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Coupling solar photo-Fenton and biotreatment at industrial scale: Main results of a demonstration plant

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Abstract

This paper reports on the combined solar photo-Fenton/biological treatment of an industrial effluent (initial total organic carbon, TOC, around 500 mg L^{-1}) containing a non-biodegradable organic substance (α-methylphenylglycine at 500 mg L^{-1}), focusing on pilot plant tests performed for design of an industrial plant, the design itself and the plant layout. Pilot plant tests have demonstrated that biodegradability enhancement is closely related to disappearance of the parent compound, for which a certain illumination time and hydrogen peroxide consumption are required, working at pH 2.8 and adding $Fe^{2+} = 20$ mg L^{-1}. Based on pilot plant results, an industrial plant with 100 m^2 of CPC collectors for a 250 L/h treatment capacity has been designed. The solar system discharges the wastewater (WW) pre-treated by photo-Fenton into a biotreatment based on an immobilized biomass reactor. First, results of the industrial plant are also presented, demonstrating that it is able to treat up to 500 L h^{-1} at an average solar ultraviolet radiation of 22.9 W m^{-2}, under the same conditions (pH, hydrogen peroxide consumption) tested in the pilot plant.

Keywords: Advanced oxidation processes; Biological treatment; Demonstration plant; Solar photocatalysis; Solar photo-Fenton

1. Introduction

The inability of conventional biological wastewater (WW) treatments to effectively remove many toxic pollutants shows that new treatment systems are needed. Rigorous pollution control and legislation in many countries has resulted in an intensive search for new and more efficient water treatment technologies. In the European Union, water policy is undergoing considerable changes at present. The adoption of the water framework directive [1] provides a policy tool that enables this essential resource to be protected. Among other measures, surface water deterioration must be prevented and bodies of water enhanced and restored, good chemical and ecological status of such water must be achieved and pollution from discharges and emissions of hazardous substances reduced by 2015 [2]. In the near future, advanced oxidation processes (AOPs) may become the most widely used water treatment technologies for organic pollutants not treatable by conventional techniques due to their high chemical stability and/or low biodegradability [3,4]. The use of AOPs for WW treatment has been studied extensively, but UV radiation generation by lamps or ozone production is expensive. Therefore, research is focusing more and more on those AOPs which can be driven by solar irradiation, that is, light with a wavelength longer than 300 nm: photo-Fenton and heterogeneous catalysis using UV/TiO_2 [5–7]. Photo-Fenton has been demonstrated to be the more effective of the two processes for treating wastewater containing pollutants at concentrations of >10 mg L^{-1} [8–12], as the reaction rate is usually much higher and separation of iron is very often not necessary. Despite its obvious potential for the detoxification of polluted water, there has been very little commercial or industrial use of the solar photocatalysis technology so far. During recent years, more installations have been erected, mainly based on non-concentrating collectors [13,14].

Partial oxidation of toxic compounds by AOPs has recently been shown to substantially increase wastewater biodegradability [15–19]. Even though AOPs for wastewater treatment have been proven to be highly efficient, their operation is currently quite expensive (tens of €/m^3) [17,20,21]. The combination of a solar AOP as a preliminary treatment, followed by an inexpensive biotreatment, would seem to be an economically attractive option. This paper therefore reports on the combined solar photo-Fenton/biological treatment of an industrial effluent containing non-biodegradable organic substances, focusing on pilot plant

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tests performed for design of an industrial plant, the design itself and plant layout.

2. Materials and methods

2.1. Chemicals and analytical methods

Technical-grade α-methylphenylglycine (MPG, $C_9H_{11}NO_2$), a bio-recalcitrant precursor used in the synthesis of pharmaceuticals, was used in this study as received at a concentration of 500 mg L^{-1}. It was tested both in clean seawater (process water before use by the pharmaceutical factory) and in the factory's wastewater (seawater after use). The composition of the wastewater (without MPG) is typically NH_4^+ = 0–40 mg L^{-1}, NO_3^- = 200–600 mg L^{-1}, COD = 200–400 mg L^{-1}, TOC = 100–200 mg L^{-1}, suspended solids = 20–100 mg L^{-1} in a seawater matrix (NaCl = 28.13 g L^{-1}, $CaCl_2 \cdot 2H_2O$ = 1.6 g L^{-1}, $MgCl_2 \cdot 6H_2O$ = 4.8 g L^{-1}, Mg $SO_4 \cdot 7H_2O$ = 3.5 g L^{-1}). Photo-Fenton experiments were performed employing iron sulphate ($FeSO_4 \cdot 7H_2O$), reagent-grade hydrogen peroxide (30%, w/v) and sulphuric acid for pH adjustment, all provided by Panreac. The photo-treated solutions were neutralized by NaOH (reagent-grade, Panreac). The mineralisation rate was monitored by measuring the total organic carbon (TOC) by direct injection of filtered samples into a Shimadzu-5050A TOC analyser. MPG concentration was analysed using reverse-phase liquid chromatography (flow rate 0.5 mL min^{-1}) with a UV detector (detection wavelength of 210 nm) in an HPLC-UV (Agilent Technololgies, series 1100) with a C-18 column (LUNA 5 μm, 3 mm × 150 mm from Phenomenex) and employing phosphoric acid at 50 mM adjusted to pH 2.5 with NaOH as the mobile phase. Hydrogen peroxide analyses were carried out by iodometric titration.

2.2. Experiment set up

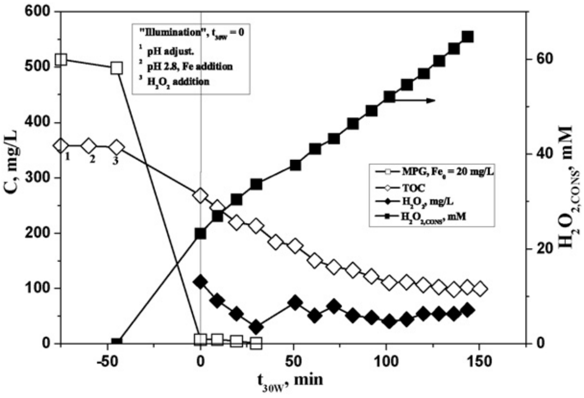

Fig. 1. Degradation (and mineralisation) of MPG (500 mg L^{-1}) dissolved in seawater by photo-Fenton at Fe = 20 mg L^{-1}. Hydrogen peroxide concentration and consumption is also shown. Points 1, 2 and 3 refer to the different steps in the procedures applied before illuminating the system (see Section 2.2 for details).

Solar driven photo-Fenton tests were carried out in a 75-L (V_T) pilot plant (total irradiated volume V_i = 44.6 L) specially developed for photo-Fenton applications installed at the Plataforma Solar de Almería (PSA, Almería, Spain). It is composed of four 1.04-m^2 compound parabolic collector (CPC) units with 50-mm-diameter absorber tubes. Details and a diagram of the pilot plant have been published elsewhere [22]. Catalyst concentration for photo-Fenton was 20 mg L^{-1} of iron. At the beginning of the treatment, with collectors covered, the pilot plant was filled with the industrial effluent (Point 1, Fig. 1). Then the pH was adjusted with sulphuric acid to 2.8–2.9, and the iron salt was added (Point 2, Fig. 1). After each addition of reagent, the liquid was well homogenised by recirculation (flow rate: 1.5 m^3 h^{-1}). Finally, an initial amount of hydrogen peroxide was added (Point 3, Fig. 1) and, during the Fenton process, a sample was taken to evaluate any effect in the dark. Afterwards, the collectors were uncovered and photo-Fenton treatment began. It should be remarked that the pilot plant has heating and cooling devices to keep the reaction-solution temperature at the 30 °C, the set point for all the experiments described in this paper. Hydrogen peroxide was measured frequently and consumed reagent was continually replaced (in small portions) to maintain the desired concentration. Solar ultraviolet radiation was measured by a global UV radiometer (KIPP&ZONEN, model CUV 3) mounted on a platform tilted 37°. Photo-Fenton treatment time was normalized to allow combination of data from several days' experiments by Eq. (1), where t_n is the experimental time (min) for each sample, UV is the average solar ultraviolet radiation (W m^{-2}) measured during Δt_n, and t_{30W} is the "normalized illumination time". In this case, time refers to a constant solar UV power of 30 W m^{-2} (typical solar UV power on a perfectly sunny day around noon).

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

Biological mineralisation of biodegradable compounds generated during preliminary oxidative processes was carried out in continuous mode in an aerobic biological reactor composed of three modules, a neutralisation tank, a conditioner tank and an aerobic immobilised biomass reactor (IBR). In this biological system, the neutralisation tank is filled with "batches" of pre-treated water from the photo-Fenton reactor and adjusted to a pH between 6.5 and 7.5 by adding 5 M NaOH measured with a portable pHmeter. NH_4Cl was added as a function of the organic carbon present in the bioreactor (C:N ratio 100:20). The wastewater mostly contains nitrogen in the form of nitrate. The pilot-plant was operated only in aerobic mode. Hence, the biomass requires nitrogen sources in reduced form, which are not sufficiently present in the wastewater. It was done mainly when clean seawater was used. The effluent is pumped from the neutralisation tank to the conditioner, where pH is controlled (between 6.5 and 7.5) with 73 mM H_2SO_4 or 80 mM NaOH solutions. Recirculated water is continuously pumped from the conditioner to the IBR and returned from the IBR by gravity. The conditioner inlet flow from the neutralisation tank is equal to the continuous outlet of the biotreatment. This could be increased as long as the TOC in the outlet retained values characteristic of background noise from the physiological bacteria activity found in conventional media. Under these conditions, continuous operation was considered to be working properly. When the TOC in the IBR outlet begins to rise, the maximum admissible organic charge in the IBR has been reached.

3. Results and discussion

3.1. Pilot plant tests

It should be remarked that the source of the wastewater employed is from a pharmaceutical factory that uses seawater as process water. The first set of experiments has been performed in clean seawater in order to determine unequivocally (the pharmaceutical effluent contains other organic compounds) if the focus contaminant (MPG) could be substantially degraded and mineralised. Previous studies have demonstrated that photo-Fenton treatment is suitable for treating MPG dissolved in model water [23] with high salinity (NaCl $35\,\mathrm{g\,L^{-1}}$) [24]. These experiments have also demonstrated that the biodegradability threshold was attained after a certain treatment time and that photo-Fenton was a more suitable treatment than TiO_2.

Results presented in Fig. 1 show that photo-Fenton ($\mathrm{Fe} = 20\,\mathrm{mg\,L^{-1}}$) is effective for treating MPG in real seawater, reaching almost complete disappearance of it during “dark Fenton”, and substantially mineralising (more than 70%) the contaminant in less than 1 h. Comparing the results of these tests with those previously obtained with MPG dissolved in a model seawater (demineralised water containing NaCl $35\,\mathrm{g\,L^{-1}}$), no significant difference is observed. But the treatment time required for substantial mineralisation of MPG was three times longer than in a previous experiment with distilled water. Treatment time required for MPG disappearance was quite similar. The effect of chloride on Fenton and photo-Fenton processes was recently reported in detail by De Laat et al. [25] and commented on in a recent review [26]. Inhibition of Fenton reactions by Cl^- is due to scavenging of OH radicals and has been described as noticeably above 0.01 M Cl^-. The effect is complicated by chlorine radical reactions with hydrogen peroxide and iron species, including the appearance of organochlorine by-products. We have detected such an inhibition effect, but it is not significant for the final goal. We have not evaluated organochlorine by-products, but we have demonstrated that wastewater biodegradability is clearly enhanced during the treatment. All the experiments were carried out at the same MPG concentration of around $500\,\mathrm{mg\,L^{-1}}$ (3 mM). The mass balance (not the reaction mechanism) of the degradation of this compound by photo-Fenton is based on Eqs. (2)–(4), where the combination of the mineralisation reaction (Eq. (2)) and the decomposition of hydrogen peroxide (Eq. (3)) are shown. According to Reaction (4), 60 mM of hydrogen peroxide should be consumed to mineralise $500\,\mathrm{mg\,L^{-1}}$ of MPG. However, 60 mM had already been consumed when 30% of the initial TOC still remained in solution. In previous stages of the treatment the situation was closer to theoretical (i.e. 30 mM of H_2O_2 to mineralise 40% of the initial TOC), but in Fig. 1 it may also be observed that at $t_{30\mathrm{W}} > 100$ min (to end of treatment) consumption of hydrogen peroxide was quite heavy considering that a consumption of 12 mM of H_2O_2 only mineralised $10\,\mathrm{mg\,L^{-1}}$ of TOC. This means that hydrogen peroxide is not consumed efficiently during the overall treatment because, as the reaction proceeds, low-molecular-weight acids such as glyoxilic, oxalic, acetic, formic acids (or their complexes with iron) are produced, and they are only slightly reactive to hydroxyl radicals.

$$\text{organic pollutant} + \mathrm{O_2} \xrightarrow{\bullet\mathrm{OH}} \mathrm{CO_2} + \mathrm{H_2O} + \text{mineral acids} \quad (2)$$

$$\mathrm{H_2O_2} \rightarrow \mathrm{H_2O} + \tfrac{1}{2}\mathrm{O_2} \quad (3)$$

$$\alpha\text{-methylpheylglycine} : \mathrm{C_9H_{11}NO_2} + 20\mathrm{H_2O_2} \rightarrow \mathrm{NH_3} + 9\mathrm{CO_2} + 24\mathrm{H_2O} \quad (4)$$

All the experiments summarised in the following figures have been repeated several times in order to correctly determine the main plant design parameters and to confirm the repeatability of the results. MPG degradation in real wastewater (see Section 2.2 for details) has also been tested with successful results, as shown in Fig. 2. MPG was completely degraded and mineralisation was also significant. Treatment time was higher than in seawater (compare Figs. 1 and 2), but results have demonstrated that photo-Fenton is also suitable for these conditions (which are those of the plant to be erected). Tests attempted to minimize the concentration of hydrogen peroxide in the photoreactor during the overall treatment. Thus, the concentration was always maintained at around $100\,\mathrm{mg\,L^{-1}}$. Under these conditions, the consumption of hydrogen peroxide for MPG degradation was similar (around 30–35 mM) to MPG dissolved in real seawater, but the treatment time also rose due to the presence of a considerable amount of other organic compounds (i.e., $250\,\mathrm{mg\,L^{-1}}$ as TOC). MPG degradation has also been tested with higher H_2O_2 concentrations and the results are also shown in Fig. 2(right). Treatment time (to degrade MPG and for the same mineralisation) was quite similar to tests with low H_2O_2, with substantially higher consumption of hydrogen peroxide. As mentioned above, hydrogen peroxide is not consumed efficiently during the overall treatment. The consumption of 30–35 mM hydrogen peroxide for MPG complete degradation is therefore a key-parameter, however, it should also be taken into account that hydrogen peroxide concentration should be maintained at around $150\,\mathrm{mg\,L^{-1}}$ to minimize consumption.

The immobilised biomass reactor (IBR) was inoculated with activated sludge (acclimatized to seawater conditions) from a pharmaceutical company. Batch recirculation mode was maintained between the conditioner tank and the IBR for approximately ten days. Measurement of total suspended solids revealed proper bacteria fixation on the supports. Neither mineral nutrient medium nor biodegradable substances were added during this step, and only pH was controlled (between 6.5 and 7.5). Dissolved oxygen concentration in the IBR of between 4 and $6\,\mathrm{mg\,L^{-1}}$ was ensured by an air blower. Before the complete batch of water pre-treated by photo-Fenton was added to the IBR, small amounts of it were added to adapt bacteria and avoid shock. Each addition was done only when the usual lowest TOC level (characteristic values of

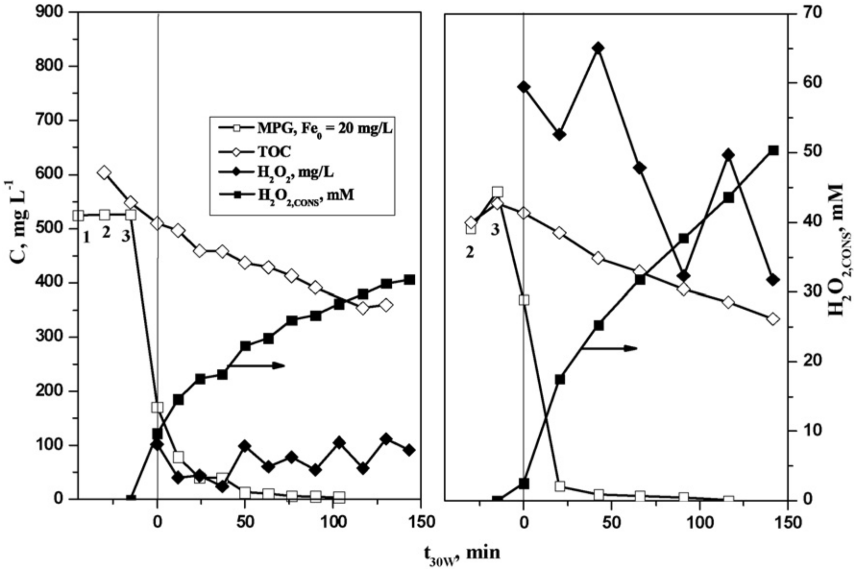

Fig. 2. Degradation (and mineralisation) of MPG (500 mg L^{-1}) dissolved in real wastewater by photo-Fenton at Fe = 20 mg L^{-1}, at low (left) and high (right) concentration of hydrogen peroxide. Hydrogen peroxide concentration and consumption is also shown. Points 1, 2 and 3 as in Fig. 1.

physiological bacteria activity, as mentioned above) had been reached.

After a certain time, the IBR was completely drained and filled with wastewater pre-treated by photo-Fenton. As previously demonstrated [23,24], wastewater can be biodegraded some time after complete disappearance of MPG. Photo-Fenton treatment time was therefore set to 150 min. At this moment most of the TOC was in the form of low-molecular-weight acids. It should also be noted that only small quantities of H_2O_2 may remain at the end in order to avoid damage to activated sludge, and therefore, no more was added after a few minutes to the end. Hydrogen peroxide was also added continuously to try to keep it at a low concentration (around 150 mg L^{-1}). The IBR neutralisation tank is filled with “batches” of pre-treated water from the photo-Fenton process. pH is adjusted (between 6.5 and 7.5) manually. The neutralized effluent is poured directly into the conditioning tank and pumped to the IBR maintaining batch recirculation mode between them. Mineralisation of the effluent is followed by measuring the TOC at regular time intervals (once or twice a day). The IBR in “batch mode” successfully treated water from the photo-Fenton pre-treatment in 4–5 days (from TOC ≈300 to 60 mg L^{-1}). Batch experiments in the IBR were conceived to demonstrate proper management of the photo-Fenton test to reach biodegradability. It should be remarked that after the so-called “adaptation” operation, and throughout all the following tests, no mineral medium was added to the IBR because the inorganic substance concentration present in the pre-treated wastewater was enough for bacteria metabolism. At this point, continuous-mode operation was started. Taking into account the results obtained from the batch experiment in the IBR, a flow of 1.6 L h^{-1} (wastewater pre-treated by photo-Fenton) was found to be the maximum that can be treated while maintaining minimum bacteria metabolism (TOC ≈60 mg L^{-1}). Based on IBR characteristics, the normalized value in the IBR was 75 mg TOC day^{-1} $L_{PR}{}^{-1}$, using PR (pall ring) supports.

3.2. Industrial plant design and set up

From the pilot plant experiments performed, it was concluded that photo-Fenton requires around 150 min of illumination time (or more) to reach the biodegradability threshold. Under these conditions, 100 m^2 of CPC collectors are necessary to treat 250 L/h (3 m^3/day, 4380 operating hours per year) of wastewater containing 500 mg L^{-1} of MPG and the IBR is able to treat half the flow rate per hour, operating 24 h per day. Fig. 3 shows the industrial plant diagram. The final solar photoreactor design consists of a recirculation tank, a centrifugal pump, a 100-m^2 solar photoreactor, polypropylene piping, accessories and the process control system. Furthermore, a reagent dosing pump (hydrogen peroxide) and three online sensors (hydrogen peroxide, pH and dissolved oxygen) are installed in the piping. A UV-A radiometer is placed at the same inclination as the solar collectors. Three CPC photoreactors (similar to those used in the pilot plant, see Section 2.2) in parallel rows illuminate a volume of 1260 L (glass tubes), with a recirculation tank that can hold up to 3 m^3. Water is pumped by a centrifugal pump at a maximum flow rate of 10 m^3 h^{-1}. The IBR tank (1 m^3), filled with 700 L of Pall rings, is connected to a conditioner tank (2 m^3) in a closed loop. The water discharged from the solar photo-Fenton reactor must be neutralized, and may need conditioning (removal of Fe^{3+} and/or H_2O_2) before it is fed to the biological process, so the neutralisation tank (5 m^3) is the first step in the biological process.

This plant is currently under testing in a program to define the optimum concentration of hydrogen peroxide (automatic control to maintain a constant concentration in dynamic conditions), determine the maximum continuous flow rate between the neutralisation tank and the bioreactor, and check the continuous effluent from the IBR outlet for accomplishing legal limits. One of the first tests done is shown in Fig. 4. This figure shows several different effects not detected in the pilot plant,

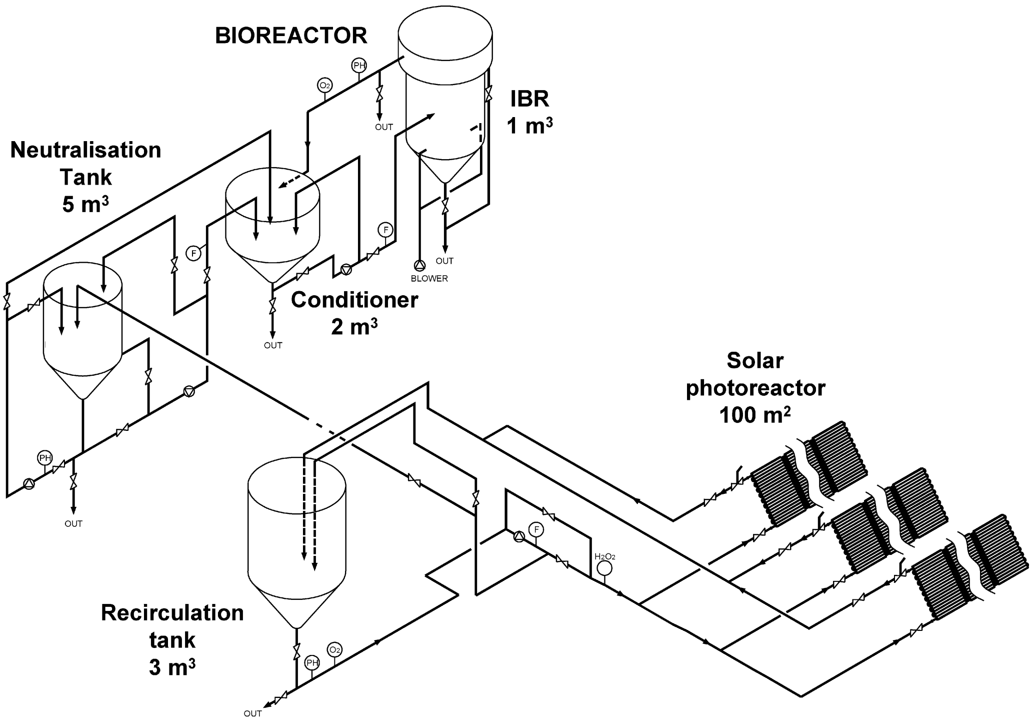

Fig. 3. Diagram of the integrated solar photo-Fenton/biotreatment industrial MPG treatment plant.

most of them related to temperature changes during the test and to the large size of the plant. It should be mentioned that temperature control is not economically feasible in a real photocatalytic plant, and this should be taken into account during plant operation. Under these conditions, temperature usually rises from morning start-up to an almost constant value for several hours around noon and decreases again during the afternoon. This may be observed in Fig. 4, where water temperature varies between 21 and 37 °C, at the same time UV irradiation increases from 16 to 30 W m^{-2} (including a partly cloudy period between 12:00 and 13:30). Under these conditions, the photo-Fenton reaction rate varied during the experiment. Sagawe et al. [27] have described differences up to five times as great between 20 and 40 °C. In recent work by our group [22], we described a similar effect with model wastewater (2.5 times faster at 35 °C compared to 20 °C). The large size of the plant caused several effects not observed at pilot plant scale. First of all, very quick decay of MPG (and TOC) was observed at the beginning of the test (between $t_{30W} = 0$ and approximately $t_{30W} = 10$ min). This decay was attributed to formation of large amounts of foam from carbon dioxide bubbles produced by pH adjustment at the beginning of the test (pH$_0$ 2.8), which retained large amounts of MPG, and as it disappeared during the photo-Fenton treatment, the MPG redissolved. The Fenton reaction also contributed to the quick decay at the beginning. In the pilot plant tests, the solar collectors were covered during preparation (pH adjustment, Fe^{2+} adding, hydrogen peroxide adding). In the industrial plant, all these preparations were done under sunlight, and therefore, Fenton and photo-Fenton took place at the same time (see Fig. 5).

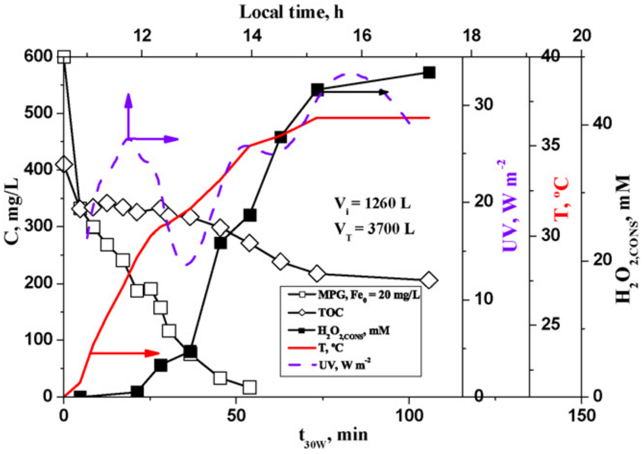

Fig. 4. Degradation (and mineralisation) of MPG dissolved in real wastewater by photo-Fenton at Fe = 20 mg L^{-1} in the industrial plant shown in Fig. 5. Hydrogen peroxide consumption, temperature behaviour and solar UV irradiation are also shown. Data are presented as a function of illumination time (Eq. (1)) and of local time.

It should be mentioned that the ratio between illuminated and non-illuminated volume is drastically different in the two plants. In the pilot plant it is $V_i/V_T = 0.6$ and in the industrial plant it is $V_i/V_T = 0.34$. The V_i/V_T ratio could be changed depending on the level of water in the recirculation tank (see Fig. 3), but it is usually minimized in order to treat as much water as possible per batch. The idea is to minimize the number of times pretreated water is emptied into the neutralisation tank and filled up again with untreated wastewater. MPG disappearance required a shorter illumination time than in the pilot plant. Moreover, at $t_{30W} = 100$ min, TOC was lower and hydrogen peroxide con-

Fig. 5. Views of the industrial plant: CPC field (up), tanks and P&I (down).

sumption was higher than in the pilot plant tests. Therefore, illumination time has been reset at around 100 min (instead of 150 min, as in the pilot plant tests). The main reason for this is the lower V_i/V_T ratio in the industrial plant. Under these conditions, the effect of Fenton reactions in the dark (in the recirculation tank) could be important [22]. With this first approach, the treatment capacity of the plant is around $500\,\mathrm{L\,h^{-1}}$, substantially higher than design ($250\,\mathrm{L\,h^{-1}}$), at an average solar ultraviolet radiation of $22.9\,\mathrm{W\,m^{-2}}$. It is worth mentioning that the average UV in the region is around $18.5\,\mathrm{W\,m^{-2}}$ [28]. Therefore, the average treatment capacity of the solar plant is around 400 L/h. A preliminary study estimated the cost per m^3 of MPG effluent treated between 7 and 10€ (30 and 70% capital and operational costs, respectively). More tests should be done to confirm these results, but pilot plant tests have proven very useful in the proper design of the industrial plant.

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