International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.9, No.06 pp 409-416, 2016

Dye degradation studies catalysed by green synthesized Iron oxide nanoparticles

D. Badmapriya, I.V. Asharani*

Department of Chemistry, School of Advanced Sciences, VIT University, Vellore, Tamil Nadu, India

Abstract : Iron oxide nanoparticles were synthesized using aqueous extract of *Piper betle* leaves through rapid single step method which could be suitably scaled up for large-scale production. The phenolic compounds present in the leaf extract were found to work as reducing and capping agent facilitating the formation of nanoparticles. The synthesized iron oxide nanoparticles were characterized by UV-Vis Spectroscopy, scanning electron microscopy, atomic force microscopy and transmission electron microscopy. Both scanning electron microscopy and atomic force microscopy analysis show that surface of the iron oxide nanoparticles were well capped by the phenolic groups present in *Piper betle.* Transmission electron microscopy analysis confirmed the spherical shape of the iron oxide nanoparticles with an average particle size of 16 nm. Energy dispersive X- ray spectroscopy showed the presence of elemental iron and oxygen indicating that the nanoparticles are essentially present in oxide form. The synthesized iron oxide nanoparticles were utilized as green catalyst for the effective decolourization of malachite green and methyl orange.
Keywords : Iron oxide nanoparticles; *Piper betle;* Methyl orange; Malachite green; Degradation.

Introduction

Metal nanoparticles have found extensive use in different applications owing to their typical optical, electrical and magnetic properties [1-3,33-45]. Different transition metal oxides including iron oxide nanoparticles (FeONPs) have been focused in various applications such as sensors [4], catalysts [5], in wastewater treatment [6], in energy storage [7], in tumor detection [8] and as antimicrobial agents [9].

There are good number of reports on the development of synthetic methods to produce FeONPs which include reduction by chemical, electrochemical, photochemical methods and heat treatment [10-13]. These methods not only use toxic chemicals but also produce toxic byproducts which have potential to become hazardous to the environment. On the other side, green methods show path to minimize the usage of toxic chemicals and reduce waste generation. Ultimately, the focus of the researchers has been on synthesizing nanoparticles through green methods using different plant extracts which serve as reducing and stabilizing agents.

Piper betle, a plant belonging to the *Piperaceae* family, has been known to possess phyto-constituents such as acetyl eugenol, trans-isoeugenol, chavicol, chavibetol, chavibetol acetate and allyl pyrocatechol diacetate [14, 15] capable of acting as reducing as well as stabilizing agents [16]. Already few reports available on green syntheses of iron oxide nanoparticles using other plant extract [17-20]. As of now, *Piper betle* leaves

have been used for only synthesizing gold and silver nanoparticles [14, 21]. Based on the rich content of phenolic compounds and since it has not been explored much for the preparation of other metal/ metal oxide nanoparticles it has been chosen for the synthesis of Fe_3O_4 NPs.

Dyes used in various industries showed their presence at a reasonable level in waste water even after treatment and pose a serious threat to the environment. These dyes are known to cause major health problems in humans which include carcinogenic and mutagenic effects [22-24].Conventional dye degradation techniques such as coagulation, flocculation, adsorption and membrane filtration [25] not only uses hazardous chemicals, but also results in incomplete degradation of dyes. Hence greener methods using biocompatible catalysts are of great interest in recent time's especially metal/ metal oxides in degradation methods. Reports are available on the degradation of methyl orange and malachite green using iron oxide nanoparticles [19,26] synthesized through chemical methods as well as green methods.

Hence in the present work, we have reported the green synthesis of FeONPs using *Piper betle* leaf extract in which the phenolic constituents act as reducing as well as stabilizing agents. The synthesized FeONPs have been utilized for catalyzing the decolourization of methyl orange and malachite green assisted by H_2O_2.

Materials and methods

Anhydrous Ferric chloride ($FeCl_3$) and hydrogen peroxide (H_2O_2) procured from Merck, methyl orange (MO) and malachite green (MG) procured from SD-Fine chemicals were used in this study. The structure of MO (C.I. 13025) and MG (C.I. 42000) were shown in the Fig.1.Fresh *Piper betle* leaves were procured from local market. Milli-Q water was used in all the experiments.

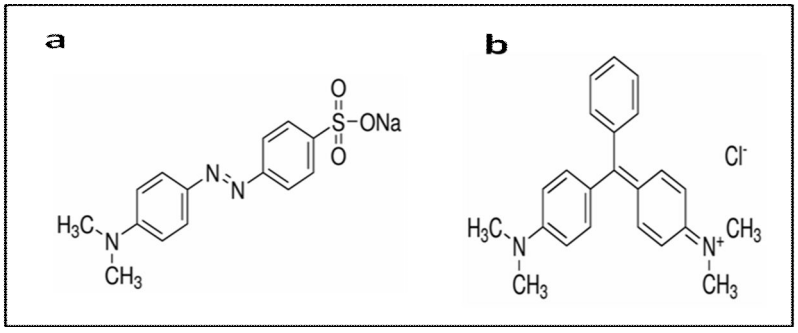


Fig.1.Structures for (a) MO and (b) MG

Preparation of FeONPs using Piper betle leaves extract

Freshly collected *Piper betle* leaves were washed several times with distilled water to remove dirt and unwanted materials. These leaves (20 g) were finely chopped and mixed with 50 mL of water in a flask, followed by stirred at 80°C for 30 minutes. The resultant extract was filtered through Whatmann filter paper and stored at 4°C for further use. For the preparation of FeONPs, a mixture of 0.1 M $FeCl_3$ solution and the *Piper betle* extract in a 1:2 (v/v) ratio was stirred for one minute on mechanical stirrer and by distinct colour change from pale brown to blackish brown. Formation of nanoparticles was seen by the change in intensity of the peaks corresponding to plant extract as well as $FeCl_3$ (shown in black and red color in Fig.2, between 220-280 nm) with an with an appearance a new broad absorbance band (shown in green in Fig. 2) in the visible region (between 500-700 nm) , in the UV-Visible spectrum [27].

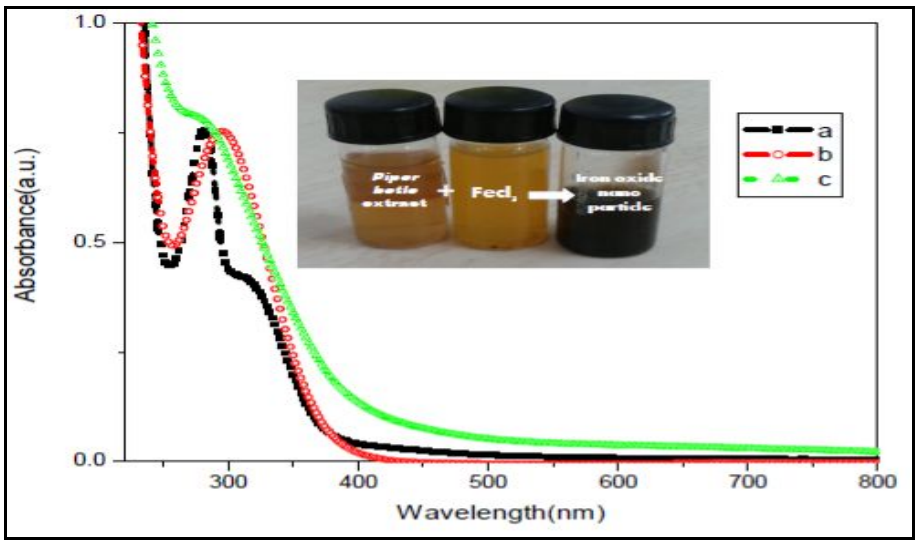


Fig.2. A UV-Vis spectrum of (a) *Piper betle* leaves extract (b) Ferric chloride and (c) FeONPs. The inset shows the photographic image of the *Piper betle* leaves extract, Ferric chloride solution and after mixing them (from left to right vials).

Characterization of FeONPs

The morphology of the FeONPs was imaged by scanning electron microscopy (SEM) using SEM Model JSM 6360 with energy dispersive X-ray spectroscopy (EDS) and Atomic force microscopy (AFM) using Nanosurf easy scan. Size and shape of the nanoparticles were obtained using TECHNAI SPIRIT G2 transmission electron microscope (TEM).

Catalytic activity of FeONPs during the degradation of dyes

Stock solutions ($1x10^{-3}$M) of MO and MG were prepared and from which required concentrations were prepared by dilution. For the degradation of MO and MG by H_2O_2, 250 µL (5×10^{-5} M) of the respective dye solutions were mixed with H_2O_2 (1:10 v/v ratio of dye to H_2O_2) in a UV-Vis quartz cuvette. In another set of dye and H_2O_2 mixture, 10 µL of synthesized FeONPs suspension was added to verify the catalytic effect of the FeONPs on the decolourization process. The progress of the decolourization for both sets of dye solutions was monitored by measuring the change in absorbance of the dye solutions on a JASCO V-670 spectrophotometer at regular interval of time.

Results and discussion

UV-Vis spectroscopic analysis

FeONPs were prepared by using the aqueous leaves extract of *Piper betle*. The formation of the nanoparticles was observed to be rapid as indicated by the colour change which occurred immediately after addition of the leaves extract to $FeCl_3$.This is supported by the appearance of a broad absorption band seen feebly in the higher wavelengths and no absorption in lower wavelengths (Fig.2) [28]. It is interesting to note that the formed FeONPs were observed to have an envelope of FeOOH in similar manner as given in a previous report [29].The formation of nanoparticles is known to take place through complexation of Fe salts followed by capping of Fe with phenolic compounds [16].

FT-IR analysis of the leaves extract

FT-IR spectrum of the *Piper betle* leaves extract was recorded to identify the functional groups of the phyto constituents responsible for the reduction of the metal precursors. FT-IR spectrum of the extract (Fig.3) shows band at 3400 cm^{-1} due to intramolecular hydrogen bonded O-H groups. In addition, the peaks at 1631 cm^{-1},1402 cm^{-1} and 1090 – 1030 cm^{-1} can be attributed to the C = O, in-plane bending vibrations of –OH, and C-O-C stretching respectively [19].

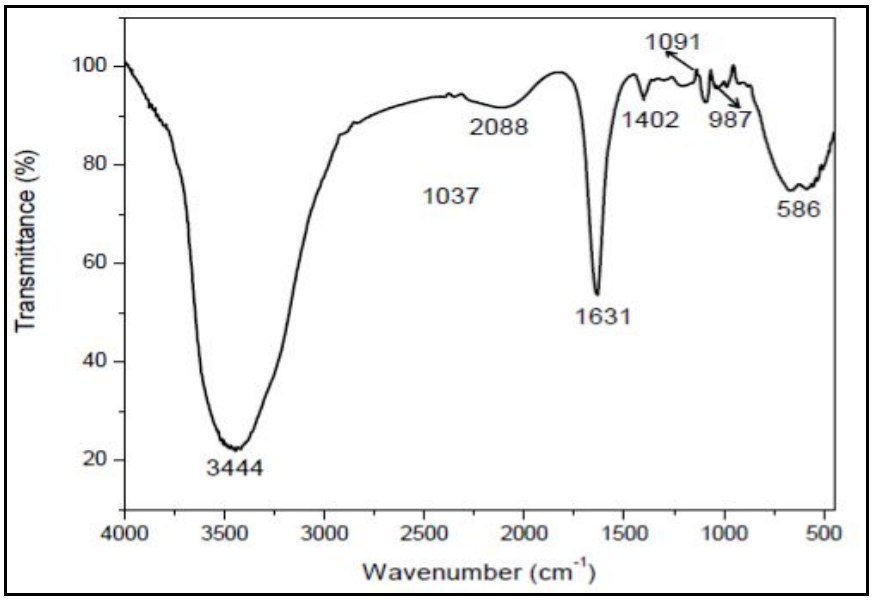


Fig.3. FT – IR spectra of *Piper betle* leaves extract

Morphology and particle size analysis of FeONPs

Both the SEM and AFM images (Fig.4) indicate the morphology as cluster of crystals due to the capping of FeONPs with phenolic compounds present in *Piper betle* extract.

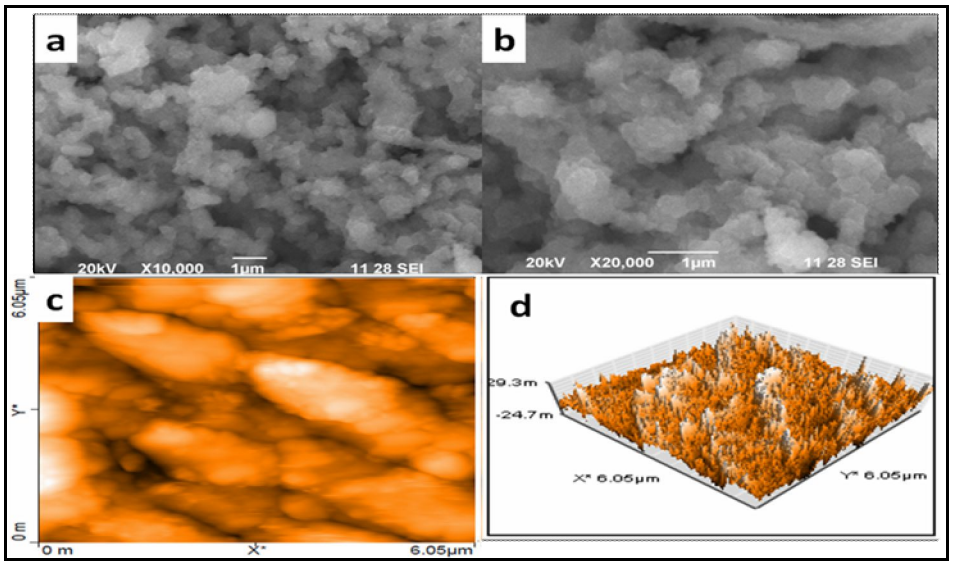


Fig.4. (a,b) SEM images of FeONPs and (c,d) AFM images of FeONPs.

The TEM images (Fig. 5) of FeONPs showed that the particles are polydispersed and spherical in shape. The average particle size calculated from the TEM images (Fig.6) is 16 nm. The presence of iron and oxygen was confirmed by EDS analysis.

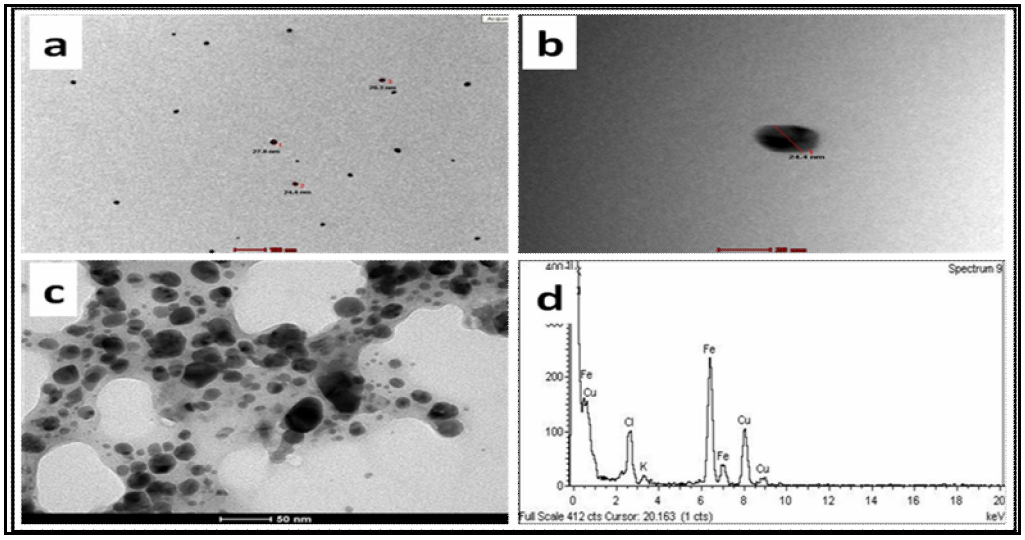
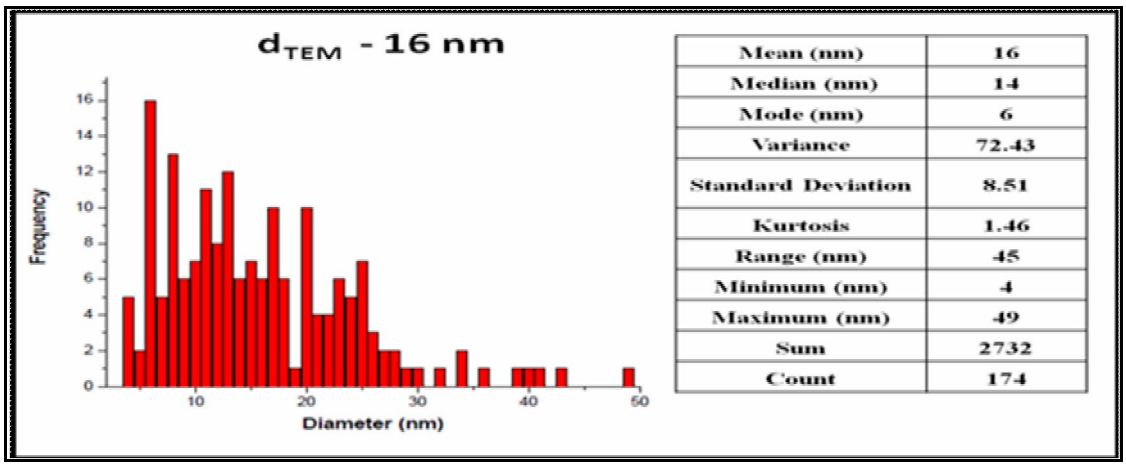


Fig.5. TEM images of FeONPs and EDS spectrum of FeONPs



Mean (nm)	16
Median (nm)	14
Mode (nm)	6
Variance	72.43
Standard Deviation	8.51
Kurtosis	1.46
Range (nm)	45
Minimum (nm)	4
Maximum (nm)	49
Sum	2732
Count	174

Fig.6. Histogram and statistical data obtained from TEM images of FeONPs

Catalytic activity of FeONPs in degradation of MO and MG

The synthesized FeONPs was used as catalyst for the decolourization of MO and MG dyes assisted by H_2O_2 as an oxidizing agent. The kinetics of degradation of MO (5×10^{-5} M) and MG (5×10^{-5} M) using H_2O_2 (1:10 v/v ratio of dye to oxidizing agent) in the presence and absence of synthesized FeONPs was monitored by UV-Vis spectroscopy and the data is shown in the [Fig. 7 (a) and (b)].

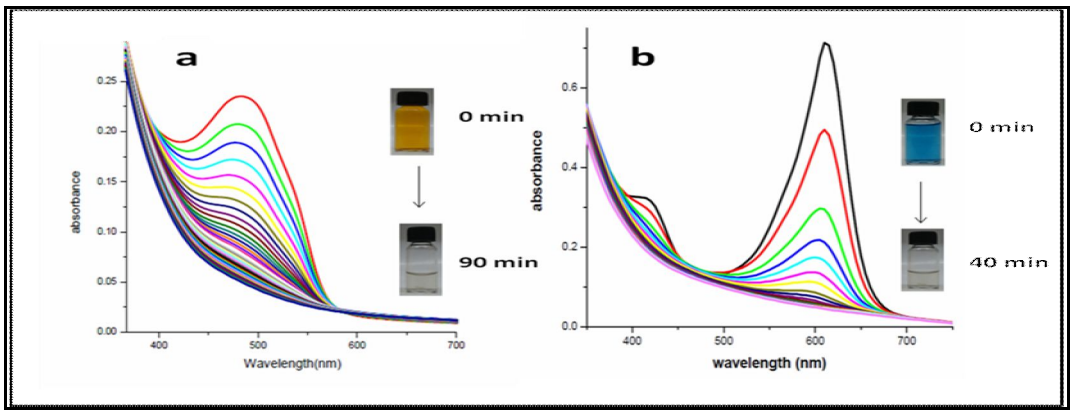


Fig.7. Kinetics of degradation of (a) MO and (b) MG using H_2O_2 in the presence of green catalyst

In the absence of catalyst, decolourization of MO and MG was not noticed even after 24 h, indicating that there was no direct oxidation pathway by peroxide. However, decolourization of MO and MG occurred only when FeONPs was introduced into the solution mixtures indicating essentiality of the NPs for promoting the decolourization which probably occur through free radicals pathway. The introduction of the nanoparticles may facilitate the formation of $OH^{\bullet}$ radical through which the degradation of the dye proceeds. Because of the higher concentration of H_2O_2 compared to the other reactants in the solution, both the reactions are seen to follow pseudo first order kinetics. The rate constants for both the dyes were calculated by plotting log (a-x) vs t [Fig.8 (a) and (b)], where 'a' is concentration at different intervals of time and 'x' is the concentration under equilibrium conditions .The rate constant for MO was found to be 0.0563×10^{-3} sec^{-1} and that of MG was 2.97×10^{-3} sec^{-1}. The degradation efficiency [Fig.9 (a) and (b)] of MO was 73.29 % and that of MG was 93 %.

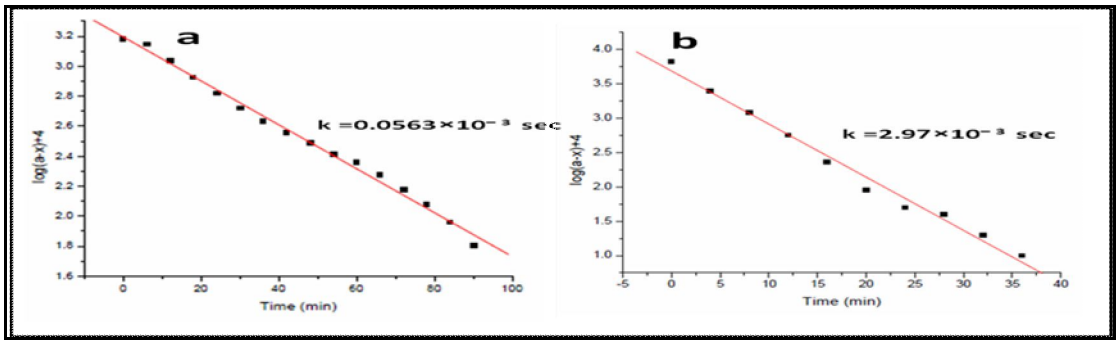


Fig.8. Kinetic data for first order plot of (a) MO and (b) MG

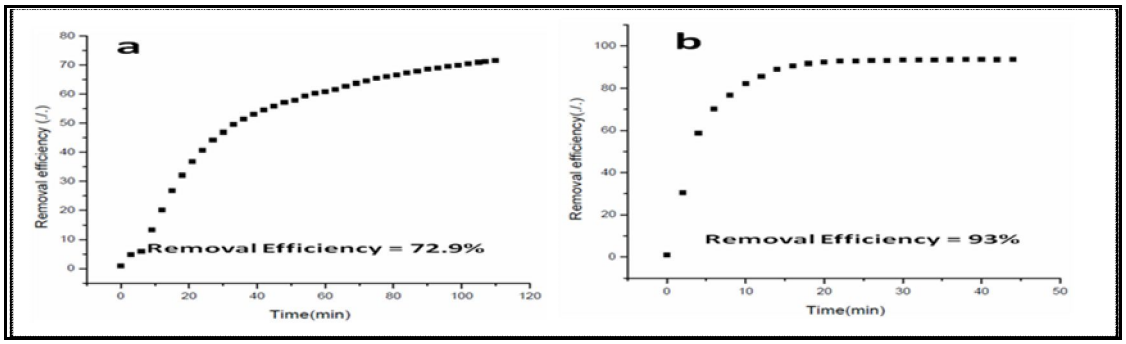


Fig.9. The degradation efficiency of (a) MO and (b) MG catalyzed by FeONPs nanocatalyst

Conclusions

In this study, an eco-friendly synthetic method for successful preparation of FeONPs using *Piper betle* extract at ambient conditions was reported. The phenolic compounds present in the *Piper betle* possibly, act as both reducing and capping agents. The synthesized FeONPs were effective in catalyzing the degradation of MO and MG dyes with H_2O_2 as an oxidizer. This could possibly pave a route for similar industrial application for dye degradation from effluent.

References

1. A.P. Alivisatos , Semiconductor clusters, nanocrystals, and quantum dots. Science, 1996, 271; 933–937.
2. V.I. Klimov, A.A. Mikhailovsky, Su. Xu, A. Malko, J.A. Hollingsworth, C.A. Leatherdale, H.J. Eisler, M.G. Bawendi, Optical gain stimulated emission in nanocrystal quantum dots, Science, 2000, 290; 314–317.
3. M. Fernández-García, A. Martínez-Arias, J.C. Hanson, J.A. Rodriguez, Nanostructured oxides in chemistry: characterization and properties, Chem. Rev. 2004,104; 4063–4104.
4. J. Chen, L. Xu, W. Li, X. Gou, α-Fe2O3 nanotubes in gas sensor and lithium–ion battery applications, Adv. Mater. 2005,17; 582–586.

5. Sugimoto M., The past, present and future of ferrites, J. Am. Cerem. Soc. 1999, 82; 269- 280.
6. Z. Cheng, A.L.K. Tan, Y. Tao, D. Shan, K.E. Ting, X.J. Yin, Synthesis and Characterization of Iron oxide Nanoparticles and Applications in the Removal of Heavy Metals from Industrial Wastewater. Int. J. Photoenergy. 2012, 1–5.
7. T. Yousefi, A.N. Golikand, M.H. Mashhadizadeh , Synthesis of iron oxide nanoparticles at low bath temperature: Characterization and energy storage studies. Mater. Sci. Semicond. Process. 2013, 16; 1837–1841.
8. AA.Ghazani, M. Pectasides, A.Sharma, CM.Castro, M.Mino-Kenudson, H.Lee, JA.Shepard, R.Weissleder, Molecular characterization of scant lung tumor cells using iron-oxide nanoparticles and micro-nuclear magnetic resonance.NBM.2014,10; 661–668.
9. N. Tran, A. Mir, D. Mallik, A. Sinha, S. Nayar, T. Webster, Bactericidal effect of iron oxide nanoparticles on Staphylococcus aureus. Intern. J. Nanomed. 2010, 5; 277–283.
10. K -C.Huang, S.H. Ehrman, Synthesis of Iron Nanoparticles via Chemical Reduction with Palladium Ion Seeds. Langmuir. 2007, 23; 1419-1426.
11. M. Starowicz, P. Starowicz, J. Żukrowski, J. Przewoźnik, A. Lemański, C. Kapusta, J. Banaś, Electrochemical synthesis of magnetic iron oxide nanoparticles with controlled size. J Nanoparticle Res.2011, 13; 7167–7176.
12. J. C. Scaiano, P. Billone,C. M. Gonzalez, L. Maretti, M. L. Marin, K. L. McGilvray, N. Yuan, Photochemical routes to silver and gold nanoparticles . Pure Appl. Chem 2009, 81:635–647.
13. S.Y. Kim, W. Song, M.W. Jung, M. Kim, C. Jeon, W.C. Choi, C.-Y. Park, Heat-driven size manipulation of Fe catalytic nanoparticles for precise control of single-walled carbon nanotube diameter. J. Phys. D: Appl. Phys. 2012, 45;255-302.
14. K. Sneha, M. Sathishkumar, S. Kim, Y.S. Yun, Counter ions and temperature incorporated tailoring of biogenic gold nanoparticles. Process. Biochem. 2010, 45; 1450–1458.
15. AM. Rimando, BH. Han, JH. Park, MC. Cantoria, Studies on the constituents Philippine *Piper betle* leaves. Arch Pharm Res. 1986,9; 93–97.
16. Mallikarjuna N. Nadagouda, Alicia B. Castle, Richard C. Murdock, Saber M. Hussainand Rajender S. Varma, In vitro biocompatibility of nanoscale zero valent iron particles (NZVI) synthesized using tea polyphenols .Green Chem. 2010, 12;114–122.
17. EC. Njagi, H. Huang, L. Stafford, H. Genuino, HM. Galindo, JB. Collins, GE. Hoag, SL. Suib, Biosynthesi of iron and silver nanoparticles at room temperature using agueous sorghum bran extracts. Langmuir, 2011, 27; 264-271.
18. B. Ahmmad, K. Leonard, Md. S. Islam, J. Kurawaki, M. Muruganandham, T. Ohkubo, Y. Kuroda, Green synthesis of mesoporous hematite (α-Fe_2O_3) nanoparticles and their photocatalytic activity, Adv Powder Technol. 2013, 24; 160–167.
19. T. Shahwan, S. Abu Sirriah, M. Nairat, E. Boyacı, A.E. Ero˘glu, T.B. Scott, K.R. Hallam, Green synthesis of iron nanoparticles and their application as a Fenton-like catalyst for the degradation of aqueous cationic and anionic dyes. Chem. Eng. J. 2011,172; 258-266.
20. M.Senthil, C.Ramesh. Biogenic synthesis of Fe_3O_4 nanoparticles using tridax procumbens leaf extract and its antibacterial activity on Pseudomonas aeruginosa. Digest Journal of Nanomaterials and Biostructures. 7:3(2012)1655-1660.
21. Z. Khan, O. Bashir, J.I. Hussain, Sunil Kumar, R. Ahmad, Effects of ionic surfactants on the morphology of silver nanoparticles using Paan (Piper betel) leaf petiole. Colloids Surf. B: Biointerfaces. 2012, 98; 85–90
22. W. Chu, C. Ma, Quantitative prediction of direct and indirect dye ozonation kinetics. Wat. Res. 2000, 34; 3153 – 3160.
23. S. Hildenbrand, FW. Schmahl, R. Wodarz,R. Kimmel,PC. Dartsch, Azo dyes and carcinogenic aromatic amines in cell culture. Jr. of Int Arch Occup Environ Health , 1999, 72; 52-56.
24. N Puvaneswari, J Muthukrishnan, P Gunasekaran, Toxicity assessment and microbial degradation of azo dyes. Indian J Exp bio. 2006, 44; 618-626.
25. V.K. Gupta, Suhas, Application of low-cost adsorbents for dye removal-A review. J. Environ. Manage. 2009, 90; 2313-2342.
26. L.L. Huang, X.L. Weng, Z.L. Chen, M. Megharaj, R. Naidu, Synthesis of iron based nanoparticles using oolong tea extract for the degradation of malachite green. Spectrochim. Acta Part A. 2014, 117; 801–804.

27. M. Andjelkovic, JV. Camp, BD. Meulenaer, G. Depaemelaere, C. Socaciu, M. Verloo, R. Verhe, Iron-chelation properties of phenolic acids bearing catechol and galloyl groups. Food Chem, 2006, 98; 23–31.
28. V. Madhavi, T.N.V.K.V. Prasad, A.V.B. Reddy, B.R. Reddy, G. Madhavi, Application of phytogenic zerovalent iron nanoparticles in the adsorption of hexavalent chromium. Spectrochim. Acta Part A. 2013, 116; 17–25.
29. Y.P. Sun, X. Li, J. Cao, W. Zhang, H.P.Wang, Characterization of zero-valent iron nanoparticles. Adv. Colloid Interface Sci.2006, 120; 47–56.
30. P.Umarani, P.Venkatesan, T.Radhakrishnan, A Study of Antimicrobial Activity of High Fluorescent Cadmium Telluride Nanoparticles, International Journal of ChemTech Research ,2016, Vol.9, No.01 pp 313-317.
31. Seeram. Hariprasad, G. Susheela Bai, J. Santhoshkumar, CH. Madhu, D. Sravani, Green synthesis of Copper Nanoparticles by *Arevalanata* Leaves Extract and their Anti Microbial Activites, International Journal of ChemTech Research,2016, Vol.9, No.02 pp 98-105.
32. S.Devasenan, N.Hajara Beevi, S.S.Jayanthi, Synthesis and characterization of Copper Nanoparticles using Leaf Extract of *Andrographis Paniculata* and their Antimicrobial Activities., International Journal of ChemTech Research ,2016, Vol.9, No.04 pp 725-730.
33. P.Umarani, P.Venkatesan, T.Radhakrishnan, A Study of Antimicrobial Activity of High Fluorescent Cadmium Telluride Nanoparticles, International Journal of ChemTech Research ,2016, Vol.9, No.01 pp 313-317.
34. Seeram. Hariprasad, G. Susheela Bai, J. Santhoshkumar, CH. Madhu, D. Sravani, Green synthesis of Copper Nanoparticles by *Arevalanata* Leaves Extract and their Anti Microbial Activites, International Journal of ChemTech Research,2016, Vol.9, No.02 pp 98-105.
35. S.Devasenan, N.Hajara Beevi, S.S.Jayanthi, Synthesis and characterization of Copper Nanoparticles using Leaf Extract of *Andrographis Paniculata* and their Antimicrobial Activities., International Journal of ChemTech Research ,2016, Vol.9, No.04 pp 725-730.
36. Gnanasangeetha D and Sarala Thambavani D; Green Zinc Oxide Nanoparticle Ingrained on Activated Silica for the Removal of As(III) from aqueous solution using Ocimum sanctum and Azadirachta indica; International Journal of ChemTech Research;2015, Vol.8, No.8, pp 44-52.
37. Manoj L, Vinita Vishwakarma; Green Synthesis and Spectroscopic characterisations of gold nanoparticles using invitro grown hypericin rich shoot cultures of Hypericum hookerianum; International Journal of ChemTech Research;2015, Vol.8, No.11 pp 194-199.
38. M. Thamima and S. Karuppuchamy; Microwave Assisted Synthesis of Zinc Oxide Nanoparticles; International Journal of ChemTech Research;2015, Vol.8, No.11 pp 250-256.
39. Joseph Sagaya Kennedy.A, Johnson.I; PL studies on NiO nanoflakes using natural Tabernaemontana Divaricata plant Leaves; International Journal of ChemTech Research;2016, Vol.8, No.11 pp 316-321.
40. S. Kavitha, R. Shilpa, D. Padmanabhan, A. Angelin; Preparation and characterization of SiO_2 nanoparticles doped carbonized Zygosaccharomyces bailli for arsenic deduction; International Journal of ChemTech Research;2015, Vol.8, No.11 pp 450-456.
41. R.Suganya, N.Krishnaveni, T.S.Senthil; Synthesis and Characterization of Zinc oxide Nanocrystals from Chemical and Biological methods and its Photocatalytic activities; International Journal of ChemTech Research;2015, Vol.8, No.11 pp 490-496.
42. Gulam Rabbani, Shivaji Jadhav, Megha Rai and Mazhar Farooqui; Synthesis and Characterization of new precursor for conducting polymer-based thin film of PANI nanocomposites containing ZnOin aqueous solution.; International Journal of ChemTech Research;2015, Vol.8, No.12 pp 386-394.
43. Savitha Elango, Kalainathan Sivaperuman; Sol-Gel mediated synthesis of tri-doped TiO_2Nanoparticles towards application of photo catalysis and its kinetic study; International Journal of ChemTech Research;2015 Vol.8, No.12 pp 588-597.
44. S. Rajeshkumar; Green Synthesis of Different Sized Antimicrobial Silver Nanoparticles using Different Parts of Plants – A Review, International Journal of ChemTech Research, 2016,Vol.9, No.04 pp 197-208.
45. Boualouache Adel, Belamri Laid, Boucenna Ali, Khalili Benyoucef, Preparation and Characterization of Metals nanostructures supported on zeolitic and clay, application in the transformation of glycerol, International Journal of ChemTech Research,2016, Vol.9, No.03 pp 491-499.

*****