

Light Harvesting Titanium Nanocatalyst for Remediation of Methyl Orange

Brajesh Kumar, Luis Cumbal

Abstract—An ecofriendly *Citrus paradisi* peel extract mediated synthesis of TiO₂ nanoparticles is reported under sonication. U.V.-vis, Transmission electron microscopy, Dynamic light scattering, and X-ray analyses are performed to characterize the formation of TiO₂ nanoparticles. It is almost spherical in shape, having a size of 60–140 nm and the XRD peaks at $2\theta = 25.363^\circ$ confirm the characteristic facets for anatase form. The synthesized nanocatalyst is highly active in the decomposition of methyl orange (64 mg/L) in sunlight (~73%) for 2.5h.

Keywords—Ecofriendly, TiO₂ nanoparticles, *Citrus paradisi*, TEM.

I. INTRODUCTION

IN recent years, the development of green techniques for the preparation of nanoparticles is advantageous over chemical agents due to their less environmental consequences. Titanium dioxide (TiO₂) is a material of great significance in many fields, e.g., photo catalysis, solar cell devices, gas sensors, biomaterials [1], [2] biomedical engineering and pharmaceutical industries [3], [4]. The nanosized TiO₂ particles are widely used to provide whiteness and opacity to products such as sunscreen lotions, paints, plastics, papers, inks, food colorants and toothpastes [4]. TiO₂ photocatalyst is emerged as a promising clean advanced oxidation technology, which could address the ever increasing global concerns for the degradation and inhibition of numerous toxic environmental contaminants based on the utilization of solar energy [5]. TiO₂ nanoparticles are known to react with O₂ and -OH adsorbed on the surface to obtain oxygen free radical and hydroxyl free radical which are capable of directly attacking the cell wall and cell membrane. Various applications of titanium dioxide include air, water and surface cleaning [6]. During the last few years, biosynthesis of the metal nanoparticles using extracts from plant have become a topic of great interest. Extracts from *Catharanthus roseus* leaf [7], *Nyctanthes arbortristis* [8], *Eclipta prostrata* leaf [9] etc. may act both as reducing and capping agents in synthesis of TiO₂ nanoparticles.

Grapefruits (*Citrus paradisi*) are unique, having red pigment in the juice vesicles and relatively high levels of

bioactive compounds. The major bioactive compounds present in grapefruits include flavonoids, limonoids, carotenoids, furocoumarins and organic acids [10], [11].

In the present study, TiO₂ nanoparticles were synthesized using *C. paradisi* outer peel extract and this nanoparticles were used as catalyst for remediation of methyl orange (MO) in the presence of direct sunlight. Methyl orange (MO) which represents azo dyes that is the largest and most versatile class of dyes widely used in chemical, textile and paper industries. Azo dyes are well known carcinogenic organic substances.

II. MATERIALS AND METHODS

A. Materials

All chemicals used were of analytical grade and used without any purification. TiO₂ (>99.0%) and methyl orange (99.5%) were purchased from the Aldrich (USA). Millipore Milli-Q water was used in all experiments. *Citrus paradisi* fruit was purchased from the local market Sangolqui, near Universidad de las Fuerzas Armadas (ESPE), Ecuador. Aqueous extract of *C. paradisi* was prepared using yellowish-green outer peel (10g) boiled with 40 mL of double distilled water at 80°C for 30 min. This extract was filtered through muslin cloth and used for further experiments.

B. Synthesis of TiO₂ Nanoparticles

Nanoparticles of Ti were prepared using the 1mM TiO₂ (aq) solution. In a typical preparation, 5 mL of the aqueous peel extract of *C. paradisi* was added in 10 mL of 1mM TiO₂ at room temperature. The mixture was stirred for complete dissolution and agitated under sonication. Ultrasound irradiation was carried out with ultrasonic processors (DAIGGER GE 505, 500 W, 20 kHz) immersed directly into the reaction solution. The operating condition was at 30 sec pulse on and 30 sec pulse off time with amplitude of 72% at 25°C for 30 minutes. After the completion of 30 min of the reaction, the color changed in to yellowish green and proof for the formation of TiO₂ nanoparticles.

C. Characterization

U.V.-vis spectra was measured using spectrophotometer (Thermo Spectronic, GENESYS™ 8, England, Quartz Cell, path length 10mm and Graph Plotted on Origin 6.1 program). The particle size distributions of nanoparticles were determined using the HORIBA, Dynamic Light Scattering (DLS) Version LB-550 program. Size and selective area electron diffraction (SAED) pattern of nanoparticles are studied on transmission electron microscopy, TEM (FEI, TECNAI, G2 spirit twin, Holland). A thin film of the sample

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was prepared on a carbon-coated copper grid by dropping a very small amount of the sample on the grid. X-ray diffraction (XRD) studies on thin films of the nanoparticle were carried out using a BRUKER D8 ADVANCE brand θ -2 θ configuration (generator-detector) x-ray tube copper $\lambda = 1.54 \text{ \AA}$ and LYNXEYE PSD detector. The diffracted intensities were recorded from 20° to 60° 2θ angles.

D. Decomposition of MO Study

Four separate sets of experiments were performed for study the decomposition of MO in direct sunlight (Table I). In set 1, 4 mL MO (64mg/L), 3 mL H₂O and 0.5 mL extract was mixed in a vial and kept in light. In sets 2, 3 and 4, the synthesized TiO₂ nanocatalyst were used; 4 mL MO, 0.5 mL extract, 2-0 mL H₂O and 1-3 mL TiO₂ nanoparticle were mixed and kept in light. All four sets of reactions were observed after 1.0, 1.5 and 2.5 hrs. The rate of MO dye decomposition was monitored by taking 4 mL samples from each set and recording the UV-vis spectra using U.V.-vis spectrophotometer (Thermo spectronic, GENESYS™ 8) by absorbance measurements at the wavelength of maximum absorption of MO (464nm) before and after degradation.

TABLE I
PHOTODEGRADATION OF METHYL ORANGE (MO) UNDER DIFFERENT
CONDITION USING TiO₂ NANOPARTICLES

MO (64mg/L), 4mL	H ₂ O	TiO ₂ (catalyst)	Extract	% Degradation		
				1.0 h	1.5 h	2.5 h
I	3 mL	-	0.5 mL	-	-	-
II	2 mL	1 mL	0.5 mL	6.1	10.8	26.3
III	1 mL	2 mL	0.5 mL	20.4	29.3	70.6
IV	-	3 mL	0.5 mL	59.1	68.5	72.3

III. RESULTS AND DISCUSSION

A. U.V.-Vis Study

Fig. 1 (a) shows the U.V.-vis absorption spectra for TiO₂ nanoparticles between 200 and 800nm. The intense band with absorption maxima around 320 to 350nm is associated to the Ti⁴⁺O²⁻ charge-transfer, corresponding to the electronic excitation from the valence band to the conduction band [12]. It has an absorption peak in 350nm (Fig. 1 (b)). It is clear that the formation of TiO₂ nanocatalyst, which was synthesized by using *C. paradisi* peel extract.

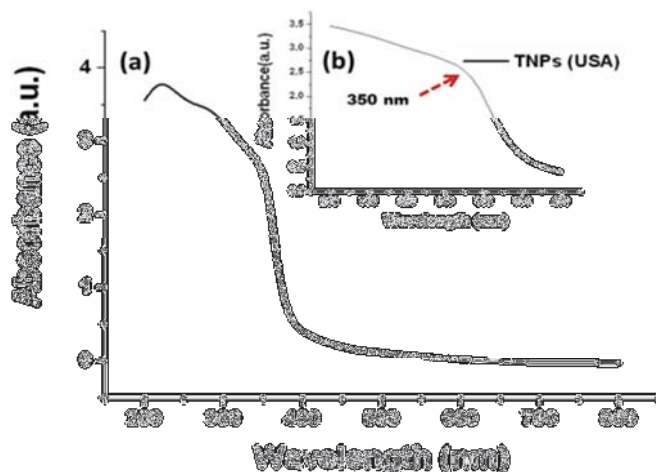


Fig. 1 U.V.-vis pattern of (a) TiO₂ nanocatalyst and (b) absorption at 350 nm

B. TEM and SAED Study

TEM images shown in Fig. 2 illustrate individual TiO₂ nanoparticles as well as a number of aggregates. The measurement of the size was performed along the largest diameter of the particles. The SAED pattern of TiO₂ nanocatalyst reveals its crystalline nature. The particles are found almost spherical in shape about 60-140 nm respectively.

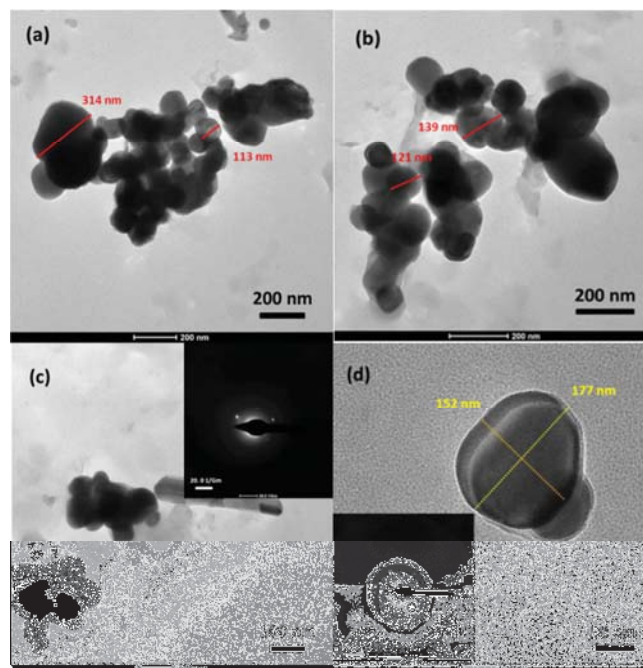


Fig. 2 (a)-(d) TEM image of TiO₂ nanocatalyst and (c, d) SAED pattern

C. DLS analysis

The DLS size distribution image of TiO₂ nanocatalyst is shown in Fig. 3. From the results, the calculated mean particle size distribution of aggregates TiO₂ nanoparticles is 2.4713 μ m and the 1.3229 μ m suggests higher stability.

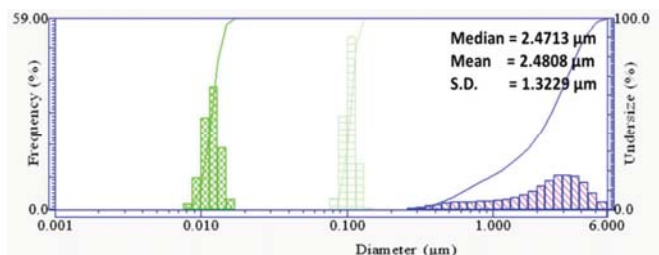


Fig. 3 DLS pattern of the prepared TiO₂ photocatalysts

D. XRD Study

Fig. 4 shows the X-ray diffraction profile of titanium. The XRD peaks at $2\theta = 25.363^\circ$ (101, Major peak), 37.924° (102) and 48.085° (103) confirm the characteristic facets for anatase form of TiO₂ [13]. It is reported as the most photocatalytically active crystalline state of TiO₂ [14].

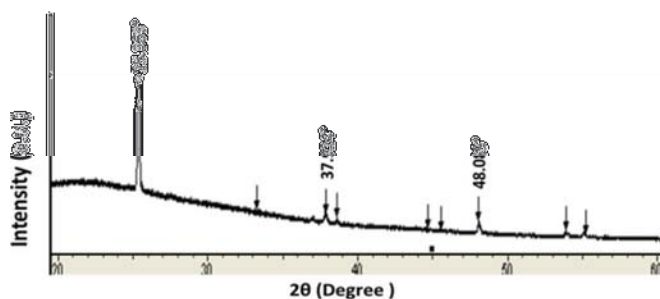


Fig. 4 XRD patterns of the prepared TiO₂ photocatalysts

E. Photocatalytic activity

The activity of the TiO₂ nanocatalyst evaluated for the degradation of MO (64mg/ L) under direct sunlight and visible light for 2.5h. Degradation of MO was found satisfactory under direct sunlight ($T = 28-32^\circ\text{C}$). But the experiments under visible light, inside laboratory were unsatisfactory. The reaction parameters were varied to get the best results as mentioned in Table I. Figs. 5 (a)-(c) shows the progression of the MO decomposition for the four different concentration of TiO₂ nanocatalyst at 1.0, 1.5, and 2.5 hrs in direct sunlight.

The average decomposition in terms of the percentage of MO in solution was calculated using the following equation:

$$\eta = [A_0 - A_t / A_0] \times 100 \%$$

where η is the rate of decomposition of MO in terms of percentage, A_0 is the initial absorbance of MO solution and A_t is the absorbance of the dyes at time t [15].

Initially, there is no degradation of MO (64 mg/ L) observed without use of nanocatalyst (MO 1). The photo degradation capacity increases with an increase in the amount of catalyst (1mM, 1-3 mL). Fig. 5 (a) explains that the degradation of MO is lowest when the amount of catalyst is 1 mL, 6.1%, which then attains maximum at a catalyst dosage of 1mL, 59.1% for 1h. It clearly indicates that, decomposition increases more than 9 times on increasing catalyst amount thrice. In Figs. 5 (b), (c), the catalyst amount of 2 mL showed 20.4 and 29.3% degradation of the MO at 1.5 and 2.5h. The degradation activity of MO is increased and saturated to 68.5 and 72.3% in

catalyst amount of 3 mL for 1.5 and 2.5 h. The degradation of MO was attributed to the higher surface area of nanocatalyst. In the valence band (VB), the holes interact with water molecules, resulting in the formation of hydroxyl radical ($\cdot\text{OH}$) and proton. Protonation of the superoxide anion, $\text{O}_2^{\cdot-}$, creates $\cdot\text{OOH}$ radicals which leads to the formation of H_2O_2 and finally $\cdot\text{OH}$ radical [16]. These $\cdot\text{OH}$ radicals are responsible for the degradation of dye molecules.

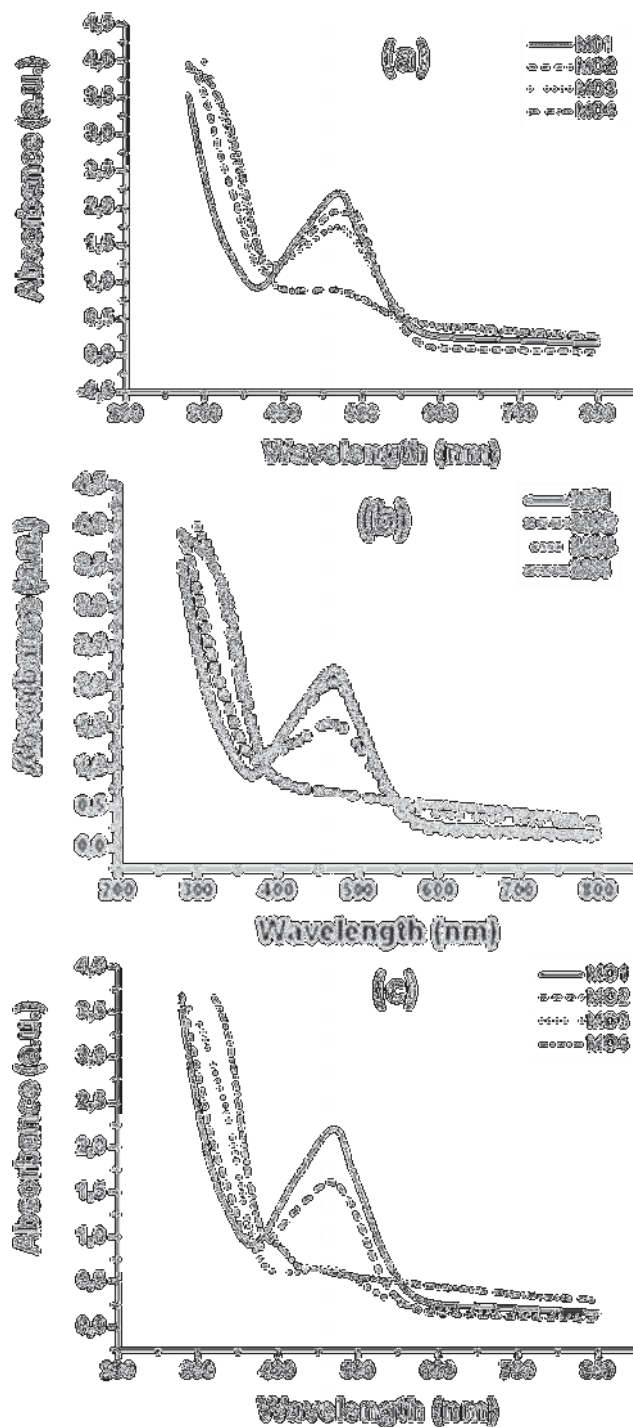


Fig. 5 Degradation of methyl orange using TiO₂ nanocatalyst in sunlight at the time (a) 1.0 h, (b) 1.5 h and (c) 2.5 h

IV. CONCLUSION

The present study shows the environmentally benign, low cost, and renewable approach for the synthesis of TiO₂ nanocatalyst using *Citrus paradisi* peel extract as an effective capping and reducing agent. XRD patterns show the existence of anatase crystalline phase of TiO₂. The formed TiO₂ nanocatalysts are highly stable and exhibited more than 72% degradation of MO in sunlight for 2.5 h.

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