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Integration of Solar Photocatalysis and Membrane Bioreactor for Pesticides Degradation

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Wastewater containing recalcitrant contaminants as pesticides can be treated by a coupled system which consists of a solar photo-Fenton pretreatment followed by a biological oxidation process. Membrane bioreactor technology (MBR) is particularly suitable for advanced biological treatment of wastewater containing biorecalcitrant compounds and shows a variety of advantages that make it a good alternative to be coupled with photo-Fenton, especially for water reclamation. In this sense, there is a lack of research about the integration of the photo-Fenton oxidation process with biodegradation in MBR. The aim of this work is to demonstrate the viability of the coupled system to treat toxic wastewater containing pesticides. The effluent obtained in the coupled system was high quality water ready to reuse, with low residual DOC concentration, absence of pesticides, absence of solids, and low turbidity values. The present study confirms that the combination of solar photo-Fenton and membrane bioreactors is an effective approach for the treatment of wastewaters polluted with pesticides, achieving carbon removal percentages higher than 95%.

Keywords activated sludge; advanced oxidation processes; membrane bioreactor; pesticides; photocatalysis; wastewater treatment

INTRODUCTION

In the last few decades, there has been a significant increase in the utilization of pesticides in the Mediterranean countries because of the increase of the intensive agriculture (greenhouses), in which the specific consumption by surface cultivated is two hundred times higher than the traditional agriculture (1). The use of these bio-recalcitrant substances contributes to water resources contamination because of their toxicity and non-biodegradability.

Wastewater containing these contaminants can be treated by Advanced Oxidation Processes (AOPs) achieving a complete mineralization. AOPs are based on the generation of hydroxyl radicals ($HO^{\cdot}$) to be used as an effective oxidant, with a higher potential than other classic oxidants like ozone or chloride (2,3,4). Even though AOPs are highly efficient, their operation is still quite expensive (tens €/m^3) compared with biological treatments (tens of cents €/m^3) (5).

An attractive alternative consists of a short pretreatment with an AOP, which converts the recalcitrant pollutants in biodegradable intermediates that can be degraded in a biological process, especially for the treatment of highly polluted wastewater (Fig. 1). This strategy reduces the overall costs of recalcitrant wastewater treatment. On the other hand, AOPs can be used as a finishing step when wastewater comprises of a high proportion of biodegradable organic carbon and low levels of recalcitrant compounds, thus bioreaction being the first stage of the integrated process (6). Combined processes of AOP and biodegradation depend on the physico-chemical properties of the raw water, and the operation schemes should be designed to address the AOP application for targeted compounds elimination (7).

Photo-Fenton has been demonstrated to be an effective AOP treatment to degrade contaminants (9,10,11,12). It is based on the Fenton reaction to generate $HO^{\cdot}$ radicals. Fe^{2+} can act as catalyst being regenerated by UV-vis radiation, which may be from the sun, reducing costs and increasing its environmental interest (10,13).

Regarding the biological treatment, membrane bioreactor (MBR) technology could be an excellent choice because it combines biological degradation with membrane filtration, and as a result improves on limitations of the conventional activated sludge treatment like the limited operational solids retention time (SRT) and the sludge settling characteristics (14).

In the last several years, a large number of studies have shown that membrane bioreactors (MBR) are particularly suitable for advanced biological treatment of wastewater containing emerging contaminants (ECs) (15) giving higher efficiencies compared with conventional activated sludge (16). The use of MBR for wastewater treatment increases the degradation of pollutants but sometimes the complete

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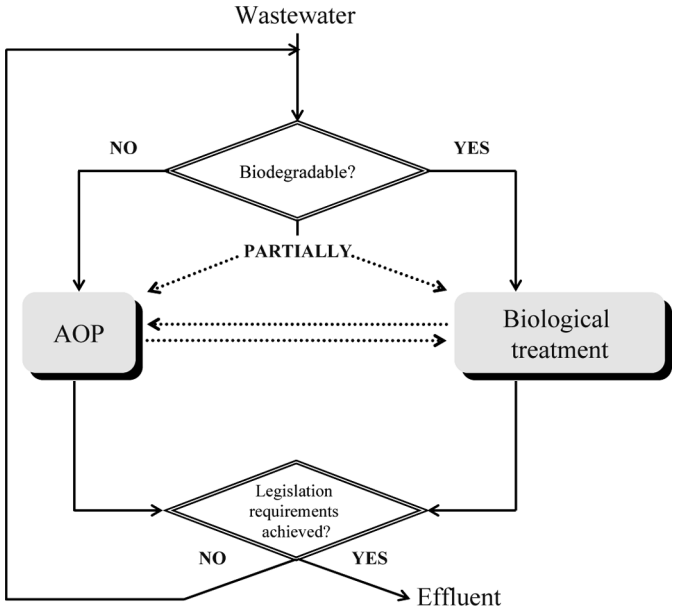

FIG. 1. General strategy of wastewater treatment (modified from Sarria et al. (8)).

biodegradation cannot be achieved. For this reason, degradation of recalcitrant pollutants must be carried out by AOPs in a previous step. The operational flexibility of both technologies allows their integration in combined processes resulting in optimized treatment performances.

Bernhard et al. (2006) studied persistent polar pollutants (P^3) degradation like pesticides, pharmaceuticals, insect repellents, flame-retardants or anionic surfactants in MBR and in activated sludge treatment (AST). The results confirm that wastewater treatment by MBR is more efficient than AST for the selected P^3. However, even under optimum adaptation conditions a complete degradation cannot be achieved in the MBR. New technologies like AOPs should be developed to prevent these contaminants entering the closed water cycles (16). Other authors confirmed C-removal rates improvement in MBRs with regard to classical treatments of different pollutants as pentachlorophenol (17), selected priority acidic pesticides (18), or different pharmaceutically active compounds (PhACs) belonging to different therapeutic groups as analgesics and anti-inflammatory drugs, antibiotics, lipid regulators, β-blockers, hypoglycaemic agents, and diuretics (14).

The most relevant advantage of MBR, compared to the classical activated sludge treatment, is the capacity to carry out biological treatment and disinfection of the effluent at the same time with an optimum control of biological degradation and a greater stability and flexibility in use (14,19–22). MBR also shows great ability to treat high strength wastes because MBR allows to work at higher solid retention time, increasing the capacity of degrading recalcitrant compounds (20), operating with high sludge concentration (23), and reducing sludge production (24). All these reasons make MBR a good alternative to be coupled with an AOP as photo-Fenton, especially for water reclamation.

Many studies have shown the potential of the AOP–biological coupled systems to treat different contaminants in wastewater from various sources (1,13,25–29). Nonetheless, there is a lack of research about the integration of the photo-Fenton oxidation process with biodegradation in MBR. The aim of this work is to demonstrate the viability of combining the photo-Fenton process with MBR to treat toxic wastewater containing a selected mixture of five commercial pesticides: Vydate®, Metomur®, Couraze®, Ditimur-40®, and Scala®. Two strategies for MBR operation were carried out: mixing the partially oxidized photo-Fenton effluent with a biodegradable synthetic wastewater and direct biotreatment of photo-oxidized pollutants without any additional carbon source.

MATERIALS AND METHODS

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. Analytical standards (>98%) for chromatographic analyses were purchased from Sigma-Aldrich. Water solubility of these compounds is 280 g L^{-1}, 25°C (oxamyl); 57.9 g L^{-1}, 25°C (methomyl); 0.61 g L^{-1}, 20°C (imidacloprid); 23.8 g L^{-1}, 25°C (dimethoate) and 0.121 g L^{-1}, 25°C (pyrimethanil).

Photochemical Reaction

Photo-Fenton experiments were carried out in a solar wastewater detoxification plant with compound parabolic collectors able to treat up to 50 L of water (2.25 m^2 irradiated surface, 22 L irradiated volume). Figure 2 presents a scheme of the coupled pilot plant, including both photo-Fenton and the membrane bioreactor, located at

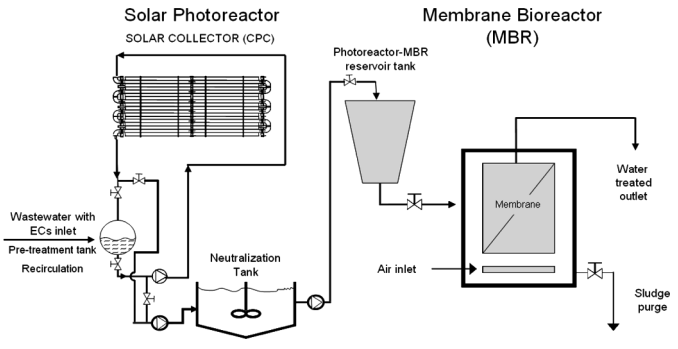

FIG. 2. Solar photoreactor-membrane bioreactor integrated system setup.

the Centro de Investigación de la Energía Solar (CIESOL, Almería, Spain).

The absorber tube has an internal diameter of 50 mm. UV radiation is measured by a global UV radiometer (KIPP&ZONEN, model CUV 3), mounted on a platform tilted 37°, which provides data in terms of incident UV ($W\,m^{-2}$). This gives an idea of the energy reaching any surface in the same position with regard to the sun. With Eq. 1, a combination of the data from several days' experiments and comparison of photoreactors installed at different sites is possible.

$$t_{30W,n} = t_{30W,n-1} + \Delta t_n \frac{UV}{30}\frac{V_i}{V_T}; \quad \Delta t_n = t_n - t_{n-1}; t_0 = 0 (n = 1) \tag{1}$$

where UV is the average solar ultraviolet radiation measured during Δt_n, t_n is the experimental time for each sample, V_T is the total volume of water loaded in the pilot plant (50 L), V_i is the total irradiated volume (22 L, glass tubes), and t_{30W} is a "normalized illumination time," which refers to a constant solar UV power of $30\,W\,m^{-2}$ (typical solar UV power on a perfectly sunny day around noon). All tests were performed at 30°C.

For the photo-Fenton reaction, the plant was loaded with 50 L of an aqueous solution of the five pesticides having a dissolved organic carbon concentration of $200\,mg\,L^{-1}$ corresponding to $\sim 40\,mg\,L^{-1}$ of DOC from each pesticide. At the beginning of the process, the collectors were covered, the pH was adjusted, and ferrous iron salt ($FeSO_4 \cdot 7H_2O$) was added. The pH was adjusted to 2.7–2.9 with H_2SO_4 and the Fe^{2+} concentration was $20\,mg\,L^{-1}$. The plant was well homogenized by turbulent recirculation after addition of each reagent.

Finally, $100\,mg\,L^{-1}$ hydrogen peroxide (reagent grade 33% w/v) was added. Then, the collectors were uncovered and the photo-Fenton reaction began. Hydrogen peroxide was measured frequently and the consumed reagent was continually replaced in order to reach the final mineralization percentage required.

Biological Treatment

Biological treatment with activated sludge was carried out in a 20-L working volume membrane bioreactor (MBR) provided with three A4 flat sheet membranes from Kubota Company with a pore size of 0.4 micrometers, built in polyethylene with a working filtering area of 0.1 square meters, giving a total filtration area of $0.3\,m^2$.

The 20-L MBR consists of a 55 cm deep cylindrical PVC tank with a 24 cm internal diameter covered by a PVC disk with ports for different probes. The MBR was provided with a pH probe (Crison 55 33), temperature and dissolved oxygen sensor (Mettler InPro6900/12/120), liquid (RS 508–2704) and gas (Omega FMA 5400/5500) flowmeters, a transmembrane pressure sensor (Delta OHM HD4V8 T), and a turbidity sensor (Hach Lange Ultraturb Plus SC100). During the course of the experiment all these parameters were registered online by a USB data acquisition card Labjack U12 (LabJack Corporation, Lakewood, CO).

Inside the MBR the aeration provides the oxygen necessary for the biological process and also provides the turbulence required to avoid solids settle and to keep clean the membrane due to the shear flow in the surface. The MBR was equipped with two aeration systems, one to keep the membranes clean and another to provide additional oxygen supply. The total air flow was $19\,L\,min^{-1}$, equivalent to 0.95 vvm. Membrane aeration was introduced through a perforated tube site at the bottom of the reactor with a flow of $15\,L\,min^{-1}$, the rest of the flow was introduced through two porous spargers which generate smaller bubbles with higher specific surface ($m^2\,m^{-3}$), giving an oxygen transfer coefficient, K_La, measured with tap water, of $19.2\,h^{-1}$.

In addition to the aeration, to prevent fouling, the MBR had a control system for sequential operation of the membranes. The reactor was equipped with three membranes but only two membranes were working at the same time, changing in 10 min cycles. In this way flux relaxation was applied maintaining the flow. This allows long operation periods without fouling troubles. During the biological treatment, effluent samples were collected automatically (Sigma 900 Portable Sampler) and filtered with 0.2-μm filters prior to analyses (Millex®-GN, 25 mm, Millipore).

Biological treatment was carried out during a period of more than one hundred days divided in four stages in which the MBR was operated as detailed in Table 1. Activated sludge was supplied by the municipal wastewater treatment plant of the city of Almería, Spain (El Bobar, Almería, Spain). The MBR was inoculated with the sludge as received from the WWTP with an initial VSS concentration around $5.5\,g\,L^{-1}$.

Stage 1 represents the reference condition, in which the feed did not include phototreated pesticides and was a synthetic urban wastewater (SW) with biodegradable carbon sources and mineral salts, with a total DOC concentration of $500\,mg\,L^{-1}$. Simulated wastewater included $3.2\,mg\,L^{-1}$ of beef extract, $6.4\,mg\,L^{-1}$ of yeast extract, $16\,mg\,L^{-1}$ of peptone, $0.8\,mL^{-1}$ of glycerol (87% v/v), and mineral salts ($16\,mg\,L^{-1}$ NaCl, $0.5\,g\,L^{-1}$ NH_4Cl, $0.5\,g\,L^{-1}$ K_2HPO_4, $0.5\,g\,L^{-1}$ KH_2PO_4, $0.5\,g\,L^{-1}$ $MgSO_4 \cdot 7H_2O$, and $10\,mL\,L^{-1}$ of trace mineral solution).

In the Stage 2 condition, the influent was constituted by the synthetic urban wastewater with biodegradable carbon sources and mineral salts, spiked with the partially oxidized pesticide solution from the photo-Fenton reaction ($132.5\,mg\,L^{-1}$ of DOC) to achieve a final concentration of the effluent equal to $500\,mg\,L^{-1}$ (SW + PTP). Pre-treated

TABLE 1
MBR operating conditions

	Stage 1	Stage 2	Stage 3	Stage 4
Feed	Synthetic wastewater (SW)	Synthetic wastewater + Photo-treated pesticides (SW + PTP)	Synthetic wastewater (SW)	Photo-treated pesticides (PTP)
Feed concentration, (mg DOC L^{-1})	500	500	500	132.5
HRT, (h)	8.3	8.3	5.5	5.5
SRT, (d)	>50	>50	>50	>50
Flow rate, (L h^{-1})	2.4	2.4	3.6	3.6
Operation time, (d)	0–54	55–86	87–91	92–102

water with pesticide intermediates of the photo-Fenton reactions was neutralized to pH 7.0 ± 0.1 by adding 0.1 N NaOH, previously to be mixed with the synthetic wastewater. In both cases, Stage 1 and Stage 2 conditions, the influent flow rate was 2.4 L h^{-1} corresponding to a hydraulic residence time of 8.3 hours and a transmembrane flux of 12 L h^{-1} m^{-2}.

Between Stage 2 and Stage 4 the bioreactor was fed with SW to return to reference, with an influent flow rate of 3.6 L h^{-1} (Stage 3).

In the Stage 4 condition, the influent was only the partially oxidized pesticide solution (PTP) from the photo-Fenton reaction. In this case, the influent flow rate was 3.6 L h^{-1} equivalent to a hydraulic residence time of 5.5 hours and a transmembrane flux of 18 L h^{-1} m^{-2}, with an initial total DOC concentration of 132.5 mg L^{-1}.

Analytical Methods

The five-pesticide solution was analyzed by HPLC (Shimadzu Lc10 with UV/Vis Shimadzu MX-10Av diode-array detector and autosampler). A reverse-phase column (Sunfire™ Waters C_{18} 150–3 mm, 5 μm) was employed. The mobile phase was acetonitrile (15%) and H_2O (85%) in a concentration gradient to 80% of acetonitrile and 20% of H_2O in 18 min (flow rate 0.5 mL min^{-1}). Detection was based on absorption at 210 nm for dimethoate and pyrimethanil, 234 nm for oxamyl and methomyl and 270 nm for imidaclorid. Samples were diluted with acetonitrile (1:1) and filtered through 0.20-μm syringe filters (Millex®-GN, 25 mm, Millipore) before HPLC injection. The sample injection volume was 20 μL.

Mineralization by photo-Fenton and biological degradation with activated sludge were followed by DOC determination in a Shimadzu-V_{CPH} TOC analyzer calibrated with standard solutions of potassium phthalate. Hydrogen peroxide concentration was determined with ammonium metavanadate in an acidic medium, which forms a red-orange peroxovanadium cation with a maximum absorbance at 450 nm (30). Biomass was determined gravimetrically (31) by measuring VSS (volatile suspended solids).

RESULTS AND DISCUSSION

There are previous studies (28,32) that show the toxicity and non-biodegradability of the selected pesticides. For the same pesticide mixture and concentration, results of *Vibrio fischeri* inhibition test and Zahn–Wellens biodegradability test have been recently referenced (32). Values close to 100% of inhibition and around 60% of biodegradability were showed by the authors. For *Vibrio fischeri* inhibition test the toxicity limit is 50%, higher values mean that the water is toxic, while for the Zahn-Wellens biodegradability test, values lower than 70% mean that wastewater is not biodegradable. Consequently, a pre-treatment with photo-Fenton is adequate to diminish the toxicity and increase biodegradability before a biological treatment.

Ballesteros Martín et al. (2009) reported that the mineralization of contaminants by photo-Fenton is closely related to the H_2O_2 dose, and consequently, complete consumption of initial H_2O_2 concentration may be used to reach a certain degree of mineralization avoiding H_2O_2 removal before biotreatment (13).

Based on previous works (13), the pesticide mixture with an initial DOC concentration of 200 mg L^{-1} was treated by photo-Fenton using a total amount of 310 mg L^{-1} of H_2O_2 to achieve a 34% mineralization, and complete removal of parent molecules of pesticides. The final DOC concentration was 132.5 mg L^{-1}.

Figure 3 represents pesticide degradation and partial DOC removal by photo-Fenton oxidation. At the early stages of the photo-Fenton reaction, molecules of pesticide are attacked by hydroxyl radicals giving rise to organic intermediates without a strong decrease in DOC concentration. In the present work, the beginning of the biological treatment was carried out just after the total pesticide degradation, when a mineralization degree of 34% had been reached.

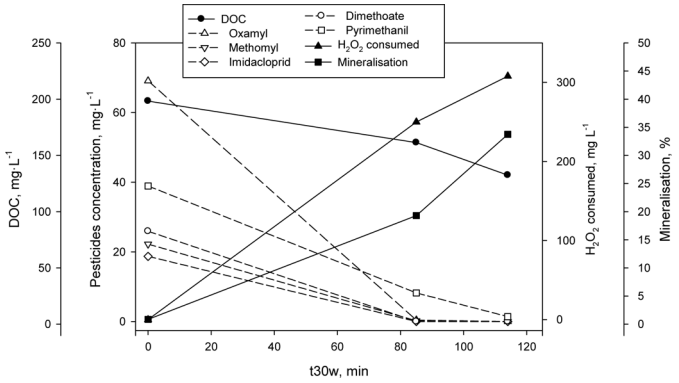

FIG. 3. DOC removal, pesticides degradation and accumulated hydrogen peroxide consumption for photo-Fenton treatment of the five-pesticide mixture up to a 34% of mineralization.

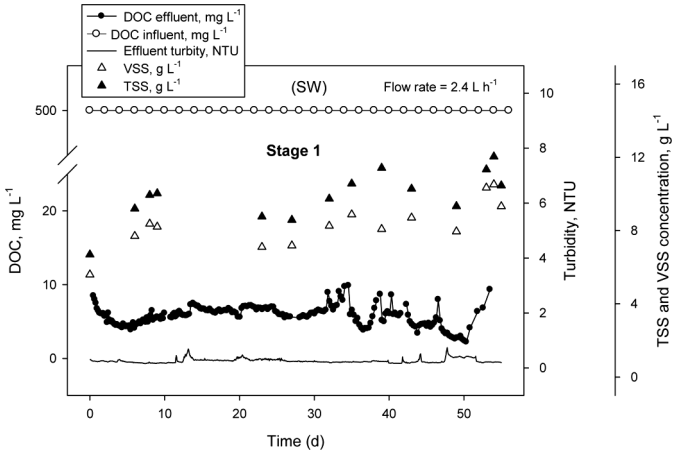

FIG. 4. Evolution of DOC, VSS, TSS, and turbidity in the MBR operating with synthetic wastewater (SW) during Stage 1.

The operational conditions in the MBR were steady during the 102 days of experiment. pH varied slightly around a mean of 6.5 and the average temperature was 17°C. The dissolved oxygen concentration slightly decreased from the beginning of the experiment due to the increase of the sludge concentration, nonetheless the oxygen concentration was always higher than 50% of air saturation not being a biological limiting factor. Transmembrane pressure (TMP) fluctuated between 40 and 80 mbar, which corresponds to an average permeability value of 270 L h^{-1} m^{-2} bar^{-1}, that is in agreement with the optimal operational values recommended by the membrane manufacturer. The reactor worked with a good stability for more than 100 days, indicating that the operational conditions, flux, transmembrane pressure and the aeration conditions, flow, and the aerator design, were suitable for the biological conditions.

Figure 4 represents a long time steady state in which the MBR was operated under Stage 1 conditions as described in Materials and Methods section. The MBR was inoculated with activated sludge from a municipal WWTP, the initial concentration of volatile suspended solids (VSS) was 5.5 g L^{-1} and the total suspended solids concentration (TSS) was 6.7 g L^{-1}.

During the experiment, the DOC concentration in the MBR effluent was lower than 10 mg L^{-1}, with averages values around 5 mg L^{-1}, which indicates that the carbon removal percentage was higher that 99%, giving a mean C-uptake rate of 59.5 mg DOC L^{-1} h^{-1} and a mean specific uptake rate of 7.2 mg DOC g VVS^{-1} h^{-1}. During this operation period, the sludge concentration (VSS) increased from 7.6 g L^{-1} to a final value of 9.3 g L^{-1} after 55 days.

Previous experiments carried out in a 6-L working volume stirred tank reactor (STR) with the same synthetic wastewater, yielded a minimum residual DOC concentration equal to 36.6 mg DOC L^{-1}, around 7 times higher than the residual DOC concentration reached in the present work. Regarding the carbon removal percentage, the STR experiment yielded 90.1% (13) compared with values higher than 99% in the MBR.

Figure 5 represents the response of the MBR to a change in the feeding composition, from synthetic wastewater (SW) (Stage 1) to synthetic wastewater spiked with the mixture of phototreated pesticides (SW + PTP) (Stage 2).

Previous works (13) have demonstrated an increase in the biological oxidation efficiency of photo-Fenton intermediates by mixing with a biodegradable carbon source (for example urban wastewater). With this strategy, acclimatized activated sludge led to complete biodegradation, achieving carbon removal efficiencies of the combined process higher than 90% in a stirred tank reactor (13).

In the present work, pre-treated water with 132.5 mg L^{-1} of dissolved organic carbon given by pesticide intermediates of the photo-Fenton reactions was neutralized to pH 7 and mixed with a biodegradable C-source as previously described to simulate mixing with an urban wastewater.

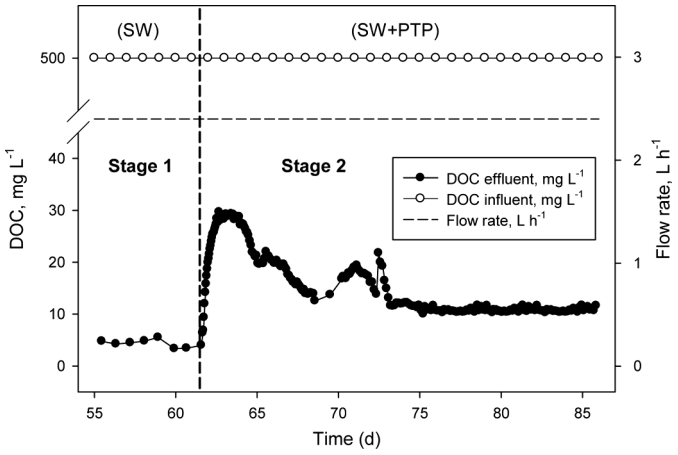

FIG. 5. Evolution of DOC in the MBR effluent during the transition between SW feeding (Stage 1) and SW + PTP feeding (Stage 2).

Consequently, in this condition, the integrated process is carried out under more pragmatic conditions like in a WWTP, where different sources of carbon are present.

DOC concentration at the beginning of the Stage 2 biotreatment was 500 mg L^{-1}, 26.5% from pesticide pretreated by photo-Fenton. The DOC concentration in the effluent of the biological treatment in the MBR varied from 5 mg L^{-1} to 30 mg L^{-1}, then decreased to become stable in the new steady state with a value around 10 mg L^{-1}. The VSS concentration in the bioreactor during the assay was 12.3 g L^{-1}, giving, in the new steady state, a C-uptake rate of 58.7 mg DOC L^{-1} h^{-1} and a specific uptake rate of 4.8 mg DOC g VVS^{-1} h^{-1}. In this case, the activated sludge spends around 10 days to complete the adaptation to the new feed. During these days the C-uptake rate decreased from 59.4 mg DOC L^{-1} h^{-1} to 56.4 mg DOC L^{-1} h^{-1} and then increased to a final and steady state value of 58.7 mg DOC L^{-1} h^{-1}. The data make obvious that the change in the feed type did not affect the stability of the bioreactor and neither the effluent quality.

Similar experiments were carried out in previous works using a stirred tank reactor (13). In this case, the steady-state DOC concentration in the outlet of the biological treatment with adapted sludge was 50 mg L^{-1}, 5 times higher than the 10 mg L^{-1} of DOC residual concentration reached in the MBR effluent.

The final carbon removal achieved by the integrated process mixing the photo-fenton effluent with biodegradable carbon sources (SW + PTP) (Stage 2) was 95.16%, lower than 99% reached during Stage 1 operation and higher than that reported for a stirred tank reactor (STR) under the same conditions (90.1%) by Ballesteros Martín et al., 2009 (13).

Oller et al. (2007) also studied the degradation of a five pesticides mixture coupling solar photo-Fenton treatment with biological oxidation in a 35-L immobilized biomass reactor (IBR) (28). The efficiency attained in the coupled photo-Fenton/biological system operated in batch mode was 85% of DOC removal (256 mg L^{-1} of initial DOC concentration), from which 23% corresponded to the photocatalytic step and 62% to the aerobic biological treatment, giving rise to a maximum treatment capacity of the aerobic IBR of 16 mg of DOC h^{-1} L^{-1} occupied by polypropylene supports colonized by activated sludge (28). In the present work, the coupled system under Stage 2 conditions achieves a final carbon removal percentage of 95.16% and a C-uptake rate of 58.7 mg DOC L^{-1} h^{-1}.

Figure 6 represents the response of the MBR to a change in the feed composition, in this case, from synthetic biodegradable wastewater (SW) (Stage 3) to phototreated pesticides effluent (PTP) without additional carbon source which corresponds to Stage 4, giving rise to a DOC concentration in the bioreactor influent of 132.5 mg L^{-1}. Therefore, before feeding the MBR with phototreated intermediates the bioreactor was fed with SW, as Stage 1, but at a flow rate 1.5 times higher. The C-uptake rate was 89.1 mg DOC L^{-1} h^{-1} higher than 59.5 mg DOC L^{-1} h^{-1} obtained during the first period of operation (days 0–54) with analogous residual DOC concentration ~5 mg L^{-1}. This shows that the MBR worked under C-limitation and that higher values of C-uptake rate would be achieved with higher DOC feeding rates.

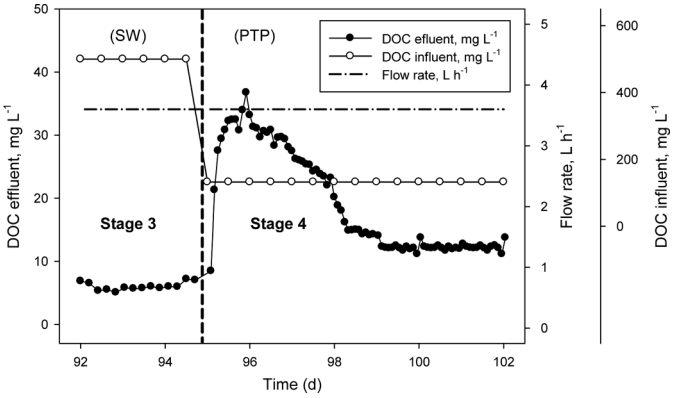

FIG. 6. Evolution of DOC in the MBR effluent during the transition between SW feeding (Stage 3) and PTP feeding (Stage 4).

Effluent DOC concentration varied from 7.0 mg L^{-1} to 32 mg L^{-1} in less than one day, and then decreased to a new steady concentration of 12.2 mg L^{-1}, with a mean sludge concentration inside the MBR of 15.3 g L^{-1}. Then, the C-uptake rate in the new steady state was 21.8 mg DOC L^{-1} h^{-1} and the specific uptake rate of 1.4 mg DOC g VVS^{-1} h^{-1}, both values appreciably lower than those obtained during the Stage 2 operation.

The final carbon removal achieved by the integrated process during Stage 4 was 94.1% higher than those reported by Zapata et al. (32), and by Ballesteros Martín et al. (13) with different bioreactor configurations.

Acclimation of activated sludge to the new feed occurred in 3 days, significantly shorter than the adaptation from Stage 1 to Stage 2, when a stable DOC effluent concentration was achieved after 10 days of operation. This fact was due to activated sludge acclimation to photo-Fenton intermediates during Stage 2 operation for 31 days. Other authors have pointed out that the faster degradation of a selection of acidic pesticides in a MBR experiment could be explained by the acclimation of the microorganisms to the influent water or to some changes in the microbial population (18).

Table 2 includes a summary of the experimental conditions carried out in order to make easier the comparison among them.

The most relevant aspects are both the increase of the specific carbon uptake rate and the decrease of the residual DOC in the effluent with the biodegradability of the feed.

Along the four experimental stages, DOC concentration in the effluent was always between 5 and 12 mg L^{-1},

TABLE 2
Steady state average values achieved in the MBR operation stages

	Stage 1	Stage 2	Stage 3	Stage 4
DOC Uptake rate, ($mg\,DOC\,L^{-1}\,h^{-1}$)	59.5	58.7	89.1	21.8
Specific DOC Uptake rate, ($mg\,DOC\,h^{-1}\,g^{-1}\,VSS$)	7.2	4.8	5.8	1.4
Effluent DOC residual, ($mg\,DOC\,L^{-1}$)	4.3	10.7	7.0	12.2
VSS concentration, ($g\,L^{-1}$)	8.6	12.3	15.3	15.3
Transition time between steady states, (d)	—	≈10	—	≈3

working with hydraulic residence time (HRT) between 5.5 and 8.3 hours. These values are lower than $50\,mg\,L^{-1}$, which is the minimal outlet concentration obtained in similar previous works using a stirred tank reactor (STR) with an adapted sludge (13), and also lower than $40\,mg\,L^{-1}$, reported by Oller et al., working in an immobilized biomass reactor (IBR) with a residence time of 27 hours (28).

The present study confirms the enhancement of the biological efficiency oxidation of the phototreated pesticides mixture when it is mixed with an additional biodegradable carbon source as Ballesteros Martín et al. (13) recommended. Additionally, the present results also verify that the use of MBR technology increases the biodegradation capacity, being able to treat the phototreated pesticides mixture without additional biodegradable carbon source.

At all experimental conditions assayed, the obtained effluent had a high quality, with low residual DOC concentration, absence of the original pesticides, absence of suspended solids, and turbidity values (NUT) below 0.5.

CONCLUSIONS

The viability of the integrated process has been demonstrated. Higher carbon removal percentage compared with conventional biotreatment has been reached in the photo-Fenton-MBR integrated process, achieving values over than 95%. The present scheme increases the operational flexibility and simplicity compared with a STR treatment. The low residual carbon in the effluent of the MBR compared with conventional biotreatment, the absence of pollutants, and the low turbidity, converted the treated water in a high quality water ready to reuse. The results confirm that a combination of solar photo-Fenton and membrane bioreactor is an effective approach for toxic wastewater treatment.

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