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Green engineering of titanium dioxide nanoparticles using *Ageratina altissima* (L.) King & H.E. Robines. medicinal plant aqueous leaf extracts for enhanced photocatalytic activity

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Abstract

In the present study, the titanium dioxide nanoparticles (TiO_2NPs) were synthesized by using *Ageratina alttissima* (L.) King & H.E. Robines. (White Snakeroot) medicinal plant aqueous leaf extracts by microwave irradiation method. The green synthesized TiO_2NPs showed the best photocatalyst due to its long thermodynamic stability and strong oxidizing power. The synthesized titanium dioxide nanoparticles were characterized by using UV-visible spectroscopy, Fourier transform infrared spectroscopy (FTIR), X-Ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), and Energy dispersive X-Ray analysis (EDX). FTIR was performed to identify the possible functional biomolecules capped on the surface of TiO_2NPs during interaction. In XRD result, the dominant peak of TiO_2 2θ value is matched with the crystallographic rutile structure which indicates the polycrystalline nature. FESEM analysis revealed the spherical shape and size of the synthesized TiO_2NPs. In this study, the degradation process of textile dyes was carried by photocatalytic activity using synthesized TiO_2NPs. The photocatalytic activity of the synthesized TiO_2NPs showed enhanced percentage of decoloring of textile dyes such as methylene blue (86.79 %), alizarin red (76.32 %), crystal violet (77.59 %), and methyl orange (69.06 %). The findings of this study clearly indicated that the synthesized TiO_2 nanoparticles *A. alttissima* be used as an alternative and eco-friendly compound to remove and degrade the pollutants released from textile and dyeing industries.

Key Words: *Ageratina alttissima* (L.) King & H.E. Robines., dyes, green engineering, titanium dioxide nanoparticles, photocatalytic activity, textile industry

1. Introduction

Nanotechnology is an emerging filed science comprises synthesis and characterization of nanoparticles (NPs) for various applications. The size, shape and morphology of the nanoparticles can be varied and modified to obtain enhanced property for suitable applications (Li *et al*., 2011a, b). NPs have enormous applications in the field of biology, chemistry, physics, sensors, catalysts, electronics, antimicrobials, optical fibers, biolabeling and agriculture (Salam *et al*., 2012). Metal and metal oxide nanoparticles have a wide range of attraction because they are essentially needed in the field of nanoscience and nanotechnology (Sankar *et al*., 2014a). Nanobiotechnology industries are expanding at an accelerated rate and deep investigation of the health and environmental effect of this nanomaterial (Mueller and Nowack, 2008). They are categorized into organic and inorganic nanoparticles, the organic nanoparticle is carbon nanoparticles and inorganic nanoparticles are including metal nanoparticles, magnetic nanoparticles, titanium dioxide, zinc oxide, and zinc sulfide (Asmathunisha and Kathiresan, 2013). Green technology has been dominated over physical and chemical methods because of its environmentally friendly, properties of being synthesized in large scale, cost-effective, free of using the higher temperature, pressure, energy, and toxic chemicals (Goodsell, 2004). With the help of stabilizing or capping agents, the possibility of preparing nanomaterials from aqueous medium has been explored recently (Shervani and Yamamoto, 2011). Titanium dioxide (TiO_2) has recently attracted much attention because of its wide potential applications in environmental remediation, electronics, sensor technology, solar cell, and other related fields (Choi *et al*., 2010; Sabry *et al*., 2016). TiO_2 offers the most successful application in photocatalysis given its excellent photoactivity, high-stability, non-toxicity, low-cost, and water-insoluble properties under most conditions. Anatase TiO_2 exhibits higher photocatalytic activity than the other TiO_2 forms. The photocatalytic activity of TiO_2 is influenced by its crystalline form and structural parameters, such as morphology, particle size, and specific surface area. Photocatalytic oxidation has been widely proven as one of the advanced oxidation processes for pollutant degradation (Chong *et al*., 2010). Many oxide semiconductors, such as TiO_2, ZnO-, and SnO_2-, have been proven as efficient photocatalysts for photocatalytic degradation of organic pollutant and photocatalytic water splitting owing to their excellent ultraviolet absorbency, relatively high photocatalytic activity, robust chemical stability, low cost and nontoxicity (Jing *et al*., 2013).

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Biological method has proved to synthesize titanium dioxide nanoparticles (TiO_2NPs) with increased rate compared to other physical and chemical methods. TiO_2NPs show vital role in photocatalytic activity to remove the environmental contaminants; it has been extensively studied as a way to resolve environment issues such as degradation of organic dyes, phenol, and reduction of CO_2 because of its photo stability, recyclability, non-toxicity, highly reactive, inexpensive, and chemically inert (Yalçýn *et al.*, 2010). TiO_2NPs have also been synthesized for the emerging microbial resistance against metal ions, and antibiotics. Previously, it was reported that titanium dioxide nanoparticles have been synthesized using plants and bacteria and it possess potential antibacterial, antifungal, anti-inflammatory and anti-leishmanial activities. TiO_2NPs are deliberated the best photocatalytic materials due to their thermodynamic stability, relative non-toxicity, and strong oxidizing power (Xu *et al.*, 2010). Green technology is identified as an alternative way to decrease the textile color dyes by using metal NPs exposure through the mechanism of photocatalytic degradation; because these non-degradable dyes are released from industries that contaminate the soil, water sources and environment globally. In textiles industries, various dyes are being used from 10-15% in synthesis and production process and yearly 7×10^5 tons of dyestuffs were released from textile industries alone. Totally about 10,000 varieties of dyes are available for commercial applications. Color dyes are highly toxic and carcinogenic to humans and animals and also responsible for causing kidney problems, liver damage and cancer (Sankar *et al.*, 2014b). Recently, it was reported that the highly toxic property of crystal violet causes cancer, methemoglobinaemia, inflammatory response in the gastrointestinal tract, cytogenetic toxicity, and eye irritation. The degradation of dyes has been achieved by using different techniques such as flocculation, electrocoagulation, UV-light degradation, and activated carbon (Kumar *et al.*, 2013). Although these methods have been used, the photocatalytic method using NPs is an impressive way to resolve the existing dye pollution in the environment effectively. In textile and paper industries, recently nanoparticles are being used to degrade the organic dyes as they exhibit enhanced photocatalytic property for degrading organic dyes under solar radiation (Kumar *et al.*, 2013). Recent reports showed that the removal of organic dyes using nanoparticles is a better choice than the common dye removal techniques like redox treatment (Kim and Hensley, 1997), electro-coagulation (Szpyrkowicz, 2005), carbon sorption (Gomez *et al.*, 2007) and UV photodegradation (Comparelli *et al.*, 2005; Sohrabi and Ghavami, 2008).

Recently, plant (Banerjee *et al.*, 2014; Roy *et al.*, 2013; Phanjom *et al.*, 2012) and microbe-mediated (Honary *et al.*, 2013) biological synthesis procedures are frequently used for synthesis of nanoparticles. But in particular, the microbe-mediated synthesis methods involve various complicated procedures and time-consuming (Li *et al.*, 2012; Bonde *et al.*, 2012). Plant medicated synthesis of nanoparticles has several advantages over other biological methods and it is rapid method to extracellular synthesis of nanoparticles in large scale. The plant *A. altissima* (White Snakeroot), is a member of *Asteraceae* family commonly located in the part of eastern half of North America (Burrows and Tyrl, 2001). Mixture of many lipophilic compounds including several benzofuran compounds such as tremtone, dehydrotremetone and 6-hydroxytremetone have been identified from this plant species (Bonner and DeGraw, 1962). It is reported that the leaves of *A. altissima* (tribe eupatorieae) having two different chromene glycosides and many lipophilic chromenes (Bohlmann *et al.*, 1977). To best of our knowledge, this is the first report on synthesis of TiO_2 NPs using *A. altissima* leaf extracts and their photocatalytic activity against different toxic dyes. The major goal of this study is to synthesis and characterization of TiO_2 – using *A. altissima* aqueous leaf extracts and also to study the photocatalytic degradation of textile dyes including methylene blue dye, Alizarin red, crystal violet and methyl orange.

2. Materials and Methods

2.1 Preparation of plant extract

To prepare aqueous leaf extract, the leaves of *A. altissima* were collected from Botanical Garden, Periyar University, Salem, Tamil Nadu, India. The fresh leaves were washed with tap water to remove the dust particles on their surface. A healthy and undamaged leaf of *A. altissima* (50 g) was cut into small pieces and homogenized using mortar and pestle. The homogenized solution was prepared by adding 200 ml of sterile distilled water. The homogenized content was boiled at 60°C for 10 min using microwave irradiation. The mixer was allowed to cool and filtered through Whatman No.1 filter paper. The filtered extract was used for nanoparticle synthesis.

2.2 Synthesis of TiO_2NPs using *A. altissima* leaf extracts

For the green synthesis of TiO_2 nanoparticles, 25 ml of filtered aqueous leaf extract was added to 5 mM of 225 ml of $TiO(OH)_4$ solution. The mixture was then incubated for 12 h. under the light condition at room temperature. The control setup was also maintained without the addition of *A. altissima* extract. The appearance of color change primarily confirmed the production of TiO_2NPs. The reaction mixture was then centrifuged at 8000 rpm for 10 min at room temperature. The supernatant was discarded and settled pellets were dissolved in appropriate volume of sterile distilled water. The nanoparticle pellet was dried and used for characterization.

2.3 Characterization of TiO_2 NPs

The green synthesis of TiO_2 nanoparticles was monitored by UV-visible double-beam spectrophotometer (UV-1800, Shimadzu, Japan) at the wavelength of 200-700 nm. Further the synthesized TiO_2 nanoparticles and plant extract were analyzed by Fourier transform infrared spectroscopy (FT-IR) which exhibited possible functional groups for the formation of nanoparticles using "Perkin-Elmer model spectrum RXI". The dried nanoparticle samples were compressed into a thin KBr disc within the range of 4000 to 400 cm^{-1} in transmittance mode. The crystalline form of TiO_2 stability and particle size distribution were characterized by X-Ray diffraction (XRD) analysis. The XRD was carried out on Rigaku miniflex II operated at a voltage of 40 kV, a current of 30 mA and scan rate of 10°/min with Cu-Kα radiation in a θ–2θ. The morphological structure of the synthesized TiO_2NPs was investigated using the field emission scanning electron microscope (FESEM, Carl Zeiss Ultra 55 model) and EDX to confirm the presence of Ti.

2.4 Preparation of photocatalytic dye solution

Green synthesized TiO_2NPs have been used for the photocatalytic degradation of different dyes such as methylene blue, methyl orange, crystal violet, and alizarin red under sunlight irradiation which act as a superior source for photocatalytic activity. The dye solutions (stock) were prepared by adding different dyes at the concentration of 10 mg/l in a bottle individually and prepared solutions were stirred for 30 min at room temperature. To prepare stock, 10 mg TiO_2NPs was added in 50 ml of dye solution. The dye and nanoparticles mixture was kept under the stirring condition for 30 min and exposed to sunlight. The mixer was then subjected to exposure of sunlight for 6 hrs and 2-3 ml of mixture was collected at different periods of time (every 1 h.) and centrifuged at 8,000 rpm for 10 min. The acquired supernatant was analyzed using UV-visible spectroscopy to measure the degradation of dye. The dye degradation rate was calculated by the following formula:

$$\text{Decolorization of efficiency}(\%) = \frac{C_0 - C}{C} \times 100$$

C_0 - Initial concentration of the dye solution

C - Concentration of the dye solution after 't' hours of exposure to sun light

2.5 Statistical analysis

All the experiments were carried out with two replicates for each treatment and repeated twice. Data were statistically analyzed using analysis of variance (ANOVA). Data were presented as the mean ± standard error (SE). The mean separations were carried out using Duncan's multiple range tests and significance was determined at the $p \geq 0.05$ % level (SPSS 20).

3. Results and Discussion

3.1 Synthesis and characterization of titanium dioxide nanoparticles

The green synthesized titanium dioxide nanoparticles were primarily confirmed by the contrast of color changes with increasing of dark brown color after incubation period. The *A. altissima* plant extract was mixed with TiO_4 solution and stored under dark conditions for 24 h. The color change was observed from light green to dark brown indicates the synthesis of TiO_2NPs. Similar results were also reported earlier for synthesis of titanium dioxide nanoparticles using *Azadirachta indica* leaf extracts (Sankar *et al.*, 2015). The UV spectrum of titanium dioxide nanoparticles synthesized using *A. altissima* leaf extracts was observed at 332 nm which confirmed the presence of titanium dioxide nanoparticles. Kumar and Cumbal (2014) also obtained peak at 350 nm in *Citrus paradsi* peel extract mediated synthesis of titanium dioxide nanoparticles.

The FTIR spectroscopy analysis of the synthesized titanium dioxide nanoparticles revealed that the presence of various functional groups were recorded at different wavelengths in the range of 3287, 2922, 1645, 1537, 1238, 1150, 1079, 1030, 687 cm^{-1} related to alcohol, phenol, ammonium ions, acyclic, aliphatic of nitro compound, aliphatic amines, vinyl, azocompounds respectively (Figure 1 a and b). The broad absorption peak of titanium dioxide nanoparticles observed at 3287 cm^{-1} represents the presence of higher concentration of alcohol, phenols with O-H stretches. The peak at 2922 cm^{-1} indicates the presence of ammonium ions with N-H stretching and medium peak at 1645 cm^{-1} shows acyclic compound with C-C stretching. The strong peak noticed at 1537 cm^{-1} represents aliphatic of the nitro compound with stretching of N-O. The aromatic ethers of C-O stretching were represented by peak at 1238 cm^{-1}. A peak observed at 1150 cm^{-1} shows alcohol compound with C-O stretching. The peak at 1079 cm^{-1} represents aliphatic amines with stretching C-N. The peak presented at 1030 cm^{-1} shows aliphatic amines with stretches of C-N. Previously, similar peaks for TiO_2NPs synthesized using *Calotropis gigantean* extract were also reported by Marimuthu *et al*. (2013). FT-IR results of *A. altissima* leaf extracts represent major peaks at 3377, 2924, 2854, 1621 and 672 cm^{-1} for its respective biomolecules. Among these peaks, the major peak at 3377 cm^{-1} shows the high concentration of broad alcohols, phenol compound with O-H stretching and intense peak at 2924 cm^{-1} indicates the alkyl group with C-H stretching. The peak at 1621 cm^{-1} represent the dienes group with stretching of C-C and the strong peak observed at 672 cm^{-1} shows vinyl biomolecule with of C-H stretching. The present result of *A. altissima* plant extract had matched with the functional groups of *Psidium guajava* plant extract reported earlier by Santhoshkumar *et al*. (2014).

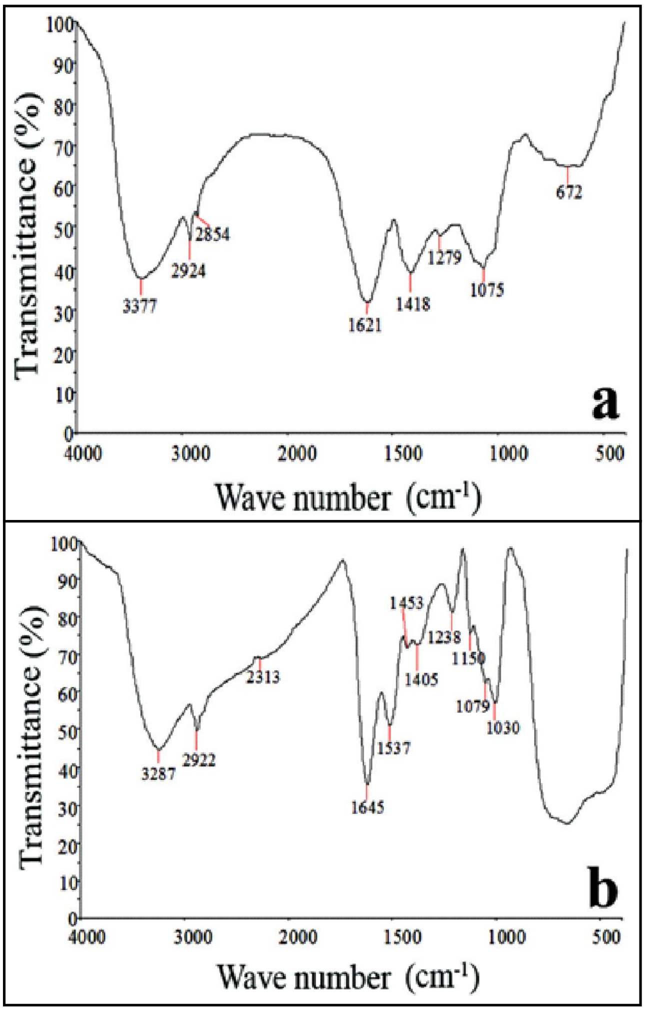


Figure 1: Fourier transform infrared spectroscopy analysis (FTIR) showing peaks for: a) aqueous leaf extract and b) biosynthesized TiO_2 nanoparticles.

The synthesized nanoparticles have morphology, agglomeration and crystallinity. The crystalline structure of the biosynthesized TiO_2 nanoparticles was confirmed by XRD analysis. The XRD pattern exhibited eight prominent peaks with 2θ at around 25.32°, 37.72°, 48.10°, 53.82°, 55.09°, 62.71°, 75.03° and 82.83°, indexed to the TiO_2 anatase values (101), (004), (200), (105), (211), (204), (215) and (224), respectively. The XRD patterns obtained was matched with the database of JCPDS No: 21-1272. XRD results confirmed the polycrystalline nature of the synthesized titanium dioxide nanoparticles (Figure 2). The dominant 2θ peak observed at 25.3264 assigned to 101 is an anatase value. Earlier, it has been reported that TiO_2 nanoparticles synthesized using *Citrus paradise* peel extract had the same 2θ value at 25.3264 anatase form of 101 rutile crystalline structures confirmed by XRD analysis (Chanathaworn *et al*., 2012; Kumar and Cumbal, 2014).

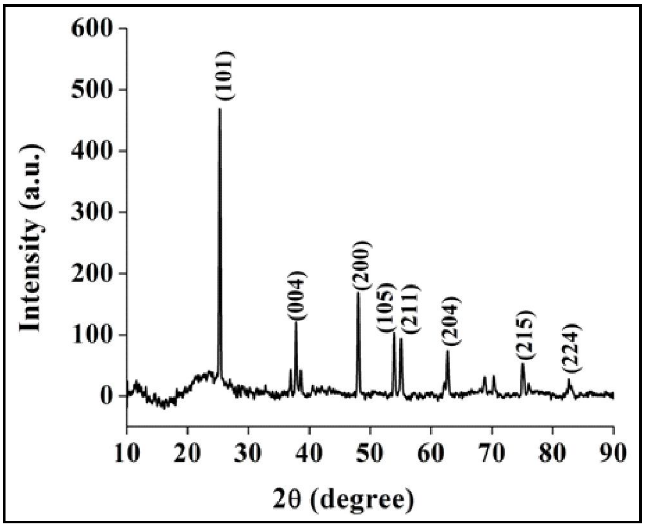
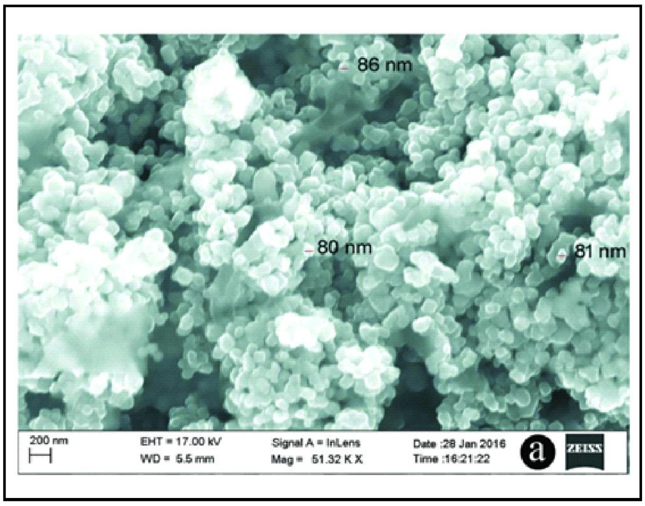


Figure 2: XRD pattern indicates the polycrystalline form of TiO_2 NP.

The topographical images were analyzed by FESEM for the surface and morphology of the synthesized TiO_2 NPs. FESEM analysis indicates that the TiO_2 NPs were found to be as spherical in shape with 60 to 100 nm in size (Figure 3a). FESEM results further showed the physical nature, the size of particles and morphology of nanoparticles at 51.32 KX magnifications which give the morphology of synthesized titanium dioxide nanoparticles. A strong peak in energy dispersive X-ray (EDX) analysis confirmed the presence of titanium dioxide in the synthesized nanoparticles (Figure 3b). Similar XRD analysis results were also reported in green synthesized titanium dioxide nanoparticles using *Mangifera indica* (Rajakumar *et al.*, 2014) and *Azadirachta indica* plant extracts (Sankar *et al*., 2015).



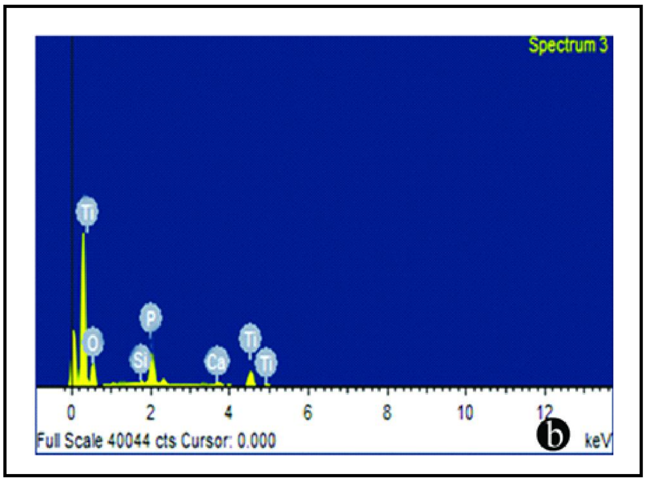
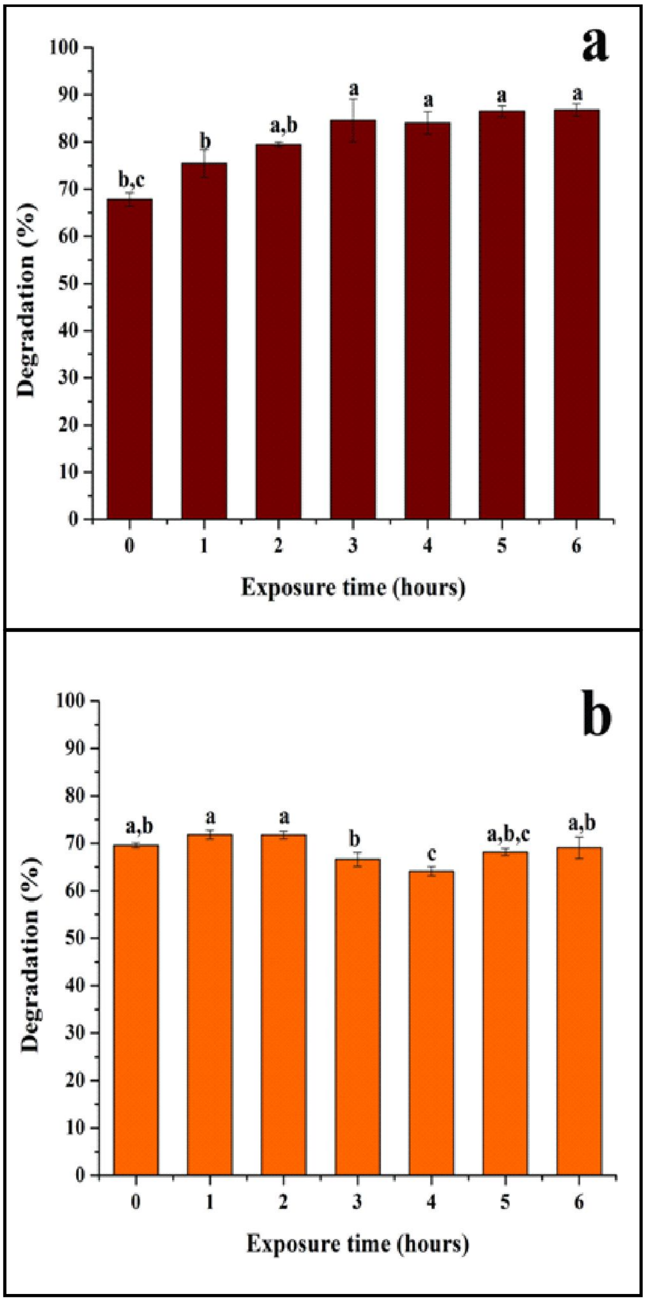


Figure 3: a) Field emission scanning electron microscopy (FESEM) image of spherical shape TiO_2 nanoparticles and b) Energy dispersive X-ray (EDX) analysis showing strong TiO_2 peaks.

3.2 Effect of titanium dioxide nanoparticles on photocatalytic activity

Artificial coloring agents (dyes) are being used in different industries like textiles, cosmetics, paper, and plastics (Sankar *et al.*, 2014b). Synthetic dyes are causing harmful effects to humans and it would cause several diseases like mutagenesis, carcinogenesis and skin diseases. It has been reported that photocatalytic degradation of textile dyes is more effective than other chemical or physical methods. In this study, the green synthesized titanium dioxide nanoparticles using A. *altissima* leaf extract showed great photocatalytic activity with enhanced degradation efficiency against several textiles dyes such as Methylene Blue, Alizarin Red, Crystal Violet, and Methyl Orange. The highest of percentage (86.79 %) of degradation was observed in Methylene Blue (Figures 4a-d). Visible range of UV arose at different wavelengths such as Methylene Blue was originated at 646 nm, Alizarin Red peak was noticed at 520 nm, Crystal Violet dye solution was derived at 580 nm and Methyl Orange solution was emanated at 464 nm. Similar results were reported for methyl orange dye solution which was originated at 464 nm in UV-spectrum (Kumar and Cumbal, 2014). It has been reported that the methyl orange was degraded by using silver nanoparticles and UV spectra was originated at 420 nm after 10 h exposure to sunlight (Selvam and Sivakumar, 2015). In the case of methylene blue, the spectra arose at 660 nm has also been reported by Roy *et al*. (2015). During the sunlight exposure, the degradation was initially confirmed by color changes; while an incubation time increased with TiO_2 NPs under sunlight exposure, the degradation efficiency of dye was also increased. Green synthesized titanium dioxide nanoparticles had acted as potential photocatalyts against different dyes used in the present study. The percent of dye degradation recorded was 86.79 %, 76.32 %, 77.59 % and 69.06 % for methylene blue, alizarin red, crystal violet, and methyl orange respectively; this result revealed the high efficiency of photocatalytic dye degradation capability of TiO_2 NPs synthesized using *A. altissima*. It is presumed that due to the presence of several potential bioactive molecules in *A. altissima* plant leaf extracts that are able to reduce the precursor TiO_4 into TiO_2NPs and these nanoparticles can effectively degrade the methylene blue and other dyes under solar irradiation. Kumar *et al.* (2013) and Kansal *et al.*

(2013) reported that the solar light was found to be more effective than other irradiation techniques for degrading dyes. During exposure to solar light, the photons hit the nanoparticles present in the colloidal mixture, the electrons on the particle surface are excited (Yu *et al.*, 2012). The excited electrons from particle surface have been accepted by the dissolved oxygen molecules in the reacting medium and are converted into oxygen anion radicals. These radicals break the organic dye into simpler organic molecules leading to the rapid degradation of the dye (Houas *et al.*, 2001; Ameta *et al.*, 2013). Accordance with Vanaja *et al.* (2014), the biosynthesized nanoparticles may act as a stable and efficient photocatalyst for degradation of dyes under visible light irradiation. The TiO_2 NPs are decisived for photocatalytic activity because of its strong oxidizing power, long-term stability, and nontoxicity (Tayade *et al.*, 2007).



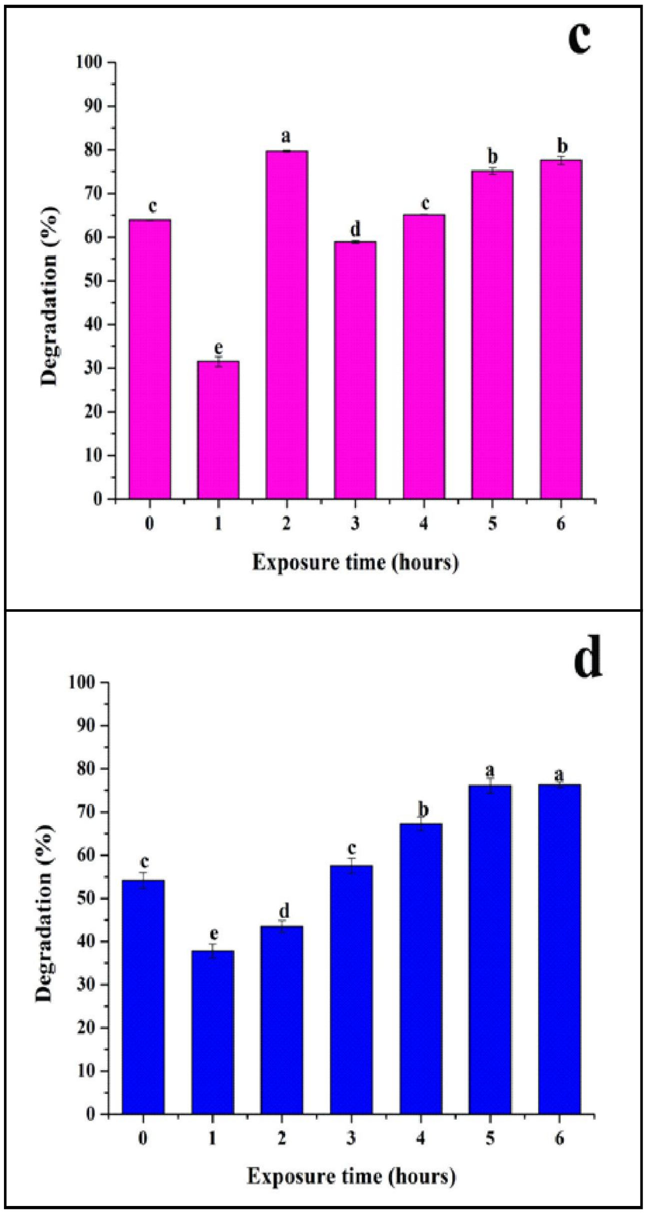


Figure 4: Degradation efficiency of TiO_2 NPs synthesized using *A. altissima* leaf extract on photocatalytic activity against: (a) methylene blue, (b) methyl orange, (c) crystal violet, and (d) alizarin red dyes. Different letters on each error bar are statistically significant at $p \geq 0.05$ level.

4. Conclusion

In summary, a simple and cost-effective method was used for synthesis of biomolecule loaded titanium dioxide nanoparticles via green technology. In the present study, the TiO_2 nanoparticles were synthesized from Titanium oxide (IV) using *A. altissima* leaf extract by using microwave irradiation method and the physico-chemical properties of titanium dioxide nanoparticles were characterized by UV-spectroscopy, FTIR, XRD, and FESEM. The biosynthesized TiO_2 nanoparticles were found to be spherical in shape with an average diameter of 60-100 nm and it was polycrystalline nature. FTIR results exhibited the presence of various functional biomolecules that acted as reducing and capping agent for conversion of TiO_4 into TiO_2 NPs. The synthesized TiO_2 nanoparticles were found to be the best photocatalyst for dye degradation. Results clearly showed that the biomolecule loaded TiO_2 nanoparticles exhibited potential dye degradation of methylene blue followed by alizarin red, crystal violet, and methyl orange under solar light. The present results suggested that the biomolecule loaded TiO_2 nanoparticles synthesized from plants could be used as effective photocatalytic agent for remediation of polluted sites by textile industry in the future.

Conflict of interest

We declare that we have no conflict of interest.

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