Synthesis and characterization of InWO$_3$ - TiO$_2$ nanocomposite material and multi application

J. Kamalakkannan, V. L. Chandraboss and S. Senthilvelan*
Department of Chemistry, Annamalai University, Annamalainagar - 608 002, India
*E-mail address: dr_senthilvel@yahoo.co.in

ABSTRACT

InWO$_3$ -TiO$_2$ nanocomposite material was synthesised by co-precipitation method and sonoication technique. The synthesized nanomaterial was characterized by FE-SEM with EDX, HR-TEM, XRD, FT-RAMAN, AFM and BET surface area measurements. The photocatalytic activity of InWO$_3$-TiO$_2$ nanocomposite material was studied from the photodegradation of malachite green (MAG) under UV-light irradiation. The photodegradation of MAG at various parameters are reported. The Photodegradation was found to follow the pseudo-first-order kinetics. The Hydroxyl radical formation in the mechanism was confirmed by fluorescence quenching technique. The antimicrobial activity of the prepared nanomaterials has also been investigated. Cyclic voltammeter (CV) measurements analysis of the prepared nonamaterial was discussed in detail. It was proposed that the catalyst was found to be stable and reusable.

Keywords: Photocatalytic activity; Antimicrobial activity; Electrochemical activity

1. INTRODUCTION

The semiconductor TiO$_2$ nanomaterial has been confirmed to be a brilliant photocatalyst and environmental remediation because of its superior photocatalytic activity under UV-Light irradiation. This nanomaterial shows stability, low cost, high thermal, non-toxicity and environmental sociability and has wide applicability [1-7]. Anatase TiO$_2$ is the most suitable photocatalyst for environmental use. Alternatively, WO$_3$ has been studied as a suitable
candidate as visible light photocatalyst [8-12]. So WO₃ doped In³⁺ give InWO₃ orthorhombic clearly. In recent years, giant efforts have been dedicated to addressing these problems by developing strategies, such as dye sensitization [13,14], impurity doping [15,16], noble metal deposition [17,18], surface modification [19-21] and semiconductor composite manufacturining [22-24]. Metal tungstate is significant additional of inorganic materials that have grand application potential in the area of catalysis [25]. Enhance MAG is an extensively used biocide dye in international aquaculture production. It is also used as a medical antiseptic, food colouring agent and food chemical addition. MAG has now become a highly controversial compound due to its toxicity to the reproductive immune system, it is carcinogenic and genotoxic also [26]. Experimental composite materials with dopants have been synthesized by coupling TiO₂ with other semiconductors such as InVO₄ [27] and WO₃ [28]. Due to cost and stability issues, TiO₂, ZnO, CdS, WO₃ and Fe₂O₃ were used for decolorizing and decomposing organic dye to mineralized products.

2. EXPERIMENTS

2.1. Synthesis of InWO₃-TiO₂ nanocomposite material

Step 1. Synthesis of InWO₃

InWO₃ synthesis was conducted in the following way. indium chloride and Sodium tungstate were first dissolved with anhydrous ethanol and deionized water respectively, the as prepared InCl₃ solution was put in a beaker, and then slowly added Sodium tungstate until it reached to 1:1 composite. Frequent magnetic stirring for 2 h was carried out to keep the reactant mixed equally. The pH of the solution was adjusted to 9 with ammonia solution. The obtained solution was placed in sonication for 40 mins to get a precipitate. The precipitate was filtered and washed with distilled water for four to six times to remove the remaining Cl⁻ and Na⁺ ions. Finally the sample was dried at 100 °C for 1 h.

Step 2. Synthesis of InWO₃-TiO₂ nanomaterial

In the second step, the obtained InWO₃ was added into tetra isopropyl orthotitanate with anhydrous ethanol and deionized water respectively. The resulting solution was stirred at room temperature for 4 h and ultra sonication was carried out for 20 min, until a precipitate was formed. The obtained precipitate was filtered and washed with distilled water and ethanol until the alkali phases were removed from the precipitate. The precipitate was together and dried in an oven at 100 °C for 12 h. The resulting powder was finally calcined at 500 °C for 3 h as shown in Scheme 1.

2.2. Chemicals

Tetra isopropyl orthotitanate (C₁₂H₂₈O₄Ti), Sodium tungstate (Na₂WO₄), Indium chloride (InCl₃), NH₃ solution, nitric acid (HNO₃-65%), were used as such. A gift sample of TiO₂-P25 (80% anatase), malachite green (C₂₃H₂₅ClN₂) are used, ethanol were the guaranteed reagents of Sigma Aldrich. The aqueous solutions were prepared by using double distilled water.
2.3. Photocatalysis

The photocatalytic activities of the photocatalysts (TiO$_2$ and InWO$_3$-TiO$_2$) were evaluated by the photodegradation of MAG. The light source was UV lamp (365 nm). The reaction was carried out at ambient temperature (303 K). In a typical experiment, aqueous suspensions of dye (40 mL, $1\times10^{-4}$ 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 (614 nm) within the Beer–Lambert law limit.

2.5. Determination of antimicrobial activity

Determination of antibacterial activity by disc diffusion method and antifungal activity by filter paper disc method as follows
Nutrient agar plates were prepared under sterile conditions and incubated overnight to identify any contamination. About 0.2 mL of working stock culture was shifted into separate nutrient agar plates and spread thoroughly using a glass spreader. Whatman No.1 discs (6 mm in diameter) were impregnated in the testing compounds dissolved in DMSO (200 mg/mL) for about half an hour. Commercially available drug disc, Ciprofloxacin (10 mg/disc) was used as positive reference standard. The discs were placed on the incubated agar plates and incubated at 37±1 °C for about 2h. Antibacterial activity was valued by measuring the zone of incubation beside the test organism. Bacteria strains and ciprofloxacin are used as a standard and results obtained. For antifungal activity by filter paper disc method with antifungal strains with Amphotericin –B as reference standard are used.

2. 6. 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.

FT-RAMAN spectra were recorded with an integral microscope Raman system RFS27 spectrometer equipped with 1024 - 256 pixels liquefied nitrogen-cooled germanium detector. The 1064 nm line of the Nd:YAG laser (red laser) was used to excite. To avoid intensive heating at the sample, the laser power at the sample was kept not higher than 15 mW. Each spectrum was recorded with an acquisition time of 18s. The surface topological studies were carried out using Atomic force Microscope (AFM) (Nano surf Easy scan2) AGILENT-N9410A-5500. The specific surface areas of the samples were determined through nitrogen adsorption at 77 K on the basis of the BET equation using a Micromeritics ASAP 2020 V3.00 H. A Shimadzu (Japan) AA6300 atomic absorption spectrometer was used to measure the concentration of Zn²⁺ ions. 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. Fluorescence technique with coumarin (1 mM of 4-hydroxycoumarin) were measured on a Hitachi F-7000 fluorescence spectrophotometer. The antibacterial activity was studied by disc diffusion method, the test compound was dissolved in DMSO (200 mg/mL) for about half an hour. Commercially available drug disc, Ciprofloxacin (10 mg/disc) was used as positive reference standard and Cyclic voltammetry (CV) measurements were carried out using CHI 60 AC electrochemical analyzer (CHI Instruments Inc. USA).

3. RESULTS AND DISCUSSION

3. 1. SEM with EDX analysis

The FE-SEM images of the prepared TiO₂ and InWO₃-TiO₂ nanocomposite material are shown in Fig 1 (a and b) respectively. The FE-SEM images exposed that individual
particles comprised of a group of elongated particles and shows the surface morphology as agglomerated various size and spherical shaped particles. The FE-SEM images of the TiO$_2$ shows an average particle size of 80 nm and InWO$_3$-TiO$_2$ shows an average particle size of 40 nm. EDX analysis conforms Ti and O are present in TiO$_2$ are shown in Fig. 1c, whereas In, W, Ti and O are present in InWO$_3$-TiO$_2$ nanocomposite material are shown in Fig. 1d.

3. 2. HR-TEM analysis

The High-resolution transmission electron microscope (HR-TEM) measurements of InWO$_3$-TiO$_2$ are shown in Fig 2a. It is established that the presence of particles are depicted from the HR-TEM micrographs well crystalline and spherical shape. InWO$_3$ are uniformly distributed on the TiO$_2$. Fig. 2b shows an average particle size as about 55 nm by selected particle area in Fig. 2a.

Fig. 1. FE-SEM images of (a) TiO$_2$ and (b) InWO$_3$-TiO$_2$ nanocomposite material, EDX analysis of (c) TiO$_2$ and (d) InWO$_3$-TiO$_2$ nanocomposite material.
Fig. 2. HR-TEM (a) Image of InWO$_3$-TiO$_2$ and (b) average Particle size selected area highlighted in Fig. 2a.
3. 3. XRD analysis

Obtained XRD of the TiO\textsubscript{2} and InWO\textsubscript{3}-TiO\textsubscript{2} nanocomposite material is shown in Fig. 3 (a, b and c) respectively. The peaks at 25.47°, 31.60°, 37.54°, 43.48°, 47.78°, 54.73° and 62.41° are the diffractions of the TiO\textsubscript{2} (101), (101), (004), (111), (200), (211) and (204) crystal planes it has a highest peak at 2\(\theta\) = 25.2 which is corresponding to the anatase phase (JCPDS No. 21-1272) of, WO\textsubscript{3} (JCPDS Card NO. 20-1324) and InWO\textsubscript{3} (JCPDS Card NO. 51-0958). XRD stick pattern of the as-synthesized InWO\textsubscript{3}-TiO\textsubscript{2} was compared to the InWO\textsubscript{3} (as per JCPDS No. 72-0746). The all JCPDS cad no reference plane indicated by 24.40°, 27.97°, 37.72°, 54.07°, 62.47°, 67.6° and 75.72° are the diffractions of the InWO\textsubscript{3} (001), (211), (224), (232), (041) and (240) crystal planes. After the increase in InWO\textsubscript{3} concentration in TiO\textsubscript{2} lattice these peaks are slowly appear. The XRD pattern of InWO\textsubscript{3}-TiO\textsubscript{2} sample shows distinct peaks of the anatase phases, without any indication of rutile phase. The size of the particles can be calculated from the Debye-Scherrer formula. \(L = \frac{0.89 \lambda}{\beta \cos \theta}\) where \(L\) is the crystalline size (nm), \(\lambda\) is the wavelength (nm), \(\beta\) is the full width at half maximum intensity (FWHM-in radian), and \(\theta\) is the Bragg diffraction angle (°). The average crystalline size of the prepared TiO\textsubscript{2} and InWO\textsubscript{3} composite material was figured out to be about 80 nm and 68 nm. The average crystalline size of the doped InWO\textsubscript{3}-TiO\textsubscript{2} nanocomposite material is almost 30 nm.

![XRD patterns](image)

**Fig 3.** XRD patterns of (a) TiO\textsubscript{2} (b) InWO\textsubscript{3} and (c) InWO\textsubscript{3}-TiO\textsubscript{2} nanocomposite material.

3. 4. FT-RAMAN analysis

The Raman spectra of TiO\textsubscript{2} and InWO\textsubscript{3}-TiO\textsubscript{2} are shown in Fig. 4. (a and b). The characteristic peaks at 143, 437, 515 and 639 cm\(^{-1}\) located around 150 and 650
corresponding to the E1g and E2g modes seen in the TiO\textsubscript{2} nanomaterial. It is recognized from the Raman active peaks of the anatase TiO\textsubscript{2} shows in Fig. 4a reported [29, 30]. This may possibly propose that it is not the simple metal oxide mixture but the chemical communication between the orthorompic InWO\textsubscript{3} and the anatase TiO\textsubscript{2} obtained (peack at 146, 398, 514 and 638 cm\textsuperscript{-1} located around 150 and 650 corresponding to the E1g and E2g modes seen in the InWO\textsubscript{3}-TiO\textsubscript{2} nanocomposite material shows in Fig. 4 b.

![FT-Raman Analysis](image)

**Fig. 4.** FT-Raman analysis of (a) TiO\textsubscript{2} and (b) InWO\textsubscript{3}-TiO\textsubscript{2} nanocomposite material.

### 3. 5. Surface topography of AFM analysis

AFM images of InWO\textsubscript{3}-TiO\textsubscript{2} nanocomposite material are shown in Fig 5a and b. It depicts polycrystalline nature with uniform distribution of tetragonal shaped grains. The observed columnar grain in 3D image shows the growth along the direction for the InWO\textsubscript{3}-TiO\textsubscript{2} and is in agreement with the XRD results. The resultant cross-sectional inspection indicates that the average breadth of InWO\textsubscript{3} -TiO\textsubscript{2} is about 89.4 nm are shown in Fig 5 b. The plane of nanosized particles in the InWO\textsubscript{3} -TiO\textsubscript{2} is more evidently reflected in three-dimensional (3D) AFM image. The Z direction from the fine surface and tetragonal shaped size of InWO\textsubscript{3}-TiO\textsubscript{2} was clearly noticed.
**Fig 5.** (a) AFM image (2 × 2 μm) of as synthesized InWO$_3$-TiO$_2$ (IWT) nanocomposite material, with scale bars 0-89.4 nm and (b) Three-dimensional (3D) AFM image of surface micelles of IWT nanomaterial (2 μm × 2 μm × 89 nm)
3.6 BET surface area analysis

![Graph showing N₂ adsorption-desorption isotherms of (a) TiO₂ and (b) InWO₃-TiO₂ nanocomposite material.](image)

**Fig. 6.** N₂ adsorption-desorption isotherms of (a) TiO₂ and (b) InWO₃-TiO₂ nanocomposite material.
The N₂ (i) adsorption/ (ii) desorption isotherms of the synthesized InWO₃-TiO₂ was representing mainly the nonporous structure according to the international union of pure and applied chemistry (IUPAC) organization [31]. It exhibited type IV pattern with the presence of hysteresis loop as exemplified in Fig. 6. A clear hysteresis at elevated relative pressure is experimental, which is related to capillary condensation coupled with large pore channels. Average pore radius of the composite was 23.133 Å. The pore size distribution of the samples thus proves the mesoporosity. The pore size distribution calculated by BJH (Barret-Joyner-Halenda) method reveals quite narrow structure and verifying good excellence of porsing. The surface area of InWO₃-TiO₂ was determined using the nitrogen gas adsorption method. The BET surface and pore volume of surface area of InWO₃-TiO₂ (103.9382 m²/g) is higher than the prepared TiO₂ (32.0876 m²/g) show in Fig 6a and 6b [32]. A sharp increase in the adsorption volume of N₂ was located in the P/P₀ (at 0.9946). This sharp increase can be recognized to the good homogeneity of the material and a pore size since the P/P₀ position of the inflection point is related to the pore size [33,34]. Increase in BET surface area increases the adsorption of dye molecules on the nanocomposite material surface. This will enhance the photocatalytic activity.

3. 2. Study of photocatalytic activity

3. 2. 1. InWO₃-TiO₂ under UV-light irradiation.

The photodegradation of MAG in aqueous medium in the presence of catalyst were studied using multi lamp UV-light irradiation at 365 nm. The effect of pH on the degradation to fast dye was investigated in the pH range 3-11. The results are reported. It is observed that the degradation increases with an increase in pH to 7 and then decreases. After 60 min of irradiation formed, The InWO₃-TiO₂ is more effective than TiO₂ in the degradation of MAG. To find out the reason for the effect of pH on degradation efficiency, colored dyes are degraded (MAG-pH = 7) presence of InWO₃-TiO₂ nanocomposite material shown in Fig 7a required to obtain (0, 33.3, 49.5, 67.4, 83 % of degradation.)
Fig. 7. (a) Primary analysis, (b-c) Kinetic of MAG degradation upon irradiation variations in \( \ln(C_0/C) \) as purpose of irradiation time and linear plot of catalysts under UV-light irradiation by TiO\(_2\) and InWO\(_3\)-TiO\(_2\) (IWT) nanocomposite material.

3. 2. 2. Kinetic study

Fig. 7.b and c show the rate which was calculated by measuring the time dependent degradation efficiency of MAG in an aqueous solution under UV-light irradiation. Photocatalytic degradation is in the order of the catalyst nanomaterial as InWO\(_3\)-TiO\(_2\) > TiO\(_2\). The photodegradation kinetics study of MAG on TiO\(_2\) and InWO\(_3\)-TiO\(_2\) were calculated by using the pseudo-first-order kinetics model eq (1)

\[
\ln(C_0/C_t) = \text{Kapp}^t \quad \text{-------- (1)}
\]

where \( \text{Kapp}^t \) is the rate constant [min], \( C_0 \) is the preliminary concentration of MAG, and \( C_t \) is the concentration of MAG at reaction time (t) [34] from the results, InWO\(_3\)-TiO\(_2\) nanocomposite material showed the maximum degradation rate constant which was higher than that of TiO\(_2\) photodegradation rate constants (\( k' \)).

3. 2. 3. Quantum yield (UV –light irradiation)

MAG dye in the monochromatic light source yields reaction quantum yield [35] by following eq- (2)

\[
\Phi = \frac{k}{2.303 I_0 \lambda \varepsilon \delta \lambda}
\quad \text{-------- (2)}
\]
where $\Phi$ is the reaction quantum yield (dimensionless), $I_0$ is the UV-light intensity of the incident light range at 200-800 nm range ($1.381 \times 10^6$) $\varepsilon_{D\lambda}$ is the molar absorptivity of MAG at 614 nm and (l) is the path length of the reaction tube and is 0.24 m for 50 mL of irradiated solution. The results of UV-light degradation quantum yields by TiO$_2$ and InWO$_3$-TiO$_2$ were (0.401 and 0.0598) respectively shown in Table 1. These results signify that the quantum yield of the InWO$_3$-TiO$_2$ catalytic process is high when compared to TiO$_2$.

**Table 1.** Quantum yield of photocatalytic degradation of MAG in aqueous solution after 60 mins under UV-light-irradiation.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% degradation</th>
<th>Quantum yield (Moles per Einstein)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>61</td>
<td>0.0401</td>
</tr>
<tr>
<td>InWO$_3$-TiO$_2$</td>
<td>61</td>
<td></td>
</tr>
</tbody>
</table>

3.2.4. Reusability

![Fig. 8. Reusability of InWO$_3$-TiO$_2$ (IWT) on MAG degradation of dye under UV-Light irradiation.](image)

To once reusability of the InWO$_3$-TiO$_2$ photocatalyst, the photocatalytic degradation properties of the photocatalyst were investigated by repeating MAG photocatalytic degradation experiments six times. After each cycle, the InWO$_3$-TiO$_2$ photocatalysts were washed thoroughly with water, MAG dye change the fresh solution of was made before each photocatalytic run in the photoreactor. The UV-light results are shown in Fig. 8 complete
degradation occurred in the 1st, 2nd 3rd 4th 5th at and 6th cycles. The results indicated that the prepared catalysts are stable and reusable. It also indicates that the photocatalytic efficiency of InWO₃-TiO₂ is decreased slowly with increase the repetition of the cycles. After the 6th cycle the efficiency of InWO₃-TiO₂ catalysts decreased when compared to the total degradation of MAG. The solution was tested for In³⁺ leaching with sodium sulfide. There is no precipitation of Indium sulfide (black color). As there is no leaching of In³⁺, this catalyst is non-hazardous and water purification technology [36].

3. 2. 5. Mechanism

![Scheme 2](image)

**Scheme 2.** (a) InWO₃- TiO₂ (IWT)-Photodegradation and Mineralization of MAG Under UV- light irradiation.

Tentative mechanism by semiconducting oxide InWO₃-TiO₂ under UV and Natural sun light irradiation towards MAG dye is proposed as follws:

\begin{align*}
1\text{MAG}_0 + \text{hv} & \rightarrow \text{MAG}_1 & \text{...(4)}
1\text{MAG}_1 + \text{ISC} & \rightarrow 3\text{MAG}_1 & \text{...(5)}
\text{InWO}_{3}\text{-TiO}_{2} (SC) + \text{hv} & \rightarrow e^- (CB) + h^+(VB) & \text{...(6)}
\text{'OH} + h^+ & \rightarrow \text{'OH} & \text{...(7)}
\text{'OH} + 3\text{MAG}_1 & \rightarrow \text{Leuco MAG} & \text{...(8)}
\text{Leuco MAG} & \rightarrow \text{Products} & \text{...(9)}
\end{align*}
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 InWO$_3$-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 (\(\cdot\)OH) by hole (h$^+$) present in the valence band of semiconductor generating \(\cdot\)OH. This \(\cdot\)OH will oxidize MAG to its leuco form, which may ultimately degrade to products. It was confirmed that the \(\cdot\)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 [37].

3. 2. 6. Effect of different concentrations of MAG

The effect of different concentration (1X$10^{-4}$, 2X$10^{-4}$ and 3X$10^{-4}$) of MAG on InWO$_3$-TiO$_2$ was investigated under UV light. This is explained on the basis that on increasing the concentration of MAG, more molecules of MAG are available for degradation. However on increasing the concentration above 1X$10^{-4}$M, the reaction rate was found to decrease. Because more molecules of MAG were degraded, excess of MAG dye may act as a filter for the incident light, preventing a sufficient intensity of light to reaching the dye molecule in the bulk of the solution. So the photodegradation of MAG was superior in lesser concentration, when compared to high concentration under UV-light irradiation are shown in Fig. 9 a.

3. 2. 7. Effect of catalyst loadings on MAG

![Fig. 9. (a) photodegradation at different concentrations and (b) photodegradation at various amount of catalyst loading. MAG dye total volume of reaction solution = 50 mL.](image)

The different loading of InWO$_3$-TiO$_2$ on MAG has been effected out in the range of 0.100, 0.150 and 0.200 g, under UV- light. The results show, the increase of catalyst loading
increases the degradation rate due to increase in the catalyst surface area, which enhances number of active sites. On higher of catalyst loading the degradation was low due to the aggregation of InWO$_3$-TiO$_2$ nanocomposite, material that cause a decrease in the number of active sites, increase the cloudiness and light scattering of InWO$_3$-TiO$_2$ nanocomposite material. This tends to decrease the passage way of irradiation through the sample. Among the catalyst loadings 0.150 g loading showed optimum activity and when compared to other catalyst loadings are shown in Fig. 9 b.

3. 2. 8. Chemical oxygen demand (COD) level

![Graph of COD reduction vs. time](image)

**Fig 10.** Chemical oxygen demand (COD) analyses by InWO$_3$-TiO$_2$ nanocomposite material under UV- light irradiation.

Fig. 10 Confirm the mineralization of MAG by chemical oxygen demand (COD) analysis. The percentage of COD reduction is given in Table 2. After 60 min irradiation under UV-Light with InWO$_3$-TiO$_2$ nanocomposite material is 88 % of COD reduction is obtained. This indicates the complete mineralization of MAG dye. Mineralization was also definite by formation of Calcium carbonate when the evolved gas (CO$_2$) through degradation was accepted into Calcium hydroxide solution [38].

-112-
Table 2. COD measurements

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>% COD reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>35</td>
</tr>
<tr>
<td>30</td>
<td>52</td>
</tr>
<tr>
<td>45</td>
<td>69</td>
</tr>
<tr>
<td>60</td>
<td>88</td>
</tr>
</tbody>
</table>

[MAG] = 1 X 10^{-4} mol L^{-1}; InWO_3-TiO_2 (0.150 g) suspension = 40 mL pH = 7 Solution and air passing with UV-light irradiation.

3. 2. 9. Hydroxyl radical analysis

Fig 11. Fluorescence spectra measured at $\lambda_{\text{max}} = 320$ nm for the InWO_3-TiO_2 (IWT) samples obtained using various time (0, 30 and 60 min) in coumarin solution (sample was illuminated for 60 min of UV-light).
Fig. 11 Shows hydroxyl radical analysis of InWO$_3$-TiO$_2$ nanocomposite material by co-precipitation method, (PL spectra of coumarin solution under UV-light irradiation as a function of irradiation time). A measured increase in the PL intensity at 373 nm is observed, this observation suggests that the fluorescence arises [39]. Caused by chemical reactions of coumarin with hydroxyl radicals formed in photocatalytic reactions [40]. Further the formed hydroxyl radicals on the surface of InWO$_3$–TiO$_2$ samples illuminated by UV light were detected by fluorescence technique.

Hence hydroxyl radical is the reactive oxidation species in InWO$_3$–TiO$_2$ sample with maximal photocatalytic activity produced than other samples [41], which is also consistent with the results of photocatalytic decomposition. The hydroxyl radical analysis further confirms that the hydroxyl radicals are active species in photocatalytic reactions. On the other hand, the formation rate of 'OH is directly related to the photocatalytic activity of InWO$_3$–TiO$_2$ nanocomposite material.

3. 3. Study of Antimicrobial activity
3. 3. 1. Determination of antibacterial activity by disk-diffusion method

The antibacterial activity of the materials (TiO$_2$ and InWO$_3$-TiO$_2$) was examined using disc diffusion method. The bacterial strains viz., (a) Bacillus subtilis (positive) (b) Vibrio cholera (Negative) are used for this study. DMSO is used as control while Ciprofloxacin is used as standard. The zone of inhibition (mm in diameter) of the materials was (1) TiO$_2$ and (2) InWO$_3$-TiO$_2$ against the tested bacterial strains is given in Table 3a. From the zone of inhibition of the materials are tested for antibacterial activity. The (2) InWO$_3$-TiO$_2$ nanocomposite material was (a) Bacillus subtilis (positive) (b) Vibrio cholera (Negative) better activity when compared to that of (1) TiO$_2$ nanocomposite material are shown in Fig. 12a and b.

3. 3. 2. Effect of antifungal activity

A filter paper disc method was employed for the in-vitro study of antifungal effects against Trigoderma veride. The results of this evaluation were compared with Amphoterin – B as a reference standard. The antifungal activity of the nanomaterials TiO$_2$, InWO$_3$ and InWO$_3$-TiO$_2$ are shown in Fig. 12c the zone of inhibition values is given Table 3b. It showed that prepared TiO$_2$, InWO$_3$ and InWO$_3$-TiO$_2$ posses significant activity almost equipotent with the standard Amphoterin – B.

The particle size place a vital role in imparting enhanced antifungal activity to the nanomaterials. The screening results indicate that InWO$_3$-TiO$_2$ was found to be active against (24). InWO$_3$-TiO$_2$ material antifungal high activity when compared (1) TiO$_2$ The result indicate InWO$_3$-TiO$_2$ material is antimicrobial high activity, resan of the nanomaterial depends on the nature and position of Indium, Tungsten and oxygen groups present in the InWO$_3$-TiO$_2$ material.
Fig. 12. Antimicrobial activity [disc diffusion method] Bacteria (a) *Bacillus subtilis* (positive) (b) *Vibrio cholera* (Negative) and (c) *Trigoderma veride*. 
Table 3. (a). Antibacterial activity [disc diffusion method]

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Bacteria</th>
<th>Standard Antibiotic</th>
<th>Zone of inhibition (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Disc</td>
<td>1 [TiO₂]</td>
</tr>
<tr>
<td>1</td>
<td>Vibrio cholera (Neg)</td>
<td>25</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>Bacillus subtilis (positive)</td>
<td>25</td>
<td>10</td>
</tr>
</tbody>
</table>

*ciprofloxacin

Table 3. (b). Antifungal activity [filter paper disc method]

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Fungi</th>
<th>Amphoteri -B</th>
<th>Zone of inhibition (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1 [TiO₂]</td>
</tr>
<tr>
<td>1</td>
<td>Trigodemo</td>
<td></td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>Veride</td>
<td></td>
<td>32</td>
</tr>
</tbody>
</table>

3.4 Study of electrochemical activity

3.4.1. Cyclic voltammeter (CV) analysis

In the prepared nanomaterial surface occurrence as the photogenerated charge carriers scatter to begin redox reactions [42,43]. Using TiO₂ and InWO₃-TiO₂ modified electrode constructed through the mechanical attachment. Fig. 13 shows the voltammogram effect of using unmodified/modified glassy carbon electrode on the electrochemical oxidation/reduction potential. In the TiO₂ modified glassy carbon electrode, the electrochemical oxidation of KCl is an irreversible process suitable to the peak (anodic current and the (Epa) peak potential of 0.0233 V and i = 1.627 e⁻⁵A). But in InWO₃-TiO₂ modified glassy carbon electrode, the deficiency of a well-defined reduction glassy carbon electrode was showing that the electrochemical redox reaction of KCl is a reversible process (enhanced anodic current and the (Epa) peak potential of 0.350 V, and i = 4.500 e⁻⁵A). These results indicates that InWO₃-TiO₂ modified glassy carbon electrode has larger adsorption–desorption and high electrochemical reaction than that of TiO₂ nanomaterial. A few literature information have indicated that glassy carbon electrodes modified with metal ion and carbon materials are created to achieve enhanced detection in comparison to bare GCE [34,44-46]. The cyclic voltammoqram result shows increase in current and improves the relation electron transferred by InWO₃-TiO₂ nanocomposite material.
Fig. 13. Cyclic voltammeter (CV) analysis of (a) uncoated GCE with 0.1 M KCl (red curve), (b) TiO\textsubscript{2} coated GCE in 0.1 M KCl (brown curve) and (c) InWO\textsubscript{3}-TiO\textsubscript{2} coated GCE in 0.1 M KCl (blue curve).

4. CONCLUSIONS

In the present work the prepared InWO\textsubscript{3}-TiO\textsubscript{2} nanocomposite material was synthesized by a simple co-precipitation method and characterized by FE-SEM with EDX, HR-TEM, XRD, FT-RAMAN, AFM and BET surface area measurements. FE-SEM and HR-TEM image shows the InWO\textsubscript{3}-TiO\textsubscript{2} was having spherical shaped structure. The EDX spectra reveal the presence of Ti, In, W and O in the catalyst. InWO\textsubscript{3}-TiO\textsubscript{2} is found to be more active than TiO\textsubscript{2}, TiO\textsubscript{2} P25 and InWO\textsubscript{3} at pH 7 for the mineralization of MAG under UV-light irradiation. The influences of operational parameters such as effect of catalyst loading, dye concentration, chemical oxygen demand (COD) level have been investigated. Hydroxyl radical formation was confirmed by fluorescence quenching technique. The InWO\textsubscript{3}-TiO\textsubscript{2}
catalysis – kinetic study was shows high quantum yield. The higher antimicrobial activity was found. Cyclic voltammetry (CV) result suggests the occurrence of current and improves the relation electron transferred. Water purification performance shows InWO$_3$-TiO$_2$ nanocomposite material can be used as a material for expanded important industrial applications.

References


[38] B. Subash, R. Krishnakumar, M. Swaminathan and M. Shanthi, ZnS–Ag–ZnO as an Excellent UV-Light-Active Photocatalyst for the Degradation of AV 7, AB 1, RR 120,


(Received 14 October 2016; accepted 02 November 2016)