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## A FACILE NOVEL SYNTHESIS OF $\text{ThO}_2/\text{Fe}_3\text{O}_4$ NANOCOMPOSITE WITH ENHANCED PHOTOCATALYTIC ACTIVITY FOR THE DEGRADATION OF MALACHITE GREEN UNDER VISIBLE LIGHT IRRADIATION

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### Keywords:

$\text{ThO}_2/\text{Fe}_3\text{O}_4$  nanocomposite, Malachite green, Photocatalysis, Catalyst, the Degradation mechanism

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**ABSTRACT:** An innovative magnetically separable  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  nanocomposite was successfully synthesized by hydrothermal method. The synthesized  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  nanocomposite was characterized by UV-DRS, FT-IR, XRD, HR-TEM, BET, and TGA techniques. XRD and HR-TEM images displayed the overall spherical shape and confirmed the formation of well crystalline  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  nanocomposite. The catalytic efficiency of  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  was explored for the removal of malachite green dye (MG) from the aqueous phase. The degradation efficiency of about 99.53% was obtained, and the degradation reaction was maximal at pH 5. The results revealed that the synthesized  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  nanocomposite showed enhanced photocatalytic activity compared to the  $\text{ThO}_2$  and  $\text{Fe}_3\text{O}_4$  samples. Based on obtained results, the most plausible mechanism for removal MG has been proposed. The  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  photocatalyst remained a robust performer even after five cycles. This nanocomposite is an effective visible light responsive material which can be used for the removal of various organic pollutants from the environment.

**INTRODUCTION:** Contamination by organic pollutants has become a major environmental concern with industrial development and increases in the human population<sup>1,2</sup>. In recent years, dyes are also an important class of pollutants that can be toxic and even carcinogenic to human beings<sup>3</sup>. Among other pollutants, malachite green (MG) is a kind of triphenylmethane dye which has been widely used in the production of ceramics, leather, textile industry, food coloring, cell coloring, wool, jute, paper, acrylic industry, parasiticide, fungicide and bactericide in aquaculture industries globally<sup>4</sup>.

However, malachite green has an adverse effect on the reproductive and immune system, and it shows potential genotoxic, carcinogenic effects, damaging effects on gill, intestine, kidney, liver, and it causes anemia, thyroid abnormalities<sup>5</sup>. Therefore, it is necessary to find an effective method to remove MG from wastewater in an efficient and cost-effective way before its release into the environment<sup>6</sup>.

In recent years, it has been proven that the photocatalytic degradation technology is an effective method for environmental remediation and efficient way for the removal of organic waste material from water system<sup>7</sup>. For photocatalytic system, the nanosized metal oxides and their composites are developed because they possess high surface area and exhibit excellent physical and chemical properties due to its promising application in the energy production and environment-friendly

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and economical approach for the degradation of organic pollutants persisting in our environment<sup>8</sup>. Recently, actinide - based nanomaterials have attracted more attention as they are considered very promising for the preparation of innovative nuclear fuels and highly efficient photocatalysts<sup>9, 10, 11</sup>. Therefore, the target synthesis of actinide oxide nanoparticles with specific sizes and shapes is of great importance for both applied and fundamental research. Among actinide oxides, ThO<sub>2</sub> has attracted increasing attention in recent years due to its usage as ceramics, sensors, solid electrolytes, optical materials, traditional nuclear industry, and catalysts<sup>12</sup>. However, a single photocatalyst always suffers from the drawback of deficient separation and transfer of charge carriers, which counteracts the high-activity performance of photocatalysts<sup>13</sup>.

Among various photocatalysts, an iron oxide containing transition metal oxides are efficient in photocatalysis. Electron transport at the interface between two semiconductors is one of the important aspects for the design of this novel material. Thus, the photogenerated charge carriers, electrons, and holes are easily separated and are utilized for redox reaction<sup>14, 15</sup>. Recently, ThO<sub>2</sub> particles were doped with iron oxides particles because of their non-toxicity, low cost, compatible magnetic and electrochemical properties, which low cost, physical and chemical stability, high catalytic activity, environmental friendliness and ease of availability<sup>16, 17</sup>.

Herein, we have designed and developed a nano-structured ThO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> nanocomposite for the photocatalytic degradation of MG dye. The effects of the concentration of malachite green, pH value, and the concentration of photocatalyst on the degradation efficiency have been investigated. The fabricated ThO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> nanoparticles showed excellent photocatalytic activity for the degradation of MG dye under visible light irradiation.

## EXPERIMENTAL:

**Materials and Methods:** All chemicals were analytical grade and used as purchased without further purification. Th(NO<sub>3</sub>)<sub>4</sub>.5H<sub>2</sub>O and FeCl<sub>3</sub>.6H<sub>2</sub>O, ethylene glycol, sodium acetate, trisodium citrate, toluene, and ethanol were purchased from Sigma Aldrich. Deionized (DI) water was used throughout the synthesis process.

**Synthesis of ThO<sub>2</sub> Nanoparticles:** In the hydrothermal preparation, 1.5 g of Th(NO<sub>3</sub>)<sub>4</sub>.5H<sub>2</sub>O powder was weighed into a 50 ml Teflon lined stainless steel autoclave, and subsequently 40 ml of toluene was added. The autoclave was sealed and maintained at 180 °C for 24 h in an electric oven, then cooled to room temperature naturally. The resulting precipitate was filtered, washed with ethanol and DI water for several times, and dried at 80 °C.

**Synthesis of Fe<sub>3</sub>O<sub>4</sub> Nanoparticles:** The Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles were synthesized *via* a hydrothermal method according to previous report<sup>18</sup>. Briefly, FeCl<sub>3</sub>.6H<sub>2</sub>O (3.3 g) and trisodium citrate (0.6 g) were dissolved in ethylene glycol (60 ml) to form a clear solution, followed by the addition of sodium acetate (6.0 g). The mixed solution was stirred vigorously for 30 min and then sealed in a Teflon lined stainless steel autoclave (100 ml capacity). The autoclave was heated and maintained at 200 °C for 10 h, and then allowed to cool to room temperature. The products were collected and washed several times with ethanol, DI water, and vacuum dried at 60 °C overnight.

**Synthesis of ThO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> Nanocomposite:** ThO<sub>2</sub> nanoparticles and Fe<sub>3</sub>O<sub>4</sub> nanoparticles were added into absolute ethanol and ultrasonically dispersed for 10 min. After being stirred for 1 h at 75 °C, the precipitate was separated, washed and dried at 80 °C for 6 h. The obtained ThO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> product was calcined at 500 °C for 2 h.

## Characterization:

**Material Characterization:** The UV-Vis diffuse reflectance spectroscopy (UV-DRS) was recorded on a UV- 2400 spectrophotometer (Shimadzu Corporation, Japan) using BaSO<sub>4</sub> as the reference. Fourier transform infrared spectra (FT-IR) were recorded with a JASCO FT-IR 460 plus spectrometer. XRD analysis was carried out using Cu K $\alpha$  radiation ( $k = 1.5418 \text{ \AA}$ ) on a JEOL JDX 8030 X-ray diffractometer. The morphology of the material was ascertained High-resolution transmission electron microscopy and the corresponding selected- area electron diffraction (HR-TEM/ SAED) was carried out on a JEOL JEM 2100 analytical scanning transmission electron microscope. The samples for TEM were prepared by placing a drop of the prepared solution on

carbon-coated copper grids, followed by drying. Photodegradation experiments were performed in a HEBER immersion type photoreactor (HIPR-MP125). TGA of samples was carried out with a TGA-50, SHIMADZU thermogravimetric analyzer at a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  up to  $800\text{ }^{\circ}\text{C}$  under nitrogen gas.

**Photodegradation Experiments:** In the evaluation of photodegradation reaction, the experiment was conducted in a cylindrical immersion type photoreactor. The initial concentration of MG dye was taken  $2 \times 10^{-5}\text{ M}$ , and the 25 mg of the  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  nanocomposite was added in the dye solutions to form a slurry. The reaction mixture was stirred in the dark for a certain time to establish the adsorption-desorption equilibrium of the dye molecules and dissolved water with the catalyst surface. Photolysis experiment of MG dye in the absence of photocatalyst under visible light was carried out by the aforementioned procedure. Further, the photocatalytic experiment was initiated by illuminating the system with visible light and after specific time intervals; certain aliquots of solution were withdrawn out with syringe at pre-determined time intervals, the dispersion was drawn and separated immediately by the adsorbent magnet and collected. The residual amount of MG dye in the solution was analyzed using a UV-Vis spectrophotometer (JASCO V-530) based on its characteristic optical absorption at 619 nm. The decolorization efficiency (%) is calculated as:

$$\text{Photodegradation (\%)} = \frac{C_0 - C}{C_0} \dots\dots\dots 1$$

Here, C is the absorption of MG solution at irradiation time of 't' min and C<sub>0</sub> is the initial absorption at t = 0 min.

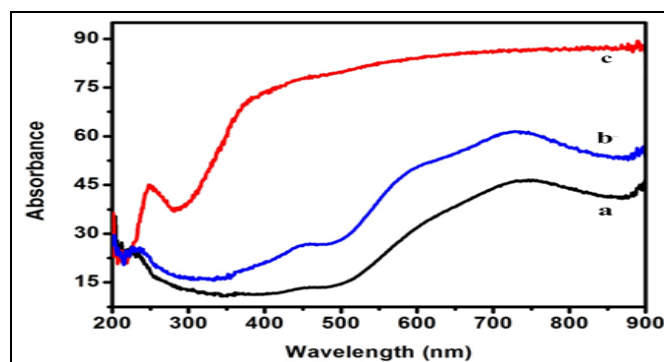
## RESULTS AND DISCUSSION:

**UV-DRS:** To understand the band structures of these materials, optical absorption study has been carried out in the wavelength ( $\lambda$ ) range 200-900 nm, as shown in **Fig. 1**. The results reveal that the absorption edge shifted to longer wavelengths as the  $\text{ThO}_2$  was doped into the surface of  $\text{Fe}_3\text{O}_4$ . The direct band gap was calculated from the UV-DRS spectra. We used the following formula for calculating band gaps from obtained diffuse reflectance spectra:

$$E = h \cdot C / \lambda \dots\dots\dots 2$$

Where, h is Planck's constant, C is the speed of light, and  $\lambda$  is cut off wavelength of recorded spectral data.

**Fig. 1a-c** shows the UV-DRS spectra of the  $\text{ThO}_2$ ,  $\text{Fe}_3\text{O}_4$  and  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  nanocomposite. The  $\text{ThO}_2$ ,  $\text{Fe}_3\text{O}_4$  nanoparticles and  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  nanocomposite show the adsorption edge of 300, 450 and 475 nm, corresponding to a band gap of 1.8 eV, 2.2 eV, and 2.7 eV respectively, which signifies its photocatalytic activity under visible-light irradiation. The absorption of the  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  nanocomposites within the visible-light range significantly increased, and a red shift in comparison with the pure  $\text{Fe}_3\text{O}_4$ . These results are attributed to the interaction between the  $\text{ThO}_2$  and  $\text{Fe}_3\text{O}_4$  nanoparticles in the composite system. The enhanced light absorption of the  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  nanocomposite leads to the generation of more photoinduced electron-hole pairs under visible-light irradiation, which subsequently results in enhanced photocatalytic activity.



**FIG. 1: UV-DRS SPECTRA OF  $\text{ThO}_2$  (a),  $\text{Fe}_3\text{O}_4$  (b),  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  (c) NANOCOMPOSITE**

**FT - IR Spectroscopy:** FT - IR measurements provided further evidence for the formation of  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  nanocomposite. **Fig. 2** illustrates the FT-IR spectra of  $\text{ThO}_2$  (a),  $\text{Fe}_3\text{O}_4$  (b) and  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  (c) nanocomposite. For all the samples, most typical band at  $3420\text{ cm}^{-1}$  was assigned to the stretching vibration of OH group and appearance of bands around  $2927\text{ cm}^{-1}$  and  $2332\text{ cm}^{-1}$  was attributed to stretching in C-H group respectively. The magnetite NPs can be seen by wide strong absorption band between  $580$  and  $630\text{ cm}^{-1}$ , especially for Fe-O bond of bulk magnetite at  $576\text{ cm}^{-1}$  <sup>19</sup> as well as those at  $1620\text{ cm}^{-1}$  can be ascribed to carboxylate groups <sup>20</sup>. This indicates that magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles are capped with citrate groups that derived from the introduction of

trisodium citrate during the solvothermal synthesis. These FT-IR spectra provided useful information that the Fe<sub>3</sub>O<sub>4</sub> were successfully bound to the ThO<sub>2</sub>.

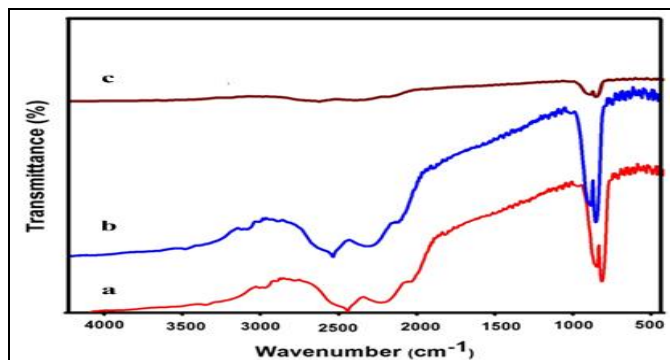


FIG. 2: FT-IR SPECTRA OF ThO<sub>2</sub> (a), Fe<sub>3</sub>O<sub>4</sub> (b), Fe<sub>3</sub>O<sub>4</sub>/ThO<sub>2</sub> (c) NANOCOMPOSITE

**XRD:** The phase and crystalline composition of the as-prepared Fe<sub>3</sub>O<sub>4</sub> and ThO<sub>2</sub> nanocomposite are examined by XRD measurements. The powder XRD pattern of the precursor is shown in Fig. 3 Fe<sub>3</sub>O<sub>4</sub> (a), ThO<sub>2</sub> (b) and ThO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> (c). All the diffraction patterns obtained were indexed to the characteristic peaks of ThO<sub>2</sub> (JCPDS card no. 65-7222). Also a typical XRD pattern of the Fe<sub>3</sub>O<sub>4</sub> showed diffraction peaks at  $2\theta = 27.56^\circ, 30.07^\circ, 35.42^\circ, 37.05^\circ, 43.05^\circ, 56.9^\circ, 62.52^\circ, 73.96^\circ$  respectively corresponding to the (111), (220), (311), (222), (400), (333), (440) and (533) reflection face-centered cubic lattice of Fe<sub>3</sub>O<sub>4</sub>, which match well with the data from the JCPDS file (Card no. 82-1533) for Fe<sub>3</sub>O<sub>4</sub>. It was observed that Fe<sub>3</sub>O<sub>4</sub>/ThO<sub>2</sub> shows the diffraction peaks at  $2\theta = 0.19$  and  $0.14^\circ$  respectively.

The average crystalline structure was calculated from the most intense peak of 220 and it was found to be 8nm respectively. The XRD patterns that can be seen there are no additional peaks, implying the absence of impurity phases in the sample. This confirms the mesoporous and crystalline nature of the material. The average crystallite size of the synthesized ThO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> nanocomposites calculated by the XRD data according to Scherrer's equation.

$$D = k \lambda / \beta \cos \theta \quad \dots\dots\dots 3$$

Where, d is the thickness of crystallite (nm), k is a constant dependent on the crystallite shape,  $\lambda$  is the X-ray wavelength (nm), B is the full width at half max in radians, and  $\theta$  is the Bragg angle of the  $2\theta$  peak.

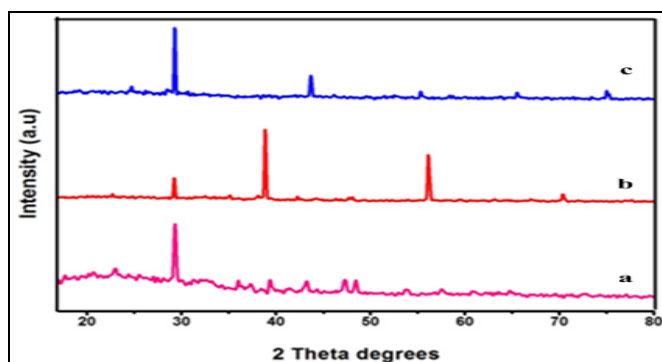


FIG. 3: (a-c) XRD PATTERN OF Fe<sub>3</sub>O<sub>4</sub>, ThO<sub>2</sub>, AND ThO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> NANOCOMPOSITE

**TEM:** The morphology, particle size, and structure of the products were characterized by TEM. The TEM images of different magnifications of ThO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> nanocomposite are shown in Fig. 4a-d. To investigate the stability of Fe<sub>3</sub>O<sub>4</sub> attached on the ThO<sub>2</sub> nanoparticles, a leaching test was conducted through treating the as-synthesized ThO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> sample fully dispersed with ethanol under sonication. Even after sonication for 30 min, the Fe<sub>3</sub>O<sub>4</sub> nanoparticles are still firmly anchored on the ThO<sub>2</sub>, suggesting the strong interaction between ThO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>. The morphology of pure ThO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> nanocomposite shows spherical shape with uniform sizes and face-centered cubic structure. The average crystallite size of ThO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> nanocomposite is 8 nm, respectively. Fig. 4d illustrates Fe<sub>3</sub>O<sub>4</sub> nanoparticles appearing black and the ThO<sub>2</sub> nanoparticles with a lighter color as observed for ThO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> nanocomposite. It is noticeable that ThO<sub>2</sub> nanoparticles are uniformly coated on the surface of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles.

The TEM images for the crystalline nature of ThO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> nanocomposite is displayed in Fig. 5a-b. The selected area electron diffraction (SAED) pattern of ThO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> nanocomposite is presented in Fig. 5c. The SAED pattern revealed several bright continuous concentric rings attributed to the diffraction from the (111), (220), (222), (400), (333) and (533) planes of ThO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>, consistent well with the XRD data. The SAED pattern indicates the well crystalline nature of the prepared photocatalysts. EDX spectroscopy was employed to investigate the chemical composition and purity of the ThO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> nanocomposite. Fig. 5d shows that the corresponding results of the EDX pattern of the ThO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> nanoparticles contain four elements of Fe, Th, Cu, and O.

The energy-dispersive X-ray spectroscopy (EDS) demonstrates the coexistence of Fe, Th, O

elements, which indicate the formation of  $\text{ThO}_2$  and  $\text{Fe}_3\text{O}_4$  nanocomposite.

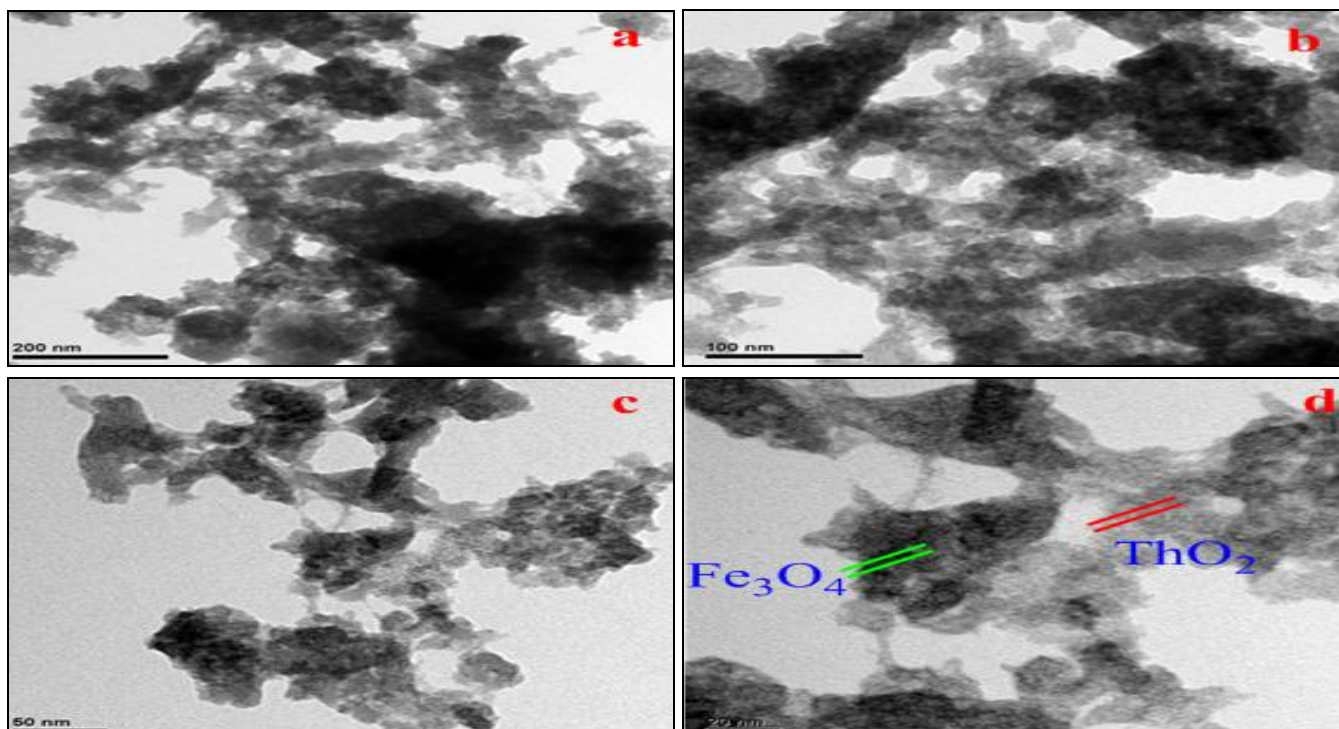


FIG. 4: (a-d) HR-TEM IMAGES OF DIFFERENT MAGNIFICATIONS OF  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  NANOCOMPOSITE

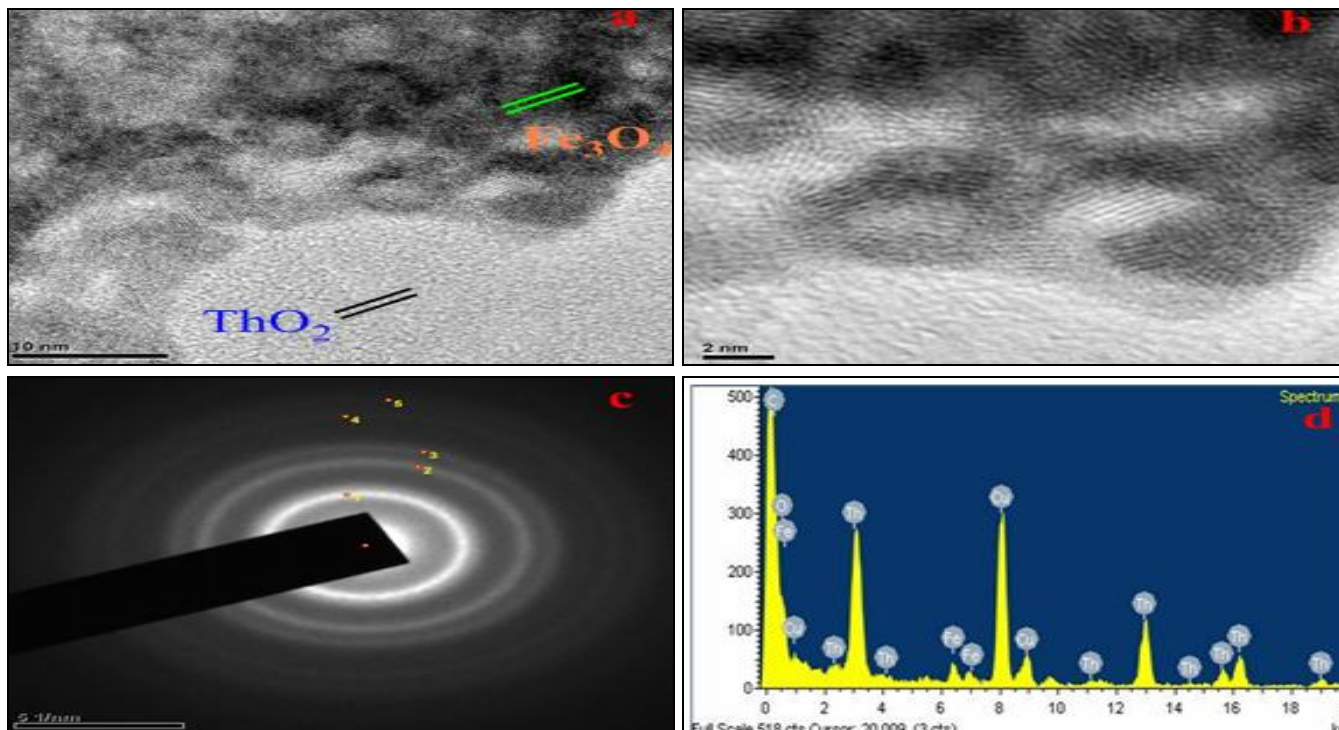


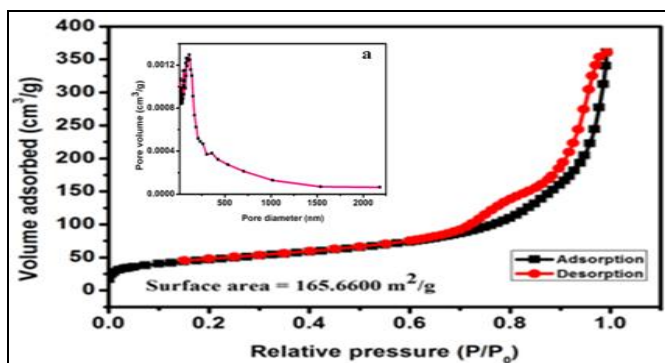
FIG. 5: (a, b) HR-TEM IMAGES OF CRYSTALLINE NATURE OF  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  NANOCOMPOSITE, (c) SAED PATTERN OF  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  NANOCOMPOSITE, (d) EDX SPECTRUM OF  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  NANOCOMPOSITE

**BET:** The specific surface area, pore volume, and size analysis were calculated using the Brunauer-Emmet-Teller (BET) method. A typical nitrogen adsorption-desorption isotherm of all the photocatalysts are shown in **Fig. 6**. All the samples

exhibit type IV nitrogen sorption isotherm with a capillary condensation step in the relative pressure ( $P/P_0$ ) range 0-1.0, indicating a well-developed mesoporosity<sup>21</sup>. The BET surface area of the nanocomposite was found to be 165.66  $\text{m}^2/\text{g}$ ,

calculated by the linear part of the BET plot. **Fig. 6a** (insert) shows that the total pore volume was observed by  $0.55794 \text{ cm}^3/\text{g}$ . The surface area, pore size, and pore volume of all the photocatalysts are presented in **Table 1**. Mesoporous structure and relatively high surface area could be responsible for its high photocatalytic activity.

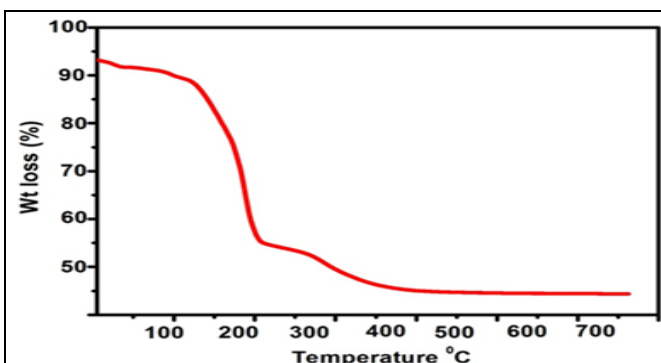
**TGA:** The TGA plot in **Fig. 7** shows the  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  nanocomposite, which shows a steady



**FIG. 6:**  $\text{N}_2$  ADSORPTION-DESORPTION ISOTHERM AND INSERT (**FIG. a**) PORE-SIZE DISTRIBUTION CURVE OF THE  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  NANOCOMPOSITE

weight loss in the temperature range of 25-700 °C. The first weight loss (40.84%) was observed between 36-200 °C, which can be attributed to the removal of physisorbed water molecules.

The second weight loss (8.77%) was occurring in the range of 270 to 400 °C due to the decomposition of bioorganic compounds in  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  nanocomposite.



**FIG. 7:** TGA ANALYSIS OF  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  NANOCOMPOSITE

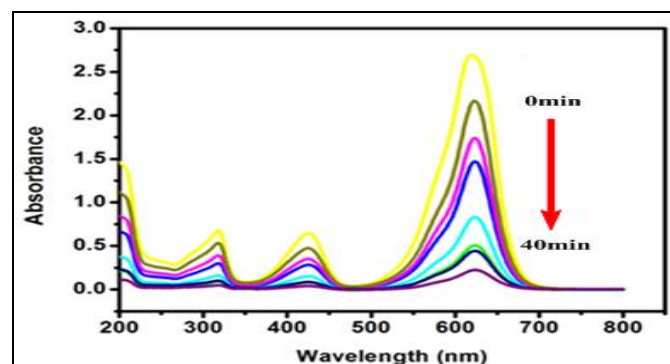
**TABLE 1: SURFACE AREA, PORE VOLUME, PORE SIZE OF SYNTHESIZED  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  NANOCOMPOSITE**

Sample name	Surface area ( $\text{m}^2/\text{g}$ ) BET result	Pore volume ( $\text{cm}^3/\text{g}$ ) BET result	Pore size (nm) BET result	Crystalline size (nm) XRD result
$\text{ThO}_2/\text{Fe}_3\text{O}_4$ nanocomposite	165.66	0.55794	1.347	8

Above the temperature of 400 °C, the pure  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  only exists, which is stable up to 600 °C.

### Photocatalytic Activity:

**Effect of Time:** **Fig. 8** shows the changes in the MG absorption spectra during photocatalytic degradation with  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  at different irradiation times varying from 0 to 40 min. More than 75% of the MG is degraded within 40 min.



**FIG. 8:** PHOTOCATALYTIC DEGRADATION OF MG AT DIFFERENT TIME INTERVALS (0-40 min) USING  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  NANOCOMPOSITE

The results show that the absorption of the visible band at 618 nm decreased and a hypsochromic shift

occurred simultaneously with increasing illumination time. The hypsochromic shift may be caused by an N-demethylation process. The absorbance peaks at 425 and 315 nm have declined, which indicates that the entire conjugated chromophore structure of MG has been destroyed.

### Effect of pH on the Photodegradation of MG:

The influence of different pH (3, 5, 7, and 9) value on the degradation efficiency of MG was investigated, which is shown in **Fig. 9**. The natural pH value of MG solution was found to be 5.2. The pH value was adjusted using dilute HCl or dilute NaOH solution for the experiment. The effect of pH on the degradation of MG was examined by changing the pH from 3, 5, 7 and 9 at a fixed amount of catalyst (0.25 g/L) and constant MG concentration (10 mg/L). **Fig. 9a** shows the effect of pH on the photodegradation of MG solution. At pH 5, it is observed that the absorption band of the MG is 619 nm. Since, the color from deep green changes to colorless, there is a rapid decrease with a slight hypochromic shift which is found at 619

nm, and there is no new absorption band in the UV range. It indicates that there would be a cleavage of the conjugated chromophore structure of the MG which would have occurred because of the formation of N-de-methylated intermediates. In the acidic pH 5, the absorption peak at 619 nm confirmed that there is adsorption of MG on  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  catalyst surface. It is found that degradation occurs (99.53%) within 40 min at pH 5. The electrons in the conduction band can be

captured by the soluble  $\text{O}_2$ , and the holes can be trapped by the surface hydroxyl, these process resulting in the formation of hydroxyl radical species ( $\cdot\text{OH}$ ), which are easily generated by oxidizing more hydroxide ions in acidic solution. Thus, the efficiency of the degradation process is enhanced in the acidic medium, especially at pH 5. Thus, the acidic medium favors the complete degradation of MG on the surface of the catalyst.

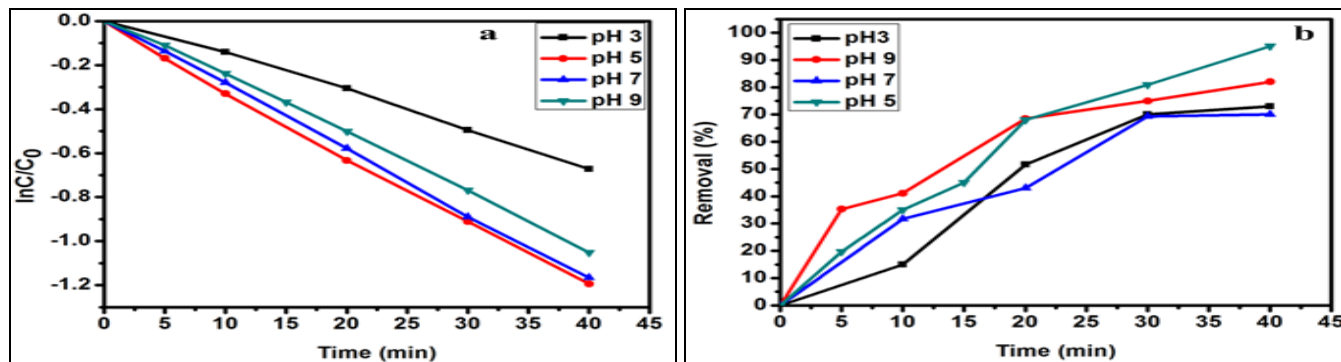


FIG. 9: (a)  $\ln(C_0/C)$  vs. IRRADIATION TIME IN MG, (b) PHOTODEGRADATION EFFICIENCY OF MG

Similar kind of report is shown by Thu *et al.*,<sup>23</sup>. The degradation yields of the cationic dyes are greater in the acidic medium than in neutral and alkaline media, which is correlated with the adsorption behavior of dyes on the catalyst surface. It shows that the degradation of malachite green followed the rate constant,  $0.481 \times 10^{-2} \text{ min}^{-1}$  ( $R^2 = 0.9925$ ). Fig. 9b illustrates the photodegradation efficiency of  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  nano-composite in which 99.53% of degradation is possible at pH 5.

**Effect of Amount of Catalyst:** The amount of photocatalyst is another factor affecting the performance of the photocatalyst. The photocatalytic study was conducted under the following conditions: a source of irradiation, visible light, type of photocatalyst ( $\text{ThO}_2/\text{Fe}_3\text{O}_4$  photocatalyst), the weight of photocatalyst (0.1 g to 0.5 g) and concentration of MG dye solution ( $2 \times 10^{-5} \text{ M}$ ). The effect of the loading of the  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  heterogeneous photocatalyst on the degradation of MG dye is shown in Fig. 10. The results reveal that the photocatalytic activity increased 80-95% after 40 min by increasing the weight of the  $\text{ThO}_2/\text{Fe}_3\text{O}_4$  photocatalyst from 0.1 to 0.5 g/L due to increased. The degree of decomposition reaction increases with the increase in the reactive sites on the catalyst, beyond which, it shows that the degradation process is reduced, because of the

scattering of light. There is a decrease in the penetration of light in the solution. When the amount of catalyst is higher in the solution, the activated molecules get deactivated by the collision of the lower energy molecules thereby increasing the turbidity of the medium and reduction in penetration of light leads to decrease in the rate of the reaction. Also, when the photocatalyst absorbs the highest light; hence, the surface area becomes high, as a result of agglomeration at higher concentration of catalyst.

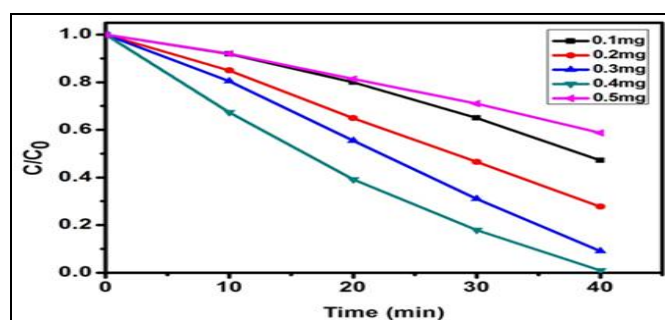
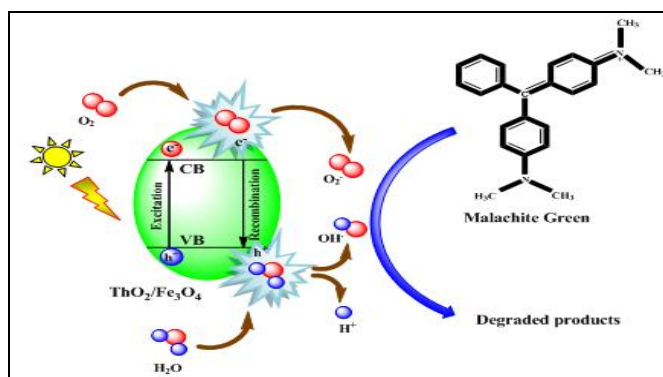


FIG. 10: EFFECT OF CATALYST DOSE ON PHOTODEGRADATION OF MG IN AQUEOUS SOLUTION

**Plausible Mechanism of MG Dye Degradation:** The mechanism of MG dye degradation is initiated by the attack of OH radicals on the malachite green cation. First, the N-demethylation occurs on the attack of OH radicals, leading to the removal of all the four methyl groups present in MG dye.

As there is a continuous generation of OH radicals in the reaction system, the attack of OH radicals occurs spontaneously on the organic moiety. On further reaction, the by-products may undergo continuous degradation due to OH radical attack to bring about a benzene ring removal and ring opening to completely mineralize the material to yield carbon dioxide and water as the end by-products<sup>24, 25, 26</sup>. A schematic representation is shown in **Scheme 1**. **Table 2** shows a comparison of previously reported MG degradation with different photocatalysts<sup>27, 28, 29, 30</sup>.

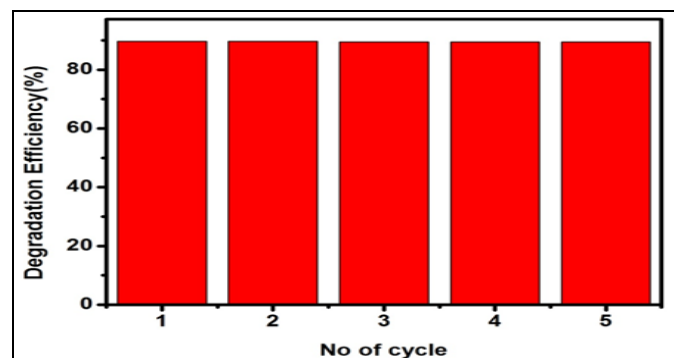


**SCHEME 1: MECHANISM FOR THE DEGRADATION OF MG USING ThO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> NANOCOMPOSITE**

**TABLE 2: COMPARISON OF PHOTOCATALYTIC DEGRADATION OF MG USING VARIOUS CATALYSTS**

MG concentration	Photocatalysts	Weight of catalyst	Time (min)	Degradation %	Reference
20 ml, 100 ppm	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /SnO <sub>2</sub>	40 mg	360	86	27
10 <sup>-5</sup> M	PANI/ZnO	0.4 g/L	300	99	28
2×10 <sup>-5</sup> M	CeFeO <sub>3</sub>	0.05 g	120	91	29
0.05 to 0.4 gL <sup>-1</sup>	ZnO	0.2 gL <sup>-1</sup>	-	93.75	30
2×10 <sup>-5</sup> M	ThO <sub>2</sub> /Fe <sub>3</sub> O <sub>4</sub>	0.5g	40	99.53	Present work

**Recyclability:** The stability of a photocatalyst during the photocatalytic reaction is an important factor for a possible industrial application. To analyze the stability of the photocatalyst, prolonged recycling studies were performed. **Fig. 11** shows the results of the repeated runs of MG degradation using the same photocatalyst. After each cycle, the photocatalyst was collected by centrifugation and then washed with distilled water until the complete removal of dye from the catalyst. Then, the catalyst was dried at 100 °C overnight and used for another cycle. The photocatalytic activity was found to be nearly the same up to five cycles.



**FIG. 11: REUSABILITY STUDY OF ThO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> CATALYST ON THE PHOTODEGRADATION OF MG**

**CONCLUSION:** In this work, the ThO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> nanocomposite was prepared and investigated as effective material for removing MG from aqueous solution. Various characterization tools such as XRD, TEM strongly evidence the formation of

ThO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> nanocomposite. Photocatalytic degradation of MG was 99.53% within 40 min. The photocatalyst was reused up to five cycles without significant change in the photocatalytic activity, which indicates the stability of the photo-catalyst. The ThO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> nanocomposite has a better specific surface area, more reactive sites, and higher stability. The facile preparation method and removal properties for MG imply the promising future of ThO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> nanocomposite in the practical application for wastewater treatment.

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