# Photocatalytic removal of Malachite Green through ZnO/$CeO_2$ nanocomposite catalyst

**Lipika Das Samanta, Somak Joyti Sahu , Sutapa Roy**

[1 ,2, 3]Department of Chemical Engineering, Haldia Institute of Technology, Hatiberia, WB 721657, India

## ABSTRACT

Processes (AOPs) have been developed to convert non-biodegradable contaminants into harmless species. Heterogeneous photocatalysis, a novel process belonging to the class of AOPs, via combination of photocatalysts, such as phtotcatalyst and ultraviolet (UV) light, is as an attractive alternative treatment method for the removal of toxic pollutants from wastewater, owing to its ability to degrade the pollutants into innocuous end-products, such as $CO_2$, $H_2$ and mineral acids. In the present work, the synthesized photocatalyst was used for removal of Malachite green (MG) through photocatalytic reaction. The ZnO/$CeO_2$ photocatalyst was prepared by co-precipitation method. The prepared catalyst was synthesized by scanning electron microscopy and BET surface analyzer. The activity of catalyst was observed. The various process parameters such as calayst loading, concentration of dye, irradiation time, pH of reaction solution were also observed. Influence of energy source and oxidizing agent were also seen. So, photocatalysis are considered very highlt competitive water treatment technologies for removal of dye.

**Keywords:** Nano composite, ZnO/$CeO_2$ photocatalyst, Photocatalytsis

## I. INTRODUCTION

Water-pollution control is now one of the major areas of scientific activity. Effluent discharge from leather, textile and dyestuff industries causing significant health concerns to environmental regulatory agencies. Color is the first contaminant to be recognized in wastewater and has to be removed before discharging into water bodies or on land [1].

Conventional water treatment methods (coagulation/flocculation/sedimentation, filtration, activated carbon adsorption and chlorination) applied as single or integrated processes are not able to eliminate microorganisms and toxic inorganic and organic compounds from drinking water sources [2, 3]. The commonly used advanced technologies for produced water treatment consist of membrane filtration, thermal distillation, adsorption, ion exchange, and advanced oxidation processes (AOPs) [4]. Among the various advanced photocatalysts were employed in different AOPs, $TiO_2$ , ZnO, is the most attractive for environmental applications due to its non-toxic nature, chemical stability, insolubility in the medium, low cost and high photocatalytic activity [5]. But some disadvantages to use these phtotocatalysts.

In metallurgical machinery, petroleum chemical industry, glass-ceramics, agriculture and functional materials due to their exceptional optical, electrical, magnetic and catalytic properties, rare earth (RE) materials are widely demoralized. Especially the overcapacity of light RE elements Ce, La and Y, the inequality utilization of RE elements severely controlled the development of RE industry. So it is very important to attempt the application of light RE elements. Light RE elements as catalysts or catalytic components has been widely applied in petroleum chemical industry, catalytic combustion of fossil fuels, automotive emissions control, the purification of industrial waste air, and solid solution fuel cells [6] and showed exceptional performance.

In most of rare earth oxides, $CeO_2$ has been successfully used as photocatalysts to degrade sewage and pollutants because of its strong redox properties of $Ce^{3+}/Ce^{4+}$ and the formation of oxygen vacancies [7, 8]. The major role of RE ions in composed photocatalysts is enhanced electron-hole pairs separation, improve optical absorption properties, modify adsorption capacity of dye and increase surface concentration of adsorbed OH group [9-11].

In the present work, the ZnO/$CeO_2$ composite catalyst was synthesized and characterized by various analytical instruments. The photocatalytic efficiency of synthesized nanocomposite catalysts for the degradation of Malachite green were investigated under operational parameters such as catalyst loadings, irradiation time, initial MG concentrations and initial pH in batch process. Influence of energy source and oxidizing agent were investigated.

## II. MATERIAL AND METHODS

### II. 1 Preparation of nanocomposite of ZnO / $CeO_2$

The ZnO/$CeO_2$ photocatalyst was prepared by co-precipitation method. The $Zn(NO_3)_2.6H_2O$ (Merck Specialties Private Limited, India) and $Ce(NO_3)_3.6H_2O$ (Loba Chemic Private Limited, India.) were main materials for the catalyst synthesis. The desired amount of $Zn(NO_3)_2.6H_2O$ and $Ce(NO_3)_3.6H_2O$ were mixed under stirring for 20 min. The required amount of NaOH (Merck Specialties Private Limited, India) was added drop-wise to attain the pH value of 10 and was stirring almost 2 h. After that the solution was then kept standing for 24 hrs to be hydrolyzed completely. The resultant sample was taken out and washed for several times by distilled water and absolute ethanol to remove excessive organic or inorganic impurities and dried overnight in oven at 120°C to obtain the hydroxide precursors. Then the dried sample was calcined in furnace at 500°C for 6 hrs. Finally, the composite oxide was obtained.

### II. 2 Catalyst Characterizations

The synthesized catalyst was characterized by Scanning Electron Microscopy (SEM) and BET surface analyzer (Quantachrome, AUTOSORB-1C, USA). The morphology was determined by SEM. Specific surface area and pore volume of the calcined samples were determined by BET surface area analyzer.

### III. 3 Experimental procedure

The removal of MG (Sigma-Aldrich) was studied by photocatalysis using synthesized ZnO (Merck Specialties Private Limited, India) and ZnO / $CeO_2$ catalysts. The reaction was carried out in a batch cylindrical glass vessel of 500 ml capacity under vigorous stirring and the UV source was placed at the top of the reactor. An 8 W ultraviolet lamp (Philips) with wavelength 218 nm was positioned. A typical reaction was carried out using 250 ml solution of MB of initial concentration 100 ppm with 400 gm/L catalyst concentration at 30ºC with a variation of ±1ºC with an UV lamp. The samples were withdrawn at specific interval of time and analyzed by UV-VIS spectrophotometer (XPLORER, XP 2001).

## III RESULTS AND DISCUSSIONS

### III.1 Catalyst characterization

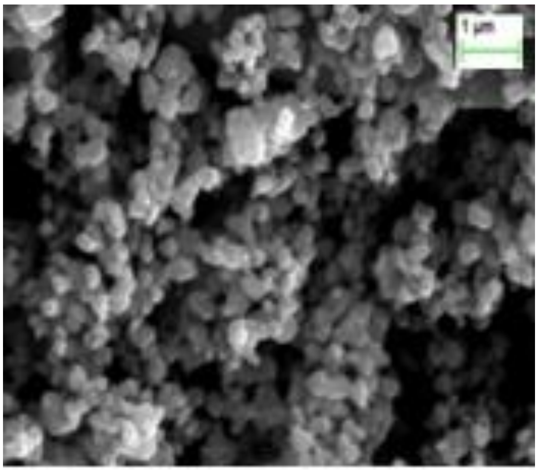

Fig. 1: SEM image of composite catalyst

The SEM image of composite presents the morphology. It is clear from the Fig. 1 that the catalyst particles are spherical in shape. Thus SEM image is clear evidence of complete homogeneity of cerium with ZnO. Single highly homogeneous aggregates are significant for photo catalysis as it can absorbs even bulky pollutants.

Quantitative as well as qualitative composition analysis of synthesized composite catalyst was determined by the EDS spectrum obtained from SEM. The composition was shown in Table 1. The surface characteristics of the catalysts were analyzed by BET apparatus. The surface area and pore volume of synthesized catalyst are 225

$m^2/g$ and 0.81 ml/g. The high surface area and pore volume of mixed oxide is due to the porous nature of the oxides formed through the co-precipitation method.

**Table 1:** composition of synthesized catalyst

| **Catalyst** | **Weight (%)** | | |
|---|---|---|---|
| | Zn | Ce | O |
| $ZnO/CeO_2$ | 46.47 | 5.39 | 48.14 |

III. 2 Selection of catalyst

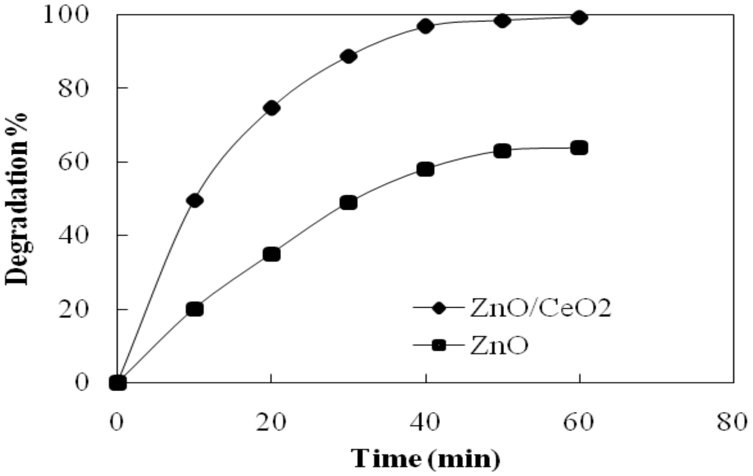

Fig. 2: Selection of catalyst

The photocatalytic removal of MG was carried out by two various catalysts which was shown in Fig .2. The results are shown in Fig. 2 by plotting percentage removal of MG as a function of time. The results indicate that $ZnO/CeO_2$ composite catalyst gives higher photocatalytic activity than ZnO. The removal depends on the BET surface area of the catalyst.

III.3 Effect of various process parameters to the photo catalytic reaction

III.3.1 Weight of catalyst

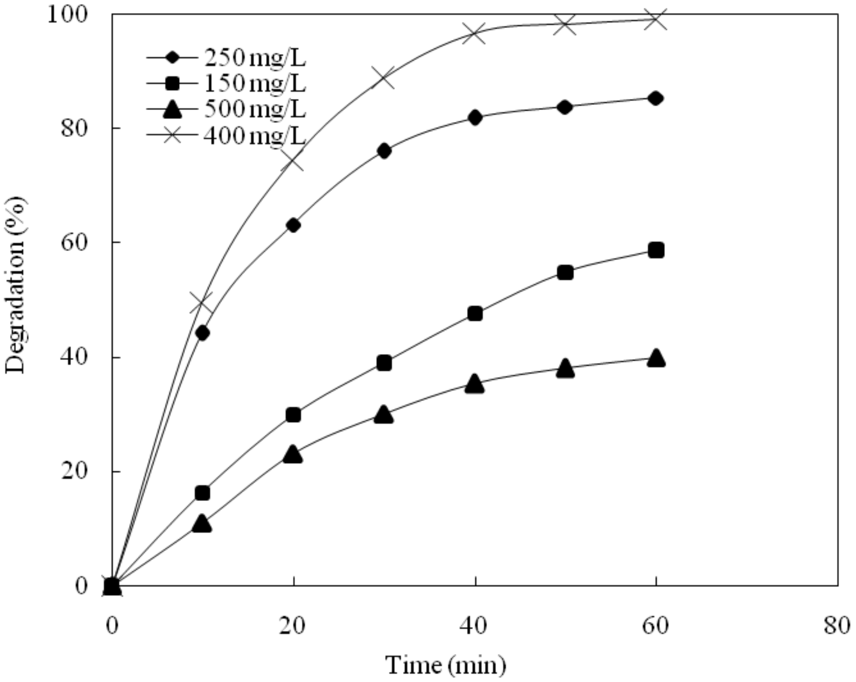

Fig. 3: Effect of catalyst weight on MB removal

The weight of catalyst driving the photo catalytic reaction is an important process parameter. In the effect of catalyst concentration on the photo catalytic removal was investigated by varying concentrations of 150 mg/L to 500 mg/L at an initial concentration of MB 100 ppm under at room temperature. The pH of the MB solution was maintained at 7. Figure 3 shows the percentage removal as a function of time for different catalyst concentration. The percentage of photo catalytic removal of MB is found to increase with increasing catalyst concentration upto 400 mg/L and then it decreases. It may be due to the fact that the number of active sites increases as the amount of catalyst increases. But when the catalyst concentration was increased beyond upto 400 mg/L the percentage removal was found to decrease. This may be due to the aggregation of catalyst particles at high concentration, causing a decrease in the number of surface active sites and decreases the removal of MB.

### III.3.2 Concentration of reactant

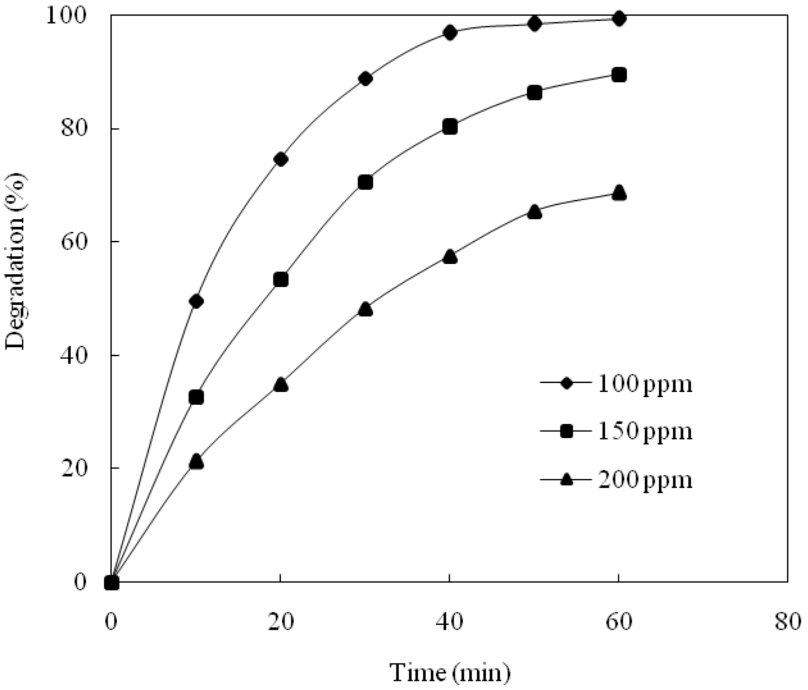

Fig. 4: Effect of dye concentration on MB removal

The concentration of pollutant is an important parameter in the catalytic removal and the removal efficiency depends on the initial concentration of the substrate. The reactions were carried out at 30 ºC using 400 mg/L catalyst concentration at pH of 7. Figure 4 shows the plot of MB removal (%) as a function of time with respect to different initial concentrations (100 mg/L to 200 mg/L) of the MB dye solution. These results show a high removal at low initial concentration of the dye (100 mg/L). As the initial concentration of the dye increases, the percentage removal of MB decreases. It has been observed that almost complete removal is possible using low concentrations of dye. The percentage removal of MB at concentration 100 mg/L is found to be 90% at 50 min, whereas for a concentration of 200 mg/L that is 69%. The possible reason for the decrease of percent removal with the increase of initial dye concentration is that, as the initial concentration of the dye increases, the increase of number dye molecules inhibits light penetration. The dye molecules do not degrade immediately because the intensity of light and the catalyst amount does not increase. As the dye concentration increases, the solution color become more intense and the path length of the photons entering the solution decreases, thereby fewer photons could reach the photocatalyst surface. Moreover, the production of $OH^{\bullet}$ and $O_2^{\bullet-}$ reduces.

### III.3.3 pH

The pH value of the original solution of MB is 7. Dilute hydrochloride acid or sodium chloride solutions were used to adjust the pH of the solution as per the requirements. The reactions were studied by varying pH from 3 to 9 at an initial concentration of MB 100 mg/L for 400 mg/L of catalyst concentration. In Fig. 5, MB is a cationic dye when dissolved in water. At low pH value (pH = 3), the adsorption was not standard.

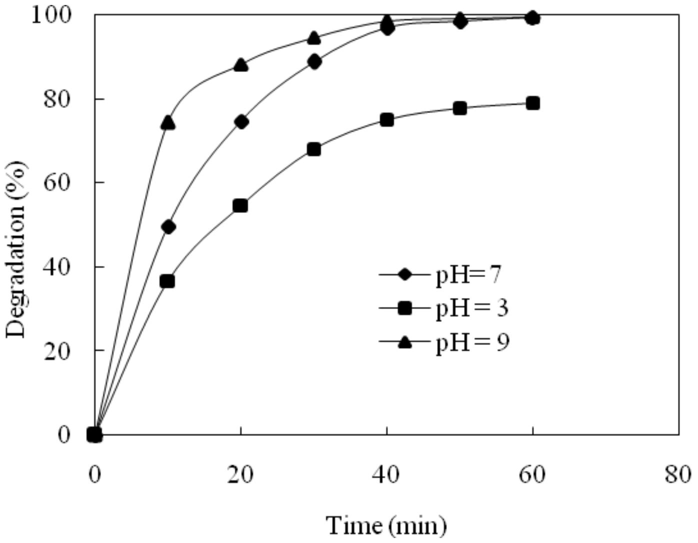

Fig. 5: Effect of pH on MB removal

However, when the solution pH increased from 3 to 9, the larger amount of MB was adsorbed on the catalyst surface and the maximum dye uptake was observed in the pH range of 9. In the acidic medium, positively charged surfaces of the catalyst tended to oppose the adsorption of cationic adsorbate species. When the pH of the dye solution became more basic, the surface tends to acquire negative charge, thereby resulting in an increased adsorption of dyes because of the rising electrostatic attraction between the positively charged dye and the negatively charged catalyst.

### III.3.4 Irradiation Time

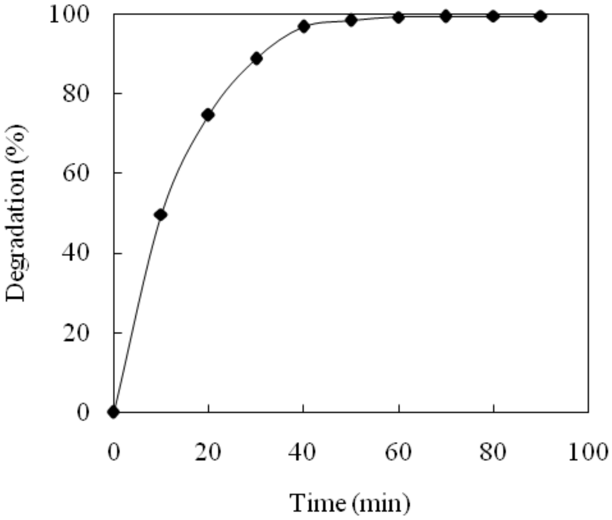

Fig. 6: Effect of reaction time on MB removal

The effect of irradiation time on the photo catalytic removal of MB of its aqueous solution was investigated from 0 to 90 min, at 100 mg/L of MB concentration, 400 mg/L catalyst concentration and pH of 7. The reaction was carried out at room temperature and result is shown in Fig. 6. The results clearly show that the photo removal efficiency increases with time up to 50 min and thereafter it levels off. This indicates that photo catalytic removal of MB with catalysts for 50 min is the optimum irradiation time.

### III.3.5 Influence of energy source and oxidizing agent

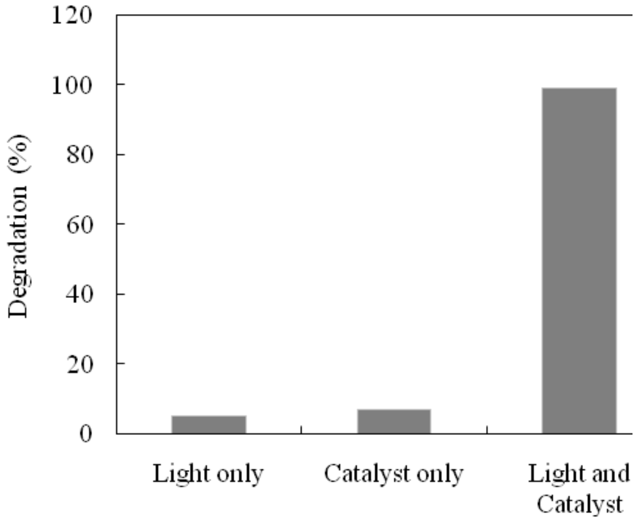

Fig. 7: Influence of energy source and oxidizing agent on MB removal

The removal of dye solution was found to be enhanced in the presence of oxidizing agent ZnO/$CeO_2$ catalyst and UV light as an energy source. The reactions were carried out at an initial concentration of MB 100 mg/L using 400 mg/L of catalyst concentration. Thus, the nature of photo removal was shown in Fig. 7. Thus, in the occurrence of catalyst, dye was removed 90.5%, approximately after 50 min UV irradiation at room temperature, but degraded 4.95% following UV irradiation without catalyst. At the same time, there were no changes (5.45%) almost in dye concentration when catalyst was used in the dark (i.e., without UV irradiation). Thus, both UV light and the catalyst photocatalyst are required for the efficient removal of MB. When catalyst absorbs UV radiation, it produces pairs of electrons and holes. The electron of the valence band of titanium dioxide becomes excited. The excess energy of this excited electron promoted the electron to the conduction band of catalyst to generate the negative-electron ($e^-$) and positive-hole ($h^+$) pair. The positive-hole of catalyst breaks separately the water molecule to form hydroxyl radical. This hydroxyl radical is responsible for the removal of dye.

## IV. CONCLUSIONS

The synthesized ZnO/$CeO_2$ catalyst was used for the photocatalytic degradation of MG from an aqueous solution. The morphology of the catalyst was confirmed by SEM and surface area was determined by BET surface analyzer. The catalyst surface was confirmed to have a positive surface charge under acidic conditions and a negative surface charge under basic conditions; therefore, acidic pH favors the degradation process. The influence of experimental parameters, namely, catalyst concentration, pollutant concentration, and pH of the solution, and their interaction at a different level was examined for MG degradation. The highest removal of MG was observed using 400 mg/L ZnO/$CeO_2$ catalyst with 100 ppm initial concentration of MG at 60 minutes of pH 7.

## REFERENCES

[1] Y. Zhang, Y. Zhang, Y. Huang, X. Chen, H. Cui, M. Wang, Enhanced photocatalytic reaction and mechanism for treating cyanide-containing wastewater by silicon-based nano-titania, Hydrometallurgy, 198, 2020, 105512.

[2] R.Dores, A. Hussain, M. Katebah, S.S. Adham, Using Advanced Water Treatment Technologies to Treat Produced Water from the Petroleum Industry. In Proceedings of the SPE International Production and Operations Conference & Exhibition, Doha, Qatar, 2012, 103-109.

[3] A. Hussain, J. Minier-Matar, A. Janson, S. Gharfeh, S. Adham, Advanced technologies for produced water treatment and reuse. In Proceedings of the International Petroleum Technology Conference, European Association of Geoscientists & Engineers, Doha, Qatar, 1, 2014, 1–11.

[4] A. Matilainen, M. Sillanpää, Removal of natural organic matter from drinking water by advanced oxidation processes, Chemosphere, 80 (4), 2010, 351-365.

[5] Y. Chen, K. Wang, L. Lou, Photodegradation of dye pollutants on silica gel supported TiO2 particles under visible light irradiation, Journal of Photochemistry and Photobiology A: Chemistry 163(1–2), 2004, 281–287.

[6] W. C. Zhan, Y. Guo, X. Q. Gong, Y. C. Guo, Y. Q. Wang, G. Z. Lu, Chin, Effect of cerium ions initial distribution on the crystalline structure and catalytic performance of CeY zeolite, Journal of Rare Earths, 35( 8), 2017, 791-799.

[7] N.S. Arul, D. Mangalaraj, T.W. Kim, P.C. Chen, N. Ponpandian, P. Meena, Y. Masuda, Synthesis of $CeO_2$ nanorods with improved photocatalytic activity: comparison between precipitation and hydrothermal process, Journal of Materials Science: Materials in Electronics, 24, 2013, 1644-1650.

[8] T. Feng, X.D. Wang, G.S. Feng, Synthesis of novel $CeO_2$ microspheres with enhanced solar light photocatalyic properties, Materials Letters, 100, 2013, 36-39.

[9] L.Y. Lin, M.H. Yeh, C.Y. Chen, R. Vittal, K.C. Ho, Surface modification of $TiO_2$ nanotube arrays with $Y_2O_3$ barrier layer: controlling charge recombination dynamics in dye-sensitized solar cells, Journal of Materials Chemistry A, 22, 2014, 8281-8287.

[10] A.N. Ökte, Ö. Yilmaz, Photodecolorization of methyl orange by yttrium incorporated $TiO_2$ supported ZSM-5, Applied Catalysis B: Environmental, 85(1-2), 2008, 92-102.

[11] C.J. Hao, J. Li, Z.L. Zhang, Y.J. Ji, H.H. Zhan, F.X. Xiao, D. Wang, B. Liu, F. Su, Enhancement of photocatalytic properties of $TiO_2$ nanoparticles doped with $CeO_2$ and supported on $SiO_2$ for phenol degradation, Applied Surface Science, 331, 2015, 17-26.