Journal of Environmental Management 131 (2013) 66-73

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Improvement of the robustness of solar photo-Fenton processes using chemometric techniques for the decolorization of azo dye mixtures

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ARTICLE INFO

Article history: Received 19 July 2013 Received in revised form 19 September 2013 Accepted 22 September 2013 Available online 18 October 2013

Keywords: Azo dye Chemometric Photo-Fenton Response surface methodologies Spectrophotometry

ABSTRACT

The aim of this study was to propose and to evaluate a strategy based on chemometric tools to improve the robustness of photo-Fenton processes during decolorization of mixtures of sulfonated azo dyes. The strategy consisted of three stages; quantification, reagent dose selection and robustness analysis. The partial least square method was used for the simultaneous quantification of acid orange 7, acid red 151, and acid blue 113, in a mixture, by using UV-visible spectra. Then, a central composite design was applied to set the best reagent dose (Fe^{2+} and H_2O_2) to obtain a decolorization of 97% for each dye. The application of the strategy allowed to predict the concentration of each dye and to select the best reagent dose to decolorize mixtures of sulfonated dyes. Also with the application of the developed strategy, a reduction of peroxide from 33 to 65% was obtained and the undesirable reactions were reduced. It was observed that the variation of dye concentrations do not affected the percentage of decolorization.

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1. Introduction

Azo compounds account for 70% of over one million tons of dyes produced per year, making them the largest group of dyes released into the environment (dos Santos et al., 2007). Biodegradation is considered a cost-competitive and environmentally-friendly alternative to degrade azo dyes; however, its robustness is highly affected by factors such as dye structure and concentration, the presence of toxic and/or recalcitrant byproducts, adaptability of microorganisms, and carbon source, among others (Barsing et al., 2011; Carneiro et al., 2010).

On the other hand, dyes may be satisfactorily degraded by means of Advanced Oxidation Processes (AOPs) like Fenton (Pignatello et al., 2006), UV/H₂O₂ (Aleboyeh et al., 2012), photo-Fenton (Malato et al., 2009; Pignatello et al., 2006; Prato-Garcia and Buitrón, 2012), heterogeneous photocatalysis (Baran et al., 2008; Kasiri et al., 2008; Sakkas et al., 2010), and electro-Fenton (Brillas et al., 2009). Nevertheless, the operative cost and the lack of strategies to deal with complex effluents apparently discourage the use of AOPs from full-scale applications (Brillas et al., 2009; Malato et al., 2009; Módenes et al., 2012). In AOPs, chemometric techniques like experimental design and response surface analyses are used to reveal the effect of dye concentration, pH, catalyst load, oxidant concentration and reaction time, within the percentage of decolorization (Alaton et al., 2009; Bezerra et al., 2008; Kasiri et al., 2008; Sakkas et al., 2010). It has been discussed that the wide range of scenarios that the model must cover (e.g., concentration changes, dye type and the presence of chemical auxiliaries) limits its effectiveness (Bezerra et al., 2008; Sakkas et al., 2010).

As dye concentration increases, both Fe²⁺ and H₂O₂ concentrations should be increased to ensure the presence of enough HO[•] radicals (Eq. (1)) to degrade the organic matter (Alaton et al., 2009; Prato-Garcia and Buitrón, 2012). This increase of the Fenton's reagent, may lead to enhance the presence of undesirable reactions, promoting the consumption of HO[•] radicals by the reagents, as indicated in Eqs. (2)–(4) (Malato et al., 2009; Pignatello et al., 2006; Prato-Garcia and Buitrón, 2012).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO' + OH^- \quad k = 53 - 76M^{-1}s^{-1}$$
 (1)

$$HO' + H_2O_2 \rightarrow HO'_2 + H_2O \quad k = 1.7 - 4.5 \times 10^7 M^{-1} s^{-1}$$
 (2)

HO' + Fe²⁺ → Fe³⁺ + OH⁻
$$k = 2.6 - 5.8 \times 10^8 M^{-1} s^{-1}$$
 (3)

$$2\text{HO} \rightarrow \text{H}_2\text{O}_2 \quad k = 5 - 8 \times 10^9 \times \text{M}^{-1}\text{s}^{-1}$$
 (4)







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^{0301-4797/\$ -} see front matter © 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.jenvman.2013.09.018