



Enhanced photocatalytic degradation of ofloxacin by co-doped titanium dioxide under solar irradiation



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ARTICLE INFO

Article history:

Received 9 September 2015

Received in revised form 20 January 2016

Accepted 21 January 2016

Available online 22 January 2016

Keywords:

Ofloxacin

Photocatalytic degradation

Nanoparticles

Co-doping

ABSTRACT

The photocatalytic degradation of Ofloxacin (OFL) was studied in aqueous solution using co-doped TiO₂ nanoparticles. The catalyst samples were synthesized by sol-gel method from Titanium isopropoxide using different concentration of Bi and Ni metal as dopant. The co-doped catalysts were characterized by (X-ray Diffraction) XRD, (Brunauer–Emmett–Teller) BET, (Scanning electron microscope) SEM and (Energy Dispersive Spectroscopy) EDS. The results revealed that the catalyst possessed spherical morphology and excellent crystalline properties. The surface area of the catalyst was found to be 74, 55 and 18.66 m²/g for 0.25 wt%, 0.5 wt% and 1.0 wt% dopant concentration, respectively. Photocatalytic capability of Bi/Ni co-doped TiO₂ nanoparticles were estimated by means of OFL degradation under different light sources. Parameters affecting the photocatalytic process such as type of catalyst, dopant concentration, catalyst concentration, different light sources and solution pH have been explored. The photo-degradation kinetics follows a pseudo first-order reaction. Bi–Ni co-doped TiO₂ showed higher activity for photocatalytic degradation of OFL under solar light compared to Degussa TiO₂. The photo-degradation process was optimized using 25 mg/L Ofloxacin with dopant concentration of 0.25 wt% and catalyst dose of 1.5 g/L. Degradation efficiency of 86% was attained at pH 3 after 6 h of solar irradiations.

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1. Introduction

The occurrence of antibiotics in the environment is an emerging environmental issue causing the selection of antibiotic-resistant microbes in wastewater treatment plants and other hot-spots with genes capable of spreading by the lateral gene transfer mechanism [1,2]. The decrease of biodegradation of leaf and other plant materials, the primary food source for freshwater biota, due to the release of antibiotics to the environment is a new relevant concern as well [3]. The investigation of the processes that may enhance their removal from water and wastewater and detoxification are in the core of scientific interest. Biotic (e.g., biodegradation) and abiotic processes (e.g., photocatalytic treatment and hydrolysis) are evaluated in order to understand the fate of antibiotics and the inherent risks they may pose to the environment. Aerobic biotransformation in the environment and during aerobic secondary treatment of wastewater has been identified as a removal mechanism for some antibiotics [4–6]. However, abiotic processes are considered to be the most important processes for their mineral-

ization or for their transformation to more biodegradable products less persistent in the environment [7].

Among antibiotics, Ofloxacin (OFL) represents a synthetic fluoroquinolone antibiotic [8] of great environmental significance due to its widespread occurrence, its genotoxic properties [9] and persistence in the environment due to its limited microbial degradation potential [8]. The chemical structure and active sites of fluoroquinolones are presented in Fig. 1. They have been found in sewage treatment plants' influents and effluents, pharmaceuticals' production and hospital effluents, ground-, river-, sea and drinking water [10]. They are sorbed onto activated sludge, inhibiting the nitrite-oxidizing bacteria activity and making activated sludge a significant reservoir of fluoroquinolones due to their long-term cycling and persistence [11,12].

In particular, OFL is known to persist in sludge-treated soils in concentrations as high as few milligrams per kilogram [13] and has recently been characterized as a high hazard to the aquatic ecosystem due to the use of the sludge on agricultural land [14]. Some fluoroquinolones are subjected to biotransformation by fungi and bacteria to a lesser extent. The degradation of OFX induced by various AOPs at a bench scale has been investigated under different experimental conditions: photocatalysis in the presence of TiO₂ [15–17] solar Fenton [16], sono photocatalysis [18], photolysis

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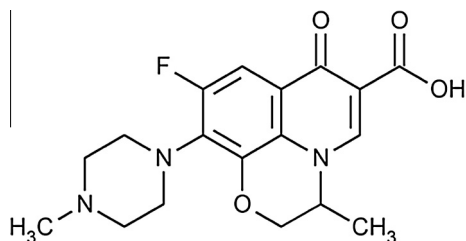


Fig. 1. Structure of Ofloxacin ($pK_{a1} = 5.45$, $pK_{a2} = 6.2$).

[19] and γ -radiolysis [20]. TiO_2 photocatalysis was also used by Michael et al. [16] to degrade 10 mg/L ofloxacin with catalyst concentration of 3 g/L. 60% degradation was obtained after 120 min of irradiation. Various methods available for the synthesis of TiO_2 photocatalyst include precipitation [21], hydrothermal, solvothermal [22], chemical vapor deposition [23] and electrospinning [24]. Among several methods available for synthesis of nanoparticles, sol-gel method is advantageous because powders of high purity and of homogenous concentrations can be synthesized at very low temperature under stoichiometry control [25]. Kundu et al. [26] studied the photocatalytic activity of Ni-doped TiO_2 prepared by hydrothermal method for the degradation of ofloxacin (25 ppm) for which almost 70% degradation has been achieved with 1 g/L catalyst dose. It has been shown by earlier studies that degradation of compound is always better by co-doped catalyst compared to Degussa P25. The result of photocatalytic degradation of methylene blue indicated that photocatalytic activity of N- and S-codoped TiO_2 (98%) was better than P25 (82%) photocatalyst due to the band-gap of N-, S-codoped TiO_2 is lower than that of P25 photocatalyst [27]. Similarly I and F has been co-doped and appeared to be better photocatalyst for methylene blue degradation in comparison to Degussa P25 [28]. Hence, sol-gel method has been followed for the synthesis of Bismuth and Nickel codoped TiO_2 (Bi/Ni- TiO_2) photocatalysts.

The photocatalytic transformation mechanisms of OFX through solar light oxidation using co-doped catalyst have not been studied earlier, even if studies involving its environmental risks are described in the literature [29,30].

2. Materials and methods

2.1. Chemicals

Ofloxacin was purchased from Sigma Aldrich and were at least of analytical grade ($\geq 98\%$). Aeroxide P25 TiO_2 powder was used for the PC experiments. All the chemicals used in this study were of analytical grade and were used as such without further purification. Bi (NO_3), $5H_2O$ and Ni (NO_3), $5H_2O$ was purchased from Loba Chem, India. Titanium isopropoxide, as source of titanium dioxide, was purchased from Sigma Aldrich. Ethanol, used as solvent, was procured from Merck. All the solutions were prepared with deionized water. Fig 1 depicts structure of Ofloxacin.

2.2. Preparation of co-doped Bi/Ni- TiO_2 nano-catalyst

Co-doped TiO_2 with varying percentage of dopant (0.25–1.0 wt %) was prepared using sol-gel method with Titanium isopropoxide (TIP) as precursor. 2.5 mL of TIP was added drop by drop to a solution of 10 mL ethanol and 2.5 mL acetylacetone at room temperature and stirred for 30 min. Then 2 mL distilled water was added to above solution. Calculated amount of Bi (NO_3), $5H_2O$ and Ni (NO_3), $5H_2O$ was added according to percentage variation of dopant from 0.25 to 1.0 wt% respectively, into prepared solution

and a stable sol was finally obtained after stirring 2 h. Then concentrated solution was placed at 90 °C for drying and dried powder was calcined at 400 °C for 2 h.

2.3. Characterization of synthesized catalyst

The above-prepared TiO_2 samples were characterized for microstructural properties by Scanning electron microscopy (Philips, SEM Analyzer). The Brunauer, Emmett and Teller (BET) surface area was obtained from nitrogen adsorption-desorption data (NOVA 2000e, USA). The chemical composition was confirmed using the electron spectroscopy for chemical analysis. The powder X-ray Diffraction (XRD) was done at room temperature using X-ray diffractometer (Cu $K\alpha$ $\lambda = 0.154$ nm) to study the crystal phase of the products. X-ray Diffraction (XRD) patterns were obtained using a Philips X-ray diffractometer with monochromatic high-intensity in a 2θ range of 20–70°. All peaks measured by XRD analysis were allocated by comparing with those of JCPDS data. Band gap has been evaluated using UV-vis diffuse reflectance spectrophotometer of Hitachi U3900H at wavelength range of 190–800 nm. The average size of the TiO_2 particles was attained by Scherrer's equation (Eq. (1)).

$$D = K \lambda / \beta \cos \theta \quad (1)$$

2.4. Experimental set-up

The degradation experiment of OFL was conducted on a self-designed, cubic, stainless steel reactor. An electric fan was installed on the side wall of the reactor for proper circulation of air. The seven UV Tubes, 36 W each with wavelength of 365 nm provided the light source. Weighed amount (0.5–2.0 g/L) of co-doped photocatalyst with dopant concentration ranging from (0.25–1.0 wt%) was well dispersed on a Pyrex glass dish (diameter 15 cm), which was placed into the reactor and was positioned at 15 cm above the bottom. A known quantity of OFL (25 ppm) was injected into vessel. The degradation experiment was allowed to run for 6 h. The concentration of OFL was periodically measured by taking samples after every 1 h and measured its absorbance.

3. Results and discussion

3.1. Characterization

Bi/Ni co-doped TiO_2 nanoparticles were prepared using sol-gel method as described in Section 2.2 and its characterization was done to analyze various parameters such as particle size, surface morphology, band-gap and surface area using XRD, SEM, UV-DRS and BET, respectively. All XRD spectra presented in Fig. 2 shows the peaks confirming anatase structure and it was observed that the prepared Bi-Ni co-doped photocatalyst consisted only of anatase and the doping would enhance the photocatalytic activity. Since Bismuth might get fused into the crystal structure of TiO_2 , reduces the band gap of TiO_2 , the co-doped photocatalyst displayed enhanced photocatalytic activity in the visible region. Nickel existing and dispersed on the surface of TiO_2 , reduces the recombination of photogenerated electron-hole pairs, increasing photo quantum efficiency, and increasing the photoactivity.

The SEM images were used to evaluate primary structure of doped TiO_2 . The morphology of the samples has been presented in Fig. 3. The photocatalysts are in the form of small agglomerates of crystals. The nanometer size of the particles resulted in an increase in surface area and a subsequent increase in the amount of photocatalytic reaction sites, which increases the photocatalytic activity. The EDS analysis of codoped TiO_2 showed significant

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