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Intensified photodegradation of organic dyes using Bi-doped ZnO nanoparticles

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ABSTRACT

Environmental threat due to the pollution of water bodies by organic dyes, which can lead to the creation of a colored layer on the surface waters and prevent the penetration of sunlight into the waters, and ultimately disrupt the life of microorganisms. In addition to all this, due to their high toxicity, it has become a serious concern for the health of humans and animals. Recently, innovative treatments based on nanotechnology for wastewater treatment processes are increasing. In this study, a simple and safe method was reported for the efficient degradation of four organic dyes (bromothymol blue, eriochrome black T, methyl red and bromocrosol green) using Bi-doped ZnO nanoparticles under sunlight. Based on the performed experiments, the Bi-doped ZnO photocatalytic activity was better than the single ZnO semiconductor. The present study can be considered as an effective step towards the photocatalytic treatment of wastewater to remove dyes using sunlight as a renewable source of energy.

KEYWORDS

Bi-doped ZnO nanoparticles, Organic dyes, Photocatalytic presses, Sunlight

I. INTRODUCTION

Clean water is necessary for the presence of life on earth. Meny pollutants such as dangerous and flammable chemicals are released into water from various industries including cosmetics, lather and textile. These toxic chemicals are especially harmful to organisms. Excessive use of water in paint-related industries causes untreated water to be discharged into water streams. Untreated water causes severe problems for the health of humans and animals (Ejhieh et al., 2010), and on the other hand, it also leads to the interruption of the food chain (El-dars et al., 2015). Due to the destructive effects of organic dyes, some methodologies such as adsorption (Chang et al., 2016), filtration (Qi et al., 2011), reverse osmosis (Yang et al., 2019) and biological processes (Ghoreishi et al., 2003) have been used to remove a wide range of organic compounds. These technologies have limitations such as complex and time-consuming operations, high costs, low efficiency, pollutant transfer from one phase to another, sludge production. Therefore, finding an effective method to remove organic pollutants from aquatic environments seems essential.

Among the pollutant removal technologies, semiconductor-based photocatalysis is widely used for degrading organic pollutants due to its low cost, excellent efficiency, and environmental friendliness (Alhaddad et al., 2022; Honarmand et al., 2023). In these processes, contaminants are converted into harmless small compounds. Zinc oxide (ZnO) is one of the most emerging n-type semiconductors employed as photocatalyst for the degradation of various pollutions (Golmohammadi et al., 2020). Single semiconductors are not able to completely remove the pollutant in a short period due to the high recombination rate of e^-/h^+ pairs (Elavarasan et al., 2022). Also, the wide band gap of single semiconductors towards UV light makes it cover only a small percentage of the solar spectrum, so it is impossible to perform photocatalytic reactions in direct sunlight (Jogamaya, 2022). Therefore, measures have been devised to increase the degradation efficiency and benefit from the renewable energy of sunlight. In order to improve the absorption of sunlight and prevent recombination processes, doping and coupling with other semiconductors have been proposed (Ghoreishian et al., 2023). Bismuth-doping semiconductor induces defects such as oxygen vacancies and ions, which provide visible photocatalytic activity and minimize the recombination of free charges (Singh et al., 2021).

In the present study, the synthesis and characterization of Bi-doped ZnO nanoparticles was reported. Their performance was investigated as an effective catalyst for the photodegradation of four organic dyes under direct sunlight.

II. EXPERIMENTAL SECTION

A. *Synthesis of Bi-doped ZnO nanoparticles*

Aqueous solutions of $Zn(NO_3)_2{\cdot}6H_2O$ and $Bi(NO_3)_3{\cdot}5H_2O$ were prepared separately in 25 mL of distilled water with concentrations of 0.1 M and 0.002

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M, respectively. Then, these two solutions are mixed in a round bottom flask and stirred vigorously at room temperature for 30 minutes. Then, NaOH solution (2 M) was added drop by drop until the pH of the solution reached above 9. The solution was continuously stirred for 5 hours under reflux conditions. After cooling the reaction mixture, the formed sediments were washed with water and ethanol three times and dried at room temperature. The obtained samples were ground to a fine powder and calcined at 550 ◦C for 2 h to achieve Bi-doped ZnO nanoparticles. Alone, ZnO nanoparticles were synthesized by the same method, except that $Bi(NO_3)_3{\cdot}5H_2O$ was not added.

B. Photocatalytic experiments

All photocatalytic tests were performed on sunny days in August between 9:00 am and 3:00 pm. The brightness of sunlight was measured at specific time intervals using a digital lux meter, and its intensity was found to be in the range of $(250 \pm 20) \times 10^3$ Lux. To carry out the photocatalytic reaction, initially, the aqueous solutions of organic dyes (bromothymol blue, eriochrome black T, methyl red and bromocrosol green) with a concentration of 10 ppm were prepared. Then, 0.05 g of nanocatalyst was added to 50 mL of each organic dye. The obtained suspensions were magnetically stirred in the dark conditions for 15 minutes to achieve the adsorption-desorption equilibrium between the organic dyes and nanocatalyst. Then the samples were transferred into the open space and the photocatalytic reactions were carried out under direct sunlight. At certain intervals, 2 mL of the suspensions were removed and centrifuged to separate the nanocatalyst and concentration of organic dyes measured by UV–Vis spectroscopy.

III. RESULTS AND DISCUSSIONS

A. Characterization of Bi-doped ZnO nanoparticles

1) X-ray Diffraction (XRD)

Fig. 1 displayed the X-ray diffraction pattern of the pure ZnO nanoparticles and Bi-doped ZnO nanoparticles. All the diffraction peaks were well matched with JCPDS card (36-1451) which belonged to the hexagonal wurtzite phase structure of ZnO nanoparticles(Rajaboopathi et al., 2017). Diffraction peaks appearing at 2θ: 31.94°, 34.64°, 36.44°, 47.74°, 56.69°, 62.99°, 66.59°, 68.09°, 69.24° and 77.34° correspond to the diffraction patterns of (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2), (2 0 1) and (2 0 2) planes, respectively. From the comparison of the diffraction patterns of pure and Bi-doped ZnO nanoparticles, it was found that the peak of 29.19° was related to bismuth. Also, the intensity of ZnO peaks after bismuth doping has decreased slightly but their position remained constant. The average crystallite sizes of Bi-doped ZnO nanoparticles were calculated by following Debye-Scherrer's formula (Sankaran et al., 2020):

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

Where D was the particle size, k was shape factor (=0.9 assuming that the particles are spherical), λ was the wavelength of the X-ray radiation, β was the maximum at half width (FWHM) and θ was the angle of diffraction. The size of Bi-doped ZnO nanoparticles was estimated from the Scherrer equation about 20 nm.

2) Fourier-transform infrared (FTIR)

FTIR spectrum of Bi-doped ZnO nanoparticles was exhibited in Fig. 2. A broad band at 3400 cm^{-1} and a short band at 1625 cm^{-1} were related to stretching and bending vibrations of O-H, respectively(Ebrahimi et al., 2021). A broad band at 1000 cm^{-1} and a sharp band at 501 cm^{-1} were assigned to vibrations of Zn-OH and Zn-O, respectively(Balogun et al., 2020). A typical peak at 1110 cm^{-1} was observed which could be due to the presence of bismuth in structure of Bi-doped ZnO nanoparticles (Singh et al., 2021). Considering that no other excess peaks were seen in the FTIR spectrum of Bi-doped ZnO nanoparticles, it can be concluded that no other unwanted compounds were fabricated in the structure of nanoparticles.

3) Field emission - Scanning electron microscope (FE-SEM)

The morphology of Bi-doped ZnO nanoparticles was studied using FE-SEM analysis. As shown in Fig. 3, the diameter of Bi-doped ZnO nanoparticles was found to be about 25 nm and was spherical with a little agglomeration.

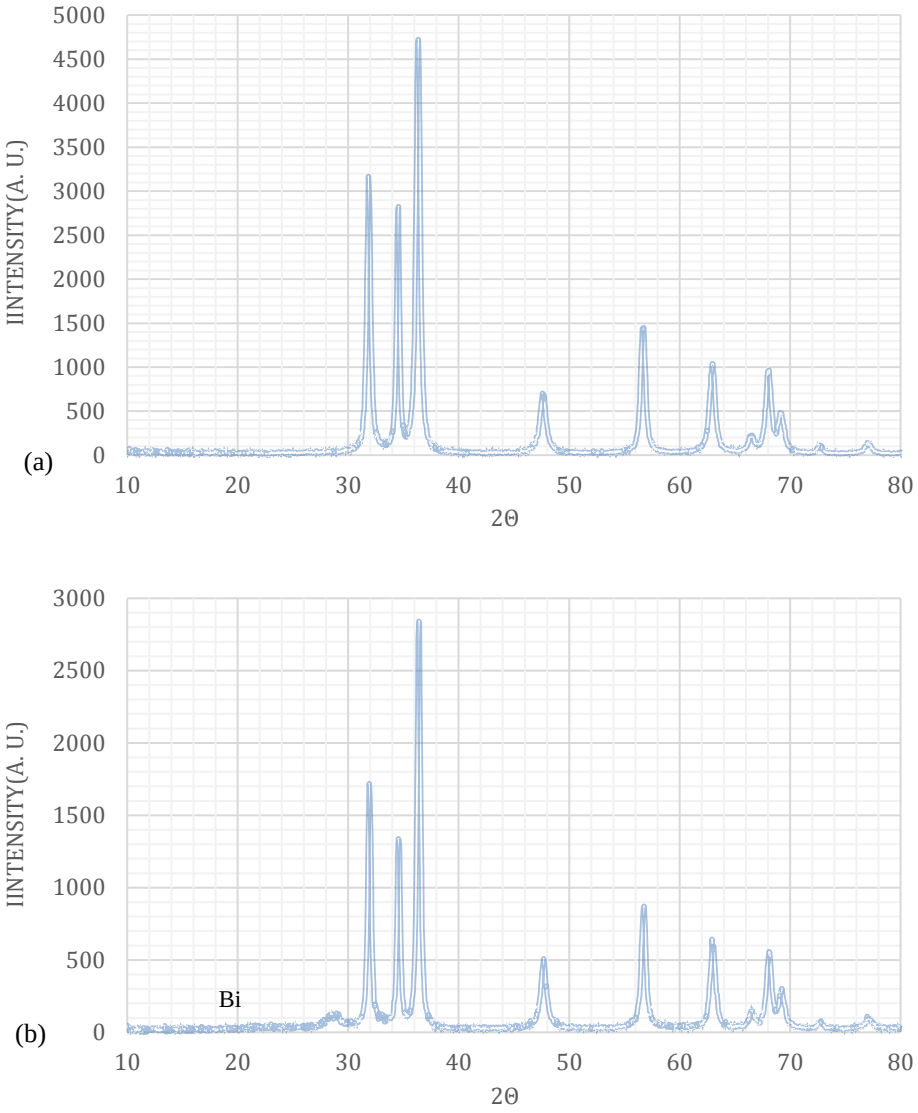


Fig. 1. XRD pattern of (a) pure ZnO nanoparticles and (b) Bi-doped ZnO nanoparticles

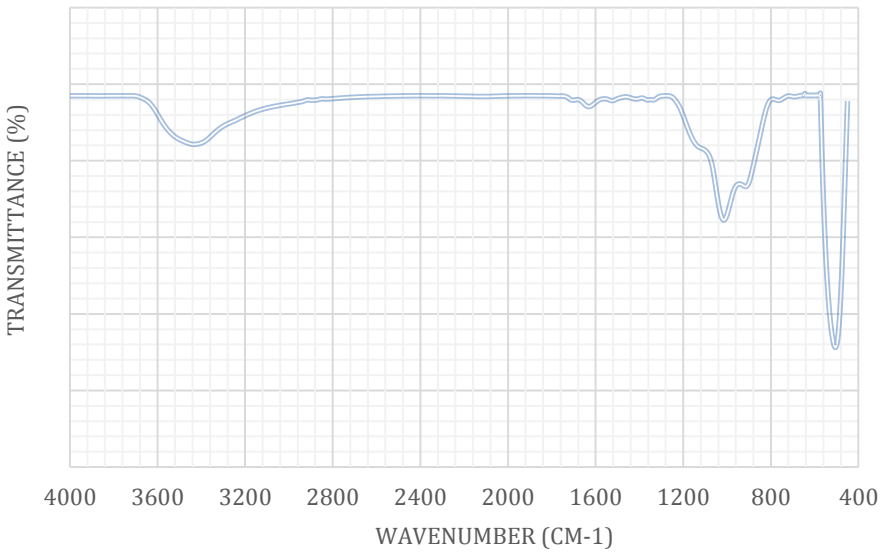


Fig. 2. FTIR spectrum of Bi-doped ZnO nanoparticles

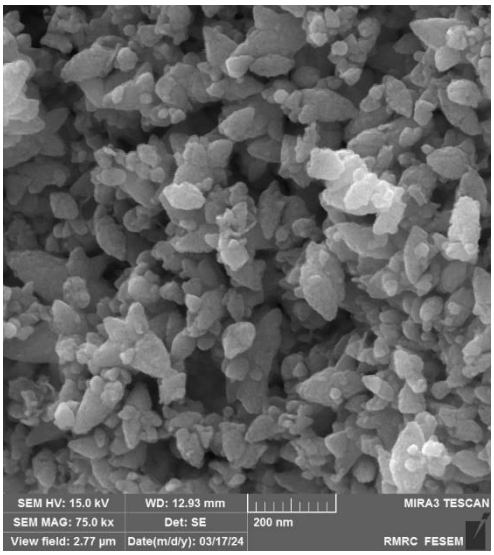


Fig. 3. FE-SEM image of Bi-doped ZnO nanoparticles

4) Photo- luminescence (PL)

PL analysis was helpful in understanding the transfer and recombination processes of the photo-induced e^-/h^+ pairs in semiconductors. Fig. 4 shows PL spectra of pure ZnO nanoparticles and Bi-doped ZnO nanoparticles. Compared with pure ZnO nanoparticles, Bi-doped ZnO nanoparticles revealed weaker fluorescence signals, entailing suppressed recombination of e^-/h^+ pairs. The results of this analysis exhibited that the excited electrons in ZnO nanoparticles are transferred to Bismuth immediately after production, which leads to a decrease in charge recombination and thus an increase in photocatalytic performance.

B. Photocatalytic Performance

In this study, the four organic dyes (bromothymol blue, eriochrome black *T*, methyl red and bromocrosol green) were used as target pollutants to study the photocatalytic performance of Bi-doped ZnO nanoparticles. As seen in Fig. 5, the photocatalytic performance of Bi-doped ZnO nanoparticles for degradation of bromothymol blue and eriochrome black *T* pollutants was better than that of methyl red and bromocrosol green. Despite all this, the Bi-doped ZnO nanoparticles could remove all the tested dyes with high efficiency without any auxiliary agent. For the effect of the presence of bismuth in the structure of the Bi-doped ZnO nanoparticles, the photocatalytic reaction of the degradation of organic dyes in the presence of pure ZnO nanoparticles was investigated. The results showed that for the complete degradation of organic dyes in the presence of pure ZnO nanoparticles, more time was needed than for Bi-doped ZnO nanoparticles. Also, to study the stability of the catalyst, its recyclability was investigated in this catalytic system for the degradation of bromothymol blue. After the completion of the reaction, the Bi-doped ZnO nanoparticles were separated from the reaction mixture and washed several times with water and ethanol. After drying, Bi-doped ZnO nanoparticles were used again in a new degradation reaction. No noticeable change in the dye degradation efficiency compared to the fresh catalyst was observed, which indicated the high stability of the catalyst.

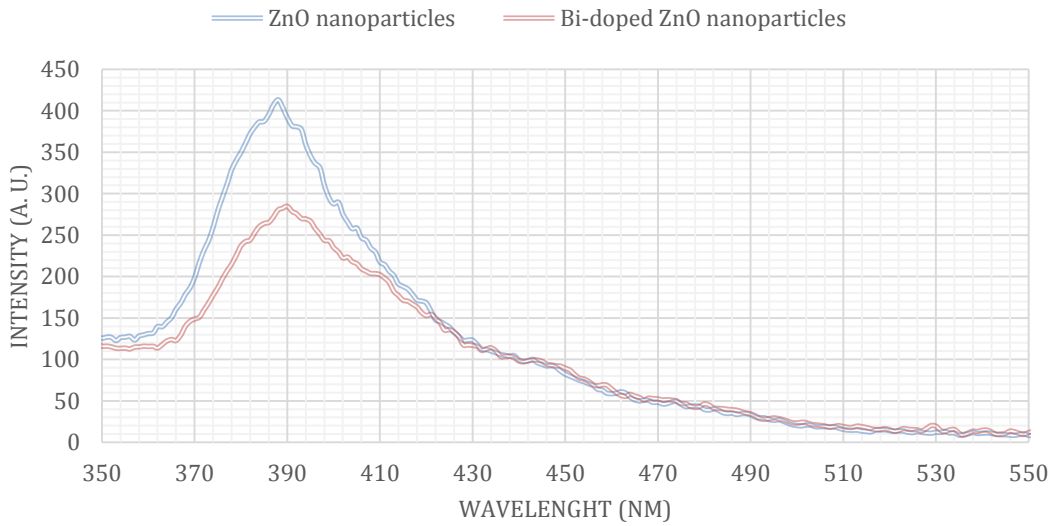
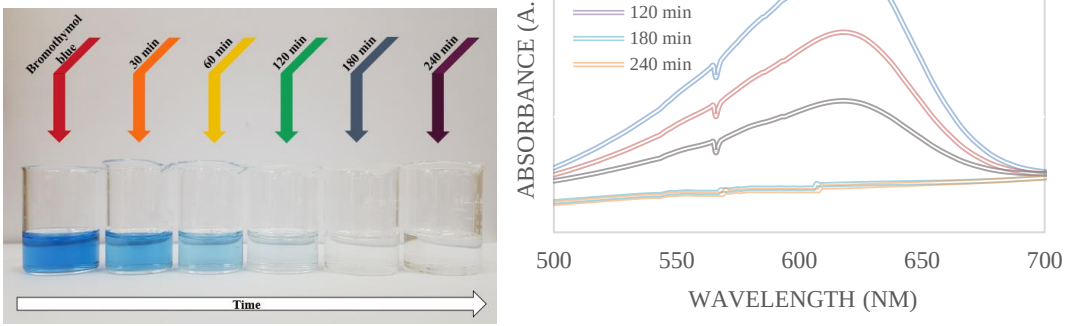
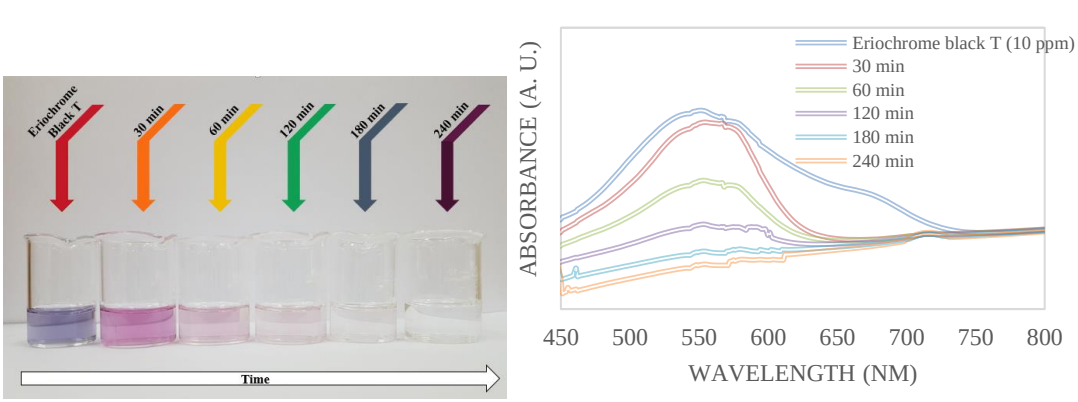


Fig. 4. PL spectra of pure ZnO nanoparticles and Bi-doped ZnO nanoparticles

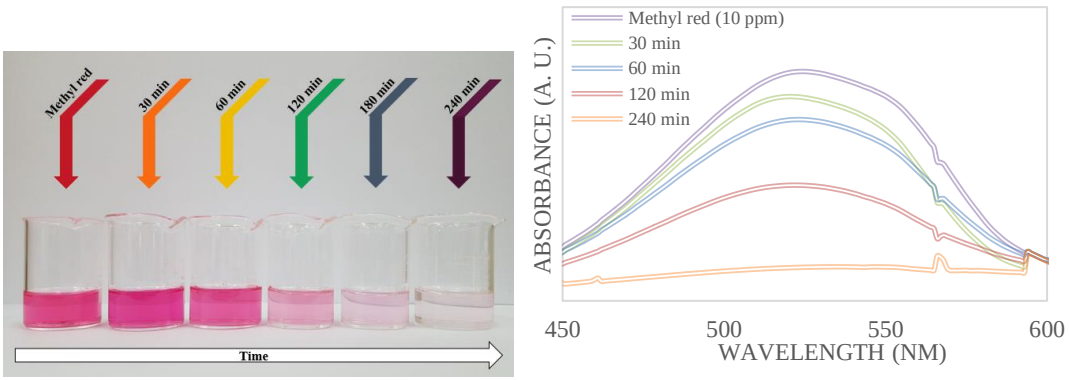
(a)



(b)



(c)



(d)

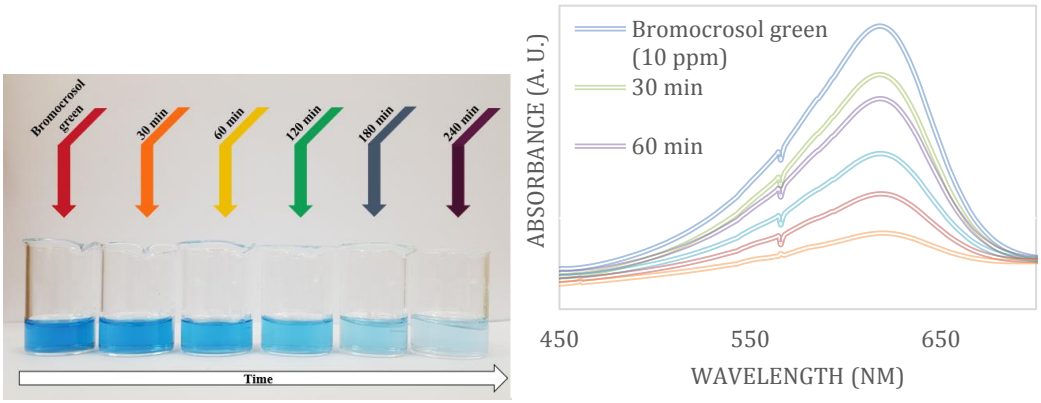


Fig. 5. UV-Vis spectra and color change of (a) bromothymol blue (b) eriochrome black T (c) methyl red and (d) bromocrosol green during photocatalytic reactions in a photocatalytic system of Bi-doped ZnO and sunlight

IV. CONCLUSION

Here, we report the synthesis of Bi-doped ZnO nanoparticles *via* a simple route. Bi-doped ZnO nanoparticles were characterized by various analyses such as XRD, FTIR, FESEM, and PL spectroscopy. The photocatalytic performance of Bi-doped ZnO nanoparticles was investigated for the degradation of four organic dyes under sunlight. The photocatalytic performance of Bi-doped ZnO nanoparticles for degradation of bromothymol blue and eriochrome black *T* pollutants was better than that of methyl red and bromocrosol green. Despite all this, the Bi-doped ZnO nanoparticles could remove all the tested dyes with high efficiency without any auxiliary agent. Based on the results obtained in this research, these types of studies are necessary to fabricate doped semiconductors with intensified photocatalytic capability in real world applications.

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