

Sunlight-induced photocatalytic degradation of rhodamine B dye by Bi_2MoO_6 microspheres

Abstract

Removal of dyes from water bodies is a significant concern throughout the world. In this study, Bi_2MoO_6 microspheres were synthesized by a hydrothermal synthetic route at 180°C , and it is effectively characterized by various techniques. The XRD peaks confirmed the orthorhombic planes of Bi_2MoO_6 . The microsphere-like morphology was revealed by FESEM and HRTEM. The photocatalytic activity of the Bi_2MoO_6 microsphere is tested against the degradation of rhodamine B under natural sunlight irradiation. About 90 % degradation of rhodamine B is observed in 90 min with the photocatalytic degradation rate of 0.028 min^{-1} . Results confirmed that the Bi_2MoO_6 microsphere could facilitate 90% degradation of RhB dye and followed the first-order kinetic model.

Gandharve Kumar*

***Corresponding Author**

Gandharve Kumar,

*Dept. of Chemistry, Faculty of Engineering,
Teerthanker Mahaveer University, Moradabad,
U.P.-244001

E- mail: gandhravk.engineering@tmu.ac.in

Ph.No.+919411802857

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Introduction

Organic dyes in aquatic environments are a significant pollutant due to their extensive usage in textile and other fabric industries (Homem and Santos, 2011; Qin et al., 2021; Rivera-Utrilla et al., 2013). Many water sources are polluted by residual dyes, which enter directly into the aquatic environment through various means like dye industries, textile industries, etc. (Dinh et al., 2017; Michael et al., 2013). Rhodamine B dye is a widely used cationic dye found in its application in coloring fabrics. Rhodamine B is water-soluble, stable in an aquatic environment, non-biodegradable, and cancer-causing in nature, which makes it harmful to humans and living species of aquatic ecosystems (Kumar et al., 2022a; Kumar and Dutta, 2022a; Kumar and Kumar, 2022; Mukherjee and Vellenki, 2022).

However, these residual dyes are not quickly metabolized, so they can easily pollute groundwater and surface water, causing harmful diseases in animals and humans (Bisht et al., 2022; Kumar et al., 2022b; Kumar and Dutta, 2022b). Due to this, several methods have been developed for wastewater remediation. Out of these techniques, semiconductor-based photocatalysts are widely utilized for the photocatalytic removal of various water pollutants (Akbari et al., 2021; Calvete et al., 2019; Durán-Álvarez et al., 2016). To date, ZnO and TiO_2 nanoparticles are the most commonly used photocatalysts for degrading organic dyes, but they require UV light for photoexcitation as their band gap is large (Nenavathu et al., 2013; Schneider et al., 2014). Recently, bismuth-based photocatalysts have been the most promising and new class of photocatalysts used in wastewater

treatment over the last few decades. Their applications cover several areas such as water-splitting, NH_3 production from N_2 , reduction of CO_2 , and degradation of water pollutants through heterogeneous photocatalysis. The band structure of these materials provides them with a suitable band gap for visible light-active and a well-distributed valence band in favor of recombination charge, enabling them to act as potential photocatalytic materials for wastewater treatment over metal oxides. Bismuth-based multi-component oxides are usually identified as stoichiometric hybrid oxides of Bi_2O_3 and metal oxides like TiO_2 , V_2O_5 , Mo_2O_3 , W_2O_3 , etc. The Aurivillius layered structure is generally determined by $[\text{Bi}_2\text{O}_2]^{2+}$ layers combined with metal oxide layers along the *c*-axis. The Bi_2MoO_6 ($n = 1$) is the simplest member of the Aurivillius family, which is a promising candidate for the photocatalytic degradation of inorganic and organic pollutants, under solar-light illumination (Das et al., 2018). In this work, we have reported the synthesis of Bi_2MoO_6 microsphere as a solar photocatalyst, and its photocatalytic activity was tested on RhB dye degradation under solar light irradiation.

Experimental Section

4 mmol bismuth nitrate pentahydrate was mixed in 20 mL of ethylene glycol, and 4 mmol sodium molybdate dihydrate was dissolved in 30 mL of ethyl alcohol. After stirring both the solutions for 30 min separately, the sodium molybdate dihydrate solution was added slowly into the bismuth nitrate pentahydrate solution with continuous magnetic stirring. After 45 min of constant stirring, the mixture was poured into a Teflon-lined stainless-steel autoclave and heated under a controlled temperature of 180 °C for 24 h. The finally prepared precipitates were washed with DI water and $\text{C}_2\text{H}_5\text{OH}$ and separated by centrifugation at 10000 RPM for 20 min, and the white product finally obtained was dried in an oven at 50 °C.

Methodology for photocatalytic experiment

The photocatalytic performance of the Bi_2MoO_6 photocatalyst was determined by observing the degradation of RhB dye (10 mg/L) solutions under exposure to natural sunlight radiation. Typically, 100 mL aqueous solution of 10 ppm RhB dye is taken into a 500 mL beaker, followed by the addition of 80 mg of Bi_2MoO_6 photocatalysts into it, which was then subjected to continuous stirring for 60 min under the dark condition. After 60 min of dark study, the beaker was kept under sunlight. 2 mL aliquot was taken from the beaker at certain intervals. The change in concentration of the RhB molecule was recorded by UV-vis spectrophotometer (UV-1800, Shimadzu, Japan) at absorbance $\lambda = 553$ nm.

RESULTS AND DISCUSSIONS

Characterization of Bi_2MoO_6

XRD analysis

The XRD spectra of pristine Bi_2MoO_6 was investigated by Bruker AXS advanced diffractometer with a scan range of 1 min^{-1} using graphite monochromatized $\text{Cu K}\alpha$ radiation (1.5418 Å) operated at 40 kilovolts. The XRD peaks for Bi_2MoO_6 were detected at $2\theta = 11.1^\circ, 28.5^\circ, 32.9^\circ, 36.2^\circ, 47.2^\circ, 55.6^\circ, 58.4^\circ$, which are matched to (020), (131), (002), (151), (062), (133), and (262) orthorhombic planes of Bi_2MoO_6 (JCPDS Card No.- 21 1272) (Figure.1). The lattice parameters are calculated to be as $a = 5.42 \text{ \AA}$, $b = 16.32 \text{ \AA}$, and $c = 5.42 \text{ \AA}$, with the average crystallite size of 14.10 nm.

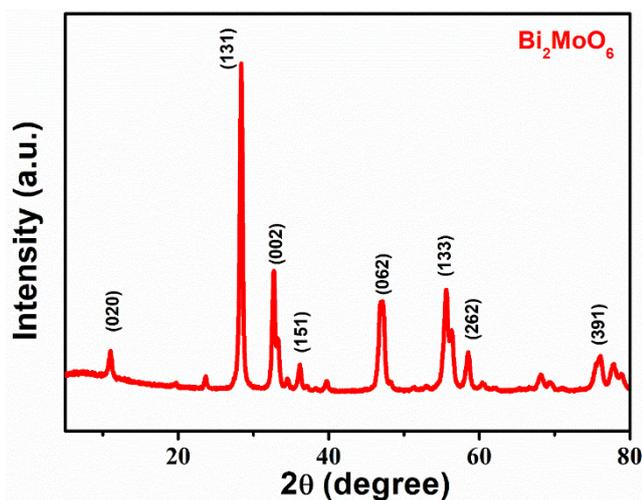


Figure.1 XRD patterns of as-synthesized Bi_2MoO_6 microspheres

Morphology of Bi_2MoO_6

The surface morphology of the Bi_2MoO_6 photocatalyst was investigated by electron microscopy. The FE-SEM image of Bi_2MoO_6 microspheres was recorded by Zeiss FESEM, Ultra-plus55 shows agglomeration of nanospikes-like structures (Figure. 2a). Similarly, the morphology of the Bi_2MoO_6 microsphere was better displayed from the HRTEM images (Figure. 2b) are recorded on a JEM-3200FS, JEOL transmission electron microscope.

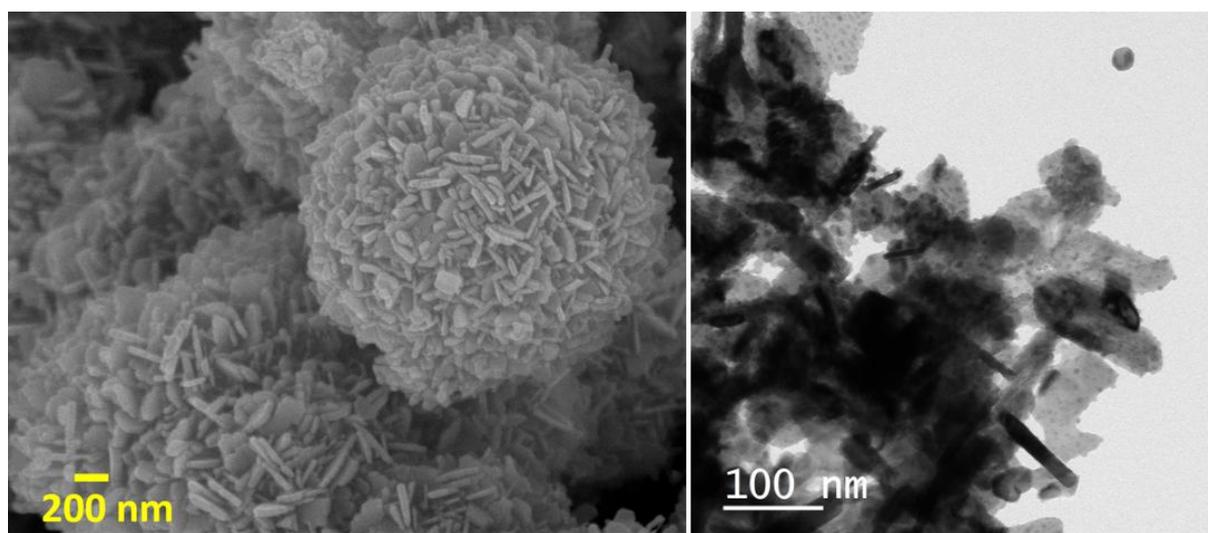


Figure.2 a) FE-SEM image of Bi_2MoO_6 microspheres; b) HR-TEM image of Bi_2MoO_6 microspheres

Photocatalytic activity

The sunlight-mediated photocatalytic degradation of RhB dye (10 mg/L) by the Bi_2MoO_6 microsphere is shown as a curve of C_t/C_0 vs. (t) time (Figure. 3). In the dark experiment firstly, the change in concentration of RhB dye was determined by the dark experiment. About 16% of RhB dye was adsorbed on Bi_2MoO_6 microspheres (Figure. 3a). The self-decomposition investigation of rhodamine B shows negligible results. The Bi_2MoO_6 microspheres show the photocatalytic performance of about 90 % rhodamine B dye degradation after 90 min of

sunlight exposure. The degradation kinetics of rhodamine B was modelled by a 1st-order kinetics model. The 1st order kinetics equation is:

$$\ln(C_0/C_t) = kt \quad (2)$$

Where C_0 is the initial dye concentration of dye, and C_t is the dye concentration at any time, whereas k (min^{-1}) is the 1st-order kinetic rate constant for RhB dye photocatalytic degradation. The photocatalytic rate constant of pristine Bi_2MoO_6 ($k = 0.028 \text{ min}^{-1}$) (Fig. 3b).

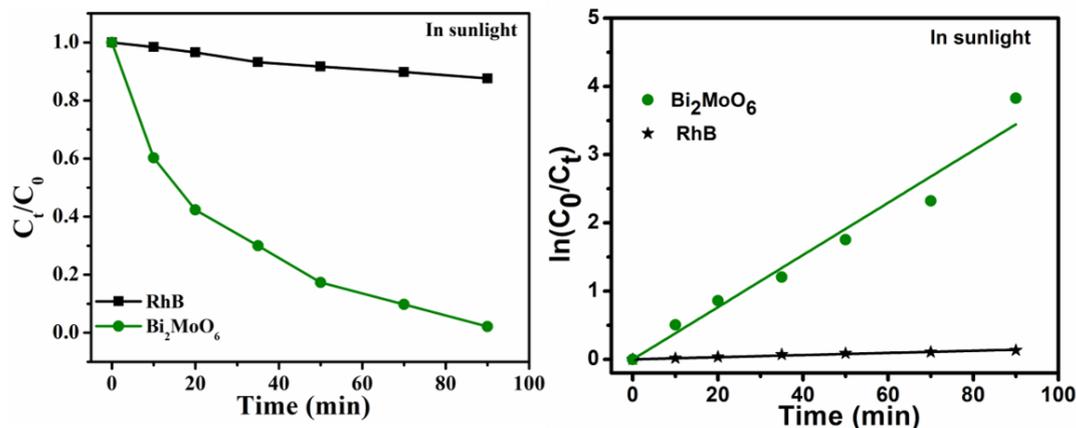


Figure. 3 a) Degradation profile (b) Corresponding 1st order kinetics curves

References:

- Akbari, M.Z., Xu, Y., Lu, Z., Peng, L., 2021. Review of antibiotics treatment by advance oxidation processes. *Environ. Adv.* 5, 100111. <https://doi.org/10.1016/j.envadv.2021.100111>
- Bisht, K., Kumar, G., Dutta, R.K., 2022. Amine-Functionalized Crystalline Carbon Nanodots Decorated on Bi₂WO₆ Nanoplates as Solar Photocatalysts for Efficient Degradation of Tetracycline and Ciprofloxacin. <https://doi.org/10.1021/acs.iecr.2c02635>
- Calvete, M.J.F., Piccirillo, G., Vinagreiro, C.S., Pereira, M.M., 2019. Hybrid materials for heterogeneous photocatalytic degradation of antibiotics. *Coord. Chem. Rev.* 395, 63–85. <https://doi.org/10.1016/j.ccr.2019.05.004>
- Das, S., Ghosh, S., Misra, A.J., Tamhankar, A.J., Mishra, A., Lundborg, C.S., Tripathy, S.K., 2018. Sunlight assisted photocatalytic degradation of ciprofloxacin in water using fe doped zno nanoparticles for potential public health applications. *Int. J. Environ. Res. Public Health* 15, 1–11. <https://doi.org/10.3390/ijerph15112440>
- Dinh, Q.T., Moreau-Guigon, E., Labadie, P., Alliot, F., Teil, M.J., Blanchard, M., Chevreuil, M., 2017. Occurrence of antibiotics in rural catchments. *Chemosphere* 168, 483–490. <https://doi.org/10.1016/j.chemosphere.2016.10.106>
- Durán-Álvarez, J.C., Avella, E., Ramírez-Zamora, R.M., Zanella, R., 2016. Photocatalytic degradation of ciprofloxacin using mono- (Au, Ag and Cu) and bi- (Au-Ag and Au-Cu) metallic nanoparticles supported on TiO₂ under UV-C and simulated sunlight. *Catal. Today* 266, 175–187. <https://doi.org/10.1016/j.cattod.2015.07.033>
- Homem, V., Santos, L., 2011. Degradation and removal methods of antibiotics from aqueous matrices - A review. *J. Environ. Manage.* 92, 2304–2347. <https://doi.org/10.1016/j.jenvman.2011.05.023>
- Kumar, G., Cilamkoti, V., Dutta, R.K., 2022a. Sunlight mediated enhanced photocatalytic degradation of antibiotics in aqueous medium using silicon doped carbon quantum dots decorated Bi₂MoO₆ nanoflakes. *Colloids Surfaces A Physicochem. Eng. Asp.* 639, 128368. <https://doi.org/10.1016/j.colsurfa.2022.128368>

- Kumar, G., Dutta, R.K., 2022a. Sunlight mediated photo-Fenton degradation of tetracycline antibiotic and methylene blue dye in aqueous medium using FeWO₄/Bi₂MoO₆ nanocomposite. *Process Saf. Environ. Prot.* 159, 862–873. <https://doi.org/10.1016/j.psep.2022.01.063>
- Kumar, G., Dutta, R.K., 2022b. Fabrication of plate-on-plate SnS₂/Bi₂WO₆ nanocomposite as photocatalyst for sunlight mediated degradation of antibiotics in aqueous medium. *J. Phys. Chem. Solids* 164, 110639. <https://doi.org/10.1016/j.jpcs.2022.110639>
- Kumar, G., Kumar, J., Bag, M., Kumar Dutta, R., 2022b. Solar light induced photocatalytic process for reduction of hexavalent chromium and degradation of tetracycline and methylene blue by heterostructures made of SnS₂ nanoplates surface modified by ZnWO₄ nanorods. *Sep. Purif. Technol.* 292, 121040. <https://doi.org/10.1016/j.seppur.2022.121040>
- Kumar, G., Kumar, R., 2022. Sunlight - induced enhanced photocatalytic reduction of chromium (VI) and photocatalytic degradation of methylene blue dye and ciprofloxacin antibiotic by - Sn₃O₄ / SnS₂ nanocomposite. *Environ. Sci. Pollut. Res.* <https://doi.org/10.1007/s11356-022-19853-0>
- Michael, I., Rizzo, L., Mc Ardell, C.S., Manaia, C.M., Merlin, C., Schwartz, T., Dagot, C., Fatta-Kassinos, D., 2013. Urban wastewater treatment plants as hotspots for the release of antibiotics in the environment: A review. *Water Res.* 47, 957–995. <https://doi.org/10.1016/j.watres.2012.11.027>
- Mukherjee, G.K.I., Vellenki, M.D.B.P., 2022. Photocatalytic degradation of tetracycline in aqueous medium using - ZnWO₄ / Bi₂MoO₆ nanocomposites under natural sunlight. *Int. J. Environ. Sci. Technol.* <https://doi.org/10.1007/s13762-022-04047-5>
- Nenavathu, B.P., Krishna Rao, A.V.R., Goyal, A., Kapoor, A., Dutta, R.K., 2013. Synthesis, characterization and enhanced photocatalytic degradation efficiency of Se doped ZnO nanoparticles using trypan blue as a model dye. *Appl. Catal. A Gen.* 459, 106–113. <https://doi.org/10.1016/j.apcata.2013.04.001>
- Qin, K., Zhao, Q., Yu, H., Xia, X., Li, J., He, S., Wei, L., An, T., 2021. A review of bismuth-based photocatalysts for antibiotic degradation: Insight into the photocatalytic degradation performance, pathways and relevant mechanisms. *Environ. Res.* 199, 111360. <https://doi.org/10.1016/j.envres.2021.111360>
- Rivera-Utrilla, J., Sánchez-Polo, M., Ferro-García, M.Á., Prados-Joya, G., Ocampo-Pérez, R., 2013. Pharmaceuticals as emerging contaminants and their removal from water. A review. *Chemosphere* 93, 1268–1287. <https://doi.org/10.1016/j.chemosphere.2013.07.059>
- Schneider, J., Matsuoka, M., Takeuchi, M., Zhang, J., Horiuchi, Y., Anpo, M., Bahnemann, D.W., 2014. Schneider et al. - 2014 - Understanding TiO₂ Photocatalysis Mechanisms and Materials(2).pdf. *Chem. Rev.* 114, 9919–9986.