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A Study of Morphology of Synthesized Nano Zinc Oxide and its Application in Photodegradation of Malachite Green Dye using Different Sources of Energy

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Abstract

Solar photo catalytic oxidation technique using semiconductors like TiO_2, ZnO etc has a land mark in the field of waste water treatment especially for the removal of organics and dye stuffs. When we use ZnO as nano particles, the efficiency of the photo catalytic activity will be enhanced. The present work deals with the photocatalytic degradation of malachite green dye using synthesized ZnO nanoparticles. The co-precipitation technique has been used for the synthesis of zinc oxide nano particles. By varying the experimental conditions, three different samples of ZnO nano particles(S_1, S_2, and S_3) were prepared. The three samples obtained by the co-precipitation technique were characterized by PXRD, FTIR, and SEM instrumental methods. The IR analysis of the spectra show a broad band between 430-419 cm-1 with shoulder shape, characteristic of Zn-O bond.. The images obtained by SEM of the samples S_1, S_2 and S_3 show Sphere and cube-like nanoparticles. The ZnO nano particles have been distributed well within the range of ~ 100nm which is the favorable property to exhibit better photo catalytic activity. From the XRD results, the size of ZnO nano particle were calculated to be 18nm, 16nm, 12nm for the three samples. The photo catalytic degradation of malachite green dye was carried out using different sources of energy like solar radiation, microwave radiation and ultra sound energy. The optimum conditions for the maximum removal of dye by photocatalytic degradation using different sources of energy were proposed by varying the experimental parameters like initial concentration of dye, dose, pH and contact time.

The photo catalytic degradation of malachite green dye obeyed pseudo first order kinetics.

Keywords: ZnO, Malachite green dye, photo degradation.

Introduction

Due to their size and shape dependent properties, nano-dimentional semiconductor materials have shown their great interest in optoelectronics, electronics, sensing, energy storing and harvesting applications. Binary semiconductor oxides such as ZnO, CdO, SnO_2 have innumerable applications and are now widely used as transparent conductive oxides Semiconductors such as nanosized TiO_2, ZnO has attracted extensive attention as photocatalyst for the degradation of organic pollutants in water and air under UV-radiation[1, 2, 3, 4]. Of these, ZnO has better ability to oxidize organic compounds. Zinc oxide is mostly a n-type, II-VI, wide direct bandgap, semiconducting material. Wurtzite zinc oxide has wide band gap(3.37ev), high excitation binding energy(=60meV) at room temperature and high dielectric constant. Being of its high optoelectronic efficiency relative to the indirect band gap of group IV crystals, it is considered as a reliable material for visible and near ultraviolet applications. When used in nanoscale its activity is much enhanced. Large scale production and extensive applications of synthetic dyes cause considerable environmental pollution. Dyes are difficult to decompose biologically & chemically. The existing methods of removal of dyes provides ways for removal of dyes from aqueous solutions, which implies their transfer from one region to other region of environment. The complete removal requires new treatment methods. In this context photodegradation of dyes offers promising hand for the treatment of industrial effluents from textile and dye industries.In this work photo catalytic degradation of Malachite green dye have been studied with ZnO nano particles. Nano zinc oxide has been used to degrade the color of malachite green dye using different sources of energy ie solar radiation, microwave irradiation and ultrasonication.

Experimental

Materials and Methods

Malachite green dye was obtained from Sd.fine chemicals, Mumbai. $ZnCl_2$ was purchased from E. Merck chemicals Ltd, Mumbai and NaOH was purchased from E. Merck chemicals Ltd, Mumbai. All the reagents and solutions were prepared by using double distilled(DD) water prepared using an all glass apparatus.

Synthesis of ZnO nano particles

ZnO nano particles were synthesized using co-precipitation method. In this method zinc oxide were prepared in three ways.In the first set, 100 mL of 1M $ZnSO_4$ solution was added to 100 Ml of 2M NaOH solution in drops. When the addition was complete, the mixture was kept at room temperature under constant stirring using magnetic stirrer for a period of 2 – 3 hours. The resultant precipitate obtained was

filtered and washed with water. The formed white precipitate $Zn(OH)_2$ was allowed to settle down, filtered using filter paper in suction pump, washed with distilled water for several times and dried in a hot air oven at 150ºC for 30 minutes. The synthesized Zinc oxide was further irradiated at 180W with microwave radiation in a microwave oven for 30 minutes. This sample will be named as S_1. The above said procedure was followed to synthesize nano ZnO in two different experimental conditions. Zincsulphate, sodium hydroxide and any one of the stabilizing agents such as Urea, Oxalic acid are used in two separate synthesis. Thus we get two more samples of zinc oxide nanoparticles. These samples will be named as S_2&S_3.

The co-precipitation reaction can be represented as follows.

$$ZnSO_4\ (aq) + 2NaOH\ (aq) \longrightarrow Zn(OH)_2\ (s) + 2Na_2SO_4\ (aq)$$

$$Zn(OH)_2 \xrightarrow{\triangle} ZnO + H_2O$$

The resultant Zinc oxide samples after irradiation were collected and stored. The samples were subjected to Powder X-Ray diffraction, Scanning electron microscopy and Fourier Transform Infra Red studies, to confirm the nano structure.

Photo catalytic Degradation Studies

Preparation dye solution

The stock solution of dye (Malachite green) with known concentration (2000ppm) was prepared and stored in brown bottles. It was diluted to get different required initial concentrations of the dye and used.

Measurement of concentration of dye solution

The stock solution is diluted to different initial concentration 2, 4, 6…8ppm for malachite green in standard measuring flasks, by making necessary dilution with required volume of DD water.

The optical density (OD) of each dye solution was measured by using UV-VIS spectrophotometer (model-No-SL-150 Elico) at 616 nm (λ_{max} value for MG dye). A plot of optical density versus initial concentration (Fig 1) was drawn. This plot was used as standard graph for the estimation of dye by interpolation technique. The values of optical density for dye solutions, before and after the removal of dye were obtained by using spectrophotometer. Using these optical densities the corresponding dye concentrations were obtained from the standard graph (Fig 1) by the interpolation technique.

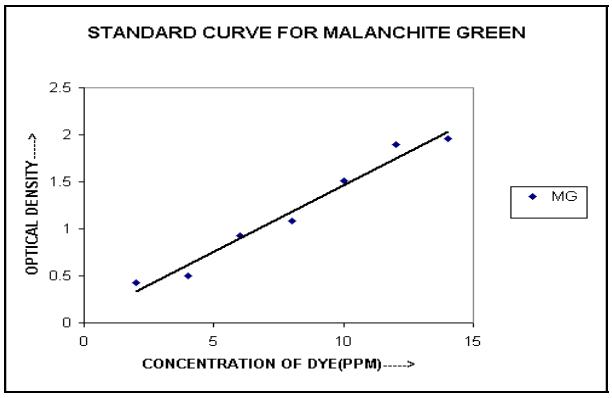

Figure 1: Standard curve for malachite green

Batch Kinetic Experiments

Stock solution of dyes (2000ppm of MG) was suitably diluted to the required initial concentration of dye with DD water. Fifty ml of the dye solution of known initial concentration (C_i) was taken in 50ml beaker.

Required amount of one of the photocatalysts (three samples of ZnO nano particles [S_1, S_2, S_3]) were exactly weighed and then transferred into the dye solution with different C_i. The beakers were then exposed to any one of the energy source, namely direct sunlight, microwave irradiation, and ultrasonication for a fixed period of contact time.

After bleaching, the OD of these solutions were measured using spectrophotometer at 616nm. Then the final or equilibrium concentrations (C_e) were obtained from the standard graph by interpolation technique.

In all the batch degradation of dye experiments, the extent of removal of the dye in terms of the value of percentage removal of dye have been calculated using the following relationships.

$$\text{Percentage removed} = 100(C_i - C_e)/C_i \qquad 1$$

Where

C_i= initial concentration of dye (ppm)

C_e=equilibration concentration of dye (ppm)

In the batch dye degradation technique, several factors govern the degradation process. The effect of various experimental parameters on degradation of malachite green dye in the aqueous suspension by zinc oxide nanoparticles was studied by varying the experimental conditions.

Results and Discussion

FT-IR analysis

The FT-IR spectra of the three samples are given in Figures:2-4. The FT-IR analysis

of the spectra shows a broad band between 430-419 cm-1. The spectra show bands at(3250 and 3500 cm^{-1}) which may be assigned to OH^- stretching vibrations of adsorbed H_2O (or) due to the residual $Zn(OH)_2$ present in the powder. The additional peaks for the samples with Frequency 1191.93, 1190.96, 1191.93 may be assigned to C-H bending vibrations. Some other peaks obtained with frequency1386.72, 1393.47, 1335.61 &1609.49, 1622.99, 1640.35 corresponds to asymmetric stretching mode of C=O and symmetric stretching mode of C=O.

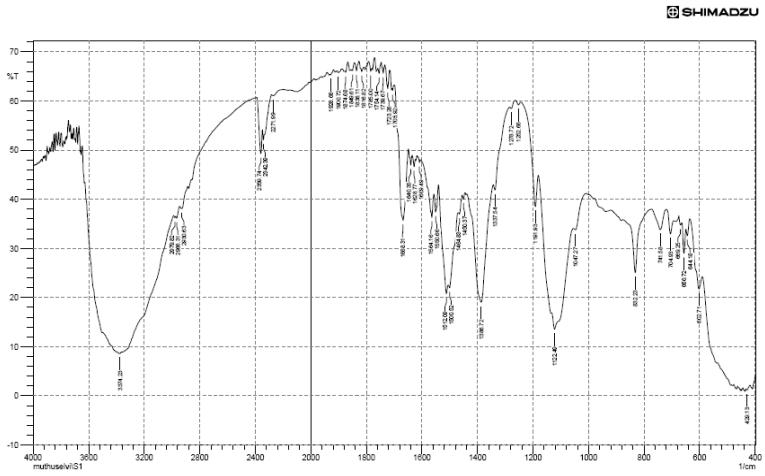

Figure 2: FT-IR Spectra for nano ZnO for sample: S_1.

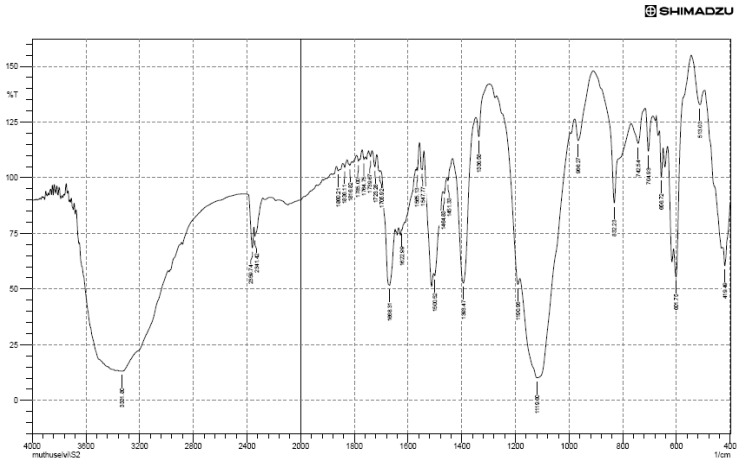

Figure 3: FT-IR Spectra for nano ZnO for sample: S_2

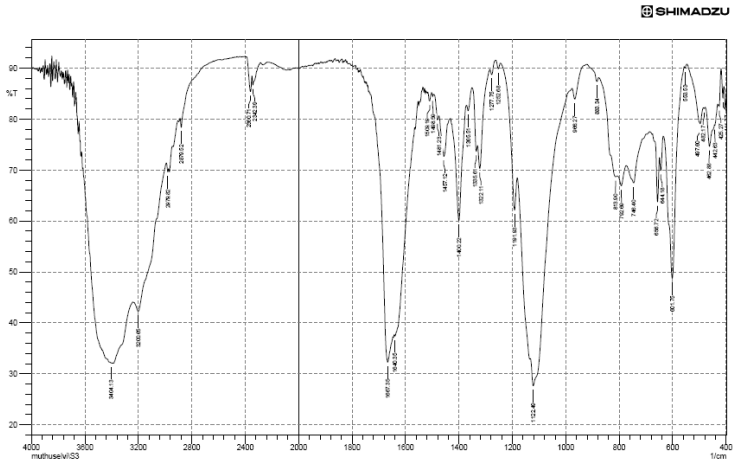

Figure 4: FT-IR Spectra for nano ZnO for sample: S_3

XRD pattern

The average particle size is determined using Debye – Scherrer's equation applied to major, peaks corresponding to maximum intensity in the XRD patterns of the three samples

(Figs. 5-7)and is found to be around 18nm, 16 nm, 12 nm for S_1, S_2, S_3 respectively.

The size of the synthesized ZnO nano particles were calculated from powder XRD pattern using Scherrer's formula.

$$t = \frac{0.9\lambda}{\beta \cos\theta}$$

Where

λ is the wavelength of incident X-Ray (1.5406Å)

β is the full width for half maximum and

θ is the Bragg's angle for the peak.

β can be calculated using the equation

$\beta = (2\theta_2 - 2\theta_1)$

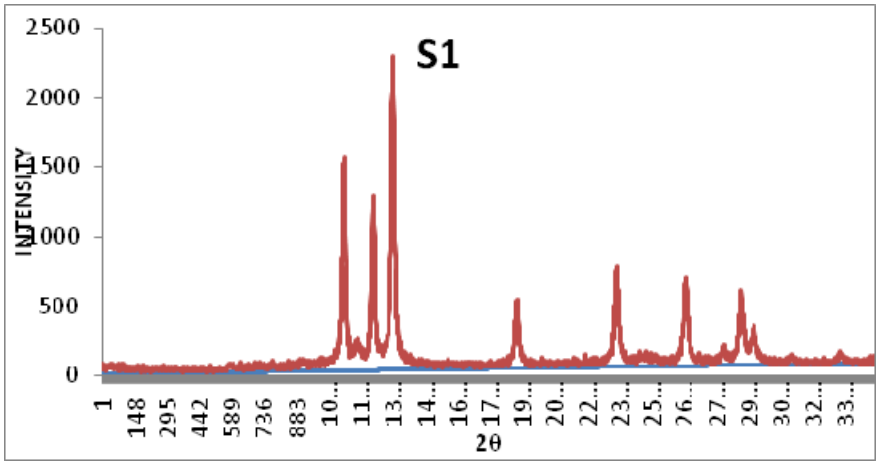

Figure 5: Powder XRD Pattern of ZnO Nanoparticle [S_1]

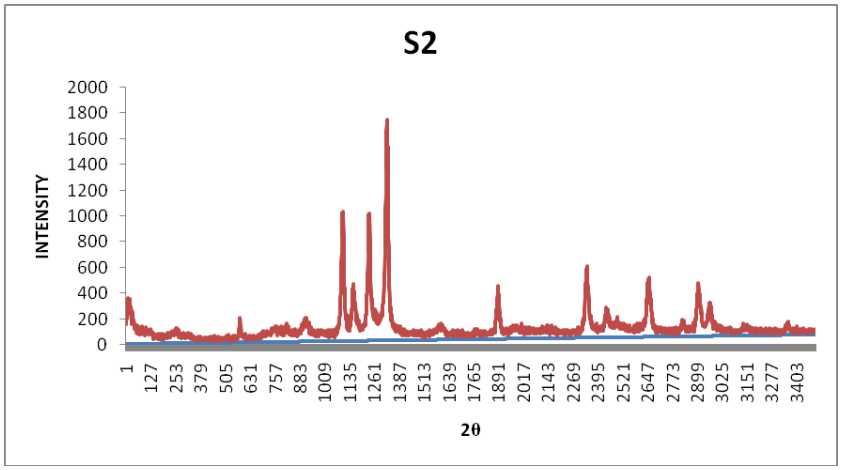

Figure:6 Powder XRD Pattern of ZnO Nanoparticle [S_2]

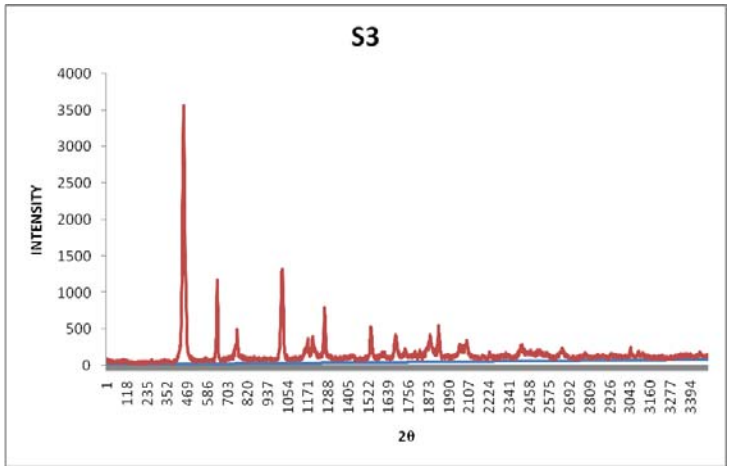

Figure:7 Powder XRD Pattern of ZnO Nanoparticle [S_3]

Scanning Electron microscope (SEM)

The images obtained by SEM of the samples S_1, $S_2$and S_3(Figures :8-10) show sphere and cube-like nanoparticles. The ZnO nano particles have been distributed well with in the range of ~ 100nm which is the favorable property to exhibit better photo catalytic activity. We can conclude that the four samples of ZnO synthesized are having particle size in the nano scale.

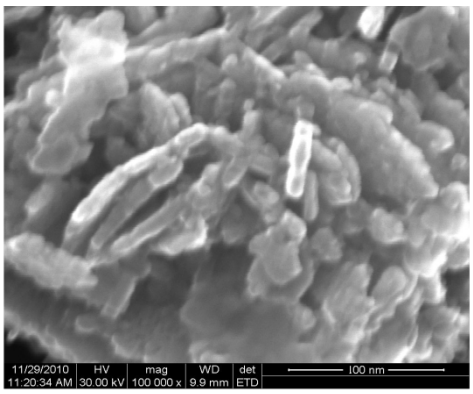

Figure:8 SEM Image for S_1

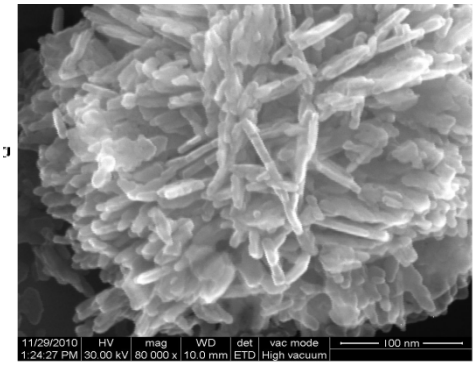

Figure:9 SEM Image for S_2.

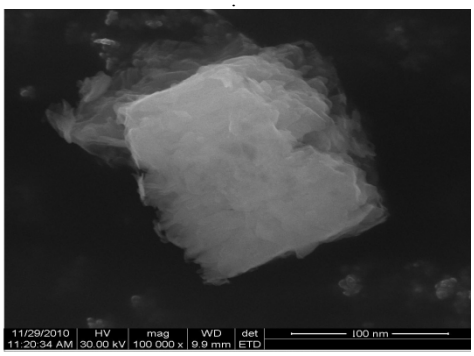

Figure:10 SEM Image for S_3

Photo catalytic degradation studies

Effect of variation of initial concentration of Malachite green dye

Keeping all other factors constant, the concentration of dye was changed from 100 ppm to 1000 ppm when it is exposed to different sources of energy and its effect on rate of bleaching was studied. The variations can be graphically represented as inFig 11.

The photo catalytic bleaching was found to decrease with increase in the concentration of dye[5].This may be due to the availability of excess of dye molecules to be degraded by a small amount of catalyst and it will be up to optimum concentration of dye. If more concentration of dye is taken, it imparts a darker colour to the solution and it may act as filter to the incident light reaching the semiconductor surface. As a consequence, the rate of photo catalytic bleaching of Malachite green decreases[6].

From this we can fix the optimum concentration for the degradation by solar radiation as 600 ppm, by microwave radiation as 600 ppm and by ultra sound energy as 600 ppm.

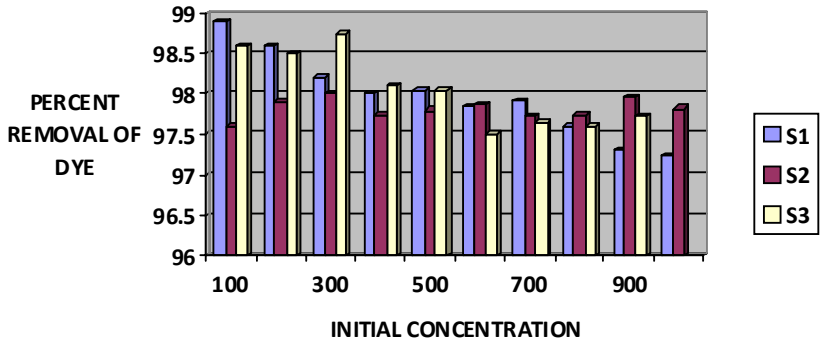

Figure 11: Effect of variation of initial concentration of dye on the photo degradation using solar radiation
Contact time -5 hr;
Dose – 200mgL^{-1};
pH – ~6.8

Effect of variation of dose of photo catalyst on the photo degradation of dyes

To study the effect of variation of dose of photo catalyst (ZnO nano particles), the initial concentrations of the dyes and initial pH (in all the beakers) were kept constant and the dose of photo catalyst (ZnO nano particles) was varied from 20 mgL^{-1} to 180 mgL^{-1}. The photo catalytic removal of dye at the optimum initial concentration and pH (normal ~ 6) were carried out following the general procedure. From the spectrophotometric analysis, the equilibrium concentration can be determined. The variations can be represented graphically as in Fig 12..Minimum amount of photo

catalyst required for the maximum removal of dye was determined and fixed as the optimum dose of photo catalyst.

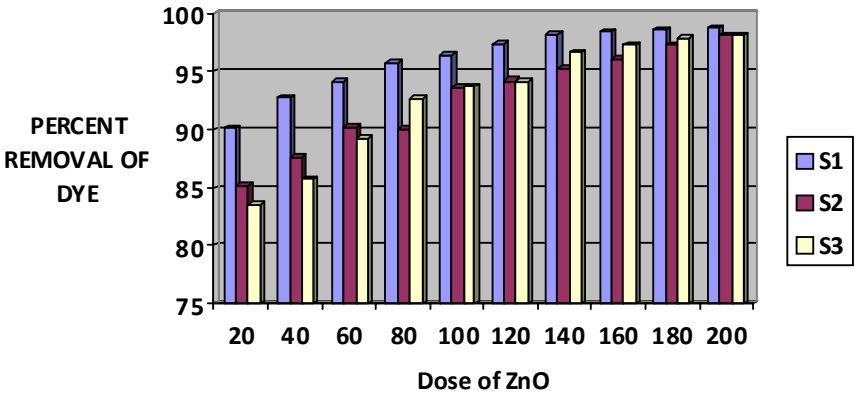

Figure 12: Effect of variation of dose of photo catalyst on the photo degradation of dye using solar radiation
Initial Concentration. – 600ppm;
pH – (~6.8);
Time – 5 hr

Effect of variation of pH of dye solution on the photo degradation

Effect of variation of pH was studied. The effect of variation of pH of dye olution on the photo degradation reaction was determined by keeping the initial concentration and dose as the optimum values in all experiments and varying pH. The initial pH of the dye solution was varied (1.8 to 10.8) by adding the required volume of 1N solution of HCl or NaOH. Then pH was measured by using digital pen pH meter (Hanna instrument, Portugal). The variation can be graphically represented as in Fig 13. It is established that surface properties of semiconductor are responsible for photocatalytic process[7, 8].

The hole generated by semiconductor creates H^+ ions in the solution from water.These protons are utilized by dissolved oxygen in solution.

$$2h^+ + H_2O \rightarrow 1/2O_2 + 2H^+ - \quad \text{(i)}$$

$$2H^+ + O_2 + 2e^- \rightarrow H_2O_2 - \quad \text{(ii)}$$

These two reactions counter balance each other to a particular extent. The surface charge on the semiconductor-electrolyte interface will play a major role in deciding the fate of this photocatalytic reaction. The surface charge on semiconductor favors the reaction when it is positive. This surface charge depends on the pH of the solution,

being positive in acidic media and negative in alkaline media. After a particular pH net charge on semiconductor surface becomes zero and is called point of zero discharge (PZC)[9].

Therefore, with increasing pH, surface concentration of dye molecules and OH^- radicals increases. However, at lower pH, ZnO gets dissolved forming salts. At higher pH, it forms Zincates $(Zn(OH)_4)_2$. All these factors are responsible for optimal value of decolourisation rate of malachite green dye. Using this study we can fix the optimum pH for the photo degradation studies at pH 7.5

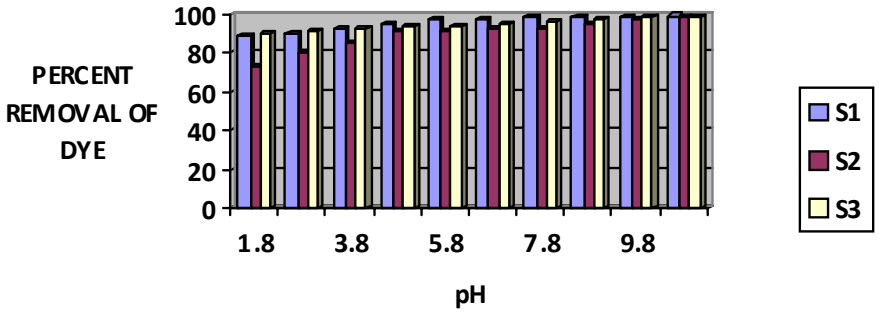

Figure 13: Effect of variation of pH of dye solution on the photo degradation using solar radiation:
Initial Concentration. – 600ppm
Contact time – 5 hr;
Dose - 200 mgL^{-1};

Effect of variation of contact time on the photo degradation of dye

In order to study the effect of variation of contact time on the removal of Malachite green of dye by the exposure to sun light and microwaves experiments were carried with optimum initial concentration of dye solution, optimum pH and optimum dose of photo catalyst[10].

The beakers containing required optimum initial concentration, and pH were taken. Then the optimum dose of photo catalyst was added and immediately they were subjected to radiation. A stop watch to note the time was started simultaneously. The beakers were removed at a different time intervals viz, ½, 1, 2, 3, 4, 5 hours and then the solutions were analyzed for the dye content.. The equilibrium concentration of the dye solution was obtained by measuring its optical density (OD). The variations are represented graphically in Fig 14.

The optimum contact time required for maximum removal was found to be 4 hrs for solar radiation and microwave radiation and 3 ½ hrs for ultra sound energy.

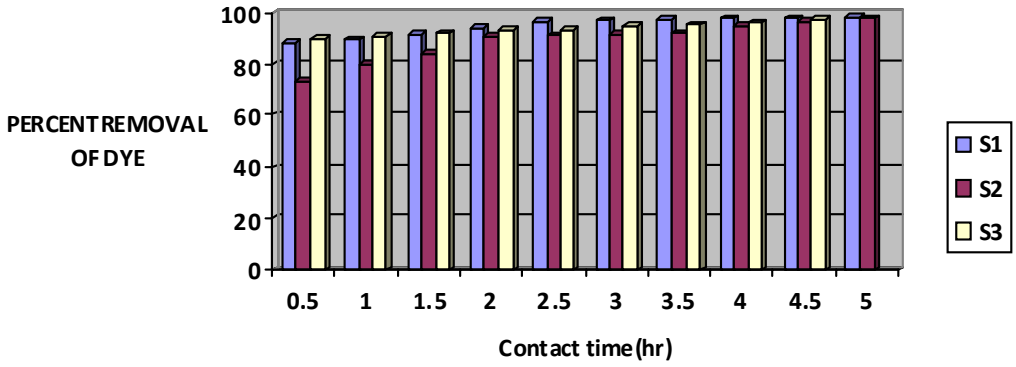

Figure 14: Effect of variation of contact time on the photo degradation of dye using microwave irradiation
Initial Concentration – 500ppm;
Dose - 20 mgL^{-1};
pH = 7.5;
Power – 100W

Kinetic studies

The plot of 2 + log O.D Versus time was found to be straight line in all the runs, suggesting that bleaching of dye by ZnO follows pseudo first order rate law[11]. Rate constant were calculated by graphs using the relation

K = 2.303 x Slope

The graphs are given in Fig 15

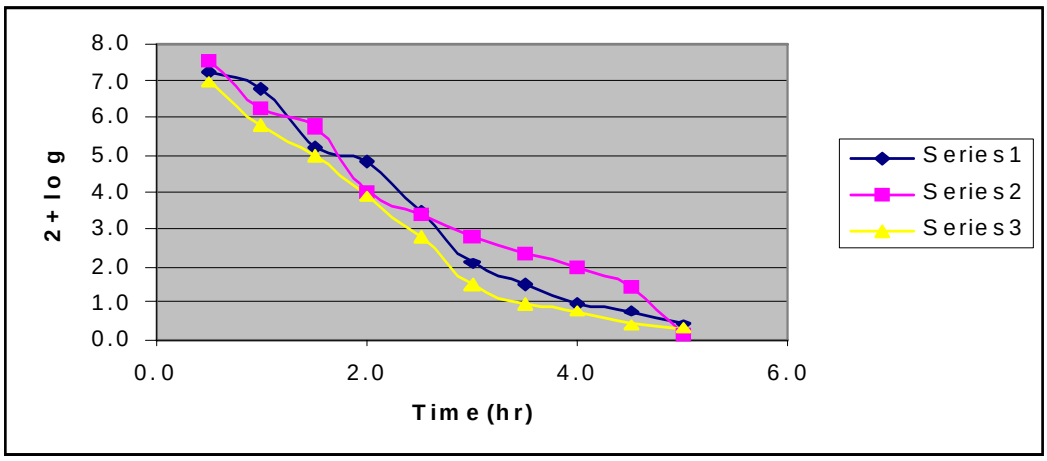

Figure 15

The calculated rate constants are tabulated in Table:1

Table 1: Rate constants for the photo degradation of Dyes.

Sample	Rate constants(K)	
	Solar radiation	Microwave radiation
Sample-1	0.1428	0.1240
Sample-2	0.1794	0.1471
Sample-3	0.2130	0.2394

Conclusion

The co -precipitation technique has been used for the synthesis of zinc oxide nano particle. By varying the experimental conditions, three different samples of nano particles were prepared. The three samples obtained by the co-prercipitation technique were characterized by PXRD, FTIR, and SEM instrumental method. The IR analysis of the spectra shows a broad band between 430-419 cm-1 with shoulder shape, characteristic of Zn-O bond. The images obtained by SEM of the samples S_1, S_2 and S_3 show sphere and cube-like nanoparticles. From the XRD results, the size of ZnO nano particle were calculated to be 18nm, 16nm, 12nm for S_1, S_2, S_3 respectively. The ZnO nano particles have been distributed well with in the range of ~ 100nm which is the favorable property to exhibit better photo catalytic activity. The size of nano particles decreased with increase in irradiation time and power of the microwave radiation. The photo catalytic degradation of dye was carried out using different sources of energy like solar radiation, microwave radiation and ultra sound radiation. Among the three different energy sources the sono chemical degradation treatment is found to be more effective than solar radiation and microwave radiation treatment with respect to time and initial concentration. The optimum conditions for maximum dye degradation was represented in Table 2.

Table 2

Radiation	Initial Concentration	pH	Dose	Contact time	% Removal
Solar	600ppm	~6.8	200mgL^{-1}	5hr	98
Microwave	600ppm	~6.8		5hr	97
Ultrasonication	600ppm	~6.8	200mgL^{-1}	2½ hr	98
			200mgL^{-1}		

The photo catalytic degradation of malachite green dye obeyed pseudo first order kinetics. So, we can conclude that photocatalytic degradationof dyes can be carried out with all the three sources of radiations, and the reaction can proceed to complete degradation. So, this technique can be used for the treatment of industrial effluents containing dyes. In places where we have plenty of sunlight, solar radiation can be used for degradation. In places where we don't have enough amount of sunlight we can use other sources of energy for the photo degradation. Also we are using minute quantities (~ 200 mgL^{-1}) of zinc oxide nano particles, and there will be no harm in mixing this small quantity of zinc in water streams, as zinc is one of the essential trace elements. These results will be helpful in designing effluent treatment plants in industries.

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