INTERNATIONAL JOURNAL OF RESEARCH IN PHARMACY AND CHEMISTRY

Available online at www.ijrpc.com

Research Article

STUDIES ON THE PHOTO DEGRADATION OF MALACHITE GREEN DYE BY THE SYNTHESIZED ZnO NANO PARTICLES WITH DIFFERENT SOURCES OF ENERGY

S. Shanthi*, R. Manjula, M. Vinulakshmi, R. Rathina Bala

The Standard Fireworks Rajaratnam College For Women, Sivakasi,Tamil Nadu, India.

ABSTRACT

Solar photo catalytic oxidation technique using semiconductors like TiO2, 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 nano particles the efficiency of the photo catalytic activity was 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, four different samples of ZnO nano particles were prepared. The four samples obtained by the Co Precipitation technique were characterized by PXRD, FTIR, and SEM instrumental method. The IR analysis of the spectra show a broad band between 540 and 480 cm-1 with shoulder shape, characteristic of Zn-O. The images obtained by SEM of the samples S_3 and S_4 show plate-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. From the XRD results the size of ZnO nano particle were calculated to be 19.33nm, 18.10nm, 11.25nm, and 8.43nm for the four samples. The photo catalytic degradation of dye was carried out using different sources of energy like solar radiation, microwave radiation and ultra sound radiation. The optimum conditions for the maximum removal of dye degradation was proposed by varying the experimental parameters like initial concentration, dose, pH and contact time .The photo catalytic degradation of malachite green dye obeyed pseudo first order kinetics.

INTRODUCTION

Large scale production and extensive applications of synthetic dyes cause considerable environmental pollution. Dyes are difficulty to decompose biologically & chemically. Therefore, a new contamination requires further treatments. In this project work photo catalytic degradation of Malachite green dye have been studied with ZnO nano particles. This study presents ZnO nano particle degradation of malachite green dye which has irritating effect on respiratory system.

EXPERIMENTAL

Malachite green dye was obtained from sd.fine chemicals, Mumbai. Two sets of synthetization were carried out in this present work. Photocatalyst ZnO nano particles were prepared by the addition was1M $ZnCl_2$ (purchased from E. Merck chemicals Ltd, Mumbai) on 2M NaOH (purchased from E. Merck chemicals Ltd, Mumbai) in absence and in the presence of starch, the mixture was kept at room temperature under constant stirring using magnetic stirrer for a period of 2 – 3 hours. All the reagents and solutions were prepared by using this DD water. The resultant precipitate obtained from set 1 was separated into two parts and labelled as Sample1 and Sample 2. Similarly the resultant precipitate obtained from set 2 was separated into two parts and labelled as Sample3 and Sample 4. The Co-Precipitation reaction can be represented as follows.

$$ZnCl_2\ (aq) + 2NaOH\ (aq) \longrightarrow Zn(OH)_2\ (s) + 2NaCl\ (aq)$$

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

The precipitates were irradiated with microwave using microwave oven.

Microwave irradiation was performed in the following schedule:

1 Sample 1 was irradiated at 180W for 1 hour.
2 Sample 2 was irradiated at 180W for 1½ hour.
3 Sample 3 was irradiated at 300W for 1 hour.
4 Sample 4 was irradiated at 300W for 1½ hour.

The resultant Zinc oxide 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 in the Removal of dye experiment.

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) 616 nm (λ_{max} value for MG dye) respectively.

A plot of optical density versus initial concentration (Fig 1). These plots were used as standard graphs for the estimation of dyes by interpolation technique. The values of optical density for dye solutions, before and after the removal of dye were also obtained by using spectrophotometer. Using these optical densities the corresponding dye concentrations were obtained from the standard graph (Fig 1) by the interpolation technique.

BATCH KINETIC EXPERIMENTS

Stock solution of dyes (2000ppm of MG) were 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 Photocatalysts (ZnO nano particles [S_1, S_2, S_3, S_4]) 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.

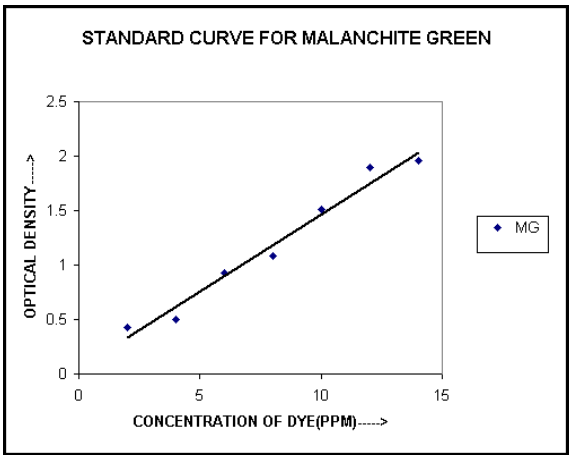

Fig. 1: Standard curve for malachite green

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.

Percentage removed $=100(C_i - C_e)/C_i$ --------1

Where

C_i= initial concentration of dye (ppm)

C_e=equilibration concentration of dye (ppm)

In the batch dye degradation technique, the effect of several factors govern the degradation process. The effect of various experimental parameters on degradation of malachite green dyes in the aqueous suspension by zinc oxide nano was studied under different experimental condition.

RESULTS AND DISCUSSION

FTIR analysis

The IR analysis of the spectra shows a broad band between 540 and 480 cm-1 with shoulder shape, characteristic of Zn-O vibrations. 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 S_3 & S_4 with frequency 1157.10 cm -1, 1071.91cm -1 may be assigned to C-H bending vibrations, of starch molecule.

XRD pattern
The average particle size is determined using Debye – Scherrer's equation applied to major, peaks corresponding to intensity and is found to be around 19.33 nm, 18.10 nm, 11.25 nm, and 8.43nm for S1, S2, S3, and S4 respectively.
The size of the synthesized ZnO nano particles was 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

$$\beta = (2\theta 2 - 2\theta 1)$$

Scanning Electron microscope (SEM)
The images obtained by SEM of the samples S3 and S4 show plate-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. When we use starch as the stabilizing agent as well as the surface sizing agent, we are able to get particles with comparatively smaller size.

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 Fig 2.
The photo catalytic bleaching was found to decrease with increase in the concentration of dye[1]. 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[2].
From this we can fix the optimum concentration for the degradation by solar radiation as 600 ppm, by microwave radiation as 500 ppm and by ultra sound radiation as 700 ppm.

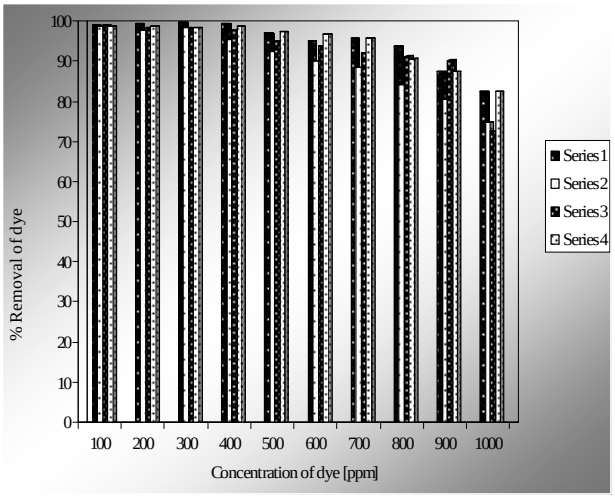

Fig. 2: Effect of variation of initial concentration of dye on the photo degradation using solar radiation
Contact time - 4 hr; Dose – 200mgL^{-1}; pH – ~6.00

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 effluents 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 are be represented graphically in Fig 3. .Minimum amount of photo catalyst required for the maximum removal of dye was determined and fixed as the optimum dose of photo catalyst.

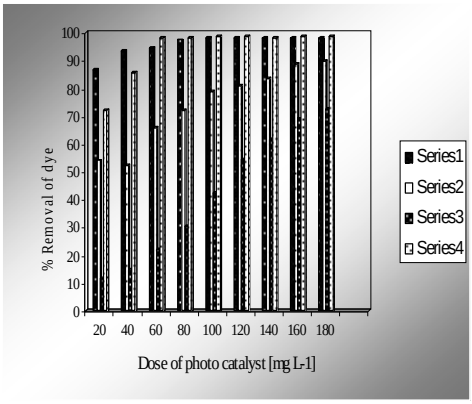

Fig. 3: Effect of variation of dose of photo catalyst on the photo degradation of dye using solar radiation

Initial Concentration. – 600ppm; pH – (~6); Time – 4 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 (1.5 to 10.5) 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 4. It is established that surface properties of semiconductor are responsible for photocatalytic process [3,4]

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

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

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

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)[5].

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

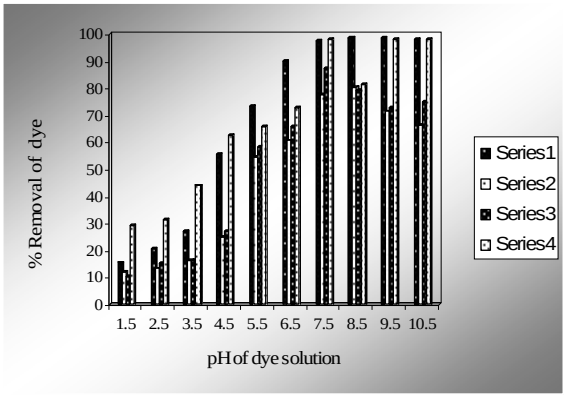

Fig. 4: Effect of variation of pH of dye solution on the photo degradation using solar radiation:

Initial Concentration. – 600ppm; Contact time – 4 hr; Dose - 20 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[6].

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. 5

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.

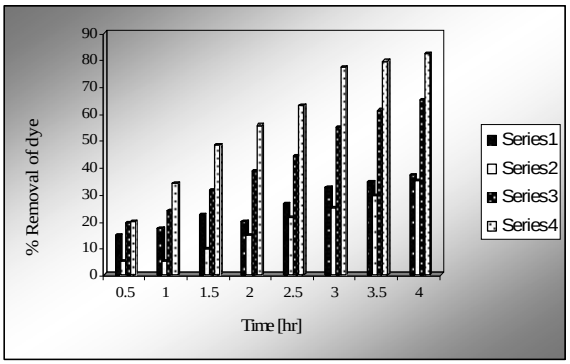

Fig. 5: Effect of variation of contact time on the photo degradation of dye using microwave irradiation

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[7]. Rate constant were calculated by graphs using the relation

K = 2.303 x Slope

The graphs are given in Fig. 6

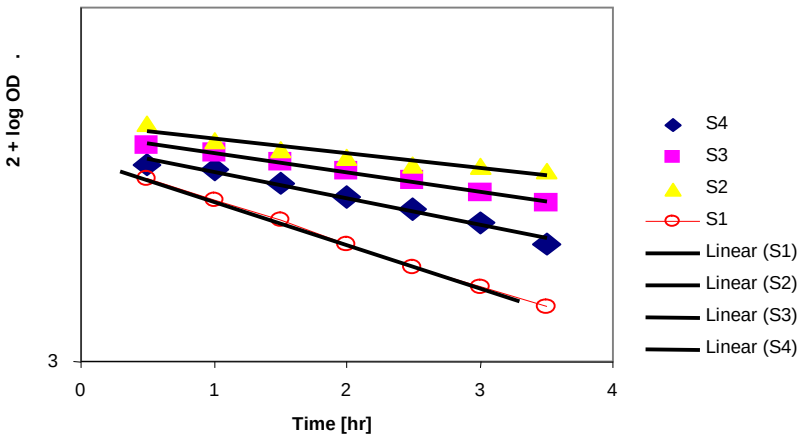

Fig. 6

Table 1: Rate constants for the photo degradation of samples

Representation of Samples	Rate constants (k)		
	Solar radiation	Microwave radiation	Ultra sound radiation
Sample 1	0.1694	0.1169	0.1850
Sample 2	0.1920	0.1317	0.2121
Sample 3	0.2479	0.3011	0.3654
Sample 4	0.4665	0.3217	0.4995

CONCLUSION

The Co Precipitation technique has been used for the synthesis of zinc oxide nano particle. The four samples obtained by the Co Prercipitation technique were characterized by PXRD, FTIR, and SEM instrumental method.

- ZnO nano particles were synthesized by applying Co Precipitation technique.
- By varying the experimental conditions, four different samples of nano particles were prepared.
- The IR analysis of the spectra show a broad band between 540 and 480 cm-1 with shoulder shape, characteristic of Zn-O
- The images obtained by SEM of the samples S_3 and S_4 show plate-like nanoparticles.
- From the XRD results shows the size of ZnO nano particle were calculated to be 19.33nm, 18.10nm, 11.25nm, and 8.43nm for S_1, S_2, S_3, and S_4 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

- 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 gram of quantities (~ 20 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.

Table 2

Radiation	Initial Concentration	pH	Dose	Contact time	% Removal
Solar	600ppm	~7.5	20mgL^{-1}	4hr	97.7
Microwave	500ppm	~7.5	20mgL^{-1}	5hr	82.5
Ultrasonication	700ppm	~7.5	20mgL^{-1}	3½ hr	99.25

REFERENCES

1. Hachem C, Bocquillon F, Zahraa O and Bouchy M. Dyes and Pigments. 2011;49:117.
2. Saquib M and Muneer M, Dyes and Pigments. 2002;53:237.
3. Zang L and Shen J. J Chem Soc Chem Commun. 1986:473.
4. Takizawa T, Watanabe T and Honda K. 2004;82:391.
5. Wang SS, Wang ZH and Zhuang QX. 2006;1:257.
6. Nasr C, Vinodgopal K, Chattopadhyay AK and Kamat PV. Res Chem Intermed. 2009;23:219.
7. Vinodgopal K, Wynkoop D and Kamat PV. Environ Sci Technol. 2008;30:1660.