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APPLICATIONS OF 2-HABT-II-GO-TiO_2: ANADVANCED MULTIPHASE COMPOSITEMATERIAL

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Abstract

In the present investigation initially 2-Hydroxyacetophenone-Biuret-Trioxane-II (2-HABT-II) terpolymer was successfully synthesized, purified and characterized in the laboratory, followed by its doping with Graphine Oxide (GO). Titanium oxide photo catalyst was then anchored on doped2-HABT terpolymer employing molecular adsorption-deposition method. The TiO_2 particles deposited on the GO doped 2-HABT terpolymeric molecules formed a coating of about 130 nm in thickness. This new modified multiphase multifunctional material was characterized by spectroscopic methods, XRD and SEM studies. An anatase type TiO_2 was uniquely developed on doped 2-HABT-II-GO polymer. Thus a multifunctional material with enhanced surface area and roomy spaces between the adjacent terpolymer molecules was resulted**.** It was tested for its metal ion uptake capacity and photo degradation property. It is evident that the material reported in this paper is an excellent photocatayst for photo degradation of dyes (methylene blue&rhodamine-d) andan efficient adsorbent for a few toxic heavy metal ions like Cd(II)&Pb(II). Thus the newly developed multiphase multifunctional material under present investigation can be successfully employed for treatment of contaminated (pullulated)water.Thus the reported material has practical applications dealing with pollution related environmental issues.

Keywords: - photo catalysis, terpolymer, adsorption, photodegredation, dye pollutants,heavy metal toxicity, water contamination

Introduction

Environmental pollution due to the indiscriminate disposal of synthetic dyes and heavy metals has been causing worldwide concern for the last few decades which can have toxic or harmful effects on many forms of the life [1-5]**.** Metals which are significantly toxic to human beings and

ecological environments, includes chromium, copper, lead, mercury, cadmium, nickel, iron etc. These heavy metals are toxic to aquatics flora and fauna even in relatively low concentration. Waste generation inclusive of organic dyes and other coloring material is an inevitable by-product of the rapid and enhanced industrialization and urbanization. These wastes cause serious and irreparable damage to the environment and are not amenable to conventional methods of waste treatment. Water used in the industries createswaste water that has potential hazard for an environment because of introducing various contaminants such as synthetic dyes into the soil and water resources. Organic dyes are environmentally harmful and too difficult to degrade by conventional chemical methods .Over past decade's significant progress has been achieved in heterogeneous photo catalysis forphotodegredation of undesirable organics in aqueous phase.Photochemistry implies that light and catalysts are necessary to initiate or to accelerate a few chemical transformations.Photocatalysts are mainly semiconducting materials e.g. Titanium oxide, silver halide etc. photocatalytic activity of photocatalyst depends on its ability to create electron pair which react with adsorbed species.Semiconductors such as TiO_2, are the most widely used catalyst in field of photocatalytic application.Lot of work is devoted to acquire high photocatalytic performance through developing new photocatalytic materials or optimizing the capacity of reported photocatalyst.Modification in the crystal structure and physiochemical properties of reported material is another effective way to enhance the photocatalytic performance.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 samples light response to visible region. Specifically speaking , when the composite photocatalyst activated by light , photo induced e^- would inject from the semiconductor with more negative conduction band(CB) level to the semiconductor with more positive CB level, while h^+ would

transfer from one with more positive valence band (VB) to the one with negative VB level. Thus widely separation of photo induced changes can be achieved, which consequently improve the photocatalytic performance. In the present investigation initially 2-Hydroxyacetophenone-Biuret-Trioxane-II (2-HABT-II) terpolymer was successfully synthesized, purified and characterized in the laboratory, followed by its doping with Graphine Oxide (GO). Then Titanium oxide photo catalyst was anchored on doped 2-HABT terpolymer employing molecular adsorption-deposition method. This new modified multiphase multifunctional material was characterized by means spectroscopic methods, XRD and SEM studies.The photocatalytic degradation efficiency of the newly developed material is studied for decolorization of methylene blue&rhodamine-d as a model dye and 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. The same material also shows an excellent toxic metal ion [(Cd(II) &Pb(II)] removal efficacy.

Material & Methods

2- Hydroxyacetophenone was prepared in the laboratory starting from phenol by its acetylation followed by Fries migration reaction. The other starting materials like biuret and trioxane etc. used in the synthesis of 2-HABT-II terpolymer were procured from reputed companies (likeMerk) and all were of analytical and pure grade .The solvent Dimethyl Suphoxide(DMSO) used also was of AR grade and double distilled under reduced pressure prior to its use in various physicochemical and spectral studies. Deionised water was used throughout the investigation.TiO_2& GO used were also of AR grade.

Synthesis & Characterization of 2-HABT-II Terpolymer

The 2-HABT-IITerpolymer was synthesized[16] & its purity was tested and confirmed by TLC. The terpolymer was characterized by physico-chemical studies like elemental analysis, molecular weight determination byconductometric titration,intrinsic viscosity, electronic, IR, proton magnetic resonance spectral studies and thermogravmetric analysis. On the basis of all physicochemical and spectral evidences the most possible structure[16] for 2-HABT-IIterpolymer is assigned which is given in Fig.1.

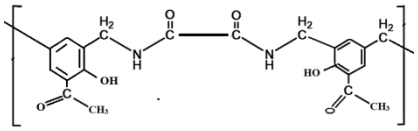

Fig.1. Structure of 2-HABT-IITerpolymer

Preparation of2- HABT-IITerpolymer Gel:

25 g of terpolymer was slowly added to 1 dm^3 of 10% wt oxalic acid with constant stirring. The mixture was heated to 318 $\pm$ 2 K to proper mixing and then allowed to cool slowly. The pinkish viscous gel is obtained at room temperature.

Preparation of GO- 2- HABT-II Composite

GO- 2- HABT-II Compositewas synthesized employing molecular adsorption deposition methodThe twice coated composite sorbent was dried in the oven under vacuum at 300 K for about 24 h and transferred to a glass bottle for storage in desiccators.

Preparation and characterization of 2-HABT-II-GO-TiO_2 (MultiphaseMultifunctional Material)

The photocatalyst2-HABT-II-GO-TiO_2 was prepared from a suspension of TiO_2 (60%) andGO-2-HABT (II) 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 hr. Powder XRD data were obtained using Cu, Kα irradiation scanning from 2 to 75^{o} at scan rate of 4^{0} min^{-1}. Thermo gravimetric analysis was carried out in a Shimadzu TGA/DTA 50 H in air flow and heating rate 10^{0}C per min. SEM analysis of pure TiO_2 and 2-HABT-II-GO-TiO_2 photocatalyst material was done for characterization.

Decolourising (photocatalytical) Reaction Studies

The photochemical reaction under solar irradiation were carried out in the month of may between 8am to 4 pm. Solar light intensity was approximately 300-700 X 10^{-3} mWm^{-2}and temperature was 308 – 318 K. The photocatalytic studies were carried out with methylene blue as well as rhodamine-d as a probe molecule at 12 X 10^{-5}mol dm^{-3} concentration and amount of photocatalyst used was 100 mg to 1000 mg. Before the reaction, the catalyst was kept in the dye solution (2 – 20 X 10^{-5}mol dm$^{-3)}$ in the dark for 1 hr. to reach adsorption equilibrium. The reaction was started on exposing the reactor to the 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-II-GO-TiO_2 photocatalyst

The thermogravimetic analysis(TGA)is an effective analytical technique to evaluate the ratio of GO-TiO_2. In fig.2,the TGA curve of 2-HABT-II-GO-TiO_2shows 15% wt loss from 30 to 120^{0}C which is due to loss of water entrapped into organic solvent molecules. The mass loss from 200 to 500^{0}C is 30% which is due to decomposition of oxygen group and carbon oxidation from GO; while GO shows the complete decomposition temperature at 750^{0}C. 2-HABT-II-GO-TiO_2shows significant lower temperature i.e. 500^{0}C for complete decomposition of the carbon from GO. This suggests that thermal stability of GO get decreased after composite formation with TiO_2 due to its catalytic effect.

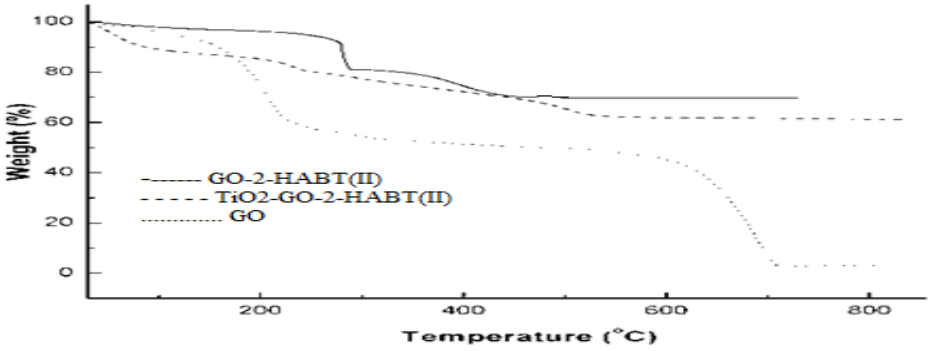

Fig. 2. TG Analysis (in air) of pure GO,GO-2-HABT(II) and 2-HABT-II-GO-TiO_2

XRD is an important tool for determining whether GO base composite are indeed present as individual graphene sheet in nanocomposite. Fig 3 show pattern of GO (curve a),2-HABT-II-GO-TiO_2(curve b) and pure 2-HABT (II) (curve c).The typical diffraction peak of GO was observed at about $2\Theta = 10.9^o$ (Fig 3a) and diffraction peak of pure 2-HABT (II) appeared at $2\Theta = 19.6^o$ (fig 3c). However after GO was disappeared into 2-HABT (II) matrix, the XRD pattern of 2-HABT-II-GO-TiO_2(Fig.3b) only show the 2-HABT (II) diffraction peak from 2-HABT (II); the diffraction of GO disappeared.

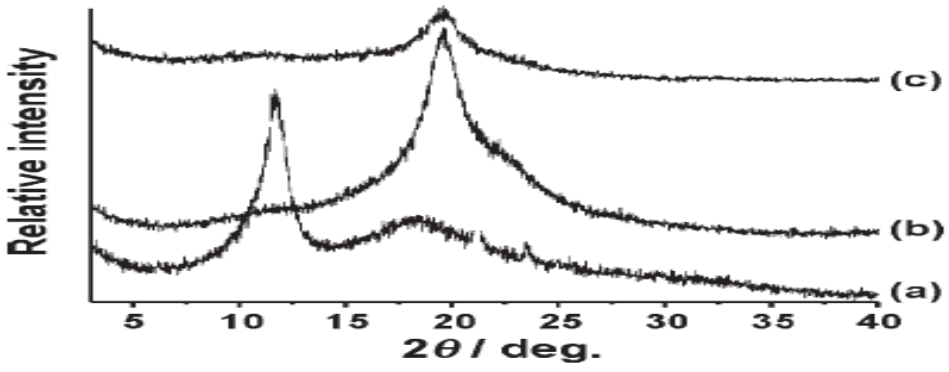

Fig. 3: XRD of pure 2-HABT (II), GO and 2-HABT-II-GO-TiO_2

SEM analysis of pure 2-HABT(II) show an agglomerated material of spherical particles(fig.4a) .SEM image of 2-HABT-II-GO-TiO_2(fig.4b) suggest the presence of TiO_2 particles located on and in the GO-2-

HABT(II)terpolymer surface. The TiO_2 particles are strongly attached to the surface of the GO-2-HABT (II) which is proved by vigorous shaking of thematerial in water for 1 hr. when TiO_2 particles could not be removed from the GO-2-HABT (II) surface.

(a) (b)

Fig. 4 (a) SEM of Pure 2-HABT(II) (b) SEM of GO-TiO_2 – 2-HABT photocatalyst

Decolorizing (Photocatalyst) Reaction

The photocatalytic studies were carried out using the dyes methylene blue and rhodamine-das probe molecules under solar irradiation (Fig.5). The reaction was carried out at an equilibrium temperature of 35^0C. It can be observed in the blank experiments (i.e. without photocatalyst) no decolourization takes place. On the other hand in the presence of the photocatalyst2-HABT-II-GO-TiO_2decolourization take place after 260 min. The experimental data proved that the reaction follows first order kinetic. Pure TiO_2 showed low decolourization after 210 min of reaction. This may be due to the location of most of the TiO_2 particles at the bottom because of little higher density. But 2-HABT-II-GO-TiO_2having lesser density and remains floating at the surface and hence showed enhanced activity. Moreover the adsorption phenomenon of dyes molecules over the surface of the polymer provided easy reaction sites and hence overall activity of photocatalyst get enhanced .Thus the TiO_2 – 2-HABT (II)photocatalystshows agood reactivity for the degradation of organic contaminants in water. Recovery and reuse of the photocatalyst

were also investigated using GO- TiO_2 – 2-HABT(II) submitted to three consecutive reactions. After each reaction the catalyst was recovered with a simple sieve and a new 12 X 10^{-5}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 approximately 15X 10^{-3} min^{-1} for the reaction. These result clearly indicate that GO- TiO_2 – 2-HABT (II)photocatalytic functional material can be used for more than 5-6 times with obtained decolourization in the range of 90 – 95 %. Theses result indicates that even after nine reactions the photocatalyst still is very active.

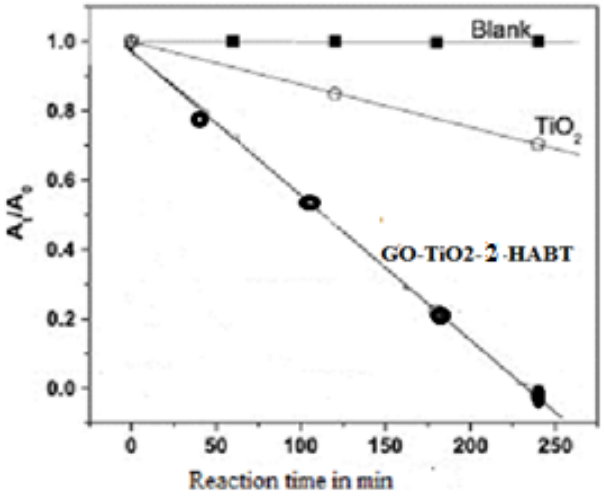

Fig.5 Discolouration curves obtained for MB in blank condition, in the presence of pure TiO_2 and 2-HABT-II-GO-TiO_2

To investigate whether the 2-HABT-II-GO-TiO_2composite surface was attacked by radicals, IR spectral analysis of the floating photocatalyst after 24 hr exposed to solar radiation were carried out. (Fig6). It was observed that very similar spectra was obtained for 2-HABT-II-GO-TiO_2before and after expose to solar radiation, suggesting that 2-HABT-II-GO-TiO_2surface oxidation by the radicals formed during photocatalytical reaction is not significant under the reactions conditions employed.

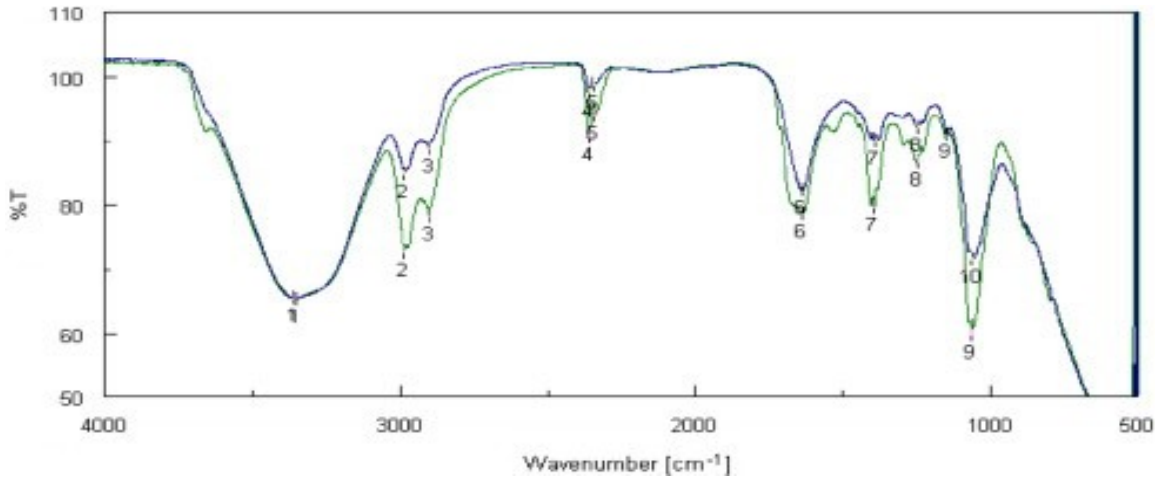

Fig.6: IR Spectra of 2-HABT-II-GO-TiO_2 photocatalyst before and after 24 hr under solar irradiation in water Before(.....); (After----------)

Removal of Metal ion (Cd &Pb)

The removal of Cd (II) &Pb (II) by 2-HABT-II-GO-TiO_2asaadsorbent was carried out at thepH 8.00.The initial concentration taken was 50 mg/lit and adsorbent dose was 3.00 gm/lit. The results are given in table 2. It can be noted that the removal of Cd (II) and Pb(II) ions increased with increasing contact time. It is evident that 2-HABT-II-GO-TiO_2 is effective for maximum removal of both the metal ions when the contact time was70 min.

Table 1

Removal of Cd(II) &Pb(II) at pH = 8.00and adsorbent dose 3.00 gm/lit with different contact time

Contact Time (in min)	10	20	30	40	50	60	70	80
% removal Cd(II)	60	65	69	72	87	90	94	96
% removalPb(II)	55	63	65	69	76	82	88	89

Conclusion

On the basis of results obtained in this investigation the following conclusion can be drawn

- 2-HABT (II)terpolymerwas successfully prepared, characterized and its most possible structure is determined.
- Anchorment of TiO_2 has successfully been done on GO-2- HABT (II)terpolymer surface.
- The newly prepared 2-HABT-II-GO-TiO_2multiphasemultifunctional material (photocatalyst) is highly active and efficient for degradation of a model dyesi.e. methylene blue and Rhodamine –d using solar radiation.
- Low density of 2-HABT-II-GO-TiO_2photocatalyst facilitated more efficient illumination due to the positioning of photocatalyst on the water surface. Moreover near to the surface there is possibility of more efficient oxygenation which is fundamental for thephotocatalytical processes.
- The dye molecules in bulk solution was supposed to be condensed around anchored TiO_2 particles because of adsorption phenomenon on 2- HABT(II) polymer matrix and hence the photocatalysis process get enhanced due to combined effect of adsorption by GO-2- HABT(II)terpolymer macromolecules and photocatalytical activity of anatase type TiO_2 .
- The study can be extended to test photo-degradation capacity of 2-HABT-II-GO-TiO_2photocatalyst for photo-degradation of other dyes and organic matter i.e.Pollutants.
- The floating type photocatalyst under present investigation can be potentially used in the treatment of contaminated waste water reservoirs located in remote areas without any special equipment installation. It can also efficiently used for the destruction of insoluble organic contaminants.
- Removal of metal ion such as Cd(II) &Pb(II) from aqueous solution is possible using2-HABT-II-GO-TiO_2multifunctional material which effectively removes more than 96% of Cd(II) and 89 % 0f Pb(II)if initialconcentration is 50mg/lit.

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