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Preparation and characterization of TiO_2 and TiO_2P25 nanomaterial and photocatalytic application

J. Kamalakkannan, B. Karthikeyan and **S. Senthilvelan***

Department of Chemistry, Annamalai University, Annamalainagar 608 002, India

E-mail address: dr_senthilvel@yahoo.co.in

ABSTRACT

TiO_2 nanomaterial was prepared by precipitation method and sonication technique. The nanomaterial was characterized by HR-SEM with EDX, TEM, XRD, FT-IR and PL analysis. The photocatalytic activity of TiO_2 was much better than that of TiO_2–P25 under UV-light irradiation at 365 nm. The photocatalytic activity was evaluated from the photodegradation of malachite green (MAG). The influence of operational parameters such as the effect of catalyst loading dye concentration and chemical oxygen demand measurements had also been investigated. The Photodegradation was found to follow the pseudo-first-order kinetics. Hydroxyl radical formation in the mechanism was confirmed by fluorescence quenching technique. It was proposed that the catalyst is found to be stable and reusable.

***Keywords*:** Photocatalytic properties, HR-SEM, HR-TEM, Reusable

1. INTRODUCTION

The dye beginning industrial effluents often poses a main environmental problem. Various dyes have been used in the textile, dyeing, leather, pulp, paper, plastic, food and cosmetics industries [1]. The coloured dyestuff discharged by these industries presents certain hazards and environmental problems [2]. Photocatalysis is one of the new techniques for the removal of dyes from wastewater [3-7] Malachite green (MAG) is an expansively used

biocide dye in global aquaculture production. It is also used as a medical purifier, food colouring agent, food additive and anthelminthic. However, MAG has now become a highly controversial compound due to the associated risks in reproductive system, protected system, carcinogenic and genotoxic properties [8,9].

TiO_2 with its know optical properties is used in paint, paper and plastics industries. The use of TiO_2 as the semiconductor photocatalyst is a well-organized method for riddance of environmental pollutants generally for the degradation of organic contaminants from water [10,11] TiO_2 is one of the most commonly used nanomaterials for photocatalytic applications suitable to its low toxicity, low cost, high chemical stability, and brilliant oxidation properties [12,13].

Titanium dioxide presents a moderately high electron–hole recombination rate due to its wide band gap energy (ca. 3.0 eV for rutile and 3.2 eV for anatase), and as an effect retards the photo activity of a system, the extent of which also depends on the synthetic method used and its work [7,14]. In the present work, the preparation of TiO_2 their characterizing by suitable analytical methods has been discussed. The photocatalytic, applications are carried out and discussed.

2. CHEMICALS

Tetraisopropyl orthotitanate ($C_{12}H_{28}O_4Ti$), A gift sample of TiO_2–P25 (80% anatase), malachite green ($C_{23}H_{25}ClN_2$) shown in Fig. 1, Con. HNO_3 and ethanol were the guaranteed reagents of Sigma Aldrich and used as such. The aqueous solutions were prepared by using double distilled water.

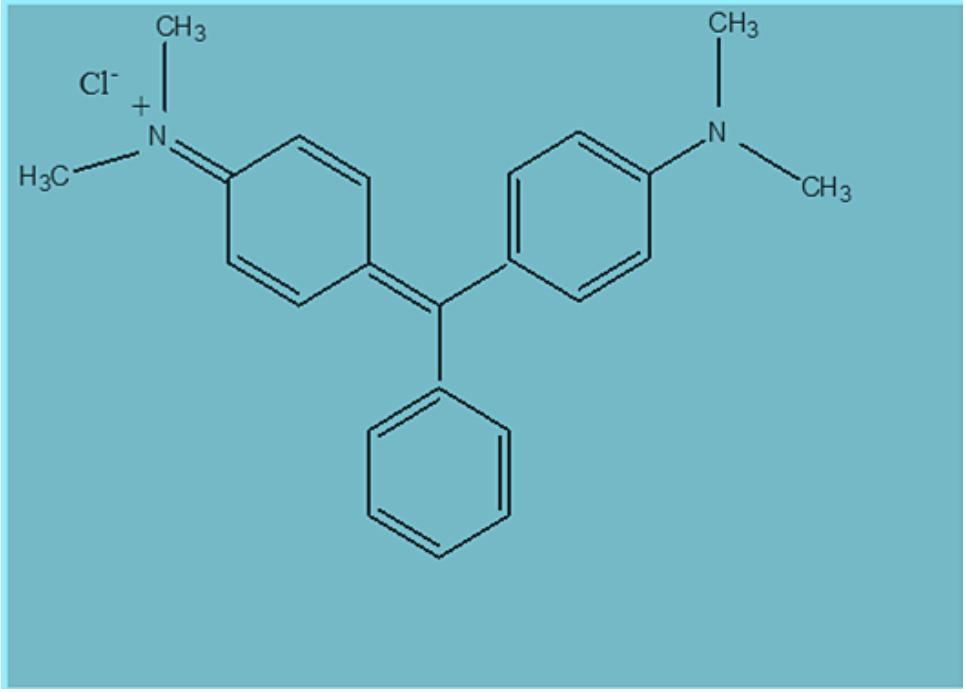
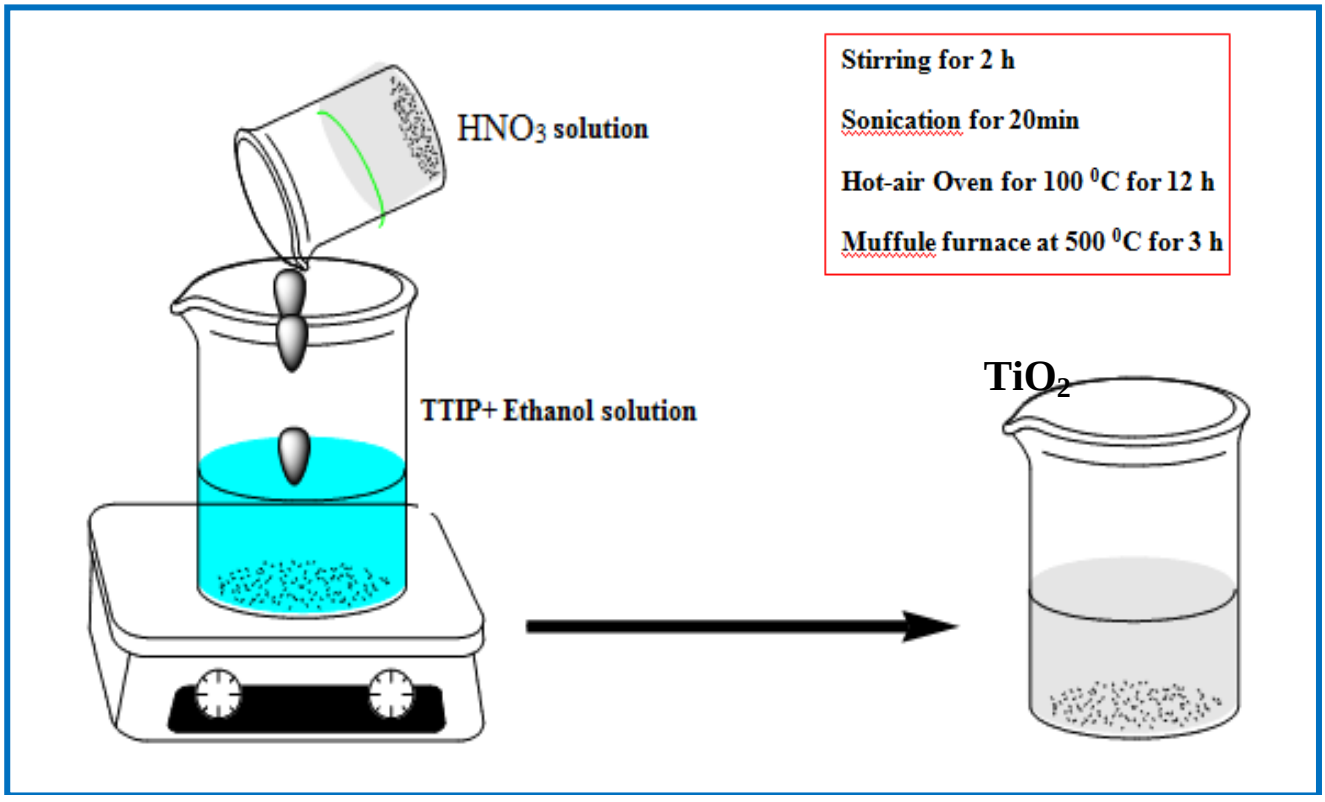


Fig. 1. Chemical structure of Malachite green (MAG).

2. 1. Synthesis of the TiO_2 nanomaterial

TiO_2 material was synthesized by the precipitation method show in **Scheme 1**. Briefly, a constant amount of tetra isopropyl orthotitanate in ethanol solution at room temperature, under vigorous stirring for 2 h than 2-3 drops of conc. nitric acid and 5 mL water was added.

The obtained solution was stirred for 1 h than ultra-sonication for 20 min, until precipitate formed. The obtained precipitate was washed with water and ethanol. Then the precipitate was collected and dried in oven at 100 °C for 12 h in air. The resulting material was finally calcined at 500 °C for 3 h, to obtain TiO_2 nanomaterial.



Scheme 1. Schematic representation for preparation of TiO_2 nanomaterial

2. 2. Photocatalysis

The photocatalytic activities of the photocatalysts (TiO_2 and TiO_2 P25) were evaluated by the photodegradation of dyes. The light source was UV lamp at 365 nm. The reaction was carriedout at ambient temperature (303 K). In a typical experiment, aqueous suspensions of dye (40 mL, 1×10^{-4} M) and 0.150 g of photocatalyst were loaded in reaction tube of 50 mL capacity. Prior to the irradiation, the suspension was magnetically stirred in dark to ensure the establishment of an adsorption/desorption equilibrium.

The suspension was kept under constant air-equilibrated condition. At the intervals of given irradiation time. The suspension was measured spectrophotometrically MAG (620 nm) within the Beer–Lambert law limit.

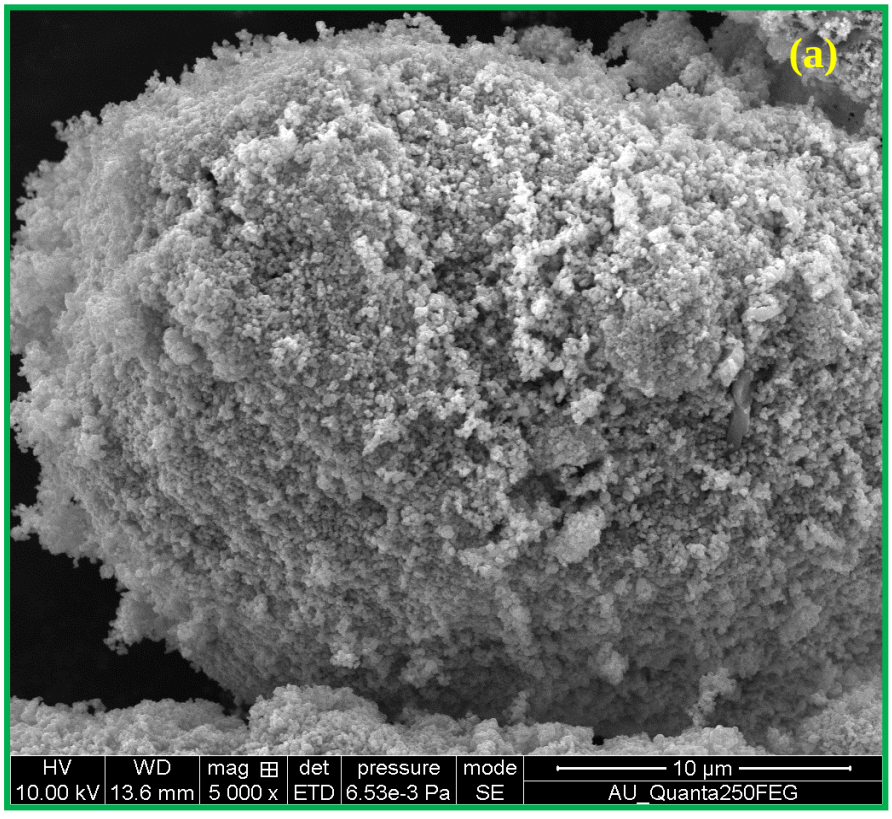
2. 3. Analytical Methods

The Scanning electron microscopy (FF-SEM) with elementary dispersive X-ray analysis (EDX) was carried out on a FEI Quanta FEG 200 instrument with EDX analyzer facility at 25 °C. The sample was prepared by placing a small quantity of prepared material on a carbon coated copper grid and allowing the solvent to evaporate. The morphology of the sample was examined using a JEOL 3010 high-resolution transmission electron microscope (HR-TEM). X-ray diffraction (XRD) spectra was recorded on the X'PERT PRO model X-ray diffractometer from Pan Analytical instruments operated at a voltage of 40 kV and a current of 30 mA with Cu Kα radiation. Photoluminescence (PL) spectra at room temperature were recorded using a Perkin-Elmer LS 55 fluorescence spectrometer. UV spectral measurements were done using a Hitachi-U-2001 spectrometer. Ultraviolet and visible (UV-vis) absorbance spectra were measured over a range of 800-200 nm with a Shimadzu UV-1650PC recording spectrometer using a quartz cell with 10 mm of optical path length.

3. RESULTS AND DISCUSSION

3. 1. HR-SEM with EDX analysis

HR-SEM image of TiO_2 are shown in Fig. 2(a.) respectively. The HR-SEM image exposed that surface morphology as agglomerated various sized and mixed has highly nanochain structure, which enhances the surface area of the nanomaterial. Fig. 2(b). EDX analysis conforms whereas Ti and O are present in TiO_2 nanomaterial.



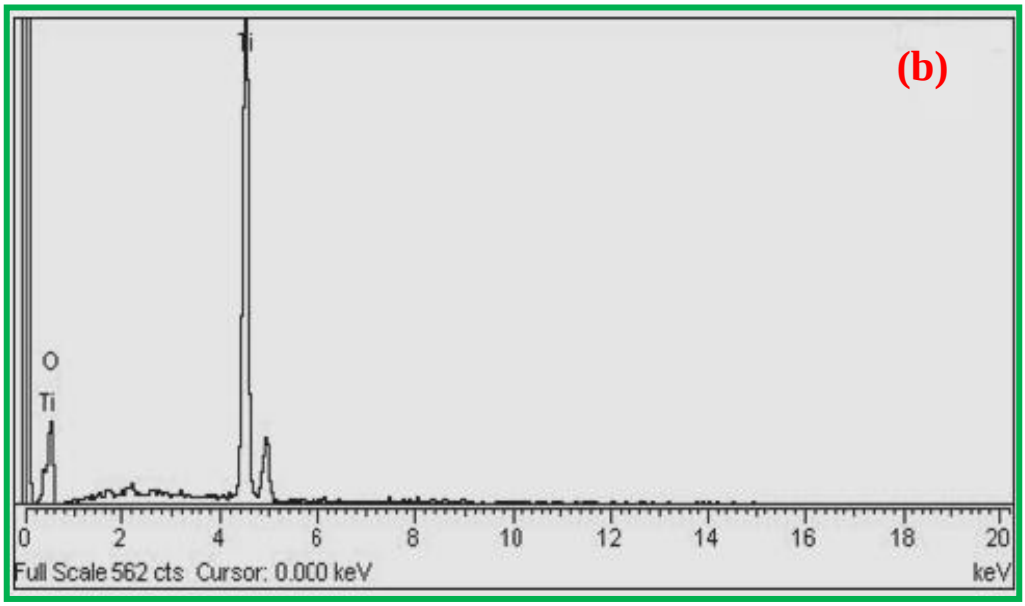


Fig. 2. HR-SEM image of (a) TiO_2 (b) EDX analysis of TiO_2 nanocomposite material

HR-SEM image of TiO_2 are shown in Fig. 2(a). respectively. The HR-SEM image exposed that surface morphology as agglomerated various sized and mixed has highly nanochain structure, which enhances the surface area of the nanomaterial. Fig. 2(b). EDX analysis conforms whereas Ti and O are present in TiO_2 nanomaterial

3. 2. XRD analysis

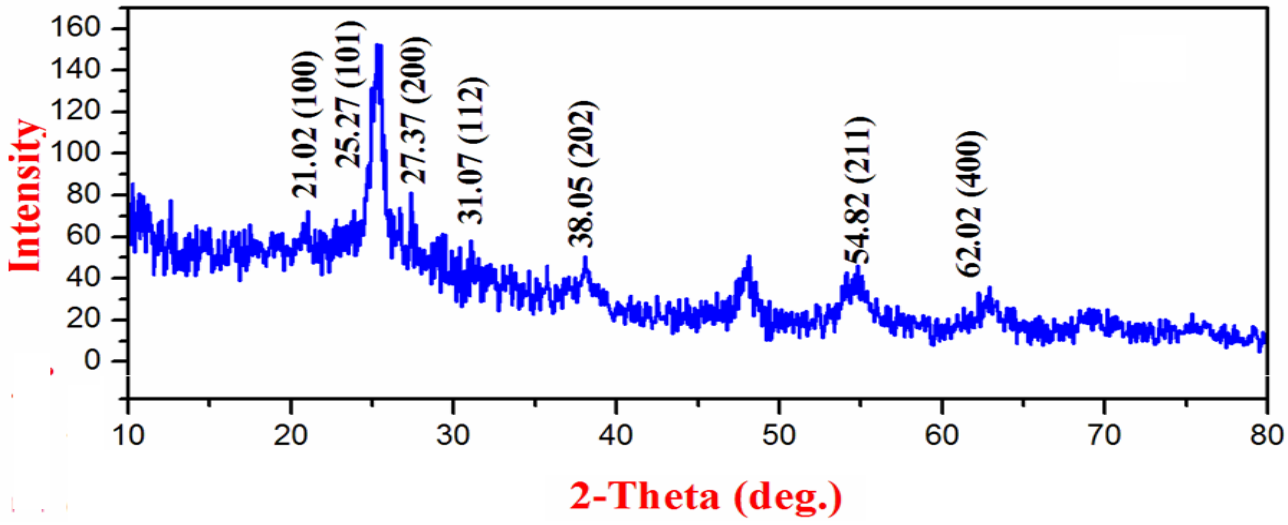


Fig. 3. XRD analysis of TiO_2 nanocomposite material

The XRD Patten of TiO_2 nanomaterial are shown in Fig. 3 respectively. The peaks at 25.22 and 54.27 are the diffractions from the TiO_2 (101) and (211) crystal planes. (Diffractions peaks of anatase phase TiO_2 (JCPDS No. 21-1272). The samples are present in TiO_2 exhibits a diffraction pattern of FCC crystal structure. The average crystalline size (L) of the particles has been calculated from the Debye–Scherrer formula, $L = 0.89\lambda / \beta \cos \theta$ where L is the crystalline size (in nm), λ is the wavelength (in nm), β is the full width at half maximum intensity (FWHM-in radian), and θ is the Bragg diffraction angle. The average crystalline size of prepared TiO_2 the average crystalline sizes of TiO_2 was 30 nm.

3. 3. FT-IR analysis

The FT-IR spectra of the prepared TiO_2 nanomaterials were shown in Figure 4. The FT-IR spectrum of shows the absorption peak at 3370-3525 cm^{-1} and 1635 cm^{-1} subsequent to stretching vibration of the ^{-}OH and bending vibration of the absorbed water molecules respectively. The main absorption peaks at 482 and 671 cm^{-1} was assigned to the Ti-O and Ti-O-Ti bonds.

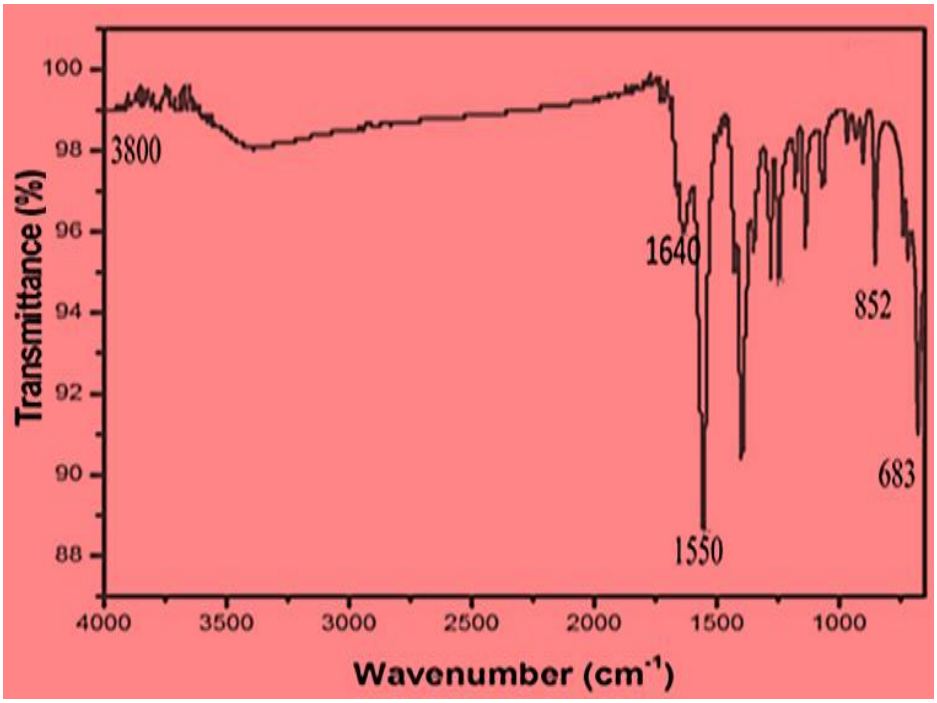


Fig. 4. FT-IR spectra of TiO_2 nanomaterial

3. 4. PL analysis

PL analysis of TiO_2 and TiO_2P25 are shown in Fig. 5. a and b, respectively. As photoluminescence occurs due to electron/hole pairs under equivalent light irradiation important to highly developed photocatalytic activity, the intensity is directly proportional to the rate of electron–hole recombination [15]. The emission spectra of synthesis TiO_2 and TiO_2p25 show that both section exhibited characteristic green emission in the range 350-600 nm. It is well-known that the PL of a nanomaterial is due to radioactive recombination

process of generated electron/hole pairs. Therefore, the decreased PL intensity of TiO_2 as a low recombination rate of electron/hole pairs, through an explanation for the enhancement in photocatalytic activity

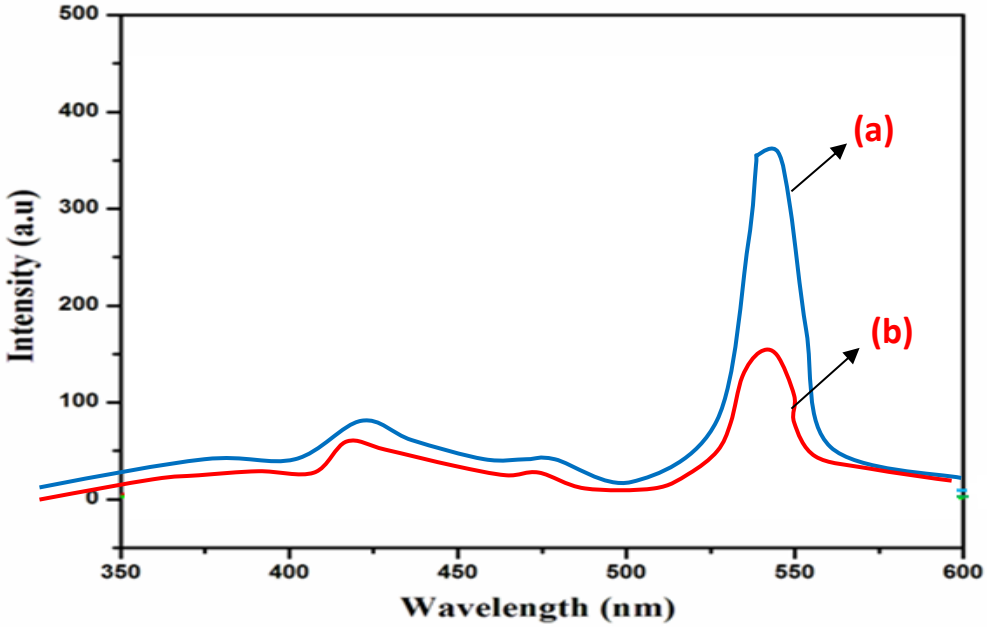


Fig. 5. PL spectra of (a) TiO_2 and (b) TiO_2 P25 nanomaterial

3. 5. Photocatalytic activity

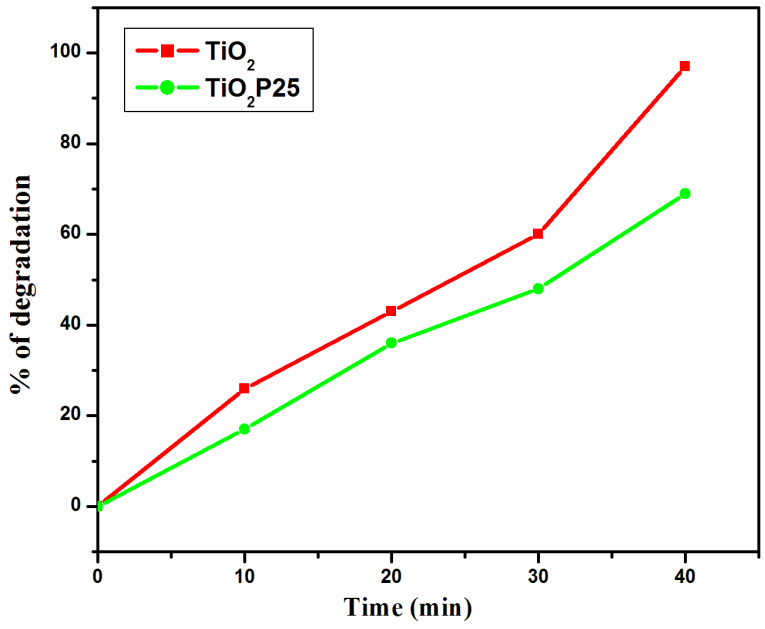


Fig. 6. TiO_2 and TiO_2P25 nanomaterial is degradation of MAG dye

TiO_2 material has superior photocatalytic activity than TiO_2P25. The MAG undergoes % of degradation from TiO_2 (0, 26, 43, 60 and 97 %) than TiO_2P25 (0, 17, 36. 48 and 69) in the presence of under UV-light at 365 nm in 40 min as shown in Fig. 6

3.6. Effect of catalyst loadings

The various amounts of the catalyst loading in photodegradation leads to increase the degradation rate. The rate is linearly related to the amount of catalyst loading. Among the three loadings 0.080 g has shown better activity and rapid degradation than other catalyst loading as shown in Fig. 7.

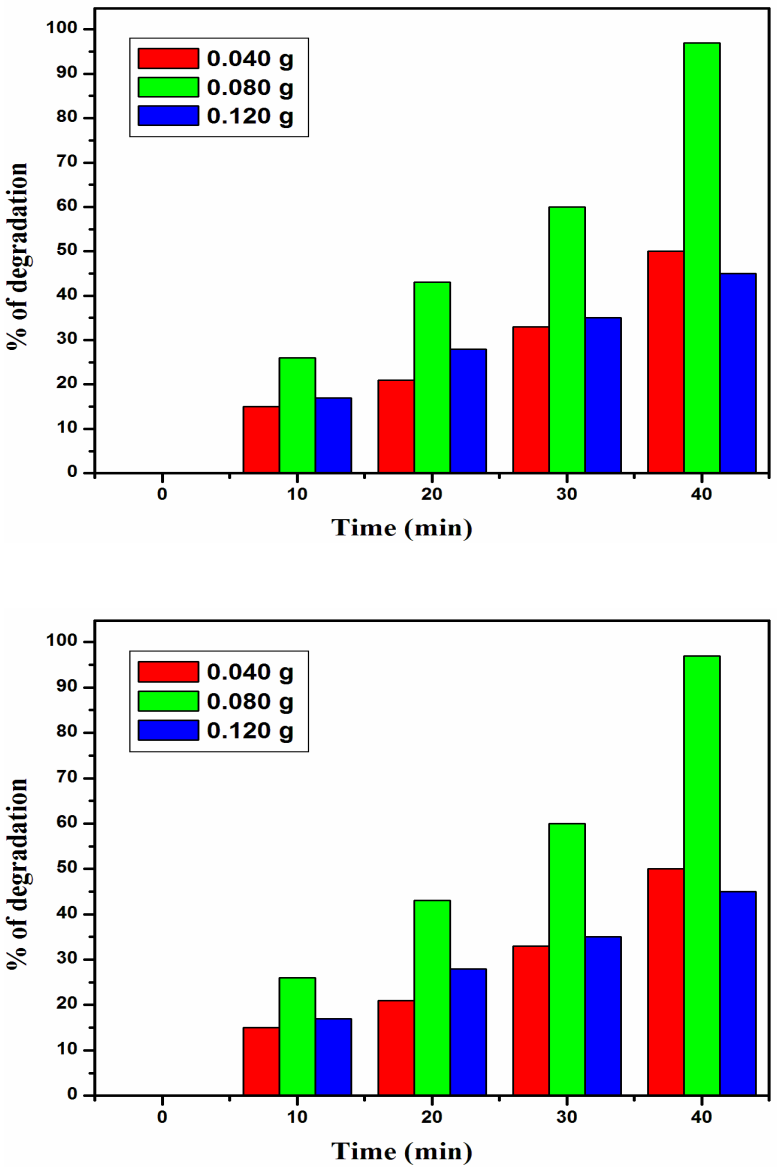


Fig. 7. Different catalyst loading upon MAG dye under UV-light irradiation by TiO_2 nanomaterial is degradation of MAG dye

3. 7. Different concentrations

The effect of different dye concentration ($1X10^{-4}$ and $1X10^{-5}$) is also inverstigated under UV light (shown in Fig. 8b). It reveals the increase in dye concentration leads the decreased activity. So photodegradation of MAG is more in lesser concentration

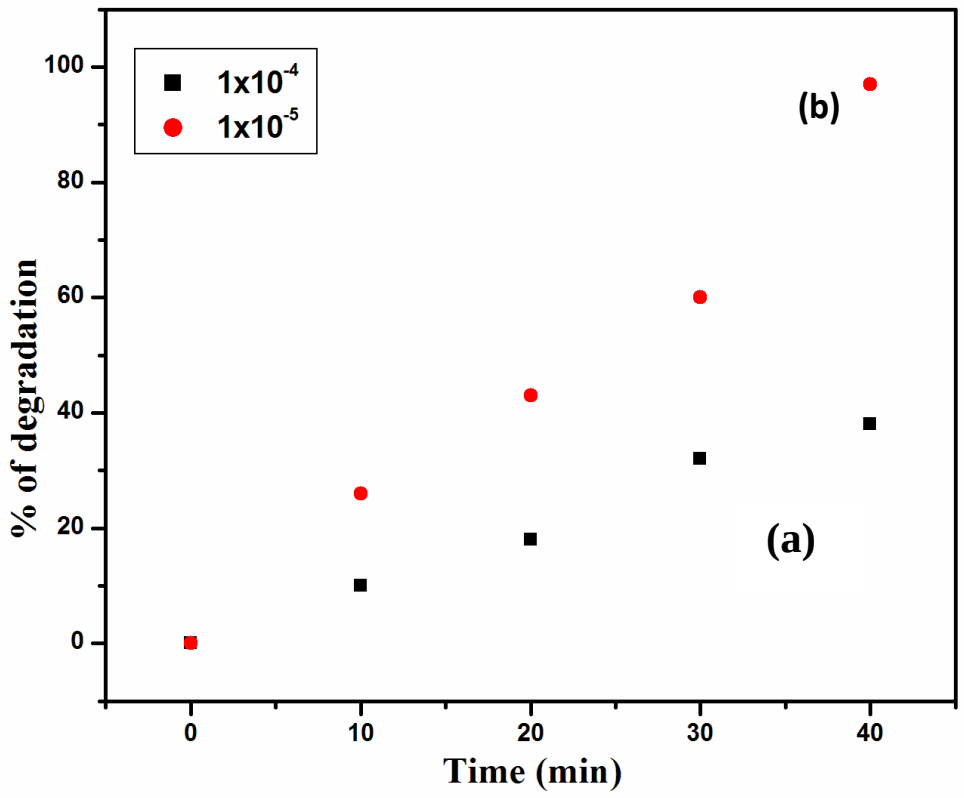


Fig. 8. Different concentration upon MAG dye under UV-light irradiation by TiO_2 nanomaterial is degradation of MAG dye

3. 8. Stability and reusability

The stability and reusability of the TiO_2 nnomaterial was achieved by repeating MAG degradation experiments for four more times. After each cycle the $InMoO_3$-TiO_2 was washed thoroughly with water, and a fresh solution of MEG was made before every run in the photoreactor.

The complete degradation occurs in the 1st cycle (100 %), 2nd cycle (99 %), 3rd cycle (98 %) and 6th (96.5 %) cycle as show in Fig.9. The results indicates that the prepared catalysts are stable and reusable. After the completion of the degradation process, the solution was tested for In^{3+} by leaching with Na_2S. There is no precipitation of In^{3+} S (black color) was found. As there is no further leaching of In^{3+}. So this responded material was non-hazardous for waste water treatment [16].

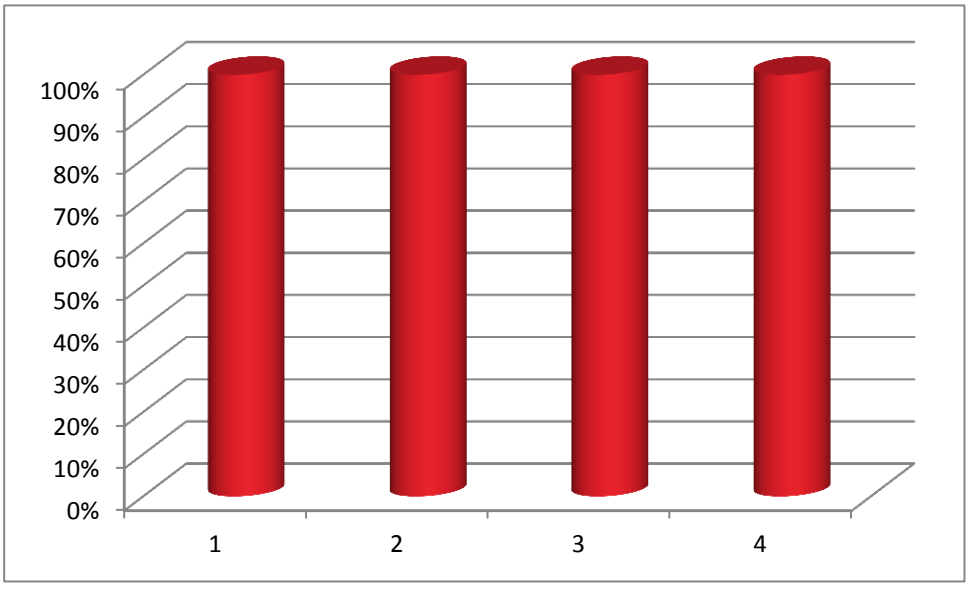


Fig. 9. Stability and reusability of TiO_2 on MAG dye concentration = $1x10^{-4}$ and irradiation time = 40 min

3. 9. Mechanism

Tentative mechanism by semiconduct oxide TiO_2 under UV-light irradiation at 365 nm towards MAG dye is proposed as follws:

$$^1MAG_0 + h\nu \rightarrow MAG_1 \quad \ldots(4)$$

$$^1MAG_1 + ISC \rightarrow {}^3MAG_1 \quad \ldots(5)$$

$$TiO_2\ (SC) + h\nu \rightarrow e^-(CB) + h^+(VB) \quad \ldots(6)$$

$$^-OH + h^+ \rightarrow {}^\bullet OH \quad \ldots(7)$$

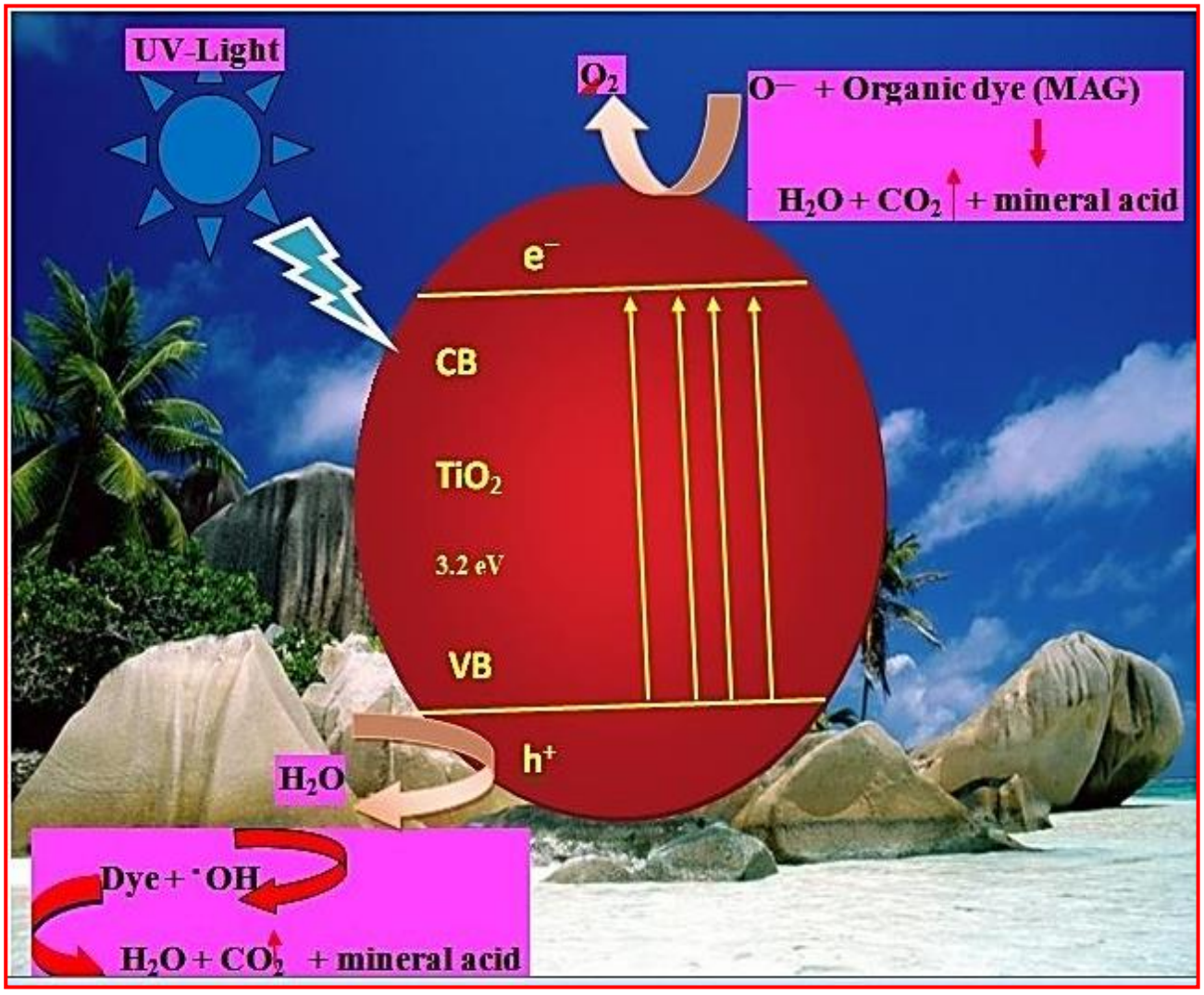
$$^\bullet OH + {}^3MAG_1 \rightarrow \text{Leuco MAG} \quad \ldots(8)$$

$$\text{Leuco MAG} \rightarrow \text{Products} \quad \ldots(9)$$

MAG dye absorbs radiation of preferred wavelength and it forms excited singlet state. promote, it undergoes intersystem crossing (ISC) to give its more stable triplet state. Along with this, the semiconducting TiO_2 (SC) also utilizes this energy to excite its electron from valence band to the conduction band.

An electron can be abstracted from hydroxyl ion (^-OH) by hole (h^+) present in the valence band of semiconductor generating $^\bullet OH$. This $^\bullet OH$ will oxidize MAG to its leuco form, which may ultimately degrade to products.

It was confirmed that the $^\bullet OH$ radical participates as an active oxidizing species in the degradation of MAG as the rate of degradation was appreciably reduced in presence of hydroxyl radical scavenger (2-propanol) Shown in Scheme 2 [7].



Scheme 2. Schematic diagram of photodegradation of MAG on TiO_2 nanomaterial under UV-light for successive mineralization.

4. CONCLUSIONS

In the present work the prepared TiO_2 nanomaterial was synthesized by a simple precipitation method and characterized by HR-SEM with EDX, XRD, FT-IR and PL, HR-SEM image shows the TiO_2 was morphology as agglomerated various sized and mixed has highly nanochain structure, The EDX spectra reveal the presence of Ti and O in the catalyst. TiO_2 is found to be more active than TiO_2P25 for the mineralization of MAG under UV-light irradiation. The influences of operational parameters such as effect of catalyst loading dye concentration. The mechanism of dye degradation in UV- light showed the superior photocatalytic activity than TiO_2 nanomaterial stable and reusable can be used as a material for expanded important industrial applications.

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