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*Review Article*

# Use of Different Natural Products to Control Growth of Titanium Oxide Nanoparticles in Green Solvent Emulsion, Characterization, and Their Photocatalytic Application

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Water, one of the crucial and the pillar resources to every living thing, could be polluted day to day by different causes such as expansion in industrialization, rapid increment in population size, the threat of climate, and growth of urbanization. The existence of a number of organic dyes, detergents, and pesticides from industrial effluents could lead to severe diseases and even to the death of human beings. Currently, remediation of those hazardous organic contaminants using semiconductor metal oxide catalysts has received extensive attention in recent years. Among the numerous nanometal oxides, titanium oxide ($TiO_2$) nanoparticles (NPs) have been well known as a significant photocatalytic material due to their suitable physiochemical behaviors such as stability, conductivity, high surface area to volume ratio, structure, and porosity nature at the nanoscale level. $TiO_2$ semiconductor nanoparticles could be synthesized via several physiochemical approaches; among those, the biogenic technique is the most selective one which involves the synthesis of NPs using different templates. Biogenic synthesis of nanoparticles is an environmentally friendly protocol that involves the use of different parts and types of biogenic sources such as bacteria, fungi, yeast, virus, and green plants or the byproducts of their metabolism, which act as both reducing and stabilizing agents. $TiO_2$ NPs obtained via the biogenic method provide a potential application for the degradation of organic dyes and other pollutants in wastewater. This method of synthesis of NPs has been given a great attention by researchers due to their nontoxicity, low cost, environmental friendliness, the usage of green solvents, and simplicity of the process. This review focuses on summarizing the synthesis of $TiO_2$ NPs using various biogenic sources, characterization, and their photocatalytic applications for the degradation of different wastes and organic dyes from polluted water.

## 1. Introduction

In the past decade, there has been a marked increase in the field of synthesis of various nanoparticles such as metallic, metal oxide, nanocomposite, and decorated nanoparticles with controlled morphologies and remarkable features, making them an extensive area of research. The possibility of synthesizing NPs with controlled particle size, shape, and crystalline nature enables NPs to be used for various potential applications, such as degradation of organic pollutants in wastewater, biomedical, biosensor, catalyst for bacterial biotoxin elimination, and for the photoanode in dye-sensitized solar cells (DSSCs) [1–3]. Among the various adapted techniques for the synthesis of nanoparticles, biogenic synthesis of nanoparticles is an environmentally friendly protocol that involves the use of different parts and types of biogenic natural sources such as bacteria (intracellular and extracellular), fungi, yeast, virus, and different parts of green plants (flower, stem, root, leaf, and fruit) or the byproducts of their metabolism, which act as both reducing and stabilizing agents to prevent the overall growth of nanoparticles during their synthesis process. Moreover, metal oxide nanoparticles such as $TiO_2$ NPs obtained via this biogenic synthesis method, a greener approach synthesis method, are safe, nontoxic, ecofriendly, and achieved with minimum energy [2, 3].

The natural environment suffers serious hazardous problems due to the release of different waste materials to the natural environment such as the accumulation of agricultural fruit and vegetable waste and industrial wastes (organic dyes, pesticides, inorganic contaminants and detergents) and due to the decomposition of toxic and poisonous gases and chemical species produced from chemical industries. Their toxicity and stability to natural decomposition and persistence in the environment have been the cause of much concern to societies and regulation authorities' worldwide. With the rapid development of industrial society and increments in population size, the threat of climate change and increasing environmental-safety threats pose a major concern. Nowadays, water pollution is becoming one of the most serious problems in the environmental fields. Wastewater effluents released from different industries such as textile, rubber, paper, and plastic contain several kinds of synthetic dyestuffs that could result in severe diseases in humans, animals, and plant species too [4, 5].

Previously, a number of different physiochemical techniques were adapted for the treatment of wastewater such as sedimentation-flocculation, coagulation, molecular sieving, ion exchange, reverse osmosis, membrane filtration, ozonation, chlorination, chemical precipitation, adsorption, photocatalysis, chemical methods, and electrochemical techniques, and many others were used to remove toxic organic/inorganic pollutants from polluted water [4–7]. However, a majority of those techniques are not efficient enough and adequate in terms of cost, energy, environmental friendless, and purification capability, and they need expensive and complicated methods and have slow adsorption rate, as well lack complete degradation of contaminants [6]. In addition to this, most organic dyes, detergents, and pesticide compounds ordinarily contain benzene and naphthalene rings that cannot be decomposed easily by conventional physical, biological, and chemical methods. Among these protocols from advanced oxidation processes, heterogeneous photocatalysis assisted by semiconductor nanometal oxides such as $TiO_2$ has been suggested as a design which is simple, operates under ambient conditions, has high stability, and cost effective, energy efficient, and environmentally safe. Also, the methods do not result in the formation of secondary pollution to the natural environment [5–7].

This is due to the fact that metal oxide semiconductor nanomaterials are inexpensive, nontoxic, possess high surface area to volume ratio, exhibiting tunable properties which can be modified by size reduction, doping, sensitizers, and composite form, affording facility for the multielectron transfer process, and capable of extended use without substantial loss of photocatalytic activity [8]. Different metal oxide materials at the nanolevel possess unique biological, optical, magnetic, mechanical, thermal, catalytic, and electrical properties and also due to the fact that as the size of the nanoparticles decreases, the surface area to volume ratio increases, which is suitable for the process of photocatalysis [6–9]. In general, various semiconductor oxide nanoparticles play an important role in various applications (Figure 1) such as self-cleaning, gas sensors, optics, photoelectrochemical devices, solar cell applications, photocatalysis, cosmetic industry, antibacterial activity, antifungal activity, antioxidant activity, and medicinal applications [10].

Among the various metal oxides, titanium dioxide ($TiO_2$) NPs are an inert, nontoxic, and inexpensive material, whose high refractive index and high capability to absorb UV light make it an interesting white pigment and environmentally friendly catalyst. The nanosized $TiO_2$ NPs are widely used to provide whiteness and opacity to products such as sunscreen lotions, paints, plastics, papers, solar cell, medicinal applications, inks, food colorants, and toothpastes. There are various methods to synthesize different metal oxide nanoparticles having various applications. According to research reports, titanium dioxide NPs could be synthesized through chemical vapour deposition [11], microemulsion [12], chemical precipitation [13], and hydrothermal [14, 15], solvothermal [16], sol-gel [17], electrochemical [18], and green [19] methods. Among the mentioned methods, green synthesis of nanomaterials is getting increased attention because of its simplicity, fastness, ecofriendliness, and nontoxic nature, and it involves the use of green solvents such as distilled water and ethanol and an economical approach [1–3]. It involves three important steps during the synthesis process such as solvent medium selection, environmental benign reducing and capping agent selection, and nontoxic substances for nanoparticles stability selection [20–22]. Figure 2 summarizes the various synthesis techniques for different nanoparticles.

Earlier studies show that the use of toxic and expensive chemicals as reducing and capping agents resulted in the production of larger particles, which again consumes extra energy and provides large particle size. Also, the chemically synthesized nanoparticles were described to exhibit less stability and added agglomeration and aggregation [23–28]. As a result, there is a necessity to improve and develop an ecofriendly protocol synthesis method that will create dispersible and stable nanoparticles of manageable size, which consumes less energy, uses green solvents, and involves easily controllable techniques. In the light of the aforementioned issues and facts in mind, this review work summarizes the recent advancement in the biogenic synthesis of $TiO_2$ NPs using various medicinal plant part extracts and microorganisms such as bacteria, fungi, algae, and yeast, characterization, and their photocatalytic applications.

So many research works were reported concerning synthesis and photocatalytic activity of titanium oxide nanoparticles. Up to the knowledge of the authors, no work was reported that summarizes on the synthesis of $TiO_2$ NPs using different sources of natural products such as different parts of green plants, bacteria (both Gram positive and Gram negative), different species of fungi (synthesized either intracellularly or extracellularly), and yeasts for the treatment of wastewater. The novelty of this work also lies on showing the possibility of production of $TiO_2$ NPs with different

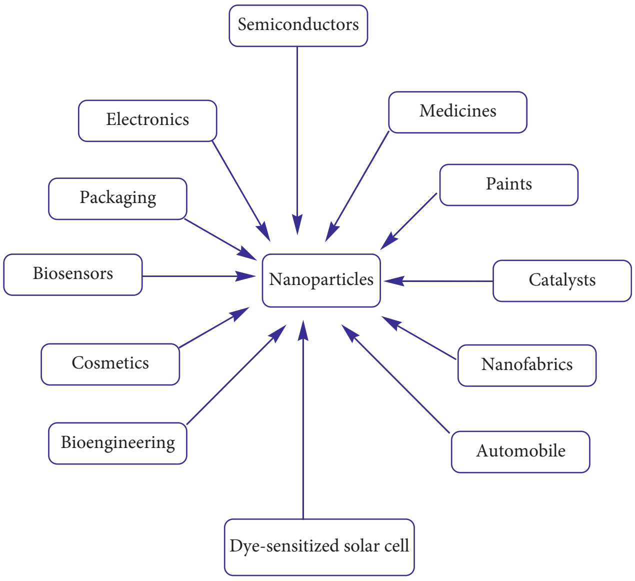


Figure 1: An overview of applications of nanoparticles [9].

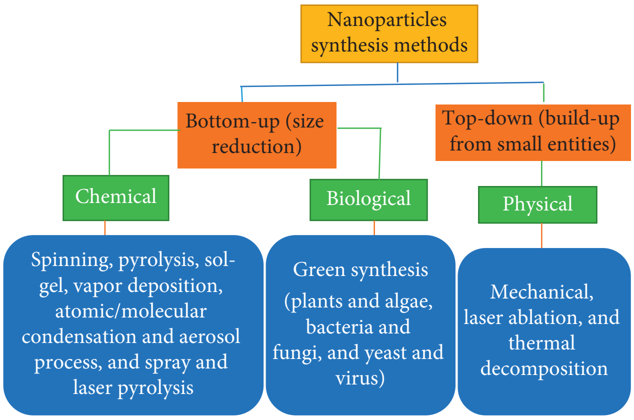


Figure 2: Synthesis methods of nanoparticles [3].

shapes and sizes following the change in the type and nature of the stabilizing/reducing role of plant extract metabolites during synthesis [29–33]. The metabolites used during nanoparticle synthesis prevent agglomeration and control the sizes of nanoparticles. It is well reported that the size of $TiO_2$ NPs could significantly affect the photocatalytic degradation of organic dyes [34]. High-surface-area (small-sized) NPs of titanium oxides are highly recommended for photocatalytic degradation of dye pollutants in waste water [32–35].

## 2. Biogenic Synthesis Methods of Titanium Oxide Nanoparticles

Green chemistry and biological processes have led to the development of an environment-friendly process for the synthesis of $TiO_2$ nanoparticles. A vast array of biological resources available in nature including living plants, plant products and plant extracts, algae, fungi, yeast, bacteria, and viruses could all be employed for the synthesis of $TiO_2$ nanomaterial. Biological methods are considered and regarded as safe, cost-effective, biocompatible, nontoxic, sustainable, and environment-friendly processes. In addition, most bioprocesses occur under normal air, pressure, and temperature, resulting in vast energy savings, high yield, and low cost [36].

*2.1. Algae-Mediated Biogenic Synthesis of Titanium Oxide Nanoparticles.* Algae are aquatic phototrophic, and recent studies have shown that some of them are not only accumulate heavy metals but are also used to biologically synthesize metallic nanoparticles. The use of algae for biosynthesis of $TiO_2$ nanoparticles has become prevalent during these days due to their easy access and efficacy. The biomolecules such as enzymes, proteins, polysaccharides, and others present in the algal extract have not relatively been well exploited for nanoparticle synthesis compared to similar other natural sources such as plants and bacteria [37]. Figure 3 shows the scheme for algae-mediated synthesis of metal/metal oxide NPs including $TiO_2$ NPs.

*2.2. Fungi-Mediated Biogenic Synthesis of $TiO_2$ Nanoparticles.* The first report of using fungi extract to biosynthesize nanoparticles dates back to a letter in nature since 1989. Fungi have attracted more attention regarding the research on biological production of $TiO_2$ nanoparticles due to their toleration and metal bioaccumulation capability, as well as their ability to secrete large amounts of enzymes [38, 39]. Previously, $TiO_2$ NPs were synthesized from a $TiO_2$ precursor by employing *Aspergillus tubingensis* fungi [40]. The study reported that the dynamic light scattering (DLS) calculated size was estimated between 1.5 and 30 nm with a polydispersity index value of 0.194. Similarly, $TiO_2$ NPs were synthesized in the presence of bulk $TiO_2$ as a precursor using *Aspergillus niger* fungi extract. They reported that the obtained $TiO_2$ NPs' size was in the range of 73.58 to 106.9 nm as it was determined via SEM [41]. It was reported that fungi are ideal biocatalysts for $TiO_2$ NPs biosynthesis, in contrast to bacteria, as they are well known for producing greater amounts of biologically active substances that make the fungus more appropriate for large-scale production of different nanomaterials too [37].

*2.3. Bacteria-Mediated Biogenic Synthesis of $TiO_2$ Nanoparticles.* In contrast to other kinds of microorganisms, bacteria were utilized to synthesize nanoparticles earlier. Due to the mild conditions, high yield, and easy purification and manipulation, bacteria become the most widely studied microorganism, with the title of "the factory of nanomaterials" [42]. Previously, different researchers made use of bacteria as a reducing and a capping agent to control the grain/overgrowth during the synthesis of titanium dioxide nanoparticles and other nanomaterials having various applications [42]. $TiO_2$ NPs were synthesized in the presence of *Aeromonas hydrophila* bacteria using the bulk form of $TiO_2$ as a precursor. The XRD pattern of the synthesized $TiO_2$ NPs estimated the size as 40.50 nm having

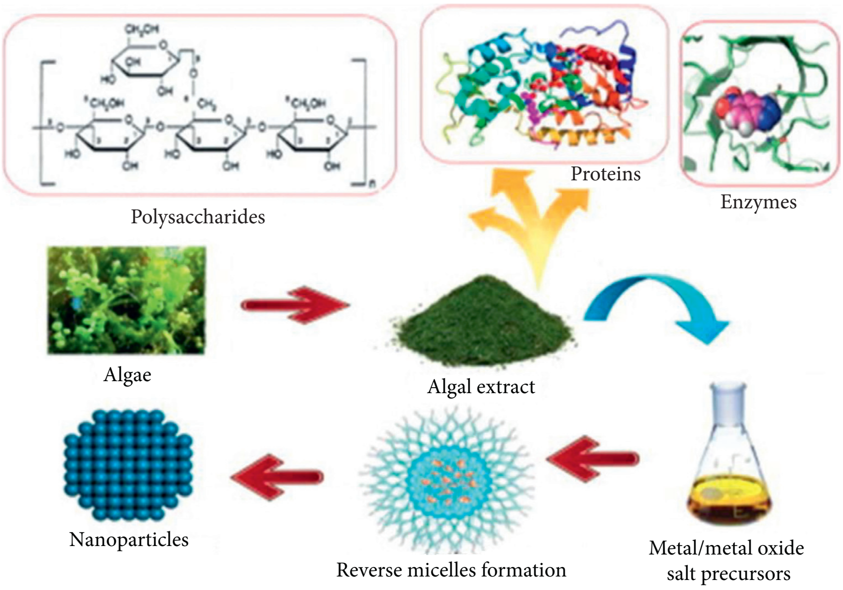


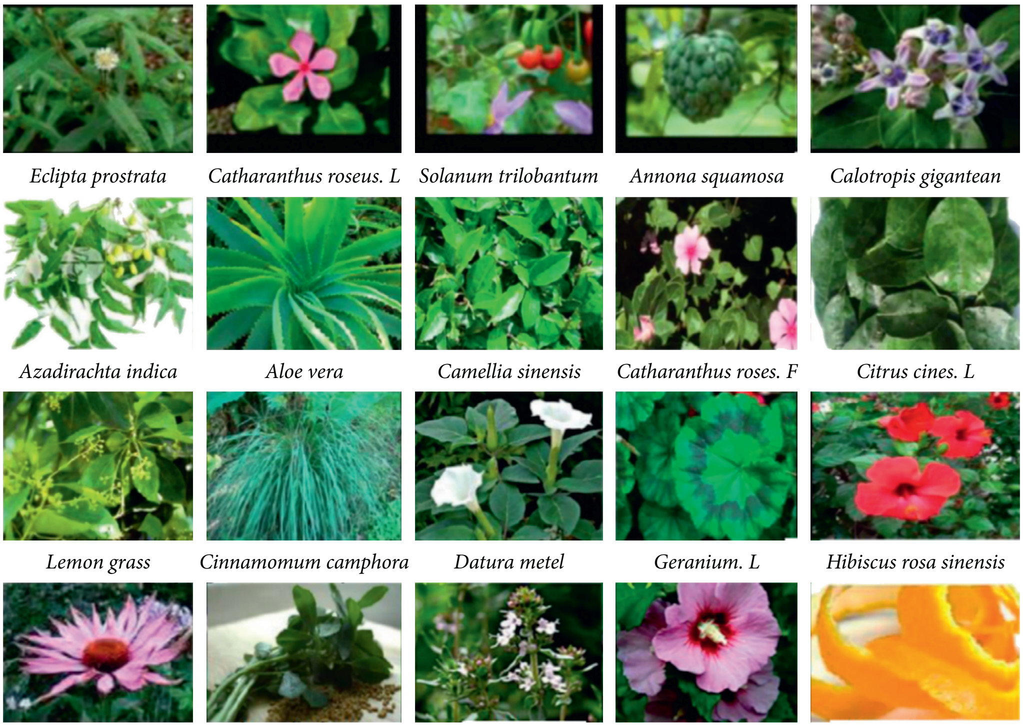
Figure 3: Algae-mediated synthesis of metal/metal oxide NPs [37].

spherical morphology as it was confirmed from FESEM analysis [43]. Moreover, a research report show that $TiO_2$ NPs were synthesized in the presence of *Planomicrobium spp.* bacteria using the bulk form of $TiO_2$ as a precursor [44, 45]. The XRD crystal size of the obtained TiO2 NPs measured was 8.89 nm. In addition, $TiO_2$ NPs were synthesized using the bacteria *Bacillus mycoides* in the presence of titanyl hydroxide as the precursor. The obtained $TiO_2$ NPs produced were predominately anatase crystal with a polydisperse size of 40–60 nm [46]. Advantages of using a bacterial system include easy handling and hereditary manipulation without much difficulty. As it was stated by different scholars, bacteria have been employed in commercial biotechnological processes such as bioleaching and bioremediation. Bacteria possess remarkable abilities to reduce heavy metal ions and are potential candidates for $TiO_2$ nanoparticles synthesis [42, 47].

*2.4. Plant-Extract-Mediated Biogenic Synthesis of $TiO_2$ Nanoparticles.* Even though different microorganisms have been employed as an alternative template for the synthesis of nanomaterials instead of using expensive and toxic organic solvents and chemicals as a stabilizer, the use of microorganisms has its own disadvantages as compared to medicinal green plants as they require advanced equipments and instruments to culture and enhance their growth before they are used for synthesis purpose and require optimization of different parameters to achieve and maintain their growth and to be used during the synthesis process. Instead, incorporating different parts of green and medicinal plants results in too ecofriendly benefits to the ecosystem. Due to the diversity of plants, nanoparticles synthesis from plant extract has known as an interesting subject across the world as different plant species are being rapidly investigated and used in nanoparticles synthesis. The use of plant extracts to synthesize $TiO_2$ nanoparticles is receiving attention in recent times because of simplicity, eco-friendly approaches, cost effectiveness, readily-scalable processes, and much product formed with the minimum cost [36]. Figure 4 shows some of the selected plant types and the different parts that were used as a template during $TiO_2$ NPs synthesis.

$TiO_2$ NPs were synthesized by the reaction between titanium tetraisoproxide and ethanolic leaf extract of *Nyctanthes arbor-tristis*. XRD result analysis revealed that the average grain size was near 100 nm having spherical morphology [48]. In our previous work [49], we have reported on the synthesis of $TiO_2$ NPs using titanium tetrabutoxide as a precursor in the presence of ethanolic root extract of *Kniphofia foliosa* as a template. The obtained XRD analysis shows the average crystalline size was estimated between 8.2 and 10.2 nm for the different volume ratios, and the FESEM result shows the obtained nanoparticles have spherical morphology. Similarly, using the $TiO\ (OH)_2$ precursor and aqueous extracts of *Eclipta prostrata* leaves as a biotemplating agent, NPs were synthesized. The obtained $TiO_2$ NPs were spherical in shape, and their size ranged from 36 nm to 68 nm [50].

Previously, TiO2 NPs were synthesized using the aqueous extract of *Psidium guajava* leaf and $TiO\ (OH)_2$ as a precursor. They reported that the average size of plant-mediated synthesized $TiO_2$ NPs was estimated as 32.58 nm [51]. Using the titanium (iv) isopropoxide precursor, $TiO_2$ NPs were also synthesized in the presence of ethanolic extract of *cassia auriculata* leaves [52]. FESEM revealed that the average particle size obtained was from 38 to 44.2 nm. In a similar fashion, $TiO_2$ NPs were synthesized using aqueous extract of orange peel as a reducing agent and titanium (iv) isopropoxide solution as a starting material, and the average crystallite size of the obtained $TiO_2$ NPs was calculated as 19 nm [53]. It has been reported that $TiO_2$ NPs were synthesized using aqueous extract of *C. giganta* flower and TiO



*Eclipta prostrata* *Catharanthus roseus. L* *Solanum trilobantum* *Annona squamosa* *Calotropis gigantean*

*Azadirachta indica* *Aloe vera* *Camellia sinensis* *Catharanthus roses. F* *Citrus cines. L*

*Lemon grass* *Cinnamomum camphora* *Datura metel* *Geranium. L* *Hibiscus rosa sinensis*

*E. purpura* *Trigonella foenum* Thyme *Alcea* Citrus cines peel

Figure 4: Some selected types of plants used as a template for $TiO_2$ NPs synthesis [36, 37].

$(OH)_2$ was used as a precursor. SEM micrograph analysis of the obtained $TiO_2$ NPs showed aggregation and spherical shape with an average size between 160 and 220 nm [29]. $TiO_2$ NPs were prepared from the aqueous leaf extract of *Ocimum basilicum L. var. Benth* using titanium (iv) isopropoxide as a precursor. The particle size of the synthesized TiO2 NPs was found as 6.97 nm as per Debye Scherrer [54]. In general synthesis of $TiO_2$ NPs using different parts of medicinal and nonmedicinal green plants, the path depicted in Figure 5 is followed.

It has been reported that phytochemicals and primary and secondary metabolites are well known as natural resources that are responsible for metal salt reductions during the green synthesis of TiO2 NPs [55]. The green-synthesized $TiO_2$ NPs show the best photocatalyst activity due to their long thermodynamic stability and strong oxidizing power. Table 1 summarizes the biogenic synthesis of $TiO_2$ NPs in the presence of different types of templates.

The table shows reports on biogenic synthesized $TiO_2$ NPs from different templates as a biological source. Due to the biodiversity of plants, bacteria, yeast, and fungi, $TiO_2$ NPs with different particle sizes, morphologies, and applications can easily be synthesized in large amount even at an industrial level [55].

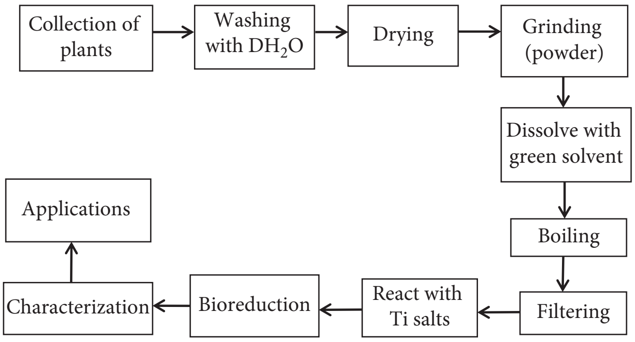


Figure 5: $TiO_2$ NPs synthetic pathway using plant extracts as green sources [53].

## 3. Characterization Techniques Used for Bioassisted Synthesized $TiO_2$ NPs

In order to check and confirm the formation of the synthesized $TiO_2$ NPs for the desired applications, a number of physiochemical and surface analysis techniques were carried out, such as morphological characterizations (scanning electron microscopy (SEM) and transmission electron microscopy (TEM)) and structural characterizations (X-ray diffraction (XRD), energy-dispersive X-ray (EDS), X-ray photoelectron spectroscopy (XPS) used for surface composition, chemical states, elemental ratio, and exact bonding nature analysis, Fourier-transform infrared (FT-IR) which provides different information about functional groups that play great role during the synthesis process, Raman spectroscopy, and Brunauer–Emmett–Teller (BET) used for the determination of surface area, pore diameter, pore size, and pore volume of the formed $TiO_2$ NPs). Total reflection X-ray fluorescence analysis (TXRF) can also be adapted to deal with elemental composition of the biogenic synthesized $TiO_2$ NPs. Particle size and surface area determination can be carried out using SEM, TEM, DLS, and XRD techniques.

Table 1: Summary of the biogenic synthesis of $TiO_2$ NPs using different templates.

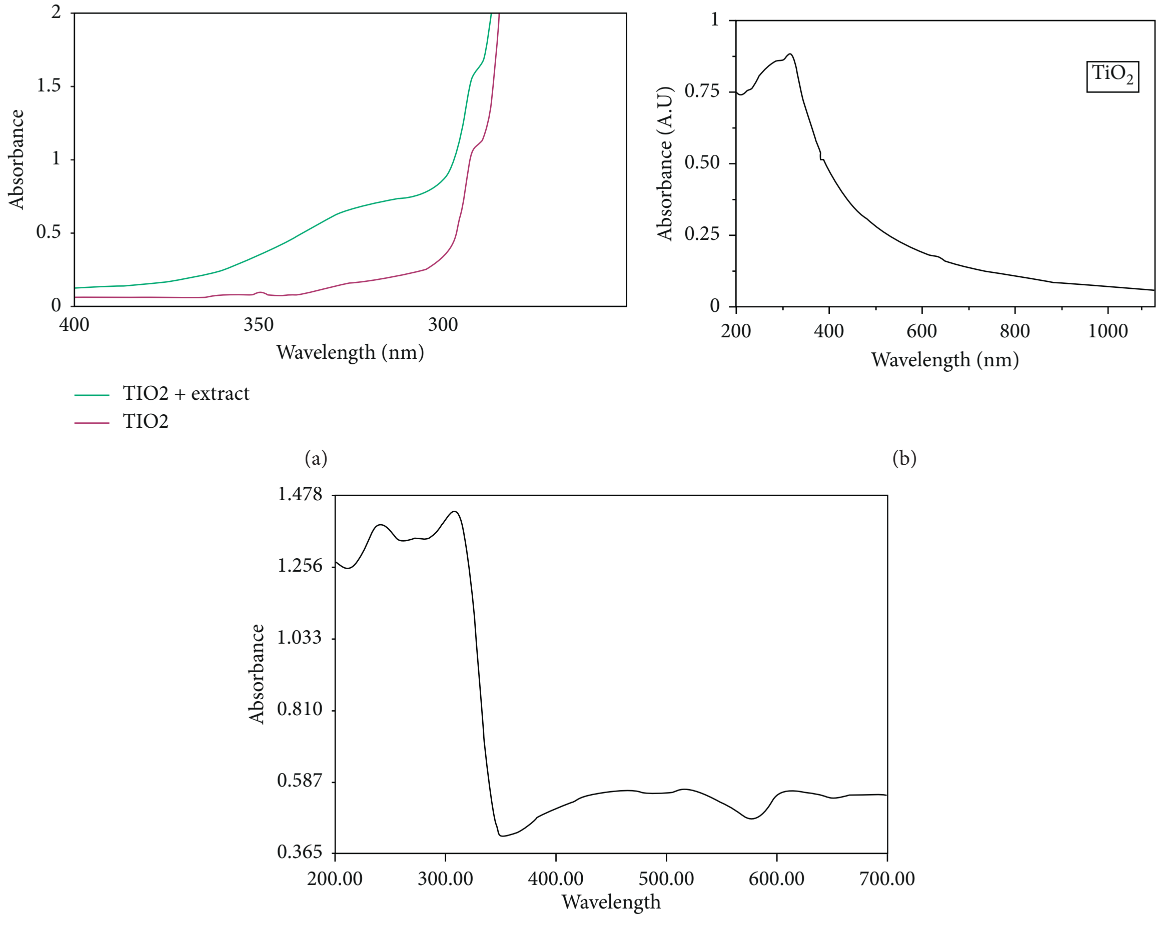
| Templates used | Size and morphology | Applications | References |
|---|---|---|---|
| *Kniphofia foliosa* | 8.2–10.2, spherical | Antibacterial | [49] |
| *Calotropis gigantea* | 10.52, spherical | Acaricidal | [56] |
| *Psidium guajava* | 32.58 | Antibacterial and antioxidant | [51] |
| *Aloe Barbadensis Miller* | 20 | — | [57] |
| *Ageratina alttissima L.* | 60–100, spherical | Photocatalytic | [58] |
| *Vitex negundo* Linn. | 10 | Antibacterial | [59] |
| *Curcuma longa* | 43.88, spherical | Biological property | [60] |
| *Vigna unguiculata* | 11.55, spherical | Antimicrobial and cytotoxic effects | [61] |
| *Eclipta prostrata* | 36, spherical | Antibacterial | [62] |
| *Nyctanthes arbor-tristis* | 100–150, spherical and cubic | — | [49] |
| *Jatropha curcas L.* | 25–100, spherical | — | [63] |
| *Albizia saman* | 41, anatase crystal | — | [64] |
| *Cassia fistula* | 38–44.2, spherical | — | [65] |
| *Taraxacum officinale* (yeast) | 50, anatase and rutile | Photocatalytic | [66] |
| *Aeromonas hydrophila* (bacteria) | 25–54 | — | [43] |
| *Planomicrobium Bacillus mycoides* (bacteria) | 8.89 | — | [45] |
| *Moringa Oleifera* | 40–60, spherical | — | [67] |
| *Aloe vera* | 12 by XRD and 30 by PSA, tetragonal | — | [68] |
| Hibiscus flower | 24.89 by XRD and 43.3 by PSA | — | [69] |
| Citrus lemon | 2000 by SEM, different shapes | Antibacterial | [70] |
| *Alcea* and thyme | 6 (thyme), 10 (alcea), polyhedron and irregular shape | Photocatalytic | [71] |
| Lignocellulosic waste | 10–20 by XRD, 24.0 ± 4.7 nm and 13.0 ± 3.3 by TEM, anatase | — | [72] |
| *Echinacea purpurea herba* | 120 by SEM | — | [73] |
| *Trigonella foenum-graecum* | 25 by XRD and 20–90 by SEM, spherical | Antimicrobial | [74] |
| *Azadirachta indica* | 56.13, spherical | — | [75] |
| *Bacillus mycoides* (bacterium) | 40–60 nm, spherical | Green solar cell and antibacterial | [46] |
| *Bacillus subtilis* (bacterium) | 10–30, spherical | Suppress aquatic biofilm growth | [76] |
| *Catharanthus roseus (Vinca rosea)* | 25–110, irregular | Effective against hippobosca maculate and *Bovicola ovis* | [77] |
| *Annona squamosal* | 40–60, spherical | — | [78] |
| *Planomicrobium sp.* | 8.89 nm irregular, spherical | — | [79] |
| *Ocimum basilicum. L Var purapurascens benth-Lamicea* | 6.97 by XRD and 50 by SEM, hexagon | — | [54] |
| Pristine pomegranate peel | 92.8, anatase phase | Antimicrobial activity for water disinfection | [80] |
| *Garcinia zeylanica* extract | 10, anatase and rutile phase | Antibacterial | [81] |
| *Cynodon dactylon* | 13–34, irregular and hexagonal shape | Antibacterial and anticancer (A549 cell lines) | [82] |

Optical and light-absorbing behaviors can be carried out using UV-Vis, PL, and DLS techniques. In addition to these techniques, electrochemical characterization can be performed using CV to determine the electronic band-gap energy. Thermal stability and behavior of the as-synthesized $TiO_2$ NPs could be characterized using TGA/DTA or TGA/DTG before the calcination step was performed.

### 3.1. Characterization by UV-Vis Absorbance Spectroscopy.

UV-Vis absorption spectroscopy is an important technique to monitor the formation and stability of titanium dioxide nanoparticles in aqueous solutions and to characterize optical properties of $TiO_2$ NPs. The absorption spectrum of $TiO_2$ NPs is sensitive to several factors, including particle size, shape, and particle-particle interaction (agglomeration) with the medium. The absorption maximum ($\lambda_{\max}$) of the synthesized nanoparticles depends on its size and shape [83, 84]. Figures 6(a)–6(c) show the absorption spectra of *Echinacea purpurea herba*-, *Hibiscus* flower-, and *Aloe vera*-extract-mediated synthesized $TiO_2$ NPs, respectively.

Figure 6(a) shows the UV-Vis absorption spectra for *E. purpurea herba*-mediated $TiO_2$ nanoparticles between 200 and 400 nm. The absorption of $TiO_2$ appears at 280 nm in UV-Vis spectroscopy. Similar studies were also reported by Roopan et al. [85]. Figure 6(b) shows the absorbance of synthesized $TiO_2$ NPs using *Hibiscus* flower extract as a template. The spectra exhibit a range between 200 and 1200 nm and the peak at 354 nm wavelength with an absorbance of 0.86 (<1), which means that it exhibits good absorbance at the UV region, as it was reported by Vijayalakshmi and Rajendran [86], and the energy band gap was estimated at 3.503 eV. Figure 6(c) proves the UV-Vis absorbance spectra of *Aloe vera* extract biogenic-synthesized



(a) (b)

(c)

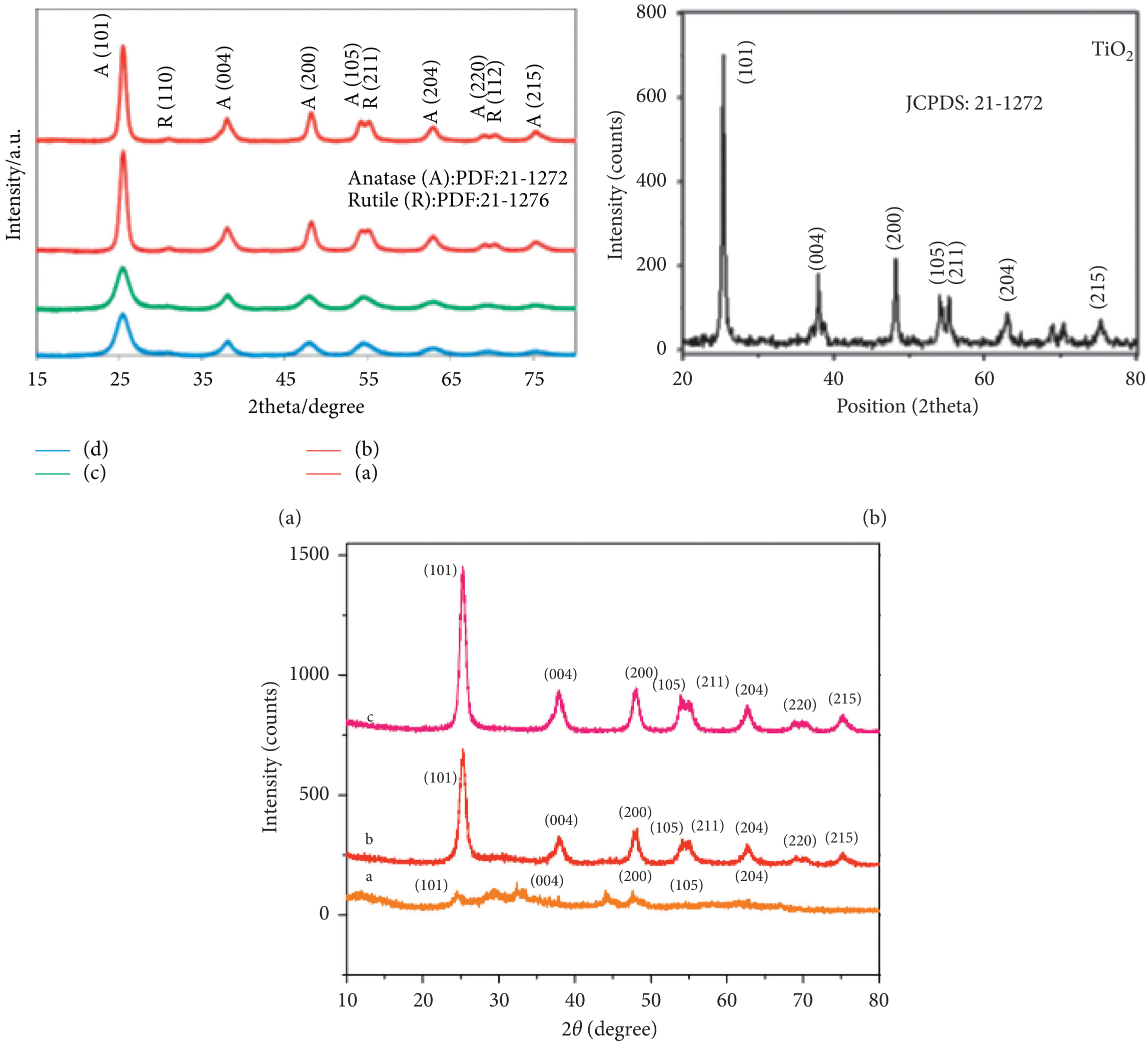
Figure 6: UV-Vis absorption spectra of (a) *Echinacea purpurea herba*-, (b) *Hibiscus* flower-, and (c) *Aloe vera*-extract-mediated synthesized $TiO_2$ NPs [68, 69, 73].

$TiO_2$ NPs. The absorption spectra of $TiO_2$ nanoparticles exhibit strong absorption below 400 nm. The spectrum of the $TiO_2$ sample calcined at 400°C indicates the absorption onset at around 393 nm with a band gap energy of 3.196 eV, which is in excellent agreement with the band gap of the anatase phase [87].

*3.2. Characterization Using XRD.* The X-ray diffraction measurement analysis technique could provide information about the structure, phase, and average crystalline size of the formed nanoparticles. Figures 7(a)–7(c) depict *Alcea*-, thyme-, *Moringa oleifera*-leaf-, and *Kniphofia foliosa*-root-extract-mediated synthesized $TiO_2$ NPs, respectively. As shown in Figure 7(a), the XRD patterns of *Alcea*- and thyme-extract-assisted synthesized $TiO_2$ NPs indicate the sharp peaks at a $2\theta$ value of $\approx 25.54$, 37.39, 47.84, 53.69, 62.12, 68.28, and 74.55, which belong to (101), (004), (200), (105), (204), (220), and (215) planes of the anatase phase as supported by the Joint Committee on Powder Diffraction Standards (JCPDS) card number of 21–1272, respectively. In addition to this, the observed peaks at a $2\theta$ value of 30.48, 54.58, and 69.89 are related to the diffraction of (110), (211), and (112) plates of the rutile phase, respectively, according to their JCPDS card number of 21–1276, as supported by the work of Hajalilou et al. [88]. From the XRD analysis result, the average crystallite size for thyme- and *Alcea*-mediated synthesized $TiO_2$ NPs was found to be about 6 and 10 nm, respectively.

Figure 7(b) proves *Moringa oleifera*-leaf-extract-based synthesized $TiO_2$ NPs, and in the XRD analysis, five diffraction peaks were observed $\approx 2\theta$ at 25.3, 37.7, 48.1, 54.0, and 62.7 with their corresponding miller indexes values of (101), (004), (200), (105), and (204), respectively, having tetragonal body-centered titanium dioxide as confirmed by the JCPDS card number of 86–1156 [89]. The average crystalline size was estimated at 12 nm, which was calculated by using Scherrer's formula. Again, Figure 7(c) displays the X-ray diffraction pattern of root of *Kniphofia foliosa* template synthesized $TiO_2$ NPs within different volume ratios of the extract and precursor salt. The diffraction peaks were observed at $2\theta$ values of $\approx 25.3$, 38.0, 47.9, 53.2, 54.8862, 62.7, 70.2, and 75.0 along with their miller index planes of (101), (004), (200), (105), (211), (204), (220), and (215), respectively.

The analysis confirms that the biosynthesized nanoparticles are in tetragonal crystal structure without any



(a) (b)

(c)

Figure 7: (a) Thyme (a), *Alcea* (b), and *Alcea* calcined at 500°C (c), and *thyme* calcined at 500°C (d), (b) *Moringa oleifera*-leaf-, and (c) root of *Kniphofia foliosa*- (a, 1 : 2, b, 1 : 1, and c, 2 : 1) extract-mediated synthesized $TiO_2$ NPs [49, 67, 71].

impurities within the detection limits of XRD as reported in [49]. The average crystalline size for the different kinds of $TiO_2$ NPs was estimated at 10.2, 8.2, and 8.5 nm for the 1 : 2, 1 : 1, and 2 : 1 volume ratio of the extract and precursor salt, respectively. As it can be observed from the XRD spectrum, $TiO_2$ NPs are synthesized within the volume ratio of 1 : 2, and the crystalline nature is lost due to the addition of an excessive amount of *Kniphofia foliosa* extract beyond the coating surface of $TiO_2$ NPs available.

*3.3. Characterization Using SEM.* Another very important characterization technique that could provide surface morphology and topography of the biotemplated synthesized $TiO_2$ NPs is field-emission scanning electron microscopy (FESEM). This analysis technique allows to determine the peculiar application of green-synthesized $TiO_2$ NPs. Figures 8(a)–8(c) (containing (A) and (B) with different magnifications) display the SEM image of citrus lemon-leaf-, *Psidium guajava*-, and *Aeromonas hydrophila*-assisted synthesized $TiO_2$ NPs, respectively.

As it can be seen in Figure 8(a), the surface morphology of citrus lemon-leaf-supported biogenic synthesized $TiO_2$ nanoparticles was measured by FE-SEM. The micrograph shows nanoscaled $TiO_2$ NPs with detailed surface morphology. The results of SEM revealed the development of titanium nanoparticles with different shapes at 15000 X magnification [70]. Figure 8(b) displays the FESEM images of *Psidium guajava*-mediated synthesized $TiO_2$ NPs, and the topographical analysis was performed based upon the surface study. Synthesized $TiO_2$ NPs were smooth and spherical in shape. The images showed the synthesized nanoparticles in 50000× resolution, which clearly gives physical morphology, particle size, and aspect ratio [51].

Again, Figure 8(c) proves the *Aeromonas hydrophila*-bacteria-mediated synthesized $TiO_2$ NPs. Also, the surface morphology of nanoparticles was investigated using the FESEM analysis technique. The nanoparticles were found to

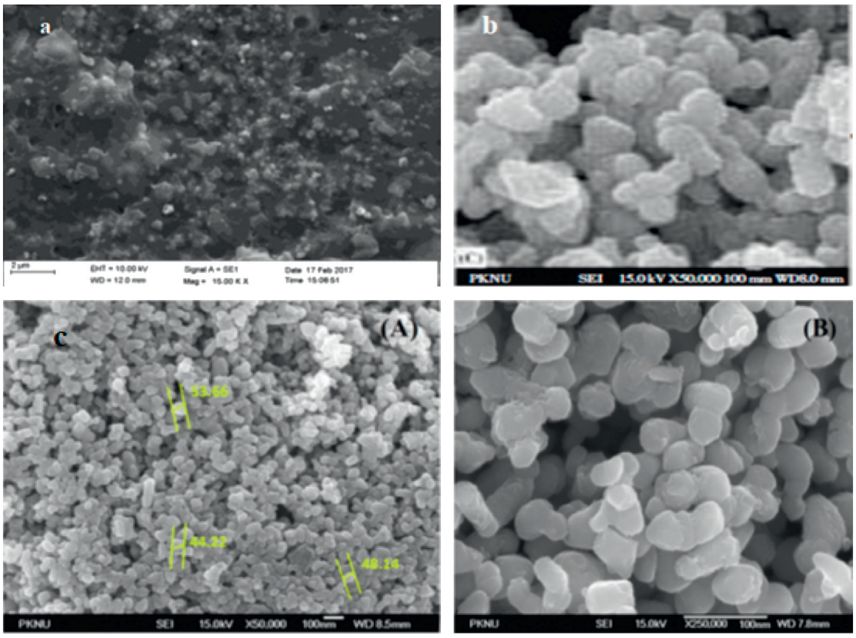


Figure 8: SEM image of (a) *citrus lemon* leaf, (b) *psidium guajava*, and (c) *aeromonas hydrophila* (A, 50000× and B, 2500×) templated synthesis of $TiO_2$ NPs [43, 51, 70].

be distributed uniformly on the surface with the formation of aggregated nanoparticles. It shows that the particles were densely dispersed with a narrow range of dispersion range [43]. Particles were nanosized with smooth surface morphology. In Figure 8(c), (A) and (B) show that the size of the synthesized $TiO_2$ NPs was found to be very consistent.

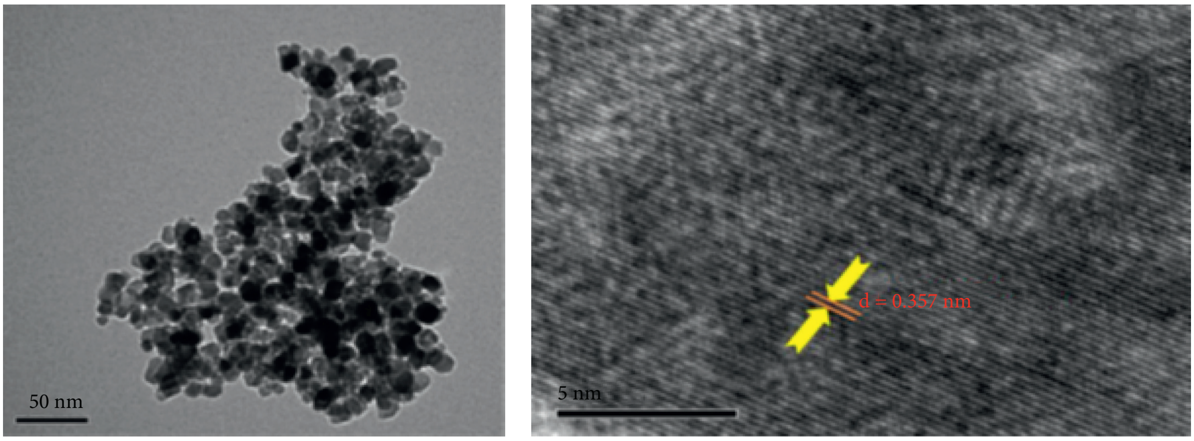
*3.4. Characterization Using TEM.* The morphology and structural arrangement of biotemplated assisted synthesized $TiO_2$ NPs could be perceived through TEM analysis. This analysis could carry out to ascertain and gain further information about the nature of the formed nanoparticles. Figures 9(a) and 9(b) display TEM micrographs of *Trigonella foenum graecum- and Aloe vera*-leaf-extract-mediated synthesized $TiO_2$ NPs.

In Figure 9(a), HR-TEM images display spherical shaped polydisperse nanoparticles, and the average particle size of *Trigonella foenum graecum*-assisted $TiO_2$ NPs was 20 nm. The TEM micrograph clearly exemplifies the individual nanoparticles formed were nearly in a spherical form with a dimension of 40–60 nm [90]. This investigational analysis indicates it is possible to get small-sized and efficient anatase $TiO_2$ nanoparticles via the biogenic method for the desired applications. Similarly, Figure 9(b) shows that $TiO_2$ nanoparticles synthesized through the biogenic method using *Aloe vera* crude extract were found to have a crystalline nature. Also, the calculated d-spacing value was estimated as $d = 0.357$ nm, and the value obtained is nearly equal to the XRD d-spacing value [74].

*3.5. Characterization Using FT- IR Spectroscopy.* The Fourier-transform infrared spectroscopy analysis technique could provide the necessary information about bioactive ingredients/molecules from the natural product that play a great role as a template during the synthesis process to prevent the overgrowth, aggregation, and then, to maintain phase stability of $TiO_2$ NPs. Figures 10(a) and 10(b) show the FT-IR spectra of *Aeromonas hydrophila- and Kniphofia foliosa*-mediated biogenic synthesized $TiO_2$ NPs, respectively.

The FT-IR spectra of *Aeromonas hydrophila*-supported synthesized $TiO_2$ NPs are indicated in Figure 9(a). The FT-IR spectrum showed characteristic bands at 3430 and 1643 $cm^{-1}$ which correspond to the surface water and hydroxyl group. The band intensities of the spectrum for the synthesized $TiO_2$ NPs are 3430, 2937, 1643, 1403, and 1079 $cm^{-1}$. These results indicated that alcohols, phenols, primary amines, lactones, and aliphatic amines are present in *A. hydrophila* which may have been participated in the synthesis process and, as a result, can maintain phase stability. As supported by the report of Coenen et al. [91], functional groups associated with these were the cause for bioreduction of the precursor salt into $TiO_2$ NPs.

Figure 10(b) consists of the FT-IR spectra of both the root extract of *k. foliosa* (a) and extract with $TiO_2$ (b) NPs. Absorption bands at 3419.46, 2926.88, 1635.14, 1319.59, 1038, and 780.44 $cm^{-1}$ are due to O–H bond stretching, C–H bond stretching of alkanes, C=O bond stretching of carbonyl groups/C=C bond stretching at $\alpha$-, $\beta$-unsaturated ketone, C–C bond stretching at the aromatic ring, C–O bond bending vibration on phenolic compounds, C–O bond stretching of the hydroxyl group, and out-of-plane C–H bending at the aromatic ring, respectively, indicating the presence of organic compounds such as knipholone anthrone, anthraquinone, and chrysophanol which were used as a capping and reducing agent [92]. The broad absorption band observed at 3433.85 $cm^{-1}$ represents O–H



(a) (b)

FIGURE 9: TEM micrograph of (a) *Trigonella foenum graecum*- and (b) *Aloe vera*-mediated synthesized $TiO_2$ NPs [68, 74].

bond stretching due to adsorbed moisture on the surface of the synthesized $TiO_2$ NPs. The weak absorption band located at 2335.14 $cm^{-1}$ is due to C=O bond stretching that could be emanated from the presence of adsorbed carbon dioxide on the surface of the NPs. The absorption band at 1629.58 $cm^{-1}$ could be due to carbon dioxide and/or due to O-H bending of molecularly adsorbed water [91]. The broad band centered at 567.13 $cm^{-1}$ represents a characteristic peak of the Ti-O-Ti bending mode of vibration, indicating formation of metal oxygen bonding [93, 94]. The absence of bands at 2926.88, 1635.14, 1319.59, 1038, and 780.44 $cm^{-1}$ in Figure 10 (b, extract + $TiO_2$ NPs) shows that organic molecules have been removed from $TiO_2$ NPs upon the calcination process.

## 4. Photocatalytic Applications of Biogenic Synthesized $TiO_2$ NPs

Photocatalysis is a reaction which uses light to activate a substance which modifies the rate of a chemical reaction without itself being involved. Photocatalytic oxidation (PCO), also known as heterogeneous photocatalysis, has been used since the mid-1970s to decontaminate water from harmful microorganisms, dyes, detergents, pesticides, and inorganic pollutants too [95]. The most commonly used and researched semiconductor nanophotocatalyst $TiO_2$ is used as the substrate, and $H_2O$ and $O_2$ are used as an adsorbate. The primary criteria for an efficient semiconductor photocatalyst are that the redox potential of the charge couple, i.e., $e/h^+$, lies within the band gap domain of the photocatalyst. A molecular description of a general photocatalytic reaction process involving $TiO_2$ is given by the following equations [96]:

$$TiO_2 + h\nu \longrightarrow TiO_2\left(e_{cb}^- + h_{vb}^+\right), \quad (1)$$

$$TiO_2\left(e_{cb}^- + h_{vb}^+ \longrightarrow TiO_2 + \text{heat}, \quad (2)$$

$$TiO_2 + H_2O_{\text{ads}} \longrightarrow TiO_2 + OH^- + H^+, \quad (3)$$

$$e_{cb}^- + O_{2\text{ads}} \longrightarrow O_2^-, \quad (4)$$

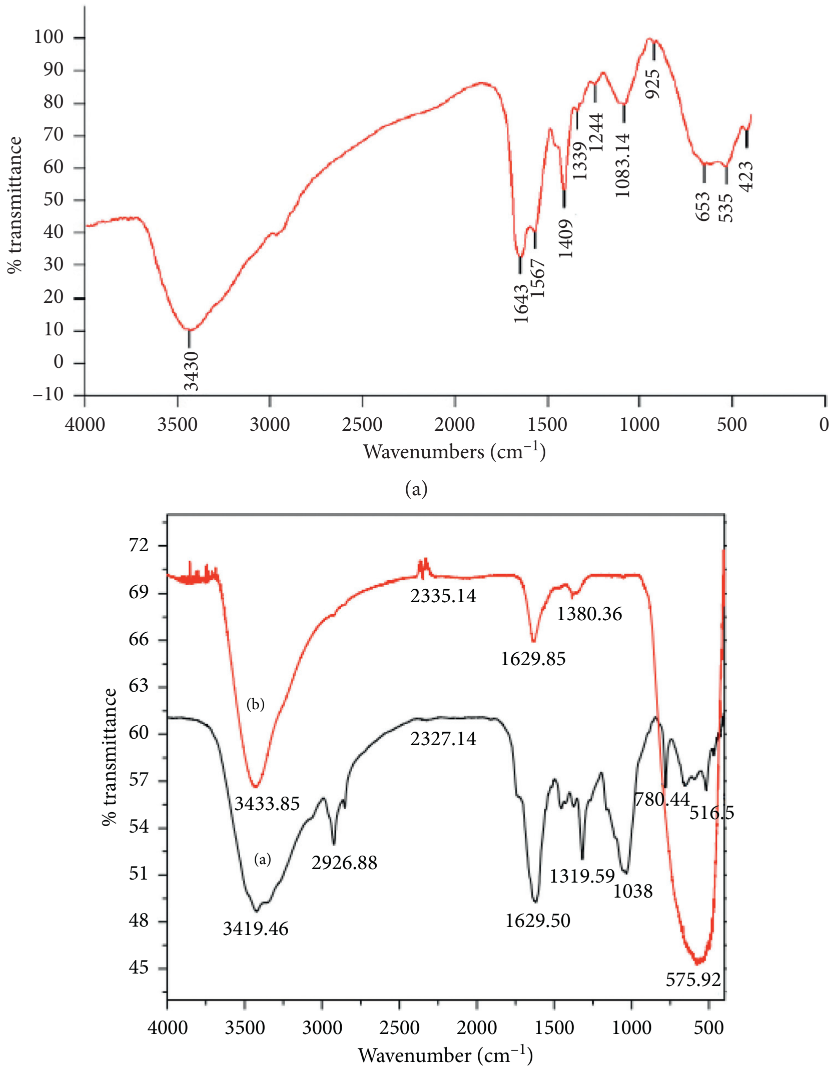
$$h_{vb}^+ + OH^- \longrightarrow OH^-, \quad (5)$$

$$OH + \text{Organic pollutants} \longrightarrow CO_2 + H_2O + \text{others}, \quad (6)$$

where CB is the conduction band, VB is the valence band, and hv is the photon energy. Figure 10 shows the schematic representation of basic working principles of photocatalysis.

As it is tried to address in Figure 11, photons with energies greater than the band-gap energy ($E_g$) can result in the excitation of valence band (VB) electrons which then promote the possible reactions with organic pollutants. The absorption of photons with energy lower than $E_g$ or longer wavelengths usually causes energy dissipation in the form of heat. The positive hole in the valence band oxidizes either pollutant directly or water to produce hydroxyl radical $^{\bullet}OH$, whereas the electron in the conduction band reduces the oxygen adsorbed on the photocatalyst ($TiO_2$). The performance of $TiO_2$ as a photocatalyst is closely related to its crystal phase, particle size, pore structure, and other morphological properties. Therefore, photocatalytic degradation (PCD) of contaminants using $TiO_2$ as a photocatalyst have been under study for disinfection, air purification, environmental cleaning, and wastewater treatment in daily life and industrial activities [95].

The photocatalytic degradation technique with $TiO_2$ NPs is generally applied for treating wastewater containing organic and inorganic contaminants due to its ability to achieve complete mineralization of the organic contaminants under mild conditions such as ambient temperature and ambient pressure [97, 98]. In particular, dye degradation is almost essential for wastewater treatment due to its sever toxicity effect. Among the three polymorphs of $TiO_2$ NPs (Anatase, Rutile, and Brookite), green-synthesized anatase $TiO_2$ exhibits high photocatalytic activity due to high absorption capacity towards organic, molecular oxygen and low rate of recombination of electron hole pairs (EHP), and



(a)

(b)

Figure 10: FT-IR spectra of (a) *Aeromonas hydrophila*- and (b) *K. foliosa*-assisted (a, FT-IR of extract and b, extract + $TiO_2$) synthesized $TiO_2$ NPs [43, 49].

due to its antifogging effect, it removes bacteria and different harmful organic materials from water [99]. Reporters state that wastewater treatment by $TiO_2$ photocatalysis has some benefits compared to conventional water treatment methods. The most important is that it can completely mineralize almost any chemicals and biological compounds, instead of just transferring them to another state [95].

Recently, the application of $TiO_2$ as a photocatalyst for the removal of organic, inorganic, and other pollutants has attracted many researchers' attention. Previous researchers reported that chlorinated pesticides could be degraded and mineralized through the photocatalytic reaction of $TiO_2$ under UV light [100, 101]. In the presence of $TiO_2$ at 300 nm irradiation, photocatalytic degradation of dicamba herbicide could be increased by 3 times compared with those without the addition of a $TiO_2$ catalyst. Figure 12 shows the degradation of methylene orange (MO) by PVP-assisted synthesized anatase $TiO_2$ NPs.

The degradation of MO using a biogenic-synthesized $TiO_2$ photocatalyst was investigated as shown in Figure 11. It is seen that a maximum of 94% degradation of MO was obtained at 1.0 g/dm$^3$ under UV light within 150 min time allocated. The obtained results were attributed to an increase in the number of active sites and photons absorbed by the catalyst. Basically, as stated by Poudyal et al. [102], titanium dioxide nanoparticles are used as a catalyst with either fixed-phase or solvent-phase methods. Both techniques have their own advantages; however, the solvent phase is more effective than the fixed phase. Since the titanium dioxide NPs remain in the wastewater treatment process, it should be separated from the solution. Figure 13 displays the UV-assisted application of titanium dioxide nanoparticles synthesized via the biogenic method using the extract of thyme and *Alcea* to remove methylene blue.

Figure 13 displays the degradation of MB before mixing (a), mixed for 30 min in a dark room (b), mixed for 30 min

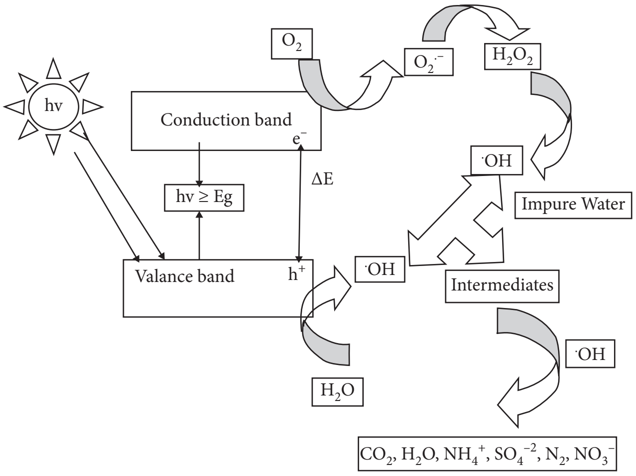


Figure 11: Basic principles of photocatalysis [95].

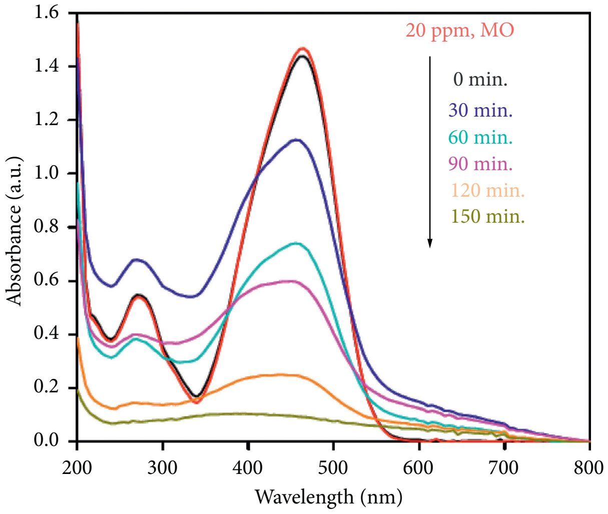
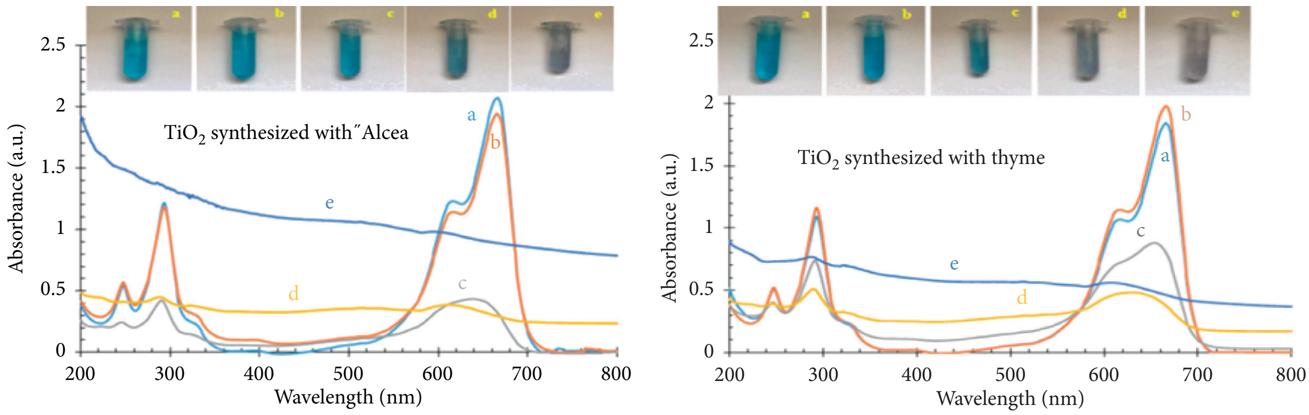


Figure 12: Degradation of MO using PVP-biogenic-assisted synthesized $TiO_2$ NPs [101].



(a)

(b)

Figure 13: (a) Alcea- and (b) thyme-mediated biosynthesized $TiO_2$ NPs for MB degradation [71].

under UV irradiation (c), mixed for 60 min under UV irradiation (d), and mixed for 90 min under UV irradiation (*e*). The absorbance of the two synthesized $TiO_2$ NPs under UV irradiation at different time intervals is depicted. As UV irradiation time increases, the absorption rate decreases. In fact, methylene blue was completely removed from the solution in both of the samples. There was no considerable change in the first 30 min of time interval; however, after 90 min irradiation, color change was observed. It was found that, by increasing the concentration of the catalyst to a specific amount, the efficiency improves. However, the excess concentration of the catalyst will have a negative effect on the radicals. This is because the catalyst particles prevent the penetration of the photons [103]. In addition to this, comparisons of the UV-Vis absorbance graphs of the two samples have indicated that $TiO_2$ NPs synthesized with *thyme* could be chosen as a better photocatalyst than *alcea*-based ones. Therefore, the UV-visible analysis of photocatalytic properties confirmed the priority of $TiO_2$ nanoparticles prepared with *thyme* extracts.

In addition to the removal of organic pollutants, $TiO_2$ photocatalyst is also applicable for the removal of different inorganic pollutants present within the wastewater. $TiO_2$ nanoparticles could be used to adsorb phosphates under UV irradiation; as supported by the work of Xie at al.[104], 95% of total phosphate was removed from surface water within 10 min. Similarly, removal of ammonia by a floating $TiO_2$ system (immobilizing $TiO_2$ nanoparticles with expanded clay aggregate granules) under solar light differences was noted on the fact that the effects of pH varied in ammonia removal [105].

## 5. Conclusions

Synthesis of nanoparticles involves the tailoring of materials at the atomic level to attain unique properties and manipulating for the desired applications. Synthesis of titanium nanoparticles would benefit from the development of clean, nontoxic, and environmentally acceptable green-chemistry procedures, probably involving organisms ranging from bacteria to fungi and algae to green plants. Green synthesis of $TiO_2$ is a better method as they give excellent manipulation on controlling the particle size growth, thus provideing considerable stabilization during the $TiO_2$ NPs synthesizing process. Currently, wastewater treatment using biogenic-assisted synthesized titanium nanometal oxides has gained great attention due to its high degradation efficiency, potential oxidation strength, high photostability, nontoxicity and noncorrosiveness, environmentally friendliness, long thermodynamic stability, abundancy, cost effectiveness, and its green nature.

## 6. Future Perspectives

It is obvious that titanium oxide nanoparticles could be synthesized using biogenic methods involving various biological sources. Synthesis of $TiO_2$ NPs at large level/industrial level using green plants will lead to a hostile environment, and it involves the use of green parts of plants. Instead, in the future, researchers should adapt and focus on synthesis of $TiO_2$ NPs using microorganisms such as fungi, algae, and bacteria by isolating from fertile and spoiled soil, characterization, culturing and use it as a template. To verify and enhance the degradation efficiency of organic dyes/pesticides and/or any water contaminants, researchers could focus on synthesizing of $TiO_2$ NPs by considering different parameters that could affect the synthesis process and, simultaneously, degradation efficiency such as calcination temperature, pH, solvent effect, volume ratio between templates and the precursor salt, and concentration of the precursor.

## Data Availability

All the necessary data are included in the review manuscript.

## Disclosure

Eneyew Tilahun Bekele is the first author.

## Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this review paper.

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