Radionuclide sorption onto nanoiron oxide: Synthesis and application to natural waters

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ABSTRACT. Expanded requirement for the lanthanides in industrial stuff resulted in intensified manufacture of lanthanide containing ores. This increases public contact to the lanthanides, both from production wastes/effluents and from various commercial products. Present study describes the efficacy of γ-Fe₂O₃ (nano maghemite) for fast adsorption of some of the long-lived, toxic and radioactive human made radionuclides from natural waters. Nanometal oxides have been successfully prepared by precipitation synthesis followed by thermal decomposition of transition metal oxides. These are further characterized by different physico-chemical techniques like XRD, UV-Vis-DRS, TEM, FTIR and BET analysis. Adsorption capacities of REEs like La(III), and Nd(III) are observed through ICPAES technique. The parameters influencing the adsorption capacity, which includes pH, contact time, initial concentration, and temperature are optimized. The adsorption kinetics and thermodynamics are analysed. These results proved that nanometal oxide (γ-Fe₂O₃) have been successfully prepared by precipitation synthesis followed by thermal decomposition of transition metal oxides, and followed a novel method to mollify the seriousness of nuclear waste contamination, which leads to successful evaluation for environmental problems.

1. Introduction

Nearly 90% of REE minerals are available in America, Australia and China. Due to the growth of industries and new advanced technologies, there is an ever raising necessity for REEs in the international market. Thus interest on proper application of REEs is important, in order to meet need of the present generation. REEs, particularly light REEs (La, Ce, Pr, Nd, and Pm) and middle–heavy REEs (Sm, Eu, Gd, and Tb) are regarded as the significant fission products in the waste of nuclear plants[1,2]. Renewal of radioisotopes from nuclear waste is an issue in present days over the globe, because of their effective application in several industries. The presence of radioactive material in natural waters has an impact on public health. REEs, the f-block in the periodic table, possesses unique physical and chemical properties, which makes them important to several critical technologies [3-5]. The widespread involvement of REEs in industry is described by their application in the for screen displays, for electromechanical devices, production of strong permanent magnets, for laser technology glass, and lenses, and in solid state microwave devices, textile industries, the ceramic, photographic, and gas mantles, as well as in medical x-ray and magnetic resonance image scanning systems. Further with the
expansion of rare earth materials in the preceding decade for plastic magnets, ceramics, superconductors etc., the rare earth elements (REEs) concentrations were developed in the environment.

Pure lanthanum is applied in the production of microscopes, lenses, hard drives in computers and in rechargeable lithium-nickel batteries, which can replace the nickel-cadmium batteries [6,7]. Neodymium (Nd) traded nearly half percent of total rare earth deal because of unique properties. Extensively applied in neodymium magnet, neodymium doped lasers and neodymium glass. Color televisions, energy-saving lamps, fluorescent lamps and glasses, contain neodymium as well [8,9]. The essentiality for toxicological readings on REEs has been mounting and REEs are getting into the environment, accumulating in organisms, and entering into the food chain. This resulted an increased exposure to REEs. Thus, estimation of REEs in environmental and natural waters became significant, and special techniques are described. Recently several investigations have conducted on recovery of REEs.

In the perspective of the safety of nuclear waste repositories, as well as for assessing radionuclide mobility in the environment or industrial wastes, the interaction of lanthanides with various sorbents has become a main subject of many studies [10].

Several techniques accessible for the sorption of REE from natural waters are adsorption, froth flotation, ozonation, co-precipitation, chemical oxidation, membrane separation, coagulation, solvent extraction, chemical precipitation and ion-exchange. Various techniques including ion exchange, chemical precipitation, membrane separation electro deposition, and adsorption etc. are used to treat natural waters containing REEs. Out of all these techniques, chemical precipitation is the most economic one but is not sufficient for dilute solutions. More effective techniques are reverse osmosis and Ion exchange, but they have rather high maintenance, heavy cost and subjected to fouling. Adsorption is one of the few promising alternatives to overcome this problem, especially using low-cost natural sorbents like agricultural wastes, zeolites, clay materials, seafood processing wastes, biomass and natural waters.

Conversely, chemical and biological techniques can never be applied due to non decomposable behavior of the REEs. Various physical and chemical techniques are being applied by a number of scientists for the adsorption of REEs from the waste water [11]. These processes are economic and successful where the soluble concentration is relatively high. Out of all these techniques, adsorption is known an assured method because of the easiness of activity and comparably less expensive in the submission of discoloration technique.

The REEs concentrations before and after adsorption are analyzed by applying inductively coupled plasma atomic emission spectrometer (ICP-AES, Shimadzu 7510). The concentrations of P and C are studied by ICP-AES technique.

Nano technology development expanded the nano materials applications in various branches for instance medication, electronic engineering, wastewater handling, cooking technology, manufacturing and house hold fields. Nanoparticles possesses surface area and surface to volume ratio because of their small size. Hence these nano particles exhibit special properties like catalytic capability and high reactivity, which proves them developed adsorbing materials than other materials [12,13].

Of the metal oxides, iron oxides are easily found in nature and also synthesized readily in the laboratory. This research is carried out my using iron oxide nanoparticles (γ-Fe₂O₃ also known as maghemite) for adsorption process. Due to four unpaired electrons in 3d orbitals of iron atoms, they have strong magnetic state moment and on subjecting to external magnetic field they attain a net magnetic moment. If the size of particles decreased to smaller than about 20 nm, they would display super paramagnetic behavior. In the past decade, because of many technological applications of iron oxide nanoparticles, a lot of attention is focused for the synthesis and application of these nanoparticles. As per the literature survey, they (γ-Fe₂O₃ also known as maghemite) are applied in removal of dyes, heavy metal ions, pigments, REEs and viruses from natural waters [5].

Iron oxide nanoparticles have superior properties compared to conventional sizes of the same material due to their high surface area to volume ratio. Thus these nanoparticles are most valuable materials due to...
their versatility in nanotechnology and related applications with significant properties which includes non-toxicity, thermal stability and characteristics such as catalytic, adsorptive magnetic and electric properties.

Adsorbent (γ-Fe₂O₃) with in nanoparticle range consists of greater outer region additionally to different non saturated reaction exterior atoms. Because of this discriminating and variable binding of effluent molecules, these nano particles exhibit large number of binding sites for interaction with different compound groups.

γ-Fe₂O₃ nanoparticles are synthesis and application for the adsorption of REEs like La and Nd is the focus of the present study. Effects of various variables like adsorbent dosage, REE initial concentration, pH on adsorption process, contact time are investigated. The adsorption kinetics and thermodynamics are studied.

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is very important technique in the determination of trace REEs because of the capability for rapid multi element detection over a wide concentration range with relatively low detection limits. Compared to other techniques such as neutron activate analysis (NAA) or inductively coupled plasma mass spectrometry (ICP-MS), ICP-AES is relatively less cost.

2. Materials and methods

Iron (II) sulfate hexahydrate (FeSO₄·7H₂O) and Sodium oxalate (Na₂C₂O₄) were used. All chemical reagents were commercial with AR purity, and used directly without further purification. All the stock solutions are prepared from reagent grade compounds using Millipore ultra pure water.

2.1 γ-Fe₂O₃ Synthesis method

2.1.1 Synthesis of metal oxalate precursors

In the typical synthesis procedure of iron metal oxalates, initially a transparent 100mL saturated sodium oxalate aqueous solution was taken into a 250mL conical flask and sonicated for half an hour for the generation of the uniform solution. Now specified amounts of metal salt (7.2 g of FeSO₄·7H₂O for FeC₂O₄·2H₂O (molar ratio is 2:1) were dissolved into 20mL of distilled water and the resultant salt solutions were added to the above saturated sodium oxalate aqueous solution by drop wise with vigorous stirring. The precipitate is collected by filtration and subsequently washed using distilled water and ethanol. Thereafter, the metal oxalate filtrate is dried at 60 °C overnight.

2.1.2 Synthesis of metal oxides

For the preparation of metal oxides (γ-Fe₂O₃) the developed corresponding metal oxalate are calcinated at 300 °C for 3 h. The heating rate was maintained about 1 °C/min. The thermal decomposition results in the liberation of gases such as CO₂, SO₂, NO₂, H₂O and so on, followed by significant shrinkage in the structure of the materials and finally γ-Fe₂O₃ metal oxide also known as maghemite is obtained. Thermal decomposition is an easy, low cost synthesis and requires small decomposition temperature in air.

The synthesized metal oxide (γ-Fe₂O₃) is characterized using XRD, FTIR, SEM-EDS, HR-TEM and BET in order to obtain the size and various functional groups, material characterization, elemental composition and surface area, porosity of the synthesized material.

3. Results and Discussion

3.1 Characterization of Nanometal oxides

The crystallinity, morphology and the size of synthesized γ-Fe₂O₃, particles are characterized by XRD, PAN analytical -X’ Pert Pro X-ray diffraction instrument; Cu Kₐ line (λ= 0.154 nm), FT-IR/Fourier Transform-Infra Red Spectroscopy (In the range of 400-4000 cm⁻¹ using KBr disc method), EDS -Energy Dispersive Spectroscopy, SEM/ scanning electron microscopy (The JEOL JSM-7600F FEG-SEM) and HR-TEM, high resolution transmission electron microscopy (HRTEM Jeol/JEM 2100) and BET.
3.2 XRD of Nano metal oxides
The synthesized oxides (γ-Fe₂O₃) were structurally characterized by XRD, using the sample scanned from 10° to 80° at a scanning rate of 0.4°/second. From Scherrer Equation (1), it was confirmed that the synthesized metal oxides (γ-Fe₂O₃) have the crystallite size of 30.22 nm. The X-ray diffraction patterns of metal oxide was depicted in the figure 1 and the data revealed that the metal oxides-γ-Fe₂O₃ (Maghemite) has nanocrystalline behavior and well matched with the standard JCPDS file No. 04-0755.

Scherrer Equation, \[ \text{Crystallite size} = \frac{0.9 \lambda}{B \cos \theta} \] (1)
Where \( \lambda \) = X-ray wavelength,
\( B \) = Full width at half maximum intensity of the peak
\( \theta \) = Bragg angle

![XRD of Nano Maghemite](image)

**Figure 1:** XRD Patterns of γ-Fe₂O₃

![FT-IR of Maghemite](image)

**Figures 2:** FT-IR Spectra of γ-Fe₂O₃
3.3 FT-IR Spectra of Nano metal oxides
The synthesized metal oxides ($\gamma$-$\text{Fe}_2\text{O}_3$, Maghemite) is characterized by FT-IR spectra shown in figure 2 in the range of 400-4000 cm$^{-1}$ using KBr disc method. The observed vibrational bands at 447 cm$^{-1}$, 548 cm$^{-1}$, 688 cm$^{-1}$ consigned to Fe-O stretching vibrations. The vibrational bands observed at above lower frequency region to confirm the formation of metal oxide. The Low intensity peaks at higher frequency regions are due to -OH bending and stretching frequencies. Generally nano materials absorb moisture from the environment, because of which low intensity peaks of -OH in the FT-IR spectra are observed.

3.4 FEG-SEM and EDS of Nano metal oxide
Morphologies of synthesized $\gamma$-$\text{Fe}_2\text{O}_3$ is investigated by SEM and SEM-EDS are shown in figure 3 and figure 4 respectively. The morphologies of the $\gamma$-$\text{Fe}_2\text{O}_3$, are in spherical structure whose dimensions is in nanometer scale.

![SEM Image](image1.png)

**Figure 3** SEM of $\gamma$-$\text{Fe}_2\text{O}_3$

![SEM-EDS Image](image2.png)

**Figure 4** SEM-EDS of $\gamma$-$\text{Fe}_2\text{O}_3$

| Element | App Conc. | Intensity | Weight% | Weight% | Atomic% |
|---------|-----------|-----------|---------|---------|---------|
| C, K    | 1.86      | 0.5716    | 3.98    | 0.09    | 10.41   |
| O, K    | 35.55     | 1.7483    | 24.87   | 0.08    | 48.78   |
| Na, K   | 0.48      | 0.5555    | 1.05    | 0.03    | 1.43    |
| Fe, K   | 52.86     | 0.9222    | 70.10   | 0.11    | 39.38   |
| Total   |           |           | 100.00  |         |         |

**Table 1:** Elemental Composition of $\gamma$-$\text{Fe}_2\text{O}_3$
3.5 BET analysis
Brunauer – Emmett – Teller (BET) analysis was employed for exploring the specific surface area and porosity. It is the general process applied to calculate the surface region of solid compounds. Here the material is chilled to liquid nitrogen hotness and depicted to a nitrogen (gas) adsorbent. The BET surface area of $\gamma$-Fe$_2$O$_3$ (Maghemite) is measured to be 98.27 m$^2$g$^{-1}$.

3.6 Batch adsorption study
The objective of this work is to adsorb REEs such as La(III) and Nd(III) from the natural waters using iron oxide ($\gamma$-Fe$_2$O$_3$) nano particles using ICPAES technique. Several experimental parameters like initial dye concentration, adsorbent dose, contact time, solution pH and temperature can affect the extent of removal of REE. Several batch adsorption studies were conducted at 313K. The adsorption studies are done to investigate the variation of REE strength, ($\gamma$-Fe$_2$O$_3$) nano particles amount (1to30 ppm) and temperature (293,303,313,323K). The experiments were conducted by varying one of the parameter while keeping other factors fixed. After fixed intervals of time (10min) the strength of the dye was monitored by applying ICP-AES technique.

The following expression explains the quantity of pollutant removed at equilibrium, $q_e$ (in mg/g), percentage of adsorption.

\[ q_e = \frac{(C_0 - C_e) \cdot V}{W} \]  

and percentage (%) of elimination = \[ \left( \frac{(C_0 - C_e)}{C_0} \right) \times 100 \] (3)

Here $C_0$ and $C_e$ explain original and equilibrium concentration of REE, V is the total volume of experimental mixture, W is adsorbent mass, C is strength of the REE at the completion of removal.

3.7 Effect of pH
Solution pH is a crucial feature in operating the adsorption capability of REE on to adsorbent ($\gamma$ Fe$_2$O$_3$). figure 5 describes the percentage removal of La(III) and Nd(III) at various pH values. 10 mg of nanoparticles were added to 10 ppm of REE solution followed by magnetic stirring. Different pH values, acidic (2), neutral (7), and basic (10) were used for adsorption studies. Graph shows that the pH of the both REE are “6.5” for the optimum adsorption on to the prepared maghemite nano particles. Hence acidic pH is preferred for further the batch adsorption studies.

![Figure 5: Effect of pH on removal of on La(III) and Nd(III) maghemite nano particles](image-url)
3.8 Effect of contact time
Several batch adsorption studies are conducted for REE (La(III) and Nd(III)) in the concentration limit from 1mg/L to 16 mg/L and 1 - 30 mg/L on maghemite nano particles respectively. The quantity of REE being removed on the surface of nano structures enhances on increasing time of contact till a plateau is reached. This explains the dynamic equilibrium state of the REE, where the quantity adsorbed on to the adsorbent maghemite is in equilibrium with that of rare earth element in the solution. At 50 and 60 minutes respectively the equilibrium was observed for both the REE on maghemite nano particles. The mechanism explains the conformation of pollutant molecules to the outer layer before the dispersal on to the surface of adsorbent and then completely entry in to the permeable arrangement of nano structures. There is repulsion or electrostatic hindrance among the adsorbed effluent on to the adsorbent surface. Finally on increasing, effluent strength, the quantity of pollutant adsorbed for every part (quantity) of maghemite (unit adsorption capability) enhances, while it decreases with increment in the adsorbent dosage because of unsaturation of adsorption sites.

3.9 Effect of adsorbent mass
Adsorption studies were carried to know about the outcome of adsorbent amount on removal of La(III) and Nd(III) on changing the quantity of adsorbent in the limits for fixed concentration of REE at constant temperature of 313K. On enhancing the adsorbent amount from 5- 20mg, adsorption percentage enhanced along less equilibrium time. The existing places on the adsorbent became restricted at higher concentration, and hence no additional adsorption, which could be explained with enhanced surface area, abundant sites for adsorption. The quantity of adsorbent mass (maghemite) is observed to be 10 mg for removal of (La(III) and Nd(III)) respectively.

3.10 Influence of initial dye concentration
REE concentration influences in the removal of effluent by maghemite nano particles at the pH value of 6.5 value at 313K is shown in figure 6 and figure 7 respectively. The pollutant concentration used in the experiment was 1 to 30 mg L⁻¹. At lower concentrations the effluent material in solution reside in binding locations those are available on adsorbent. This grades an appropriate adsorption. The concentration of the REE was determined with various time intervals varying between 0 to 60 minutes. It is observed, the adsorption/removal of La(III) could be fast from the starting of the investigation and at the end, reached to equilibrium. Similar trend is observed in Nd(III) also. From the above results equilibrium time was 40 min, fixed throughout the experiment.

![Figure 6: Effect of La(III) initial concentration on maghemite nano particles](image-url)
This isotherm explains the adsorption is appropriate near homogeneous phases, and is specific on the surface of adsorbent which is observed to be monolayer. The linear Langmuir isotherm model is given as

\[
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m^L \cdot b_L}
\]

Where the terms represent their own words. The important properties of Langmuir isotherm is explained by a fixed numerical value which is dimensionless and known as equilibrium parameter \( R_L \).

\[
R_L = \frac{1}{1 + b_L \cdot C_0}
\]

The rate of \( R_L \) expresses the behavior of Langmuir isotherm, which is irreversible \( (R_L = 0) \), favourable at conditions of \( 0 < R_L < 1 \), and Linear at \( R_L = 1 \) or not favorable at \( R_L > 1 \).

Figure 8 represents the Langmuir isotherms of La(III) and Nd(III) by the adsorption onto maghemite nano particles. The experimental value is in correlation with graphical value of \( Q \) for both REEs. From the result it is observed that maghemite nano particle has better adsorption capacity over the selected REEs.

**Table 2. Langmuir adsorption isotherm coefficients**

| Isotherm Model | Parameter | La(III) | Nd(III) |
|---------------|-----------|---------|---------|
| Langmuir      | \( Q_{max} \) (mg/g) | 26.77   | 33.33   |
|               | \( K_L \) (L/mg)      | 2.4836  | 5.8824  |
|               | \( R^2 \)             | 0.9379  | 0.9989  |
Figure 8. Langmuir adsorption isotherms of La(III) and Nd(III) on maghemite nano particles at 313 K

3.12 Adsorption kinetics

Adsorption of effluents on the surface of maghemite (iron metal oxide) is impacted by three mass exchange techniques that are outside dissemination of effluent (REE) atoms from the fluid stage to the surface of solid. Adsorption on solid, IPD of effluent materials in interior of the pores. The adsorption procedure is normally quick instead of inner and outside dissemination. But in elaboration, adsorption equilibrium time proposes that the interior dispersion manages the response rate. In this context the adsorption of effluent was applied to PFO and PSO expressions in evaluating the kinetics of adsorption technique. The result of the adsorption kinetics was gained for proposed REEs. The issues are observed in Table 3. The adsorption kinetic plots can be presented in figure 9. Usually the correlation coefficient (R²) value is the base and from which best fit can be selected.

3.13 Pseudo second order kinetic model

The data is treated for PSO kinetic form. The linear formula of the equation can be presented

\[ \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \]

Here  
\( q_e \) (mg/g) = strength of adsorbate at equilibrium  
\( q_t \) (mg/g) = adsorbate strength at a given time t  
\( K_2 \) (g/mg min) = PSO rate constant.

The linear graph of \( \frac{t}{q_t} \) vs ‘t’ can pursue the data of \( q_e \), \( K_2 \) from the slope, intercept correspondingly. From the observation, the correlation coefficient values are nearly ideal (R² > 0). This indicates a better conformity with experimental, theoretical values. Furthermore better correlation is established among \( q_e \) values determined applying PSO model and experimental investigation.
Figure 9: Pseudo second order kinetic model of La(III) and Nd(III) on maghemite nano particles at 313K.

Table 3. Pseudo second order kinetic model of La(III) and Nd(III) on maghemite nano particles at 313K.

| REE     | Qₑ (mg/g) (Experimental) | Qₑ (mg/g) (Calculated) | K₂ | R²  |
|---------|--------------------------|------------------------|----|-----|
| La(III) | 22.8                     | 24.93                  | 0.0063 | 0.9963 |
| Nd(III) | 29.8                     | 28.4                   | 0.0027 | 0.9980 |

From the observations it is concluded that the adsorption kinetics of La(III) and Nd(III) on maghemite nano particles at 313 K.

3.4 Thermodynamic parameters
The thermodynamic parameters includes Entropy (ΔS°), Enthalpy (ΔH°) and Gibb’s free energy (ΔG°). They are calculated from the given equation:

\[
K_D = \frac{C_S}{C_e}
\]

\[
\Delta G^o = -RT \ln K_D
\]

\[
\ln K_D = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}
\]

Here \( K_D \) = the constant at equilibrium
\( C_S \) = Quantity of effluent adsorbed (mg/g)
\( C_e \) = Equilibrium strength of effluent in the reaction mixture (mg/L).
R = Universal gas constant (8.314 mol/K)
T = Absolute temperature (K).

Linear plot is obtained for \( \ln K_D \) vs 1/T. From the slope, intercept the data of \( \Delta H^o \) and \( \Delta S^o \) are determined.
Table 4. Thermodynamic parameters of La(III) and Nd(III) on maghemite nano particles at 313 K.

| REE    | $\Delta H^\circ$ (kjourles/mol) | $\Delta S^\circ$ (joule/K/mol) | $\Delta G^\circ$ (kjourles/mol) |
|--------|-------------------------------|-------------------------------|-------------------------------|
| La(III)| 2.3                           | 0.0158                        | -2.6454                       |
| Nd(III)| 5.9                           | 0.0276                        | -14.5388                      |

Figure 10. Thermodynamic parameters of La(III) and Nd(III) on maghemite nano particles at 313 K.

These parameters have special role in the calculation of heat change and deciding the spontaneous behavior in the adsorption technique. The negative sign of $\Delta G^\circ$ explains adsorption process of REEs is spontaneous and favorable. The value of $\Delta H^\circ$ are negative for both effluents, describes, exothermic behavior of the adsorption. The value of $\Delta S^\circ$ indicates the entropy decrease at solid-liquid interface. Generally, adsorption is described to be physisorption or chemisorptions. $\Delta H^\circ$ for physisorption limits from -4 to -40 KJ mol$^{-1}$ and chemisorption ranges from -40 to -800 KJ mol$^{-1}$. The data in the Table 4 informs the La(III) and Nd(III) on maghemite nano particles at 313 K is may be due to physical binding.

4. Conclusions
From the above results and discussion it is concluded that $\gamma$-Fe$_2$O$_3$ also known as maghemite nano particles are successfully prepared and applied in the adsorption of rare earth elements like Lanthanum and neodonium from the natural waters. ICPAES technique is applied for the entire study and factors effecting like initial concentration of adsorbate, adsorbent, pH, contact time are also investigated. The study extended to calculation of thermodynamic parameters and explained the feasibility of the reaction. The pseudo second order kinetics best fit into the model. Hence $\gamma$-Fe$_2$O$_3$ nano particles are considered as better adsorbents in the removal of radioactive nuclides from natural waters.

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