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BISMUTH DOPED ZnO/MoO$_2$ COMPOSITES FOR THE CATALYTIC DEGRADATION OF METHYLENE BLUE

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ABSTRACT. From past years, the demand of clean water has been increased due to shortage of portable fresh water. Parallel, the use of composite materials for the catalytic degradation of pollutants particularly dyes in industrial effluents has attracted good attention. In this work, bismuth doped ZnO/MoO$_2$ composites were synthesized by co-precipitation method using bismuth chloride, zinc sulphate and sodium molybdate as starting precursors. The structural/morphological studies of these composites were accomplished by UV–Visible spectroscopy, Fourier Transform Infrared Spectroscopy and Scanning Electron Microscopy. The catalytic activity of the bismuth doped ZnO/MoO$_2$ composites was investigated by degradation of methylene blue (MB) dye. The degradation of MB was observed to be 75% at only 45 sec and enhanced catalytic activity was observed by increasing Bi content in synthesized composites.

Keywords: *ZnO/MoO$_2$ composites; Bismuth doping; Methylene blue; Catalytic degradation*

INTRODUCTION

Metal oxides have recently attained rapid attention for remediation and environmental protection. The degradation of dyes in waste water from textile industry is really a challenging task and such dyes are a huge source of water contamination. To cope with this challenge, significant consideration has been paid to resolve this issue and as such catalytic properties of metal oxides were improved by doping them with variety of metals [1].

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Among several metal oxides used for this purpose, TiO_2 and ZnO have been broadly reported for degradation process of dyes due to their remarkable properties. ZnO has recently been reported more advantageous over TiO_2 because of its low cost and high catalytic activity. Moreover, it has similar conduction and valence bands to that of TiO_2 [2]. ZnO is also a good semiconducting material of II–VI type, with a wide band gap (3.37 eV) and a large excitation binding energy (60 meV) at room temperature thus making it good for photocatalytic applications [3].

Catalytic properties of zinc oxide have been enhanced either by doping or by developing ZnO based composites such as ZnO/metal [4], ZnO/metal oxide [5] and ZnO/polymer [6]. Doping is considered to be more useful in this regard. A large number of dopants such as transition metals as well as rare earth elements have been reported to enhance the catalytic properties of ZnO [7-10]. Combination of different metal oxides can reduce the band gap, hence, extending the absorbance range to visible region to achieve a higher photocatalytic activity [11-14]. Some notable examples of such combinations are $CuO–TiO_2$ [15], $WO_3–TiO_2$ [16], ZnO/TiO_2 [17], ZnO/SnO_2 [11], TiO_2/MgO [18], and SnO_2/ZnO [19].

$NaBH_4$ supported by a catalyst is a well-known reducing agent for the reduction of MB dye. Composites synthesized by doping have been reported to assist $NaBH_4$ [20, 21]. Keeping in view the literature background, in this study, molybdenum oxide is chosen for modifying ZnO [22, 23] while bismuth ion is selected as a dopant because of its previously reported role in enhancing catalytic properties of ZnO [24]. According to accessible literature, there is no work reported on the synthesis of Bi-doped ZnO/MoO_2 composite material for catalytic degradation of MB. Therefore, in this study, we report the preparation of Bi-doped ZnO/MoO_2 composite material together with its catalytic reduction efficiency.

RESULTS AND DISCUSSION

Bismuth doped ZnO/MoO_2 composites were synthesized by co-precipitation method followed by annealing process. These composites were subsequently characterized by different spectroscopic techniques. UV-Visible Spectrum of the composite was recorded by UVD-T90+ Spectrophotometer in the range 200-800 nm and exhibit maximum wavelength at 255 nm (Figure 1). The single absorption indicates homogeneity across the sample of composite.

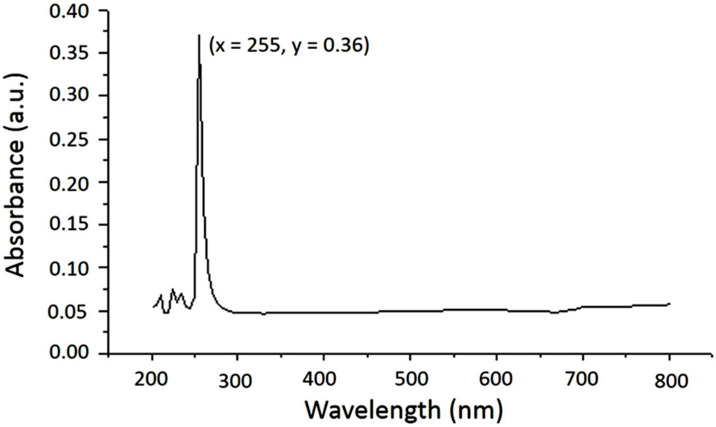

Figure 1. UV-Vis spectrum of Bi-doped ZnO/MoO$_2$ (1%) composites

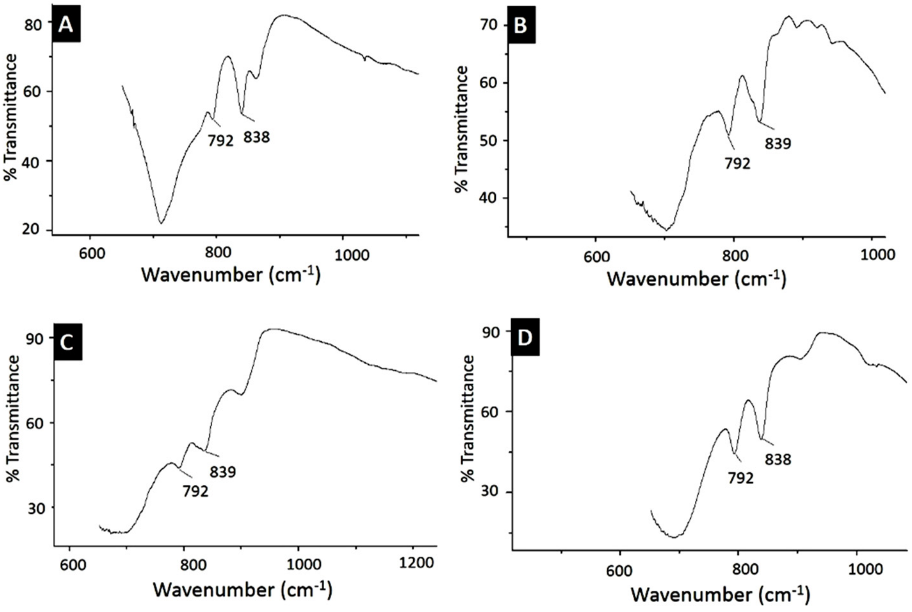

Figure 2.A: FT-IR Spectrum of 0.4% Bi-doped ZnO/MoO$_2$ composite;
B: FT-IR Spectrum of 0.6% Bi-doped ZnO/MoO$_2$ composite;
C: FT-IR Spectrum of 0.8% Bi-doped ZnO/MoO$_2$ composite;
D: FT-IR Spectrum of 1% Bi-doped ZnO/MoO$_2$ composite

FT-IR spectral data provided valuable information about the functional groups present in the synthesized bismuth doped ZnO/MoO_2 composites. The FT-IR spectra of Bi-doped ZnO/MoO_2 composites were recorded in the range 4000-400 cm^{-1}. The spectrum of bismuth doped metal oxide composites showed a broad band at 740-990 cm^{-1} which was assigned to Bi-O stretching mode vibrations [25] while the peak observed at 792 cm^{-1} is assigned to Mo-O in MoO_2 [26]. The band observed around 400-650 cm^{-1} is attributed to the zinc oxide bending vibrations [27]. FT-IR spectra of ZnO/MoO_2 composites with variable concentrations of dopant i.e. bismuth were recorded and compared. All the spectra showed bands around same frequency which confirmed the formation of bismuth doped ZnO/MoO_2 composite (Figure 2).

The surface morphology of Bi-doped ZnO/MoO_2 appears to be dense globular and rod-like structures with high porosity as shown by the SEM micrograph of the prepared composite (Figure 3).

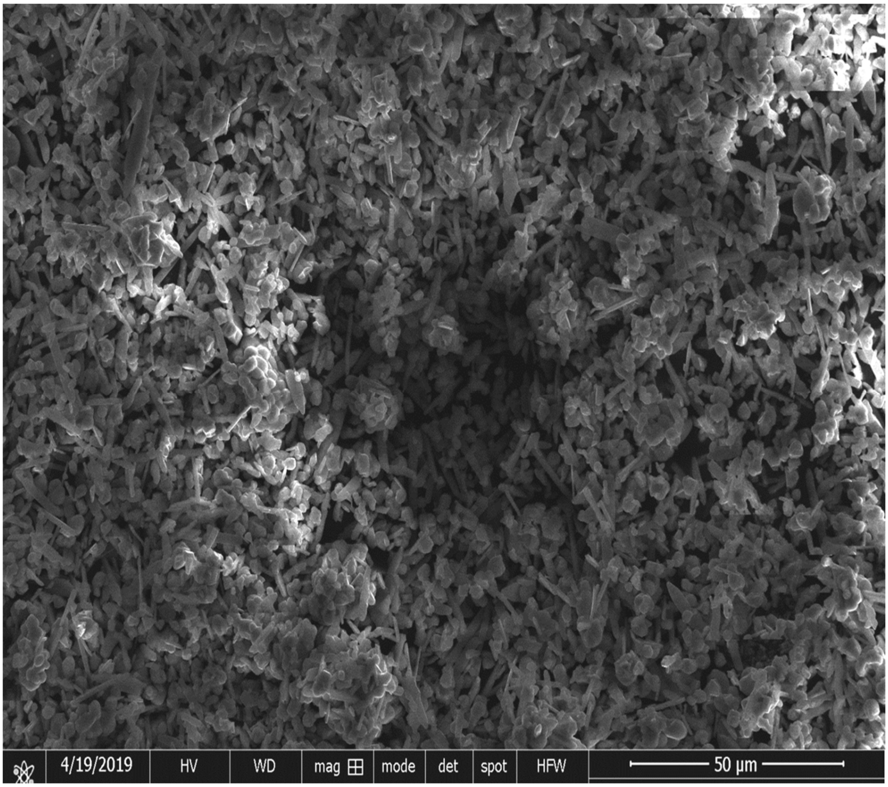

Figure 3. SEM micrograph of the prepared Bi-doped ZnO/MoO_2 composite (1%)

Catalytic degradation of MB by synthesized composites

To investigate the role of bismuth doped ZnO/MoO$_2$ composites as catalyst, degradation of MB was studied in the presence of NaBH$_4$ by adding variable concentration of composites as well as in the absence of composite. NaBH$_4$ is a well-known reducing agent and its efficiency is associated with its high electron injection capacity [28]. The rate of degradation was observed in the range 400-800 nm at room temperature. Overall, Bi doped ZnO/MoO$_2$ composites have shown enhanced catalytic activity for the degradation of MB. The different color of MB in its oxidized and reduced form make it good candidate for catalytic study. Figure 4A contains

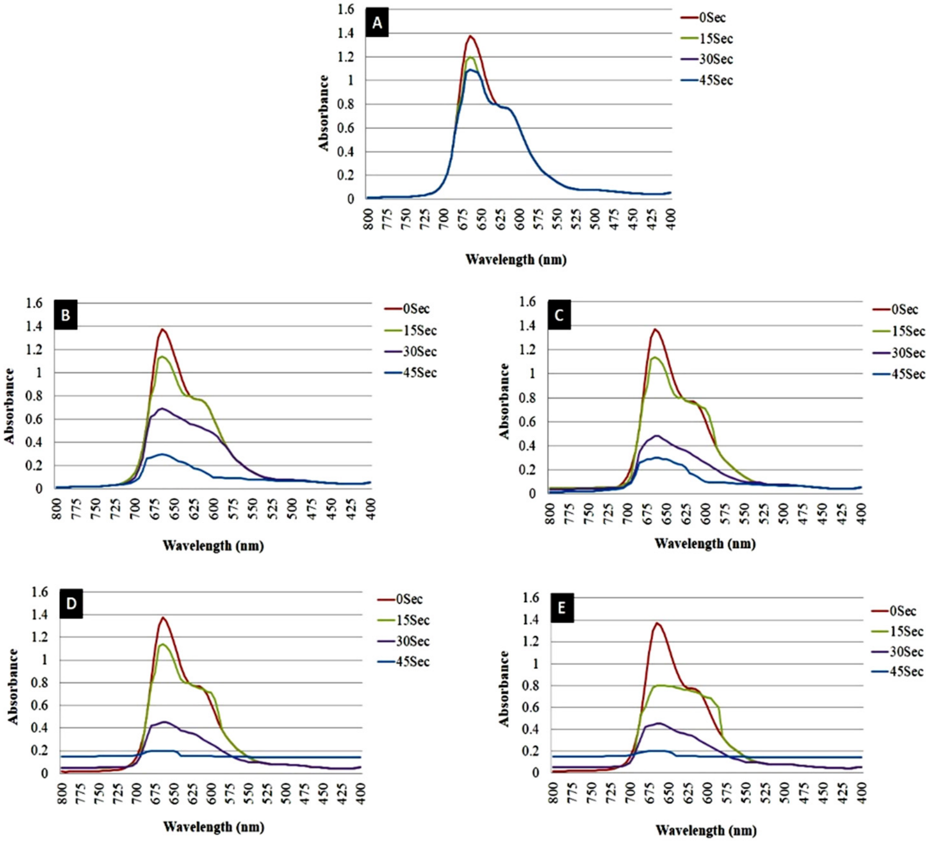

Figure 4. Catalytic degradation of MB using NaBH$_4$ with Bi-doped ZnO/MoO$_2$ composites **A:** without composites; **B:** Bi-doped ZnO/MoO$_2$ composites (0.4%); |**C:** Bi-doped ZnO/MoO$_2$ composites (0.6%); **D:** Bi-doped ZnO/MoO$_2$ composites (0.8%); **E:** Bi-doped ZnO/MoO$_2$ composites (1%)

absorption spectra of MB in the absence of composite and shows that absorption peaks of the MB solution diminish gradually with time and finally solution becomes colorless. Moreover, in this case, the absorption peak of MB at 665 nm was found to decrease slowly with the increase in the reaction time indicating a slow degradation rate in the absence of composite.

In the same manner degradation of MB was investigated by adding variable concentration (0.4% to 1.0%) of synthesized composite as catalyst. The results are graphically represented in Figure 4(B-E). Generally, it has been observed that by increasing the concentration of Bi doping in composite, rate for MB degradation was completed in less time interval. So, it can be concluded that the addition of bismuth composite enhances the degradation of the dye and maximum efficiency was observed especially in case of 1% bismuth doped ZnO/MoO_2 composite as compared to other compositions. This enhanced reduction efficiency is might be due to provision of large surface by the Bi doped ZnO/MoO_2 composites which cannot be achieved in its absence. Moreover, these findings are in agreement with previously reported catalytic property of Bi doped ZnO composites [24].

CONCLUSIONS

The bismuth doped ZnO/MoO_2 composites were successfully synthesized by a facile, simple, and low cost co-precipitation method. The catalytic efficiencies of bismuth doped ZnO/MoO_2 composites for degradation of MB were reported. Bismuth doped ZnO/MoO_2 was found to be an efficient catalyst to degrade MB dye, an environmental hazard.

EXPERIMENTAL SECTION

Chemicals used

Zinc sulphate $ZnSO_4 \cdot 7H_2O$, Sodium molybdate Na_2MoO_4, Bismuth chloride $BiCl_3$, Sodium hydroxide NaOH, Tetrahydrofuran C_4H_8O used were of analytical grade and purchased from sigma Aldrich. These were used as such without any further purification. Spectroscopic analysis of the composites was performed by mean of UV-Vis spectrophotometer (Labomed spectrophotometer system; model UVD-T90+), FT-IR spectrometer (Agilent FTIR spectrophotometer; model CARY-630; range 4000-650 cm^{-1}) and SEM (Nova Nano 450-SEM field emission scanning electron microscope (FESEM).

Fabrication of Bismuth doped ZnO/MoO$_2$ composites

Bi^{3+} doped ZnO/MoO$_2$ composites were successfully prepared by simple co-precipitation method (Figure 5). Appropriate amounts of zinc sulphate (1 mM), sodium molybdate (1 mM) and bismuth chloride (0.4 – 1.0 %) were dissolved in 10 mL deionized water separately and stirred for few minutes until solutions became transparent. To the solution of bismuth chloride, solutions of zinc sulphate and sodium molybdate were added together with stirring on hot plate. Then, NaOH (2 mol %) was added drop wise in the above resulting mixture and stirred again vigorously by keeping the pH at 7. This resulted yellow colored precipitates, which were filtered, washed several times with deionized water, ethanol and finally dried in oven at 80°C for 2 hours. The dried precipitates were crushed with mortar and pestle to obtain fine powder and then placed in muffle furnace at 650°C for 4 hours to anneal at the rate of (5 °C/min).

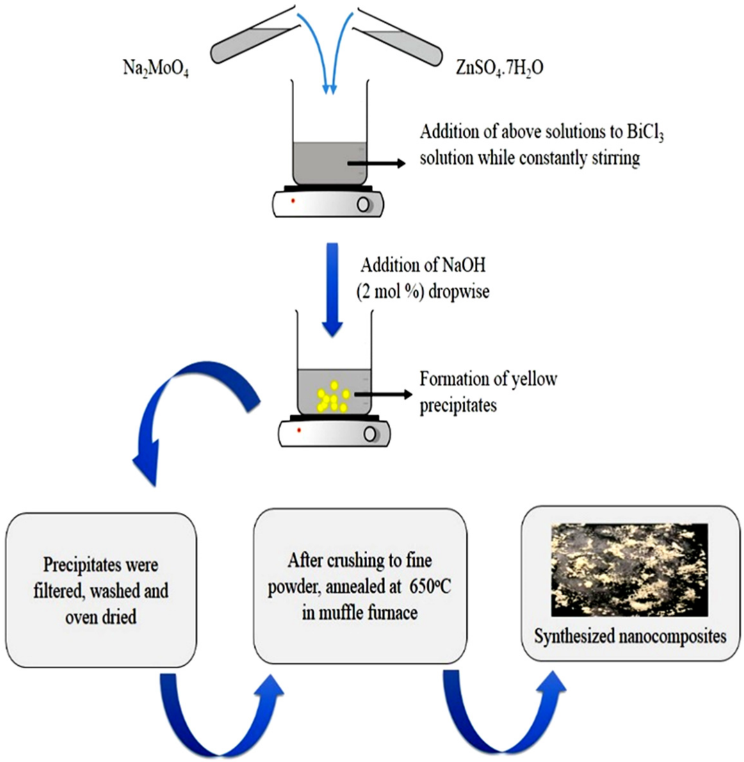

Figure 5. Schematic representation for the synthesis of Bi doped ZnO/MoO$_2$ composites

Degradation of MB using Bi doped ZnO/MoO_2 composites

MB solution (2.0 mmol, 5 mL) was mixed with $NaBH_4$ (0.2 g) in the presence of variable amount (0.4 – 1.0%) of Bi-doped ZnO/MoO_2 catalyst at room temperature. The degradation of dye was noted by UV/Visible Spectrometer after every 15 seconds. The degradation rate of MB dye was calculated by using the following equation:

$$\text{Degradation rate} = \frac{Ao-A}{A} x100$$

where A_o shows initial absorbance, and A corresponds to variable absorbance.

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