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Photocatalytic degradation of Malachite Green using Zn doped SnO_2 compounds

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ABSTRACT

The photocatalytic degradation of Malachite Green dye on $Sn_{1-x}Zn_xO_2$ *(x= 0, 0.1, 0.2, 0.3 & 1) samples have been carried out using sunlight. The samples prepared by co-precipitation method and sintered at* 600^0C *were characterized by XRD, FTIR and DRS methods. Some solid state properties like electrical resistivity have been carried out.*

The doped samples showed higher photocatalytic activity. The effect of process parameters like pH, light and amount of catalyst on the degradation of dye has also been assessed. COD measurements were carried out to confirm the degradation. A tentative mechanism of the photocatalytic process has been assigned.

Keywords: COD, Malachite Green dye, photodegradation, $Sn_{1-x}Zn_xO_2$***, sunlight***

I. INTRODUCTION

The discharged wastes from various industries and dyes are the major source of coloured effluents and many times non-biodegradable pausing threat to the environment. Dyes are insufficiently removed by conventional sewage plant treatment [1]. Therefore semiconductor photocatalysis using various semiconductors such as TiO_2, ZnS, CdS, Fe_2O_3, ZnO, CeO_2 etc. have been used for the degradation of organic & inorganic dye pollutants [2-4].

In photocatalysis use of UV light for the treatment of huge quantity of industrial effluents is not feasible or economical. In the countries where ample amount of sunlight is available, photocatalysis involving sunlight will be a more economical and eco-friendly. So there is a need of an effective photocatalyst which can degrade pollutants under sunlight or visible light irradiation [5].

Insertion of transition metal ions on the photocatalyst structure can significantly enhance the photonic efficiency either by widening the light absorption range or by modifying the redox potential of the photoproduced radicals [6, 7]. Photocatalysis of Malachite Green has been studied by Trabelsi et al [8] and others [9 -11]. The present work is about photodegradation of malachite green over $Sn_{1-x}Zn._xO_2$ photocatalyst using solar radiation.

II. EXPERIMENTAL

$Sn_{1-x}Zn_xO_2$ (x = 0, 0.1, 0.2, 0.3 & 1) were prepared by co-precipitation method as described by Borker et al [4]. In this process $SnCl_2.2H_2O$ and $ZnSO_4.7H_2O$ of AR grade were taken in stoichiometric proportion and dissolved in distilled water to obtain a clear homogenous solution. To this 10% AR Grade NaOH solution was added with constant stirring till a white precipitate was formed which was then digested on a water bath for 3 h. The precipitated hydroxide mixture was subjected to oxidation by dropwise addition of 30% H_2O_2 with continuous stirring. The precipitate was filtered, washed with distilled water and dried at 100°C. It was then heated to 400 ^{0} C for 4 h. Finally, the precipitate was homogenized well in a mortar & then sintered at 600°C for 8 h to form solid solution.

The diffraction patterns were recorded on Rigaku X-ray diffractometer using Cu K α radiation, filtered through Ni absorber, at a scanning rate of 0.1°/min. The infra-red absorption spectra were recorded (Shimadzu model 8101A) to find the formation of metal-oxygen bond. Electrical resistivity (ρ) of the samples were measured by two- probe method from room temperature to 100^0 C. The diffuse reflectance spectra of the samples were recorded by UV-Vis-NIR Spectrophotometer at room temperature in the range 200- 800 nm. Chemical analysis was carried out to check the composition of the sample.

Photocatalytic degradation of malachite green was studied using prepared samples in the presence of sunlight during 10.00 am to 2.00 pm. 100 ml of the 10^{-5} M dye solution along with 150 mg of prepared photocatalyst was kept in sunlight. The degradation rate was monitored by measuring absorbance of the dye solution after every hour using UV-visible spectrophotometer (SPECTRO 119). The reaction was carried out at various experimental conditions like change in pH, with different amount of photocatalyst and with and without sunlight. The pH was measured with pH meter. The pH of the solution was adjusted by using previously standardized 1N HCl and 1N NaOH. COD values were determined to confirm the mineralization of the dye. Recovery of the photocatalyst sample was also calculated.

III. RESULTS AND DISCUSSION

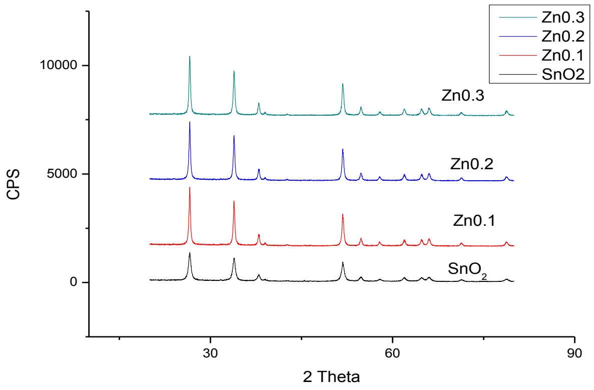

Fig.1. XRD pattern of SnO_2, $Sn_{0.9}Zn_{0.1}O_2$, $Sn_{0.8}Zn_{0.2}O_2$ and $Sn_{0.7}Zn_{0.3}O_2$

The formation of monophasic oxides were checked by recording X- ray powder diffractogram of all the samples such as $Sn_{1-x}Zn_xO_2$ (x = 0, 0.1, 0.2, 0.3 and 1.0). Fig.1 shows the XRD pattern of $Sn_{1-x}Zn_xO_2$ (x = 0, 0.1, 0.2 and 0.3) oxides calcined at 600°C. Pure SnO_2 is in tetragonal phase and ZnO is in hexagonal phase. $Sn_{0.9}Zn_{0.1}O_2$, $Sn_{0.8}Zn_{0.2}O_2$ and $Sn_{0.7}Zn_{0.3}O_2$ are in tetragonal phases and the crystal lattice parameter (4.447°A) is smaller than that of calculated pure SnO_2 (4.725°A). It may be due to the insertion of Zn atom into SnO_2 crystal lattice. Since the radius of Zn^{2+}(0.74A°) ion is smaller than that of the Sn^{4+} (0.80°A), the SnO_2 crystal lattice parameter decreases. On increasing x of $Sn_{1-x}Zn_xO_2$ from 0.4 to 0.9, the xrd diffraction peaks due to SnO_2 becomes weak and ZnO phases are observed. So only small amounts of ZnO can be introduced into the SnO_2 crystal lattice to form solid solution and excess ZnO remains in hexagonal phase.

FTIR studies were performed to ascertain the metal- oxygen bonding nature of the product. Evolution of bands at 480 cm^{-1} and 540 cm^{-1} are observed in the samples as x increased, which are due to Zn-O stretching vibrational modes. These two bands are of strong intensity in ZnO.

Electrical resistivities of the samples were measured by two probe method from room temperature to 100°C. Plots of log resistivity (ρ) versus 1000/T for $Sn_{1-x}Zn_xO_2$ samples show decrease in resistivity with rise in temperature indicating semiconducting behavior.

The band gap energy of these compositions was calculated using diffuse reflectance spectroscopy, which is shown in table 1. The doped samples show increase in band gap which helps in inhibiting electron-hole recombination by charge separation.

Table 1 Band gap energy of the $Sn_{1-x}Zn_xO_2$ samples

Sample	Band gap energy (eV)
SnO_2	3.97
$Sn_{0.9}Zn_{0.1}O_2$	4.07
$Sn_{0.8}Zn_{0.2}O_2$	4.09
$Sn_{0.7}Zn_{0.3}O_2$	4.05
ZnO	3.28

Photocatalytic degradation of Malachite Green dye was carried out using prepared samples. MG dye has absorption in visible region at λ_{max} 620nm in water. Measuring the absorbance of the solution at this wavelength monitors the progress of photocatalytic degradation. The reaction was studied for various experimental conditions like amount of catalyst, without using catalyst and with catalyst, only dye and different pH. The dye is unable to degrade in absence of sunlight and photocatalyst. The optimum amount of catalyst was found to be 150 mg for the degradation of 100 ml of 10^{-5} M Malachite Green dye solution as shown in Fig 2. The rate of dye degradation increased with the amount of photocatalyst which may be attributed to the increase in the exposed surface area of the semiconductor. But after a certain limit (150 mg), if the amount of photocatalyst is increased further, there will be a saturation point. According to Kartal et al [11] the amount of photocatalyst affects both the number of active sites on photocatalyst as well as penetration of light through the suspension.

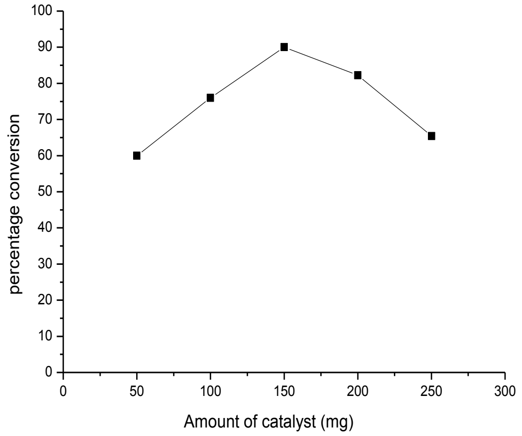

Fig. 2 Optimization of catalyst amount

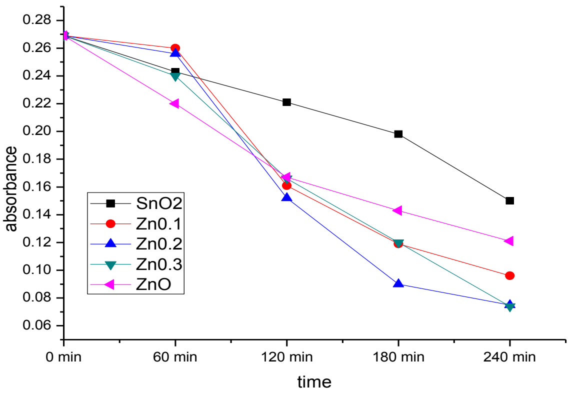

Fig.3 Degradation of malachite green at pH 7

Under solar irradiation, along with catalyst the dye is degraded completely within 240 minutes time interval. Absorption spectra obtained after completion of the dye degradation indicate that the degradation products are colourless. Thus the photocatalytic degradation provides an efficient way to mineralize the dye. The photocatalytic degradation of Malachite Green over different compositions of $Sn_{1-x}Zn_xO_2$ (x= 0, 0.1, 0.2, 0.3& 1) at neutral pH is shown in Fig.3. It was observed that SnO_2 is a good photocatalyst for the degradation of dye. A significant increase in the photocatalytic activity was observed by the substitution of Zn^{2+} in SnO_2 crystal lattice. $Sn_{0.8}Zn_{0.2}O_2$ shows the highest conversion value. This may be due to increase in band gap energy which inhibits the electron hole recombination.

Dye degradation was studied at different pH conditions, which is one of the important factors. It has been observed that degradation of dye is faster in alkaline pH, ie at pH 10. In alkaline medium, there is greater probability for the formation of hydroxyl radical ($OH^{\cdot}$), which can act as an oxidant, thus increasing the rate of photodegradation of the dye [5]. Fig. 4 shows the degradation of MG dye at pH 10.

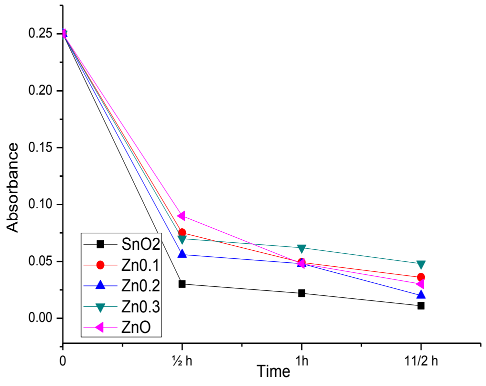

Fig. 4 Photodegradation of Malachite Green at pH 10

Increasing the pH of the dye solution from 4 to 10 increases the photocatalytic reaction after 240 min irradiation time. The photocatalytic degradation was faster in alkaline pH than in acidic pH range. At alkaline pH the negative surface of the semiconductor with OH^- ions act as an efficient trap for the photo-generated holes and produce hydroxyl radicals. At higher pH, the hydroxyl radical and 0_2^- radical can easily diffuse from the negative surface of semiconductor into the bulk of the reaction solution. Hence hydroxyl radical is responsible for dye degradation. At higher pH, the absorption spectra do not change considerably, only less time is required for the dye degradation to complete.

At acidic pH range the removal efficiency is minimum. This is because at low pH value the semiconductor particle agglomeration reduces the dye adsorption as well as photon absorption. But at low pH the concentration of H^+ is in excess and H^+ ions interact with dye linkage decreasing the electron densities at that linkage. Consequently, the reactivity of hydroxyl radical by electrophilic mechanism decreases. COD values are related to the total concentrations of organics in the solutions. From measured COD values, the COD removal efficiency values were calculated. The reduction in the estimated COD values from 100mg/L to 70 mg/L in 4 h of irradiation indicated the photodegradation of Malachite Green dye. Under present investigation, it was observed that the recovery of the photocatalyst was found to be about 98 % for MG. Also pH of the dye solution remains almost same before and after degradation.

IV.MECHANISM

Many people have suggested various mechanisms for the degradation of dye pollutants [4, 10]. On exposure to solar radiation, the semiconductor (SC) will be excited by light to give SC*. This excited state will provide an electron (e^-) in the conduction band leaving a hole in the valence band. This electron is then trapped by molecular O_2 forming O_2^- ions. The valence band hole generates hydroxyl radical ($OH^{\cdot}$) from hydroxyl ions, which can easily attack the adsorbed dye, thus leading finally to their complete mineralization. Scheme 1 suggests one of these mechanisms.

$SC + hv \rightarrow SC^*$

$SC^* \rightarrow e^-_{CB} + h^+_{VB}$

$e^-_{CB} + O_2 \rightarrow O_2^-$

$O_2^{-} + H_2O \rightarrow 2OH^{-} + 2OH^{\cdot} + O_2$
$h^{+}_{VB} + OH^{-} \rightarrow OH^{\cdot}$
$OH^{\cdot} + MG \rightarrow$ Leauco form
Leuco form → degraded products

Scheme 1

V. CONCLUSION

SnO_2 forms solid solution with Zn up to 30 % mole maintaining tetragonal structure. A significant increase in the photocatalytic activity was observed by substitution of Zn^{2+} in SnO_2 crystal lattice. $Sn_{0.8}Zn_{0.2}O_2$ shows the highest conversion value. This may be due to improvement in band gap energy which inhibits the electron hole recombination. It was found that Malachite Green dye can be degraded efficiently using semiconductor photocatalysts with sunlight. The dye degrades to a colourless solution after a period of 240 min irradiation time. The mechanism involves the formation of $OH^{\cdot}$ radical, which is an active oxidizing agent for the degradation of dye. Decrease in COD values indicate the mineralization of the dye. Photocatalyst can be recovered and reused.

RERERENCES

[1] B. Neppolian, S. Sakthivel, B. Arabindoo, M. Palanichamy and V. Murugesan, TiO_2 Assisted Photodegradation of Reactive Yellow 17 Using Batch Reactor, *Recent Trends in Catalysis* V. Murugesan, B. Arabindoo, M. Palanichamy, Narosa Publishing House, New Delhi, 1999, 78-81.

[2] S. Sakthivel, S. U. Geissen, D. W Bahnemann, V. Murugesan , A. Vogelpohl , Enhancement of photocatalytic activity by semiconductor heterojunctions:α-Fe_2O_3, WO_3 and CdS deposited on ZnO, J. Photochem. Photobiol. A: Chem 148, 2002, 283-293.

[3] M. R.Hoffmann, S.T Martin., W. Choi, D. W. Bahnemann, Environmental applications of semiconductor photocatalysis, Chem. Rev. 95, 1995, 69-96.

[4] P. Borker, A. V Salker, Photocatalytic degradation of textile azo dye over $Ce_{1-x}Sn_xO_2$ series, Mater. Sc. Eng. B 133, 2006, 55-60.

[5] T.Y. Zhang, T. Oyama, S. Horikoshi, H. Hidaka, J. C.Zhao, N. Serpone, Photocatalyzed N- demethylation and degradation of methylene blue in titania dispersions exposed to concentrated sunlight, Sol. Ener. Mater. Sol. Cells, 73, 2000, 287-303.

[6] H. Hidaka, Photodegradation of surfactants with TiO_2 semiconductor for the environmental wastewater treatment, Proc. Indian. Acad. Sci (Chem Sci) 110, 1998, 215 -228.

[7] H. Trabelsi, P. Atheba, G. K. Gbassi, M. Ksibi, P. Drogui, Sunlight- activated photocatalysis of Malachite Green using a TiO_2/Cellulosic fibe, Inter. J Hazard. Mater 1, 2012, 6-10.

[8] C. C. Chen, C. S. Lu, Y. C Chung, J. L Jan, UV light induced photodegradation of Malachite Green on TiO_2 nanoparticle, Inter. J. Hazard. Mater, 141, 2007, 520-528.

[9] S. Afshar, H. S. Jahromi, N. Jafari, Z. Ahmadi, M. Hakamizadeh, Degradation of Malachite Green Oxalate by UV and visible lights irradiation using Pt/TiO_2/SiO_2 nanophotocatalysts", Scientica Iranica F, 18 ,3, 2011, 772-779.

[10] K. L Ameta, N. Papnai, R. Ameta, Photocatalytic degradation of Malachite Green using nano-sized cerium iron oxide, Orbital: Electron. J. Chem. 6(1), 2014, 14 -19.

[11] O. E. Kartal, M. Erol, OguzH, Chem. Eng. Technol. 24, 2001, 645.