



Photocatalytic Degradation of Evans Blue Dye by $PbTa_2O_6$ Synthesized by Solid State Method

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ABSTRACT

This article reports synthesis of $PbTa_2O_6$ photocatalyst by ecofriendly solid state mechanochemical method with green chemistry approach. The synthesized photocatalyst was characterized by various analytical investigative techniques such as UV DRS, FTIR, XRD, SEM with EDAX and TEM with SAED for structural confirmation. Band gap of synthesized $PbTa_2O_6$ was found to be 4.38 eV and XRD pattern was confirmed as hexagonal crystal phase. SEM shows agglomerated crystalline particles. The photocatalytic property of synthesized catalyst was examined by photodegradation of Evans blue as a representative dye systematically. The degradation follows first order kinetics with rate constant $4 \times 10^{-3} \text{ min}^{-1}$.

Keywords: Photocatalyst; Green chemistry; SEM; TEM; XRD; EDAX

INTRODUCTION

There are several types of dyes used by Indian textile manufacturer. The production of dyestuff and pigment by Indian textile industries is close to 80,000 tonnes. Major part of India is having their bread and butter from textile industry as a result of these the textile industry of India takes up to 80% share of total consumption of dyestuff and pigment [1]. With the growing industrialization and market competition large variety of dyes and chemicals are used to make more and more attractive shades [2]. Waste water containing textile dye is becoming a burning issue regarding water pollution. A considerable concentration of dye found in waste water due to incomplete use and washing. Literature survey shows that, different water treatment methods by different researchers have adopted to minimize water pollution, which includes physical techniques are employed for treatment of waste water such as adsorption [3], membrane filtration, biological technique involving biodegradation [4] and chemical treatment involving coagulation [5], floatation, ion exchange, ultrasonic mineralization and advance oxidation process. Physical method such as adsorption, sedimentation, chemical methods involves, ozonation, biological methods involve use of different microbes for removal of textile dye present in water. Since these dye have complicated obstinate molecular structure above suggested methods are markedly insufficient water treatment technique since most of these technique causes pollution and removal of added chemicals are found difficult.

Mineralization of organic water pollutant using interaction between ultraviolet radiation and semiconductor catalyst has a strong potential as it is widely demonstrated in recent years. Visible light induced photocatalyst have received considerable attention because visible light occupies main part of solar light. Number of metal oxide used as photocatalyst. There are two types of photocatalysis that is homogenous photocatalysis and heterogeneous photocatalysis. In the present study focus is given on heterogeneous photocatalysis which is two phase system, which consist of utilizing the near UV radiation to photoexcite a semiconductor catalyst in presence of oxygen. Homogeneous photocatalysis is an advance oxidation process which uses Hydrogen peroxide (H_2O_2), O_3 and

Fenton's reagent for effective detoxification of pollutants [6]. Advance oxidation process involving heterogeneous photocatalysis is a promising technique for degradation of dyes present in waste water [7]. In this photocatalysis process hydroxyl radical generated possess higher oxidation potential (2.8 eV) compared to other common oxidants like hydroperoxy radical (1.70 eV), Chlorine Dioxide [8]. In photocatalysis it is aimed to produce more and more hydroxyl radicals to efficiently degrade the dye pollutant [9]. Photocatalytic detoxification employs heterogeneous photocatalysis in presence of UV light to achieve mineralization of toxic pollutant [10]. From literature survey in last couple of decades many catalyst like TiO_2 , WO_3 , PbSnO_3 , ZnO , CeO_2 , CdS and ZnS have been significantly used for dye degradation and this compound were used as photocatalyst [11-17]. Now a days researcher are focusing on synthesis of different mixed metal semiconductor photocatalyst which could show significant results for detoxification of dye pollutant. Semiconductor photocatalyst shows different application such as gas sensing, for coating on automobile, fuel cell and also shows magnetic properties [18-20].

After studying the water pollution survey and the important of photocatalysis for removal of dye pollutant there is need to synthesize different photocatalyst and test their activity for dye degradation. In this article PbTa_2O_6 synthesized by simple solid state mechanochemical method using green chemistry approach.

EXPERIMENTAL SECTION

There are several methods which are being used for synthesis of photocatalyst such as Sol gel method, Photo-deposition method, Calcination and organic synthesis methods. All above methods are complicated difficult in operation and cost effective and causes pollution. Solid state mechanochemical method is a green technique, in which no solvent is used and easy to carry out. For this purpose, a solid state mechanochemical synthesis method, with a green chemistry approach was employed. For synthesis of PbTa_2O_6 Starting reagent used were PbO (Cassella Chem, 99.9% purity) and Ta_2O_5 (Chemsworth, CAS No- 13124-61-0, purity 99.9%). For preparation of mixed metal oxide equimolar mixture metal oxides taken and grinded with mortar and pestle to acquire fine powder which was further calcined at 500°C for 4 hours. Again the obtained powder was further calcined at 800°C following milling after each interval of 3 hours. The calcination was continued for next 20 hours with milling. At the end mixture was heated up to terminal temp.

Photocatalytic degradation of Evans blue dye by PbTa_2O_6 is conducted under specially designed photoreactor containing UV-visible light source. In quartz glass tube Evans blue dye solution containing catalyst was exposed to the UV-visible light. Decrease in absorbance with time was recorded on Equiptronics model no EQ-825 UV-visible spectrophotometer. To study effect of dye concentration on catalyst, different concentration of dye solution with same amount of catalyst was studied. Also to study the effect of catalyst concentration, different amount of catalyst with same concentration of dye solution was utilized.

RESULTS AND DISCUSSION

The photo-absorption of photocatalyst depends on the mobility of electron hole pairs, which determines the probability of electron and holes to reach reaction sites on the surface of photocatalyst. The optical property of synthesized product was studied by using Perkins Elmer -950 λ UV spectrophotometer. The catalyst was scanned over the wavelength range of 200 to 800 nm. Figure 1 represents the UV-Diffused spectrum of synthesized PbTa_2O_6 catalyst and it shows adsorption edge cut off at 283 nm with corresponding band in visible region. The band gap energy for synthesized compound was found to be 4.46 eV.

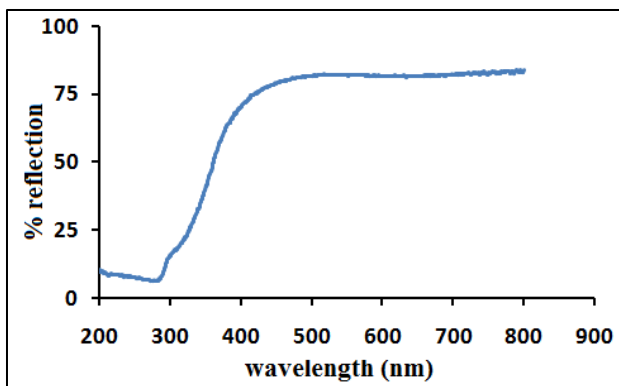


Figure 1: UV-visible diffused reflectance spectra of synthesized PbTa_2O_6

The vibrational frequency of synthesized catalyst was studied by Shimadzu FTIR 8400S, in the range of 400-4000 cm^{-1} . The infrared absorption spectrum of synthesized PbTa_2O_6 catalyst is shown in Figure 2. Vibrational frequency band at 442 and 517 cm^{-1} indicates the presence of Pb-O and frequency around 600 cm^{-1} indicate the presence of Ta-O vibrations PbTa_2O_6 .

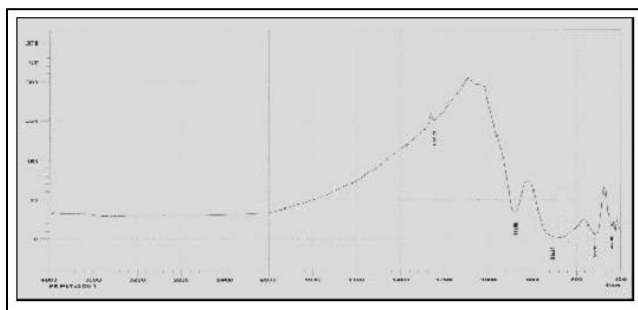


Figure 2: Infra-red spectra of PbTa_2O_6

The structural properties of material was studied by using X-ray diffractometer, Rigaku-D/MAX 2500 with Cu-K α radiation having $\lambda = 1.5406 \text{ \AA}$. X-ray powder diffractogram matches of synthesized PbTa_2O_6 shown in Figure 3. The d-line Pattern of X-ray diffractogram matches well with standard JCPDS data card no.20-0598. The peaks at scattering angles (2θ) 28.54, 43.09, 52.21, 57.54 and 57.80 corresponding to the reflection planes 300, 321, 413, 006, 333 confirming hexagonal phase of synthesized compound.

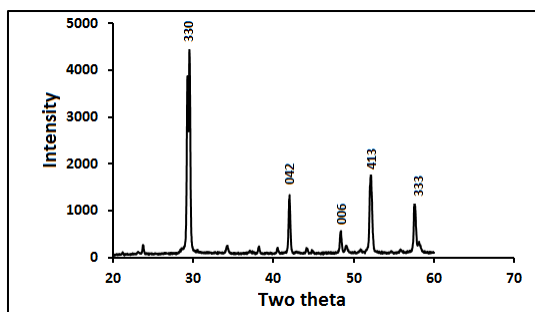


Figure 3: XRD analysis of synthesized PbTa_2O_6

The surface morphology and associated chemical composition of synthesized photocatalyst was checked by using a scanning electron microscope (SEM) FEI company QUANTA 200-3D coupled with EDAX. It is clear from Figure 4 that very fine particles of PbTa_2O_6 are joined with each other forming cluster of particles. It appears the polycrystalline nature of PbTa_2O_6 . The EDAX data furnishes elemental conformity with the respective molar

proportions taken for synthesis. The observed mass percentage of Ta in PbTa_2O_6 is 54.29%, Pb in PbTa_2O_6 is 31.22% and O in PbTa_2O_6 is 14.47% as expected.

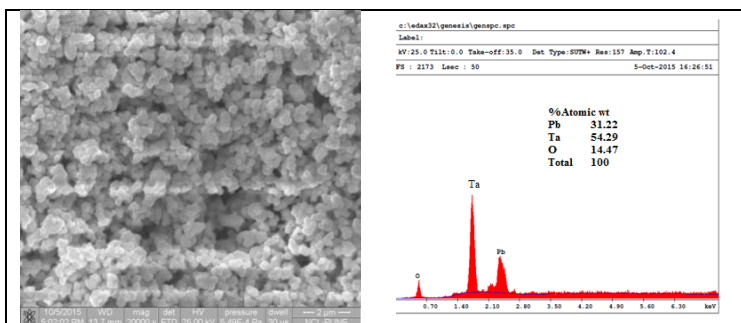


Figure 4: SEM image and EDAX analysis of synthesized PbTa_2O_6

The TEM image along with selected area of diffraction pattern (SAED) recorded for the sample corresponding to the PbTa_2O_6 is shown in Figure 5. The dark spot in SAED Micrograph can be alluded to PbTa_2O_6 nanoparticles. The SAED Pattern associated with such spot reveals occurrence of PbTa_2O_6 which is in good agreement with XRD data. From the TEM image it is clear that, the average particle size of crystallites 107 nm. The dark spot at different d line matches with XRD pattern. The dark spot in SAED at distance 107 nm well matches with planes of XRD pattern confirming synthesis of PbTa_2O_6 as hexagonal phase.

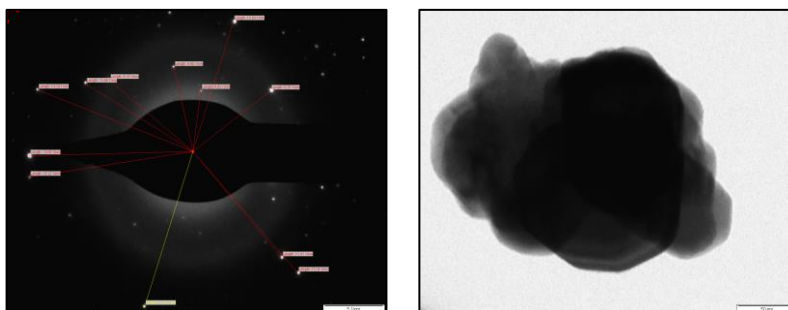


Figure 5: TEM images and SAED analysis of synthesized PbTa_2O_6

Photodegradation of Evans Blue Dye

Photocatalytic property of synthesized catalyst was evaluated by studying photodegradation of Evans Blue dye. Evans blue dye used for dyeing of textile like tissue, cotton and silk. The structure of Evans blue dye is shown in Figure 6, with molecular formula $\text{C}_{34}\text{H}_{24}\text{N}_4\text{O}_{14}\text{S}_4$ and molecular weight 960.817 g. The dye is a water soluble shows maximum absorbance at 610 nm. Initially 0.2 g of catalyst was stirred in 20 ppm dye solution and exposed to the UV-visible light in photoreactor. The decrease in absorbance with time shows that the degradation of Evans blue dye and it was recorded on spectrophotometer. The same procedure was adopted for 0.3 and 0.5 g catalyst to study effect of catalyst amount on degradation. The degradation of Evans blue dye is depicted in Figure 7. The result implies that the photodegradation rate is faster with 0.5 g photocatalyst this may be higher number holes and electron ejected on exposure to the light. The Figure 8 represents different concentration of dye solution with same amount of catalyst.

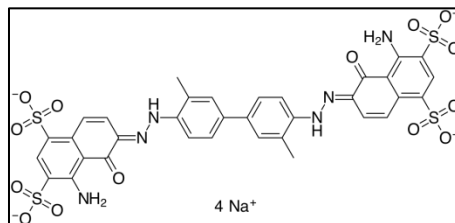


Figure 6: Structure of Evans blue dye

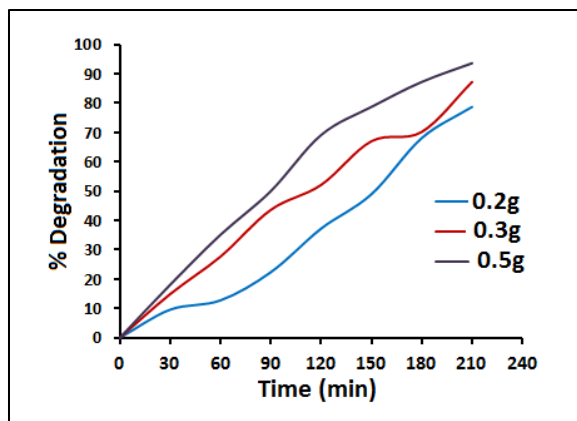
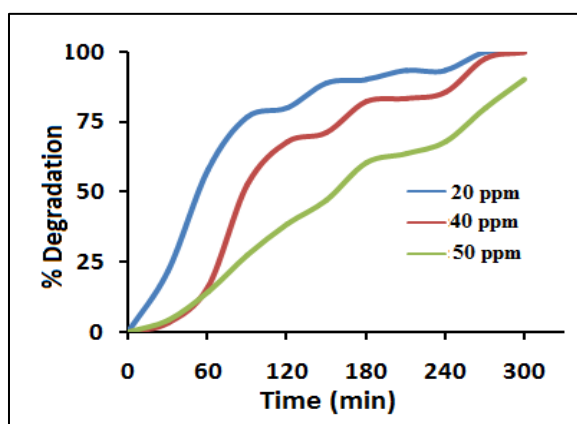
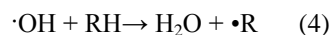
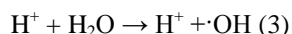
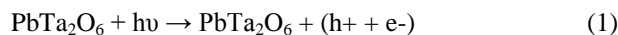
Figure 7: Effect of catalyst PbTa₂O₆ concentration on Evans blue dye degradation

Figure 8: Effect of dye concentration on degradation

The mechanism of photodegradation can be explained as follows. When aqueous suspension of the photocatalyst PbTa₂O₆ was irradiated with light energy greater than the band gap energy of the semiconductor oxide, conduction band electrons (e⁻) and valance band holes (h⁺) are formed. The photogenerated electrons react with absorbed molecular O₂ reducing it to superoxide radical anion O₂⁻, and photogenerated holes can oxidize organic molecules directly or the OH and the H₂O molecule adsorbed at catalyst surface to OH radical. These will act as strong oxidizing agent and can easily attack on organic molecule or those located close to the surface of the catalyst, thus leading to complete mineralization, Equations 1-5 represent the probable pathway of the degradation.



The photodegradation follows first order kinetics with rate constant 4×10^{-3} per min as shown in Figure 9.

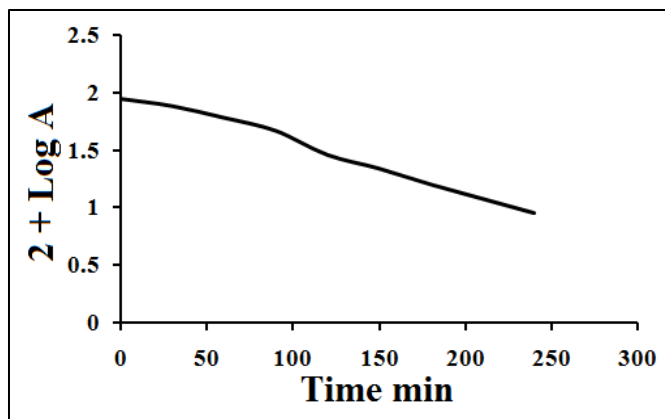


Figure 9: Kinetic study of degradation of Evans blue dye

CONCLUSION

Photocatalyst PbTa_2O_6 successfully synthesized by solid state mechanochemical synthesis with green chemistry approach. The synthesized catalyst is hexagonal crystallite phase having average particle size 107 nm. The band gap energy of synthesized catalyst is found to be 4.38 eV. The photocatalyst possess good photocatalytic activity as Evans blue dye effectively degraded and result resembles with other researcher [21]. The degradation follows first order kinetics with rate constant 4×10^{-3} per min.

ACKNOWLEDGEMENT

The authors are thankful to B.C.U.D, Savitribai Phule Pune University for financial support to carry out this research work. The authors are thankful to IISER Pune, NCL Pune, SAIF, IIT Bombay for valuable analysis.

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