Energy-efficient carbon-doped titanium dioxide nanoparticles: synthesis, characterization, and catalytic properties under visible LED irradiation for degradation of gemifloxacin

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Abstract

Synthesis and characterization of energy-efficient visible-light-responsive carbon-doped titanium dioxide nanoparticles (C-TiO₂NP) is reported. The characterization results of C-TiO₂NP using BET, TEM, DLS, and XRD indicate the following: (1) the C-TiO₂NP have high surface area (77.02 m²/g), (2) size range of 5.00–10.00 nm and (3) zeta potential of 19 (pH 4.0), 4 (pH 7.0) and –21 (pH 10.0) while (4) the XRD results shows a peak pattern indicating that C-TiO₂NP is mostly in the anatase phase. The photocatalytic properties of C-TiO₂NP is investigated in this study using gemifloxacin antibiotic under LED in the visible region ($\lambda_{\text{max}} \sim 450$ nm). Results shows that C-TiO₂NP have significant catalytic properties under LED visible light (up to ~ 74% within 60 min). On the other hand, no degradation is observed for control TiO₂NP using LED visible light under equivalent experimental conditions. Using control TiO₂NP with H₂O₂ under LED visible light results in a percentage degradation of ~ 33.0%. Upon using C-TiO₂NP with H₂O₂, the %degradation increases from ~ 33.0 to 64.0%. Although H₂O₂ generally enhances the activity of bare TiO₂NP under UV irradiation, the %degradation under LED in the presence of C-TiO₂NP and H₂O₂ (~ 64%) is smaller than that in the presence of C-TiO₂NP only (~ 74%). Results demonstrates the applicability of C-TiO₂NP as an energy-efficient and cost-effective photocatalyst under LED visible light for pharmaceutical wastewater treatment.

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Graphical abstract

Keywords Photocatalytic degradation · Photodegradation · Titanium dioxide · Carbon doped titanium dioxide nanoparticles · Gemifloxacin

1 Introduction

Heterogeneous photocatalysis is a promising technology for the removal of toxic organic and inorganic contaminants from water. Photocatalysts designed to work with energy-efficient light sources have recently attracted a lot of attention [1]. Processes involving UV irradiation are energy demanding while those involving solar light requires a large surface area for installation. Moreover, the efficiency of daylight as an energy source is highly dependent on the duration of the day, intensity and direction of light as well as environmental conditions. Such factors limited the use of sunlight in water treatment applications [2, 3].

Recently, solid-state technology resulted in the development of light emitting diodes (LEDs) that are compact, economic, and environment-friendly. LED can produce light of high spectral purity and are available in both chip and bulb types. Ultraviolet LED has been widely used for the photocatalytic degradation of organic pollutants and recently, visible LED was used for the same purpose. In addition, LED can overcome the outlined limitations of conventional light sources commonly used in photocatalytic degradation experiments [4, 5].

Advances in nanotechnology allowed the synthesis of nanomaterials with unprecedented opportunities to meet emerging environmental issues such as water treatment and water desalination [6]. Currently, advanced oxidation processes (AOPs) involving novel nanomaterials have been

widely investigated to eliminate residuals of pharmaceuticals and other toxic organic pollutants from wastewater [7, 8]. Heterogeneous photocatalysis; in particular has been considered superior to other processes for water treatment with respect to (1) lack of hazardous chemicals, (2) minimum waste, (3) low energy consumption when compared to thermal [9], biological [10] or chemical methods such as ozonation [11], solar-Fenton method [12], and sonophotocatalytic degradation [13].

Titanium dioxide nanoparticles (TiO_2NP) are a widely used photocatalyst for wastewater treatment [14]. TiO_2NP are cost-effective, nontoxic and attain long-term chemical and photostability with high decomposition and mineralization rates [15]. However, conventional TiO_2NP suffer from the main limitation that is the wide energy bandgap (3.2 eV). This limited the usability of TiO_2NP to UV irradiation < 400 nm [16]. Various attempts have been directed towards extending the applicability of TiO_2NP to the higher wavelength range by lowering its bandgap [8, 17, 18]. Doping with other metals, nonmetals or both resulted in a significant improvement [19–21]. In literature, hematoporphyrin/N-doped TiO_2 nanohybrids have been successfully used under solar irradiation with a high degradation efficiency [22].

The persistence of fluoroquinolones (FQs) is well documented in various ecosystems [16, 23, 24]. Several studies demonstrated that wastewaters containing FQs are associated with serious health problems such as genotoxicity and carcinogenicity. Induction of antibiotic resistance is

also a major concern especially with the rapid emergence of resistant bacteria worldwide, endangering the efficacy of antibiotics [25–27]. Gemifloxacin (GEM) is an oral broad-spectrum quinolone for the treatment of chronic bronchitis and pneumonia. It acts by inhibition of both DNA gyrase and topoisomerase IV thus inhibiting DNA synthesis that is essential for bacterial growth [28–30]. It has a high oral bioavailability (~ 71.00%) and it does not undergo significant metabolism thus GEM is excreted unchanged [31]. In addition, inadequate industrial wastewater treatment has also contributed to the presence of GEM in wastewater even at low concentration levels 0.20 µg/L [32].

Wastewater treatment has been considered one of the vital challenges studied recently [33]. Our research group has investigated the use of various types of NPs for industrial wastewater treatment including bare and modified TiO₂NPs [34–36]. Herein, we aim to develop C-TiO₂NP with an excellent photocatalytic response under visible light irradiation. Furthermore, the synthesized particles were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), dynamic light scattering (DLS), and Brunauer–Emmett–Teller (BET) surface area distribution from nitrogen adsorption–desorption isotherm. The photocatalytic performance was evaluated using GEM as a model pollutant.

2 Experimental

2.1 Chemicals

Titanium tetrachloride solution, TiO₂NP (< 100 nm, surface area > 14.0 m²/g, cat. no. 677469), HPLC-grade acetonitrile and methanol were purchased from Sigma-Aldrich. Analytical grade Na₂SO₃ and H₂O₂ (33%, v/v), KOH and glucose were purchased from El Nasr (Egypt). GEM standard was kindly supplied by Hikma Pharmaceuticals (Egypt). Ultrapure water was obtained using a MilliQ UF-Plus system (Millipore, Germany) with a resistivity of at least 18.2 MΩ cm at 25 °C and total organic carbon (TOC) value below 5 ppb.

2.2 Reversed-phase liquid chromatography

2.2.1 RP-HPLC using isocratic elution

Initially, an isocratic HPLC method was developed and validated using a Shimadzu HPLC with an isocratic pump controlled with Class-VP software (Shimadzu Corporation, Japan) equipped with UV–Vis detector and Zobrax C18[®] column (4.60 × 250.00 mm, 5 µm). The effect of mobile phase composition and pH on the efficiency of separation were investigated. Analysis was carried out at room

temperature with a mobile phase of 10 mM ammonium acetate (pH 3.5): acetonitrile (70:30 v/v) at a flow rate of 1.0 mL/min, and detection at 270 nm. Separation efficiency was demonstrated using GEM photodegraded sample (150.00 µg/mL GEM, pH 7.0 in the presence of 0.6 mg/mL commercial-grade TiO₂NP, 1.25 mM H₂O₂, 254 nm for 22.5 min) and system suitability parameters were calculated according to the US Pharmacopeia 2011 [35].

2.2.2 RP-HPLC using gradient elution

A previously developed HPLC assay [34] was used to determine GEM in the presence of its photodegradation products under different conditions. Briefly, the analysis was performed using Agilent 1200 HPLC with a gradient pump system controlled with Chemstation software (Agilent Technologies, Germany) equipped with UV–Vis detector and Luna C18[®] column, (4.60 × 250.00 mm, 5 µm) at flow rate of 1.0 mL/min and detection at 270.0 nm. The mobile phase composition was Solvent A: 10 mM ammonium acetate buffer (pH 4.0) and Solvent B: acetonitrile. The gradient elution was programmed as follows: 0–2 min, 25.0% (B); 2.0–8.0 min, 25.0–40.0% (B); 8.0–10.0 min, 40.0–25.0% (B); 10.0–12.0 min, 25.0% (B). Analysis of GEM photodegraded sample (150.00 µg/mL GEM, pH 7.0 in the presence of 0.6 mg/mL commercial-grade TiO₂NP, 1.25 mM H₂O₂, 254 nm for 22.5 min) was carried out and system suitability parameters were calculated as per the US Pharmacopeia [35].

2.3 Synthesis of NP

A previously reported sol–gel procedure [20] was used to prepare both TiO₂NP and C-TiO₂NP photocatalysts. In a typical experiment, 6 mL of titanium tetrachloride was added dropwise with stirring to 100 mL of ultrapure water in a conical flask immersed in an ice bath. Glucose (180.15 mg) was added to a final concentration of 0.01 M. The solution was heated for 1 h at 95 °C, then left to cool to room temperature. The pH was adjusted to 8.0 and heated again at 95 °C for another 1 h. The precipitate was isolated by centrifugation at 7000 rpm for 15 min, then washed with deionized water to remove excess chloride ions and dried in an oven at 120 °C. The NP gel suspension was performed using an oven at 120 °C instead of the calcination process and a high anatase phase for synthesized NP was obtained. Carbon doping process results in a shift in the band gap of TiO₂NP to generate an excellent response under the LED visible light. Similar conditions were employed in previous studies; 50 °C [39], 60 °C [40], 100 °C [41] and 200 °C [42] and the results were highly anatase crystalline particles. The control TiO₂NP photocatalyst was

prepared using a similar procedure except for the addition of glucose.

2.4 Characterization of TiO₂NP and C-doped TiO₂NP

A set of characterization techniques has been implemented since no single technique can reveal all the properties of the proposed NPs [43]. Correlation of the results obtained using different techniques would lead to a better understanding of the characteristics of target samples.

2.4.1 TEM

The morphology and size distribution of the synthesized TiO₂NP and C-TiO₂NP were inspected using a transmission electron microscope (Model 2100; JEOL, Japan). One drop of the sample was placed on a copper grid followed by drying in air and examination at 160 kV.

2.4.2 XRD

The formation and crystallographic characteristics of TiO₂NP and C-TiO₂NP were analyzed using X-ray diffraction equipment (Model X'Pert PRO, Netherlands) with a secondary monochromator, Cu-radiation ($\lambda = 1.542\text{\AA}$) at 45 kV, 35 mA and scanning speed 0.02°/s. The diffraction peaks between $2\theta = 2^\circ$ and 60° , corresponding spacing (d , $\text{\AA}$), and relative intensities (I/I_0) were obtained.

2.4.3 BET

The Brunauer–Emmett–Teller surface area detailed analysis and pores size distribution was performed using a nitrogen adsorption analyzer (NOVA touch 4LX, USA) equipped with Quantachrome TouchWin software (version 1.11). Samples were degassed for 2 h before conducting the studies.

2.4.4 DLS

A Zetasizer Nano ZS-ZEN 3600 (Malvern Instruments Ltd, UK) with DTS Nano version 6.12 software) was used to determine the mean diameter, particle size distribution and polydispersity index (PDI). The average zeta potential of both NP in different pH (4.0, 7.0 and 10.0) was determined at 25 °C for 2 min through a combination of phase-analysis light scattering and laser Doppler velocimetry to check particle electrophoretic mobility.

2.5 Photodegradation studies

Irradiation under visible light was carried out using a Venus LED lamp ($\lambda_{\text{max}} \sim 450\text{ nm}$, 73 K Lux), China in an

air-ventilated cabinet. The intensity of the light was determined using a LUX meter (model LX-101, China). Also, UV irradiation module with a calibrated UV lamp 6 W, 254 nm, 1012 $\mu\text{W}/\text{cm}^2$ (Vilber Lourmat, France) housed in a cabinet with air ventilation was used.

2.5.1 Photocatalytic properties of TiO₂NP under UV light

Initially, the photocatalytic properties of the synthesized TiO₂NP versus commercial-grade TiO₂NP under UV light has been evaluated. Throughout this study, 25 mL GEM solution (150 $\mu\text{g}/\text{mL}$, pH 7.0), 0.6 mg/mL NP, and 1.25 mM H₂O₂ were placed in Petri dishes. Then the reaction mixture was subjected to UV irradiation for 22.5 min while stirring at low speed. At the end of the irradiation period, samples were filtered using 0.2 μm syringe filter. Sodium sulfite was added to stop the reaction as previously described [34, 37]. Samples were completed to volume (25 mL), stored frozen, and protected from light until analysis. The percentage of degradation was calculated relative to an equivalent control sample that has not been subjected to irradiation.

2.5.2 Photocatalytic properties of C-TiO₂NP under visible light

Aliquots of GEM standard (50 $\mu\text{g}/\text{mL}$, pH 7.0) were placed in Petri dishes either alone or in the presence of 0.8 mg/mL C-TiO₂NP/TiO₂NP. The reaction mixture was subjected to LED visible light for 60 min then samples were filtered through 0.2 μm syringe filter, completed to volume (25 mL) and processed as described above. The percentages degradation of GEM under LED visible light irradiation using either C-TiO₂NP or TiO₂NP were calculated as described above.

2.5.3 Effect of H₂O₂

The effect of H₂O₂ on the photocatalytic activity of C-TiO₂NP was evaluated. Results were compared to those obtained using H₂O₂ alone. Aliquots of 25 mL buffered GEM solution (50 $\mu\text{g}/\text{mL}$, pH 7.0) were placed in Petri dishes in the presence of 2 mM H₂O₂ and (0.8 mg/mL) of C-TiO₂NP. Then the reaction mixture was subjected to LED visible irradiation as described and appropriate amount of Na₂SO₃ was added at the end of the irradiation period as previously described [34, 37]. Samples were then filtered and stored until analysis using gradient HPLC method. Results were compared to those irradiated in the presence of H₂O₂ and equivalent control sample which has not been subjected to irradiation.

3 Results and discussion

In this study, Carbon was selected as a suitable dopant to modify the band gap of TiO₂NP to enable photocatalytic activity under visible light illumination. Further, LED was chosen as an excellent visible light source due to its economic, long lifetime, high spectral purity and energy efficiency as well as its ability to produce visible light with minimal heating to the samples. This was crucial to evaluate the photocatalytic activity of the C-TiO₂NP under controlled temperature conditions.

Initially, a set of preliminary studies were established before synthesis of the modified C-TiO₂NP. Such studies included the synthesis of control TiO₂NP using a reported modified sol–gel method [20] to ensure the validity of synthesis protocol. Comparison of the performance of the synthesized TiO₂NP versus that of the commercially available grade was carried out using an isocratic HPLC assay and GEM as a model for a hazardous pollutant from pharmaceutical industry [34]. Characterization of synthesized NPs was carried out and promising results were obtained as described below in more detail. The efficiency of the modified C-TiO₂NP was determined under LED irradiation either alone or after addition of H₂O₂ using a gradient HPLC [34] assay. The reusability of the C-TiO₂NP has also been investigated. In all experiments, analysis results

of each sample were compared to those obtained using equivalent control sample which has not been subjected to any irradiation. Degradation percentage was obtained according to the area under the peak for each sample chromatogram.

3.1 Reversed-phase liquid chromatography

A photodegraded GEM sample was prepared and used to demonstrate the specificity and suitability of the assay. Careful optimization of the mobile phase composition and pH was required due to the complexity of degraded sample either under UV irradiation or LED irradiation. Validation was carried out according to ICH guidelines [38]. System suitability parameters were calculated to evaluate the efficiency of separation and summarized in Table 1.

RP-HPLC with isocratic elution A mobile phase composed of 10 mM ammonium acetate (pH 3.5): acetonitrile (70:30 v/v) at a flow rate of 1 mL/min and detection at 270 nm was performed. A linear relationship was obtained between the integrated peak area and GEM concentration 3.125–200.00 µg/mL.

RP-HPLC with gradient elution A mobile phase of 10 mM ammonium acetate buffer (pH 4.0) as solvent A and acetonitrile as solvent B at a flow rate of 1.0 mL/min and detection at 270.0 nm. A linear relationship was obtained

Table 1 Summary of system suitability and validation parameters for the proposed RP-HPLC assays

Parameters	Isocratic RP-HPLC assay	Gradient RP-HPLC assay
<i>System suitability</i>		
Retention time	4.6	7.1
Resolution (Rs) ^a	2.48 and 5.54	3.65 and 2.70
Peak symmetry	0.8	0.7
Column capacity (K)	2.35	2.15
Number of theoretical plates (N)	8970	19,755
<i>Validation</i>		
Accuracy (mean ± SD) ^b	100.51 ± 0.78	100.79 ± 0.69
Precision (RSD%)		
Repeatability ^c	0.68	0.68
Intermediate precision ^d	0.60	0.89
<i>Linearity</i>		
Regression equation	y = 145.07x – 85.845	y = 163.42x + 376.11
Correlation coefficient (r)	0.9999	0.9997
Range	3.125–200.00 µg/mL	5.00–100.00 µg/mL
LOD	1.49 µg/mL	1.50 µg/mL

^aCalculated for the main peak with the pre and post eluting peaks (Figs. 5c, 6B)

^bAverage of nine determinations

^cThe intraday, average of nine determinations over three concentration levels repeated within the same day

^dThe inter-day, average of nine determinations over three concentration levels repeated over three different days

between the integrated peak area and GEM concentration 5.00–100.00 $\mu\text{g/mL}$.

3.2 Characterization of the prepared nanoparticles

3.2.1 TEM

The size, morphology, and dispersion of TiO_2NP and $\text{C-TiO}_2\text{NP}$ were examined using TEM as shown in Fig. 1. TEM images of TiO_2NP and $\text{C-TiO}_2\text{NP}$ showed that the size

ranges were 5–15 nm and 5–10 nm, respectively. Regarding their small size, the particles were estimated to have a high surface area thus can act as a good catalyst. Results indicated that the doping process did not significantly alter the size of the particles. Differences between TiO_2NP and $\text{C-TiO}_2\text{NP}$ in TEM images confirmed the successful synthesis of the latter in the nano-range. On the other hand, images obtained at higher magnifications suggested that the $\text{C-TiO}_2\text{NP}$ seems to be somehow different in morphology as previously reported [19]. Having

Fig. 1 Transmission electron micrograph of TiO_2NP (**A**, **C** and **E**) and $\text{C-TiO}_2\text{NP}$ (**B**, **D** and **F**) at different magnifications

a close look at Fig. 1 of TEM for C-TiO₂NP, the bright and darker areas show particles with the same composition; the contrast difference is solely a consequence of the overlapping particles. The high-resolution TEM image Fig. 1F demonstrates that there are particles consist of titania and the difference of grey scale between layers is due to the overlapping particles. Thus, lighter ones are forming a monolayer and the darker regions are overlapped particles. Consequently, it can be stated, that the showed particles are carbon doped titania NPs and not nanocomposite system. Several TEM images for

carbon-doped titanium were reported elsewhere [40, 42], that are in a good agreement with our results.

3.2.2 XRD

X-ray diffraction analysis was carried out to determine the crystalline nature of the C-TiO₂NP. The XRD patterns of the prepared photocatalysts are shown in Fig. 2. The peaks at 2θ 27.6, 41.1, 43.8 and 68.4 correspond to the diffraction (110), (200), (210) and (301) reflection from crystal planes of the rutile phase of TiO₂, while the peaks at 2θ 36.1, 39.5, 53.9, 56.2, 62.5, 64.3, 70.4 and 74.8 were due to the

Fig. 2 XRD pattern of **A** TiO₂NP and **B** C-TiO₂NP

(101), (112), (105), (211), (204), (116), (310) and (215) mirror planes of the anatase phase [44–46]. The prepared C-TiO₂NP showed higher intensity for two peaks; 27.6 and 36.1 that suggested higher crystallinity. On the other hand, a significant decrease or disappearance of other peaks; 41.1, 43.8, 62.5, 64.3 and 74.8 occurred when compared to that of TiO₂NP. The C-TiO₂NP sample did not show detectable dopant (Carbon) related peak, which may be due to the addition of low concentration of carbon which may have moved either into the substitutional sites or into the interstitial positions of the titanium dioxide crystal structure [47]. Such results indicated transformation from rutile to anatase phase due to doping. It has been reported that the anatase phase of titanium dioxide has higher photocatalytic activity [19, 48, 49]. Thus, it could be concluded that the prepared catalysts exhibits the desired phase for the purpose of the photocatalytic activity. Such results are in agreement with the previously reported results [38, 50, 51]. Several studies reported earlier that TiO₂ and carbon doped TiO₂ NPs prepared at different low temperature such as 50–200 °C [39–42] resulted in pure NP with high crystallinity. The highly crystalline nanoparticles obtained in this study were also produced using a low-temperature synthesis protocol, which is more advantageous than other methods using high temperature procedures.

3.2.3 BET

The surface area and average pore radius of TiO₂NP and C-TiO₂NP were 79.91 m²/g, 2.56 nm for TiO₂NP and 77.02 m²/g, 3.01 nm for C-TiO₂NP. The total pore volume for pores with a radius of less than 140 nm at P/Po=0.99 was found to be 1.0251 and 1.1602 cc/g for TiO₂NP and C-TiO₂NP, respectively. Results of BET surface area analysis were generally in agreement with those of TEM where it was concluded that both control and doped particles were almost equal in size. Figure 3 shows the nitrogen adsorption–desorption isotherm of control (A) TiO₂NP and (B) C-TiO₂NP. Both types exhibited a type IV adsorption isotherm, which has the typical characteristics of mesoporous materials [21]. Furthermore, Barret–Joyner–Halender (BJH) pore size distributions of the analyzed samples showed a narrow pore size distribution as shown in Fig. 3C TiO₂NP and d C-TiO₂NP. It was believed that a photocatalyst with high surface area has a superior photocatalysis efficiency since high surface areas always allow higher contact/adsorption of pollutants.

3.2.4 DLS

3.2.4.1 Size The hydrodynamic size of TiO₂NP and C-TiO₂NP were (170 nm, PDI 0.12) and (190 nm, PDI 0.27), respectively. DLS measures the hydrodynamic size and

is able to detect aggregates of NPs [43]. In this case, the hydrodynamic size of both types was relatively close which was in agreement with other techniques. However, there was a relatively wide difference in size detected by DLS when compared to other techniques. Taking in consideration that the PDI was relatively small for both TiO₂NP and C-TiO₂NP, it could be concluded that the size detected by DLS is not due to aggregation but due to an attached layer of ions and molecules in solution [52].

3.2.4.2 Zeta potential The surface charge has always been associated with both the stability of NPs and efficiency as a photocatalyst [35, 53]. Since the surface charge could vary according to pH, in this study the zeta potential was measured over a pH range 4.0–10.0, as described above. Figure 4A shows the effect of pH on zeta potential where the charge of TiO₂NP and C-TiO₂NP at pH 4.0, 7.0 and 10.0 were 20.0, −3.0 and −27.0 mV and 19.0, −4.0 and −21.0 mV, respectively. In agreement to the previously published reports [1, 54], the zeta potential of titanium-based NPs was positive at acidic pH, negative at alkaline pH with the point of zero charge (PZC) close to pH 7.0. This finding has been considered while selecting the experimental conditions in photodegradation experiment of GEM in order to avoid electrostatic repulsion between the drug and the NPs.

3.3 Photocatalytic degradation study

As explained above, titanium-based NPs has a PZC close to pH 7.0 (Fig. 4A) while GEM has two main ionizable groups with pKa 5.53 and pKa 9.23 (Fig. 4B) [34]. GEM exists as a zwitterion between pH 5.53 and 9.23 thus at pH 7.0 where TiO₂NP or C-TiO₂NP are close to PCZ, repulsion between GEM and catalyst NPs will be minimal [34].

3.3.1 Photocatalytic properties of TiO₂NP

Preliminary studies were carried out using the following experimental conditions: 150 µg/mL GEM, pH 7.0, 0.6 mg/mL NPs and 22.5 min UV irradiation in presence of 1.25 mM H₂O₂ and promising results were obtained. The efficiency of synthesized TiO₂NP; in terms of pattern and percentage of degradation was quite similar to the commercial TiO₂NP (~ 94.0%) Fig. 5. Results obtained using the isocratic HPLC method verified the reliability of the synthesis protocol that will be used later on for the synthesis of C-TiO₂NP [34]. The amount of sodium sulfite required to stop the reaction in this experiment was calculated to be stoichiometrically equivalent to the added H₂O₂ (1:1 M ratio).

Fig. 3 N_2 adsorption(Θ)—desorption(Θ) BET isotherm of: **A** TiO_2NP and **B** $C-TiO_2NP$. The inset shows the BJH pore size distributions from the adsorption branch of isotherm for **C** TiO_2NP , **D** $C-TiO_2NP$

Fig. 4 **A** Zeta potential of TiO_2NP (...) and $\text{C-TiO}_2\text{NP}$ (—) at different pH (4.0, 7.0 and 10.0). **B** The theoretical isoelectric point of GEM through different pH

3.3.2 Photocatalytic properties of $\text{C-TiO}_2\text{NP}$

Initially, the stability of GEM at pH 7.0 under LED visible irradiation for 60 min was verified. This experiment was conducted to ensure that any decrease in GEM concentration upon LED visible irradiation was solely due to the effect of the catalyst, not the light. In the absence of any photocatalyst, approximately no degradation was noted as shown in (Fig. 6A). The photocatalytic activity of synthesized NPs was demonstrated throughout two experiments conducted at the same experimental conditions but after addition of either TiO_2NP or $\text{C-TiO}_2\text{NP}$ (0.8 mg/mL). The percentage degradation was ~0% and 74.0% in the presence of equivalent amounts of TiO_2NP (Fig. 6B) and $\text{C-TiO}_2\text{NP}$ (Fig. 6C), respectively. Lack of any degradation with TiO_2NP under LED irradiation was expected and in agreement with the photocatalytic characteristics of TiO_2NP . On the other hand, the percent degradation under LED visible irradiation in the presence of $\text{C-TiO}_2\text{NP}$ confirmed the successful modification of the band gap of $\text{C-TiO}_2\text{NP}$ as result of carbon doping.

3.3.3 Effect of H_2O_2

The ability of H_2O_2 to enhance photodegradation of GEM in the presence of TiO_2NP has been demonstrated by our research group [34]. In this study, the effect of the addition of H_2O_2 to experiments conducted using $\text{C-TiO}_2\text{NP}$ was investigated. In the absence of the photocatalyst, H_2O_2 resulted in approximately ~33.0% degradation (Fig. 6D) which was attributed to degradation via hydroxyl radicals. Upon addition of $\text{C-TiO}_2\text{NP}$, the percentage degradation was increased from 33.0 to 64.0% (Fig. 6D, E). Such results were significantly lower than that obtained using $\text{C-TiO}_2\text{NP}$ under LED light without adding H_2O_2 (74.0%) Fig. 6C. Thus, adding H_2O_2 in presence of $\text{C-TiO}_2\text{NP}$ has negatively impacted the performance of the photocatalyst. Photodegradation experiments using $\text{C-TiO}_2\text{NP}$ were also carried out under LED irradiation in two consecutive cycles. Percentage degradation of 74.0% and 46.0% were obtained in Cycle 1 and 2, respectively (Fig. 7). Such decrease was attributed to either the partial loss of the photocatalyst between the two cycles or the impact of H_2O_2 on the

Fig. 5 Chromatogram of isocratic HPLC method showing the result of **A** control GEM sample (150.00 $\mu\text{g/mL}$) at pH 7.0 and photodegradation at pH 7.0 with 1.25 mM H_2O_2 upon exposure to UV light for

22.5 min in the presence of **B** 0.6 mg/mL commercial-grade TiO_2NP and **C** synthesized TiO_2NP

Fig. 6 Comparison of degradation (%) of GEM (50 $\mu\text{g/mL}$ at pH 7.0) under visible light irradiation for 60 min using: LED light alone, LED with 0.8 mg/mL TiO_2NP , LED with 0.8 mg/mL C- TiO_2NP , LED with 2 mM H_2O_2 and LED with 2 mM H_2O_2 and 0.8 mg/mL C- TiO_2NP . **A**

Chromatograms of gradient HPLC method and the inset **B** shows Bar chart summarizing the results, *a* LED light alone, *b* LED with 0.8 mg/mL TiO_2NP , *c* LED with 0.8 mg/mL C- TiO_2NP , *d* LED with 2 mM H_2O_2 and *e* LED with 2 mM H_2O_2 and 0.8 mg/mL C- TiO_2NP

Fig. 7 **A** Chromatograms of gradient HPLC method showing the analysis results of GEM through the regeneration study of C-TiO₂NP (1st Cycle, 2nd Cycle) and the insert **B** Comparison of degradation

rates (%) of GEM through the regeneration study of C-TiO₂NP (1st Cycle, 2nd Cycle)

surface of C-TiO₂NP. Further investigations are required in order to investigate this observation.

4 Conclusion

In this study, nanocrystalline visible-light responsive C-TiO₂NP were synthesized by a low temperature sol–gel procedure. The C-TiO₂NP have been employed as an economic photo catalyst for GEM degradation (74% within 60 min) under LED irradiation in the visible light region. A detailed characterization was carried out using TEM, XRD, BET, and DLS. The size of the synthesized C-TiO₂NP was in the nano range with a pH-responsive charge/zeta potential. The C-TiO₂NP attained good crystallinity, high surface area, and a reduced bandgap that enabled photocatalytic activity in the visible light range. This modification offered an efficient economic alternative to TiO₂NP that is active in the UV light range.

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Compliance with ethical standards

Conflict of interest The authors certify that they have NO affiliations with or involvement in any organization or entity with any financial interest, or non-financial interest in the subject matter or materials discussed in this manuscript.

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