



# Synthesis of mixed Oxides of Cerium-Iron Nanostructures for Effective Removal of Heavy Metals from Waste Water

Vivekananthan.V, Selvapriya.A, Janani.D and Narendhar.C

Department of Nanotechnology, Sri Ramakrishna Engineering College Coimbatore-22, Tamilnadu, INDIA

Available online at: [www.isca.in](http://www.isca.in)

Received 30<sup>th</sup> November 2013, revised 5<sup>th</sup> February 2014, accepted 15<sup>th</sup> March 2014

## Abstract

*Cerium-iron oxide, as a mixed form or as a multi ferrite composite can be a potent material to remove organic and inorganic contaminants through affinity based binding. Being semi conducting in nature they also exhibit elevated photo-catalysis at nanoscale. This effect of photo catalysis can be utilized for degradation of dyes. The cerium-iron core-shell nanostructures were formed by simple co-precipitation technique and analyzed for stability over a period of one week. The stable suspensions were subjected to particle size analysis and zeta potential measurement. Polystyrene is a rigid polymer which can be used to fabricate a simple matrix over with a layer of cerium-iron oxide composite can be coated. This matrix will be used as a column in a simulated reactor which can effectively permeate water and remove the organic and inorganic contaminants in a normal atmospheric and environmental condition. Having high affinity for the heavy metals like cadmium and arsenic iron nanoparticles serve as the chemical affinity provider and cerium acts as a photocatalyst. The waste water can be analyzed by UV Visible spectroscopy for the amount of contaminants present before and after the treatment process to measure the distribution of the heavy metals in the samples.*

**Keywords:** X-Ray diffraction spectroscopy, UV-visible spectroscopy, photo-catalysis, polystyrene, iron-cerium oxide nanoparticles..

## Introduction

The world health organization estimates that about 25% of the diseases facing humans today occur due to long term exposure to environment pollutions including air, soil and water pollution. Improper management of industrial waste<sup>1</sup> is the main cause of environmental pollution. Heavy metals are mainly responsible that are responsible for polluting ground water that are harmful to both plants and animals.

Different contaminants are released to wastewater with the rapid industrialization of human society, including heavy metal ions, organics, bacteria, viruses, and so on, which are serious harmful to human health. Among all water contaminations, heavy metal ions, such as  $Pb^{++}$ ,  $Cd^{++}$ ,  $Zn^{++}$ ,  $Ni^{++}$  and  $Hg^{++}$  are highly toxic and are non-biodegradable, can cause severe health problems in animals and human beings.

The harmful effects of Cd lead a number of acute and chronic disorders, such as renal damage, emphysema, hypertension, testicular atrophy, and skeletal malformation in fetus<sup>2</sup>. Wastewater from many industries, including chemical manufacturing, battery manufacturing industries, metallurgical, leather tanning, and mining contain these heavy metal ions. These wastewater with heavy metal ions are discharged into natural water directly, not only threat the aquatic organisms, but may be enriched by precipitation, adsorption, and harmed human health through the food chain. Thus, the removal of such

toxic metal ions from wastewater is becoming a crucial issue. Heavy metals like arsenic, cadmium and mercury are an important contributor to various forms of carcinogenesis, cardiovascular, inflammatory and neurodegenerative<sup>3</sup> diseases.

Dyes and pigments are a growing pollution problem in the industrial and household wastewater as a result of their extensive use and relative stability towards degradation. The dyes from various industries are engineered to be resistant to all kinds of treatments without fading. They need to sustain both alkaline and acidic environment; they need to withstand washing with soaps, bleaching agents and microbiological fading, to be resistant to light and ultraviolet irradiation etc. Obviously, the better the stability of dyes achieved in the consumer products, the worse problem they cause in the wastewater stream<sup>4</sup>.

Dyes are able to color water even in concentrations as low as 1mg/liter. Textile wastewater contains typically a much higher amount of the dye content: 200 mg/liter, which gives intense coloration. While color is easily recognizable in the water stream, an additional environmental hazard comes from the fact that many dyes are either toxic or become toxic when being gradually decomposed in the ecosystem. Hence the ecosystem will get unbalanced. The dyes undergo bioaccumulation in living organisms<sup>4</sup>.

Many dyes are carcinogenic (can cause mutations in organisms), as well as genotoxic (can damage DNA). Dyes preserve their ability to absorb sunlight in water and as they reduce the photosynthetic capability of aquatic plants and microorganisms, even when the dilution of the wastewater camouflages the presence of the dye<sup>4</sup>.

The problem of bioaccumulation of dyes in the aquatic organisms is mounting because of the multiple sources of the dye contamination such as industries on textile, food processing, paper and printing, cosmetic, pharmaceutical, detergent, pesticide and leather tanneries<sup>4</sup>.

Iron-Cerium oxide, in mixed oxides state or as a multi ferrite composite can be a potent material to remove these contaminants through affinity based binding and subsequent removal of these heavy metals. Being semi conducting in nature they also exhibit elevated photo catalysis at Nanoscale.

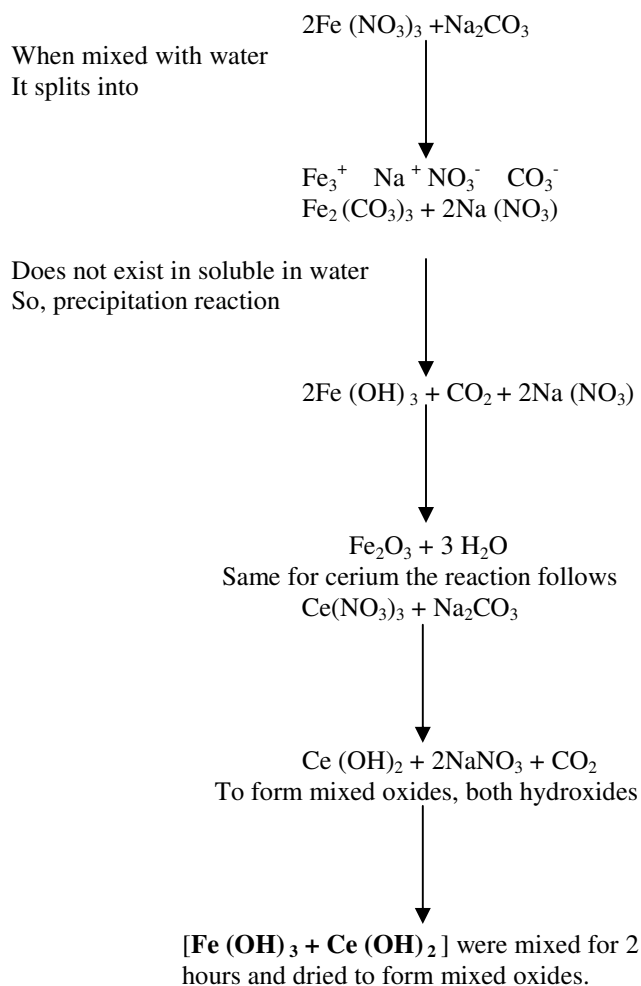
Iron oxide having outstanding stability, cost-effectiveness, oxidative power, high resistance to corrosion, and environmentally friendly properties could fulfill many requirement of a good photocatalyst<sup>5</sup>. And affinity towards heavy metals can used to remove heavy metal contaminations. One more significant advantage of this material is its absorbance in the visible region, which covers 43% of solar light. However, this semiconductor material has low band gap energy, poor conductivity and high chances for electron-hole ( $e^-$ - $h^+$ ) recombination<sup>6</sup>, which limits its photo catalytic application. In order to address these issues, many attempts have been made such as incorporation of heteroatom (e.g., Si, Bi, Ti, Mn, Pt. and Ta), quantum confinement, and architectural control<sup>7</sup>.

Ceria is known to be the best material due to its redox behavior ( $Ce^{4+}$   $Ce^{3+}$ ), oxygen storage capacity (OSC) etc.  $CeO_2$ -based materials have various applications such as three-way catalysts (TWC), fuel cell processes, catalytic wet oxidation, and hybrid solar cells. Energy Band gap of ceria is 3.1 eV as reported by many researchers which is transparent to the visible light and absorbing only UV light from the solar spectrum where only 5 % solar light is available. The mixed oxides systems have the ability to obtain structures in combinations with the properties that neither individual oxide possesses. Coupling of two semiconductors (e.g.,  $CdS/TiO_2$ ,  $CdS/ZnO$ ,  $TiO_2/SnO_2$ , and  $CdSe/TiO_2$ ) with suitable energetics can significantly improve the selectivity and enhance the charge separation yield<sup>8</sup>. The combination of ceria with  $Fe_2O_3$  would be an efficient photo catalyst and will fulfill the seeking property of individual material<sup>7</sup>. To enhance the redox property and thermal stability of pure  $CeO_2$ ,  $Fe_2O_3$  is often mixed.

## Material and Methods

Iron nitrate, cerium(III) nitrate hexahydrate, sodium carbonate. All chemicals are purchased from Sigma Alderich and Merck and used without any further purification.

**Method of Syhthesis:**  $Fe(NO_3)_3 \cdot 9H_2O$  and  $Ce(NO_3)_3 \cdot 6H_2O$  were taken individually and added to the aqueous solution of  $Na_2CO_3$  and both the solutions was mixed and stirred for 2 hours the precipitate was washed for several times using purified water and dried at  $110^\circ C$  in a hot air oven for 3 hours. Then the powder was collected and calcined at  $400^\circ C$  for 3 hours. Then the size of the particles was analyzed using particle size analyzer.



## Results and Discussion

**Observation:** i. When using liquor ammonia as precipitating agent, particle size could not be controlled since it is a fast precipitating agent. In all the three cases noted in table particles size were found to be more than 500nm. ii. Using ammonia in cold bath results in poly dispersed particles. iii. Using surfactant can control the growth of the particles. iv. Since surfactant is amphiphilic it has hydrophobic tail and hydrophilic head, so it can control growth of particles. v. Using sodium hydroxide reduce the size below 500nm, but to get controlled size without using surfactant slow precipitating agent must be used

**Table-1**  
**Size Analysis**

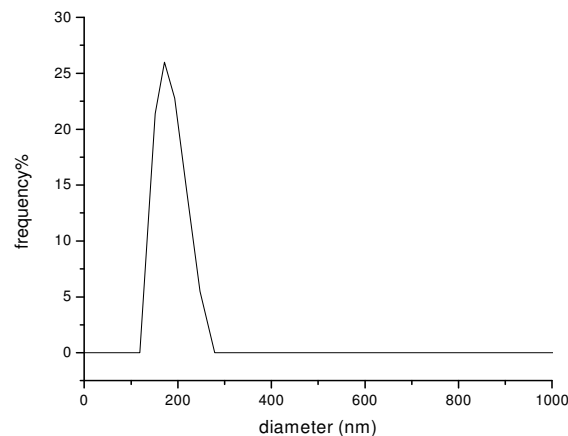
| Precursor used | Precipitating agent used | Optimum conditions | Particle size Mean(nm)  |
|----------------|--------------------------|--------------------|-------------------------|
| Cerium         | Liquor ammonia           | Room temperature   | 652.5nm(poly dispersed) |
| Iron-cerium    | Liquor ammonia           | Room temperature   | 704.7nm                 |
| Iron-cerium    | Liquor ammonia           | Cold bath          | 204.4nm(poly dispersed) |
| Cerium         | Sodium hydroxide         | Room temperature   | 273.7nm(poly dispersed) |
| Iron           | Sodium hydroxide         | Room temperature   | 466.7nm                 |
| Iron cerium    | Sodium hydroxide         | Room temperature   | 815.5nm                 |
| Iron cerium    | Sodium hydroxide         | Cold bath          | 189.2nm(poly dispersed) |

**Table-2**  
**Size analysis**

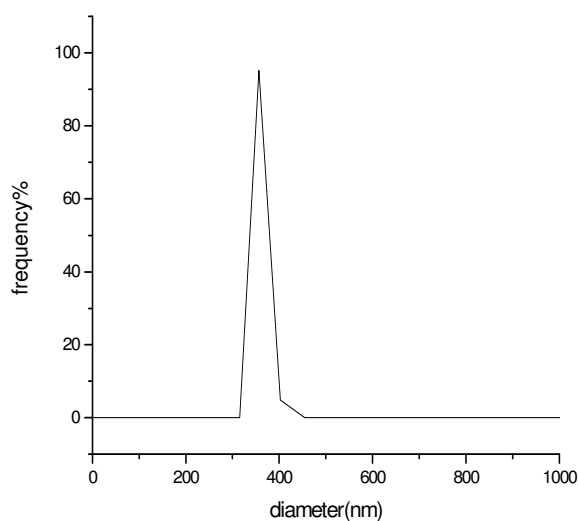
| Precursor used | Precipitating agent used | Optimum conditions | Particle size mean(nm) |
|----------------|--------------------------|--------------------|------------------------|
| Iron           | Sodium carbonate         | Room temperature   | 168.9                  |
| Cerium         | Sodium carbonate         | Room temperature   | 337.7                  |
| Iron cerium    | Sodium carbonate         | Room temperature   | 164.2                  |

**Observation:** i. Iron and cerium were mixed individually with sodium carbonate the size was not completely reduced. ii. When it was mixed together and stirred for few hours' size of the particle is controlled. This is because of Competitive inhibition. iii. Competitive inhibition is a form of enzyme inhibition by which an enzyme may bind either the inhibitor or the substrate but never both at the same time

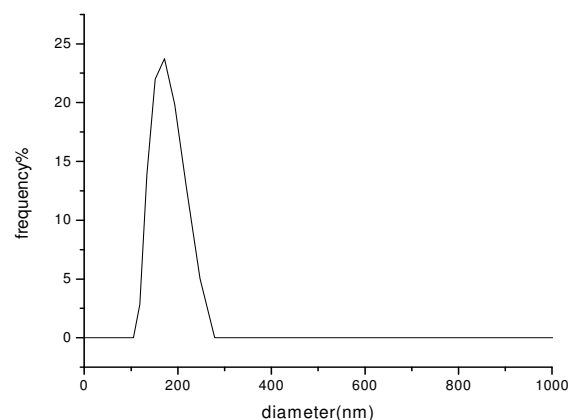
**Results-Particulate Analyser:** The most important methods for the characterization of particles in the nanometer and micrometer range are dynamic and static laser light scattering (laser diffraction). The static laser light scattering can be used for the analysis of emulsions, suspensions and dry samples. For liquid samples scattering occurs due to Brownian motion<sup>9</sup>.



**Figure-2**  
**Particle Size Analyzer Result for Iron Oxide**



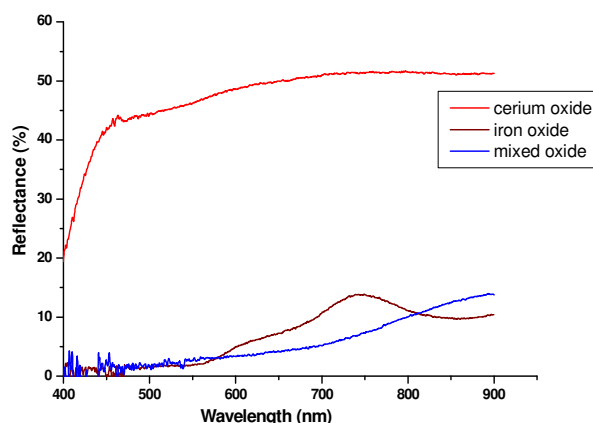
**Figure-1**  
**Particle Size Analyzer Results for Cerium Oxide**



**Figure-3**  
**Particle Size Analyzer Result for Iron-Cerium Oxide**

**UV-Visible Analysis:** It refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared (NIR)) ranges. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state<sup>10</sup>, while absorption measures transitions from the ground state to the excited state.

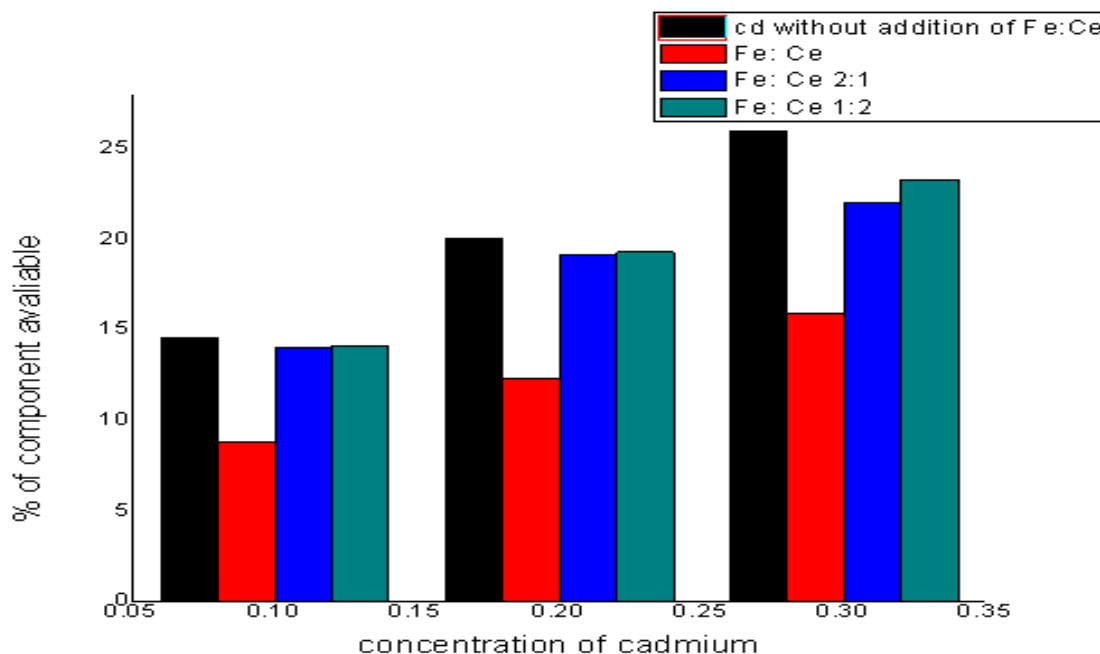
**Observation:** i. The graph is plotted for different concentration of cadmium. From the result it is observed that at the equal ratio of iron- cerium binding of heavy metal was efficient. ii. Binding efficiency was analyzed for various heavy metals like chromium and lead. In all the cases the results are similar and plotted in graph.



**Figure-4**  
 UV Analysis to show variation in the formation of mixed oxides

**Table-3**  
 Heavy Metal Binding for Cadmium

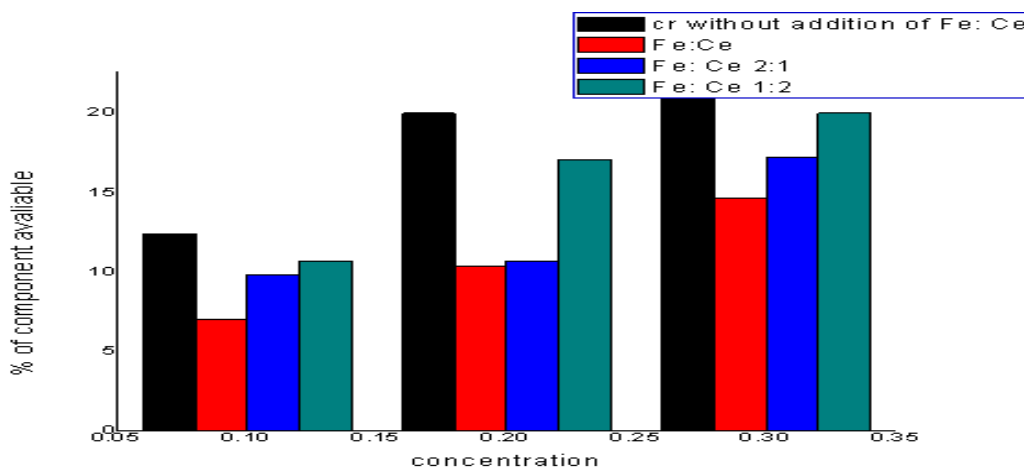
| Concentration of cadmium | % component available before the addition of iron-cerium | % component available after the addition of iron-cerium(equal ratio) | % component available after the addition of iron-cerium(Fe(2):Ce(1)) | % component available after the addition of iron-cerium(Fe(1):Ce(2)) |
|--------------------------|--|--|--|--|
| 0.1                      | 14.6   | 8.8  | 14   | 14.1   |
| 0.2                      | 20   | 12.3   | 19.1   | 19.3   |
| 0.3                      | 26   | 15.9   | 22   | 23.3   |



**Figure-5**  
 Cadmium without Addition of FE: CE

**Table-4**  
**For chromium**

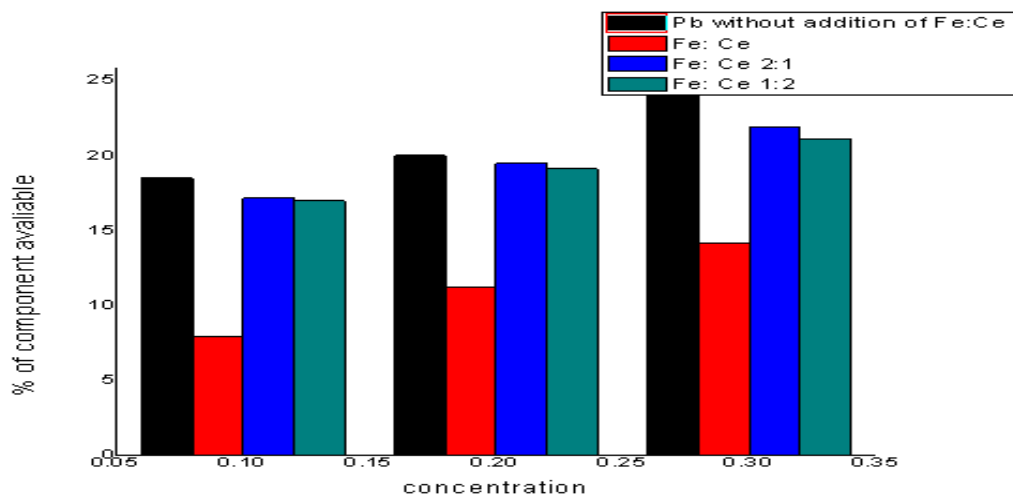
| Concentration of chromium | % component available before the addition of iron-cerium | % component available after the addition of iron-cerium(equal ratio) | % component available after the addition of iron-cerium(Fe(2):Ce(1)) | % component available after the addition of iron-cerium(Fe(1):Ce(2)) |
|---------------------------|--|--|--|--|
| 0.1                       | 12.4   | 7  | 9.83   | 10.7   |
| 0.2                       | 20   | 10.4   | 10.7   | 17.1   |
| 0.3                       | 21   | 14.65  | 17.2   | 20   |



**Figure-6**  
**Chromium without Addition of FE : CE**

**Table-5**  
**For lead**

| Concentration of lead | % component available before the addition of iron-cerium | % component available after the addition of iron-cerium(equal ratio) | % component available after the addition of iron-cerium(Fe(2):Ce(1)) | % component available after the addition of iron-cerium(Fe(1):Ce(2)) |
|-----------------------|--|--|--|--|
| 0.1                   | 18.5   | 7.9  | 17.17  | 17   |
| 0.2                   | 20   | 11.2   | 19.5   | 19.13  |
| 0.3                   | 24   | 14.12  | 21.9   | 21.07  |



**Figure-7**  
**Lead Without Addition of FE : CE**

## Conclusion

The synthesis of mesoporous and nanostructured iron-cerium mixed oxide for heavy metal removal, degradation of organic contaminations and dye degradations. UV-Visible spectroscopy reveals the formation of mixed oxide. Removal of heavy metals was analyzed by using UV-Visible spectrometry

## Reference

1. Xue Y., Luan Q.F., Yang D., Yao X. and Zhou K.B., Direct Evidence for Hydroxyl Radical Scavenging Activity of Cerium Oxide Nanoparticles, *Journal of Physical Chemistry C* (2011)
2. Narendhar C., Murugu mohan kumar S., Regitha M., Karpanai selvan B., Selvapriya A. and Janani D., Facile Synthesis of Iron Oxide Nanoparticles and Their Antimicrobial Activity, *Asian Journal of Chemistry*; **25**, Supplementary Issue (2013)
3. Luciano Carlos, Fernando S. García Einschlag, Mónica C. González and Daniel O. Mártire, Applications of Magnetite Nanoparticles for Heavy Metal Removal from Wastewater, *doi.org* (2013)
4. Gajendra Kumar Pradhan and Parida K.M., Fabrication of iron-cerium mixed oxide: an efficient photo catalyst for dye degradation, *International Journal of Engineering, Science and Technology*, **2(9)**, (2010)
5. Sayan Bhattacharya, Synthesis, characterization and arsenic (III) sorption behavior of Cerium Aluminum mixed oxide nanoparticles: An effective sorbent in arsenic remediation, Sayan Bhattacharya, *J. Ecosyst Ecogr* (2012)
6. Jinyi Deng, Subarna Banerjee, Susanta K. Mohapatra, York R. Smith and Mano Misra, Bismuth Iron Oxide Nanoparticles as Photocatalyst for Solar Hydrogen Generation from Water, *Journal of Fundamentals of Renewable Energy and Applications*, **1** (2011)
7. Korsvik C., Patil S., Seal S. and Self W.T., Superoxide dismutase mimetic properties exhibited by vacancy engineered ceria nanoparticles, *Chem Commun (Camb)* (2007)
8. Andra predescu, Avram nicolae, Adsorption of zn, cu and cd from waste waters by means of maghemite nanoparticles, *U.P.B. Sci. Bull., Series B*, **74(1)**, (2012)
9. Dowding J.M., Dosani T., Kumar A., Seal S. and Self W.T., Cerium oxide nanoparticles scavenge nitric oxide radical (NO), *Chem Commun (Camb)* (2012)
10. Xiangtao Wang, Yifei Guo, Li Yang, Meihua Han, Jing Zhao and Xiaoliang Cheng, Nanomaterial as Sorbents to Remove Heavy Metal Ions in Wastewater Treatment, *Environmental and Analytical Toxicology* (2012)
11. Pirmohamed T., Dowding J.M., Singh S., Wasserman B., Heckert E., Karakoti A.S., King J.E., Seal S. and Self W.T., Nano ceria exhibit redox state-dependent catalase mimetic activity, *Chem Commun (Camb)* (2010)
12. Melissa S. Wason Cerium oxide nanoparticles: potential applications for cancer and other diseases, *American journal translation research*, (2013)
13. Jing Hu, Guohua Chen and Irene M.C. Lo, Selective Removal of Heavy Metals from Industrial Wastewater Using Maghemite Nanoparticle: Performance and Mechanisms, *ASCE 0733-9372* (2006)
14. Ghosh N.N., Synthesis of Nanostructured Magnetic Mixed-Oxide Ferrite Powders by Using A Novel Chemical Method, *Mat. Res. Soc. Symp. Proc.*, **720** (2002)