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Decontamination of industrial wastewater containing pesticides by combining large-scale homogeneous solar photocatalysis and biological treatment

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ABSTRACT

This work evaluates the technical feasibility of large-scale combined solar photo-Fenton/aerobic biological treatment targeting the treatment of a real industrial wastewater polluted with commercial pesticides. Photo-Fenton experiments were carried out under sunlight in a CPC-based plant (150 m^2 of solar collectors and the total photo-reactor volume 1060 L). The biological reactor was an immobilized biomass reactor (IBR, 2× 1230 L) filled with Pall®Ring supports colonized by activated sludge from a municipal wastewater treatment plant. The first study performed was focused on the decontamination of wastewater containing a selected mixture of five commercial pesticides (Vydate®, Metomur®, Couraze®, Ditimur-40® and Scala®) at 500 mg/L of initial dissolved organic carbon (DOC). Real wastewater containing pesticides was tested at two different initial DOCs (200 and 500 mg/L). The solar photo-Fenton was always performed in batch mode at pH adjusted to 2.8 and with 20 mg/L of Fe^{2+}, while the biological reactor was operated both in batch and continuous mode. Mineralization was followed by measuring DOC and chemical oxygen demand (COD) and the composition of the real wastewater was determined by liquid chromatography electrospray time-of-flight mass spectrometry (LC-TOF-MS). It has been demonstrated that photo-Fenton is able to enhance biodegradability of real wastewaters containing biorecalcitrant compounds at concentrations up to 500 mg/L but it has been also pointed out that the process should be optimized by a proper selection of treatment time and H_2O_2 dose.

1. Introduction

The recent growth of intensive agriculture in the Mediterranean basin has not only caused the high consumption of scarce fresh water resources, but also water pollution due to the presence of pesticides. These substances, though often chemically stable and recalcitrant, are not eliminated in conventional water treatments and represent a threat to both public health and the environment due to their persistence and long term toxicity. Consequently, they have been designated as priority substances (PSs) in EU legislation [1]. With this regulation, the EU intends to ensure the correct use and discharge of said substances in order to minimize their harmful environmental impact. However, this type of contamination is not yet controlled and there is a need for the development and optimization of feasible technologies to solve the problem.

It is well known that advanced oxidation processes (AOPs) are effective methods for eliminating these compounds [2,3]. Moreover, the integration of a preliminary solar AOP and a conventional biotreatment has been described as an economically and effective option to reduce the high operation costs of the AOPs [4,5]. However, there are no large-scale industrial applications as it is such a novel process but very attractive combined systems have recently been proposed to treat different kinds of industrial wastewater [6–10]. This work evaluates the technical feasibility of large-scale combined solar photo-Fenton/aerobic biological treatment targeting the treatment of a real industrial wastewater polluted with commercial pesticides. This technology has been tested in ALBAIDA RESIDUOS S.L., a company that selectively collects the empty plastic pesticide containers used in the greenhouses of the area of El Ejido (Spain) for recycling (around 2 million containers per year, corresponding to 30,000 ha of greenhouses). These containers are shredded and washed, producing water contaminated with pesticides which has usually been treated by solar photo-Fenton since the start-up of the plant in 2004 [11]. This photocatalytic plant has recently been upgraded, including the combination of

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photo-Fenton and biotreatment start-up, and the first results are presented here. The goal is to increase the treatment capacity of the plastic recycling plant and, therefore, it is necessary to increase the wastewater treatment facility through a proper combination of photo-Fenton and biotreatment. With this procedure, it will also be possible to recycle the water inside the plant. The quality attained after the biotreatment should be enough for reusing the water for plastic washing. Therefore, the start-up and operation of the combined system with model wastewater and real wastewater with different contaminant loads, jointly with the operation of the bioreactor in batch and continuous mode, is presented here.

2. Experimental

2.1. Chemicals

The photo-Fenton experiments were performed using $FeSO_4{\cdot}7H_2O$, reagent-grade hydrogen peroxide (30%, w/v) and sulfuric acid (96%, w/v) for pH adjustment, all purchased from Panreac. Diluted solutions of H_2SO_4 (96%) and NaOH (60%), both from Panreac, were used from the pH control in the IBR.

2.2. Analytical determinations

Mineralization was followed by measuring the dissolved organic carbon (DOC) through direct injection of filtered samples into a Shimadzu-5050A TOC analyzer with an NDIR detector. Total iron concentration was monitored by colorimetric determination with 1,10-phenanthroline, according to ISO 6332, using a Unicam-2 spectrophotometer. Hydrogen peroxide was analyzed through a spectrophotometric method using ammonium metavanadate, according to the technique proposed by Nogueira et al. [12]. Chemical oxygen demand (COD) was measured with Merck® Spectroquant kits (ref. 14541). Ammonium concentration was determined with a Dionex DX-120 ion chromatograph equipped with a Dionex Ionpac CS12A 4 mm × 250 mm column. Anion concentrations (NO_3^- and NO_2^-) were determined with a Dionex DX-600 ion chromatograph using a Dionex Ionpac AS11-HC 4 mm × 250 mm column. The composition of the real wastewater was determined by a rapid, automated screening method for determining pesticide using liquid chromatography electrospray time-of-flight mass spectrometry (LC-TOF-MS) based on the use of an accurate-mass database (ca. 300 compounds in 20 min) [13]. The high-performance liquid chromatography (HPLC) system (consisting of vacuum degasser, autosampler, and a binary pump) (Agilent series 1100, Agilent Technologies, Santa Clara, CA) was equipped with a reversed-phase XDB-C18 analytical column of 4.6 mm × 50 mm and 1.8 μm particle size (Agilent Technologies, Santa Clara, CA). This system was connected to a time-of-flight mass spectrometer Agilent MSD TOF (Agilent Technologies, Santa Clara, CA) equipped with an electrospray interface operating in the positive ion mode. LC-MS accurate-mass spectra were recorded across the range of 50–1000 m/z. Solid-phase extraction using Oasis™ HLB cartridges was applied before chromatographic analysis.

2.3. Experimental set-up

2.3.1. Solar reactor

Photo-Fenton experiments were carried out under sunlight in a CPC-based plant, installed in the ALBAIDA company facilities in Almeria. Fig. 1 shows a view of the solar collector field. It consists of 4 parallel rows of 14 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 the total photo-reactor volume is 1060 L. A schematic diagram of the plant has recently been published [14]. The 14 modules in each row are connected in series so the water flows from one module to another and finally to a tank. As the CPCs have a concentration factor of approximately 1 and there is no thermal insulation, the maximum temperature reached inside the photo-reactor is around 40 °C. Batch mode treatments handle between 1500 and 2000 L each run.

Fig. 1. View of one of the rows of the solar collector field.

The real industrial wastewater generated in the washing of commercial pesticide containers in ALBAIDA has a heterogeneous nature (variable DOC, ionic concentration and pesticide content). The wastewater was collected and stored (approximately 1200 L of wastewater per 1000 kg of plastic containers, corresponding to an initial rate of DOC between 200 and 500 mg/L). For the decontamination of this wastewater, batches of 2000 L were treated by photo-Fenton in the solar reactor. This volume of water was added in the photocatalytic plant and homogenized by turbulent recirculation for half an hour. Then, the pH was adjusted to 2.7–2.9 and iron salt was added (20 mg/L of Fe^{2+}). The last step was the addition of hydrogen peroxide, starting, at that moment, the photo-Fenton reaction. Hydrogen peroxide was measured frequently and consumed reagent was continuously replaced until the desired mineralization was reached. The photo-treated effluent was then discharged in a tank of 5000 L for neutralizing its pH before the biological treatment. This tank received the water from several batches of the photocatalytic plant and it was used as a water source for the biological reactor.

2.3.2. Biological system

The selected biological reactor was an immobilized biomass reactor (IBR). The plant is comprised 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 from a conventional, municipal wastewater treatment plant (1230 L each tank), centrifugal pumps, air blowers, two dosing pumps (H_2SO_4 and NaOH), tubing and valves (see Fig. 2). In the conditioner tank, dissolved oxygen concentration (DO) and pH are measured online using CRISON electrodes (6050 and 55,026, respectively) and automatically controlled, with a range of 4–6 mg/L for DO and 7–7.5 for pH. The system can be operated in batch or continuous mode. In batch mode (valves 1 and 2 are closed), the partially photo-treated water (pH previously adjusted to 7 in the neutralization tank) is charged in the conditioner tank and it is maintained in the system with a constant recirculation flow between the two IBRs and the conditioner tank until achieving the desired point in the biological treatment. The recirculation flow rate was set to 1500 L/h with flow control (FC) “a”. In continuous mode, the photo-treated water is charged and neutralized in the neutralization tank. In this case, valves 1 and 2 must be open

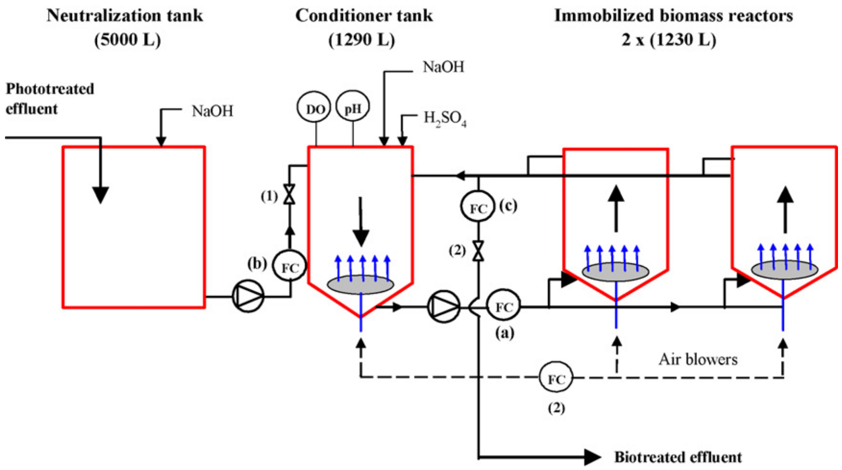


Fig. 2. Flow diagram of the biological system.

at the same flow (flow control b and c) in order to reach the stationary state. In this study, the inlet and outlet flow were fixed at 120 L/h and the hydraulic residence time (t_R) was 20 h, taking into account the maximum capacity of the biological system. The t_R is the relation between the total volume of the system (2500 L) and the flow rate (120 L/h). The bioreactor was operated after a gradual adaptation period of the biomass to the photo-treated pesticide effluent. Start-up of the biological reactor began with immobilization of the sludge on the ring supports. For this aim 50 L of activated sludge from conventional wastewater treatment plant, 100 L of raw water and certain amount of mineral solution were added to the bioreactor. After 2 days of recirculation in batch mode at 1500 L/h, the biomass was completely fixed on the supports, according to suspended solids control.

3. Results and discussion

The first study performed in the described installation (combination of photo-Fenton and biological treatment) was focused on the decontamination of wastewater containing a selected mixture of five commercial pesticides: Vydate® (10%, w/v oxamyl, $C_7H_{13}N_3O_3S$, 47.7 g DOC/L), Metomur® (20%, w/v methomyl, $C_5H_{10}N_2O_2S$, 360 g DOC/L), Couraze® (20%, w/v imidacloprid, $C_{16}H_{22}ClN_3O$, 395 g DOC/L), Ditimur-40® (40%, w/v dimethoate, $C_5H_{12}NO_3PS_2$, 500 g DOC/L) and Scala® (40%, w/v pyrimethanil, $C_{12}H_{13}N_3$, 285 g DOC/L). This model wastewater was used for plant start-up and commissioning, due to our previous experience with this mixture at pilot plant scale [15]. According to this work, the minimum requirement for successful disposal of the wastewater from chemical pre-oxidation (photo-Fenton) to biological post-treatment was the elimination of the active pesticide ingredients, as was also demonstrated by toxicity (*Vibrio fischeri* tests) and biodegradability assays (Zahn–Wellens test). Coming back to the first experiment performed in ALBAIDA photo-Fenton/biological treatment plant, the conditions of the simulated water before the photo-Fenton process were 500 mg/L of initial DOC (20% from each commercial pesticide: 180 mg/L oxamyl, 45 mg/L methomyl, 43 mg/L imidacloprid, 68 mg/L dimethoate, 80 mg/L pyrimethanil, dissolved in tap water from ALBAIDA installations) and 20 mg/L of Fe^{2+}. The photo-Fenton treatment was extended until the total degradation of the active ingredients (34% of mineralization, 330 mg/L of DOC, 20 mM of H_2O_2 consumed). This effluent was then discharged into the IBR (after adjusting the pH to around 7). The water was slightly diluted with fresh water during operational procedures (draining from the solar collector field and pH adjustment). The dilution was mainly provoked by the fluxing of CPC tubes to guarantee the complete disposal of the treated wastewater to the neutralization tank. The initial conditions of the water before biotreatment were 250 mg/L of DOC and 465 mg/L of COD. After 6 days of biotreatment in batch operation, 160 mg/L of the initial DOC was reduced (the final DOC was 80 mg/L). Fig. 3 summarizes results of the pesticide mixture degradation and DOC elimination during the combined chemical and biological treatment. In addition, the global efficiency of the combined system in terms of DOC reduction was 84, 34% corresponding to the photo-Fenton treatment and 50% to the biological stage.

In Fig. 3 the average oxidation state (AOS) is also shown. During any AOP treatment, AOS usually increases as a function of treatment time and attains almost a plateau after a certain time. These results suggest that more oxidized organic intermediates are formed at the beginning of the treatment and after a certain time the chemical nature of most did not vary substantially anymore, even if the AOP was prolonged [16]. The formation of more oxidized intermediates is an indirect indication of the ability of the treatment to improve biodegradability [17]. This parameter can be calculated as 4 × (DOC − COD)/DOC [18], in which DOC and COD are expressed in moles of C/L and of O_2/L, respectively, at the sampling time. In Fig. 3, AOS increased gradually throughout the experiment, which means that the organic content of the wastewater (initially containing five commercial pesticides) was gradually more and more oxidized. The photo-Fenton process was stopped before reaching a stable AOS with regard to biodegradability tests and taking into

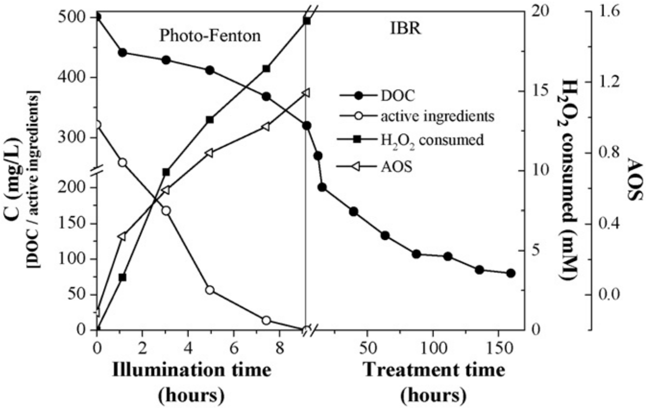


Fig. 3. Degradation of the pesticides and mineralization of the mixture by the combined system photo-Fenton/IBR at pre-industrial scale (DOC_0: 500 mg/L). Hydrogen peroxide consumption and average oxidation state (AOS) evolution during photo-Fenton process is also shown.

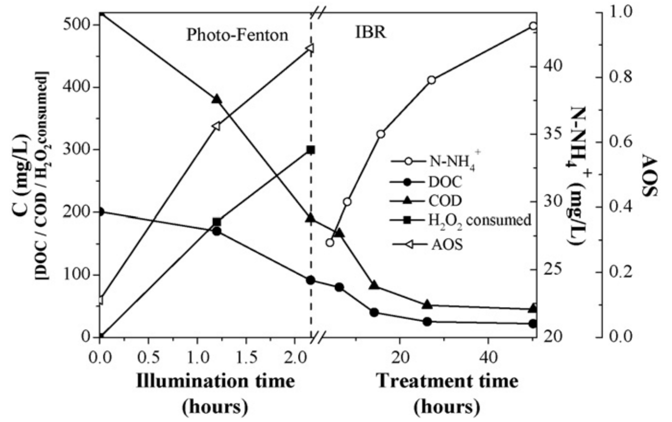


Fig. 4. Mineralization of the real wastewater (DOC and COD), H_2O_2 consumed, AOS evolution and $N–NH_4^+$ concentration in the combined system photo-Fenton/IBR (DOC_0: 200 mg/L; 20 mg/L Fe).

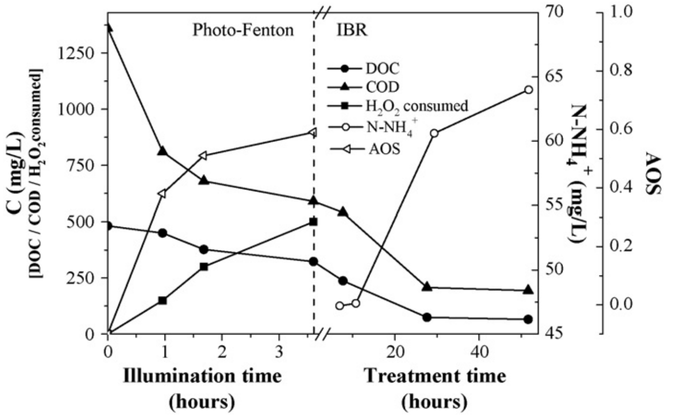


Fig. 5. Mineralization of the real wastewater (DOC and COD), H_2O_2 consumed, AOS evolution and $N–NH_4^+$ concentration in the combined system photo-Fenton/IBR at pre-industrial scale (DOC_0: 480 mg/L; 20 mg/L Fe).

account that the AOP treatment time should be minimized to optimize the cost of the overall process. Regarding the former results, different considerations were taken into account for treating real wastewater produced from the washing of pesticide containers: (i) biodegradability was enhanced when active ingredients of the pesticides were removed but the remaining DOC exhibited a low biodegradation rate (160 mg/L of DOC was mineralized in 6 days) and (ii) the composition of the real wastewater is so variable that it is very difficult to adjust the initial dose of H_2O_2 to carry out the photo-Fenton process until complete degradation of the active ingredient is attained. Consequently, it was decided to adopt a compromise solution and to extend photo-Fenton treatment to a larger mineralization degree in order to ensure pesticide degradation and to increase the biodegradability of the remaining DOC in order to increase the biodegradation rate. It was also decided to compare the operation of the combined treatment at two different initial DOCs, in order to determine any advantage concerning treatment time between both alternatives. It is necessary to comment that wastewater is produced from washing empty pesticide containers and, therefore, initial DOC could be controlled by washing more or less containers per batch. Therefore, the proposed strategy for the combined system was: extending the photo-Fenton process until 40–50% of mineralization before discharging the partially oxidized solution in the IBR. The solar photo-Fenton was always performed in batch mode at pH adjusted to 2.8 and with 20 mg/L of Fe^{2+}, while the biological reactor was operated both in batch and continuous mode, as commented below.

Two different sets of experiments in the combined system were performed operating both photo-Fenton and IBR in batch mode with different initial DOC content (approximately 200 and 500 mg/L). In the first case ($DOC_0 = 200$ mg/L), 54% mineralization was achieved in the photo-Fenton process, with a H_2O_2 consumption of 9 mM. The DOC of the photo-Fenton effluent was 92 mg/L and the concentrations of $N–NH_4^+$ and $N–NO_3^-$ were 25 and 5 mg/L, respectively. The photo-treated water was then discharged into the neutralization tank in order to adjust the pH to around 7 before the biological step. After 26 h of biotreatment, the DOC was reduced to 25 mg/L, attaining 22 mg/L after 48 h and 18 mg/L after 120 h. This means that continuing the biotreatment after the first day was not so efficient. However, nitrification was not achieved and there was an accumulation of $N–NH_4^+$ in the system (45 mg/L at the end of the process), the $N–NO_3^-$ remained constant (4.5 mg/L $N–NO_3^-$) and no $N–NO_2^-$ was detected. This problem and the possible solutions are later discussed in the text. The overall efficiency of DOC removal in the combined system was 89% (54% corresponding to the photo-Fenton process and 35% to the biological step). Fig. 4 shows the mineralization of the wastewater in the combined system, the H_2O_2 consumed, the AOS evolution and the concentration of ammonium during the biological step. It is necessary to note the enhancement attained in the biotreatment process, as a higher percentage of DOC was removed in IBR in a shorter time, compared with the results with model wastewater containing five pesticides shown in Fig. 3. It could be justified as a consequence of a longer photo-Fenton treatment (until 50% mineralization), but with the initial concentration being different ($DOC_0 = 200$ mg/L, compared with 500 mg/L in the model wastewater containing five pesticides), this statement should be reinforced with real wastewater experiments at 500 mg/L as follows.

In the second set of experiments (DOC_0: 480 mg/L) the DOC was reduced to 300 mg/L in the photocatalytic step (37.5% mineralization) with 15 mM of H_2O_2 consumed (see Fig. 5). The concentrations of $N–NH_4^+$ and $N–NO_3^-$ in the photo-Fenton effluent were 50 and 10 mg/L, respectively. It is interesting to note that using a similar H_2O_2 dose that, in the experiment with simulated wastewater containing five pesticides, a higher mineralization was attained. Therefore, it means that the organic content of the real wastewater contained less persistent contaminants than the model wastewater. The neutralized mixture was treated in the bioreactor, and after 5 days the final DOC was 52 mg/L but after only 1.5 days the DOC was 75 mg/L. Similar to the experiment with DOC_0 around 200 mg/L, continuing the biotreatment after 2 days did not improve the efficiency outstandingly. Again, the process of nitrification did not occur, finishing with a higher ammonia concentration in the system outlet (78 mg/L of $N–NH_4^+$; 11 mg/L $N–NO_3^-$). The increase of ammonium concentration during the biological process can be explained because the heterotrophic biomass is able to transform some amines (commonly present in the photo-treated samples due to the nitrogenous pesticide nature) into ammonium, which accumulates in the bioreactor outlet due to the absence of nitrifying bacteria. Therefore, the reason why the nitrification process did not take place might be that the IBR was not properly colonized by nitrifying bacteria. This highlights the fact that the biomass must be progressively and carefully acclimated before introducing the partially treated effluent by photo-Fenton. In this case, the overall efficiency of the coupled system, in terms of initial DOC elimination, was 84% (37.5% photo-Fenton and 46.5% IBR) after 2 h of photo-Fenton and 1.5 days of biotreatment, respectively. The enhancement attained in biotreatment time compared with the results shown in Fig. 5 was around 5 days. These results reinforce the importance of AOS, as in this case (compared with the results shown with the model wastewater containing five pesticides) the AOS stabilized during the photo-Fenton process and

Table 1
Main pesticides detected in real wastewater sample by LC-TOF-MS using an accurate-mass database.

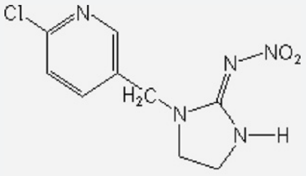
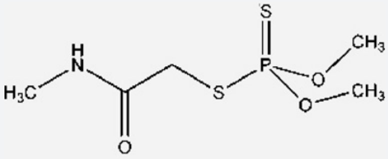
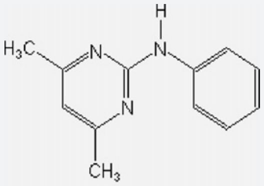
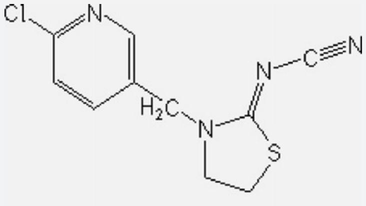
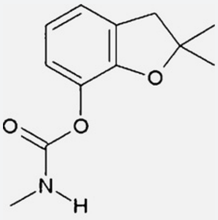
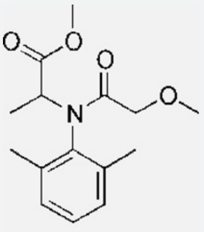
Compound	R_t (min)	Experimental mass $[M-H]^+$	Calculated mass $[M-H]^+$	Error (mg/L)	Score	Initial conc. (μg/L)	% Reduction (in photo-Fenton)	% Reduction (combined system)
 **Imidacloprid** $C_9H_{10}ClN_5O_2$	6.40	255.0525	255.0523	0.61	92.43	695	89.2	96.4
 **Dimethoate** $C_5H_{12}NO_3PS_2$	6.56	228.9995	228.9996	−0.42	94.59	877	85.2	99.4
 **Pyrimethanil** $C_{12}H_{13}N_3$	8.29	199.1113	199.1109	1.7	93.98	850	26.2	42.7
 **Thiacloprid** $C_{10}H_9ClN_4S$	7.32	252.0241	252.0236	1.78	95.24	563	69.8	84.2
 **Carbofuran** $C_{10}H_{12}O_2$	8.43	164.0836	164.0837	−0.74	98.4	168	71.4	100
 **Metalaxyl** $C_{15}H_{21}NO_4$	8.85	279.1473	279.1471	0.77	90.9	192	71.4	100

Table 1 (*Continued*).

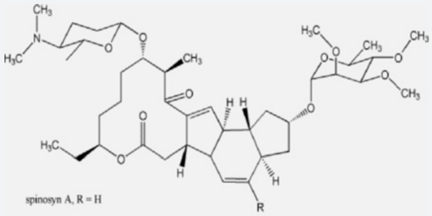
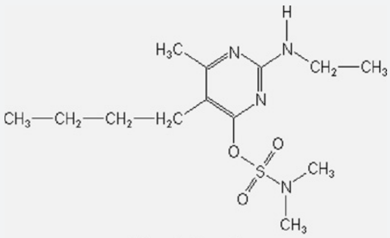
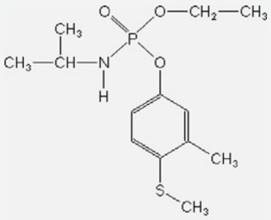
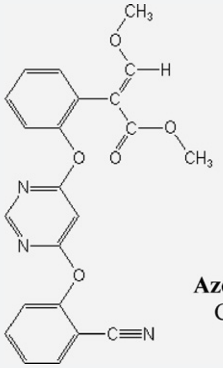
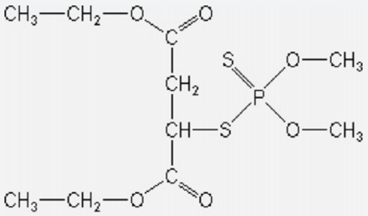
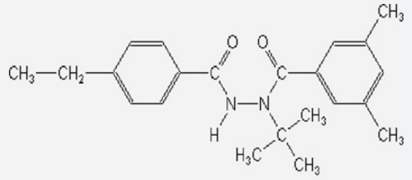
Compound	R_t (min)	Experimental mass $[M-H]^+$	Calculated mass $[M-H]^+$	Error (mg/L)	Score	Initial conc. (μg/L)	% Reduction (in photo-Fenton)	% Reduction (combined system)
 **Spinosyn A** $C_{41}H_{65}NO_{10}$	9.14	731.4604	731.4608	−0.67	88.79	140	62.9	100
 **Bupirimate** $C_{13}H_{24}N_4O_3S$	9.44	316.1562	316.1569	−2.33	88.86	38	71.1	100
 **Fenamiphos** $C_{13}H_{22}NO_3PS$	10.04	303.1057	303.1058	−0.34	89.76	36	66.7	100
 **Azoxystrobin** $C_{22}H_{17}N_3O_5$	10.14	403.1172	403.1168	0.84	96.21	491	73.3	99.4
 **Malathion** $C_{10}H_{19}O_6PS_2$	10.75	330.0362	330.0361	0.31	94.1	1065	83.3	100

Table 1 (*Continued*).

Compound	R_t (min)	Experimental mass [M−H]$^+$	Calculated mass [M−H]$^+$	Error (mg/L)	Score	Initial conc. (μg/L)	% Reduction (in photo-Fenton)	% Reduction (combined system)
 **Tebufenozide** $C_{22}H_{28}N_2O_2$	11.05	352.2225	352.2224	0.4	70.59	74	63.5	100

therefore the biotreatment of the wastewater pre-oxidized by photo-Fenton was easier. Considering the DOC removal, the treatment time and the H_2O_2 consumption, it can be stated that the best option would be to start the treatment at the higher DOC (DOC_0 around 500 mg/L). In this case, the higher time required for photo-Fenton is proportional to the organic content removed but the H_2O_2 is used more efficiently (9 mM and 15 mM for 200 and 500 mg/L of DOC, respectively), the biotreatment time being similar in both cases (main DOC elimination during the first 24 h). Furthermore, it is very important to notice how the accumulation of N–NH_4^+ during both biological treatments (40 and 60 mg/L, respectively) present a toxic effect on the DOC elimination by drastically reducing the organic load biodegradation rate in the following hours.

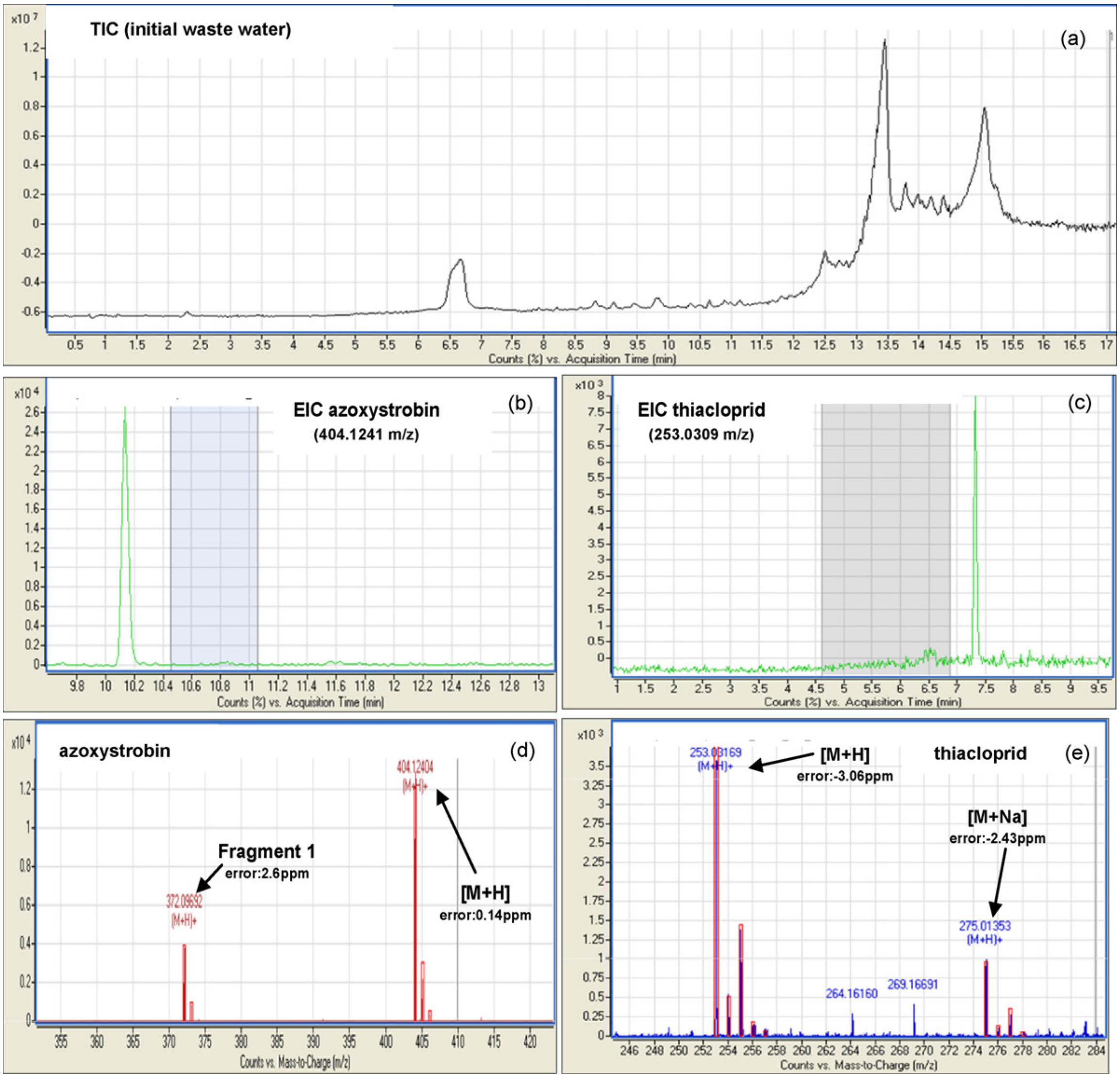


Fig. 6. Screening pesticides in initial sample of real wastewater by LC-TOF-MS: (a) total ion chromatogram; (b) extracted ion chromatogram of azoxystrobin; (c) extracted ion chromatogram of thiacloprid; (d) accurate-mass spectra of azoxystrobin (R_t 10.14 min); (e) accurate-mass spectra of thiacloprid (R_t 7.32 min).

In the experiment with the highest organic load (DOC$_0$: 480 mg/L), the identification and quantification of the pesticides present in real wastewater was performed, during the combined system, by liquid chromatography with a time-of-flight mass spectrometry detector (LC-TOF-MS) based on the use of an accurate-mass database. Three samples were taken and analyzed during the photo-Fenton process: initial (phF 1, DOC: 480 mg/L), intermediate (phF 2; DOC: 375 mg/L, 9 mM H_2O_2 consumed) and final (phF 3; DOC: 300 mg/L, 15 mM H_2O_2 consumed); and two during the biological treatment: initial (IBR 1; DOC: 280 mg/L) and final (IBR 2; DOC: 75 mg/L).

Recently, several multi-residue methods have been developed and are being used to detect the presence of many contaminants (ca. pharmaceuticals and/or pesticides) at low levels in the environment [19–21]. In this context, LC-TOF-MS has demonstrated to be a powerful tool for the identification of trace compounds of complex matrices and/or for confirming their presence based on accurate-mass measurements [22,23]. The most important characteristic of this analytical technique is that the accurate-mass determination allows us to obtain specific information for a given molecule plus an additional confirmation if more fragments are present in the spectra.

In this work, we used a rapid automated screening method developed by Mezcua et al. [13] to verify the presence of 300 compounds in less than 20 min. Therefore, after chromatographic analysis the samples were processed with the database-searching tool of the software (Qualitative Mass Hunter). For this purpose, two steps were performed: (1) the extraction of the compounds (molecular feature extraction) from the raw data (full-scan TOF-MS positive ion mode spectra) and (2) a database search. The first process is a search for compounds by molecular feature controlling some parameters (peak filter and relative abundance). The second step is to identify and search for the presence of target compounds in the sample. In this step the csv Excel file created is employed as a database. The defined search criteria are accurate-mass tolerances and retention time tolerance.

Twelve active ingredients in diverse concentration ranges were identified in the initial sample of the real wastewater (see Table 1). Total ion chromatogram (TIC) of initial real wastewater and extracted ion chromatogram (EIC) of two pesticides present in the matrix, are shown in Fig. 6(a). Azoxystrobin mass spectra show the $[M+H]^+$ and "Fragment1" at m/z 404.1168 and m/z 371.0896, respectively. Ferrer and Thurman [24], identified this "Fragment1" as a particular azoxystrobin fragment that offers specific information useful for an unequivocal confirmation of this pesticide. A similar situation was observed for thiacloprid that presented two signals in mass spectra. The first one at m/z 275.01353 attributed to the sodium adduct and the second one at m/z 253.03169 that corresponds with the protonated molecule $[M+H]^+$. Moreover, thiacloprid presents Cl and S atoms in its elemental composition ($C_{10}H_9ClN_4S$). In this case, the isotope signature of the compound is useful for a quick check and partial confirmation of the formula, especially since most pesticides show an interesting A+2 ion from a halogen or sulfur atom [25].

Three pesticides identified by LC-TOF-MS in real wastewater were contained in the model mixture previously studied (imidacloprid, dimethoate and pyrimethanil, see Fig. 7). The evolution of the concentration of pesticides during the different stages of the combined process is shown in Fig. 7. The differences between the samples phF 3 and IBR 1 are due to the change in pH (from 2.8 to 7.5).

As it can be observed, the concentration of all the pesticides decreased gradually throughout the process (the greater part during the photo-Fenton process) and after the biological treatment, the majority were totally removed, except for two of them (pyrimethanil and thiacloprid), that were found in the range of µg/L. Table 1 shows the reduction of each pesticide (in percentage) in the photo-Fenton stage and in the integrated system. The reduction of the pesticides in the IBR may be due to the addition of two factors: the change in the pH and the possible adsorption of the compounds on the biomass, likely in an immobilized bioreactor where the biomass is forming biofilms.

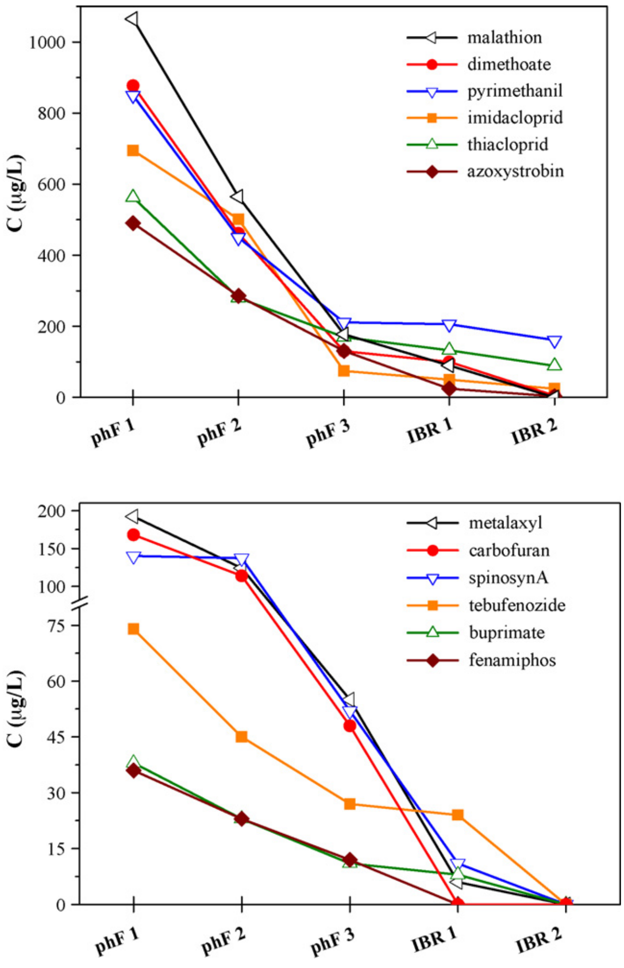


Fig. 7. Evolution of pesticide concentration in the real wastewater during the different stages of the combined system photo-Fenton/IBR.

The last step for evaluating the plant was operating the aerobic biological system in continuous mode, taking into account the results of the batch mode operation. Due to photo-Fenton plant size, more than one batch was necessary to have enough effluent to feed the bioreactor. Therefore, the effluents of two consecutive photo-Fenton runs were collected in a reservoir tank. The pH of the mixture was raised to 7 before the biological treatment. The total volume of the photo-treated solution was 3500 L and the DOC 190 mg/L. The influent flow rate to the IBR was set to 120 L/h (t_R = 20 h) taking into account the daily biological treatment capacity achieved in batch mode (165 mg DOC/day), the volume to be treated and the target of reducing 75% of the initial DOC (190 mg/L). Fig. 8 shows the system operating for 32 h in these conditions. As it can be observed, the bioreactor operation was kept stable during that time, reaching a constant 70% DOC reduction in the effluent with a residual DOC of 60 mg/L, which was highly similar to the intended target and therefore demonstrated the reliability of the results obtained in batch mode. It also confirms the consistency of the procedure followed for the design of the combined treatment. Therefore, the plant will continue operating in batch mode by photo-Fenton and in continuous mode by biotreatment using a

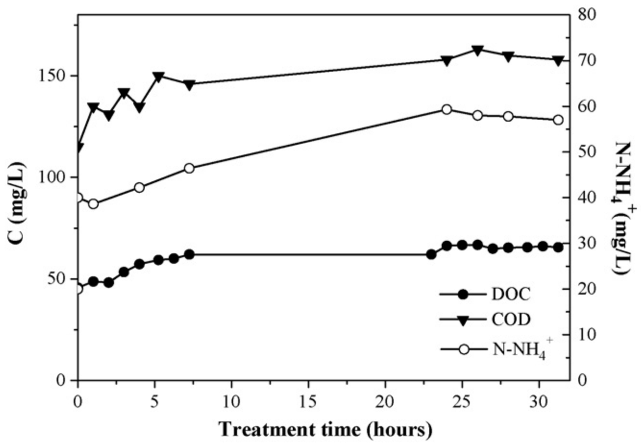


Fig. 8. Continuous operation of the IBR. Evolution of the DOC, COD and nitrogen from ammonium in the effluent after treatment.

reservoir tank in between both processes. Nevertheless, nitrification was not successful in the continuous operation mode (60 mg/L of N–NH_4^+ and 15 mg/L of N–NO_3^- in the treated effluent).

The results show that the combined system was able to eliminate the pesticides and reduce the DOC and COD (more than 80% mineralization) of the wastewater, being a feasible approach for the decontamination of such recalcitrant wastewaters. However, in this case, nitrification was not achieved during the biological step and there was an accumulation of nitrogen in the effluent (40–80 mg/L of N–NH_4^+ and 5–15 of N–NO_3^-), which occasionally exceeds the Spanish limits of permitted discharge (70 mg/L N: 50 mg/L of N–NH_3 and 20 mg/L of N–HNO_3) [26]. As it has been previously stated, this can be explained by considering that in the start-up of the bioreactor it was not fully colonized by nitrifying bacteria. Therefore, a strong effort should have been made to successfully develop the nitrifying population through a progressive and longer term adaptation process to high-ammonium concentrations, since nitrifying bacteria grows much slower than the heterotrophic population. Due to the nature of the wastewater, the content of nitrogen in the photo-treated water was very high, as nitrogen is commonly present in the structure of many pesticides and other constituents. For example, n-methyl pyrrolidone, n-methyl piperazine, or ammonium salts (as ammonium sulfate and ammonium thiocyanate) are additives commonly present in the commercial formulations of pesticides. The fact that the water that came into the bioreactor contained a considerable amount of NH_4^+ and NO_3^- (between 20 and 50 mg/L) may also inhibit the slender nitrifying bacteria present in the IBR by the excess of substrate and the presence of nitrification first stage products [27,28]. Nevertheless this problem is not critical, as the solution will be to perform the inoculation and start-up of the biological system again, considering the need for a longer and more gradual adaptation process to nitrogenous forms, permitting the growth of nitrifying bacteria. It has been demonstrated that, after a correct adaptation period of the biomass, aerobic biological systems are able to treat high-ammonium concentrations (between 200 and 300 mg N/L) without nitrifier inhibition [29–31]. Moreover, several immobilized biological systems (as fixed biofilms) have been demonstrated to be successful for carbon and nitrogen removal [32–35]. A re-inoculation of the biological reactor is being considered and further tests will be done in order to operate the combined system to obtain water more suitable to be discharged.

Another possible solution would be implementing a biological configuration focused on nitrogen removal. The conventional systems are the combination of aerobic/anoxic/anaerobic reactors for nitrification/denitrification. Moreover, there have been recent developments regarding novel nitrogen-removal technologies to treat high-ammonium level wastewaters, as the combination of nitritation and anaerobic ammonium oxidation (nitritation/ANAMMOX) [36] or shortcut biological nitrogen removal (SBNR) [37]. However, nitrogen removal is not the target of the present work. The key issue of this study is the operation of the photocatalytic stage until the upgrading of wastewater biodegradability. It has been demonstrated that with a proper selection of photo-Fenton process conditions, the organic content of the effluent could be upgraded until being biodegradable and therefore it could be biotreated on-site. In general, the objective of the AOP should be to convert the biorecalcitrant effluents into effluents compatible with any sewage system, usually with conventional municipal wastewater treatment plants.

4. Conclusions

It has been demonstrated that photo-Fenton is able to enhance biodegradability of real wastewaters containing biorecalcitrant compounds at DOC up to 500 mg/L but it has been also pointed out that the process should be optimized by a proper selection of treatment time and H_2O_2 dose.

Operational conditions should be selected in a suitable range (longer treatment time and higher H_2O_2 dose than the minimum pre-determined at lab scale or with model wastewaters) ensuring proper managing of real wastewaters of unpredictable composition.

This coupled technology can be applied in industrial plants with difficult access to the municipal sanitation and sewage system, making possible the direct discharge of the effluent or its reutilization in industrial facilities. On the other hand, the correct operation of the solar photo-Fenton systems could very often permit the disposal of the pretreated wastewater in conventional sewage systems.

This paper is also highlighting the importance of applying a consistent methodology for operating these systems, as each wastewater should be studied on a case-by-case basis.

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