



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

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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 waste¹ 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 fetus². 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 neurodegenerative³ 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 stream⁴.

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 organisms⁴.

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 dye⁴.

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 tanneries⁴.

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.

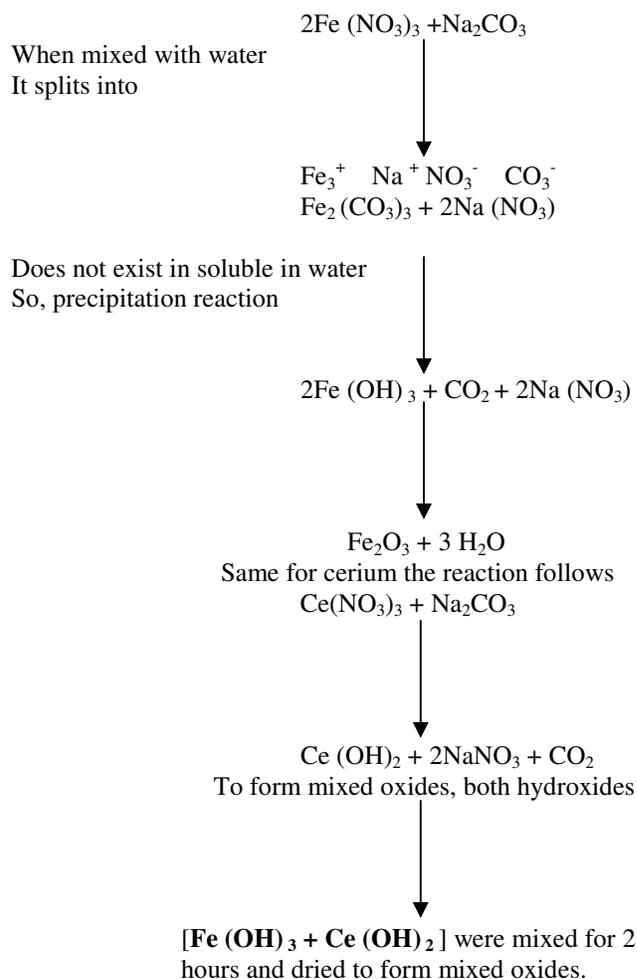
Iron oxide having outstanding stability, cost-effectiveness, oxidative power, high resistance to corrosion, and environmentally friendly properties could fulfill many requirement of a good photocatalyst⁵. And affinity towards heavy metals can used to remove heavy metal contaminations. One more significant 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^+) recombination⁶, 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 control⁷.

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 yield⁸. The combination of ceria with Fe_2O_3 would be an efficient photo catalyst and will fulfill the seeking property of individual material⁷. 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 motion⁹.

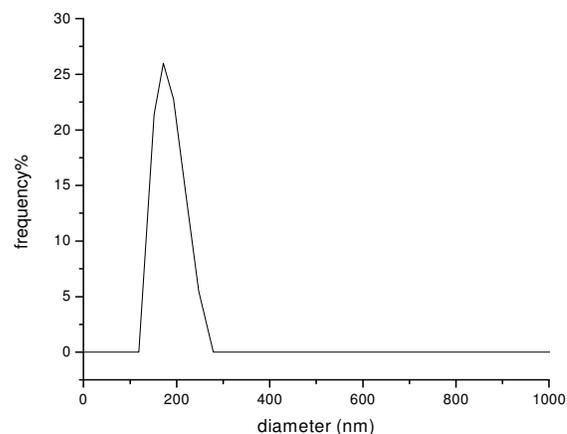


Figure-2
Particle Size Analyzer Result for Iron Oxide

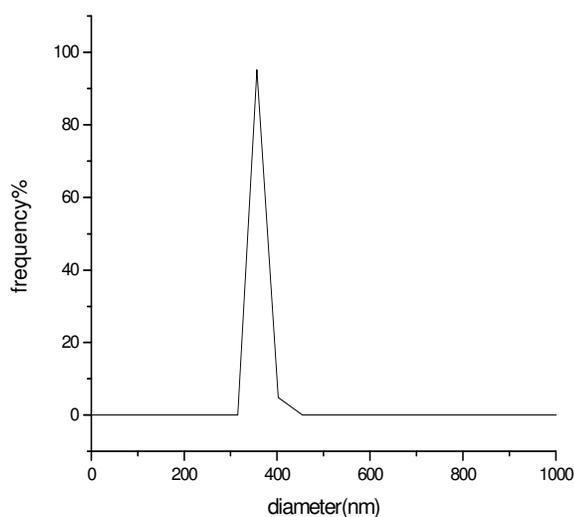


Figure-1
Particle Size Analyzer Results for Cerium Oxide

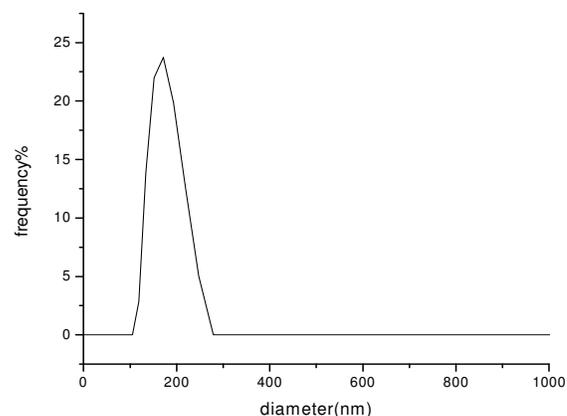


Figure-3
Particle Size Analyzer Result for Iron-Cerium Oxide

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 state¹⁰, 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.

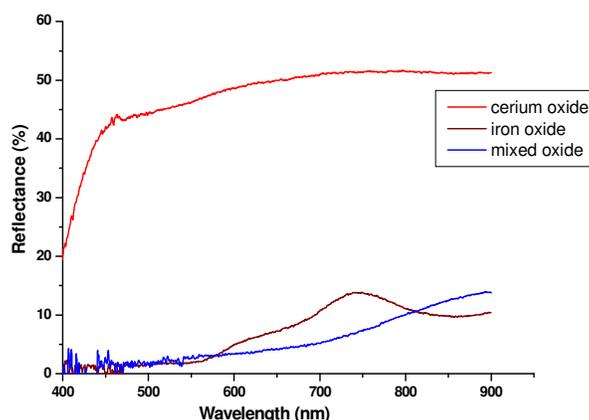


Figure-4
 UV Analysis to show variation in the formation of mixed oxides

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

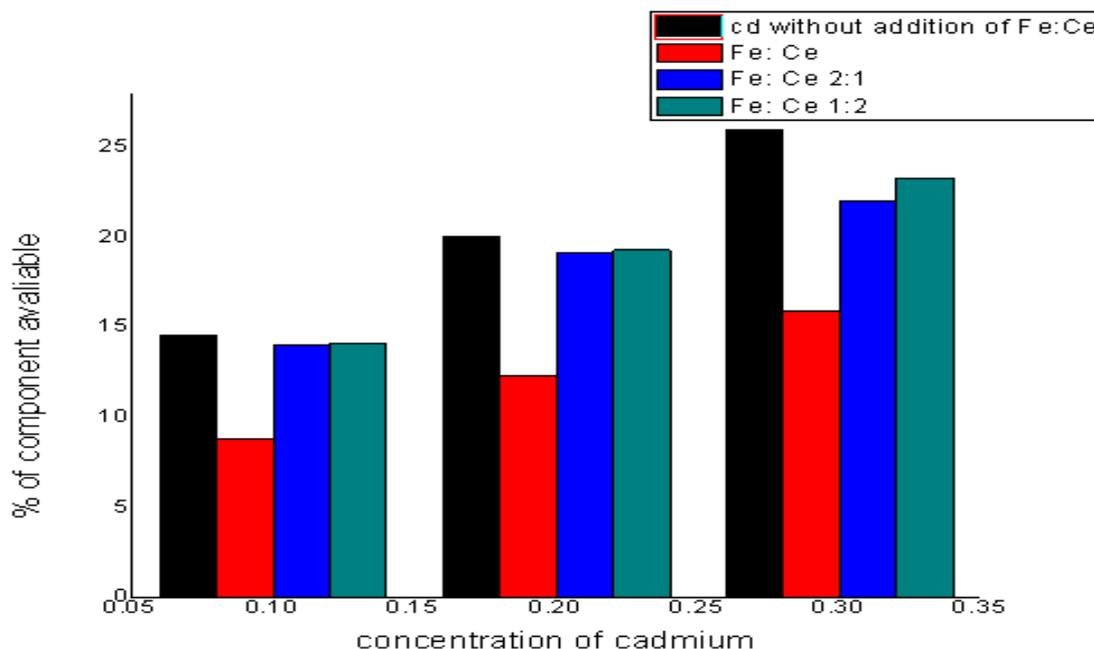


Figure-5
 Cadmium without Addition of FE: CE

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

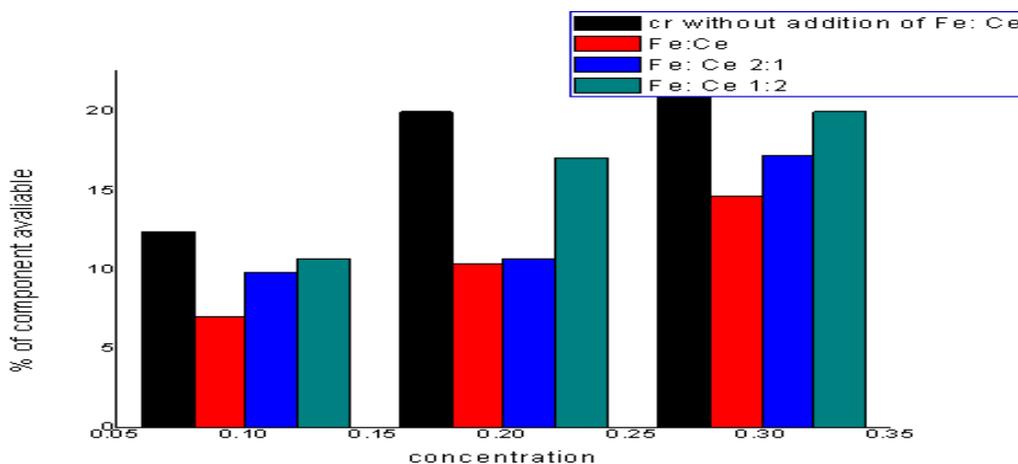


Figure-6
Chromium without Addition of FE : CE

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

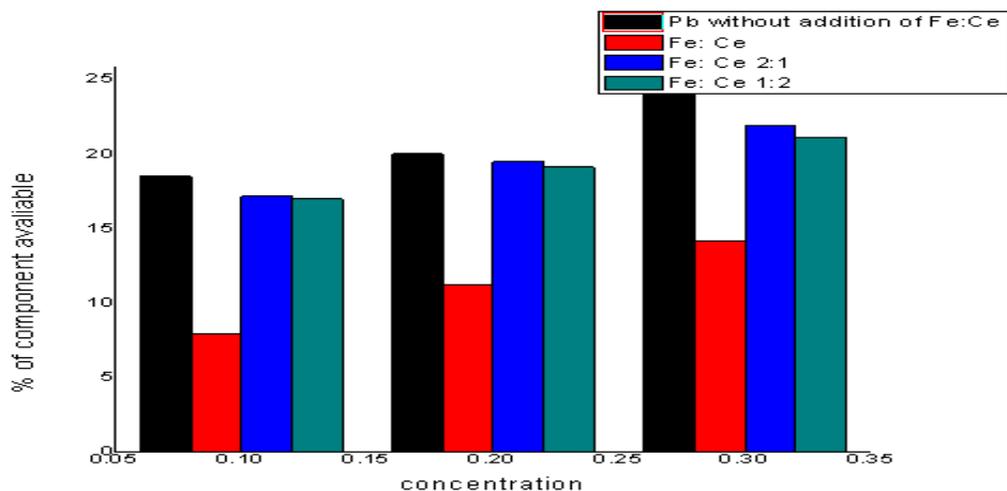


Figure-7
Lead Without Addition of FE : CE

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

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