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Optimal recipe design for Paracetamol degradation by advanced oxidation processes (AOPs) in a pilot plant

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Abstract

This work addresses the optimization of the batch process recipe of an Advanced Oxidation Process (AOP) aimed at reducing paracetamol (PCT) and Total Organic Carbon (TOC) concentrations from a given effluent. The kinetic model by Cabrera Reina et al. (2012) is adapted to model the treatment, the problem is next formulated as a dynamic optimization problem and dosage of hydrogen peroxide is addressed by means of a piecewise constant strategy, which is compared with other dosage protocols. Results show that cost reductions can be obtained when applying the model-based optimization techniques proposed, and hint new opportunites for AOPs enhancement.

Keywords: model-based optimization, process design, photo-Fenton process, advanced oxidation process (AOP).

1. Introduction

Advanced Oxidation Processes (AOPs) are treatment technologies aimed at degrading and mineralizing recalcitrant organic matter from wastewater through reaction with hydroxyl radical ($^{\bullet}OH$). Recently, these technologies have been proposed as a solution to treat emerging contaminants, especially pharmaceuticals and personal care products (Pignatello et al., 2006). AOPs' reactions can be further promoted by iron catalysts (Fe^{2+}) and UV irradiation, giving rise to photo-Fenton systems.

The optimal design, operation, and control of these processes can be driven by challenging process systems engineering tools that combine AOPs science, photo-Fenton chemistry, and leading technologies with model-based optimization strategies. However, the use of optimization tools requires the availability of reliable models.

A significant amount of work has been devoted to identify intermediate products, model kinetic mechanisms, and identify key variables in AOPs systems, where interaction of complex reactions occurs (Andreozzi et al., 2000). For instance, operational variables such as reagent dosage, pollutant load, pH, and UV source, have been investigated as variables affecting the accomplishment of degradation targets.

Most preliminary AOPs studies were based on design of experiments (DOE) techniques (Pérez-Moya et al., 2008; Arslan-Alaton et al., 2010; Dopar et al., 2011), and they provide limited information regarding intermediate products and side reactions. That entails the risk of making wrong design or operational decisions. In contrast, rigorous models have been reported, describing in detail the degradation mechanism of simple

molecules –namely formic acid (Rosetti et al., 2004; Farías et al. 2009). The very recent work by Cabrera Reina et al. (2012) addresses the degradation of Paracetamol (PCT) by introducing a kinetic model aimed at describing the evolution of the system in terms of lumped observable variables such as Total Organic Carbon (TOC). In all these studies hydrogen peroxide dosage arises as a critical issue to be managed due to the presence of secondary reactions scavenging this reactant.
However, studies seeking for the optimal design of AOPs are still not found. In this context, the optimal recipe design problem is tackled in this work for the case of PCT remediation in an AOPs pilot plant by using model-based optimization tools.

2. Problem Statement

This work considers the optimization of the batch process recipe to be implemented in an AOPs pilot plant in order to process PCT solutions and reduce PTC and TOC concentrations below given limits. The objective is to drive the process at minimum processing cost, while fulfilling a set of environmental constraints –*i.e.* maximum Fe allowed in effluents–, operational restrictions –*i.e.* maximum treatment horizon desired–, and plant physical restrictions –*i.e.* reactor capacity and available lamp intensity.
Specifically, the decisions that are considered are the initial concentration of reactants Fe^{2+} and H_2O_2 for the photo-Fenton degradation ($C_{Fe^{2+},0}$ and $C_{H_2O_2,0}$) and the feed-forward trajectories of the H_2O_2 dosage along the batch time horizon ($q_{H_2O_2}$).

3. Optimization model

The problem can formulated as a dynamic optimization problem. The material balances in the batch reactor compose a differential-algebraic equations (DAE) system. Particularly, the model presented by Cabrera Reina et al. (2012) is adapted to predict the kinetic behavior of process variables, namely concentrations for PCT, H_2O_2, Fe^{2+}, Fe^{3+}, dissolved oxygen (DO), $OH^{\bullet}$ radical, and TOC (dummy intermediates, as well). Hence, the Fenton-like reaction is added to the model (Kušić et al., 2006).
The optimization model includes constraints to force final PCT and TOC levels:

$$C_{PCT}(t_{end}) / C_{PCT,0} \leq 0.1\ \% \qquad (1)$$

$$C_{TOC}(t_{end}) / C_{TOC,0} \leq 10.0\ \% \qquad (2)$$

Regarding the objective function to be minimized (ϕ), it includes the cost of reagents Fe^{2+} and H_2O_2 and the cost of electricity consumption in the lamp:

$$\phi = Cost_{Fe^{2+}} + Cost_{H_2O_2} + Cost_{\varepsilon} =$$
$$= p_{Fe^{2+}} C_{Fe^{2+},0} V_{total} + p_{H_2O_2}(C_{H_2O_2,0} V_{total} + \int q_{H_2O_2} dt) + p_{\varepsilon} I A_w t_{end}, \qquad (3)$$

where $p_{Fe^{2+}}, p_{H_2O_2}, p_{\varepsilon}$ are the prices for raw materials and electricity, $C_{Fe^{2+},0}$ and $C_{H_2O_2,0}$ are the initial concentrations of Fe^{2+} and H_2O_2, V_{total} is the reaction volume, $q_{H_2O_2}$ is the input flow H_2O_2 along time, I is the lamp intensity, A_w is the irradiation surface and t_{end} is the final processing time. Given the pilot plant, the installation of new equipment elements is not considered, and investment cost contributions are not included in Eq. 3.
The boundaries of the decision variables are defined as follows: initial concentration for Fe^{2+} is set between 0 and 0.179 mM, which also satisfies the legal iron concentration allowed in effluents (DOGC). In the case of H_2O_2, the typical concentrations range for AOPs is taken (0-45 mM). The reaction volume is set to the maximum plant treatment capacity (V_{total}=15 L) and the lamp intensity to the lamp radiation installed (I=36

W/m^2). The available processing time (t_{end}) is set to the maximum time horizon, which is also a free-decision variable.

4. Optimization tools

4.1. Pareto frontier for cost function ϕ versus processing time t_{end}

The processing time t_{end} only appears in the objective function (Eq. 3) related to the electricity cost contribution $Cost_e$. However, t_{end} is a decision variable that indirectly affects ϕ dramatically: an increase of t_{end} leads to a reduction of reagents consumption and, consequently, a reduction of $Cost_{Fe^{2+}}$ and $Cost_{H_2O_2}$. Therefore, its value will tend to the upper bound in the optimal solution.

In order to elucidate the trade-off between the cost and the allowed time, the Pareto frontier is first constructed. For that, the objective function (Eq. 3) is minimized with different upper bounds for the processing time: $t^u_{end} \in \{0.7h,\ldots,10h\}$. In this step, the initial values $C_{Fe^{2+},0}$ and $C_{H_2O_2,0}$ are continuous, time-independent control variables. Then, the optimization problem is solved as a direct-sequential approach in Matlab, with no discretization or characterization of the dosage profile $q_{H_2O_2}$, which is fixed to zero.

4.2. Dosage profile $q_{H_2O_2}$ optimization for a given processing time t_{end}

Once the processing time t_{end} has been selected, the dynamic profile of H_2O_2 addition rate is optimized, together with $C_{Fe^{2+},0}$ and $C_{H_2O_2,0}$. In that step, two different types of dosage profiles are used: (i) a given dosage protocol and (ii) a piecewise constant (PWC) profile with a finite number of time discretizations.

- **Dosage protocol.** This dosage protocol (Fig. 1) consists of an initial load of reagent, and a constant addition of the remaining during a specific time interval (Yamal-Turbay et al., 2012). The addition profile is characterized by the total amount of H_2O_2 ($H_2O_{2,total}$), the fraction of total reagent that is completed at initial time t_0 (y_0), the starting time of the dosage (t_{ini}), and the continuous dosage span (Δt_{add}). The dosage protocol is a particularization of a PWC profile with two single step functions to start and to stop the reagent addition. It was previously introduced for practical issues regarding experimentation. The dosage protocol results in an optimization problem with continuous time-independent control variables ($H_2O_{2,total}$, y_0, t_{ini}, and Δt_{add}) characterizing a dynamic profile, without a discretization of control variables, which is solved by a direct-sequential approach in Matlab.

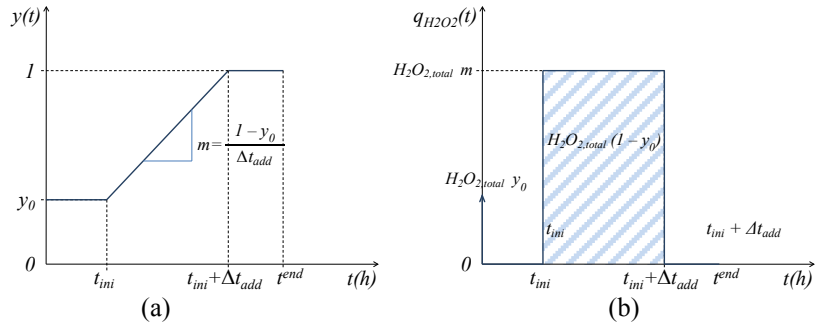

Figure 1: The pre-established dosage protocol: (a) fraction added $y(t)$ (b) input flow $q_{H_2O_2}(t)$.

- **Piecewise constant (PWC) profile.** The problem statement can be easily expanded and the solution further improved by considering more dosage intervals. In that case, the problem is transformed into a dynamic optimization (DO), where dosage is now

characterized by the discretization of $q_{H_2O_2}(t)$ into a finite number of intervals. Thus, a direct-simultaneous strategy is used by discretizing the corresponding DAE system and the process and control variables to obtain a non-linear programming (NLP) model. Orthogonal collocation in finite elements (Čižniar et al., 2005) is used at that step, using 16 finite elements. Next, the NLP is solved using GAMS / CONOPT.

4.3. Handling inequalities in the optimization model

Inequalities with process variables, such as the constraints for the final PCT and TOC concentrations (Eq. 1 and 2), can be transformed into penalization terms for the objective function (Eq. 3). This strategy is used in the implementations in Matlab, which otherwise require special tool-packages. For instance, Eq. 2 is transformed into the following quadratic penalty function:

$$Penalization_{TOC} = 1000\ (C_{TOC}(t_{end})/C_{TOC}(t_0) - 0.1)^2 \qquad (4)$$

Other penalty-like terms could be used, such as logarithmic or inverse barrier functions.

5. Results and discussion

An AOP recipe is optimized to treat 15 L of effluent with 0.52 mM of PCT in a pilot plant with fixed capacity (volume, lamp intensity, area and wavelenght, etc.). An elimination of 99.9% of substrate and 90% of TOC is set to be attained. The boundaries for the control variables are: $C_{Fe^{2+}} \in [0,\ 0.179\ \text{mM}]$, $C_{H_2O_2} \in [0,\ 45\ \text{mM}]$, and $t_{end} \in (0,\ t^u_{end})$, $t^u_{end} \in \{0.7h, \ldots, 10h\}$, and the prices of reactants and energy are $p_{Fe^{2+}}$=12.62 €/mol, $p_{H_2O_2}$=3.17 €/mol, p_ε=0.1456 €/kw·h. The results obtained are compared to a base case where typical values $C_{Fe^{2+},0}$=0.14 mM and $C_{H_2O_2,0}$=132.3 mM are used with no dosage.

5.1. Pareto frontier

The Pareto frontier for the cost function ϕ versus processing time t_{end} obtained through the process recipe optimization with no dosage is presented in Figure 2. The most critical trade-offs are obtained between 0.7 h and 3h. At lower final times, the TOC elimination of 90% is not achieved. Upper final times do not affect to the reactant consumption, and processing cost tends to $6.98 \cdot 10^{-2}$ € per batch.

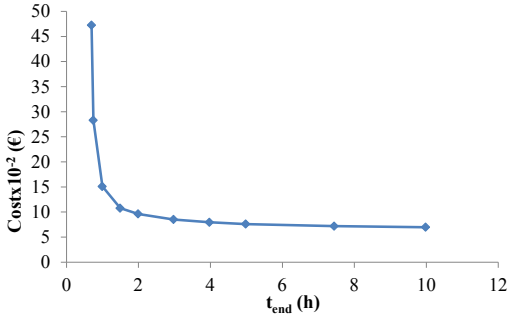

Figure 2: Pareto frontier for cost function ϕ versus processing time t_{end} (no dosage is considered).

A processing time of 2 hours is selected, with a treatment cost of $9.62 \cdot 10^{-2}$ € per batch. Although the PCT and TOC elimination can be achieved at lower processing times, the interest was set on reducing the cost at the expense of extending the reactor occupation.

5.2. Dosage profile $q_{H_2O_2}$ optimization for t_{end}=2 hours

The process recipe is further improved using both the dosage protocol and the PWC profile optimization. This way, a reduction of the processing cost is obtained, from

$9.62 \cdot 10^{-2}$€ to $9.30 \cdot 10^{-2}$€ and $9.13 \cdot 10^{-2}$€ per batch, respectively. The improvement related to the base case is given in Table 1, along with other key indicators of the process. In addition, the corresponding profiles are presented at Figure 3 for each case.

Table 1: Key performance indicators (KPIs) in the base case and optimal solutions

KPI	Base case	No dosage	Dosage protocol	PWC dosage profile
Processing cost (10^{-2} €)	44.57	9.62	9.30	9.13
Processing cost reduction (%)	-	78.4[a]	79.1[a] (3.3[b])	79.5[a] (5.1[b])
Fe^{2+} consumption (mmol)	2.100	2.459	2.425	0.268
H_2O_2 consumption (mmol)	132.3	20.5	19.6	18.1
Time 99.9% PCT reduction (h)	0.13	0.49	0.64	0.69
Time 90% TOC reduction (h)	0.89	1.99	1.99	2.00
Final PCT elimination (%)	100	100	100	100
Final TOC elimination (%)	99.42	90.1	90.1	90.0

[a] Improvement regarding base case. [b] Improvement regarding optimal solution without dosage

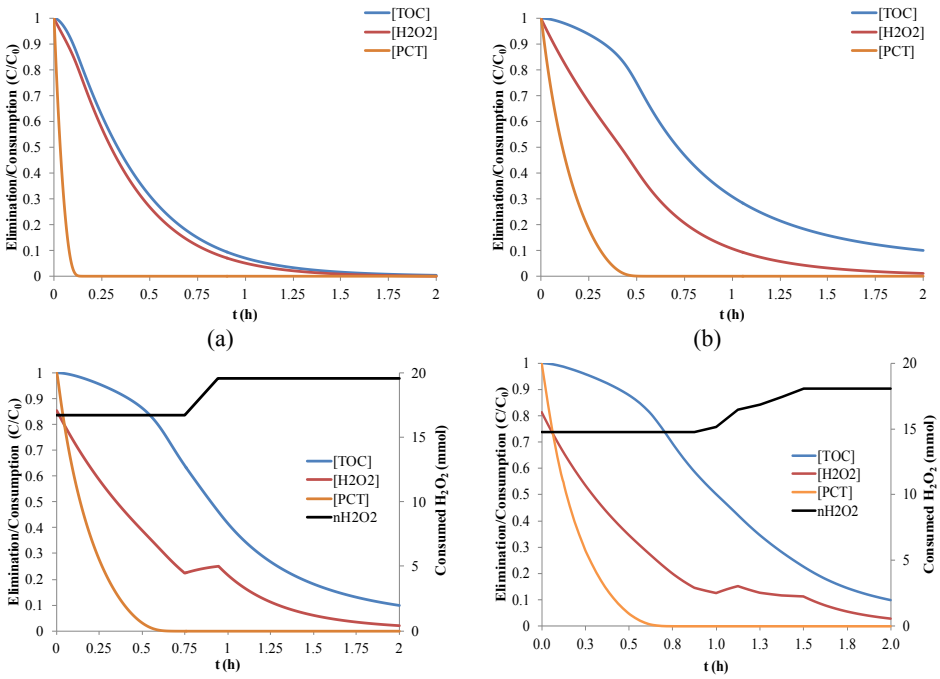

Figure 3: Control ($q_{H_2O_2}$) and process (normalized C_{TOC}, $C_{H_2O_2}$ and C_{PCT}) variable profiles: (a) base case, (b) optimal solution with no dosage, (c) with dosage protocol, and (d) with PWC profile.

6. Conclusions

The model-based recipe and process optimization regarding H_2O_2 dosage is presented as a promising approach for Advanced Oxidation Processes (AOPs). The treatment of Paracetamol solutions in a pilot plant has been addressed as a case study where operational decisions are crucial to improve the processing and economic performance while fulfilling specific degradation targets. The results demonstrate that the processing

time is a variable of crucial influence over the processing cost (increasing the time from 0.7 to 10 hours reduces the processing cost from $47.26 \cdot 10^{-2}$ to $6.97 \cdot 10^{-2}$ € per batch), and this decision variable tends always to its upper bound. The performance improvement attained through the dynamic optimization of H_2O_2 dosage trajectory is quantitatively minor for this case (5.1% regarding the optimal solution without dosage). However, the methods introduced have shown a promising approach to the optimization AOPs. Future work will undertake the implementation of the optimal recipes at the pilot plant scale. Hence, the effect of the lamp intensity will be studied as a decision variable, as well as design or retrofit issues such as the equipment configuration and use of serial reactors.

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