Synthesis and Characterization of TiO_2 for Photocatalytic Degradation of Methylene Blue

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ABSTRACT

Synthesis of TiO_2 using the sol-gel method and evaluation as a photocatalyst in the photodegradation of methylene blue on visible light irradiation in a closed reactor have been carried out. The synthesis involved hydrolysis and condensation of titanium isopropoxide in ethanol and deionized water, followed by drying and calcination. The synthesized TiO_2 nanoparticles were characterized using FTIR spectroscopy, Scanning Electron Microscopy (SEM) and UV-Vis spectroscopy. Photocatalytic experiments were conducted under UV light irradiation to assess the degradation efficiency of TiO_2. The degradation of Methylene Blue was monitored through UV-Vis spectrophotometry by measuring the absorbance at 269 nm. The results demonstrated that TiO_2 exhibited significant photocatalytic activity. The photocatalytic performance was influenced by factors such as catalyst loading, initial dye concentration, and pH of the solution. This study highlights the potential of TiO_2 nanoparticles as effective photocatalysts for the treatment of dye-contaminated wastewater, offering a sustainable approach to mitigating environmental pollution.

Keywords: *Titanium dioxide, methylene blue, photocatalytic degradation, nanoparticles.*

1. Introduction

Nanoscience and technology are rapidly developing fields that are providing revolutions in all scientific fields [1]. Nanoscience is the study that deals with the structure of materials that are on an ultra-small scale. The changes in the physical and chemical properties occur at the nano level which is one billionth of a meter. Nanotechnology revolutionizes a diverse range of fields right from health care to manufacturing. One example of nanoscience is the carbon nanotube (CNT). They are designed at the nanoscale but they create macro scalar structures stronger than steel. Heavy metal NPs of lead, mercury, and tin are so rigid and stable that their degradation is not easily achievable, which can cause environmental toxicities [2].

Rapid industrialization and urbanization have resulted in complex and severe water pollution problems. These water pollution problems have posed serious threats to the ecological environment and food safety [3]. The contribution of the industrial sector to water pollution is significant. The textile industry is the main problem out of all other industries that release dyes that contaminate the water [4]. Because of the potential toxicity of the dyes and their visibility on the surface of the water, the removal and degradation of organic dyes have been a matter of considerable interest. Some effective methods to degrade these organic dyes in wastewater like chemical oxidation, membrane filtration, ion exchange, physical adsorption, etc. were identified. However, these methods failed to degrade the organic dyes completely and caused secondary pollution [5,6].

The photo catalytic degradation of organic compounds is an important branch of the broader subject of photo catalysis. Semiconductor particles are ideal photo catalysts for this reaction. The use of semiconductor particles as photo catalysts for the initiation of redox chemical reactions continues to be an active part of the investigation. In this regard, some attempts have been made to study the photo catalytic oxidation of methylene blue with TiO_2 nanoparticles [7]. Photo catalytic degradation involving titanium dioxide appeared to be an effective method and promising technology for the treatment of wastewater.

Titanium dioxide is one of the nanomaterials that have been used due to its unique properties. Titanium oxide nanoparticles can provide improved UV protection while also having the additional advantage of removing the cosmetically unappealing whitening related to sunscreen in their nano-form. The nano-titanium dioxide is also used in coatings to form self-cleaning surfaces in plastic garden chairs. Water is created as a sealed film on the coating, and the dirt dissolves in the film after which the next shower will remove the dirt and clean the chairs [8].

Titanium dioxide which is also a known semiconductor shows unique characteristics such as easy processing control, non-hazardous, inexpensive, environmentally friendly, enhanced photocatalytic efficiency, efficient utilization of visible and solar light, and simplicity. The nano-sized TiO_2 was synthesized from the organometallic precursor-titanium tetra isopropoxide (TTIP). Titanium isopropoxide is not hazardous or toxic to the environment and provides an easy approach to the production of titanium dioxide nanoparticles. The organic dye that was used in the experiment for the photocatalytic degradation was Methylthionium chloride commonly called methylene blue. It is a thiazine dye that exists at a large scale in the textile wastewater which is discharged into the nearby environment without proper management [9]. The effects of methylene blue include gastrointestinal upset, headache, and dizziness.

2. Materials and Methods

2.1 Materials required

Scanning Electron Microscope (SEM), FTIR spectrometer, UV-Vis spectrophotometer, magnetic stirrer, UV lamp, and LT furnace.

Titanium tetra isopropoxide (TTIP, 98+ % solution), hydrochloric acid (1.0 M solution), ethanol, (95 %, solution), and deionized water.

2.2 Preparation of Titanium Dioxide Nanoparticles by Sol-Gel Process

Titanium isopropoxide (TTIP) was the precursor. It was dissolved in ethanol and stirred for 30 minutes using a magnetic stirrer. In this step, to investigate the effect of pH upon the sample properties, a mixture of deionized water and hydrochloric acid (HCl) was added to the solution dropwise to adjust the pH range to 6 because below or above this pH the particle size decreases. The concentration of acid was 1 M. A homogeneous solution was obtained after stirring for 2 hrs at room temperature with a magnetic stirrer. A sol was formed after stirring, and then the sol was left to age for 24 hrs to form the gel. To obtain the nanoparticles, the gel was dried at 100° C for 1 hr to evaporate water and other organic materials. The dried gel was calcined in the LT furnace at 350°C at a heating rate of 10 °C / min for 3 hrs soaking time to obtain the desired TiO_2 nanoparticles.

2.3 Preparation of Methylene blue dye

0.1g of methylene blue was dissolved in 500 mL distilled water. From this 1 mL was taken and diluted with 99 mL of distilled water. A duplicate was also performed and both were kept in UV light for 45 minutes. At a 15-minute time interval, the solutions were collected in vials and observed for degradation.

1 ml of methylene blue was added with 99 mL water. To this, 25 mg of titanium dioxide nanoparticles were added and left in darkness for 30 minutes inside the UV lamp. After 30 minutes, the lamp was turned on. The solution was left inside the lamp for 2 hours. This solution was collected at 15-minute time intervals in vials. Similarly, this procedure was carried out with 50 mg of titanium dioxide nanoparticles. After keeping the samples under UV light for 2 hours, the samples were characterized under a UV-Vis spectrophotometer for the investigation of photocatalytic degradation.

3. Results and Discussion

The synthesized TiO_2 nanoparticles were characterized under SEM, UV–VIS spectrophotometer, and FTIR spectrometer. Their surface morphology, absorbance in UV spectrum and Infrared spectrum were investigated.

3.1 Scanning Electron Microscope (SEM)

The surface morphology of the synthesized TiO_2 nanoparticles was characterized by SEM analysis as shown in Fig. 1&2 and they were obtained in 20 µm and 2 µm diameter. The synthesized TiO_2 nanoparticles were found to have a fine surface without any cracks.

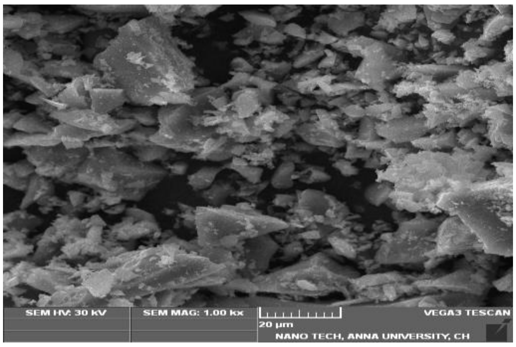

Fig. 1. SEM image of TiO_2

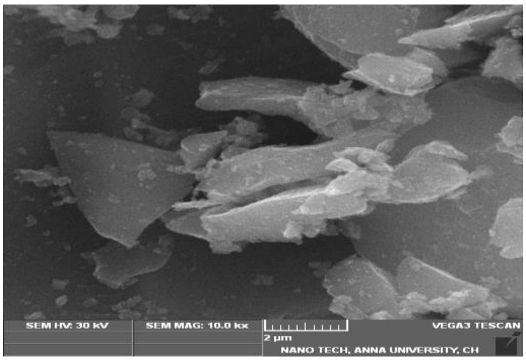

Fig. 2. SEM image of TiO_2

3.2 FTIR Spectroscopy

The synthesized TiO_2 nanoparticles were characterized under FTIR. The spectrum obtained from the FTIR is shown in Fig.3.Investigating the surface chemistry of the nanoparticles would help to have a better view of their properties. The FTIR spectroscopy was performed to investigate the chemical bonding between the Ti and O atoms in the range 4000 to 400 cm^{-1}.

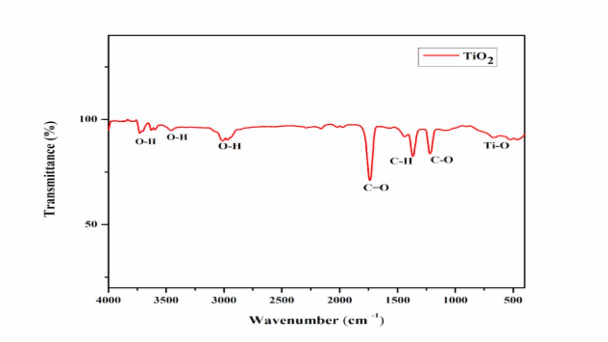

Fig. 3. FTIR of TiO_2

The peaks obtained between 3700 $cm^{-1}$and 3000 cm^{-1}refer to the characteristic stretching vibrations of the hydroxyl (O-H) group which were obtained due to the alcoholic group of ethanol, which was initially used to dissolve the precursor TTIP. The peak at 1739 cm^{-1} refers to the carboxyl (C=O) group resulting from residual organic species. The peak at 1368.24cm^{-1} is attributed to the alkane (C-H) group of the (CH_3-CH_2-) linkage. The alkane and the carboxyl groups come from the precursor TTIP and ethanol used in the synthesis process. The peak at 1221 cm^{-1} refers to the ether group (C-O) from ethanol. The broadband from 900 to 400 cm^{-1} region is ascribed to the Ti-O stretching. The peak at 671.10 cm^{-1} in the range of 900–400 cm^{-1} is the contribution from the anatase phase of Ti-O.

3.3 UV-Vis spectroscopy

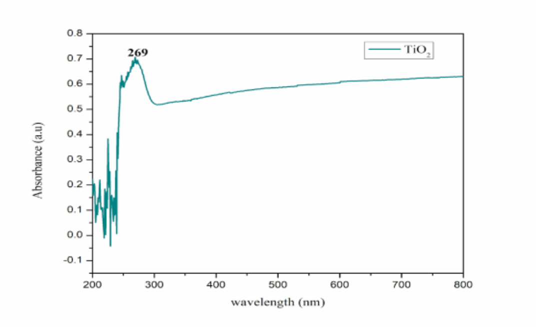

Fig. 4. UV-VIS absorption spectrum of TiO_2 nanoparticles

Before the photocatalytic activity of TiO_2, it is necessary to record the light absorption. The spectrum of UV-visible absorbance is shown in Fig.4. The maximum absorption peak of TiO_2 ranges between 250 and 450 nm which is dependent on the irradiation, physical, and chemical nature of the sample, and the surface impurities. The powder sample of TiO_2 nanoparticles was mixed with the solvent (ethanol) and kept inside the UV-Vis spectrophotometer. A blank solution was also placed as a reference. At 269 nm, strong absorption was observed for the TiO_2 nanoparticles.

3.4 Photocatalytic degradation of methylene blue

The TiO_2 nanoparticles were added to the aqueous solution of methylene blue and degradation studies were investigated using a UV-VIS spectrophotometer.

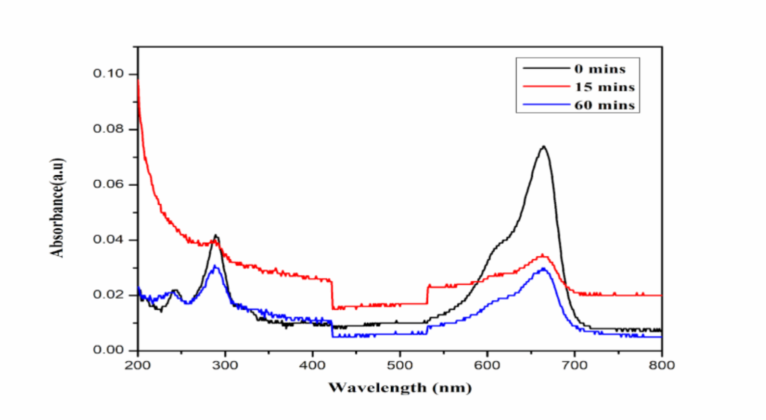

Fig. 5. 25 mg of TiO_2

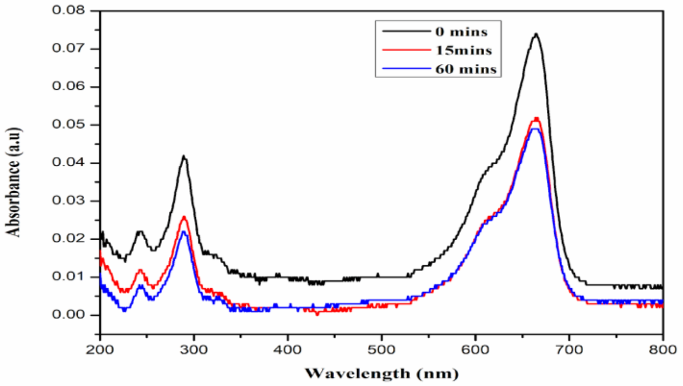

Fig. 6. 50 mg of TiO_2

Initially, 25 mg and 50 mg of TiO_2were added to 0.1 g of methylene blue, and the solution was kept under a UV lamp for photocatalytic degradation. The effect of TiO_2 on the degradation of methylene blue was studied by absorption studies.

Fig. 5 is the UV absorption spectrum of methylene blue in the presence of 25 mg of TiO_2.It is clear from the UV absorption spectrum that TiO_2facilitates the degradation of methylene blue. The absorbance of methylene blue has decreased from 0.075 to 0.035 after 15 minutes and after 1 hour it has decreased to 0.03.

Fig.6 is the UV absorption spectrum of methylene blue in the presence of 50 mg of TiO_2.The absorbance of methylene blue has decreased from 0.075 to 0.05 after 15 minutes and after 1 hour it has decreased to 0.045. The decrease in the absorbance shows the photocatalytic degradation of methylene blue in the presence of TiO_2.

From these absorption studies it is clear that 25 mg of TiO_2 has better efficiency than 50 mg for the degradation of methylene blue. However, future studies should be carried out to optimize the experimental conditions to obtain maximum degradation of methylene blue.

4. Conclusion

TiO_2 nanoparticles were synthesized by a simple and cost-effective method. The SEM image shows that the metal oxide particles were in nano size. FTIR spectra and UV-Vis spectroscopy studies confirmed the presence of a Ti-O bond. The degradation studies of methylene blue in the presence of metal oxide also confirm the efficiency of synthesized TiO_2 nanoparticles in the photocatalytic activity.

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