Photocatalytic efficiency of Ho_2O_3-ED-HPV in Bisphenol-A Removal

K. Selvakumar, V. Ramani, K. Thirumalai, A. Arun, M. Swaminathan

Abstract*: Hydrothermally synthesized Ho_2O_3-ED-HPV was characterized by DRS-UV, FT-IR, SEM and EDX analysis.Catalyst surface has clustered microsponge-like structure with more number of cavities. To investigate the catalytic properties of Ho_2O_3-ED-HPV nanoparticles, the photodecomposition of bisphenol-A with ultraviolet light was performed.

***Keywords* : Bisphenol-A, Heteropoly acid, Ho_2O_3-ED-HPV, Photocatalyst.**

I. INTRODUCTION

Pharmaceutical compounds are vital for many benefit purposes in modern society, but drug companies simultaneously release chemicals that are most poisonous in the environment [1]. Furthermore, drugs and their intermediates may enter the environment through a variety of ways, such as discharge of treated sewage, landfills and sewage lines [2, 3]. Although various physical and biological processes in ecosystem reduce many drug contaminants, some amount of these pharmaceutical compounds are found in a variety of aquatic environments [4-6]. Various industries, including pharmaceuticals, chemicals and paints, are booming in India and they discharge their waste directly or partially in streams [7].

Bisphenol-A (BPA) is an extensively used Endocrine-Disrupting Chemicals (EDCs) and is known for its wide use in polycarbonate plastics and epoxy resins [8, 9]. During the BPA production and application process, a large amount of BPA is discharged into the natural environment [10].

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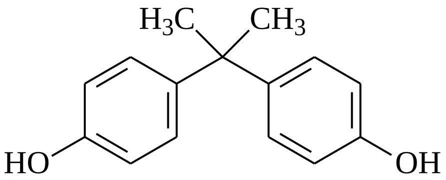


Bisphenol A (2, 2-bis (4-hydroxyphenyl) propane, BPA)

Since environmental pollution crossed the threshold of natural purification, advanced oxidation process has become a must for the effective wastewater treatment with high efficiency. Nowadays, advanced oxidation processes specifically photocatalysis is used for the degradation of toxic chemicals. Semiconductor photocatalysis is a ‘green approach’. Photocatalysts play a vital role as they can make use of solar light. Semiconductor oxides such as titania, zinc oxide are widely used as photocatalysts for environmental remediation.

Degradation of a toxic molecule is caused by the catalytic material by the absorption of photons, particularly of those wavelengths found in sunlight such visible light and ultraviolet light. Photodegradation processes depend on the experimental conditions: the presence of molecular oxygen, the nature of the chromophores, and / or the impurities that induce degradation by absorbing UV photons. Photo-oxidative degradation (i.e.) in the presence of molecular oxygen, has been well documented for many materials. Photocatalysts, when they are present in nano size, have more efficiency in the degradation. Ho_2O_3 is an attractive rare earth metal oxides due to its unique optical and electrical properties [11, 12]. Until now, Ho_2O_3 has been prepared by thermal decomposition of holmium nitrate and oxalate [13], holmium carbonate and carbamide-containing complex of holmium [14, 15]. The development of an easy and reliable pathway for the synthesis of Ho_2O_3 nanoparticles is of great importance for the potential study of its properties. Morphology and particle size have been shown to have a major impact on the properties of nano-structured materials [16, 17]. Hence it is important to investigate favorable and appropriate procedures for the formation of Ho_2O_3 nanoparticles and to control its particle size and shape.

Heteropoly acid (HPA) material has great activity as oxidation / acid catalyst in most of the reactions [18, 19]. HPA has photophysical and photochemical properties, similar to semiconductors. [20,21]. However, several reports state that HPAs are active only under UV radiation. In order to make them visible active and to increase surface area modification of HPA is carried out. HPA compounds are supported on a montmorillonite clay [22] and TiO_2 [23] to obtain insoluble catalysts with increased surface area.

Furthermore, support metal oxide and other materials improve the catalytic activity of the catalysts due to the synergistic effect [24]. In the present work, a nanocomposite with Ho_2O_3, ethylene diamine (ED) and heteropoly vanadate (HPV) was prepared by hydrothermally and its photocatalytic activity was investigated. ED was used as a binder for Holmium oxide and Heteropoly vanadate.

II. EXPERIMENTAL SECTION

A. Materials

The analytical grade Holmium oxide (Ho_2O_3), ethylene diamine, ethylene glycol, ethanol, disodium hydrogen phosphate, sodium metavanadate and sodium tungstate dehydrate were obtained from Himedia. Analytical standard Bisphenol-A was received from Sigma–Aldrich.

B. Preparation of Catalysts

Preparation of Ho_2O_3-ED

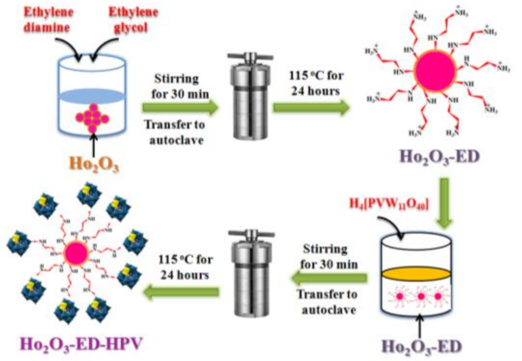
0.5 g of Ho_2O_3, dispersed in 20 ml ethylene glycol and 40 ml ethylene diamine (ED) was sonicated for 30 min and transferred into autoclave and maintained for 24 h at 115 °C. The product was filtered and washed by ethanol and deionized water and dried at 60 °C in vacuum.

Preparation of heteropoly-11 -tungsto-1-vanadophosphoric acid, $H_4[PVW_{11}O_{40}].32H_2O$ (HPV)

HPV was prepared by the literature procedure [25]. In a typical procedure 0.71 g of disodium hydrogen phosphate (Na_2HPO_4) was dissolved in 10 mL of water and mixed with 0.61 g of sodium metavanadate ($NaVO_3$) which was dissolved in 10 mL of boiling water. The mixture was allowed to cool down to room temperature and acidified with 1 mL conc. sulphuric acid which turned the reaction mixture into red colour. 17.76 g of sodium tungstate dihydrate ($Na_2WO_4.2H_2O$) dissolved in 20 mL of water was added to the reaction mixture and 8.4 mL of conc. sulphuric acid was added slowly to the reaction mixture with vigorous stirring while the dark red colour was faded. The HPV was then extracted using 80 mL of diethyl ether and separated as heavy oily etherate (bottom layer) followed by evaporation in a vacuum desiccator. $H_4[PVW_{11}O_{40}].32H_2O$ (HPV) was obtained as crystalline yellow solid (70 %).

Synthesis of Ho_2O_3-ED-HPV

0.1 g of $H_4[PVW_{11}O_{40}]$ (HPA) was dissolved in 80 mL ethanol and then 0.8 g of Ho_2O_3-ED added to it. It was transferred to autoclave, maintained at 115 °C for 24 h. The black product was separated as described above.



Scheme 1. Schematic representation of Ho_2O_3-ED-HPV composite synthesis.

C. General procedure for photocatalytic degradation of Bisphenol A

Bisphenol-A (BPA) was used to evaluate the photocatalytic performance of the Ho_2O_3-ED-HPV samples. 40 mg portion of the catalyst was dispersed in 50 mL of BPA aqueous solution with the concentration of 30 µM in 100 mL beaker. Solution was allowed to reach an adsorption–desorption equilibrium in 30 min by stirring under dark condition. After stirring, the solution was transferred to photoreactor tube and irradiated by UV light (λ = 365 nm). 3 mL of the reaction solution was sampled with 10 min interval and centrifuged. Its absorbance was measured at 276 nm by an UV–visible spectrophotometer to monitor its concentration.

III. RESULTS AND DISCUSSIONS

A. DRS-UV spectra analysis

The DRS-UV-visible spectra of Ho_2O_3, Ho_2O_3-ED and Ho_2O_3-ED-HPV are shown in Figure 1. The absorbance of the Ho_2O_3-ED-HPV was higher than Ho_2O_3 and Ho_2O_3-ED. The band gap (Eg) was determined using DRS information and Tauc's formula. Band gaps of Ho_2O_3, Ho_2O_3-ED and Ho_2O_3-ED-HPV nanocomposites were calculated from the K-M plot (Fig. 2). The energy band gaps for the prepared photocatalyst Ho_2O_3, Ho_2O_3-ED and Ho_2O_3-ED-HPV were found to be 5.07 eV, 3.48 eV and 3.35 eV respectively.

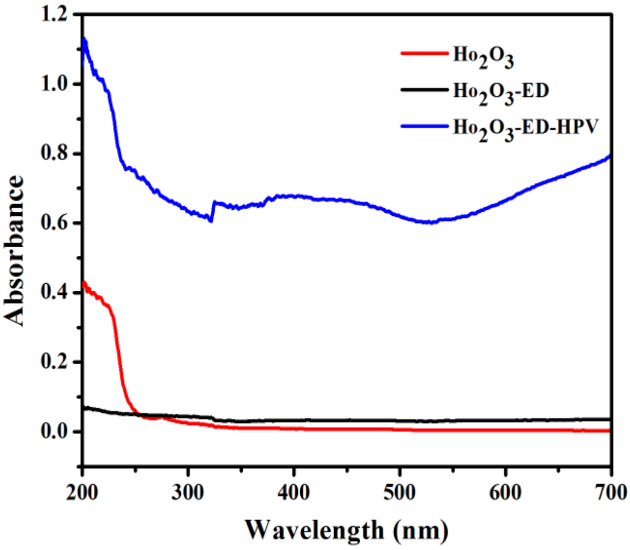


Fig. 1. DRS-UV absorption spectrum of Ho_2O_3, Ho_2O_3-ED and Ho_2O_3-ED-HPV.

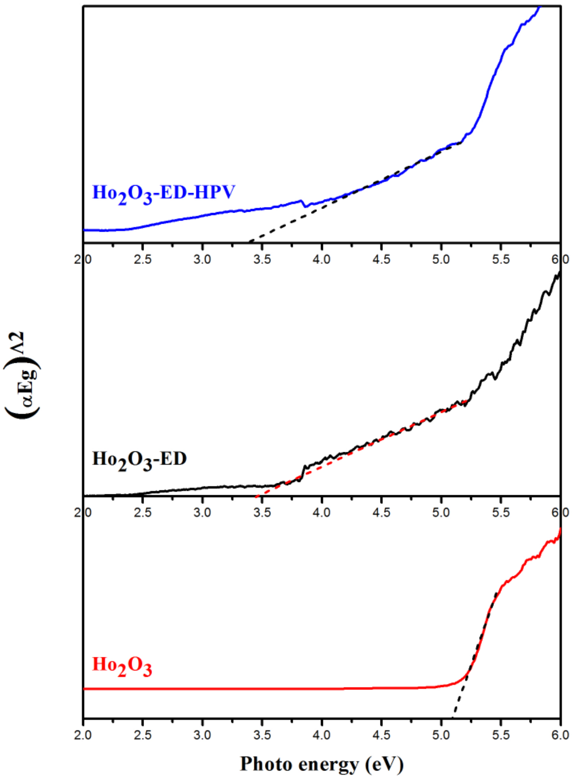


Fig. 2. DRS-UV Tacu's plot of of Ho_2O_3, Ho_2O_3-ED and Ho_2O_3-ED- HPV.

B. FT-IR spectra analysis

The composite material was analyzed by FTIR spectroscopy (Fig. 2). In figure 2a, the broad bands observed at 1527 cm^{-1} are indexed to CO_3^{2-} species [26]. In FTIR of Ho_2O_3-ED-HPV (Fig. 2c), the characteristic W-O symmetric and antisymmetric stretching and O-W-O symmetric and antisymmetric deformation vibrations in tungstate groups are absorbing at 1105, 949 and 795 cm^{-1} [27].

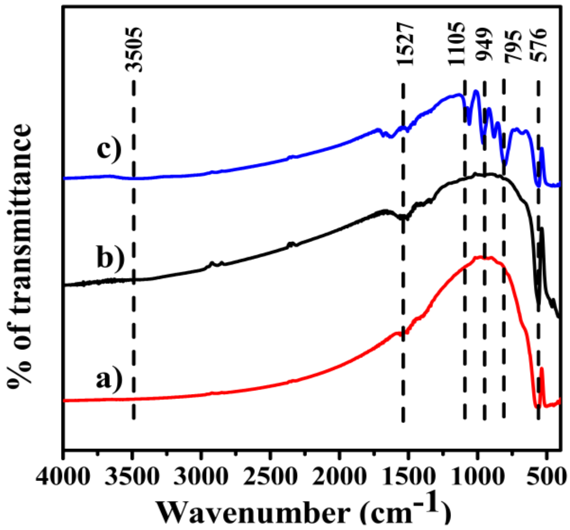


Fig. 3. FT-IR spectrum of a) Ho_2O_3, b) Ho_2O_3-ED and c) Ho_2O_3-ED- HPV

C. SEM and EDX analysis

The SEM images of Ho_2O_3-ED-HPV are shown in Fig. 4. Ho_2O_3-ED-HPV shows a clustered microsponge-like structure morphology. The presence of elements Ho, O, C, N, P, V and W in the catalyst was confirmed by EDX recorded from the selected area (Fig. 5). Multi-elemental EDS mapping images of Ho, O, C, N, P, V and W are shown in Fig. 6. Apparently, the corresponding C, N, P, V and W maps evidenced bright spots corresponding to the calcified area and illustrated a homogeneous distribution of these elements in the cross-section view.

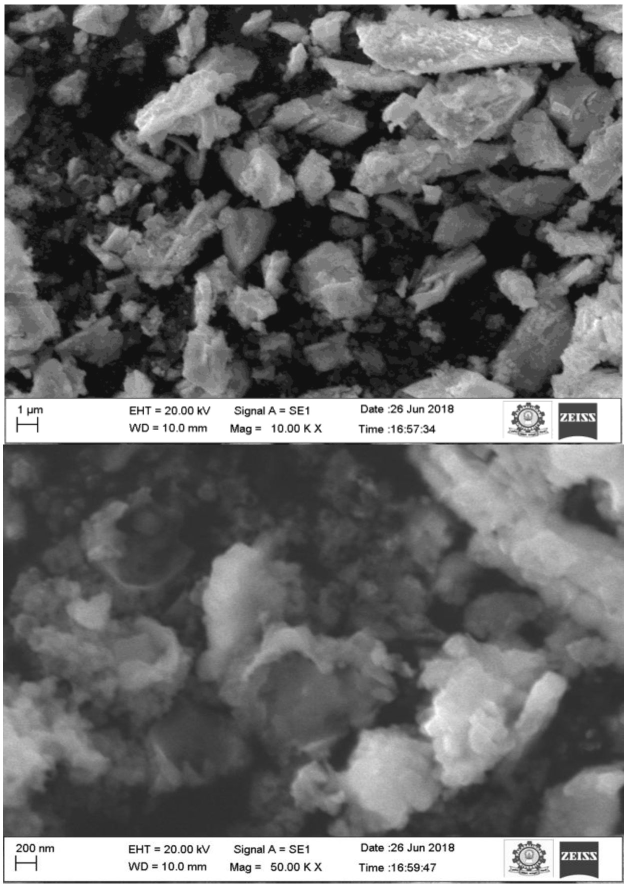


Fig. 4. SEM image of Ho_2O_3-ED-HPV

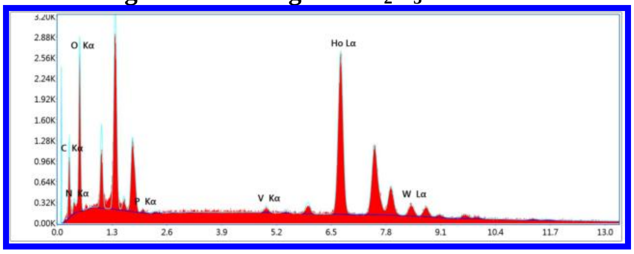


Fig. 5. EDX spectrum of Ho_2O_3-ZnO-ED-HPV

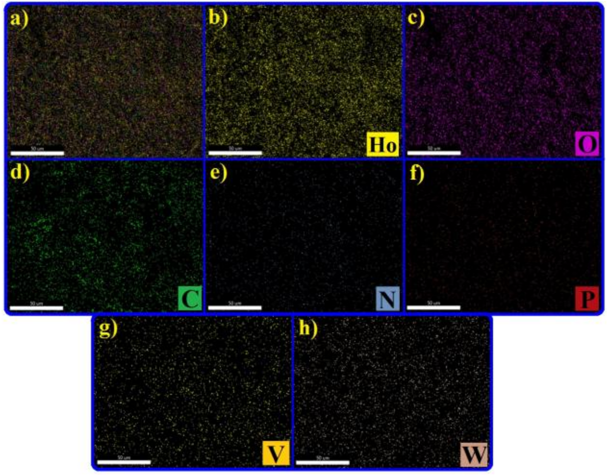


Fig. 6. SEM-EDX digital mapping images of elements Ho, O, C, N, P, V and W.

D. Optimization of Photocatalytic degradation

Effect of different catalysis

To optimize photodecomposition efficiency, the effect of various catalysts, their dosages were done. Photocatalytic degradation of BPA with Ho_2O_3, Ho_2O_3-ED and Ho_2O_3-ED-HPV was carried out and the results are shown in figure 7. Ho_2O_3-ED-HPV is more active than other catalysts of Ho_2O_3 and Ho_2O_3-ED.

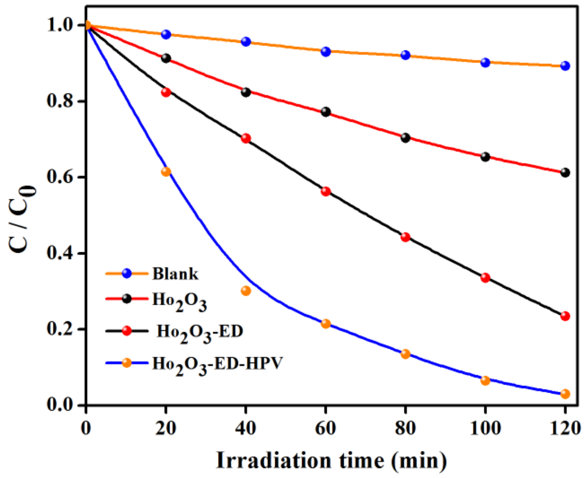


Fig. 7. Photodegradation of BPA solution under Different catalysts (catalysts: 40 mg, BPA conc.: 3 X 10^{-5})

Effect of different dosage catalyst

The optimum catalyst dosage of Ho_2O_3-ED-HPV study is reported in Fig. 8. Photodegradation of BPA increases up to 40 mg of Ho_2O_3-ED-HPV and decreased thereafter. Therefore, increase in catalyst amount increases photodegradation efficiency due to increase in the reactive sites of catalyst [28]. At higher amount of catalyst, activity decreases as the surface area decreases due to aggregation.

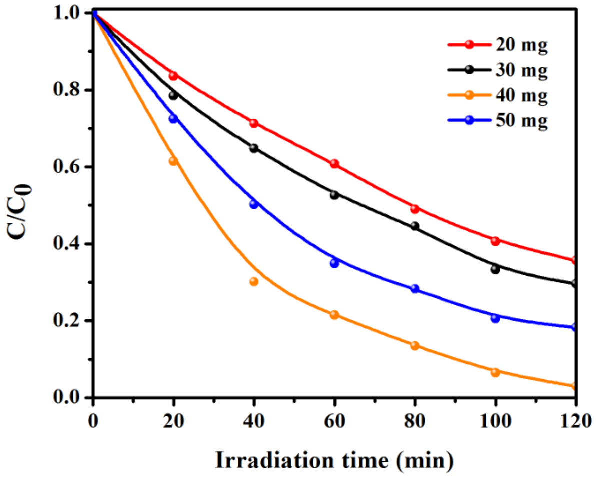


Fig. 8. Photodegradation of BPA solutions under different dosage of Ho_2O_3-ED-HPV nanocomposites (BPA conc.: 3 X 10^{-5}).

Reusability of the catalyst

After the complete degradation of BPA solution the catalyst was separated and reused for four consecutive runs of photodecomposition under the same conditions. Figure 9 shows a slight decrease in efficiency in each run. Photodegradation of BPA by Ho_2O_3-ED-HPV remained 91 % for used catalyst even at 5th run. The results confirm the recyclability and of the catalyst.

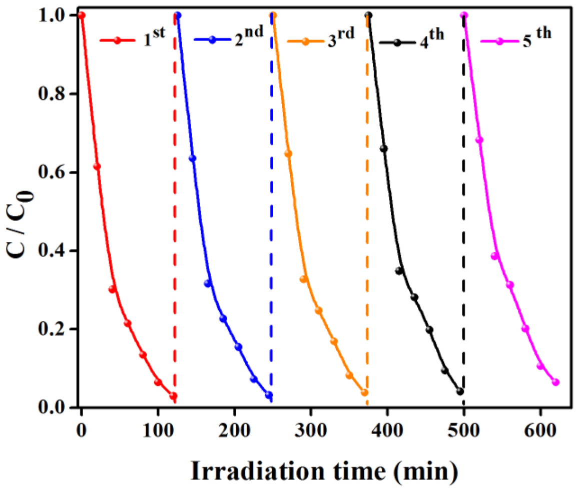


Fig. 9. Reusability of the Ho_2O_3-ED-HPV photocatalyst.

Degradation Mechanism

To investigate the degradation mechanism of BPA, scavengers for different reactive oxidizing species (ROS) were used. Triethanolamine (TEOA (h+)), benzoquinone (BQ ($\cdot O^{2-}$)) and isopropyl alcohol (IPA ($\cdot$OH) were utilized as the scavengers [29, 30]. Degradation of BPA with Ho_2O_3-ED-HPV is highly suppressed by BQ (figure 10). Therefore, the superoxides radicals are playing main role in the degradation process. Photodegradation efficiency is slightly reduced with TEOA and IPA. Main species involved in degradation of BPA with Ho_2O_3-ED-HPV is superoxide.

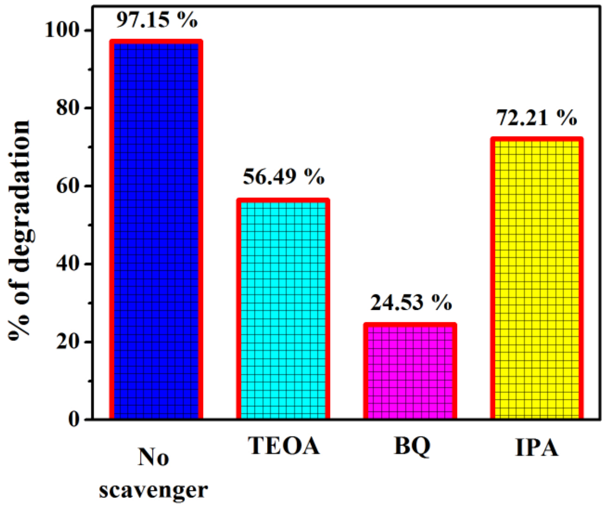


Fig. 10. Effect of scavengers on Photodegradation of BPA BPA conc. 4 X 10^{-5}; Ho_2O_3-ED-HPV- 40 mg; IPA-0.1 mmol / TEOA-1 mmol / BQ-0.1 mmol, irradiation time 120 min)

IV. CONCLUSION

The Ho_2O_3-ED and Ho_2O_3-ED-HPV nanocomposite were hydrothermally and characterized. The FTIR spectral analysis of Ho_2O_3-ED-HPV catalyst displays the characteristic bands of metal oxide, ED and HPV. SEM and EDX analysis reveals that catalyst surface has clustered microsponge-like structure with more cavities. Ho_2O_3-ED-HPV is found to be efficient in the degradation of bisphenol-A.

The photodegradation of BPA solution was completed in 120 min under UV light irradiation. Superoxide radicals play the main role in the degradation of BPA.

Further, the Ho_2O_3-ED-HPV photocatalyst has good chemical stability and reusability.

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