Visible light induced photocatalytic degradation of azo dye by Bi_2O_3 nanoparticles synthesized using greener route

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Abstract-The present investigation describes the photocatalytic treatment of methyl orange dye using Bi2O3 nanoparticles synthesized by greener way. A novel monoclinic α- Bi2O3 was synthesized by adopting the sustainable green synthetic strategy from the source of rambutan (Nephelium lappaceum L.) fruit peel extract as a natural ligation agent. The bio synthesized product was characterized using X-ray diffraction studies (XRD), ultra violet-visible diffuse reflectance spectra (UV-DRS), field emission scanning electron microscope (FE-SEM), energy dispersive X-ray spectroscopy (EDX) and ultra violet-visible absorption spectrophotometer (UV-Abs). The photocatalytic activity of bio synthesized α- Bi2O3 was investigated using methyl orange dye under artificial visible light illumination. The results revealed that the bio synthesized product proved significantly a better activity against azo dye. The plausible mechanism for the formation of Bi2O3 nanoparticles with rambutan peel extract was also proposed.

Keywords: Bi2O3 nanoparticles, greener route, photocatalytic activity, visible light, azo dye

1 Introduction

In recent years, textile dying operations discharged untreated effluent containing a complex mixture of colored and toxic compounds into the waterways and create both environmental and aesthetic problems. To resolve these environmental concerns, various endeavors have been carried out via photocatalytic oxidation technology as a means of wastewater remediation process. Photocatalytic processes are of pervasive interest because photo assisted catalytic degradation assures to be a versatile, economic, environmentally benign technology [1]. In this technology, light and catalysts are necessary to bring out a chemical reaction. The catalysts characterized by semiconductors usually are metal oxides [2].

Among the various metal oxides, Bi_2O_3 is one of the non-TiO_2 semiconducting metal oxides and proves the better photocatalytic activity under visible light irradiation. Bismuth oxide has excellent optical and electrical properties such as wide band-gap (2.8 eV), high refractive index, high dielectric permittivity and high photoconductivity [3].
Further, Bi_2O_3 has been extensively used in gas sensors, photovoltaic cells, optical coatings, fuel cells, super capacitors and photocatalysts, etc [4]. There have been a large number of synthetic pathways were explored to produce Bi_2O_3 nanoparticles such as sonochemical synthesis[4], Microwave assisted method[5], hydrothermal method[6], chemical deposition method[7], template-free aqueous method[8], ultrasonic assisted hydrothermal method[9].But, increasing environmental concerns over chemical synthesis have resulted in attempts to develop Bio synthetic approaches. One of them is the synthesis of nanoparticles using plant extracts [10].

This work highlights the synthesis of Bi_2O_3 nanoparticles from the bio source rambutan (Nephelium lappaceum L.) fruit peel extract [11] and their photocatalytic activity was screened by the photocatalytic decomposition of azo dye like methyl orange(MeO) under visible light illumination .

2. Materials and Methods

2.1 Materials

The Nephelium lappaceum L. (rambutan fruit) was procured from local market at Kanchipuram, Tamilnadu, India. Bismuth nitrate [Bi $(NO_3)_3.5H_2O$], Ethanol and Methyl orange (MeO) were purchased from Merck chemicals Ltd., India without further purification. Double distilled water was used throughout the experiment. The structure and absorption spectrum of methyl orange was shown in Fig. 1.

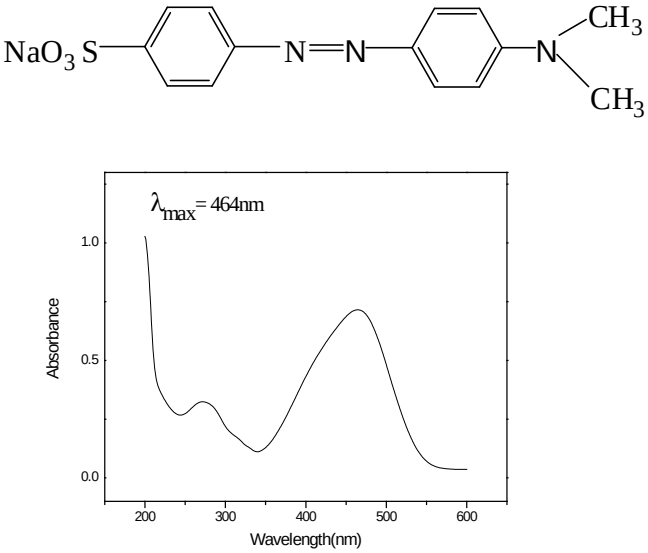


Fig.1 (a) Structure of Methyl Orange

2.2 Preparation of the Extract

Fresh peels of Nephelium lappaceum L. were washed thoroughly with running water and subsequently cut into small pieces and placed in a hot air oven at 50°C until complete dryness. About 3 g of finely dried Nephelium lappaceum L. peels were boiled with 40 ml double distilled water and 20 ml ethanol (2:1) for 10 min. The temperature was maintained at 80°C during extraction. The extract obtained was filtered through Whatman No. 1 filter paper and the filtrate was collected in 100 ml conical flask and stored in refrigerator for further use. [10]

2.3 Bio-synthesis of Bismuth Oxide Nanoparticles

Initially, 0.1 M aqueous solution of bismuth nitrate [Bi $(NO_3)_3.5H_2O$] was prepared. Later, 10ml of Nephelium lappaceum L. extract was added drop wise to 50ml of 0.1M bismuth nitrate pentahydrate and stirred at 80°C for 2h. The particles formed after adequate time of stirring were collected by centrifugation at 10000 rpm for 10minutes. Later, the centrifuged particles were washed with water and again subjected to centrifugation at 5000 rpm for 10 minutes. The centrifuged sample was dried in an air oven and powdered using mortar and pestle. This powdered sample was calcined in a muffle furnace at 500°C to get pure Bi_2O_3 nanoparticles.

2.4 Instrumentation

A powder X-ray diffractometer (JEOL IDX 8030 instrument operating at 40 kV with a current of 30mA using Cu Kα) was used to determine the crystalline phases present in the sample. The optical studies were carried out with diffuse reflectance spectrophotometer (DRS) Shimadzu (UV 2450) UV–VIS– instrument in the wavelength range of 200–800 nm using BaSO4 as standard .The surface morphology of the powder was observed using a field emission scanning electron microscope (FESEM-SUPRA 55) - CARL ZEISS, GERMANY. Degradation of MeO solution was recorded from SHIMADZU UV-1650 PC UV-Visible spectrophotometer.

2.5 Photocatalytic activity studies

The photocatalytic activities of as synthesized samples were analyzed by 100ml of 10 ppm concentrated solution of methyl orange under artificial visible light illumination. Prior to illumination, the solution was magnetically stirred for 45 min to reach adsorption/desorption equilibrium. Then, the solution was illuminated using 150W Tungsten lamp with air bubbling in a photo reactor. During the illumination, 3ml reaction solution was withdrawn using Millipore syringe periodically and measured the absorbance at 464nm using ultra violet-visible spectrophotometer. At the end, decolorisation efficiency was calculated using the formula,

$$\frac{(A0-At)}{A0} \times 100$$

Where A_0 is the absorbance before irradiation and A_t is the absorbance at time t [12].After decolorize the methyl orange dye, degradation efficiency was measured using COD values.

The chemical oxygen demand (COD) was measured by dichromate method as follows: 10.0 mL of potassium dichromate solution (0.250 mol/L) and 10.0 mL of dye solution before or after treatment were poured into a vessel with a reflux apparatus. After switching on the cooling water, 30 mL of silver sulfate/sulfuric acid was poured into the vessel. Turn on the heater and keep the solution boiling for 2 h. Wash the condensator with 20 mL of deionized water, dilute the solution to 140mL, and cool it to room temperature. Ammonium iron (II) sulfate was used to measure the residual dichromate quantitatively using 1, 10-phenanthroline as an indicator. The solution quickly turned from yellow to cyan, and to mahogany finally indicating the end of titration. The volume of consumed ammonium iron (II) sulfate was recorded as V2. The COD was calculated according to Equation,

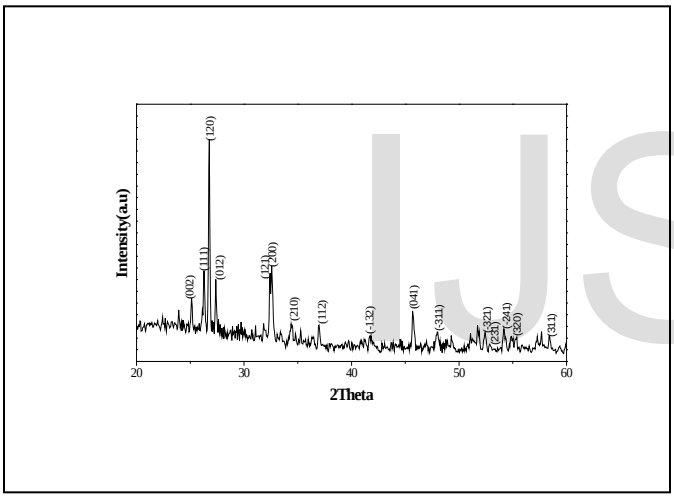
$$COD\ (mg/l) = [C\ (V1-V2) \times 8000]/V0$$

Where C is the concentration of ammonium iron (II) sulfate, mol/L; V1 is the volume of consumed ammonium iron (II) sulfate in blank experiments (mL) and V0 is the volume of a sample (mL).

3. Results and Discussion

3.1. X- ray diffraction studies

Fig.2 shows the X-ray diffraction pattern of bio synthesized Bi_2O_3 nanoparticles. Several dominant 2θ peaks were observed in Fig.1 (a). According to JCPDS data (76-1730), the distinct diffraction peaks at 2θ = 27.39 °C, 33.25 °C, 33.03 °C, 26.90 °C and 28.01 °C can be well indexed to the monoclinic phase of crystalline α - Bi_2O_3 (1 2 0), (2 0 0), (1 2 1), (1 1 1) and (0 1 2) crystal planes of Bi_2O_3 . Any other characteristics peaks are not found, indicating that the as-prepared Bi_2O_3 is pure. The strong and sharp diffraction peaks implied that the as- prepared Bi2O3 nanoparticles possess good crystalline nature. The size of the nanoparticles was calculated through the Scherer's formula, $D=0.94\lambda/\beta \cos\theta$, Where D is the average crystal size, β is the half-height width of the diffraction peak, θ is the diffraction angle, and λ is the X-ray wavelength (0.1541 nm).The average particle size of the bio synthesized Bi_2O_3 was 73nm .



3.2. Morphological Studies

The size and morphology of the nanparticles was studied using field emission scanning electron microscopy (FESEM). SEM analysis of bio synthesized Bi_2O_3 nanoparticles was shown in Fig. 3, which depicts the particles were agglomerated and peal shaped like structure having smooth surface with a thickness of 84.12 nm, which has a very large specific surface area and this, may lead to augmenting the optical properties [13] and it might be beneficial for its photocatalytic activity improvement because large surface area can enhance more photon absorption [14].

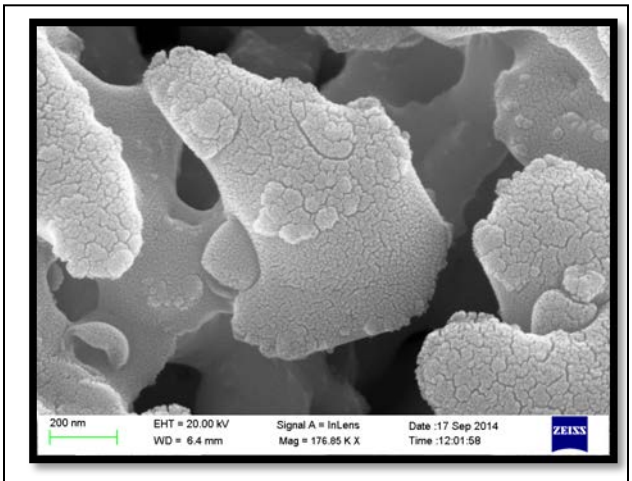


Fig.3 FESEM image of Bio synthesized Bi2O3

3.3. Elemental analysis

Fig. 4 shows the Energy Dispersive X-ray (EDX) spectrum of as prepared bio synthesized Bi_2O_3. The spectrum reveals only the presence of Bi and O peaks which indicates the presence of pure Bi2O3 without any impurities. The small peak rises at 2.1-2.2 keV due to gold, which is coated on the sample before recording SEM.

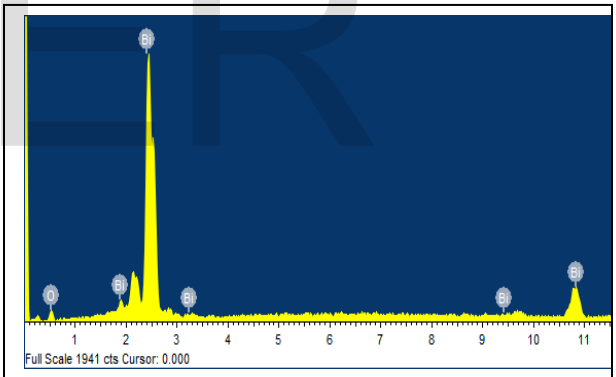


Fig.4 EDX spectrum of Bio synthesized Bi2O3

3.4. Optical Studies

The optical property of the bio-synthesized Bi2O3 was investigated using UV–Vis diffuse reflectance spectroscopy, which is shown in Fig. 5. It clearly shows that, their absorption edges are located at 443 nm for bio-Bi2O3, suggesting that the photocatalysts can be excited by visible light irradiation. The color of the photocatalyst is pale yellow, which accord with its absorption spectrum. The strong absorption spectrum reveals that the visible light absorption is not due to the transition from the impurity but due to band-gap transition.

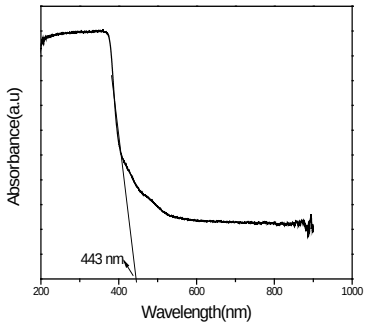


Fig.5 UV- DRS spectrum of bio synthesized Bi_2O_3

The band gap energy of the photo catalyst was determined from the following formula, Eg = 1240/ λ eV, Where, Eg is the band gap energy (eV), his Planck's constant (6.626 x 10-34Js), C is the light velocity (3 x 108 m/s) and λ is the wavelength (nm) [15].According to this formula, the band gap energy of bio synthesized Bi2O3 was estimated to be 2.6 eV respectively, similar values were reported in literatures[7,11].

3.5 Photocatalytic degradation of Methyl orange dye

The photocatalytic activity of bio synthesized Bi2O3 samples was analyzed by monitoring the degradation of the methyl orange dye. A dark experiment was carried out to confirm that the photo-degradation reaction did not proceed without the presence of the light. Fig.6 shows the decolorisation efficiency percentage of methyl orange aqueous solution at various time intervals in the presence of Bi2O3 sample. It reveals the bio-synthesized Bi2O3 nanoparticles showed 94.80% degradation of methyl orange aqueous solution in 240 mins of the reaction.

The surface area, morphology and particle size play a decisive role in photocatalytic activity studies. The plate structured bio synthesized Bi_2O_3 nanoparticles may have high surface area. It is reported that the high surface area of photocatalyst enhances dye adsorption and succeeding photocatalytic activity.

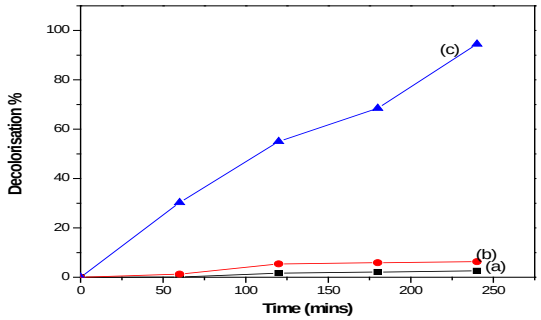


Fig.6 Degradation Efficiency of (a) Dye +visible light only (Blank) (b) Dye + Bio synthesized Bi_2O_3 only (Dark) (c) Dye+Bio synthesized Bi_2O_3+visible light

3.6 Mineralization Studies of dye

The COD test is an effective technique to find out the organic strength of water and COD measurement in terms of quantity of oxygen required for the oxidation of organic matter present in the dye into CO_2 and H_2O.The COD values were calculated before and after photocatalytic treatment. While the visible light induced photocatalytic treatment of azo dye, the decrease in COD values from 88.8 mg/l to 14.1 mg/l confirms the mineralization of MeO dye along with color removal was observed.

4. Conclusion

Bi_2O_3 is prepared using environmental green synthetic method and their structural, optical properties and degradation studies are studied. With the addition of plant extract act as a ligation agent as well as capping agent. The XRD pattern confirms the formation of Bi_2O_3, specifically pure monoclinic α- Bi_2O_3 obtained. The optical properties confirms, the adsorption edges located at 443 nm, suggesting that the photocatalysts can be excited by visible light irradiation. To analyze the photocatalytic activity of α- Bi_2O_3, photodegradation of methyl orange under visible light was used as a model reaction. The results indicate that α-bismuth oxide is potential for effective degradation.

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