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RESEARCH ARTICLE

**NEW SURFACE MODIFIED TERPOLYMER: A SMART PHOTOCATALYTIC
FUNCTIONAL MATERIAL**

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ABSTRACT

Dye pollutants are alarming hazardous compounds causing serious diseases such as cancer, hormone deficiency and bronchitis. Research is essential to develop alternate/more effective technique for removal of dye pollutants. In the present investigation, initially, 2-hydroxyacetophenone–biuret-trioxane (2-HABT) terpolymer was successfully synthesized, purified and characterized in the laboratory. Then, titanium oxide photocatalyst was anchored on 2-HABT terpolymer using molecular adsorption–deposition method. The titanium oxide particles, deposited on the 2-HABT terpolymeric molecules, formed a coating of about 100 nm in thickness. This newly modified functional photocatalytic material was characterized by means of infrared spectroscopy, X-ray diffraction and scanning electron studies. An anatase-type titanium oxide was uniquely developed. This new TiO₂-2-HABT photocatalyst exhibited an excellent photocatalytic activity in the photodegradation of quite concentrated dyes. The dye molecules in bulk solution was supposed to be condensed around titanium oxide particles because of the adsorption phenomenon on 2-HABT polymer molecules, and, therefore, the photocatalytic process was enhanced due to the combined effect of adsorption by 2-HABT terpolymer macromolecules and photocatalytic activity on anatase-type titanium oxide. It was observed that the decolorization of contaminated water occurred within a short-time interval. Thus, it can be concluded that the functional photocatalytic material, reported in article, can be successfully used for water and wastewater treatments.

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INTRODUCTION

Catalyst used in photochemical reaction is called photocatalyst. Photocatalysts are mainly semiconducting materials such as titanium oxide, silver halide and so on. The photocatalytic activity of the photocatalyst depends on its ability to create electron–hole pairs that react with the adsorbed species. Waste generation inclusive of organic dyes and other coloring material is an inevitable by-product of the rapid and enhanced industrialization and urbanization. Dye pollutants are alarming hazardous compounds causing serious diseases such as cancer, hormone deficiency and bronchitis. (Ollis *et al.*, 1991) These wastes cause serious and irreparable damage to the environment and are not amenable to conventional method of waste treatment. Wastewater from industries have potential hazard for the environment by introducing various contaminants, such as synthetic dyes, into the soil and water resources. Organic dyes are harmful to the environment and are too difficult to degrade by conventional chemical methods. Over the past few decades, a significant progress has been achieved in heterogeneous photocatalysis for photodegradation of undesirable organics in aqueous phase. Semiconductors,

such as titanium oxide, are the most widely used catalysts in the field of photocatalytic applications. Fujishima *et al.* (2000) Significant work has been devoted to acquire high photocatalytic performance by developing new photocatalytic materials or optimizing the capacity of the reported photocatalysts. Over 150 photocatalysts, including oxides, sulfides, nitrides and hydroxides, have been reported in the literature, which are able to degrade pollutants and to split water for hydrogen production. (Osterloh 2008; Kabra *et al.*, 2004) Modification in the crystal structure and physicochemical properties of reported material is another effective way to enhance the photocatalytic performance. Doping with anions or cations, loading with noble metals (platinum, palladium, gold etc.) and compositing with other semiconductors (cadmium, zinc oxide, tin dioxide, tungsten trioxide etc.) are the few known techniques for improving the photocatalytic potency of photocatalytic materials. (Leung *et al.*, 2010; Linsebigler *et al.*, 1995) Among them, coupling with other semiconductors provide a unique opportunity not only to enhance the separation efficiency of photogenerated electrons (e^-) and holes (h^+) but also to extend the light response to the visible region in the samples. Specifically, when the composite photocatalyst is activated by light, the photoinduced electrons (e^-) are injected from the semiconductor with more negative conduction band (CB) level to the semiconductor with more positive CB level, while holes (h^+) transfer from one with more

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positive valence band (VB) to the one with negative VB level. Thus, a wide separation of photoinduced changes can be achieved, which consequently improves the photocatalytic performance. However, it should be noted that the reason for improvement of composite photocatalyst is not only due to the effect described above but also due to some other factors, such as the enhancement of surface acidity or alkalinity (Akurati *et al.*, 2008; Fu *et al.*, 1996) and the surface population of (hydroxyl) OH groups, (Anderson and Bard 1997; Du *et al.*, 2008; Janus *et al.*, 2006) which can promote the adsorption of reacting substances and facilitate the generation of OH radicals. Photocatalysts are nanoscale metal oxide materials (titanium oxide is often used). They get coated on the substrate surface and begin strong catalytic degradation due to the interaction with light. They can degrade toxic and harmful dyes effectively in the water. They can remove odor and stains. Titanium oxide has been considered to be the dominant photocatalyst due to its properties such as superior photocatalytic oxidation ability, non-photocorrosive, non-toxic and inexpensive characteristics. (Alberici *et al.*, 1997); Beauchet *et al.* 2007) The concentration of pollutants in ambient water is quiet low, and the adsorption of pollutants on titanium oxide photocatalyst is often limited due to small specific surface area, leading to very low photocatalytic degradation efficiency.

The possible way to overcome this is to add a coadsorbent to the titanium oxide photocatalyst to enhance its adsorptive and photocatalytic activities. (Jorio *et al.*, 1998; Sun *et al.*, 2010) Silica gel has attracted considerable interest as an excellent support, as it is transparent to near UV light, has large specific surface area and strong sorbability. (Zhang *et al.*, 2006; Demeestere *et al.*, 2007; An *et al.*, 2005 Shapovalov 2010) Several efforts have been directed toward the improvement of the photocatalytic activity of titanium oxide in order to increase its efficiency for the treatment of wastewater. (Shapovalov 2010; Chong *et al.*, 2010; Alonos *et al.*, 2009) Some of these approaches are as follows: doping with transition metals, surface modification by noble metals (such as palladium, gold and platinum) and coupling with various semiconductors. (Zielinskaa *et al.*, 2010; Wanga *et al.*, 2010; Qamar 2010; Silva *et al.*, 2010; Tristao *et al.*, 2006) Use of thin titanium oxide films in rotating disk and solar reactors is again an attempt to increase the photocatalytic activity by improving the illumination and oxygenation process. In the present investigation, initially, 2-hydroxyacetophenone– biuret-trioxane (2-HABT) terpolymer was successfully synthesized in the laboratory. It was purified and characterized using physicochemical and spectral methods. Then, titanium oxide photocatalyst was anchored on 2-HABT terpolymer using molecular adsorption–deposition method. The titanium oxide particles deposited on the 2-HABT terpolymeric molecules formed a coating of about 100 nm in thickness. This newly modified functional photocatalytic material was characterized by means of infrared (IR) spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The photocatalytic degradation efficiency of the newly developed material is studied for decolorization of methylene blue as a model dye. The material under investigation has been observed to be a very good photocatalyst and can be successfully applied

for water and wastewater treatment with special reference to dyes and other organic pollutants.

MATERIALS AND METHODS

2-Hydroxyacetophenone was prepared in the laboratory starting from phenol by its acetylation followed by Fries migration reaction. The other starting materials such as biuret and trioxane and so on, used in the synthesis of 2-HABT terpolymer, were procured from companies (such as Merck, Mumbai, India) and all were of analytical and pure grade. The solvent, dimethyl sulphoxide (DMSO), was of analytical reagent (AR) grade and double distilled under reduced pressure prior to its use in various physicochemical and spectral studies. Deionized water (DI) was used throughout the investigation. Titanium oxide was also of AR grade.

Synthesis and characterization of 2-HABT terpolymer

The 2-HABT terpolymer was synthesized by condensing 2-hydroxyacetophenone and biuret with trioxane in the molar ratio of 3:3:2. Hydrochloric acid (2M) was used as a catalyst. The reaction mixture was heated at 382 K in an electrically heated oil bath for about 5 h. Voltage regulator was applied to maintain constant temperature of the bath. The solid mass obtained was immediately removed from the flask as soon as the reaction was complete. The separated polymeric mass, having resinous texture, was washed repeatedly with DI hot water and dried. The dried mass was washed with petroleum ether to remove the unreacted starting materials or 2-HA-trioxane copolymer formed if any. The terpolymer was purified by dissolving it in 2.5 N sodium hydroxide solution and reprecipitating it by dropwise addition of 1:1 (v/v) hydrochloric acid/DI water. The purification by precipitation process was repeated twice. The resulting terpolymer sample was washed with boiling water several times, filtered and dried in vacuum at room temperature. The purified terpolymer was finally ground well to pass through a 300 mesh sieve and kept in vacuum over silica. The yield of Terpolymer was found to be 70%. The purity of terpolymer was tested and confirmed by thin layer chromatography method. The terpolymer was characterized in light of studies such as elemental analysis, molecular weight determination by conductometric titration method, intrinsic viscosity, electronic, IR, proton magnetic resonance spectral studies and thermogravimetric analysis. On the basis of all physicochemical and spectral evidences, the most possible structure for 2-HABT terpolymer is assigned as given in Figure 1. (Gurnule *et al.*, 2003).

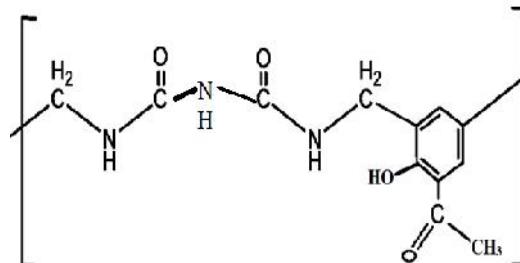


Fig.1. Structure of 2-HABT terpolymer. 2-HABT, 2-hydroxyacetophenone–biuret–trioxane

TiO₂-2-HABT photocatalyst (smart functional material) preparation and characterization

The photocatalyst TiO₂-2-HABT was prepared from a suspension of titanium oxide (70%) and 2-HABT dissolved in DMSO at 350 K (Tristao *et al.*, 2006). The solvent was evaporated and the obtained material was ground to 2–4-mm beads and dried under vacuum at 350 K for 5 h. Powder XRD data were obtained using Cu K irradiation scanning from 2 to 75° at a scan rate of 4°/min. Thermogravimetric analysis was carried out in a Shimadzu TGA/DTA 50H in air and heating rate of 10°C per min. SEM analysis of pure titanium oxide and TiO₂-2-HABT photocatalyst material was performed for characterization.

Decolorizing (photocatalytical) reaction studies

The experiments for photochemical reactions, under solar irradiation, were carried out in the city of Nagpur (India) in the month of May between 10 a.m. and 2 p.m. Solar light intensity was approximately $370\text{--}970 \times 10^{-3}$ mW/m², and the temperature was in the range of 310–320 K. The photocatalytic studies were carried out with rhodamin-d(RD) as a probe molecule at 16×10^{-5} mol/dm³ concentration, and the amount of photocatalyst used was 100–1000 mg. Before the reaction, the catalyst was kept in the dye solution ($2\text{--}16 \times 10^{-5}$ mol/dm³) in the dark for 1 h to reach adsorption equilibrium. No stirring was done in the reaction in order to avoid oxygenation of the solution and to stimulate the used photocatalyst. The reaction started on exposing the reactor to sunlight and, during 250 min, aliquots of 1 ml were collected at the reactor bottom and analyzed spectrophotometrically.

RESULTS AND DISCUSSION

Characterization of TiO₂-2-HABT photocatalyst

The thermogravimetric analysis (Figure 2) shows that the pure 2-HABT terpolymer decomposes completely at 838 K. The weight loss of the prepared photocatalyst showed titanium oxide content of ~70%. This result suggests that all titanium oxide added in the preparation was incorporated in the polymer beads. XRD analysis of pure titanium oxide and TiO₂-2-HABT photocatalyst showed very similar pattern with diffraction lines at 25.4, 37.8, 48.2, 53.8 and 55.3° (Figure 3). These results suggest that no change in crystalline structure occurred during the preparation of the photocatalyst. SEM analysis of pure titanium oxide shows an agglomerated material composed of spherical particles (Figure 4(a)). The SEM image for TiO₂-2-HABT photocatalyst (Figure 4(b)) suggests the presence of titanium oxide particles on the 2-HABT Terpolymer surface. The titanium oxide particles are strongly attached to the surface of the terpolymer, which is demonstrated by vigorous shaking of the material in water for 1 h, when titanium oxide particles could not be removed from the 2-HABT terpolymer surface.

Photocatalytic (decolorizing) reaction

Photocatalytic studies were carried out using the dye rhodamin-d as probe molecule under solar irradiation (Fig.5).

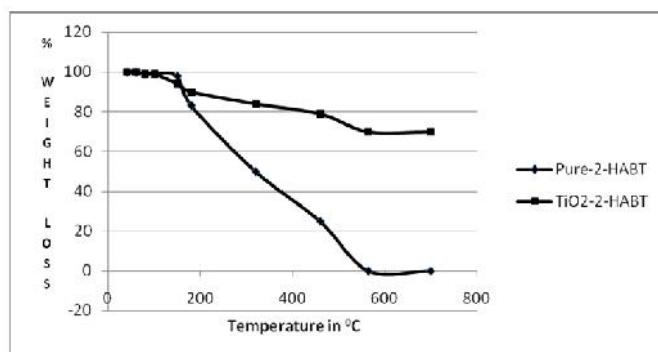


Fig. 2. TG analysis (in air) of pure 2-HABT and TiO₂-2-HABT photocatalyst

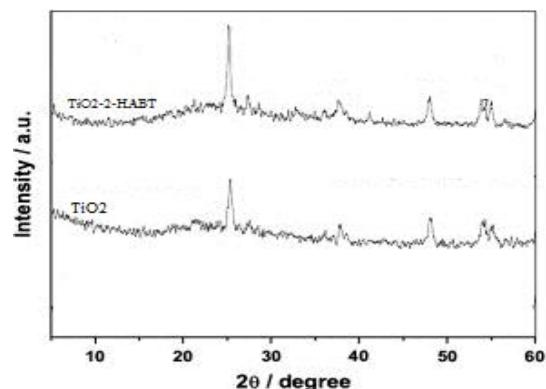
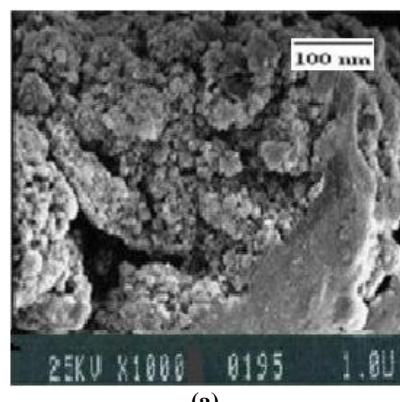
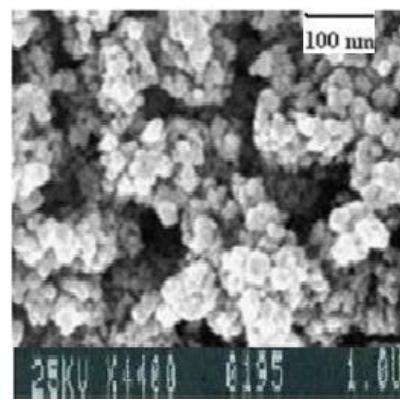


Fig.3. XRD of pure titanium oxide and TiO₂-2-HABT photocatalyst



(a)



(b)

Fig.4. (a) SEM of pure titanium oxide and (b) SEM of TiO₂-2-HABT photocatalyst

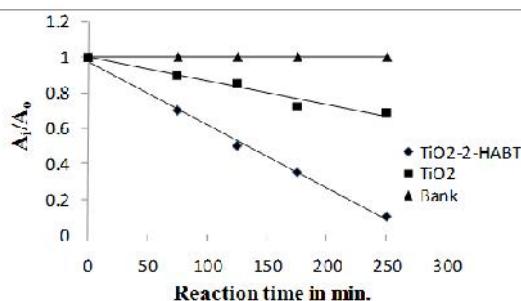


Fig.5. Discoloration curves obtained for RD in blank condition, in the presence of pure titanium oxide and TiO₂-2-HABT

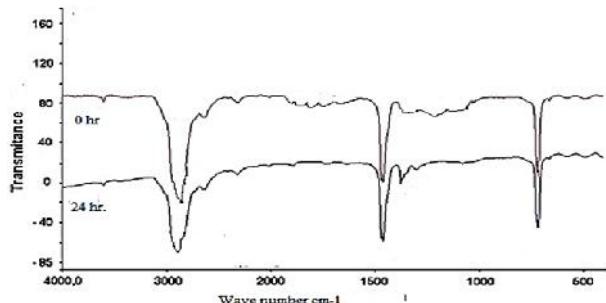


Fig.6. IR spectra of TiO₂-2-HABT photocatalyst before and after 24 h under solar irradiation in water

The reaction was carried out at an equilibrium temperature of 40°C. No decolorization takes place in the blank experiments (i.e. without the photocatalyst). On the other hand, in the presence of the photocatalyst TiO₂-2-HABT, decolorization takes place after 220 min. The experimental data proved that the reaction follows first-order kinetics. Pure titanium oxide showed low decolorization after 175 min of reaction. This may be due to the location of most of the titanium oxide particles at the bottom because of slightly higher density. But TiO₂-2-HABT, having lesser density, remains floating at the surface and hence showed enhanced activity. Moreover, the adsorption phenomenon of dye molecules over the surface of the polymer provided easy reaction sites, and hence, the overall activity of the photocatalyst was enhanced. Thus, the TiO₂-2-HABT photocatalyst shows a good reactivity for the degradation of organic contaminants in water. Recovery and reuse of the photocatalyst were also investigated using TiO₂-2-HABT submitted to three consecutive reactions. After each reaction, the catalyst was recovered with a simple sieve and a new 17×10^{-5} mol/dm³ dye solution was used. The decolorization and kinetic studies were performed for each reaction. The decolorization remains nearly 100% and rate constant is approximately 18×10^{-3} min⁻¹ for the reaction. These results clearly indicate that TiO₂-2-HABT photocatalytic functional material can be used for more than five to six times with obtained decolorization in the range of 95–99%. These results indicate that, even after nine reactions, the photocatalyst is still very active. To investigate whether the 2-HABT polymer surface was attacked by radicals, IR spectral analysis of the floating-type photocatalyst was carried out after 24-h exposure to solar radiation (Fig. 6). Very similar spectra were obtained for 2-HABT before and after exposure to solar radiation, suggesting that the 2-HABT surface oxidation, by the radicals

formed during photocatalytical reaction, is not significant under the reaction conditions used.

Conclusion

On the basis of the results obtained in this investigation, the following conclusions can be drawn:

- Terpolymer (2-HABT) has been successfully prepared, characterized and its most possible structure has been determined.
- Anchorage of titanium oxide has been successfully performed on 2-HABT terpolymer surface.
- The newly prepared TiO₂-2-HABT photocatalyst (smart functional material) is highly active and efficient for the degradation of a model dye rhodamin-d using solar radiation.
- Low density of TiO₂-2-HABT photocatalyst facilitated more efficient illumination due to the positioning of the photocatalyst on the water surface. Moreover, near the surface, there is the possibility of more efficient oxygenation, which is fundamental for the photocatalytical processes.
- The dye molecules in bulk solution were supposed to be condensed around anchored titanium oxide particles because of the adsorption on 2-HABT polymer matrix. Hence, the photocatalysis process is enhanced due to the combined effect of adsorption by 2-HABT Terpolymer macromolecules and photocatalytical activity of anatase type titanium oxide.
- The study can be extended to test photodegradation capacity of TiO₂-2-HABT photocatalyst for photodegradation of other dyes and organic matter, i.e. pollutants.
- The floating-type photocatalyst, in the present investigation, can be potentially used in the treatment of contaminated wastewater reservoirs located in remote areas without the need for any special equipment. It can also be efficiently used for the destruction of insoluble, organic contaminants.

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