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ORIGINAL PAPER

Decolorization of Methylene Blue Dye Using Sonocatalytic Followed by Photocatalytic Process

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Abstract The aim of the present investigation is to study the different methods to improve the photocatalytic decolorization using visible light photocatalyst. In this investigation, ZnO/Bi_2O_3 composite was prepared using hydrothermal method, and it is studied for the decolorization of methylene blue (MB) dye. Enhancement of decolorization has been done by ultrasonication followed by photocatalytic process. Considerable improvement was observed in sonocatalysis followed by photocatalytic process. Various operating parameters have been studied and optimized for the maximum decolorization of dye wastewater. It is observed from the present result that the sonocatalysis followed by photocatalysis is found to be the more efficient method for the treatment of wastewater.

Keywords Decolorization · Hydrothermal method · Methylene blue dye · Photocatalysis · Sonocatalysis · ZnO/Bi_2O_3 catalyst

Introduction

Wastewater generated from the textile industry causes color and odor and it contains high amount of COD and BOD. The large volume of wastewater released to the environment not only causes adverse effect to human health but also reduces the freshwater resources. Hence, it is not only important to treat the effluent but also to conserve freshwater. Water conservation and water loss reduction is always an integral part of the management of freshwater. Generally, the traditional tertiary process is used to remove color and odor and to clean the wastewater. But the major disadvantage in this method is that it releases toxic carcinogenic products. Hence, to overcome the disadvantage, several oxidation methods such as Fenton process [1], ozonation, sonication [2–5], and photocatalytic process [6–8] are introduced.

Fenton process produces iron sludge during the treatment process, and separation of iron through precipitation is a tedious process. It also needs limited pH range of about 2 to 3 [9]. Ozonation treatment process has the disadvantage of limited half-life period. In the sonication process, sound released creates excess pressure and temperature among the bubbles that break the bonds of the molecules. But the removal efficiency is very low, since it cannot degrade the higher pollutant volume. Hence, photocatalytic treatment has been selected to treat the effluent since only light irradiation is used and no chemicals will involve in this process which is a major advantage. But photocatalytic process as an individual process is rather slow. Therefore, to enhance the degradation efficiency, many hybrid advanced oxidation processes (AOPs) such as electro-Fenton, UV/ H_2O_2, O_3/H_2O_2 photo-Fenton, and sonophotocatalytic process are used to degrade the effluent [10, 11]. Various ferrites, oxyhalides, semiconductor oxides, and vanadates such as WO_3, $BiVO_4$, Cu_2O, ZnO, CeO_2, BiOBr, and GO are used as a photocatalyst [12–15]. In order to enhance the photocatalyst, various methods such as doping and composites of various catalysts are reported in the literature [16]. Sharm and Lee [17] investigated nickel-doped titanium nanocomposite as an adsorbent and a photocatalyst for naphthalene removal from aqueous phase. The author reported that 2.5 times higher removal was achieved by the nanocomposite in the presence of visible light compared to TiO_2 alone. The same authors [18] also investigated and synthesized cobalt oxide-loaded TiO_2 further supported with reduced graphene

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oxide for the degradation of 2-chlorophenol under visible light irradiation. The authors observed that the incorporation of cobalt oxide-loaded TiO_2 supported with reduced graphene oxide might improve the photocataytic activity and reported 98.2 % degradation efficiency.

The Bi_2O_3 catalyst can be excited by visible light with a band gap of 2.8 eV and it has been proven to be an efficient photocatalyst [14]. But Bi_2O_3 alone shows lower photocatalytic activity, due to its higher recombination rate. The catalyst having higher recombination rate will have lower photocatalytic efficiency [19]. For this, heterojunction may be done. Heterojunction is combination of two dissimilar semiconductors of different energy band gaps in order to slow down the recombination rate. Hence, heterojunction or coupling of semiconductors had been selected in order to restrain the recombination. Here, ZnO is taken for coupling since it has higher potential in photocatalytic activity of wide energy band gap (3.2 eV). In this experiment, the p-n type semiconductor of ZnO/Bi_2O_3 is used. The objective of the present work is to prepare the ZnO/Bi_2O_3 catalyst using hydrothermal method and study the sonocatalytic followed by photocatalytic decolorization of synthetic dye wastewater.

Materials and Methods

Synthesis of Zinc Oxide-Bismuth Oxide Catalyst Using Hydrothermal Method

Commercial ZnO and Bi_2O_3 powders were purchased from Sigma Aldrich and used without any further purification. The composites were prepared according to Maryam et al., [20] where the commercial zinc oxide of about 0.5 g was dissolved in 0.2 mol of NaOH. On continuous stirring, about 0.5 g of commercial bismuth oxide was added. The mixture was taken in Teflon-lined stainless steel autoclave and kept in temperature of 80 °C for 24 h. The solution was then decanted and washed by distilled water and ethanol for five times and the resulting precipitate was dried in the hot air oven for 12 h at 60 °C.

Experimental

The experiment for the present investigation is carried out in an ultrasonicator followed by photochamber. Synthetically, prepared methylene blue (MB) dye is taken in the sonicator. Sonicator consists of cylindrical jacketed stainless steel reactor equipped with inbuilt piezoelectric transducer placed at the rectangular bottom and an external generator is used. The bath type can deliver fixed frequency of 36 kHz. The setup is connected to AC power supply. After sonication, the solution is subjected to photocatalytic process. The photocatalytic apparatus consists of three 300 W xenon lamps consisting of magnetic stirrer to maintain the uniform mixing of the solution. It has UV filter cap so that it will not allow light of range below 420 nm. Cooling fans are provided in the chamber to control the temperature. Experiments were conducted for sonocatalytic followed by photocatalytic process. After a definite time interval, the samples were collected from the conical flask and were analyzed for color removal.

Result and Discussion

XRD (X-Ray Diffraction) Measurement

An XRD pattern of ZnO/Bi_2O_3 composite is shown in Fig. 1. The peaks were formed according to Maryam et al. [20]. The

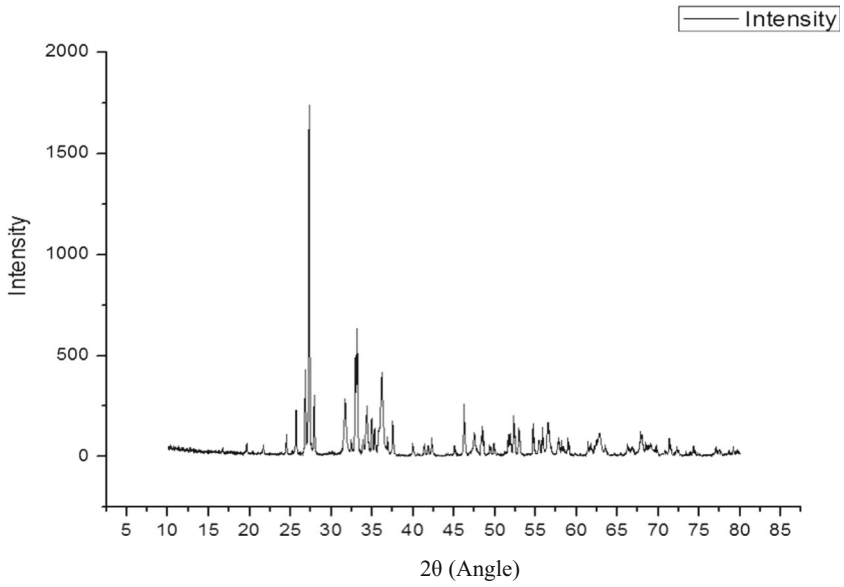

Fig. 1 XRD result of the catalyst used for the sonocatalysis followed by photocatalysis process at angle 2 theta

peaks formed at 27.2° and 33.7° confirm the presence of Bi_2O_3 (JCPDS No. 71-2274). The peaks formed at 31.69°, 34.9°, and 36.1° indicate the presence of zinc oxide (ZnO) (JCPDS No . 79-2205). The other peaks formed in the analysis show the crystalline nature of the sample. Thus, from the XRD analysis, it shows that the ZnO/Bi_2O_3 composite had been formed.

Band Gap Energy of Photocatalyst

UV DRS of the ZnO/Bi_2O_3 catalyst is shown in Fig. 2. It is noticed from the figure that the maximum wavelength was observed at 463 nm. The band gap has been calculated using the formula ($E = 1240/\lambda$ where λ is the wave length) and found to be 2.67 eV. It is evident that ZnO (3.2 eV) and Bi_2O_3 (2.8 eV) form a composite (ZnO/Bi_2O_3) having the band gap energy of 2.67 eV which can be used effectively as a visible light photocatalyst.

Decolorization of Methylene Blue Dye on Individual and Sequential Process

The effect of different processes such as sonolysis, photocatalysis, and sonication (catalyst is not added during sonication) followed by photocatalysis and sonocatalysis (catalyst is added during sonication) followed by photocatalysis on color removal of methylene blue dye is shown in Fig. 3. For all processes, 10 mg $L^{-1}$of MB dye concentration was taken and 1 g L^{-1} ZnO/ Bi_2O_3 catalyst has been added. In photocatalytic process, 93.97 % of color removal was achieved at the end of 135 min. The reason behind this is that due to heterojunction of two semiconductors, the electrons that get excited due to the light irradiation get transferred from ZnO to Bi_2O_3 due to the band gap energy of about 3.2 eV and 2.8 eV, respectively. Also, the electron holes get transferred from Bi_2O_3 to ZnO, due to this recombination rate gets reduced and OH radicals formed. In sono followed by photocatalytic process about 94.3 % of color removal was achieved at the end of 120 min. The reason behind is that due to sonication $OH^{\bullet}$, radicals formed will be higher and hence the color removal occurs in faster rate than that of individual process. In sonocatalysis followed by photocatalysis process, about 94.4 % of color removal was observed within 105 min. This is due to the reason disaggregation of catalyst by ultrasonic vibrations, thus increasing surface area of catalyst [21]. In sonocatalysis method, only 10.2 % removal was observed. There is no further color removal that was observed in the process. It is evident from all processes that efficient color removal at lesser time was achieved by sonocatalysis followed by photocatalysis.

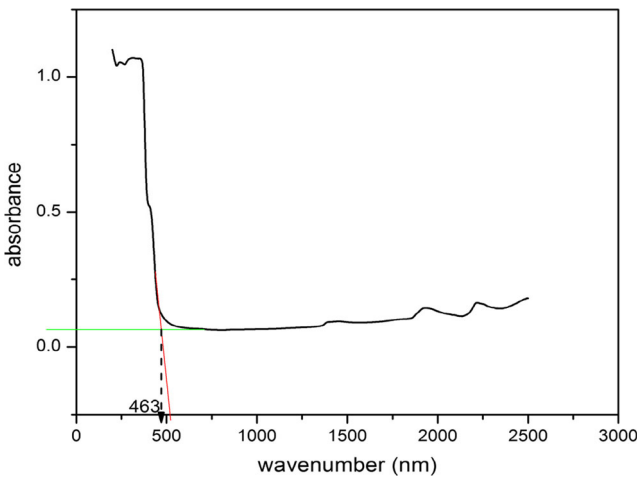

Fig. 2 UV DRS of the ZnO/Bi_2O_3 catalyst

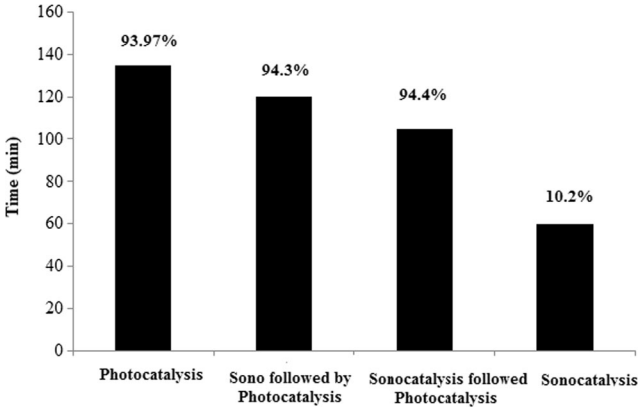

Fig. 3 Decolorization of MB dye individual and sequential process. Initial methylene blue dye concentration: 10 mg L^{-1}, catalyst dosage: 1 g L^{-1}, light intensity: 300 lx

Effect of Light Intensity

The effect of light intensity on percentage color removal has been studied for an initial dye concentration of 10 mg L^{-1} with 1 g L^{-1} of catalyst. The dye solution was sonicated and then kept in photocatalytic chamber. The light intensity has been varied and the result is shown in Fig. 4. It is observed from the figure that percentage color removal increases with increase in light intensity. This is due to that at the low light intensity, the light travelled to reach the catalyst will be low which results in less hydroxyl radical formation.

Effect of Catalyst Dosage

The effect of catalyst dosage on percentage color removal is shown in Fig. 5. It is observed from the figure that as the amount of catalyst increases, the time to achieve the color removal gets decreased. This is due to increase in surface area as catalyst dosage increases.

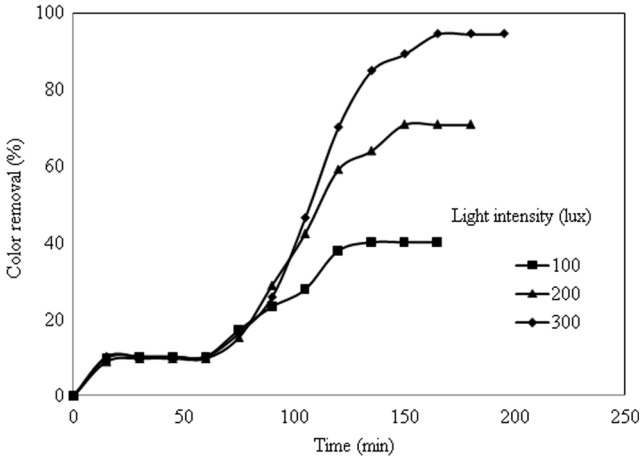

Fig. 4 Effect of light intensity on percentage color removal of MB dye. Initial methylene blue dye concentration: 10 mg L^{-1}, catalyst dosage: 1 g L^{-1}

Effect of Initial Dye Concentration

The effect of initial dye concentration on percentage color removal is shown in Fig. 6. It is observed from the figure that by increasing dye concentration, the percentage color removal gets decreased and the time taken for color removal of methylene blue increased. It is further noticed from Fig. 6, for 20 mg L^{-1}, 40 mg L^{-1}, and 60 mg L^{-1} dye, the color removal was constant beyond 330 min and for the 80 mg L^{-1} dye, the color removal was constant after 420 min. This is due to the reason that the higher concentration of dye solution absorbs the visible light and only certain amount of light is used for photo catalytic process thus decreasing formation of $OH^{\bullet}$ radical. Hence, the percentage color removal is more for less dye concentration.

Effect of pH

The effect of pH on percentage color removal is shown in Fig. 7. It is observed that at neutral pH, the color removal

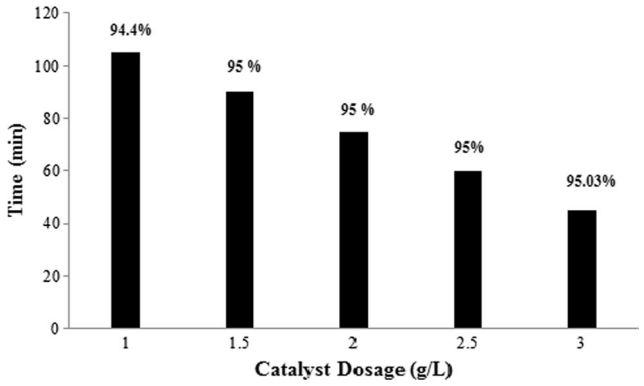

Fig. 5 Effect of catalyst dosage on percentage color removal of MB dye. Initial MB dye concentration: 10 mg L^{-1}, light intensity: 300 lx

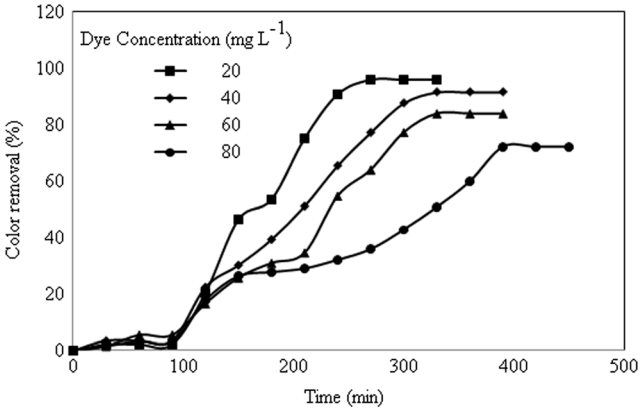

Fig. 6 Effect of initial dye concentration on percentage color removal of MB dye. Catalyst dosage: 1 g L^{-1}, light intensity: 300 lx

was 97 %, and at pH 4, the color removal was 63 %. Also, the color removal gets decreased from 97 to 89 % at pH 11. At acidic conditions, ZnO gets dissoluted [22], and hence the color removal will be very low. The higher efficiency at neutral pH may be due to the reason that surface charge density of the catalyst may have been changed from positive to negative [23]. Since methylene blue is cationic and charge density of the catalyst is negative, it leads to electrostatic attraction and thus increasing the removal efficiency. At alkaline pH, it again decreases because hydroxyl groups formed will be more leading to scavenging effect, in which initially color removal is higher, but later on, the color removal decreases with increasing time due to decomposition of the catalyst.

Reusability of the Catalyst

To test the reusability, the already used catalyst was washed with ethanol and kept in air oven. The dried catalyst was then taken and used in the photocatalytic pro-

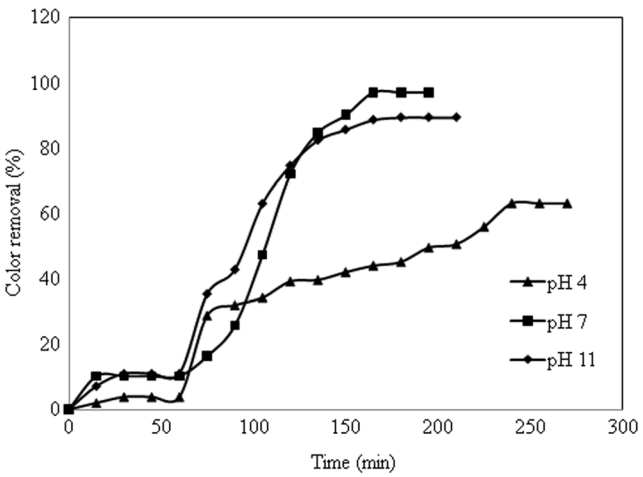

Fig. 7 Effect of pH on percentage color removal of MB dye. Initial MB dye concentration: 10 mg L^{-1}, catalyst dosage: 1 g L^{-1}, light intensity: 300 lx

cess. The effect of reusability of the catalyst is shown in Fig. 8. It is observed from the figure that the percentage color removal decreases (91, 87, and 81 %, respectively) as the number of reusable cycle of catalyst increases.

Kinetics of Photocatalytic Process

Kinetic study of methylene blue color removal has been performed for different initial dye concentrations. The kinetics of the color removal can be written as follows:

$$-\frac{dC}{dt} = kC \tag{1}$$

The equation can be written as a pseudo first order reaction with respect to color removal:

$$-\ln\left(\frac{C_t}{C_0}\right) = kt \tag{2}$$

Where C_0 is the initial absorbance of the dye, C_t is the absorbance of the dye as a function of time, t, and k is the rate constant. The term $-\ln (C_t/C_0)$ was plotted versus time and the slope gives k value of rate constant. The k value for the percentage color removal in each experimental condition is calculated. The kinetics study of methylene blue for color removal for various initial concentrations is shown in Fig. 9. It is observed from the figure, $-\ln (C_t/C_0)$ versus time "t" follows the straight line. The correlation coefficients are regarded as an index of the goodness-of-fit to the first order kinetics. The R^2 values of dye decolorization of photo catalysis process are typically ≥0.920. It can be observed from the figure that the color removal follows the first order kinetics having the rate constants of 0.015, 0.008, and 0.006 min^{-1} for 20, 30, and 40 mg L^{-1} of initial concentration of dye solution.

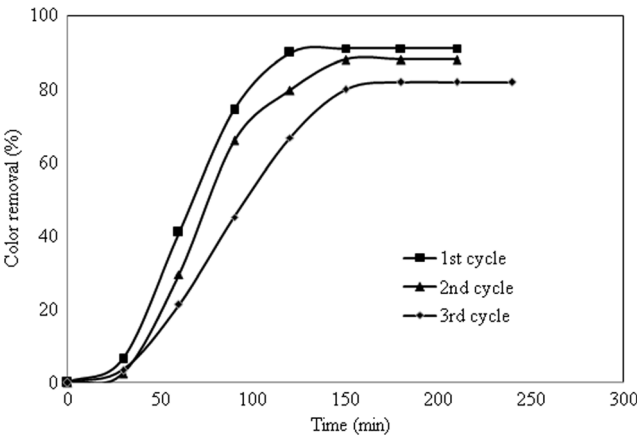

Fig. 8 Effect of catalyst reusability on percentage color removal of MB dye. Initial MB dye concentration: 10 mg L^{-1}, catalyst dosage: 1 g L^{-1}, light intensity: 300 lx

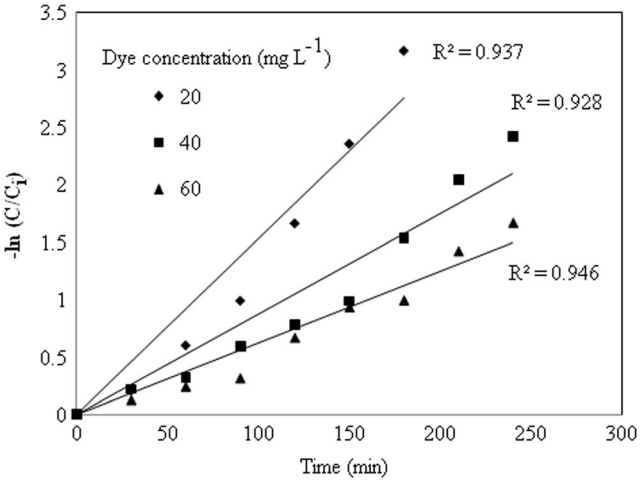

Fig. 9 Kinetics MB dye color removal using photo catalysis. Catalyst dosage: 1 g L^{-1}, light intensity: 300 lx

Conclusion

The ZnO/Bi_2O_3 composite catalyst was prepared and its photocatalytic property was investigated. The effect of various combinations of processes such as sono followed by photocatalysis and sonocatalysis followed by photocatalysis were experimentally investigated. It has been observed that all the processes achieved good color removal efficiency while in combination of process; reaction gets faster than that of the individual process. The effect of catalyst dosage, initial dye concentration, pH, and light intensity also has been experimentally investigated on color removal of the dye. The band gap of the photocatalyst had been found by UV-diffuse reflectance spectroscopy and found out to be 2.67 eV. The reusability of the catalyst was tested for three cycles; the percentage color removal was found out to be 91, 87, and 81 %, respectively.

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