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Novel TiO_2 coupled Bi_2O_4 Nanocomposites for effective removal of aqueous Rose Bengal dye under UV-A light illumination

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ABSTRACT

Novel hetero structured TiO_2/Bi_2O_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_2O_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 decolonization and mineralization of the dyes because of the presence of aromatic functional group in the dyes 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 TiO_2 in a large scale is still limited due to its disadvantages of wide band gap (Eg = 3.2 eV for anatase TiO_2) and rapid recombination of photogenerated charge carriers. To tackle the problem and enhance the efficiency, the development of novel TiO_2-based photocatalysts is necessary. TiO_2 under UV light irradiation electron–hole pairs is generated. It will also generate various oxygen species such as $^{\bullet}OH$, $O_2^{\bullet-}$, $HO_2^{\bullet-}$, 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 (ë > 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 (Bi_2O_4) and TiO_2 nanoparticlesis 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.

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 TiO_2/Bi_2O_4 Catalyst

The preparation of TiO_2/Bi_2O_4 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).

Results and Discussion

The detailed characterization of TiO_2/Bi_2O_4 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% TiO_2/Bi_2O_4 nanocomposite are shown in Fig. 1a-d is different magnification. The lattice fringes in HR-TEM images of the TiO_2/Bi_2O_4 catalyst are shown in Fig. 1e. The SAED image of TiO_2/Bi_2O_4 nanocomposites (Fig. 1f) shows both the bright rings and crystalline spots and also reveals that the polycrystalline nature of the TiO_2/Bi_2O_4 composites.

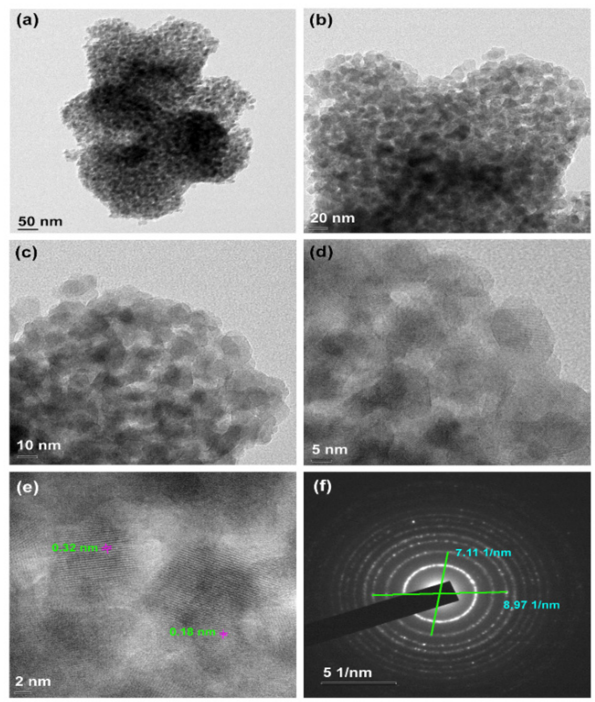

Fig. 1. HR-TEM images of TiO_2/Bi_2O_4: a) 50 nm, b) 20 nm, c) 10 nm, d) 5 nm, e) 2 nm and f) SAED pattern

Photocatalytic degradation of RB by TiO_2/Bi_2O_4 catalyst with UV light

Primary analysis

The photocatalytic activities of the TiO_2/Bi_2O_4 nanocomposite with 13, 16, 19 and 21 wt% loading of Bi_2O_4 were analyzed by their ability to degrade RB.

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/TiO_2/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 TiO_2 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% TiO_2/Bi_2O_4/dark) (curve f) at 90 min. The degradation of dye on irradiation with TiO_2/Bi_2O_4 catalyst of different weight percentage of Bi_2O_4 is shown in curves d, e, g and h. Catalyst loaded with 19 wt% Bi_2O_4 loaded TiO_2 shows a higher degradation (curve g, 88%). This demonstrates that 19 wt% TiO_2/Bi_2O_4 is a more effective photocatalytic for RB degradation than the other catalyst, which is chosen as the optimum catalyst for further studies.

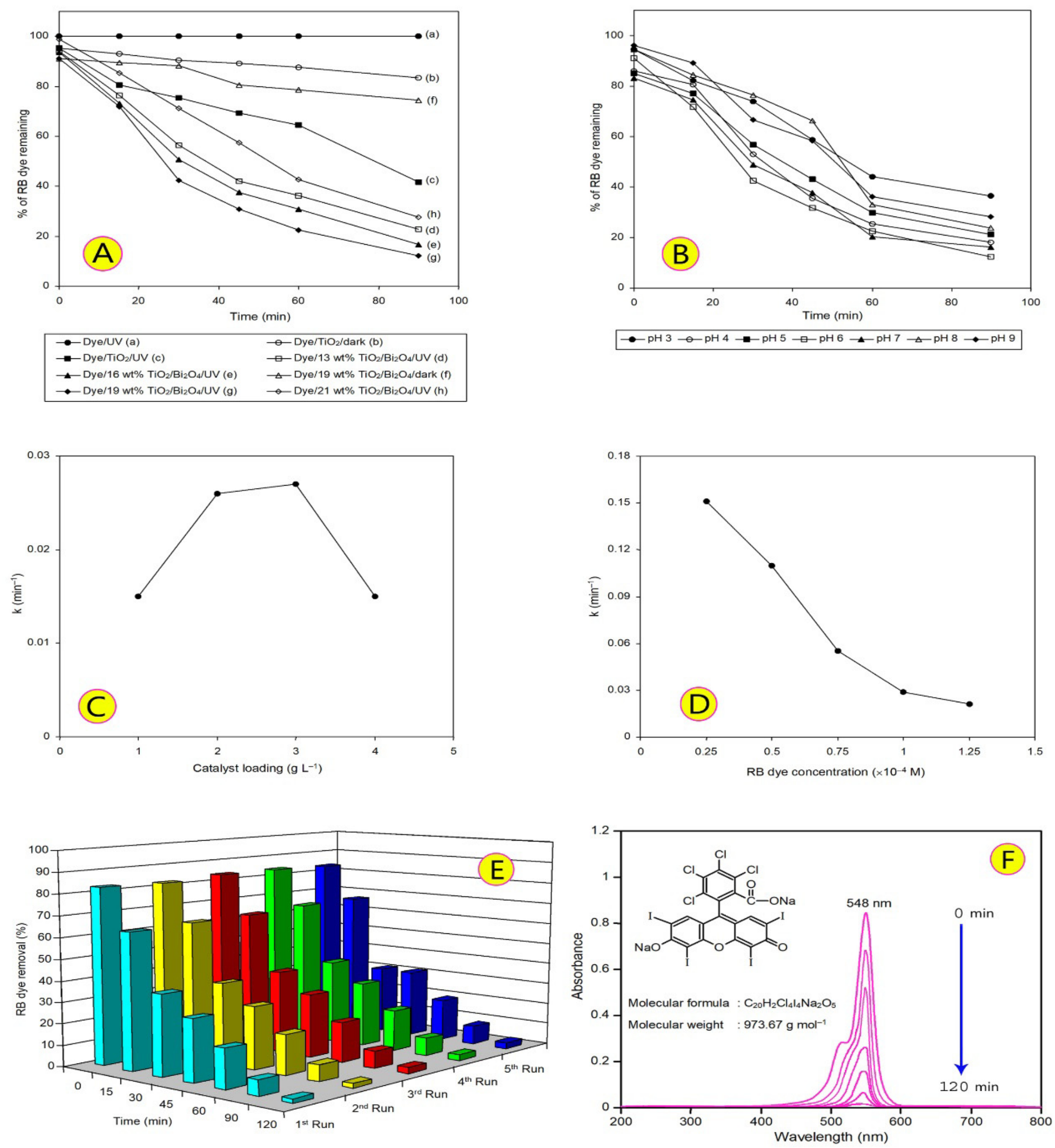

Fig. 2. A) Primary analysis of TiO_2/Bi_2O_4 catalyst with RB dye under UV light. [RB] = 1 ´ 10^{-4} M, 19 wt% TiO_2/Bi_2O_4 = 2 g L^{-1}, airflow rate = 8.1 mL s^{-1}, pH = 6.0, I_{UV} = 1.381 ´ 10^{-6}einstein L^{-1} s^{-1}. **B)** Effect of pH,**C)**Effect of catalyst loading, **D)** Effect of dye 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 as experiment at various pH values, ranging from 3 to 9 with a constant amount of dye (1 × 10^{-4} 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 decreases. Hence, the optimum pH for efficient degradation of RB on TiO_2/Bi_2O_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_2O_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 × 10^{-4} M decreased the degradation rate constant from 0.151 to 0.021 min^{-1} (15 min) (Fig. 2D). This indicates that TiO_2/Bi_2O_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 $^{\cdot}OH$ 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_2O_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_2O_4.

Complete mineralization

In order to confirm the mineralization of dye, COD measurements were made for the degradation of RB with TiO_2/Bi_2O_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_2O_4 process. Moreover complete mineralization was also confirmed by overlay absorption spectrum Fig. 2F.

Table 1. COD measurements under optimum conditions

Catalyst	0 min	60	90	120	150 min
	COD reduction %				
TiO_2/Bi_2O_4	0	32	47	79	96

[RB] = 1×10^{-4} 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_2O_4nanocomposite 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/$Bi_2O_4$was tested under natural UV-A light irradiation. The Maximum photocatalytic degradation of RB was observed at 1×10^{-4} 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.

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