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Systematic optimization approach for the efficient management of the photo-Fenton treatment process

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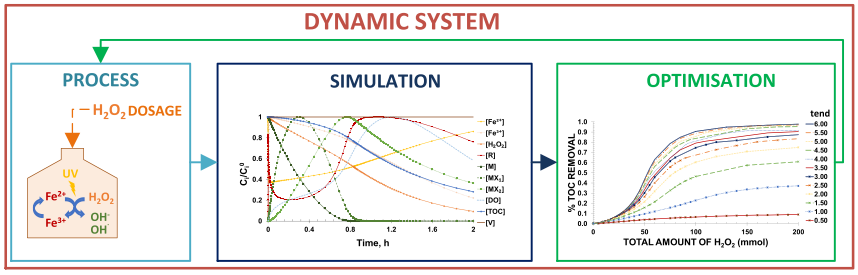
HIGHLIGHTS

- The optimization of H_2O_2 dosage for efficient photo-Fenton operation is addressed.
- A direct simultaneous optimisation method using available kinetic models is proposed.
- A multi-objective optimization framework is provided for exploiting existing models.
- Pareto solutions are given considering economic and environmental issues.
- A practical decision-making oriented overview of the process is provided.

GRAPHICAL ABSTRACT



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ABSTRACT

The photo-Fenton process is a photochemical process that has proved to be highly efficient in degrading new potentially harmful contaminants. Despite of this, scarce attention has been paid to the development of systematic procedures and optimisation strategies to efficiently operate such a process. The present work aims at investigating the effectiveness of a model-based approach in carrying out the dynamic optimisation of the recipe of a photo-Fenton process, performed in fed-batch mode (reactant dosage).

This work has addressed and solved multiple optimisation problems, searching for the optimal hydrogen peroxide (H_2O_2) dosage profile, and Pareto frontiers have been built accordingly in order to point out the interaction between three main process efficiency parameters, such as processing time, total amount of H_2O_2 used, and Total Organic Carbon (TOC) removal. Such a study allows mapping the best operating conditions and provides a decision-making oriented overview of the process. An economic study has also been carried out with the aim of finding out the optimal H_2O_2 dosage profile that guarantees the minimum operating cost under a varying set of operational and environmental constraints, such as TOC removal.

This work has adopted and properly adapted the model by Cabrera Reina et al. (2012) in order to describe the evolution of the system under a flexible reactant dosage. Cabrera Reina et al. (2012) proposed a semi-empirical kinetic model to track paracetamol degradation using the photo-Fenton process and experimentally validated this model for a pollutant load range between 4 and 25 mmol L^{-1} of TOC (e.g. industrial wastewaters). Dynamic optimisation has been addressed applying a direct simultaneous optimisation method using this extended model. Results have been presented and discussed in regard of optimal H_2O_2 dosage under both economic and environmental constraints. The model-based optimisation approach has allowed a fast practical recipe adjustment with reduced experimental work.

Abbreviations: H_2O_2, Hydrogen peroxide; Fe^{2+}, Ferrous ion; Fe^{3+}, Ferric ion; R, Free radicals; TOC, Total organic carbon; M, Parent organic compound present at the beginning of the reaction; MX_1, Partially oxidized organic: first intermediate; MX_2, Partially oxidized organic: second intermediate; DO, Dissolved oxygen; DO^*, Dissolved oxygen saturation concentration.

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Nomenclature

$F(t)$	Inlet flow-rate, L h^{-1}
$f_i(t)$	Molar inlet flow-rate for each component i, mmol h^{-1}
V	Total volume of the reactor, L
$V_{irradiated}$	Irradiated volume of the reactor, L
$F(t)\ V^{-1}$	Dilution factor for the fed-batch operation, h^{-1}
I	Irradiance, W m^{-2}
$[C_i]^{IN}$	Concentration of component i in the inlet flow, mmol L^{-1}
$[C_i]$	Concentration of component i inside the reactor, mmol L^{-1}
$[C_i]^0$	Initial concentration of component i inside the reactor, mmol L^{-1}
tt′	Time, h
τ	Final reaction time (reaction span), h
$\chi(t)$	TOC removal at a generic time t, (adimensional)
$\chi(\tau)$	Final TOC removal (at τ), (adimensional)
$A(t)$	Amount of H_2O_2 employed at a generic time t, mmol
$A(\tau)$	Total amount of H_2O_2, mmol
k_j	Kinetic constants for each reaction j, (units according to the kinetic expression)
r_i	Reaction rate for component i, mmol L^{-1} h^{-1}
$g1_{DO}$, $g2_{DO}$, $c1_{DO}$	Stoichiometric coefficients in the dissolved oxygen balance, (adimensional)
K_La	Gas–liquid mass transfer coefficient in the dissolved oxygen balance, h^{-1}
$c_{N,\ N=1,\ 2,\ 3}$	Unit cost coefficients, (several units)

1. Introduction

In the last years, research, development and implementation of Advanced Oxidation Processes (AOPs) (Andreozzi et al., 1999), both for industrial and urban wastewaters, have received considerable attention. AOPs have emerged as the only feasible option for the treatment of hardly biodegradable or toxic substances that can resist or damage conventional biological treatments (Oller et al., 2011) and for the treatment of the so-called Contaminants of Emerging Concern (CECs). CECs are a group of chemicals that are being detected in waters in very low concentrations (ng L^{-1} and μg L^{-1}) thanks to new and more powerful analytical techniques, and that may be included in future environmental regulations depending on the results of the investigations on their effects on human health and the environment.

Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC tackle the issue of priority substances in the field of water policy, states the importance of CECs monitoring and updates the list of priority substances. According to the European Commission, another important goal will also be the reinforcement of the risk assessment of pharmaceutical products (Ribeiro et al., 2015).

Although AOPs are considered clean technologies for this challenge, they are also expensive due to the consumption of energy and chemical reagents, which increases with treatment time. Hence, the achievement of a practical application of AOPs is required. For that goal, the key issue is the achievement of design and operation approaches providing optimal economic and environmental performance of AOPs.

The photo-Fenton process can be described as an extension of the Fenton process. The Fenton process (Fenton, 1894) occurs by means of addition of hydrogen peroxide to Fe^{2+}salts according to the Eq. (1):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\cdot} \quad (1)$$

The Photo-Fenton process is based on the use of UV–VIS light irradiation at wavelength higher than 300 nm that allows Fe^{2+} regeneration by the photolysis of Fe^{3+} complexes (Kiwi et al., 1993; Pulgarin and Kiwi, 1996), as presented in Eq. (2):

$$Fe(OH)_2 \xrightarrow{h\nu} Fe^{2+} + OH^{\cdot} \quad (2)$$

The Photo-Fenton process is of added interest among AOPs, for the possibility of developing high efficient and cost effective treatment systems by exploiting solar energy and the combination with biological technologies (Pouran et al., 2015). Moreover, it has showed to be highly successful for both micropollutants remediation (Miralles-Cuevas et al., 2014) and the treatment of high-strength organic wastewaters (Pouran et al., 2015). The review by Wang et al. (2016) stressed that the photo-Fenton process has been applied to treat different kinds of wastewaters such as olive-oil mill, textile, pesticide, cosmetic, dye, fermentation brine, green olives, pharmaceutical, cork cooking, pulp mill and phenolic wastewaters.

In the last years a remarkable experimental effort has been made to better understand the photo-Fenton process as a whole. As pointed out in a review by Pignatello et al. (2006), several studies performed at laboratory scale have investigated the role of H_2O_2 consumption, the processing time and the mineralization rate, which are key process efficiency parameters that affect the overall kinetics. Subsequently, Zapata et al. (2010) published an important study, performed at pilot plant scale, evaluating the effect of temperature, dissolved iron concentration, and dissolved organic carbon (DOC) as well as their relationship to such key process efficiency parameters.

More recently, Pouran et al. (2015) have stressed that a significant number of studies have addressed the investigation of the main factors affecting photo-Fenton performance (% DOC or %TOC removal), such as contaminant loads, Fenton reagents concentrations, pH and temperature, by the use of multivariate experimental design based on the response-surface methodology.

Conversely, only few studies (Moreno-Benito et al., 2013) have adopted a model-based approach for determining the best operating conditions that can help the development of practical applications.

In the optimisation of batch wise operation of photo-Fenton processes, the hydrogen peroxide dosage strategy plays a crucial role. Experimental results have highlighted the activation of inefficient reactions scavenging hydrogen peroxide, the most expensive process reactant, which can be avoided or reduced by proposing a proper flexible set of operational conditions (i.e. the recipe) with gradual dosage (Yamal-Turbay et al., 2012, 2013).

According to the literature survey, up until now, the determination of an efficient H_2O_2 dosage profile has been faced mostly following an experimental approach (Prieto-Rodríguez et al., 2011) based on manual H_2O_2 dosing that has led to low process performance or, for control purposes (Ortega-Gómez et al., 2012).

Hence, the main novelty of this work is a systematic dynamic model-based optimisation strategy that takes advantage of kinetic models and enables a practical recipe adjustment in a fast and reliable way, with reduced experimental work and with a novel decision-making focus based on both economic and environmental factors.

The success of an optimisation strategy also depends on the availability of reliable and computationally affordable models.

Regarding photo-Fenton kinetic modelling, two main approaches can be found in literature, such as empirical models (Kusic et al., 2006; Pérez-Moya et al., 2008) that cannot be scaled up and do not address the process dynamics, and First Principles Models (FPMs) (Jeong and Yoon, 2005; Conte et al., 2012) that are unaffordable even for very simple molecules.

Therefore, a compromise solution was adopted such as the semi-empirical kinetic (shortcut) model by Cabrera Reina et al. (2012) based on simplified photo-Fenton reactions and lumped parameters (for parent compound, intermediates and free radicals). This model