Removal of cerium ions from aqueous solution by hydrous ferric oxide – A radiotracer study

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A B S T R A C T

Radiotracer technique has been used to study the removal behavior of Ce (III) ions from aqueous solutions by synthesized and well characterized hydrous ferric oxide (HFO). Adsorptive concentration (10^{-4}–10^{-8} mol dm^{-3}), pH (*ca* 4.0–10.0) and temperature (303–333 K) were examined for assessing optimal conditions for removal of these ions. The uptake of Ce (III) ions, which fitted well for Freundlich and D-R isotherms, increased with increase in the temperature and no significant desorption took place in the studied temperature range. The presence of some anions/cations affected the uptake of metal ion markedly. Irradiation of hydrous ferric oxide and tungsten oxide by using a 11.1×10^9 Bq (Ra–Be) neutron source having a neutron flux of 3.9×10^6 cm^{-2} s^{-1} with associated γ-dose rate of 1.72 Gy/h did not influence the extent of adsorption of Ce (III) significantly.

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1. Introduction

The management of radioactive wastes happens to be an important aspect of recent researches [1]. Reprocessing of spent fuel primarily consists of the removal of radionuclides, followed by volume reduction and finally ceramization before the ultimate disposal of such wastes. Many conventional methods for recovering metals, radionuclides and lanthanides from aqueous solutions are known. Adsorption of cerium, because of its importance as a radiotoxic fission product in radioactive waste, has been the subject of several investigations on different materials. Several polymers, clay minerals, dead biomass and metal oxides have been used as adsorbent for removal of toxic heavy metals [2–4].

Wulfsberg [5] study indicates that the hydrated Ce^{3+} ion ($[Ce(H_2O)_n]^{3+}$) will remain in solution at different environmental pH. Berry et al. [6–9] observed that cerium has localized in the cell, particularly in the lysosomes, where it is concentrated and precipitated in an insoluble form in association with phosphorus.

Radioactive fallout from the testing of nuclear weapons indiscriminately contaminates either the oceans, land, or both, depending upon existing meteorological conditions. To the present time probably the greatest quantity of fission products added to the oceans has come from weapon tests. Additional fission products in the oceans in the future will originate as wastes from laboratories, power reactors, and plants producing nuclear fuels and materials for nuclear weapons. With the possibility of increased contamination of the oceans with fission products there is a need for determination of the uptake, accumulation, and loss of individual radionuclides by marine organisms [10,11].

2. Materials and methods

2.1. Synthesis of hydrous ferric oxide (HFO)

The HFO was synthesized by slow addition of 1.0 M ammonium hydroxide to a solution of ferric chloride at pH 7.5 under constant stirring [12]. The precipitate thus formed was filtered and washed with distilled water. The precipitate was then mixed with hydrochloric acid solution at pH 4.0 and aged at 330 K. After 2 h of aging, the synthesized product was thoroughly washed with double distilled water till it was free from chloride ions. The solid was dried in a hot air oven at 315 K and then sieved to obtain particles of 120–170 mesh size, before using it as adsorbent.

2.2. Infrared and X-ray diffraction analysis

Infrared spectra of synthesized HFO in the range 200–4000 cm^{-1} were measured by a KBr disc method using Jasco FT/IR5300 spectrophotometer. The synthesized compound was also characterized by X-ray diffraction (XRD) technique using a Rigaku, X-ray diffrac-

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tometer; and data resembled as per ASTM File no. 33-664, pp. 481 for HFO.

2.3. Sorption measurements

Cerium (III) as its sulphate salt was used and stock solution (1.0 mol dm^{-3}) of metal ion was prepared in double distilled water. The solution was further standardized via the standard method of Flaschka [13] and then diluted to obtain the desired experimental concentrations (10^{-2}–10^{-7} mol dm^{-3}). The radioactive cerium (^{141}Ce, $t_{1/2}$ = 33 d) as its respective sulphate in dilute H$_2$SO$_4$ (ca 166.5 × 10^6 Bq) was obtained from the Board of Radiation and Isotope Technology (BRIT), Mumbai (India). A very small amount of this radionuclide was used to label the Ce (III) adsorptive solution to obtain a measurable radioactivity of minute aliquots of withdrawn samples from bulk.

The sorption experiments were performed by stirring, at regular intervals, and equilibrating 0.1000 g of HFO with 10.0 cm^3 of labeled adsorptive solution [Ce (III)] of desired concentration. The equilibrated solution was centrifuged for phase separation and then supernatant solution was analyzed for its β-activity measurements using an end-window GM-counter (Nucleonix, Hyderabad, India). Radioactivities of some samples were also checked for their γ-activity using a Multi Channel Analyzer (Nucleonix, Hyderabad, India). Procedures for estimation of the amount adsorbed and evaluation of other parameters were identical to those given earlier [14].

2.4. Irradiation of adsorbents

HFO was irradiated with neutrons and (-rays from a 11.1 × 10^9 Bq (Ra–Be) neutron source having an integral neutron flux of 3.9 × 10^6 n cm^{-2} s^{-1}, associated with a nominal (-dose of ca 1.72 Gy h^{-1} (total dose: from 41.28 Gy to 123.84 Gy for 24–72 h of irradiation). Irradiated absorbents were then employed along with unirradiated materials for the uptake of Ce (III) from aqueous solutions.

3. Results and discussion

3.1. Effect of metal ion concentration

Concentration effect for the adsorption of Ce (III) on HFO was carried out by varying the adsorptive concentrations (10^{-2}–10^{-7} mol dm^{-3}) at 303 K. It was observed that initially a fast uptake of metal ions occurred, which became slower with the lapse of time and an apparent equilibria between the two phases achieved within ca 75 min for Ce-HFO of contact time. No further uptake was observed even after 24 h of contact. Moreover, the smooth and continuous curves leading to saturation for the uptake of Ce (III) ions over HFO infer about the adsorption of metal ions occurring in a single step and not accompanied by any complexity. The amount of Ce (III) adsorbed at equilibrium increases from 0.843 × 10^{-8} to 0.559 × 10^{-3} mol g^{-1} with an increase in adsorptive concentration from 10^{-7} to 10^{-2} mol dm^{-3}. The relative change in the uptake, i.e., percentage adsorption, increased from 55.9 to 84.3% for Ce (III) with the increase in the bulk dilution from 10^{-2} to 10^{-7} mol dm^{-3}. This increase in the percentage adsorption is explicable on the basis of the fact that a relatively smaller number of adsorptive species would be available at higher dilution for deposition on an equal number of surface sites of adsorbents [15].

3.2. Equilibrium modeling

The concentration dependence data were further utilized in equilibrium modeling of the removal process by using the Fre-
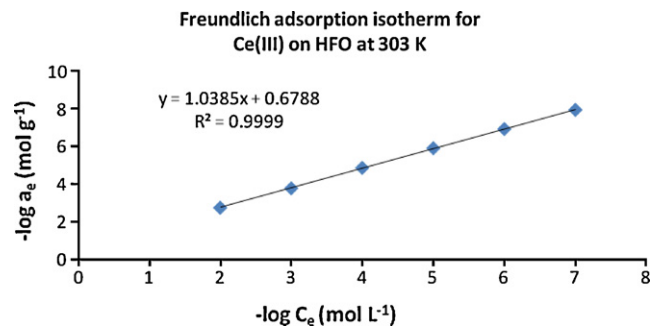

Fig. 1. Freundlich adsorption isotherm of Ce (III) on hydrous ferric oxide at 303 K.

undlich and Dudinin–Raushkevich (D–R) adsorption isotherms. It has been observed that the concentration data fitted well by Freundlich and D–R isotherms.

The Freundlich adsorption isotherm is given in logarithmic form, used for modeling concentration dependence data:

$$\log a_e = \frac{1}{n} \log C_e + \log K \tag{1}$$

here a_e and C_e are the amounts adsorbed (mol g^{-1}) at equilibrium and equilibrium bulk concentration (mol dm^{-3}), respectively and $1/n$ and K are the Freundlich constants which correspond to adsorption intensity and adsorption capacity, respectively. In order to find out these constants a plot has been drawn between log a_e vs log C_e (cf Fig. 1) and straight line was found the system. The linear plot confirm about the monolayer coverage of Ce (III) at the surface of adsorbent. The value of $1/n$ and K were 0.874 and 1.00 × 10^{-2} mol g^{-1}, respectively. The fractional values of $1/n$ ($0 < 1/n < 1$) obtained for the system was considered to be due to the heterogeneous surface structure of adsorbent with an exponential distribution of surface active sites [16]. The higher numerical values of K confirm the significant affinity of Ce (III) for HFO.

To establish the chemisorption phenomenon, the Dubinin–Radushkevich (D–R) isotherm was applied in the form:

$$\ln a_e = \ln X_m - \beta \varepsilon^2 \tag{2}$$

where a_e is the amount of adsorbate adsorbed per unit weight of adsorbent (mol g^{-1}), X_m is the adsorption capacity of adsorbent per unit weight (mol g^{-1}), ε is the Polanyi potential = RT ln[1 + (1/C_e)], C_e is the equilibrium concentration of cerium in solution (mol l^{-1}), a R is the gas constant, T is the temperature (K) and β is a constant related to the sorption energy (mol^2/kJ^2).

If $\beta < 0$, this is related to the adsorption free energy, E, via the relationship:

$$E = \frac{1}{(-2\beta)^{1/2}} \tag{3}$$

The plot of ln a_e versus ε^2 for the adsorption of Ce (III) ions onto HFO is shown in Fig. 2. The values of β, X_m and E obtained from this plot were 0.80 × 10^{-9} mol^2/kJ^2, 5.63 × 10^2 mol g^{-1} and 7.91 kJ mol^{-1}, respectively. The numerical value of the adsorption free energy (E) was of the magnitude expected for a chemisorption uptake [17].

3.3. Effect of temperature

The effect of solution temperature varying from 303 to 333 K in steps of l0 K on chemisorption of Ce (III) ions by HFO has been investigated; the initial concentration of Ce (III) being kept at 1.0 × 10^{-5} mol dm^{-3} at pH 6.80. It was observed that with the increase in temperature the uptake of metal ion increased from

Dubinin-Radushkevich adsorption isotherm for Ce(III) on HFO at 303K

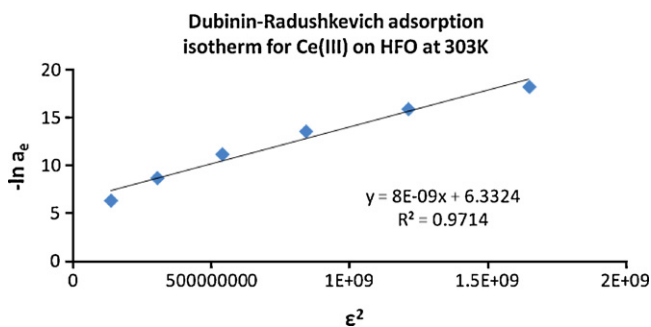$y = 8E-09x + 6.3324$
$R^2 = 0.9714$

Fig. 2. Dubnin–Radushkevich adsorption isotherm of Ce (III) on hydrous ferric oxide at 303 K.

Table 1
Thermodynamic parameter for adsorption of Ce (III) ions on hydrous ferric oxide as a function of temperature.

Temperature (K)	Rate constant $(min^{-1}) \times 10^2$	Energy of activation $(kJ\,mol^{-1})$	Enthalpy change $(kJ\,mol^{-1})$	Entropy $(kJ\,K^{-1}\,mol^{-1}) \times 10^2$
303	11.56	5.26 ± 0.04	11.27 ± 0.04	8.64 ± 0.03
313	12.34			
323	12.97			
333	14.13			

0.446×10^{-6} to 0.791×10^{-6} mol g^{-1} at equilibrium. This increase in adsorption of metal ions may be either due to acceleration of slow adsorption steps or due to creation of some new active sites [16] or due to transport against a concentration gradient, and/or diffusion controlled transport across the energy barrier [18].

A kinetic study for the uptake of Ce (III) ions over HFO has also been worked out, which follows the first order rate law obeying Lagergren equation:

$$\log(a_e - a_t) = \log a_e - \frac{k_1 \cdot t}{2.303} \qquad (4)$$

where a_e and a_t are the amounts adsorbed at equilibrium and at contact time intervals t and k_1 is the adsorption rate constant. The values of adsorption rate constants at different temperatures have been estimated from the slopes of straight lines obtained from log $(a_e - a_t)$ vs time and the values are listed in Table 1. These values increase with the increase in temperature, which is in conformity to expectations as chemisorption increases with the increase in temperature for non-physical type adsorption.

The Arrhenius plots of log k_1 vs $1/T$ (Fig. 3) gave the activation energy for the adsorption process of Ce (III) on HFO as 5.26 ± 0.04 kJ mol^{-1}. The low value of activation energy indicates that the process of uptake can occur even under normal conditions of temperature and pressure and also indicates about the strong force of attraction operating during the adsorption.
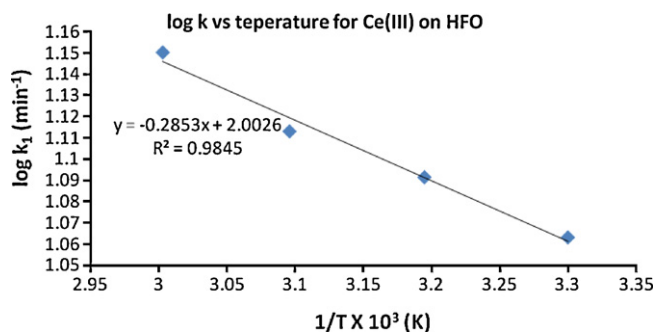
log k vs teperature for Ce(III) on HFO

$y = -0.2853x + 2.0026$
$R^2 = 0.9845$

Fig. 3. Bt vs. time plots for cerium sulphate solution of 1.0×10^{-2} mol dm^{-3} and 1.0×10^{-7} mol dm^{-3} concentrations [temperature: 303 K].

Variation of log Kd with temperature for Ce(III) on HFO
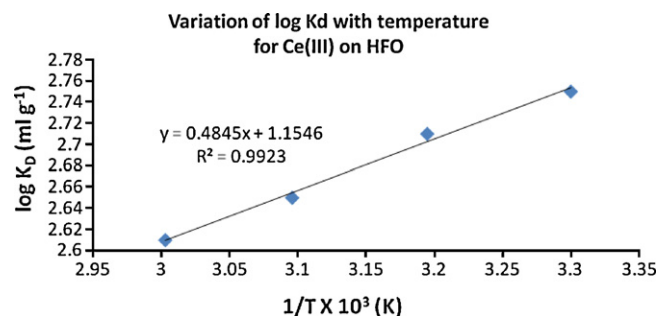
$y = 0.4845x + 1.1546$
$R^2 = 0.9923$

Fig. 4. Variation of log k_1 vs $1/T$ for adsorption of Ce (III) on hydrous ferric oxide. [Initial concentration of Ce (III): 1.0×10^{-5} mol dm^{-3}; pH: 6.80.]

The change in standard enthalpy ΔH^0 during the adsorption process has been evaluated using van't Hoff equation

$$\log K_D = -\frac{\Delta H^0}{2.303\,RT} + \text{constant} \qquad (5)$$

$$K_D = \frac{\text{Radioactivity absorbed/g of adsorbent}}{\text{Radioactivity of equilibrat ed solution/ml}} = \frac{R_0 - R_e}{R_e} \times \frac{V}{m} \qquad (6)$$

where R_0 is the initial radioactivity of the adsorbate and R_e is the radioactivity of the supernatant solution at equilibrium, V is the volume of the sorptive solution (ml), and m is the mass of the adsorbent used (g) and where K_D, ΔH^0, R and T have their usual meaning. The values of ΔH^0 (at 303 K) found from the slopes of straight lines (Fig. 4) obtained by plotting log K_D vs $1/T$ are found to be 11.27 ± 0.04 kJ mol^{-1}. The positive value of ΔH^0 confirms the endothermic nature of the adsorption process [19] and the numerical value indicates an ion exchange type mechanism [17] for the uptake.

Furthermore, the changes in standard free-energy and entropy has also been calculated by using following equations:

$$\Delta G^0 = -RT \ln K \qquad (7)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (8)$$

where symbols have their usual significance. The value of ΔG^0 was found to be negative. It is indicative of the fact that the adsorption of Ce (III) ions on HFO is spontaneous in nature (*cf.* Table 1). The positive value of ΔS^0 infers an increase in the degree of freedom of sorbate ions operative due to more randomness following the chemisorption process.

3.4. Kinetic studies

To establish the practical utility of adsorption, kinetic data have been treated by the models given by Boyd et al. [20], which is valid under the experimental conditions used. This is in accordance with the observations of Reichenberg [21] as given by the following equations:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 Bt) \qquad (9)$$

and

$$B = \frac{\pi D_i}{r^2} \qquad (10)$$

where F is fractional attainment of equilibrium at time t, D_i the effective diffusion coefficient of adsorbate in the adsorbent phase, r the radius of adsorbent particle assumed to be spherical and n is an integer. The fractional attainment of the equilibrium can be
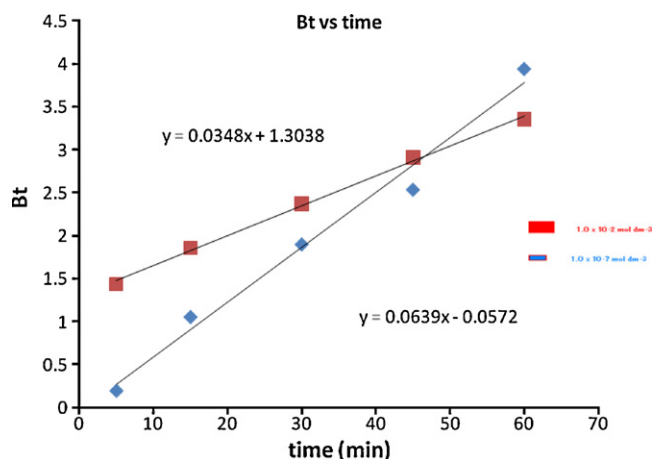
Fig. 5. Variation of log K_D vs $1/T$ for adsorption of Ce (III) on hydrous ferric oxide. [Initial concentration of Ce (III): 1.0×10^{-5} mol dm^{-3}; pH: 6.80.]

determined with the following equation:

$$F = \frac{Q_t}{Q_\infty} \tag{11}$$

where Q_t and Q_∞ are the amounts adsorbed after time t and infinite time (24 h), respectively. For every calculated value of F, corresponding values of Bt are calculated from Eq. (9). The linearity test of Bt versus t plots (Fig. 5) is employed to find out the particle diffusion-control mechanism. At the lower concentration, the Bt versus t plots did not pass through the origin signifying the adsorption to be film diffusion, but at higher concentrations the same were linear up to a certain point and passed through the origin indicating the adsorption to be a particle diffusion in nature.

3.5. Desorption study

HFO with preadsorbed Ce (III) was washed with double distilled water to ensure the removal of adhering species and subsequently the adsorbent was dried in an electric oven at 383 K. The desorption of preadsorbed Ce (III) on these solids was studied in Ce (III) solution (1.0×10^{-5} mol dm^{-3}) at different temperature (i.e., 303–333 K) at pH 7.0. The very low values of percentage desorption at different temperatures (cf Table 2) indicates that the desorption process is
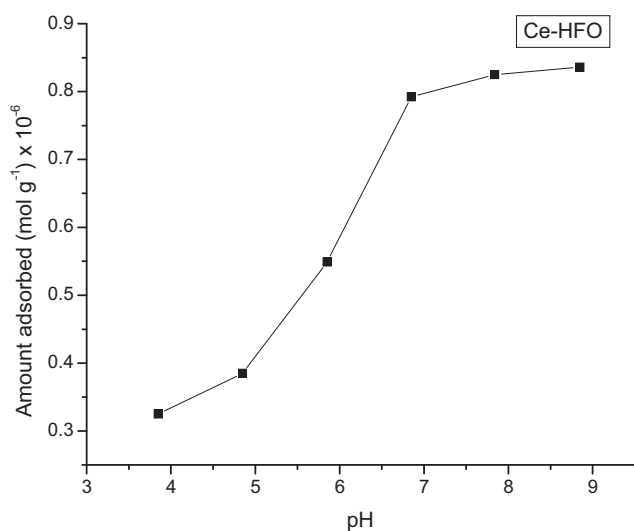

Fig. 6. Time variation of adsorption of cerium ions on hydrous ferric oxide at various pH of cerium sulphate sloution. [Initial concentration of Ce (III): 1.0×10^{-5} mol dm^{-3}.]

Table 2
Temperature-variation study on amount of Ce (III) adsorbed and desorbed on hydrous ferric oxide at equilibrium. [Initial adsorptive concentration = 1.0×10^{-5} mol dm^{-3}; pH = 7.00.].
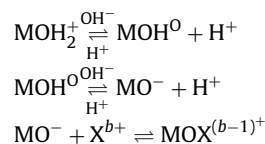
Temperature (K)	Percentage adsorbed at equilibrium (%)	Desorption in equilibrium bulk concentration (%)
303	79.1	4.4
313	80.5	4.5
323	82.9	4.6
333	84.2	6.2

almost independent of temperature. Thus a low value of desorption, unaffected by increase of temperature shows that the process of adsorption for Ce (III) is irreversible in nature. It also indicates that a major part of Ce (III) was probably bound to the HFO surface through strong interaction and converted to a final stable adsorption phase.

3.6. Effect of pH

Cerium (III) occurs with its stable +3 oxidation state and exists with its various forms on varying the pH of solution. In order to find out the mechanism involved at the solid/solution interface, the study has been extended for the adsorption of Ce (III) on the surface of HFO as a function of adsorptive pH at a constant temperature (303 K) and using Ce (III) solution of 1.0×10^{-5} mol dm^{-3}. The increase in the pH from 3.5 to 8.5 results in increase in Ce (III) uptake (Fig. 6). On the other hand HFO has a reported P_{ZPC} at 8.4 [22]. The HFO surface below the P_{ZPC} will be positively charged due to the presence of excess of H$^+$ ions from the solution, therefore there will be competitive adsorption between the proton and Ce (III) ions. Beyond the P_{ZPC} value the oxide surface becomes negatively charged and also the concentration of the H$^+$ ions is reduced comparatively to the ratio of Ce (III) ions present for adsorption. In the acidic solution the HFO does not dissolve. From pH 4.6 to pH 7.0 the uptake of Ce (III) ions is moderate but beyond pH 8.0 there is a sharp increase in the uptake, because for the pH beyond P_{ZPC} the solid adsorbent is negatively charged, and hence attracts Ce (III) ions.

The cationic exchange behavior of adsorbent for Ce (III) is due to the existence of a pH-dependent surface charge according to the following mechanism:

$$MOH_2^+ \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} MOH^O + H^+$$

$$MOH^O \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} MO^- + H^+$$

$$MO^- + X^{b+} \rightleftharpoons MOX^{(b-1)+}$$

where MO is the metal oxide and X^{b+} is the cationic species.

3.7. Effect of added cations

The adsorption capacity of any adsorbent is highly dependent upon the individual nature of adsorbent and adsorbate species and the pH of the bulk solution. In addition, adsorption depends more or less significantly on the characteristics of added species in the bulk of the system.

The effect of six fold concentrations (6.0×10^{-5} mol dm^{-3}) of some cations (viz. Na$^+$, K$^+$, Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}) towards the uptake behavior of HFO for the removal of Ce (III) through independent experiments (Table 3) clearly indicates that the presence of Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+} do hamper the uptake of Ce (III) ions to some extent. However, the presence of Na$^+$ and K$^+$ did not affect the removal of toxic metal ion markedly. The suppression in the adsorption of Ce (III) ions on the HFO surface in the presence of

Table 3

Influence of added cations (six fold) on the adsorption of Ce (III) on hydrous ferric oxide. [Initial concentration of adsorptive solution 1.0×10^{-5} mol dm^{-3}, pH = 6.80.].

Added cation	Percentage adsorbed (%)
Nil	79.1
Na$^+$	75.5
K$^+$	76.5
Ca^{2+}	68.1
Mg^{2+}	70.9
Sr^{2+}	72.5
Ba^{2+}	70.6

Table 4

Effect of irradiation on hydrous ferric oxide by neutron (Ra–Be) source on the adsorption of Ce (III) ions. [Initial concentration of adsorptive solution $\times 10^{-5}$ mol dm^{-3}.].

Time of irradiation (h)	Total dose (Gy)	Amount of metal ion adsorbed (mol g$^{-1} \times 10^{-6}$)
Nil	Nil	0.791
24	41.28	0.772
48	82.56	0.725
72	123.84	0.690

several cations is explicable on the basis of competition of metal ions for the solid surface [15].

3.8. Effect of irradiation

The effect of irradiation on radiation stability of HFO towards removal behavior of Ce (III) has been assessed by carrying out the experiments using a 11.1×10^9 Bq (Ra–Be) neutron source having an integral neutron flux of 3.9×10^6 n cm^{-2} s^{-1} and associated with a concomitant γ-dose rate of 1.72 Gy h^{-1} (total dose: from 41.28 Gy to 123.84 Gy for 24–72 h of irradiation). It is evident from the results (Table 4) that irradiation [upto the doses used] shows some sintering effect but do not appreciably affect the adsorption of Ce (III) ions. Similar result of decrease in the adsorption of Sr^{2+} ions on irradiated alumina surface was reported by Newton [23].

4. Conclusion

HFO was found to be effective in rapid and efficient removal of micro concentrations of Ce (III) toxic ions from aqueous solutions. The adsorption process follows Freundlich and D–R adsorption isotherm with endothermic/irreversible nature. The uptake of metal ions are affected to varying degrees by adding diverse ions to the bulk solution prior to the adsorption process. The adsorbent shows good radiation stability towards ionizing radiations and may have potential use in radiotoxic waste management.

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