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Exploration of Dye Degradation Potential of Eco-friendly Synthesized TiO_2 Nanoparticles Using Extract of *Acacia nilotica*

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Abstract

Nowadays the requirement for clean water in human population is growing day by day. The different factories and industries like pharmaceutical, textile, food processing, and chemical industries are the major cause of water contamination by adding an organic dyes. The aim of present study is to synthesize the green nanoparticles for the purification waste water. The TiO_2 nanoparticles were prepared using crude extract of local plant *Acacia nilotica.* The TiO_2 nanoparticles initially were confirmed by color change and later by UV-spectroscopy. The size and shape of TiO_2 nanoparticles were assessed by using field emission scanning electron microscope (FESEM). The Energy Dispersive X-ray spectrometric analysis (EDs) was performed to measure the elements concentrations. Dye removing potential of prepared TiO_2 nanoparticles were performed using methylene blue induced dye mixture. The result showed that the synthesized TiO_2 nanoparticles were round and spherical in shape ranging from 50-120nm with average of 60 nm. EDs confirmed the TiO_2 presence in nanoparticles. The synthesized TiO_2 nanoparticles showed 75% dye removing capacity after 2 hours of exposure. In conclusion, TiO_2 nanoparticles were highly effective for removing dye from water; therefore these TiO_2 nanoparticles can be used as best source for water treatment for removing dyes from waste water.

Keywords: TiO_2 nanoparticles, *Acacia nilotica*, Waste-water, Dye removing, Methylene blue

Introduction

Fresh and healthy water is very important for the animal, humans and plants. Aquatic life especially fishes is dependent on germ free and high quality water for their healthy life [1]. Nowadays the requirement for clean water in human population is growing with the time. The contaminated water from various foundations continues to contaminate the normal water capitals and also the system of water cleaning systems. The different factories and industries like pharmaceutical, textile, food processing, leather, printing and chemical industries are the major cause of water contamination by adding an organic contaminants from their various industries [2-5].

Ecosystem contamination has been a vital problem for today's civilization because of rapid increases of various factories around the world especially the dye factories. Waste of various colored dye material generates severe difficulties to the environment and the people's health. Because these dye material may produce caner and different mutations in human and different aquatic animals. That's why it is very important to regulate and damage the factories waste in the form of dyes earlier the may cause harmful and acute hazard to the normal environment. In textile and different food processing industries mostly methylene blue is used for different purposes such as for silk, leather and wood products. In some food industries rhodamine is also used and some industries utilized methylene orange [6, 7].

The enormous research on TiO_2 has been evident from literature in various areas of basic and applies sciences because of its high reducing capacity for the breakdown of organic contaminants, without any side effects, minimum price, elemental strongest, rich resilience and visible life transparency. During the dye water purification, initially water decomposes into hydrogen and oxygen molecules in the existence of ultra violet radiations without being electric field applied [8, 9].

The UV light generated pores of TiO_2 decompose the water molecules and reducing the closest molecule of light activated area. Whereas the electrons interact with the oxygen molecule to generate oxides of superoxide. Treatment of wastewater services around the globe mostly are natural biological related technology. Therefore, while pollutants removal the TiO_2 in the waste water treatment change the both oxygen dependent and oxygen independent process [10, 11]. Importantly, elimination of nitrogen has been highly important than other material especially in the existence of TiO_2 nanoparticles [12].

The plant *Acacia nilotica* locally named as Babul or Kikar is a well-known average sized tree and is widely dispersed in humid and subhumid countries. It has wide range of pharmacological benefits with well-known anti-oxidant potential. *A. nilotica* contains a variety of phytochemicals such as tannins, steroids, terpenes, oleosins, alkaloids, phenols, phenolic, oleosins, phenolic glycosides and essential oils. This plant is well known for its immense source f phenolics mainly gallic acid, and (-) epigallocatechin-5, 7-digallate [13-15].

The *A. nilotica* richly studied and found active against range of disease such as its flowers, gum, bark, leaves, roots and seeds are anti-oxidant, antidiabetic, antimutagenic, anit-cancer, antipyretic, anti-allergic and anti-microbial. This plant is also used in many folk medicines against indigenous diseases [16]. The aim of the present study is to investigate the dye degradation efficacy of TiO_2 nanoparticles.

Materials and Methods

Selection of Plant

Acacia nilotica Lam (Mimosaceae) 'Babul' was collected from Jamshoro and identified and confirmed by Dr. Jamal Mangi Assistant Professor, Institute of Plant sciences, University of Sindh, Jamshoro, Pakistan.

Preparation of the Plant Extract

The collected whole plant was washed five times with distilled water to eliminate the allied impurity. Approximately 500 g of superbly plants pieces was positioned in 2000 mL of methanol and then the mixture was kept in shady places for a week. After that mixture was filtered with Whatmann filter (110 mm). Plant extract was dried in vacuum oven at 40°C. Afterwards, collected crude methanolic extract was used for synthesis of nanocatalyst, filtrated methanol extract was used for synthesis of TiO_2 nanoparticles.

Synthesis of TiO_2 Nanoparticles

Titanium dioxide was purchased from Sigma Aldrich (CAS. 13463-67-7). Methanol extract of 100 mL was placed in flask and 1 mM solution of TiO_2 was added drop wise and kept in incubation with stirring till the change of mixture color from yellow to brown color. Change of color specifies the foundation of TiO_2 nanoparticles.

Characterization of TiO_2 Nanoparticles

The synthesized TiO_2 nanoparticles were inspected by ultra violet visible spectroscopic examination. The form and size of the prepared TiO_2 nanoparticles were calculated by means of a field emission scanning electron microscope

(JEOL JSM, USA). Fourier-transform infrared spectroscopy (FTIR) was achieved by construction of potassium bromide (KBr) disk on crushing TiO_2 nanoparticles with KBr and measured on a Shimadzu FTIR–8400S instrument (Kyoto, Japan). Energy Dispersive X-ray spectrometric analysis (EDs) was done to measure out the elements concentrations in the prepared TiO_2 nanoparticles.

Dye Degradation Activity of Synthesized TiO_2 Nanoparticles

The photocatalytic potential of these prepared TiO_2 *nanoparticles* was examined by degradation of methylene blue under visible light using already reported method [17]. Firstly, dried 20 mg of TiO_2 nanoparticles was placed with 100 mL methylene blue dye solution (2.49 mg/L) and the solution was kept mixing for 30 min in shady atmosphere before uncovering to observable light. After few minutes, 10 mL sample was obtained from the solution, centrifuged to obtain fresh supernatant mixture of the dye and lastly was then analyzed using the wavelength from 200 to 800 nm through the Shimadzu-1800 UV–Vis spectroscope to investigate the dye degradation potential of synthesized TiO_2 nanoparticles.

Results and Discussion

The synthesis and reduction of TiO_2 nanoparticles by plant extract was examined by means of UV-visible spectroscopic investigation. Throughout the addition of TiO_2 solution into *A. nilotica* extract, the immediate alteration in color of the mixture from light yellow to dark brown proposed the foundation of TiO_2 nanoparticles. Recently, world health organization assessed that more than 783 million humans in the world not properly using clean water for drinking, therefore from literature it's evidenced that 1.87 million children mortality because of contaminated water [18]. Different water purification strategies are taken as unachievable in less developed countries such as Pakistan, because they require enormous amount of money and investment, huge resource of water because of its cast humans need to pay for the clean water [19]. Due to the shortage of water peoples have to accumulate their own water from outside their residence and pile the water in their homes because they can use it during water shortage. In this whole process water collection, storage and transportation water is at high risk of contamination from microbes and other pollutants. The scanning electron microscopic images of our study in comparison to other study indicated that methods, and totaling of phytochemical and components in the formation of nanoparticles can decrease the TiO_2 particle self-assembling which is an innate characteristic of majority of TiO_2 nanoparticles [20, 21].

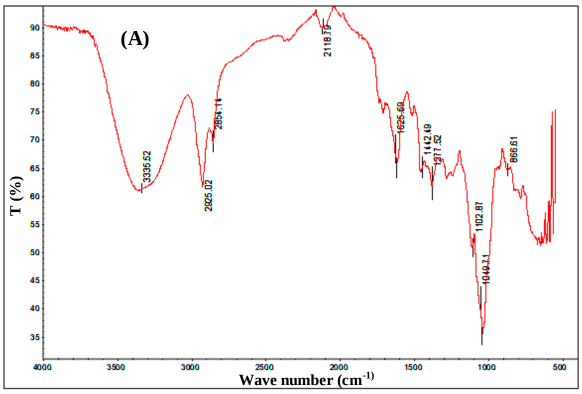
Fourier Transform Infrared (FTIR) Analysis

Fourier transforms infrared (FTIR) analysis of prepared TiO_2 nanoparticles by using *A. nilotica* methanol extract. The IR band appeared at 3401 cm^{-1} in *A. nilotica* extract is typical sign of the O–H and it was moved to 3370 cm^{-1} in TiO_2 nanoparticles. Another clear transfer in the wave pattern matching to amide (1600 to1640 cm^{-1}) indicated that involvement of amino ($–NH_2$) or COO^- (carboxylate) in *A. nilotica* methanol extract preparing superficial of TiO_2 nanoparticles constant (Fig.1 and Table 1).

Table 1. **FTIR spectral bands of prepared TiO_2 nanoparticles and *A. nilotica* methanol extract.**

	Observed spectral Bands (cm^{-1})	Suggested groups
A.N	TiO_2NPs	
3401	3370	O–H
1600	1640	($–NH_2$) or COO^- (carboxylate)

A.N= crude extract of *A. nilotica*



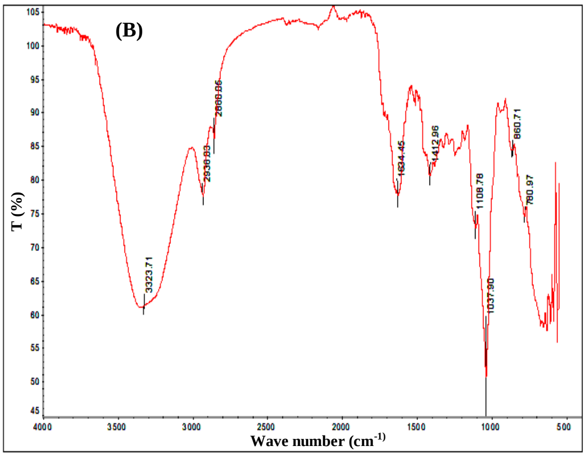


Figure 1. **(A) FTIR spectrum of prepared TiO_2 nanoparticles (B) FTIR spectrum of *A. nilotica* methanol extract**

Energy-dispersive X-ray Spectrometric (ED) Analysis

TiO_2 nanoparticles and crude extract of *A. nilotica* were examined for elemental investigation and occurrence of TiO_2 using energy dispersive (ED) X-ray spectrometric method. Elements indicated in EDS spectrum (Fig. 2A) are the ingredients of the *A. nilotica* extract used for the preparation of TiO_2 nanoparticles. On the other side in (Fig. 2B) prominent signs in ED spectrums in TiO_2 are authorize the amalgamation of the TiO_2 nanoparticles.

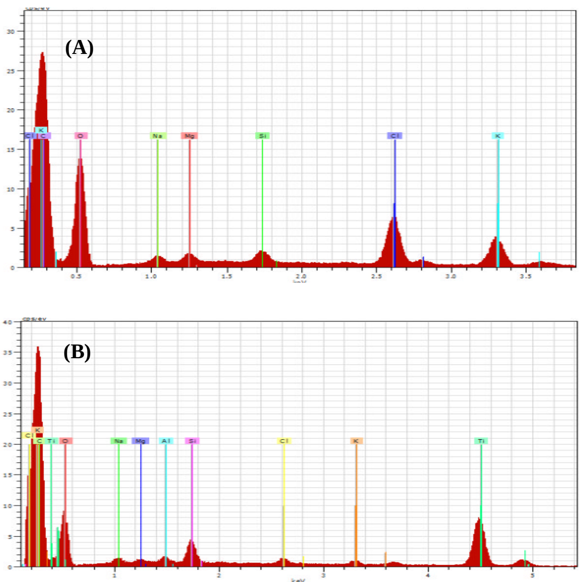


Figure 2. **(A) EDS spectrum of *A. nilotica* methanol extract. (B) EDS spectrum of prepared TiO_2 nanoparticles**

Field Emission Scanning Electron Microscopy (FESEM)

The FESEM results of TiO_2 and crude extract of *A. nilotica* indicated that majority of the TiO_2 nanoparticles were round and few were in rod shaped and the sizes of TiO_2 nanoparticles were ranges from 50-120 nm but most of them were 60 nm (Fig. 3).

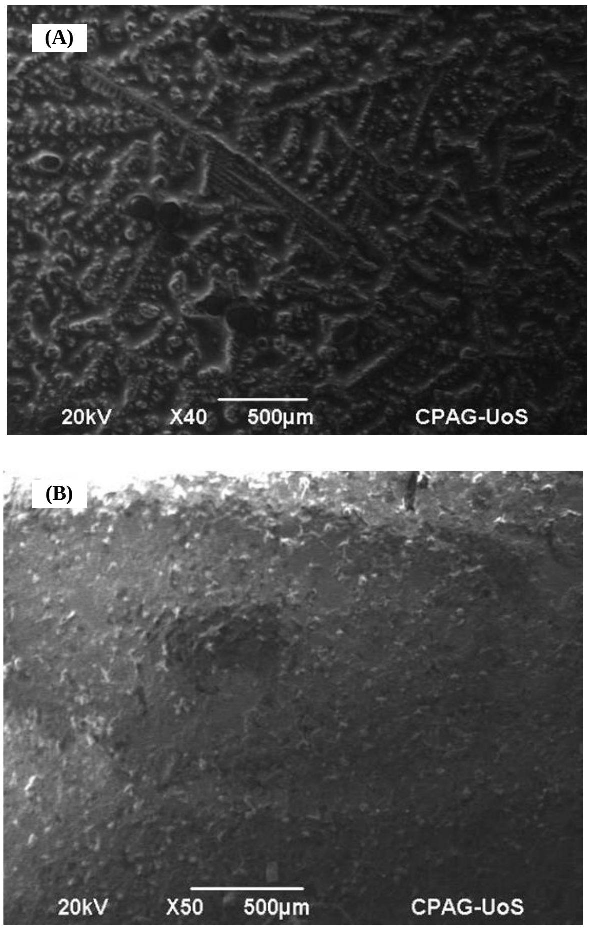


Figure 3. **(A) FESEM of TiO_2 nanoparticles (B) FESEM of *A. nilotica* methanol extract**

Dye Degradation Activity of Synthesized TiO_2 Nanoparticles

The dye degradation potential of TiO_2 nanoparticles was assessed by UV treatment by the degradation of methylene blue. The removal of dye competence to anticipated dye methylene blue by the synthesized TiO_2 nanoparticles as a result of response time. The result of dye elimination by

TiO_2 nanoparticles under the influence of UV source was obtained approximately 75%, after 2 hours (Table 2). Present study focused on the photocatalytic degradation of methylene blue. Synthesized TiO_2 nanoparticles showed significant potential of dye removal from water. Subsequently the absorbance is straight relation with the concentration of solution. The removal of methylene blue was assessed through the strength if absorbance as it reduces with times. The primary concentration of methylene blue was measured as highest absorbance spectrum for zero treatment time [22].

The outcome of in decreasing in absorbances at different concentrations of TiO_2 is recognized to maximum level of loading as indicated that he increase in TiO_2 loading which as impact on removal of methylene blue dye. Acacia is well known for its different pharmacological activities. Highly significant removal of different pollutants can be obtained through using of acacia bark. This study plant has capacity of enhancing the water quality through removing pathogen and maintaining the color and turbidity of water without any cytotoxic effects [23].

Table 2**. Dye degradation by prepared greenTiO_2 nanoparticles.**

Time (min)	*dye reduction (%)
30	5
60	15
90	45
120	75

***TiO_2 nanoparticles = 20 mg; Methylene blue 100 mL**

Conclusion

Synthesis of TiO_2 nanoparticles by using extract of *Accacia nilotica* was rapid and inexpensive. Prepared nanoparticles were characterized using various techniques such as UV-Visib spectroscopy, FTIR, EDs and FESEM. The TiO_2 nanoparticles were proved to be highly potent for removal of dye from industrial waste water. These nanoparticles could be useful for the removal of dye from waste water.

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