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Enhanced photocatalytic degradation of norfloxacin in aqueous Bi_2WO_6 dispersions containing nonionic surfactant under visible light irradiation

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HIGHLIGHTS

- TX100 strongly enhanced the adsorption and photodegradation of NOF in Bi_2WO_6 dispersions under visible light irradiation (400–750 nm).
- Cu^{2+} (10 mM) significantly suppressed the photocatalytic degradation of NOF.
- FT-IR demonstrated that the NOF adsorbed on Bi_2WO_6 was completely degraded.
- Three possible photocatalytic degradation pathways of NOF were proposed, according to the HPLC/MS/MS analysis.

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ABSTRACT

Photocatalytic degradation is an alternative method to remove pharmaceutical compounds in water, however it is hard to achieve efficient rate because of the poor solubility of pharmaceutical compounds in water. This study investigated the photodegradation of norfloxacin in a nonionic surfactant Triton-X100 (TX100)/Bi_2WO_6 dispersion under visible light irradiation (400–750 nm). It was found that the degradation of poorly soluble NOF can be strongly enhanced with the addition of TX100. TX100 was adsorbed strongly on Bi_2WO_6 surface and accelerated NOF photodegradation at the critical micelle concentration (CMC = 0.25 mM). Higher TX100 concentration (>0.25 mM) lowered the degradation rate. In the presence of TX100, the degradation rate reached the maximum value when the pH value was 8.06. FTIR analyses demonstrated that the adsorbed NOF on the catalyst was completely degraded after 2 h irradiation. According to the intermediates identified by HPLC/MS/MS, three possible degradation pathways were proposed to include addition of hydroxyl radical to quinolone ring, elimination of piperazynilic ring in fluoroquinolone molecules, and replacement of F atoms on the aromatic ring by hydroxyl radicals.

1. Introduction

The increasing antibiotic resistance of microorganism and antibiotic resistance in human body aroused by the presence of antibiotics in natural water gains great public attention [1]. Many antibiotics detected in aquatic environment, even at trace levels, may cause antibiotic resistance and lead to an adverse effect to aquatic wildlife, the ecosystem and human health [2,3]. Fluoroquinolones (FQs) is one of the most consumed antibiotics and has a total consumption of about 44 million kilograms every year in the world [4]. Norfloxacin (NOF), a second generation synthetic FQs, is widely used in veterinary medicine and treatment of human infections. Three of the primary sources of antibiotics entering the environment are medicine, agriculture, and pharmaceutical industry. Because a large portion of the administered doses are excreted, a substantial amount of NOF is released to the environment. NOF has poor solubility in water and easily deposits on aquatic sediments and soil. Thus, its environmental occurrence, transfer, fate, and potential risk during water treatment should be the focus of our concern.

Among the removal technologies of heavy metals and FQs from water, including adsorption, biological treatment, and advanced oxidation/reduction process (AO/RP) [5–11], AO/RP has been

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proved to be a highly efficient and low cost method, and received considerable attention. AO/RP with the highly reactive hydroxyl radical (•OH), hydrated electrons (e_{aq}) and hydrogen atoms (H•) as main active species can effectively degrade these soluble biorefractory antibiotics [6]. The widely used photocatalyst, namely TiO_2, can mainly be excited by light in the ultraviolet region during oxidation process [12]. However, the exciting light in the UV region only accounts for 4% of the solar light in the complete spectrum of sunlight, which significantly limits the application of TiO_2 in photocatalysis. Bismuth tungstate (Bi_2WO_6) was reported to have an excellent photodegradation efficiency under visible light (400–800 nm) [13–16]. In previous studies, Bi_2WO_6 prepared by hydrothermal method displayed a certain photocatalytic activity capacity to NOF and Rhodamine under simulated solar light irradiation [17–21]. However, the poor solubility of NOF in aquatic environment limits the photocatalytic capacity to NOF.

In recent years, the use of surfactant solutions in prior extraction/washing steps for removal of organic contaminants from solid phases has been largely applied in sediment or soil remediation. It also gives a particular insight into potential use of dissolved surfactants in the photocatalysis treatment of complex poorly soluble pollutant in aqueous solution.

It should be noted that some surfactants can be completely decomposed by photocatalysis [22], so theoretically, they can compete with the target substrate for active sites on the semiconductor surface and thus retard the degradation of contaminants. Pramauro et al. indicated that the degradation of some aromatic pollutants in the presence of surfactants bearing alkyl chains is possible, although at relatively low reaction rates [23,24]. The possible beneficial effects arising from adsorption of surfactants onto the semiconductor surface were examined [25,26]. Hidaka et al. proposed the use of amphiphiles in photocatalysis and their resistance to radical attack and found that different types of surfactants have various effects on the photocatalytic process [27], depending on the pollutant hydrophobicity, solution pH, and surfactant concentration. Although the addition of surfactants will compete with the target pollutant for active sites on the catalyst, the degradation of poorly soluble substances can be strongly enhanced with the formation of surfactants micelle in aqueous solution. It was reported that introduction of anionic surfactant in TiO_2 dispersions induces the aggregation of cationic dyes, allowing the poorly soluble dye adsorbed on the photocatalyst surface, which strongly accelerated the photodegradation under visible light irradiation [28–30]. However, the specific mechanism of the complex system still remains unknown. What is more, many researchers have investigated the degradation pathway of pharmaceuticals in biological treatment and UV light treatment, but few researchers paid attention to the degradation intermediates during the visible light treatment [31,32]. It is necessary to investigate the efficiency of photocatalysis in degradation of antibiotics, such as NOF, in presence of surfactants under visible light. The degradation pathway and products of the pharmaceuticals during photo treatment process under visible light should also be our concern.

Triton X-100 (TX100), a nonionic surfactant, is capable of solubilizing hydrophobic contaminants that are relatively water insoluble. Previous study confirmed that TX100 was effective in removing polycyclic aromatic hydrocarbons and benzoapyrene from soils [33,34]. Besides, nonionic surfactants are preferable to anionic and cationic surfactants due to the following reasons: (1) They are less nontoxic [35]. (2) They are easily biodegradable and purchased [36]. We conducted this study to evaluate the feasibility of the photocatalytic decomposition of the target NOF by Bi_2WO_6 in surfactant micelles (TX100) and the impacts of the following coexisting substances on the photocatalytic degradation of NOF by Bi_2WO_6: inorganic anions (SO_4^{2-}, NO_3^-, and HCO_3^-) and inorganic cations (K^+, Ca^{2+}, Cu^{2+}, and Mg^{2+}). Fourier-transform infrared (FTIR) spectroscopy was used to determine whether the adsorbed NOF on the catalyst was degraded. Furthermore, photodegradation products during the treatment process and pathways of photocatalytic degradation of NOF were also investigated.

2. Materials and methods

2.1. Reagents

Norfloxacin ($C_{16}H_{18}FN_3O_3$, purity 99.8%) was purchased from Aladdin-Reagent Company, Shanghai. Triton X-100 were purchased from Aldrich Chemical Co., Ltd. Bismuth tungstate was synthesized using bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$) and sodium tungstate dihydrate ($Na_2WO_4{\cdot}2H_2O$) as precursors, which were purchased from Chemical Technology Co., Ltd., Tianjin, China. The preparation method is illuminated in Supplementary material. The salts including sodium sulfate (Na_2SO_4), sodium nitrate ($NaNO_3$), sodium bicarbonate ($NaHCO_3$), potassium chloride (KCl), magnesium chloride ($MgCl_2$), copper sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$) and calcium chloride ($CaCl_2$) were obtained from Chemical Technology Co., Ltd., Tianjin, China. The mobile phase solvent for HPLC analysis (i.e., acetonitrile, formic acid) came from Tedia Company. All other reagents were of analytical purity. Solutions were prepared with high-purity water (18.25 M cm^{-1}) from a Milli-Q water purification system.

2.2. Surface tension measurements

The CMC for the TX100 containing systems was measured according to the Wilhelmy plate method using an interfacial tensiometer (Tensiometer K14 Krüss, Germany), and were performed in the absence and the presence of Bi_2WO_6. The mean value of the five measurements set at a temperature of 25 ± 1 °C was accepted as a result.

2.3. Photocatalytic degradation

Typically, photocatalytic degradation was performed in an aqueous Bi_2WO_6 suspension prepared by mixing 100 mg Bi_2WO_6 powder with 100 mL of solutions containing NOF and TX100 at an appropriate concentration. Prior to irradiation, the suspensions were stirred in the dark for 30 min to achieve the adsorption–desorption equilibrium. The light source, which was 300 W Xe lamp (CEL-HXF300 AULTT, Beijing, China) with a 400 nm cut off filter. At regular irradiation time intervals, 2 mL reaction solution was withdrawn and filtered through 13 mm × 0.45 μm membrane for NOF analysis.

2.4. Characterizations

FTIR spectra were obtained using a spectrometer (Spectrum GX, PerkinElmer, USA) within the 4000–400 cm^{-1} region at a 4 cm^{-1} resolution. About 2 mg of the milled sample was ground with 200 mg of KBr (FTIR grade) and compressed into a pellet under a vacuum at a pressure of 75 KN cm^{-2} for 3 min.

Crystallographic information of Bi_2WO_6 was obtained by X-ray diffraction (XRD, 43 Rigaku D/MAX-RB, Cu Kα radiation, Japan). The data were collected in the 20–80° 2θ range with 0.4° steps and a counting time of 5 s per step.

UV–vis diffused reflectance spectra (DRS, Shimadzu, UV-3150, Japan) of Bi_2WO_6 were obtained on a Hitachi U-3010 spectrometer, using $BaSO_4$ as the reference.