Chapter 7

Photocatalytic Degradation of Levofloxacin by Cu doped TiO₂ under Visible LED Light

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Abstract

Degradation performance of Cu-TiO₂ photocatalytic materials against a widely used antibiotic drug levofloxacin (LFX) was investigated under visible LED light source of 40 W. Cu-TiO₂ (0.25-1.0 wt%) nanomaterials are prepared through reverse micelle mediated modified sol-gel method. Characterization of synthesized Cu-TiO₂ samples are performed by XRD, UV-Vis, and DLS techniques. The doping of 0.5 wt% copper in TiO₂ shown lower crystallite size (5.79 nm) and visible light absorption characteristics with energy band gap of 2.84 eV. 0.5 wt% Cu-TiO₂ photocatalyst has shown significant LFX degradation of 75.5% with catalyst loading of 1 g/L and initial pollutant concentration of 50 mg/L.

Keywords

Cu-TiO₂, Doping, Photocatalyst, Degradation, Levofloxacin, Visible LED Light

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1. Introduction

Water pollution through antibiotics is a huge challenge for industries, municipal bodies and environmental protection agencies. Based on chemical structure of antibiotics, it is categorized mainly into macrolides, tetracyclines, fluoroquinolones and sulphonamides [1]. Extensively used different fluoroquinolones (FQs) are detected in industrial and municipal wastewater as well as in surface and ground water resources in different countries of the world viz. Argentina, China, Egypt, India, Iran, Pakistan, and Spain [2-9]. Moreover, Levofloxacin (LFX) which is one of the widely used FQs class antibiotic for different bacterial infections is observed in wastewater due to its persistency to biodegradation [10-13]. Existence of LFX in water is toxic to cyanobacteria which is crucial member of nutrient cycle in aquatic ecosystem [14,15]. Conventional processes like flocculation and sedimentation are found ineffective towards LFX removal from drinking water treatment plant and removal efficiency of LFX by conventional activated sludge process is less than 50% in sewage wastewater treatment plant [16,17]. In vicinity of pharmaceutical industrial sector, significant concentration of LFX has been observed in water resources due to less upgradation of industrial wastewater treatment plant [6].

Hence, the role of advanced wastewater treatment technologies is becoming critically important to resolve the obstacle associated with LFX pollution in water resources. Adsorbents like carbon, Al₂O₃ and SiO₂ based nanomaterials have shown effective removal of levofloxacin [18-20]. However, the adsorption process only transferred the aqueous pollutants from one phase to another, which generated contaminants adsorbed solid residues [21]. In view of this, advanced oxidation processes (AOPs) are much explored due

to their effective degradation of various pollutants to addresses environmental issues related especially pharmaceutical and dye contaminants [22-26]. Amongst the various AOPs, nanomaterials assisted photocatalytic processes have shown promising results in degradation of LFX [27-30]. TiO₂ based nanomaterials are investigated for LFX and other FQs antibiotics degradation under UV, solar and visible light source due to their features like non-toxicity, chemical stability and high oxidizing capacity [31-39].

Selection of the light source is crucial in the photocatalytic process, which influences the degradation performance as well as energy consumption. Conventional UV light source like mercury lamps have shown limitations like high energy consumption, contains hazardous mercury and cooling water requirement for controlling the temperature inside the photocatalytic reactor [40]. Light emitting diodes (LEDs) as light source are shown to provide advantages such as longer life compared to conventional light source, less utilization of energy and also it is not harmful to the environment [41]. UV LED is employed by few researchers in photocatalytic reactors, but UV LED is considerably costlier than visible LED [42]. Moreover, Visible LED light sources are safer for operational personnel with respect to process safety, whereas UV light is harmful to human and caused skin diseases [43].

Wide band gap energy semiconductor material TiO₂ (anatase phase ~ 3.2 eV) has shown effective photo catalytic activity mainly under a UV light source. Also, TiO₂ material hardly absorb the solar light as the natural light source is comprised of less than 5% UV region [44]. For development of visible light active TiO₂ based nanomaterials, doping of metal and non-metal, heterojunctions semiconductor and other strategies are utilized which altered the photocatalytic properties such as decreasing band gap energy and delaying the electron-hole pair recombination rate [45]. Metal doping is one of the most widely used strategies, which effectively shifting band gap edge towards visible light wavelength and also helps in charge carrier separation [46,47]. There are different metals such as Ag, Au, Fe, Ni, Zn and Cu which are reportedly utilized for development of visible light active metal doped TiO₂ nanomaterials [48-53]. Copper metal is cheaper and readily available as compared to costlier noble metals. It is observed that through electron trapping, copper dopant is reported to play a vital role in delaying rate of charge carrier recombination. Also, copper metal doping onto TiO₂ is shifting the band gap energy towards the visible light region [54-56].

Most commonly synthesize methods for metal doped TiO₂ nanomaterials are sol-gel and hydrothermal [57,58]. Synthesis of nanomaterials through reverse micelle mediated method provides better control over the morphology of nanomaterials. Synthesizing the nanomaterials with narrow particle size distribution (PSD) in the reverse micelle method

is more convenient compared to other methods as reverse micelle acts as nanodomains during the hydrolysis reaction [59,60].

Hence, in the present work, the reverse micelle mediated modified sol-gel method is used for synthesizing Cu-TiO₂ materials with different copper doping concentrations (0.25-1.0 wt%). Synthesized Cu-TiO₂ materials are utilized to degrade the environmentally harmful LFX antibiotic under visible light LED source in order to develop the sustainable photocatalyst based environmental remediation process.

2. Materials and methods

2.1 Materials and reagents

For synthesizing Cu doped TiO₂ materials, precursors titanium tetraisopropoxide (TTIP) (> 98%) and copper (II) nitrate trihydrate extra pure (≥ 99 %) are purchased from Spectrochem Pvt. Ltd., Mumbai and Merck Specialities Pvt. Ltd., Mumbai respectively. Triton X-114 (laboratory grade) is purchased from Sigma-Aldrich Chemicals Pvt. Ltd., Bangalore. Hexane (fraction from petroleum) and Toluene (≥ 99.0 %) are procured from S D Fine-Chem Limited, Mumbai and Merck Specialities Pvt. Ltd., Mumbai separately. Pharmaceutical drug levofloxacin (LFX) is received from Rhombus pharma private limited, Gujarat.

2.2 Preparation of Cu-TiO₂ photocatalyst

Reverse micelle nanodomains mediated modified sol-gel method is utilized for synthesis of Cu doped TiO₂ materials. The molar ratio of solvent/surfactant/CuNO₃ aqueous solution/TTIP precursor is kept at 11/1/1/1. Solvent is consisted the hexane and toluene, which is taken in 7:3 volume ratio and triton x-114 is taken as surfactant. Reverse micelle is formed with intense mixing of surfactant and solvent mixture. For preparation of various (0.25-1.0 wt%) Cu doped TiO₂ materials, suitable concentration of CuNO₃ solution is added at very slow rate into the solvent-surfactant reverse micelle mixture. Swelling of reverse micelle is initiated due to addition of copper nitrate aqueous solution. In this hydrated reverse micelle solution, TTIP is added at slow rate, where hydrolysis is taken place inside the reverse micelle which act as a nanocarriers. At the end of the complete addition of TTIP, gel solution is reserved under stirring condition for around 15 H. To separate the gel from the solvent-surfactant mixture, it is centrifuged at 8000 rpm for 10 min. After gel is exposed to air for around six hours, drying is carried out at 130°C for 18 H in a hot air oven. Dried sample is calcined at 400°C for 4 H by using muffle furnace, where temperature increment rate is around 10°C/min. Samples 0.25 wt%, 0.5 wt%, 0.75

wt% and 1 wt% Cu-TiO₂ are designated as 0.25CuT, 0.5CuT, 0.75CuT and 1.0CuT respectively.

2.3 Characterization

For phase identification and measurement of crystallite size, XRD experiment is performed using Bruker AXS (D8 advance) X-ray powder diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$), where scanning of Cu-TiO₂ sample is in 2θ range of 10-85°. For determining light absorbance behavior of Cu-TiO₂ sample, Ultraviolet- Visible- Near IR (UV-Vis-NIR) spectroscopy is performed using Agilent Cary 5000i spectrophotometer. The average particle size and particle size distribution (PSD) of is analysed using dynamic light scattering (DLS) using Malvern particle size analyser NanoZS, where Cu-TiO₂ samples are dispersed in Millipore water and sonicated for around 30 min to isolate the agglomerated particles.

2.4 Photocatalytic degradation

For degradation of LFX (50 mg/L) under visible light irradiation, Philips 40 W LED is utilized as visible light source, where catalyst loading of Cu-TiO₂ samples are 1 g/L. Batch reactor volume is 350 ml and continuous aeration is provided through purging inside the photoreactor. Stirring condition of 300 rpm is kept for complete dispersion of photocatalyst in a levofloxacin aqueous solution. Sample is taken out at regular time interval and it is centrifuged at 9500 rpm for 10 min for separating Cu-TiO₂ nanomaterials. The absorption spectra of LFX is analysed in a UV-vis spectrophotometer. The rate of degradation is determined through change in λ_{max} of LFX (288 nm). Degradation is estimated using Eq. (1) as follow:

$$\text{Degradation (\%)} = [(C_0 - C)/C_0] \times 100 \quad (1)$$

Where C_0 is initial concentration of LFX and C is concentration of LFX after visible light irradiation at any time t .

3. Results and discussion

3.1 Characterization of Cu-TiO₂ photocatalyst

X-ray diffraction profile for Cu doped TiO₂ samples calcined at 400°C are shown in Fig. 1. For TiO₂ anatase phase (denoted as A), diffraction peaks at 25.3°, 37.9°, 48.1°, 54.1°, 55.1° and 62.7° related to (101), (004), (200), (105), (211), and (204) orientations of TiO₂ anatase phase (ICDD No.01-089-4921) [61,62]. Fraction of anatase phase (X_A) in Cu-TiO₂

samples are calculated by $X_A = 1/(1 + 1.26 I_R/I_A)$, peak intensities of anatase (101) and rutile (110) is corresponded to I_A and I_R respectively. Crystallite size is calculated by using Scherrer formula $D = 0.94\lambda/\beta\cos\theta$, D is corresponding to average crystallite size, λ is X-ray radiations' wavelength ($1.5406\text{\AA}$), β is represented the full width at half maximum (FWHM) and θ is bragg angle [63]. Average crystallite size and anatase (%) are specified in Table 1, where 0.5CuT sample is exhibited lowest crystallite size. In higher Cu doped TiO_2 samples, crystallite size is increased, possibly due to enhancement of crystallization of TiO_2 [64]. Synthesized Cu doped TiO_2 samples are consisted nearly identical anatase phase in the range of 93-95%.

Figure 1. X-ray diffraction patterns of Cu- TiO_2 samples.

Absorbance profile of Cu- TiO_2 materials through UV-vis spectroscopy analysis are shown in Fig. 2a. It is observed that with increment in copper doping, absorbance edge is shifted towards higher wavelength. For determining band gap energy of the materials, tauc plot of light energy $(\alpha h\nu)^2$ vs. energy $(h\nu)$ is plotted as shown on Fig. 2b, where it is found that band gap energy is decreased with increasing the Cu doping concentration. Values of band gap energy for synthesized samples are given in Table 1. Similar kind of observation is found for hydrothermally and sol-gel synthesized Cu doped TiO_2 nanomaterials, where declining trend is observed in band gap energy with increase in copper doping onto TiO_2 [65,66].

Figure 2. (a) Absorbance spectra profile of Cu-TiO₂ samples, (b) tauc plot.

Number average particle size of synthesized Cu-TiO₂ samples are analysed using DLS technique. It is found that particle size in the range of 50-70 nm for 0.25, 0.5 and 0.75 wt% Cu-TiO₂ samples as shown in Table 1. However, for 1.0CuT sample, particle size is relatively high, which may be due to high rate of agglomeration of nanomaterials in aqueous medium.

Table 1: Characteristics of Cu-TiO₂ samples.

Nanomaterials	Average crystallite size (nm) ^a	Number average particle size (nm) ^b	Anatase (%)	Band gap energy (eV)
0.25CuT	8.10	55.0	93.99	2.93
0.5CuT	5.79	50.2	95.14	2.84
0.75CuT	8.22	70.8	94.11	2.76
1.0CuT	9.17	131.3	94.20	2.57

^a using Scherrer formula; ^b using DLS technique

4. Degradation performance of Cu-TiO₂ towards LFX under visible LED light

To study the effect of Cu doping concentration on degradation performance under visible light LED, initial LFX concentration and photocatalyst concentration are kept constant as 50 mg/L and 1 g/L respectively. Also, to perform photolysis, effect of 40 W visible LED on degradation of LFX (50 mg/L) is checked, where only around 5% LFX is degraded under 6 H light irradiation. With doping of Cu onto TiO₂, band gap is tuned and it is reduced sufficiently to absorb the visible light wavelength. With using 0.5CuT material, more than 75% degradation of LFX is observed under visible light source in 6 H time span as shown in Fig. 3. Other Cu-TiO₂ samples are also shown good photocatalytic activity against LFX. This suggested that synthesized Cu doped TiO₂ nanomaterials are shown considerable degradation performance against antibiotic aqueous solution under visible light source. The photocatalytic degradation efficiency is observed in the order of 0.5CuT>0.25CuT>0.75CuT>1.0CuT.

Kinetics of degradation of LFX is simulated by Langmuir-Hinshelwood model as follow [67]:

$$-\ln (C/C_0) = kt \quad (2)$$

Where, C₀ is initial concentration of LFX, C is concentration of LFX after visible light photocatalytic degradation, t is irradiation time (min) and k is first order rate constant (min⁻¹).

Figure 3. Degradation of LFX with and without presence of Cu-TiO₂ samples under 40W visible LED (initial LFX concentration = 50 mg/L, catalyst loading = 1 g/L).

Figure 4. Kinetics of LFX degradation for Cu-TiO₂ samples (initial LFX concentration = 50 mg/L, catalyst loading = 1 g/L).

Table 2: First-order rate constant for LFX degradation with different Cu doped TiO₂ samples.

Nanomaterials	$k \times 10^3 \text{ (min}^{-1}\text{)}$	R^2
0.25CuT	4.25	0.97
0.5CuT	4.42	0.98
0.75CuT	3.01	0.97
1.0CuT	1.62	0.97

Kinetics for photocatalytic degradation of LFX using different Cu doped TiO₂ photocatalyst is shown in Fig. 4 and their rate constant values are given in Table 2. It is found that degradation performance is slightly enhanced, when copper doping concentration increases from 0.25 to 0.5 wt%. Moreover, it is found that 1.0CuT material has shown lowest photocatalytic activity, even though its band gap energy is low enough to absorb the significant photon energy from visible light source.

Conclusion

Cu-TiO₂ nanomaterials with different copper doping concentration is successfully synthesized through reverse micelle mediated modified sol-gel method. With increment in copper doping onto TiO₂, band gap wavelength is more shifted towards visible light region. Amongst the synthesized various Cu-TiO₂ materials, 0.5CuT is found to be having lower crystallite and particle size as well as the most efficient candidate for photocatalytic degradation of LFX under visible LED light, where more than 75% LFX degradation is taken place in 6 H time span.

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