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SYNTHESIS AND CHARACTERIZATION OF BiOI AND ITS APPLICATION IN WASTE WATER TREATMENT

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Abstract

The main objectives of the present research work are to synthesize BiOI photocatalyst by simple solvothermal method and to characterize the synthesized BiOI photocatalyst by the Fourier Transform Infrared (FT-IR) spectroscopy, X- ray Diffractometer (XRD) and Field Emission Scanning Electronic Microscopy (FE- SEM). Also, the photocatalytic performance of BiOI compound towards the photodegradation of Rhodamine B, Methylene Blue and Acid Orange 7 dyes under visible light irradiation have been investigated and reported. The maximum degradation was witnessed for Acid Orange 7 dye when compared to the other two dyes. A suitable photocatalytic degradation mechanism has been proposed based on the observed results.

Keywords: BiOI photocatalyst, Photodegradation, Solvothermal.

1. Introduction

The Earth is a watery place. About 71 percent of the Earth's surface is water-covered, and the oceans hold about 96.5 percent of all Earth's water. Water also exists in the air as water vapour, in rivers and lakes, in icecaps and glaciers, in the ground as soil moisture and in aquifers. Of all the water on Earth, just 3% is fresh water. Fresh water is vital to life and yet it is a finite resource.

When harmful microorganisms and chemical substances contaminate bodies of water, they cause the water quality to decrease and potentially make it toxic. Water pollution is the presence of chemical, physical, or biological components or factors producing a condition of impairment of given water body with respect to some beneficial use. It happens when chemicals or dangerous foreign substances are introduced to water, including chemicals, sewage, pesticides and fertilizers from agricultural runoff, or metals like lead or mercury [1]. Water pollution due to waste effluents of the textile industry is seriously causing various health problems in humans. Among the chemical pollutants, organic dyes, are one of the major contaminants of industrial wastewater. According to a recent survey, textile dyeing is the second-largest pollutant of water worldwide and the fashion industry produces 20 percent of the world's wastewater [2].

When water is polluted and decontamination becomes necessary, the best purification approach should be chosen to reach the decontamination objectives. A purification process generally consists of five successive steps.
(1) preliminary treatment or pre-treatment (physical and mechanical)
(2) primary treatment (physicochemical and chemical)
(3) secondary treatment or purification (chemical and biological)
(4) tertiary or final treatment (physical and chemical) and
(5) treatment of the sludge formed (supervised tipping, recycling or incineration) [3].

And one of the recently emerged way to treat the waste water is by means of photocatalysis. It is a low-cost and environment friendly technology and has demonstrated a significant potential for water pollution purification; it has received extensive attention in recent decades. The key is that a large number of photocatalysts have been developed. And one of them is Bismuth Oxyiodide which is proven to be a useful candidate in treatment of waste water polluted with organic dye.

Bismuth oxyhalides (BiOX) has drawn extensive interests of researchers. BiOX compounds with layered tetragonal matlockite structures represent good optical, electrical and magnetic properties, and have been widely applied in the potential fields of catalysis, ionic conductors, photochromic devices, ferroelectric materials, pigments and solar cells. Especially, BiOX perform as a family of promising photocatalysts due to their good photocatalytic activities under both ultraviolet and visible light irradiation [4]. The large space of Bismuth oxyiodide layered structure can polarize the related atoms and orbitals. The induced dipole can separate the hole-electron pair efficiently and promote photocatalytic reactions. On the other hand, BiOI has an indirect-transition band-gap, so the excited electron has to travel a certain k-space distance to be emitted, which reduces the recombination probability of the excited electron and the hole.

BiOI photocatalysts of various morphologies have been successfully fabricated, such as BiOI nanoparticles, BiOI

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nanoplates and BiOI 3D microspheres were synthesized. They all exhibit good photoactivity under visible light irradiation. For these attributes, BiOI is considered an excellent visible light photocatalyst [5].

2. Experimental session

2.1 Materials and methods:

Bismuth nitrate pentahydrate ($Bi(NO_3)_3.5H_2O$, 99.5%), was obtained from Qualigens chemicals, India. Potassium iodide (KI, 99%) and Acid Orange 7 were acquired from Sigma-Aldrich. Rhodamine B and Methylene Blue were procured from S.D. Fine chemicals Ltd., India. All chemicals were of analytical grade and were used without further purification.

In brief, 2.5 mmol Bi(NO3)3·5H2O and 2.5 mmol KI was uniformly dispersed in 25 mL and 20 mL of ethylene glycol to make solution A and solution B respectively. Then solution B was dripped into solution A , with constant stirring for 30 min. After which, the obtained yellow solution was transferred into the 50 mL Teflon-lined autoclave at 120° C for 16 h. Finally, the obtained product was rinsed with deionized water and filtered and then dried at 80° C for 4 h.

3. Results and discussion

3.1 XRD Studies

XRD analysis was carried out to investigate the phase structures of the catalysts. The XRD pattern of the BiOI photocatalyst is shown in Fig. 1. The diffraction peaks in the Fig. 1 at 2θ for 29.6°, 33.1°, 43.6°, 55.1°, corresponds to (102), (111), (113) and (212) diffraction planes respectively. The XRD pattern of BiOI is in good agreement with the standard data (JCPDS 10-0445) with tetragonal phase. The estimated lattice constant of 3D-BiOI with a tetragonal crystal structure is found to be a = b =3.994 Å and c =9.149 Å respectively. The purity of the prepared material was confirmed by the absence of peaks related to impurity phases [6,7].

3.2 FT-IR Spectroscopy Studies

The functional groups and chemical bonding of the synthesized material are investigated by FTIR spectroscopy. The FTIR spectra of BiOI is presented in Fig. 2. In the FTIR spectrum of BiOI, the strong absorption was mainly located in the 400–700 cm^{-1}, as a result of the stretching vibrations of Bi–O, Bi–O–I bonds [8]. The peak positioned at 489 cm^{-1} may be assigned to the symmetrical vibration frequency of the Bi-O bond. The sharp and intense peak at 1398 cm^{-1} is due to the O–H deformation vibration of the tertiary C–OH group. This peak might be due to the adsorption of ethylene glycol on the catalyst surface during the fabrication process. Besides, the sharp band at 1616 cm^{-1} and the broadband at 3470 cm^{-1} can be attributed due to the bending (δ (O-H)) and stretching (ν (O–H)) frequencies of the hydroxyl group [7].

3.3 Morphological Analysis

The morphological nature of the solvothermally synthesized BiOI photocatalyst was analyzed by FE-SEM**.** The different magnifications of the SEM images of BiOI can be seen in Fig.3 (a,b) which displays the 3D- nanoflower morphology of BiOI photocatalyst and it is composed by the compilation of many 2D nano-sheets, to form 3D nano flower like structure. The surface state and structural morphology of photocatalysts can play vital roles in enhancing the PCA. The above results of the FESEM analysis indicates that the BiOI sample with well-structured surface was expected to favour effective charge carrier separation, leading to improved towards PCA removal. Consequently, the recombination is decreased due to the localized features of the surface [9,10,11].

3.4 Photocatalytic Degradation Studies

The photocatalytic degradation of the synthesized BiOI photocatalyst was examined by the degradation of various dyes RhB, MB and AO7. The degradation experiments were executed using 250 W tungsten halogen lamp as visible light source. In this experiment, 75 mg of the photocatalyst sample was dispersed in 75 mL of dye solution.

Also, the absorption studies of the photocatalyst on RhB, MB and AO7 were carried out in the dark to identify the time taken to reach adsorption- desorption equilibrium. It was found that the equilibrium between the catalyst and dye was established after 45 min. After having established the equilibrium with 75 mg of photocatalyst, the dyes were irradiated for 60 min. It was found that the photocatalyst exhibited higher degradation efficiency for RhB (49%), still lesser for MB (34%) and then for AO7 (30%).

In order to investigate the rate of the photocatalytic reaction, the photocatalytic degradation results are linearly fitted with the first-order kinetic equation as given below,

$\ln(C_0/C_t) = kt$

here, C_0, C, t and k are respectively the initial concentrations of the pollutant, the concentration of the dye at any moment of the reaction, radiation time and the rate constant. The value of k can be determined from the slope of the graph $\ln(C_0/C)$ vs (t). According to the Fig. 4 the diagram $\ln(C_0/C)$ Vs (t) is the straight line, which could be deduced that RhB, MB and AO7 photocatalytic degradation follows the first order reaction [6]. From Fig. 5, the rate constant (k) values are calculated as 0.00819, 0.0065, and 0.00526 min^{-1} for RhB, MB and AO7 respectively.

3.5 Effect of Photocatalyst

The decolorization spectra of RhB, MB and AO7 dyes collected at different time intervals are obtained from Fig. 6-8 respectively. The photocatalytic activity of the BiOI sample was observed with respect to the absorbance variation at the maximum wavelength (λmax) of dye. The extinction spectra were recorded in the wavelength range 400-800 nm. From these spectra, it was observed that the maximum absorption peak centered at 554,484 and 664 nm for RhB, MB and AO7 degradation over BiOI respectively. The respective peak intensities decreased gradually after visible light irradiation for 60 min, indicating the oxidative degradation of the RhB, MB and AO7 dyes. During the progress of the degradation experiments, the frequent decrease in the extinction indicated a decrease in the dye concentration with respect to time, which is visually con-

firmed by the decoloration of the reaction solution. This observation confirms that a redox reaction took place on the surface of BiOI photocatalyst.

3.6 General Mechanism Of BiOI Photocatalyst

In the photocatalysis process, BiOI absorbs the light energy (hν) equal or higher than its band gap (Eg), which results in the creation of holes (h^+) and electrons (e^-) in the valence band (VB) and conduction band (CB), respectively, as also described by (Eq.(1)). Then, the photogenerated e^- and h^+ react with oxygen (O_2) and water (H_2O), adsorbed on the surface of BiOI, to generate superoxide radical anions ($O_2^{\cdot-}$) and hydroxyl radicals ($OH^{\cdot}$). The large redox potentials of these radicals ($O_2^{\cdot-}$ and $OH^{\cdot}$) lead to the photodecomposition of the pollutants as shown in Eqs. (2–4).

$BiOI + h\nu \rightarrow h^+ (VB) + e^-(CB)$ (1)

$e^- (CB) + O_2 \rightarrow O_2^{\cdot-}$ (2)

$h^+ (VB) + H_2O \rightarrow H^+ + OH^{\cdot}$ (3)

$OH^{\cdot} + O_2^{\cdot-} +$ Pollutants $\rightarrow$ Degradation Products (4)

This also clearly indicate that the degradation efficiency was well enhanced after the addition of BiOI photocatalyst. This degradation is due to the open 3D flower like specific surface area of the photocatalyst which is responsible for adsorbance of the dye [10]. Moreover the reactive oxygen species interactions in the photocatalyst and the species demonstrated that degradation occurs due to generation of $OH^{\cdot}$ and $O_2^{\cdot-}$ [12].

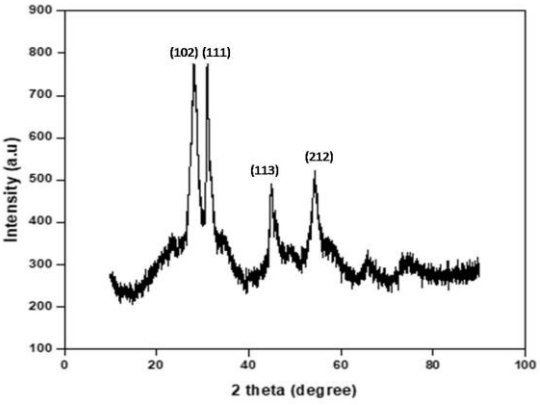

Fig. 1 XRD pattern of the BiOI photocatalyst.

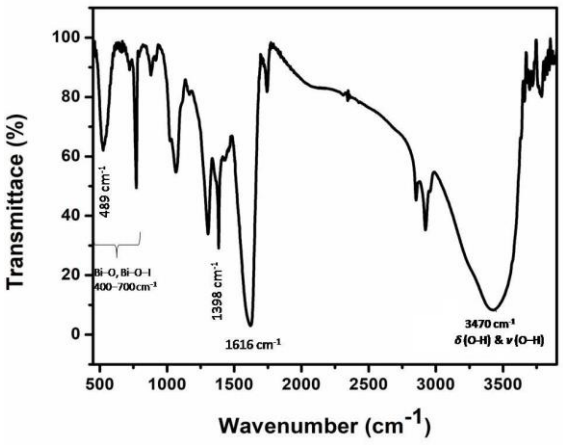

Fig.2 FTIR Spectra of BiOI photocatalyst.

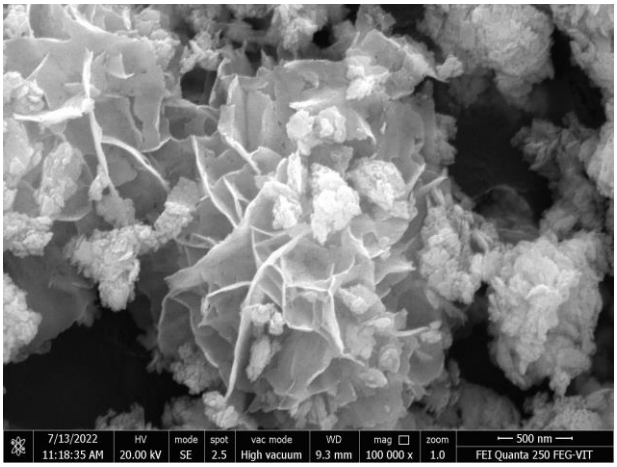

Fig. 3(a)

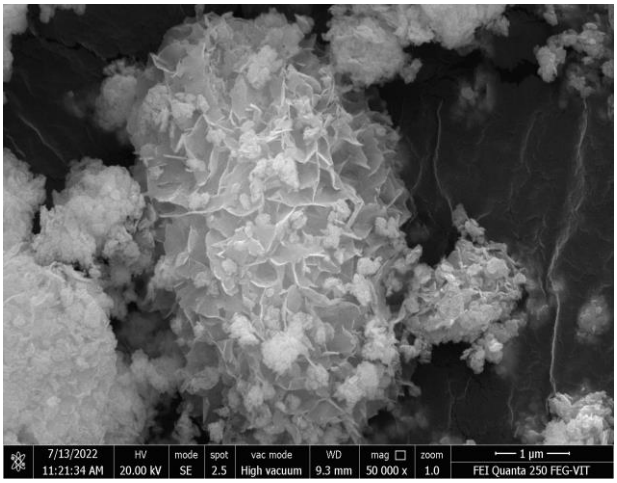

Fig. 3(b)

Fig. 3 SEM images of pure BiOI at different magnifications.

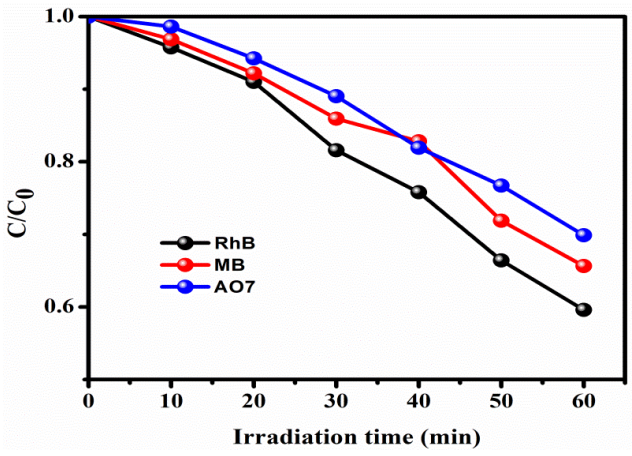

Fig.4 Photocatalytic degradation of 1×10^{-5} M, 2×10^{-4}M and 5×10^{-5} M concentration of RhB, MB and AO7 respectively at various time intervals over 0.75 g/L BiOI photocatalyst.

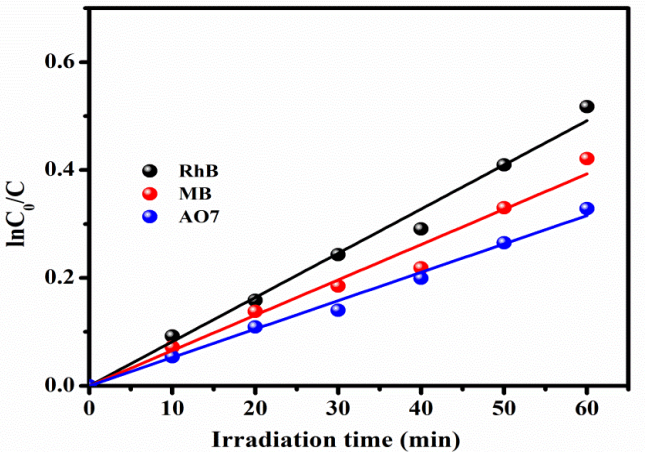

Fig.5 First order kinetic study of photocatalytic degradation of RhB, MB and AO7 at various time intervals over BiOI photocatalyst.

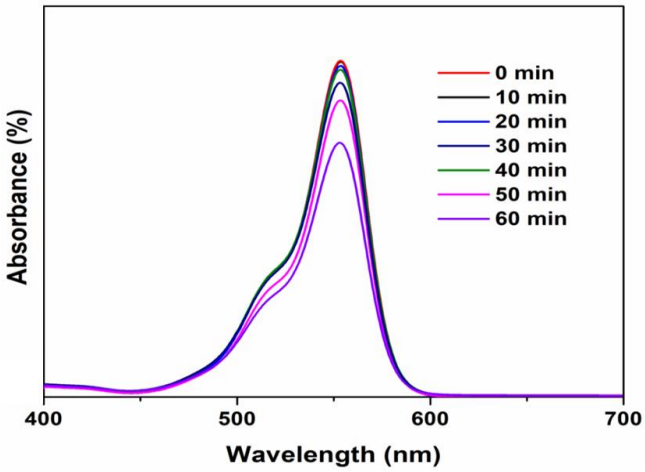

Fig. 6 UV- Vis absorption spectra of RhB degradation at different time intervals over the BiOI catalyst.

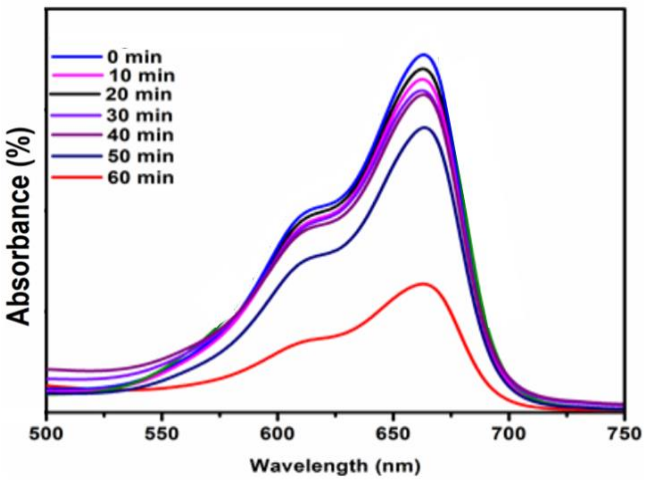

Fig.7 UV- vis absorption spectra of MB degradation at different time intervals over the BiOI catalyst

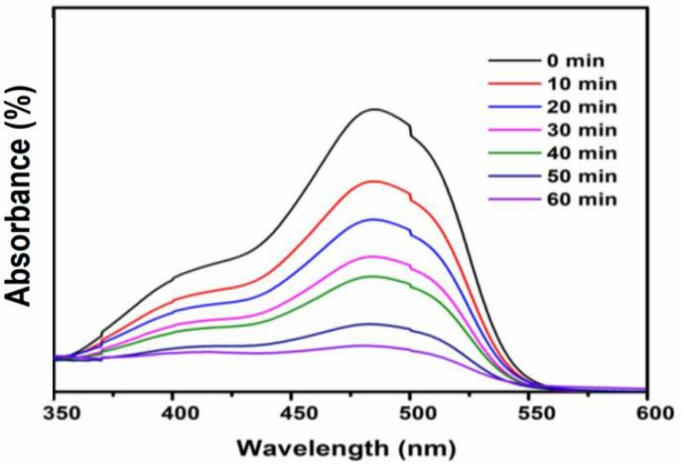

Fig.8 UV- Vis absorption spectra of AO_7 degradation at different time intervals over the BiOI catalyst.

4. Summary And Conclusion

In this work, we investigated the influence of BiOI photocatalyst on the photocatalytic degradation of RhB, MB and AO7. The BiOI was synthesized by solvothermal route. The as-synthesized BiOI was characterized by X- ray Diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). The photocatalytic activities of the BiOI photocatalyst were tested in the photo degradation reaction of RhB, MB, AO7 aqueous solution under visible light irradiation. The photocatalytic experiments demonstrated that the BiOI showed greater photocatalytic degradability of RhB than for MB and AO7, which may be due to the strong absorption in visible region, enhanced charge separation efficiency of the photocatalyst and this may be due to its anionic nature. This study demonstrates that BiOI can be a good candidate for photocatalytic decontamination of environmental pollutants. Yet further modification and composites with BiOI are synthesized for the effective degradation of the organic dye pollutants.

References

[1] Melissa Denchak, Water Pollution: Everything You Need to Know, NRDC movement, 2022.

[2] E.G. Solozhenko, et al., 1995, Decolourization of azo-dye solutions by Fenton's oxidation, Elsevier, Water Research Volume 29, 9, 2206-2210.

[3] Grégorio Crini et al., Advantages and disadvantages of techniques used for waste water treatment, Springer, Environmental Chemistry Letters, 2019, 17, 145–155.

[4] Jinfeng Zhang, et al., Direct Z- scheme porous g-C_3N_3/BiOI heterojunction for enhanced visible- light photocatalytic activity, Elsevier, Journal of Alloys and Compounds, 2018, 766, 841- 850.

[5] Liqun Ye, et al., Synthesis of highly symmetrical BiOI single-crystal nanosheets and their {001} facet-dependent photoactivity, Mater.Chem., Journal of Materials Chemistry, 2011, 21, 12479.

[6] Rong Hao et al., Efficient adsorption and visible-light photocatalytic degradation of tetracycline hydro-

chloride using mesoporous BiOI microspheres, Elsevier, Journal of Hazardous Materials, 2012, 209–210, 137-145.

[7] Ahmad Najafidoust, et al., Sono-solvothermal design of nanostructured flowerlike BiOI photocatalyst over silica-aerogel with enhanced solar-light-driven property for degradation of organic dyes, Elsevier, Separation and Purification Technology, 2019, 221, 101-113.

[8] Wenlian William Lee et.al, Synthesis of bismuth oxyiodides and their composites: characterization, photocatalytic activity and degradation mechanisms, RSC Adv., 2015, 5, 23450-23463.

[9] Rongan He, 3D BiOI-GO composite with enhanced photocatalytic performance for phenol degradation under visible- light, Elsevier, Ceramics International, 2015, 41, 3511- 3517.

[10] Yang Liu, et al., Heterogeneous activation of per sulfate for Rhodamine B degradation with 3D flower sphere-like BiOI/Fe_3O_4 microspheres under visible light irradiation, Elsevier, Separation and Purification Technology, 2018, 192, 88-98.

[11] Malathi Arumugam et. al, Solvent-mediated synthesis of BiOI with a tunable surface structure for effective visible light active photocatalytic removal of Cr(VI) from wastewater, Elsevier, Environmental Research ,2021, 197, 111080.

[12] Yasmin Vieira, et al., Reactive oxygen species-induced heterogeneous photocatalytic degradation of organic pollutant Rhodamine B by copper and zinc aluminate spinels, SCI, Journal of Chemical Technology and Biotechnology, 2020, 95, 791-797.