Degradation of Dyes by Implementation of Biogenically Synthesized Zinc Oxide

Sandeep Ramesh Gadhave[1], Jayshree Parikh[2], Haribhau Ramrao Aher[3]

[1]Research Scholar, Department of Chemistry, JJTU University, Rajasthan, India
Email: *srgdrug95[at]gmail.com*

[2]Associate Professor, Department of chemistry, JJTU University, Rajasthan, India

[3]Principle, Arts, Commerce and Science College, Kolhar, India

Abstract: ***Green synthesized zinc oxide nanoparticles and its application in degradation of malachite green dye. Degradation carried out in presence and absence of zinc oxide nanoparticles as catalyst in dark condition, resulting with degradation efficiency of 4.11 % without catalyst and 19.02 % in presence of catalyst. Photocatalytic degradation of malachite green dye was carried out through various parameters, as comparative study was conducted in presence of sunlight for zinc oxide nanoparticles, precursor salt, leaves extract of Michelia Champaka plant. Comparative study for degradation of malachite green dye results as, degradation conducted in presence of zinc oxide nanoparticle as catalyst degrades 83.06% of dye, zinc nitrate salt degrades 17.33% of dye, Leaves extract of Michelia Champaka degrades 74.16% of dye and malachite green dye self - degradation in sunlight is 4.74%. Degradation study was carried for 180minutes to attain maximum degradation of dye.***

Keywords: Degradation, Malachite green, Photocatalytic, sunlight, nanoparticles

1. Introduction

Nanotechnology a recent advance, fortunately the ability to prepare enamors peaked nanomaterial of any size and shape, leads to the revolution of new biocidal agents. Now a days "a wonder of modern medicine" known as nanomaterial's as its elevated benefits towards antibiotics resistant organism[1]. Metallic nanoparticles correspond a various function unobserved in bulk phase but ingratiated of their exclusive catalytic, magnetic, optical, electronic and antimicrobial, wound healing and anti - inflammatory properties, fillers, opacifiers, disinfectants, agents, drug delivery materials etc. Nano science is one of the emerging theories in the in synthesis of micro scale materials and compactable in the areas of physics, chemistry, biology, material science, medicine and clinical field[2]. The green method for inorganic material synthesis is a valuable route to chemists, biologists and material scientists. Plant extracts as rich source of biological motilities act as a capping agent and reducing agent for the synthesis nanoparticles. Hence plant extract employed in fabrication of nps due to its property of redox potential[3]. Zinc nanoparticles (ZnNPs) have attentiveness due to its high electrical conductivity, low electrochemical migration, magnificent solder ability, high melting point, optical, and catalytic properties being used in, sensors, solar cells, information storage, heat transfer systems, textiles, water treatment, and antimicrobial coating material in surgical tools, Rubber production, LCD and solar cells manufacturing and LCDs, as a whitener in pigment productions, electronics, chemical fibers and textiles, antifouling paints[4]. In contrast the synthesis of ZnNPs is inexpensive as that of noble metal nanoparticles of platinum (Pt), silver (Ag), and gold (Au) [5, 6, 7].

This recent work is based on plant mediated synthesis of nanoparticles with zinc acetate. *Michelia champaka* (Marathi - son Chapa, Hindi - Champa), family - Magnoliaceae, consist of 12 - genera and 220 - species of evergreen trees and shrubs native to tropical, sub - tropical south and south east asia.

2. Experimental method for preparation of nanoparticles

2.1. Excerpts of *Michelia Champaka* leaves were organized by boiling the 100gm of Michelia Champaka leaves dried powder of meshed size in 1000ml of double distilled water for the duration of 90 minutes at a temperature of 60°C. Since the continuous heating concentrates the extract of *Michelia Champaka* leaves and decrease in volume up to 900ml is obtained. The change in color of suspension is observed as brownish in color from the absolute colorless nature. Further cooled at RT for 1 hour[8, 9]. Further this leaves suspension is subjected to filtration process through employment of leaves extract to Whatmann filter paper number 1. Slow and steady filtration takes time and obtained filtrate with an absolute pale brown color suspension, which is subjected to container bottle for storage at 4°C and obtained purified suspension of *Michelia Champaka* leaves was employed for the further experimental preparation of nanoparticles[10].

2.2 Formation of ZnO nps.

1) Preparation of Zn nitrate solution - The exact weighed amount of zinc nitrate hexahydrate (0.03397gm) was transferred to the standard calibrated measuring flask of glass containing 200ml of distilled water and dissolved in it. Further it was volume up to the mark by using double distilled water to yield an exact solution of 1mM zinc nitrate solution[11].
2) Formation of ZnO nps using plant extract - Synthesis of nanoparticles of zinc oxide was pleasured from the old method and modified it into newer method of synthesis for the growth of nanoparticles with increased yield. The *Michelia Champaka* leaves extract and 1mM of

zinc nitrate solution was introduced for mixing in a beaker, in the ratio of 1: 1, as 1mM of 20ml Zn (NO) $_3$ solution was poured in 20ml of *Michelia Champaka* leaves abstract suspension drop by drop for about half hour of duration on magnetic stirrer with continuous stirring. As the addition of 1mM zinc nitrate solution increases with time, the *Michelia Champaka* leaves extract changes its color from pale brown to milky white in origin, hence this is the starting of generation of ZnO nps[12, 13]. Further the light milky white suspension of ZnO nps was transferred into a 100ml of conical flask and heated continuously for the time duration of 40 minutes at 60°C, with continuous stirring, as the formation of pale white suspension occurs. The formed suspension of nanoparticles was subjected to centrifugation at 3000 rpm for about 30 minutes. The obtained pale white zinc oxide nano forms were collected in silica crucible and ovened at 80°C for time duration of 3hours.

2.3 Degradation of malachite green dye

Implementation of green synthesized zinc oxide nanoparticles for the degradation of green color molecules of malachite green dye to resist the exploitation of environmental toxicity. Malachite green dye is the stimulation of dimethyl aniline and benzaldehyde for the formation of chromophoric group. The study for performed on malachite green dye with accordance of zinc oxide nanoparticles as follow,

2.3.1. Performance of malachite green dye in presence catalyst and in absence of catalyst as reaction carried out in dark environment[14].

2.3.2. Photo degradation of malachite green dye in presence of bright sunlight as,

a) Degradation reaction in presence of catalyst and sunlight[15].
b) Degradation reaction in presence of precursor salt zinc nitrate hexahydrate in sunlight[16].
c) Degradation reaction proceeds with solar radiation on *Michelia Champaka* aqueous leaf extract in sunlight.
d) Degradation of malachite green dye in solar radiation in absence of catalyst.

2.3.3 Degradation of malachite green dye in presence in presence and absence of zinc oxide nano catalyst in dark condition.

I) Preparation of malachite green dye solution in absence of catalyst - Malachite green dye of about 1mg/liter dissolved in distilled water and transferred to 1liter of volumetric flask and diluted up to the mark with double distilled deionized water and prepared dye solution was protected from sunlight as it was wrapped with aluminum foil and placed on magnetic stirrer for formation of homogeneous mixture in absence of catalyst[17].

II) Preparation of malachite green dye solution in presence of catalyst - Approximately 1mg/liter of malachite green dye measured accurately and transferred to distilled water containing 50mg of catalyst as the solution is stirred well for homogeneity. The solution is stirred continuously for duration of 30 minutes and further wrapped with aluminum foil to avoid sunlight. The total volume of one liter of dye solution placed in dark for a duration of one hour with continuous stirring to undergo the adsorption - desorption process. The activity of degradation of malachite green dye solution in presence and absence of catalyst carried out by removal of 3 ml of aliquots from the stock solution and subjected to ultra violet visible spectrophotometer for analysis[18]. The aliquots were removed for every 15 minutes of time interval from zero minutes up to 180 minutes of time duration. The spectrophotometric studies revels that the maximum degradation of malachite green dye solution was observed as 4.11% in 180 minutes time interval which is a very lower. The degradation occurred in dark condition give 4.11% of degradation, as this must be because of interaction of dye molecules within them self - producing the repulsive charge. The degradation observed with presence of zinc oxide nanoparticle catalyst in dark environment gives a result of 19.02% of malachite green dye degradation in the maximum time condition of 180 minutes. Malachite green dye is an azo dye and contain (- N=N -) as an azo group, which is a chromophoric group and responsible for strong green color of dye. Zinc oxide nano catalyst till some extent was capable to bind the chromophoric azo group but unable to disturb the chromophoric group and hence the low rate of degradation is observed. The higher rate of malachite green dye solution degradation can be achieved if there is complete destruction in the chromophoric band which is possible in presence of radiation, as solar or sunlight. Result presented in graph 1.1.

2.4 Photo catalytic degradation of malachite green dye by various methods as comparative study.

2.4.1 Photo catalytic degradation of malachite green dye under solar irradiation and zinc oxide nanoparticles as precursor material - The pre - prepared solution of malachite green dye employed for experiment in dark condition with zinc oxide nanoparticle catalyst was implemented in this experiment.100ml of malachite green dye solution was abstracted and to it 10mg of zinc oxide nanoparticle catalyst was added with vigorous stirring. The solution was kept in dark for 30 minutes for undergoing the process of adsorption - desorption. Further the malachite green dye solution dye solution was mounted in sunlight for about 1.5 hour on magnetic stirrer with continuous stirring. The solution of 3ml was abstracted from the stock solution and subjected to centrifugation and filtration then proceeds to ultra - visible spectrophotometer for observations. This process was repeated for every 15 minutes and continues up to 180 minutes time.

Observations obtained specify that, the degradation of malachite green dye solution was increasing slowly and steadily in presence of zinc oxide nanoparticle catalyst. The maximum rate of malachite green dye solution degradation was 83.06% in 180 minutes of time. The observed rate of malachite green dye solution degradation is optimum high as the change in color was observed from green to very light faint green colored solution which was nearly to colorless nature. The change in color of malachite green dye solution with increasing time; result that there is nearly complete breakdown of the chromophoric group. It is also estimated that the optimum rate of malachite green dye solution degradation is because the nanoparticles of zinc oxide when exposed to sunlight, where the energy is optimum, the movement of election occurs from the valence band towards the conduction band, as the cavities or the holes are generated in the valence band. Further the electrons that are appeared in the conduction band has the ability to absorb the molecular oxygen and gives the production of O_2^- radicals, and cavities or holes that are generated in the valence band give the formation of hydroxyl radicals OH^* which are produced due to reaction with water (H_2O). Further as the hydroxyl radicals $OH^*$are considered as a strong oxidizing agent, they have the ability to convert or decompose the malachite green dye molecule into the simple organic species or compounds as there is the continuous generation of oxygen species. Hence the higher malachite green dye solution degradation efficiency of 83.06%.

2.4.1.2 Photo - induced reaction of degradation of malachite green dye in presence of sunlight and presence of zinc nitrate hexahydrate salt as a precursor - The malachite green dye solution of dark experiment without catalyst was introduced in this experiment.100ml of malachite green dye solution abstracted from the stock solution and to it 0.5 gm is of zinc nitrate - salt was added and stirred for obtaining homogenous mixture. The solution mixture was transferred to centrifugation at 6000 rpm for 20 minutes. The observation of the solution mixture revels the complete dissolution of salt. Further the malachite green dye solution was mounted in bright sunlight for absorption of radiation. After one hour a 3ml of sample from the malachite green dye solution is removed and subjected to ultra violet visible spectrophotometer. The sample removal process is carried out for every 15 minute and carried out up to 180 minutes.

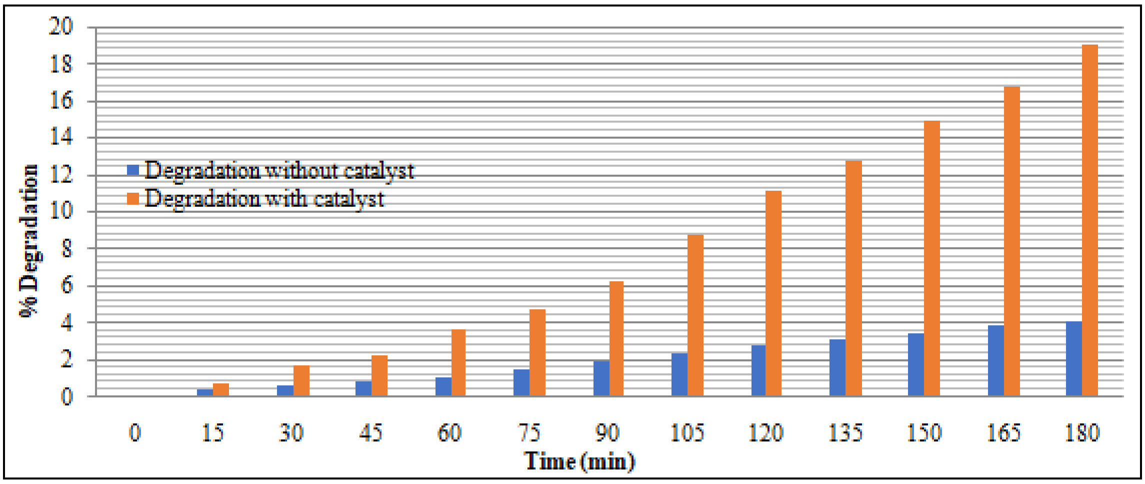
The observation obtained from the dye degradation of malachite green evolves the malachite green dye solution degradation rate of 17.33% in 180 minutes. The percentage of degradation increase with increase in time. The rate of malachite green dye solution degradation varies along with time duration because the penetration of radiation through the dye molecule is not adsorbed by the surface molecule of zinc ion in a solvent. The degradation of dye that has occurred is due to the chemical composition zinc nitrate salt which it binding towards the molecules of malachite green dye through water molecules. It can be also assumed that zinc nitrate molecules contain large size of particles and hence the surface area decrease for absorption of the radiation and hence low rate of degradation of malachite green dye solution.

2.4.1.3 *Michelia champaka* leaf extract mediated photo catalysis of degradation of malachite green dye - The malachite green dye solution from the stock of dark experiment carried out without catalyst, as 100ml of the dye solution was utilized for this current experiment. The concentrated leaf extract of *Michelia champaka* was freshly prepared and about 10 ml of leaf abstract was added to the malachite green dye solution. The color of solution change from orange to pale orange, as the immediate reaction occurs as the volume of solution is increased. The prepared solution of malachite green dye solution dye is stirred for few minutes and exposed to sunlight. After a half hour of exposure to sunlight the 3ml of solution is derived from the exposed solution and subjected toward analysis. This process of removal of 3ml of abstract is carried out for every 15 minutes and continued up to 180 minutes.

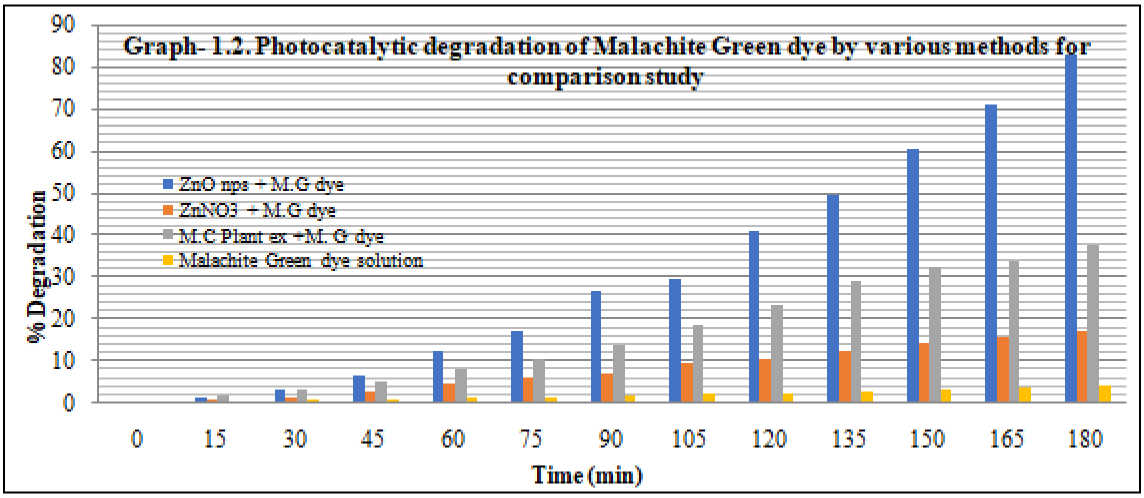
The results from the observation can be stated as the rate of degradation of malachite green dye solution increase with increase in time and with exposure of dye solution to sunlight. The maximum rate of malachite green dye solution degradation was obtained at 180 minute which was of 74.16%. The degradation percentage increases slowly and steadily for higher absorbance of dye, evaluated by ultra violet visible spectrophotometer. The change in color of dye solution observed, demonstrate that as the time increase the solution in sunlight become lighter in color and again as the maximum time increase the solution become faint colorless in nature and this observation cleared the increase rate of degradation of malachite green dye. The degradation of 74.16% may be because of the phytoconstituents present in leaf extract of plant which is responsible for oxidation and acts as a capping agent. The phytoconstituents present in the aqueous leaf extract are also responsible for malachite green dye solution degradation. The sunlight is absorbed on the surface of malachite green dye molecule and penetrates through the dye molecules, which result in destruction of chromophoric group of malachite green dye. The phytoconstituents present in the *Michelia Champaka* leaf extract acts as the reducing agent and bring the reduction of organic moitietes into simpler organic compounds and hence higher the penetration of radiation on the surfaces of malachite green dye molecules and hence higher the rate of degradation of malachite green dye.

2.4.1.4 Photo catalytic degradation of malachite green dye in solar radiation in absence of catalyst - 100ml of malachite green dye solution previously prepared was utilized for this experiment. The malachite green dye solution without any further treatment was subjected in sunlight for one - hour durations. The aliquots of 3ml were removed from the malachite green dye solution and subjected towards ultra violet visible spectrophotometer. This process is too repeated for every 15 minute and continued up to 180 minutes.

The result obtained from the observation states that maximum degradation of malachite green dye without any catalyst gives the rate of 4.74% in 180 minutes of time. The degradation takes place very slowly and the rate of malachite green dye solution degradation is also low. The low rate of malachite green dye solution degradation is because of large group of molecules of dye embedded together on the surface of solution. The layer of dye molecules on the surface of solution restricts the penetration of light into the medium of solution. The malachite green dye solution degradation that has occurred is the self-degradation of malachite green dye. There are no active sites present in the solution, so this is also a reason for low degradation of dye. Result presented in graph 1.2.



Graph 1.1: Degradation of Malachite Green dye solution in dark condition in presence and absence of zinc oxide nanoparticles



3. Conclusion

Zinc oxide nanoparticles derived with Michelia Champaka leaves extract relived for degradation of malachite green dye degradation in presence and absence of catalyst as ZnO nps, as maximum degradation was observed when the experiment was carried out in photo radiation (sunlight). Parametric experiment with various parameters as, catalyst, metal salt, leaves extract and self - degradation of dye was carried in sunlight.

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