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RESEARCH ARTICLE

DEGRADATION OF METHYL ORANGE USING PHOTO CATALYST (ZNO) AND DOPED CU-ZNO NANO PARTICLES BY ADVANCED OXIDATION PROCESS

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ABSTRACT

The ZnO and 1%, 2% copper doped ZnO nano particles were synthesized, by using the chemical precipitation method. The resulting nano particles were characterized by X-ray diffraction, scanning electron microscopy, UV visible spectroscopy. Photo catalytic degradation of methyl orange in aqueous solution by ZnO and Copper doped ZnO under UVC (464 nm) irradiation was studied. The Scherrer equation for X-ray diffraction spectra was used to determine the crystallite sizes of ZnO and Cu-ZnO nano particles. The average crystallite size of un-doped ZnO was found to be 21.65 nm, while the crystallite sizes of 1% and 2% were 31.64 nm and 29.39 nm respectively. Effect of catalyst dosage, initial concentration of methyl orange on the degradation rate constant were also studied, effect of copper doping on degradation and in addition reusability aspects of nano particles where also studied which revalue's that reused nano particles exhibited same results as that of virgin particles.

INTRODUCTION

Contaminated waste water such as effluents from industries include changed chemicals especially synthetic dyes plays important task in environment pollution (Inam Ulla *et al.,* 2012). There are numerous techniques of subtraction of dyes from waste water. Some of them are, by flotation, precipitation, oxidation, filtration, coagulation, ozonation, supported liquid membrane, and also biological process (Nurul Shareena Aqmar Bte Mohd Sharif 2009). These methods just accomplish something in transferring organic compounds from water to a new phase, consequently creating inferior pollution (Madhusudhana *et al.,* 2012) and these techniques have one or further last part products requirements to be extra management (Inam Ulla *et al.,* 2012; Nurul Shareena Aqmar Bte Mohd (Sharif 2009). Recently, scientific and research community have shown their great interest on metal oxide Nano structures and their applications due to their easy, safe, environmental friendly, economical synthesis procedure and technological applications in the water and air purification by degradation and adsorption of organic/inorganic pollutants and toxic gases (Singh ?). Photo catalysis is a hopeful method for solve countless existing ecological issues. Semiconductor absorbents propose the possible for removal of organic pollutants (Rahmatollah Rahimi *et al.,* ?). Amongst them semiconductor based photo catalytic degradation could be considered as the most efficient. This particular technique involves the use of semiconductor as catalysts which act as the medium of oxidation. Currently, TiO2 and ZnO are largely deployed as the semiconducting materials suitable in the treatment of pollutants (Susheela Bai Gajbhiye *et al.,* 2012). ZnO is a unique and key inorganic material that has been involved an wide-ranging explore due to its characteristic description and work of fiction applications in extensive areas of science and technology. It has numerous properties like semiconducting, piezoelectric, piezoelectric, catalysis, optoelectronics and fine particles metallurgy. In addition, the optical properties of ZnO nano particles play a incredibly significant role in optoelectronic, catalytic and photochemical properties (Samria Bagheri *et al.,* 2013). Doping of ZnO with transition metals can straight to ferromagnetic properties at room temperature, strength form dilute magnetic semiconductors (DMSs) and is an efficient way to tune the properties of ZnO. The doping TM will produce some untenanted states that will as a result alter of the band gap energy. The presence of a dopant ion in the ZnO lattice can influence also the photo catalytic capability of the nano particles (Voicu, O. Oprea *et al.,* 2013)

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MATERIALS AND METHODS

Experimental section

Synthesis of the Undoped and doped with Cu zinc oxide samples have been prepared by precipitation method. Analytical grade of purity zinc sulphate, sodium hydroxide and

copper sulphate were used as starting materials. In this study, a 0.1M of zinc nitrate ($Zn(NO_3)_2{\cdot}4H_2O$) in 100ml aqueous solution was kept under constant stirring using magnetic stirrer to completely dissolve the zinc nitrate for one hour and 0.2M of sodium hydroxide (NaOH) in 100ml aqueous solution was also prepared in the same way with stirring of one hour. After complete dissolution of zinc nitrate, 0.2M NaOH aqueous solution is added under high speed constant stirring, drop by drop (slowly for 45 min) touching the walls of the vessel. The reaction is allowed to proceed for 2 hrs after complete addition of sodium hydroxide. The beaker is sealed at this condition for 2 h. After the completion of reaction, the solution was allowed to settle for overnight and further, the supernatant solution is separated carefully. The precipitate was separated by filtration, washed several times with distilled water to pH value 7 and dried in air. For preparation of the final catalyst samples, the corresponding precursors were heated for 3 h at 500 ºC in air (Satyanarayana talam *et al.,* 2012).

In similar same manner 1%, 2% and 4% of copper doped zinc oxides were prepared. While preparing copper doped zinc oxide the required amount of copper weight was taken. Here varying amount of copper is mixed along with along with zinc nitrate and NaOH is added drop by drop and remaining procedure will be same as above preparation method.

(i) For kinetic measurements, a CARY 50 Bio UV-Vis Spectrophotometer (Varian BV, The Netherlands) with temperature controller and HPLC system (Agilent 1100 series, USA) were used.
(ii) For degradation study, mercury lamp (PHILIPS, TUV 25W T5, E_{max} =254 nm) mounted inside the UV cabinet was used. The typical light intensity illuminated on the surface of reaction mixture was 0.04 mW cm^{-2}.

Characterization

For characterization of nanoparticles, a Siemens X-ray Diffractometer (Cu source) (XRD) AXS D5005 was used to identify the particle size of the doped TiO_2. The surface morphologies were examined using a Scanning electron microscope (SEM) JEOL JSM 6360 to decide whether the coatings have suitable surface morphologies for photo catalytic degradation or not.

X-ray diffraction (XRD)

Figure-1 represents the prototype of ZnO nano fine particles and also 1%, 2% copper doped zinc oxide particles.XRD peaks shows that the equipped material consists of particles in nano size range. XRD outline analysis is done using Siemens X-ray diffracto meter (AXS D5005), the peak strength location and width, full width at half maximum (FWHM) data ie.0.3858 °. The diffraction peak was found to be 36.2549° and further it also confirms the prepared nano powder was of majorly containing zinc oxide particles. Nevertheless it do not contain significant XRD peaks other than ZnO peaks. Diameter of these nano particles was calculated using Debye scherrer formula.

$d = 0.89\lambda / \beta \cos\theta$

Where 0.89 is Scherrer's constant, λ is the wavelength of X-rays, θ is the Bragg diffraction angle, and β is the full width at half-maximum (FWHM) of the diffraction peak corresponding to plain. The particles size was found to be 21.65nm of ZnO and that of 1%and 2% is 31.64 and 29.39 respectively.

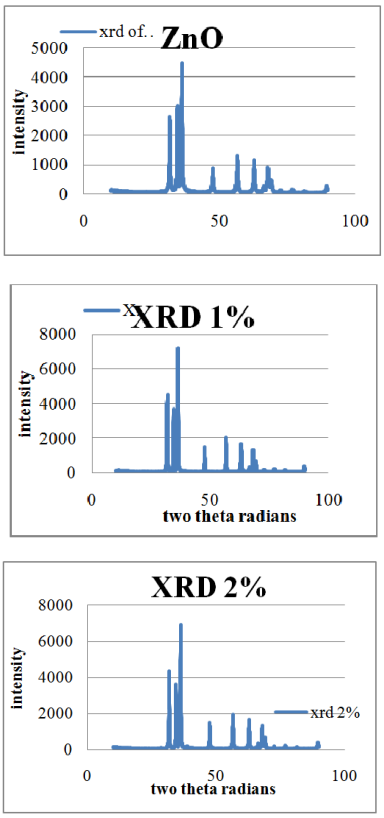

Figure 1. XRD plots of pure ZnO and 1%, 2% copper doped zinc oxide shows maximum peak

Scanning Electron Microscopy (SEM)

The SEM pictures of ZnO nano particles and 1% and 2% copper doped zinc oxide are shown in Figure-2 at dissimilar magnifications by means of SEM JEOL (JSM 6360). These films confirm the structure of ZnO nano particles. These pictures substantiate the approximate oval in shape and are arranged in groups to form a needle like structure. The particular area electron diffraction pattern shows distinct bright rings which conform preferential orientation of nano crystals as an alternative of asymmetrical.

UV–Vis Spectroscopy

Zno nano particles elucidation was equipped by ultrasonically dispersed them in absolute ethanol the greatest peak was found to be 374nm.The band gap (Eg) of ZnO nano particles is premeditated by using the formula Eg = hc/λ, where h = Planck's constant, c = velocity of light and λ = wavelength. The resultant band gap was found to be 3.32eV. In that of 1% and 2% is 3.30 and 3.290 (Samria Bagheri *et al.,* 2013).

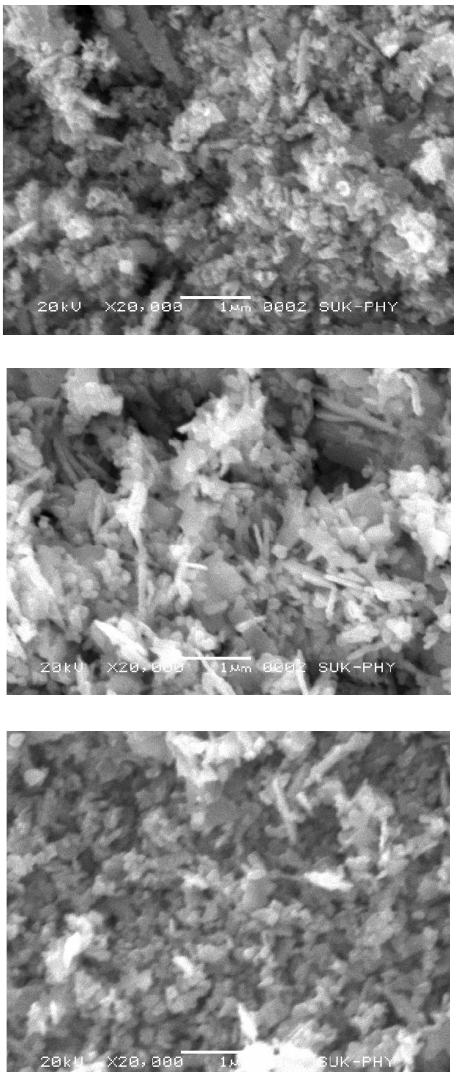

Figure 2. SEM images of ZnO and 1%, 2% copper doped zinc oxide at higher magnification

The Photo catalysis Process

The photo catalysis study was carried out by taking known concentration of methyl orange in a beaker to investigate the photo catalytic degradation. A dose of 100 mg l^{-1} ZnO nano particles were added. It was placed in a photo catalytic chamber under 25 W UV- lamp (Phillips) with a wavelength peak at 254 nm with continuous stirring for adsorption–desorption equilibrium and then exposed to UV light. At the interval of every 20 minutes, the solution was taken out and centrifuged at 1000 rpm for 10 min. The concentration of methyl orange was measured at 4649 nm using UV visible spectrophotometer (Varian CARY 50 Bio UV-Vis Spectrophotometer).

RESULTS AND DISCUSSION

Variation of Methyl orange Concentration by UV Alone without Catalyst

It is imperative from mechanistic and submission points of vision to study the reliance of photo catalytic response speed on the methyl orange concentration. Therefore, the control of substrate concentration on the degradation rate was deliberate at different concentrations altering from ($0.5x10^{-5}$) M to ($5x10^{-5}$) M in 100ml.The rate of response is calculated for maximum degradation i,e $1.1376E^{-06}$ M/sec. The degradation rate for the putrefaction and mineralization of the dye as a role of substrate concentration employing UV. It is observed that the degradation rate is originated to decrease with the increase in substrate concentration from ($0.5x10^{-5}$) M to ($5x10^{-5}$) M. This might be due to that as the early concentrations of the dye increase the colour of the irradiating combination becomes additional and additional strong which prevents the dispersion of light to the surface of the substrate molecule. Their concentrations will decrease with increase in concentration of the dye as the beam photons are smaller amount then the molecules of dye and also all molecules of drug or dye do not approach in contact with light. Subsequently, the degradation efficiency of the dye decreases as the dye concentration

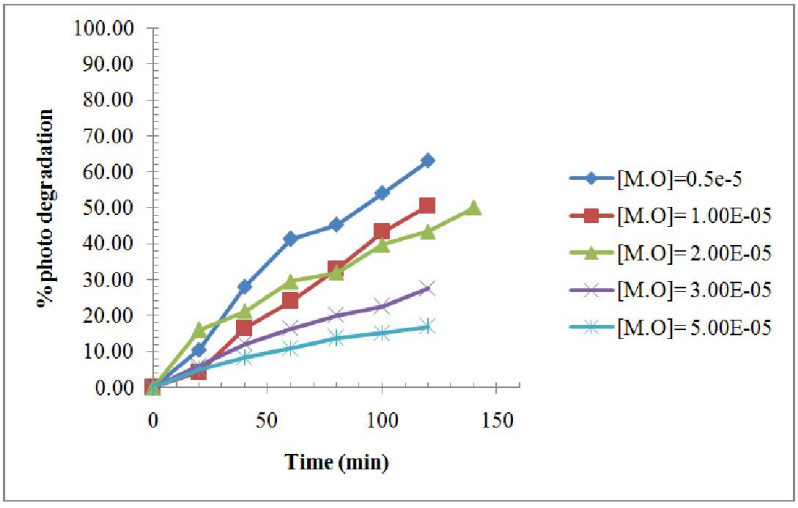

Figure 3. Effect of methylene blue concentration under UV alone

increases (Yadollah Abdollahi *et al.,* 2012; Ankita Ameta *et al.,* 2013; Haque *et al.,* 2006). Graphical representation is shown in Figure 3.

Variation of methyl orange concentration

In a view to study the dependence of photo catalytic reaction rate on the substrate concentration, the degradation kinetics of methyl orange has been investigated employing different concentrations of dye presented. As a function of substrate concentration, employing zinc oxide in UV light. It is interesting to note that degradation rate under UV light source increases with increase in substrate concentration from $0.5x10^{-5}$M to $1x\ 10^{-5}$M. A further increase in the methyl orange concentration may be leads to a decrease in the degradation rate.

When the methyl orange concentration increases from $0.5x10^{-5}$M to $1x\ 10^{-5}$M, the catalytic sites may be sufficient enough to withstand the increased concentration leading to higher rate of photo degradation. With further increase in concentration of methyl orange, more and more molecules of the compound gets adsorbed on the surface of the photo catalyst, as result of which, the requirement of catalyst surface needed for the degradation also increases. However, the generation of relative amount of $OH^{\bullet}$ and O_2^{-} on the surface of catalyst do not increase as the intensity of the light, irradiation time, amount of catalyst and quantity of oxidizing agent. Consequently the rate of photo degradation decreases with increase in concentration of methyl oragne (Santhosh *et al.,* 2008; Wing *et al.,* 2008). The rate reaction is calculated for maximum degradation i,e $4.04293E^{-07}$ M/sec M/sec. Graphical representation is shown in Figure-4.

as the quantity of catalyst is increased, the rate of photo degradation of dye increases but routinely the response rate become practically constant after a definite amount (0.1gm) of the semiconductor. This might be due to the truth that as the amount of semiconductor is increased, the existing surface area also increases, but after a definite limit, if the amount of photo catalyst is further increased there will be no increase in the showing surface area of the photo catalyst. It may be considered like a saturation point over which any increase in the quantity of semiconductor has insignificant or no consequence on the rate of photo catalytic degradation of dye, as any increase in the amount of semiconductor after this saturation point will only increase the width of the layer at the bottom of the clarification (Samria Bagheri *et al.,* 2013; Yadollah Abdollahi *et al.,* 2012; Ankita Ameta *et al.,* 2013; Haque *et al.,* 2006). It is observed that the saturation point is increased on by means of vessels of higher dimensions. The rate reaction is calculated for maximum degradation i,e $8.10713E^{-07}$ M/sec.

The adsorption of the methyl orange on the surface of the photo catalyst was investigated by string the aqueous solution in the dark for 24h in a round bottomed flask containing varying amounts of photo catalyst. Analysis of the samples after centrifugation indicates no observable loss of the dye. Graphical representation is shown in Figure-5.

Effect of Copper Doing on Degradation

The amount of doped semiconductor also affects the process of dye degradation. Different % copper doped photo catalyst was used (1% and 2%) the results are shown in graph -6.

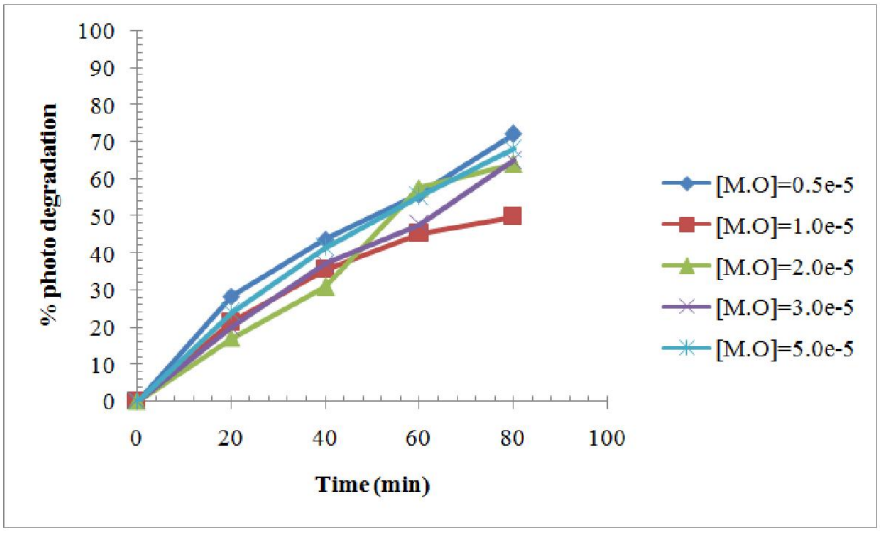

Figure 4. Effect of methylene blue variation under UV irradiation with constant catalyst of 0.1gm

Effect of Variation of amount of photo catalyst

The effect of the photo catalyst dosage on the degradation kinetics of methyl orange was investigated using different concentration of ZnO varying from 0.05 mg/L to 0.250 mg/L of $3.0x10^{-5}$ methyl orange solution. It have been observed that

The degradation is less because the amount of dopent is very small. Further increasing the concentration of dopent the degradation increases very less and it can be noted from characterization then band gap of the doped particles is greater than ZnO particles. So that excitation of electrons was very less consequently degradation decrees. The rate reaction is

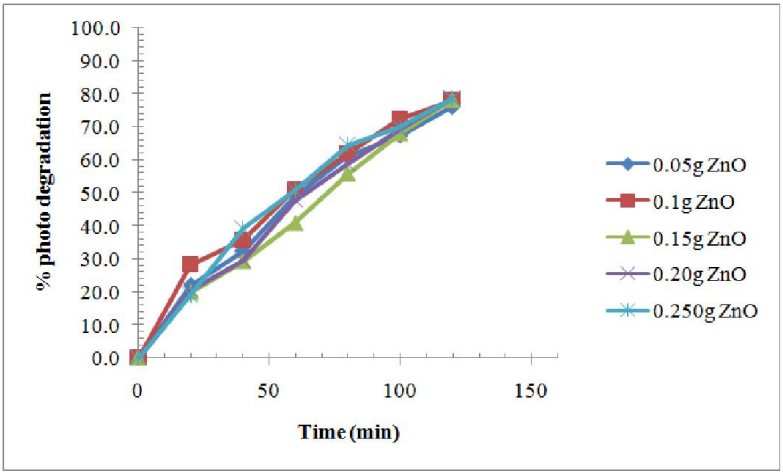

Figure 5. Effect of varying photo catalyst loading with constant methyl orange [3x10^{-5}] M under UV

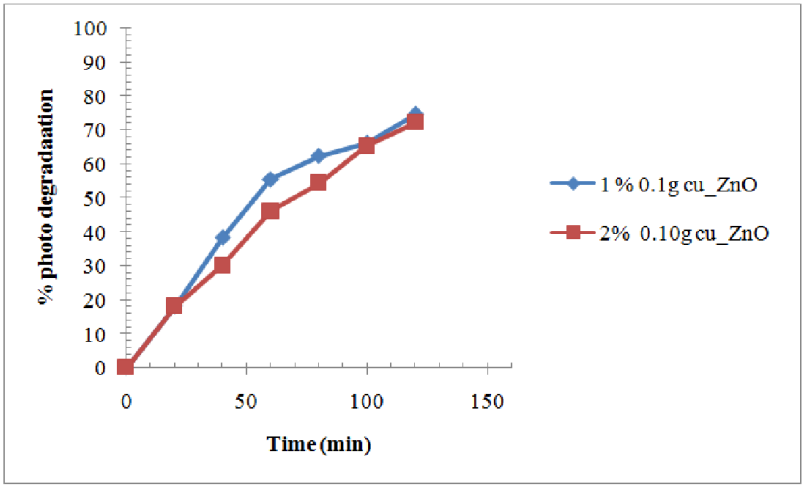

Figure 6. Effect of copper doped ZnO on methyl orange at concentration 3x10^{-5} M.

calculated for maximum degradation i,e 7.99381E^{-07} M/sec. Doping of ZnO with transition metals ions has also been studied. Similarly to metal doping. The use of transition metals ions allows for electron trap that suppress electron hole recombination. The holes is then able to migrate towards the surface of the catalyst and oxidize the adsorbed organic compound. It is concluded that a doping threshold exists where only small concentration produce a positive effect on the photo catalytic rate. Some transition metals actually decrease the photo catalytic rate due to increase in electron hole recombination by creating recombination centres. It is noted that not all transition metal produce a positive result. Some transition metals produce a positive result (Zhong Lin Wang 2004; Milenova *et al.,* 2013).

Conclusion

Copper doped (1% and 2%) ZnO and ZnO wurtzite nanoparticles, prepared by the precipitation method, have been tested in the reaction of methyl orange under UV irradiation. The average sizes of the crystallites of doped and undoped ZnO are below 50 nm. The percentage of purity of photo catalyst plays a vital role in bringing about degradation. Hence the studies on characterization of the same were done using XRD and SEM. The results of these test further conformed the obtained sample is ZnO, by characterization particle size is calculated and come to know the prepared ZnO is pure and does not contain any other impurities other than ZnO. Doping of ZnO with transition metals ions has also been studied. It is concluded that a doping threshold exists where only small concentration produce a positive effect on the photo catalytic rate. Some transition metals actually decrease the photo catalytic rate due to increase in electron hole recombination by creating recombination centres. It is noted that not all transition metal produce a positive result. Some transition metals produce a positive result. This result is an indication that segregation of doping element is occurring on the surface of the ZnO particles. The pure ZnO samples exhibit the best photo catalytic properties.

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