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UV-LED/ilmenite/persulfate for azo dye mineralization: The role of sulfate in the catalyst deactivation

Jefferson E. Silveira [a,*], Wendel S. Paz [b,*], Patricia Garcia-Muñoz [a], Juan A. Zazo [a], Jose A. Casas [a]

[a] Chemical Engineering, Autonomous University of Madrid, Cantoblanco, 28049 Madrid, Spain
[b] Department of Condensed Matter Physics, Autonomous University of Madrid, Cantoblanco, 28049 Madrid, Spain

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ABSTRACT

This work investigates the effect of UV-LED on the persulfate (PS) activation with natural ilmenite ($FeTiO_3$) in the oxidation of azo dye Disperse Blue 3 (DB3). The high induction period and the scarce ability of this mineral to activate PS can be overcome by using UV irradiation to increase the $SO_4^{\bullet -}$ generation via photoreduction of Fe(III) to Fe(II) on the ilmenite surface, main responsible of $SO_4^{\bullet -}$ formation in iron-based catalysis. The effect of several operating conditions such as persulfate dose (20–100% of the theoretical stoichiometric amount), reaction temperature (30–70 °C) and mineral concentration 320 mg L^{-1} has been studied. Under optimum conditions (320 mg L^{-1} of ilmenite, pH_0: 3, using 100% of stoichiometric amount of PS at 70 °C under UV-LED radiation) more than 95% TOC reduction and 92% PS decomposition were reached after 180 min. The progressive deactivation of $FeTiO_3$ through successive experiments can be explained, according to density functional theory (DFT) calculations, by the formation of a passivation layer due to adsorption of SO_4^{2-} on the $FeTiO_3$ surface.

1. Introduction

The growth in the use of synthetic dyes has been accompanied by large volumes of industrial effluent causing environmental damage to the living organisms [1]. There are several types of synthetic dyes which are widely used in paper, cosmetics, food, pharmaceutical and textile industries [2,3]. Among them, azo dyes are the most common used in textile industry, representing about 70% of all commercial dyes. These compounds contain an azo group (—N=N—) as chromophore, associated with aromatic systems linked to other groups such as —OH and —NO_2 [4,5].

Advanced oxidation processes (AOP's) based on the in situ hydroxyl radical ($HO^{\bullet}$) generation have been widely used as a feasible way to mineralize azo dyes. Electrochemical oxidation [6], solar photoelectro-Fenton [7], photocatalytic degradation [8] and ozonation [9] represent some of those alternatives to $HO^{\bullet}$ generation.

Activated persulfate based AOP's constitutes an alternative to the aforementioned procedures. The persulfate anion (PS) is a strong oxidant, with a redox potential of 2.01 V [10]. Furthermore, PS can be induced to generate a stronger sulfate radical ($SO_4^{\bullet -}$), with a standard redox potential varying between 2.5 and 3.1 V [11]. Many studies have demonstrated the oxidation of azo dyes by activated persulfate. Frontistis et al. [12] demonstrated the effectiveness of using PS/UV for methyl orange decolorization. Kordkandi and Forouzesh [13] have applied thermally activated persulfate to treat aqueous methylene blue. Xu and Li [14] reported the degradation of azo dye Orange G by Fe^{2+} activated persulfate. In addition, Teel et al. [15] compared the activation of persulfate with 13 naturally occurring minerals found in surface and subsurface soils, for in situ chemical oxidation, among them cobaltite, pyrite, siderite and ilmenite. However, those results revealed a scarce ability to decompose persulfate in a natural groundwater system.

Ilmenite ($FeTiO_3$) as a titanate of ferrous iron mineral, is a antiferromagnetic semiconductor, with a band gap varying between 2.4 and 2.9 eV with potential applications in chemical catalysts and photocatalysts reactions [16–18]. At room temperature and atmospheric pressure, $FeTiO_3$ adopts an ordered corundum structure [8,9] of space group R_{3}^{-}, in which Fe(II) and Ti(IV) form alternating layers along the rhombohedral axis of the crystal, with oxygen layers between them. Layers of Fe and Ti alternate with a cation ordering of Ti-Fe-V-Fe-Ti (V: vacant sites) along the c axis.

So far, the application of ilmenite as catalyst in AOP's processes is limited by a high induction period and a low activity [19]. These

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* Corresponding authors.
E-mail addresses: jeffersonano@gmail.com (J.E. Silveira), wpascal1@gmail.com (W.S. Paz).

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drawbacks can be overcome by using UV irradiation to improve the efficiency via photoreduction of Fe(III) to Fe(II) in the ilmenite surface, decreasing the induction period [20,21]. In this sense, Fe(II) plays an important role in $SO_4^{\bullet -}$ generation in iron-based catalysis. Liang et al. [22] found that Fe (II), but not Fe(III), activates PS. Light emitting diodes (LEDs) have become an alternative to conventional UV sources [21] due to a higher current-to-light conversion efficiencies, compactness, suitability for periodic illumination, narrow band emission, no disposal problems and long life [23,24].

This work outlines the combination of temperature and UV LED radiation (λ: 400–405 nm) with the aim of improving catalytic properties of ilmenite mediated activation of persulfate toward textile dye DB3 mineralization, allowing the use of this raw mineral as an inexpensive and sustainable catalyst.

The anthraquinone azo dye DB3 ($C_{17}H_{16}N_2O_3$) has been chosen as a target compound because of their toxic and mutagenic characteristics [25]. The contribution of sulfate upon the $FeTiO_3$ surface passivation during PS activation has been also studied by performing *ab initio* band calculations based on the density functional theory using the plane-wave pseudopotential method as implemented in Quantum Espresso code.

2. Material and methods

2.1. Reactants

Disperse blue 3 was provided by Sigma Aldrich (dye content 20%). The simulated disperse azo dye aqueous solution was prepared by complete dissolving 80 mg (16 mg of dye) in 1 L deionized water. The average COD of the resulting solution was 112 mg L^{-1} (measured in triplicate). Persulfate (98%) was purchase from Panreac (Spain). The chemicals used either as potassium iodide (KI) (99%), sodium carbonate (Na_2CO_3) (99%), sodium bicarbonate ($NaHCO_3$) (99.7%), sodium sulfate (Na_2SO_4) (99%), dichloromethane (CH_2Cl_2) (99.8%), *tert*-butyl alcohol (TBA), (99.5%), ethanol (EtOH) (95%) were purchased from Sigma-Aldrich (U.S.A). The ilmenite (Ref. 50110700) was provided by Marphil S.L. (Spain). Titanium dioxide (TiO_2) was purchased from Degussa Corporation.

2.2. Ilmenite characterization

Experimental band-gap determination was carried out plotting $(\alpha h\upsilon)_n^1$ versus $h\upsilon - E_g \pm E\ (\Omega)$ (where $n = 2$ for indirect semiconductors) giving a linear absorption edge and its cut with base line corresponds to band-gap energy. The diffuse reflectance spectra were recorded with a UV–vis Agilent Varian, Cary 5000. The iron and titanium content of fresh and used ilmenite was determined by total reflection X-ray fluorescence, using a TXRF spectrometer 8030c (detection limit 0.007 and 0.02 mg L^{-1} for Fe and Ti respectively). The crystalline phases in the catalyst were analyzed by X-ray diffraction (XRD) using a Siemens model D-5000 diffractometer with Cu Kα radiation (λ = 1,54 Å). Ilmenite was characterized by X-ray Photoelectron Spectroscopy (XPS) with a Kα Thermo Scientific apparatus with an Al Kα (hv = 1486.68 eV) X-ray source using a voltage of 12 kV under vacuum (2×10^{-7} mbar) condition. For the peak analysis a Shirley type background was used. Peaks were fitted with Gaussian and Lorentzian functions using the XPS Peak 4.1 software [26]. The BET specific surface area (S_{BET}) of the catalyst was characterized from nitrogen adsorption-desorption isotherms at 77 K using a Micromeritics Tristar 3020 apparatus. The samples were previously outgassed overnight at 150 °C to a residual pressure of 10^{-3} Torr [21].

2.3. DFT model setup and calculations methods

The first-principle calculations were carried out based on the frame-work of density functional theory (DFT), as implemented in the Quantum ESPRESSO package [27]. The generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) [28] was adopted for exchange-correlation functional. Since GGA-PBE functionals usually underestimate the band gaps, fail to correct treat *d* orbitals in transition-metal oxides due to unphysical self-interaction and GGA-PBE incorrectly predict a metallic state, we use here the hybrid nonlocal exchange-correlation functional (HSE06) [29] in an attempt to get more reliable values, possibly closer to the experimental ones.

The HSE functional, with its fraction of screened short-ranged Hartree-Fock exchange, yields reasonably accurate predictions for energy band gaps in semiconductors [30,31]. The electron-ion interaction is described using the norm-conserving Troullier-Martins pseudopotentials [32] are employed in PBE and HSE calculations. The energy cut-off for the plane wave basis set is put at 100 Ry with a charge density cut-off of 400 Ry. We have used a Monkhorst-Pack [32] scheme with a 6 × 6 × 3 k-mesh for the Brillouin zone integration.

The complete hexagonal unit cell of $FeTiO_3$ ilmenite is shown in Fig. 2. All calculations were carried out under rhombohedral symmetry constraints. The $FeTiO_3$ was simulated in the supercell approach under structure optimizations based on the experimental lattice structure obtained from the American Mineralogist Crystal Structure Database [33].

2.4. Typical reaction procedure

The UV-LED system consisted of a glass jacketed batch reactor (the reaction volume was set at 250 mL) placed in a magnetic stirrer (200 rpm). A commercial LED strip (SMD 5050) which radiates at 405 nm was placed around the external wall of the reactor. The irradiance corresponding to LED radiation was 10 W m^{-2} with a power of 19 W. The reaction temperature was controlled between 30 and 70 °C with a thermal batch recirculation system (Julabo 13) (Fig. S1). The PS dose was varied between 20% (0.34 g L^{-1}) and 100% (1.7 g L^{-1}) of the stoichiometric theoretically needed for complete mineralization of COD (12 g PS/g COD). The ilmenite concentration was 320 mg L^{-1} (preliminary studies showed that the higher amounts not increase the reaction rate). The reusability of ilmenite was appraised in three successive experiments. The catalyst recovered by filtration and dried overnight at 60 °C after each run.

2.5. Analytical methodology

Reaction samples were instantly placed in an ice bath and immediately analyzed after centrifugation at 3500 rpm for 10 min. The mineralization degree of DB3 was determined measuring the total organic carbon (TOC) by TOC-V CSH, Shimadzu, Japan. A gas chromatography-mass spectrometry (GC–MS) system in electron impact ionization mode was used for the aromatic by-products with a CP-3800/Saturn 2200, Varian, equipped with an automatic injector CP-8200/SPME, solid-phase micro extraction [34]. Short-chain organic acids were analyzed by ion chromatography with chemical suppression (Metrohm 790 IC) using a conductivity detector. A Metrosep A supp 5-250 column (25 cm length, 4 mm diameter) was used as stationary phase and an aqueous solution containing 3.2 mM Na_2CO_3 and 1 mM $NaHCO_3$ was used as the mobile phase at a flow rate of 0.7 mL min^{-1} [21]. The residual PS was determined by colorimetric method [35]. The iron released from the ilmenite was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) using an ICP-MS Elan 6000 PerkinElmer Sciex (with detection limit of 0.045 ppb). The acute