Improving photo-Fenton process by hydrogen peroxide dosage strategies. Dissolved oxygen performance indicator

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Abstract

Fenton and photo-Fenton are Advanced Oxidation processes driven by the supply of hydrogen peroxide (H₂O₂). However, excessive hydrogen peroxide supply results in unproductive reactions and causes the process performance to decay. Thus, the goal of this work is to systematically compare different H₂O₂ dosage strategies using a new approach based on monitoring dissolved oxygen as a performance indicator, which is assumed to directly reveal the inefficient consumption of H₂O₂. The systematic approach proposed is a preliminary test to establish a general methodology to define an optimal dosage scheme.

Keywords: Photo-Fenton process, hydrogen peroxide dosage, dissolved oxygen indicator

1. Introduction

H₂O₂ supply is inherent to Fenton and photo-Fenton processes, since it is the source of the highly oxidant hydroxyl radicals. However, an excessive hydrogen peroxide supply favours reactions consuming such radicals, which is an adverse effect. A product of such reactions is oxygen, and dissolved oxygen concentration (DO) is an interesting measure that can be used as an indirect estimation of the extent of this effect. Thus, the determination of the H₂O₂ dosage scheme minimizing such scavenging reactions and maximizing process efficiency is a crucial issue to be addressed.

Supplying the total amount of hydrogen peroxide in convenient portions along the reaction time to improve process performance is reported elsewhere. However, the determination of the best partition as well as the addition timing is not resolved. To address dosage in a systematic way, a pre-established H₂O₂ dosage protocol was proposed to improve the performance of the photo-Fenton process (Yamal-Turbay et al. 2012). 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 render enough operation flexibility.

On the other hand, the adaptive addition of H₂O₂ depending on monitored process variables, such as DO, has been also investigated (Prieto-Rodríguez et al. 2011; Ortega-Gomez et al. 2012) to overcome the limitations of a pre-fixed scheme. However, lacking of a reliable model, such approach heavily relies on the underlying hypothesis of a convenient DO set-point.

In order to produce a deeper understanding of the relationship between dosage and DO, a research work is proposed to systematically compare different H₂O₂ dosage strategies based on dissolved oxygen as performance indicator (assuming a direct relation with the inefficient consumption of H₂O₂). The approach conceived consists in dividing the reaction span in three stages and addressing them separately, assuming their different qualitative effects in the reaction outcome.

A first effect (initial stage) is given by the initial H₂O₂ addition (the reaction kick-off, A₀); this was studied using from 20% to twice the stoichiometric amount of H₂O₂, S (from 0.2S to 2S), and measuring the initial mineralization rate ($-d[TOC]/dt|_{t=0}$) as a performance indicator. A second effect (transition stage), is given by a continuous dosage of H₂O₂ aimed at keeping the previous mineralization rate; for a fixed H₂O₂ inlet flow, this was studied by dosing until different DO levels (DO_{stop}) were attained at time θ and measuring the DO change rate ($d[DO]/dt|_{t=\theta}$) as a performance indicator. A last effect, during a final automatic control stage, would be given by the dosage of H₂O₂ driven by an automatic system tuned to control DO. This last effect strongly depends on the decisions made at the previous stages. Hence, this work addresses the study of the first two stages aimed at discussing the ulterior influence on the automatic dosage. Table 1 summarizes the experimental design for these two stages.

Table 1: Stages of the experimental approach.

Stage	Decision variables	Measured outcome
Initial	Initial H ₂ O ₂ amount: $0.2S \leq A_0 \leq 2S$	$-d[TOC]/dt _{t=0}$
Transition	Stop level for dosage: $4\text{mg/L} \leq \text{DO}_{\text{stop}} \leq 12\text{ mg/L}$ (@ H ₂ O ₂ flow 0.287 mL/min)	$d[DO]/dt _{t=\theta}$

2. Materials and methods

Photo-Fenton experiments were performed in a 15-L pilot plant composed by a glass jacketed reservoir tank and a glass annular photo-reactor, and equipped with an Actinic BL TL-DK 36 W/10 1SL lamp (UVA-UVB). The irradiated volume of the latter is 1.5 L, or rather 10% of the total volume: pH was adjusted to 2.8, hydrogen peroxide was used at 33% (w/w), and iron sulphate (FeSO₄·7H₂O) was adopted as the source of ferrous ion (Fe²⁺). Paracetamol dissolved in water (100 mg/L) with an initial total organic carbon (TOC) concentration equal to 65 mg/L was selected as model wastewater. Duplicate measurements were performed. Total organic carbon (TOC) concentration was determined with a TOC (TOC-VCSH/CSN Shimadzu; Kyoto, Japan) analyser. PCT concentration was measured via HPLC Agilent 1200 series (Agilent Technologies) and H₂O₂ concentration was measured by using the spectrophotometric method.

3. Results and discussion

For the first stage, the results showed that the highest initial mineralization rates ($-d[TOC]/dt|_{t=0}$) are obtained for concentrations between 0.4S and 0.8S (Figure 1). Thus, an initial concentration of 0.4S was selected for the assays in the second stage because exceeding this concentration produced no improvement on process efficiency, while below 0.4S the process was slower (probably due to the lack of radicals).

For the second stage, continuous dosage was fixed at 0.287 mL/min according to preliminary assays. This continuous addition is expected to keep the mineralization rate ($d[TOC]/dt$). Figure 2 A represents the normalized TOC degradation curves and Figure 2B represents the DO evolution.

Figure 1: Normalized TOC degradation curves as a function of initial H_2O_2 initial dosage

Figure 2: A) Normalized TOC degradation curves as a function of initial H_2O_2 initial dosage plus a continuous flow rate in 0.287 mL / min that stop addition after specific DO_{stop} value. B) DO evolution

Attaining a DO value of 4 mg/L (DO_{stop}) seems the most promising result. Longer dosage produces higher H_2O_2 concentrations, but this excess is not effectively used because the reaction rate ($-d[TOC]/dt$) is obviously decreasing and the reagent consumption is rising up. The results obtained were compared in order to determine the best dosage conditions bearing in mind a future subsequent addition of H_2O_2 (third control stage) that would, from this point on, automatically determine H_2O_2 dosage level (OP) from the measured DO (PV) and a convenient DO value (SP).

4. Conclusions

The dosage strategy proposed was implemented and assessed at each stage. Given the quantitative criterion, the quantitative results obtained allowed sorting out the alternatives and identifying the best one. The work contributes in the continue progressing towards improving photo-Fenton process by hydrogen peroxide dosage strategies of photo-Fenton processes.

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 wants to thank SERC Chile (FONDAP/15110019). Sara Miralles Cuevas wants to thank the Spanish Ministry of Science, Innovation and Universities for her Juan de la Cierva Scholarship.

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