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Newly developed 4-HABT-AgI-ZnO nanophotocatalytic functional material for wastewater treatment

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ABSTRACT

Initially, 4-hydroxyacetophenone–biuret–trioxane (4-HABT) terpolymer was successfully synthesized, purified and characterized in the laboratory. A nanophotocatalyst, AgI-ZnO, was prepared using precipitation followed by hydrolysis method. Then, it was anchored on 4-HABT terpolymer using molecular adsorption–deposition method. The AgI-ZnO nanoparticles, deposited on the 4-HABT terpolymeric molecules, formed a coating of about 90 nm in thickness. This newly modified functional nanophotocatalytic material was characterized by means of infrared spectroscopy, X-ray diffraction and scanning electron microscopy studies. This new 4-HABT-AgI-ZnO nanophotocatalyst exhibited an excellent photocatalytic activity in the photodegradation of quite concentrated aqueous solutions of dyes. The dye molecules in bulk solution was supposed to be condensed better around AgI-ZnO particles because of the adsorption phenomenon on 4-HABT terpolymer molecules, and, therefore, the photocatalytic process was enhanced due to the combined effect of adsorption by 4-HABT terpolymer macromolecules and photocatalytic activity on AgI-ZnO. It was observed that the decolorization of contaminated water occurred within a short-time interval. Thus, it can be concluded that the functional nanophotocatalytic material, reported in this research paper, can be successfully used for water and wastewater treatments.

Keywords*:* Terpolymers, AgI-ZnO nanostuctures, visible spectrum photocatalyst, photo catalytic degradation, surface modified polymeric functional materials.

INTRODUCTION

Organic compounds are broadly used in industries and in daily life, have become regular pollutants in water bodies. As they are known to be lethal and carcinogenic, an effective economic treatment for eliminating the organic pollutants in water has been found to be an insistent demand. Environmental and energy issues are the most important concerns faced by human beings. Organic pollutants released from industrial wastes are highly toxic even at relatively low concentration, and thus can cause severe diseases in human beings.[1-3] Photocatalysis under sunlight is promising way for the removal of water contaminants because of its abundant, cheap and clean characteristics.[4-5] 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 zink oxide, are the most widely used catalysts in the field of photocatalytic applications.[6] Ag nanoparticles(nps) with inimitable surface plasmon resonance property have fascinated much attention recently in the field of photo catalysis. Ag halides, classical photosensitive materials in photographic film, are potential photocatalysts due to their narrow band gap of 2.25 ev. Recently the binary Ag/AgX photocations have been designed to improve photocatalytic activities of the photocatalysts.[7] Keeping in view the importance of ZnO and AgI in photodegradation process, a new modified 4-HABT-AgI-ZnO nanophotocatalyst has been developed and its photocatalytic activity for methylene blue(MB) dye decomposition has been studied and reported in the present research article.

MATERIALS AND METHODS

4-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 4-HABT terpolymer, were procured from reputed companies and all were of analytical/chemically 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. The other chemicals used like silver nitrate, potassium iodide and zinc nitrate etc. were also of AR grade.

Synthesis and characterization of 4-HABT terpolymer

The 4-HABT terpolymer was synthesized by condensing 4-hydroxyacetophenone and biuret with trioxane in the molar ratio of 3:3:2 in presence of hydrochloric acid (2M) as a catalyst. The purity of terpolymer was tested and confirmed by thin layer chromatography(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 4-HABT terpolymer has been assigned as given in figure 1.[8]

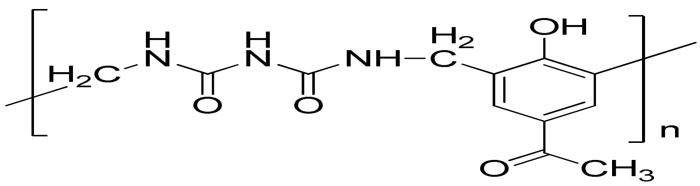

Fig.1. Stucture of 4-HABT terpolymer

Preparation of AgI - ZnO nanoparticles

In 100 ml beaker 20 ml 0.04 M $AgNO_3$ solution was taken and 20 ml 0.04 M of KI solution was added into it drop wise with constant stirring for 60 min to form the AgI suspension. This AgI suspension and Zinc nitrate solutions were added simultaneously in to 100 ml beaker containing 0.4 M alkali solution and kept for 2 hrs at $55^{\mathbf{0}}$C with constant stirring. Completion of reaction was confirmed by formation of precipitate. The reaction mixture was filtered, washed with DI water followed by ethanol. The product was dried under vacuum and stored in air tight bottles.

Preparation and characterization of 4-HABT-AgI-ZnO nanophotocatalyst

The nonophotocatalyst 4-HABT-AgI-ZnO was prepared from a suspension of AgI-ZnO(60%) and 4-HABT dissolved in DMSO at 350K. 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 Kα irradiation scanning from 2 to 75° at a scan rate of 4°/min. SEM analysis of 4-HABT-AgI-ZnO nanophotocatalystic material was performed for characterization.

Photocatalytical reaction studies

Photochemical reactions, under solar irradiation, were carried out when the solar light intensity was approximately 350–950 × 10^{-3}mW/m^2, and the temperature was in the range of 310–320 K. The photocatalytic studies were carried out with MB as a probe molecule at 10 × 10^{-5}mol/dm^3 concentration, and the amount of photocatalyst used was 25–250 mg. Before the reaction, the catalyst was kept in the dye solution (2–16×10^{-5} mol/dm^3) in the dark for 1h 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 and, during 240 min, aliquots of 1ml were collected at the reactor bottom and analyzed using spectrophotometric method.

RESULTS AND DISCUSSION

Characterization of 4-HABT-AgI-ZnO nanophotocatalyst

XRD analysis of plane AgI-ZnO and 4-HABT-AgI-ZnO nanophotocatalyst showed very similar pattern with diffraction lines at 25·42, 37·83, 48·21, 53·87 and 55·33° (Figure 3). These results suggest that no change in crystalline structure occurred during the preparation of the improved photocatalyst. SEM analysis of 4-HABT-AgI-ZnO nanophotocatalyst shows an agglomerated material composed of nano size(90-150nm) oval/sherical particles (Figure 3) and suggestive of the presence of AgI-ZnO particles on the 4-HABT terpolymer surface. The AgI-ZnO particles are strongly attached to the surface of the terpolymer, which is demonstrated by vigorous shaking of the material in water for 1h, when AgI-ZnO particles could not be removed from the surface of 4-HABT terpolymer.

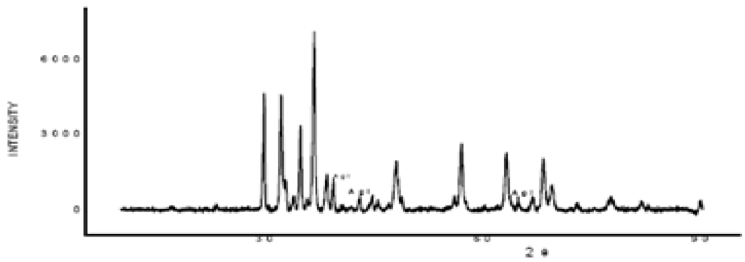

Fig 2. XRD spectrum of 4-HABT-AgI-ZnO

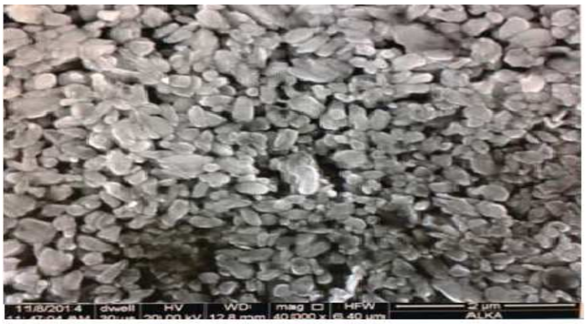

Fig.3 SEM microghraph of 4-HABT-AgI-ZnO nanophotocatalyst

Photocatalytic Decolorization Reaction

Photocatalytic studies were carried out using the dye methylene blue(MB) as probe molecule under solar irradiation (Figure 4). The reaction was carried out at an equilibrium temperature of 40°C. No decolorization takes place in the blank experiments (i.e.in absence of photocatalyst). In presence of plane AgI-ZnO photodegradation is observed but with comparatively slow rate.

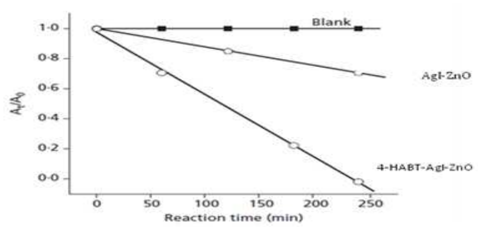

Fig.4. Decoloration curves obtained for MB in blank condition,in the presence of plane AgI-ZnO and 4-HABT-AgI-ZnO nanophotocatalyst

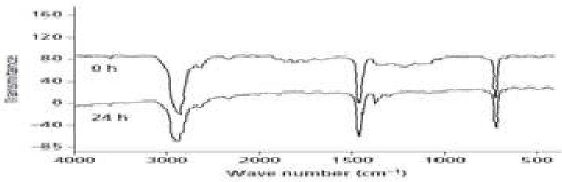

Fig.5. IR spectra of 4-HABT-AgI-ZnO photocatalyst before and after 24 h under solar irradiation in water.

On the other hand, in the presence of the newly developed 4-HABT-AgI-ZnO improved nanophotocatalyst, decolonization takes place within 210 min. This may be due to the location of most of the AgI-ZnO at the bottom because of slightly higher density. But 4-HABT-AgI-ZnO nanophotocatalyst, 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, 4-HABT-AgI-ZnO nanophotocatalyst, the newly developed functional material, shows very good reactivity for the degradation of organic contaminants in water. Recovery and reuse of the photocatalyst were also investigated using 4-HABT-AgI-ZnO submitted to five consecutive reactions. After each reaction, the catalyst was recovered with a simple sieve and a new 16×10^{-5} mol/dm^3 dye solution was used. These results clearly indicate that 4-HABT-AgI-ZnO nanophotocatalyst functional material can be used for more than five times with obtained decolorization in the range of 95–99%. These results indicate that, even after five reactions, the nanophotocatalyst is still very active. To investigate whether the 4-HABT polymer surface was attacked by radicals, IR spectral analysis of the floating-type nanophotocatalyst was carried out before and after 24-h exposure to solar radiation (Fig. 5). Very similar spectra were obtained for 4-HABT before and after exposure to solar radiation, suggesting that the 4-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:

■4-HABT terpolymer can be successfully prepared, characterized and its most possible structure has been determined.

■Anchorment of AgI-ZnO has been successfully performed on 4-HABT terpolymer surface.

■The newly developed 4-HABT-AgI-ZnO photocatalytic functional material is highly active and efficient for almost 100% degradation of a model dye, methylene blue, using solar radiation.

■Low density of 4-HABT-AgI-ZnO 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 AgI-ZnO particles because of the adsorption on 4-HABT polymer matrix. Hence, the photocatalysis process is enhanced due to the combined effect of adsorption by 4-HABT terpolymer macromolecules and photocatalytical activity of AgI-ZnO.

■The study can be extended to test photodegradation capacity of 4-HABT-AgI-ZnO photocatalyst for photodegradation of other dyes and organic pollutants.

■Thus this floating-type newly developed improved nanophotocatalyst, 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 soluble/insoluble organic contaminants.

■The newly developed nanophotocatalic functional material presented in this research article has potential applications in pollution control.

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