Photocatalytic performance and interaction mechanism of reverse micelle synthesized Cu-TiO₂ nanomaterials towards levofloxacin under visible LED light

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Received: 22 June 2021 / Accepted: 15 November 2021 / Published online: 28 November 2021
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Abstract

The degradation performance of Cu-TiO₂ nanomaterials towards levofloxacin (LFX) antibiotic was investigated under an environmentally benign visible LED light source. Cu-TiO₂ nanomaterials were prepared using the reverse micelle sol–gel method with different copper content ranging from 0.25 to 1.0 wt% concerning titania. Characterization of Cu-TiO₂ samples was performed by XRD, TEM, UV–Vis, BET, ICP-MS, FTIR and XPS techniques. 0.5 wt% Cu-TiO₂ showed crystallite size below 6 nm, surface area (69.85 m²/g) and significant visible light absorption capacity. Both Cu¹⁺ and Cu²⁺ are formed in lower Cu-doped TiO₂ samples, whereas only Cu²⁺ is present in higher Cu-doped TiO₂ samples as evident in XPS analysis. 0.5 wt% Cu-TiO₂ has shown the optimum photocatalytic degradation of 75.5% under 6 h. of a visible light source. FTIR analysis of LFX adsorbed Cu-TiO₂ materials indicated the pollutant–catalyst interaction, where the declining trend was observed in photocatalytic degradation efficiency for higher Cu-doped TiO₂ samples due to copper-LFX complex formation. Copper-LFX complexes are formed due to the presence of Cu²⁺ in higher Cu-doped TiO₂ nanomaterials, which might have hindered the photocatalytic activity under visible light. Effects of initial pollutant concentration, catalyst loading and visible light intensity on the degradation of LFX are studied. Photocatalytic degradation pathways of LFX using best performing Cu-TiO₂ material were also proposed based on the LC–MS analysis.

Graphical abstract

Keywords Reverse micelle · Cu-TiO₂ · Levofloxacin · Photocatalytic degradation · Visible LED light

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1 Introduction

Consumption of antibiotics has increased at a swift rate throughout the world due to their inhibiting action towards the harmful bacterial species, viruses and many other microorganisms [1]. Levofloxacin (LFX) is one of the excessively utilized fluoroquinolone-based antibiotics due to its excellent ability in curing bacterial infections. Discharge of LFX through industrial wastewater is an alarming situation, as LFX is persistent in the environment and its toxicological effects would suppress the growth of aquatic and other useful microorganisms [2–5]. This existing environmental status related to LFX and other antibiotics pollution in the aquatic environment has demanded the development of sustainable advanced wastewater treatment techniques. Heterogeneous photocatalysis processes employing doped metal oxides and composites including carbon nanomaterials have gained much attention due to their proficiency in degrading the diverse complex organic aqueous contaminants like pharmaceutical, dye and, pesticide [6–10]. Among the different photocatalytic nanomaterials, TiO_2 has received noticeable consideration, especially in the environmental remediation of various aqueous organic pollutants, due to its features like low cost, non-toxicity, high photochemical stability and high reactivity [11]. However, the rapid rate of electron–hole pair recombination and poor visible light photocatalytic activity in bare TiO_2 materials are key challenges to research communities [12]. To overcome these challenges, the development of visible light active TiO_2 based nanomaterials was emphasized for the past few decades through different approaches like metal doping, non-metal doping, dye sensitization and coupling with other semiconductors [13, 14]. Metal dopant plays a dual role in the enhancement of the photocatalytic activity of TiO_2 by means of reducing the bandgap energy and improving the charge carrier separation, where Ag, Au, Ni, Fe, Cu, Mg and Cr are examples of the most commonly used metal dopants [15]. The use of copper metal is economically viable compared to noble metals like silver and gold and also the prevention of electron–hole pair recombination through redox reactions of Cu^{1+} and Cu^{2+} contribute to boost up the efficiency of photocatalyst based reactions [16, 17]. In recent times, many researchers have utilized Cu-doped TiO_2 nanomaterials due to their effectiveness in degrading the complex organic pollutants (pharmaceuticals, dyes, etc.) and antimicrobial ability against diverse bacterial species [18–21].

There is a significant contribution of nano-dimensional materials in heterogeneous photocatalysis-based environmental remediation processes due to its advantage of available surface area compared to their bulk materials [22].

Size control, distinct physicochemical and allied properties of nanomaterials are ongoing research approaches for enhancing the process efficiency of photocatalytic-based advanced wastewater treatment processes [22, 23]. Commonly used synthesis methods for nanomaterials are sol–gel, reverse micelle sol–gel, co-precipitation, hydrothermal and solution combustion [24–26]. The reverse micelle sol–gel method has provided significant control over the nanoparticle size and particle size distribution (PSD) compared to the conventional sol–gel route [27]. The reverse micelle-mediated method also ensures that nanomaterials are synthesized with a high degree of uniformity in terms of morphology [28]. Light irradiation source in the photocatalytic-based process must be selected precisely as it influences the activation capability of photocatalyst, process economics and safety [29, 30]. The utilization of visible LEDs in photocatalyst-based wastewater treatment processes has added more environmental and economical edge over the conventional UV light irradiation source due to their features like longer operating lifetimes and robustness [31, 32].

In present investigation, Cu- TiO_2 (0.25–1wt%) nanomaterials with a high degree of monodispersity are fabricated with using reverse micelle sol–gel method. Synthesized Cu- TiO_2 materials are utilized to degrade the environmentally harmful LFX antibiotic under visible LED light irradiation source. Effects of interaction of LFX molecules with lower and higher Cu-doped TiO_2 nanomaterials onto photocatalytic degradation performance are not much explored by researchers as per our best knowledge. The interaction behavior of LFX with Cu- TiO_2 samples (with different Cu-doping concentration) and their mechanism are addressed here by using FTIR characterization, to correlates their photocatalytic activity under visible light. The effects of process parameters (initial pollutant concentration, catalyst loading and visible light intensity) on degradation performance is investigated. Degradation pathways of LFX using optimum performing Cu- TiO_2 material under visible LED light are also proposed to understand its degradation mechanism.

2 Experimental procedure

2.1 Chemicals and materials

For lab-scale synthesis of Cu- TiO_2 nanomaterials, Toluene ($\geq 99.0\%$) and Hexane (fraction from petroleum) were purchased from Merck Specialties Pvt. Ltd., Mumbai, and S D Fine-Chem Limited, Mumbai, respectively. Triton X-114 (laboratory grade) was acquired from Sigma-Aldrich Chemicals Pvt. Ltd., Bangalore. Copper (II) nitrate trihydrate extra pure ($\geq 99.0\%$) and titanium tetra isopropoxide (TTIP) ($> 98\%$) were obtained from Merck Specialties Pvt. Ltd.,

Mumbai, and Spectrochem Pvt. Ltd., Mumbai, respectively. LFX antibiotic was obtained from Rhombus pharma private limited, Gujarat.

2.2 Synthesis of Cu-TiO₂

Cu-TiO₂ nanomaterials with different Cu-dopant amounts (0.25, 0.5, 0.75, 1 wt%) were synthesized through the reverse micelle sol–gel method and its schematic diagram is shown as in Fig. 1. The reverse micelle was formed by mixing hexane–toluene mixture (7:3 volume ratio) and triton X-114 (0.0111 molar) under continuous stirring condition of 700 rpm and it was kept for 1 h. The aqueous core was generated due to the slow addition of 0.0111 molar CuNO₃ aqueous solution (for copper doping) into the reverse micelle mixture. Swelling of reverse micelle arises subsequently through this inclusion, resulting in the formation of

Fig. 1 Schematic diagram for the synthesis of Cu-TiO₂ nanomaterials through reverse micelle sol–gel method

hydrated reverse micelle. This hydrated reverse micelle mixture was kept at 700 rpm stirring for 1 h. and TTIP (0.0111 molar) was added with controlled rate. Titania precursor was hydrolysed in generated reverse micelle nanocarriers, which was kept for 15 h under stirring of 700 rpm. The generated sol–gel mixture was centrifuged at 8000 rpm for 10 min and resulted in the separation of solvent–surfactant mixture from gel product. Drying of gel was carried out in a hot air oven at 130 °C for 18 h, which was further calcined for 4 h in muffle furnace at 400 °C. Cu-TiO₂ materials with Cu doping amount of 0.25wt%, 0.5wt%, 0.75wt% and 1wt% are termed as 0.25CuT, 0.5CuT, 0.75CuT and 1.0CuT, respectively.

2.3 Characterization

For determining phase and crystallite size of Cu-TiO₂ samples, X-ray diffraction (XRD) analysis was performed using Bruker AXS (D8 advance) instrument with 2θ range of 10–80°. Average crystallite size was estimated using Debye–Scherrer equation shown in Eq. 1 [33] as follows:

$$D = \frac{0.94\lambda}{\beta \cos \theta}, \quad (1)$$

where D is average crystallite size of nanomaterial, $\lambda = 1.5406$ Å, θ is bragg angle of diffraction and β is full width at half maximum (FWHM) intensity peak.

Ultraviolet–Visible–Near IR (UV–Vis–NIR) spectroscopy was performed for determining the band gap energy of Cu-TiO₂ samples using Agilent Cary 5000i spectrophotometer. Brunauer–Emmett–Teller (BET) surface area and allied properties of Cu-TiO₂ nanomaterials was investigated through N₂ gas mediated adsorption–desorption isotherm analysis using ASAP 2010, Micromeritics. The field emission scanning electron microscope (FE-SEM) of JEOL, JSM-7600 F model was utilized for analysing morphology of Cu-TiO₂ samples. To find out actual copper dopant content in Cu-TiO₂ nanomaterials, ICP-MS was carried out using Thermo Fisher Scientific iCAP RQ ICP-MS. For determining chemical state information of Cu-TiO₂ materials, X-ray photoelectron spectroscopy (XPS) was performed using ThermoFisher scientific (Nexsa base) instrument. To determine functional group present in fresh Cu-TiO₂ and after dark adsorption of LFX onto Cu-TiO₂ samples, fourier transforms infrared (FTIR) spectroscopy was performed using Shimatzu (IRPrestige-21).

2.4 Photocatalytic degradation study of Cu-TiO₂

Photocatalytic degradation of LFX was carried out in a photocatalytic reactor with a cooling jacket under a constant stirring condition with the help of a magnetic stirring system. Under the visible light source (Phillips visible LED of

40 W), 350 mL aqueous pollutant solution was taken in the reactor. The influence of catalyst loading (0.5, 1 and 2 g/L) under constant LFX concentration was studied for studying photoactivity behavior. The effect of initial LFX concentration (25, 50 and 100 mg/L) on degradation performance at constant catalyst loading was checked. Moreover, effect of visible light source with lower intensity (i.e., Philips 14 W LED) on LFX degradation was examined under identical conditions of catalyst loading and initial pollutant concentration. All the experiments of photocatalytic degradation were carried out in triplicate in order to exhibit the reproducibility and the average value has been reported (detailed information is given in ESI: Table S1–S11). Agilent Cary 5000i spectrophotometer was utilized here for determining the LFX concentration through absorbance intensity during photocatalytic degradation treatment, at λ_{max} of 288 nm. Photocatalytic degradation is determined based on the equation degradation (%) = $[(C_0 - C)/C_0] \times 100$, where C_0 is the initial LFX pollutant concentration (mg/L) and C is LFX pollutant concentration (mg/L) after visible light irradiation at any time t . To explore the degradation pathways of LFX during the photocatalytic degradation process at a different time interval, liquid chromatography–mass spectrometry (LC–MS) was carried out on Agilent 6645 Q-TOF LC/MS instrument. During LC–MS analysis, the electrospray interface (ESI) was an ion source and positive ion mode was used for scanning the fragment. Buffer solution and

acetonitrile were utilized as mobile phases for the separation of intermediates.

3 Results and discussion

3.1 Characterization of synthesized Cu-TiO₂ catalysts

The XRD patterns of Cu-TiO₂ samples (calcined at 400 °C) are shown in Fig. 2a, where diffraction peaks of Cu-TiO₂ nanomaterials are well-matched with the anatase phase of TiO₂ crystal (ICDD 01-089-4921) [34]. The average crystallite size of Cu-TiO₂ samples are shown in Table 1. Peak related to copper was not observed due to the lower range of copper doping concentration (i.e., 0.25–1.0wt%). Among all the synthesized Cu-TiO₂ samples, 0.5CuT exhibited the lowest crystallite size, and crystallite size is calculated using the Scherrer equation [33]. Here, crystallite sizes of Cu-TiO₂ samples are much smaller compared to conventional sol–gel synthesized Cu-TiO₂ nanomaterials due to the utilization of reverse micelle nanodomains during the synthesis [35]. The absorption wavelength is shifted towards the visible light region with increment in the Cu doping onto TiO₂ shown in Fig. 2b. A tauc plot (inset of Fig. 2b) of light energy ($\alpha h\nu$)² versus energy ($h\nu$) was utilized for calculating the band gap energy of Cu-TiO₂ nanomaterials and their respective values are tabulated in Table 1.

Fig. 2 **a** XRD pattern of 0.25, 0.5, 0.75 and 1wt% Cu-TiO₂ nanomaterials (calcined at 400 °C). **b** Absorbance spectra profile of Cu-TiO₂ nanomaterials (inset: tauc plot). **c** N₂ adsorption–desorption isotherm curve of Cu-TiO₂ nanomaterials

Table 1 The actual Cu doping concentration, average crystallite size, optical and surface properties of Cu-TiO₂ nanomaterials

Nanomaterials	Cu ^a (wt%)	Average crystal- lite size (nm) ^b	Band gap energy (eV) ^c	BET Surface Area ^d (m ² /g)	Pore volume ^e (cm ³ /g)	Pore diameter ^e (nm)
0.25CuT	0.20	8.10	2.93	50.003	0.0648	3.439
0.5CuT	0.42	5.79	2.84	69.858	0.0839	3.337
0.75CuT	0.66	8.22	2.76	59.045	0.0745	3.343
1.0CuT	0.75	9.17	2.57	41.619	0.0571	3.499

^aThe actual Cu doping concentration was determined by ICP-MS analysis^bThe average crystallite size was determined using Scherrer formula^cThe band gap energy was calculated using Tauc plot^dThe BET surface area was determined using N₂ adsorption analysis^ePore volume and pore diameter were found based on BJH desorption

BET surface area, pore-volume and pore diameter of synthesized Cu-TiO₂ samples are given in Table 1. For Cu-TiO₂ nanomaterials, BET surface area is increased from 50 to 69.8 m²/g, when Cu doping is increased from 0.25wt% to 0.5wt% Cu onto TiO₂. Nanoparticles with higher surface area (0.5CuT sample) might improve the adsorption and desorption mechanism with involved pollutant molecules, which assisted in boosting up the photocatalytic activity [36]. However, further increment in Cu doping concentration onto TiO₂ resulted in the decline in specific surface area. This decrease in surface area of higher Cu doped TiO₂ (1.0CuT sample) indicates Cu occupancy on the surface of TiO₂ which reduces the active sites [37]. The nitrogen adsorption–desorption isotherm of Cu doped TiO₂ materials is shown in Fig. 2c. Isotherm curve is matched with type IV isotherm, which revealed that synthesized Cu-TiO₂ samples were mesoporous materials [38].

The morphological characteristics of the synthesized 0.5CuT sample are analysed by TEM as shown in Fig. 3a–c and its particle size distribution is shown in inset of Fig. 3a. The mean diameter of 0.5CuT is around 10.5 nm with a polydispersity index (PDI) of 0.086. This result indicated that the reverse micelle-assisted synthesis method in a current investigation has promoted the fabrication of monodispersed nanoparticles. Individual functioning of nucleation and growth stages during nanomaterial synthesis are unique characteristics of the reverse micelle-based method which facilitated the formation of the nanoparticles with narrow PSD [39].

XPS analysis is carried out to find out elemental composition, where the existence of titanium, oxygen and copper was confirmed by survey spectrum of 0.5CuT and 1.0CuT samples as shown in Fig. 4a and b, respectively. It was reported that oxidation states of copper and its binding energy are altered due to loading of lower and higher copper doping onto TiO₂ [40, 41]. Hence, XPS spectra for Cu2p_{3/2} are deconvoluted here and compared to explore the

oxidation states of copper in lower Cu-TiO₂ sample (0.5CuT) and higher Cu-TiO₂ sample (1.0CuT). 0.5CuT material (Fig. 4c) exhibited binding energy of Cu2p_{3/2} level at 932.18 and 933.08 eV related to Cu¹⁺ from Cu₂O and at 933.68 eV corresponded to Cu²⁺ from CuO [42, 43]. However, only the Cu²⁺ oxidation state has appeared in the case of 1.0CuT sample and the associated peak is observed at 933.58 eV as shown in Fig. 4d.

3.2 Photocatalytic degradation of LFX by Cu-TiO₂ nanomaterials under visible LED light

Cu-TiO₂ samples with different Cu doping concentrations have been checked for the degradation of LFX antibiotics with fixed initial pollutant concentration (50 mg/L) and catalyst loading (1 g/L) conditions. Photocatalytic performance towards LFX was slightly improved from 73.7 to 75.5% under 6 h of visible LED light irradiation, when Cu doping onto TiO₂ is increased from 0.25 to 0.5 wt% as shown in Fig. 5a. However, degradation efficiency was significantly declined to 40.5% in case of the 1.0CuT sample.

Interaction of LFX antibiotic pollutants with Cu-TiO₂ nanomaterials must be probed to gauge this interesting photocatalytic behavior of Cu-doped TiO₂ samples, especially with higher Cu doping. In the present study, FTIR analysis for pure and LFX adsorbed Cu-TiO₂ samples were carried out and compared to determine the adsorptive sites of LFX with low and higher Cu-doped TiO₂ materials. LFX adsorbed 0.25CuT, 0.5CuT, 0.75CuT and 1.0CuT samples are labelled as L0.25CuT, L0.5CuT, L0.75CuT and L1.0CuT, respectively. Figure 6a, b exhibits a peak at 1631 cm⁻¹ for all pure and LFX adsorbed Cu-TiO₂ samples, which is a distinctive peak representing the O–H–O bending of TiO₂ [35]. LFX is showing the peak of C=O stretching of the carboxylic group at 1724 cm⁻¹, which disappeared for both L0.25CuT and L0.5CuT samples as shown in Fig. 6a [44, 45]. This suggested that adsorption of LFX with Cu-TiO₂ material (with low Cu doping) might

Fig. 3 TEM images of synthesized 0.5CuT sample (a–c). inset image: particle size distribution is determined from measurement of 100 particles from TEM image (a)

have transpired through COOH groups. As per Fig. 6b, the peak at 1620 cm^{-1} corresponded to C=O stretching of pyridone group of LFX is shifted to 1587 cm^{-1} and peak related to COOH groups also disappeared in case of L0.75CuT and L1.0CuT sample [46, 47]. Shifting of the peak of the pyridone group revealed that LFX may be forming the complexes with copper sites in higher

Cu-doped TiO_2 materials [48]. Also, copper complexes with LFX through pyridone are probably due to the existence of copper in the form of copper (II), which might play a decisive role in this kind of coordination with LFX [49]. The sole existence of Cu^{2+} state as per the XPS $\text{Cu}2p_{3/2}$ spectra of 1.0CuT sample (Fig. 4d) is also strongly suggesting that copper (Cu^{2+}) is forming a complex with LFX,

Fig. 4 XPS wide spectra for **a** 0.5CuT sample. **b** 1.0CuT sample. Deconvoluted XPS $\text{Cu}2p_{3/2}$ spectra for **c** 0.5CuT sample. **d** 1.0CuT sample

Fig. 5 **a** Effect of different Cu-TiO₂ samples on photocatalytic degradation of 50 mg/L of LFX at catalyst loading of 1 g/L under 40 W visible LED source. **b** Effect of initial pollutant concentration on photocatalytic degradation of LFX at 1 g/L loading of 0.5CuT catalyst under 40 W visible LED source. **c** Effect of catalyst loading on photocatalytic degradation of 50 mg/L of LFX under 40 W visible LED source. **d** effect of photolysis (40 W LED), catalysis (0.5CuT loading: 1 g/L), 14 W LED-mediated photocatalytic degradation of 50 mg/L of LFX (0.5CuT loading: 1 g/L), 40 W LED-mediated photocatalytic degradation of 50 mg/L of LFX (0.5CuT loading: 1 g/L)

which impeded the photocatalytic activity of higher Cu-doped TiO₂ materials towards LFX.

However, no peak shifting related to the pyridone group was observed in LFX adsorbed lower Cu-doped

TiO₂, i.e., L0.25CuT and L0.5CuT samples which might be due to very less existence of Cu^{2+} on the TiO₂ surface. XPS $\text{Cu}2p_{3/2}$ spectra of 0.5CuT sample (Fig. 4c) also supported this hypothesis, where Cu^{2+} are existed in lesser

Fig. 6 FTIR spectra of pure and LFX adsorbed Cu-TiO₂ samples **a** Cu-TiO₂ material with lower Cu doping, **b** Cu-TiO₂ material with higher Cu doping

proportion compared to Cu¹⁺. This suggests that Cu²⁺ does not much influence the degradation of LFX in the case of lower Cu-doped TiO₂ photocatalytic materials.

Overall, a significant declining trend was observed in the photocatalytic degradation efficiency in the 1.0CuT sample compared to 0.5CuT. It indicated that the existence and magnitude of Cu²⁺ on the surface of Cu-TiO₂ materials is the leading influencing factor in the case of levofloxacin degradation.

Based on the IR spectra interpretation during adsorption of LFX with Cu-TiO₂ samples and XPS analysis of Cu-TiO₂, the interaction mechanism of LFX molecules with lower and higher Cu-doped TiO₂ samples has been proposed and illustrated as Fig. 7a, b. There is probably more chance of incorporation of copper doping ions into TiO₂ structure at lower Cu doping rather than getting accumulated on the surface due to nearly identical ionic radii of Cu²⁺ (0.72 pm) and Ti⁴⁺ (0.68 pm) [50]. Also, peak related to copper complex formation with LFX has not been observed in LFX adsorbed lower Cu-doped TiO₂ materials in FTIR (Fig. 6a). This suggested that for lower Cu-doped TiO₂ samples the population of Cu on the surface of Cu-TiO₂ is extremely low and much of the interaction of LFX has occurred through the carboxylic group onto the TiO₂ surface as shown in Fig. 6a. Hence, higher photocatalytic performance towards LFX was observed

Fig. 7 Proposed interaction mechanism of LFX molecules with **a** Cu-TiO₂ particle with low copper doping, **b** Cu-TiO₂ particle with high copper doping

in the case of 0.25CuT and 0.5CuT materials due to the almost negligible formation of copper-LFX complexes.

However, interaction behavior of Cu-TiO₂ particle with higher copper doping with LFX pollutant is peculiar compared to lower Cu-doped TiO₂ materials, where copper complex formation with LFX through pyridone group was observed along with the carboxylic group. Here, most of the Cu dopants remained on the surface due to higher copper loading and only a few doping ions were able to enter into the interior lattice of TiO₂ [51]. The interaction mechanism of LFX molecules with Cu-TiO₂ particles with high copper doping (Fig. 7b) has been proposed based on FTIR interpretation (Fig. 6b), where LFX interacts with significant adsorption sites of copper and creates the surface complexes. The formation of copper-LFX complexes in substantial proportion is a key hypothesis that is proposed here for suppressed photocatalytic performance in higher Cu-doped TiO₂ materials vis a vis lower Cu-doped TiO₂ materials.

Effect of initial LFX concentration on degradation performance is checked where 0.5CuT photocatalyst is utilized. It is observed that with increment in initial LFX concentration, degradation efficiency is decreased as shown in Fig. 6b. The degradation efficiency for initial LFX concentration of 25, 50 and 100 mg/L is found as 88.7%, 75.5% and 71.2%, respectively. Degradation efficiency is decreased at higher concentrations of pollutant, which might be due to more adsorption of pollutant molecules which resulted in unavailability of catalytic surface for developing the hydroxyl radicals [52, 53].

0.5CuT is also employed for checking the effect of photocatalyst amount on the degradation performance of LFX under visible light. It is observed that with increasing catalyst loading, degradation efficiency is enhanced as shown in Fig. 6c. Degradation performance is found as 70.8%, 75.5% and 88.6% for the catalyst loading of 0.5 g/L, 1 g/L and 2 g/L, respectively. This increment of degradation efficiency could be due to a large number of active sites available for interaction at higher catalyst loading [54, 55].

For checking the photocatalytic potential of 0.5CuT sample towards LFX under 40 W visible LED light, it is compared with photolysis (under 40 W LED light only) and catalysis using 0.5CuT (without any light). Degradation under photolysis and adsorption of LFX during catalysis during 6 h. are found as 5.7% and 10.2%, respectively, as shown in Fig. 5d. 0.5CuT sample significantly enhanced the degradation efficiency of LFX up to 75% under 40 W visible LED in 6 h, which is mainly due to the photocatalytic effect. Effect of lower visible light intensity on degradation of LFX is also checked, where 0.5CuT is shown 31.8% under 6 h. of illumination of 14 W LED.

3.3 Plausible degradation pathways of LFX using 0.5CuT nanomaterial under 40 W visible LED light irradiation

LFX pollutant was degraded through multiple pathways, primarily involving the oxidative degradation and subsequently other pathways viz. defluorination, demethylation, decarboxylation and ring-opening [56, 57]. Possible degradation pathways of LFX using 0.5CuT material under visible LED light are shown in Fig. 8. LFX (C₁₈H₂₀FN₃O₄) was observed at $m/z = 362$ during $[M + H]^+$ ion mode of analysis. From parent ion, product L1 ($m/z = 319$) was formed through loss of CO₂ as per pathway I, while product L2 ($m/z = 342$) was produced through loss of F as illustrated in pathway II. Product L3 ($m/z = 340$) was generated due to dehydrogenation of product L2, and product L4 ($m/z = 298$) can be formed by two separate ways, i.e., through decarboxylation of L3 and defluorination of L1 [58–60]. Through the pathway III, product L5 ($m/z = 348$) may be formed due to demethylation of LFX parent ion and L6 ($m/z = 290$) was produced through loss of CO₂ and CH₃ from product L5. Product L7 ($m/z = 265$) was formed from L6 through the ring-opening of the piperazinyl group and product L8 ($m/z = 203$) was formed by means of depiperazinylization of L7 [55, 61]. The pathway IV suggested that product L10 ($m/z = 101$) can be formed due to discharge of piperazinyl substituent, i.e., L9 ($m/z = 261$) from the LFX compound [33, 62]. Product L11 ($m/z = 279$) was generated due to oxidation of piperazinyl ring from LFX based on pathway V, which further formed product L12 ($m/z = 167$) with the removal of C₆H₇FN group and product L13 ($m/z = 149$) through dehydration of L12 [56, 59, 63]. Due to oxidation and decarboxylation of L11, product L14 ($m/z = 235$) was formed and subsequently, L15 ($m/z = 221$) was produced through demethylation [64]. Through the involvement of reactive hydroxyl radicals, product L16 ($m/z = 359$) was formed by substitution of fluorine group with a hydroxyl group in LFX compound as per pathway VI, and L17 ($m/z = 290$) was produced due to ring-opening of piperazinyl group and loss of COOH group. Product L18 ($m/z = 261$) was formed by means of the piperazine side chain oxidation process, where C₃H₈N is removed from L17 [65–67]. Further, these products can mineralize into carbon dioxide and water due to successive oxidation [68]. Overall, it was observed that with the major contribution of in-situ generated highly reactive OH[•] radicals, LFX was successfully degraded through various pathways during the visible LED light-mediated photocatalytic process [69, 70]. Figures S1–8 (supplementary information) shows the LC-MS spectra of LFX after photocatalytic degradation of LFX at 30, 45, 60, 90, 180, 240, and 300 min.

Fig. 8 Plausible degradation pathways of LFX using 0.5CuT material under 40 W visible LED light irradiation (* Not detected)

4 Conclusions

In this work, reverse micelle sol–gel method is utilized here for synthesizing different Cu–TiO₂ nanomaterials (0.25–1.0wt% Cu) with a high degree of monodispersity for the degradation of Levofloxacin under a visible LED light source of 40 W. UV–vis confirms that the bandgap edge is more shifted towards the visible light region with increment in copper doping onto TiO₂. Based on XRD and BET results, it was observed that 0.5CuT sample has displayed lower crystallite size and higher specific surface area compared to other Cu–TiO₂ samples. TEM result confirmed that the 0.5CuT sample showed homogeneous morphology due to reverse micelle-controlled synthesis. XPS analysis revealed that lower Cu-doped TiO₂ sample (0.5CuT) consisted both copper oxidations states (Cu¹⁺ and Cu²⁺), while the only Cu²⁺ exists in case of the higher Cu-doped TiO₂ sample (1.0CuT). It was found that higher Cu-doped TiO₂ samples are less efficient in degrading LFX compared to lower Cu-doped TiO₂ under visible light of 40 W LED. FTIR interpretation of pure and LFX adsorbed Cu-doped TiO₂ samples validates the formation of copper–LFX complexes in higher Cu-doped TiO₂ samples through the pyridone group. Cu²⁺ oxidation state and its higher accumulation facilitated the copper–LFX complexes and affected the photocatalytic potential of higher Cu-doped TiO₂ materials. Photocatalytic performance is affected through the existence of copper–LFX

complexes, which is proposed here based on the interaction mechanism of LFX molecules with both lower and higher Cu-doped TiO₂ materials. 0.5CuT nanomaterial is found to be the most efficient candidate for photocatalytic degradation of LFX (75%) under a 40-W visible LED light possibly due to synergetic effects of visible light absorption, higher specific surface area and lesser copper–LFX complexes' formation. Photocatalytic degradation was found to be directly proportional to catalyst concentration and light intensity, while it is inversely proportional to an initial concentration of the LFX pollutant. LC–MS analysis showed strong oxidative degradation of the model pollutant LFX, almost leading to mineralization. Overall, Cu-doped TiO₂ nanomaterials have ample potential in the field of environmental remediation application due to its high visible-light photocatalytic activity.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s43630-021-00141-8>.

Acknowledgements We deeply acknowledge Gujarat Pollution Control Board (GPCB), Gandhinagar, Gujarat, India, for providing Ph.D. fellowship (Grant ID: Ph.D./R&D/05/444437). We are thankful to Padma Shri Dr. H. M. Desai, Vice-chancellor, Dharmsinh Desai University for providing research facilities, and Dr. B. N. Suhagia, Dean, Faculty of Pharmacy for his valuable direction in pharmaceutical pollutant selection. We also thank Dr. Bhavesh Bharatiya, School of Chemistry, University of Bristol, England for his useful contribution and discussion about the schematic diagram for the synthesis of

Cu-TiO₂ nanomaterials through reverse micelle sol-gel method in the manuscript.

Funding We deeply acknowledge Gujarat Pollution Control Board (GPCB), Gandhinagar, Gujarat, India, for providing a Ph.D. fellowship (Grant ID: Ph.D./R&D/05/444437).

Availability of data and materials Not applicable.

Code availability Not applicable.

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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