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Research Article
Synthesis and Characterization of Sn/ZnO Nanoparticles for Removal of Organic Dye and Heavy Metal

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Abstract

Background and Objective: Environmental pollution from human activities is a major challenge of civilization today. This study aimed to use Sn doped ZnO nanoaprticles for the purification polluted water from dye and heavy metal. **Materials and Methods:** The Sn doped ZnO nanoparticles have been synthesized using a simple chemical method and characterized by XRD, SEM and AFM. The degradation efficiency of Sn/ZnO nanoparticles was studied against methyl orange dye along with Cr(VI) by using a UV-vis spectrophotometer (SI-210 Double Beam UV Visible Spectrophotometer (Elico)). **Results:** The results demonstrated that the photocatalyst was efficient at 200 mg L^{-1}, the maximum amount of degradation (80.2 %) have been observed for MO/Cr(VI) after 2 h. **Conclusion:** The photocatalytic performance of the Sn/ZnO nanoparticles was stable after the nanoparticles were reused 5 times. The photocatalytic ability of the Sn-doped ZnO film allowed the development of a low cost, high efficiency and environmentally friendly material for water treatment applications using sunlight.

Key words: ZnO nanoparticles, photocatalyst, dye degradation, methyl orange dye, AFM

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Synthetic dye usage has increased in the textile and dyeing industries because of their ease and cost-effectiveness. The environmental problem associated with the use of dyes is their lose during dyeing process since the fixation efficiency ranges from 60-90%[1]. Effluents discharged from textile and dyeing industries causes serious environmental threats due to its high contamination of color and heavy metals. Many dyes resistant to biodegradation, difficult to be broken down its structure biologically. Methyl orange dye is hard to be degraded, can cause harmful effects on living organisms. If the heavy metals are ingested they can cause serious health disorders[2]. The Cr(VI) is toxic for humans and is associated with the development of various health disorders[3]. Therefore, it is necessary to treat heavy metal and dye contaminated effluent prior to its discharge to the environment. Conventional treatment of most organic dyes has significant disadvantages. Adsorption has many advantages over other methods. The adsorbents may be of mineral, organic, zeolites, nanoparticles/nano composites, agricultural wastes, biomass and polymeric materials[4,5].

Plenty of natural source energy available from the sun light could be used to degrade some organic dyes in the presence of photo catalyst upon solar light irradiation[6]. So, this study was aimed to synthesize eco-friendly heterogeneous photocatalyst able to decompose dye and adsorb heavy metal from industrial waste water. Therefore, Sn doped ZnO nanoparticles have been synthesized using a simple chemical method and degradation efficiency of Sn/ZnO nanoparticles was studied against methyl orange dye along with Cr(VI).

MATERIALS AND METHODS

Materials: All chemicals $Zn(NO_3)_2.2H_2O$, $SnCl_4.5H_2O$, methyl orange and solvents were purchased from Merck and were used without further purification. Potassium chromate salt was used to make all chrome standard solutions used in the experiments. A stock solution of 1000 mg L^{-1} was prepared by dissolving the potassium chromate in distilled water. Working standards were then prepared by appropriately diluting the stock solution.

Synthesis of Sn doped ZnO nanoparticles: The Sn doped ZnO nanoparticles have been synthesized using a simple chemical solution method. The stock solutions of starting materials 50 mM $Zn(NO_3)_2.2H_2O$, 50 mM $SnCl_4.5H_2O$ and 100 mM NaOH were prepared using deionized water as solvent for each sample. The solution of NaOH was dropped into the solution of $Zn(NO_3)_2.2H_2O$ under continuous magnetic stirring till the formation of white precipitates of $Zn(OH)_2$. The precipitates were filtered off and washed with distilled water. The precipitates of $Zn(OH)_2$ were first dried in air at room temperature and then calcined at 250°C for 24 h to attain fine crystalline ZnO nanoparticles. For the preparation of Sn doped ZnO, 50 mM $SnCl_4.5H_2O$ was added to 5 g of calcined ZnO nanoparticles. The sample was agitated and heated at 110°C for 30 min. The powder was cooled to room temperature, calcined at 300°C for 2 h and then grounded. Total preparation time of solid product was 25 h. The product obtained was labeled as Sn-doped zinc oxide (Sn-ZnO).

X-ray diffraction (XRD) patterns: The X-ray diffraction (XRD) patterns of ZnO-Sn nanoparticles were carried out by a X-ray diffractometer (PANalytical PW 340/60 X'pert PRO) which was operated with Cu Kα ($\lambda = 1.5406$ A^0) radiation. The synthesized products were characterized using a VEGA3 TESCAN (Czech Republic) scanning electron microscope (SEM) and AFM images were obtained using atomic force microscope (Veeco-di CPII).

Photocatalytic degradation experiment: The photocatalytic activity of the prepared Sn-ZnO photocatalyst was evaluated for simultaneous degradation of MO dye and hexavalent chromium. Batch tests were performed as per the following procedure: 0.2 g Sn-ZnO nanoparticles photocatalyst was added in 100 mL solution prepared by mixing (Cr (VI) (20-50 mg L^{-1})) and MO (10-50 mg L^{-1}) in a beaker and the mixture was stirred in dark for 40 min to allow the physical adsorption of dye molecules on catalyst particles reaching the equilibrium. The photo degradation experiments were carried out under natural sunlight. Reaction samples were collected at regular intervals and immediately centrifuged to remove suspended particles before recoding absorbance. The concentration of MO and Cr(VI) were determined by measuring the absorption intensity at their maximum absorbance wavelengths of 661 and 540 nm, respectively, by using a UV-vis spectrophotometer (SI-210 Double Beam UV Visible Spectrophotometer (Elico)) with a 1cm path length spectrometric quartz cell and then calculated from calibration curve. The percentage of dye degradation was calculated from the following equation:

$$\text{Dye degradation (\%)} = \frac{A_0 - A_t}{A_0} \times 100$$

where, A_0 is absorbance of dye at initial stage, A_t is absorbance of dye at time "t".

The percentage removal of Cr(VI) was calculated according to the following equation:

$$\text{Removal of Cr(VI) (\%)} = \frac{C_0\text{-Ce}}{C_0} \times 100$$

where, C_0 and C_e are the initial and final concentrations of Cr(VI) metal ion in the solution phase.

Effect of Sn/ZnO load on the degradation of MO/Cr(VI) mixture: The effect of amount of photocatalyst on the rate of simultaneous photocatalytic degradation of MO and Cr(VI) was observed by taking different amounts of Sn-ZnO (100-300 mg L^{-1}) keeping other factors constant.

Effect of initial concentration of methyl orange and chromium (VI): The effects of MO and Cr(VI) concentrations on the rate of their photocatalytic degradation were observed at different concentrations (10-50 mg L^{-1}) of MO and Cr(VI).

Effect of pH of the solution: The effect of pH on the rate of photocatalytic degradation of MO/Cr(VI) mixture was investigated in the pH range of 2-12. The pH was maintained each time by using 1 M HCl or 1 M NaOH and measured using a pH meter.

Recycling/reuse of the Sn-ZnO photocatalyst: The recycling and reuse of the photocatalyst for the degradation of MO/Cr(VI) mixture was also tested. For each experiment, the 200 mg L^{-1} of Sn-ZnO photocatalyst was added into the MO/Cr(VI) solution with an initial concentration of 10 mg L^{-1} MO and 20 mg L^{-1} Cr(VI) in 1:1 ratio, pH maintained at 4. The degradation efficiency was calculated after contact time of 120 min. The experiment was carried out five times with the same, reused Sn-ZnO photocatalyst.

RESULTS AND DISCUSSION

Characterization of Sn-ZnO nanoparticles: From the XRD pattern in Fig. 1, it is obvious that the sample has typical wurtzite crystal structures with two characteristic peaks. The strong peaks located at 34.04 and 36.63° corresponding to the miller index of (002) and (101) phases of ZnO. No peaks related with Sn were detected, demonstrating that the Sn atoms were completely dissolved in the ZnO lattice.

The microstructure and morphology of nanoparticles were analyzed using SEM. Figure 2 shows the micrographs of the samples of Sn/ZnO nanoparticles. The Sn/ZnO nanoparticles are heterogeneous in nature. Anisotropic growth of crystal results from the driving force of the dopant on ZnO lattice, hence, Sn-doped ZnO nanostructures have a granular shape as shown in Fig. 2[7].

Atomic force microscopy: AFM images have been used to estimate the grain size of the samples. Figure 3a and b shows both 2D and 3D images obtained using an AFM (Atomic Force Microscope) for Sn doped ZnO nanoparticles. The sampling areas used were [5×5 μm]. Micrographs reveal that films are closely packed and granular in nature; signature of agglomeration of grains is almost absent. Uniform brightness contrast exhibits absence of impurities or clusters[8,9]. The measured roughness parameter was 3.45 nm.

Effect of Sn/ZnO load on the degradation of MO/Cr(VI) mixture: It is necessary to find out the optimum loading of photocatalyst for efficient removal of dye[10]. Hence, a series of experiments were carried out to find the optimum amount of the photocatalyst Sn/ZnO by varying its amount from 100-300 mg L^{-1}. The percent degradation of dye versus time of degradation by varying the photocatalyst weight is recorded is given in Fig. 4. To achieve highest photocatalytic reaction rate, the optimum amount of the photocatalyst was found to be 200 mg L^{-1}. The observed dependence of reaction

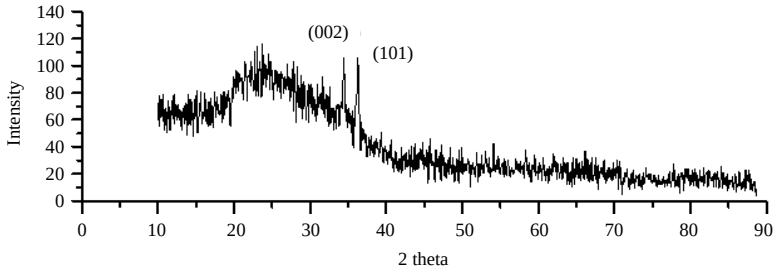

Fig. 1: XRD spectrum of Sn-ZnO nanoparticles

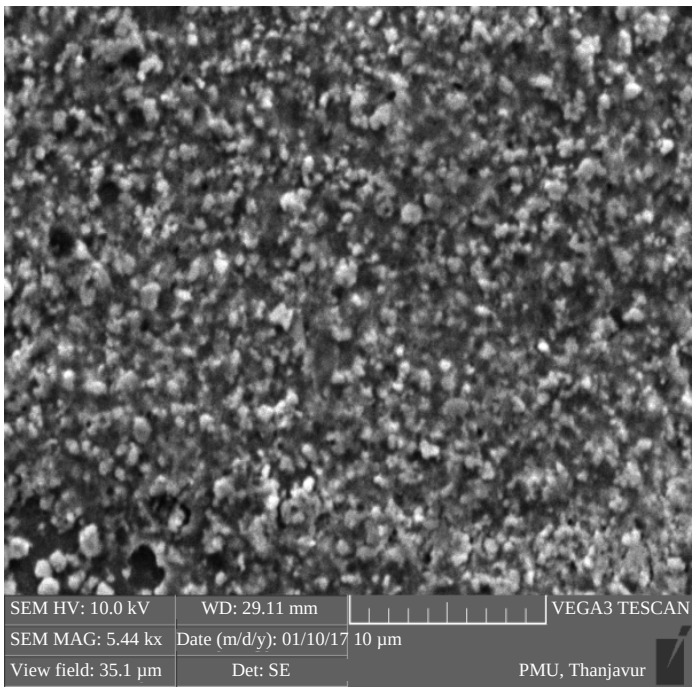

Fig. 2: SEM micrograph of Sn doped ZnO nanoparticles

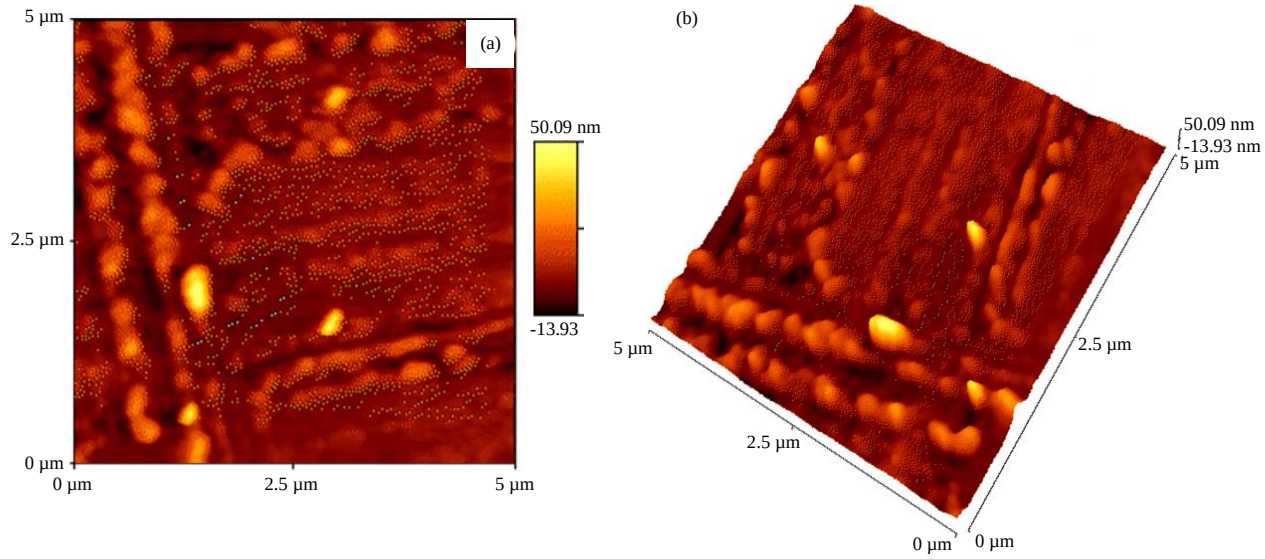

Fig. 3(a-b): AFM images of Sn doped ZnO nanoparticles (a) 2D image and (b) 3D image

rate on the amount of photocatalyst can be explained in terms of the availability of active sites at the adsorbent surface and the level of light penetration in the reaction medium[11]. Upon increasing the amount of photocatalyst up to 200 mg L^{-1} percent degradation increases due to the increase in the adsorbent total surface area and thus, the number of active sites, available for the photocatalytic reaction. However, excess photocatalyst, above this optimal load, would induce more aggregation (particle-particle interactions) of photocatalyst making a significant fraction of the catalyst inaccessible either to the adsorbing dye or to the radiation[12]. The degradation efficiency decreases after achieving an optimum value of photocatalyst load. Therefore, 200 mg L^{-1} of the photocatalyst was selected as the optimal amount of photocatalyst for the subsequent experiments.

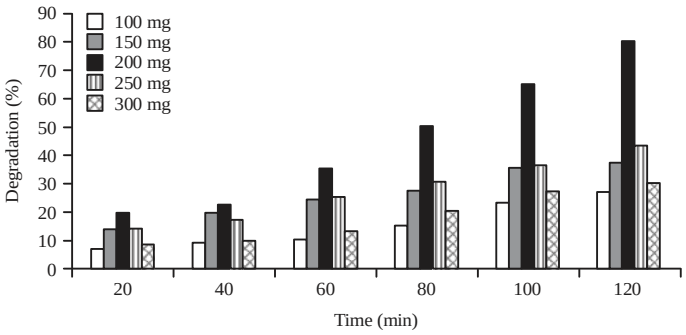

Fig. 4: Percent degradation of MO/Cr(VI) Vs. time by varying the amount of Sn/ZnO (100-300 mg)

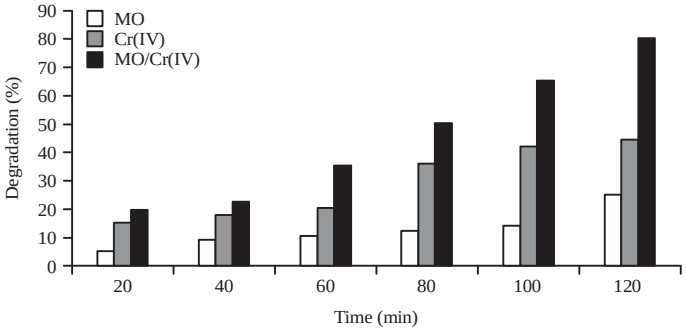

Fig. 5: Percent degradation of MO, Cr(VI) and MO/Cr(VI) Vs. time

Effect of initial concentration of methyl orange and chromium (VI): The comparative study of % degradation of MO dye , Cr(VI) and MO/Cr(VI) mixture in solutions with the concentration of 200 mg L^{-1} for the Sn-ZnO nanoparticles under sunlight shown in Fig. 5. The result shows that 25.1, 44.4 and 80.2% degradation have been observed for MO, Cr(VI) and MO/Cr(VI) at 2 h, respectively using initial concentrations of MO 10 mg L^{-1}, Cr(VI) 20 mg L^{-1} and MO/Cr(VI) in 1:1 ratio of MO and Cr(VI). From the figure the % degradation of MO/Cr(VI) mixture are higher than that of the MO and Cr(VI) individually[13]. This may be because in the metal ion-organic compound system, organics receives holes from the valance band directly or indirectly and get oxidized. The enhancement in the rate and extent of MO degradation confirmed that Cr(VI) is an efficient scavenger of photogenerated electrons. Similarly, the presence of MO significantly promoted the reduction rate of Cr(VI) because of the promoter effect by photocatalytic degradation of the dye as shown in Fig. 5.

Effect of pH: The effect of pH on MO/Cr(VI) removal efficiency by Sn/ZnO nanoparticles was determined at pH 2, 4, 6, 8, 10 and 12. For each experiment, the 200 mg L^{-1} of adsorbent was added into the MO/Cr(VI) solution with an initial concentration of 10 mg L^{-1} MO and 20 mg L^{-1} Cr(VI) in 1:1 ratio. The degradation efficiency was calculated after contact time of 120 min. The results were presented in Fig. 6, from the results, the optimum pH for removal efficiency of Sn/ZnO was observed as 4. High removal of Cr(VI) at low pH is probably due to reduction of hexavalent chromium to trivalent chromium ions, which is easier in removal[14]. The favorable of low pH can be attributed to the neutralization of negative charges on the surface of the adsorption by excess hydrogen ions, thereby facilitating the diffusion of hydrogen chromate ions $(HCrO_4)^-$ and their subsequent adsorption. By increasing pH $(HCrO_4)^-$ species shifts to forms $(CrO_4)^-$ and $(Cr_2O_7)^-$. The decrease in adsorption of Cr(VI) by increasing pH is due to completion between the anions $(CrO_4)^-$ and OH^- [15,16].

Figure 7 shows the results obtained regarding the recycling and reuse of the photocatalyst for photocatalytic degradation of MO/Cr(VI) mixture. The experiment was carried out under the following conditions; for each experiment, the 200 mg L^{-1} of adsorbent was added into the MO/Cr(VI) solution with an initial concentration of 10 mg L^{-1} MO and 20 mg L^{-1} Cr(VI) in 1:1 ratio. The degradation efficiency was calculated after contact time of 120 min. The results show that the photocatalytic activity remained nearly unchanged after five uses, which indicates that the photocatalyst is stable in the photocatalytic oxidation of

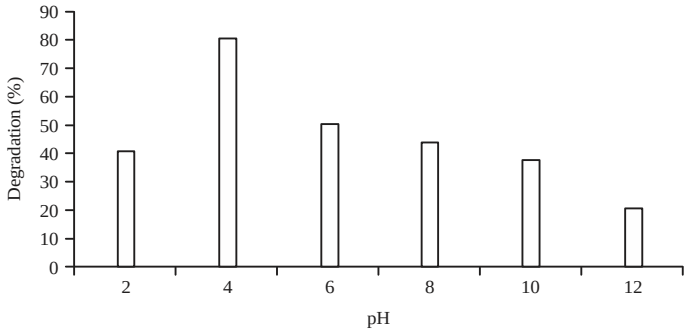

Fig. 6: Percent degradation of MO/Cr(VI) at 120 min by varying the pH of the solution keeping MO/Cr(VI) concentration and Sn/ZnO amount as constant

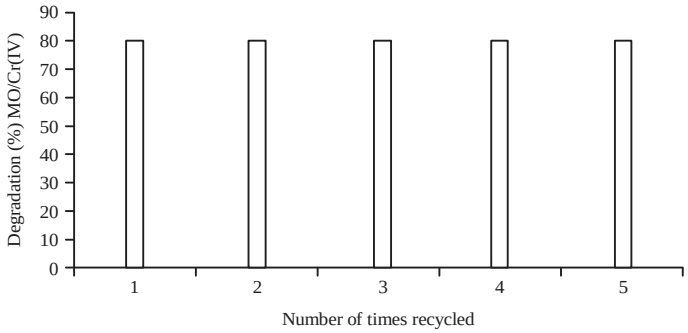

Fig. 7: Recycling of the photocatalyst for degradation of MO/Cr(VI) mixture

MO/Cr(VI) mixture. This results also agreement with previous reports[17]. Therefore, this photocatalyst can be separated and recycled while maintaining its stability, making it a promising material for environmental remediation.

CONCLUSION

In this study, the Sn doped ZnO nanopowders were successfully synthesized via chemical method and calcined at 300°C. Photocatalytic performances of Sn/ZnO nanoparticles were evaluated using MO, Cr(VI) and MO/Cr(VI) solutions as the indicator under the natural sunlight. The results demonstrated that the photocatalyst was very efficient, 80.2% degradation have been observed for MO/Cr(VI) after 2 h. This study provided a simple yet efficient way to synthesize Sn/ZnO based photocatalysts in large scale. Also, the "superlong" nature of Sn-doped ZnO nanoparticles suggests that the photocatalysts are recyclable.

SIGNIFICANT STATEMENT

In wastewater systems containing heavy metals with other organic pollutants, the most promising methods to treat such complex systems are the photocatalytic ones which consume cheap photons from the sun light. These photo catalysts serve as electron relays, from the organic substrates to metal ions. Hence, this study would help the researcher in determining mechanism of ZnO nanoparticle as they induce both degradation of organic pollutants and metal ions.

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