Novel TiO$_2$ coupled Bi$_2$O$_4$ Nanocomposites for effective removal of aqueous Rose Bengal dye under UV-A light illumination

T. Vimala$^{1,2}$, A. Sivarajan$^1$*, T. Rajachandrasekar$^3$ and K. Veeravelan$^3$

$^1$Department of Chemistry, Govt. Arts College, Tiruchirappalli 620 022, (Affiliated to Bharathidasan University, Thiruchirappalli-24) Tamilnadu, India
$^2$Department of Chemistry, S.T.E.T. Women’s College (Autonomous) (Affiliated to Bharathidasan University, Thiruchirappalli-24), Mannargudi 614 016, Tamilnadu, India
$^3$Photocatalysis Laboratory, Department of Chemistry, M.R. Govt. Arts College, Mannargudi 614 001(Affiliated to Bharathidasan University, Thiruchirappalli-24), Tamilnadu, India

(Received 17 August, 2023; Accepted 26 October, 2023)

ABSTRACT

Novel hetero structured TiO$_2$/Bi$_2$O$_4$ nanocomposite was successfully synthesized by hydrothermal and sol-gel method. High-resolution transmission electron microscope (HR-TEM) analysis clearly indicates the particles with spherical and hexagonal structure and sizes of most of the particles are below 50 nm. The photocatalytic performance of Rose Bengal (RB) dye was studied. The photocatalysts showed high degradation rate and complete mineralization ability for Rose Bengal under UV-A light. The effect of operational parameters such as effect of pH, Catalyst suspension, Initial dye concentration and reusability were observed. Hence the catalyst can be reused for continuous treatment of waste water.

Key words: Photocatalysis, TiO$_2$/Bi$_2$O$_4$, Rose Bengal, Nanocomposite, Wastewater treatment

Introduction

Conservative method used to address the rising problem of wastewater pollution due to organic dyes are partial to decolourization and mineralization of the dyes because of the presence of aromatic functional group in the dye and stability of the dye in wastewater (Konstantinou, et al., 2004). Considerable attention has therefore been focused on the use of photocatalytic process as an effective technology for the treatment of wastewater containing organic dyes (Rajasri et al., 2022). Photocatalytic degradation by semiconducting nanoparticles is mainly considered as potential and effective technology for the mineralization of dye into ecological friendly compounds (Muthuvel, et al., 2021). Nanoparticals have emerged as sustainable alternative to conventional bulk materials, as robust, high surface area heterogeneous photocatalysts and catalyst supports (He et al., 2011). The nano sized particles have high surface to volume proportion which increase the exposed, which increase the exposed surface area of the active component of the catalyst, enhances the contact between reactants and catalyst (Tabor, P., et al., 2010). TiO$_2$ and ZnO are found to be best among are photocatalyst because of their wide band gap energy, biological and chemical process, ease of synthesis and applicability (Suppuraj, et al., 2020).

Compared to other materials, titanium dioxide (TiO$_2$) as an excellent photocatalyst has drawn the
most attention due to its unique characteristics in the band position and surface structure, as well as its biological and chemical inertness, non-toxicity, resource abundance, and resistance to photo corrosion. However, the implementation of pure TiO₂ in a large scale is still limited due to its disadvantages of wide band gap (Eg = 3.2 eV for anatase TiO₂) and rapid recombination of photogenerated charge carriers. To tackle the problem and enhance the efficiency, the development of novel TiO₂-based photocatalysts is necessary. TiO₂ under UV light irradiation electron–hole pairs is generated. It will also generate various oxygen species such as ‘OH, O₂⁻, HO₂⁻, etc. by redox reactions. To achieve a high photocatalytic activity, it is essential to suppress recombination of electron–hole pairs. The photosensitized spectrum occupies only a little of the whole solar energy. The visible light-sensitive photocatalysts have received considerable attention because visible light (λ > 400 nm) occupies the main part of the solar spectrum. Therefore, the development of efficient visible light-sensible photocatalysts is becoming one of the most challenging topics recently (Gowthami, et al., 2020). Recently, the composite of Bismuth oxide (Bi₂O₄) and TiO₂ nanoparticles is being considered as a potential photocatalyst in air and water purification. The composite has three advantages: the increasing absorptivity of pollutants, extended light absorption range, and facile charge transportation and separation.

Results and Discussion

The detailed characterization of TiO₂/Bi₂O₄ by FT-IR, XRD, SEM-EDX and UV-DRS analysis was reported in our earlier paper (Vimala et al., 2024).

HR-TEM

High resolution-transmission electron microscopy (HR-TEM) images of the prepared 19 wt% TiO₂/Bi₂O₄ nanocomposite are shown in Fig. 1a-d is different magnification. The lattice fringes in HR-TEM images of the TiO₂/Bi₂O₄ catalyst are shown in Fig. 1e. The SAED image of TiO₂/Bi₂O₄ nanocomposites (Fig. 1f) shows both the bright rings and crystalline spots and also reveals that the polycrystalline nature of the TiO₂/Bi₂O₄ composites.

Fig. 1. HR-TEM images of TiO₂/Bi₂O₄: a) 50 nm, b) 20 nm, c) 10 nm, d) 5 nm, e) 2 nm and f) SAED pattern

Photocatalytic degradation of RB by TiO₂/Bi₂O₄ catalyst with UV light

Primary analysis

The photocatalytic activities of the TiO₂/Bi₂O₄ nanocomposite with 13, 16, 19 and 21 wt% loading of Bi₂O₄ were analyzed by their ability to degrade RB.

Experimental

Materials

The commercial Rose Bengal (RB) dye (C.I. No. 45440) from Hi-Media Chemicals, titanium isopropoxide, isopropanol (AVRA), sodium bismuthate (Hi-Media) was used as received. The experimental solution was prepared using distilled water. Chemical oxygen demand (COD) was determined by following the protocol mentioned earlier in the literature (Muthuvel et al., 2014).

Methods

Fabrication of the TiO₂/Bi₂O₄ Catalyst

The preparation of TiO₂/Bi₂O₄ nanocomposite, photocatalytic degradation experiments and characterization techniques are reported earlier (Vimala et al., 2024; Rajasri et al., 2022; Suppuraj et al., 2020; Gowthami et al., 2020).
Experiments were performed under different controlled conditions and the results are presented in Fig. 2A. The dye is found to be resistant to self-photolysis in the presence of UV light (curve a). In presence of a dye/TiO₂/dark, decrease of 17% in dye concentration occurs and remains almost constant up to 90 min (curve b). When the dye is on irradiation with TiO₂ under UV light, 59% degradation was observed at 90 min (curve c). A decrease in the dye concentration (26%) occurs when it is treated with dye (19 wt% TiO₂/Bi₂O₄/dark) (curve f) at 90 min. The degradation of dye on irradiation with TiO₂/Bi₂O₄ catalyst of different weight percentage of Bi₂O₃ is shown in curves d, e, g and h. Catalyst loaded with 19 wt% Bi₂O₃ loaded TiO₂ shows a higher degradation (curve g, 88%). This demonstrates that 19 wt% TiO₂/Bi₂O₄ is a more effective photocatalytic for RB degradation than the other catalyst, which is chosen as the optimum catalyst for further studies.

Fig. 2. A) Primary analysis of TiO₂/Bi₂O₃ catalyst with RB dye under UV light. [RB] = 1 × 10⁻⁴ M, 19 wt% TiO₂/Bi₂O₄ = 2 g L⁻¹, airflow rate = 8.1 mL s⁻¹, pH = 6.0, IUV = 1.381 × 10⁻⁶ einstein L⁻¹ s⁻¹. B) Effect of pH, C) Effect of catalyst loading, D) Effect of dye concentration, E) Reusability, F) Structure of Rose Bengal (RB) dye and its overlay absorption spectrum.
Effect of pH

The solution pH plays a key role in advanced degradation processes such as photocatalytic degradation. We carried out an experiment at various pH values, ranging from 3 to 9 with a constant amount of dye (1 \times 10^{-4} \text{ M}) and catalyst (2 g L^{-1}). Increases in the photocatalytic degradation percentage 64 to 88\% (90 min) in pH 3-6 (Fig. 2B). Above pH 6, the photocatalytic degradation was decreased. Hence, the optimum pH for efficient degradation of RB on TiO_{2}/Bi_{2}O_{4} is pH 6. The electrostatic attraction between the dye molecules and catalyst is greatly improved at pH 6 (Buvaneswari et al., 2015). The observed enhancement in the degradation and decolorization of RB at pH 6 can be attributed to the presence of excess hydroxyl groups on the catalyst surface. These results in the formation of more hydroxyl radicals (·OH) and then the photodegradation and decolorisation of RB increased.

Effect of catalyst loading

The experiment of RB with 19 wt\% TiO_{2}/Bi_{2}O_{4} was carried out by different concentration using UV light irradiation is shown in Fig. 2C. The increase of catalyst concentration from 1-3 g L^{-1}, the rate of degradation efficiency increases from 0.015 to 0.027 min^{-1} (45 min). Further increase in catalyst amount above 3 g L^{-1}, decreases the degradation efficiency. This may be explained on the basis that increasing concentrations of catalyst increase the surface area of the loaded catalyst, thus causing an increase in the rate of reactions. Beyond this point, the percentage of reaction decreased with an increase in the amount of catalyst. At a concentration above 3 g L^{-1} of catalyst, the removal percentage is decreased. This condition is observed due to an increase in the amount of light reflected by the catalyst, which consequently results in a decrease in the amount of light that penetration the catalyst (Kalal et al., 2015). Thus, 3 g L^{-1} catalyst concentration was found to be the optimum concentration and was used as the catalyst dosage for further photocatalytic reactions.

Effect of dye concentration

It is important both from the mechanistic and application point of view, to study the dependence of the photocatalytic reaction on the substrate concentration. The effect of various initial dye concentration on the photocatalytic degradation has been investigated. Increase of the initial dye concentration from 0.25 to 1.25 \times 10^{-4} \text{ M} decreased the degradation rate constant from 0.151 to 0.021 min^{-1} (15 min) (Fig. 2D). This indicates that TiO_{2}/Bi_{2}O_{4} catalyst can also work well at high initial concentrations of RB. The results showed that the dye degradation and decolorization decrease with the increasing dye concentration. At a higher initial dye concentration, but with a constant concentration of OH radicals the relative concentration of radicals was lower, which led to a decreased degradation and decolorization efficiency (Ji et al., 2011).

Reusability

A stability test of TiO_{2}/Bi_{2}O_{4} was carried out and the result is presented in Fig. 2E. It can be seen that the degradation rate of RB slightly decrease to 92\% after five consecutive reaction runs, indicating a good photocatalytic stability of TiO_{2}/Bi_{2}O_{4}.

Complete mineralization

In order to confirm the mineralization of dye, COD measurements were made for the degradation of RB with TiO_{2}/Bi_{2}O_{4} under optimum conditions. COD reduction values for the dye at different times of UV irradiation are given in Table 1. COD values show 96\% COD reduction (RB) for 150 min UV irradiation. These results confirm the mineralization of the dye with TiO_{2}/Bi_{2}O_{4} process. Moreover complete mineralization was also confirmed by overlay absorption spectrum Fig. 2F.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>0 min</th>
<th>60</th>
<th>90</th>
<th>120</th>
<th>150 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO_{2}/Bi_{2}O_{4}</td>
<td>7</td>
<td>7</td>
<td>9</td>
<td>7</td>
<td>96</td>
</tr>
</tbody>
</table>

[RB] = 1 \times 10^{-4} \text{ M}, catalyst suspended = 3 g L^{-1}, airflow rate = 8.1 mL s^{-1}, pH = 6, irradiation time = 150 min.

Conclusion

Novel TiO_{2}/Bi_{2}O_{4} nanocomposite was prepared by facile hydrothermal method and sol-gel method and it was characterized by HR-TEM analysis. Moreover, the photocatalytic activity of TiO_{2}/Bi_{2}O_{4} was tested under natural UV-A light irradiation. The Maximum photocatalytic degradation of RB was observed at 1 \times 10^{-4} \text{ M}, pH 6 and 3 g L^{-1} of catalyst concentration. The catalyst is highly stable and reusable for multiple runs. Hence it is an effective for industrial applications.
References


