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# Use of rice husk as an effective sorbent for the removal of cerium ions from aqueous solution: kinetic, equilibrium and thermodynamic studies

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## ABSTRACT

In this research, the sportive removal of cerium ions (Ce (IV) from aqueous solution by rice husk (RH) has been studied in batch mode at ambient temperature. The effect of operational parameters such as contact time, amount of sorbent, initial concentration of metal ion and temperature on the percentage removal of Ce (IV) from aqueous solution was investigated. The Fourier transform infrared spectroscopy, scanning electron microscopy and energy dispersive X-ray analysis techniques were used to confirm the sorption of Ce (IV) onto RH. Kinetics models including pseudo-first-order, pseudo-second-order, Elovich, liquid film diffusion, modified Freundlich equation and Bangham equation were used to study the sorption kinetics. Results showed that the sorption data fitted-well to the pseudo-second-order kinetic model. Experimental data was also subjected to Linear and Nonlinear forms of Langmuir, Freundlich, and Dubinin-Radushkevivh isotherms and attained results exhibited that the sorption data fitted well to nonlinear and linear sorption isotherms. Thermodynamic study indicated that the sorption of Ce (IV) onto RH was an endothermic process and spontaneous in nature. Moreover, the recovery of Ce (IV) and regeneration of sorbent (RH) was carried out by employing various desorbing media.

*Keywords:* Sorption; Rice husk; Cerium ion; Sorption isotherms; Thermodynamics

## 1. Introduction

Rare earth elements (REEs) have received considerable attention because of their special properties and a wide range of applications [1]. They are largely employed in the field of medicine, nuclear energy, chemical engineering, electronics, metallurgy and computer. Cerium as the most abundant and one of the members of group has some well-established applications that are totally different from other member of REEs. However, the high purity is usually needed for its utilization industry, where it is employed, for example, for sulfur control in steels, ceramic, catalyst support, pyrophoric

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alloys, publishing powders, etc. It is accompanied by other REEs in its minerals, as well as in spent nuclear fuel [2]. The environmental behavior of REEs has attracted great interest in the environmental impact assessment of disposed long-lived radioactive waste.

Many conventional methods namely chemical precipitation [3], ion exchange [4], floatation [5], coagulation [6], membrane processes [7], solvent extraction [8] and sorption [9–11] have been developed to separate heavy metals from aqueous solutions. Sorption as the most famous method to remove heavy metals exhibited several advantages such as easy operation, high efficiency, low cost and production of less sludge volume [12]. Many types of materials such as activated carbons [13], carbon nanotubes [14], zeolites [15], chitosan [16], clays [17] and agricultural wastes [18] have been revealed to remove metal cations from aqueous solutions.

In our previous work, we have reported the use of plant leaves and anion exchange membrane for removal of dyes from aqueous solution via sorption process. In the present research, we will use RH as an effective sorbent for the removal of Ce (IV) from aqueous solutions at room temperature. As Pakistan is one of the world's major producers of rice (5.2 million tons annually) and its husk which forms 20%–23% of the whole rice grain is considered as unwanted waste material that actually poses a disposal problem for mill owners. Its basic composition is proteins, cellulose, hemicellulose and lignin, containing hydroxyl and carboxyl functional groups available to interact with cations [19,20]. The sorption study of Ce (IV) onto RH has not been reported so far to the best knowledge of the authors.

In this manuscript, we reported the batch sportive removal of Ce (IV) from aqueous solution in detail at ambient temperature. The effect of contact time, amount of sorbent (RH), initial concentration of Ce (IV) and temperature on the percentage removal of Ce (IV) was studied in detail. Experimental data for sorption of Ce (IV) onto RH was revealed by sorption kinetic models, linear and nonlinear isotherms and thermodynamics. Further, the recovery of Ce (IV) and regeneration of sorbent (RH) was investigated.

## 2. Experimental setup

### 2.1. Reagents

All the reagents used were of analytical grade and used without further modifications. The temperature of solutions was maintained by dipping the culture tube in water bath of Gallen kamp thermo stirrer (UK) for thermodynamic studies. The precision of the temperature in the water bath was ±0.1°C. Deionized water was used throughout this research.

### 2.2. Sorbent

The husk of basmati rice (botanical name: Oryza sative) was obtained from a rice mill in the Punjab Province of Pakistan. All experimental work was conducted from the same batch of rice to eliminate any effect of seasonal variation in the rice sample. The required samples were thoroughly washed with water to remove dust particles and were oven dried at 80°C till constant weight was obtained. The dried husk was stored in a pre-cleaned airtight container and was used without any physical or chemical pre-treatment. The chemical analysis of husk samples of basmati rice was carried out by employing neutron activation analysis (NAA) and atomic sorption spectrometry (AAS) techniques for their trace metal contents and obtained results have been reported elsewhere [21]. The results showed that the amount of metals such as Na, K, Pb and Fe were present in µg per g of sample. Silica contents were found to be 18.27 (0.62%) of RH. The trace amount of elements present in RH was analyzed by adopting standard procedure. The sorption capacity of cerium for different sorbent is represented in Table 1.

### 2.3. Batch sorption

A known amount of RH was taken into a 25 cm$^3$ secured cap culture tube along with 4 cm$^3$ of standard acid solution and a fixed amount of stock radiotracer with known amount of cerium concentration solution was added. Subsequently, the contents were equilibrated on a wrist-action mechanical shaker (Vibromatic [USA]) at a rate of 500 rpm for a specific time. Then it was centrifuged at 5,000 rpm for phase separation and the supernatant solution was withdrawn for activity measurement. The radioactivity of solutions before ($A_i$) and after ($A_f$) equilibrium was measured with a NaI well type scintillation counter (Canberra Inc.) coupled with a counter-scaler (Nuclear Chicago). A volume of 1.0 cm$^3$ was usually used to measure the activity. All experiments were conducted at ambient temperature. The percentage sorption of cerium from the solution was calculated using the following expression:

$$\% \text{ Adsorption} = \frac{A_i - A_f}{A_i} \times 100 \quad (1)$$

where $A_i$ and $A_f$ are the initial and final radioactivity of metal ions (counts/min) into the solution respectively.

### 2.4. Characterization

#### 2.4.1. Fourier transform infrared spectroscopy (FTIR) analysis

FTIR spectra of was recorded by using the technique attenuated total reflectance (ATR) with FTIR spectrometer

Table 1
Adsorption capacity of cerium for different sorbents

| Sorbents | Capacity (mg/g) | References |
|---|---|---|
| HPMBP loaded Ca alginate beads | 20.60 | [38] |
| Hydrated ferric oxide | 1.40 | [39] |
| Crab shell | 5.85 | [40] |
| Wood sawdust | 36.00 | [28] |
| Granular activated carbon | 12.00 | [28] |
| Activated charcoal | 24.04 | [41] |
| Resin purolite C100 | 0.098 | [42] |
| Hydrated MnO$_2$ | 1.75 | [43] |
| Rice husk | 0.101 | This work |

(Vector 22, Bruker) having resolution of 2 cm$^{-1}$ and a total spectral range of 4,000–400 cm$^{-1}$.

### 2.4.2. Microscopic characterization

Morphological characterization of RH was successfully done through a field emission scanning electron microscope (FE-SEM, Sirion200, FEI Company, USA).

### 2.4.3. Energy dispersive X-ray (EDX) analysis

The successful sorption of Ce (IV) onto RH was proved by EDX analysis.

### 2.4.4. Batch desorption

Batch desorption of Ce (IV) was carried out by immersing certain quantity of metal loaded sorbent into aqueous solution of HCl (1 mole/L), $H_2SO_4$ (1 mol/L), and $HNO_3$ (2 mol/L) as a desorbing media for five minutes.

## 3. Results and discussion

### 3.1. FTIR

The sorption of Ce (IV) onto RH was confirmed by FTIR analysis of virgin and cerium loaded RH samples. The FTIR spectrum of virgin RH is represented in Fig. 1(a). The characteristic absorption band at 3,400–3,200 cm$^{-1}$ is assigned for surface O–H stretching whereas aliphatic C–H stretching had a broad band at 2,921–2,851 cm$^{-1}$. The peaks at 1,737.8, 1,435.6 and 1,365.4 cm$^{-1}$ are associated with C=O stretching, OH bending of the adsorbed $H_2O$ and aliphatic C–H bending respectively [22]. The peaks at 1,217.0, 1,365.4, 1,737.8 and 1,027.4 cm$^{-1}$ are associated to carboxyl group on RH in the range of reported peaks at 1,208–1,230, 1,367–1,371, 1,740 and 1,029 cm$^{-1}$ for carboxyl group [23,24]. Furthermore, the peak at 1,074.0 cm$^{-1}$ corresponds to anti-symmetric stretching vibration of Si–O, whereas at 476.2 cm$^{-1}$ indicates the bending vibration of Si–O–Si bond [23,25,26].

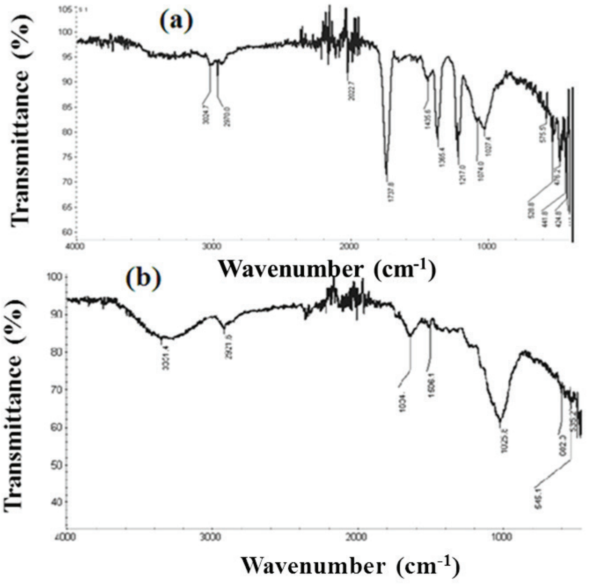

Fig. 1. FTIR spectrum of (a) virgin rice husk and (b) cerium loaded rice husk.

After the sorption of cerium onto RH, the changes in the frequencies were important to look into the functional groups, which were responsible for the sorption of it. Fig. 1(b) depicts the FTIR spectrum of cerium loaded RH. The band intensity of these peaks reduced confirming their involvement during sorption. The changes in the peaks position (2,927.6, and 1,634.3 cm$^{-1}$) and peaks intensities (1,026.0 cm$^{-1}$) were observed for cerium. These findings suggest that lesser stretching due to the binding of metal ions with carboxyl and silanol groups present in RH. It proves the successful adsorption of Ce (IV) onto RH.

### 3.2. Scanning electron microscopy and EDX test

The morphological features of RH were investigated by using scanning electron microscopy (SEM) in detail. The SEM micrographs of RH before and after sorption of cerium ions are presented in Fig. 2(A). It has been observed that the roughness of RH diminishes as sorption of Ce (IV) proceeded. Most of the sites which were present before metal ions sorption were filled up resulting into smoother surface.

The presence of energy peak confirmed the sorption of Ce (IV) which was revealed by EDX analysis of RH and presented in Fig. 2(B). The peaks for cerium energy lines present in the range of 0.80–5.670 keV by EDX pattern. This all proves the successful sorption of Ce (IV) onto RH.

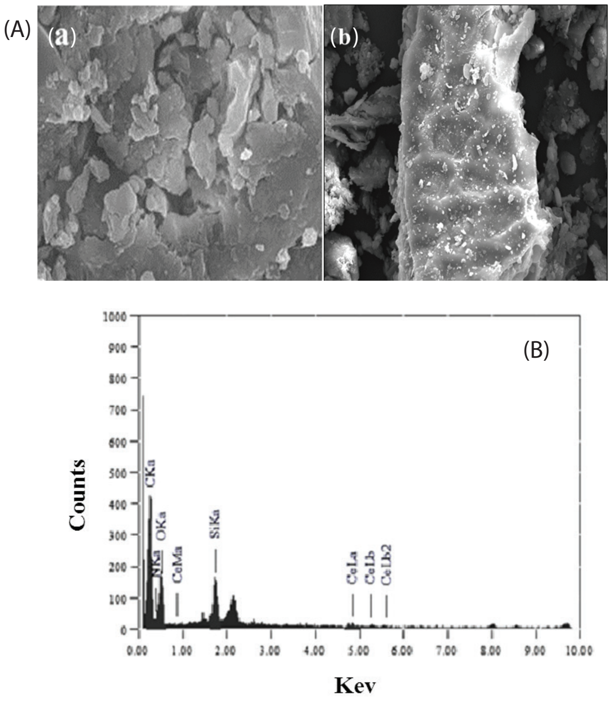

Fig. 2. (A) scanning electron microscopy (SEM) image of (a) virgin and (b) cerium loaded rice husk. (B) Energy dispersive X-ray image of cerium loaded rice husk.

### 3.3. Effect of operational parameters

The effect of operational endowments such as contacts time, mass of sorbent, initial concentration of Ce (IV) and temperature on the percentage removal of Ce (IV) from aqueous solution has been investigated in detail. These are given below:

#### 3.3.1. Effect of contact time

The influence of contact time on the percentage removal of Ce (IV) was studied keeping other parameters such amount of RH, concentration of Ce (IV), temperature and shaking speed constant by using 4 cm$^3$ of metal ions solution with optimized weight of RH and results are presented in Fig. 3. The removal of Ce (IV) is found to be enhanced from 61.1% to 76.6%. The sorption of Ce (IV) was very fast in first few minutes and then there was no large change in percentage removal, after this equilibrium was established and no further significant increase in sorption appeared with contact time. The fast reaction in the start may be because of existence of large number of empty sites onto RH and interaction was developed between Ce (IV) and sorption sites. When all the surface sites were occupied then the sorption slowed down due to movement of metal ions deep into interior pores of RH. Another reason could be that the large number of vacant sites helped fast sorption and when these sites were occupied than there was a competition for lesser remaining sites for the metals ions to be adsorbed which slowed down the rate of sorption until equilibrium was established. The equilibration time for cerium was 25 min which is much less than reported 1 h equilibrium time in literature for cerium and lanthanum by tangerine peel [27] and sawdust [28].

#### 3.3.2. Effect of amount of sorbent

The effect of amount of RH onto the percentage removal of Ce (IV) was studied keeping the other endowments constant by taking 4 cm$^3$ of cerium ions solution. The amount of sorbent (RH) was varied from 0.025 to 0.35 g for metal ions under this study and attained results are represented in Fig. 4. The percentage removal of Ce (IV) is found to be enhanced with increasing the amount of RH up to certain amount beyond which no significant enhancement in the percentage removal of Ce (IV) was observed. The percentage removal of Ce (IV) is found to be increased from 43.5% to 71.6% for 3.6 × 10$^{-5}$ mol L$^{-1}$ cerium in 1.0 × 10$^{-4}$ mol L$^{-1}$ HNO$_3$ solutions. Similar result was reported by researcher for cerium sorption onto tangerine peel [27]. The amount of RH optimized for further investigation Ce$^{4+}$ was 0.25 because after these amounts the change in percentage sorption was very less.

#### 3.3.3. Effect of initial concentration of cerium ion

The initial metal ion concentration is particularly important and sorption of metal ions is dependent on it. The effect of intial concentration of Ce (IV) was studied keeping the other endowments such as contact time, RH dosage, shaking speed and temperature constant. At low metal ion concentration, metal ions are adsorbed onto some of the sorption sites leaving others vacant while with increasing metal ions concentration these sites are filled completely. Fig. 5 showed the effect of initial concentration of Ce (IV) on the percentage removal of Ce (IV) by RH. The percentage removal of Ce (IV) from aqueous solution is found to be decreased with increasing initial concentration of Ce (IV) from 5 to 60 mg L$^{-1}$. Due to saturation of sorption sites some of the metal ions were left unabsorbed at higher initial concentration of Ce (IV). More binding sites were available at low concentration of metal ions. The number of ions competing for available binding sites onto the RH was increased with increasing the concentration. Similar results were reported by various researchers [29–31].

#### 3.3.4. Effect of temperature

The effect of temperature on the percentage removal of Ce (IV) from aqueous solution by RH was investigated using

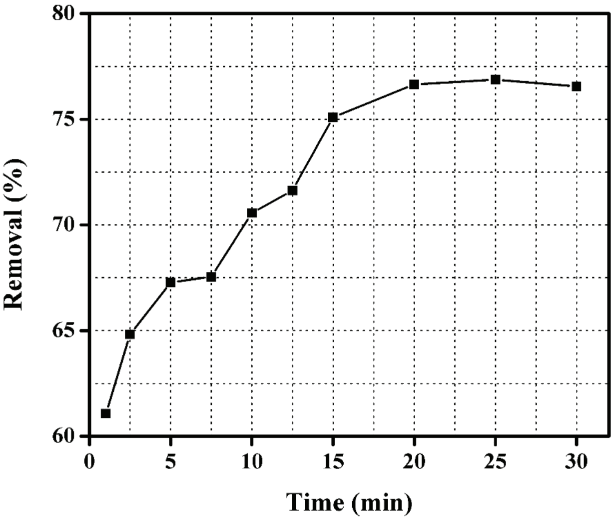

Fig. 3. Effect of contact time on the sorption of Ce (IV) onto RH.

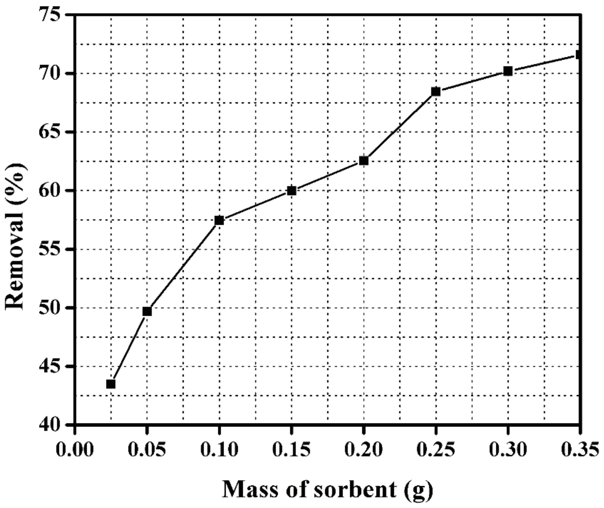

Fig. 4. Effect of amount of RH onto the sorption of Ce (IV).

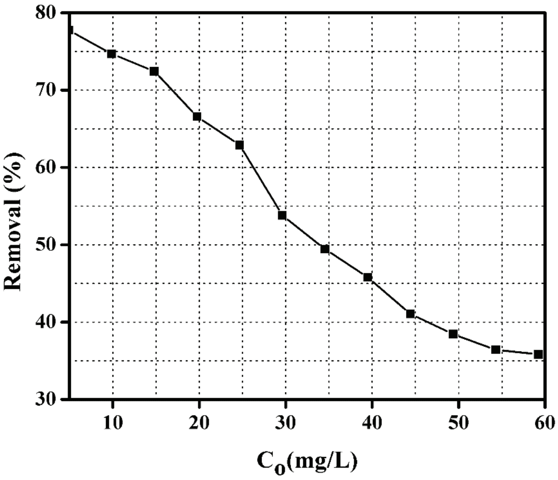

Fig. 5. Effect of initial concentration on the sorption of Ce (IV) onto RH.

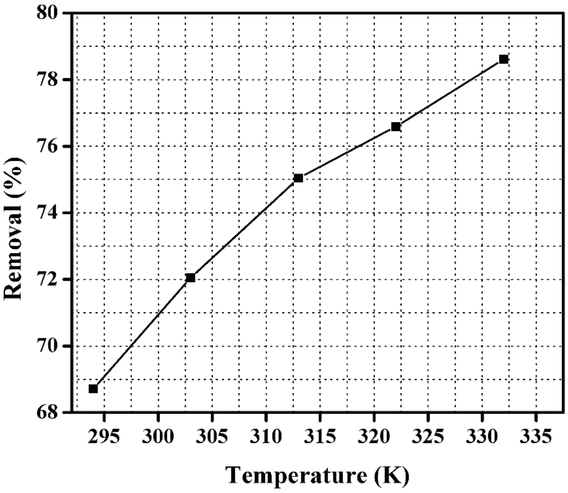

Fig. 6. Effect of temperature on the sorption of Ce (IV) onto RH.

the optimized conditions and attained results are denoted in Fig. 6. There was an increase in the sorption of metal ions for all adsorbate–adsorbent systems with a rise in temperature which indicates higher sorption at elevated temperatures. The percentage sorption of Ce (IV) is found to be increased with increase in temperature from 278 to 333 K under the optimized experimental conditions. The increase in sorption for Ce (IV) by increasing temperature may be either due to acceleration of some originally slow sorption steps or to the creation of some new active sites on the surface of the sorbent. Similar results have been reported for the sorption of mercury and antimony onto RH [32,33], nickel on Saccharum bengalense [34], lanthanum removal on Platanus orientalis leaf powder [35] and thorium sorption by carbon nanotubes and zeolitic tuff [36,37].

### *3.4. Sorption kinetics*

#### *3.4.1. Pseudo-first-order model*

The linearized form of the Lagergren Pseudo-first-order rate equation is given by [44].

$$\mathrm{loq}(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \tag{2}$$

where $q_e$ and $q_t$ are the sorbed amount of Ce (IV) at equilibrium and time t repectively and $k_1$ (/min) is the rate constant of pseudo-first-order sorption model. The plot of $\log(q_e - q_t)$ vs. time for sorption of Ce (IV) onto RH is depicted in Fig. 7. The values of $k_1$ and $q_e$ were calculated from slop and intercept and are given in Table 2. These plots are linear, however the linearity of these curves does not necessarily assure the mechanism due to the inherent disadvantage of correctly estimating equilibrium sorption capacity [45]. The correlation cofficient ($R^2$) was 0.840. Moreover, the difference between experimental sorption capacity ($q_{e,\mathrm{exp}}$) and calculated sorption capacity values ($q_{e,\mathrm{cal}}$) is very large for sorption of Ce (IV) onto RH. Hence the pseudo-first-order model does not explain the rate process.

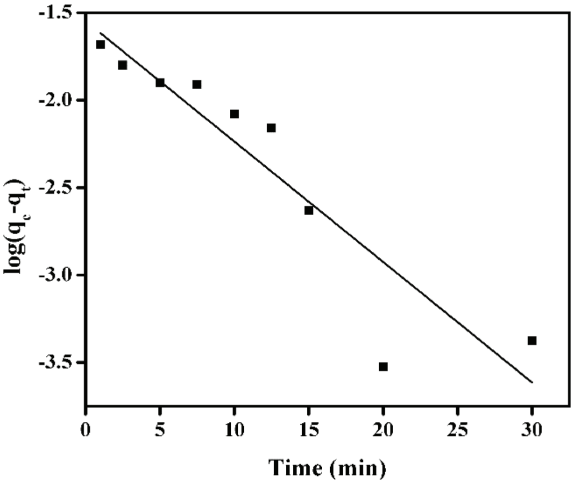

Fig. 7. Pseudo-first-order kinetics for sorption of Ce (IV) onto RH.

Table 2
Pseudo-first-order, pseudo-second-order and Elovich model rate constants

| Pseudo-first order | | Pseudo-second order | | Elovich model | |
|---|---|---|---|---|---|
| $q_{e\,(\mathrm{exp})}$ | 0.10 | $q_e$ | 0.103 | α | 1,026 |
| $q_{e\,(\mathrm{cal})}$ | 0.028 | $k_2$ | 12.5 | β | 166.7 |
| $k_1 \times 10^{-2}$ | 2.9 | – | – | – | – |
| $R^2$ | 0.840 | $R^2$ | 0.999 | $R^2$ | 0.934 |

$q_e$: mg/g; $k_1$: (/min); $k_2$: g/mg.min; α: mg/g.min; and β: g/mg.

#### *3.4.2. Pseudo-second-order model*

The linearized form of pseudo-second kinetic model is expressed as [46]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where $k_2$ (g/mg.min) is the rate constant of pseudo-second-order model. The plot of $t/q_t$ vs. $t$ for pseudo-second-order model for sorption of Ce (IV) onto RH is represented in Fig. 8. The value of sorption capacity ($q_e$) can be measured from slope and is given in Table 2. This value is in good agreement with the experimental value (0.103 mg/g). The value of correlation cofficient is is close to unity ($R^2$ = 0.999) which represents that the experimental data fitted well to the pseudo-second-order model.

### 3.4.3. Elovich model

The most interesting model to describe the activated chemisorption is the Elovich equation [47].

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{4}$$

where $\alpha$ (mg/g.min) and β (g/mg) are constant. The parameter $\alpha$ is considered as initial sorption rate (mg/g.min) and β is related to the extent of surface coverage and activation energy for the chemisorption. Fig. 9, depicts the graphical representation of Elovich model. The values of $\alpha$ and β were measured from intercept and slope of plot and attained results are given in Table 2. The correlation cofficient ($R^2$) was 0.934 lower than that of pseudo-second-order model.

### 3.4.4. Liquid film diffusion model

The liquid film model is expressed as [48].

$$\ln\left(1 - \frac{q_t}{q_e}\right) = -K_{\text{fd}}t \tag{5}$$

where $K_{\text{fd}}$ is liquid film diffusion rate constant. The plot of $\ln(1 - q_t/q_e)$ vs. time is a straight line for liquid film model and is represented in Fig. 10. The value of $K_{\text{fd}}$ was measured from slope of the linear plot and is given in Table 3. The value of correlation coefficient ($R^2$) was 0.836 which is lower than pseudo-second-order model. The inability of the plot to pass through the origin represents that it was not only the rate determining but there also involves other mechanisms. It shows that the liquid film diffusion model cannot be sufficient to explain the experimental data and other models are also needed.

### 3.4.5. Modified freundlich equation

The modified freundlich equation was orignally developed by Kuo and Lotse [49].

$$q_t = kC_o t^{1/m} \tag{6}$$

where $q_t$ is the amount of sorbed Ce (IV) (mg/g) at time $t$, $k$ is the apparent sorption rate constant (L/g.min), $C_o$ is the initial concentration (mg/L) of metal ions, $t$ is the contact time (min) and $m$ is the Kuo-Lotse constant. The values of $k$ and $m$ were employed to study the influence of Ce (IV) surface loading and ionic strength on the sorption process. The linear form of modified Freundlich equation is given as:

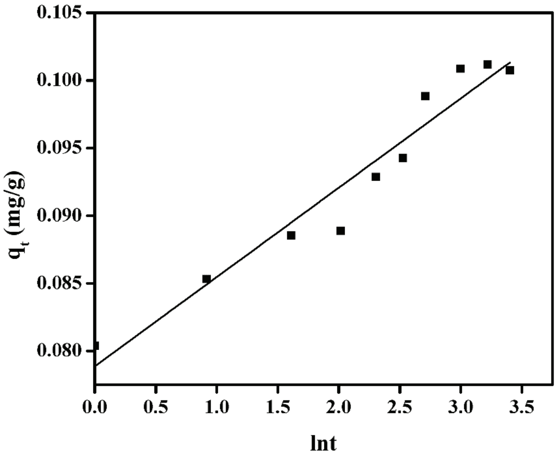

Fig. 9. Elovich model for sorption of Ce (IV) onto RH.

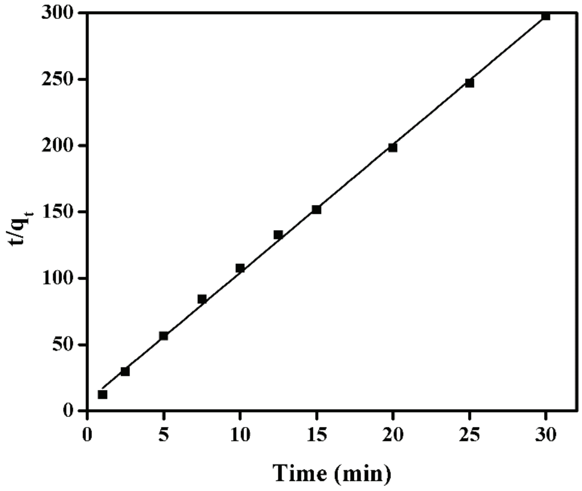

Fig. 8. Pseudo-second-order kinetics for sorption of Ce (IV) onto RH.

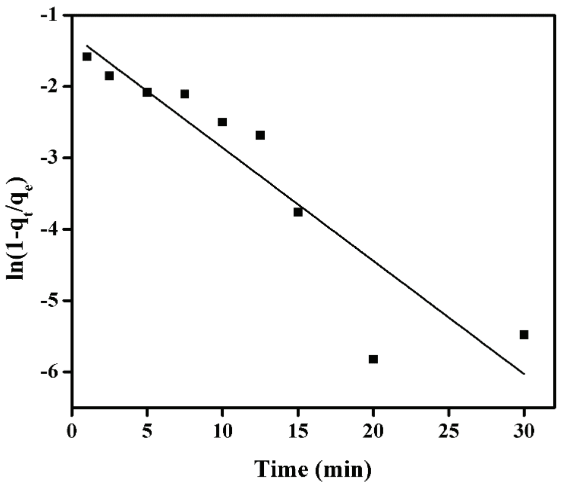

Fig. 10. Liquid film diffusion model for sorption of Ce (IV) onto RH.

Table 3
Liquid film diffusion model, modified Freunlich equation and Bangham equation rate constant

| Liquid film diffusion model | | Modified Freunlich equation | | Bangham equation | |
|---|---|---|---|---|---|
| $k_{fd}$ | 0.15 | $m$ | 13.9 | $k_o$ | 0.032 |
| $C_{fd}$ | –1.27 | $k$ | 0.01 | $A$ | 0.072 |
| $R^2$ | 0.836 | $R^2$ | 0.967 | $R^2$ | 0.946 |

$k_{fd}$: (/min); $k$: L/g.min; and $k_o$: mL/g/L.

$$\ln q_t = \ln\left(kC_o\right) + \frac{1}{m}\ln t \tag{7}$$

Fig. 11 shows the graphical representation of modified Freundlich equation. The parameters $m$ and $k$ were attained from the slope and intercept of plot of ln$t$ Vs. ln$q_t$ and are given in Table 3. The value of correlation coefficient is 0.967.

### 3.4.6. Bangham equation

Bangham equation [50] is given as

$$\log\left(\frac{C_o}{C_o - q_t m}\right) = \log\left(\frac{k_o m}{2.303\,V}\right) + \alpha\log t \tag{8}$$

where $C_o$ is the initial concentration of Ce (IV) solution (mg/L), $V$ is volume of solution (mL), $q_t$ is amount of Ce (IV) sorbed (mg/g) at time $t$, $m$ is weight of sorbent used (g/L). $\alpha$ (<1) and $k_o$ (mL/(g/L) are constants. The plot of log($C_o$/$C_o$–$q_t m$) vs. log$t$ is shown in Fig. 12. The values of $\alpha$ and $m$ were determined from slope and intercept and are given in Table 3. The double logarithmic plot did not give linear curves for Ce (IV) sorption onto RH indicating that the diffusion of sorbate into pores of the sorbent is not the only rate controlling step [51,52]. It may be that both RH and pore diffusion were significant to different extent in the sorption of Ce (IV) from aqueous solution.

## 3.5. Sorption isotherms

For the application of sorption process on the commercial level, proper quantification of the sorption procedure is required. Sorption equilibrium is necessary for the analysis and design of the sorption process it provides fundamental data of physicochemical method for evaluating the applicability of the process as a unit operation. For this purpose the experimental data was analyzed using Langmuir, Freundlich and Dubinin-Radushkevich sorption isotherms.

### 3.5.1. Langmuir sorption isotherm

The Langmuir isotherm has been used by various workers for the adsorption study of a variety of systems [53]. Langmuir model supposes homogeneity of the sorbing surface and no interactions between sorbed species having uniform energies of sorption onto the surface and no trans-migration of sorbate species in the plane of the surface. The difference in sorption capacities of two sorbents for same sorbate is believed to be largely due to the physicochemical properties of them or the chemistry of solution containing sorbing species.

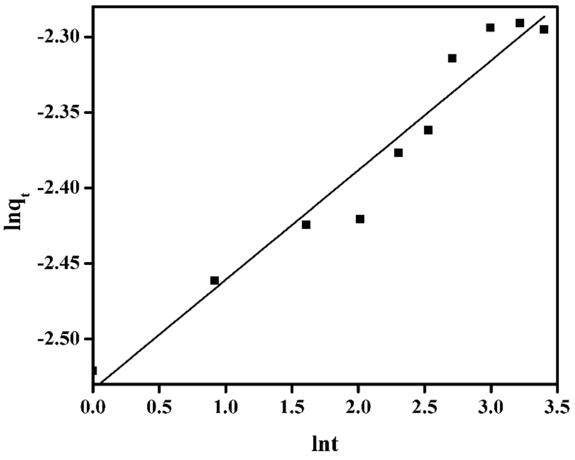

Fig. 11. Modified Freundlich equation plot between ln$t$ vs ln$q_t$ for sorption of Ce (IV) onto RH.

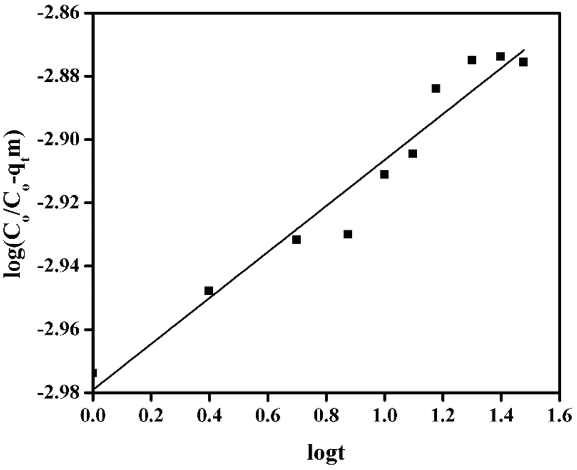

Fig. 12. Bangham equation plot between log$t$ vs. log($C_o$/$C_o$ – $q_t m$) for sorption of Ce (IV) onto RH.

Langmuir sorption isotherm may be expressed as:

$$C_{\text{ads}} = \frac{Q_m k_L C_e}{1 + k_L C_e} \tag{9}$$

The above nonlinear Langmuir isotherm can be linearized as:

$$\frac{C_e}{C_{\text{ads}}} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \tag{10}$$

where $C_e$ is the metal ions concentration of solution (mol L$^{-1}$) at equilibrium and $C_{\text{ads}}$ is the amount sorbed per unit mass onto sorbent at equilibrium (mol g$^{-1}$). The constant $Q_m$ is the monolayer sorption capacity (mol g$^{-1}$) and $K_L$ (L mol$^{-1}$) is related to the energy of sorption. In general $Q_m$ and $K_L$ are the functions of pH, ionic media and ionic strength. The value of $Q_m$ for Ce (IV) was computed by nonlinear and linear forms of Langmuir isotherm. Wavemetrices IGOR Pro 6.1.2 software was used for the calculation of isotherm parameters while using non-linear equations. The non-linear form of Langmuir isotherm model for the sorption of Ce (IV) onto RH are represented in Fig. 13, and the attained constants are given in Table 4. Similarly, the linearized form of Langmuir isotherm model for sorption of Ce (IV) onto RH is represented in Fig. 14, and attained endowments are given in Table 5. To compare the application of different forms of the models, the regression coefficient '$R^2$' and Chi-square test '$\chi^2$' were used as determining tools for the best-fit of sorption isotherm equations which may be calculated by the following expressions:

$$R^2 = \frac{\sum\left(C_{\text{ads,cal}} - \acute{C}_{\text{ads,exp}}\right)^2}{\sum\left(C_{\text{ads,cal}} - \acute{C}_{\text{ads,exp}}\right)^2 - \sum\left(C_{\text{ads,cal}} - C_{\text{ads,exp}}\right)^2} \tag{11}$$

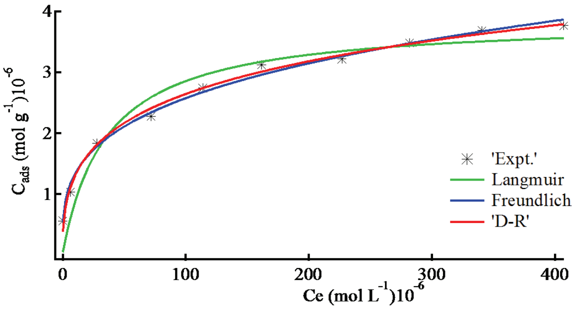

Fig. 13. Nonlinear plots of Langmuir, Freundlich and D-R isotherms for sorption of Ce (IV) onto RH.

Table 4
Langmuir, Freundlich and Dubinin Radushkevivh isotherms parameters by nonlinear method

| Isotherms | Parameters | | $\chi^2$ |
|---|---|---|---|
| Langmuir isotherm | $Q_m$ | $K_L$ | $7.01 \times 10^{-13}$ |
| | $3.87 \times 10^{-6}$ | 28,016 | |
| Freundlich Isotherm | $K_F$ | $n$ | $7.15 \times 10^{-13}$ |
| | $(3.696 \pm 0.385) \times 10^{-6}$ | $3.456 \pm 0.145$ | |
| D-R Isotherm | $C_m$ | $\beta$ | $7.4 \times 10^{-12}$ |
| | $(9.485 \pm 0.503) \times 10^{-6}$<br>$E = 14.13 \pm 0.660$ | $(2.506 \pm 0.117) \times 10^{-3}$ | |

$Q_m$: mol/g; $K_L$: L/mol; $K_F$: (mg/g) (L/mg)$^{1/n}$; $C_m$: mol/g; β: mol$^2$/J$^2$; and $E$: kJ/mol.

$$\chi^2 = \sum \frac{\left(C_{\text{ads}} - C_{\text{ads},m}\right)^2}{C_{\text{ads},m}} \tag{12}$$

where $C_{\text{ads,exp}}$ is the experimental sorption at time $t$ (mol g$^{-1}$), $C_{\text{ads,cal}}$ is the calculated sorption at time $t$ (mol g$^{-1}$), $\acute{C}_{\text{ads,exp}}$ is the average of $C_{\text{ads,exp}}$ (mol g$^{-1}$), $C_{\text{ads}}$ is the equilibrium capacity from experimental data (mol g$^{-1}$), and $C_{\text{ads},m}$ is the calculated equilibrium capacity from the model (mol g$^{-1}$). The computed value of '$R^2$' for linear equation is given in Table 5 and Chi-square '$\chi^2$' for nonlinear equation is shown in Table 4. The similarity of the data obtained from a non-linear model is usually established by comparison with the experimental data, $\chi^2$ would be a smaller number and vice versa, whereas

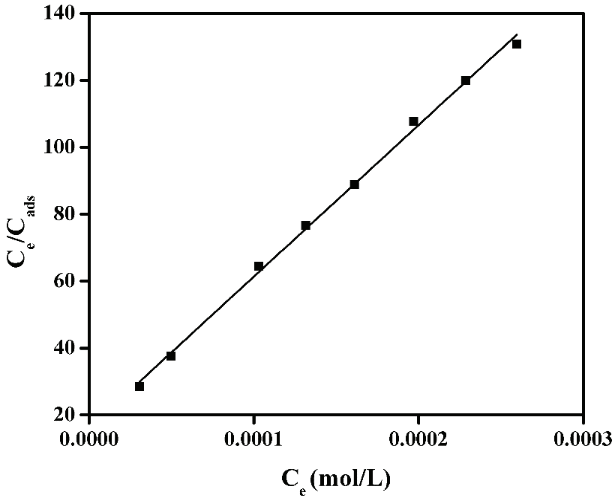

Fig. 14. Linear form of Langmuir isotherm for sorption of Ce (IV) onto RH.

Table 5
Langmuir, Freundlich and Dubinin-Radushkevivh isotherms parameters by linear method

| Isotherms | Parameters | | $R^2$ |
|---|---|---|---|
| Langmuir isotherm | $Q_m$ | $K_L$ | 0.9872 |
| | $3.91 \times 10^{-6}$<br>$R_L = 0.047–0.470$ | 31,576 | |
| Freundlich Isotherm | $K_F$ | $n$ | 0.993 |
| | $3.8 \times 10^{-5} \pm 3.1 \times 10^{-7}$ | $3.433 \pm 0.099$ | |
| D-R Isotherm | $C_m$ | $\beta$ | 0.980 |
| | $(8.03 \pm 0.047) \times 10^{-6}$<br>$E = 15.08 \pm 0.743$ | $(2.171 \pm 0.170) \times 10^{-3}$ | |

$Q_m$: mol/g; $K_L$: L/mol; $K_F$: (mg/g) (L/mg)$^{1/n}$; $C_m$: mol/g; β: mol$^2$/J$^2$; and $E$: kJ/mol.

for linear models, maximum value of '$R^2$' is considered to be more favorable.

An essential feature of a Langmuir isotherm can be expressed in terms of a dimensionless constant 'separation factor' parameter, '$R_L$' that is used to predict if an adsorption system is "favorable" or "unfavorable" and can be expressed as follows:

$$R_L = \frac{1}{\left(1 + k_L C_o\right)} \tag{13}$$

where $C_o$ is the initial concentration of metal ions (mol L$^{-1}$) and $K_L$ is the Langmuir sorption equilibrium constant (Lmol$^{-1}$). The value of $R_L$ indicates the sorption process to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The values of $R_L$ for sorption of Ce (IV) was calculated from Langmuir constant $K_L$ and initial concentrations of metal ion and results are summarized in Table 5 which confirmed that the sorption of Ce (IV) onto RH was favorable indicated by the fractional values of $R_L$ between one and zero.

### *3.5.2. Freundlich isotherm model*

Freundlich isotherm was proposed by Herbert F. Freundlich which is mathematically defined as:

$$C_{\text{ads}} = K_f C_e^{1/n} \tag{14}$$

The linearized form of Freundlich isotherm:

$$\log C_{\text{ads}} = \log K_f + \frac{1}{n} \log C_e \tag{15}$$

where $C_e$ is the concentration of sorbate at equilibrium in aqueous solution (mol L$^{-1}$) and $C_{\text{ads}}$ is the sorbed concentration per unit mass of adsorbent (mol g$^{-1}$). '$K_f$' and '$n$' are the Freundlich constants indicating the sorption capacity and sorption intensity respectively. The good fit of sorption data to Freundlich isotherm indicates that there is almost no limit to the amount sorbed and multilayer sorption will occur. The linear form of Freundlich sorption isotherm for the sorption of Ce (IV) onto RH is represented in Fig. 15, and attained parameters are given in Table 5. The experimental data was also subjected to nonlinear form of Freundlich isotherm and attained values of $K_f$ and $n$ are given in Table 4. The value of $n$ signifies the heterogeneous surface of the RH. The values of '$n$' ranges from 2 to 10 indicating good sorption, 1 to 2 moderate sorption and less than one indicates poor sorption [54].

### *3.5.3. Dubinin-Radushkevich model*

The nonlinear Dubinin-Radushkevivh (D-R) equation can be represented as:

$$C_{\text{ads}} = C_m \exp\left(-\beta\varepsilon^2\right) \tag{16}$$

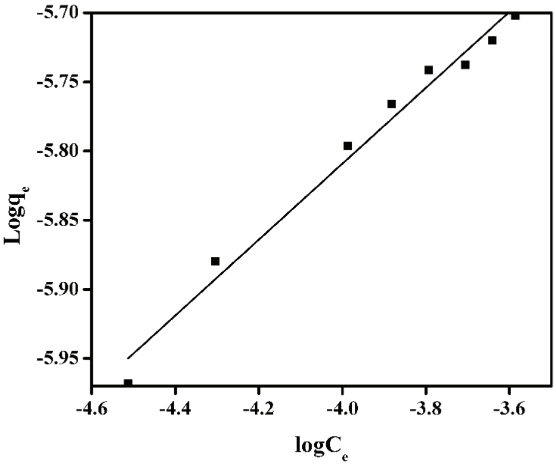

Fig. 15. Linar form of Freundlich isotherm for sorption of Ce (IV) onto RH.

where $C_{\text{ads}}$ is the amount of Ce (IV) sorbed onto RH, $C_m$ (mol g$^{-1}$) is the maximum amount of metal ions that can be sorbed onto RH under the optimized experimental conditions, β is the constant related to sorption energy and ε (Polyanyi potential) = $RT\ln(1 + 1/C_e)$ where $R$ is the universal gas constant (kJ mol$^{-1}$ K$^{-1}$), $T$ is the absolute temperature (K) and $C_e$ is the equilibrium concentration of metal ions in solution (mol g$^{-1}$). The linearized form of D-R isotherm:

$$\ln C_{\text{ads}} = \ln C_m - \beta\varepsilon^2 \tag{17}$$

From β value, the mean sorption energy ($E$) can be computed as [55]:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{18}$$

which is the mean free energy of transfer of one mole of solute from infinity to the surface of sorbent.

The plots of straight line were obtained by using linear form of D-R isotherm of Eq. (17) and are presented in Fig. 16. The values of $C_m$ and β were calculated from intercepts and slopes of plot of $\ln C_{\text{ads}}$ vs. $\varepsilon^2$ using a least square fit program and are given in Table 5. The D-R constants ($C_m$) for sorption of Ce (IV) onto RH was $8.033 \times 10^{-6} \pm 4.738 \times 10^{-8}$ mol g$^{-1}$ evaluated from intercept of straight lines using least square fit program.

The β value of $(2.171 \pm 0.170) \times 10^{-3}$ was used for the determination of sorption free energy ($E$) and the calculated $E$ values were $15.08 \pm 0.743$ kJ mol$^{-1}$. The chemisorption phenomenon is operative for Ce (IV) sorption and higher numerical values of $E$ is for stronger bond between metal ions and sorption sites onto RH.

The D-R constants for nonlinear form were computed from the plot of $C_{\text{ads}}$ vs $C_e$ by using a computer program Wavemetrices Igor Pro 6.2.1.2 and are given in Table 4 along with their respective ($\chi^2$) values which can be used as best fitting tool in nonlinear method. The values of '$C_m$' and 'β' along with calculated sorption free energy are also given in Table 4.

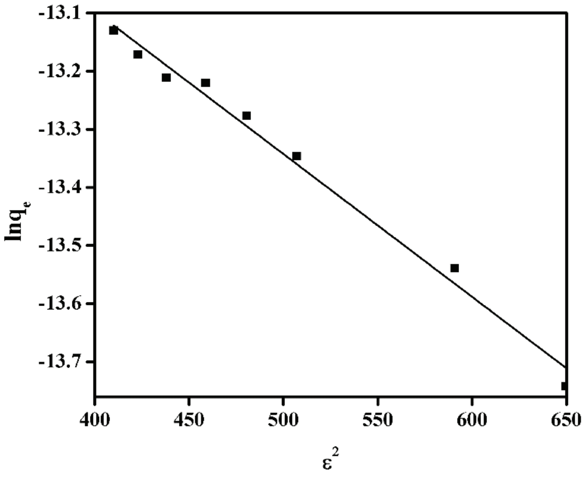

Fig. 16. Linar form of Dubinin Radushkevich (D-R) isotherm for sorption of Ce (IV) onto RH.

The nonlinear plots of sorption of Ce (IV) onto RH are given in Fig. 13. Low numerical values of '$\chi^2$' for nonlinear and high values of '$R^2$' linear plots showed that the experimental data obeyed well.

### 3.6. Sorption thermodynamics

Sorption thermodynamic depicts the feasibility and spontaneity of the sorption process. The endowments such as change in Gibb's free energy ($\Delta G^o$), enthalpy ($\Delta H^o$) and entropy ($\Delta S^o$) were determined from equations below.

$$\ln Kc = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{19}$$

$$K_c = \frac{C_a}{C_e} \tag{20}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{21}$$

where $K_c$, $C_a$, $C_e$, $R$, $T$ are the equilibrium constant, amount of Ce (IV) (mol/L) sorbed onto the sorbent per litre (L) of the solution at equilibrium, equilibrium concentration (mol/L) of Ce (IV) in solution, general gas contant (8.31 J/mol.K) and absolute temperature (K) respectively. Similarly $\Delta G^o$, $\Delta H^o$ and $\Delta S^o$ are the change in Gibb's free energy (KJ/mol), enthalpy (KJ/mol) and entropy (J/mol.K) respectively. Fig. 17, represents the plot of ln$K_c$ vs. $1/T$ for the sorption of Ce (IV) onto RH. The values of sorption enthalpy ($\Delta H^o$) and entropy ($\Delta S^o$) for Ce (IV) sorption onto RH were calculated from slope and intercept of Fig. 17 and are shown in Table 6. On the other hand, the values of Gibb's free energy ($\Delta G^o$) for sorption of Ce (IV) onto RH were also measured from Eq. (21) and are represented in Table 6. The values of Gibb's free energy ($\Delta G^o$) decreases with rise in temperature representing the decrease in feasibility of sorption at higher temperature. Further, the negative values of $\Delta G^o$ for the sorption of Ce (IV) onto RH exhibit that the sorption process is spontaneous in nature. The positive value of enthalpy ($\Delta H^o$) depicts that the sorption of Ce (IV) onto RH is an endothermic. Similarly the positive value of entropy ($\Delta S^o$) represents the enhancement in randomnes at the sorbent-sorbate interface during the sorption of Ce (IV) onto RH.

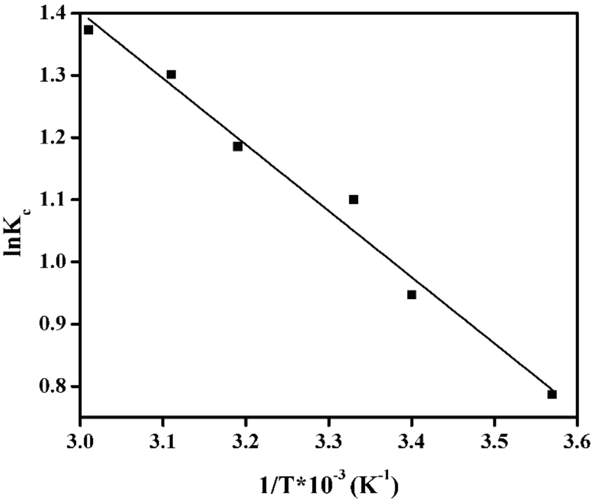

Fig. 17. Plot of $1/T$ vs. ln$K_c$ for sorption of Ce (IV) onto RH.

Table 6
Thermodynamic parameters for sorption of Ce (IV) onto RH

| | | $\Delta G$ (KJ/mol) | | | | |
|---|---|---|---|---|---|---|
| $\Delta H$ (KJ/mol) | $\Delta S$ (J/mol) | 280 K | 294 K | 303 K | 322 K | 332 K |
| 8.65 | 38.2 | –10.70 | –11.20 | –11.70 | –12.30 | –12.70 |

### 3.7. Recovery of Ce (IV)

Recovery of Ce (IV) and regeneration of the sorbent are important aspects of wastewater treatment. Attempts were made to desorb the loaded Ce (IV) from the RH surface by employing various desorbing media. For these purpose mineral acids such as hydrochloric, sulphuric and nitric acid solutions of different molarities were employed by employing batch mode. For regeneration of Ce (IV) fixed amount of metal loaded sorbent was shaked with varied volumes and concentrations of HCl, $H_2SO_4$ and $HNO_3$ for specific intervals of time. For the desorption of cerium ions from RH, a series of experiments were performed with varying concentration of acid solutions, $HNO_3$ solution gave maximum recovery of cerium (~95%) with 2.0 mol L$^{-1}$ solutions. Similarly, for aqueous solution of HCl (1.0 mol/L) and $H_2SO$ (1.0 mol/L) the recovery of cerium was 55% and 60% respectively. The lower concentration of HCl and $H_2SO_4$ was used because their higher concentration was damaging for the cerium loaded sorbent. The attained result was consistent with phenomena explained in the effect of acid concentration that the sorption was decreased with increasing the concentration of acids as sorbing media.

## 4. Conclusions

In this manuscript, the batch sorption of Ce (IV) onto RH from aqueous was invetigated in detail. The percentage removal of of Ce (IV) was increased with contact time, mass of sorbent and temperature whereas decreased with initial concentration of metal ions. Sorption kinetics studies revealed that experimental data for sorption of Ce (IV) onto RH fitted well to pseudo-second-order kinetics. Attained experimental data was also subjected to nonlinear and linear forms of langmuir, Freundlich and D-R isotherms and obyed all isotherms but good fitted to lagmuir isotherm model. Sorption thermodynamic results indicate that the sorption of Ce (IV) onto RH was endothermic and spontaneous process. Moreover, the recovery of cerium was attained maximum for $HNO_3$ (2.0 mol $L^{-1}$) solution. It exhibited that the RH could be utilized as a good sorbent for removal of Ce (IV) from aqueous solution at ambient temperature.

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## Symbols

| | |
|---|---|
| $C_o$ | Initial concentration of Ce (IV), mg/L |
| $C_t$ | Concentration of Ce (IV) at time $t$, mg/L |
| $W$ | Weight of sorbent, g |
| $V$ | Volume of sorbate, $dm^3$ |
| $k_1$ | Rate constant of pseudo-first-order model, /min |
| $k_2$ | Rate constant of pseudo-second-order model, g/mg.min |
| $\alpha$ | Initial sorption rate, mg/g.min |
| $\beta$ | Extent of surface coverage and activation energy for the chemisorption, g/mg |
| $K_{fd}$ | Liquid film diffusion rate constant |
| $k$ | Apparent sorption rate constant, L/g.min |
| $m$ | Kuo-Lotse constant |
| $K_L$ | Langmuir constant, L/mg |
| $q_m$ | Langmuir monolayes sorption capacity, mg/g |
| $K_f$ | Freunlich constant |
| $T$ | Absolute temperature, K |
| $R$ | Gas constant, 8.31 J/mol.K |
| $\Delta G°$ | Change in Gibb's energy |
| $\Delta S°$ | Change in entropy |
| $\Delta H°$ | Change in enthalpy |

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