



2-HABT-ZnO: An Excellent Visible Spectrum Nano Photocatalytic Functional Material

*Rahangdale P.K.

*Bhawabhuti Mahavidyalaya, Amgaon-441902 (India)

*Corresponding Author, email: pralhadrahangdale@gmail.com; Contact No.: +91 9881010726

Abstract

This research article reports the laboratory synthesis of 2-Hydroxyacetophenone-biuret-trioxane (2-HABT) terpolymer followed by anchoring of ZnO photocatalyst employing molecular adsorption-deposition method. The ZnO particles, deposited on the 2-HABT terpolymeric molecules, formed a coating of about 90 nm in thickness. This newly modified functional photocatalytic material was characterized by means of infrared spectroscopy, X-ray diffraction and scanning electron studies. This new 2-HABT-ZnO photocatalyst exhibited an excellent photocatalytic activity in the photodegradation of quite concentrated dyes in presence of visible spectrum of light. The dye molecules in bulk solution were supposed to be condensed around zinc 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 of nano zinc 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 the article has potential applications for water and wastewater treatments with special reference to degradation of dyes.

Keywords: - Photocatalytic materials; Terpolymer; Surface modification of polymers; Pollutant Dyes; Adsorption-deposition process.

Introduction

Catalyst used in photochemical reaction is called photocatalyst. Photocatalysts are mainly semiconducting materials such as titanium oxide, silver halide, zinc oxide and so on. The photocatalytic activity of the photocatalyst depends on its ability to create electron-hole pairs which react with adsorbed species.

Population growth and the resultant development of large high-density urban populations together with global industrialization have resulted in global warming and the buildup of chemical and biological contaminants throughout the biosphere, but most notably in soils, sediments and various aquatic bodies¹. 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. Semiconductors, such as TiO₂ & ZnO, are the most widely used catalysts in the field of photocatalytic applications². Over 150 photocatalysts, including oxides, sulphides, nitrides and hydroxides, have been reported in the literature which are able to degrade pollutants and to split water for H₂ production^{3,4}. Doping with anions or cations, loading with noble metals (Pt, Pd, Au, etc) and compositing with other semiconductors (Cd, ZnO, SnO₂, WO₃, etc) are the few known techniques for improving the photocatalytic potency of photocatalytic

materials^{5,6}. When the composite photocatalyst is activated by light, the photo induced 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 positive valence band (VB) to the one with negative VB level. Thus wide separation of photo induced charges can be achieved, which consequently improve the photocatalytic performance⁷. 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^{8,9} and the surface population of OH groups¹⁰⁻¹² which can promote the adsorption of reacting substances and facilitates the generation of hydroxyl radicals. Photocatalysts are nanoscale metal oxide materials. 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. TiO₂ 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^{13,14}. Addition of a co-adsorbent to the TiO₂ photocatalyst is one of the way to enhance its adsorptive and photocatalytic activity^{15,16}. Silica gel has attracted considerable interest as an excellent support

since it is transparent to near UV light, has large specific surface area and strong sorbability¹⁷⁻¹⁹. Several efforts have been directed towards the improvement of the photocatalytic activity of TiO₂ in order to increase its efficiency for the treatment of waste water²⁰⁻²². Some of these approaches are: doping with transition metals, surface modification by noble metals (such as Pd, Au and Pt) and coupling with various semiconductors²³⁻²⁷.

Keeping the above literature aspect in mind, initially, 2-Hydroxyacetophenone-Biuret-Trioxane (2-HABT) terpolymer was successfully synthesized in the laboratory. It was purified and characterized using physicochemical and spectral methods. The zinc oxide photocatalyst was anchored on 2-HABT terpolymer employing molecular adsorption-deposition method. The ZnO particles deposited on the 2-HABT terpolymeric molecules formed a coating of about 90 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 **congo red** 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 etc., used in the synthesis of 2-HABT terpolymer were procured from Merck, Mumbai, India and all were of analytical reagent/chemically pure grade. The solvent Dimethyl Sulphoxide (DMSO) was double distilled under reduced pressure prior to its use in various physicochemical and spectral studies. Deionized water was used throughout the investigation.

Synthesis & Characterization of 2-HABT Terpolymer

The 2-HABT Terpolymer was synthesized by condensing 2-Hydroxyacetophenone and Biuret with trioxane in the molar ratio 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

hours. 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 unreacted starting materials or 2-HA-Trioxane copolymer formed if any. The terpolymer was purified by dissolving it in 2.5 N NaOH solution and reprecipitating it by dropwise addition of 1:1 (v/v) HCl/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 TLC 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 Fig.1.

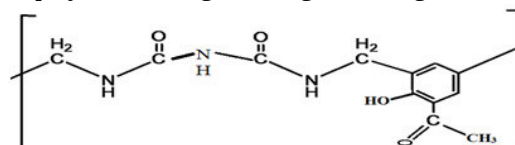


Fig.1. Structure of 2-HABT Terpolymer
Preparation and characterization of 2-HABT-ZnO nano Photocatalyst functional material

2-HABT-ZnO, the new photocatalyst, was prepared from a suspension of ZnO (60%) and 2-HABT dissolved in DMSO at 357K. The solvent was evaporated and the obtained material was ground to 3-4 mm beads and dried under vacuum at 327 K for 5hr. Powder XRD data was obtained using Cu, K α irradiation scanning from 2 to 75° at a scan rate of 4° min⁻¹. Thermo gravimetric analysis was carried out in a Shimadzu TGA/DTA 50 H in air and heating rate of 10°C per min. SEM analysis of pure and 2-HABT-ZnO photocatalyst material was performed for characterization.

Photocatalytical Reaction Studies

Photochemical reactions, under solar irradiation were carried out in the month of May between 10 am to 2 pm. Solar light intensity was approximately $350\text{--}950 \times 10^{-3} \text{ mW m}^{-2}$ and temperature was in the range of 308 – 318 K. The photocatalytic studies were carried out with **congo red** as a probe molecule at $16 \times 10^{-5} \text{ mol dm}^{-3}$ concentration and the amount of photocatalyst used was 100 mg to 1000 mg. Before the reaction the catalyst was kept in the dye solution ($2 - 16 \times 10^{-5} \text{ mol dm}^{-3}$) in the dark for 1 hr. to reach adsorption equilibrium. The reaction started on exposing the reactor to sunlight and,

during 240 min aliquots of 1 ml were collected at the reactor bottom and analyzed spectrophotometrically.

Results and Discussion Characterization of 2-HABT-ZnO photocatalyst

The TG analysis (Fig.2) shows that the pure 2-HABT terpolymer decomposes completely at 838 K. The weight loss for the prepared photocatalyst showed ZnO content of ~75%. This result suggests that all ZnO_2 added in the preparation was incorporated in the polymer beads.

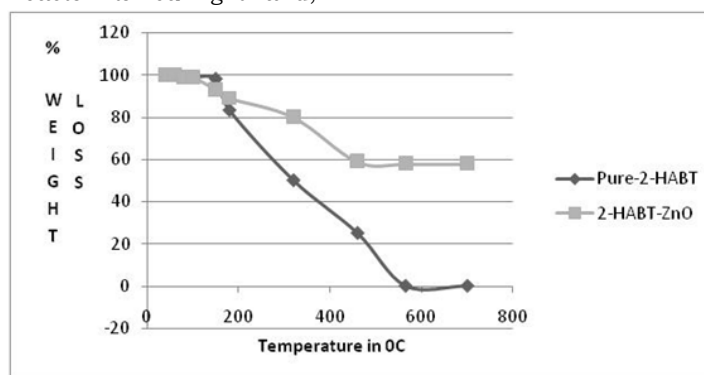


Fig. 2. TG Analysis (in air) of pure 2- HABT and 2-HABT-ZnO

XRD analysis of pure ZnO and 2-HABT-ZnO photocatalyst showed very similar pattern with diffraction lines at $25.6; 37.7; 48.3; 53.6; 55.2^\circ$

(Fig. 3). These results suggest that no major change in crystalline structure occurred during the preparation of the photocatalyst.

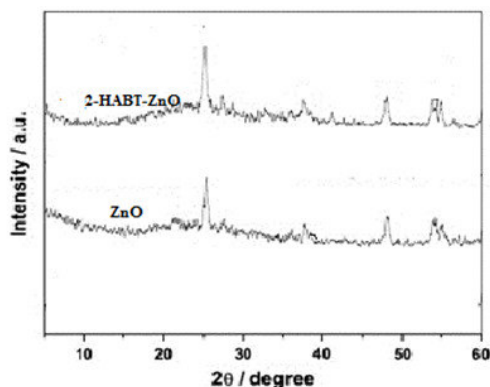


Fig. 3 : XRD OF Pure ZnO and 2-HABT-ZnO Photocatalyst

SEM analysis of pure ZnO shows an agglomerated material composed of spherical particles (Fig. 4 a). The SEM image for 2HABT-ZnO photocatalyst (Fig. 4 b) suggests the presence of ZnO particles on the 2- HABT terpolymer surface. The ZnO particles are strongly attached to the surface of the

terpolymer which is demonstrated by vigorous shaking of the material in water for 1 hr when ZnO particles could not be removed from the 2- HABT terpolymer surface. SEM images also prove nano size of the photocatalyst material under investigation.

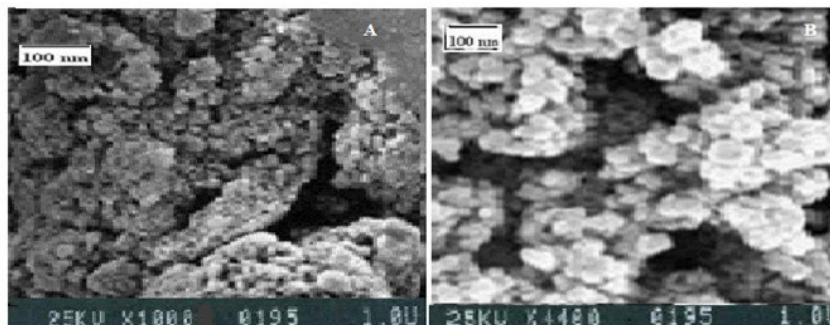


Fig. 4 (a) SEM of Pure ZnO (b) SEM of 2-HABT-ZnO nano photocatalyst

Decolorizing (Photocatalytic) Reaction

Photocatalytic studies were carried out using the dye **congo red** as probe molecule under solar irradiation (Fig.5). The reaction was carried out at an equilibrium temperature of 313K. No decolourization takes in the blank experiments (i.e., without ZnO photocatalyst). On the other hand, in the presence of the photocatalyst 2-HABT-ZnO, decolourization takes place after 210 min. The experimental data proved that the reaction follows first order kinetics. Pure ZnO showed low decolourization after 200 min of reaction. This may be due to the location of most of the ZnO particles at the bottom because of slightly higher density. But 2-HABT-ZnO, 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 2-HABT-ZnO photocatalyst shows a good reactivity for the degradation of organic contaminants in water. Recovery and reuse of the photocatalyst were

also investigated using 2-HABT-ZnO submitted to three consecutive reactions. After each reaction, the catalyst was recovered with a simple sieve and a new $16 \times 10^{-5} \text{ mol dm}^{-3}$ dye solution was used. The decolourization and kinetics studies were performed for each reaction. The decolourization remains nearly 100 % and rate constant is approximately $17 \times 10^{-3} \text{ min}^{-1}$ for the reaction. These results clearly indicate that 2-HABT-ZnO photocatalytic functional material can be used for more than 7 times with obtained decolourization in the range of 94 – 98 %. These results indicate that, even after seven 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 photocatalyst was carried out after 24 hr 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 photocatalytic reaction, is not significant under the reaction conditions employed.

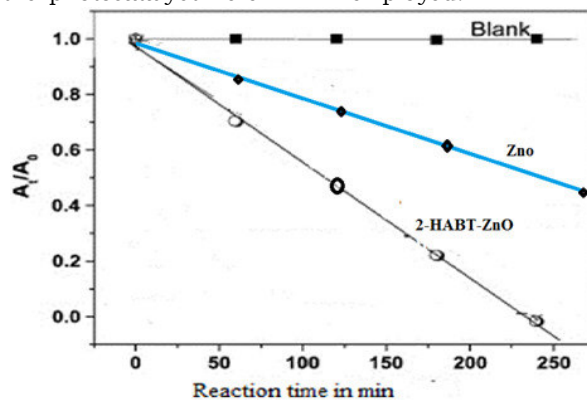


Fig.5 Discolouration curves obtained for Congo Red in blank condition, in the presence of pure ZnO and 2-HABT-ZnO

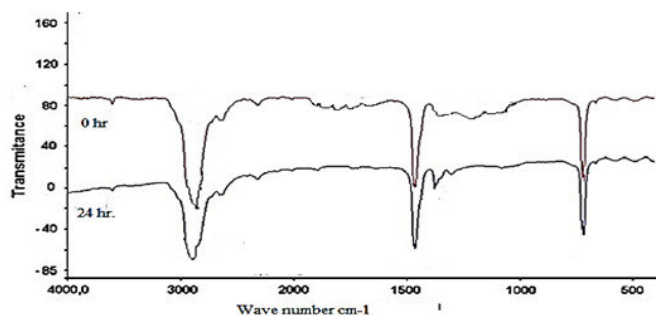


Fig.6 :IR Spectra of 2-HABT-ZnO photocatalyst before and after 24 hr under solar irradiation in water

Conclusions

On the basis of the results obtained in this investigation the following conclusions have been drawn

- 2-HABT terpolymer can be successfully prepared, characterized and its most possible structure has been determined.
- Anchoring of ZnO has been successfully done on 2- HABT terpolymer surface.
- The newly prepared 2-HABT-ZnO functional material (photocatalyst) is highly active and efficient for degradation of a model dye **congo red** using solar radiation.
- Low density of 2-HABT-ZnO photocatalyst facilitated more efficient illumination due to the positioning of the photocatalyst on the water surface. Moreover, near to 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 ZnO 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 ZnO.
- The study can be extended to test photo-degradation capacity of 2-HABT-ZnO photocatalyst for photo-degradation 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 waste water 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.
- The material under investigation has potential application in water/waste-water treatment

Scope for future work

The new nano material, 2-HABT-ZnO, can be tested for its photocatalytic degradation potency for other synthetic dyes/colored

organic matter and adsorption studies for abatement of toxic heavy metal pollutants.

Acknowledgements

The author is thankful to Dr. R.B. Kharat, Ex-Director, Institute of Science, Nagpur and Dr. L.J Paliwal, Professor, PGTD of Chemistry, RTM Nagpur University, Nagpur for their valuable guidance, moral support, timely help and constant encouragement during the course of this investigation. Thanks are also due to the Principal, Science College, Congress Nagar, Nagpur for providing the necessary laboratory facilities. The author is also thankful to the Managing Director of Deenee Chemical Laboratory(DCL), Chandrapur for providing access to the UV-Visible spectrophotometer and other instrumental facilities as and when required.

References

1. Yazdani F, Allahdadi I, AbasAkbari G. Impact of superabsorbent polymer on Yield and Growth Analysis of Soybean (*Glycine max L.*) under drought stress condition, *Pakistan J. Bio. Sci.*, **2007** 10(23): 4190-4196
2. Fujishima, A.;Rao, T.N.; Tryk, D.A. Titanium dioxide photocatalyst, *J. Photochem. Photobiol.*2000,C 1,1-21
3. Papaconstantinou, E.Photochemistry of polyoxometallates of molybdenum and tungsten and/or vanadium, *Chem. Soc.Rev.***1989**, 18,1-31
4. Osterloh, F.E.Inorganic materials as catalysts for photochemical splitting of water, *Chem.Mater.***2008**, 20, 35-54
Kabra,K.; Chaudhary, R;Sawhney, R.L.Treatment of hazardous organic and inorganic compounds through aqueous-phase photocatalysis: a review, *Ind. Eng. Chem.Res.* **2004**,43,7683-7696
5. Leung, D.Y.C.;Fu,X.;Wang, C.;Ni, M.;Leung, M.K.H.; Wang, X. Hydrogen production over titania-based photocatalysts, *ChemsusChem***2010**,3, 681-694.
6. Linsebigler, A.L.;Lu, G.Q.;Yates, J.T. Photocatalysis on TiO₂ Surface-principles,

- mechanisms, and selected results, *Chem.Rev.* **1995**,95, 735-758
7. Akurati, K.K.; Vital, A.; Dellemann, J.-P.; Michalow, K.; Graule, T.; Ferrari, D.; Baiker, A. Flame-made WO₃/TiO₂nanoparticle: relation between surface acidity structure and photocatalytic activity, *Appl. Catal.***2008**,B79, 53-62.
 8. Fu, X.;Clark, L.;Yang, Q.; Anderson, M. Enhanced photocatalytic performance of titania-based binary metal oxides: TiO₂/SiO₂ and TiO₂/ZnO₂, *Environ. Sci Technol.* **1996**,30, 647-653.
 9. Anderson, C.; Bard, A.J. Improved Photocatalytic activity and characterization of mixed TiO₂/SiO₂ andTiO₂/Al₂O₃ materials, *J.Phys. Chem.***1997**,B 101, 2611-2616.
 10. Du, P.; Bueno-Lopez ,A.; Verbaas, M.;Almeida, A.R.; Makkee, M.;Moulijn, J.A.;Mul, G. The effect of surface OH-population on the Photocatalytic activity of rare earth-doped P25-TiO₂ in methylene blue degradation, *J.Catal.* **2008**,260, 75-80.
 11. Janus, M.; Inagaki, M.;Tryba, B.; Toyoda, M.; Morawski, A.W. Carbon-modified TiO₂photocatalyst by ethanol carbonization, *Appl.Catal***2006**,B. 63, 272-276.
 12. Alberici, R.M.;Jardim, W.E.Photocatalytic destruction of VOCs in the gas phase using titanium dioxide, *Appl.Catal.***1997**,B-Environ. 14, 55-68.
 13. Beauchet, R.; Magnoux, P.;Mijoin, J.Catalytic oxidation of volatile organic compounds (VOCs) mixture (isopropanol/o-xylene)on zeolite catalysts,*Catal. Today***2007**, 124,118-123.
 14. Jorio,H.; Kia red, K.; Brzezinski, R.; Leroux, A.; Viel, G.; Heitz, M. Treatment of air polluted with high concentration of toluene and xylene in a pilot-scale bipfilter, *J. Chem. Technol. Biotechnol.***1998**,73, 183-196
 15. Sun, L.;Li, G.Y.; Wan, S.G.; An, T.C. Mechanistic study and mutagenicity assessment ofintermediates in photocatalytic degradation of gaseous toluene,*Chemosphere***2010**,78, 313-318.
 16. Zhang, M.L.;An, T.C.; Fu, J.M.;Sheng, G.Y.;Wang, X.M.;Hu, X.H.;Ding, X.J. Photocatalytic degradation of mixed gaseous carbonyl compounds at low level on adsorptive TiO₂/SiO₂photocatalyst using a fluidized bed reactor, *Chemosphere***2006**,64,423-431.
 17. Demeestere, K.;Dewulf, J.;VanLangenhove, H. Heterogeneous photocataysis as an advanced oxidation process for the abatement of chlorinated, monocyclic aromatic and sulfurous volatile organic compounds in air; state of arts, *Crit. Rev. Environ.Sci.Technol.***2007**,37,489-538.
 18. An, T.C.;Zhang, M.L.;Wang, X.M.;Sheng, G.Y.;Fu, J.M.Photocatalytic degradation of gaseous trichloroethene using immobilizedZnO/SnO₂ coupled oxide in flow-through photocatalytic reactor, *J.Chem.Technol.Biotechnol.* **2005**, 80, 251-258.
 19. Shapovalov, V.I.Nanopowders and films of titanium oxide for photocatalysis; a review, *Glass. Phys.Chem.* **2010**,36,21-157.
 20. Chong, M.N.; Jin, B.; Chow, C.W.K.; Saint, C.Recent developments in photocatalytic water treatment technology. *A review, Water Res.***2010**,44, 2997-3027.
 21. Alonos, M.D.H.;Frenso, F.;Suarezza, S.; Coronado, J.M. Deve lopment of alternative photocatalysts. To TiO₂ challenges and opportunities, *Energy Environ.Sci.***2009**, 2, 1231-1257.
 22. Zielinskaa, A.;Kowalskaa, E.; Sobczakd, L.W.;Lackab, I.; Gazdac, M.; Ohtanie, B.; Hupkaa, J.; Zaleskaa, A. Silver-doped TiO₂ prepared by microemulsion method; surface properties,bio and photoactivity, *sep. purify. Technol.***2010**, **72**, 309-318.
 23. Wanga, C.;Aoa,Y.; Wanga, P.; Houa, J.; Qjana, J.; Zhanga,S. Preparation , Characterization, photocatalytic properties of titania hallow sphere doped with cerium. *J. Hazards. Mater.***2010**, 178, 517-521.
 24. Qamar, M.Photodegradation of acridine orange catalyzed by nanostructure titanium dioxide modified with platinum and silver metals, *Desalination***2010** , 254, 108-113.
 25. Silva,S.S.; Magalhaes,F.; Sansiviero,M.T.C.Nanocompositos semiconductors ZnO/TiO₂Testes fotocataliticos,*Quim.Nova.* **2010**, 33,85-89.
 26. Tristao, J.C.;Magalhaes, F.; Corio, P.; Sansiviero, M.T.C. Electron characterization and photocatalytic properties of CdS/TiO₂ .Semiconductor composite, *J. photo-chem., Photobiol.A.***2006** , 181,152-157.

