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 50-120 nm 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 of 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.
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.

**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 to 1640 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).

**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].

**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$_2$ NPs                    |                  |
| 3401                               | O–H              |
| 1600                               | (–NH$_2$) or COO$^-$ (carboxylate) |

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

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).

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 of 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 green TiO$_2$ 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 *Acacia 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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