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Photocatalytic and Antibacterial Potency of Titanium Dioxide Nanoparticles: A Cost-Effective and Environmentally Friendly Media for Treatment of Air and Wastewater

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Abstract: Titanium dioxide nanoparticles (TiO₂-NPs) were synthesized via a facile hydrothermal method. X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM), X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared (FTIR), and Raman spectroscopy were used to study the structure, morphology, chemical composition, and functional group attached to the as-synthesized TiO₂-NPs. These NPs were then used to test their efficacy against various microbes and their potency as effective catalysts. TiO₂-NPs are found to have the maximum antibacterial activity against Gram-negative bacterial strains rather than Gram-positive bacteria. The photocatalytic activity of the TiO₂-NPs was investigated for the photodegradation of 10 ppm bromophenol blue (BPB) dye by using 0.01 g–0.05 g of catalyst. TiO₂-NPs exhibited the removal of 95% BPB, respectively, within 180 min. The TiO₂-NPs' antibacterial and catalytic properties suggest that these may be used in environmental remediation as a cost-effective and environmentally friendly wastewater and air treatment material.

Keywords: nanoparticles; titanium dioxide; photocatalyst; antibacterial; water treatment

1. Introduction

Titanium dioxide (TiO₂) nanoparticles (NPs) are among the most widely used engineered nanostructures of TiO₂. Most of the TiO₂ applications are due to their structural and electronic properties. These mainly consist of three phases which include anatase, rutile, and brookite [1]. Due to its greater photocatalytic activity [2], anatase has the highest number of industrial applications compared to rutile and brookite [3]. At the beginning of the twentieth century, the mass production of TiO₂-NPs started as a non-toxic substitute for a white dye used in paints. It has various applications as a white pigment in manufacturing plastics, paper, ink, paints, and as a coating material for welding rods. Ultrafine TiO₂-NPs [4] are widely used in other industrial products, such as cosmetics, toothpaste, pharmaceuticals, and skincare products [3,5–7].

TiO₂-NPs constitute a semiconductor (n-type) with a wide-band gap having various applications in wastewater treatments dye-sensitized solar cells, photoionized devices, and lithium batteries [8]. TiO₂-NPs have specific medicinal properties and have been used in

many biomedical applications such as artificial hips, dental implants, bone plates, coatings, scaffolds, and also in gene and drug delivery systems [9,10]. Interest in the synthesis of TiO₂-NPs and their applications are due to their biocompatibility [5,11] antimicrobial properties [8,12–14], high chemical stability, specific surface area, and catalytic activity [15]. Due to the wide range of applications, TiO₂-NPs have considerable potential for human exposure. People can be exposed to these nanoparticles through oral, respiratory, or dermal routes. TiO₂-NPs have been used in the food industry since 1996 when the US Food and Drug Administration approved it as a food supplement [16–19]. TiO₂-NPs are also used as nanocarriers for drug delivery [20] and as a nano-drug for treating diseases [21].

Materials containing TiO₂ are widely used for water purification as photocatalysts [15,22,23]. Particularly, these oxides materials are used for the degradation of dyes including methyl orange [24,25], methylene blue [26], rhodamine 6G, rhodamine B (RhB) [27–29] etc., and phenolic compounds including nitrophenol [30], chlorophenol 1, 2 [31], phenol [32]. These studies found a connection between the degradation rate and the structural properties of the catalysts, including specific surface area [33,34] and crystallinity [35]. Dlamini et al. [36], used 1 g/L of TiO₂-NPs and reported 85% degradation of BPB dye which is a much higher concentration. Su et al. [37] reported the complete degradation of methyl orange (MO) by using TiO₂ (0.6 g/L) in 420 min. Wang et al. [38], synthesized TiO₂/P3HT and used 450 mL of MO solution with an initial concentration (10 mg/L) and catalyst (0.45 g) for photocatalytic degradation. Moreover, 88.5% of degradation was reported after 10 h of irradiation time.

The purpose of this study was to synthesize TiO₂ using a hydrothermal route and to study its antibacterial and photocatalytic properties for the removal of dye pollutants. Moreover, the factors affecting the photodegradation efficiency, including catalyst concentration, dye concentration, and initial pH were also evaluated. The catalyst was characterized by FESEM, XPS, XRD, Raman, FTIR, and UV-Vis spectroscopy. The results showed that TiO₂ nanoparticles have a higher photocatalytic degradation capacity for BPB dye. These results will provide better guidance to researchers working in the fields of photocatalysis and environmental remediation. In terms of bacteria and dyes, it may be useful in the treatment of polluted water.

2. Results and Discussion

Using a field emission scanning electron microscope (FE-SEM), the morphology of the as-synthesized TiO₂-NPs is examined. Figure 1a,b depict the details obtained concerning the morphology or structure of the TiO₂-NPs at lower and higher magnification. At lower magnification, the TiO₂-NPs appear to be small sphere-like structures (nano-spheres). At higher magnification, almost all the TiO₂-NPs in the micrograph are in the nanometer range. Most of the smaller sized particles are packed close to one another at the bottom. The smaller the particle, the lower it lands, followed by a slightly larger particle, etc. On the other hand, the larger particles at the end appear to be largely separated from one another. Nanoparticles of different sizes (larger and smaller) can be seen and observed in the current micrograph. As a result, the biggest particles are on top, followed by the smallest particles at the bottom of the sample. This result adds to the proof that the TiO₂-NPs were synthesized by using a top-down method. The average particle size, according to the FE-SEM data, is less than 100 nm.

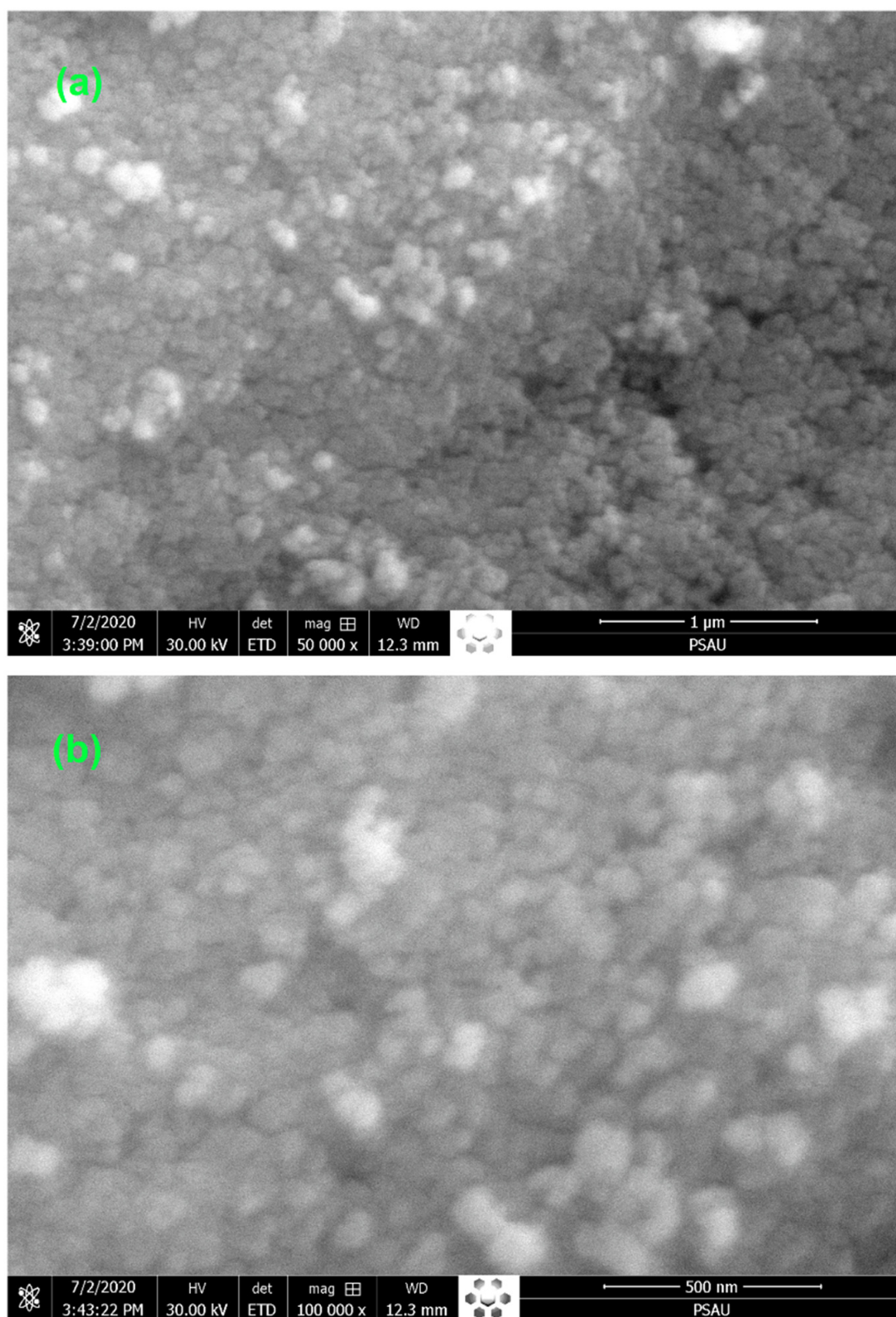


Figure 1. FESEM micrograph of the as-synthesized TiO_2 nanoparticles at (a) lower and (b) higher magnification.

Figure 2 displays the X-ray diffraction pattern of the as-synthesized TiO₂-NPs. It is an analytical technique for determining TiO₂-NPs crystallinity and phase formation. The XRD analysis was carried out at 298 K by using a nickel-filtered Cu radiation source ($K\alpha = 1.5418 \text{ \AA}$) in an X-ray diffractometer. The strength data were collected over a two-degree scale from 10 to 80 degrees. Diffraction peaks were found at 23.17°, 25.71°, 27.92°, 36.57°, 37.53°, 38.32°, 41.71°, 48.52°, 54.46°, 55.51°, 57.09°, 69.30°, 70.71° and 75.48°, respectively. Crystalline TiO₂-NPs phases were identified using the X' Pert High Score by comparing it to the standard data of the JCPDS No. 01-075-1537 (anatase) and 01-082-0514 (rutile). As a result, all of the peaks in the as-synthesized TiO₂ refers to (101), (110), (103), (004), (112), (111), (200), (105), (211), (220), (116), (220) and (202) planes. By using the Debye–Scherrer equation, the crystallite size of the synthesized nanoparticles is calculated. XRD results show that the average crystallite size of (TiO₂-NP) is 15 nm.

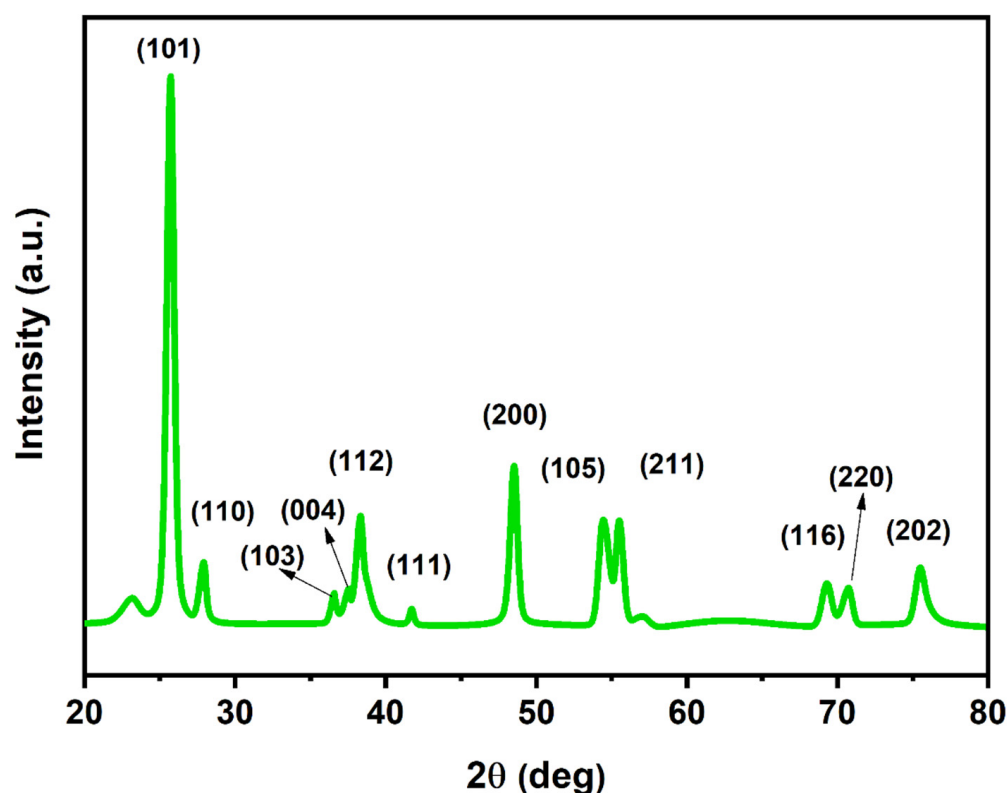


Figure 2. X-ray diffraction pattern shows sharps peaks for the crystalline nature and different phases of the synthesized TiO₂.

X-ray photoelectron spectroscopy (XPS) was used to investigate the bonding properties, valence states, and quantitative study of the electronic structures of the synthesized TiO₂-NPs. The wide Ti 2p and O 1s spectra in the XPS study confirm no other precursor elements or magnetic contamination in the synthesized sample, as shown in Figure 3. The XPS survey in Figure 3a shows the peaks labeled to the respective elements' binding energies. In Figure 3b, two sharp peaks are observed for Ti⁴⁺ in TiO₂, corresponding to the spin-orbit of Ti 2p_{3/2} and Ti 2p_{1/2} at binding energies of 463 and 468 eV, respectively. There is no perceivable peak shift. This demonstrates that Ti atoms have the same oxidation state [39]. Figure 3c shows the magnified O 1s peak. The peak at 533 eV is thought to be caused by bulk oxygen in TiO₂ [40]. In all spectra, the FWHM is nearly the same (1.35 eV).

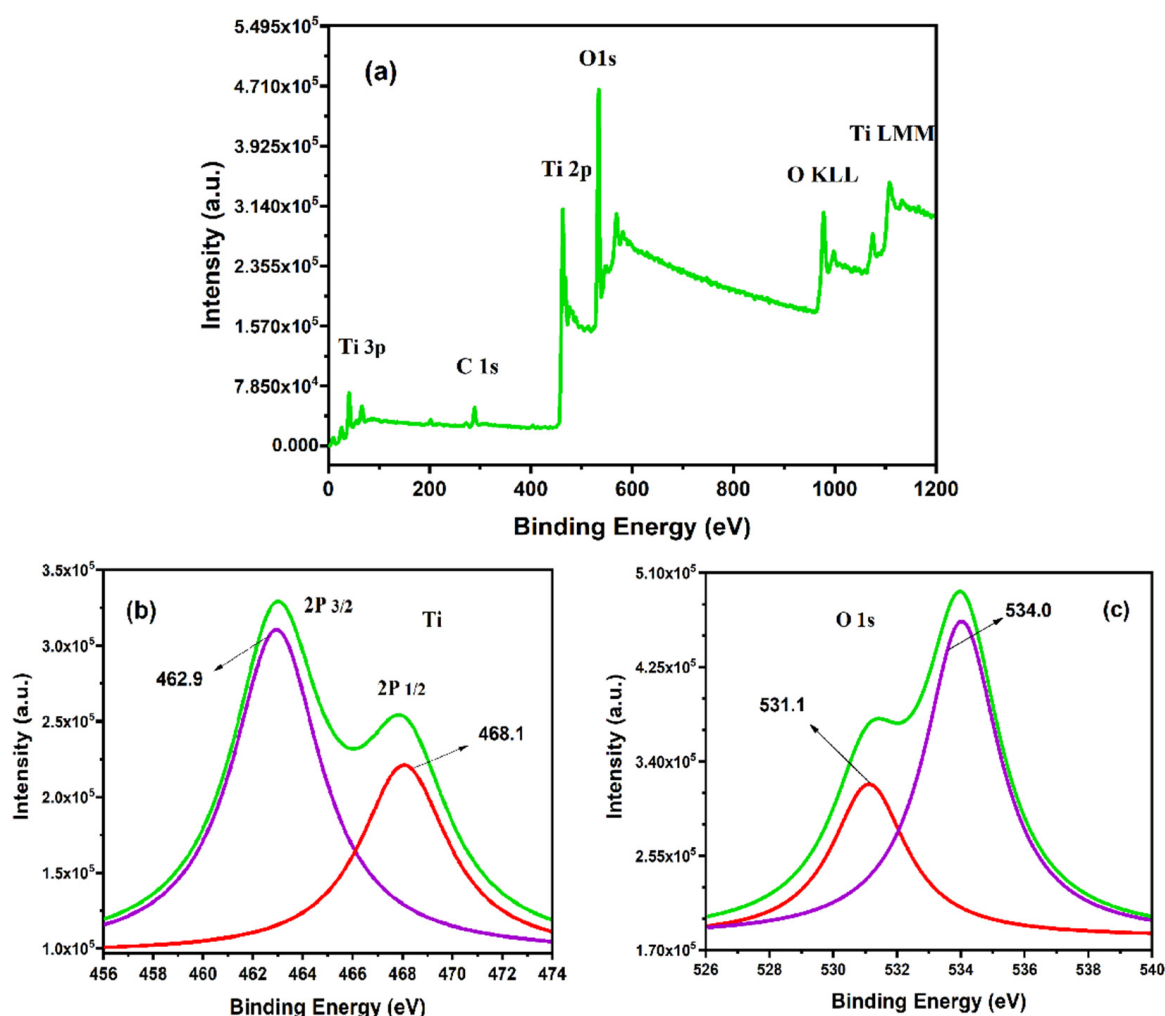


Figure 3. (a) XPS survey of the as-synthesized TiO₂ nanoparticles; (b) high-resolution Ti 2p; and (c) O 1s XPS spectra.

In Figure 3a, escorting to the higher binding energy side of the peak involves many components resulting from TiO₂ surface hydroxylation (when it is mounted, the electrode is exposed to air). These are attributable to both acidic and fundamental hydroxyl groups and absorbed water at the outermost surface. We observe that the O 1s spectrum is similar to those recorded on the untreated (as grown) single crystal of anatase [41] and rutile exposed to vapor and liquid water [42,43].

The chemical elucidation of the synthesized TiO₂-NPs was performed by using the spectrum obtained from FTIR, as shown in Figure 4. The presence of unsettled Ti–O–Ti stretching vibrations could be attributed to a wide band in the 400–900 cm^{−1} range. Furthermore, two bands at 1644 and 3395 cm^{−1} were linked to the O–H group bending and stretching vibrations.

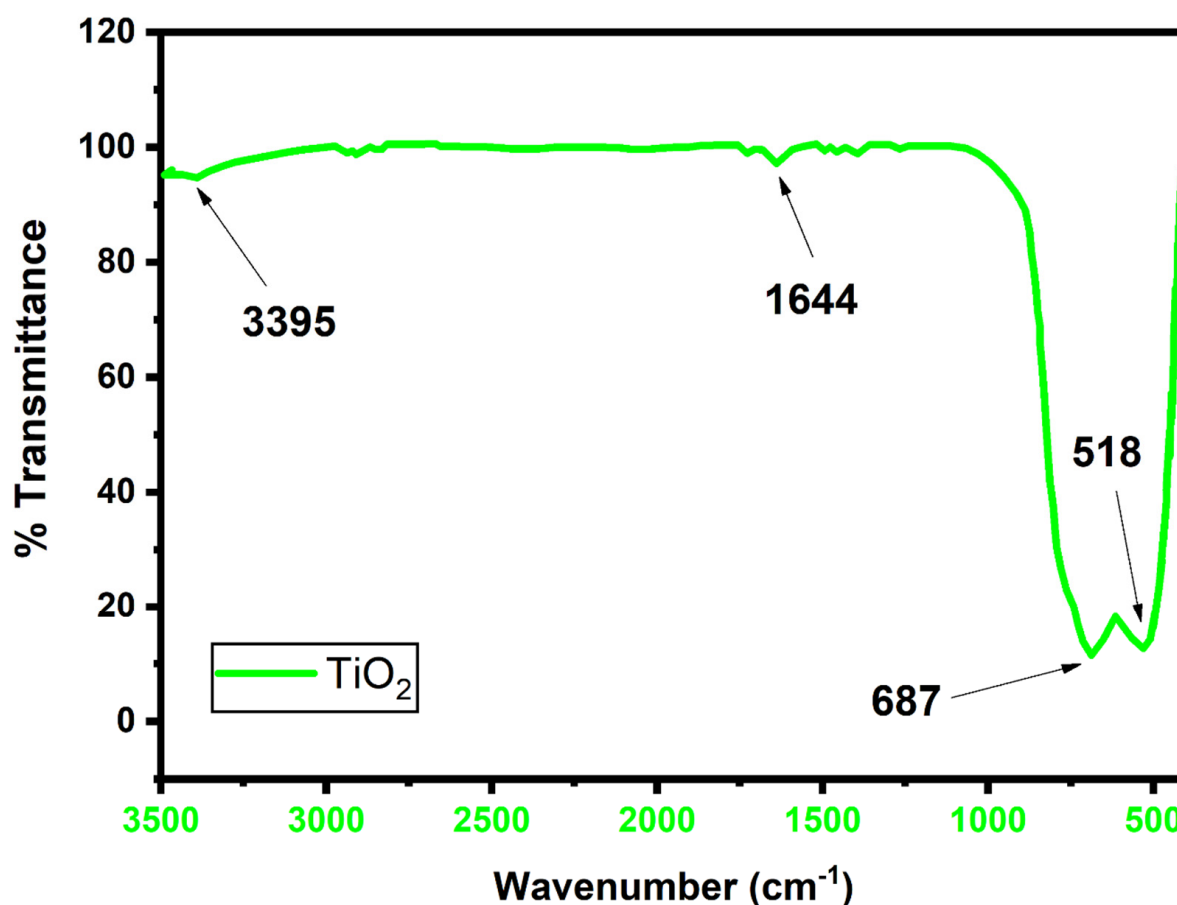


Figure 4. Spectrum obtained from FT-IR analysis of TiO₂-NPs.

The intense and low intensity E_g modes in the Raman spectrum of TiO₂-NPs appearing at 144 and 193 cm^{-1} [44], respectively, are shown in Figure 5. The peaks of B_{1g} , ($A_{1g} + B_{1g}$), and E_g are located at 399, 516, and 637 cm^{-1} , respectively. The symmetric, asymmetric, and bending vibrations of the Ti–O–Ti bond trigger vibrational modes in TiO₂ [45,46]. The peak tagged by E_g represents Ti–O stretching mode, while the peaks at 516 cm^{-1} and 399 cm^{-1} represent Ti–O stretching mode (the only O is moving) and O–Ti–O bending mode (only Ti is moving), respectively [46,47].

The antibacterial susceptibility of synthesized TiO₂-NPs was observed against ATCC bacterial strains. In this study, a total of four bacterial strains; *Pseudomonas aeruginosa* (ATCC[®] 10145), *Escherichia coli* (ATCC[®] 33876), *Klebsiella pneumonia* (ATCC[®] BAA-1144 used as Gram-negative bacteria, while as a Gram-positive bacteria, *Staphylococcus aureus* (ATCC[®] 11632) were used. It has been observed that the strains were sensitive to TiO₂-NPs and inhibit the growth against all doses in tested bacterial strains. Figure 6 showed that with the increase in TiO₂-NPs concentration, the diameter of ZOI also increased. The highest growth inhibition by TiO₂-NPs was observed against *K. pneumoniae* and it was the most sensitive among all the used strains. TiO₂-NPs were observed to inhibit Gram-negative strains more than the Gram-positive strains. Among Gram-negative strains: *P. aeruginosa*, *K. pneumonia*, and *E. coli* formed a ZOI of 15 ± 0.27 , 20 ± 0.21 , and 23 ± 0.19 mm, respectively. Gram-positive strain: *S. aureus* forms a 19 ± 0.14 mm of ZOI for all the doses as shown in Table 1. This suggests that the TiO₂-NPs can be used to tackle resistance against drugs among bacteria in clinical as well as environmental applications. TiO₂-NPs have been shown to prevent or destroy bacterial cells by adhering to the cell wall, causing the leakage and damage of intracellular contents, hydroxyl radicals, the generation of reactive oxygen species, and the release of Ti^{4+} ions [48–50]. In comparison with the published literature, our results show better antibacterial potency against selected microbial strains [51–56].

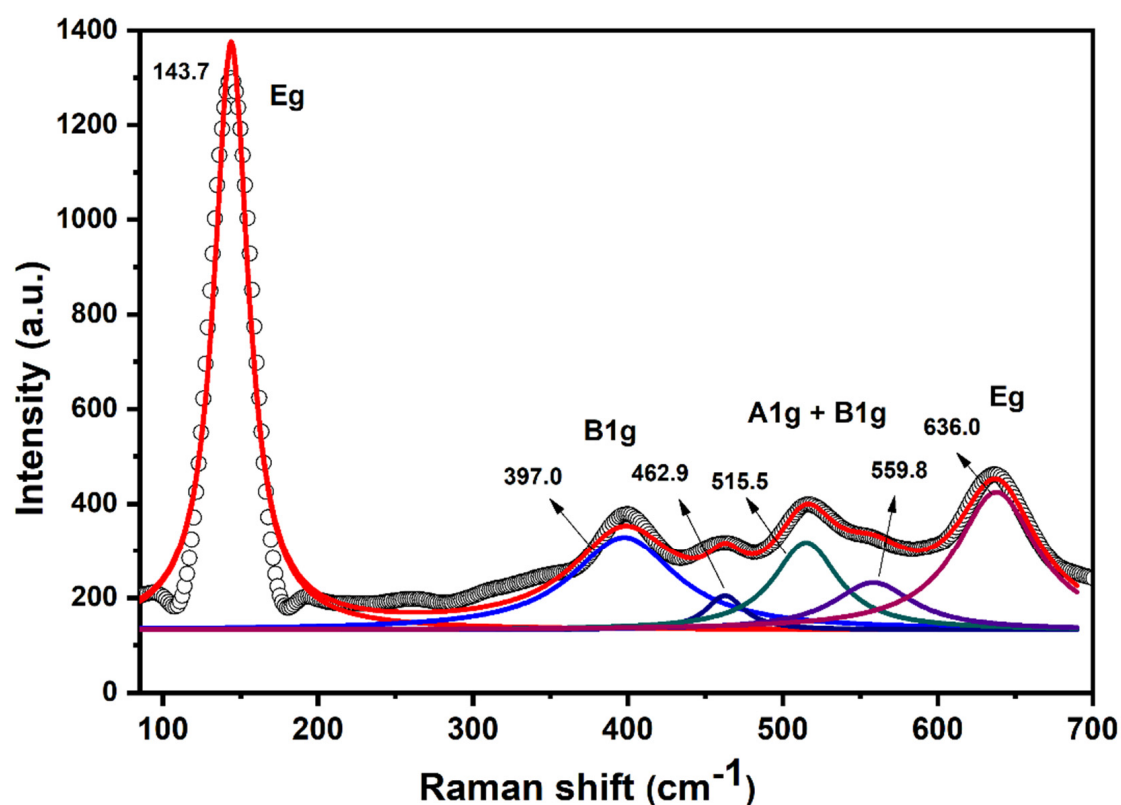


Figure 5. Raman spectroscopy of Titanium dioxide nanoparticles shows the intense and low intense E_g modes appear at 144, 193 cm^{-1} .

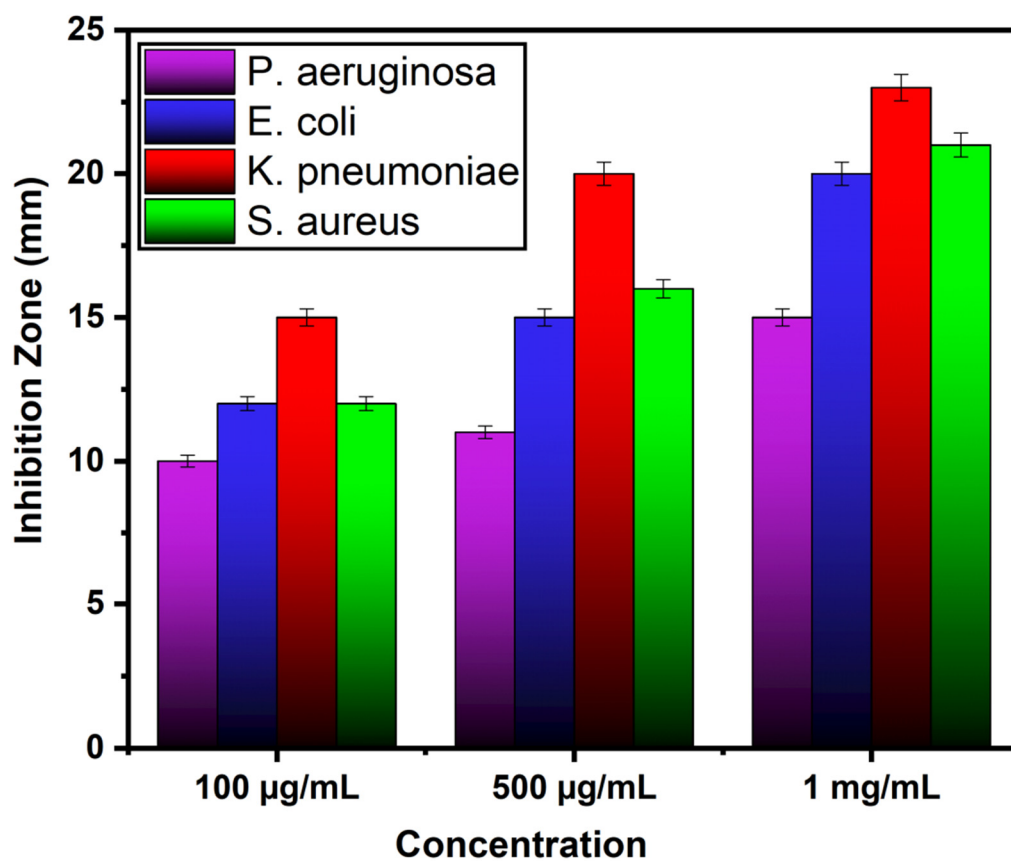


Figure 6. Bar graph showing the diameter of the zone of inhibition (in mm) produced by pure TiO_2 NPs.

Table 1. The table summarizes the experimental parameters and detail of the bacteria.

Bacteria		TiO ₂		
		100 µg/mL	500 µg/mL	1 mg/mL
Gram negative	<i>P. aeruginosa</i>	10 ± 0.19	11 ± 0.22	15 ± 0.27
	<i>E. coli</i>	12 ± 0.11	15 ± 0.13	20 ± 0.21
	<i>K. pneumoniae</i>	15 ± 0.16	20 ± 0.18	23 ± 0.19
Gram positive	<i>S. aureus</i>	12 ± 0.14	16 ± 0.12	19 ± 0.14

The bromophenol blue (BPB) degradation by TiO₂-NPs in ultraviolet (UV) light with respect to time is shown in Figure 7a. From the relative intensity of absorption spectra (UV-Visible), the dye degradation was calculated. In the current work, the BPB shows an absorbance peak at 591 nm and is found to be inversely proportional to UV irradiation time. This proposes that with an increase in irradiation time, the degradation of dye was enhanced. The percentage (%) degradation of BPB is shown in Figure 7b, where a sluggish increment is observed in % degradation and the amount of dye degraded within 180 min was found to be 84 ± 3%. The proposed photodegradation mechanism of organic dye by TiO₂ consists of the fact that TiO₂ is initially photoexcited for the generation of electrons in the conduction band and holes in the valence band. An advanced electron creates a hole (+ive), which can respond to water, causing the formation of hydroxyl radicals. These radicals are responsible for the degradation in dyes and are known as a strong oxidizing agent [36,57]. It is also possible that the reduction in dissolved oxygen by photogenerated electrons results in the formation of the superoxide anion radical. These anion radicals are also a powerful oxidizing agent, capable of attacking any absorbed organic molecules or molecule situated near the catalyst's surface, resulting in the degradation of organic dye molecules [58].

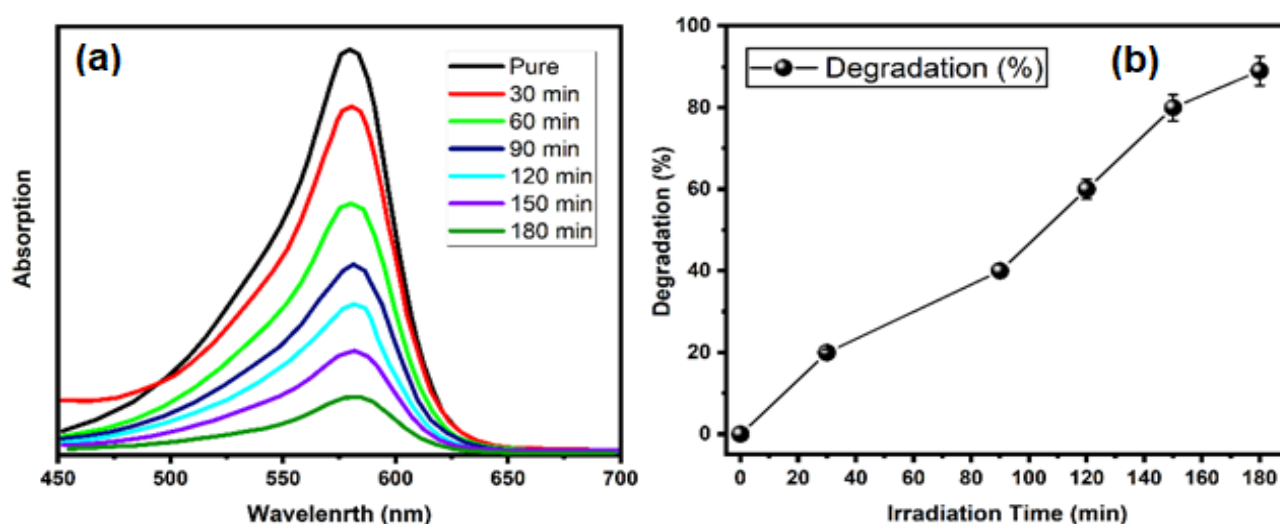


Figure 7. (a) Absorption spectra (UV-Vis) of photodegraded bromophenol blue by TiO₂ and, (b) their % degradation at various time intervals.

Textile industries waste contains dye with various different pH. It is therefore necessary to investigate role of pH in dye degradation. pH has an important role not only in the size of catalyst aggregates, the formation of hydroxyl radicals, and the influencing features of textile wastes, but also affects the position of conduction, valence bands and charge on the catalyst [57,59]. The pH study of TiO₂ at various pH (4, 6, 8, 10) was carried out with a constant dye concentration (10 ppm) for 180 min (irradiation time). Solution pH was controlled by adding NaOH and HNO₃. The effect of pH on BPB degradation is

shown in Figure 8, which shows a direct variation of solution pH with dye degradation. Results showed that at pH 4, around 70% of the dye decomposed. When solution pH changes to higher values, an increase in the BPB decomposition is observed, i.e., 80%, 85%, and 95% for the pH values 6, 8, and 10, respectively. The formation of hydroxyl radicals might be causing the high degradation of BPB dye. Similarly, when using TiO_2 and ZnO as photocatalysts, it was previously found that the discoloration/degradation of Reactive Black 5 and Reactive Orange 4 dye increased with increasing pH [60].

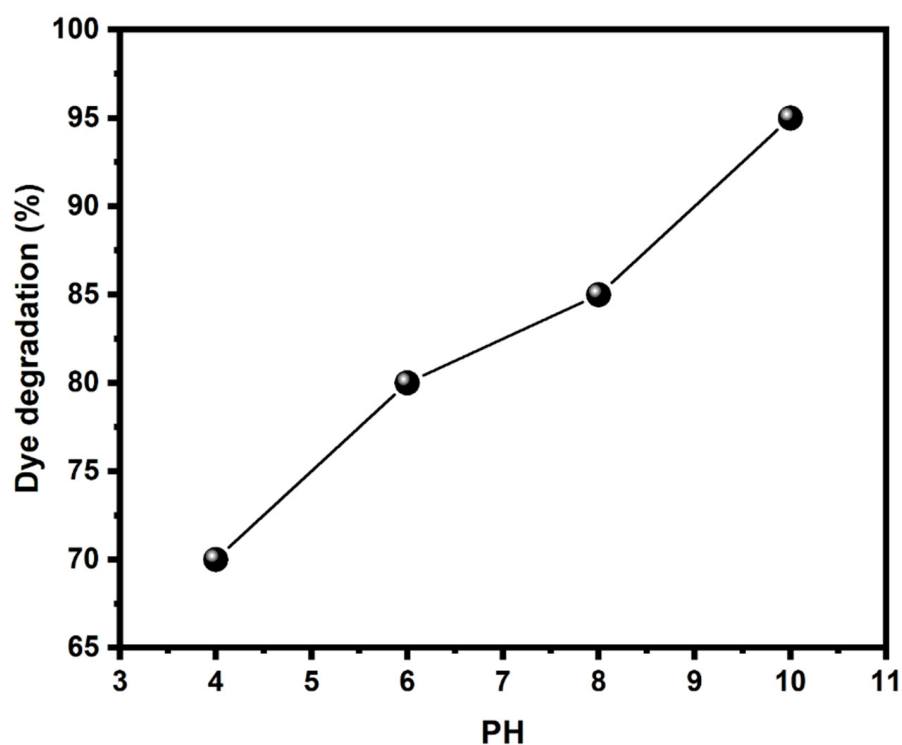


Figure 8. Effect of PH on degradation bromophenol blue.

The effect of the amount of catalyst has also been investigated by using various quantities of catalysts (0.01 g, 0.02 g and 0.05 g). The absorption spectra of BPB in aqueous solution using various concentrations of catalysts (TiO_2 -NPs) before and after degradation is shown in Figure 9a. From the spectra, it is observed that the photodegradation of BPB increases with the increase in catalyst concentration. An increase in active sites might be a reason for the enhancement of degradation due to an increase in the amount of catalyst. Due to this increase, the number of superoxides and hydroxyl radicals increases, which results in the degradation of dye. The % degradation of BPB dye by using various concentrations of catalyst is shown in Figure 9b, which shows that 0.01 g, 0.02 g, and 0.05 g of TiO_2 -NPs (catalyst) degraded 30%, 55%, and 75% in 180 min (3 h), respectively. The variation in photodegradation was also observed due to the variation in dye (BPB) concentration. Different concentrations (10, 20, 50, 75 and 100 ppm) of BPB were used and 85%, 70%, 55%, 40%, 30%, respectively, were decomposed with a constant amount of catalyst (0.05 g). It was observed that the rate of degradation decreased as the concentration of BPB increased as shown in Figure 10. This might be due to the absorbance of dye molecules on the catalyst surface, which absorbs UV light instead of catalyst (TiO_2). This also reduces the formation of hydroxyl radicals by blocking the active sites of photocatalysts with dye molecules [61]. In comparison with the published literature, our result shows better catalytic activity in terms of pH, time, dye concentration, catalyst concentration and will be a potential candidate for the wastewater and air treatment materials [54,62–66].

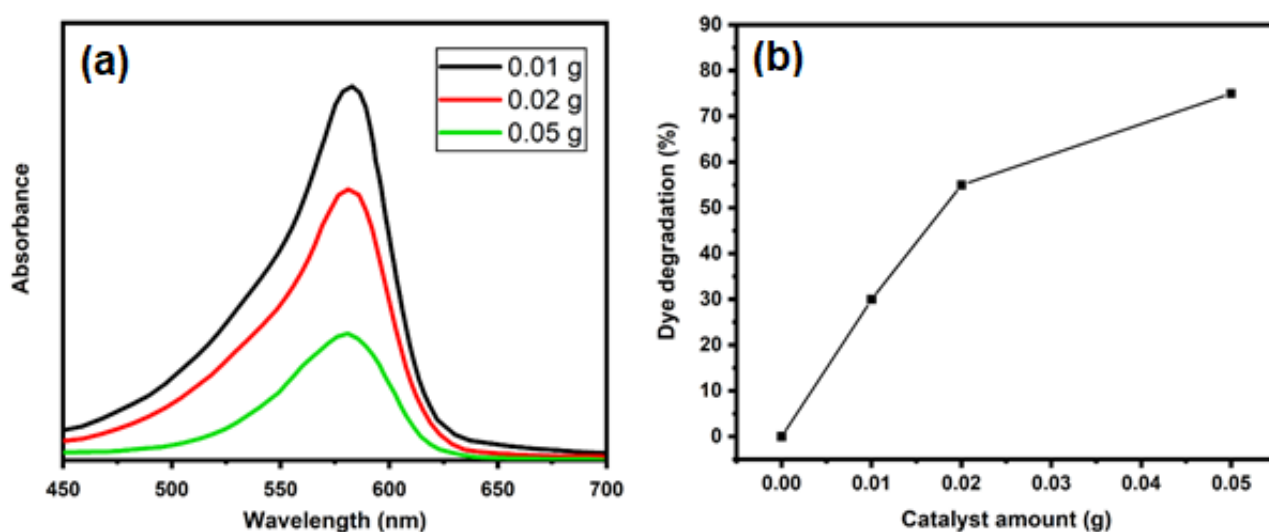


Figure 9. (a) Absorption spectra (UV-Vis) of photodegraded bromophenol blue by various concentrations of TiO_2 and, (b) their % degradation at various catalyst amounts.

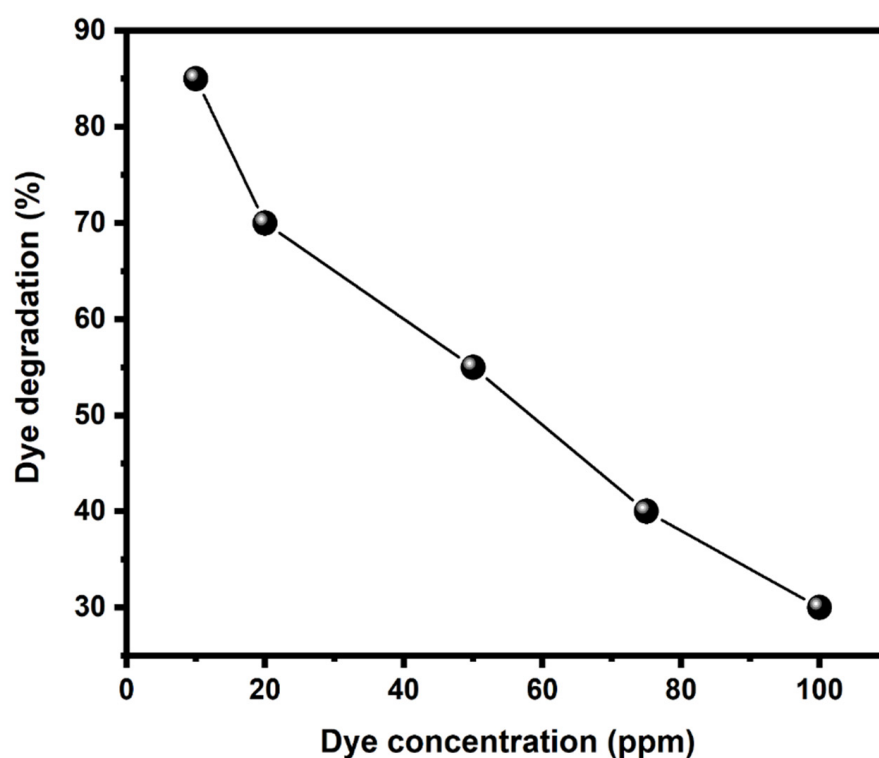


Figure 10. Effect of dye concentration on degradation (%) by TiO_2 .

3. Materials and Methods

3.1. Sample Preparation

Industrial titanium dioxide PC500 (in a total amount of 2.8 g; purchased from Sigma Aldrich, New York, NY USA) was used to synthesize TiO_2 -NPs. The bulk TiO_2 was vigorously mixed with 100 mL sodium hydroxide (from a 0.5 M aqueous solution) at room temperature for 1 h. After that, the homogenous mixture was mounted in an autoclave (Teflon-lined; purchased from HighTech, Islamabad, Pakistan) and heated at 150 °C for 15 h. The precipitate was then washed many times with deionized water and ethanol. Afterward, it was dried in the oven at 120 °C.

3.2. Characterization

X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared (FTIR), UV-Visible (UV-Vis) spectroscopy, and Raman spectroscopy were used for the characterization of the as-synthesized material. A Bruker D8 (Berlin, Germany), JSM 7600F, JEOL (Tokyo, Japan), Kratos Axis Ultra DLD apparatus (Manchester, UK), Shimadzu model IRAffinity-1S (Shimadzu Corporation, Kyoto, Japan), Jenway 6300 UV-Visible spectrophotometer (Jenway 6300, Staffordshire, UK), and Dispersive Micro Raman System (In via, Renishaw, Wotton-under-Edge, UK) were used for XRD analysis, FESEM analysis, XPS analysis, UV-Vis analysis and Raman analysis, respectively.

3.3. Antibacterial Activity of Synthesized TiO_2 -NPs

The antibacterial efficacy of as-synthesized TiO_2 -NPs was investigated by the adapted broth culture method [12], separately against various clinical bacterial isolates sub-cultured from their pure cultures. The fresh cultures were used and incubated for 24 h at 37 °C after transferring the stock solution on nutrient agar. Bacterial isolate cultures containing 1.5×10^8 CFU/mL (0.5 McFarland) bacteria. Various concentrations (0.1, 0.5, 1 mg/mL) of TiO_2 -NPs were prepared. A 40 μL concentration from the prepared solution was transferred to each well (4 mm). After the overnight incubation at 37 °C, the zone of inhibition (ZOI) was measured around each well in millimeters. The control (ciprofloxacin) was used as a standard and was not exposed to the nanoparticles. The mean value was been reported and carried out in triplicate.

3.4. Catalytic Activity of TiO_2 -NPs

The dye-degrading abilities of the TiO_2 -NPs were studied separately by using bromophenol under UV irradiation using OSRAM UV lamp. Four OSRAM UV lamps with a wavelength of 254 nm were used in the FL-PhR. (Puritec Germicidal lamp HNS 8 W G5, made in Rome, Italy). Each lamp had a power of 8 watts, for a total of 32 watts. Moreover, 0.05 g of TiO_2 -NPs as a catalyst was poured in 10 mL of 10 ppm solution of bromophenol (BPB). The solution was exposed to UV light on a rotary shaker (100 rpm) for 3 h (180 min) at room temperature. UV spectrophotometer was used to analyze the absorption behavior and degradation rate.

4. Conclusions

TiO_2 -NPs were synthesized by using a simple hydrothermal method. FE-SEM, XRD, XPS, RAMAN, FT-IR, and UV-Vis spectroscopy was used to study the morphology, structure, chemical composition, functional groups attached, and photocatalytic properties of TiO_2 -NPs. The synthesized NPs have excellent antimicrobial activity against the tested microbes and open the doors for the formation of a different type of antibacterial activity content. The results show that 95% of BPB (dye) was degraded within 180 min and the degradation rates at pH 4, 6, 8, 10 were 70%, 80%, 85%, and 95%, respectively. This suggests that for THE rapid photodegradation of BPB, high pH is congenial. According to the catalyst concentration analysis, 30% dye was degraded by 0.01 g of catalyst (TiO_2), which increased up to 84% by 0.05 g. The excessive active sites may be responsible for the increased degradation with an increase in catalyst amount. As a result, the number of superoxides and hydroxyl radicals increases led to the significant photodegradation of dye. The antibacterial and catalytic properties of TiO_2 suggest that it can be used in wastewater and air treatment materials that are cost-effective and environmentally friendly.

Author Contributions: Conceptualization, Z.R., A.K. (Awais Khalid), P.A., M.F., A.S., I.U.R. and S.S.; data curation, Z.R., A.K. (Awais Khalid), P.A., M.U.K. and A.K. (Ajmal Khan); formal analysis, Z.R., A.K. (Awais Khalid), P.A., M.U.K., A.S., S.S. and A.K. (Ajmal Khan); funding acquisition, P.A. and A.S.; investigation, Z.R., A.K. (Awais Khalid), P.A., M.F., M.U.K. and I.U.R.; methodology, Z.R., A.K. (Awais Khalid), P.A., A.S., I.U.R. and A.K. (Ajmal Khan); project administration, P.A. and A.S.; resources, P.A., M.F., M.U.K. and A.K. (Ajmal Khan); software, M.F., M.U.K., I.U.R. and S.S.;

supervision, P.A. and M.F.; validation, Z.R., A.K. (Awais Khalid), P.A., M.U.K., A.S., S.S. and A.K. (Ajmal Khan); visualization, P.A., M.U.K. and A.S.; writing—original draft, Z.R., A.K. (Awais Khalid) and P.A.; writing—review and editing, Z.R., A.K. (Awais Khalid), P.A., M.F., M.U.K., A.S., I.U.R., S.S. and A.K. (Ajmal Khan). All authors have read and agreed to the published version of the manuscript.

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