



## Green Synthesis of TiO<sub>2</sub> using Syzygium Cumini Leaf Extract and Evaluation of their Photocatalytic Activity

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### ABSTRACT

Green Synthesis of TiO<sub>2</sub> using *Syzygium cumini* leaf extract was synthesized by standard impregnation method. The prepared sample was characterized by UV and FT-IR. The photocatalytic activity of the novel photocatalyst was evaluated using methylene blue (MB) as a target pollutant. The composite sample exhibit enhanced photocatalytic performance under visible light irradiation than pureTiO<sub>2</sub>.

Keywords: Composite Photocatalyst, Methylene blue, *Syzygium cumini* leaf

### I. INTRODUCTION

Provision of sustainable energy is essential for the global economic development and human well-being. More than 80% of our current energy production comes from carbon-based fossil fuels such as coal, oil, and natural gas [1]. Most of the semiconductor photocatalysts have band gap in the UV region i.e; equivalent to or larger than 3.2 eV. The large band gap absorbing only UV light is a major drawback in its potential application [2]. Number of methods have been investigated and found to shorten the band gap is to doping of nonmetals and co-doping with polymer materials. The novel photocatalyst exhibits activity for the removal of organic pollutants under visible light irradiation [3], clearly demonstrating that the TiO<sub>2</sub> photocatalyst possess an interesting electronic property as well as high thermal and chemical stability, many methods have been used to extend the photocatalytic performance such as doping with metals or non-metal elementals [4] and coupling with other semiconductors [5]. These methods are effective because the high surface area and small particle size it enhances e<sup>-</sup>-h<sup>+</sup> pairs separation.

In this work, for the first time Green Synthesis of TiO<sub>2</sub> using *Syzygium cumini* leaf extract composite was synthesized by impregnation method. The composite should increase the visible light harvesting efficiency by increasing the surface area and to evaluate the photo degradation of MB under visible-light irradiation.

### II. MATERIALS AND METHOD

#### 2.1 Synthesis of Photocatalysts

##### 2.1.1 Synthesis of pure TiO<sub>2</sub> Photocatalyst

The pure TiO<sub>2</sub> sample was synthesized by thermal treatment of precursor TiO<sub>2</sub> it was placed in a crucible with a cover under ambient pressure in air. After dried at 80 °C for 24 hr, the precursor was put in a Muffle furnace and heated to 550 °C for 3 hr with a heating rate of 10 °C min<sup>-1</sup>. The resultant yellow product was collected and ground into a powder for further use [6].

##### 2.1.2 Preparation of *Syzygium cumini* leaf Extract

At first *Syzygium cumini* leaves, collected from the campus, were thoroughly washed with double distilled water to remove any dirt adhered to the surface. Now leaves were allowed to dry at 60°C temperature, these dry leaves were ground well and obtained powder was collected and stored. Leaf extract was prepared by mixing 20 g of powder with 100 mL of double distilled water and heating the mixture at 80°C for 60 min in water bath. Extract obtained after heating was filtered using Whatman filter paper and was used as a capping/ stabilizing agent for the synthesis of composite TiO<sub>2</sub>.

##### 2.1.3 Green Synthesis of TiO<sub>2</sub> using *Syzygium cumini* leaf Extract

Green synthesis of TiO<sub>2</sub> composite photocatalyst was synthesised by an impregnation method. Synthesis involved mixing calculated quantities of the above prepared TiO<sub>2</sub> powder and *Syzygium cumini* leaf extract in the ratio 1:1 was dispersed in 1 M HCl. The dispersion was magnetically stirred for 3

hr. After that the product was collected by centrifugation and washed with ethanol and deionized water. Finally, the sample was dried at 80 °C in an oven for 1 hr. The obtained TiO<sub>2</sub> composite modified with *Syzygium cumini* leaf extract was in the form of yellow powder [7].

## 2.2 Characterization Techniques

UV-Visible spectral data were collected over a spectral range 200-800 nm with Shimadzu UV-3101 PC spectrophotometer. FT-IR spectra in transmittance mode were recorded for a solid mixture of sample and KBr in the form of pellets on a SHIMADZU FTIR spectrometer.

## 2.3 Evaluation of Photocatalytic Activity

The photocatalytic degradation of Rh-B was performed under the natural sunlight in the presence of CNU composite photocatalysts. In the photocatalytic treatment of dye, a known concentration of Rh-B dye solution 1x10<sup>-5</sup> M was prepared in deionized water resulting in a solution with pH 7.6 was taken in a beaker. 0.1 g photocatalyst was added to the 50 ml (2 g/l) of dye solution. Before irradiation of the dye solution, the suspension was stirred for 30 min in the dark to realize adsorption-desorption equilibrium in the presence of catalyst. The dye solution was agitated with an electromagnetic stirrer at a constant speed of 790 rpm. The dye solution was directly exposed to sunlight radiation in an open atmosphere. At given intervals of irradiation a known volume of sample along with the catalyst particles were collected, centrifuged and then filtered through Millipore filter paper. The filtrates were analysed by UV-Visible spectrophotometer. The determination wavelength is 553 nm for Rh-B dye, which is the maximum absorption wavelength.

The degradation efficiency of dye is calculated by the following equation

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

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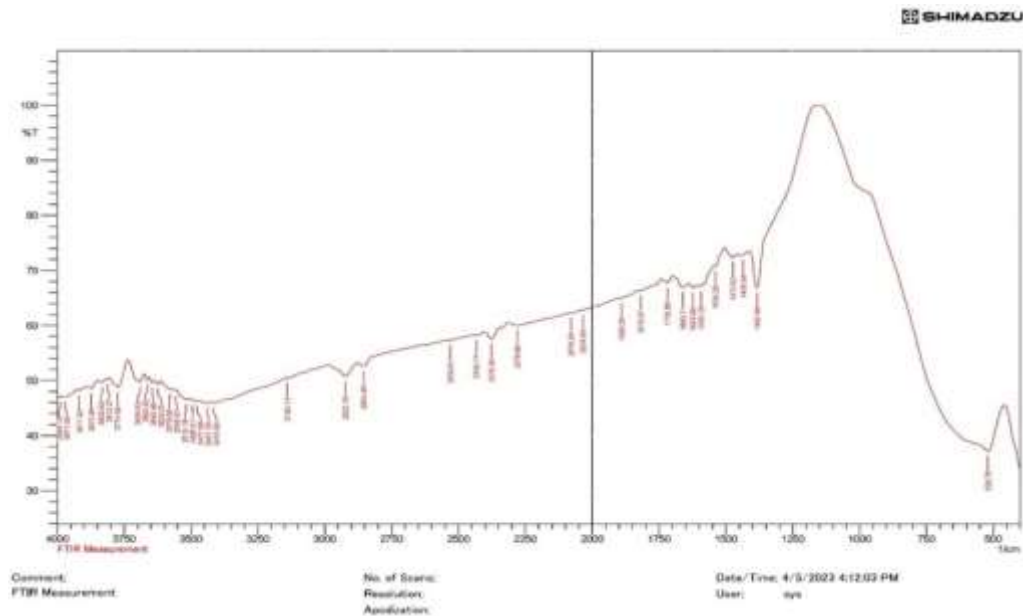
## III. RESULTS AND DISCUSSION

### 3.1 Characterization Technique

#### 3.1.1 FT-IR Analysis

The molecular geometry, information about its functional groups and inter/intra molecular interactions of the resulting composite photocatalysts are characterized by FT-IR spectroscopy. Fig 3.1 shows the FT-IR spectrum of modified TiO<sub>2</sub> sample. The main characteristic peaks of modified sample can be assigned as follows: The main absorption bands at 1435, 1473, 1539 and 1411 cm<sup>-1</sup> are allocated to aromatic C-N stretching and the conjugated C=N stretching can be seen at 1593 and 1539 [9]. Moreover, the small bands at 2376 cm<sup>-1</sup> can be assigned likely to the stretching vibration modes of NH<sub>2</sub> and NH groups, while the bands at 3917-3774 cm<sup>-1</sup> corresponds to the absorbed moisture i.e., the presence of water molecule [10].

According to the result, the absorption spectrum revealed the presence of various bio compounds in the leaf sample of *Syzygium cumini*. Strong- broad and weak-broad bands around 3689.83 cm<sup>-1</sup> to 3415.93 cm<sup>-1</sup> represented -OH group of alcohol. The band between 2922.16 cm<sup>-1</sup> and 2854.65 cm<sup>-1</sup> represented -CH group of alkanes and the band around 1718.58 cm<sup>-1</sup> showed strong C=O stretching of aldehyde. The band around 1660-1539 cm<sup>-1</sup> revealed that the presence of C=C stretching of conjugated alkenes have medium di substitute (trans) groups in the leaf sample. The spectrum shows an intense band at 520.78 cm<sup>-1</sup> corresponding to Ti-O-Ti vibrations, which conform the formation of TiO<sub>2</sub> sample as well as the leaf extract sample containing halo compounds with strong stretching of -C-I groups [75]. 1718.58 cm<sup>-1</sup> showed strong C=O stretching of aldehyde. The band around 1660-1539 cm<sup>-1</sup> revealed that the presence of C=C stretching of conjugated alkenes have medium di substitute (trans) groups in the leaf sample. The spectrum shows an intense band at 520.78 cm<sup>-1</sup> corresponding to Ti-O-Ti vibrations, which conform the formation of TiO<sub>2</sub> sample as well as the leaf extract sample containing halo compounds with strong stretching of -C- I groups [8].



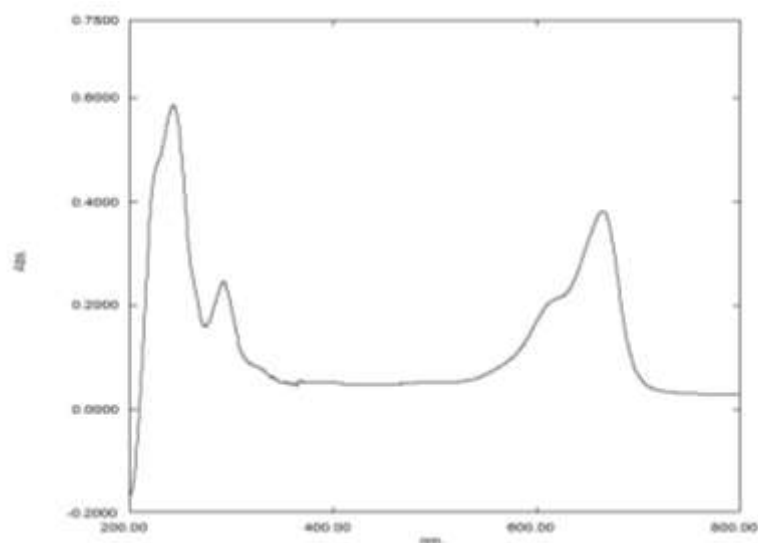
**Fig 3.1** FT-IR spectrum of modified TiO

### 3.1.1 Photocatalytic Activity Measurements

To Evaluate the photocatalytic activity of prepared sample TiO<sub>2</sub> modified by *Syzygium cumini* leaf extract towards dye degradation. Methylene Blue (MB) was used as the model pollutant for the degradation. The suspensions of the catalyst in dye solution were subjected to sunlight for 180 minutes with continuous stirring. After every 30 minutes, 5 ml aliquots were pipette out and centrifuged. The Photocatalytic degradation of the dye was monitored using UV spectroscopic analysis technique. The absorbance of the clear supernatants was determined at 688.5 nm wavelength against blank solution.

### 3.2 Degradation of Dye during the Course of Reaction

Fig. 3.2, depicts the spectrum of MB dye. Fig. 3.3 depict the degradation spectrU of MB dye using modified TiO<sub>2</sub> photocatalyst. From the figure it is explained that as the reaction time increases, the primary absorption peak of MB at 688.5 nm almost disappears at the end of 180 minutes irradiation. It indicates that the main chromophores in the MB dye solution are destroyed using modified TiO<sub>2</sub> photocatalyst and proves that 97 % dye is decomposed in the system.



**Fig. 3.2** UV Spectrum of Methylene Blue Dye.

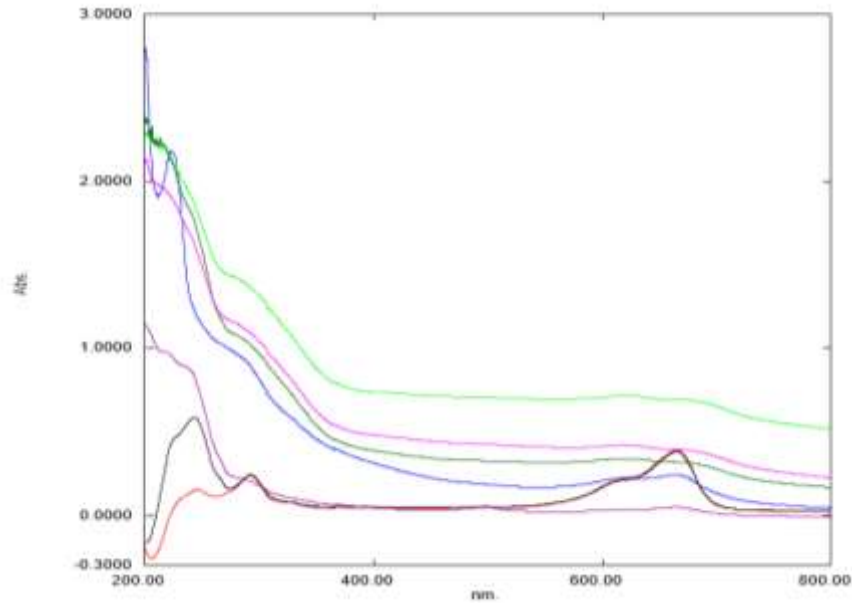


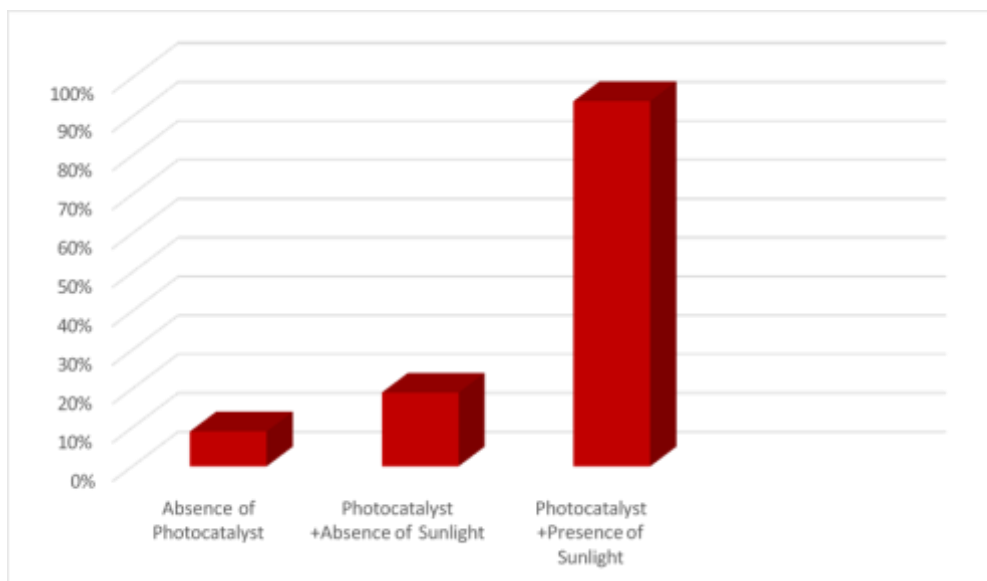
Fig. 3.3 Combined Degradation Spectra of Dye during the Course of Reaction.

### 3.3 Efficiency of Photocatalyst

Efficiency of photocatalytic process of methylene blue dye can be given in the Table-1 and Fig 3.4

**Table -1** Degradation Efficiency of Modified TiO<sub>2</sub> Photocatalyst.

Photocatalyst	Efficiency %
Without Photocatalyst in the Presence of Sunlight at pH 8.6	9
Photocatalyst in the Absence of Sunlight at pH 8.6	19
Photocatalyst in the Presence of Sunlight at pH 8.6	94



**Fig 3.** Degradation Efficiency of Methylene Blue Dye.

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#### IV. CONCLUSION

In this study the photodegradation of methylene blue under sunlight can be effectively done in the presence of modified photocatalyst. Time is an important factor for the degradation reaction. In this irradiation experiments, the irradiation time was 180 minutes and the time interval was 30 minutes. About 97 % of the Methylene Blue was degraded in the presence of synthesized photocatalyst within 180 minutes irradiation time. The synthesized sample was characterized by FTIR spectroscopy, it was found that an intense band at  $520.78\text{ cm}^{-1}$  corresponding to Ti-O-Ti vibrations, which conformed the formation of  $\text{TiO}_2$  sample as well as the leaf extract of *Syzygium cumini* sample containing halo compounds with strong stretching of -C-I groups. It was found that the use of natural renewable and eco-friendly leaf extract was used for synthesis of modified  $\text{TiO}_2$  photocatalyst. It exhibits excellent photocatalytic activity against dye molecules and can be used in water purification systems and dye effluent treatment.

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