Journal of the Taiwan Institute of Chemical Engineers 000 (2017) 1–8

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Optimization of Disperse Blue 3 mineralization by UV-LED/$FeTiO_3$ activated persulfate using response surface methodology

Jefferson E. Silveira[a,*], Elis Marina Turini Claro[b], Wendel S. Paz[a], Adriana S. Oliveira[a], Juan A. Zazo[a], Jose A. Casas[a]

[a] *Chemical Engineering, Autonomous University of Madrid, Cantoblanco, 28049 Madrid, Spain*
[b] *São Paulo State University (UNESP), Institute of Biosciences, Department of Biochemistry and Microbiology, Av. 24 A, 1515, Bela Vista, 13506-900 Rio Claro, SP, Brazil*

ARTICLE INFO

Article history:
Received 28 August 2017
Revised 14 December 2017
Accepted 15 December 2017
Available online xxx

Keywords:
Optimization
Box-Behnken design
$FeTiO_3$
Photo-reduction

ABSTRACT

Response surface methodology based on Box-Behnken design (BBD) was successfully applied for the optimization of the UV-LED/$FeTiO_3$ activated persulfate (PS) process. Disperse Blue 3 (DB3) azo dye oxidation was carried out in a quartz jacketed stirred batch reactor using 405 nm UV at 10 W/m^{-2} as radiation source. The effects of temperature, catalyst concentration and persulfate dose upon the total organic carbon (TOC) removal were investigated. Optimum operating conditions were found to be: ilmenite: 320 mg/L^{-1}, PS: 1.56 g/L^{-1} and 67 °C. Under these conditions, 96% mineralization was achieved. Ecotoxicity of the final effluent was evaluated using *Aliivibrio fischeri* bacteria, finding a negligible toxicity.

1. Introduction

The continuous demographic growth, the steep expansion of the industrial sector and the discharge of effluents in water bodies contribute to an increasing pressure over hydrological resources, causing an irreversible reduction in fresh water availability [1]. The synthetic dyes industries are considered a representative example of water polluting industry, in which raw effluents contain recalcitrant and potentially carcinogenic compounds [2].

Nowadays, over 100,000 different dye structures have been synthesized and more than 0.7 million tons/year of dyes are produced, with applications in textile, paper, leather, cosmetics, food and pharmaceutical industries [3,4]. Worldwide, 280,000 tons of textile dyes are discharged in industrial effluents annually [5]. Among these compounds, azo dyes represent the largest group used in textile dyeing and printing industries and they account for around 70% of the world dye production. These are aromatic and heterocyclic compounds containing an azo group (–N=N–) as chromophore, linked to other groups such as –OH and $–NO_2$ [6,7].

Traditional treatment methods are not effective in the removal of azo dyes due to their complex structure, which confers them high stability and chromaticity. Thus, more effective water treatment technologies are required [8]. Advanced oxidation processes (AOPs), which rely primarily on the generation of the free radicals to degrade organic compounds, have shown a great potential. These techniques consist of the activation of oxidants to provide a clean way of generating highly oxidizing radical species [9].

Recently, sodium persulfate (PS) anion has emerged as a promising oxidant, and has been effectively used for azo dye treatment [10]. PS presents high solubility, high stability and wide operative pH range in aqueous solution. However, reactions of PS with organic substances in water are generally slow at ambient temperature, therefore it is necessary to activate PS generating a stronger sulfate radical ($SO_4^{\bullet-}$, $E_0 = 2.5–3.1$ V), to accelerate the degradation rate [8,11]. Generally, PS activation can be accomplished by a transition metal ion which acts as a catalyst. Because Fe is a relatively nontoxic and inexpensive specie among the transition metal catalysts, it has been widely studied for this purpose [12]. Several types of Fe-based catalysts in different AOPs have been used for the chemical activation of persulfate, including the polycrystalline $FeTiO_3$ (natural ilmenite) [13]. Ilmenite is an antiferromagnetic semiconductor, with a band gap between 2.3 and 2.9 eV with potential applications in chemical catalytic reactions [14].

One of the main drawbacks of this mineral is the high induction period and lower activity in comparison to other materials [14]. This problem can be solved by using UV radiation to improve the efficiency via photoreduction of Fe(III) to Fe(II) in the ilmenite surface (Eq. 1), decreasing the induction period. So far, this strategy ($FeTiO_3$/UV) has been tested for advanced oxidation processes us-

---

[*] Corresponding author.
E-mail address: jefferson.silveira@uam.es (J.E. Silveira).

https://doi.org/10.1016/j.jtice.2017.12.015
1876-1070/© 2017 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

Please cite this article as: J.E. Silveira et al., Optimization of Disperse Blue 3 mineralization by UV-LED/$FeTiO_3$ activated persulfate using response surface methodology, Journal of the Taiwan Institute of Chemical Engineers (2017), https://doi.org/10.1016/j.jtice.2017.12.015

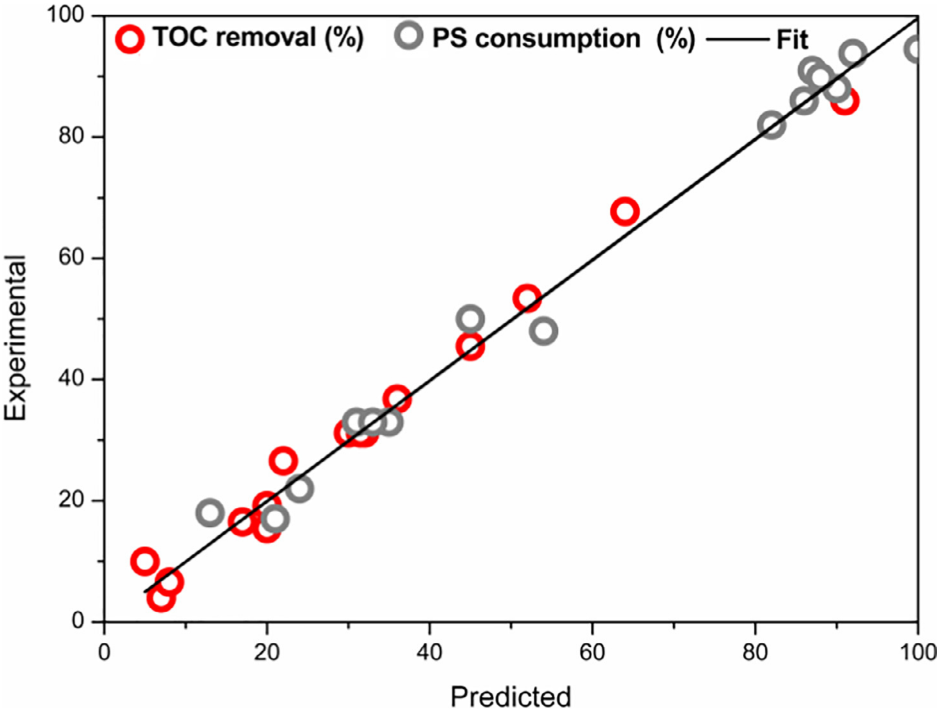

Fig. 1. Predicted *versus* actual plot for TOC removal and PS consumption on DB3 mineralization.

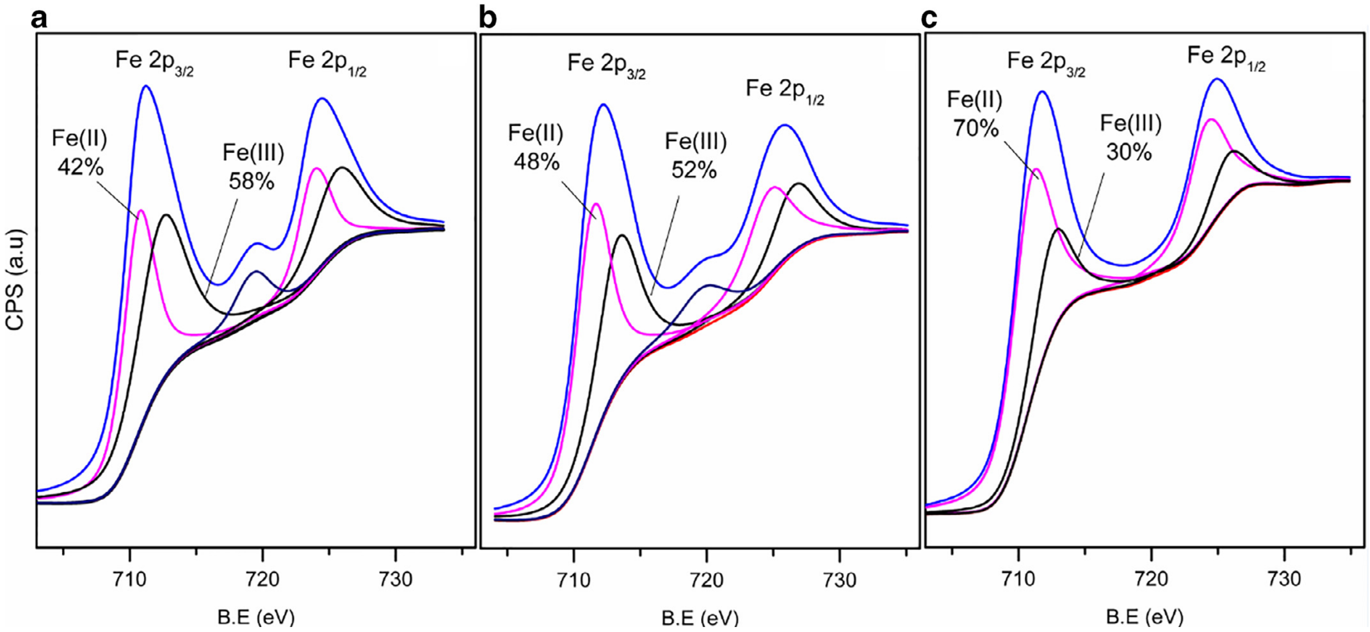

Fig. 2. XPS spectra of Fe 2p for raw ilmenite, photo-reduced and photo-reduced in dye presence. Experimental conditions: $[DB3]_0 = 80$ mg/L, $[PS]_0 = 92\%$, ilmenite = 320 mg/L, $pH_0 = 3$, $t = 180$ min.

ing H_2O_2 as oxidant for the degradation of phenol [14,15].

$$\text{ILM} - \text{Fe(III)} \xrightarrow{h\nu} \text{ILM} - \text{Fe(II)} \quad (1)$$

In addition, Cheng et al. [16] and Bokare and Choi [17] suggest that, in presence of colored substances like organic dyes, visible light irradiation can also reduce Fe(III) to Fe(II) via intermolecular electron transfer from an excited dye state, Eqs. (2,3).

$$\text{dye} + \text{visiblelight} \rightarrow \text{dye}^* \quad (2)$$

$$\text{dye}^* + \text{Fe(III)} \rightarrow \text{Fe(II)} + \text{dye}^{\bullet +} \quad (3)$$

The increase in source of Fe(II) promotes the activation of PS to produce $SO_4^{\bullet -}$and $HO^\bullet$ (Eqs. 4,5) [18–20].

$$\text{Fe(II)} + S_2O_8^{2-} \rightarrow \text{Fe(III)} + SO_4^{\bullet -} + SO_4^{2-} \quad (4)$$

$$SO_4^{\bullet -} + H_2O \rightleftarrows HO^\bullet + H^+ + SO_4^{2-} \quad (5)$$

Ultraviolet light emitting diodes (UV-LEDs) are a promising source of UV radiation and become an alternative to photocatalytic reactions. They present potential advantages over conventional UV lamps such as instant on/off ability, tunable radiation to control

Please cite this article as: J.E. Silveira et al., Optimization of Disperse Blue 3 mineralization by UV-LED/FeTiO$_3$ activated persulfate using response surface methodology, Journal of the Taiwan Institute of Chemical Engineers (2017), https://doi.org/10.1016/j.jtice.2017.12.015