Defect State Modulation of TiO₂ Nanostructures for Photocatalytic Abatement of Emerging Pharmaceutical Pollutant in Wastewater Effluent

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1. Introduction

Frequent appearance of emerging pharmaceuticals in aquatic environment especially wastewater, surface, and groundwater poses an immense challenge in order to provide clean water globally. Detection of such pharmaceutical pollutants, varying from μg/L to ng/L level, arises primarily due to unscientific discharge of effluents from pharmaceutical industries, hospitals, household, and agricultural wastes. As a consequence, ecological risk of such emerging pollutants in the aquatic environment may lead to endocrine disorder, mutagenesis, and development of multiresistant pathogenic microorganisms, becoming threat to human, animals, and plants life.

Antipyrine (ANT) is considered one of the most frequently detected pharmaceutical emerging pollutants in waste and surface water. Several reports ascribed the presence of ANT up to the μg/L level in aquatic environment due to improper treatments of industrial, hospital, agricultural, and household effluents. Toxicity assay ascribed its influence in aquatic ecosystems and human life (lungs, mucosa damage). To overcome unwanted ecotoxicological effects of ANT, advanced oxidation processes are most effective technology in comparison to conventional wastewater treatment processes (ultrafiltration, reverse osmosis, adsorption, etc.), which possess limitations in practical usage. Out of various advanced oxidation processes, semiconductor-based photocatalysis is highly appealing and sustainable that can effectively degrade organic pollutants via generation of reactive oxygen species (ROS) in water.

Different semiconductor-based photocatalysts, e.g., ZnO, TiO₂, and SnO₂, are widely used for the degradation of ANT from wastewater. Among proposed photocatalysts, TiO₂ is one of the most active materials for the degradation purpose as it has...
superior properties such as low cost, high stability, biocompatibility, nontoxicity, and ease of preparation.\cite{10, 11} Several literatures are reported for the degradation of dye, toxic metal, and emerging pollutants using TiO₂ as an active photocatalyst.\cite{12-14} UV-assisted complete photocatalytic degradation of ANT was reported by Durán et al. using spinning disc reactor with good efficacy up to ten cycles.\cite{15} Similar observation was reported by Sousa et al. for the degradation of a number of emerging pollutants using TiO₂ nanoparticle.\cite{16} However, rapid charge carrier recombination and poor solar spectra utilization (only UV photon absorption ability) make TiO₂ impractical for industrial-scale wastewater treatment application. Several strategies like doping of metal/nonmetal, heterojunction, dye/polymer sensitization, etc. have been adopted in order to alter charge carrier dynamics that can maximize the light harvesting ability.\cite{13, 17}

Recently, much effort has been made over the construction of defect from surface to bulk within the semiconductor that plays a crucial role to alter overall charge transport dynamics. A size-dependent correlation between surface/bulk defect with particle size was reported by Wu et al.\cite{18} Improved photocatalytic activity for the particle size >10 nm arises due to predominant bulk effect, while surface defect plays crucial role for enhancement in photocatalytic activity for the particle size < 10 nm. Recently, theoretical investigations revealed that the trap state modulation within TiO₂ can alter overall charge transport efficiency and can be useful for solar harvesting application. Distortion of TiO₂ crystal via introducing oxygen vacancy/Ti³⁺ may alter overall active sites of TiO₂ and may facilitate utilization of wider range of solar spectra for enhanced solar harvesting application. Several methods like hydrogen reduction, metal reduction, electrochemical reduction, and plasma treatment have been employed in order to formation of distorted TiO₂ crystal lattice.\cite{19} Incorporation of Ti⁴⁺ and oxygen vacancy within black TiO₂ nanotube by Cui et al. was found to accelerate photoelectrochemical water splitting ability due to enhanced visible light absorption and better charge transport ability.\cite{20}

Improvement in dye-sensitized solar cell efficiency using black TiO₂ was reported by Periyat et al. due to enhanced IR absorption ability.\cite{21} Therefore, wide range absorption spectrum of TiO₂ after creation of defect is supposed to be a key factor for the alteration of optical properties and functionality. Recently, defective TiO₂ has shown significant absorption in the visible spectrum, which eventually resulted in higher photocatalytic degradation of contaminants present in water.\cite{19, 22} Further, boron-doped black TiO₂/g-C₃N₄ nanocomposite showed enhanced removal efficiency of As(III) from aqueous solution.\cite{23} However, correlation between bulk to surface defects on the photocatalytic properties for the degradation of emerging pollutants is not fully understood and is one of the motives in the present work. In photocatalysis, decomposition of pollutants has been generally carried out via batch scale which suffers several limitations for practical wastewater treatment applications.\cite{24, 25} There are very few studies where development of prototype reactor is reported for actual decontamination of wastewater.\cite{26, 27} Tayade et al. developed photocatalytic reactor using TiO₂ for potential removal of industrial dyes under UV light illumination.\cite{28} Sand-coated TiO₂ was used in reactor by Ramadan et al. for photocatalytic degradation of phenol under UV light.\cite{14} From practical application point of view, usage of defected TiO₂ in reactor under continuous operation for the degradation of emerging pollutants under visible light is not reported in the literature and is another motive for this work.

In this article, we have synthesized TiO₂ microspheres using hydrothermal method. We further created different extent of defects within TiO₂ using NaBH₄ under inert atmosphere. Role of defect has been discussed toward degradation of emerging pharmaceutical pollutant (ANT) under visible light illumination. We have also explored detailed mechanistic pathways and intermediates generated during photocatalytic degradation of ANT. We further developed a continuous reactor where defected TiO₂ was coated over glass beads and employed for photocatalytic degradation of ANT under visible light illumination.

2. Experimental Section

2.1. Reagents

Titanium (IV) iso-propoxide (TTIP), ANT (C₁₅H₁₂N₂O₂), and sodium borohydride (NaBH₄) were purchased from Sigma-Aldrich. All the other chemicals used were of analytical grade and were used without further purification.

2.2. Synthesis of TiO₂ Microspheres

First, TiO₂ microspheres (TiO₂-MS) were synthesized using the hydrothermal technique.\cite{12} At first, 5 mL of TTIP was mixed with 45 mL of acetone and stirred the solution for 20 min. After this step, the resulting solution was transferred to a 100 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 12 h. The system was allowed to cool down to the ambient temperature naturally. The precipitates at the bottom of the solution were collected and washed multiple times with acetone and ethanol, and dried at 80 °C for 3 h. The dried sample was kept inside the muffle furnace for annealing at 400 °C for 4 h in the presence of air in order to improve its crystallinity.

2.3. Synthesis of Defective TiO₂ Using NaBH₄

Defective-TiO₂ was synthesized by manifesting defects inside the crystal lattice using a reducing agent (NaBH₄) with little modification.\cite{29} First, 1.2 g of TiO₂-MS was mixed with 2.4 g of NaBH₄ (TiO₂:NaBH₄ = 1:2 weight ratio) and kept inside the tabular furnace at 400 °C under an inert atmosphere (N₂) for different reduction period of time (3, 5, and 8 h) and samples were termed as DT3, DT5, and DT8, respectively. The samples were then cooled down naturally and washed multiple times with deionized (DI) water to remove excess NaBH₄ and were dried at 60 °C overnight.

2.4. Fabrication of Glass Beads Coated with Defective TiO₂ (DT5)

Borosilicate glass beads (Ø ≈ 3 mm) were sonicated in mixture of DI water and ethanol (1:1) for 2 h to remove any impurity present. After sonication, beads were washed with DI water multiple times and were kept for drying at 100 °C for 4 h. The coating of DT5 photocatalyst was carried out as using the procedure
developed by Miranda-Garcia et al.\textsuperscript{[30]} At first, 5 g DT5 catalyst was added in 150 mL of isopropyl alcohol and sonicated for 30 min. After that, 20 μL nitric acid was added to the suspension and again sonicated for 30 min. In the next step, 500 mg PEG 600 was added to the suspension and kept for the sonication (30 min). After preparing the suspension, the glass beads were coated using dip coating method. The beads were dipped inside the suspension of 2 min and taken out for drying. This step was repeated for multiple times in order to form a thick layer of the photocatalyst on the surface of glass beads. Finally, glass beads were calcinated at 400 °C for 2 h.

2.5. Characterization Methods

Field emission scanning electron microscope (FESEM, MIRA3 series, Czech Republic) was used to investigate the surface morphology of the as-prepared photocatalyst. Highly magnified images of the samples were acquired using high-resolution transmission electron microscopy (FEI Titan G2 60–300 (300 kV), HRTEM). Energy dispersive X-ray spectroscopy (EDX, Oxford Instrument) linked to FESEM was performed to measure the composition of the samples. X-ray diffraction (XRD) patterns for the samples were obtained by employing a scanning rate of 2° min\(^{-1}\) in the 2θ range from 10° to 80° on two circle diffractometers (Rikagu MiniFlex 600) equipped with Cu Kα radiation (at 40 mA and 40 kV). Diffuse reflectance spectroscopy (DRS) measurement was carried out using a UV–vis spectrophotometer (Cary 7000 UMS, Agilent). X-ray photoelectron spectroscopy (XPS, PHI 5000 Versa Prob2) was used to analyze the elemental composition of the samples. Surface area and the pore sizes were analyzed using BET surface area analyzer (Autosorb I, Quatachrome Corp.), with nitrogen gas as the standard absorptive gas with all samples degassed at 80 °C prior to measurements. For analyzing the concentration of ANT, high-pressure liquid chromatography (HPLC) (Agilent, US) equipped with UV-detector and C18 column (4.6 × 250 mm, Agilent) was used. The mobile phase was a mixture of 25% HPLC grade acetoneitrile and 75% HPLC grade water. Before injecting, samples were filtered with a 0.22 μm filter membrane. The flow rate was set to 1.00 mL min\(^{-1}\), and the injection volume was 10 μL. HPLC UV-detector wavelength was set to 254 nm for the detection of ANT. Intermediates generated after photocatalysis were analyzed with liquid chromatography equipped with single quadrupole mass spectrometry (LC–MS) system to investigate different pathways of the degradation of ANT.

2.6. Photocatalytic Activity Test

The photocatalytic activity of the prepared catalyst was studied toward degradation of ANT. The photocatalytic degradation of ANT (initial concentration \(C_0 = 10 \text{ ppm}\)) was carried out in a glass petri dish of 10 cm diameter with 5 g L\(^{-1}\) of catalyst loading. The batch setup (petri dish) was equipped with three visible light lamps (36 W each) on the top of the reactor. The suspension was continuously stirred using the magnetic stirrer to avoid agglomeration of the catalyst. The suspension was kept in the dark to achieve absorption equilibrium for 2 h. After the adsorption equilibrium is achieved, the suspension was irradiated with the visible light (Philips MASTER PL-L 36 W lamp, \(\lambda \geq 400 \text{ nm}\)). Then, after every 30 min of interval, 2 mL of suspension was collected for further analysis till the complete degradation was achieved. The collected samples were centrifuged using a microcentrifuge and then filtered with 0.22 μm syringe filter before injecting the sample for HPLC analysis. The percentage degradation \(\%\text{DE}\) of ANT was evaluated using Equation (1)

\[
\%\text{DE} = \left( \frac{C_0 - C}{C_0} \right) \times 100
\]

where \(C_0\) is the initial concentration of ANT and \(C\) is the concentration at various time intervals during the experiment.

For continuous flow degradation of ANT, a prototype packed bed reactor was designed. Simplicity of the reactor design and ease of the operation were focused while fabricating the prototype reactor to facilitate its scale-up in the near future. Briefly, the reactor assembly consists of a reservoir, borosilicate glass tube, peristaltic pump, and three visible light lamps. The glass tube (height 45 cm, dia meter 3 cm) holds the catalyst, i.e., the defected TiO\(_2\) coated over silica beads, making it a packed bed-type reactor. Tapered end of the glass tube further assisted with narrow tube fitting prevents beads to elute in the flowing stream while allowing the contaminants to flow across the packed bed. Total superficial volume of the reactor without the catalyst was found to be 315 mL, whereas after charging the catalyst operating volume of the reactor was reduced to 115 mL. Reactor was clamped at both ends and kept horizontal during the reaction. Visible lamps were placed around the reactor such that radiation falls over the catalyst from all the sides. A peristaltic pump was used to deliver the solution of ANT to the reactor. Rotation speed of pump was calibrated with the flow rate using DI water solution before pumping the actual solution. A constant flow rate of ANT was kept throughout the experiments. A reservoir filled with ANT was placed at the inlet of the pump and outlets were collected periodically. Complete recycle was obtained by connecting outlet back to the reservoir.

3. Results and Discussion

The phase crystallinity of TiO\(_2\)-MS, DT3, DT5, and DT8 samples was examined using XRD. Figure 1a shows the XRD patterns of the synthesized TiO\(_2\)-MS, DT3, DT5, and DT8 samples. The characteristic diffraction peaks for TiO\(_2\)-MS were consistent with anatase phase (JCPDS card no. 21-1272), which indicates well crystallinity of TiO\(_2\) in anatase phase. As observed, there was no significant change in the XRD peak positions for TiO\(_2\) after the creation of defects, which indicate that the crystallinity of samples was maintained in anatase phase. Intact crystallinity after creation of defect within the TiO\(_2\) lattice is well consistent with several reported literature.\textsuperscript{[29,31,32]} Apart from the crystallinity phase, reduction in peak intensity was observed with creation of different extent of defect within TiO\(_2\) lattice. The reduction in peak intensities for 101 peaks at \(2θ = 25.34°\) follows the order: DT8 (1149) > DT5 (1221) > DT3 (1311) > TiO\(_2\)-MS (1311). It was concluded that with an extended period of heating, the reducing agent (active hydrogen generated by NaBH\(_4\))\textsuperscript{[29]} tends to create more defects deep inside the TiO\(_2\) lattice via deformation of wide range crystal surface of TiO\(_2\). Morphology of the...
as-synthesized TiO$_2$-MS was analyzed using FESEM as shown in Figure 1b. The average diameter of the microspheres was found to be $\approx 2.94 \, \mu m$ (Figure 1c). Figure 1d shows FESEM image of dispersed TiO$_2$-MS. After creating defects inside the lattice of TiO$_2$-MS, there was no noticeable change in the structure and the morphology, as shown in Figure S1, Supporting Information.

To further investigate morphology and the crystallinity of the TiO$_2$-MS, TEM and HRTEM were performed as shown in Figure 2. TEM images (Figure 2a,b) of TiO$_2$-MS confirm the porous nature of the synthesized photocatalyst, and the structure was composed of many tiny size nanoparticles (size $\approx 20 \, nm$). During further analysis of HRTEM image (Figure 2c), high crystallinity of TiO$_2$-MS was observed and interplanar distance was found to be 0.36 nm, which corresponds to (101) crystal plane of anatase TiO$_2$, which is consistent with XRD results.$^{[31,33,34]}$

Selected area electron diffraction (SAED) patterns (Figure 2d) from HRTEM analysis further demonstrate the presence of high crystallinity within the crystal lattice as lattice fringe with interplanar distance of 0.36 nm ($d_{101}$) clearly observed.$^{[32,34]}$

Morphology and crystallinity were retained well for all the samples after creation of defects via NaBH$_4$ (Figure S2–S4, Supporting Information).

Further, in order to analyze mesoporosity of the as-synthesized samples (TiO$_2$-MS and DT5), N$_2$ adsorption–desorption measurement was performed. A typical type IV isotherm with an H2 hysteresis loop observed for both TiO$_2$-MS and DT5 samples (Figure 3a,b). A narrow pore size distribution was observed

Figure 1. a) XRD pattern of TiO$_2$-MS, DT3, DT5, and DT8 samples, b) FESEM image of TiO$_2$-MS (low magnification), c) particle size distribution, and d) FESEM image of TiO$_2$-MS (high magnification).

Figure 2. a,b) TEM image, c) HRTEM image, and d) SAED pattern of TiO$_2$-MS.
for both TiO2-MS and DT5, as shown in Figure 3.c.d. From the results, the average pore sizes were 6.4 and 6.3 nm for TiO2-MS and DT5 samples, respectively. In addition, total pore volume was 0.356 and 0.363 cc g⁻¹ for TiO2-MS and DT5 samples, respectively. The specific surface area was calculated by the BET method found to be comparable for both TiO2-MS (111.3 m² g⁻¹) and DT5 (114.7 m² g⁻¹).

XPS was used to analyze the presence of Ti³⁺, Ti⁴⁺, Ti—O and O—H group in the as-synthesized samples. Hydroxyl groups (—OH) have an important role to play in the degradation process. The characteristic peaks for 2p orbital of Ti³⁺ (460 eV) and Ti⁴⁺ (458.6 and 464.4 eV) were identified within the spectrum as shown in Figure 4 and are in agreement with the reported literature. The ratio of Ti³⁺ and Ti⁴⁺ was calculated using the area under the peak of the respective oxidation state. The ratio (Ti³⁺/Ti⁴⁺) was found to increase with the increase in defects in TiO2-MS. Ti³⁺/Ti⁴⁺ ratios are tabulated in Table 1. In XPS spectra of O 1s (as shown in Figure 5), two peaks are exhibited with binding energies of 529.7 and 530.82 eV, which corresponds to TiO₂ and Ti-OH species, respectively. This confirms that oxygen has a bond with titanium and OH groups are present on the surface of the catalyst.

Figure 6 shows UV–vis absorption spectra for TiO2-MS, DT3, DT5, and DT8 samples. The as-prepared samples show a steep edge around 380 nm, which signifies that all the prepared catalysts are highly active in UV region (<400 nm) (Figure 6a). After the creation of defect within the surface of TiO2-MS, the improvement in absorption of light in the visible region was observed. The enhancement of absorption in the visible range was explained due to the decrement in the bandgap. Figure 6b shows Tauc plot, which was used to determine the bandgap of TiO2-MS, DT3, DT5, and DT8 samples. The results show that the bandgap decreases in the order: TiO2-MS > DT3 > DT5 > DT8. The defect creation was explained from the decrement in the bandgap through Ti³⁺ or oxygen vacancies. These defects helped to achieve light absorption at the higher wavelength (visible), which is consistent with several reported literature.

The photocatalytic activity of TiO2-MS, DT3, DT5, and DT8 samples was evaluated toward the degradation of a pharmaceutical compound, ANT with an initial concentration of 10 ppm under visible light irradiation, as shown in Figure 7a. Prior to illumination, photocatalyst was saturated with ANT under dark condition for 2 h in order to attain the adsorption–desorption equilibrium. Under the dark condition, it was observed that there

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![Figure 3](image-url) **Figure 3.** Nitrogen adsorption–desorption isotherm of a) TiO2-MS and b) DT5 samples. Pore size distribution pattern for c) TiO2-MS and d) DT5.
was no significant adsorption of ANT on the photocatalyst surface. On the other hand, pristine TiO\textsubscript{2} exhibits 55\% degradation of ANT within 4 h under visible light illumination. After creation of defect within TiO\textsubscript{2} by NaBH\textsubscript{4}, an improvement in photocatalytic is observed. Efficient photocatalytic activity by defective TiO\textsubscript{2} was due to improved absorption in the visible region and creation of Ti\textsuperscript{3+} defect within crystal lattice. DT5 exhibits almost complete degradation of ANT, while further increase in defect (DT8) decreased photocatalytic activity. Under identical conditions, no degradation of ANT was observed in the absence of the photocatalyst. HPLC chromatogram for the degradation of ANT is shown in Figure S5, Supporting Information. It is reported that TiO\textsubscript{2} preferably follow pseudo-first-order reaction kinetics model for the removal of organic pollutants in water\cite{22,43,44}. The following equation was used to calculate the rate constant (min\textsuperscript{-1}) for the photocatalytic reactions

\[ \ln \frac{C}{C_0} = -Kt \] (2)

Here, \(C\) and \(C_0\) (mg L\textsuperscript{-1}) are the instantaneous and initial concentration of ANT. \(K\) stands for pseudo-first-order rate constant (min\textsuperscript{-1}), and \(t\) is the time of irradiation (min). Calculated rate constant values (Figure S6, Supporting Information) for the photocatalytic reactions are found to be 0.0037 (TiO\textsubscript{2}-MS), 0.0103 (DT3), 0.0130 (DT5), and 0.0065 (DT8) min\textsuperscript{-1}. Thus, rate constant for DT5 sample (0.013 min\textsuperscript{-1}) was found to be significantly higher compared to other samples, \(\approx\)3.8 times of TiO\textsubscript{2}-MS.

The photocatalyst loading is one of the critical parameters which affects the overall photocatalytic activity. To optimize the photocatalytic performance, a comparative study was carried out with different catalyst loading (3, 5, 7, and 9 g L\textsuperscript{-1}) of DT5 photocatalyst, keeping others parameters constant. The reason behind the selection of DT5 photocatalyst is that it exhibits best photocatalytic performance among all the photocatalyst. Photocatalytic activity for different loading concentrations is shown in Figure 7b. It was observed that loading of 5 g L\textsuperscript{-1} for the catalyst showed the best photocatalytic performance. Lower photocatalytic activity for 3 g L\textsuperscript{-1} demonstrated that the

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### Table 1

| Sample name | Ti\textsuperscript{3+/Ti4+} |
|-------------|--------------------------|
| TiO\textsubscript{2}-MS | 0.096 |
| DT3         | 0.103 |
| DT5         | 0.127 |
| DT8         | 0.342 |

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Figure 4. High-resolution XPS spectra of Ti 2p for a) TiO\textsubscript{2}-MS, b) DT3, c) DT5, and d) DT8 samples.
loading of the photocatalyst is too low to provide enough surface area for the photocatalysis. On the other hand, inefficient photocatalytic activity for higher loading photocatalyst (7 and 9 g L$^{-1}$) attributed to scattering of light and agglomeration of photocatalyst particles.\cite{45} The photodegradation mechanism was illustrated by carrying out the photocatalytic reaction in the presence of different ROS scavengers to investigate the role of ROS for the degradation of ANT. It is reported that during photocatalysis, various ROS are generated, i.e., h$^+$, e$^-$, hydroxyl radical (OH$^-$), and superoxide radical (O$_2^-$), which are mainly accountable for the photodegradation of organic compounds.\cite{46} Here, we have used isopropanol (IPA) (ROS: hydroxyl radical), ascorbic acid (ROS: superoxide radical), and ammonium oxalate (AO) (ROS: hole and hydroxyl radical) as the ROS scavengers in order

![Figure 5. High-resolution XPS spectra of O 1s for a) TiO$_2$-MS, b) DT3, c) DT5, and (d) DT8 samples.](image)

![Figure 6. a) UV–vis absorption spectra, and b) Tauc plots for TiO$_2$-MS, DT3, DT5, and DT8 samples.](image)
to illustrate the role of ROS during photocatalytic degradation of ANT. The effect of such scavengers on the photocatalytic activity is shown in Figure 7c. Significant retardation of photocatalytic activity was observed after addition of IPA, AO, and ascorbic acid. These results demonstrate that holes (h\(^+\)), hydroxyl radicals (OH\(^-\)), and superoxide radical ion (O\(_2\)\(^-\)) play a predominant role in the photocatalytic degradation of ANT. Stability and durability of the photocatalyst play a key role for real-life application of the photocatalyst. Therefore, recycling experiment was carried out in order to investigate the photocatalytic performance of DT5 sample for repetitive cycles. Figure 7d shows the photocatalytic activity of DT5 sample for consecutive five cycles. The results indicate that photocatalytic activity does not change even after fifth cycles. Excellent performance of the photocatalyst for each consecutive cycle throughout the experiment implies that the photocatalyst is highly stable and did not show any sign of photocorrosion during the degradation of ANT. During photocatalytic reaction, ROS helps to oxidize ANT into smaller molecules and further completely mineralizes it into CO\(_2\) and H\(_2\)O. A comparison of performance for various photocatalysts for the degradation of ANT is shown in Table 2.

The literature related to mechanism for the degradation of ANT using photocatalyst is limited. The intermediates during photocatalytic degradation of ANT were identified using LC–MS technique (Figure S7, Supporting Information) and the observed m/z ratios were matched with the previous literature of ANT degradation. The peak at m/z = 204.8 is proposed to be due to the addition of hydroxyl groups in the structure of ANT. There are three possible structures (A1, A2, and A3) for monohydroxylated ANT, as shown in Figure 8. The two hydroxylated compounds (A2 and A3) oxidize to form aldehyde group (m/z = 203) represented as A6 and A7. A1 undergoes pyrazole ring opening to form A5 at m/z = 220.2, which further breaks to form A9 due to oxamoyl chain loss, giving the peak at m/z = 164.8. The peak at m/z = 112.6 corresponds to dephenylation from ANT to form A4. A4 further oxidizes to give A8.
which has a peak at $m/z = 144.8$. Eventually, smaller organic compounds mineralize into inorganic molecules, i.e., CO$_2$, H$_2$O, NH$_4^+$, NO$_3^-$, and NO$_2^-$.

Schematic for the degradation of ANT using defective TiO$_2$ is shown in Scheme 1. Inefficient photocatalytic activity for TiO$_2$-MS under visible light illumination is correlated from weak absorption of visible light of the solar spectrum and poor charge carrier separation. However, improvement in visible light absorption and efficient electron and hole separation after defect formation within TiO$_2$ (DT3, DT5, and DT8) resulted in a significant enhancement in the photocatalytic activity. Improvement in photocatalytic activity can be correlated from the creation of defects within TiO$_2$, where successful reduction Ti$^{4+}$ to Ti$^{3+}$ takes place by NaBH$_4$. This leads to the efficient extraction of an electron by diminishing electron–hole separation, where Ti$^{3+}$ acts as a charge carrier center within TiO$_2$ lattice. Therefore, efficient generation ROS via hole of the valence band (VB) and electron in the conduction band (CB) predominantly

**Table 2.** A comparative study of the photocatalytic degradation of ANT using different photocatalysts.

| Photocatalyst                          | Light source | Initial pollutant concentration [mg L$^{-1}$] | Irradiation time [min] | Degradation efficiency [%] | References |
|---------------------------------------|--------------|---------------------------------------------|-------------------------|-----------------------------|------------|
| H$_2$O$_2$/TiO$_2$                     | UV           | 50                                          | 120                     | 100                         | [15]       |
| CoFe$_2$O$_4$/TiO$_2$                  | UV           | 0.1                                         | 50                      | >99                         | [53]       |
| TiO$_2$/ZnO/clay                       | Solar        | 15                                          | 600                     | 70                          | [9]        |
| Zn-doped TiO$_2$/clay                  | Solar        | 10                                          | 360                     | 90                          | [54]       |
| ZnO-TiO$_2$/delaminated montmorillonite coated with Ag | Solar       | 5                                           | 360                     | 95                          | [55]       |
| Fe$_2$O$_3$@BC/ACF                      | Visible      | 10                                          | 480                     | 100                         | [7]        |
| Defective-TiO$_2$                      | Visible      | 10                                          | 240                     | 100                         | Our work   |

**Figure 8.** Proposed photocatalytic degradation mechanism for ANT.
degrade the ANT under visible light illumination. Best photocatalytic activity for DT5 sample is due to efficient charge carrier separation and improved visible light absorption. On the other hand, weak photocatalytic activity for DT3 is ascribed from inefficient defect by Ti$^{3+}$ on the surface of TiO$_2$. On the other hand, an excess defect within DT8 resulted in creation of more Ti$^{2+}$ within the crystal lattice of TiO$_2$, which facilitates more internal recombination between electron and hole pair. This leads to reduction in ROS production, which is responsible for an inefficient photocatalytic activity for DT8.

For practical wastewater treatment application, we have coated defective TiO$_2$ (DT5) on glass beads to immobilize the particles, and these coated beads were used in the continuous reactor. Figure 9a shows the SEM images of defected TiO$_2$ (DT5) over glass beads. Uniform distribution of DT5 over glass beads was observed with average size \( \approx 3 \mu m \). These coated glass beads were charged in the prototype reactor for investigation of their photocatalytic performance in the dynamic flow conditions. Figure S8, Supporting Information, illustrates the reactor setup for the continuous experiment. After flushing DI water, 2 ppm ANT solution was flown through the reactor at the same flow rate for 2 h to achieve the steady-state and adsorption equilibrium. After 2 h of continuous flow, the outlet concentration was found to be the same as the inlet concentration confirming the adsorption–desorption equilibrium, and 400 mL of 2 ppm ANT solution was taken for the photocatalytic degradation reaction. The reaction was conducted in complete recycle mode. The lamps were switched ON to start the degradation reaction and readings were taken at regular intervals of 30 min. Figure 9b shows the degradation of ANT under visible light illumination. No degradation of ANT was observed in the absence of catalyst confirming no photolysis or any effect form the reactor setup. Almost complete degradation was achieved after 10 h of continuous irradiation. Excellent photocatalytic activity by defective TiO$_2$ in continuous operation demonstrates superiority of the photocatalyst for detoxifying wastewater effluents. Stability of the photocatalyst during photocatalysis is very important as leaching of catalyst into water causes secondary contamination. In our reactor system, no leaching of TiO$_2$ in the water was observed (Figure 9c). This confirms that there is no possibility of the secondary pollution in water via usage of the photocatalyst. There are very few studies where development of prototype reactor is reported for actual treatment of wastewater. Our developed reactor is highly efficient compared to earlier reported due to its low cost, easy operation under visible light, and ability to degrade emerging pollutants under continuous operation.

4. Conclusions

In this work, we have successfully synthesized TiO$_2$-MS via a facile hydrothermal approach. Defect state modulation of TiO$_2$-MS using NaBH$_4$ improved visible light absorption to the different extents via variation of the reduction time. The as-synthesized defective TiO$_2$ (DT3, DT5, and DT8) exhibited improved visible light photocatalytic activity toward the degradation of ANT in comparison to TiO$_2$ without defects. Excellent photocatalytic activity by DT5 toward the degradation of ANT was ascribed due to enhanced visible light absorption and improved charge carrier separation because of Ti$^{3+}$ acting as a trap state and thus facilitating electron–hole separation. The lower extent of defect in DT3 leads to inefficient charge carrier separation, which resulted in poor photocatalytic activity. The best photocatalytic activity for DT5 was correlated with the enhancement of bulk defect compared to the surface because of Ti$^{3+}$, where Ti$^{3+}$ acts as a recombination center and thereby reducing the charge carrier recombination. Excellent recyclability indicates applicability of DT5 for wastewater treatment applications. Further increase in defects within the TiO$_2$ crystal lattice facilitated charge carrier recombination, which resulted in decrease in photocatalytic activity (DT8). For practical applications, we further developed a continuous reactor, where we immobilized DT5 over glass spheres. Developed prototype reactor demonstrated efficient visible photocatalytic degradation of ANT under continuous operation. Therefore, developed photocatalysts are promising for real-world wastewater treatment applications in near future.
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

antipyrine, defects, photocatalysts, TiO₂, visible light illumination, wastewater remediation

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