



An improved hybrid strategy for online dosage of hydrogen peroxide in photo-Fenton processes

Yu Xiangwei^a, Moisès Graells^a, Sara Miralles-Cuevas^b, Alejandro Cabrera-Reina^b,
Montserrat Pérez-Moya^{a,*}

^a Universitat Politècnica de Catalunya, Av. Eduard Maristany, 16, 08019 Barcelona, Spain

^b Programa Institucional de Fomento a la Investigación, Desarrollo e Innovación (PIDi), Universidad Tecnológica Metropolitana, Santiago, Chile

ARTICLE INFO

Editor: Despo Kassinos

Keywords:

Photo-Fenton process
Hydrogen peroxide dosage
Dissolved oxygen
Control
Wastewater

ABSTRACT

This work addresses the challenge of designing H₂O₂ dosage strategies for improving photo-Fenton applications, as well as for further understanding the effect of the dosage. The developed strategy focuses on the limitations of the current solution schemes by adopting a hybrid methodology between open and closed loop approaches and it is based on three different stages: (i) one-shot initial H₂O₂ addition (ii) continuous H₂O₂ dosage until reaching a specific dissolved oxygen (DO) level and (iii) on-off control of H₂O₂ dosage using DO slope as control variable. The proposed strategy is validated in the remediation of a Paracetamol solution (100 mg L⁻¹) and the results are assessed using H₂O₂ consumption and mineralization rate and level as performance criteria. The final tuning of the proposed strategy consists of: (i) only 40% of the stoichiometric H₂O₂ concentration, (ii) continuous feeding of H₂O₂ until a 4 mg L⁻¹ DO concentration is attained, and (iii) on-off control dosage selecting DO slope set-points in 0.1 and 0.2 mg L⁻¹ min⁻¹. These scheme and settings show an improvement of the process performance by ~ 15% with respect to the same H₂O₂ amount in a single-addition. This work contributes to improving photo-Fenton operations and designing more efficient processes.

1. Introduction

Hydrogen peroxide (H₂O₂) supply is inherent to Fenton and photo-Fenton processes, since it is the source of the highly oxidant hydroxyl radicals. However, an excess of H₂O₂ favors reactions consuming such radicals, which is an adverse effect, (Eqs. (1) and (2)) and is downgrading process performance [20]



Thus, the determination of the H₂O₂ dosage scheme minimizing such scavenging reactions and maximizing process efficiency is a crucial issue to be addressed. This is the reason why some authors [14] claim that the supply of H₂O₂, as a means to set the concentration of hydroxyl radicals, is the most significant operational parameter for the photo-Fenton process affecting both the reaction outcome and the cost of the process.

A considerable number of works has been devoted to empirically determining operational conditions supplying H₂O₂ in convenient

portions along the reaction time to improve process performance. While many proposed approaches have shown to be valuable in particular experimental setups, determining a general strategy is still pending [8, 21].

Splitting the total supply of H₂O₂ into several portions and adding them at different times has been reported to produce improvements over no dosage. However, the use of arbitrary amounts and time intervals prevents the solutions from being reported as optimal. Some researchers reported that sequential addition of discrete amounts of H₂O₂ leads to better results than adding a great initial dose [1,6]. Other previous works reported that adding H₂O₂ at a constant rate into the reactor along the reaction time increases the process efficiency [12,16,18].

To address dosage in a more systematic way, a pre-established H₂O₂ dosage protocol was proposed to improve the performance of the photo-Fenton process [22]. Although such dosage protocol can be successfully adjusted, it is limited to an initial addition and an initial dosing time, and only two degrees of freedom cannot accurately represent the operation flexibility.

Determining convenient schemes for adding finite amounts of

* Corresponding author.

E-mail address: montserrat.perez-moya@upc.edu (M. Pérez-Moya).

reactant at prefixed time intervals has been a natural preliminary approach to the dosage problem. Yet, this neglects the continuous nature of the problem. In this regard, Yu et al. [23] have recently addressed the open-loop continuous dosage of H_2O_2 as a dynamic optimization problem, which consists in determining a control law (the recipe) that drives the process through a feasible trajectory at a continuous time interval and minimizes a given cost function at the end of the interval. However, lacking an accurate and reliable dynamic model describing the process response to the dosage, the practical solution of such dynamic optimization problem was achieved through a coarse discretization and the experimental evaluation of a reduced set of dosage schemes.

Furthermore, all these works address the problem in an open-loop approach. No feedback is contemplated and the output does not affect the control action, the dosage, which is pre-set. However, a robust on-line approach should consider closed-loop strategies adjusting the dosage in response to disturbances and deviations of the desired output (this would further set another problem: i.e. the agreement of a quantitative assessment of the desired output at each time t , or at the end of a given time horizon). Towards this end, on-line measurements are needed and a practical and reliable observable should be adopted to guide the control action.

Oxidation reduction potential (ORP) and dissolved oxygen concentration (DO) are parameters that can easily be measured on-line. As these variables show significant changes during the photo-Fenton process, they can be envisaged as practical means to infer the process evolution [17,19,20]. Certainly, without a model explaining the correlation, the inference is purely empirical, but it could lead to practical results. For instance, Martínez, [11] proposed an extremum-seeking control cascade for automating Advanced Oxidation Processes (AOPs) and successfully implemented it for a photo-Fenton process, although no justification was provided for targeting at constantly driving ORP readings to its achievable maximum.

A practical alternative to ORP is dissolved oxygen (noted as DO when referred to the on-line signal). Since a product of the scavenging reactions is oxygen (O_2), Eq. (3), DO concentration is a sensible and promising measure that can be used as an indirect estimation of the extent of this effect. Prieto-Rodríguez et al. [17] reported that excess H_2O_2 decomposes to generate O_2 , which is directly suggesting the inefficient consumption of H_2O_2 . Therefore, the adaptive addition of H_2O_2 depending on the monitored DO has also been investigated, and practical improvements have been reported [14]. However, since a convenient fixed DO set-point is adopted, the approach cannot be considered general and further improvement could be attained (optimality is not guaranteed).



Again, the lack of an accurate and reliable dynamic model prevents a rigorous approach towards the optimal dosage scheme. Thus, practical dosage strategies still need to be developed to improve practical applications and to further understanding the nature of the dosage. Since both open and closed loop approaches provide partial advantages, a hybrid approach is presented.

Considering the strategies reported in literature as a starting point, this work focuses on the development of a systematic, reliable and generalized H_2O_2 dosage methodology for the treatment of a highly concentrated aqueous paracetamol solution by photo-Fenton process. The approach conceived consists in dividing the reaction span and consequently H_2O_2 dosage in three stages and addressing them separately, assuming their different qualitative effects in the reaction outcome: (1) initial H_2O_2 addition aimed at increasing initial mineralization rate, which is mainly influenced by a thermal Fenton reaction, (2) continuous H_2O_2 addition aimed at reaching a suitable H_2O_2 concentration in the reaction bulk for the photo-Fenton process and (3) automatic H_2O_2 dosage based on a control system aimed at keeping the H_2O_2 concentration constant at such concentration. In order to validate and assess the performance of this dosage strategy, a highly concentrated

acetaminophen (paracetamol commercial name) aqueous solution was generated as model pollutant, using mineralization rate, mineralization level and H_2O_2 consumption as performance criteria.

Assuming the concentration of the H_2O_2 solution given (33% w/v as usual) the dosage scheme has five degrees of freedom. While there is only one degree of freedom in the first stage, flexibility increases up to three degrees of freedom for the last stage. Table 1 presents the decision variables considered, along with the nomenclature used, and Fig. 1 shows a qualitative image of the dosage scheme.

2. Materials and methods

2.1. Reagents

Paracetamol (98% purity) was supplied by Sigma-Aldrich. Hydrogen peroxide (reagent-grade, 33% w/v) was provided by Panreac. Heptahydrate ferrous sulfate ($FeSO_4 \cdot 7H_2O$) used as ferrous ion source was purchased from Merck. Sulfuric acid (H_2SO_4 95%) was acquired from Fisher.

2.2. Pilot plant

The photo-Fenton experiments were performed in a batch-mode pilot plant, Fig. 2, consisting of a 13.5 L glass reservoir tank, a 1.5 L glass tubular photo-reactor, a centrifugal pump (Iwaki Magnet Pump, MD-30RZ-220, 1-16HP-220 V) and connecting tubing. Total reaction volume was 15 L for all experiments in this research. The radiation source is a Philips Actinic BL TL 36 W/10 1SL lamp (UVA-UVB), the incident photon power, $E = 3.36 \times 10^{-4}$ einstein min^{-1} (300 and 420 nm) was measured using potassium ferrioxalate actinometry. On-line measurement sensors are equipped for pH (Hamilton Polilyte HTVP 120), temperature and DO (Hamilton Oxsens) monitoring. H_2O_2 is automatically dosed through a peristaltic pump (Watson Marlow, OEM 313 24 V) and a PLC program (Siemens SIMATIC S7-1200) managed by the plant SCADA system (InTouchR® software).

2.3. Analytical methods

Total organic carbon (TOC) concentration was measured by a TOC (TOC-VCSH/CSN Shimadzu; Kyoto, Japan) analyzer. H_2O_2 concentration was determined by means of the spectrophotometric method developed by Nogueira et al. [13]. The absorption at 450 nm was detected via a U-2001 UV-vis spectrophotometer (Hitachi, Tokyo, Japan). Iron concentration in the reaction bulk was measured in filtered samples using the 1,10-phenanthroline method according to ISO 6332 [9].

2.4. Experimental procedure

The conditions of all the photo-Fenton experiments are described as follows: the pilot plant was filled with 15 L of distilled water including 100 $mg L^{-1}$ of dissolved Paracetamol, which is equivalent to 63 $mg L^{-1}$ of TOC. Afterwards, the pH was adjusted to optimum acidic conditions (2.8) with H_2SO_4 and, then, 20 $mg L^{-1}$ pre-dissolved $FeSO_4 \cdot 7H_2O$ were added. After a homogenization period of 10 min, the first sample was

Table 1
Dosage decision variables.

	Initial addition (1)	Constant flow (2)	On-off control (3)
Decision variables	<ul style="list-style-type: none"> Initial added volume (V_0) 	<ul style="list-style-type: none"> Flow ($F_1 = dV/dt$) DO set point (SP_1) 	<ul style="list-style-type: none"> Flow ($F_2 = dV/dt$) Upper control limit (SP_2) Lower control limit (SP_2)

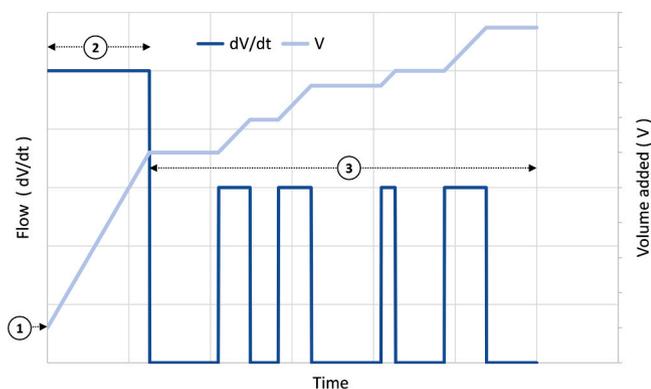


Fig. 1. Qualitative illustration of the H_2O_2 dosage scheme: (1) Initial addition (2) Constant flow and (3) On-Off control.

taken for initial iron and TOC measurements. Finally, H_2O_2 was added and the UV lamp switched on immediately after in order to trigger the photo-Fenton process. Duplicate TOC and iron measurements were always performed.

Experiments with hybrid H_2O_2 dosing strategies were performed following the three-stage procedure described next:

- 1. Initial stage (open-loop):** Single one-shot addition at the beginning of the experiment, t_0 . The initial H_2O_2 concentrations produced by this supply ranged from 94.5 to 944.7 mg L^{-1} , i.e. from 20% to twice the H_2O_2 stoichiometric amount (S) for 100 mg L^{-1} paracetamol (from 0.2S to 2S).
- 2. Transition stage (close-loop):** Continuous automatic addition of H_2O_2 (a peristaltic pump controlled by a SCADA maintained a prefixed flow rate, 0.287 mL min^{-1}) until the set DO level was attained. The DO level settings ranged from 4 to 12.5.
- 3. Final stage (closed-loop):** An on-off controller was employed to automatically add H_2O_2 depending on the DO slope. A fixed rate

H_2O_2 flow (0.287 mL min^{-1}) was turned off when the DO slope exceeded a maximum threshold and it was turned on when the DO slope fell below a minimum threshold (different threshold values were tested as explained in Section 3.3.2).

3. Results and discussion

The dosage strategy presented in this work consists in dividing the reaction span in three stages and addressing them separately, assuming their different qualitative effects in the reaction outcome and the significant differences on the dissolved oxygen production rate along the treatment, which hinders the use of this parameter as a control variable with a single set point.

3.1. Initial stage: hydrogen peroxide initial addition

The process was initially determined by the classical Fenton chain reaction, known also as thermal Fenton, meaning that it is driven by thermal energy from the surroundings rather than photochemical energy [15]. This step is characterized by a high H_2O_2 consumption, which is immediately afterwards reflected in a high HO^\bullet production and fast mineralization rate, suggesting the necessity of a high single initial H_2O_2 dose for the reaction kick-off. Thus, to determine the most adequate conditions at this stage, the effect of the initial H_2O_2 addition on process performance was evaluated using different initial concentrations. Based on the theoretical stoichiometric H_2O_2 concentration needed to achieve the complete mineralization of the wastewater (noted as S), different concentrations in the range from 20% (94.5 mg L^{-1}) to 200% (944.7 mg L^{-1}) of this theoretical concentration were selected. This range was assumed to represent very different situations from exhaustive H_2O_2 limitation to significant H_2O_2 excess. By way of example, the notation used for the initial addition experiments was 0.2S for 20% and 2S for 200% stoichiometric concentrations. As depicted in Fig. 3, the results showed a saturation effect of the mineralization rate ($\text{mg of TOC removed min}^{-1}$) above $\approx 0.4\text{S}$. In spite of increasing the initial H_2O_2

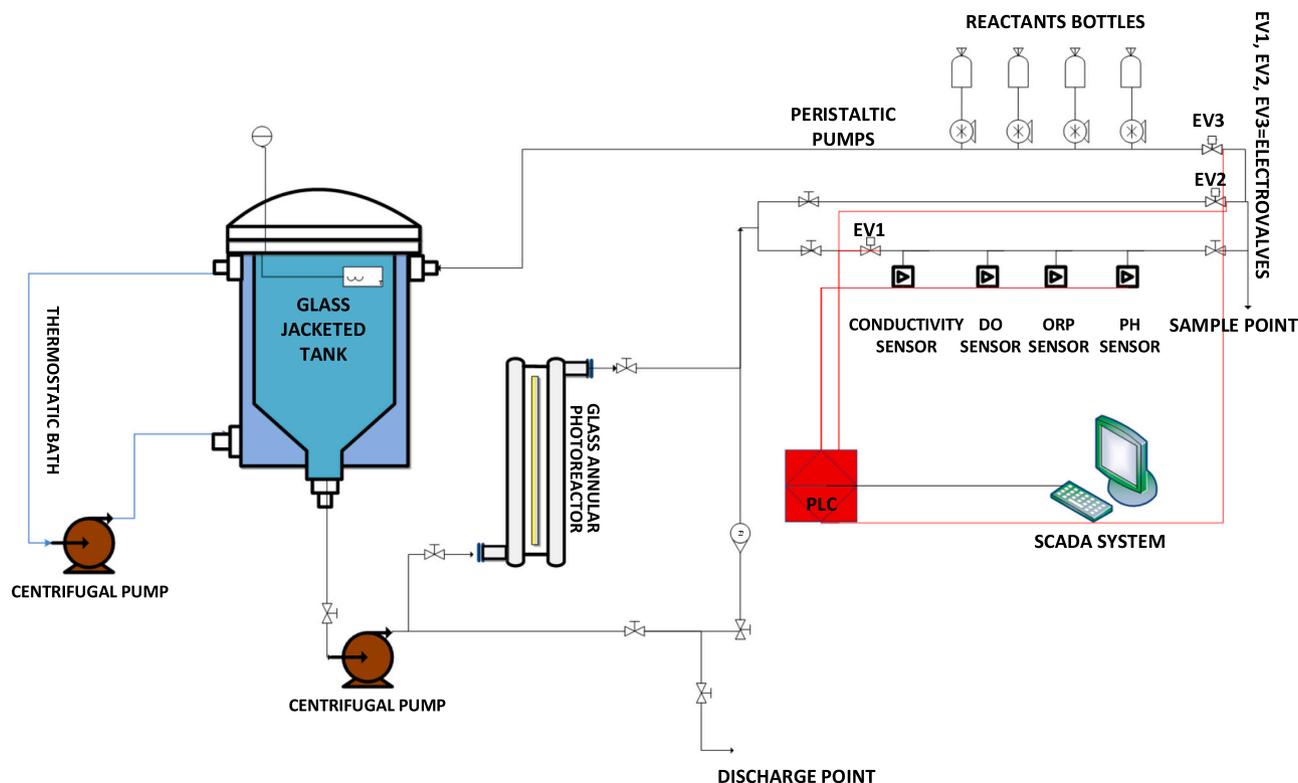


Fig. 2. Pilot Plant schematic representation.

concentration, the mineralization rate reached a maximum value equivalent to $\approx 0.025 \text{ mg TOC min}^{-1}$ after 5 min of reaction time. Below 0.4S, there was a lack of H_2O_2 in the reaction bulk so that not enough HO^\bullet were produced, limiting the decontamination process. In contrast, above 0.4S there was no improvement of process performance since side reactions were favored. H_2O_2 can be auto-decomposed to water and dissolved oxygen. The use of simplified photo-Fenton mechanisms suggested that HO^\bullet may recombine or react with H_2O_2 and also yielding dissolved oxygen [3]. Therefore, the high amount of radicals produced together with the high amount of H_2O_2 initially present in the reaction bulk, increased the occurrence of reactions that are not related to organic matter oxidation but to dissolved oxygen generation. This is also in accordance with the H_2O_2 consumptions obtained, which increased linearly with the initial amount of H_2O_2 added to the photo-reactor (Fig. 3). Whilst only 139 mg L^{-1} of H_2O_2 were consumed after 5 min of reaction time when 0.4S were used for the initial addition, this value increased linearly up to 675 mg L^{-1} for 2S. Thus, since above 0.4S H_2O_2 was unnecessarily consumed, this value was selected as the optimum initial addition for the rest of the study. Fig. 4 reinforces the conclusions withdrawn from Fig. 3. Initial additions beyond 0.4S show a clear increase in the DO signal that reflects the H_2O_2 excess in the system. This indicates an inefficient use of the reagent, which is deemed to be partially spent in competitive reactions.

3.2. Transition stage: continuous H_2O_2 addition

While the first addition was prefixed, the addition at the second stage was variable according to the time required to attain a convenient DO level with a constant predetermined flow. Despite the simplicity, this second stage was performed closed-loop and the control action (the end of the constant flow) depended on the measured response of the system. In this way, the transition stage considered a continuous H_2O_2 addition aimed at keeping the initially reached maximum mineralization without (significant) H_2O_2 accumulation using online DO signal as reference to stop the dosage once this accumulation started to occur. Each assay of this experimental series followed the same procedure: (i) 0.4S H_2O_2 (188.9 mg L^{-1}) initial addition and (ii) fixed H_2O_2 continuous addition ($0.287 \text{ mL min}^{-1}$ equivalent to $94.71 \text{ mg min}^{-1}$) from the beginning of the experiment until reaching the corresponding DO set up.

During the initial min of the treatment, there was a decrease in the dissolved oxygen concentration due to Dorfman mechanism (Fig. 5), which is characterized by carbon-centered free radicals ($\text{R}\cdot$) reaction with dissolved oxygen [7,10]. Even though DO signal diminished to concentrations close to zero after ≈ 3 min of reaction time; the mineralization rate was kept at maximum level. This was validated by an additional experiment at higher H_2O_2 addition rate (1.47 mL min^{-1} equivalent to 484 mg min^{-1}) from the beginning of the experiment until

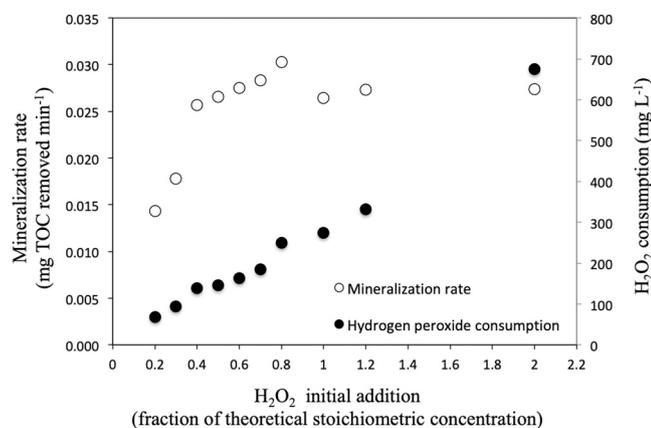


Fig. 3. Effect of the H_2O_2 initial addition on mineralization rate and H_2O_2 consumption after 5 min of reaction time.

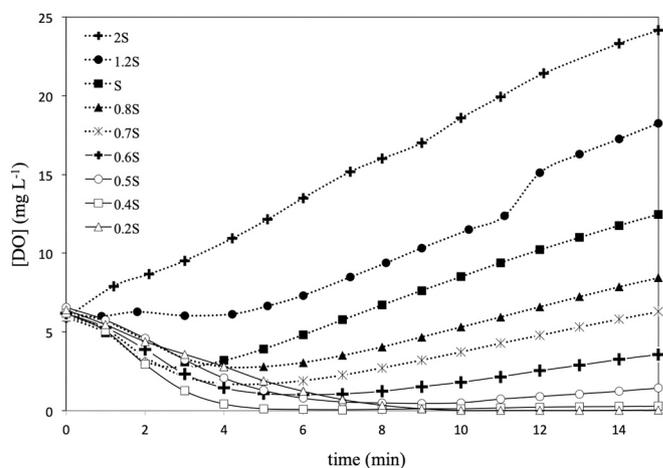


Fig. 4. Effect of the H_2O_2 initial addition on DO evolution during the initial stage experiments.

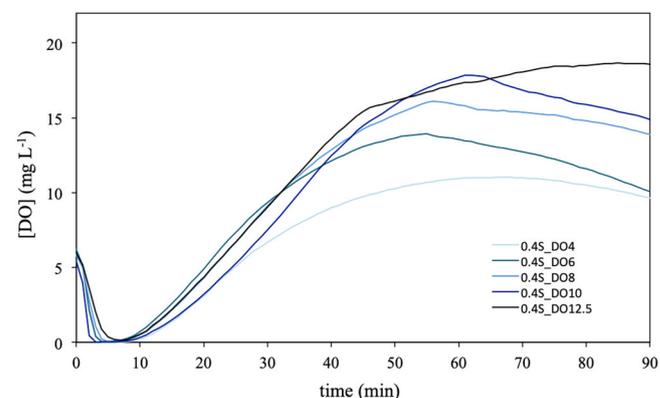


Fig. 5. DO evolution profiles for the transition stage experiments in which different DO set points for H_2O_2 dosage pump stop were studied.

16.5 min, when DO reached the highest concentration of the whole experimental series (12.5 mg L^{-1}). Although this change in the operating conditions allowed DO concentration not to decrease to zero, it did not improve the mineralization rate (data not shown). It is important to note that this is not in accordance with the results obtained by Santos-Juanes et al. [19], who reported that such a low DO value indicates a lack of H_2O_2 in the reaction bulk. Probably, the higher wastewater TOC concentration selected for that work, the differences in the experimental set-up (photo-reactor) and the different irradiance levels available during the experiments were responsible of the differences in the information provided by the DO signal. This points out the necessity of developing generalized H_2O_2 dosage strategies that must be afterwards locally optimized.

From ≈ 5 min, DO signal started to increase (Fig. 5). The selected DO concentrations at which the H_2O_2 dosage pump was stopped were 4, 6, 8, 10 and 12.5 mg L^{-1} (noted in Fig. 5 as DO4, DO6, DO8, etc.), which corresponded to 22, 24, 29, 35 and 39 min of operation time, respectively. From this point on, experiments were codified as follows: "initial addition_DO set point selected for H_2O_2 dosage pump stop". By way of illustration, 0.4S_DO6 is the notation for the experiment with 0.4S initial addition and continuous H_2O_2 addition from the beginning of the experiment until DO signal reaching 6 mg L^{-1} .

The results showed no significant differences in the mineralization rates up to 45 min, indeed, the average pseudo-first order kinetic constants related to TOC mineralization of this experimental series were in the range from $4.8 \cdot 10^{-3}$ to $5.6 \cdot 10^{-3} \text{ min}^{-1}$ with no trend related to the DO signal. The ratios of TOC removed to H_2O_2 consumed (mg/mg) were

obtained at 15, 30 and 45 min of reaction time for the different transition stage experiments (duplicate assays; the average value is shown in Fig. 6-A). Indeed, they are extremely similar, independently of the DO set-point selected. The H_2O_2 concentration curves demonstrated that, between 15 and 25 min of reaction time, the H_2O_2 started to accumulate in the system, which was detrimental for process performance due to side reactions proliferation (Fig. 6-B). While the H_2O_2 concentration remained in the range from 90 to 100 mg L^{-1} between 5 and 15 min of operation time, this concentration increased up to 110–140 mg L^{-1} after 30 min depending on the experiment. In addition, to keep H_2O_2 dosage after DO concentration achieving 4 mg L^{-1} not only involved H_2O_2 accumulation, but also the unnecessary increase of H_2O_2 consumption. Consequently, 4 mg L^{-1} of DO (22 min) was selected as reference to stop the H_2O_2 dosage pump in the transition stage.

3.3. Final stage: automatic H_2O_2 dosage

After the simple close-loop control performed during the transition stage, a more flexible close-loop strategy was adopted for the final stage. The final on-off automatic control presented automatically cuts and restarts the H_2O_2 dosage pump (0.287 mL min^{-1}) depending on the value attained by the DO slope, which will be justified in the following subsections.

3.3.1. Drawbacks of DO as control variable

Maintaining $\approx 100 \text{ mg L}^{-1}$ of H_2O_2 during the photo-Fenton treatment of industrial wastewaters is reported as a suitable operational condition since it does not limit the mineralization rate (i.e. it grants an acceptable propagation rate for side reactions). Several works on the sequential (manual) addition of H_2O_2 have used this reference value to decide when to add H_2O_2 as well as the amount to add [2,4,5]. Thus, at the end of the transition stage, it can be assumed that the mineralization was at maximum rate and the H_2O_2 at optimum concentration. Accordingly, the objective of the final stage is to define an automatic dosage strategy aimed to maintain $\text{H}_2\text{O}_2 \approx 100 \text{ mg L}^{-1}$ up to the end of the process. Although DO concentration has been successfully used as control signal with this objective [14,17], the DO concentration value obtained at the end of the transition stage (4 mg L^{-1}) does not allow this possibility in this particular case. Oxygen saturation concentration in water at 25 °C was 8.3 mg L^{-1} ; this means that dissolved oxygen will automatically increase to this value as the final stage progresses even without dissolved oxygen generation reactions. Furthermore, since Dorfman mechanism is not relevant anymore after the initial reaction

min, dissolved oxygen will never decrease again to 4 mg L^{-1} independently of H_2O_2 addition. Therefore, control systems like the one proposed by Ortega-Gómez et al. [14] based on a single DO signal set point cannot be adopted as a generalized solution because control set up cannot be selected at 4 mg L^{-1} ($\approx 50\%$ saturation concentration). It is fair to comment that the amount of H_2O_2 needed will increase when treating waters with a higher initial pollution load leading to higher DO values and this will allow the use of a control systems based on DO. However, this is not the only disadvantage of using DO concentration as a reference variable to obtain information about H_2O_2 concentration variation in the reaction bulk. This parameter presents an important delay in its response to H_2O_2 changes in the reaction system, as depicted in Fig. 7, which corresponds to a preliminary experiment of the final stage. This assay followed the above-proposed strategies for the initial and transition stages (0.4S_DO4, i.e. 0.4S H_2O_2 initial addition and continuous H_2O_2 addition until DO signal reaching 4 mg L^{-1}) and, during the final stage, alternated H_2O_2 dosage and no dosage periods every 10 min. From the start of the final stage (22 min) DO signal always increased, even when H_2O_2 concentration in the system diminished due to no dosage periods. This means that DO signal provided misinformation about process performance. After 85 min, when the dosage was definitively stopped until the end of the experiment, 16 min were

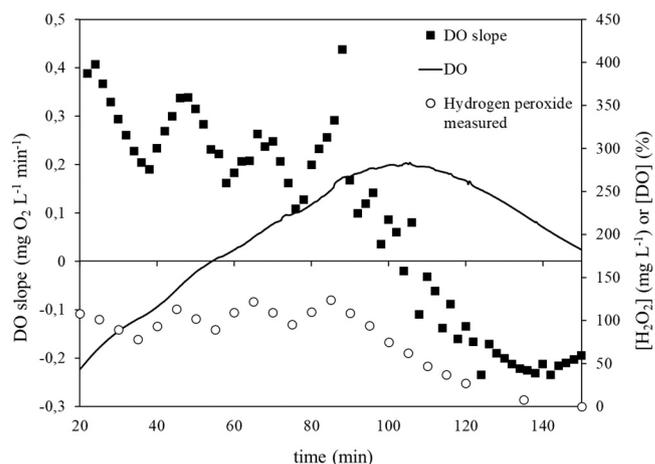


Fig. 7. Comparison between DO and DO slope ($\Delta t = 2 \text{ min}$) responses to changes in H_2O_2 concentration in the reaction bulk during the final stage.

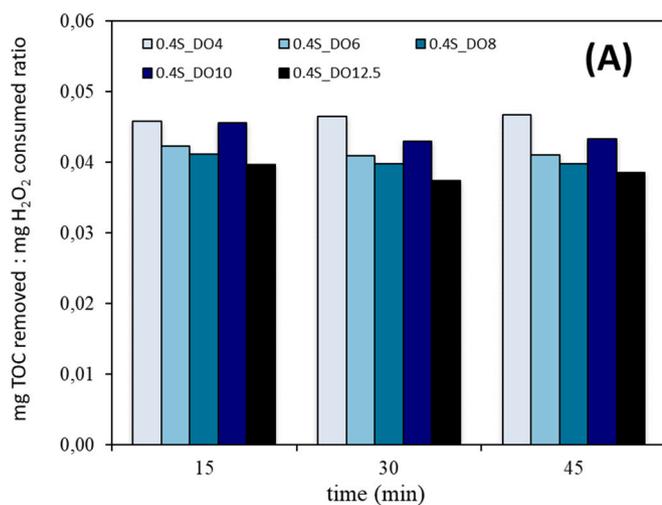
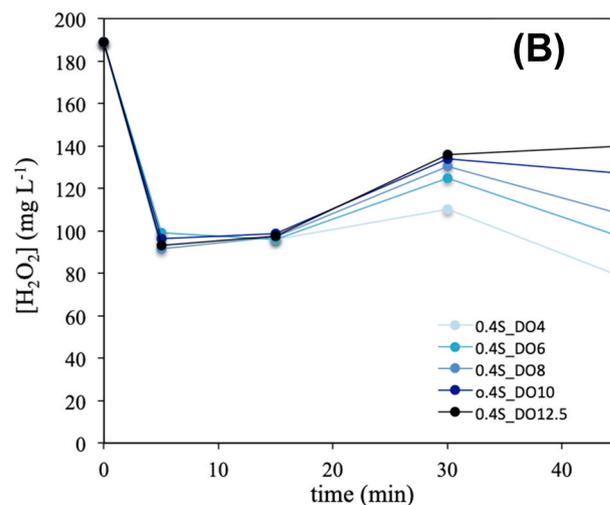


Fig. 6. H_2O_2 concentration curves (A) and mg of TOC removed to mg of H_2O_2 consumed ratio calculated at different reaction times (B) obtained for the experiments of the transition stage.



needed to observe a decrease in the DO signal, which is indeed a very high response time. Since DO seems to be useful only under certain conditions, efforts were focused on finding new options to select a new control variable.

Despite the drawbacks commented above, slight variations in the DO curve trend could be observed each time the H_2O_2 dosage pump was switched on/off. This suggests the significance of the information that the DO slope may bring. Consequently, the DO slope evolution is also provided in Fig. 7. DO slope of the already available experiments was calculated by means of Eq. (4) to delve into the information provided by this parameter.

$$DO_{slope} = \frac{\Delta DO}{\Delta t} = \frac{\overline{DO}_1 - \overline{DO}_2}{\Delta t} \quad (4)$$

Where \overline{DO}_1 is the average DO corresponding to the time period from “t- Δt ” to “t” and \overline{DO}_2 is the average DO corresponding to the time period from “t-2 $\cdot\Delta t$ ” to “t- Δt ”, being Δt a certain period of time that can be selected by the user. By way of illustration, the DO slope calculated on a 2 min basis (Δt) corresponding to minute 8 can be obtained as the difference between the average DO from minute 6 to minute 8 and the average DO from minute 4 to minute 6, divided by 2 min.

Different values of Δt from 1 s to 3 min were used to compare the different DO slope responses. The results showed that the response of this variable started to be representative of the H_2O_2 concentration behavior when Δt was in the range from 1 to 2 min. For instance, during the H_2O_2 concentration decrease observed from minute 22 to 35 in the above-mentioned preliminary experiment of the final stage (Fig. 7), DO always tended to increase, however, DO slope ($\Delta t = 2$ min) decreased accordingly with a slight delay. Lower values of Δt based on a few seconds showed almost constant responses because the changes in DO signal were zero or extremely low, while calculations based on Δt of around half a minute were in general representative but presented an important dispersion, as occurs with DO signal.

3.3.2. New control strategy based on DO slope

The control strategy presented was based and tuned according to these observations. Given that the DO slope presented a faster and more representative response to H_2O_2 concentration changes than DO and, additionally, that any value could be selected as set-point independently of the DO level, a control system to tune DO slope ($\Delta t = 2$ min) and consequently H_2O_2 concentration during the final stage of the photo-Fenton process is proposed. Notation for these experiments follows the one selected for previous stages and adds the specific code for this step, which gives practical information about H_2O_2 dosage pump automatic control. By way of illustration, 0.4S_DO4_L0.2_H0.35 means 0.4S H_2O_2 initial addition, continuous H_2O_2 addition until DO reaching 4 mg L⁻¹ and H_2O_2 automatic dosage with H_2O_2 dosage pump stop when DO slope reaches 0.35 mg L⁻¹ min⁻¹ and H_2O_2 dosage pump re-start when DO slope reaches 0.20 mg L⁻¹ min⁻¹.

According to Fig. 7, DO slope values of ≈ 0.2 – 0.3 mg L⁻¹ min⁻¹ can be associated to H_2O_2 concentrations of ≈ 100 mg L⁻¹ in the reaction bulk. In this way, a first experiment was carried out using an on-off control system tuned to control DO slope values between 0.20 mg L⁻¹ min⁻¹ (low limit, H_2O_2 dosage pump switch on) and 0.35 mg L⁻¹ min⁻¹ (high limit, H_2O_2 dosage pump switch off). The results showed slight H_2O_2 accumulation from 70 min so that the H_2O_2 concentration in the system almost reached 140 mg L⁻¹ at the end of the experiment, indicating that the selected control range could be improved. The average H_2O_2 concentration during the final stage of this experiment was 113 ± 18 mg L⁻¹. Therefore, the control limits were diminished to 0.15 and 0.25 mg L⁻¹ min⁻¹, which allowed a more precise control of the H_2O_2 concentration resulting in an average value of 102 ± 8 mg L⁻¹. Thus, the proposed strategy was validated since, with a very simple control system, the H_2O_2 concentration could be controlled with an acceptable accuracy. As can be seen in Fig. 8, no difference was found in

the mineralization profiles obtained between both control strategies, therefore, the DO slope limits were again decreased to 0.10 and 0.20 mg L⁻¹ min⁻¹ in order to maintain a lower H_2O_2 concentration in the reaction bulk during the experiment. Again, an equivalent mineralization profile with respect to the previous experiments was obtained. The average H_2O_2 concentration of this assay during the final stage was 81 mg L⁻¹. However, two different zones can be observed after the initial addition period (Fig. 8). From ≈ 60 min up to the end of the experiment, the H_2O_2 concentration about 70 mg L⁻¹, which was the primary objective of reducing the DO slope. In contrast, from ≈ 25 min to ≈ 60 min, the H_2O_2 concentration decreased from ≈ 100 mg L⁻¹ to 70 mg L⁻¹. Based on the obtained results, which indicate that 70–80 mg L⁻¹ of H_2O_2 concentration is a better option than 100 mg L⁻¹, the DO set-point of the transition stage could also probably be diminished without any significant decontamination efficiency lose.

3.4. H_2O_2 dosage validation

It is important to note that the objective of this work was not to optimize the H_2O_2 dosage, but to develop a methodology to do it. No additional experiments using lower DO slope set-points or diminishing the DO set-point of the transition stage were carried out because it makes no sense to optimize the treatment of a simple synthetic wastewater. Real wastewaters will for sure lead to higher H_2O_2 consumption due to the presence of radical scavengers in the water matrix and to longer treatment times. In contrast, to validate the developed H_2O_2 dosage methodology, four additional assays using different H_2O_2 single one-shot additions in the range from S to 2S were performed.

The amount of TOC removed was significantly lower for all the experiments in which H_2O_2 was completely added from the beginning of the assays due to side reactions proliferation as a consequence of H_2O_2 excess. While 63, 66, 66 and 65 % of TOC were removed for the S, 1.1S, 1.2S and 2S single one-shot addition experiments, respectively, the TOC removed with the 0.4S_DO4_L0.10_H0.20 experiment increased up to 75 % (Fig. 9-left). Furthermore, the H_2O_2 consumption of the latter experiment was only 464 mg L⁻¹, i.e. 98% of the theoretical stoichiometric concentration needed to achieve the wastewater complete mineralization, i.e. almost equivalent to the one of the S experiment. Thus, the TOC removed: H_2O_2 consumed ratio (Fig. 9-right), which varied between 0.13 and 0.07 mg of TOC mg of H_2O_2 ⁻¹ in the single addition experiments, was meaningfully higher for the 0.4S_DO4_L0.10_H0.20 experiment (0.16 mg of TOC mg of H_2O_2 ⁻¹)

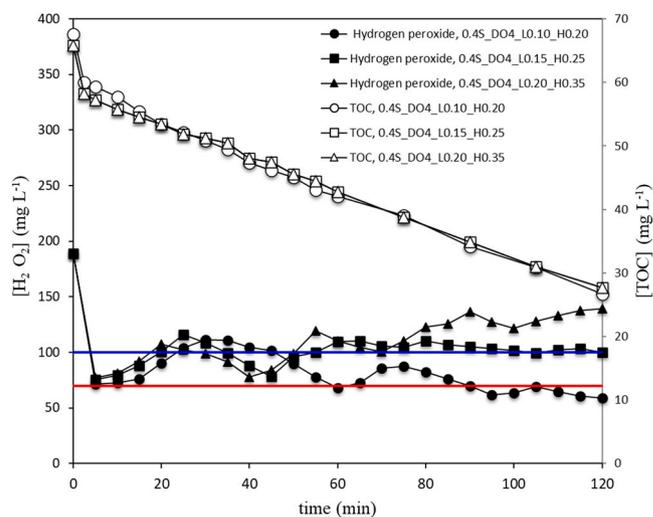


Fig. 8. Comparison of H_2O_2 concentration curves (full symbols) and TOC mineralization profiles (empty symbols) using different DO slope set-points during final stage experiments. The horizontal lines represent different H_2O_2 concentration objectives to maintain during the final stage experiments.

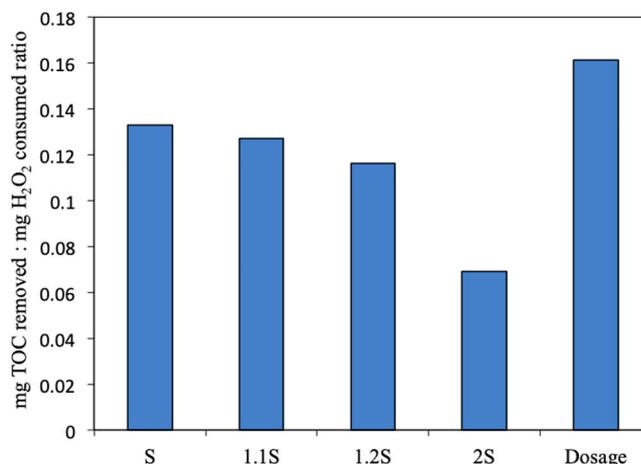
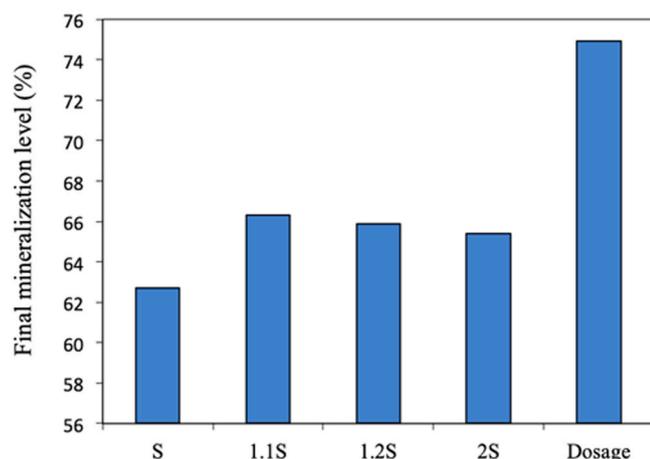


Fig. 9. Comparison of the % TOC removed (left) and the TOC removed:H₂O₂ consumed ratio obtained for the single addition experiments and the assay in which the developed H₂O₂ dosage strategy was used.

validating the utility of the developed dosage strategy.

4. Conclusions

This work contributes to a new insight towards improving photo-Fenton process by designing efficient hydrogen peroxide dosage strategies. In order to address the limitations of current approaches, a flexible hybrid method combining both open and closed loop dosage approaches was formalized and discussed. The novel dosage scheme is based on three different stages: the initial stage, the subsequent continuous H₂O₂ feed (transition stage), and the final on-off control stage.

The scheme results in five decision variables to be adjusted: the initial concentration of H₂O₂, the slope of the continuous H₂O₂ feed in the transition stage (the flowrate and the DO set-point serving as the termination criterion), and the upper and lower limits of the slope of monitored DO that trigger the on-off control of such a H₂O₂ feed.

Results show that there exists a set of values for the decision variables that can be determined and that leads to enhancing the efficiency of the photo-Fenton operations. In the case studied, the experimental results showed that, for the same Paracetamol sample, the best settings for the flexible scheme proposed increased the process performance (the ratio TOC removed to H₂O₂ consumed) by ~ 15% with respect to the single initial addition option. Compared with other works reporting a value of 100 mg L⁻¹ as a convenient set-point to be kept for the H₂O₂ concentration during the dosage, this work shows that it can be decreased to 70–80 mg L⁻¹, which means increased H₂O₂ savings.

Thus, this work shows quantitative and qualitative enhancements of the photo-Fenton process performance through more flexible H₂O₂ dosage strategies and indicates that designing and tuning more efficient dosage strategies is still an open issue.

Further improvements of this methodology should focus on the treatment of more complex wastewaters (water matrix effect, different TOC concentrations and pollutants, etc.), the possibility of using variable DO slope set-points during the final stage, and the use of more complex control systems such as PI or PID.

CRedit authorship contribution statement

Yu Xiangwei: Investigation, Methodology, Visualization, Data curation. **Moisés Graells:** Conceptualization, Methodology, Funding acquisition, Writing - review & editing. **Sara Miralles-Cuevas:** Conceptualization, Writing - original draft, Writing - review & editing. **Alejandro Cabrera-Reina:** Conceptualization, Data curation, Writing - original draft, Writing - review & editing. **Montserrat Pérez-Moya:** Conceptualization, Data curation, Formal analysis, Resources,

Methodology, Supervision, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the Spanish "Ministerio de Economía, Industria y Competitividad (MINECO)" and the European Regional Development Fund, both funding the research Project AIMS (DPI2017-87435-R). Yu Xiangwei particularly acknowledges the State Scholarship Fund of China Scholarship Council (No. 201706950041). A. Cabrera-Reina and S. Miralles-Cuevas want to thank SERC Chile (ANID/FONDAP/15110019) and ANID/FONDECYT/1200460.

References

- C.V.D.S. Almeida, M.S. Macedo, K.I.B. Eguliz, G.R. Salazar-Banda, D. D. Queissada, Indanthrene blue dye degradation by UV/H₂O₂ process: H₂O₂ as a single or fractioned aliquot? *Environ. Eng. Sci.* 32 (2015) 930–937, <https://doi.org/10.1089/ees.2015.0171>.
- M.M. Ballesteros Martín, J.A. Sánchez Pérez, J.L. Casas López, I. Oller, S. Malato Rodríguez, Degradation of a four-pesticide mixture by combined photo-Fenton and biological oxidation, *Water Res.* 43 (2009) 653–660, <https://doi.org/10.1016/j.watres.2008.11.020>.
- A. Cabrera Reina, L. Santos-Juanes, J.L. García Sánchez, J.L. Casas López, M. I. Maldonado Rubio, G. Li Puma, J.A. Sánchez Pérez, Modelling the photo-Fenton oxidation of the pharmaceutical paracetamol in water including the effect of photon absorption (VRPA), *Appl. Catal. B Environ.* 166–167 (2015) 295–301, <https://doi.org/10.1016/j.apcatb.2014.11.023>.
- A. Cabrera Reina, S. Miralles-Cuevas, J.L. Casas López, J.A. Sánchez Pérez, Pyrimethanil degradation by photo-Fenton process: influence of iron and irradiance level on treatment cost, *Sci. Total Environ.* 605 (2017) 230–237, <https://doi.org/10.1016/j.scitotenv.2017.06.217>.
- A. Cabrera Reina, S. Miralles-Cuevas, G. Rivas, J.A. Sánchez Pérez, Comparison of different detoxification pilot plants for the treatment of industrial wastewater by solar photo-Fenton: are raceway pond reactors a feasible option? *Sci. Total Environ.* 648 (2019) 601–608, <https://doi.org/10.1016/j.scitotenv.2018.08.143>.
- W. Chu, K.H. Chan, C.Y. Kwan, K.Y. Choi, Degradation of atrazine by modified stepwise-Fenton's processes, *Chemosphere* 67 (2007) 755–761, <https://doi.org/10.1016/j.chemosphere.2006.10.039>.
- L.M. Dorfman, I.A. Taub, R.E. Bühler, Pulse radiolysis studies. I. Transient spectra and reaction-rate constants in irradiated aqueous solutions of benzene, *J. Chem. Phys.* 36 (1962) 3051–3061, <https://doi.org/10.1063/1.1732425>.
- B.M. Esteves, C.S.D. Rodrigues, L.M. Madeira, Synthetic olive mill wastewater treatment by Fenton's process in batch and continuous reactors operation, *Environ. Sci. Pollut. Res.* 25 (2018) 34826–34838, <https://doi.org/10.1007/s11356-017-0532-y>.

- [9] ISO 6332, Water Quality – Determination of Iron – Spectrometric Method using 1,10-phenanthroline, 1988.
- [10] A. Kunai, S. Hata, S. Ito, K. Sasaki, The role of oxygen in the hydroxylation reaction of benzene with Fenton's reagent. Oxygen 18 Tracer Study, *J. Am. Chem. Soc.* 108 (1986) 6012–6016, <https://doi.org/10.1021/ja00279a057>.
- [11] E. Martínez, Extremum-seeking control of redox processes in wastewater chemical treatment plants, *Comput. Aided Chem. Eng.* 24 (2007) 865–870, [https://doi.org/10.1016/S1570-7946\(07\)80167-2](https://doi.org/10.1016/S1570-7946(07)80167-2).
- [12] J.M. Monteagudo, A. Durán, I. San Martín, M. Aguirre, Effect of continuous addition of H₂O₂ and air injection on ferrioxalate-assisted solar photo-Fenton degradation of Orange II, *Appl. Catal. B Environ.* 89 (2009) 510–518, <https://doi.org/10.1016/j.apcatb.2009.01.008>.
- [13] R.F.P. Nogueira, M.C. Oliveira, W.C. Paterlini, Simple and fast spectrophotometric determination of H₂O₂ in photo-Fenton reactions using metavanadate, *Talanta* 66 (2005) 86–91, <https://doi.org/10.1016/j.talanta.2004.10.001>.
- [14] E. Ortega-Gómez, J.C. Moreno Úbeda, J.D. Álvarez Hervás, J.L. Casas López, L. Santos-Juanes Jordá, J.A. Sánchez Pérez, Automatic dosage of hydrogen peroxide in solar photo-Fenton plants: Development of a control strategy for efficiency enhancement, *J. Hazard. Mater.* 237–238 (2012) 223–230, <https://doi.org/10.1016/j.jhazmat.2012.08.031>.
- [15] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced oxidation processes for organic contaminant destruction based on the fenton reaction and related chemistry, *Crit. Rev. Environ. Sci. Technol.* 36 (2006) 1–84, <https://doi.org/10.1080/10643380500326564>.
- [16] D. Prato-García, G. Buitrón, Evaluation of three reagent dosing strategies in a photo-Fenton process for the decolorization of azo dye mixtures, *J. Hazard. Mater.* 217 (2012) 293–300, <https://doi.org/10.1016/j.jhazmat.2012.03.036>.
- [17] L. Prieto-Rodríguez, I. Oller, A. Zapata, A. Agüera, S. Malato, Hydrogen peroxide automatic dosing based on dissolved oxygen concentration during solar photo-Fenton, *Catal. Today* 161 (2011) 247–254, <https://doi.org/10.1016/j.cattod.2010.11.017>.
- [18] D. Sannino, V. Vaiano, P. Ciambelli, L.A. Isupova, Mathematical modelling of the heterogeneous photo-Fenton oxidation of acetic acid on structured catalysts, *Chem. Eng. J.* 224 (2013) 53–58, <https://doi.org/10.1016/j.cej.2013.01.078>.
- [19] L. Santos-Juanes, J.L.G. Sánchez, J.L.C. López, I. Oller, S. Malato, J.A. Sánchez Pérez, Dissolved oxygen concentration: a key parameter in monitoring the photo-Fenton process, *Appl. Catal. B Environ.* 104 (2011) 316–323, <https://doi.org/10.1016/j.apcatb.2011.03.013>.
- [20] M. Tokumura, R. Morito, R. Hatayama, Y. Kawase, Iron redox cycling in hydroxyl radical generation during the photo-Fenton oxidative degradation: dynamic change of hydroxyl radical concentration, *Appl. Catal. B Environ.* 106 (2011) 565–576, <https://doi.org/10.1016/j.apcatb.2011.06.017>.
- [21] N. Wang, T. Zheng, G. Zhang, P. Wang, A review on Fenton-like processes for organic wastewater treatment, *J. Environ. Chem. Eng.* 4 (2016) 762–787, <https://doi.org/10.1016/j.jece.2015.12.016>.
- [22] E. Yamal-Turbay, M. Graells, M. Pérez-Moya, Systematic assessment of the influence of hydrogen peroxide dosage on caffeine degradation by the photo-Fenton process, *Ind. Eng. Chem. Res.* 51 (2012) 4770–4778, <https://doi.org/10.1021/ie202256k>.
- [23] X. Yu, A. Somoza-Tornos, M. Graells, M. Pérez-Moya, An experimental approach to the optimization of the dosage of hydrogen peroxide for Fenton and photo-Fenton processes, *Sci. Total Environ.* 743 (2020), 140402, <https://doi.org/10.1016/j.scitotenv.2020.140402>.