A practical time discretization methodology for adjusting the dosage profile in photo-Fenton processes

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Abstract
This work is aimed at systematically determining conditions enhancing the performance of Photo-Fenton processes and improving the mineralization of aqueous solutions containing emergent pollutants. Current investigations cannot provide definitive solution approaches yet and optimizing H_2O_2 dosage is still a challenge. Thus, this work adopts recipe optimization concepts based on time discretization for experimentally addressing the optimization of the dosage profile. Results show the practicability of the solution, and discussion provides insight for the generalization of an optimization procedure.
Keywords: Photo-Fenton, H_2O_2 dosage profile, recipe optimization

1. Introduction

Photo-Fenton processes are effective for mineralizing aqueous solutions containing emergent pollutants. Accordingly, a number of works has been dedicated to determining conditions enhancing their performance (Pouran et al.,2015). Despite improvements, solutions are still far from optimal. Using H_2O_2 is essential, but excess is recognized counterproductive. Hence, research sought for adequate concentration ratios of H_2O_2 to contaminant and iron (Pignatello et al.,2006). Constant ratios suit steady operation, but time-varying batch processes require H_2O_2 concentration to be controlled to maximize performance. Thus, optimizing H_2O_2 dosage challenges current research. The experimental tuning of pre-established protocols systematically improves the dosage profile of photo-Fenton processes (Yamal et al., 2012), but considering too few degrees of freedom produces solutions too far from optimal. Conversely, the lack of detailed dynamic models hinders model-based optimization (Jung et al., 2015). Success cases have been reported for polymerization reactors (Jang et al., 2016; Nie et al., 2014), but recipe optimization of photo-Fenton processes has been hardly addressed (Audino et al., 2019). Using recipe optimization concepts and a practical time discretization, a methodology is proposed for experimentally optimizing the dosage profile. Assume a single objective J to be maximized. J is the outcome of the operation after a fixed reaction time T and after the addition of a fixed volume V^{TOT} of reactant solution (H_2O_2) that can be dosed in different ways during this time horizon. This definition excludes the minimization of the reaction time or the reactant consumption (alternative or complementary) objectives, but further problem extensions may be envisaged stemming from it.

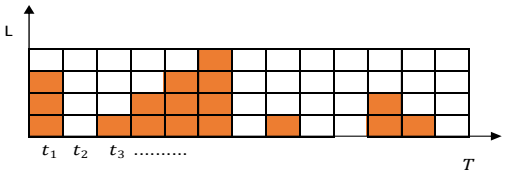

Figure 1. Discretization of the dosage profile

Assume the reaction time T is discretized in $i = 1,2,3 \dots N$ time slots, each of duration $\Delta t = T/N$, and $L \in \mathbb{N}$ dosage levels. Hence, for each time slot i the dosage $x_i \in \{0,1, \dots, L\}$ needs to be determined so that:

$$\max J = f(\mathbf{x})$$

s.t.

$$X^{TOT} = \sum_i x_i, \qquad \Delta V_i = \left(\frac{V^{TOT}}{X^{TOT}}\right) \cdot x_i \quad \forall i,$$

$$F^{min} \le F_i = \frac{\Delta V_i}{\Delta t} \le F^{max} \quad \forall i$$

which in turn allows determining the necessary dosage flows F_i for each time slot.

2. Design of Experiments

While this problem statement defines a comprehensive theoretical framework to address the dosage problem, it also poses an unaffordable solution space of $(L+1)^N$ experimental assays. Hence, a practical way to address the design of experiments is by identifying and removing the clearly unrealistic alternatives or the non-informative assays. Some simplifications are next proposed in regard of the granularity adopted and the practicality of the solutions attained.

A first issue is the simplification of the dosage level to a binary decision for each time slot i; thus, $x_i \in \{0,1\}$. Further considerations include setting $x_1 = 1$ 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). Particularly, in this work the time horizon T is set to 2h and the slot duration Δt is set to 15 min, which leads to $N = 8$ and 2^N=256 alternatives to be explored. However, four slots (the first and the three last ones) are given preset dosage values so that only 2^{N-4}=16 assays are finally planned. Those assays are given in Table 1.

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.

ID (dec)	ID (bin)	S1	S2	S3	S4	S5	S6	S7	S8	Fraction per slot
0	0000	1	0	0	0	0	0	0	0	1
1	0001	1	0	0	0	1	0	0	0	1/2
2	0010	1	0	0	1	0	0	0	0	1/2
3	0011	1	0	0	1	1	0	0	0	1/3
4	0100	1	0	1	0	0	0	0	0	1/2
5	0101	1	0	1	0	1	0	0	0	1/3
6	0110	1	0	1	1	0	0	0	0	1/3
7	0111	1	0	1	1	1	0	0	0	1/4
8	1000	1	1	0	0	0	0	0	0	1/2
9	1001	1	1	0	0	1	0	0	0	1/3
10	1010	1	1	0	1	0	0	0	0	1/3
11	1011	1	1	0	1	1	0	0	0	1/4
12	1100	1	1	1	0	0	0	0	0	1/3
13	1101	1	1	1	0	1	0	0	0	1/4
14	1110	1	1	1	1	0	0	0	0	1/4
15	1111	1	1	1	1	1	0	0	0	1/5

3. Experimental Settings

The present study sets the outcome to be minimized as the Total Organic Carbon concentration measured at the end of the fixed reaction time (i.e. $J = -[TOC]_T$). Paracetamol (PCT) is chosen as model pollutant and the mineralization of the PCT solution is then performed at pilot plant scale using a SCADA system to perform and assess the different dosage profiles. The reaction system includes a 13.5 L glass jacked reservoir tank and a 1.5 L glass tubular photoreactor. The irradiation source is an Actinic BLTL-DK 36 W/10 1SL lamp (UVA-UVB). Finally, the experimental conditions are: 40 mg L^{-1} PCT, 189 mg L^{-1} H_2O_2 (33% v/w), 10 mg L^{-1} Fe(II), pH = 2.8, T = 25°C, and reaction time 120 min.

4. Results and Discussion

The planned experiments were compared against a blank assay consisting in the addition of the whole amount of hydrogen peroxide at once, at time zero. This reference allowed proving the improved performance presented by the assays including dosage (Fig.1, A). The promising results obtained suggests that the systematic approach proposed will allow determining the best dosage strategy from the completion of the ongoing experimentation.

The analysis of the profile of the hydrogen peroxide concentration along the reaction time, given by each corresponding dosage profile (Fig.2, B) will provide further information in regard of the consumption of hydrogen peroxide and the efficiency of the process.

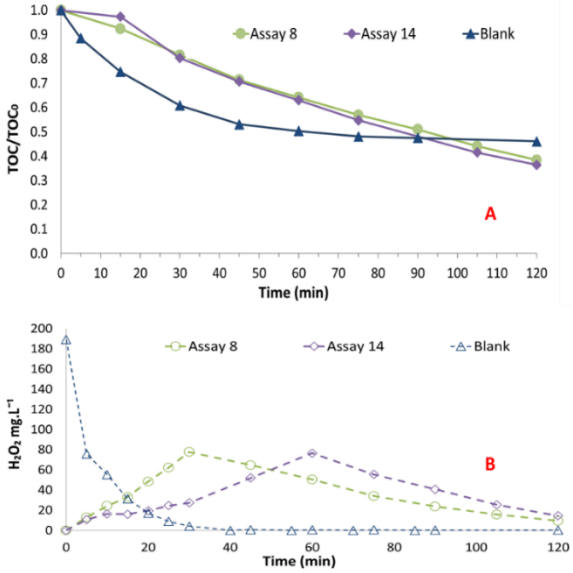

Figure 2. A). Evolution of normalized TOC results of experiment blank, assay 8 and assay 14. B). H_2O_2 concentration evolution for the same experiments.

5. Conclusions

The present work develops a recipe optimization concept based on time discretization for experimentally addressing the optimization of the dosage profile. The problem statement focus in defining a comprehensive theoretical framework to address the dosage problem from a systematic approach. A particular simplification of the dosage level to a binary decision for each time slot i; is proposed in order to discuss a easily an affordable experimental design. Result should be systematically processed in order to optimize the recipe (best dosage scheme for this particular case). Next step is further insight for progressing towards model-based optimal control of photo-Fenton processes.

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