Effect and Safety Evaluation of Hydrothermal Synthesis on Graphene and GO/MgO Nanocomposite for Visible light Photocatalytic Activity

S. Krishna Moorthy, D. Murugesan, N. Ponpandian, C. Viswanathan*
Department of Nanoscience and Technology, Bharathiar University, Coimbatore-641046, Tamilnadu, India

Abstract
Nanocomposites, a unique of organic and inorganic semiconductor, have been prepared by the chemical method. The magnesium oxide and Graphene composites were synthesized by hydrothermal method. Synthesized particles were examined under the characterization studies like XRD, UV-Vis, FTIR, TEM and FESEM. The GO/MgOnanocomposite were used in the visible light Photodegradation for the degradable dyes of Methylene Blue and Methylene Violet. In actual photocatalyst is a chemical species which may be a metal oxide semiconductor or a composite as light activated catalysts in the destruction of organic and inorganic materials or particles. The photocatalysts determines both the surface specific area and the photon conversion efficiency.

Keywords: Nanocomposite; Photocatalyst; Methylene Blue; Methylene Violet; TEM

1. Introduction

A simple one step hydrothermal strategy using non-toxic and cost effective precursors has been developed to prepare graphene oxide nanocomposites for removal of dye pollutants. A nanocomposite is a material, in which one of the components has atleast one dimension that is nano scope in size of the particles. The matrix itself comprises a resign and filler, the goal of which is to improve the characteristics of the resin while reducing the production cost. From a mechanical point of view the filler- resign system behaves as a homogeneous material, and the composite is considered as being made of a matrix and reinforcement. Most of the composite materials consist of one or more discontinuous phases of distributed in one continuous phase. Hybrid components are that which are with several discontinuous phases of different natures, the discontinuous phases usually harder and with superior mechanical properties that continuous phase is called matrix.

Methylene blue (MB) and Methylene Violet (MV) are the dyes where widely used in industries such as textiles, paper, plastics, tannery and paint industries. In addition, dyes are commonly toxic and some causes cancer and mutagenic. The longtime of dyes in water reservoirs, rivers, lakes and ponds sometimes causes food chain contamination, resulting in adverse effects on human being and animal health. Therefore, removal of pollutants from waste water has attracted considerable attention in the recent trends. To remove the dyes from contamination media such as chemical oxidation, solvent extraction, catalytic degradation, photodegradation, homogeneous and heterogeneous photo dye degradation in organic and inorganic forms. Adsorption is one of the promising processes for the removal of heavy metal ions from water. Some of the adsorbent materials for heavy metal ion removal are activated carbon and CNTs, etc., for the removal of Pb, cadmium and other heavy metal ions. However, the cost of adsorbent becomes relatively high when pure sorbents are used. Photodegradation of dye has been a successful method for the eradication of dyes from effluent water, which further helps in water purification.

Graphene oxide (GO) is a highly effective absorbent of dyes and they can be used to remove BB and MV from aqueous solution. GO and nanocomposite can be directly used as an effective absorbent for the decoloration of MB and MV, which is widely applied to dye cotton, wood, and silk. GO has a huge absorption capacity for MB and MV, which is competitive with other high performance absorbents. The fast absorption process of MB and MV onto GO is one advantage. The absorption capacity of GO is regulated by many influencing factors, such as temperature, pH value, ionic strength, and dissolved organic and inorganic matter.

There is a wide variety of water pollutants, which includes by products and wastage of industries, factories, organic matter, pathogens, and etc. water pollution is a burning problem all over the globe, which requires some eco-friendly methods for its purification. The biggest consumers of water are textiles; tannery, electroplating and paper industries and therefore, these industries are also considered of mostly responsible for creating water pollution. Degradation has emerged as a process for removal of organic and inorganic pollutants, which are present in the effluents released by the industries.

2. Experimental section

2.1 Materials

All chemical were analytical grade and used as received without further purification. Graphite flakes (~105 µm flakes), Magnesium Nitrate ($MgNO_3$) and Sodium hydroxide (NaOH) is supplied by Sigma Aldrich. Potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), sulphuric acid (H_2SO_4 98%), hydrogen peroxide (H_2O_2) and ethanol were purchased from Himedia Laboratory Pvt. Ltd.

2.2 Synthesis GO/MgO nanocomposite

Hydrothermal synthesis is a method for growing single crystals from an aqueous solution in an autoclave at high temperature and pressure. 30 mg of Graphene sheets were dispersed in 30 distilled water and sonificated for 1 hour the solution become brown color which indicates the dispersion of GO. To the above GO solution 0.01M of Tin (II) chloride dihydrate ($SnCl_2$)2H_2O and 0.01M of Zinc chloride ($ZnCl_2$) were added and kept at continues stirring. Then ammonia is added to adjust the pH upto 10 and then the above solution is transfer to the autoclave at 180^oC for 12 Hours. The solution washed with distilled water and ethanol, and then kept for drying over night at 80^oC. Finally, GO/ZnO and GO/SnO_2 nanocomposites were prepared.

2.3 Characterization

The nanocomposite of graphene and its composites were examined under the characterization techniques such as were carried out by using X-Ray diffractometer (XRD) measurements were carried out at room temperature using a PANalyticalX'pert-pro diffractometer with Cu Kα_1 radiation (λ = 1.5406 Å) over a scanning interval (2θ) from 10 to 80^o. The average crystalline sizes were estimated using Scherrer formula from the X-ray line broadening. The morphological and elemental analyses of the GO/MgOnanocomposites structures is observed by Field Emission Scanning Electron Microscopy (FESEM) (FEI Quanta-250 FEG) coupled with EDX spectroscopy. FTIR spectrum of GO and GO based nanocomposites were studied by using a Therma Nicolet Nexus 670 spectrophotometer between 4000 and 400 cm^{-1}. The optical absorption properties of the as synthesized nanocomposites were analyzed by using UV-Vis absorption spectrophotometer. Raman spectroscopy is used to study vibrational, rotational and other low-frequency modes in a system. Raman spectroscopy is a suitable technique to characterize carbonaceous materials, particularly for distinguishing ordered and disordered crystal structures of carbon. The Raman spectra of the samples were measured on a HORBIA JobinYvon Raman spectrometer, equipped with an excitation source of He-Ne laser (632.8 nm), CCD camera and scan resolution held at 2 cm^{-1}.

2.4 Photocatalytic Activity:

20 mg of the photocatalysts (binary/ternary nanocomposites) were taken and dispersed in 50 ml of aqueous solution of MV and BB separately. The solution were mixed by using a magnetic stirrer constantly in the presence of dark environment for 15 minutes After, these solution was placed or allowed to irradiated in the sun light. During the exposure of dye solution to the visible sun light source, aliquots were taken out at intervals of every 30 minutes and the concentration of MV and BB were determined by UV-Vis Spectrometer. Absorption spectrum is obtained by a plot between absorbance versus irradiation time and the efficiency of decolorization was determined in term of change in intensity of absorption maximum of the dyes. The efficiency of decolorization is calculated using formula

$$C_0 - C/C_0 * 100\% \qquad (1)$$

Where,

$\mathbf{C_0}$ – Initial concentration of dye solution, **C** – Concentration of dye after irradiation

3. Result and Discussion

3.1 Physico-chemical properties of GO/MgO

3.1.1 XRD of GO/MgO

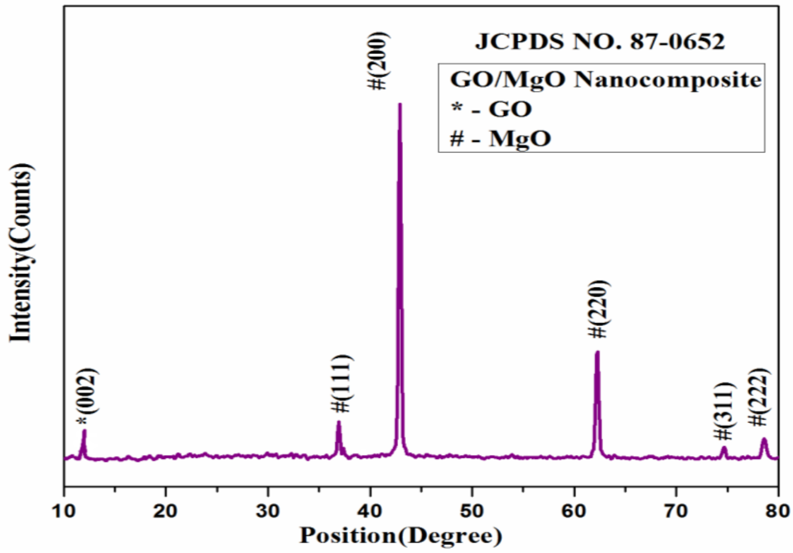

Fig1. X-ray Spectrum for GO/MgO

The XRD spectra of GO/MgO nanocomposite were shown in Fig.1 shows a sharp peak at 11.9^{o} although the high content of GO in the composite makes that the intensity much higher the peaks are observed at 36.0, 42.4, 62.2, 74.1 and 78.1^{o} corresponds to the (h k l) values of the peaks (111), (200), (220), (311) and (222) respectively. The corresponding speaks are very well were matched with (**JCPDS#87-0652)** of ZnO. The average crystallite size is calculated for GO/MgO by using Scherer formula equation is about 18 nm.

3.1.2 FTIR of GO/MgO

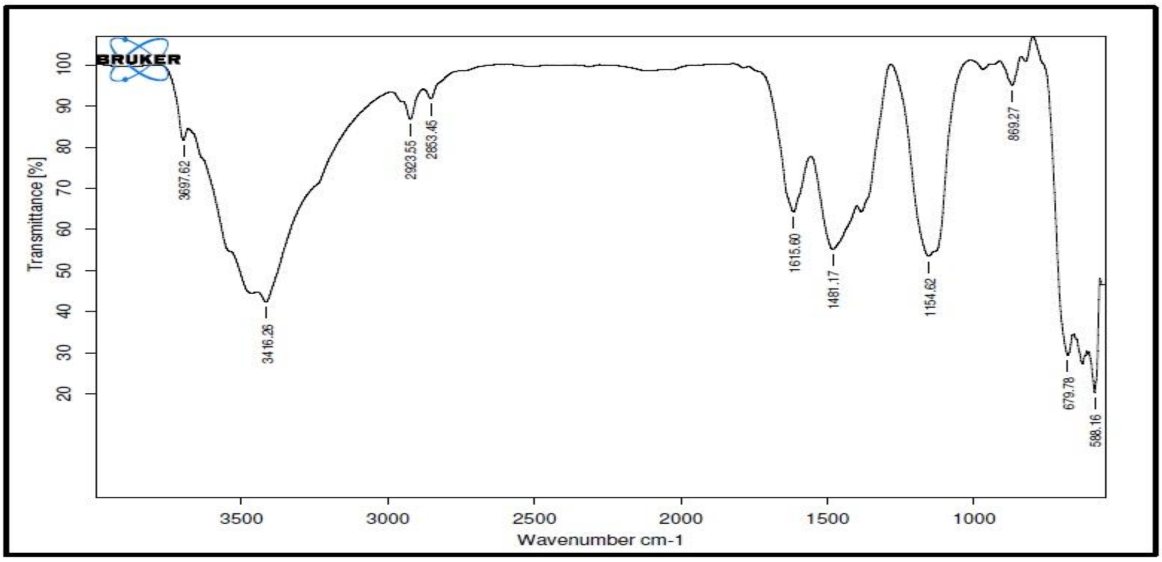

Fig2. FTIR Spectra for GO/MgO

The FTIR spectrum of the nanocomposites are exhibits C-OH stretching vibration attributed at 3416 and 2923 cm^{-1}, and other characteristic vibrations such as, O-H were absorbed at 2853 cm^{-1}. The C=C attributed at 1615 cm^{-1} are corresponding SP^2

hybridization.. The C=C attributed at 1615 cm^{-1} are corresponding SP^2 hybridization. The C-OH stretching vibration attributed at 3416 cm^{-1} could be ascribed to the vibrations of the adsorbed water molecules. The peak at 679 cm^{-1} corresponds to the stretching vibrations of the terminal MgOH. The peak at 869 cm^{-1} region corresponds to the stretching modes of the Mg-O-Mg. The peak at 588 cm^{-1} corresponds to the stretching vibrations of the terminal Sn-OH.

3.2 Morphology Analysis of GO/MgO

3.2.1 FESEM and TEM

The morphology of the synthesized GO/MgO was observed by using FESEM images as shown in Fig.3. The FESEM images of GO/MgO were synthesized by a hydrothermal technique. From these micrographs the MgO nanoparticles are grown on GO sheets. The obvious from the image of the particle are agglomerated and uniformly spherical in shape and the particle size ranges from 18 to 25 nm.

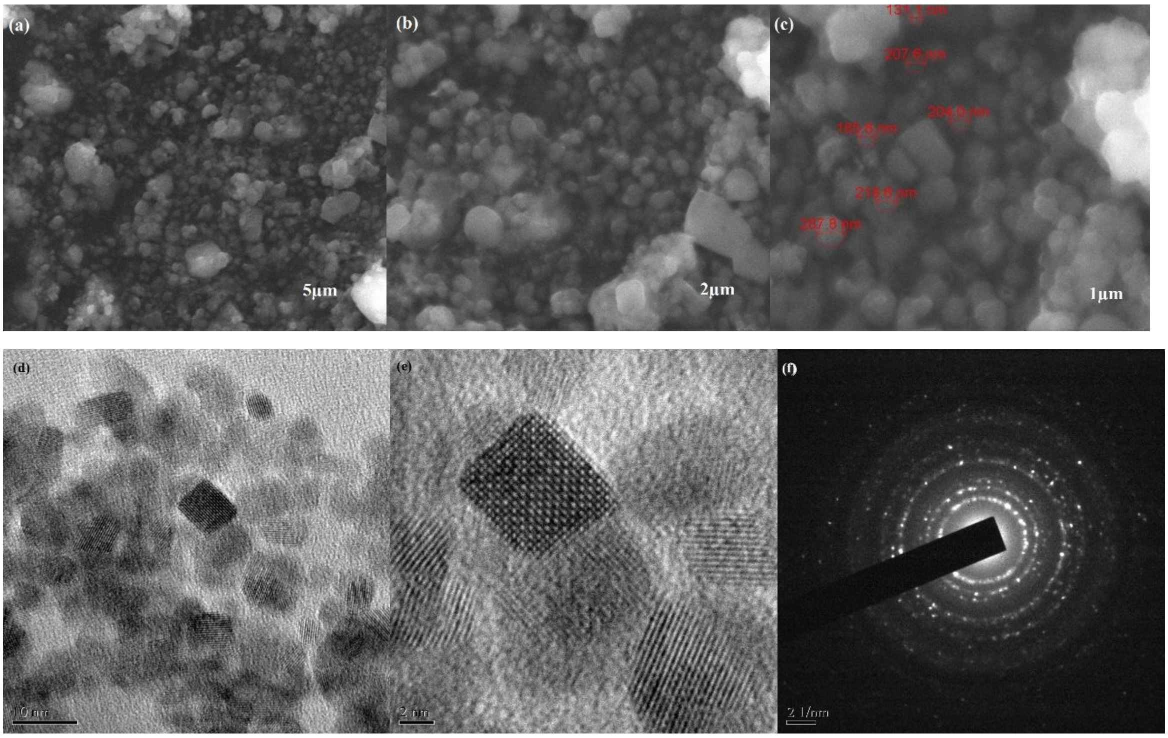

Fig.3 Shows (a & c) FESEM images of GO/MgO and (d& f) TEM images GO/MgO with different magnifications

A drop of sample is placed on a piece of parafilm, place the carbon coated copper grip wait for 5-10 minutes, and drain the excess with help of filter paper, wash with distilled water and stained with 2% uranyl acetate and observed under transmission electron . The below images show the agglomerates of small grain and some dispersed Nanoparticles. The particle size histograms of GO/MgO nanocomposite show that the particles were in the range from 10 to 50 nm width mean diameter of 20 nm. The diffraction pattern of the TEM image shows the presence of polydispersed GO/MgO nanocomposite.

4. Photocatalytic Activity of GO/MgO

4.1 Photodegradation

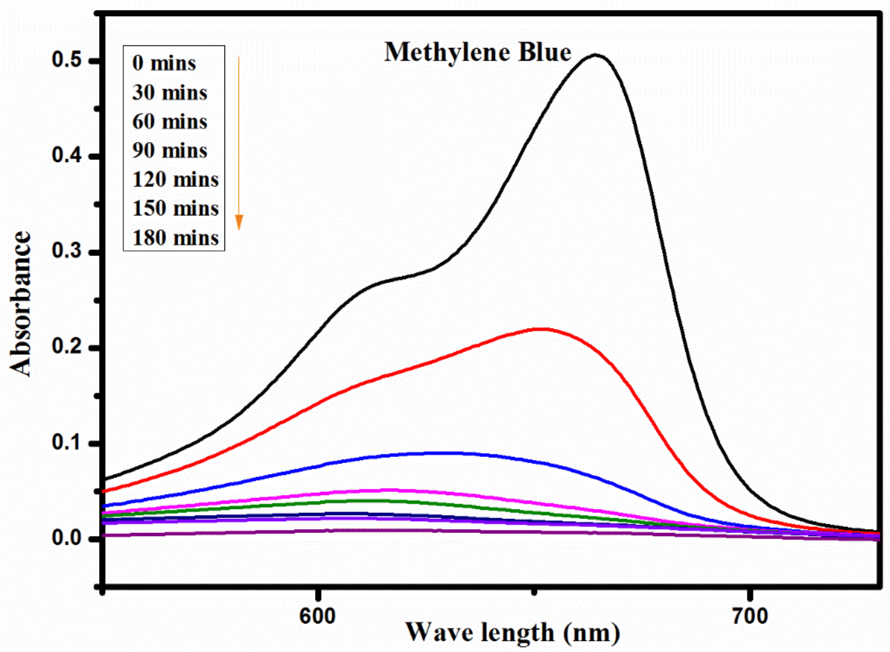

Fig.4 UV-Visible absorbance spectra for photodegradation of MB for GO/MgO

Photocatalytic activity of GO/MgOwhere represented in the following Figures. It is clearly proved that, the dyes such as Methylene Blue (MB) and Methylene Violet (MV) were degraded for the nanocomposites at faster efficiency rate. The experiment process carried out with good quantity of variation in the dyes concentration in water under the visible sunlight. The following Figures show the degradation with time interval of 30 minutes in the span of 6 h duration. Based on the above degradation mechanism, the high surface area of sphere like GO/MgO nanocomposites sufficiently produces active oxygen radicals which are basically responsible for the degradation of MB and MV.

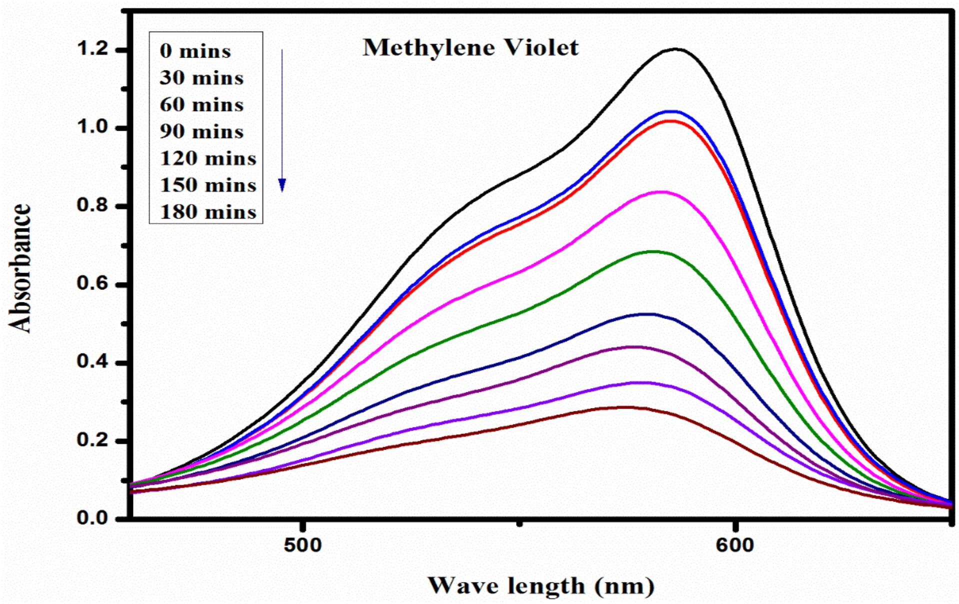

Fig.5 UV-Visible absorbance spectra for photodegradation of MV for GO/MgO

4.2 Efficiency of Degradation

4.2.1 Methylene Blue (MB)

The Photodegradation of the GO/ZnO and GO/SnO_2 nanocomposites were studied and determined under visible sunlight. Although the photodegradation a level in the samples were close, it was found little higher degradation in GO/SnO_2 nanocomposites compare to the GO/ZnOsamples degradation at 90 to 150 minutes. After the complete degradation at about 210 minutes the higher degradation in GO/SnO_2 nanocomposites compare to the other two samples. From the degradation time of 210 minutes the degradation rate is saturated constantly

4.2.2 Methylene Violet (MV)

Photodegradation of the GO/ZnO and GO/SnO_2 nanocomposites were studied and determined under visible sunlight. Although the photodegradation a level in samples were close to, it was found little higher degradation in GO/SnO_2 nanocomposites compare to the GO/ZnO samples degradation minutes. After the complete degradation at about 210 minutes the higher degradation in GO/SnO_2 nanocomposites compare to the other two samples. From the degradation time of 180 minutes the degradation rate is saturated constantly.

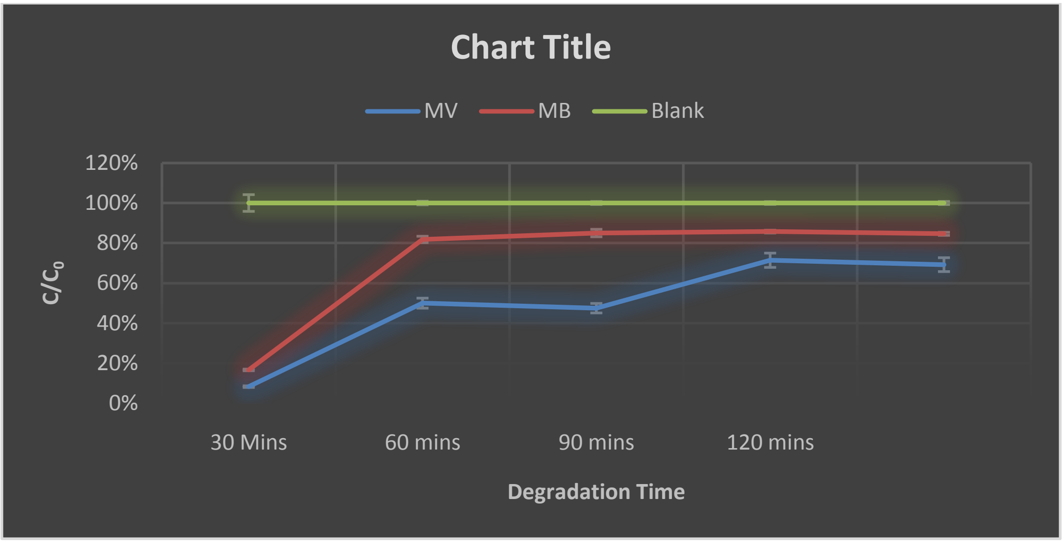

Fig.8 Efficiency of Photodegradation rate, (a) GO/ZnO and (b) GO/SnO_2 nanocomposites

5. Conclusion

A simple and cost effective hydrothermal method is used to prepare GO/MgOnanocomposite. The obtained samples were characterized by using various analytical techniques to find out their Physico-chemical, functional and catalytic properties. The photodegradation and photocatalytic activity of the GO/MgOnanocomposite were studied by using Methylene Blue and Methylene Violet dyes and determined under visible sunlight. Therefore, the experimental results are clearly exhibits all our as-prepared nanocomposite are excellent visible light photocatalyst towards the degradation of MV and BB under visible light irradiation. Specifically, GO/MgO nanocomposite provide excellent degradation efficiency of MB with rapid time.

References

1. David J. Lockwood (2004). Introduction to Nanoscale Science and Technology, FRSC National Research Council of Canada Ottawa, Ontario, Canada. Kluwer Academic Publishers, New York.
2. Charles P. Poole Jr., Frank J. Owens (2003). Introduction To Nanotechnology-Wiley-Interscience, John Wiley & Sons Ltd.
3. Bandyopadhyay AK (2008). Nano Material, New Age International (P) Ltd., Publishers
4. Robert kelsall, Ian Hamley, Mark Geoghegan (2005). Nanoscale Science and Technolog, Copyright 2005 John Wiley & Sons Ltd.

5. Masuo Hosokawa, Kiyoshi Nogi, Makio Naito and Toyokazu Yokoyama (2007). Nanoparticle Technology Handbook (2007) Elsevier.
6. Kavitha KS, Syed Baker, Rakshith D, Kavitha HU, Yashwantha Rao HC, Harini BP and Satish S (2013). Plants as Green Source towards Synthesis of Nanoparticles. *International Research Journal of BiologicalSciences*,Vol. 2(6), 66-76.
7. Ayeshamariam A, TajunMeeraBegam M, Jayachandran M, Praveen Kumar G and M Bououdina (2012). Green Synthesis of Nanostructure Materials for Antibacterial and Antifungal Activity. *International Journal of Bioassays*, Vol. 02 (01), 304-311.
8. Akl M. Awwad and Ninda (2012). A Green and Facile Approach for Synthesis of Magnetite Nanoparticles. *Nanoscience and Nanotechnology*, Vol. 2(6), 208-213.
9. SohailYasin, Lin Liu, and Juming Yao (2013).Biosynthesis of Silver nanoparticles by Bamboo Leaves Extract and Their Antimicrobial Activity. *Journal of Fibre Bioengineering and Informatics* Vol. 6:1, 77-84.
10. Maensiri S, Laokul P, Klinkaewnrong J, Phokha S, Promarak V and Seraphin S (2008). Indium oxide (In2O3) nanoparticles using Aloe veraplant extract: Synthesis and optical properties. *Journal of Optoelectronics and Advanced Materials*, Vol. 10, 161 – 165.
11. MonalisaPattanayak and Nayak PL (2013). Ecofriendly Green Synthesis of Iron Nanoparticles from Various Plants and Spices Extract. *International Journal of Plant, Animal and Environmental Science.* Vol. 3, 68-78.
12. Gnanasangeetha D and SaralaThambavani D (2013). One Pot Synthesis of Zinc Oxide Nanoparticles via Chemical and Green Method. *Research Journal of Material Sciences*, Vol. 1(7), 1-8.
13. Sangeetha Nagarajan and KumaraguruArumugamKuppusamy (2013).Extracellular synthesis of zinc oxide nanoparticles using seaweeds of gulf of Mannar, India. *Journal of Nanobiotechnology*, Vol.11(39), 1-11.
14. Joy Sarkar, Manosij Ghosh, Anita Mukherjee, Dipankar Chattopadhyay and Krishnendu Acharya (2013). Biosynthesis and safety evaluation of ZnO nanoparticles. *Bioprocess Biosystem Engineering*, Springer-Verlag Berlin Heidelberg.
15. Rajiv P, SivarajRajeshwari and RajendranVenckatesh(2013). Bio-Fabrication of zinc oxide nanoparticles using leaf extract of Partheniumhysterophorus L. and its size-dependent antifungal activity against plant fungal pathogens.*SpectrochimicaActa Part A: Molecular and Biomolecular Spectroscopy*, Vol.112, 384–387.

16. Wani AH and Shah MA (2012). A unique and profound effect of MgO and ZnO nanoparticles on some plant pathogenic fungi. *Journal of Applied Pharmaceutical Science*, Vol. 02(03), 40-44.
17. Mathibela Elias Aphane (2007). The Hydration of Magnesium Oxide with Different Reactivities by Water and Magnesium Acetate. University of South Africa.
18. HenristC, Mathieu JP, Vogels C, Rulmont A, ClootsR (2003). Morphological study of magnesium hydroxide nanoparticles precipitated in dilute aqueous solution. *Journal of Crystal Growth*, Vol.249, 321–330.
19. Tran X. Phuoc Tran X. Phuoc, Howard H, Donald V. Martello , Yee Soong , Minking K. Chyu (2008). Synthesis of Mg (OH)2, MgO, and Mg nanoparticles using laser ablation of magnesium in water and solvents. *Optics and Lasers in Engineering*, Vol.46, 829– 834.
20. Ismail Cakmak and Horst Marschner (1992).Magnesium Deficiency and High Light Intensity Enhance Activities of Superoxide Dismutase, Ascorbate Peroxidase, and Glutathione eductase in Bean Leaves. *Plant Physiology*, Vol.98, 1222-1227.
21. Dalip Kumar,Buchi Reddy V,Braj G. Mishra,Rana RK,allikarjuna N. Nadagoudaand Rajender S. Varma (2007).Nanosized magnesium oxide as catalyst for the rapid and green synthesis of substituted 2-amino-2-chromenes. *Tetrahedron*, Vol.63, 3093–3097.
22. Avinash C. Pandey, Sharda S. Sanjay and Raghvendra S. Yadav (2010). Application of ZnO nanoparticles in influencing the growth rate of Cicer arietinum. *Journal of Experimental Nanoscience*, Vol. 5(6), 488-97.
23. Daniel I Arnon(1949). Copper Enzymes in Isolated Chloroplasts. Polyphenoloxidase in Beta Vulgaris. *Plant physiology*, Vol.24, 1-14.
24. Hamtmut K Lichtenthaler and Alan R Wellburn (1955). Determinations of total carotenoids and chlorophylls a and b of leaf extracts in different solvents. *Biochemical Society Transaction*, Vol.11, 591-593.
25. BoenHoung, Chen-Ju Huang, 2006, “Structure and properties of Ag embedded Al doped ZnO nanocomposite thin films prepared through a sol-gel process”. Surface & Coatings technology, Vol. 201, 3188-3192.
26. Xu-Chen Song, Yi Fan Zheng, E Yang, G Liu, 2010, “Photocatalytic activities of Cd doped ZnWO4 nanorods prepared by hydrothermal process”. J. Hazd Mater.

27. Bandara, J., Kuruppu, S. S., Pradeep, U. W., 2006, "The promoting effect of MgO layer in sensitized photodegradation of colorants on TiO2/MgO composite oxide". Colloids and Surfactants A: Physicochem. Eng. Aspects, Vol. 276, 197-202.