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Scale-up strategy for a combined solar photo-Fenton/biological system for remediation of pesticide-contaminated water

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ABSTRACT

This work is proposing a design strategy for an industrial combined solar photo-Fenton/aerobic biological system for the decontamination of wastewater polluted with commercial pesticides. The two possibilities (photo-Fenton/bio and Bio/photo-Fenton) of the combined system were evaluated (using different analytical tools and bioassays, mainly DOC, COD, toxicity and biodegradability) in pilot plant and the most successful was scaled-up. Photo-Fenton (20 mg/L of Fe^{2+}) was carried out in compound parabolic collectors (CPC) at an initial DOC of 500 mg/L (100 mg/L of each commercial pesticide). The biological pilot reactor was an Immobilized Biomass Reactor (IBR) filled with polypropylene Pall Ring® supports colonized by activated sludge. The industrial plant has a total collector surface of 150 m^2, total photo reactor volume of 1060 L and the scaled-up biological treatment plant (also an IBR) consists basically of two IBRs (1230 L each).

The photo-Fenton treatment at pilot plant scale was able to reduce toxicity (from 96% to 50% of inhibition) and increase biodegradability (from 50% to 95%) of the wastewater and the most suitable point for combining it with the biological treatment was after the total elimination of the active ingredients. The efficiency of the combined photo-Fenton/bio system in terms of mineralization was 94%, of which 35.5% corresponds to the AOP and 58.5% to the aerobic biological treatment. The combination Bio/photo-Fenton was not successful. The efficiency of the industrial-scale combined system (photo-Fenton/bio) was 84%, 35% corresponding to the photo-Fenton treatment and 49% to the biological stage.

1. Introduction

Recent growth of surface and groundwater pollution is one of the main current worldwide concerns. An increasing number of pollutants coming from human development, mainly generated by industry, are polluting water resources. For instance, the enormous growth of intensive agriculture along the Mediterranean coast in recent years has polluted water with pesticides. These substances are often toxic and recalcitrant, and conventional biological treatments are ineffective for their elimination. As a result, they have been designated as priority substances (PSs) in EU legislation [1]. Advanced oxidation processes (AOPs) have been demonstrated as effective methods for oxidizing these substances [2,3], although their high operating costs are a significant drawback for industrial application. One proposed cost-cutting measure is the use of renewable energy resources, i.e., sunlight as the source of radiation for running the AOP [4]. Another attractive way of reducing costs is the integration of AOPs with biological treatment in a combined technology [5–7]. In these integrated systems, AOPs are usually employed as a pretreatment to enhance the biodegradability of wastewater containing recalcitrant pollutants. Although several combined systems have been proposed as a solution for the treatment of different kinds of industrial wastewater, they are still not in general commercial or industrial use. This may be because most of the research on these systems is limited to evaluation of overall parameters such as BOD_5, COD and DOC and use of activated sludge from treatment plants in small laboratory devices, very often working with model wastewaters prepared by dissolving a single compound in demineralized water.

This work intends to go a step forward in this direction; by proposing a design strategy for an industrial combined solar photo-Fenton/aerobic biological system for the decontamination of wastewater polluted with commercial pesticides. For this purpose, a mixture of commercial pesticides in natural water was selected as the model waste water because it is close to real biorecalcitrant waste water containing different compounds (pesticides + formulation components). After preliminary laboratory testing, the feasibility of the two possibilities (photo-Fenton/

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bio and Bio/photo-Fenton) of the combined system was evaluated in pilot plant, being the most successful applied at industrial scale to upgrade the treatment in a commercial solar photo-Fenton installation. Such an industrial solar photo-Fenton system has been in operation since 2004 at ALBAIDA Recursos Naturales y Medio Ambiente S.A., a company that selectively collects empty plastic pesticide containers from the greenhouses in El Ejido (southeastern Spain) for recycling. These containers are shredded and washed, contaminating the rinse water with pesticide residues. The rinse water is then treated by solar photo-Fenton [8]. This photocatalytic plant has recently been upgraded to include the photo-Fenton and biotreatment combination, using the strategy included in this paper.

2. Experimental

2.1. Chemicals

Commercial formulations of Vydate® (10%, w/v oxamyl, $C_7H_{13}N_3O_3S$), Metomur® (20%, w/v methomyl, $C_5H_{10}N_2O_2S$), Couraze® (20%, w/v imidacloprid, $C_{16}H_{22}ClN_3O$), Ditimur-40® (40%, w/v dimethoate, $C_5H_{12}NO_3PS_2$) and Scala® (40%, w/v pyrimethanil, $C_{12}H_{13}N_3$) were used as received. Fig. 1 shows the pesticide chemical structures. Analytical standards (>98%) for chromatographic analyses were purchased from Sigma–Aldrich.

Distilled water used in the pilot plant was supplied by the Plataforma Solar de Almería (PSA) distillation plant (conductivity < 10 μS/cm, Cl^- = 0.2–0.3 mg/L, NO_3^- < 0.2 mg/L, organic carbon < 0.5 mg/L). The photo-Fenton experiments were performed using $FeSO_4{\cdot}7H_2O$, reagent-grade hydrogen peroxide (30%, w/v) and sulfuric acid all purchased from Panreac. For industrial-scale experiments, the compounds were dissolved in natural water (2 mS/cm; 350 mg/L Cl^-, 80 mg/L SO_4^{2-}, 3 mg/L of dissolved organic carbon, DOC).

2.2. Analytical determinations

High-performance liquid chromatography HPLC (Agilent Technologies, Series 1100) with a UV-DAD detector and a C-18 column (Phenomenex LUNA 5 μm, 3 mm × 150 mm) was used to monitor the pesticide concentrations during degradation. The mobile phase consisted of a mixture of 15% HPLC-grade acetonitrile and 85% ultrapure water (Millipore Co.). Mineralization was followed by measuring the dissolved organic carbon (DOC) by direct injection of filtered samples into a Shimadzu-5050A TOC analyzer. Samples were filtered with 0.22 μm PTFE filters (Millipore Millex® GN). Hydrogen peroxide was analyzed by a spectrophotometric method using ammonium metavanadate [9]. Chemical oxygen demand (COD) was measured with Merck® Spectroquant kits (ref: 1.14541.0001). The absorbance was measured with a Merck Spectroquant® NOVA 30 photometer (an external calibration curve was used).

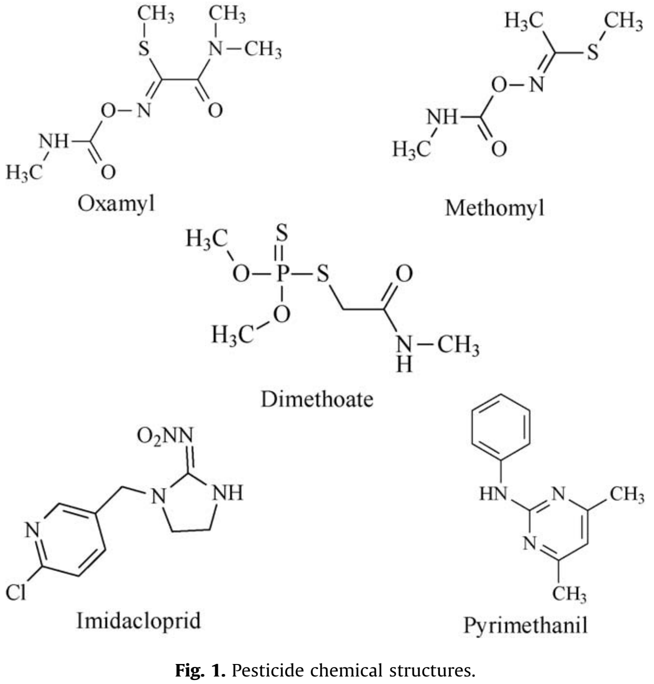

Fig. 1. Pesticide chemical structures.

2.3. Toxicity and biodegradability assays

A commercial assay marketed as Biofix®Lumi-10 was employed to evaluate the toxicity at different stages of the treatment using a freeze-dried specially selected strain of the marine bacterium *Vibrio fischeri* (NRRL number B-11177). Hydrogen peroxide present in the samples was removed prior to toxicity analysis using catalase (2500 U/mg bovine liver; 100 mg/L) acquired from Fluka Chemie AG (Buchs, Switzerland) after adjusting the sample pH to between 6 and 8. Toxicity was also analyzed by respirometry using a BMT Respirometer (SURCIS, S.L). The biodegradability of the pesticide mixture was evaluated by an adaptation of the Zahn–Wellens (Z–W) test (Directive 88/303/EEC). The biodegradation process was monitored at appropriate regular time intervals, by DOC analysis of the filtered solution. The ratio of DOC eliminated after each interval to initial DOC compared to the DOC in a blank reference is expressed as the percentage of biodegradability. When this percentage reaches 70%, the test sample is considered biodegradable [9].

2.4. Experimental set-up

2.4.1. Solar reactors

(a) *Pilot plant*: Photo-Fenton experiments were carried out under sunlight in a pilot plant specially developed for photo-Fenton applications installed at the Plataforma Solar de Almeria (PSA). A diagram of this system has been published elsewhere [10]. It consists of four compound parabolic collector (CPC) modules. Solar ultraviolet radiation (UV) was measured by a global UV radiometer (KIPP&ZONEN, model CUV 3) mounted on a platform tilted 37° (the same as the CPCs). With Eq. (1), combination of the data from several days' experiments and their comparison with other photocatalytic experiments is possible [11].

$$t_{30\mathrm{W,n}} = t_{30\mathrm{W,n-1}} + \Delta t_\mathrm{n}\frac{\mathrm{UV}}{30}\frac{V_\mathrm{i}}{V_\mathrm{T}}; \quad \Delta t_\mathrm{n} = t_\mathrm{n} - t_\mathrm{n-1} \qquad (1)$$

where t_n is the experimental time for each sample, UV is the average solar ultraviolet radiation measured during Δt_n, and $t_{30\mathrm{W}}$ is a "normalized illumination time". In this case, time refers to a constant solar UV power of 30 W/m (typical solar UV power on a perfectly sunny day around noon). V_T is the total volume of the water loaded in the pilot plant (75 L), V_i is the total irradiated volume (44.6 L).

All photo-Fenton experiments were carried out at an initial DOC of 500 mg/L (100 mg/L of DOC coming from each commercial pesticide). The pesticide mixture was added directly to the plant and homogenized by turbulent recirculation for half an hour. With the collectors covered, the pH was adjusted to 2.7–2.9 and iron salt was added (20 mg/L of Fe^{2+}). Then the hydrogen peroxide was added and the collectors were uncovered, which is when photo-Fenton began.

(b) *Industrial plant*: The reactor configuration is similar to the pilot plant described, but larger. It has 4 parallel rows of 14

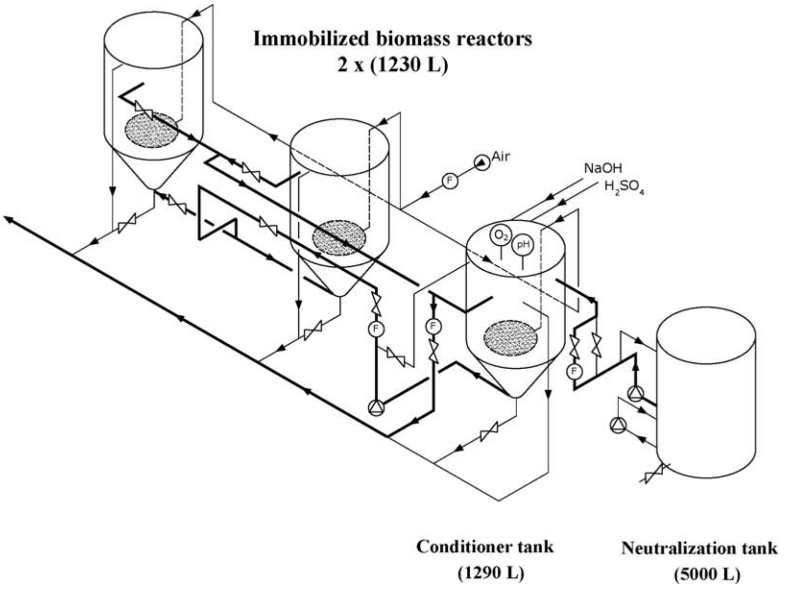

Fig. 2. Flow diagram of the biological system.

photocatalytic reactor modules (20 tubes/module, 2.7 m^2/module) mounted on a 37°-tilted platform (local latitude). The total collector surface is 150 m^2 and total photo reactor volume is 1060 L. The industrial-scale experiments were also performed with 500 mg/L of initial DOC, 20 mg/L of Fe^{2+} and pH adjusted to 2.7–2.9. In this case, a matrix of raw water was employed to approximate real wastewater conditions and the operating temperature was not controlled. A diagram of the plant has been previously published [12].

2.4.2. Biological system

(a) *Pilot plant*: The IBR consists of a 160-L flat-bottom tank filled with 90–95 L of polypropylene Pall Ring® supports colonized by activated sludge. The system is also provided with a 100-L conditioner tank with a pH control system (between 6.5 and 7.5), which is connected to the IBR by a recirculation pump. The system was operated in batch mode with a recirculation flow of 500 L/h. Dissolved oxygen; pH and temperature were automatically measured and registered. Furthermore, dissolved oxygen was also automatically kept between 4 and 6 mg/L. Total operating volume in the pilot scale experiments was 150 L. Start-up and adaptation of the biological reactor began with immobilization of the sludge (50 L of activated sludge from conventional wastewater treatment plant + 100 L raw water) on the ring supports. After this, biomass was grown by adding biodegradable carbon sources, urban wastewater and glucose (DOC_0: 100–300 mg/L), and ammonium chloride (carbon/nitrogen ratio 100/20) as required. The second phase in the start-up was adaptation of the biomass to the photo-treated pesticide effluent in two steps:

(1) Addition of 300 mg/L of DOC: 70% easily biodegradable carbon source (glucose + lactose) and 30% of partially photo-treated pesticide mixture.
(2) Addition of 300 mg/L of DOC: 30% easily biodegradable carbon source and 70% partially photo-treated pesticide mixture.

Total suspended solids, DOC and pH were used to evaluate the IBR state throughout the adaptation process (45 days).

(b) *Industrial plant*: Based on the pilot plant results, a scaled-up biological treatment plant (also an IBR) was designed and installed at ALBAIDA for combined treatment (photo-Fenton/IBR). The plant consists of a neutralization tank (5000 L), a conditioner tank (1290 L), two immobilized biomass reactors (IBRs) filled with Pall®Ring supports colonized by activated sludge (1230 L each tank), centrifugal pumps, a blower, two dosing pumps (H_2SO_4 and NaOH), tubing and valves (see Fig. 2). In the biological system, dissolved oxygen and pH were automatically kept in a range of 4–6 mg/L and 6.5–7.5, respectively. The industrial biological system was operated also in batch mode with a recirculation flow of 1500 L/h and the adaptation process of the biomass to the pesticide effluent was similar to the one carried out at pilot plant scale and explained before.

3. Results and discussion

3.1. Toxicity and biodegradability evolution during photo-Fenton process

In a previous study, it was demonstrated that photo-Fenton could be employed as a pretreatment to enhance the biodegradability of a mixture of five commercial pesticides [Vydate®, Metomur®, Couraze®, Ditimur-40® and Scala®] with an initial DOC of 200 mg/L [13,14]. A gradual decrease in toxicity and increase in biodegradability were observed just after total degradation of the active ingredients contained in the commercial formulations. In view of this experience, the combined system was studied at an initial DOC of 500 mg/L in order to find out whether the larger amount of intermediates generated when using higher concentrations would cause any substantial change in toxicity and biodegradability behavior. Furthermore, this study is also of interest for predicting the impact on the industrial integrated system of real waste water containing variable amounts of pesticides from the plastic pesticide bottle shredding and washing operations. If the system is robust enough, it could greatly simplify control of the washing process. The first step was to study the toxicity and biodegradability of the pesticide mixture at 500 mg/L of initial DOC. The original DOC of 500 mg/L (100 mg/L DOC from each pesticide) corresponded to 210 mg/L oxamyl, 47 mg/L methomyl, 45 mg/L imidacloprid, 63 mg/L dimethoate and 85 mg/L pyrimethanil. As optimized in previous experiments, other parameters were operating temperature 35 °C and 20 mg/L of Fe^{2+} [13,14]. During the process, partly photodegraded samples with different DOCs (from 500 to 150 mg/L) were collected. At the end of the experiment (after 430 min of illumination time) the

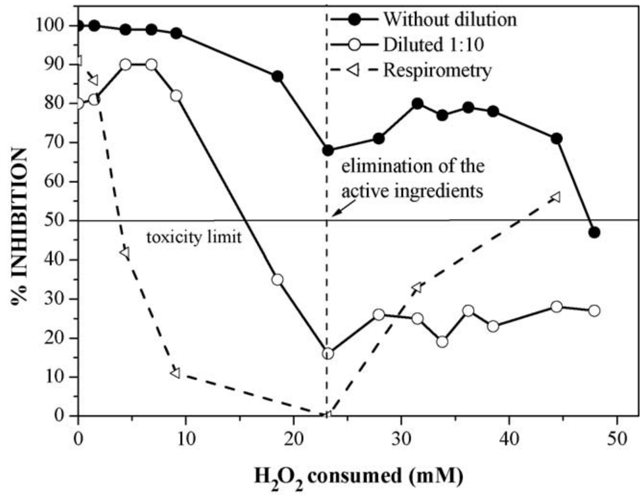

Fig. 3. Toxicity expressed as percentage of inhibition (evaluated with *Vibrio fischeri* and activated sludge) of samples partially treated by photo-Fenton as a function of H_2O_2 dose.

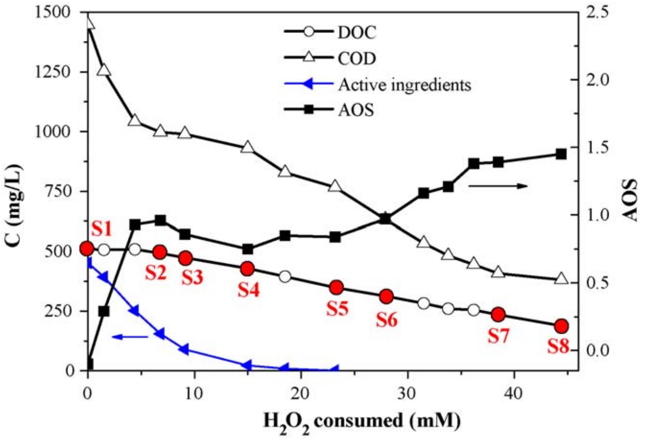

Fig. 4. DOC, COD and AOS during photo-Fenton degradation of the pesticide mixture. Active ingredients refer to the sum of five pesticides. Samples selected for Zahn–Wellens test are shown.

total mineralization was 70% and H_2O_2 consumption was 48 mM. The active ingredients were completely eliminated after 23 mM of H_2O_2 consumed (DOC = 345 mg/L). The relation between the hydrogen peroxide consumption and the illumination time during the photo-Fenton process was 0.1 mM H_2O_2/min approximately.

Toxicity was monitored using two different assays: *V. fischeri* and respirometry tests. *V. fischeri* toxicity analyses revealed that inhibition decreased from 96% to 70% after the total elimination of the active ingredients, as shown in Fig. 3. The toxicity of these samples was also evaluated in 1:10 dilutions and exactly the same inhibition tendency was observed, dropping from 80% to 20% (Fig. 3). These results confirm that photo-Fenton degradation of the pesticide mixture was able to gradually reduce the toxicity of the initial solution. Due to the limited expressiveness of *V. fischeri*, toxicity was also studied with a respirometry assay. In general, the combination of different microorganism populations makes activated sludge more resistant to toxic effluents than *V. fischeri*. As shown in Fig. 3, as soon as the active ingredients were eliminated by photo-Fenton process, the activated sludge did not show toxicity (23 mM of H_2O_2 consumed, 345 mg/L DOC). This means that the compounds present at this stage of degradation did not have a toxic impact on the sludge. However the final inhibition of 56% correlates with the inhibition measured in the *V. fischeri* assay. Toxicity is related to the intermediates formed and a more detailed study based on advanced analytical tools (as Mass Spectrometry) would be necessary to determine the toxicity of each degradation product. In addition, the other components of the formulation and their intermediates should be taken into account. But that is out of the scope of this study, mainly because the results were coherent and gave sufficient information regarding our main goal, which was to determine the stage of degradation when toxicity decreases substantially, as a tool for deciding when to apply biodegradability tests. Considering the results above, the total elimination of the active ingredients might be a key point of the treatment. Afterwards, respirometry and *V. fischeri* tests show that toxicity increases, which could be (or not) related to biodegradability, as discussed below.

In addition to DOC, COD was also measured during photo-Fenton treatment to evaluate the average oxidation state (AOS) of the solution. AOS can also provide indirect information on biodegradability, as it indicates variations in the qualitative composition of the effluent that could lead to changes in solution biodegradability/toxicity [15]. This parameter can be calculated by Eq. (2) [16], in which DOC and COD are expressed in moles of C/L and of O_2/L, respectively, at the sampling time. COD, DOC and AOS during pesticide mixture degradation by photo-Fenton are shown in Fig. 4.

$$\mathrm{AOS} = \frac{4(\mathrm{DOC} - \mathrm{COD})}{\mathrm{DOC}} \tag{2}$$

As photo-Fenton is an oxidation process, it formed more oxidized organic intermediates at the beginning of the process (Note how fast COD decreases until H_2O_2 of 10 mM) without substantial mineralization (very low, as measured by DOC, until H_2O_2 of 10 mM). After a certain amount of H_2O_2 consumption, COD and DOC behave similarly, stabilizing the AOS [17]. After 25 mM H_2O_2, another increase in AOS, though not so sharp, and another steady state after 35 mM of H_2O_2 were observed, indicating that the very different intermediates formed go through different oxidation-mineralization steps. Formation of more oxidized intermediates usually demonstrates indirectly improved wastewater biodegradability.

Biodegradability of the mixture during phototreatment was evaluated in eight samples by the Zahn–Wellens (Z–W) test along 28 days. Among the different samples taken during photo-Fenton, four of them (S1, S2, S3 and S4) contained varying amounts of the active ingredients of the commercial pesticides (see Fig. 4). The results are summarized in Fig. 5. S1 (highest concentration of the active ingredients) was non-biodegradable (around 50% of biodegradability in 28 days), whereas the rest of the samples were biodegradable according to the Z–W test. S2, S3 and S4 were biodegradable after a long period of 8 days or more. However, once the active ingredients had been eliminated (S5: 345 mg/L of DOC), all the samples became biodegradable in a short time (5 days or less). S6, S7 and S8 had the highest biodegradation percentages. This demonstrates that the most suitable point for combining photo-Fenton with the biological treatment was after the total elimination of the five active ingredients, somewhere between S5 (23 mM H_2O_2) and S6 (27.7 mM H_2O_2). In the first four samples, the evolution of the five active ingredients concentration during the 28 days of test was also monitored. The amount of oxamyl was dramatically reduced due to its hydrolysis (as it is commented later), while the rest of the compounds remained constant in the solution, confirming that they are non-biodegradable.

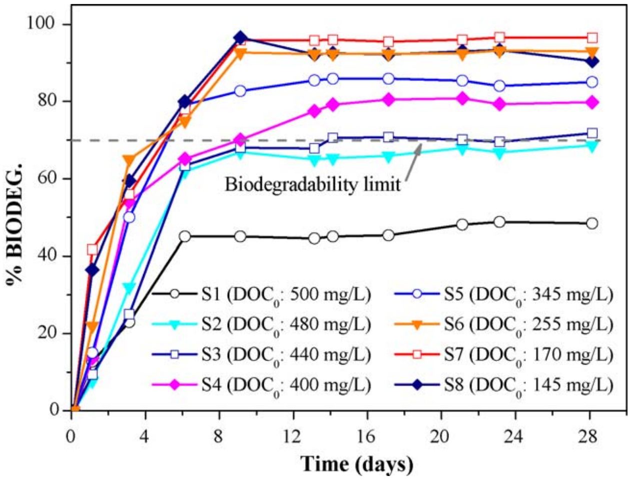

Fig. 5. Zahn–Wellens (Z–W) biodegradability analysis of samples taken during photo-Fenton. The H_2O_2 doses corresponding to S1, S2, S3, S4, S5, S6, S7 and S8 are 0, 6.3, 11.3, 16.4, 23, 27.7, 36.6 and 39.1 mM, respectively.

3.2. Combined photo-Fenton/biological system

3.2.1. Pilot plant scale

The first approach was to test the degradation of the commercial pesticide mixture in the combined photo-Fenton/ biological (AOP-BIO) system. To do this, the five commercial pesticides at 465 mg/L of initial DOC were degraded by photo-Fenton. The photo-Fenton process was continued until total elimination of the active ingredients, according to the above biodegradability results. This partly oxidized effluent was then discharged into the IBR system after adjusting the pH to around 7. After 3 days of biotreatment, the DOC had dropped to 28 mg/L. The results found in the IBR are more favorable than in Z–W test (higher percentage of biodegradation in less treatment time). Fig. 6 shows an overview of mixture degradation in the integrated treatment. Overall mineralization efficiency of the combined system was 94%, of which 35.5% corresponds to the AOP and 58.5% to the aerobic biological treatment.

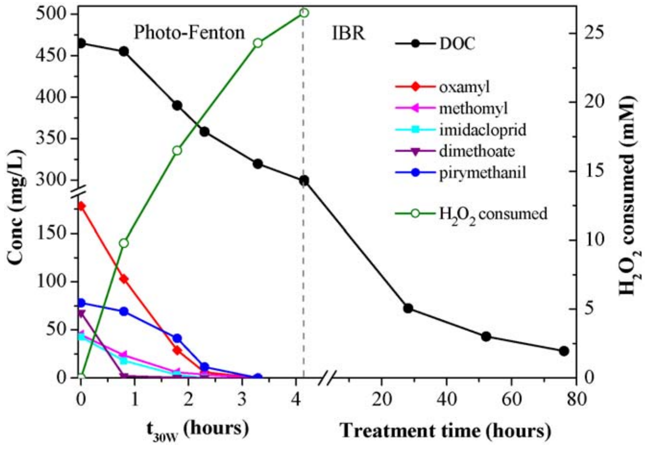

Fig. 6. Degradation of the pesticides and mineralization of the mixture by the combined system photo-Fenton/IBR at pilot plant scale. Hydrogen peroxide consumption during photo-Fenton process is also shown.

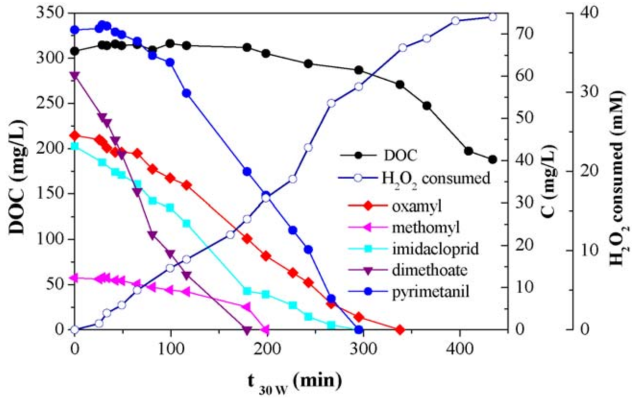

Fig. 7. Mineralization of the pesticide mixture ($DOC_0 = 320$ mg/L), pesticide degradation and H_2O_2 consumption during photo-Fenton applied after biological treatment.

Although the combination photo-Fenton/IBR system successfully degraded the mixture of pesticides, a second approach was tried to see which option was better. According to analyses of S1 (Fig. 5), 45% of biodegradability took place without any photo-Fenton pretreatment. As the formulations of commercial pesticides could contain biodegradable additives, the percentage of biodegradability of the untreated sample was not completely negative (45% biodegradability) and immobilized biomass systems are usually more robust than the suspended activated sludge, the treatments were also tested in the reverse combination at pilot plant scale (IBR/photo-Fenton). After 1 day of biotreatment, the original DOC was reduced 35% (320 mg/L of residual DOC). No biomass toxicity response to exposure to the mixture was observed. The concentrations of oxamyl and methomyl were dramatically reduced by 75% and 80% during the biotreatment to 40 and 10 mg/L, respectively, in 1 day, while the rest of the compounds remained constant in the solution. However, all these pesticides have been reported as non-biodegradable substances [18,19]. These results are discussed below. After adjusting the pH to 2.8, the partially degraded mixture was then treated by photo-Fenton at 20 mg/L of Fe^{2+} (Fig. 7). After 435 min of illumination time, only 120 mg/L of DOC were mineralized with a consumption of 40 mM of H_2O_2. The active ingredients were completely eliminated after 340 min of illumination time (twice as long as with photo-Fenton/IBR) and 30 mM of H_2O_2 was consumed (in the same range as photo-Fenton/IBR). But it can easily be concluded that to reach 28 mg/L DOC (reached at the end of photo-Fenton/ IBR) photo-Fenton treatment would have to be extremely long and a huge amount of H_2O_2 consumed. It was therefore very clear that the advantage in biodegradability enhancement achieved in the first approach (photo-Fenton/IBR) cannot be compensated in the second (IBR/photo-Fenton), as not only the non-biodegradable ingredients of the commercial pesticides must be removed by the AOP, but all the intermediates formed.

As mentioned above, the concentrations of oxamyl and methomyl were dramatically reduced during the biotreatment (in the second approach) to 40 and 10 mg/L. Oxamyl is known to be hydrolyzed at neutral pH [20]. In this case, the hydrolyzed product (oximino metabolite, $C_5H_{10}N_2SO_2$) was also detected and its concentration gradually increased although not at the same rate as oxamyl disappeared, and only 19% of the reduction was related to oxamyl hydrolysis. In view of these results, further biodegradability tests were performed. To study possible adaptation of the biomass to the active ingredients after long exposure to the pesticide-polluted water, another Z–W test was performed, but this time using biomass extracted from the IBR. Biodegradability was studied in two separate solutions of 200 mg/L of original DOC each (for consistent results in the Z–W) with Couraze (445 mg/L oxamyl) and Metomur (150 mg/L methomyl). The results are shown in Fig. 8a and b. The methomyl solution reached 70% biodegradability in 6 days of biotreatment, while oxamyl reached 60% in 28 days. Both compounds completely disappeared from the

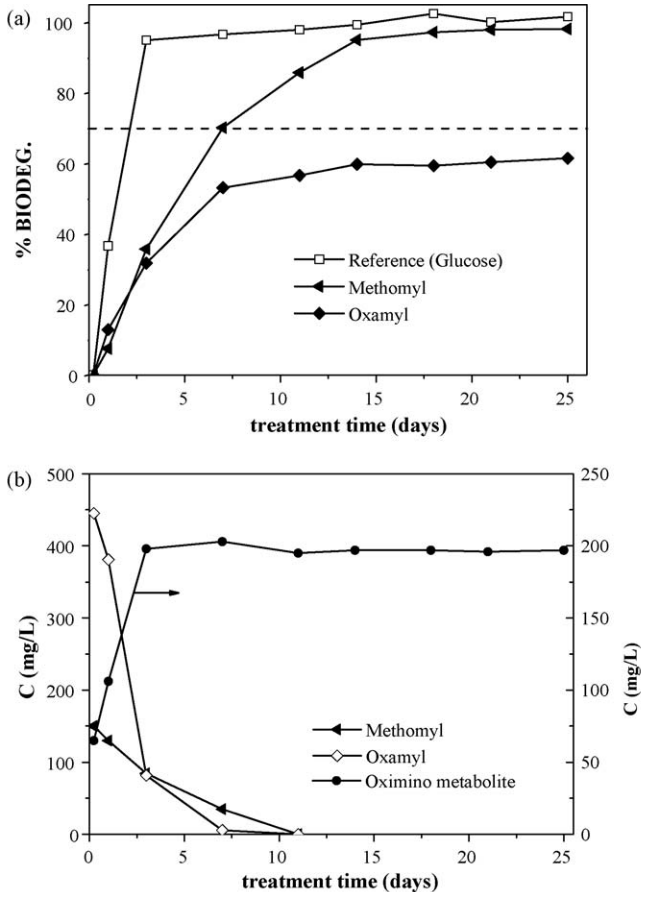

Fig. 8. (a) Zahn–Wellens (Z–W) biodegradability analysis of oxamyl and methomyl solutions (DOC: 200 mg/L). (b) Oxamyl, methomyl and oximino metabolite concentration during Z–W test.

initial solutions after 12 days. It was found that 61% of the original oxamyl was hydrolyzed into the oximino metabolite after 3 days of Z–W test. However, the oximino metabolite remained in solution after 28 days. Therefore, 100% of methomyl and 39% of oxamyl had disappeared during the Z–W test with adapted biomass extracted from the IBR. To disregard any adsorption of methomyl or oxamyl on the biomass, an extraction was performed using acetonitrile, but neither oxamyl nor methomyl were detected in the extracted solution. It may therefore be stated that oxamyl and methomyl (non-biodegradable compounds by conventional activated sludge) can be biodegraded by specifically adapted biomass.

3.2.2. Industrial scale

After the preliminary tests, the combined photo-Fenton/IBR system was reproduced in an up-scaled system designed from the pilot plant results to prove the feasibility of the technology. The commercial pesticide mixture and the experimental conditions (500 mg/L of initial DOC and 20 mg/L of Fe^{2+}) were maintained. The photo-Fenton treatment was also extended until complete degradation of the active ingredients (34% mineralization, 600 min illumination time and 20 mM of H_2O_2 consumed). Fig. 9 shows the degradation of the five active compounds, the mineralization of the mixture (reduction in COD and DOC) and the AOS during photo degradation over hydrogen peroxide consumption. As observed, the H_2O_2 required for complete elimination of the active ingredients is in the same range as in the pilot plant (20–25 mM) and the AOS curve is also positive. This proves that H_2O_2 consumption of a specific wastewater could be used as a reference parameter for controlling the most important factor of a combined photo-Fenton/biological system, the moment when the waste water reaches the desired purification (defined by certain DOC mineralization and disappearance of the key compounds) for transfer from the AOP to the biotreatment. It should be mentioned that H_2O_2 analyses are quick and easy and can be applied during normal operation of treatment plants.

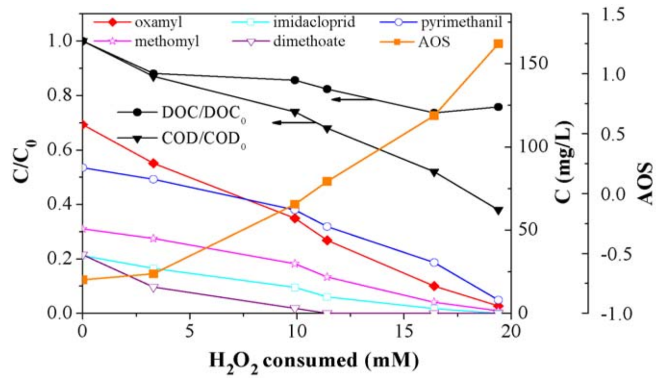

Fig. 9. Degradation and mineralization of the pesticide mixture (DOC_0 = 500 mg/L; COD_0: 1575 mg/L) over H_2O_2 consumed during the photo-Fenton treatment at industrial scale and the AOS curve during the photo-Fenton process.

This effluent was discharged into the IBR (after adjusting the pH to around 7). The water was slightly diluted with fresh water during operation (draining the solar collector field and adjusting the pH). The starting conditions of the water before biotreatment were 280 mg/L of DOC and 465 mg/L of COD. After 5 days of biotreatment, DOC was reduced 71% (80 mg/L of final DOC). The efficiency of the industrial-scale combined system was 84%, 35% corresponding to the photo-Fenton treatment and 49% to the biological stage. Results are summarized in Fig. 10.

Although the pesticide mixture was successfully degraded in both combined systems, two points deserve special mention in the industrial plant experiments. First, photo-Fenton degradation was much slower (600 min compared to 250 min illumination time for the elimination of the active ingredients at pre-industrial and pilot plant scale, respectively). This significant increase in the illumination time can be attributed to:

(i) Water in the industrial plant was salty (around 2 mS/cm) groundwater, and the effect of salts on the photo-Fenton reaction rate is well known [21,22].
(ii) The temperature in the photoreactor of the industrial plant was around 20 °C, in winter in South-Spain, which was much lower

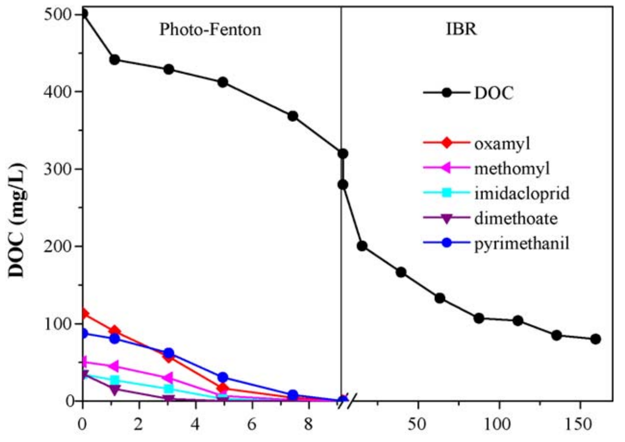

Fig. 10. Pesticide degradation and mineralization of the mixture by the industrial-scale combined photo-Fenton/IBR system (DOC_0: 500 mg/L, 20 mg/L Fe^{2+}).

than at pilot plant scale (operated at 35 °C). It is well-known that photo-Fenton is faster at 35 °C than at 20 °C [23,24].

Another fact is that industrial-scale IBR efficiency in terms of DOC reduced per volume of sludge supports and time was considerably lower than in the pilot plant (50 versus 160 mg DOC reduced/day L of Pall Ring supports, respectively). This may be due to the difference in the bioconsortia formed in the two bioreactors, and also the higher salinity of the water in the industrial-scale plant. Moreover, biotreatment DOC reduction efficiency, expressed as DOC reduction per litre and day, was quite slow (40 mg DOC reduced/L day) compared to typical biotreament of municipal wastewater (250–300 mg DOC/L day). The behavior of biological systems may be influenced by many factors, but mainly by biomass adaptation, the source of feed waste water previously employed, the salt content and the type of compounds generated by the photo-Fenton treatment, that might be not as easy to biodegrade as found in the Z–W tests. The water partly treated by photo-Fenton was the only carbon source in both bioreactors. However, the biological treatment in the normal operation of the industrial plant, would have be enhanced by specific biomass adaptation to this particular waste water, which takes several months.

4. Conclusions

A strategy targeting the design of an industrial-scale combined solar photo-Fenton/aerobic biological system for the decontamination of biorecalcitrant wastewater has been described. It is recommended that for adequate design of this type of treatment, a detailed study be done in each particular case using different analytical tools and bioassays, mainly DOC, COD, toxicity and biodegradability. It has been demonstrated that the H_2O_2 dose is a critical parameter for design and control of operation of the combined system.

It is important to notice the wide difference in efficiency found in the biological treatment stage when the integrated system was scaled-up. This highlights how decisive and restrictive (for the treatment of very specific and variable wastewater), start-up and growth can be in implementing a new biological reactor, even more so when the biotreatment is performed in an immobilized biomass reactor which is much more resistant than a conventional sequencing batch reactor. Therefore, even small modifications in microorganism populations already developed in an IBR could be extremely difficult and time consuming, and in some cases could require re-inoculation of the whole biological system. These results highlight the limitations of the results obtained in small laboratory devices and working with model wastewaters to design a proper treatment.

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