Trends in Applied Sciences Research

ISSN 1819-3579

Academic
Journals Inc.

www.academicjournals.com

OPEN ACCESS Trends in Applied Sciences Research

ISSN 1819-3579
DOI: 10.3923/tasr.2017.1.9

Research Article
Preparation of Modified Nanoparticles of Zinc Oxide for Removal of Organic and Inorganic Pollutant

Shady Mohamed El-Dafrawy, Salah Fawzy and Shawky Mohamed Hassan

Department of Chemistry, Faculty of Science, Mansoura University, Mansoura, Egypt

Abstract

Background and Objective: Water pollution is a worldwide issue that attracted the researcher's attention. It involves the release of toxic substances, pathogenic germs, easy-soluble substances, radioactivity, etc. These pollutants affect human health, aquatic living and microorganisms. This study aimed to use modified ZnO nanoparticles as an affordable technique for the purification of water from dyes and heavy metals. **Materials and Methods:** In attempt to improve methylene blue photodegradation rates using ZnO, a series of tin oxide (SnO_2) doped ZnO photocatalysts were synthesized using sol-gel method with a doping molar ratios (0, 0.01, 0.02, 0.04 and 0.05 M) SnO_2/ZnO. The prepared photocatalysts were characterized by XRD (X-Ray Diffraction), Scanning Electron Microscope (SEM), Transmission Electron Microscopy (TEM) and Diffuse Reflectance Spectra (DRS) in order to investigate their morphology, structures and band gab. **Results:** The crystallinity and the average grain sizes of ZnO decreased with increasing the amount of SnO_2. The DRS showed a reduction in band gap energy from 3.27-3.10 eV by increasing SnO_2 molar ratio. The percentage of degradation dropped, when the initial dye concentration increased. The amount of adsorbed metals on SnO_2 doped ZnO surface increased by increasing SnO_2 molar ratio then decreased at 0.05 M SnO_2 doped ZnO. **Conclusion:** The SnO_2 doped ZnO photocatalyst demonstrated the highest photodegradation efficiency which was about 100% in 90 min and higher adsorption efficiency to all studied heavy metals which was nearly 100% to all metals in 1 h.

Key words: Sol-gel, SnO_2 doped ZnO, methylene blue, photocatalysts, adsorption

Received: September 13, 2016 Accepted: November 07, 2016 Published: December 15, 2016

Citation: Shady Mohamed El-Dafrawy, Salah Fawzy and Shawky Mohamed Hassan, 2017. Preparation of modified nano ZnO for removal of organic and inorganic pollutant. Trends Applied Sci. Res., 12: 1-9.

Corresponding Author: Shady Mohamed El-Dafrawy, Department of Chemistry, Faculty of Science, Mansoura University, Mansoura, Egypt
Tel: 00201007783311

Competing Interest: The authors have declared that no competing interest exists.

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

INTRODUCTION

Organic pollutant such as dye is one of these pollutants that require much oxygen to decompose and very stable to many water treatment methods[1,2]. Dye is used widely in several industries such as producing fabric, food, furniture and paint. The waste water released from factories contains enormous amount of dyes and organic chemicals produced by industrial processes which is discharged into the environment[3,4].

Many synthetic dyes and their metabolites are toxic, mutagenic and carcinogenic[5]. Also, methylene blue can cause permanent injury to humans and animals on inhalation and ingestion and the risk of the presence of this dye in water may be arisen from the burning effect of eye, nausea, vomiting and diarrhoea[6,7]. Generally, the presence of these pollutants in water causes severe problems to human beings and aquatic life[8].

Acute heavy metal intoxications may damage central nervous function, the cardiovascular and gastrointestinal systems, lungs, kidneys, liver, endocrine glands and bones. Increased heavy metal exposure has been implicated in several degenerative diseases of these same systems and may increase the risk of some cancers[9].

Photocatalysis has attracted attention since the discovery of the Fujishima and Honda in the early 1970's[10], (they discovered that photolysis of water could occur using semiconductor photocatalysts). This discovery suggested a large number of potential applications, such as photovoltaic cells, degradation of pollutants and photolysis of water. Since then, photocatalysis has been a subject of serious research.

One of the major advantages of photocatalytic processes over the existing technologies is that there is no further need for secondary treatments. The process can be summarized as follows:

$$\text{Organic pollutants}+O_2 \rightarrow CO_2+H_2O+\text{mineral acid} \quad (1)$$

The ZnO is one of the most important and widely used photocatalysts as it has the advantages of being cheap, efficient, safe and eco-friendly[11]. In this respect, Advanced Oxidation Process (AOPs) have emerged as promising water treatment technologies for the complete destruction of organic contaminants in water[12,13].

This study was aimed to synthesize nontoxic, environmental friendly and affordable heterogeneous photocatalyst able to mineralize and decompose dyes in wastewater and adsorb heavy metals from water. Therefore, the photodegradation efficiency of ZnO and SnO_2/ZnO was studied against methylene blue dye as a water pollutant. Also, the adsorption of various heavy metals on ZnO and SnO_2/ZnO photocatalysts in neutral conditions were studied.

MATERIALS AND METHODS

Reagents: All inorganic and organic chemicals (zinc acetate dihydrate, tin chloride dihydrate, sodium hydroxide, 2-methoxy ethanol and methylene blue) were of analytical grade.

Preparation of pure tin oxide and zinc oxide catalysts: Zinc acetate dihydrate was used as a precursor to prepare ZnO by sol-gel method. Zinc acetate dihydrate was dissolved in 0.1 M 2-methoxy ethanol by stirring at 70°C for 30 min. Then 28% sodium hydroxide solution was added to the prepared solution drop wise till the solution reached pH 9 to form gel[14]. The obtained gel was left overnight then dried for 20 h at 130 °C to produce xerogel. The xerogel was calcined for 2 h at different temperatures (400, 500, 600 and 700°C) to obtain crystalline nanoparticles of zinc oxide (ZnO). Pure tin oxide (SnO_2) was prepared in the same manner using tin chloride dihydrate as starting material[14].

Preparation of tin oxide doped zinc oxide catalysts: Starting with zinc acetate dihydrate, 8.12 g of zinc acetate dihydrate were dissolved in 370 mL of 0.1 M 2-methoxy ethanol by stirring at 70°C for 30 min. Preparation of 0.1 M 2-methoxy ethanol solution of tin chloride dihydrate was by the same way and added drop wise under vigorous stirring to the previously prepared solution of zinc acetate dihydrate. The obtained solution was vigorously stirred for 2 h at 70°C. The amount of tin chloride dihydrate solution was with molar ratio equal to 0.01/1, 0.02/1, 0.04/1 and 0.05/1 SnO_2/ZnO. The NaOH solution was added drop wise until pH reached the value of 9 where gel is actually formed. The obtained gels were dried for 20 h at 130°C to produce xerogel. Finally, the photocatalysts were obtained by calcining the xerogels for 2 h at different temperatures (400, 500, 600 and 700°C)[14].

Catalyst characterization: X-ray diffraction (XRD) is a non-destructive method for identification and quantitative analysis of various crystalline forms of metal oxides[15]. Patterns were obtained with hand pressed samples mounted on a Philips PW 1830 goniometer using the Cu K_α line (λ = 0.15458 nm) radiation under 40 kV and 100 mA and scanning with the 2θ ranging from 10-80°.

The ZnO and SnO_2 doped ZnO topography was determined by a Jeol JSM-840 Scanning Electron Microscope (SEM) under high vacuum and acceleration voltage of 200 KeV. The samples were deposited onto carbon tape and coated with gold in a Blazers plasma sputterer (30 sec at 30 mA).

Transmission Electron Microscopy (TEM) was carried out using a JEOL 2010 instrument with resolving power 0.2 nm, accelerating tension being 200 keV. Samples diluted in ethanol solution were deposited onto Formvar-coated, carbon-reinforced, 3 mm diameter copper electron microscopes grids and left to air-dry prior to analysis[16].

The UV-Vis transmission spectra of the as-synthesized ZnO and SnO_2 doped ZnO were recorded by the HP Hewlett Packard 8452 A Diode Array Spectrophotometer over the wavelength range of 200-1000 nm. The DRS measurements were used to obtain band gap values[17].

The photocatalytic activities of photocatalysts were evaluated by measuring the degradation ratio of methylene blue as a model pollutant in water under a Shimadzu MPC-2200 UV/Vis spectrophotometer. The methylene blue degradation was carried out at 20°C with external lamp (400 W UV/Vis lamps, Mercury lamp).

The prepared ZnO and SnO_2 photocatalysts were used to remove heavy metals (Cu, Cd, Fe and Pb) from water via adsorption process.

The total metal concentration in solution was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

RESULTS AND DISCUSSION

XRD analysis for ZnO and SnO_2 doped ZnO: The XRD patterns of ZnO, SnO_2 and SnO_2/ZnO samples of different molar ratios calcined at 600°C are shown in Fig. 1. The indexed peaks showed that ZnO nanoparticles exhibited hexagonal wurtzite structure (JCPDS card number: 36-1451) and SnO_2 nanoparticles had tetragonal structure (JCPDS card number: 41-1445) and no other phases were detected. ZnO nanoparticles were well crystalline at 600°C whereas SnO_2 particles were almost amorphous at the same calcination temperature.

The average grain sizes of the SnO_2/ZnO samples were determined by using the diffraction peak (101) for ZnO. The crystallinity and the average grain sizes of ZnO decreased with increasing the amount of SnO_2 from 35-18 nm[18-21]. The mean grain sizes decreased with increasing SnO_2 molar ratio because Sn^{4+} ion (0.71°A) is smaller than Zn^{2+} ion (0.74 °A). Therefore, the more Zn^{2+} ions are substituted with Sn^{4+} ions, the more reduction in crystals size occur.

SEM analysis for SnO_2 doped ZnO: The SEM images of selected samples of pure ZnO and SnO_2 doped ZnO photocatalysts with different concentrations of SnO_2 (0.01, 0.04 and 0.05) are illustrated in Fig. 2. The SEM images show that all the samples were agglomerated to some extent. The average sizes appeared quite close to those

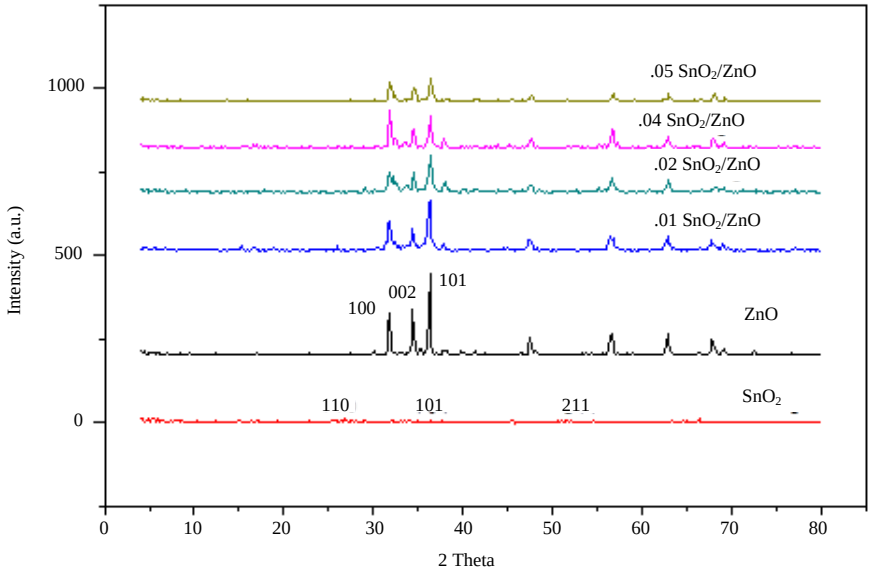

Fig. 1: XRD pattern for ZnO and SnO_2 doped ZnO calcined at 600°C

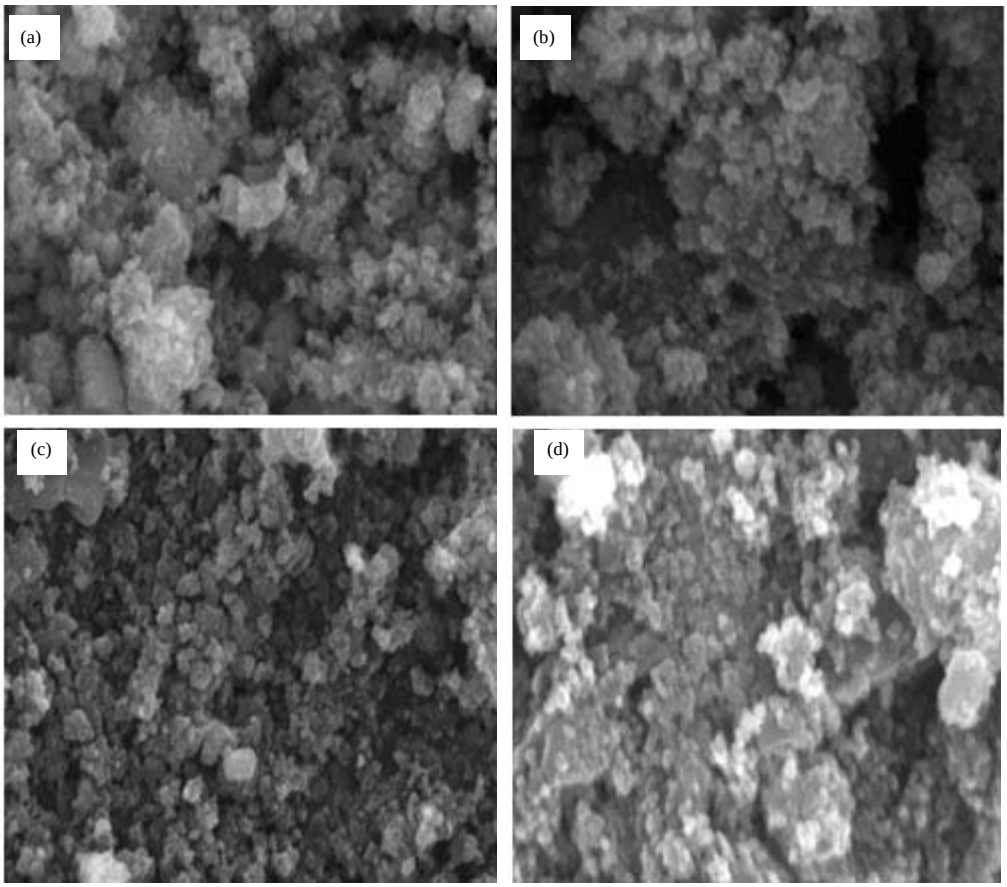

Fig. 2(a-b): SEM images for (a) ZnO, (b) 0.01 M SnO_2/ZnO, (c) 0.04 M SnO_2/ZnO and (d) 0.05 M SnO_2/ZnO

calculated from the XRD patterns. The particles of pure ZnO photocatalyst was successfully synthesized[22] as shown in Fig. 2a. The micrographs of the mixed oxides in Fig. 2b-d revealed the presence of both the hexagonal phase for ZnO and tetragonal phase for SnO_2. The SEM images showed also that tetragonal phase increased with increasing SnO_2 molar ratio. The small crystallites of the different phases were interwoven with each other forming tightly bound nanoclusters[23].

TEM analysis SnO_2 doped ZnO: The representative TEM images of selected samples, pure ZnO and SnO_2 doped ZnO (0.01, 0.04 and 0.05) are illustrated in Fig. 3. The TEM observations showed relative coincidence with XRD analysis in size of crystals and the phase of both ZnO and SnO_2. According to the TEM image in Fig. 3a, ZnO sample was composed of nanoparticles with sizes in the range of about 30 nm and each nanoparticle was attached to several other nanoparticles. The TEM observations also showed that ZnO nanoparticles had a spherical shape and were agglomerated to some extent. The images in Fig. 3(b-d) showed a mixture of hexagonal and tetragonal phases indicating that SnO_2 tetragonal phase is present and indicated that tetragonal phase increased with increasing SnO_2 molar ratio. The images showed that crystals size decreases by increasing amount of SnO_2 in accordance with XRD analysis[22].

UV-Vis absorption spectra: The absorbance values were substituted in Kubelka-Munk equation to get $(\alpha h\nu)^2$ values. The $(\alpha h\nu)^2$ values were plotted against the light energy and the band gap values were determined by extrapolation of the linear part of $(\alpha h\nu)^2$ to $h\nu$ axis[17-24].

The E_g values of ZnO and SnO_2 were 3.27 and 3.55 e.V, respectively. The band gap values of the samples containing ZnO and SnO_2 ranged between 3.10 and 3.16 e.V and were lower than those of both pure oxides. In general, the band gap energies of mixed oxides were very close to that of pure ZnO because the amount of SnO_2 was relatively low.

Photocatalytic activity

Effect of SnO_2 doping concentration on photoactivity of ZnO: The effect of SnO_2 as a dopant on the photocatalytic

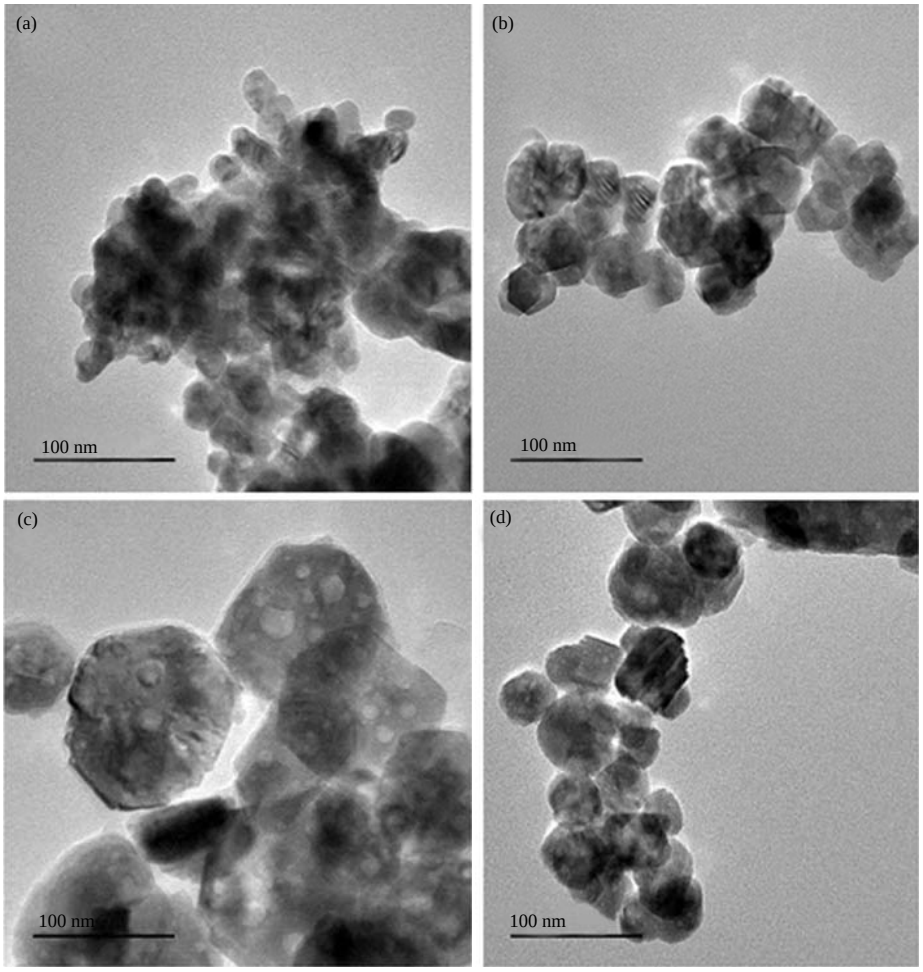

Fig. 3(a-b): TEM images for (a) ZnO, (b) 0.01M SnO_2 doped ZnO, (c) 0.04 M SnO_2/ZnO and (d) 0.05 M SnO_2/ZnO

activity of ZnO in decomposing methylene blue is illustrated in Fig. 4a. The SnO_2 had very law photocatalytic activity due to its law crystallinity. The ZnO showed appreciable photocatalytic activity due to its crystallinity. All the SnO_2/ZnO samples were more active than the two pure oxides. The sample 0.04 M SnO_2/ZnO revealed the highest photocatalytic activity then the photocatalytic activity decreased at 0.05 M SnO_2/ZnO.

Effect of calcination on photoactivity of SnO_2 doped ZnO: The effect of the calcination temperature on the photocatalytic activity of the 0.04 M SnO_2/ZnO sample are illustrated in Fig. 4b. The best photocatalytic activity was obtained when the sample was calcined at 600°C, whereas the photocatalysts calcined at 500 and 700°C were less active. The increase in calcination temperature from 400-600°C enhanced the photocatalytic activity due to increase of the crystallinity. At 700°C the photocatalytic activity decreased due to growth of the size of the particles leading to a low surface area.

Effect of initial pH: The effect of initial pH due to the amphoteric property of ZnO was studied, it is very important to investigate the effect of pH in the dye solution on the reactions that take place on ZnO surface, as pH is a main factor that influences the surface charge profile of the photocatalysts[25].

In this study, experiments were carried out at the same conditions except that pH of the methylene blue aqueous solution was adjusted within the range of 3-12 using diluted NaOH or HNO_3 solution.

The photocorrosion of ZnO is most rapid in a strong acidic environment (pH lower than 4). Photocorrosion of

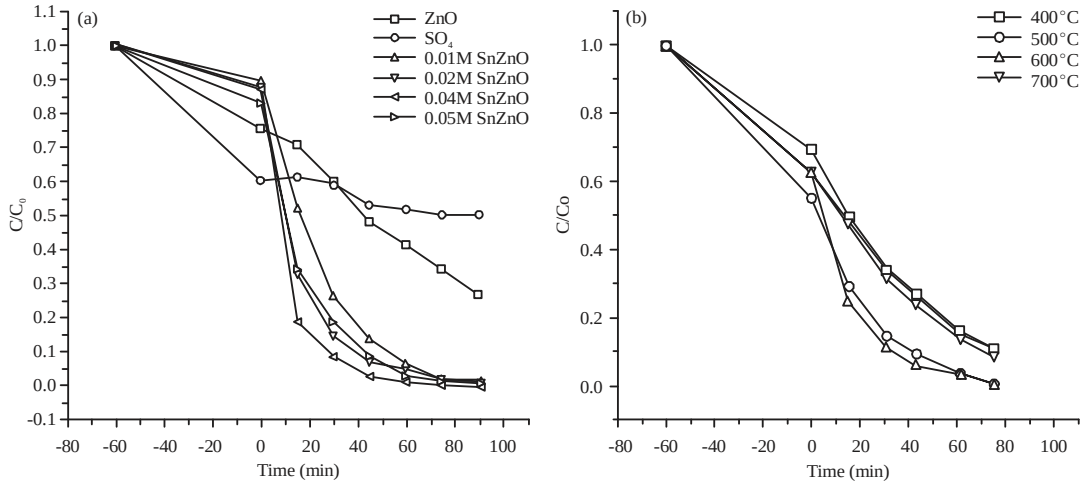

Fig. 4(a-b): Photodegradation curves of methylene blue on (a) ZnO, SnO_2 and SnO_2 doped ZnO and (b) 0.04 M SnO_2/ZnO, treated under different temperatures

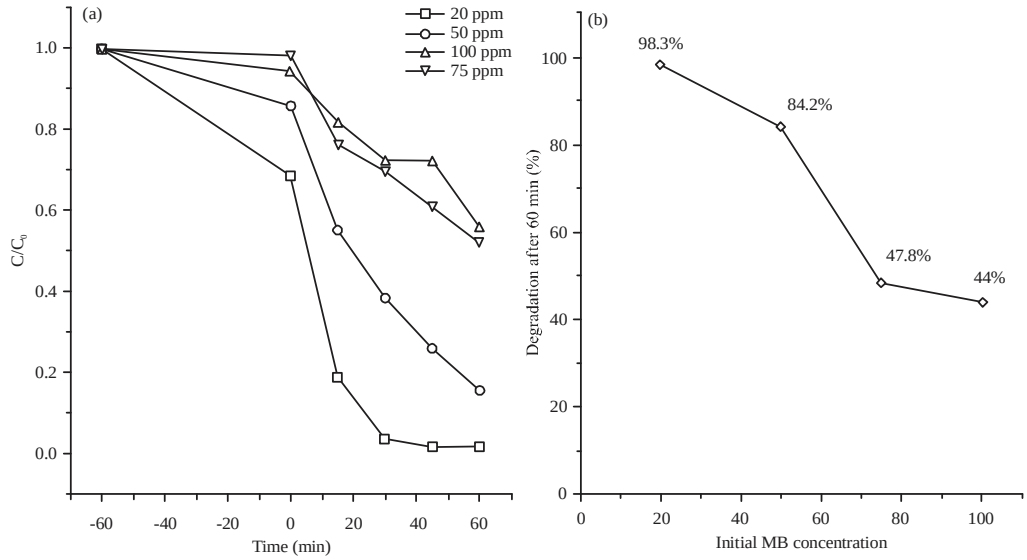

Fig. 5(a-b): (a) Effect of initial concentration of methylene blue on the photodegradation efficiency of 0.04 SnO_2/ZnO, (b) Degradation for methylene blue after 60 min at pH 10 over 0.04 M SnO_2/ZnO

ZnO is less severe with increasing pH and no photocorrosion takes place at pH higher than 10[26].

More importantly, in alkaline solution, large quantities of OH^- ions are present on the catalyst surface and in the reaction medium, which promotes the formation of hydroxyl radicals ($OH^•$)[27-30].

It is very well-known that for pH values higher than the point of zero charge (P_{ZC}), which is about pH = 9.48 for 0.04 M SnO_2/ZnO, the surface becomes negatively charged and it is the opposite for pH<9.48.

Being a cationic dye methylene blue molecule is easily adsorbed to ZnO particles with negative surface charge. These methylene blue cations can be oxidized directly by photo-generated OH^-. That is why the high degradation ratios were achieved in alkaline and neutral pH regions[31].

Effect of initial concentration of methylene blue: Dye concentration was investigated using initial concentrations of methylene blue (20, 50, 75 and 100 ppm), 0.05 mg of photocatalyst and 50 mL of dye solution at pH = 10. The Photodegradation of 0.04 M SnO_2/ZnO at different dye concentrations is illustrated in Fig. 5a. It can be observed that the photodegradation efficiency decreased by

Table 1: Rate constants and correlation coefficients for photocatalytic degradation of methylene blue for 0.04 M SnO_2/ZnO

C_i (mg L^{-1})	k_{app}	R^2
20	0.0769	0.999
50	0.0276	0.995
75	0.0104	0.995
100	0.0085	0.999

Table 2: Adsorption of heavy metals over ZnO and SnO_2 doped ZnO

	Removal (%)			
Samples	Cd	Cu	Fe	Pb
ZnO	99.03	97.39	100	97.64
0.01 M SnO_2/ZnO	99.2	97.42	100	97.94
0.02 M SnO_2/ZnO	99.46	97.64	100	99.33
0.04 M SnO_2/ZnO	99.63	99.18	100	99.92
0.05 M SnO_2/ZnO	99.01	99.1	100	99.07

increasing the dye concentration. As the concentration of dye increases, amount of dye adsorbed on the photocatalyst surface increases, consequently generation of hydroxyl radicals will be reduced. Furthermore, as the concentration of methylene blue increases, the fewer photons reach the photocatalyst surface. As a result, the production of hydroxyl radicals that can attack the pollutants will decrease and photocatalytic efficiency decreases[32,33].

The percentage of degradation dropped from 98.3-84.2% when the initial dye concentration increased from 20-50 ppm after 60 min of irradiation was observed at Fig. 5b and to 47.8% for 75 ppm dye solution. Beyond 75 ppm, the reduction in photodegradation efficiency is not very significant.

Kinetic studies of methylene blue degradation using ZnO and SnO_2/ZnO under UV/Vis light: The results show that the photocatalytic decomposition of methylene blue by 0.04 M SnO_2/ZnO can be described by the first-order kinetic model. The plots of the concentration data gave a straight line. The correlation coefficient (R) for the fitted line and the rate constants (k_{app}) are calculated and their values are grouped in Table 1. R^2 is a measure of the strength and direction of the linear relationship between ln (C_o/C) and time (t). The more R^2 values approach 1, the more the relation will be linear indicating that the reaction is first order reaction[27].

Adsorption of heavy metals over ZnO: Many factors can affect the efficiency of heavy metal removal such as nanoparticles size, morphology and pH of the medium[34]. The ZnO and SnO_2 doped ZnO were investigated to remove heavy metals from water by adsorption process.

Adsorption of heavy metals on ZnO and SnO_2 doped ZnO is illustrated in Table 2. The amount of adsorbed metals on SnO_2 doped ZnO surface increased by increasing SnO_2 molar ratio then decreased at 0.05 M SnO_2 doped ZnO. All samples showed high efficiency in removal of all metals.

CONCLUSION

Pure ZnO, SnO_2 and SnO_2 doped ZnO photocatalysts were synthesized using sol-gel method. It was found that all the doped samples had stronger light absorption in UV/Vis light range when compared with the pure ZnO. The doped ZnO photocatalysts showed enhanced photocatalytic activity in methylene blue photodegradation greater than pure ZnO under UV/Vis light irradiation. The 0.04 M SnO_2 doped ZnO photocatalyst demonstrated the highest photodegradation efficiency which was about 100% in 90 min and higher adsorption efficiency to all studied heavy metals which was nearly 100% to all metals in 1 h. The 0.04 M SnO_2/ZnO sample was used to study the effect of calcination, pH and initial dye concentration of dye. It showed best photodegradation efficiency at 600°C and the photocatalytic activity increased by increasing pH of the medium. Also, it was observed that photodegradation rates decreased by increasing initial concentration of methylene blue.

SIGNIFICANCE STATEMENT

This study indicated that the best photodegradation efficiency showed at 600°C and the photocatalytic activity increased by increasing pH of the medium. As well SnO_2 doped ZnO remove heavy metals from water by adsorption process.

ACKNOWLEDGMENT

The technically contents and ideas presented in this study are solely the author's interpretations. The authors thank the reviewers for their critical and constructive reviews which helped in improving this study.

REFERENCES

1. Gambhir, R.S., V. Kapoor, A. Nirola, R. Sohi and V. Bansal, 2012. Water pollution: Impact of pollutants and new promising techniques in purification process. J. Hum. Ecol., 37: 103-109.
2. Reddy, D.H.K. and S.M. Lee, 2012. Water pollution and treatment technologies. J. Environ. Anal. Toxicol., Vol. 2. 10.4172/2161-0525.1000e103.
3. Udom, I., M.K. Ram, E.K. Stefanakos, A.F. Hepp and D.Y. Goswami, 2013. One dimensional-ZnO nanostructures: Synthesis, properties and environmental applications. Mater. Sci. Semiconductor Process., 16: 2070-2083.

4. Akpan, U.G. and B.H. Hameed, 2009. Parameters affecting the photocatalytic degradation of dyes using TiO_2-based photocatalysts: A review. J. Hazard. Mater., 170: 520-529.
5. Sumanjit, T.P.S. Walia and R. Kaur, 2007. Removal of health hazards causing acidic dyes from aqueous solutions by the process of adsorption. J. Online Health Allied Sci., Vol. 6.
6. Ma, C., Z. Zhou, H. Wei, Z. Yang, Z. Wang and Y. Zhang, 2011. Rapid large-scale preparation of ZnO nanowires for photocatalytic application. Nanoscale Res. Lett., Vol. 6. 10.1186/1556-276X-6-536.
7. Rehman, S., R. Ullah, A.M. Butt and N.D. Gohar, 2009. Strategies of making TiO_2 and ZnO visible light active. J. Hazard. Mater., 170: 560-569.
8. Ayed, L., K. Chaieb, A. Cheref and A. Bakhrouf, 2009. Biodegradation of triphenylmethane dye Malachite Green by *Sphingomonas paucimobilis*. World J. Microbiol. Biotechnol., 25: 705-711.
9. Lakherwal, D., 2014. Adsorption of heavy metals: A review. Int. J. Environ. Res. Dev., 4: 41-48.
10. Fujishima, A. and K. Honda, 1972. Electrochemical photolysis of water at a semiconductor electrode. Nature, 238: 37-38.
11. Chan, S.H.S., T.Y. Wu, J.C. Juan and C.Y. Teh, 2011. Recent developments of metal oxide semiconductors as photocatalysts in advanced oxidation processes (AOPs) for treatment of dye waste-water. J. Chem. Technol. Biotechnol., 86: 1130-1158.
12. Thiruvenkatachari, R., S. Vigneswaran and I.S. Moon, 2008. A review on UV/TiO_2 photocatalytic oxidation process (Journal review). Korean J. Chem. Eng., 25: 64-72.
13. El-Dafrawy, S.M., 2016. Structural and photocatalytic of MCM doped ZnO nanoparticles and it's application in removal of iron, cadmium and lead ions from water. J. Catal. Catal. Res., 1: 1-9.
14. Ahmed, M.T., M.I. Abd-Elhamid, A. Sarhan and A. Hassan, 2017. Characteristic and thermal stimulated depolarization current of poly (vinyl chloride-co-vinyl acetate-co-2-hydroxy propyl acrylate) ZnO nanocomposite. Global J. Phys., 5: 585-594.
15. Rao, K.N., K.M. Reddy, N. Lingaiah, I. Suryanarayana and P.S. Prasad, 2006. Structure and reactivity of zirconium oxide-supported ammonium salt of 12-molybdophosphoric acid catalysts. Applied Catal. A: Gen., 300: 139-146.
16. Saravanan, R., V.K. Gupta, V. Narayanan and A. Stephen, 2013. Comparative study on photocatalytic activity of ZnO prepared by different methods. J. Mol. Liquids, 181: 133-141.
17. Kisch, H., 2013. Semiconductor photocatalysis-mechanistic and synthetic aspects. Angewandte Chem. Int. Edn., 52: 812-847.
18. Hanna, A.A., S.M.A. Mousa, M.A. Sherief and G.M. Elkomy, 2010. Sol-gel preparation, characterization and electrical properties of nanosized gallium doped zinc-oxide. J. Am. Sci., 6: 295-300.
19. Hayat, K., M.A. Gondal, M.M. Khaled, S. Ahmed and A.M. Shemsi, 2011. Nano ZnO synthesis by modified sol gel method and its application in heterogeneous photocatalytic removal of phenol from water. Applied Catal. A: Gen., 393: 122-129.
20. Lin, C.C. and Y.J. Chiang, 2012. Preparation of coupled ZnO/SnO_2 photocatalysts using a rotating packed bed. Chem. Eng. J., 181: 196-205.
21. Hamrouni, A., H. Lachheb and A. Houas, 2013. Synthesis, characterization and photocatalytic activity of ZnO-SnO_2 nanocomposites. Mater. Sci. Eng.: B, 178: 1371-1379.
22. Sun, J.H., S.Y. Dong, J.L. Feng, X.J. Yin and X.C. Zhao, 2011. Enhanced sunlight photocatalytic performance of Sn-doped ZnO for Methylene Blue degradation. J. Mol. Catal. A: Chem., 335: 145-150.
23. Hamrouni, A., N. Moussa, F. Parrino, A. di Paola, A. Houas and L. Palmisano, 2014. Sol-gel synthesis and photocatalytic activity of ZnO-SnO_2 nanocomposites. J. Mol. Catal. A: Chem., 390: 133-141.
24. Butler, M.A., 1977. Photoelectrolysis and physical properties of the semiconducting electrode WO_2. J. Applied Phys., 48: 1914-1920.
25. Vignesh, K., M. Rajarajan and A. Suganthi, 2014. Visible light assisted photocatalytic performance of Ni and Th co-doped ZnO nanoparticles for the degradation of methylene blue dye. J. Ind. Eng. Chem., 20: 3826-3833.
26. Ramaswamy, V., N.B. Jagtap, S. Vijayanand, D.S. Bhange and P.S. Awati, 2008. Photocatalytic decomposition of methylene blue on nanocrystalline titania prepared by different methods. Mater. Res. Bull., 43: 1145-1152.
27. El Hakam, S.A., S.M. El-Dafrawy, S. Fawzy and S.M. Hassan, 2014. Structural, photocatalytic and antibacterial activity of ZnO and ZrO_2 doped ZnO nanoparticles. Int. J. Sci. Res., 3: 779-787.
28. Sakthivel, S., B. Neppolian, M.V. Shankar, B. Arabindoo, M. Palanichamy and V. Murugesan, 2003. Solar photocatalytic degradation of azo dye: Comparison of photocatalytic efficiency of ZnO and TiO_2. Solar Energy Mater. Solar Cells, 77: 65-82.
29. Daneshvar, N., D. Salari and M.A. Behnasuady, 2002. Decomposition of anionic sodium dodecylbenzene sulfonate by UV/TiO_2 and UV/H_2O_2 processes a-comparison of reaction rates. Iran. J. Chem. Chem. Eng., 21: 55-62.
30. El-Hakam, S.A., A.I. Ahmed, E. Abdel-Galil, S.M. El-Dafrawy and A.A. Al-Khamri, 2017. Removal of methylene blue and brilliant green dyes from aqueous solution by Ag_2O/MCM-41 nanoparticles. Res. J. Pharm. Biol. Chem. Sci., 8: 2604-2622.

31. Yang, Z., P. Zhang, Y. Ding, Y. Jiang, Z. Long and W. Dai, 2011. Facile synthesis of Ag/ZnO heterostructures assisted by UV irradiation: Highly photocatalytic property and enhanced photostability. Mater. Res. Bull., 46: 1625-1631.
32. Mahmoudi, Z., S. Azizian and B. Lorestani, 2014. Removal of methylene blue from aqueous solution: A comparison between adsorption by iron oxide nanospheres and ultrasonic degradation. J. Mater. Environ. Sci., 5: 1332-1335.
33. El-Hakam, S.A., A.I. Ahmed, S.M. El-Dafrawy, A.A. Ibrahim and M.S. Adly, 2016. Application of nanostructured graphene oxide/titanium dioxide composites for photocatalytic degradation of methylene blue dye under UV-visible light. Int. J. Modern Chem., 8: 27-37.
34. Singh, S., K.C. Barick and D. Bahadur, 2013. Functional oxide nanomaterials and nanocomposites for the removal of heavy metals and dyes. Nanomater. Nanotechnol., Vol. 3. 10.5772/57237.