An Efficient Photocatalytic Degradation of Methyl Blue Dye by Using Synthesised PbO Nanoparticles

ASHOK V. BORHADE*, DIPAK R. TOPE and BHAGWAT K. UPHADE

Chemistry Research Center,
HPT Arts and RYK Science College, Nasik 422005, India
ashokborhade2007@yahoo.co.in

Received 31 August 2011; Accepted 8 November 2011

Abstract: We report here the synthesis of visible light sensitive PbO and Ni doped PbO nanoparticles by hydrothermal method and characterized by UV-DRS, photoluminescence spectroscopy (PL), FTIR, X-ray diffraction (XRD), SEM, EDAX and TGA. Further an efficient approach has been developed for degradation of methyl blue (MB) in aqueous medium. The photodegradation of dye was monitored as a function of dye concentration, pH and catalyst amount has been determined. The reduction in the chemical oxygen demand (COD) revealed the mineralization of dye along with colour removal.

Keywords: Hydrothermal method, PbO nanoparticles, Photocatalyst, Visible light, Methyl blue dye.

Introduction

To develop more efficient photocatalyst, there is an urgent need for photocatalytic systems, which are able to operate effectively under visible light irradiation. The use of naturally available visible light has recently drawn much attention. Removal of organic dyes by photocatalytic degradation is emerging as an effective treatment method. Nowadays, photocatalyst is becoming more popular in water purification. The discharge of large quantity of coloured water from industries possess serious environmental problems. The colorization of water due to the presence of dyes may have an inhibitory effect on the process of photosynthesis and thus may affect the aquatic ecosystem. The coloured molecules absorbs visible light, decreasing the amount of light available for photosynthesis.

There are many methods for eliminating water pollutants. Widely used semiconductor photocatalysts like ZnO and TiO₂ shows very low photoactivity under visible light excitation. Photocatalytic degradation of azo dye readily in water using ZnO¹, the photocatalytic degradation of acid red B dye using TiO₂² was studied earlier. The photocatalytic degradation of methyl orange by zinc ferrite doped titania has also been reported³. Use of semiconducting iron (II) oxide in photocatalytic bleaching of some dye has been reported by Ameta⁴. A number of systems have been reported, they include transition metal doped TiO₂⁵, nitrogen doped TiO₂⁶ and photosensitization of dye pollutants^{7,8}. Thus, the removal of dyes from coloured effluents is one of the major

environmental problem. Many industries discharge untreated waste water on land causing pollution to surface water, ground water and soil^{9,10}. The dye like rhodamine B¹¹, reactive red-2¹² and malachite green¹³ was removed by activated carbon. The herbicide (thiram) was photocatalytically degraded by using TiO₂ in presence of visible light¹⁴. The PbO nanoparticles also used in sensor¹⁵, Li - ion batteries¹⁶, Lead -acid batteries¹⁷ and biomedical application¹⁸. Due to high concentration of organics in the effluents and the higher stability of modern synthetic dyes, the conventional biological treatment methods are ineffective for the complete colour removal and degradation of organics and dyes¹⁹.

Transition metal oxides with nanostructure have attracted considerable interest in many areas of chemistry, physics and material science. So, attempt was made to prepare materials that have absorption's extending towards visible range and thereby allowing the use of the main part of solar spectrum. The PbO nanoparticle was synthesized by different methods²⁰⁻²⁵. In the present study PbO and Ni doped PbO assisted photocatalytic degradation of methyl blue is reported.

Experimental

A mixture of 2.5 mmol of citric acid and 0.1 N sodium hydroxide (10 mL) and a little water is added to a magnetically stirred methanolic solution of 2 mmol lead nitrate at room temperature over 20 min. The reaction mixture was stirred for 2 h at room temperature. The white solid product was filtered by vacuum, washed with distilled water and dried in an oven at 110 °C for 2 h. The solid product was calcined at 500 °C for 2 h.

Synthesis of 3% and 7% Ni doped PbO nanoparticles

1 gm PbO nanoparticles were added to an aqueous solution of sodium hydroxide (1 N, 10 mL) in a Teflon autoclave. After vigorous shaking for several minutes nickel sulphate solution (3% or 7%) was added to the reaction mixture. It was then stirred for another fifteen minutes. The reaction mixture was heated in an oven at 120 °C for 6 h. The solid product was vacuum filtered off, washed with hydrochloric acid (0.1 N) and dried in an oven at 110 °C for 2 h.

Characterization

The samples prepared by the hydrothermal method were characterized by FTIR (Schimadzu 8400S model). FTIR was used to observe the stretching of metal oxygen bond. UV-DRS spectra were recorded by using a Schimadzu UV 2450 spectrophotometer at room temperature. Photoluminescence (PL) spectrum at room temperature was recorded by Perkins Elmer spectrophotometer by using xenon arc lamp as the light source. The thermal stability was carried out using Perkins Elmer Thermal Analyzer up to 1000 °C in air at the heating rate of 20 °C/min. PbO nanoparticles calcined at 500 °C was employed for the powder XRD studies using Philips - 1710 diffractometer with Cu K α radiation $\lambda = 1.54 \text{ \AA}$. A scanning electron microscope (SEM) with EDAX recorded by using JEOL JEM - 6360 was used to study the surface morphology of the lead oxide powder. The interaction of the nickel dopant with the host PbO semiconducting material by electron spins resonance (ESR) spectroscopy. The ESR spectrum was recorded by E-112 EPR spectrometer Varian, USA.

Photocatalytic degradation

In photocatalytic degradation, methyl blue dye (50 mL) and the catalyst (PbO or Ni doped PbO photocatalyst) were taken in a beaker and exposed to sunlight. The dye solutions were mixed properly with a magnetic stirrer during the reaction process. Dye solutions of about 2-3 mL were taken out at regular interval and their absorbance was recorded at 610 nm using spectrophotometer (UV- Vis Ultra Spec CL - 540). The control experiments were also conducted under visible light without catalyst to measure any possible direct photocatalysis of this dye. Photocatalytic degradation of methyl blue was evaluated at different pH, with various amounts of dye and various amounts of PbO photocatalysts, while all the reactions were carried out at 25 °C.

Results and Discussion

Synthesis and characterization of PbO nanoparticles

The FTIR spectra of PbO, 3% and 7% Ni doped PbO nanoparticles are shown in Figure 1. The FTIR spectrum of PbO shows a broad band with very low intensity at 3446 cm^{-1} corresponding to the vibration mode of OH group indicating the presence of small amount of water adsorbed on the PbO nanoparticle surface. The band at 1408.08 cm^{-1} is due to OH bending of water. Bands at 574 , 682 and 844 cm^{-1} are attributed to the Pb - O vibrations. A new band at 920 cm^{-1} and 1047 cm^{-1} appeared in the 3% Ni doped PbO nanoparticle due to presence of nickel ion. The 7% Ni doped PbO nanoparticle shows a new strong band around 808 and 908 cm^{-1} . The diffused reflectance spectra (Figure 2) shows band at 396 nm corresponds to PbO nanoparticle. Compared with bulk PbO, the blue shift observed in the PbO nanoparticle is due to the size effect. The band gap energy for PbO nanoparticle is calculated from $E = h\nu = hc/\lambda$. The band gap energy of PbO nanoparticles is 3.13 eV . In 3% Ni doped PbO nanoparticle band shift from 396 nm to 402 nm and band gap energy has 3.08 eV . While in 7% Ni doped PbO nanoparticle band shift from 396 nm to 407 nm and band gap energy is found to be 3.04 eV . The band position shows that absorption extending towards visible range (Figure 2).

Figure 1. IR spectra of PbO and Ni doped PbO nanoparticles.

Figure 2. UV- DRS spectra of a) PbO nanoparticle, b) 3% Ni doped PbO nanoparticle, c) 7% Ni doped PbO nanoparticle.

Figure 3 depicts the photoluminescence spectrum (PL) of nano-size PbO particles synthesized in water, sodium hydroxide and citric acid. It shows a weak band at 370 nm, a broad blue emission band at 473 nm and a strong green - yellow emission band at around 500 nm. The ultraviolet band is attributed to the band - edge excitation recombination and the visible band is related to the defects in PbO nanostructures. The origin of blue emission from the undoped PbO is associated with the intrinsic defect centers such as oxygen vacancy, lead vacancy or oxygen interstitial. The observation of strong 473 nm blue band emission indicates the existence of oxygen vacancy concentrated on PbO nanoparticle surface. A strong band around 500 nm may be due to oxygen defects and gives green - yellow emission. This green - yellow emission is observed in PL spectra due to recombination of photogenerated holes with singly ionized charge state of specific defect²⁶.

Figure 3. PL spectrum of PbO nanoparticle.

Figure 4 represents the typical XRD pattern of PbO nanoparticle. It shows peaks at angles 29.1, 30.4, 32.5, 37.7, 49.4, 50.9, 53.3, 56.2 and 63.7, which correspond to the reflection from 111, 002, 200, 210, 022, 220, 222, 311 and 131 crystal planes respectively. The XRD pattern is in agreement with the orthorhombic structure of PbO (JCPDS Card No. 76 - 1796) with a space group $Pca 2_1$ (29). Sharp diffraction peaks indicate good crystallinity of PbO nanoparticles. The broadening of peaks indicates that the particles are of nanometer scale, which is in good agreement with observed SEM images. The XRD patterns of 3% Ni doped PbO nanoparticles show new peaks at 26.5, 31.8 and 48.6. The XRD pattern of 7% Ni doped PbO nanoparticle shows new peaks at 18.6, 31.9 and 48.6. The change in diffraction patterns is due to encapsulation of nickel ion in PbO nanoparticle (Figure 4). The particle size was calculated using Scherrer formula.

Figure 4. XRD pattern of PbO, 3% and 7% Ni doped PbO nanoparticles.

The average particle size can be estimated from the extrapolation of the plot (Figure 5) and the crystal size (ϵ) was obtained 69 nm based on the intercept inverse, *i.e.*, $1/\epsilon = 0.144 \times 10^{-8}$, which yields $\epsilon = 69$ nm. The average particle size of 3% Ni and 7% Ni doped PbO nanoparticles was found to be 64 and 61 nm respectively. As the doping level increases, the particle size decreases slightly. This may be due to the fact that dopant ions inhibit crystal growth and sintering between grains during heat treatment.

Figure 5. Particle size determination.

The morphology and size of the synthesized PbO samples were investigated using scanning electron microscopy (SEM). SEM microstructures of samples have been presented in Figure 6(a-c). The surface of the catalyst presents a spongy discrete particle appearance. The elemental analysis (EDAX) indicates that calcined PbO nanoparticles contain 100% PbO. The Ni doped PbO nanoparticles contain 3% Ni and 7% Ni ion (Figure 6b & c). Thermogravimetric analysis (TGA) shows that there is no considerable loss in weight. TGA curve proves the existence of lead oxide which does not decompose up to 580 °C (Figure 7). The ESR spectrum shows that the PbO and Ni doped PbO semiconducting nanoparticles consist of unpaired electrons. From the ESR signal, the effective g value for unpaired electrons was observed to be 2.00277, which gives a clear evidence of paramagnetism in the PbO nanomaterial (Figure 8).

Figure 6 a)

Figure 6 b)

Figure 6 c)

Figure 6. SEM images and EDAX of a) PbO nanoparticle, b) 3% Ni doped PbO nanoparticle, c) 7% Ni doped PbO nanoparticle.

Figure 7. TGA spectrum of PbO nanoparticle.

Figure 8. ESR spectrum a) PbO nanoparticle, b) 3% Ni doped PbO nanoparticle.

Photodegradation studies of MB

Photodegradation process assisted by semiconducting PbO nanoparticles depends on various parameters like nature and concentration of organic substance, concentration and

type of the semiconductor photocatalyst, light source and intensity, pH and temperature.²⁷ Earlier report shows that, the photocatalytic degradation of dyes follows first-order kinetics.^{28,29} The present investigation also reveals that PbO nanoparticles induced photocatalysis of MB follows pseudo-first order kinetics with respect to MB concentration (Table 1). The rate constant (Figure 9a) for this reaction is obtained by using the expression $K = -2.303 \times \text{Slope}$ is found to be $K = 3.015 \times 10^{-4} \text{ sec}^{-1}$ (Table 1 & 2).

Table 1. A Typical Run- Dye = 1.5×10^{-4} M/L, Photocatalyst = 50 mg.

Time, min	O.D	2 + log O.D
00	1.071	2.000
30	0.663	0.821
60	0.540	1.732
90	0.330	1.518
120	0.170	1.230
150	0.072	0.857
180	0.025	0.397

Table 2. Effect of pH on rate constant.

pH	K (sec^{-1}) $\times 10^{-4}$
2.0	1.322
4.0	1.509
6.0	3.326
8.0	6.930
10.0	0.146
12.0	4.107

Effect of initial dye concentration

The effect of MB concentration on degradation was studied by varying the concentration from 1×10^{-4} M to 7×10^{-4} M and keeping PbO (50 mg/50 mL) as constant. The degradation of MB was found to be decrease at high initial dye concentration (Figure 9b). The active surface on the catalyst available for reaction is very crucial for the degradation. At constant amount of catalyst when dye concentration increases, very few active sites of photocatalyst are available for reaction. At high concentration of dye, solution becomes more intense coloured and path length of photons entering the solution decreased. As an effect of this only few photons reached to the catalyst surface. Due to this the production of hydroxyl radical and superoxide radicals are limited and photodegradation was found to be negligible.

Effect of pH

The pH of the dye solution was adjusted using varying concentration of HCl and NaOH. The maximum degradation of dye was recorded at the pH 10 (Figure 9c). The pH affects not only the surface properties of PbO photocatalyst but also the dissociation of dye molecules and the formation of hydroxyl radicals. At alkaline conditions more hydroxyl radicals were formed and hence enhance the rapid degradation of dye solution.

Effect of amount of PbO photocatalyst

Photodegradation of MB dye was carried out by taking different amounts of PbO and keeping dye concentration constant at 3×10^{-4} M (Figure 9d). It was found that the rate of degradation increases up to 75 mg/50 mL of the PbO photocatalyst, beyond which it shows a drastic reduction. The increase in degradation activities of MB dye with PbO photocatalyst amount may be due to an increase in the active sites available on the catalyst surface for the reaction, which in turn increases the rate of radical formation. The reduction in the degradation of dye, when the catalyst amount is increased beyond 75 mg/50 mL is due to light scattering and the reduction in light penetration through the solution. With a higher amount the deactivation of activated molecules by collision with ground state molecules dominates the reaction.

Figure 9. a) Rate constant of dye degradation, b) Effect of amount of dye on dye degradation, c) Effect of pH on dye degradation, d) Effect of amount of photocatalyst on dye degradation.

Effect of nature of PbO photocatalyst

Experiments were carried out with different photocatalyst such as PbO, 3% and 7% Ni doped PbO and keeping MB dye concentration 3×10^{-4} M (Figure 10). It was found that degradation of MB was more with 3% and 7% Ni doped PbO than PbO photocatalyst. The presence of Ni ion in PbO photocatalyst shifts the absorption of light towards visible range. The band gap energies for 3% Ni and 7% Ni doped PbO photocatalyst was minimum as compared to band gap energy of PbO photocatalyst. Due to this Ni doped PbO are more effective as compared to PbO photocatalyst.

Figure 10. Effect of nature of photocatalyst, a) PbO photocatalyst, b) 3% Ni doped PbO photocatalyst, c) 7% Ni doped PbO photocatalyst.

Efficiency of reused PbO photocatalyst

The PbO nanoparticle photocatalyst used in the photocatalytic reaction was dried at 40 - 50 °C in a hot air oven before it was reused as such in the succeeding photocatalytic experiment. The photodegradation efficiency of PbO photocatalyst shows a smaller change after repetitive use. It indicates the cost effectiveness of this method.

Estimation of chemical oxygen demand (COD)

The chemical oxygen demand (COD) was widely used to measure the organic strength of waste water. The COD of the dye solution was estimated before and after the treatment. The reduction in the COD values of the treated dye solution indicates the mineralization of the dye molecules. The degradation efficiency is calculated from following equation. The results obtained are reported in Table 3. In the present work maximum 91.11% degradation efficiency was obtained.

$$\text{Photodegradation efficiency} = \frac{\text{Initial}_{\text{COD}} - \text{Final}_{\text{COD}}}{\text{Initial}_{\text{COD}}} \times 100$$

Table 3. Chemical Oxygen Demand (COD) in methyl blue dye.

Dye Solution, M / L	Initial COD, mg/L	Final COD, mg /L	Photodegradation efficiency, %
1×10^{-4}	26.4	8.0	69.69
2×10^{-4}	40.0	10.4	74.00
3×10^{-4}	73.6	17.6	76.08
4×10^{-4}	128.0	18.4	85.62
5×10^{-4}	216.0	19.2	91.11

Conclusion

PbO, 3% and 7% Ni doped PbO semiconducting nanoparticles was successfully synthesized by hydrothermal method. The PbO nanoparticles have orthorhombic structure with particle size 69 nm. The 3% Ni and 7% Ni doped PbO have particle size 64 and 61 nm respectively. Encapsulation of nickel ion in PbO decreases the particle size which enhances the photocatalytic activity of PbO photocatalyst. The PbO and Ni doped PbO semiconducting nanoparticles exhibit significant photocatalytic activity for the organic dye. The degradation of dye catalyzed by PbO and Ni doped PbO semiconducting nanoparticles under visible light

followed a radical type mechanism. The result shows the reduction in the chemical oxygen demand (COD) for dye along with colour removal using PbO nanoparticles.

Acknowledgment

Authors are thankful to Principal, HPT Arts and RYK Science College Nasik and Principal, P.V.P College Pravaranagar, for providing necessary laboratory facilities and Department of Physics, Pune University for providing characterization facilities.

References

1. Daheshwar N, Salari D and Khataee A R, *J Photochem. and Photobio. A: Chem.*, 2003, **157(1A)**, 111.
2. Wang J, Ma T, Zhang G, Zhang Z, Zhang X, Jiang Y, Zhao G and Zhang P, *J Cat Comm.*, 2007, **18 (1)**, 607.
3. Cheng P, Deng C, Gu M and Shangguan W, *J Mater Sci.*, 2007, **42**, 9239.
4. Ameta R, Vardia J, Punjabi P B and Ameta S C, *Ind J Chem Tech.*, 2006, **13**, 114.
5. Nagaveni K, Sivalingam G, Hegde M S and Madras G, *J Appl Catal B*, 2004, **48**, 83.
6. Asahi R, Morikawa T, Ohwaki T, Aoki K and Taga Y, *Science*, 2001, **293**, 269.
7. Ji H, Ma W, Huang Y, Zhao J and Wang Z, *J Chin Sci Bull.*, 2003, **48**, 2199.
8. Zhao W, Chen C, Li X and Zhao J, *J Phys Chem B*, 2002, **106 (19)**, 5022.
9. Nigam P, Armour G Banat I M, Singh D and Marchant R, *J Bioresour Technol.*, 2000, **72**, 219.
10. Khan T A, Singh V V and Kumar D, *J Sci Ind Res.*, 2004, **63**, 355.
11. Ramuthai S, Nandakumar V, Thirucheli M, Avivoli S and Vijayakumaran V, *E-J Chem.*, 2009, **6 (S1)**, S 363.
12. Karthikeyan S, Sivakumar B and Sivakumar N, *E-J Chem.*, 2010, **7 (S1)**, S175.
13. Baskaran P K, Venkatraman B R and Avivoli S, *E-J Chem.*, 2011, **8 (1)**, 9.
14. Thakare S R and Bhawe N S, *E-J Chem.*, 2005, **2(1)**, 62.
15. Konstantinov K, Ng S H, Wang J Z, Wang G X, Wexler D and Liu H K, *J Power Sources*, 2006, **159 (1)**, 241.
16. Li S, Yang W, Chen M, Gao J, Kang J and Qi Y, *J Mater Chem And Phy.*, 2005, **90 (2-3)**, 262.
17. Wang J, Zhong S, Konstantinov K, Ahn J H, Liu H K and Dou S X, *J Meta Nanocryst Mater.*, 2007, **15-16**, 367.
18. Shah M A, *J Biomed Nanosci Nanotech.*, 2006, **1(1)**, 3.
19. Souther R H and Alspaugh T A, *J Water Pollution Control Federation*, 1957, **29**, 804.
20. Jia B and Gao L, *J Mater Chem Phys.*, 2006, **100 (2-3)**, 351.
21. Raju V, Murthy S, Gao F, Lu Q and Komarneni S, *J Mater Sci.*, 2006, **41(5)**, 1475.
22. Chen S and Li N, *J Mater Chem.*, 2002, **12**, 1124.
23. Zhou Q, Liu X Y, Liu L, Li Y G, Jiang Z Y and Zhao D Y, *J Chem Lett.*, 2005, **34 (9)**, 1226.
24. Juan C L, Mao Z.S, Shen W Z, Jun Z.Z and Xin D H, *J Mater Lett.*, 2005, **59(24-25)**, 3119.
25. Jiang X, Wang Y, Herricks T and Xia Y, *J Mater Chem.*, 2004, **14 (4)**, 695.
26. Hsieh C T, Chen J M, Lin H H and Shih H C, *J Appl Phys Lett.*, 2003, **83**, 3383.
27. Ferraz A M C, Maser S and Jonhaeuser M J, *Fuel.*, 1999, 1567.
28. Panduranga A, Kamal S, Uma S, Palanichamy M and Murugesan V, *Ind J Chem Technol.*, 2001, **8**, 496.
29. Lachheb H, Puzenat E, Houas A, Ksibi M, Elaloui E, Guillard C and Herrmann J M, *J Appl Catal B Environ.*, 2002, **39**, 75.