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EFFECT OF VARIOUS METAL IONS IMPREGNATION ON PHOTOCATALYTIC ACTIVITY OF ZnO

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ABSTRACT

The effect of various metal ions on photocatalytic activity of ZnO was studied by impregnation of ZnO with Ag^+, Cd^{2+} and Fe^{3+} ions. Impregnation was done with metal ions of varying concentrations such as 0.5, 1.0, 1.5 atom percentage and the samples were calcined at different temperatures for 2 h. The catalysts were characterized by XRD and SEM. Band gaps of ZnO and metal ion impregnated ZnO were calculated from UV-Visible Diffuse Reflectance Spectroscopic studies. The photocatalytic activity of ZnO was studied by degradation of Rhodamine 6G from aqueous solutions. Enhanced photocatalytic activity was observed by Ag^+ impregnation, where as the activity was hindered by Cd^{2+} and Fe^{3+} impregnations.

Key Words: *Photocatalysis, impregnated ZnO, Rhodamine 6G, Dye degradation, Textile effluents*

INTRODUCTION

Textile waste-waters contain large quantities of dye effluents which are toxic and non-biodegradable. These effluents cause a lot of damage to the environment by releasing toxic and carcinogenic substances [Bouzdia *et al* 2004)]. As a consequence, dyes have become a major source of environmental pollution. Some physical and chemical techniques are currently available for the treatment of dye effluents [Robinson *et al* (2001,) Zamora *et al* (1999), Ladakowicz *et al* (2001), Georgiou *et al* (2001)], but these processes are not destructive merely transfer dye from liquid to solid phase causing secondary pollution [Chaudari and Sur (2000), Stock *et al* (2000)].

Recently, it has been demonstrated that semiconducting materials mediating photocatalytic oxidation can be an alternative to conventional methods for the removal organic dye effluents from water [Fox and Dulay (1993), Legrini *et al* (1993), Hoffmann *et al* (1995), Ollis *et al* (1993), Turchi and Ollis (1990)]. The illumination of these particles with light energy greater than the band gap energy of the semiconductor produces excited high energy states of electron and hole pairs that can migrate to the surface of the particle and initiate a wide range of redox reactions, which can lead to complete mineralization of organic pollutants. Among various semiconducting materials TiO_2 and ZnO were used extensively for degradation of these dyes. TiO_2 is the most commonly used effective photocatalyst for degradation of wide range of organic chemicals [Kusvuran *et al* (2005), Khodja *et al* (2001)]. The main disadvantage of TiO_2 is it absorbs UV light and rapid recombination of electron hole pairs also limits the efficiency of TiO_2. ZnO is another semiconductor, which is investigated in recent years as potential photocatalyst [Akyol *et al* (2004)].

The modification of semiconductors with metal ions has attracted significant attention especially in heterogeneous photocatalysis since it extends the absorption by photocatalyst into visible region or it decreases the recombination of electron-hole pair [Gupta and *et al* (2006)]. However, the activity of the doped photocatalyst substantially depends on the dopant ion nature, concentration, method of preparation and thermal treatment [Malati and Wong (1984), Tahiri *et al* (1998), Litter (1999)].

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In this study, ZnO doped by various metal ions such as Ag(I), Cd(II) and Fe(III) were characterized by XRD, SEM and UV-Vis Diffuse Reflectance Spectroscopy techniques. The photocatalytic activity of doped ZnO was studied by degradation of R6G in aqueous solutions.

MATERIALS AND METHODS

Materials

Zinc Oxide and Rhodamine 6G were obtained from Merck India. All the solutions were prepared using double distilled water. All the chemicals used in the study were of analytical reagent grade.

Preparation of metal-impregnated ZnO photocatalyst

Silver impregnated ZnO containing 1 atom% of silver was prepared by the following procedure. Silver nitrate solution containing 105 mg in 100 mL was added to 5 g of ZnO and the mixture was stirred for 4 h. The suspension was allowed to stand for 24 h. The water was then evaporated by heating at 100 ^{0}C for 16 h. Silver doped ZnO of 0.5 and 1.5 atom percent were prepared by taking 52.5 mg and 157.5 mg of silver nitrate and following the same procedure. The dried solids were grounded to fine powder in an agate mortar and calcined at 200, 400 and 600 ^{0}C for 2 h in muffle furnace.

The above procedure was used for preparation of cadmium and Iron impregnated ZnO by taking corresponding amounts of Cadmium nitrate and Ferric nitrate for 5 g of ZnO.

Characterization

XRD and SEM: The catalysts were characterized for their structure and morphology by XRD (X-ray diffraction) and SEM (scanning electron microscopy). The XRD patterns of the powdered samples were recorded by Bruker 8 D advanced X-ray diffractometer and SEM images of the samples were taken by using Philips XL 30 ESEM Scanning electron microscope.

UV-Vis Diffuse Reflectance Spectroscopy: UV-Vis spectroscopy was used to characterize the optical absorption properties of ZnO and metal ion impregnated ZnO. The UV-Vis absorption spectra of the samples were recorded in the wavelength range 200-800 nm using Shimadzu UV 3600 UV-Vis-NIR spectrometer in diffuse reflectance mode (DRS) using $BaSO_4$ as reference. Spectra were recorded at room temperature and the data were transformed through Kubelka-Munk function.

Photocatalytic studies: The experimental setup for the photocatalytic degradation consisted of a 250 mL Borosil beaker with water circulation outside. The beaker was placed on a magnetic stirrer, above which a high pressure mercury vapour lamp (125 W, Philips) emitting visible light was placed. 100 mL of the dye solution was taken in the beaker and ZnO or metal ion impregnated ZnO (M-ZnO) at a dose of 1 gL^{-1} was added to it. The distance of the light source from the upper level of dye solution in the beaker was 18 cm. The solution was stirred in the dark for 5 min to establish the adsorption equilibrium. The zero time reading was taken and the solution was then irradiated. Aliquots were taken at regular time intervals and centrifuged to analyse the percent degradation of the dye.

Analysis

The percent degradation of Rhodamine 6G (R6G) was found out spectrophotometrically by measuring absorbance of the dye solution at λ_{max} 518 nm. The decolourisation efficiency (%) was calculated as

$$\text{Efficiency (\%)} = \frac{C_0 - C}{C_0} X \ 100$$

where C_0 is the initial concentration of dye and C is the concentration of dye after irradiation.

RESULTS AND DISCUSSION

Catalyst characterization

XRD and SEM analysis: The XRD patterns obtained for powdered ZnO and Ag-ZnO of various concentrations of silver loading 0.5, 1.0, 1.5 atom% dried at 100 ^{0}C are shown in Figure 1 indicating well indexed phases of ZnO Wurtzite structure (JCPDS No. 36-1451). Impregnation of ZnO with Ag^+ ions doesn't show any change in crystal structure may be due to low percent of silver loading and surface deposition. Similar effect was observed for Cd^{2+} and Fe^{3+} impregnated ZnO (Figures 2 and 3). The

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intensity of peaks increased with silver doping and is decreased with cadmium and iron doping on ZnO. No change in peak positions were observed even after calcination of samples at 200, 400, 600 ^{0}C. The SEM images of ZnO and doped ZnO are given in Figure 4, which shows that ZnO particles are in different shapes and sizes and, doping does not change the morphology of ZnO. Some agglomeration of particles was observed in Cd^{2+} doped ZnO.
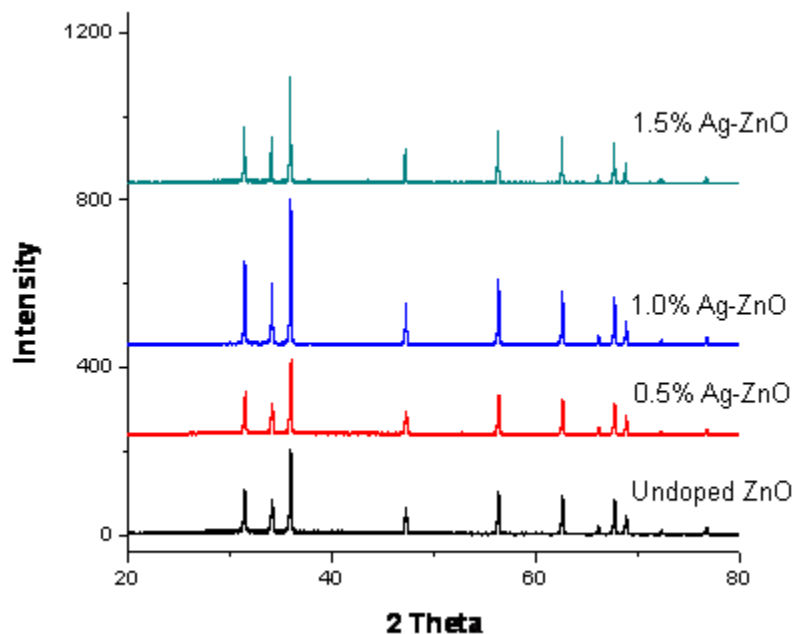

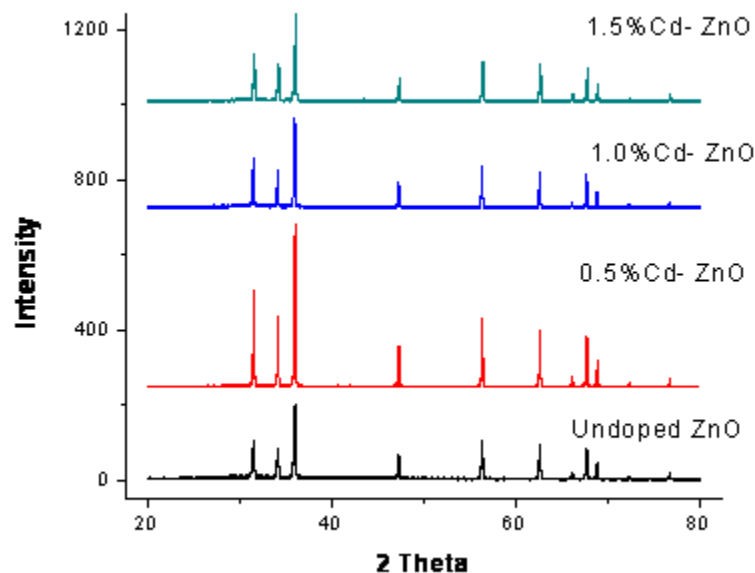**Figure 1: Powdered XRD patterns of ZnO and various atom% of Ag$^+$doped ZnO.**

Figure 2: Powdered XRD patterns of ZnO and various atom% of Cd^{2+}doped ZnO.
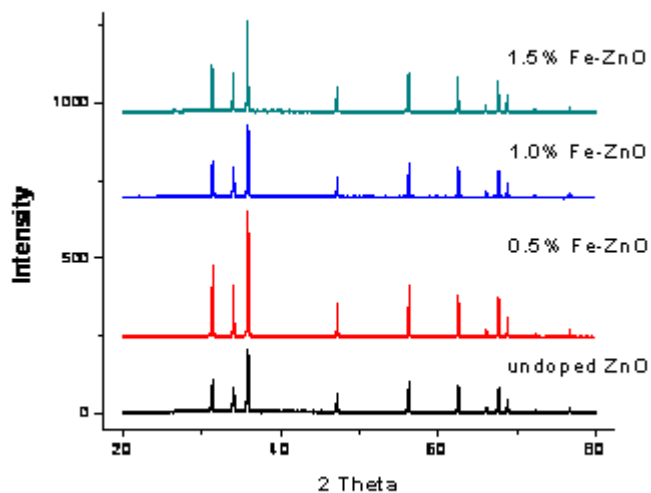
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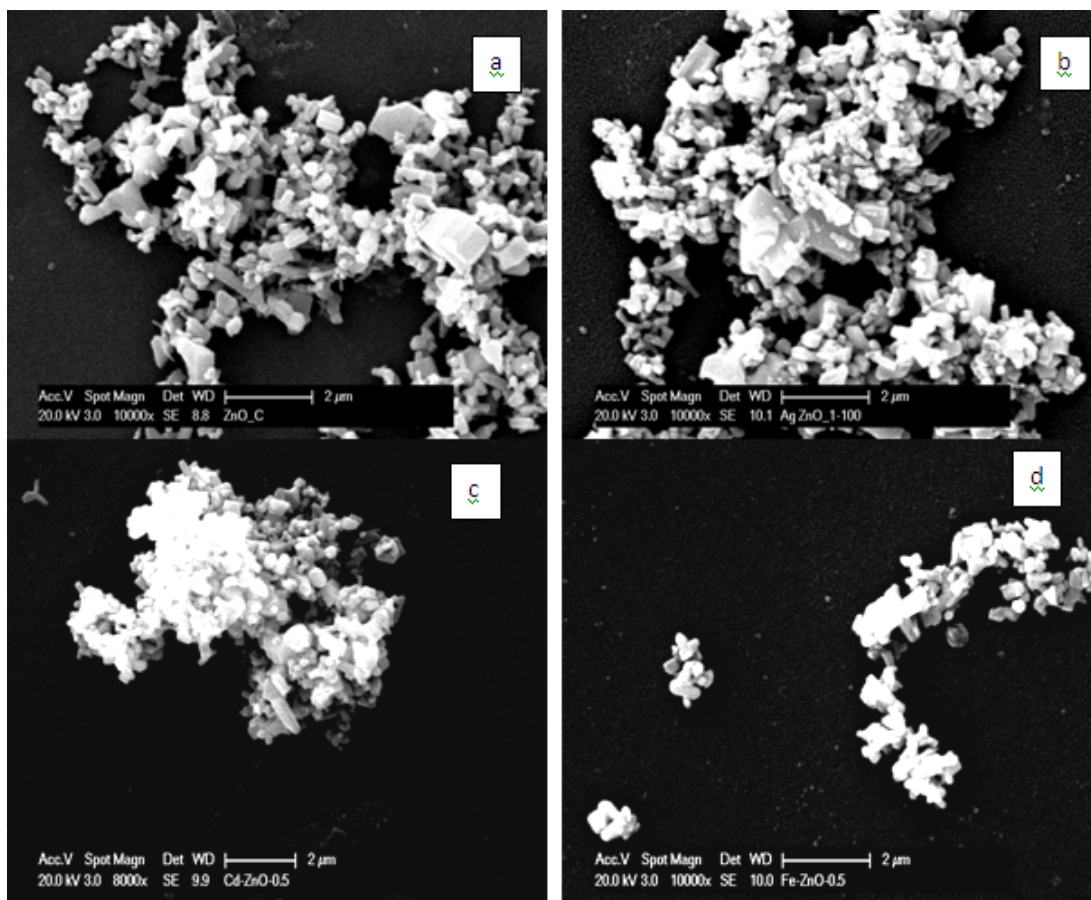**Figure 3: Powdered XRD patterns of ZnO and various atom% of Fe^{3+}doped ZnO.**

Figure 4: SEM images of a) Undoped ZnO and b) Ag^{+} doped ZnO; c) Cd^{2+} doped ZnO d) Fe^{3+} doped ZnO.

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Diffuse reflectance analysis: Figure 5 shows UV-Vis absorption spectra of ZnO as well as ZnO doped with 0.5, 1.0, 1.5 atom% of different metal ions. All the samples have a strong absorbance below 400 nm. The addition of metal ions does not change the absorption maximum of ZnO significantly, but a slight red shift in the absorption maximum was observed in the case of 1 atom% silver doped ZnO. The low absorbance values of 1 atom % Ag-ZnO and 1.5 atom% of Cd-ZnO over their preceding concentrations is due to lower amounts of sample taken for diffuse reflectance studies. The band gap energies of ZnO and doped ZnO samples were calculated by extrapolating the linear portion of the plots of modified Kubelka-Munk function, $[F(R)h\nu]^2$ versus the photon energy (hν) [Cimitan *et al* (2009)] shown in Figure 6. Table 1 shows the band gap energies of undoped and metal ion doped ZnO samples. The band gap energy is decreased slightly in the case of 1 atom% of silver doping compared to undoped ZnO, which supports the red shift in absorption spectra. No change in band gap energy of cadmium and iron doped ZnO samples.

Table 1: Band gap energies (eV) of ZnO and metal ion doped ZnO

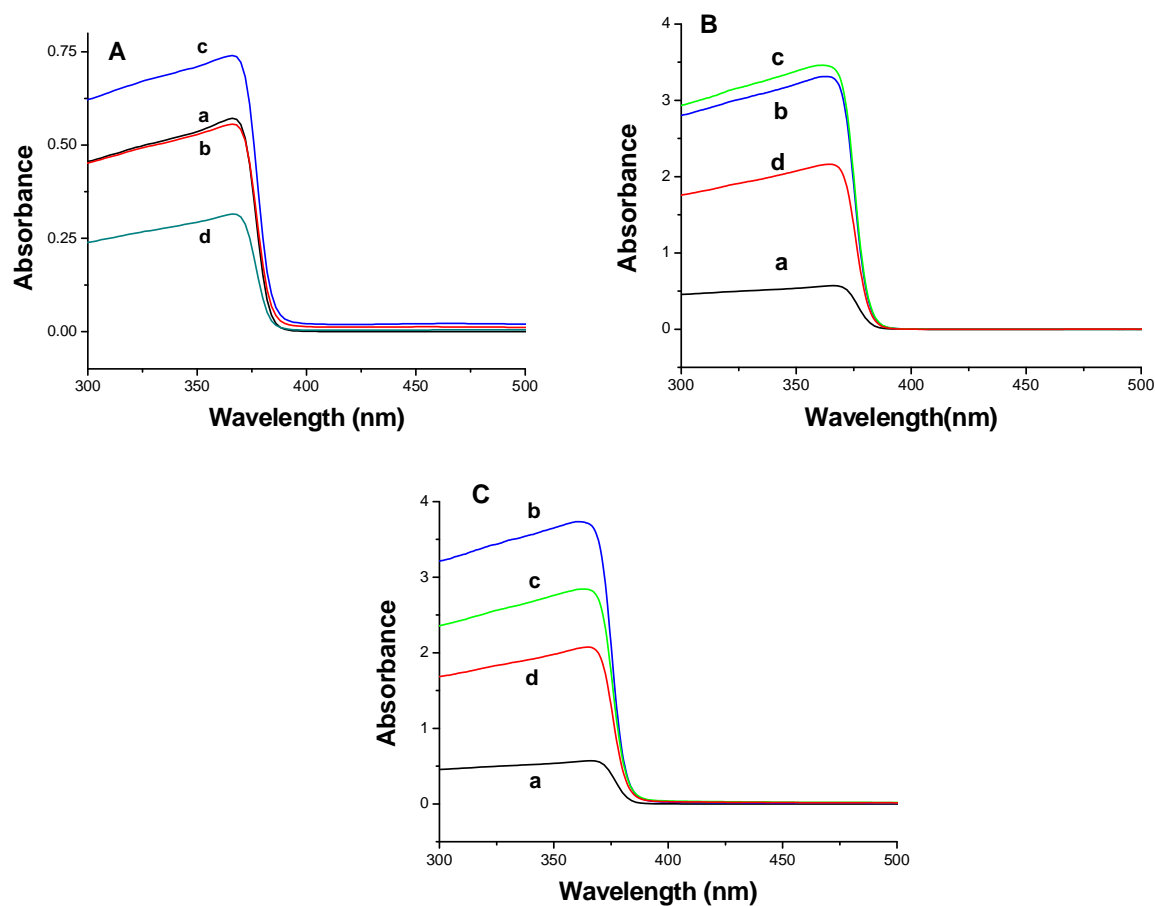| Percent Doping	Band gap energy (eV)		
	Ag-ZnO	Cd-ZnO	Fe-ZnO
0.5	3.28	3.28	3.28
1.0	3.27	3.28	3.28
1.5	3.28	3.28	3.28

Figure 5. UV-Vis absorption spectra of ZnO and doped ZnO; (A) Ag-ZnO, (B) Cd-ZnO, (C) Fe-ZnO and a- undoped, b-0.5 atom %, c-1.0 atom % and d-1.5atom %
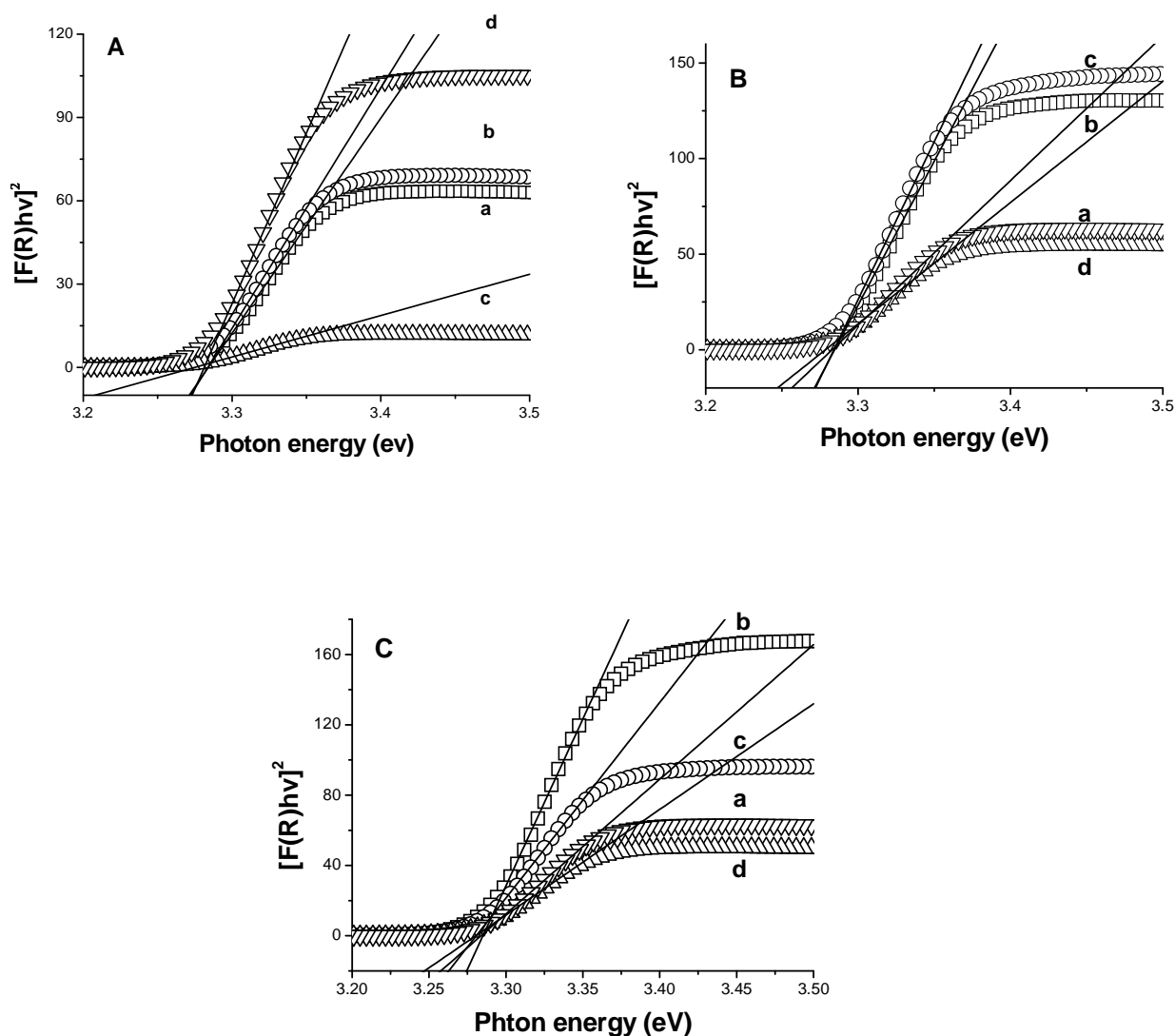
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Figure 6. Kubelka-Munck function versus photon energy plots for ZnO and doped ZnO; (A) Ag-ZnO, (B) Cd-ZnO, (C) Fe-ZnO (a- undoped, b-0.5 atom %, c-1.0 atom % and d-1.5atom %)

Photocatalytic degradation

The aqueous solutions of R6G (1.04×10^{-4} M) were found to degrade up to 72% and 86% on visible light irradiation for 1 h in the presence of ZnO (1 gL^{-1}) and Ag-ZnO (1 gL^{-1}), respectively. The degradation efficiency of Ag-ZnO was found to be higher than ZnO as shown in Figure 7.

The effect of calcination temperature of Ag-ZnO on degradation of R6G was also studied. The percent degradation decreased with increase in calcination temperature. Samples heated at 100 and 200 ^{0}C have high activity than samples calcined at 400 and 600 ^{0}C for 2 h. Higher temperature calcinations have a negative effect on photocatalytic activity because the presence of silver promotes the densification and grain growth of ZnO at higher temperatures by forming a silver island in the ZnO matrix, which causes

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the reduction in active surface sites of the photocatalyst for the adsorption of dye and for the absorption of light (Georgekutty *et al.* 2008). The degradation efficiency also varied with concentration of silver ion doping. With increase in silver doping from 0.5 to 1.5 atom percent, the degradation efficiency was found to be maximum for 1 atom percent of silver doping on ZnO. This is the optimal concentration of Ag doping on ZnO by this method.

The enhancing effect of Ag doping may be explained by its ability to trap electrons and this process reduces the recombination of charges and favours the oxidation of the substrate [Subbarao *et al* 2003]. Higher concentrations of silver doping could be unfavourable to photocatalytic efficiency. It is assumed that silver doping below optimum value acts as electron-hole separation center [Hermann *et al* (1986)], where as above optimum value it can also act as charge carrier recombination center. This is because the possibility of hole capture increases by large number of negatively charged Ag particles on ZnO which reduces the photocatalytic activity (Scalafani and Hermann 1998).

In case of cadmium doped ZnO, the photocatalytic activity is decreased when compared to pure ZnO. Increase in percentage of cadmium doping from 0.5 to 1.5 atom percent further lowered the photocatalytic activity (Figure 8). The photodegradation studies of calcined Cd-ZnO samples showed that the degradation efficiency is decreased with increase in calcinations temperature.

The photocatalytic activity of Fe-ZnO was found to be much lower than Pure ZnO and the activity was further decreased with increase in percent of Fe doping from 0.5 to 1.5 atom percentage (Figure 9). Calcinations of samples also have a negative effect on photocatalytic activity. Table 2 shows the percent degradation of R6G on undoped and metal ion doped ZnO after irradiation for 1h. Iron (III) can also acts as the recombination centers for the photogenerated electrons and holes according to the following equations. When the dopant concentration increases, the recombination rate will increase and compete with the redox processes (Zhu *et al.* 2006).
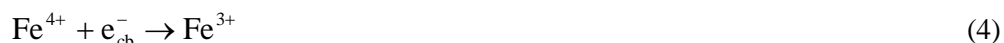
$$Fe^{3+} + h_{vb}^{+} \rightarrow Fe^{4+} \tag{1}$$

$$Fe^{3+} + e_{cb}^{-} \rightarrow Fe^{2+} \tag{2}$$

$$Fe^{2+} + h_{vb}^{+} \rightarrow Fe^{3+} \tag{3}$$

$$Fe^{4+} + e_{cb}^{-} \rightarrow Fe^{3+} \tag{4}$$

Table 2: The percent degradation of R6G on ZnO and doped ZnO calcined at various temperatures.

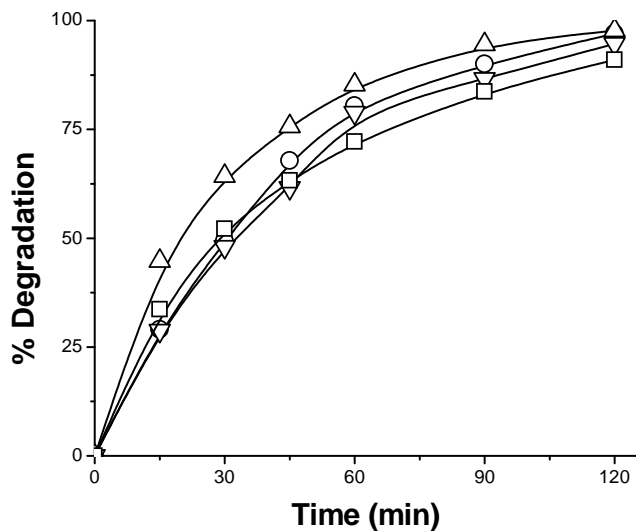| Sample	Percent degradation after 1h of irradiation				
	Uncalcined	$100^{0}C$	$200^{0}C$	$400^{0}C$	$600^{0}C$
Undoped ZnO	72.13				
1.0%Ag-ZnO		85.23	76.47	58.32	50.85
0.5%Cd-ZnO		69.55	61.91	42.45	33.87
0.5%Fe-ZnO		61.33	47.00	33.33	12.12

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Figure 7. Effect of silver doping on degradation of R6G. [R6G] = 1.04 x 10^{-4} M, [Catalyst] = 1gL^{-1};
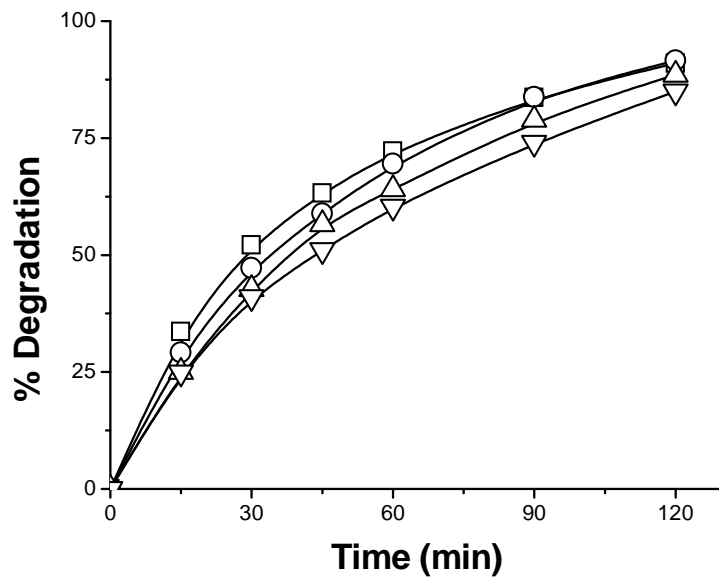(□) Undoped ZnO, (○) 0.5% Ag-ZnO, (Δ) 1.0% Ag-ZnO, (∇) 1.5% Ag-ZnO.

Figure 8. Effect of cadmium doping on degradation of R6G. [R6G] = 1.04 x 10^{-4} M, [Catalyst] = 1gL^{-1};
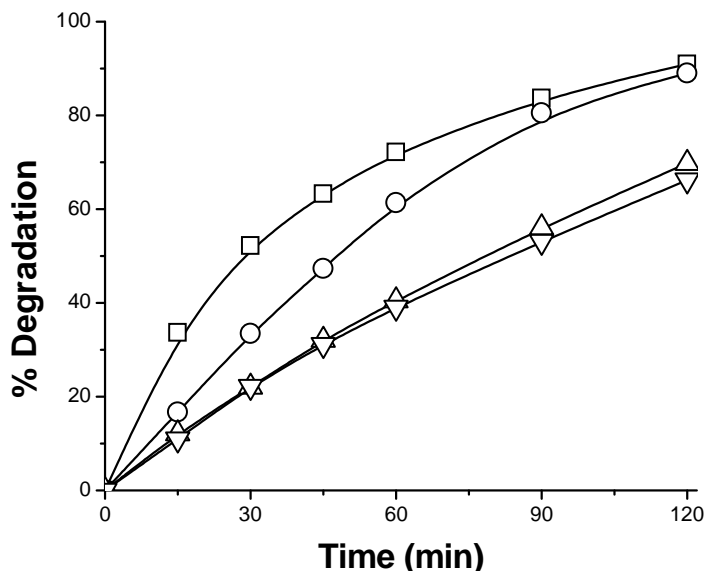(□) Undoped ZnO, (○) 0.5% Cd-ZnO, (Δ) 1.0% Cd-ZnO, (∇) 1.5% Cd-ZnO.

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Figure 9. Effect of iron doping on degradation of R6G. [R6G] = 1.04 x 10^{-4} M, [Catalyst] = 1gL^{-1};
(□) Undoped ZnO, (○) 0.5% Fe-ZnO, (Δ) 1.0% Fe-ZnO, (∇) 1.5% Fe-ZnO.

Conclusions
Silver doping on ZnO enhanced the phocatalytic activity and 1atom percent is the optimum loading for silver. Calcination of doped ZnO samples has a negative effect on photocatalytic activity.
Cadmium and Iron doping has reduced the photocatalytic activity of ZnO. This may be due to high concentration of Cd and Fe on the surface of ZnO which acts as charge recombination centers.
No change in the band gap energy of ZnO by this method of doping with different metal ions. The reason could be due to deposition of metal ions on the surface rather than intrusion in to the crystal lattice of ZnO.

ACKNOWLEDGEMENTS

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