



Full Length Article

Enhanced catalytic performance of a bio-templated TiO₂ UV-Fenton system on the degradation of tetracyclineXiaodan Yu^a, Xinchun Lin^c, Wei Feng^c, Weiguang Li^{b,*}^a School of Environment, Harbin Institute of Technology, Harbin 150090, PR China^b State Key Laboratory of Urban Water Resource and Environment, School of Environment, Harbin Institute of Technology, Harbin 150090, PR China^c Key Laboratory of Groundwater Resource and Environment Ministry Education, College of Environment and Resources, Jilin University, Changchun 130021, PR China

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ABSTRACT

Biomorphic TiO₂ was successfully fabricated using maize straw as a template. The morphology and structure analysis revealed that the as-prepared TiO₂ retained the original pore morphology of the maize straw material. The framework of the maize-straw-templated TiO₂ (T-TiO₂) consisted of a cubic grid structure derived from lamellar TiO₂ nanosheets. The results of UV–vis diffuse reflectance spectra and PL spectra revealed that the C-doping derived from maize straw template promoted the photoresponse properties of TiO₂. Efficient hybrid AOPs (advanced oxidation processes) combining T-TiO₂ photo-catalytic oxidation with a Fenton-like reaction for TC oxidation was first investigated, and then, the synergistic degradation effect was discussed in this article. As a result, the synergistic operation of the UV/Fenton/T-TiO₂ photocatalytic hybrid process exhibited significant activity towards the degradation of TC (50 mg/L) over a wide pH range of 3.0–9.0 with a remarkably low iron ion dosage (1 mM). Moreover, the degradation kinetics can be well fitted by the pseudo-first order model, where a kinetic constant of 0.09378 min⁻¹ was achieved, substantially higher than those of the UV/Fenton/N-TiO₂ (0.04419 min⁻¹), UV/Fenton (0.03343 min⁻¹), Fenton (0.0172 min⁻¹), UV/H₂O₂ (0.01412 min⁻¹), UV/T-TiO₂ (0.00209 min⁻¹) and UV (0.00027 min⁻¹) systems. The high synergistic effect probably occurred because of (1) the high surface activity of T-TiO₂ as photocatalyst, which yielded a remarkably enhanced optical absorption capacity for the lamellar structure, and (2) the efficient reduction of Fe³⁺ to Fe²⁺ by the photoinduced electrons from T-TiO₂.

1. Introduction

At present, tetracycline (TC) is one of the most widely used antibiotics in therapeutic medicine and animal feed [1]. Because of the transmission of the majority of unabsorbed TC to environment and its potentiality to threaten human health and water ecosystem, the treatment of TC in aqueous solutions has attracted researchers' attention. Various treatment processes have been reported, such as AOPs [2,3], membrane filtration [4], and biodegradation [5], but the success has not been as good as expected. Among them, AOPs have received considerable attention over the last decade as an effective and suitable technology for the remediation of wastewater contaminated with toxic and persistent organic pollutants [6]. The Fenton process, as one of the most popular AOPs, simply combines hydrogen peroxide (H₂O₂) with ferrous ions (Fe²⁺) to generate powerful hydroxyl radicals ([•]OH) that possess a high standard oxidation potential of 2.8 eV and are able to mineralize most organic pollutants [7–9]. In the Fenton system, Fe²⁺

acts as a catalyst to decompose H₂O₂ to [•]OH, while the ferric ion (Fe³⁺) is less reactive than Fe²⁺ in [•]OH production from H₂O₂. In the chain reactions of the Fenton system, the cycle of Fe³⁺ to Fe²⁺ is the rate-limiting step, therefore, controlling the generation of [•]OH. UV illumination can promote the transformation of Fe³⁺ to Fe²⁺ by Fe(OH)²⁺ photolysis (Eq.(1)) [10], which supports a decline in the Fe²⁺ requirement of the UV-Fenton reaction. In theory, it may be feasible to run the UV-Fenton reaction with a low dosage of iron ions, allowing the effluent iron concentration to meet the emission standards. On the other hand, the Fenton system can efficiently oxidize organic pollutants only under acidic conditions (pH: 3 ~ 4). In most cases, with the Fenton system, under the initial neutral condition, the precipitation of iron ions to amorphous ferric oxyhydroxides inhibits the chain reaction.



Recently, several studies have shown that the combination of photocatalysts with the Fenton system can lead to a drastic enhancement in

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hydroxyl radical production by offering synergistic reaction routes to key mechanisms involving hydroxyl radical formation [8,11,12]. The Fenton system suppresses electron–hole recombination by scavenging the conduction band electrons of photoexcited TiO_2 to increase the lifetime of the valance band holes and generate more radicals [13]. Whereas the photogenerated conduction band electrons enhance the reduction of Fe^{3+} to Fe^{2+} and accelerate the chain reactions of the Fenton process [14].

Moreover, photocatalytic oxidation is a friendly and efficient AOPs for TC degradation [15,16]. Among the various semiconductor photocatalysts, titanium dioxide (TiO_2) is an attractive material with conspicuous merits such as thermal and chemical stability, nontoxicity, and catalytic performance [17]. The morphology of the catalyst has a great influence on the catalyst [18]. Nanostructures with unique morphologies and properties, such as nanosheets, nanotubes, nanowires, and nanospheres, have received considerable attention [19–21]. Among them, TiO_2 nanosheets with a fully exposed surface allow for the utilization of all surface active sites, which yield a high catalytic activity [22]. Thus high dispersity is important for maintaining a large surface area with a large number of reactive sites. For TiO_2 nanosheets, we need to search a method to prevent undesirable layer-by-layer stacking. Currently, a great deal of research has been reported on the preparation of TiO_2 nanosheets by different techniques, such as the sol-gel method [23], supercritical method [24], hydrothermal method [19,25], etc. However, these traditional methods are cumbersome, costly, time consuming and cause environmental pollution. Template-based syntheses are an ideal technique to fabricate biomorphic advanced functional materials with predetermined structural properties. Existing biological tissues such as wood [26,27], butterfly wings [28], egg shell membrane [29], and sorghum straw [30] often have various types of hierarchical multi-layered porous structures. Bio-template technology combining the hierarchical porous structure of different biomaterials with the functional properties of inorganic materials gives a unique multi-scale structure and the superior performance of bionic materials. Some of these materials synthesized using biological templates have a high porosity and large specific surface area. Biological templates based on assemblies can effectively increase the contact surface of a reaction and improve the performance of materials.

In this work, we designed and prepared T- TiO_2 by a bio-template synthesis method. Maize straw provided a wide variety of biomorphic pores and channels and was used as a template to prepare a hierarchical porous material. T- TiO_2 had a high photocatalytic activity because it replicated the micro-/nanostructures suitable for collecting light to promote the light-harvesting efficiency [31]. Meanwhile, the synergetic effect of the T- TiO_2 photocatalysis and the UV-Fenton reaction in TC oxidation was discussed. The influences of T- TiO_2 on the UV-Fenton process were examined by studying the various operational parameters such as concentration of TC, molar ratio of H_2O_2 and Fe^{2+} , initial pH value and dosages of TiO_2 on the efficiency of the process. Overall, the excellent activity showed that the introduction of the T- TiO_2 photocatalyst overcame the major drawbacks of the UV-Fenton process, such as strict pH range limits and high initial dosages of Fe^{2+} .

2. Experimental

2.1. Reagents and chemicals

All chemicals used in this study were analytical reagent grade and used without further purification. Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), Sodium thiosulfate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), tetrabutyl titanate (TBT) and sulfuric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium hydroxide (NaOH) was purchased from Beijing Chemical Works. Hydrogen Peroxide 30% (H_2O_2) was purchased from Shenyang East China Reagent Plant. 5-Dimethylpyrroline-oxide (DMPO) was obtained from J&K Scientific Ltd. Tetracycline (TC) HCl ($\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8$ HCl) was purchased from Genview Scientific, Inc. All

solutions were prepared in deionized water.

2.2. Synthesis and characterization of TiO_2 (with and without template)

T- TiO_2 was prepared using the calcination method. First, natural straw was cut into small pieces with a thickness of approximately 1–2 mm and were extracted for 5 h with 250 mL of 5% weak aqua ammonia as the extracting solution with heating. After extraction, the natural straw was washed with distilled water and dried at 60 °C in vacuum for later use. Next, 50 mL TBT was added to 150 mL absolute ethyl alcohol from an aqueous mixture. The as-prepared straw (2 g) was added to a mixed solution, which was soaked and kept at 60 °C for 24 h, and then, filtered and washed with absolute ethyl alcohol several times. After drying at 60 °C, the as-prepared products were calcinated at 550 °C for 4 h in a tube furnace at a heating rate of 10 °C/min to form the T- TiO_2 . The normal TiO_2 (N- TiO_2) was prepared by a similar procedure but in the absence of the straw template.

X-ray diffraction (XRD) patterns of all powders were obtained on a Rigaku D/Max 2550 diffractometer (Rigaku Corporation, Japan) using a Cu K α radiation source ($\lambda = 1.54056$) at a scan rate of 10° min⁻¹ to determine the crystal phase of the obtained samples. The acceleration voltage and the applied current were 3 kV and 20 mA, respectively. The surface morphology was characterized by field-emission scanning electron microscopy (FE-SEM, NOVA-230, FEI, America). Transmission electron microscopy (HRTEM) images were obtained on an FEI Tecnai G2 F20 electron microscope with an acceleration voltage of 120 kV. The chemical composition was analyzed using X-ray photoelectron spectroscopy (XPS, ESCA LAB 220-XL, Al K α radiation). The Brunauer-Emmett-Teller (BET) surface area and pore-size distribution were measured by N₂ adsorption and desorption by Micromeritics ASAP 2020 instrument. UV–vis DRS measurements were carried out using a Shimadzu U-4100 UV–vis spectrophotometer equipped with an integrating sphere attachment. Analysis range was from 200 to 800 nm, and Al₂O₃ was used as a reflectance standard. PL spectra of TiO_2 were measured by FLS920 with excitation wavelength of 325 nm.

2.3. Experimental procedure

The as-prepared TiO_2 was investigated by the photodegradation of TC in an aqueous solution under UV irradiation. All catalytic reactions were conducted in a glass beaker with constant stirring (750 rpm), and sulfuric acid or NaOH was used to adjust the solution pH to the desired value. The photoFenton reaction was started by adding a certain amount of H_2O_2 to the solution, which was irradiated by a 10 w UVC-lamp (L: 220 mm, D: 80 mm, Konche, Shenzhen) providing an irradiation of 220–275 nm. Sample volumes of 4 mL were collected at given time intervals and immediately filtered with 0.45 μm membrane filters. To assess the stability and reusability of the catalyst, 5 consecutive cycles were conducted within 90 min, with each cycle retesting the heterogeneous catalyst.

2.4. Analytical methods

The concentrations of the remnant TC and Fe^{2+} were measured by a UV–vis spectrophotometer at wavelengths 357 nm and 510 nm, respectively, and Fe^{2+} required the use of a phenanthroline reagent as a color indicator.

The electron spin resonance (ESR) technique (with DMPO; Bruker A200 spectrometer) was employed to qualitatively analyze the formation of radical species. The settings for the ESR spectrometer were as follows: center field, 3360 G; sweep width, 100 G; microwave frequency, 9.751 GHz; and power, 6.33 mW.

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