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STRATEGIES FOR HYDROGEN PEROXIDE DOSING BASED ON DISSOLVED OXYGEN CONCENTRATION FOR SOLAR PHOTO-FENTON TREATMENT OF COMPLEX WASTEWATER

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ABSTRACT

Hydrogen peroxide consumption is known to be one of the key parameters of the photo-Fenton process responsible for its high operating costs. The purpose of this study was to find out whether adding dissolved oxygen to the reaction medium in a continuous stream of pure oxygen or air with different H_2O_2 dosage strategies could improve the Dorfman mechanism, generating secondary oxidation species that could boost mineralization, and consequently, diminish H_2O_2 consumption. Experiments confirmed less efficient COD elimination. Additional DO slightly increased H_2O_2 consumption, as it initiated a series of reactions generating hydroxyl radical scavengers and H_2O_2 self-decomposition slowing down the reaction. At the same time, the study highlighted that automatic H_2O_2 dosing based on DO setpoints would be a highly attractive control option, however, more detailed studies on the initial amount of hydrogen peroxide and dosing rates must be undertaken.

Keywords: Automatic H_2O_2 dosing, Dissolved oxygen, Injection of pure oxygen or air, Wastewater decontamination

1. Introduction

The potential of the photo-Fenton process as an alternative technology for the treatment of wastewater containing organic pollutants not removable by conventional techniques (due to their high chemical stability, low biodegradability, or high toxicity) is widely recognized (Pignatello *et al.*, 2006). However, its main drawback is its operating costs. In recent years, research has focused on making this advanced oxidation process less-expensive, for example, by using solar radiation instead of UV lamps as a photon source. In addition, a detailed economic evaluation of the photo-Fenton process pointed out that optimizing the amount of reagent required is essential to lower the final cost (Sánchez Pérez *et al.*, 2013). The main reagents affecting operating cost are hydrogen peroxide and acid. Assuming that for highly polluted wastewater the process is carried out under optimal pH (around pH = 2.8) and addition of acid is unavoidable, the role of H_2O_2 dosing becomes essential to improve the treatment's economic competitiveness. On one hand, hydrogen peroxide concentration is directly related to the amount of hydroxyl radicals generated, and on the other, hydrogen peroxide competes with pollutants for the

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hydroxyl radical. Therefore, the amount of hydrogen peroxide added should be a balance between high enough mineralization rates (efficient hydroxyl radical reactions) and moderate hydroxyl radical scavenging.

The photo-Fenton process has been described by several authors as a reaction system including over 30 well-known reactions (Pignatello *et al.*, 2006; Burns *et al.*, 2010). Direct oxidation of Fe(II) by dioxygen is exceedingly slow at pH levels where Fe (III) is soluble and therefore does not contribute to Fenton of photo-Fenton reactions below pH 4. The most important of these reactions when hydrogen peroxide and oxygen are in solution can be summarized as follows:

$Fe(II)+H_2O_2 \rightarrow Fe(III)+HO^\bullet+HO^-$	$k=53\text{-}76\ M^{-1}s^{-1}$	Reac. 1
$HO^\bullet+R \rightarrow R^\bullet$		Reac. 2
$R^\bullet+O_2 \rightarrow ROO^\bullet$	$k \approx 10^9 M^{-1}s^{-1}$	Reac. 3
$ROO^\bullet+RH \rightarrow ROOH+R^\bullet$		Reac. 4
$ROO^\bullet+ H_2O \rightarrow ROH+ HO_2^\bullet$		Reac. 5
$O_2^{\bullet -}+H^+ \leftrightarrow HO_2^\bullet$; $pK_a=4.8$		Reac. 6
$HO_2^\bullet+ H_2O_2 \rightarrow HO^\bullet+H_2O+O_2$	$k=3\ M^{-1}s^{-1}$	Reac. 7
$Fe(III)+H_2O_2 \rightarrow Fe(II)+ HO_2^\bullet+H^+$	$k=9.1x10^{-7}M^{-1}s^{-1}$	Reac. 8
$Fe(III)+ HO_2^\bullet+H^+ \rightarrow Fe(II)+O_2+H_2O$	$k<2x10^3M^{-1}s^{-1}$	Reac. 9
$Fe(II)+ HO_2^\bullet+H^+ \rightarrow Fe(III)+ H_2O_2$	$k=1.2x10^6M^{-1}s^{-1}$	Reac. 10
$HO^\bullet+H_2O_2 \rightarrow H_2O+ HO_2^\bullet$	$k=4.7x10^7M^{-1}s^{-1}$	Reac. 11
$2H_2O_2 \rightarrow O_2+2H_2O$		Reac. 12
$2\ HO_2^\bullet \rightarrow H_2O_2+ O_2$	$k=8.3x10^5M^{-1}s^{-1}$	Reac. 13

As reaction of hydrogen peroxide with hydroxyl radicals finally produces oxygen (Reac. 11 and 13), and this reagent is also decomposed into water and oxygen (Reac. 12), monitoring dissolved oxygen (DO) has been suggested as an easy, measurable tool for studying progress of the photo-Fenton process and H_2O_2 consumption efficiency (Gernjak *et al.*, 2006; Prieto-Rodríguez *et al.*, 2011; Santos-Juanes *et al.*, 2011). Generation of too much oxygen is indicative of inefficient reaction conditions, whereas a decrease in dissolved oxygen concentration (to near zero) indicates participation of competitive superoxide radicals (Reac. 3-11) in the degradation of organic compounds and so low hydrogen peroxide concentrations available (Kunai *et al.*, 1986). Therefore, based on DO measurements, different strategies for optimizing hydrogen peroxide consumption have been proposed. For example, (Ortega-Gómez *et al.*, 2012) developed a system model (DO-H_2O_2) using the reaction curve method with an anti-windup proportional integral (PI) controller which achieved a 50% decrease in hydrogen peroxide consumption for decontamination of waste water containing paracetamol as a model pollutant. The behavior of the DO-H_2O_2 relationship has also been examined in tests of H_2O_2 automatic dosing strategies keeping DO between desirable set points (Prieto-Rodríguez *et al.*, 2011). These studies also showed the importance of the Dorfman mechanism (Dorfman *et al.*, 1962) during the first stages (Reac. 3-5) of photo-Fenton in which DO is actually consumed.

As a follow-up to such previous studies, different H_2O_2 dosing strategies, along with continuous supply of pure oxygen or air to the reaction medium, were analyzed to see whether external contribution of oxygen leads to lower H_2O_2 consumption for a specific level of degradation of complex wastewater.

2. Material and methods

2.1. Chemicals and reagents

Commercial formulations of five pesticides: 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. Distilled water used in the pilot plant was supplied by the Plataforma Solar de Almería (PSA) distillation plant (conductivity < 10 µS cm^{-1}, Cl^- = 0.2–0.3 mg l^{-1}, NO_3^- < 0.2 mg l^{-1}, organic carbon < 0.5 mg l^{-1}). Solar photo-Fenton experiments were performed using iron sulfate ($FeSO_4.7H_2O$), reagent grade hydrogen peroxide (30%, w/v) and sulfuric acid for pH adjustment (around 2.6-2.8) to avoid iron salt precipitation, all provided by Panreac (analytical grade). Pure oxygen (industrial quality) was also used as purchased from Carburos Metálicos S.A.

2.2. Analytical determinations

Mineralization was followed by measuring the dissolved organic carbon (DOC) by direct injection of filtered samples with 0.2 µm syringe-driven filters into a Shimadzu TOC-VCSN analyzer with an NDIR detector. Total iron concentration was monitored by colorimetric determination with 1,10-phenanthroline, following ISO 6332, using a Unicam-2 spectrophotometer. Hydrogen peroxide concentration was measured in a spectrophotometer at 410 nm based on the formation of a yellow complex from the reaction of titanium (IV) oxysulfate with H_2O_2 following DIN 38409 H15. Chemical oxygen demand (COD) was measured with Merck® Spectroquant kits. The absorbance was measured with a Merck Spectroquant® NOVA 30 photometer (an external calibration curve was used).

2.3. Experimental set-up

2.3.1. Solar photo-reactor

Solar photo-Fenton experiments were performed in a Compound Parabolic Collector (CPC) solar pilot plant specially developed for solar photo-Fenton applications (Malato *et al.*, 2009) and operated in batch recirculation mode. The reactor loop consists of a continuously stirred tank, a centrifugal recirculation pump (1.5 m^3 h^{-1}), and connecting tubing and valves. The solar collector is composed of four 1.04-m^2 CPC units (total area of 4.16 m^2). The total reactor volume is 75 L (V_T) and the total illuminated volume is 44.6 l (V_i). The temperature inside the reactor was kept at 35 °C using a temperature control system consisting of trace heating in the tubing, and cooling by a heat exchanger with a secondary cooling water cycle. For a detailed diagram of this solar reactor see (Maldonado *et al.*, 2007).

Dissolved oxygen (DO) and pH in the pilot plant were measured online by WTW® Sensolyt IQ system electrodes. All the online data acquisition instruments transmitted their measurements by analogical output of their respective controllers to a series of distributed I/O modules (Advantech® ADAM 4000 series). Custom SCADA (Supervisory Control and Data Acquisition) software for this was programmed in National Instruments® Lab-VIEW 7.0 at the Plataforma Solar de Almería. In the experiments in which hydrogen peroxide was automatically dosed as a function of dissolved oxygen, 30% w/v H_2O_2 solution was added to the batch recirculation tank by an Alldos® diaphragm dosing pump (Alldos® Primus 208 Etron Profi E26-0.8, at 1 ml min^{-1}). This pump was activated by the abovementioned SCADA software when the DO low setpoint was reached, and turned off when it reached the high setpoint.

Solar ultraviolet radiation (UV) was measured by a global UV radiometer (KIPP&ZONEN, model CUV3). Equation 1 was used for treatment of data acquired during the experiments, where t_n is the experimental time for each sample, UV (kJ l^{-1}) is the average solar ultraviolet radiation measured during Δt_n, A_T is the total illuminated area of collectors (m^2), V_T is the total volume of the pilot plant and $Q_{UV,n}$ is the accumulated energy (per unit of volume, kJ l^{-1}) incident on the reactor for each sample taken during the experiment.

$$Q_{UV,n+1}=Q_{UV}+\Delta t_n\cdot\overline{UV}_{G,n+1}\cdot\frac{A_i}{V_T};\ \Delta t_n=t_{n+1}-t_n \qquad \text{Eq. 1}$$

2.3.2 Experimental Procedure

Based on previous related work (Prieto-Rodríguez *et al.*, 2011) three different solar photo-Fenton treatments of waste water containing five commercial pesticides were carried out to determine whether H_2O_2 consumption could be reduced when working with a continuous supply of air or pure oxygen to remove at least 60% COD. This wastewater was used as a model because it was sufficiently complex to simulate different waste waters, and because our group has had long experience with it, making evaluation of the effect of adding oxygen on a well-known photo-Fenton process more consistent. The main purpose was to try and reinforce the Dorffmann mechanism for removal of organics, lowering H_2O_2 consumption and reducing the amount of sunlight required, as the Dorffmann mechanism is a “dark process”.

Experiments performed were: (i) Solar photo-Fenton with pure oxygen injected directly into the recirculation tank and excess hydrogen peroxide of 200-500 mg l^{-1}; (ii) Solar photo-Fenton under the same conditions as before, but injecting air; and (iii) Solar photo-Fenton with air injection and automatic dosing of H_2O_2 based on DO setpoints, instead of an excess of hydrogen peroxide.

The covered solar photo reactor was filled with 75 l of water and an amount of each of the five commercial pesticides necessary for 40 mg l^{-1} of DOC was added to the system, for a starting total DOC of 200 mg l^{-1}. Unfortunately, this could not be done with precision, since formulation ingredients usually caused foam and some of the DOC to not dissolve in water. As a consequence, the initial COD and DOC measured was usually not constant at the beginning of the treatment but the foam disappeared after a few minutes of treatment. After at least 15 min of homogenization, a sample was taken. Then, depending on the experiment, oxygen or air was injected into the reactor and maintained until the end of the experiment. Once DO was saturated in solution, the pH was adjusted to 2.8 with sulfuric acid. Afterwards, iron salt was added (20 mg l^{-1} Fe^{2+}) and well homogenized for 15 min. Fe concentration was the optimum for CPC photoreactor according to previous optimization (Malato *et al.*, 2004; Zapata *et al.*, 2009). At that moment, collectors were uncovered and the first dose of H_2O_2 was added, starting photo-Fenton. Samples were taken every 15 min, quickly filtered and analyzed. For those experiments in which it was attempted to keep hydrogen peroxide in excess (between 200-500 mg l^{-1}) throughout the test, reagent consumed was continuously replaced.

3. Results and discussion

3.1. Solar photo-Fenton with injection of pure oxygen

At the beginning of the experiment, the reaction medium was over-saturated with pure oxygen to around 32 mg l^{-1} of DO. Figure 1 presents the DOC and COD degradation profiles, changes in DO, and H_2O_2 consumption during the experiment. Once the photo-Fenton reaction began, DO quickly decreased during the first few minutes to 19 mg l^{-1}. After that, DO slowly but continuously decreased to below 1 mg l^{-1}, which is to now, the strongest COD reduction.

Reaction mechanisms in which dissolved oxygen is involved may take place during the first stage of the Fenton process, when it could be considered a soup-like radical. These mechanisms are maintained by the continuous injection of pure oxygen. That is, peroxo-organic radicals ($ROO^{\bullet}$) produced by the Dorfman mechanism (Reac.3) can participate in another series of reactions (Reac. 4 and 5), generating hydroperoxyl radicals, which are less reactive than hydroxyl radicals, mainly generated in solution at acid pH (Reac. 6) (Pignatello *et al.*, 2006), and can also react with the iron salts in solution (Reac. 9-10) generating more hydrogen peroxide and dissolved oxygen (Utset *et al.*, 2000). The most favored reaction, under these conditions, is Reac. 10, which caused generation of more H_2O_2, and a negative effect according to Reac. 11 (very high kinetic constant), capturing hydroxyl radicals. Reac. 10 also converted Fe(II) into Fe(III), impeding the efficiency of the Fe(II)-based Fenton reaction (Reac. 1). On the other hand, an excess of hydrogen peroxide could also start to self-decompose by Reac.12. Due to these alternative mechanisms, overall decontamination slows down, as observed at the beginning of the treatment, where DOC remained constant for a longer time than in the experiment without O_2 as reported previously (Prieto-Rodriguez *et al.*, 2011).

Taking into account that an input stream of pure O_2 was kept up until the end of the experiment, the DO profile observed in Figure 1 confirms its consumption throughout the process. Nevertheless, the heavy consumption of H_2O_2 in this experiment compared to the other one without injecting oxygen (Prieto-Rodriguez *et al.*, 2011), in which 60% of COD (with 6.9 kJ l^{-1}) was removed after consuming only 12 mM

(408 mg l^{-1}) of H_2O_2 must be highlighted. In this experiment, 60% of COD was eliminated after 28.4 kJ l^{-1} of accumulated UV energy and H_2O_2 consumption of 18 mM (612 mg l^{-1}). This shows that injection of pure oxygen into the reaction matrix has a negative effect on the solar photo-Fenton treatment of complex waste water.

Therefore, in an attempt to reduce this negative effect, in experiments described in Sections 3.2 and 3.3, air was continuously bubbled into the photo-reactor instead of pure oxygen.

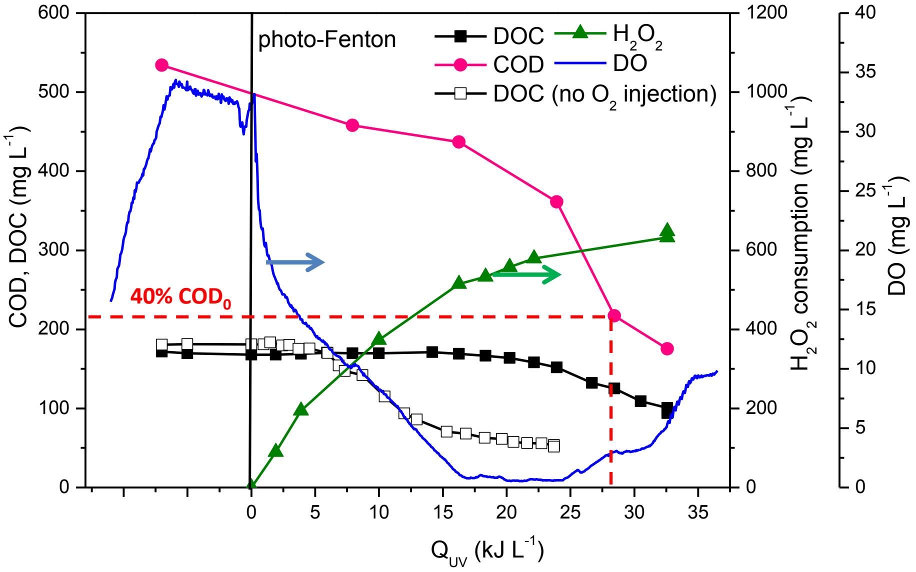

Figure 1. DOC and COD, H_2O_2 consumption and DO concentration during solar photo-Fenton with pure oxygen injection and excess of H_2O_2. DOC during solar photo-Fenton with the same initial conditions previously reported (no O_2 injection) (Prieto-Rodriguez *et al.*, 2011)

3.2. Solar photo-Fenton with air injection

Figure 2 shows the results of the experiment with air injection.

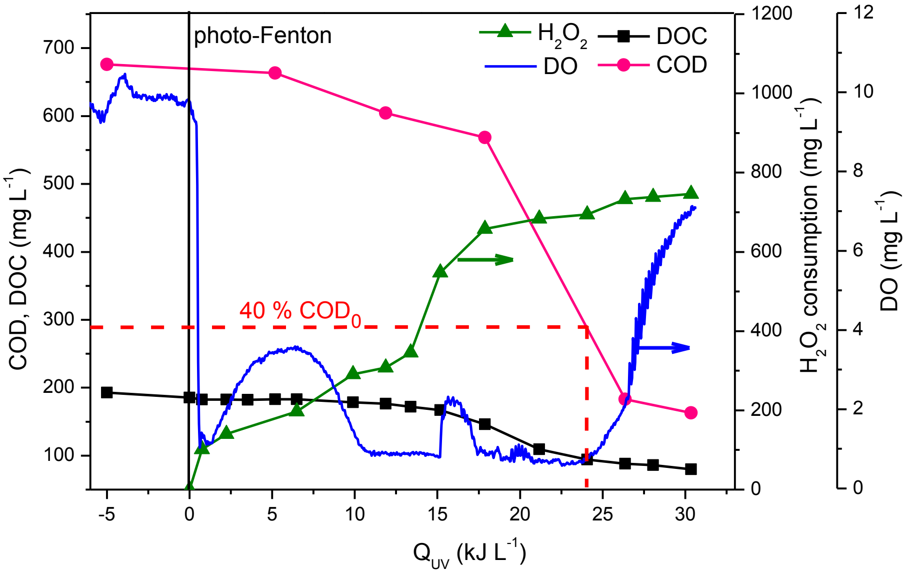

Figure 2. DOC and COD evolution, H_2O_2 consumption and DO concentration during solar photo-Fenton with air injection and excess H_2O_2

This test was carried out with the same initial operating conditions described in Section 3.1, except oxygen was continuously supplied by injecting air into the reaction tank, up to a maximum of 9.5 mg l^{-1} of DO.

As observed, COD remained almost constant during a shorter period of time and less accumulated energy was required for its degradation to begin, at approximately 13 kJ l^{-1} instead of 18 kJ l^{-1}, as previously observed when pure oxygen was injected. In this case, 20.5 mM (695 mg l^{-1}) of H_2O_2 was consumed to remove 60% of the initial COD (Q_{UV} = 24.2 kJ l^{-1}). This high consumption also shows inefficient replacement of H_2O_2 by O_2 from air, at least at the beginning of solar photo-Fenton. However, DO was rather low during the experiment, increasing only at the end of the treatment, when 60% of COD was mineralized. This substantial increase in DO may have been due to inefficient use of H_2O_2, because Reac.10 was generating H_2O_2 at the same time as Reac.12 (H_2O_2 decomposition) was producing oxygen, balancing the overall consumption of H_2O_2. This demonstrates the active participation of DO due to other undesirable reactions.

Again, as discussed in the section above, both oxidants were in excess (H_2O_2 and O_2) during most of the degradation process, but they were inefficient for removal of organics compared to H_2O_2 alone. Although in this case air was used instead of pure oxygen, it is clear that DO was also in excess giving rise to the undesirable mechanisms described in Section 3.1.

3.3. Solar photo-Fenton process with air injection and automatic dosing of H_2O_2

This experiment was done to evaluate the efficiency of DOC degradation and H_2O_2 consumption with DO from continuous injection of air , and using a very low amount of automatically controlled hydrogen peroxide. These operating conditions were maintained by an automatic H_2O_2 dosing system with on-off control according to low and high DO setpoints based on previously published results (Prieto-Rodriguez *et al.*, 2011). The DO control setpoints tested were 5 (on) and 7 (off) mg l^{-1} and the inlet flow rate was 1 mg l^{-1} min^{-1} of H_2O_2. With these set points, DO decreased to a minimum of approximately 2 mg l^{-1} at the beginning, even though automatic H_2O_2 dosing started when DO went below 5 mg l^{-1}. Afterwards, the DO concentration increased due to accumulation and self-decomposition of H_2O_2 to over 7 mg l^{-1}, when automatic dosing turned off. In order to start the degradation chain reaction (first steps Reactions 1 and 2) an initial amount of 0.2 mM (8 mg l^{-1}) of H_2O_2 was added right at the beginning.

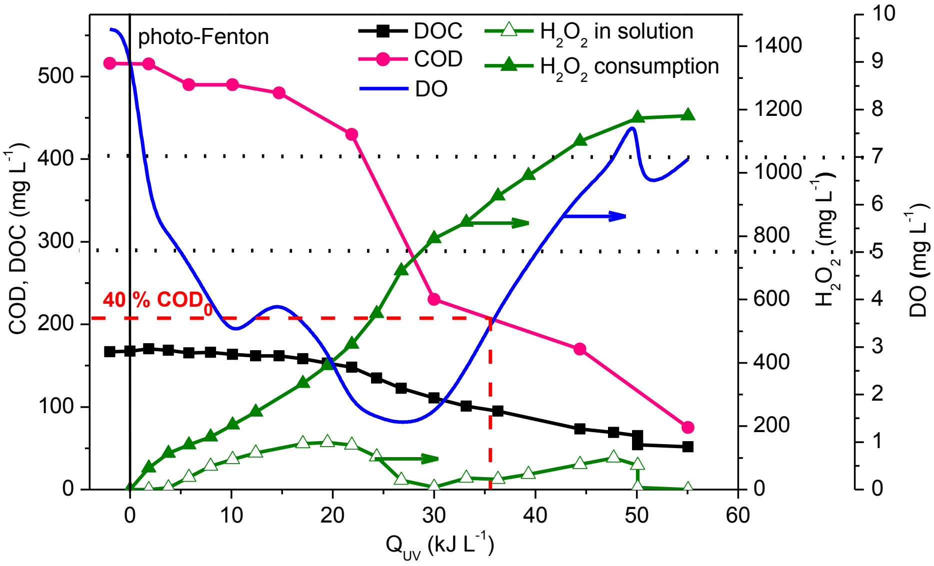

Figure 3. DOC and COD, H_2O_2 consumption and DO concentration during solar photo-Fenton with continuous air injection and automatic dosing of H_2O_2. DO setpoints (5 and 7 mg l^{-1}) are also shown (dotted lines). H_2O_2 in solution is also shown

H_2O_2 accumulated as observed in Figure 3. In this case, H_2O_2 reached a maximum of 148 mg l^{-1} at 19.4 kJ l^{-1} (see Figure 3), when rapid mineralization started. A sharp COD reduction from 17% (at 19.4 kJ l^{-1}) to 60% elimination was observed with H_2O_2 consumption of 11.5 mM (390 mg l^{-1}, see Figure 3). In this case, when 60% of the initial COD was removed (Q_{UV} = 36.3 kJ l^{-1}), around 900 mg l^{-1} of H_2O_2 had been consumed. Therefore, the H_2O_2 consumption was higher than for the two previous cases (see Sections 3.1 and 3.2). Although automatic dosing based on DO setpoints had been shown to be efficient in previous work (Prieto-Rodriguez *et al.*, 2011), in this case higher hydrogen peroxide consumption is related to the low initial hydrogen peroxide dose (8 mg l^{-1}), which did not permit proper evolution of Reacs. 2 and 3. As DO rapidly decreases from the beginning, a higher initial H_2O_2 would be recommendable. Excess oxygen supply seems also to have had a negative effect, as H_2O_2 was inefficiently consumed.

3.4. Comparison of key parameters

The main parameters used to observe the effectiveness of solar photo-Fenton in remediation of a complex waste water by direct injection of additional dissolved oxygen into the reaction medium are summarized in Table 1, which shows DOC elimination percentages, H_2O_2 consumption and the accumulated energy (Q_{UV}, kJ l^{-1}) needed to eliminate 60% of COD. We selected 60% COD elimination, because for complex and biorecalcitrant industrial waste water, this is usually the point at which wastewater biodegradability is sufficiently enhanced to end the chemical oxidation step, and proceed to final polishing with a conventional biological system (Ballesteros *et al.*, 2009; Oller *et al.*, 2011). Attending to the results, behavior of DOC was consistent as its degradation was always slower and reached lower degradation than COD. It is well known that to reduce COD is not needed complete mineralisation, as it is for DOC.

Table 1. Percentage of DOC mineralized, accumulated energy and hydrogen peroxide consumption required to eliminate 60% of COD

Exp.	Description	% DOC mineralized	Q_{UV} (kJ l^{-1})	H_2O_2 consumed (mg l^{-1})
i	Pure O_2 injection + H_2O_2 in excess (200-500 mg l^{-1})	27.1	28.4	612
ii	Air injection + H_2O_2 in excess (200-500 mg l^{-1})	49.6	24.2	695
iii	Air injection + H_2O_2 automatic dosage	44.3	36.3	900

4. Conclusions

It was demonstrated that an injection of air or pure oxygen in the photo-Fenton reaction medium along with excess H_2O_2 causes generation of radicals ($HO_2^{\bullet}$) that are less reactive than hydroxyl radicals, leading to longer irradiation and higher hydrogen peroxide consumption to be necessary for desired degradation of organics. So it may be concluded that aeration of the photoreactor is not recommendable.

Automatic control of H_2O_2 based on DO setpoints has been proven extremely useful and efficient for photo-Fenton to progress properly based on “online” measurements (DO), instead of “offline”, such as H_2O_2 experimental determination. Nevertheless, H_2O_2 consumption was higher when this reagent was controlled by DO setpoints than in the companion experiment with H_2O_2 continuously added in excess because of the extremely low starting dose of hydrogen peroxide. However, this would be easy to solve in any industrial implementation just by adding a larger amount of H_2O_2 at the beginning, and continuing beyond the automatic DO setpoint control.

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References

Ballesteros Martín M.M., Sánchez Pérez J.A., García Sánchez J.L., Casas López J.L. and Malato Rodríguez S. (2009), Effect of pesticide concentration on the degradation process by combined solar photo-Fenton and biological treatment, *Wat. Res.*, **43**(15), 3838-3848

Burns J.M., Graig P.S., Shaw T.J. and Ferry J.L. (2010), Multivariate Examination of Fe(II)/Fe(III) Cycling and Consequent Hydroxyl Radical Generation, *Environ. Sci. Technol*., **44**(19), 7226-7231.

DIN 38409-15 (1987). German standard methods for the examination of water, waste water and sludge; general measures of effects and substances (group H); determination of hydrogen peroxide and its adducts (H 15) DeutschesInstitut Fur Normung E.V. (German National Standard).

Dorfman L.M., Bühler R.E. and Taub I.A. (1962), Absolute rate constant for the reaction of hydroxyl radicals with benzene in water, *J. Chem. Phys*., **36**(2), 549-550.

Gernjak W., Fuerhacker M., Fernández-Ibañez P., Blanco J. and Malato S. (2006). Solar photo-Fenton treatment - Process parameters and process control, *Appl. Catal. B: Environ.,* **64**(1-2), 121-130.

Kunai A., Hata S., Ito S. and Sasaki K. (1986). The role of oxygen in the hydroxylation reaction of benzene with Fenton's reagent. 18O tracer study, *J. Am. Chem. Soc.,* **108**(19), 6012-6016.

Malato Rodrıguez S., Blanco Galvez J., Maldonado Rubio M.I., Fernandez Ibañez P., Alarcon Padilla D., Collares Pereira M., Farinha Mendes J. and Correia de Oliveira J., Engineering of solar photocatalytic collectors, *Sol. En.*, **77**, 513-524, 2004.

Malato S., Fernández-Ibáñez P., Maldonado M.I., Blanco J. and Gernjak W. (2009). Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends, *Catal. Today*, **147**, 1–59.

Maldonado M.I., Passarinho P.C., Oller I., Gernjak W., Fernández P., Blanco J. and Malato S. (2007), Photocatalytic degradation of EU priority substances: a comparison between TiO2 and photo-Fenton in a solar pilot plant, *J. Photochem. Photobiol. A: Chem.,* **185**, 354-363.

Oller I., Malato S. and Sánchez-Pérez J.A. (2011), Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination-A review, *Sci. Tot. Environ.,* **409**(20) 4141-4166.

Ortega-Gómez E., Moreno Úbeda J.C., Álvarez Hervás J.D., Casas López J.L., Santos-Juanes Jordá L. and Sánchez Pérez J.A. (2012), Automatic dosage of hydrogen peroxide in solar photo-Fenton plants: Development of a control strategy for efficiency enhancement, *J. Hazar. Mat.,* **237–238**, 223-230.

Pignatello J.J., Oliveros E. and MacKay A. (2006), Advanced oxidation processes for organic contaminant destruction based on the fenton reaction and related chemistry, *Crit. Rev. Environ. Sci. Technol.*, **36**(1), 1-84.

Prieto-Rodríguez L., Oller I., Zapata A., Agüera A. and Malato S. (2011), Hydrogen peroxide automatic dosing based on dissolved oxygen concentration during solar photo-Fenton, *Catal. Today*, **161**(1), 247-254.

Sánchez Pérez J.A., Román Sánchez I.M., Carra I., Cabrera Reina A., Casas López J.L. and Malato S. (2013), Economic evaluation of a combined photo-Fenton/MBR process using pesticides as model pollutant. Factors affecting costs, *J. Hazar. Mat*., **244-245**, 195-203.

Santos-Juanes L., Sánchez J.L.G., López J.L.C., Oller I., Malato S. and Sánchez Pérez J.A. (2011), Dissolved oxygen concentration: A key parameter in monitoring the photo-Fenton process, *Appl. Catal. B: Environ.,* **104**(3-4), 316-323.

Utset B., Garcia J., Casado J., Domenech X. and Peral J. (2000), Replacement of H_2O_2 by O_2 in Fenton and photo-Fenton reactions, *Chemosphere*, **41**, 1187-1192.

Zapata A., Velegraki T., Sánchez-Pérez J.A., Mantzavinos D., Maldonado M.I. and Malato S., Solar photo-Fenton treatment of pesticides in water: Effect of iron concentration on degradation and assessment of ecotoxicity and biodegradability, *Appl. Catal. B: Environ*., **88**, 448–454. 2009.