An experimental approach to the optimization of the dosage of hydrogen peroxide for Fenton and photo-Fenton processes

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Abstract

The determination of the hydrogen peroxide dosage scheme that minimizes hydrogen peroxide consumption while meeting the specified treatment outcome is crucial for Fenton and photo-Fenton processes. The challenge is building a methodology that provides the optimal dosage profile. However, the lack of detailed dynamic models prevents exploiting model-based optimization methods that have proved successful in other applications. Thus, this work addresses this challenge by providing a problem formulation identifying and discussing objectives and constraints, and the nature of the optimal solution. From this point, the work presents a novel dosage model and a consequent methodology aimed at experimentally optimizing the dosage profile along a discretized time horizon following recipe optimization concepts. The approach is parallel to the numerical solution of the model-based optimization problem posed by hydrogen peroxide dosage. The proposed methodology is validated in the remediation of a Paracetamol (PCT) solution, and the obtained results are assessed and discussed in regard of the evolution of the concentration of hydrogen peroxide, the contaminant (PCT), and Total Organic Carbon (TOC). The concentration of dissolved oxygen (DO), which is also monitored, allows providing a more comprehensive explanation of the nature of the process.

Abbreviations: AOPs, Advanced Oxidation Processes; H_2O_2, Hydrogen peroxide; PCT, Paracetamol; TOC, Total Organic Carbon; DO, Dissolved Oxygen

Keywords

Photo-Fenton; Hydrogen peroxide dosage; Recipe optimization; Experimental design; Dissolved oxygen monitoring; Hydrogen peroxide consumption

1. Introduction

The application of advanced oxidation processes (AOPs) to the degradation of recalcitrant organic matter has been extensively studied over the last decades. Among AOPs, the Fenton process, stemming from the work by Henry Fenton in the 1890s, has received increasing attention as it has proved to be highly efficient in the treatment of wastewaters containing non-biodegradable contaminants and producing extensive toxicity reduction. The advantages of the Fenton process are the need of a reagent easy to obtain, the flexibility of the operations, a short reaction time, and harmless by-products (Pignatello et al., 2006). In addition, the Fenton process takes place at ambient temperature and barometric pressure.

In the Fenton process, hydrogen peroxide (H_2O_2) and a Fe(II) catalyst produce highly reactive hydroxyl radicals ($HO^{\bullet}$), (Eq. 1-2), which unselectively react with organic matter, concomitantly with the oxidation of Fe (II) into Fe(III).

The presence of UV-vis light ($\lambda \leq 580nm$) allows reducing Fe(III) again into Fe (II), which in turn produces further $HO^{\bullet}$ radicals (Eq. 3) and results in a cycle continuously supplying $HO^{\bullet}$ until H_2O_2 is depleted. Shorter wavelengths ($\lambda \leq 310nm$) cause peroxide photolysis (Eq. 4) and the direct production of extra $HO^{\bullet}$. Therefore, the oxidation rate of photo-Fenton results much higher than that of the Fenton process.

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + HO^{\bullet} \qquad \textbf{\textit{Eq. 1}}$$

$$Fe(III) + H_2O_2 \rightarrow Fe(II) + H^+ + HO_2{}^{\bullet} \qquad \textbf{\textit{Eq. 2}}$$

$$Fe^{III}(OH)^{2+} + hv \rightarrow Fe^{2+} + HO^{\bullet} \quad \textit{Eq. 3}$$

$$H_2O_2 + hv \rightarrow 2\,HO^{\bullet} \quad \textit{Eq. 4}$$

Improved versions of the Fenton process are classified according to their hydroxyl radical production and include Photo-Fenton, electro-Fenton, sono-Fenton, photo-electro-Fenton, photo-sono-Fenton and sono-electro-Fenton.

This work focuses on the Photo-Fenton process, an effective method that takes place on the presence of Fenton reagents and UV radiation, including natural sunlight, which has been reported to reduce the operation cost.

The $HO^{\bullet}$ radical is the key species attacking organic molecules in an efficient but non-selective manner. However, an unnecessarily high concentration of $HO^{\bullet}$ (if H_2O_2 is added in excess) can cause unproductive reactions (Eq. 5-6) downgrading process performance (Tokumura et al., 2011):

$$HO^{\bullet} + HO^{\bullet} \rightarrow H_2O_2 \quad \textit{Eq. 5}$$

$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \quad \textit{Eq. 6}$$

Using H_2O_2 is essential, but oversupplying is counterproductive. The supply of hydrogen peroxide, as a means to control the concentration of hydroxyl radicals, is the most important operational parameter for the photo-Fenton process affecting both reaction outcome and process cost (Ortega-Gomez et al., 2012). Accordingly, a number of works has been dedicated to determining conditions enhancing process performance through a sensible hydrogen peroxide supply. Despite the progress reported by recent works (Yamal-Turbay et al., 2012; Pouran et al., 2015; Wang et al., 2016; Esteves et al., 2018), solutions are still partial and far from optimal.

Most proposals are heuristic strategies that are useful in particular situations, although they that cannot provide the optimal solution. However, optimization is a systematic strategy leading not to an improved solution but to the solution for which is proved that no other better solution exists.

Initially, research sought for adequate concentration ratios of H_2O_2 to contaminant and iron (Pignatello et al., 2006) in an attempt to minimize the scavenging effect. However, constant ratios may suit steady operation, but time-varying batch processes (such as these addressed in this work and those usually reported in the literature –e.g. Pouran et al., 2015) require H_2O_2 supply to be continuously adapted to maximize the final operation performance. Thus, the real research challenge is the optimization of a continuous time-dependent H_2O_2 dosage profile.

Monteagudo et al. (2009) and Zazo et al. (2009) proved that continuously dosing H_2O_2 along the reaction time can increase oxidation efficiency beyond that obtained by administering a total dose of H_2O_2 at the beginning of the reaction (henceforth no dosage). H_2O_2 discretized dosage by splitting the total supply into several portions and adding them at different times has also been reported to produce improvements respect no dosage. However, the use of arbitrary time intervals prevents the solutions to be reported as optimal. Some researchers reported that sequential addition of discrete amounts of H_2O_2 leads to better results than adding a great initial dose (Chu et al., 2007; Almeida et al., 2015). Other previous works reported that adding H_2O_2 at a constant rate into the reactor along the reaction time increases the process efficiency (Monteagudo et al. 2009 Prato-Garcia et al., 2012). However, other researchers have drawn completely opposite conclusions (Chidambara and Quen, 2005; Zhou et al., 2016). Certainly, this divergence shows that dosage is still an open issue deserving attention, particularly with regard to a systematic approach and the standardized comparison of methods and results. Other works have addressed H_2O_2 dosage as a continuous control problem. Santos-Juanes et al. (2011) used the on-line monitoring of dissolved oxygen (DO) to regulate the dosage of H_2O_2 and greatly improve the operation performance. Despite the practical achievement, the strategy relies on the expert setting of an indirect factor (DO set-point) assumed to reveal the operation performance, and it cannot be proved optimal. A general systematic strategy based on an accurate statement of an optimization problem is still pending.

On the other hand, the optimization of similar problems has been successfully reported, such as the optimization of batch and fed-batch operations by model-based approaches (Biegler, 2018; Jang et al., 2016; Nie et al., 2014). The general dynamic optimization problem addressed consists on determining a control law (the recipe) that drives the process through a feasible trajectory on a continuous time interval and minimizes a given cost function at the end of the interval. The ordered set of decisions made along the given time horizon and the practical discrete approximation required by the numerical solution

approach is in the basis of this work.

Nevertheless, for Fenton and photo-Fenton processes, the lack of suitable dynamic models hinders model-based optimization to a great extent (Qin and Badgwell, 2003; Jung et al., 2015), and the idea of model-based optimization to determine the best hydrogen peroxide supply profile along a batch run (the recipe) has been hardly addressed (Audino et al., 2019).

Since, the optimization of the operation of the photo-Fenton process, and particularly of the H_2O_2 dosage problem, is a continuous optimal control problem that should be formulated and addressed as such, this work uses recipe optimization concepts and a convenient time discretization to propose a practical methodology for experimentally addressing the optimization of hydrogen peroxide dosage profile. The adoption of this approach favors the convergence with the model-based optimization approach.

The proposed methodology is tested through its application to the remediation of a Paracetamol (PCT) solution. Furthermore, taking into account that several authors (Prieto-Rodríguez et al., 2011; Ortega-Gómez et al., 2012) have proposed using the variation of the concentration of dissolved oxygen (DO) for tactically adjusting hydrogen peroxide supply, this work also measures and discusses the response in DO concentration in order to provide deeper insight into the nature of the process.

2. Dosage modelling and problem formulation

Dosing hydrogen peroxide in batch Fenton and Photo-Fenton processes is a decision-making problem. Once admitted the existence of dosage alternatives, the problem consists in selecting a feasible alternative satisfying the given constraints and, eventually, the alternative producing the best outcome, the so-called optimal decision. Heuristic rules (tactical step moves based on local information) provide fast and practical decision-making support, but they do not drive to the optimal decision (the full set of moves for which the inexistence of any better alternatives for the complete problem can be proved), and they lean towards concealing misconceptions (mistaking the goal). Conversely, optimization techniques seek for the optimum at the expense of analyzing and quantitatively assessing all the alternatives (explicitly or implicitly, in the case of efficient search methods).

This work addresses the optimization of hydrogen peroxide dosage in batch Fenton and Photo-Fenton

processes. Accordingly, this work undertakes a systematic problem analysis and formulation (including declared assumptions and simplifications) that contributes a methodological approach aimed at stirring discussion and further research. Next, this section sets system boundaries and operational constraints, offers the definition of an objective function quantitatively assessing the outcomes of the decisions, and proposes a search method. The search can be performed using a mathematical abstraction accurately representing the system under study, or experimentally (Box et al., 2005). Lacking convenient kinetic models, this work undertakes an experimental approach, which is more expensive but consistent with the model-based optimization approach used for solving similar dynamic optimization problems in industrial applications (Biegler, 2018; Jang et al., 2016; Nie et al., 2014).

A first assumption is batch operation. While continuous operation might be the choice for industrial solutions, most of the academic research focuses on batch assays (Pouran et al. 2015), probably because of the operational costs. Dosage in batch processing poses a dynamic optimization problem: determine the dosage level at each infinitesimal time interval (the trajectory of the control action) that minimizes (or maximizes) a given integral function at the end of a given finite interval.

The discrete approximation applied in the numerical solution of the model-based approach is for the experimental approach not only inevitable, but required of additional simplification.

2.1. Problem formulation

The proposed dosage model assumes a single objective J to be minimized by the operation of a Fenton or photo-Fenton reactor. J is the outcome of the operation after some reaction time T and after the addition of some total amount A of reactant (e.g. volume of H_2O_2 solution). As Fenton and photo-Fenton processes are mostly operated in batch, this outcome has to be a fix value that describes the performance of the process, such as an economic indicator or the final concentration of a given species. Likewise, the method could be applied to continuous processes by selecting a derivative (e.g. reaction rate) as an indicator.

Fig 1. General discretization of the dosage profile. Theoretical framework.

A fraction f ($0 \leq f \leq 1$) of this total amount A can be dosed following different schemes during the

time horizon, while the remaining fraction ($A_0 = (1-f)\cdot A$) is assumed to be added at once at the very beginning. Assume the reaction time T is discretized in $i = 1,2,3 \dots N$ time slots, each of duration $\Delta t = T/N$, and $L \in N$ dosage levels as represented in Figure 1 (in the limit, $N, L \to \infty$, this discretization allows considering time and supply as a continuous decision variables). Hence, for each time slot i the dosage level $x_i \in \{0,1,2 \dots, L\}$ needs to be determined so that the balance and flow constraints on A are satisfied and the outcome $J = f(\boldsymbol{x}, f, A, T)$ is minimized (Eq. 7).

The formulation of the dosage model includes the integral of dosage bits (X, Eq. 8) that determines the incremental addition at each time interval (ΔA_i, Eq. 9). Hence, Eq. 10 allows determining and bounding (e.g. pumping capacity) the corresponding dosage flows F_i for each time slot.

$$J = f(\boldsymbol{x}, f, A, T) \qquad \textbf{\textit{Eq. 7}}$$

s.t.

$$X = \sum_i x_i \qquad \textbf{\textit{Eq. 8}}$$

$$\Delta A_i = \left(\frac{f\cdot A}{X}\right)\cdot x_i \quad \forall i \qquad \textbf{\textit{Eq. 9}}$$

$$F^{min} \le F_i = \frac{\Delta A_i}{\Delta t} \le F^{max} \quad \forall i \qquad \textbf{\textit{Eq. 10}}$$

The outcome $J = f(\boldsymbol{x}, f, A, T)$ could be inexpensively determined through a convenient mathematical model f, if available, or experimentally. This work relies on the experimental measurement of the objective function J for exploring and assessing the alternatives and detecting the best one. The infinite solution space and the too expensive experimental search requires some further assumptions to positively address such identification.

In regard of decision variables, the following experimental work assumes a given time horizon T (thus, excluding the minimization of the reaction time) and disregards the consideration of any initial amount of reactant ($f = 1 \to A_0 = 0$). The total amount A will be also assumed fixed, but some assays will be

presented providing insight and discussion concerning the stoichiometric amount. Thus, the general dosage problem presented is addressed in a reduced form consisting in determining the maximum distance we can drive on this road given this time and this amount of fuel; lacking a map of the road, the problem is addressed by methodically planning and executing a series of runs.

In regard of the modelling parameters N and Δt, this work proposes a first discretization aimed at achieving the practicality required by the evaluation of the methodology. Besides, the work also explores an alternative in order to offer data and discussion on the effect and sensitivity of such parameter values. Other implementations are deemed for future research and, in the same way that further problem extensions, may be envisaged stemming from the proposed formulation.

2.2. Design of Experiments

While this problem statement defines a comprehensive theoretical framework to address the dosage problem (consistent with the numerical solution of the optimization problem, if a reliable process model was available), it also defines an unaffordable solution space of $(L+1)^N$ experimental assays. Thus, this work also analyses the practical ways to address the corresponding design of experiments by identifying and removing unrealistic solutions. Further simplifications are discussed in regard to the granularity adopted and the practicality of the solutions attained.

A first issue to decide is the objective function. As stated in the previous section, it has to be a final indicator of the performance of the process of a batch process. Among other complex alternatives (economic and/or environmental impacts), this work sets the outcome to be minimized as the Total Organic Carbon (TOC) concentration measured at the end of a given reaction time (i.e. $[TOC]_T$). The particular choice of TOC at the end of a time horizon, is commonly used by many authors, including those addressing hydrogen peroxide dosage (Herney-Ramirez et al., 2010; Pouran et al., 2015). TOC is a valuable index of water quality as it reveals the extent of mineralization of mother starting (pollutants plus the formed intermediates). The reagent to be dosed is Hydrogen peroxide, and its amount A is defined in terms of volume of water solution (reagent-grade, 33% w/v).

Moreover, the dosage level is simplified to a binary decision for each time slot i; thus, $x_i \in \{0,1\}$ (Figure

2A). Further considerations include setting $x_i = 1$ for the first slot (since no reaction is expected otherwise) and setting $x_i = 0$ for the last slots in the series (since the reaction is expected to continue for a while without further dosage) as represented in Figure 2B. These are practical assumptions (e.g., the first time slot could have no duration, in order to consider an initial immediate addition of reactant), and they can be revised later on depending on the results.

Fig 2. Discretization of the dosage profile (A) considering binary decisions and (B) fixing first and last time slots.

The time horizon T is set to 120 minutes. This reaction time is fixed according to the preliminary experiments using a single H_2O_2 addition. The monitoring of the H_2O_2 concentration (Figure 3B) shows that the stoichiometric amount of H_2O_2 is almost exhausted after 120 minutes. Thus, the slot size Δt is the last decision to be made. It is set to 15 min, which leads to $N = 8$ and $2^N = 256$ alternatives to be explored. Since there are four slots assumed to be determined beforehand (the first and the last three) the solution space is again reduced and only $2^{N-4} = 16$ assays are finally planned. For the sake of illustration, assume a finer partition given by a Δt value reduced to 5 min (only to one third). Hence, $N = 24$ and the alternatives to be explored would be $2^{N-4} = 1048576$, which is experimentally unaffordable.

Table 1. Design of experiments. The dosage level (0, 1) is given for the eight time slots S1 to S8; the preset values for slots S1, S6, S7 and S8 are shadowed. The reactant fraction to be dosed at each active slot is also given.

3. Materials and methods

Paracetamol (98% purity) was purchased from Sigma-Aldrich. Hydrogen peroxide (reagent-grade, 33% w/v) was purchased from Panreac. Heptahydrate ferrous sulfate ($FeSO_4 \cdot 7H_2O$) used as the ferrous ion was acquired from Merck. Sulfuric acid (H_2SO_4 95%) from Fisher was used for pH adjustment. Ammonium metavanadate (NH_4VO_3 98.5%) was used for H_2O_2 measurement. HPLC gradient grade Methanol (MeOH) was acquired from J.T. Baker Inc. and ultra-pure solvents (Milli-Q® water) were prepared for HPLC mobile phase. Distilled water was used as water matrix for solution preparation.

The experimental setup is an automated photochemical pilot plant. The reaction system includes a 13.5 L glass jacked reservoir tank and a 1.5 L glass tubular photo-reactor (10 % of the total volume) with an irradiated height of 130 mm). 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. The recirculation fluid is driving through the reservoir tank and the photo-reactor by a centrifugal pump (Iwaki Magnet Pump, MD-30RZ-220, 1-16HP-220V). Sensors are also equipped for measuring pH (Hamilton Polilyte HTVP 120), intensity of UV radiation on the external surface (Sglux UV_Surface_A_4-20mA_cable), temperature and dissolved oxygen (Hamilton Oxysens). H_2O_2 dosage is automatically performed through a peristaltic pump (Watson Marlow, OEM 313 24V) and a PLC (Siemens SIMATIC S7-1200) managed by the plant SCADA system (InTouchR® software).

3.1. Analytical methods

Total organic carbon (TOC) concentration was determined with a TOC (TOC-VCSH/CSN Shimadzu; Kyoto, Japan) analyzer. Samples were taken every 15 min and kept in the ice to slow down further oxidation.

PCT concentration was measured via HPLC Agilent 1200 series (Agilent Technologies) with UV-DAD array detector. The chromatographic column was a 5 µm 4.6 mm×150 mm Akady Ultrabase C-18. 20 µl samples, the detection wavelength was set to 243 nm and the temperature was fixed to 25℃. The eluent was a mixture of methanol and water (25:75) with a flow rate of 0.4 mL min^{-1} (Yamal-Turbay et al., 2015), retention time was 7.3 min under these conditions. Samples were taken at different times and were previously treated with methanol (in proportion 50:50) in order to stop further degradation of PCT.

H_2O_2 concentration was measured by using the spectrophotometric method (Nogueira et al., 2005). The absorption at 450 nm was detected via a U-2001 UV–vis spectrophotometer (Hitachi, Tokyo, Japan).

3.2. Experimental procedure

The conditions of the photo-Fenton experiments were: pH adjusted to 2.8 ± 0.2 using H_2SO_4 and temperature 26-28 ºC. The initial solution in the reactor was prepared with 15 L of distilled water and 0.6122 g of model pollutant PCT and 0.7468 g of $FeSO_4 \cdot 7H_2O$ (40 mg L^{-1} PCT and 10 mg L^{-1} Fe(II)).

The total amount of hydrogen peroxide to be dosed, A, is set to be the stoichiometric concentration (considering H_2O_2 as the only oxidant in the media, Eq. 11), S, for the given amount of PCT: this is 9.545 g (8.5909 mL of solution 33% w/v), which corresponds to a concentration of 189 mg L^{-1} (S).

$$C_8H_9NO_2 + 21H_2O_2 \rightarrow 8CO_2 + 25H_2O + H^+ + NO_3^- \qquad \textit{Eq. 11}$$

Table 2. List of assays carried out using 40 mg L^{-1} PCT and 189 mg L^{-1} of H_2O_2 (the corresponding to the stoichiometric amount, S).

The UV light was switched on as soon as $FeSO_4 \cdot 7H_2O$ and PCT were added in order to guarantee its stabilization. The execution of the dosage program started 10 min after to ensure perfect mixing. The dosage of the H_2O_2 solution followed the specific values set for experiment and shown in Table 2, and the specific dosage time intervals 0, 15, 30, 45, 60 min. All experiments were repeated twice, the average values were obtained to exhibit the TOC conversion, PCT degradation, and H_2O_2 evolution.

4. Results and discussion

4.1 Preliminary results

Preliminary tests were performed to a 40 mg L^{-1} PCT sample to identify the contribution to the mineralization of PCT of factors such as reagent and irradiation. The tests (Figure 3) were performed at pH= 2.8 ± 0.2 and T = 26-28℃, and the loads of the Fenton reagents were [Fe(II)] = 10 mg L^{-1} and [H_2O_2] = 189 mg L^{-1} (corresponding to the stoichiometric amount, S).

Fig 3. (A) Evolution of TOC concentrations upon blank assays. (B) Comparison of Fenton and photo-Fenton process: evolution of TOC and H_2O_2 concentrations

The results of these tests can be summarized as follows:

- Negligible mineralization was attained in all the blank tests (Figure 3A), even in the assays with sole H_2O_2, sole irradiation, and the combination of both.

- The comparison between the results of the Fenton and the photo-Fenton processes (Figure 3B) shows that UV irradiation significantly enhanced the conversion attained. This is due to already mentioned role of UV-vis light, which increases the mineralization from 23.3 % to 57.15 %.

Once demonstrated the higher mineralization capacity of the photo-Fenton process, the next step is studying the effect of H_2O_2 dosage on the performance of photo-Fenton processes aimed at determining the best dosage scheme.

4.2 Base case

The 16 dosage schemes planned (Table 2) were first performed for 40 mg L^{-1} PCT and the stoichiometric amount of H_2O_2 (S, 189 mg L^{-1}) to be dosed along a time horizon of two hours (T= 120 min). Clearly, the stoichiometric amount cannot be expected to achieve total mineralization. However, it is useful for providing reference results for quantitative comparison.

Additional measurements were taken beyond this time horizon for TOC (up to 240 min, in order not to miss further reaction progress), while measurements for PCT were interrupted earlier, as they fell below the detection limits of the analytical techniques.

Table 2 presents the assays using the binary code, which clearly express the dosage profile. The label NO_DOSAGE refers to the assay for which the same total amount of H_2O_2 was supplied all at once at the beginning. All these assays were repeated twice and variability of TOC concentration was found to be low (below 4 %). Therefore, from here on, only the average of all these repeated measurements is presented.

All these assays show that PCT completely reacts within the first 45 min. However, the time required for PCT concentration to drop below the detection limits depends on the number and size of the dosing bits (the distribution of the H_2O_2 supply along the time). For a first assay, G1 = {0000}, no presence of PCT is detected after 15 min; for the group of assays G2 = {0001, 0010, 0100, 1000}, no presence of PCT is detected after 25 min; for the groups G3 = {0011, 0101, 0110, 1100, 1001, 1010}, G4 = {0111, 1011,

1101, 1110}, and G5 = {1111}, tending to continuous supply, the time spans from 25 to 45 min.

The higher the number of the dosing bits (the lower the H_2O_2 amount added in each time slot), the slower the PCT elimination. Figure 4 shows the hydrogen peroxide present in the system for each group. NO_DOSAGE is the assay producing the PCT fastest elimination, while the rest G1 (0.573 mL/min at first dosing interval), G2 (0.286 mL/min at each dosing interval), G3 (0.286 mL/min), G4 (0.286 mL/min), and G5 (0.286 mL/min), result increasingly slower. Thus, these results allow concluding that, only in regard to PCT removal, the most concentrated reactants at the beginning, the best performance, which suggests that the scavenging effect should be expected later and involved with intermediate products.

Fig 4. Hydrogen peroxide profiles (A) all assays (B) with two doses, G2 (C) with three doses, G3 (D) with four and five doses, G4 and G5.

The evolution of the concentration of H_2O_2 is studied and presented in the above set of figures (Figure 4). The dashed line plotting the evolution when H_2O_2 is added all at once at the beginning (NO_DOSAGE) reveals that the same amount, S, of H_2O_2 is consumed much faster and exhausted by 135 min. On the other hand, other dosing schemes produce H_2O_2 profiles that span longer and may exhibit peaks and valleys (Figures 4B and 4C), which may be interpreted as a gap between supply and demand. This seems not the case for the more continuous dosage given by G4 and G5 (Figure 4D), although this cannot be deemed as the most efficient.

The identification of the best protocol is given by Figure 5 (according to the objective function set to be minimized, $J = [TOC]_{120}$) and is revealed to be 1000 (61.90% conversion) and 0000 (61.70% conversion), which is an improvement of 4.75 percent points NO DOSAGE (57.15% conversion). This may seem a minor improvement, but it can be much more significant in regard of process economy. Despite this numerical value, the improvement is shown to be systematically determined by the dosage modelling proposed and the experimental design derived accordingly. On the other hand, 0011 and 0001 are revealed to have worse performance than NO_DOSAGE; indeed, this can be attributed to a demand of H_2O_2 that is attended too late (although it can be expected to have an effect beyond $T = 120$ min). The comparative details of these extreme situations are given in Figures 6.

Fig 5. TOC conversion after 120 min under photo-Fenton treatment. The total amount of hydrogen peroxide added during 120 min is the stoichiometric quantity. Table 2 summarize the dosing strategies.

Fig 6. Hydrogen peroxide inlet flow, measured hydrogen peroxide concentration, and reference concentration (the one that would result from the addition to a non-reacting system): (A) 0001 (the worse scheme) (B) and 1000 (the best scheme)

Finally, the evolution of dissolved oxygen concentration (DO) is also monitored for tactical purposes and for a more complete interpretation of the underlying nature of the process (Figure 7). DO level has been interpreted as a practical indicator of process efficiency (Santos-Juanes et al., 2011). Thus, while low DO levels might indicate the need for more H_2O_2, the rising of DO might indicate an unproductive decomposition of hydrogen peroxide that should be avoided.

Fig 7. Evolution of DO level for assays NO_DOSAGE, 1000 and 0001.

Accordingly, Figure 7 might suggest that NO_DOSAGE, providing more moderate peaks and valleys, should produce the best performance, which is obtained by 1000. Conversely, both assays 1000 and 0001, experience a smoother start. This shows that, although DO is a practical indicator, the relationship between this indicator and the performance (minimizing TOC, or cost, or any other objective function that may be proposed) is not direct and deserves attention beyond this first experimental design proposed to illustrate the methodology.

On one hand, the aggregate and indirect information provided by the DO level at time $t < T$ cannot anticipate the outcome of the process at time T, and it cannot drive decisions to an optimal outcome. On the other hand, the change in the DO level (its derivative at time $t < T$) may provide local information that could eventually drive tactical decisions (adding H_2O_2). In this regard, the change of the DO level is a robust measurement, since it is relative and insensitive to offsets and interferences caused by side reactions and intermediate products. However, developing an accurate correlation of the level of dissolved oxygen with these factors, including delays due to the diffusion of the dissolved oxygen, is complex challenge out of the scope of this paper.

4.3 Extended cases

This section investigates some of the implicit assumptions accepted up to this point.

The proposed dosage model assumes a general single objective J that for the base case was TOC concentration after 120 min: $J = [TOC]_{120}$. In addition to this objective function, the total amount of hydrogen peroxide to be added was set to be the stoichiometric ($A = S$) and the initial amount was set to be zero ($A_0 = 0$). Finally yet importantly, the intervals were arbitrarily fixed to 15 min. Such decisions are not inherent to the methodology and they could be controlled to achieve better performance.

4.3.1 Objective function

A first extension in the objective function consists in changing the reaction time. Thus, a new set of assays was performed for a time horizon of four hours (T= 240 min), and the conversions obtained for $J = [TOC]_{240}$ were ranked and compared with those in the previous section. For this extended reaction span, the best conversion was 6 percent points higher than that obtained without dosage.

A new objective function can also be proposed by considering the reverse approach: the earliest time to achieve a specified conversion. Given the same conversions, such a time is obtained by the linear interpolation of the measured values. For instance, the time required for reaching 70% conversion show that while 240 min are required if no dosage is applied, only 167 min (73 min less) are required for the most efficient dosage protocol (1000).

4.3.2 Hydrogen peroxide amount

The first set of assays were planned with a total amount of hydrogen peroxide, A, equal to the stoichiometric amount. This is an assumption based on the idea that an ideal dosage protocol should exist that would cause no hydrogen peroxide dissipation in any unproductive reaction. However, more than the stoichiometric amount could achieve better performance. Therefore, this sub-section explores the effect of different amounts of hydrogen peroxide. Certainly, the idea of A as decision variable instead of a fixed parameter is implicit in the problem formulation (Eq.7), but attempting such an extended optimization problem is out of the scope of this work.

In Figure 8 and from this point on, experiments are codified using the same ID (bin) from Table 2, plus the amount of hydrogen peroxide referred to the stoichiometric amount, S, specifically S (189 mg L^{-1}), 1.2S (226.8 mg L^{-1}), and 2S (378 mg L^{-1}).

366 **Fig 8.** Evolution of the TOC concentration (normalized) for the assays S_NO DOSAGE, 2S_NO
367 DOSAGE and S_1000_08.

368 Figure 8 shows how the best dosage protocol (S_1000_08) reaches similar mineralization value (68 %,
369 150 min) than NO_DOSAGE assay with double hydrogen peroxide amount (2S_No Dosage). The
370 methodology allows to save half of the hydrogen peroxide amount.

371 **4.3.3 Hydrogen peroxide initial amount (A_0)**

372 DO performance allows analyzing the appropriate initial amount of hydrogen peroxide in order to avoid
373 the marked decrease in oxygen consumption general produced in dosage assays at early stages of the
374 oxidation process. Towards this end, a new set of experiments were performed to obtain a new set of
375 outcomes at 120 min for different initial amounts of hydrogen peroxide (Table 3).

376 **Table 3.** TOC conversions obtained at 120 min with different hydrogen peroxide amounts (A) and initial
377 amounts (A_0) and the conversion obtained. The stoichiometric amount (S) is 189 $mg \cdot L^{-1}$.

378 **Fig 9.** Evolution of the DO concentration for the assays given in Table 3.

379 Figure 9 presents the corresponding DO profiles. For this particular case (the dynamics of the photo-
380 Fenton process are strongly dependent on the nature of the organic matter to be degraded), 0.2S obtain
381 flatter DO performance at the first time reactions.

382 It is worth noting that DO levels attain levels far beyond saturation. As commented previously, DO
383 absolute values usually depend on many factors (pressure, temperature, salinity…) in addition to those
384 specifically provided by the Photo-Fenton reacting environment (intermediates, radicals…). Other works
385 monitoring DO in Photo-Fenton processes also report similar values noticeably exceeding DO saturation
386 (Santos-Juanes et al. 2011, Ortega-Gómez et al. 2012). This works also propose the reactions producing
387 O_2. Another important factor to observe is process dynamics, and the accumulation caused by O_2
388 production rates larger than the oxygen diffusion rate. This effect is included in the model introduced by
389 Cabrera-Reina et al. (2012).

390 **4.3.4 Time discretization**

Finally, time discretization is addressed in this last experiment. Related to the interval time slots only two options were tested (from 15 to 5 min) the results (Figure 10) evidence a clear effect of this parameter. Further studies are required in order to optimize it.

Fig 10. Evolution of the DO concentration for the assays with different time discretization.

All these results are exploring different variations of the initial experimental design open promising research lines. The development of a methodology for determining the best dosage protocol for the photo-Fenton process deserves the attention of future work.

5. Conclusions

This work presents a comprehensive theoretical framework to address the problem of hydrogen peroxide dosage for Fenton and photo-Fenton processes in a systematic way. The work proposes a problem formulation that provides a new insight into the nature of the decision-making problem, and allows further discussion of tactical and strategic solution approaches. The framework is based on the underlying dynamic optimization essence of the problem. A natural discretization scheme is adopted to develop a new dosage model for which advantages and limitations are discussed. With the aim to overcome the current lack of models that provide model-based solution approaches, this work is expected to shed new light to the dosage problem by addressing it from an experimental approach.

A practical experimental design is proposed and assumptions are made to reduce the dosage level to a set of binary decisions, as well as fixing reaction time and the total amount of hydrogen peroxide. This experimental approach is consistent with the model-based optimization approach and sets a framework to further develop and validate a mathematical model for the dosage. Accordingly, a complete set of dosage schemes were implemented and assessed for the study of paracetamol (PCT) degradation.

The quantitative results obtained allow sorting out the alternatives and identifying the best dosage profile, which increases TOC conversion by 4.75 percent points (after 120 minute). Additionally, complementary measurements allowed to further discuss the complex nature of the different interconnected processes causing such an outcome. All the treatments under study attained the total elimination of initial PCT within a minimum time of 7 min and maximum time of 45 min (over a time horizon of 120 min). The

measurement of the corresponding DO concentration allowed concluding that no simple relation seems to exist between the observed DO values and the final outcome of the process at the end of the time horizon (e.g. $[TOC]_T$). However, the study of DO profiles in parallel to the corresponding dosage profiles might provide meaningful and practical correlations for tactical purposes.

Other objectives and configurations were studied to envisage new aspects to be explored. Thus, decisions not inherent to the methodology (the total amount of hydrogen peroxide to be added, the initial amount of hydrogen peroxide, the intervals time slots) were modified and tested to achieve better system performance. When the goal was to minimize TOC concentration after 240 min ($J = [TOC]_{240}$), the mineralization was further improved (by to 6 percent points) with the same amount of hydrogen peroxide.

Conversely, attending the inverse objective (the earliest time required to meet a certain TOC value) led to determining that the same mineralization was achieved within 167 min or 240 min, depending on the dosage protocol. The effect of an initial amount of hydrogen peroxide was also addressed and studied. When the monitoring of the DO levels was included, the marked decrease in oxygen consumption produced at early stages of the oxidation process was shown to be moderated. Finally, changing time discretization (from 15 to 5 min) revealed that this is a very influencing aspect deserving further studies and that future work should continue progressing towards a model-based optimal control of photo-Fenton processes.

Notation

Table 4. Notation for the mathematical model.

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