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Photo-Fenton and biological integrated process for degradation of a mixture of pesticides

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Abstract

A solution of mixed pesticides (alachlor, atrazine, chlorfenvinphos, diuron, isoproturon) was considered for degradation employing photo-Fenton as a preliminary step before biotreatment. Photo-Fenton degradation is an important sub-process in the integrated photobiological process for removal of biorecalcitrant chemicals. Shortening the photo-Fenton treatment time has a critical impact on the economical feasibility of the integrated process. In this study, photo-Fenton was proved to enhance biotraitability of a mixture of biorecalcitrant substances (pesticides). During the photocatalytic process, dissolved organic carbon (DOC) measurements, liquid and ionic chromatography analyses, acute toxicity evaluation using Microtox™ and the Zahn–Wellens biodegradability testing were provided to characterize the photo-treated solutions. In order to find out the best moment for coupling of photocatalytic and biological processes, different times of photo-Fenton pretreatment were tested for biotreatment. The partially photo-treated solutions were fed to eight parallel continuously operated packed-bed bioreactors during 28 days. Considering the coupled system, it was shown that the pre-treated solutions obtained with only 1 g l^{-1} H_2O_2 (irradiation time, $t_{30\,W} = 0.6$ h) exhibited higher than 80% of DOC degradation. In this case, the packed-bed bioreactors contributed to more than 50% of the total carbon conversion of the pesticide solution.

Keywords: Pesticide treatment; Photo-Fenton; Biotreatment; Packed-bed bioreactors

1. Introduction

Agrochemicals such as insecticides, herbicides and fungicides are classified among the most dangerous toxicants. Due to their high toxicity, biological treatment of agro-industrial effluents is often perturbed and sometimes blocked. It is more important to test the mixture of these substances rather than the individual chemical species because of the possible presence of combine synergistic and/or antagonistic effects.

In this study, five pesticides were chosen including alachlor, atrazine, chlorfenvinphos, diuron and isoproturon. These compounds are considered Priority Substances by the EU [1] not only from their intrinsic toxicity but also because of their extremely easy transport in the environment that represents a risk to both surface and groundwater.

Several oxidative degradation procedures (AOPs, advanced oxidation processes) have been developed in the field of the chemical treatment of water for the elimination of pesticides: TiO_2/UV, Fenton reagent, O_3, O_3/UV and O_3/H_2O_2. Of these, photo-Fenton process was demonstrated particularly efficient for mineralization of pesticides [2–5]. The Fenton method requires H_2O_2, Fe^{2+} salts and acidic pH. Under these conditions highly reactive and unselective oxidants, OH radicals, are produced. With UV–vis light, the formed Fe^{3+} complexes are photolysed, which enables regeneration of Fe^{2+} (catalyst): the process is called photo-Fenton.

Photo-Fenton and other AOPs for wastewater treatment have been extensively studied [6], but their use remains limited due to high operational costs, generation of UV radiations by lamps, H_2O_2 consumption in case of photo-Fenton [7–9]. Hence, the combination of photo-Fenton as a preliminary treatment, followed by a biotreatment was considered to be a feasible process for pesticide removal. Simple biodegradability and ecotoxicity tests can fail to predict accurately whether process coupling

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would be effective. This is particularly true for toxicity tests as in several cases chemical oxidation may lead to increased toxicity being accompanied by increased biodegradability [10]. Many papers have yet related the feasibility of the coupling, using the Zahn–Wellens procedure to assess the biocompatibility of the photo-treated solutions of individual pesticides [11–13]. The Microtox™ acute toxicity measurement was also studied as a predictive tool to facilitate the biocoupling [14]. In this study, the biotraitability of the photodegraded solutions was more precisely investigated using packed-bed bioreactors operated during 28 days.

The paper reports: (1) the results of the preliminary experiments that demonstrated the biological incompatibility of the solution of mixed pesticides without any photo-Fenton pretreatment; (2) the photo-Fenton degradation of the mixed pesticides. The chemical and biological characteristics of the photo-treated solutions were evaluated in order to select different stages of the photocatalytic reaction to be tested for the subsequent biotreatment; (3) the results of the biotreatment, which was carried out using several bioreactors operated in parallel and continuously fed by various pre-treated solutions of mixed pesticides; (4) the overall carbon degradation efficiency of the tested photo-Fenton/bioreactor coupled systems.

2. Materials and methods

2.1. Chemicals

The chemical compounds used in this study consist of: alachlor (95%, technical grade $C_{14}H_{20}ClNO_2$, Aragonesas Agro S.A.), atrazine (95%, technical grade $C_8H_{14}ClN_5$, Ciba-Geigy), chlorfenvinphos (93.2%, technical grade $C_{12}H_{14}Cl_3O_4P$, Aragonesas Agro S.A.), diuron (98.5%, technical grade $C_9H_{10}Cl_2N_2O$, Aragonesas Agro S.A.) and isoproturon (98%, technical grade $C_{12}H_{18}N_2O$, Aragonesas Agro S.A.). Analytical standards of all pesticides (for chromatographic analyses) were purchased from Sigma–Aldrich. Demineralised water was used to prepare the mixture of pesticides. Ferrous iron sulfate ($FeSO_4{\cdot}7H_2O$), hydrogen peroxide (30%, w/v) and sulphuric acid used for pH adjustment (around 2.7–2.8) were reagent grade.

2.2. Analytical determinations

Mineralization was followed by measuring the dissolved organic carbon (DOC) by direct injection of filtered samples into a Shimazu-5050A TOC analyser provided with an NDIR detector and calibrated with standard solutions of potassium phthalate. Pesticide concentration was analyzed using reverse-phase liquid chromatography (flow 1 ml min^{-1}) with UV detector in a HPLC-UV (Varian 9012, 9100, 9065) with an ODS-2 column (Waters 4.6 mm × 250 mm, from Phenomenex) and a guard column (Waters 4.6 mm × 10 mm): alachlor (H_2O/acetonitrile 40/60, 224 nm), atrazine, isoproturon, chlorfenvinphos and diuron (acetic acid (1%)/acetonitrile 80/20–40/60 (0–30 min) and 40/60 (30–35 min), 249 nm). Ultra pure distilled-deionised water obtained from a Milli-Q (Millipore Co.) system and HPLC-grade organic solvents were used to prepare all the solutions. Cation concentrations were determined with a Dionex DX-120 ion chromatograph equipped with a Dionex Ionpac CS12A 4 mm × 250 mm column. Isocratic elution was done with H_2SO_4 (10 mM) at a flow rate of 1.2 ml min^{-1}. Anion concentrations were measured with a Dionex DX-600 ion chromatograph using a Dionex Ionpac AS11-HC 4 mm × 250 mm column. The gradient programme was pre-run 5 min with 20 mM NaOH, injection, 8 min 20 mM NaOH and 7 min NaOH 35 mM, flow rate 1.5 ml min^{-1}. H_2O_2 concentration was determined by iodometric titration.

2.3. Toxicity measurements

Microtox™ acute toxicity testing was performed with *Vibrio fischeri* using a Model 500 Analyzer (Azur Environment, Workingham, England). Hydrogen peroxide present in the samples from photo-Fenton experiments was removed prior to toxicity analysis using catalase (2500 U/mg bovine liver; 100 mg l^{-1}) acquired from Fluka Chemie AG (Buchs, Switzerland) after adjusting the sample pH to 7. Samples from photo-Fenton treatment were filtrated (0.22 μm filter, Schleicher and Schuell, G-Dassel) before toxicity testing. Measurement of toxicity was performed within 24 h after irradiation. Stored samples should be frozen before analysis. Toxicity is expressed as toxicity units, $TU = 100/EC_{50}$, where EC_{50} is the concentration which causes 50% reduction of the bioluminescence (*Vibrio fischeri*). All chemicals for the bioassays were obtained from a commercial supplier (Tetra Technique, Veyrier, Switzerland).

2.4. Biodegradability assessment

The Zahn–Wellens test was carried out according to the EC protocol (Directive 88/302/EEC). The activated sludge obtained from a secondary effluent of the treatment plant of Morges (Switzerland) was used as inoculum. The fresh activated sludge was centrifuged at 10,000 rpm during 7 min at 20 °C, and washed once with mineral medium. According to the guidelines of the Zahn–Wellens test, the ratio between the carbon content of the experimental sample and the dry-weight of the inoculum was ranged between 1 and 4 (average 3.2). Aeration and homogenization were guaranteed. Preliminary experiments were performed to check that neither volatilization nor adsorption occurred during the testing period of 28 days.

2.5. Experimental set-up

2.5.1. Photo-Fenton experiments

The photocatalytic experiments were performed using 0.5 l Pyrex flask with a cut-off at $\lambda = 290$ nm placed into Hanau Suntest Simulator.

The radiation source employed was a xenon lamp and the total radiant flux (80 mW cm^{-2}) was measured with a YSI Corporation powermeter. The lamp had a λ distribution with about 0.5% between 300 and 400 nm. The profile of the photons emitted between 400 and 800 nm followed the solar spectrum. Based

Table 1
Description of the photo-Fenton procedure

Time (h)	Irradiation time $t_{30\,W}$ (h)	Operation	Objective
0	−0.75	Preparation of the solution of mixed or single pesticides ($30\,mg\,l^{-1}$ per pesticide); acidification pH 2.7 (H_2SO_4)	Fenton reaction
0.25	−0.5	One gram per liter $FeSO_4{\cdot}7H_2O$ ($[Fe^{2+}] = 2\,mg\,l^{-1}$)	
0.50	−0.25	Pre-determined amount of H_2O_2	
0.75	0	Radiation on	Photo-Fenton reaction
–	–	Control of the remaining amounts of H_2O_2	Monitoring of the photo-Fenton reaction
–	–	Neutralization of the solution (NaOH) when $[H_2O_2] = 0$	Stabilization of the solution; iron precipitation
–	–	Filtration (0.45 μm)	Iron removal analyses of the physico-chemical and biological parameters

on Eq. (1), the actual time for the irradiation was calculated for the experiment:

$$t_{30\,W,n} = t_{30\,W,n-1} + \Delta t_n \frac{UV}{30}, \quad \Delta t_n = t_n - t_{n-1} \tag{1}$$

where t_n is the experimental time for each sample, UV the average solar ultraviolet radiation emitted during Δt_n, and $t_{30\,W}$ the "normalized illumination time". Thus, time refers to a constant solar UV power of $30\,W\,m^{-2}$ (typical solar UV power on a perfectly sunny day around noon). This calculation allows the comparison with other photocatalytic experiments. Negative time is used to report the dark period, i.e. the Fenton process.

The aqueous suspensions were magnetically stirred throughout irradiation, opened to air. Extreme care was taken to ensure uniform experimental conditions during the partial degradations, since several experiments were necessary to be run in order to continuously feed the bioreactors. Table 1 summarizes the overall photo-Fenton procedure.

2.5.2. Biotreatment experiments

As illustrated in Fig. 1, eight aerated packed-bed bioreactors were operated in parallel. Each bioreactor consisted of a 0.24 l glass column containing ca. 0.15 l packing expanded clay colonized by activated sludge from the wastewater treatment plant of Morges (Switzerland). Liquid in the columns was circulated with peristaltic pumps. The effluent of the photocatalytic stage was circulated through the bottom of the column, which operated as an up-flow reactor. In order to homogenize the bacterial population throughout each column and between all of them (in

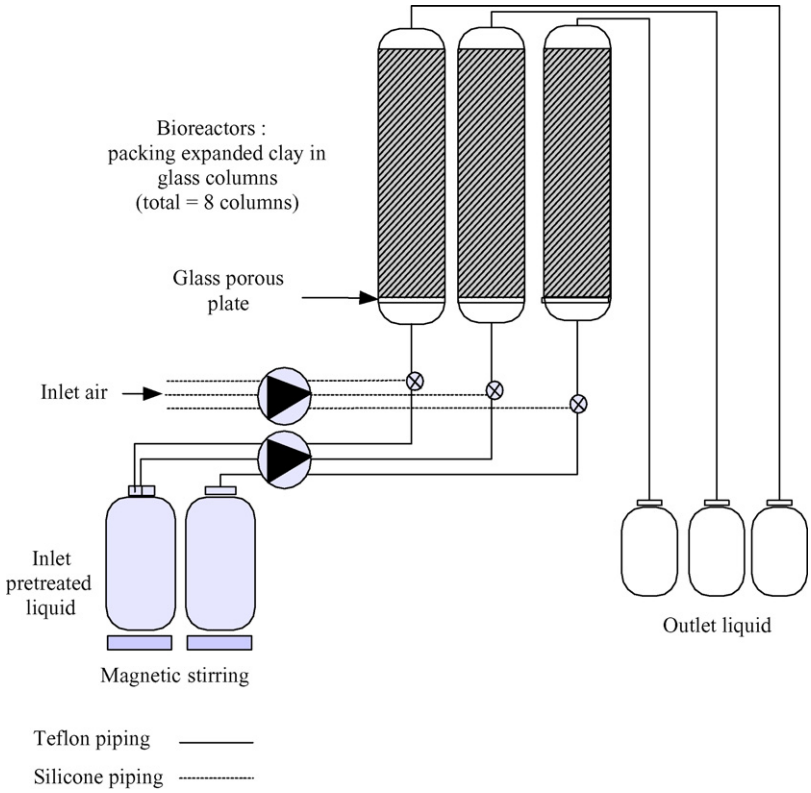

Fig. 1. Experimental setup used for investigation of the photocatalytic-biological coupling treatment of the mix of pesticides. Only three bioreactors out of eight are illustrated.

Table 2
Physico-chemical and biological properties of the pesticides (NB: non-biodegradable; B: biodegradable)

Compound	Molecular formula	Solubility in water at 25 °C (mg l^{-1})	EC_{50} ± 95% confidence interval (mg l^{-1})	Biodegradability (Zahn–Wellens test)	Initial concentration (mg l^{-1})
Alachlor	$C_{14}H_{20}ClNO_2$	239	105 ± 8	NB	30
Atrazine	$C_8H_{14}ClN_5$	34	89 ± 6	B	30
Chlorfenvinphos	$C_{12}H_{14}Cl_3O_4P$	125	18 ± 1	NB	30
Diuron	$C_9H_{10}Cl_2N_2O$	41	86 ± 5	NB	30
Isoproturon	$C_{12}H_{18}N_2O$	65	29 ± 2	NB	30

fact, eight biofilters were run simultaneously), wastewater from the primary decantor was recirculated inside the biofilter from upside down during a few days.

The pH was controlled and adjusted at 7 using 1 M H_2SO_4 or 2 M NaOH solutions. The required nutrients for bacterial activity were provided after photo-treatment with a concentrated mineral medium, so that volume remained unchanged. The aeration was about 0.03 l h^{-1} and the O_2 concentration was checked by means of a dissolved oxygen (DO) probe (Ingold AG, Urdorf, Switzerland) on top of the column. All the glass vessels were protected from illumination with aluminum sheets. Agitation was maintained before and after biotreatment using magnetic stirring. Temperature was 25 °C.

2.6. Data analyses

Validation of toxicological bioassays as well as biodegradability assessments was ensured since all the quality control data were considered acceptable according to the official guidelines (OECD, U.S. Environmental Protection Agency (EPA) Office of Pollution Prevention and Toxics (OPPT), and the European Commission) and other established criteria (e.g., response to the negative controls, use of reference substances: phenol for Microtox™, diethylene glycol for Zahn–Wellens testing [14]).

Photocatalytic and biodegradability experiments were at least duplicated and all samples were analyzed in triplicate. Toxicity data were computed and EC_{50} values were calculated according to the gamma method, using linear regression analysis of transformed DOC concentrations as natural logarithm data versus percentage inhibition. All correlation coefficients were >0.90.

Statistical analysis of all experimental results was carried out using analysis of variance (ANOVA). For all laboratory experiments, α was set at 0.05.

3. Results and discussion

3.1. Biocompatibility of the mixed pesticide solution

Before considering any photocatalytic treatment of the mixture of pesticides, a solution of the mixed compounds (alachlor, atrazine, chlorfenvinphos, diuron, isoproturon) was first tested for biodegradability using the Zahn–Wellens procedure [15]. This test was carried out under similar conditions that of a wastewater treatment plant using activated sludge. A parallel control experiment using diethylene glycol (0.5 g l^{-1}) was carried out to test if the sludge was active. The diethylene glycol was in fact degraded as much as 96% in 6 days.

Under the tested conditions, the mixture of pesticides was proved biorecalcitrant. The concentrations of DOC and of each pesticide (HPLC) in the mix remained unchanged, even after 28 days. This observation also indicates that bacteria cannot adapt to degrade these chemicals. This result is concomitant with previous experiments performed with the single compounds and using the same biodegradability testing procedure [15]. In that study, no biodegradation has been observed for each compound tested alone, except for atrazine (see Table 2).

A supplementary test to measure the biodegradation of the mix of pesticides was carried out in batch mode in the packed-bed bioreactors shown in Fig. 1. Even under theoretically favorable conditions, such as the presence of co-substrates and adapted bacteria, as well as a strict control of pH, temperature and aeration, the test confirmed that the solution of mixed pesticides is non-biodegradable in the tested conditions. Three techniques were used to follow this test: (a) respirometric measurements with an O_2 probe in both the inlet and outlet of the biofilters, (b) determination of single pesticide concentrations by HPLC and (c) measurements of DOC as a function of time.

3.2. Chemical and biological characteristics of the photo-treated pesticide solution

Photo-Fenton degradation is an important sub-process in the integrated photocatalytic-biological coupled process for removal of biorecalcitrant chemicals. Shortening the photo-Fenton treatment time has a critical impact on the economical feasibility of the integrated process. For this purpose, it is very important to gather information concerning both chemical and biological characteristics of the solution during the photocatalytic pre-treatment. DOC analyses, concentrations of the initial compounds and of other inorganic species produced during the photo-Fenton process were monitored in the course of the photocatalytic experiments. Acute toxicity was also measured using the Microtox™ system and biodegradability was assessed according to the Zahn-Wellens method.

Decreasing DOC concentrations are representative of the oxidative reactions that occur in the experimental solution during the photocatalytic treatment. During the photo-Fenton reaction, degradation progress depends simultaneously on the irradiation time and on the amounts of H_2O_2 which are really consumed. In order to find out which parameter was the most representative of the degradation progress, several photoreactions have been

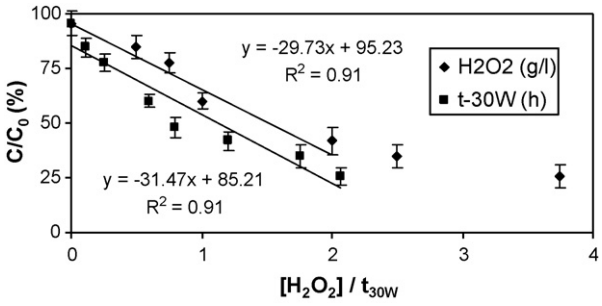

Fig. 2. DOC evolution of the solution of mixed pesticides as a function of the irradiation time ($t_{30\,W}$) and the consumed amounts of H_2O_2 during photo-Fenton. Error bars represent 95% confidence intervals.

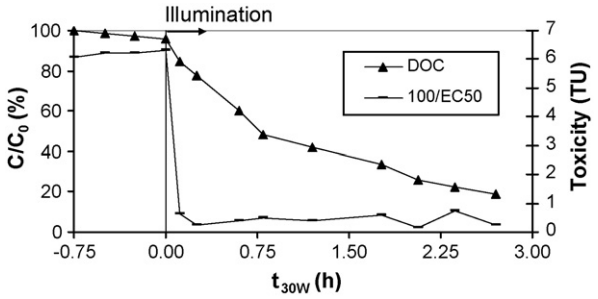

Fig. 3. Evolution of toxicity (expressed as $100/EC_{50}$) and DOC of the solution of the mixed pesticides as a function of the irradiation time ($t_{30\,W}$) during photo-Fenton. Negative time is related with the obscurity phase. Data correspond to the average value of at least six measurements.

achieved to determine the relation between the amounts of consumed H_2O_2, the illumination time and the degradation ratios. Fig. 2 presents the evolution of the DOC contents as a function of either the irradiation time or the consumed H_2O_2 during the photo-Fenton degradation of solutions of mixed pesticides. As shown in Fig. 2, evolution of global mineralization can be well illustrated by both H_2O_2 consumption and the illumination time. Therefore, the progress of the photo-Fenton process could be equally defined by one of the two parameters. In fact, the concentration of H_2O_2 was precisely followed in order to avoid any residual amount of H_2O_2 in the photo-treated solution, because H_2O_2 may damage the bacterial cells and thus limit the consecutive biotreatment. No remaining H_2O_2 was also required for toxicity analyses. Thus, to obtain one precise degradation ratio, the exact amount of H_2O_2 was introduced in the solution of pesticides. Then irradiation was provided until no remaining H_2O_2 was measured. For that reason, in this study, the initial concentrations of H_2O_2 are also the H_2O_2 concentrations really consumed during the photo-Fenton process.

Fig. 2 shows that the degradation ratio tends to stabilize at H_2O_2 concentrations above $2\,g\,l^{-1}$. Beyond this threshold, higher amounts of H_2O_2 as well as a higher irradiation time are necessary to extend degradation. In fact, the mineralization of the mixed pesticide solution was difficult to achieve. Long irradiation period and its consequent high time and energy consumption, as well as the high H_2O_2 amounts result in a rather expensive treatment. Electricity represents about 60% of the total operational cost when photoprocesses are driven by electrical generation of photons instead of direct solar irradiation. This underlines the aim of the study to shorten the photocatalytic treatment time in order to promote the biodegradation.

In this paper, the illumination time ($t_{30\,W}$, described in Section 2.5.1.) was chosen to characterize the advancement of the photo-Fenton process, because it is a useful parameter in practical applications. Fig. 3 represents the chemical degradation of the mix of pesticides as a function of the illumination time course ($t_{30\,W}$). Evolution of the overall Microtox™ acute toxicity is also pictured, toxicity being expressed in TU ($=100/EC_{50}$ [16]). A sharp decrease in toxicity was observed at the beginning of the photo-Fenton process, followed by a stable toxic level during all the rest of the photo-treatment. This indicates that the intermediates formed during the photo-assisted pre-treatment are less toxic than the initial compounds. This is different from the behavior observed with the photo-Fenton degradation of the single pesticides [14]. Indeed, even if many fluctuations have been mentioned, mainly depending on the intermediate by-products generated by each tested compound, it has been shown that toxicity of single pesticide solutions tends to increase during the first stages of the photo-treatment and then decreases. So it seems that whenever the substances are mixed, toxicity presents a global behavior which tends to decrease as soon as the photo-Fenton begins. It has already been stated that toxicity is not an additive data [17]. Moreover, as illustrated in Table 3, comparison between the irradiation times necessary to degrade the single and the mixed compounds reveals that the photo-Fenton process is more efficient for treating the mixing solution, even if incomplete mineralization was achieved. Rapid decomposition of mixed pesticides may be caused by photo-sensitized

Table 3
Comparison of the illumination time ($t_{30\,W}$) necessary to remove 100% of the parent molecule of pesticide (HPLC data) and 80% of DOC during the photo-Fenton treatment of both single and mixed pesticides

Compound	Illumination time, $t_{30\,W}$ (h)			
	100% removal of initial compound		80% DOC removal	
	Single	In mixture	Single	In mixture
Alachlor	0.28 ± 0.01	0.05 ± 0.04	1.20 ± 0.02	
Atrazine	0.94 ± 0.05	0.85 ± 0.03	>3.50	
Chlorfenvinphos	0.25 ± 0.01	0.05 ± 0.01	1.13 ± 0.03	2.50 ± 0.02
Diuron	0.37 ± 0.02	0.25 ± 0.01	0.68 ± 0.02	
Isoproturon	0.66 ± 0.03	0.50 ± 0.02	1.28 ± 0.30	

reactions of pesticides, which may generate large amount of activated oxygen species and excited organic molecules during photo-irradiation. The interplay between iron complexes and the organic molecules may also been favored in the case of mixed pesticides. It results in an increased reactivity of the system and may smooth the overall evolution of toxicity during the photo-degradation.

The evolution of the five initial compounds was followed during the pre-treatment process by HPLC measurements. At 0.15 h of photo-treatment, when about 20% of DOC removal was observed, mainly every parent pesticide was eliminated (only 3% atrazine and 4% chlorfenvinphos were left). Thus, complete disappearance and total dechlorination (23 mg l^{-1} chloride was expected for the tested concentrations) of all pesticides were attained very easily. The elimination of the initial bio-recalcitrant compound was required in order to test the biocompatibility of the photo-treated solution [18]. The slow decrease of DOC compared with the pesticide evolution indicated an accumulation of intermediate products. The nitrogen balance was also checked during the photo-Fenton process, because the release of ammonia and nitrate was indicator of the by-product degradation. The slow mineralization rate observed at the end of the photo-treatment was concomitant with the incomplete release of nitrogen as NH_4^+ or NO_3^-. From previous experiments [11], it has been concluded that the most resistant intermediates were due to the phenylurea pesticides (diuron and isoproturon) and atrazine. In particular, the stable triazine ring and the formation of urea could justify the remaining 10% DOC measured at the end of the photo-Fenton process. It also explains why the observed 80% DOC removal in mixture has taken more time than for every other single pesticide photo-irradiation experiment except atrazine. Limitation can thus be related to the by-products generated by the photo-degradation of atrazine. Indeed, more than 3.5 h have been necessary to obtain 80% of DOC removal during photo-treatment of single atrazine and photo-degradation of the mixed solution has needed more than 2.5 h to obtain 80% DOC removal.

In the case of the mixed pesticide solution, toxicity and biodegradability were found to be related. Indeed, as illustrated in Fig. 3, before irradiation (i.e. during the Fenton process), the solution of the mixed pesticides was toxic up to 6 TU and biorecalcitrant according to the test of Zahn–Wellens. On the contrary, after illumination (i.e. during the photo-Fenton process) the partially treated solutions exhibited a lower toxicity, approximately 0.5 TU (see Fig. 3), and were biodegradable according to the Zahn–Wellens test. These results are in accordance with previous experiments which demonstrated that biocompatibility was achieved after complete disappearance of the initial biorecalcitrant substance [11].

Therefore, it is interesting to test the biotreatability of the solutions partially degraded by the photo-Fenton process.

3.3. Photochemical–biological coupled flow treatment

The above-mentioned results presenting the concomitant decrease of toxicity and increase of biodegradability of the treated solution of mixed pesticides suggest the photo-Fenton as a promising pre-treatment process. Therefore, a photochemical–biological coupled flow reactor can be considered for the complete mineralization of the solution of the mixed pesticides. The aim of the study was also to determine the best moment for coupling, in order to limit the cost of the photocatalytic treatment. For that purpose, successive steps of pre-treatment were selected during the photo-Fenton process and tested for biotreatment in several biological fixed bed reactors. The bioreactors (see Fig. 1) were operated in continuous mode, whereas the photo-chemical treatment was operated in batch mode. Table 4 gives the characteristics of different pre-treated solutions which were tested for biocoupling. Each partially treated solution was tested in triplicate: three columns were operated in parallel and were compared to the control bioreactors. Control bioreactors consisted of a bioreactor fed with only the mineral medium and a bioreactor operated with the initial solution of no photo-treated mixed pesticides. A preliminary test using diethylene glycol was performed in each bioreactor in order to check both the activity of the bacteria and the correct operating mode of each column.

Table 4
Photocatalytic characteristics and biodegradability assessment of the pre-treated solutions tested with the photo-Fenton/bioreactor coupled system (NB: non-biodegradable; PB: partially biodegradable; ND: not-determined)

Sample	$t_{30\,W}$ (h)	H_2O_2 (g l^{-1})	C/C_0 (%)	Biodegradability (Zahn–Wellens)
A	0	0	96	NB
B	0.11	0.50	85	PB
C	0.25	0.75	76	PB
D	0.60	1.00	60	PB
E	0.80	1.23	48	ND
F	1.20	2.00	42	ND
G	1.76	2.50	35	ND
H	2.06	3.75	26	PB

The pre-treatment of the solution was made in photocatalytic reactors using the photo-Fenton process. After photo-treatment, the solutions were neutralized (pH around 6.5–7), which also provoked the precipitation of the iron. Solutions were centrifuged and filtrated before biotreatement. Sequential batches of the photo-treatment process were carried out so that the input flow rate into the biological reactors was 0.12 l day^{-1}. This flow rate was maintained during at least 28 days. A relatively steady-state condition for DOC removal was observed in the columns after 48 h.

Various experiments were performed in order to compare the efficiency of the coupled photocatalytic and biological treatments of the mixture of pesticides based on the advancement of photodegradation. Fig. 4 illustrates the experimental results obtained with the coupled system. Data correspond to the average values obtained after 28 days of biotreatment in the columns. Fig. 4 shows the DOC removal efficiency which was attributed to both photo-Fenton and biotreatment, as a function of the photoreaction time presented in Table 4. A maximum degradation efficiency of 90% was obtained with the coupling system. It was achieved with pre-treated solutions E, F, G and H. Thus, beyond an irradiation time of 0.80 h (1.25 g l^{-1} H_2O_2, sample E), intensi-

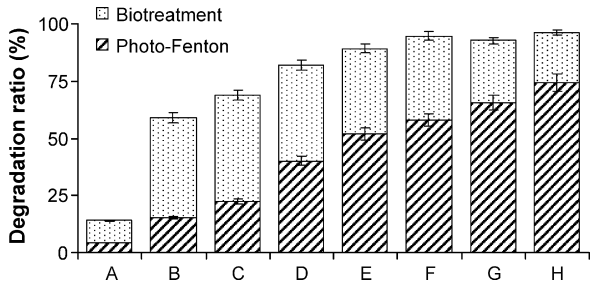

Fig. 4. Relative contribution of photocatalysis and biotreatment for the degradation of the solution of the mixed pesticides. Characteristics of the samples A–H are listed in Table 2. Error bars represent 95% confidence intervals.

fying the photo-Fenton reaction is useless to enhance the global degradation ratio. So it means that beyond this threshold, the more intensive the photo-treatment, the less important the biological contribution to achieve the global degradation. In fact, more than 80% of DOC were degraded in the coupled system with pre-treated solutions using only 1 g l^{-1} H_2O_2 ($t_{30\,W}$ = 0.6 h, sample D). This global degradation degree is already an interesting result for an industrial application of the integrated process. In this case, the biological treatment contributes to more than 50% of the total carbon conversion of the pesticide solution. It should be noticed that using a recirculation loop in biological system can have important effect on the total removal capacity and intensification of the integrated process. Since the toxicity of the pesticide solution becomes low after partial photo-Fenton process, the adaptation of bacteria is expected to enhance the biotreatment.

4. Conclusion

The photocatalytic treatment of the solution of the mixed pesticides was successfully achieved with the photo-Fenton process. In this study, photo-Fenton degradation was considered as a sub-process in the integrated photocatalytic-biological coupled system for removal of the biorecalcitrant pesticides. In particular, it was aimed to shorten the photo-treatment time in order to enhance the economical feasibility of the integrated process. The Microtox^{TM} acute toxicity evaluation and the Zahn–Wellens tests for biodegradability assessment were shown to be two relevant indicators to determine the best moment for coupling. Biotreatability of the partially photo-degraded solutions was investigated more accurately using several biological fixed bed reactors which were continuously operated during 28 days.

The obtained concomitant decrease of toxicity and increase of biodegradability of the partially photo-treated solution of mixed pesticides confirmed that photo-Fenton is a promising pre-treatment process capable to enhance the biotreatability of waters contaminated with biorecalcitrant chemicals (pesticides).

Finally more than 80% of DOC was degraded in the coupled system for the pesticide solutions which were photo-treated during only 0.6 h ($t_{30\,W}$) and needed 1 g l^{-1} H_2O_2. This step of photo-Fenton treatment proved to be the most relevant moment for coupling because in this case, the biological treatment contributed to more than 50% of the total carbon conversion of the pesticide solution. Recirculation of the bioreactor effluents is now prospected in order to improve the global degradation degree of the contaminated waters.

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