BIOCOMPATIBLE SYNTHESIS OF TiO_2 NANOPARTICLES USING *Aloe vera* EXTRACT AND ITS APPLICATION FOR TEXTILE DYE DEGRADATION

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Abstract

Discharge of hazardous dyes from textile industries in fresh water bodies like lakes, rivers and ground water has become a serious problem, since these water bodies are major source for domestic purposes. These pollutants have complex chemical structure and therefore it is very difficult to remove by traditional water purification methods. In this study, we green synthesized Titanium dioxide (TiO_2) nanoparticles (NPs) using *Aloe vera* leaf extract. The synthesized nanoparticles were used for the degradation of Methylene blue (MB) dye. The synthesized TiO_2 nanoparticles have been characterized by UV-vis spectroscopy, XRD, FT-IR and SEM which revealed that the TiO_2 nanoparticles were crystalline in nature with size from 40-60nm and oval in shape. Photocatalytic activity was carried out under UV light which enhanced the degradative ability of TiO_2 NPs. The degradative ability for further characterized by Uv-Vis spectra which confirmed he reduction of MB dye by green synthesized TiO_2 nanoparticles.

Key words: TiO_2 nanoparticles, *Aloe vera*, green synthesis, dye degradation, bioremediation

INTRODUCTION

Many of the major problems that humanity is facing in the twenty first century are related to water quantity and/or water quality issues (Educ, *et al.*, 2009). These problems are going to be more aggravated in the future by climate change, resulting in higher water temperatures, melting of glaciers, and an intensification of the water cycle (Huntington, *et al.*, 2006) with potentially more floods and droughts (Oki, *et al.*, 2006). With respect to human health, the most direct and most severe impact is the lack of improved sanitation, and related to it is the lack of safe drinking water, which currently affects more than a third of the people in the world. Additional threats include, for example, exposure to pathogens or to chemical toxicants via the food chain (e.g., the result of irrigating plants with contaminated water and of bioaccumulation of toxic chemicals by aquatic organisms, including seafood and fish) or during recreation (e.g., swimming in polluted surface water). For all practical purposes, water pollution is the addition by humans of something to the water that alters its chemical composition, temperature, or microbial composition to such an extent that harm occurs to resident organisms or to humans. While chemical pollution has implication for human health, both directly from toxic chemicals in drinking water, and indirectly from the accumulation of toxic compounds by organisms that are then eaten by people.

Water pollution from different sources such as agricultural run-off, effluents from textile, paper and pulp mill, industries provide large amounts of harmful waste containing dyes. Dyes are an important class of synthetic organic chemical compounds that are generally non-biodegradable and their removal provides crucial ecological problems. The use of these colored dyes (among others, methylene blue, acid red 14, remazol red RR, reactive blue 19, methyl orange) provides a major source of environmental contamination (Wua, *et al.,* 2010, Li., *et al.*,2016). The release of colored wastewater to the environment is a considerable source of toxic and aesthetic pollution and eutrophication due to the stability of modern dyes. Conventional biological treatment methods of industrial wastewater are ineffective and often result in an intensively colored discharge from the treatment plants (Sharma, *et al.,* 2009). Extensive use of these dyes in the industries has become an ever increasing part of industrial effluents. In fact, of 450,000 tons of organic dyes annually that have been produced worldwide, more than 11% are lost as effluents during manufacture and application processes (Chaloupk, *et al.*, 2010). Removal of these dyes is necessary to protect environment. In recent times nanotechnology has provided a great platform in various fields includng bioremediation. Many researchers have explored the catalytic and dye degradation using nanoparticles. In the present study green synthesized Titanium dioxide nanoparticles using *Aloe vera* extracts was used for the degradation of Methylene blue dye.

MATERIAL AND METHODS

Preparation of plant extract

Fresh plants of *Aloe vera* leaves were collected from garden. The leaves were washed with tap water followed by distilled water for 5 times to remove adhering debris, associated epifauna/ epiphytes. After cleaning, fresh material was cut into small pieces and preserved at a temperature of 28 ^{0}C until it was used. The shade dried *Aloe vera* leaves were macerated as to make coarse powder using mortar and pestle.

50 g of leaves were mixed with 100 ml of distilled water and boiled at 100 ^{0} C to get extract. Then the extract was filtered through a Whatman No.1 filter and was stored in a refrigerator at 4 ^{0}C until further analysis. (Yuvasree, et al., 2013)

Preparation of precursors:

Precursors for Titanium oxide (TiO_2) nanoparticles (NPs) (Titanium oxide) were purchased from Sigma Aldrich chemicals, India and prepared freshly. Precursor for preparing TiO_2 nanoparticle was 2mM of titanium oxide was dissolved in 100 ml of double distilled water. (Bhakya., *et al.*, 2015*)*

Synthesis of TiO_2 nanoparticles using *Aloe vera* extract:

20ml of leave extract were adding with 100 ml of distilled water that contains Titanium oxide nanoparticles (TiO_2 -NPs). The mixture was stirred up continuously for 4 hours at 70^{0} C. By this process, the NPs were formed and then it was filtered and washed repeatedly by using distilled water to remove by-products. The nanoparticles were dried at 100 ^{0} C for overnight and calcinated at 500 ^{0} C for 4 hours. (Pusit Pookmanee, *et al.*, 2009*)*

Characterization of green synthesized TiO_2 nanoparticles:

UV–visible spectra analysis was performed for all samples and the absorption maxima were analyzed at a wavelength of 200–700 nm using UV– visible spectrophotometer (UV-160 v, Shimadzu, Japan). The biosynthesized TiO_2 nanoparticles were examined for the presence of biomolecules using FTIR spectrum (Thermo Scientific Nicolet 380 FT-IR Spectrometer). The crystalline nature of particles was evaluated by using X-ray diffraction method (XRD) which recorded by XPERT-PRO diffract meter using Cu-kα radiation wavelength of 1.5406˚A. The studies on size and shape of silver nanoparticles were performed by Scanning electron microscopy (SEM) was performed using HITACHI-4800**.** JEOL 2010, operated at 200 kV and equipped with an energy dispersive spectroscopic.

Photocatalytic degradation of methylene blue activity:

Methylene blue (MB) also known as methyl thioninium chloride, is a medication and dye, a heterocyclic aromatic dye, in the textile has increased in the last few years (Kang *et al.*, 2000). The UV–visible band of MB monomer in water appears normally at 665 nm corresponding to the transition of MB (Shahwan *et al.*, 2011).

In this experiment, 3.2 mg of MB dye was dissolved in 500 ml distilled water and it is considered as a stock solution. The dye was sonicate for 10 mins to dissolve completely. Then 100ml of MB dye was taken in the petri dish. The relative absorbance of band at 665 nm is plotted as a function of time to evaluate the reduction reaction rate in the absence of titanium dioxide nanoparticles (30 min). 50 mg of TiO_2 was added to the dye. The plot of relative absorption intensity with wavelength in a regular interval of time (15 min) reveals that the complete reduction of MB is accomplished in less than 20 min in the presence of TiO2 nanoparticles. The decreasing trend of the absorption intensity indicates the reduction of MB, but in a slow pace. Increased degradation of MB has been achieved through the inclusion of TiO_2 colloid which is shown by a strong decrease in the absorption intensity. The size dependent catalytic property has been investigated. In the present reduction reaction TiO_2 nanoparticles exhibit an awesome performance as a catalyst. (Kang, *et al.*, 2000, Shahwan, *et al.*, 2011)

RESULT AND DISCUSSION

Now a days performance and minimization of electronic devices is very important aspect compare to rest of parameters, in which nano materials play very important role. Everyone is focused on nanotechnology because of its vast of applications in almost all types of industries from textiles to medicine including electronics. Titanium dioxide is solid inorganic substance, which is a white colour metal oxide.TiO_2 is poorly soluble, non-flammable, thermally stable and not classified as hazardous.

In present study, TiO_2 nanoparticles of *Aloe vera* leaf extracts were synthesized and their photocatalytic degradation of methylene blue activities was performed. This study is the first attempt to evaluate photocatalytic degradation of methylene blue potential of TiO_2 nanoparticles synthesized from *Aloe vera*. The green synthesis of TiO_2 nanoparticles was accomplished through new effortless green chemistry process, using the *Aloe vera* extract as a reducing and capping agent. The formation of TiO_2 NPs was monitored by visual exam. The color of solution altered from green to pale white color through the reaction, showing the formation of *Aloe vera* mediated TiO_2 NPs showed in Figure 1a, 1b, 1c and 1d. Nanoparticles attract more researchers for the future developments in the area of medicine, healthcare and agriculture due to their diverse remarkable and captivating range of biological applications.

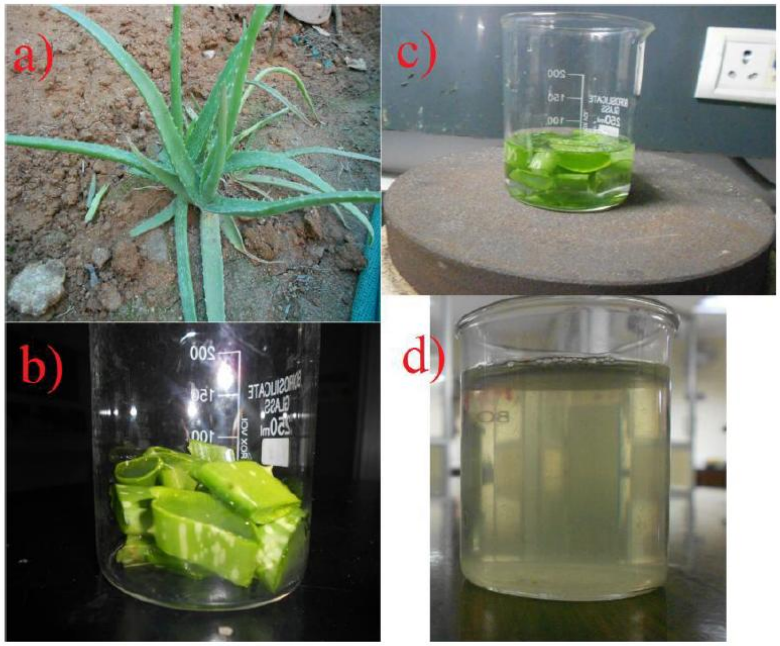


Figure: 1 a) *Aloe Vera* plant, b) Separated pieces of *Aloe Vera*, c) In boiling Boiling process, d) Extract of Aloe vera leaves extract

Synthesis of TiO_2 nanoparticles both the precursor and the reducing agent were mixed in a clean sterilized flask in 1:1 proportion. Then the solutions were centrifuged at 12,000 rpm for 15 min, consequently dispersed in double distilled water to remove any heavy-handed biological materials with constant stirring at 50- 60°C. Sedimented NPs were given three washing with double distilled water at 12,000 rpm for 15 min. Finally NPs were lypholized to obtain a fine powder. The green synthesized bio-nanoparticles TiO_2 power preparation showed in figure 2.

a) Synthesis of TiO_2 b) Pellet of TiO_2 NPs c) TiO_2 NPs powder

Figure : 2 Green synthesis of TiO_2 by using *Aloe Vera* plant extract

UV spectrum:

UV-Vis spectroscopy absorption spectra of TiO_2 NPs formed in the reaction media has absorbance maxima at 350 nm. A peak specific for the synthesis of TiO_2 nanoparticles was obtained at 350-370 nm by UV-Visible spectroscope in Figure 3.

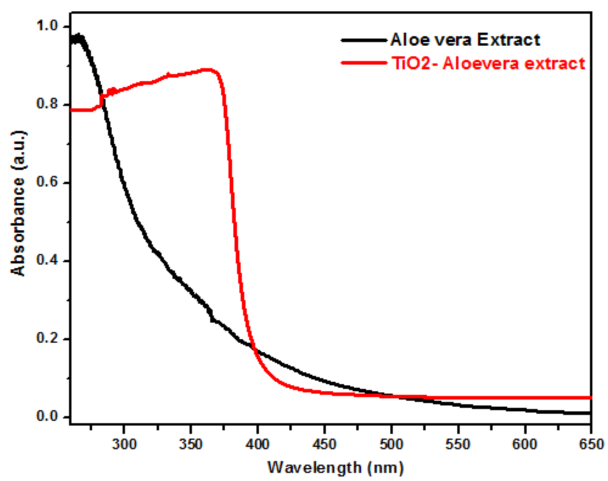


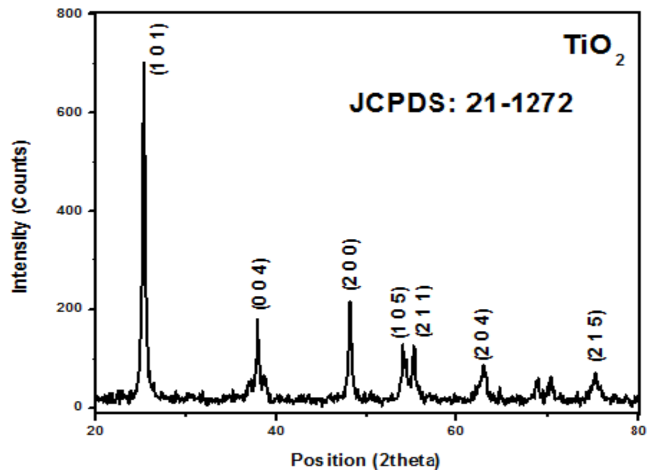
Figure: 3 (a) UV-absorption spectra of TiO_2 formed in the reaction media by

Aloe vera

Absorption spectra of TiO_2 formed in the reaction media have absorbance maxima at 360 nm. A peak specific for the synthesis of TiO_2 nanoparticles was obtained at 200-430 nm by UV Visible spectroscope. Nanoparticle synthesis is an emerging area of research in the scientific world. Wide range of application in different aspects of human life is the reason for the great attraction of researchers towards this field. Green chemistry procedure, probably involving organisms ranging from bacteria to fungi and even plants would benefit the development of clean, nontoxic and environmentally acceptable synthesis and assembly of nanoparticles.

XRD analysis

The XRD pattern of TiO_2 nanoparticles obtained from green synthesis were as shown in Figure 4. The result showed that the structure was in tetragonal structure and these results were



good agreement with JCPDS card number 21-1272.

Figure 4: XRD Pattern of TiO_2 nanoparticles

Peaks were absorbed at 25^0, 38^0, 48^0, 53^0, 55^0, 62^0 and 75^0 along with miller indices values (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 1), (2 0 4) and (2 1 5) respectively. The XRD spectra indicated that particles were of acceptable crystallinity with the cubic structure form of TiO_2 nanoparticles and aggregations formed due to the action of stabilizing agents in the *Aloe Vera* extract.

FTIR analysis:

FT-IR Analysis of TiO_2 Nanoparticles FT-IR determinations were carried out to study the interaction of functional groups and possible biomolecules of *Aloe vera* extract responsible for the biosynthesis of TiO_2 nanoparticles.

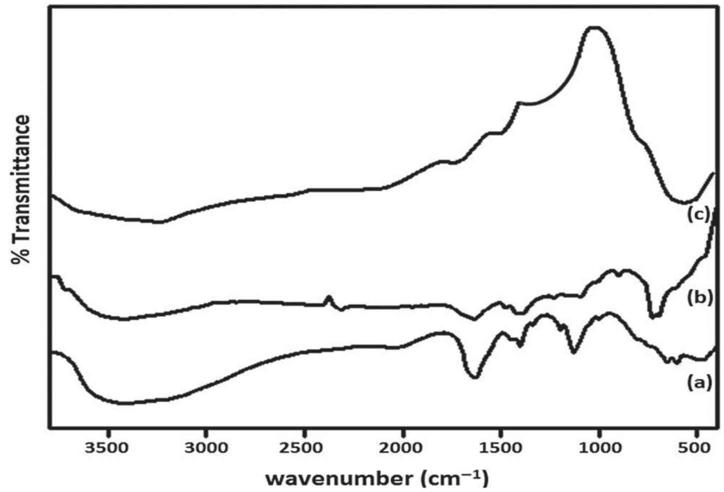


Figure: 5 FT-IR spectra of (a) *Aloe vera* extract (b) prepared sample and (c) calcinated TiO2 nanoparticles

Figure 5 (a) could be assigned to the stretching mode of –OH group of phenolic compounds of *Aloe vera* extract. The absorption band at 1630 cm^{-1} and 1460 cm^{-1} are characteristic of C=O stretching vibrations possibly from amino acids of proteins. The peak at 1401 cm^{-1} could be attributed to the –NH deformation or –OH deformation frequency possibly from amino acids or phenolic groups. The peak at 1128 cm^{-1} is due to the presence of C–OH stretching vibration of secondary alcoholic groups. The peaks appeared below 1000 cm−1 could be assigned to the presence of aromatic substituted rings. The peaks at around 700–600 cm^{-1} may be due to the C–H out of plane bending vibrations. The peak at 464 cm^{-1} is due to rocking vibration of NO_2 from aromatic nitro compounds of *Aloe vera* extract. This results is comparable with the study of Garnweitner, *et al.*, (2012) and Mali, *et al.*, (2013).

The characteristic peak of functional groups of *Aloe vera* extract is slightly shifted with the decreased intensity which is clearly observed in the FT-IR spectrum of as-prepared sample (Fig. 5(b). Moreover, the broad band at 3400 cm^{-1} with less intensity can be related to –OH vibration of Ti–OH group and water molecules of the as prepared sample. A small absorption band at 1620 cm^{-1} was caused by bending vibration of coordinated H_2O as well as from the Ti–OH. Particularly it is noticeable that the peak of –C–OH stretching vibration at 1122 cm^{-1} is completely disappeared in the spectrum of prepared sample thereby it is undoubtedly predictable that the functional moieties of *Aloe vera* extract played a significant role for the formation of titanium hydroxide precursor. Additionally a strong intense peak appeared at low energy region of 645 cm^{-1} which may be due to stretching mode of Ti–O– Ti bonds of TiO_2 network, confirms the facilitation of the starting material, titanium oxide to amorphous and hydrated TiO_2 precursor by *Aloe vera* extract (Ba-Abbad, *et al.,* 2012, Gao, *et al.,* 2004).

In the case of calcinated TiO_2 nanoparticles spectrum which is shown in Figure 5(c), the intensity of the peaks characteristic of *Aloe vera* extract are greatly reduced or completely disappeared whereas the intensity of peak characteristic of Ti–O–Ti bonds of TiO_2 at 630–650 cm^{-1} is greatly enhanced the TiO_2 precursor by calcination (Rajakumar, *et al.*,2012).

SEM (Scanning Electron Microscope):

SEM analysis was performed with the titanium nanoparticle to learn the structure of the nanoparticles. Small amount of sample was taken on a copper grid coated with carbon and dried under mercury lamp. The oval shaped smooth surfaced nanoparticle was observed as shown in Fig.6 a). This image was observed within the magnification of 1µm (Sharmila Devi, *et al.*, 2014).

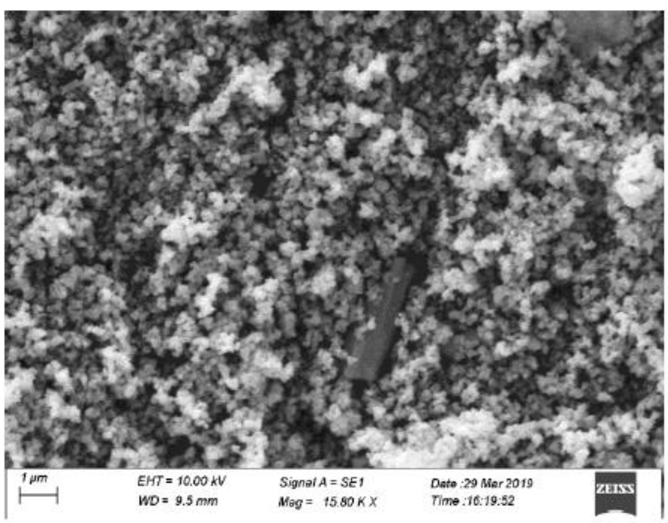


Figure. 6 a) SEM analysis of TiO2 NPs in l µ m magnification

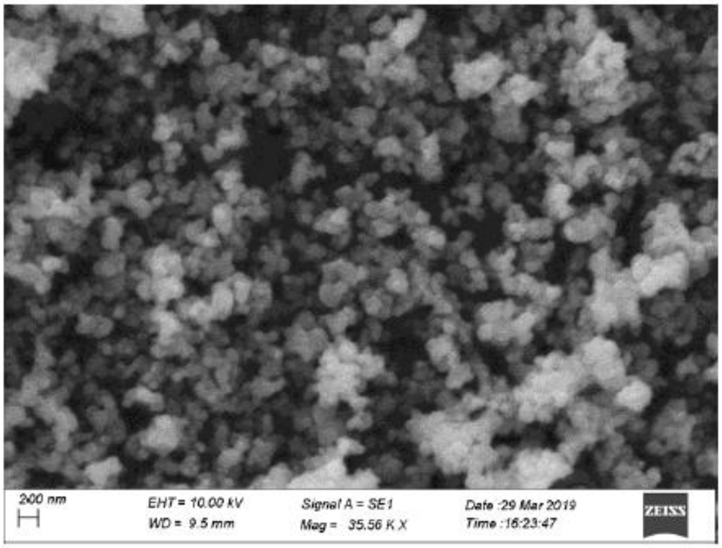


Figure. 6 b) TiO2 NPs shows the range 40-60nm

The TiO_2 nanoparticle were showing irregular particles structure. The size was ranging from 40nm to 60 nm (Ouyang, *et al.*, 2012).

Photocatalytic degradation of methylene blue:

Photocatalytic activities of *Aloe Vera* mediated Titanium oxide nanoparticle (TiO_2 NPs) were evaluated *via* photocatalytic degradation of MB dye under UV irradiation shown in Figure. 7

Figure. 7 Photocatalytic degradation of methylene blue (MB)

A blank test was conducted initially for MB dye results in minimal degradation (9%) shows less photolysis with no color change. Subsequently degradation was carried out in the presence

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of catalyst accounting for 84.35%, when exposed to UV light irradiation in figure 8. Results demonstrate relatively complete reduction (84.35%) of MB occurs within 105 min under UV lamp. The dye degradation rate was highly depended on the morphology and crystallinity of biosynthesized TiO_2 NPs.

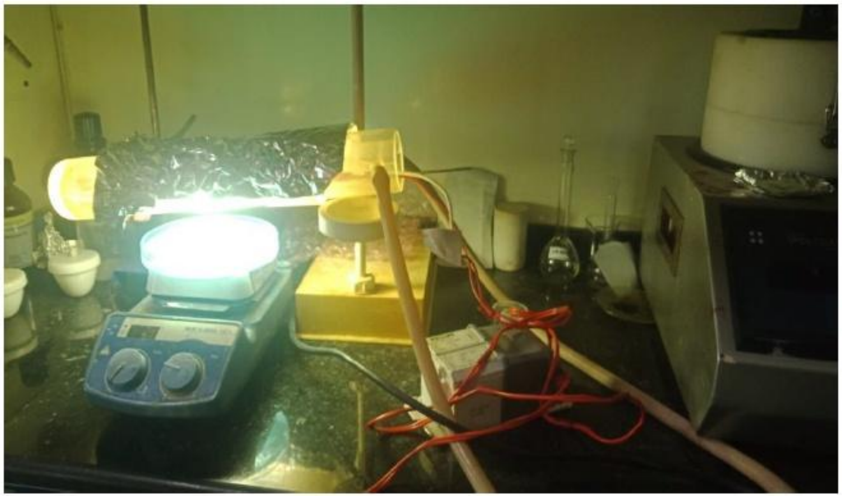

Figure. 8 phtocatalytic UV – light set up

The above results revealed, green synthesis of *Aloe vera* mediated TiO_2 NPs exhibited higher degradation efficiency (84.35%) achieved when using tungsten halogen lamp (150 W) due to the formation of nano-hetero junctions compared to various synthetic methods like physically and chemically based approaches. Kumar and co-workers (2013) have reported similar biosynthesized TiO_2 NPs comparing solar light irradiation techniques, and UV-light irradiation. This approach was commenced to be faster in decolorizing methylene blue (84.35% within 105 min.) in the presence of a catalyst.

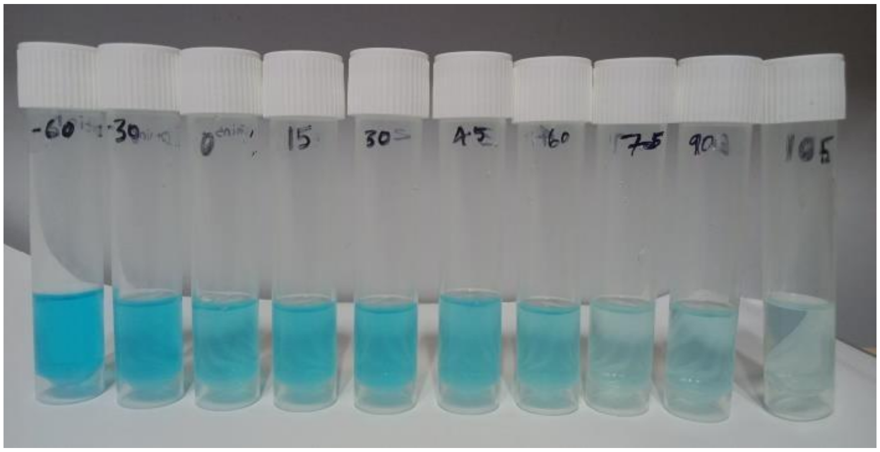

Figure. 9 Photodegradation characterization studies by visible color change of green synthesized *Aloe vera* mediated TiO_2 NPs.

Organic dyes were widely used in various industrial processes and discharged into the environment, resulting in them being common contaminants in wastewater. Most of the dyes are stable, recalcitrant, colorant, and even potentially carcinogenic and toxic. The deleterious effects of dyes on human health and ecosystems have driven researchers to develop facile and effective methods to treat dye wastewater.

UV–VIS test for methylene blue degradation:

According to absorbance spectrum of samples, maximum absorbance of all samples occurs at 660 nm wavelength. First absorbance spectrum was taken at zero time (i.e. before illumination UV light and TiO2 catalyst) and peak has highest value. After illumination starts every an hour, absorbance spectrum were recorded and showed that peak value reduces moderately. This shows that during experiment absorbance value decrease with exposure to time and finally after 1.5 h absorbance peak become nearly smooth while solution blue color also become color less with passing time. N-dealkylation of dyes containing auxochromic alkylamine groups plays an important role in photocatalytic degradation (Dariani, *et al.*, 2016) Fig. 9 and 10 shows the color of Methylene blue solutions becomes weaker when part of the methyl groups degrade, and hypochromic shift occurs. Hence, N-demethylation of Methylene blue occurs as described in the pathway at first, and finally Methylene blue depredated into H2O, CO2, and other inorganic molecules. (Zhang, *et al.*, 2001)

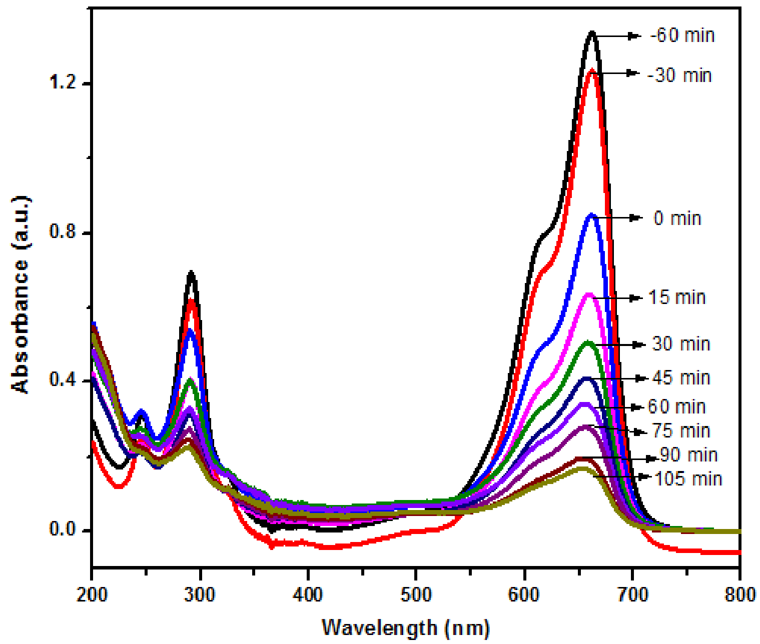

Figure. 10 Photodegradation of MB dye under UV light using green synthesized *Aloe vera* mediated TiO_2 NPs.

The higher photocatalytic performance of TiO_2 NPs could be explained by strong visible light absorption and the presence of TiO_2^+ nanoparticles resulting in a low recombination rate of e^-/h^+ pairs (Yola *et al.*, 2014; Auffan *et al.*, 2009). Degradation of MB concluded by reduction intensity of absorption peak due to SPR effect i.e., charge-density oscillation generates at the interface of metal and dielectric medium. Therefore, these it is clear thus the green TiO_2 NPs can be act as an effective alternative catalyst against toxic agents achieved by photocatalysis with upon UV-light illumination.

CONCLUSION

In this study TiO_2 nanoparticles have been successfully prepared by green synthesis using *Aloe vera* extracts. The biosynthesized nanoparticles were implemented for removal of textile dye from its aqueous solution. Effective destruction of dyes is made possible by photocatalysis in the presence of TiO_2 suspensions. Various operational parameters affect the activities of *Aloe vera* mediated TiO_2 NPs photocatalysts. Since the influence of the parameters has been in some cases controversial, it is therefore necessary to study the nature of the sample to be degraded, as this will provide a clue on the type of photocatalyst to be used in its degradation. Enhanced photocatalytic performances were towards MB dye achieving 84.35% within 105 min under UV light irradiation. The better understanding of the photocatalytic process and the operative conditions could give great opportunities for its application for the removal of dye from textile industries.

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