

**Synthesis, Characterization and Visible light driven
Photocatalytic Applications of Bi₂WO₆ Nanoparticles
towards Congo red Dye Degradation**

A

Dissertation

Submitted in the partial fulfilment

FOR THE DEGREE OF
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By

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Under the guidance of

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DECLARATION

The work embodied in this report is an original investigation carried out by me, on the topic entitled “**Synthesis, Characterization and Visible light driven Photocatalytic Applications of Bi₂WO₆ Nanoparticles towards Congo red Dye Degradation**” for partial fulfilment of degree in Master of Science (Chemistry), NIT Rourkela. To the best of my knowledge and belief, this work has not been submitted to any other University or Institution to confer any Degree or Diploma of similar nature.

Durga Prasad Rout

CERTIFICATE

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This is to certify that the dissertation entitled “**Synthesis, Characterization and Visible light driven Photocatalytic Applications of Bi_2WO_6 Nanoparticles towards Congo red Dye Degradation**” submitted by **Durga Prasad Rout** to the Department of Chemistry, National Institute of Technology, Rourkela, Odisha, for the award of the degree of Master of Science is a record of bonafide research work carried out by him under my supervision and guidance. I am satisfied that the dissertation has reached the standard fulfilling the requirements for the regulations relating to the nature of the degree.

N.I.T. Rourkela

Date:

Dr. Braja Gopal Mishra

Supervisor

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CONTENTS

	Page No
Chapter 1	
INTRODUCTION	
1.1 Introduction	06
1.2 Objective of the present work	08
Chapter 2	
MATERIAL AND METHODS	
2.1 Synthesis of Bi ₂ WO ₆ nanoparticles	09
2.1.1 Amorphous-citrate method (AC)	09
2.1.2 Urea hydrolysis method (UH)	09
2.2 Characterization	10
2.3 Degradation of Congo-Red dye	10
Chapter 3	
RESULTS AND DISCUSSION	
3.1 Characterization of Bi ₂ WO ₆ Photocatalyst	11
3.2 Photocatalytic degradation of congo red dye	16
3.3 Conclusion	19
References	20

CHAPTER 1

INTRODUCTION

1.1 Introduction

In recent years, environmental pollution and its impact on all forms of life are of principal concern. The industrial discharge from various chemical, agrochemical and textile industries contains significantly higher amount of toxic organic chemicals and carcinogenic compounds such as persistent organic pollutants, pesticides, dyes, suspended solids, pathogens and soluble refractory organic compounds. These pollutants enter into the water sources causing serious water pollution which drastically affect all forms of life. The treatment of polluted aqueous sources is of great importance and a sustainable approach to obtain portable water for all sections of our society. Although various methods have been developed to remove these contaminant which includes adsorption [1, 2], nano filtration [3] electro coagulation [4], biological treatment [5], chemical and electrochemical degradation [6]. Each of these methods has certain disadvantages in terms of economy, scaling, by-products formation, energy consumption and disposal problems. It is highly necessary to devise advanced processes which can bring about complete mineralization of the organic pollutants using minimum experimentation steps and less consumption of energy. In this context, the complete mineralization of organic pollutants by photocatalytic process using solar energy and low band gap semiconductor nanoparticles as catalyst is an exciting proposition. Congo-red dye is one of the organic pollutants which are found in the effluent water from the textile industry, paper industry and biological labs. Congo red is a carcinogenic and toxic dye which causes severe health problem to human being as well as affect the aquatic life. Hence several attempts have been made to remove congo red by

adsorptive removal from aqueous sources using clay materials [7], hydroxyapatite-chitosan composite [8], activated carbon [9], cattail root [10] and natural and acid-treated kaolinite and montmorillonite [11] as adsorbent. The detoxification of congo red containing aqueous effluent by ozone treatment has also been studied [12,13]. Most of the earlier works on removal of congo red focus on adsorption technique where the subsequent disposal of the pollutant is a concern. It is highly desirable to convert congo red dye to environmentally acceptable products by oxidation process. The conventional oxidation processes which rely on the use of oxidants such as H_2O_2 , tertiary butyl hydrogen peroxide along with metal ions as catalyst generate a significant quantity of byproducts. Hence it is highly desirable to develop catalytic method for degradation of congo red which are clean, environmentally acceptable, less energy consuming and utilizes molecular dioxygen as oxidant. In order to achieve this objective, in this work we have utilized Bi_2WO_6 semiconductor nanoparticles as visible light driven photocatalyst for degradation of congo red from aqueous sources using air as oxidant.

The bismuth tungstate (Bi_2WO_6) is the simplest member of the Aurivillius family of layered perovskites of general formula $[Bi_2O_2][A_{n-1}B_nO_{3n+1}]$ ($A=Ca, Sr, Ba, Pb, Bi, Na, K$ and $B=Ti, Nb, Ta, Mo, W, Fe$). It is “A” cation-deficient bismuth-layered compounds with $n=1$ in the structural formula [14]. Several methods have been devised for the synthesis of this important compound which include solid state reaction [15], amorphous complex method [16], mechanochemical synthesis [17] solvothermal [19,20], hydrothermal [18,21], and microwave assisted hydrothermal methods [23], sol-gel method [22]. Urea hydrolysis and amorphous citrate methods are two versatile methods for synthesis of complex oxide nanoparticles. Urea being a mild hydrolysing agent, the kinetics of hydrolysis can be controlled to a large extent by proper choice of preparative parameters to generate oxide nanoparticles of desired morphology and

shape. Similarly, the amorphous citrate method which utilizes citric acid as a dispersing as well as coordinating agent provides an efficient organic framework for dispersion of the precursor metal ions. The amorphous citrate precursor contains molecularly dispersed metal ions coordinated to the citrate backbone which upon calcination provides oxide nanoparticles. Using urea hydrolysis [24-29] and amorphous citrate method [30-33] many novel materials have been synthesized. The preparation of Bi_2WO_6 by amorphous citrate method and urea hydrolysis has not been studied so far. Since the photocatalytic property of a semiconductor particle depends on surface area, band gap, crystallinity, morphology and exposed facets, it will be an interesting proposition to synthesize this material using these methods and explore its catalytic applications.

In this work for the first time Bi_2WO_6 has been synthesized via urea hydrolysis and amorphous citrate method and used as photocatalyst for degradation of congo red dye under visible light irradiation in aqueous medium.

1.2 Objective of the present study

The main objective of the present research work include

- (1) Synthesis of layered tungstate (Bi_2WO_6) nanomaterials by using urea hydrolysis and amorphous citrate methods.
- (2) Characterization of the surface morphology, structure, surface area, particle size and electronic properties of the synthesized nanoparticles.
- (3) To study the applicability of the Bi_2WO_6 nanoparticles as photocatalyst for complete mineralization of congo red from aqueous sources.

CHAPTER 2

MATERIAL AND METHODS

2.1. Preparation of Bi_2WO_6 nanoparticles

In this present study, Bi_2WO_6 (BWO) nanoparticles have been synthesized via two different synthetic methods; amorphous citrate method and urea hydrolysis method. In both the synthesis method ammonium tungstate ($\text{N}_{10}\text{H}_{40}\text{W}_{12}\text{O}_{41}$) and bismuth carbonate ($(\text{BiO})_2\text{CO}_3$) are have been used as precursor compound.

2.1.1. Amorphous citrate method (AC)

Stoichiometric amount of ammonium tungstate, bismuth carbonate and same amount of (equimolar quantity with respect to total metal ions) citric acid were taken and made a paste with minimum water. The thick paste was then heated in an oil bath at 60°C for 15 minutes to obtain a transparent gel. On evacuation the transparent gel a solid residue was obtained. This solid residue was then immediately transferred to a pre-heated furnace at 160°C and put for 2 h to get the amorphous citrate precursor. This amorphous precursor then grind and calcined at 500°C for 6 h to get Bi_2WO_6 (BWO-AC) nanomaterials.

2.1.2. Urea hydrolysis method (UH)

Stoichiometric amount of metal salt (ammonium tungstate + bismuth carbonate) was dissolve in 75 ml of water (solution-A), and a little molar excess of urea was dissolve in 100 ml water (solution-B). Solution A and B were mixed and refluxed at 100°C for 10 h leading to the formation of a precipitate. The precipitate was washed three times using double distilled water and then collected by centrifugation at 5000 rpm for 15 min. This precipitate was dried at 100°C for 24 h, made a homogeneous powder by grinding and calcined at 500°C for 6 hour in order to get Bi_2WO_6 (BWO-UH) nanoparticles.

2.2. Characterization

The synthesized BWO material were analysed using different analytical techniques in order to get information on the physicochemical characteristics. The XRD patterns of the BWO materials was recorded using a Rigaku, Ultima-IV Multipurpose X-ray diffraction system using Ni filtered $\text{CuK}\alpha_1$ ($\alpha = 1.5405\text{\AA}$) radiation in the range of $20\text{--}60^\circ$ at a scan rate of 5° per minute. The optical properties of the samples were analysed by recording the UV-visible diffuse reflectance spectra using Jasco V-650 spectrometer fitted with BaSO_4 coated integration sphere in diffuse reflectance (DRS) mode. The particle morphology of the BWO sample were studied by taking Field Emission Scanning Electron Micrographs using a Nova NanoSEM microscope model FEI operating at an acceleration voltage 15 kV. Transmission electron micrographs (TEM) of the BWO-AC material was recorded using JEM-2100 HRTEM equipment using carbon coated copper grids. The specific surface area of the BWO materials was determined by BET method using N_2 adsorption/desorption at 77K on an AUTOSORB 1 Quantachorme instrument.

2.3. Degradation of Congo-Red dye

The photocatalytic property of Bi_2WO_6 was evaluated for the degradation of congo red dye (CR) under visible light irradiation in aqueous media. In a typical experiment, 100 mL of 10^{-5} M dye solution was taken to which 50 mg of the catalyst was dispersed by sonication for 10 minute under dark condition. To obtain adsorption desorption equilibria, the dye solution containing the dispersed catalyst particles was stirred in dark for further 30 minutes before it is exposed to the visible light source. The dye solution was irradiated using a 125 watt Hg vapour lamp. After equal interval of time, 2 ml of the solution was taken out of the reaction mixture and centrifuged at 6000 rpm for 10 minutes to remove the catalyst particles. The concentration of dye in the supernatant was analysed by UV-visible spectroscopy. In order to optimize the degradation reaction parameter, catalyst obtained using different synthetic methods, the catalyst amount, concentration of starting dye solution and the irradiation time was varied.

CHAPTER 3

RESULT AND DISCUSSION

3.1 Characterization of the Bi_2WO_6 photocatalysts

The XRD profile of Bi_2WO_6 material synthesized by amorphous citrate method and urea hydrolysis method are shown in *figure 1*. The dominant peaks at 2θ value 28.3, 32.7, 47.1, 55.8, 58.5 degree with d spacing value 3.14, 2.62, 1.92, 1.64, 1.57 corresponds to the orthorhombic phase of Russellite Bi_2WO_6 (JCPDS 79-2381). The observed XRD peaks corresponds to reflection from the (131), (002), (202), (133) and (262) planes of Bi_2WO_6 . In case of amorphous citrate method (AC) phase pure Bi_2WO_6 is obtained.

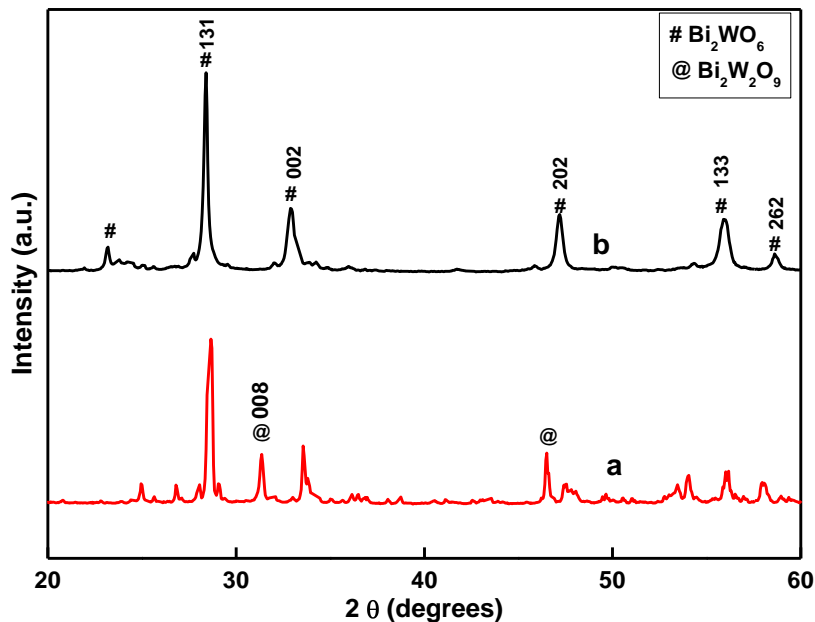


Figure 1. XRD profile of (a) BWO-UH and (b) BWO-AC materials.

For BWO-UH sample, in addition to the peaks corresponding to Bi_2WO_6 russellite phase, a less intense but well defined XRD peak is observed at 2θ value of 31.3° which corresponds to the reflection from (008) plane of $\text{Bi}_2\text{W}_2\text{O}_9$ (JCPDS 33-0221). The XRD study indicated that the BWO-UH system contains mixed phase system with Bi_2WO_6 as major and $\text{Bi}_2\text{W}_2\text{O}_9$ as minor phase. In amorphous citrate process, citric acid has been used as ligand, which can coordinate to the metal ions resulting in a homogeneous distribution of the precursor metal ions in the reaction mixture. Where as in case of urea hydrolysis method, the liberated ammonia from urea can hydrolyze the metal ions into the corresponding hydroxides. The subsequent calcination of these precursor material yield the complex oxide phase. The ligation property and the evolved heat during calcination play a very crucial role in deciding the phase purity and crystallinity of the material. The particle size of the BWO material calculated using Scherrer equation ($D = 0.9\lambda/\beta\cos\theta$; β = full width at half maxima, D = volume average crystallite size, λ = wavelength of X-ray radiation) is found to be about 8-10 nm.

The UV-Visible DR spectra of BWO material are presented in [Figure 2](#). The optical absorption features of BWO-AC and BWO-UH is nearly similar.

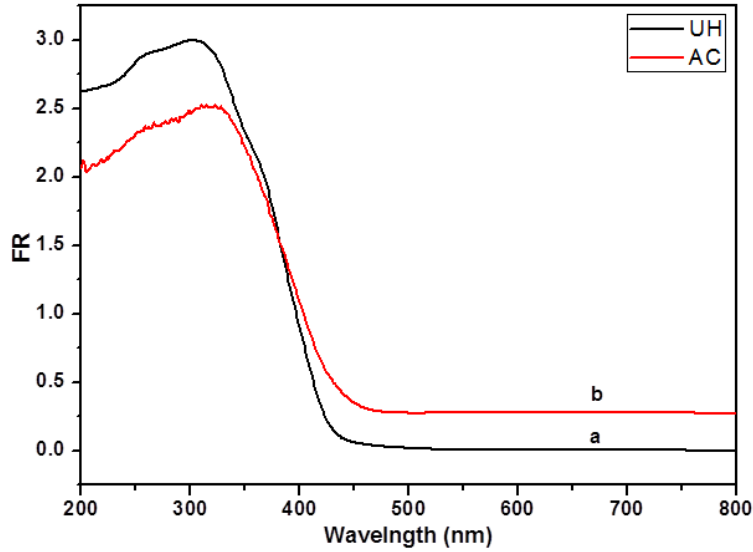


Figure 2. UV-Vis-DRS spectra of (a) BWO-UH and (b) BWO-AC materials.

However, the absorption edge for BWO-UH and BWO-AC materials appears at 450 nm and 470 nm, respectively. The band gap of the BWO material is calculated from the plots of $[F(R) \cdot hv]^2$ as a function of photon energy (Tauc plot) (figure 3).

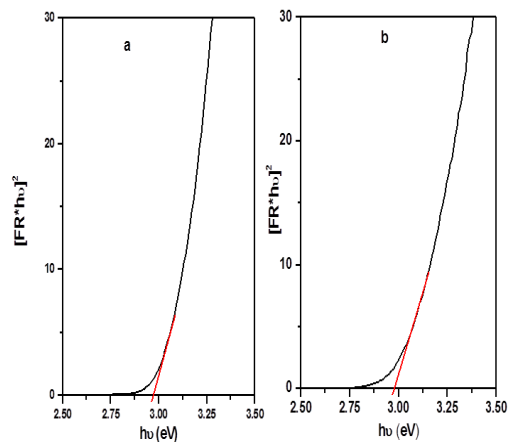


Figure 3. Plots of $[F(R) \cdot hv]^2$ as a function of photon energy for the (a) BWO-UH and (b) BWO-AC Materials.

The band gap of BWO-UH and BWO-AC materials are found to be 2.92 eV and 2.95 eV respectively. Both the Bi_2WO_6 material shows significant light absorption in the UV-visible region. The band gap observed in this study is slightly higher than the band gap observed for Bi_2WO_6 material synthesized by solid state reaction and other techniques (~ 2.8 eV). The higher band gap obtained for both the BWO-AC and BWO-UH material can be ascribed to the quantum confinement effect due to the presence of small nanoparticles with size less than 10 nm. The steep curves of DR-spectra in both the cases signify that visible light absorption is due to band gap transition rather than transitions from impurity level [15].

The morphological features of the BWO materials have been studied by using field emission scanning electron microscopy. The FESEM image of BWO materials are presented in figure 4.

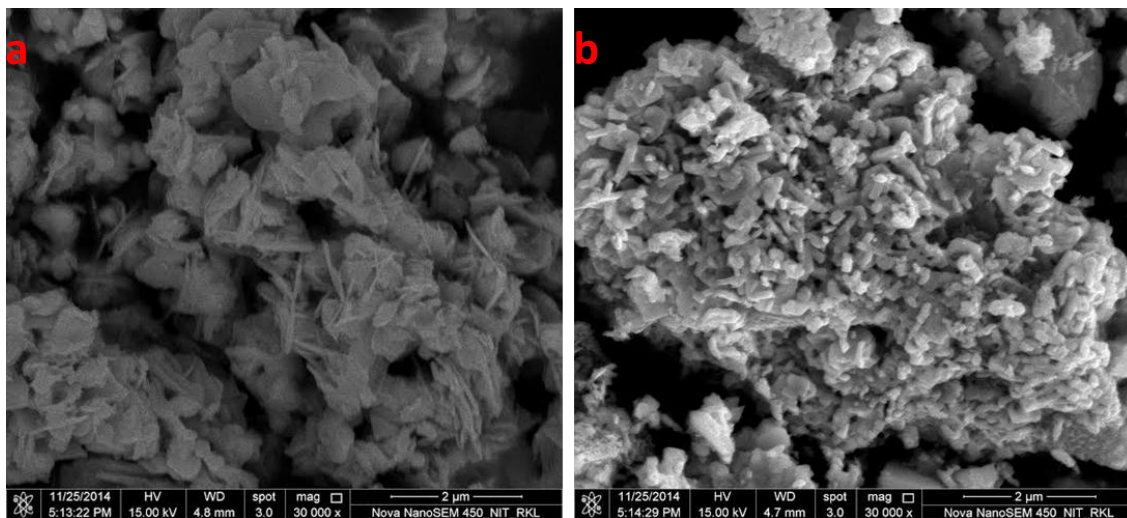


Figure 4. FESEM image of (a) BWO-UH and (b) BWO-AC materials

Both the materials show different morphology. The FESEM image of BWO-UH shows sheets like particles having different shapes and sizes distributed throughout the sample. The BWO-AC

material on the other hand exhibits a mixed particle system with rectangular shape and small near spherical particles in an agglomerated state. The HRTEM image of BWO-AC material is presented in [figure 5](#). Uniformly distributed spherical particles with size in the range of 5-10 nm are present throughout the sample.

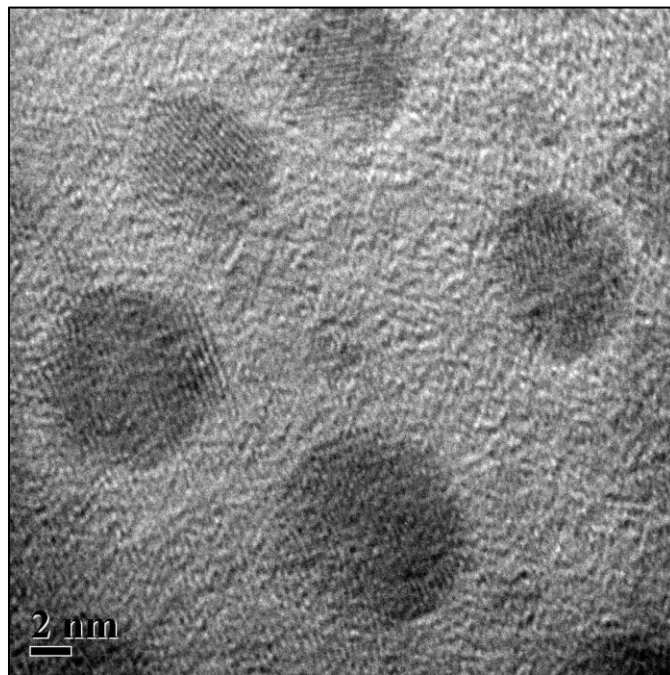


Figure 5. HRTEM image for BWO-AC material.

The surface area of BWO materials was evaluated using N₂ sorption method. The BWO-UH and BWO-AC materials are nonporous in nature and exhibit surface area of 25 m²/g and 35 m²/g, respectively.

3.2 Photocatalytic degradation of congo red dye

The catalytic application of BWO material synthesized via urea hydrolysis and amorphous citrate method have been evaluated by the degradation of congored dye in aqueous solution under visible light irradiation. The changes in the concentration of congored with respect to irradiation time are monitored by examining the variations in maximal absorption in UV–visible spectra at 498 nm. **Figure 6 and 7** represents the concentration changes of conogored at 498 nm as a function of irradiation time during the degradation process in aqueous solution catalyzed by 50 mg each of BWO-UH and BWO-AC materials respectively.

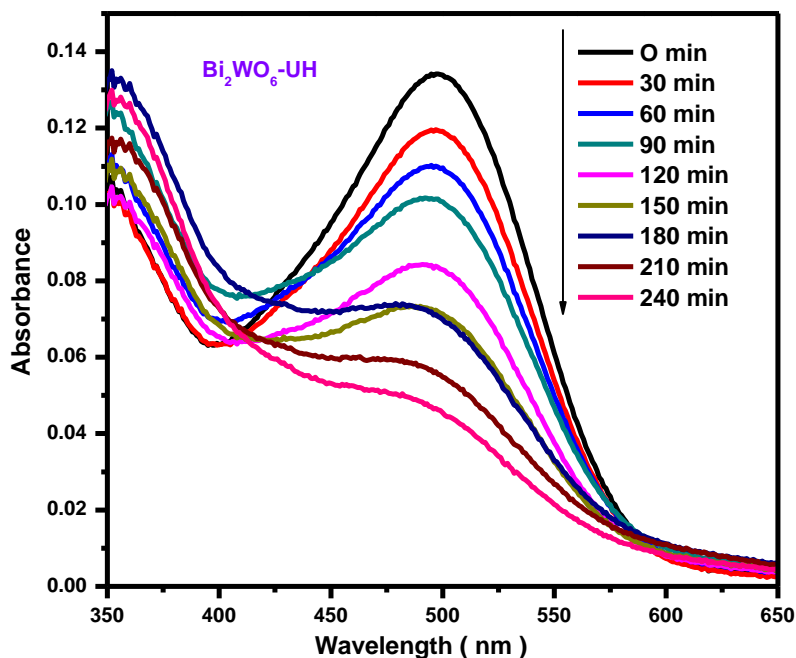


Figure 6. UV-Visible spectra of aqueous solution of congored with respect to different irradiation time under visible light irradiation in presence of 50 mg of BWO-UH catalyst.

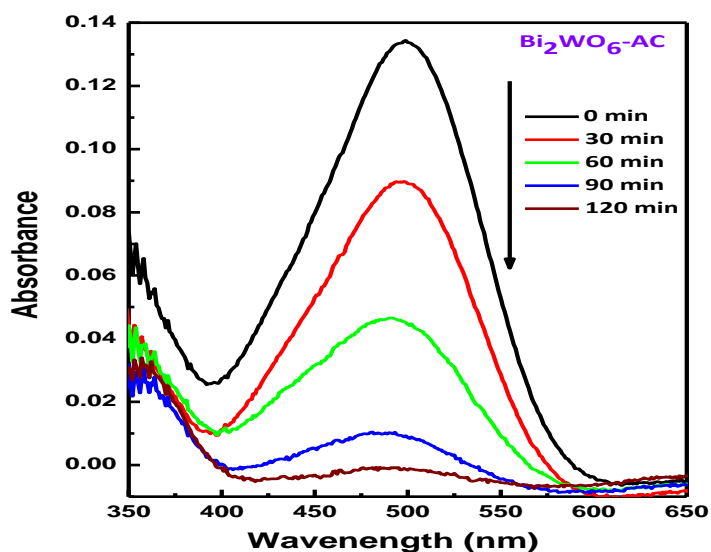


Figure 7. UV-Visible spectra of aqueous solution of congored with respect to different irradiation time under visible light irradiation in presence of 50 mg of BWO-AC catalyst.

In order to confirm that the reaction is truly photocatalytic in nature, blank reaction (without catalyst) as well as reaction under dark condition in presence of catalyst was carried out. No significant changes in the concentration of the dye are observed after 6h of reaction indicating the reaction to be photocatalytic in nature. The percentage degradation of congo red with respect to irradiation time is plotted in figure 8 for both BWO-UH and BWO-AC materials.

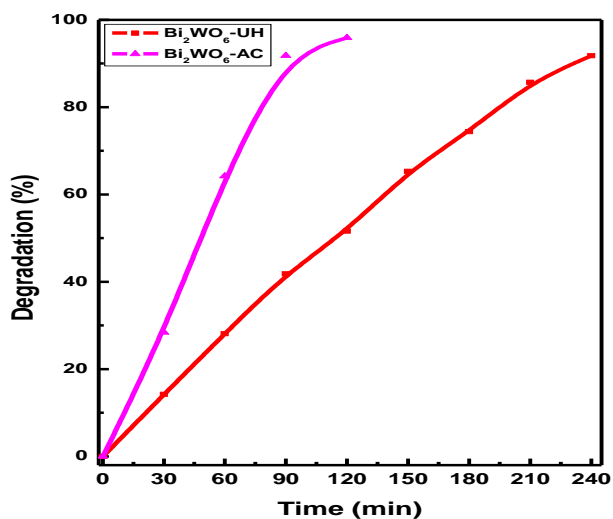


Figure 8. Comparison of the photocatalytic activity of BWO-UH and BWO-AC material for photocatalytic degradation of congored under visible light irradiation.

The BWO-AC material shows greater degradation efficiency for congo red degradation then the BWO-UH material as indicated by the higher initial rate of degradation observed in fig. 8. Within 120 minutes more than 95% of the dye is degraded by using 50 mg of BWO-AC material (Table 1).

Table 1. Degradation efficiency of BWO material with respect to catalyst amount and irradiation time.

Catalyst	Degradation % (60 min)		Degradation % (120 min)		Degradation % (180 min)	
	25 mg	50 mg	25 mg	50 mg	25 mg	50 mg
BWO-UH	16.2	28.1	31.5	51.6	59.6	74.4
BWO-AC	36.1	64.4	62.0	95.8	76.4	97.6

3.3 Conclusions

In this work we have studied the synthesis, characterization and catalytic application of Bi_2WO_6 nanoparticles for degradation of congo red from aqueous sources. The Bi_2WO_6 nanoparticles were synthesized using two novel methods namely amorphous citrate method and urea hydrolysis method. Phase pure Bi_2WO_6 was obtained in amorphous citrate method which have been ascribe to the homogeneous distribution of metal ions in the precursor due to the inherent ligating capacity of citric acid. The Bi_2WO_6 synthesized by urea hydrolysis method contain a mixed phase system with Bi_2WO_6 as major and $\text{Bi}_2\text{W}_2\text{O}_9$ as minor phase. UV-visible spectral study indicated that the Bi_2WO_6 material exhibit significant visible light absorption suitable for photocatalytic applications. The BWO material exhibit quantum confinement effect as manifested from the higher band gap value of ~ 2.9 eV observed in this study. Distinctly different morphology was observed for BWO material depending upon the method of synthesis. The BWO-UH material exhibits flake like particles whereas the presence of BWO quantum dots and rectangular shape particles are observed in case of BWO-AC particles. The particle size of the BWO-AC quantum dots are found to be in the range of 6-8 nm from TEM study. The BWO material synthesized by both methods display promising photocatalytic activity for degradation of congored from aqueous sources under visible light irradiation. The experimental data indicated that the BWO-AC material is more efficient as compare to BWO-UH. In this work we have developed a facile, environmentally friendly, economic and efficient method for degradation of congored using Bi_2WO_6 nanoparticle as photocatalyst.

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