



Photocatalytic degradation of textile wastewater in presence of hydrogen peroxide: Effect of cerium doping titania



Azza Touati^a, Tijani Hammedi^a, Wahiba Najjar^{a,*}, Zouhaier Ksibi^a, Sami Sayadi^b

^a Université Tunis El Manar, Faculté des Sciences de Tunis, LR01ES08 Laboratoire de Chimie des Matériaux et Catalyse, El Manar, 2092 Tunis, Tunisie

^b Centre de Biotechnologie de Sfax, Laboratoire de Bioprocédés Environnementaux, B.P. 1177, 3018 Sfax, Tunisie

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ABSTRACT

Ce–TiO₂ catalysts synthesized through sol–gel method were explored for textile wastewater photocatalytic degradation in presence of H₂O₂. Synthesized materials were characterized by X-ray diffraction, Raman spectroscopy, UV–visible diffuse reflectance spectroscopy, N₂ physisorption at 77 K and H₂–temperature programmed reduction. Suitable amount of cerium (1%) significantly inhibits the electron–hole pairs recombination and reduces the energy gap values of the materials. 1% Ce–TiO₂ catalyst demonstrated superior catalytic performances permitting a 40% and 55% of TOC and color conversions, respectively. The relationship between photocatalytic activity and physicochemical properties was discussed. Environmental impact of textile wastewater was evaluated by the bioluminescence test using the LUMISTox.

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1. Introduction

The presence of dangerous organic pollutants in water represents a major problem with a global concern. Textiles industries, especially, pollute the water sources due to the random use and discharge of various types of dyes [1]. These effluents are highly variable in composition with relatively low biological oxygen demand (BOD) and high chemical oxygen demand (COD) contents [2]. Textile wastewater contains varieties of dyes and chemicals that make the chemical composition of textile industry effluents an environmental challenge [3]. Actually, the treatment of textile wastewater is still difficult. In the last few years, a more promising technology based on advanced oxidation process (AOP) has been studied extensively through which a broad range of organic pollutants can be oxidized quickly and non-selectively [4,5]. Heterogeneous photocatalysis has proven to be an effective technique compared to other AOP thanks to titanium dioxide. It's characterized by its photo-stability, its chemical and biological inert nature, its availability and its low cost [6]. The photocatalytic activity of TiO₂ is one of its most distinctive features, and is largely determined by properties such as the crystalline phase, crystallite size, specific surface area, and porous structures. Many studies have been carried out in this field [7]. Heterogeneous

photocatalysis is now considered an increasingly attractive approach for the degradation of organic pollutants.

In order to improve the photocatalytic activity of TiO₂, several studies have shown that selective ion doping is one of the most effective means [8]. Compared to many metal ions, lanthanides ions are considered as the ideal dopants to modify the crystal structure, the electronic structure and the optical properties of TiO₂ [9]. They are able to form complexes with various Lewis bases through the interaction between the f-orbitals of the lanthanide metal and the functional groups of Lewis bases, thus providing an effective adsorbability of organic pollutants on TiO₂ surface [10–12]. Owing to their special electronic structure 4fⁿ5d^y, these metals are endowed with different optical properties and the redox coupling of Lnⁿ⁺/Ln⁽ⁿ⁻¹⁾⁺ is able to form the labile oxygen vacancies with relatively high mobility of bulk oxygen species [13].

In particular, the TiO₂ doped with lanthanides ions via sol–gel process has much higher photocatalytic activity than that of pure TiO₂ [14]. In fact, sol–gel process is one of wet chemistry reactions for the synthesis of metal oxide catalysts through the polymerization of inorganic precursors, like metal alkoxide or halide, and colloidal solution [15].

Among them, cerium doping attracted more interest, probably due to the following reasons: (1) the redox couple Ce³⁺/Ce⁴⁺ makes cerium oxide shift between CeO₂ and Ce₂O₃ under oxidizing and reducing conditions; (2) the different electronic structures between Ce³⁺ (4f¹5d⁰) and Ce⁴⁺ (4f⁰5d⁰) could result in different optical properties and catalytic properties [16–21].

* Corresponding author. Tel.: +216 23265760.

E-mail address: najjarwahiba2014@gmail.com (W. Najjar).

It's reported that studies on photocatalytic oxidation of real industrial effluents in the presence of H_2O_2 were initiated because adding H_2O_2 as oxidant was proposed as a further way of supplementing the low photonic efficiency of conventional UV photocatalysis [22]. Photocatalysis can be achieved by direct charge transfer of UV generated charge carriers to or from the adsorbed reactant [23]. Alternatively, the UV-generated hole may react with an OH^- to form a hydroxyl radical [24]. Thus, hydroxyl radicals are expected to be the active intermediates in both the hydrogen peroxide photolysis and the TiO_2 photocatalysis. The importance of H_2O_2 as a source of hydroxyl radicals occurs because, in contrast to the very low photonic efficiency of heterogeneous generation of hydroxyl radicals at the surface of TiO_2 [25] the quantum efficiency for the homogeneous photolysis of H_2O_2 ($H_2O_2 \rightarrow 2OH^-$) is maximum [26], in fact, H_2O_2 photolysis degrades many industrial pollutants including azo dyes. However, considering that UV absorption by H_2O_2 is negligible above 280 nm, the process requires UV-C irradiation. In contrast, addition of H_2O_2 is expected to increase degradation rates induced by 254 nm radiation. It has been shown that H_2O_2 addition to P25 accelerates the UV-C degradations of the azo-dyes, which exists in majority in the industrial textile effluents [27–29]. According to our knowledge, no study was reported on the photocatalytic performance of cerium doped TiO_2 materials for the oxidation of textiles wastewater in presence of hydrogen peroxide.

This study reports the photocatalytic oxidation of a real industrial effluent under [H_2O_2 /UV/catalyst] system over Ce– TiO_2 materials synthesized via sol–gel method. Physico-chemical characterization of synthesized catalysts has been discussed. The effect of the cerium doping content and the H_2O_2 concentration on the photocatalytic activity has been also investigated. The evolution of gap energy value versus Ce percentage has been deeply studied. Environmental impact of the process has been evaluated for the optimized photocatalytic test.

2. Experimental

2.1. Photocatalysts synthesis

Titanium (IV) isopropoxide ($Ti(O-i-Pr)_4$), 97%, cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$), 99%, purchased from Aldrich were applied. A series of catalysts with different molar ratio of Ce/Ti were prepared with different cerium content such as 0.2, 0.4, 0.6, 1 and 2% via sol–gel method. For the synthesis of 1% Ce– TiO_2 , the detailed process was described as follows: Under moderate stirring, 0.054 g of cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) and 12.5 mL of absolute ethanol (C_2H_5OH) were introduced in a flask with a ground neck. After that, 1.6 mL of the complexing agent, ethylacetoacetate ($C_6H_{10}O_3$) was added and finally followed by 3.8 mL of ($Ti(O-i-Pr)_4$). The mixture was stirred for 30 min and then was hydrolyzed by adding dropwise a 2.25 mL of nitric acid (0.1 mol L^{-1}). The agitation was stopped by the formation of a gelatinous precipitate “the gel” which was transferred to an autoclave (Equilabo) for the heating process according to the supercritical conditions of the solvent (Ethanol) (243°C , 64 bar). Then, the resultant powder was calcinated at 500°C in oxygen atmosphere for 3 h ($10^\circ\text{C min}^{-1}$). Other catalysts were prepared in a similar manner.

2.2. Photocatalysts characterization

The photocatalysts were structurally characterized by XRD which measurements were carried out by XPERT-PRO diffractometer with a nickel-filtered $Cu K\alpha$ radiation source ($\lambda = 1.54056 \text{ \AA}$) (40 kV, 30 mA). The Raman scattering system consisted of a DILOR RTI 30 triple monochromator spectrometer coupled with a

Spectraphysics argon-ion laser model 164. The 514.5 nm emission line, with an incident power of 400 mW was always used. The temperature, monitored by a thermocouple, was achieved by a liquid nitrogen flow. The specific surface areas and the porosities of the powders were determined by a MICROMERITICS ASAP 2020 apparatus coupled with a computer. UV–visible diffuse reflectance spectra were obtained with Perkin Elmer Instrument, equipped with an integrating sphere RSA-PE-20 type in the range 200–900 nm. Temperature programmed reduction (TPR) was carried out with a flow-type reactor. Hydrogen (5 vol.% in Ar) was passed through a reaction tube containing the sample under atmospheric pressure at 20 mL min^{-1} . The tube was heated with an electric furnace at $10^\circ\text{C min}^{-1}$, and the amount of H_2 consumed was monitored with a ThermoFinnigan 1100 TPD/R/O gas chromatograph equipped with a TC detector.

2.3. Photocatalysis procedure

The photocatalytic activities of the samples were evaluated by a real textile wastewater degradation and decolorization under UV irradiation in presence of H_2O_2 . The solution was vertically exposed to a UV lamp (Apelex, VL-15 C, $\lambda = 254 \text{ nm}$, 30 W) by 15 cm in all experiments. Industrial effluent was supplied by a textile factory (Ksar Helal, Tunisia) using different dyes and chemicals including detergents, salts and surfactants. Typically, the catalyst (1 g L^{-1}) was introduced into the textile effluent solution. The dispersion was magnetically stirred in darkness for 15 min before irradiation to establish the adsorption–desorption equilibrium between the effluent and the surface of the photocatalyst. Subsequently, the suspension was subjected to UV irradiation and hydrogen peroxide. During the photocatalytic reaction a small volume of the suspension was withdrawn from the photoreactor at selected time intervals and centrifuged at 4000 rpm for 15 min to remove off the suspended catalyst particles to be, then, analyzed. The whole reaction lasted for 24 h.

Total organic carbon TOC was measured using a SHIMADZU TOC_VCBH model analyzer.

The decolorization of the samples during the irradiation was determined by UV–visible spectrophotometer using a SHIMADZU UV-1800 apparatus.

The percentages of TOC and color removals were calculated, respectively as:

$$\text{TOC removal}(\%) = \frac{(\text{TOC}_0 - \text{TOC})}{\text{TOC}_0} \times 100$$

$$\text{Color removal}(\%) = \frac{(A_0 - A)}{A_0} \times 100$$

where TOC_0 , TOC , A_0 and A are initial TOC, TOC after irradiation at various time interval, initial absorbance, and the absorbance after irradiation at various time interval, respectively.

The decolorization rate constants k (min^{-1}) were calculated by the slopes of the tangent to the curves of photodecoloration at the instant $t = 0$.

The microtoxicity test consists of the inhibition of the bioluminescence of *Vibrio fischeri* LCK480 using the (Dr. Lange GmbH, Düsseldorf, Germany) LUMISTox system and according to ISO 11348-2 (1998) [30].

3. Results and discussion

3.1. XRD and Raman analysis

X-ray diffraction (XRD) analysis was employed to find out the purity of the sol–gel prepared TiO_2 and Ce doped TiO_2 matrix and

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