

Eco-Friendly And Solvent Free Synthesis Of Cerium Oxide Nano Particles Using Methacrylic Acid As Organic Dispersant. An Extended Application to the Removal of Orange G Dye.

A.Sridhar¹, M.Selvaraj², S.S.Jayanthi^{3,*}

Department of Chemistry, Guru Nanak College Velachery, Chennai -42 Tamil Nadu, INDIA

*Department of Chemistry, Guru Nanak College, Velachery, Chennai -42

Corresponding Author: S.S.Jayanthi

ABSTRACT

Cerium oxide nanoparticles have been synthesized by microwave method using cerium nitrate and methacrylic acid as precursors. The material was structurally characterized by XRD and SEM and the optical characterization was carried out using UV-visible and Photoluminescence spectro fluorimeter techniques. The X ray studies reveal the face centered cubic structures for cerium oxide nano particles. The purity of the sample was confirmed using XRD and EDAX. The absorption studies are used to confirm the bleaching of the dye in the presence of cerium oxide nano particle. The decolourization of the dye and also the decrease in the absorption peak confirms the removal of the dye..

Keywords: Solvent free synthesis, Optical properties, Blue shift, Luminescence, bleaching of dye.

Date of Submission: 15-08-2017

Date of acceptance: 09-09-2017

I. INTRODUCTION:

Cerium oxide (CeO₂) and ceria based materials have been investigated widely in recent years due to their potential applications in catalysis [1-6] and photo catalysis [7, 8], electronic, ceramic and gas sensors, solid oxide fuel cells (SOFC) and solar cells [9-13].etc., CeO₂ is a chemically stable oxide which has an outstanding capacity to store or release oxygen due to the variation in the oxidation state between +3 and +4. This varying oxidation state, make cerium to play an important role in scavenging reactive oxygen and nitrogen species which makes it a suitable candidate in nano biology and regenerative medicine[14].

Several methods have been reported to synthesize CeO₂ nanostructures with different morphologies, such as hydrothermal [15, 16] solvothermal [17, 18] microwave-assisted hydrothermal [19] microemulsion [20], chemical precipitation [21] urea-nitrate combustion [22], reverse micelle route [23] and sonochemical [24] etc. Among these preparation methods, microwave-assisted method is a simple and economic way to prepare nanomaterials. Hence this method has been successfully applied for the preparation of a variety of nanosized inorganic materials.

The synthesis of cerium oxide nano particles reported by H. Yang *et al.* [26] using microwave from ceric ammonium nitrate and sodium hydroxide in aqueous medium V. D. Araujo *et al.* [27] reported

microwave assisted hydrothermal synthesis using cerium nitrate and sodium hydroxide Hui Wang *et al.* [28] reported preparation of CeO₂ by microwave induced method using cerium ammonium nitrate, Hexa methylene tetramine, Poly ethylene glycol, in 100ml distilled water. B. S. Shirke [29] synthesized cerium oxide nano particle using propylene glycol as a precursor in a microwave method. In all the above methods, in addition to the precursor they used other materials to maintain the pH. Hence there are lot of possibility for the contamination But in our method, we limit the use of reagents and hence the chance of contamination is very less. We already reported the formation of zinc oxide and cerium oxide nano particle using conventional solid state method using glycerol as stabilizing agent [30]. In this current investigation, we bring out the effect of changing the dispersant.

Synthetic dyes are widely used in a number of industries such as textile and leather industries, paper printing, cosmetics, and pharmaceuticals. It is estimated to be more than 10000 commercially available dyes with over 7×10⁵ tons of dye-stuff produced annually. Azo dyes represent about 60-70% of the dyes used in textile industry. Some of them show aquatic toxicity or allergenic effects and under reductive conditions they produce aromatic amines that are carcinogenic. Azo dyes represent a class of synthetic, colored, organic compounds which are characterized by the presence of one or more azo

bonds. These dyes belong to the most toxic ones compared to other forms of dyes. Large quantities of these dyes (10-15% of the total world production) are released into the waste water (typical concentration 10-200 mg L⁻¹), the presence of which poses a major threat to the aquatic organisms as well as animals and humans because of their non-biodegradability, toxicity and potential carcinogenic nature.

The methods such as filtration, coagulation, flocculation, ion exchange, photo catalytic degradation are unsatisfactory for wastewater treatment because are expensive and may produce more toxic by-products. Among the various available water treatment techniques, adsorption is the most reliable and efficient technique for dye removal, despite a fact that usually the adsorbent needs to be regenerated what increases the cost of the process. In our current study, one of the major effluents from the textile industry is Orange G and it is eliminated using Cerium oxide nano particle.

II. 2. EXPERIMENTAL:

Cerium nitrate hexa hydrate Ce(NO₃)₂.6H₂O. A.C.S. reagent (sigma Aldrich 99% purity by weight) and the Methacrylic acid were obtained from Merck. All the reagents used were of analytical grade purity and hence were used without further purification. About 4.3 g of cerium nitrate hexa hydrate was mixed with few drops of methacrylic acid and kept in the microwave for 3 minutes (30 seconds on and off method). The amount of methacrylic acid (stabilizing agent) was adjusted after several trials. The substance was crumbled into yellow crystalline powder. The yellow crystalline powder was annealed at 500 °C for 6 hours. To study the bleaching of the orange G dye, 0.05 g of cerium oxide nano particle was added to the dye solution.

III. RESULTS AND DISCUSSION:

3.1 Structural characterization:

3.1.1 XRD studies:

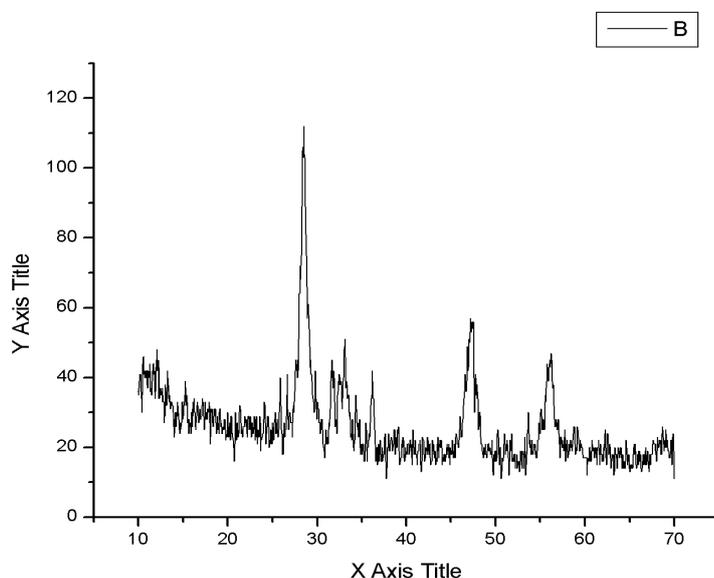


Fig.1. XRD spectrum of cerium oxide nanoparticle synthesized using microwave

The x-ray diffraction pattern was studied using scifert - X -ray diffractometer with a CuK α (1.5406Å) radiation. The diffracted intensities were recorded from 10° to 70° angle. The absence of extra peak claims the purity of the substance and also confirms the complete conversion of Cerium nitrate into CeO₂. In both the methods, all the diffraction peaks agreed well with the standard values for the face centered cubic structure of cerium oxide and matches well with the JCPDS number 81-0792. The crystalline size of the sample was obtained from Scherrer's formula.

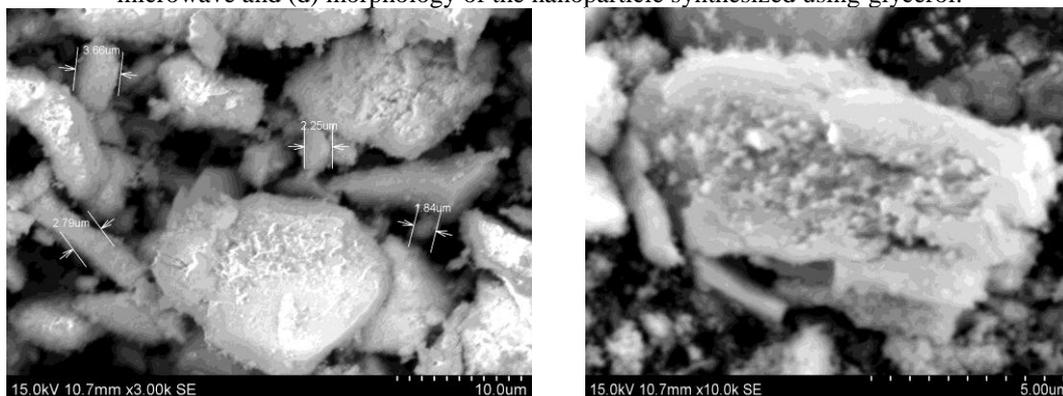
$$D = 0.9\lambda / \beta \cos\theta \quad \text{eq (1)}$$

Where D-Crystallite size, λ - Wavelength (1.5406 Å), β -Full width at the half maximum of the peak (111) = 0.2525 θ - is the diffraction angle which is half of $2\theta = 28.74$

The average crystalline size found to be around 56 nm It was found that the size decreases by microwave heating. The average particle size of the products prepared by conventional and microwave-assisted method are calculated to be ca. 59 and ca.56 nm respectively.

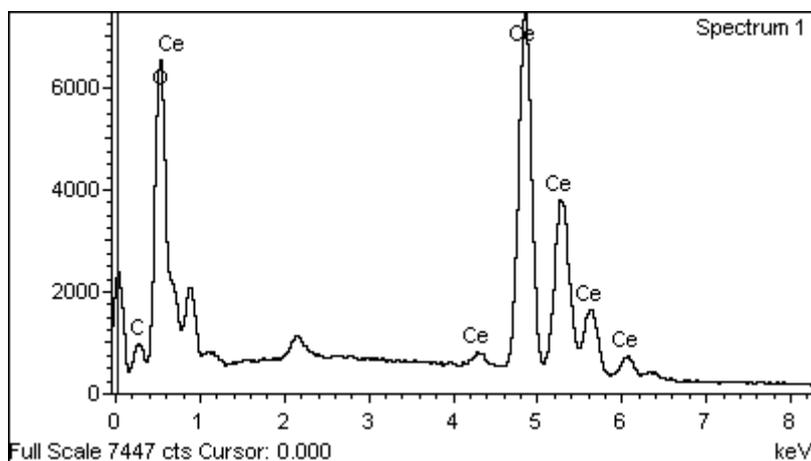
3.1.2 FESEM and EDAX analysis:

Fig. 2. SEM images of cerium oxide nanoparticles. (a) morphology of the nanoparticle synthesized using microwave and (d) morphology of the nanoparticle synthesized using glycerol.



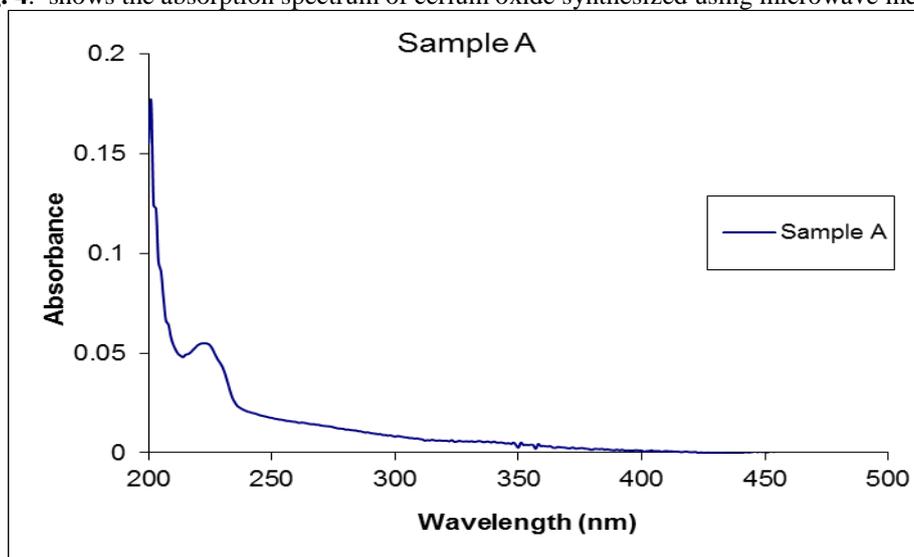
The SEM image show particle aggregates of irregular shapes and larger size. The EDAX analysis

represented in Fig. 3 shows peaks only for Cerium and Oxygen which assures the purity of the sample.



3.1.3 Optical Characterization and Structural characterization:

Fig. 4. shows the absorption spectrum of cerium oxide synthesized using microwave method.



Cerium oxide nano particle synthesized using methacrylic acid shows a absorption peak at 226 nm due to the charge transfer between the oxygen and cerium in CeO₂. The absorption peak shows a blue-shift (from 310 nm to 226 nm) along with change in the mode of organic dispersant from glycerol to methacrylic acid. The blue shift confirms the size reduction in CeO₂ when prepared using

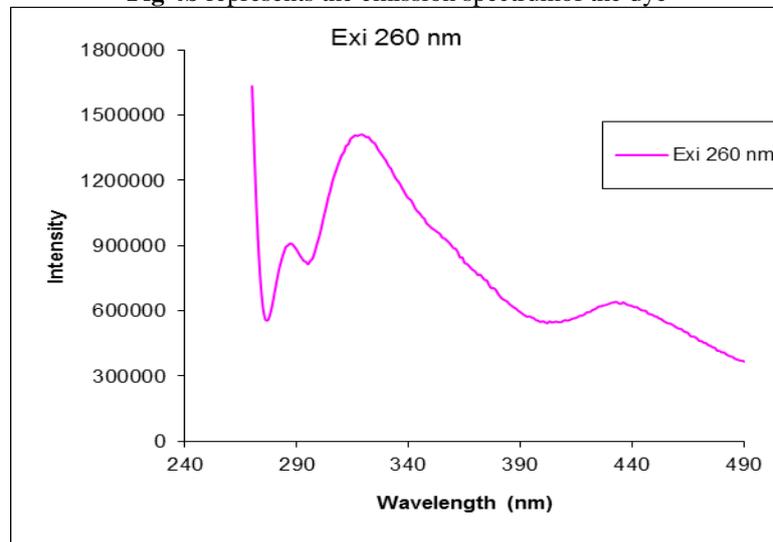
methacrylic acid as organic dispersant. [32]. the approximate bandgap value calculated from the λ_{max} using the formula given below.

$$\text{Energy band gap} = 1.2/\lambda_{max} \text{ (eV)} \quad (2)$$

The band gap value calculated from the above equation is around .

3.1.4 Luminescence spectral studies :

Fig 4b represents the emission spectrum of the dye



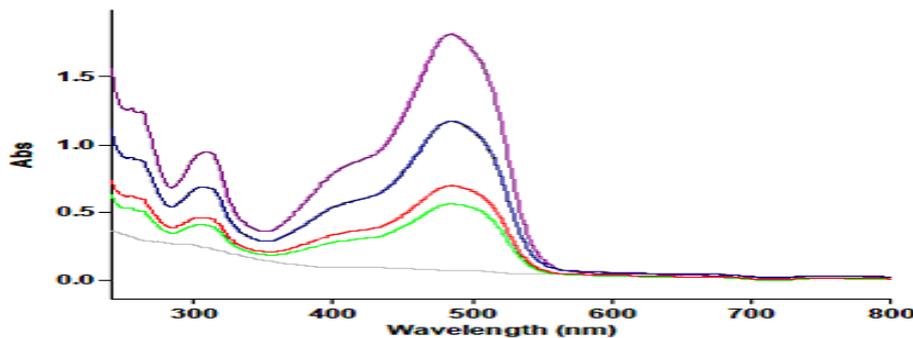
The emission spectrum of cerium oxide nanoparticles shows peaks around 318 and a shoulder was observed around 436 nm. The peaks are blue shifted compared to the peaks observed for cerium oxide prepared using glycerol (378 nm, 438 nm and 484 nm)[ref]. The investigation showed that the emission bands ranging from 400 to 500 nm for CeO₂ sample are attributed to the hopping from different defect levels of the range from Ce 4f to O 2p band [33]. In addition to this, the intensity of the peaks are very high compared to the conventional cerium oxide. This is due to the abundant defect such as dislocations which is useful for fast oxygen transportation. The appearance of emission peak

depends upon the mode of preparation and the presence of voids [34].

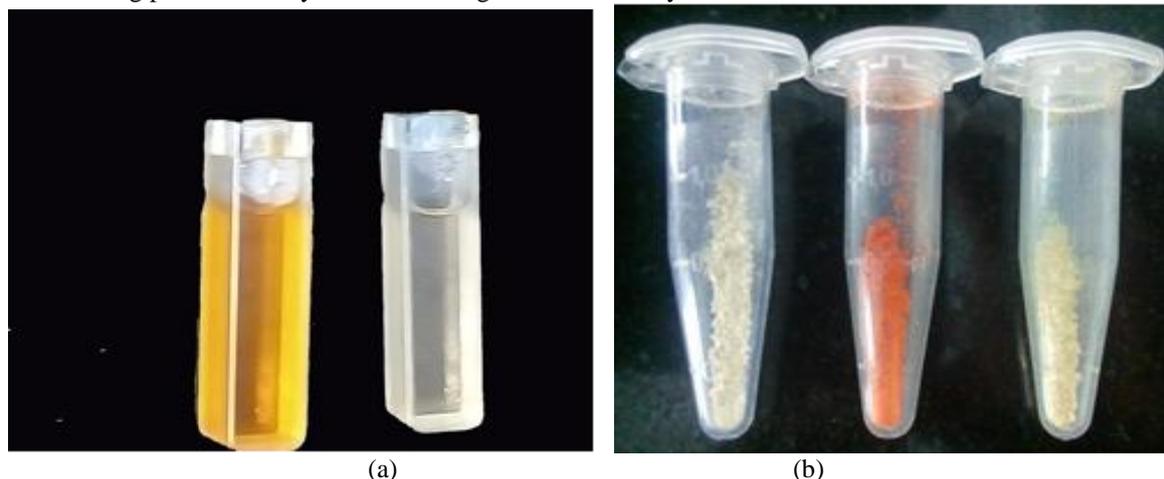
3.1.5 Removal of Orange G using cerium oxide nano particle:

The orange G dye shows strong emission around 480 nm. The absorption decreases completely in the presence of cerium oxide nano particle. The spectrum recorded shows decrease in the absorption and the peak completely disappears after 25 minutes. Cerium oxide is an excellent adsorbent and hence all the dye got adsorbed on the nano particle. The nano particle is recovered from the dye by just adding a pinch of bleaching powder.

Fig 6 represents the reduction of the dye, 5b shows the decolourised water



The following pictures clearly indicate the degradation of the dye



(a) 1-the Orange G dye before adsorption and 2 –after adsorption
(b) (1st vial–Pure ceriumoxide), (2nd vial – cerium oxide after adsorption) and (3rd vial represents cerium oxide after bleaching)

IV. CONCLUSION

The CeO₂ nanoparticles were successfully synthesized by the solvent free and ecofriendly method using methacrylic acid as organic dispersant. The structural and optical characterization was carried out using XRD, SEM, absorption and fluorescence measurements respectively. The structural morphology changes with the change in the organic dispersant. The shape changes from to irregular and the size reduces from 56 nm to . The XRD spectrum shows the nanoparticles are crystalline pure phase CeO₂ nanoparticles with face centered cubic structure and the mean grain size was around 59 nm. The absorption shows blue shift in the absorption maximum from 310 nm to 226 nm which reflects the smaller size of the particle. The compound shows luminescence spectra with maxima at 318 nm and 436 nm. The cerium oxide nano particle acts as an adsorbant and it bleaches the orange dye effectively which was confirmed from the absorption studies, In future, the CeO₂ can be used as a potential dye remover from the waste water.

ACKNOWLEDEMENT

The authors acknowledge the **National centre for ultrafast Process, Department of Nuclear physics and Centre for Nanoscience and Nanotechnology, University of Madras** to carry out the characterization studies. The authors also acknowledge the **Management, Guru Nanak College** to carry out the synthesis in the Research Lab.

REFERENCES

- [1]. B. Parthasarathi, S.T. Aruna, K.C. Patil, M.S. Hedge, *J. Catal.* 186(1999) 36-44
- [2]. E. Florence, G. Florence, B. Jacques, *J. Catal.* 206(2002) 363-367.
- [3]. V. Solinas, E. Rombi, I. Ferino, M.G. Cutrufello, *J. Mol. Catal. A* 204 (2003) 629-635.
- [4]. D. Girija, S. Bhojya Naik, C. N. Sudhamani and B. Vinay Kumar, *Arch. of App. Sci. Research*, 3(2011) 373-382.
- [5]. S. Scire, S. Minico, C. Crisafulli, C.Satriano, A. Pistone, *Appl. Cat. B: Environmental*, 40 (2003) 43-49.
- [6]. A.Abad, P. Concepción, A. Corma and H. García, *Angew. Chem. Int. Ed.* 44(2005) 4066–4069.
- [7]. S. B. Khan, M. Faisal, M. M. Rahman, A. Jamal, *Science of the Total Environment*, 409 (2011) 2987–2992.
- [8]. SB Khan, M. Faisal, MM. Rahman, K Akhtar, AM.Asiri, A Khan, KA. *Int. J. Electrochem. Sci.*, 8 (2013) 7284 – 7297.
- [9]. J Saranya, KS Ranjith, P Saravanan, D Mangalaraj, RT RajendraKumar, *Mater. Sci. Semicond. Process.* 26 (2014) 218–224.
- [10]. N. Izu , I Matsubara , T Itoh , T Akamatsu , W Shin, the special issue *Gas Sensors – 13*(2013) 3252-3261.
- [11]. P. Jasinski, T.Suzuki, H.U.Anderson, *Sens. Actuators, B* 95 (2003)73–77.
- [12]. Y. Ma, X. Wang, S. Li, M. S. Toprak, B. Zhu, M. Muhammed, *Adv. Mater.* Vol. 22 (2010) 1640–1644.
- [13]. Corma, A., Atienzar, P., Garcia, H. & Chane-Ching, J. Y. *Nat. Mater.* 3 (2004) 394–397.
- [14]. Can Xu, Xiaogang Qu, *NPG Asia Materials* (2014) 6, e90.

- [15]. Masui T, Hirai H, Imanaka, J. of Mater. Sci. Lett. 21 (2002) 489–491.
- [16]. K Kaneko, K Inoke, B Freitag, Ana B. Hungria, Paul A. Midgley, Thomas W.Hansen, J Zhang, S Ohara and T Adschiri, *Nano Lett.*, 7(2007) 421–425.
- [17]. A.B. Sifontes, G. Gonzalez, J.L. Ochoa, L.M. Tovar, T. Zoltan, E. Can˜izales, *Materials Research Bulletin* 46 (2011) 1794–1799.
- [18]. Dengsong Zhang, Fuhuan Niu, Hongrui Li, Liyi Shi, Jianhui Fang, *Powder Technology* 207 (2011) 35–41.
- [19]. G. Feng, L. Qingyi, K. Sridhar, *J. of nanosci. and nanotech* 6 (2006), 3812-3819.
- [20]. E Kockrick, C Schragea, A Grigasa, D Geigerb, S Kaskela. *J. Solid State Chem.* 181(2008) 1614–1620.
- [21]. J. Jasmine Ketzial and A. Samson Nesaraj, *J. Ceram. Process. Research*, 12(2011) 74-79.
- [22]. G. Avgouropoulos and T. Ioannides, *Appl. Catal., A*, 244(2003) 155–167.
- [23]. S. Sathyamurthy, K. J. Leonard, R. T. Dabestani and M. P. Paranthaman, *Nanotechnology*, 16(2005) 1960-1964.
- [24]. L. Yin, Y. Wang, G. Pang, Y. Koltypin, A. Gedanken, *J. Colloid Interface Sci.* 246 (2002) 78-84.
- [25]. P. lidstroˆm, J. Tierney, *Microwave assisted organic synthesis—a review*, *Tetrahedron* 57 (2001) 9225
- [26]. H. Yang, C. Huang, A. Tang, X. Zhang, W. Yang, *Materials Research Bulletin*, 40 (2005) 1690–1695.
- [27]. V. D. Araujo, W. Avansi, H. B. de Carvalho, M. L. Moreira, E. Longo, C. Ribeiro and M. I. B. Bernardi, *CrystEngComm*, 14 (2012) 1150-1154.
- [28]. Hui Wang, Jun-Jie Zhu, Jian-Min Zhu, Xue-Hong Liao, Shu Xu, Tao Ding and Hong-Yuan Chen, *Phys. Chem. Chem. Phys.*, 4 (2002) 3794–3799.
- [29]. B.S.Shirke, A.A. Patil, P.P.Hankare, K. M. Garadkar *Journal of material Science, Material electronics*, 22 (2011), 200-203.
- [30]. (a) M. Saravanan, S. Dhivakar, S.S. Jayanthi, *Mater. Lett.*, 67 (2012) 128-130.
- [31]. S.S. Jayanthi, *Nano science and Nanotechnology an Indian journal*, NSNTAIJ, 8 (2014), 274 -278.
- [32]. Chyi-Ching Hwang, Ting-Han Huang, Jih-Sheng Tsai, Cheng-Shiung Lin, Cheng-Hsiung Peng *Materials Science and Engineering B* 132 (2006) 229-238.
- [33]. Chenguo Hu, Zuwei Zhang, Hong Liu, Puxian Gao, Zhong Lin Wang, *Nanotechnology* 17 (2006) 5983- 5987.
- [34]. Y.W. Zhang, S.Rui, C.S.Liao, C.H.Yans, *J. Phys. Chem. B*, 107(2003) 10159-10167.
- [35]. A.C. Cabrala, L.S.Cavalcanteb, R.C.Deusc, E.Longod, A.Z.Simˆoes,n, F.Mouraa, *Ceramics International*, 40(2014) 4445–4453.

International Journal of Engineering Research and Applications (IJERA) is **UGC approved** Journal with Sl. No. 4525, Journal no. 47088. Indexed in Cross Ref, Index Copernicus (ICV 80.82), NASA, Ads, Researcher Id Thomson Reuters, DOAJ.

A.Sridhar. “Eco-Friendly And Solvent Free Synthesis Of Cerium Oxide Nano Particles Using Methacrylic Acid As Organic Dispersant. An Extended Application to the Removal of Orange G Dye.” *International Journal of Engineering Research and Applications (IJERA)*, vol. 7, no. 9, 2017, pp. 01–06.