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Effective removal of lanthanum ions from aqueous solution using rice husk: impact of experimental variables

Shagufta Zafar[a,b], Muhammad Imran Khan[c,d,*], Majeda Khraisheh[e,*], Shabnam Shahida[f], Nasir Khalid[g], Muhammad Latif Mirza[b]

[a] *Department of Chemistry, The Govt. Sadiq College Women University Bahawalpur, Pakistan, email: shg_zf@yahoo.com (S. Zafar)*
[b] *Department of Chemistry, The Islamia University of Bahawalpur, Pakistan, email: mlatifmirza@gmail.com (M.L. Mirza)*
[c] *School of Chemistry and Material Science, University of Science and Technology of China, Hefei 230026, Anhui, China, email: raoimranishaq@gmail.com (M.I. Khan)*
[d] *Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, Fujian, China*
[e] *Department of Chemical Engineering, College of Engineering, Qatar University, Doha, Qatar, email: m.khraisheh@qu.edu.qa (M. Khraisheh)*
[f] *Department of Chemistry, The University of Poonch, Rawalakot, Azad Jammu & Kashmir, Pakistan, email: shabnamshahida01@gmail.com (S. Shahida)*
[g] *Chemistry Division, Pakistan Institute of Nuclear Science and Technology, PO Nilore, Islamabad, Pakistan, email: mkhalid@gmail.com (N. Khalid)*

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ABSTRACT

The focus of the present work is to optimize different experimental parameters such as nature of electrolyte, pH, amount of adsorbent, ions concentration, equilibration time, temperature, and operating mode. The effective removal of lanthanum ion (La^{3+}) using biomaterial such as rice husk (RH) was determined by radio-tracer technique. The adsorption phenomenon was verified by FTIR, SEM and EDX techniques. The adsorption data was well fitted to linear and nonlinear forms of Freundlich, Langmuir and Dubinin-Radushkevich isotherm models with characteristic Freundlich constants of $n = 2.087 \pm 0.084$ and $K = 2.81\times10^{-4} \pm 6.387\times10^{-6}$ mol/g and Langmuir constants of $Q_m = (1.046\pm0.105)\times10^{-5}$ mol/g and $K_L = 5347 \pm 995$ dm^3/mol. The sorption free energy was 10.78 ± 0.641 kJ/mol indicating the chemisorption interaction between the La^{3+} ions and the RH with pseudo 2nd order kinetics. Thermodynamic parameters were evaluated using Van't Hoff equation with ΔG values indicating spontaneity of the process. A positive ΔH value of 28.563 kJ/mol suggested an endothermic nature of the adsorption. Freundlich adsorption capacity of La^{3+} ions was 2.81×10^{-4} mol/g for RH indicating that it locally available cheaper material is good alternative for costly commercial adsorbents and may be used for waste management of radionuclide's.

Keywords: Lanthanum; Rice husk; Biosorbent; Isotherms; Kinetic; Thermodynamics

1. Introduction

Rare earth elements (REE), due to their unusual spectroscopic characteristics and unique properties are considered as one of the most critical groups of raw materials [1]. They are associated with the increasing demands of clean energy, high-tech, superconductors, ceramics, and nuclear industries [2]. Lanthanum (La), one of the lanthanide elements, currently gathered special attention as its alloys are utilized in a number of industries [3] such as rechargeable batteries, fiber optics, scintillation detectors, medical applications, surgical laser, color televisions, camera and telescope lenses, fluorescent and energy saving lamps and glasses, organic synthesis and radio analytical chemistry [4–6]. The

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*Corresponding author.

disposal or storage of industrial effluents containing lanthanum are of concern due to its carcinogenic effects at high concentrations [7]. In addition, it may produce hyperglycemia, low blood pressure, malfunction of spleen, liver and lungs, impaired calcium absorption mechanism, and pneumoconiosis at low to intermediate levels [8–13].

Many methods exist for the removal of lanthanum from aqueous solution. These include ion exchange [14], electrophoresis [15], electro-dialysis [16] and solvent extraction [17,18]. Although many advantages exists, disadvantages, such as high consumption of chemicals and generation of large amount of sludge are known to be hinder their large scale use. The adsorption process has been employed extensively due to its high efficiency, ease of operation and low maintenance cost [19,20]. This has initiated research in new, low-cost materials for possible use as adsorbents. The adsorbents used for lanthanum removal include resins [4,21,22], tangerine peel [23], natural clinoptilolite tuff [24], magnetic alginate-chitosan gel beads [25], aluminosilicates [26], bamboo charcoal [27], leaf powders [28,29], activated carbon [30], biomasses [31,32], bentonite [33], soil materials [34] and microorganisms [35]. These adsorbents are either less efficient or time consuming. The optimized time of 60 min have been reported for the absorptive removal of lanthanum from aqueous solutions by Platanusorientalis leaf powder [29] and tangerine peel [23]. Hence, there is a need to exploit some other more economical, efficient and rapid procedure for this purpose.

This work deals with a series of experiments to assess the utility of indigenous, low cost material (rice husk) as an adsorbent for the removal of lanthanum from aqueous solutions. 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. Rice husk's basic composition is proteins, cellulose, hemicellulose and lignin, containing hydroxyl and carboxyl functional groups available to interact with cations [36–38]. The adsorption study of lanthanum on RH has not been reported so far to the best knowledge of the authors.

2. Experimental

2.1. Preparation of radio-tracer

The radio-tracer of lanthanum used in this study was prepared by irradiating a known weight of spec-pure lanthanum nitrate ($La (NO_3)_3$) from Johnson & Mathey UK, in a 10 MW swimming-pool type reactor (PARR-1) of Pakistan Institute of Nuclear Science and Technology (Islamabad), for an appropriate time at a neutron flux of 4.5×10^{13} $cm^{-2}\,s^{-1}$. After a suitable cooling time, the target which is an irradiated sample was dissolved in water and diluted it to a suitable volume. The radio nuclidic purity of the tracer was checked on 4K series of 85 Canberra Multichannel analyzer (Chicago) coupled with a 25 cm^3 Ge (Li) detector.

2. 2. Reagents

All the reagents used were of analytical grade and used without further modifications. Deionized water was used throughout this work. For thermodynamic studies, the temperature of solutions was maintained by dipping the culture tube in water bath of Gallen kamp thermo stirrer (UK). The precision of the temperature in the water bath was ± 0.1°C. FTIR analysis of RH was carried out by using a Thermo Nicolet- 6700 FT-IR spectrophotometer having a total spectral range of 4000–400 cm^{-1}. The morphology of RH was investigated by using scanning electron microscopic (SEM) (JSM 6490A Analytical Electron Microscope, Jeol, Japan).

2.3. Adsorbent

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 as such 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 absorption spectrometry (AAS) techniques for their trace metal contents and the results have been reported elsewhere [39]. 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 of amount of elements present in RH were analysed by adopting standard procedure.

The Scanning Electron Microscopy (SEM) images of raw RH and lanthanum-loaded RH were recorded at different magnifications from 100 to 10,000 and attained results are represented in Fig. 2.

2.4. Adsorption measurements

The adsorption studies of lanthanum ions from aqueous solutions onto RH has been carried out by optimizing different physico-chemical endowments namely; nature of electrolytes, initial pH of adsorbing media, amount of adsorbent, equilibration time, concentration of adsorbate and temperature, using batch method and radio-tracer technique. The criterion for the optimization was the selection of parameters where maximum adsorption occurred. All the reported results are the average of at least triplicate independent measurements. The determined relative standard deviation was within ± 3.6% unless otherwise specified.

A known amount of adsorbent (rice husk) was taken in a 25 cm^3 secured cap culture tube along with 4 cm^3 of standard acid solution and a fixed amount of stock radio-tracer, with known amount of lanthanum 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, centrifuged at 5000 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 (296 ± 1 K) unless otherwise specified.

The percentage adsorption of metal ion from the solution was calculated using the following expression:

$$\% \, adsorption = \frac{A_i - A_f}{A_i} \times 100 \qquad (1)$$

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

2.5. Diagram of lanthanum ions speciation

Diagram of lanthanum species distribution, as a function of pH for La^{3+} ions, was simulated for a defined lanthanum ions concentration, using nitrate ions as reference employing HYDRA (Hydrochemical Equilibrium-Constant Database) software [40]. Using these software metal ions speciation can be stimulated which is helping us in understanding that at which pH La^{3+} is present in which form.

3. Results and discussions

3.1. Characterization of rice husk

The RH was characterized by various physico-chemical methods such as moisture, ash and volatile contents, porosity, bulk density and pH_{pzc}, and instrumental techniques like scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), Fourier transport infra-red spectroscopy (FTIR), and BET. Ash and moisture contents, porosity, bulk density and pH_{PZC} were determined and found to be 20.11%, 2.61%, 70.66%, 0.305 g cm^{-3} and 5.841 respectively.

3.2. FTIR, SEM and EDX analysis

The adsorption of lanthanum ions onto RH was verified by observing the perturbation in the absorption peaks in FTIR spectra of virgin and lanthanum loaded RH samples and obtained results are shown in Fig. 1. The characteristic absorption band at 3400–3200 cm^{-1} is assigned for surface O–H stretching, whereas aliphatic C–H stretching had a broad band at 2921–2851 cm^{-1}. The peaks at 1737.8, 1435.6 and 1365.4 cm^{-1} are associated with C=O stretching, OH bending of the adsorbed H_2O and aliphatic C–H bending respectively [41]. The peaks at 1217.0, 1365.4, 1737.8 and 1027.4 cm^{-1} are associated to carboxyl group on RH in range of reported peaks at 1208–1230, 1367–1371, 1740 and 1029 cm^{-1} for carboxyl group [42,43]. Furthermore, the peak located at 1074.0 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 [42,44,45]. The shifting in C=O stretching peak position from 1027.4 to 1018.6 cm^{-1} and 1737.8 to 1730.6 cm^{-1} and disappearance of peak at 1074.0 cm^{-1}were observed after lanthanum adsorption onto RH which suggest that stretching occurs to a lesser extent due to the binding of lanthanum ions with carboxyl and silanol groups present in RH. The decrease in intensity of peaks at 1737.8 and 1216.3 were observed which confirms the involvement of C=O functional group in lanthanum ions adsorption. It was also observed that a new peak at 445.7 cm^{-1} has been observed after the adsorption of lanthanum onto RH. Similar observations of minor shifts and decrease in the intensities of the FTIR peaks after the adsorption of metal ions on different biosorbents were reported [42,46–48].

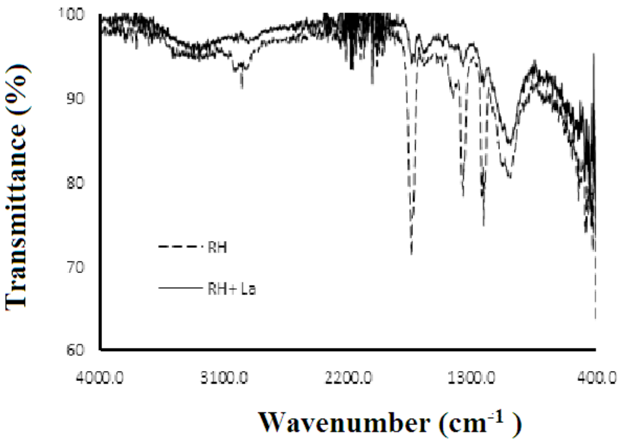

Fig. 1. FTIR spectrum of virgin and lanthanum loaded rice husk.

The SEM images of magnification at 5000 have been shown in Fig. 2, which indicate that the surface of RH is irregular and porous containing pores ranging from 100–180 nm (Fig. 2a). The observed smoothness of the surface of lanthanum loaded RH is the indicative of the adsorption process (Fig. 2b).

Similarly, the determined composition of RH by EDX revealed the presence of C, O and Si (in percentage levels), whereas the lanthanum energy peaks in the range of 0.55 to 5.45 keV (Fig. 3), also confirm the adsorption of lanthanum onto the RH.

3.3. Effect of operational parameters

3.3.1. Effect of acid concentration

The chemistry of solution changed with various chemical compounds and electrolytes which may alter the surface properties of the adsorbent, therefore, the adsorption behavior of 9.98 × 10^{-5} mol/L lanthanum ions was checked in mineral acid solutions of HNO_3, HCl, H_2SO_4 and $HClO_4$ having a concentration range from 0.0001 to 1.0 mol/L using 300 mg of RH. The concentration of lanthanum, amount of 300 mg of RH and equilibration time of 25 min was selected arbitrarily. The results presented in Fig. 4a show that maximum adsorption of lanthanum ions was observed at 0.0001 mol/L of HNO_3. With further increase in acid concentration the adsorption of lanthanum was started decreasing up to 1.0 mol/L of acid solution. Similar trend was observed by all acids used. The decrease in adsorption of lanthanum ions at higher acid concentration may be attributed to the competition between the excess of H^+ ions in the medium and positively charged lanthanum ions. It was also observed that maximum adsorption of lanthanum ions occurred from 0.0001 mol/L HNO_3 as compared to the

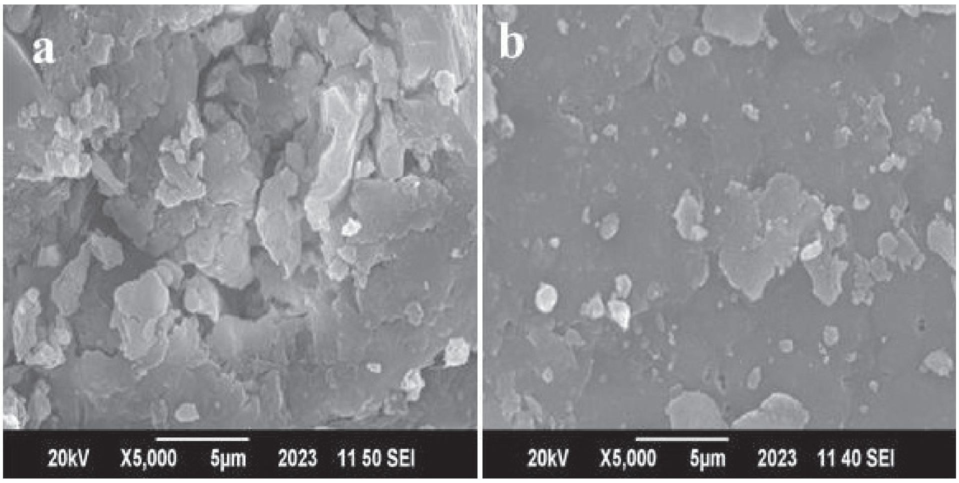

Fig. 2. Scanning electron microscopic (SEM) image of (a) virgin and (b) lanthanum loaded rice husk.

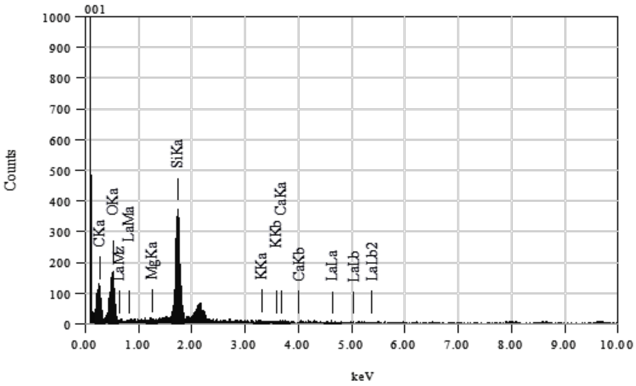

Fig. 3. Energy dispersive X-ray image of lanthanum loaded rice husk.

other acids, therefore, this concentration of HNO_3 was used for all the subsequent experiments regarding the optimization of adsorption conditions for lanthanum ions onto RH.

3.3.2. *Effect of pH*

The adsorption of lanthanum from aqueous solutions is dependent on the pH of the solution, which affects the surface charge of the adsorbent, degree of ionization and speciation of the adsorbate species. The adsorption behaviour of lanthanum ions was therefore, studied from the aqueous solutions of different pH values ranging from 1.0 to 10.0, using 300 mg of RH and 4 cm^3 of 9.98 $\times 10^{-5}$ mol/L of lanthanum ions. The results obtained are shown in Fig. 4b. With the increase in solution pH, the uptake of La^{3+}ions was increased, the maximum adsorption of lanthanum ions on RH occurred at pH 7, there was no significant increase in adsorption with further increase in pH of the medium. The distribution of lanthanum species as a function of pH was simulated using Hydra software [49] as lanthanum concentration and shown in Fig. 4c. It has been observed that the dominant specie is La^{3+} up to pH 7. The concentration of La^{3+} species start decreasing after this pH while $LaOH^{2+}$ concentration start increasing. After the pH 8.3, the fraction of $La(OH)_3$ concentration start increasing which is indication of lanthanum hydroxide precipitation. This fact indicated that adsorption of lanthanum ions occurs for pH below than 8.3, since there is no chemical precipitation in this range for studied lanthanum concentration. The adsorption of lanthanum at neutral pH could be attributed to the cellulose part of the RH, where site-binding adsorption might be occurring. This could be due to the surface complexation phenomenon with various amino acids present in RH and fibrous contents. The complexation is facilitated by acidic dissociation at higher pH, which is essentially dependent upon the respective proton dissociation constants. The removal of lanthanum could, therefore, be due to the mixed effect of "ion exchange" and surface complexation phenomenon on the surface of RH. Similar results have been reported for the adsorption of lead and antimony on RH [50,51].

3.3.3. *Effect of sorbent amount*

The effect of the amount of adsorbent on the adsorption efficiency of lanthanum ions was checked by shaking 4 cm^3 of 9.98 × 10^{-5} mol/L of La^{3+} solution in 0.0001 mol/L HNO_3 and shaking time of 10 min. The amount of rice husk was varied from 25 to 350 mg and the results are shown in Fig. 4d, which revealed that 300 mg of rice husk was sufficient for the maximum removal of lanthanum from the aqueous solution used and this amount of rice husk was used for further investigations.

3.3.4. *Effect of equilibrium time and kinetic models*

The effect of equilibrium time upon adsorption of La^{3+} ions onto RH was studied using 4 cm^3 of 1.996 × 10^{-4} mol/L of lanthanum solution in 0.0001 mol/L of $HNO_{3,}$ with 300 mg of RH. The equilibration time was varied from 0.5–30 min and attained results are shown in Fig. 5a, which shows that the percentage adsorption increases with the increase in equilibration time. Maximum adsorption was observed at 25 min, beyond which there was no signifi-

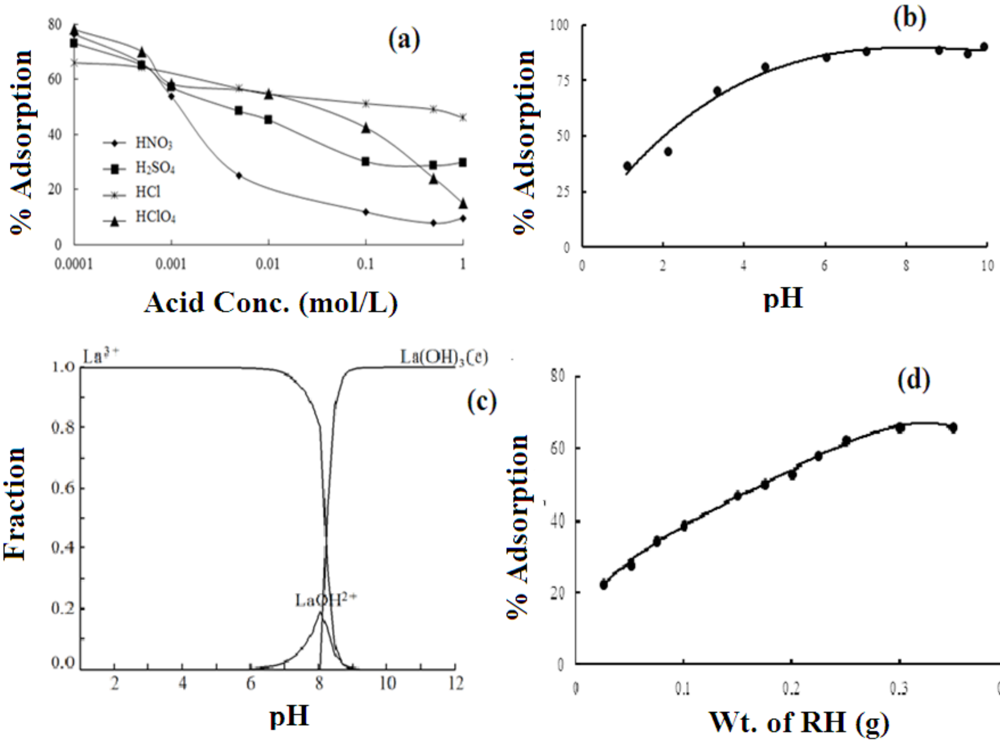

Fig. 4. Effect of operational parameters on the adsorption of lanthanum ions on rice husk; (a) effect of acid concentration (b) effect of pH (c) Lanthanum speciation as a function of pH (d) effect of amount of adsorbent.

cant variation in the adsorption occurred. Therefore, this equilibration time was considered to be sufficient for the adsorption of lanthanum on RH and was used for all the subsequent experiments.

The kinetic data obtained for the adsorption of La^{3+} ions onto RH was also evaluated for the first order Lagergren [52] [Eq. (2)] and pseudo-second order [53] [Eq. (3)] models using the linearized forms as:

$$\log\left(Q_e - Q_t\right) = \log\ Q_e - \frac{k_1}{2.303}t \qquad (2)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e}t \qquad (3)$$

where Q_e is amount of lanthanum adsorbed at equilibrium (mg/g), Q_t is amount of lanthanum adsorbed at time "t" (mg/g), t is time (minutes), k_1 is rate constant of the first order model (/min), k_2 is rate constant of the pseudo-second order model (g/mg·min). The plot of log ($Q_e - Q_t$) against "t" for pseudo first order with R^2 0.9927 is given in Fig. 5a. The plot of t/Q_t against "t" for pseudo-second order kinetic model with straight line ($R^2 = 0.9944$) is shown in Fig. 5b. The kinetic parameters for the pseudo-first order and pseudo-second order models are given in Table 1. The higher correlation coefficient and good correspondence between the calculated (0.312 ± 0.009 mg/g) and experimental (0.302 mg/g) values of sorption capacity show that the experimental kinetic data is more near to the pseudo-second order rate equation.

The nature of the adsorption either via film diffusion or intra-particle diffusion mechanism was verified by using the Morris–Webber [54] and Reichenberg [55] equations:

The sorption data was subjected to Morris-Webber equation:

$$Q_t = k_p t^{0.5} \qquad (4)$$

where Q_t is the adsorbed concentration (mg/g) at time "t" and k_p is the intra-particle transport rate constant of the Morris–Webber model. The plot of Q_t against $t^{0.5}$ is shown in Fig. 5d, which depicts intercept equal to 0.150 ± 0.005. If the value of intercept is zero then it can concluded that intra-particle diffusion mechanism was only operative mechanism but in this case other mechanisms also taking part in the adsorption of lanthanum onto RH.

The sorption data was subjected to Reichenberg equation:

$$X = \left(1 - \frac{6}{\pi^2}\right)e^{-B_t} \qquad (5)$$

where

$$X = \frac{Q_t}{Q_e} = \frac{\text{Amount of metal adsorbed at time "t"}}{\text{Amount of metal adsorbed at equilibrium}}$$

The value of B_t is a mathematical function of X that can be calculated for each value of X by using the relationship:

$$B_t = -\ 0.4977 \ln\left(1 - X\right) \qquad (6)$$

The plot of B_t versus time is a straight line (Fig. 5c) with a correlation factor of 0.9927, which indicates that film diffusion mechanism also involved in sorption of lanthanum onto RH.

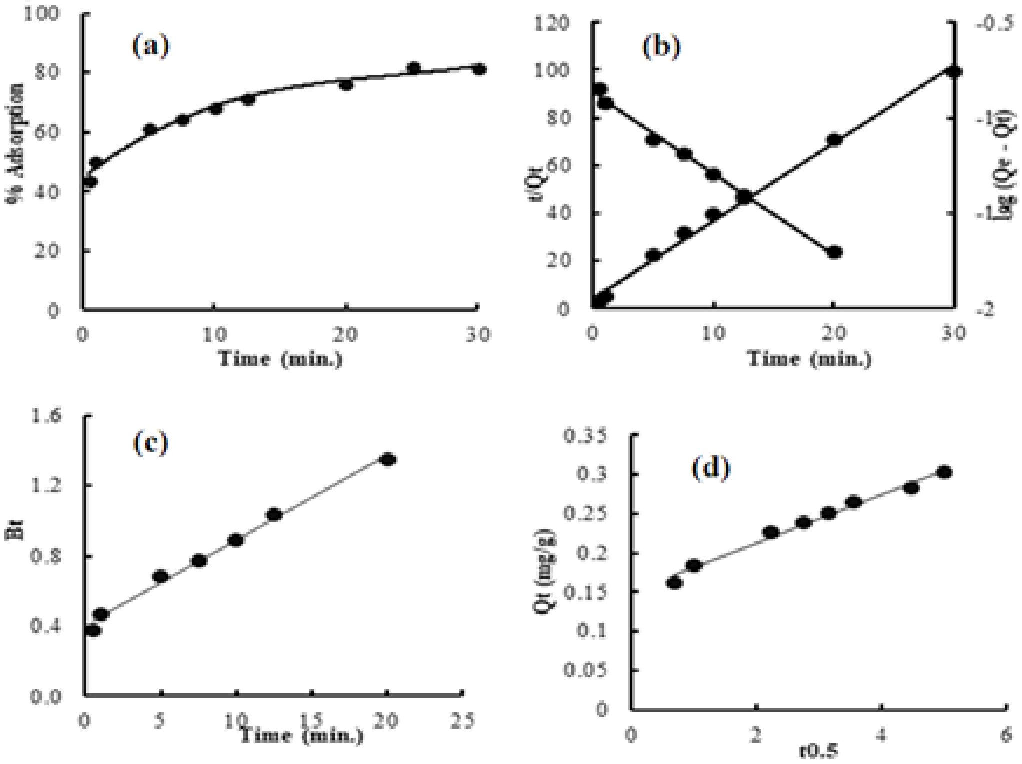

Fig. 5. Effect of equilibration time and various kinetic models for adsorption of lanthanum ions on rice husk; (a) Percentage removal (b) Pseudo 1st and 2nd order models (c) Reichenberg kinetic model (d) Morris Webber Kinetic model.

Table 1
Determined kinetic parameters for adsorption of La^{3+} ions on rice husk

Model	Rate constant (*k*)	Q_e (mg g^{-1})/C	% Error	R^2
Pseudo 1st order	0.097 ± 0.0037	0.134 ± 0.002	55.714	0.9927
Pseudo 2nd order	2.066 ± 0.598	0.312 ± 0.009	–3.173	0.9944
Morris Webber	0.031 ± 0.002	0.150 ± 0.005		0.9838
Reichenberg	0.0484 ± 0.0018	0.405 ± 0.190		0.9927
Experimental Q_e	= 0.302 (mgg^{-1})			

3.3.5. Effect of lanthanum ions concentration

The dependence of La^{3+} ions concentration on adsorption by RH was studied under the optimized conditions of 300 mg adsorbent weight and 25 min equilibrium time. The initial sorptive concentration of La^{3+} ions was varied from 9.98×10^{-5} to 1.39×10^{-3} mol/L. It was observed that the adsorption of lanthanum was decreased with the increase in initial concentration of lanthanum ions. This can be explained in terms of relatively lesser number of active sites at higher concentrations of lanthanum.

The results of the La^{3+} ions varying concentration adsorption onto RH were analyzed in terms of linear and nonlinear forms of Freundlich, Langmuir and D-R adsorption isotherm models. To compare the application of different models, the coefficient of determination "R^2" for linear plots and Chi-square test "χ^2" for nonlinear plots were used as determining tools for the best-fit equations which may be calculated by the following expressions:

$$R^2 = \frac{\Sigma(C_{Ads,cal} - C_{Ads,exp})^2}{\Sigma(C_{Ads,cal} - {}_{Ads,exp})^2 - \Sigma(C_{Ads,cal} - C_{Ads,exp})^2} \tag{7}$$

and

$$\chi^2 = \Sigma \frac{\left(C_{Ads,cal} - C_{Ads,exp.}\right)^2}{C_{Ads,exp.}} \tag{8}$$

where $C_{Ads,exp}$ is experimental adsorption capacity (mg/g), $C_{Ads,cal}$ is calculated adsorption capacity (mg/g) and $\acute{C}_{Ads,exp}$ is average of C_{Ads}, exp. (mg/g). The Freundlich adsorption isotherm was used to analyzed the experimental data for lanthanum ions adsorption onto RH [56]. It was found that the Freundlich adsorption isotherm was capable of describing the data over the concentration range studied. The nonlinear form of the Freundlich isotherm used was:

$$C_{Ads} = KC_{Eq}^{\ 1/n} \tag{9}$$

Where as linearized form of Freundlich isotherm used was:

$$\log C_{Ads} = \log K + \frac{1}{n}\log C_{Eq} \tag{10}$$

where C_{Ads} is amount of lanthanum adsorbed on RH at equilibrium (mol/g), C_{Eq} is equilibrium concentration of lanthanum in solution (mol/L), K and $1/n$ are characteristic Freundlich constants. A plot of log C_{Ads} versus log C_{Eq} yields a straight line with R^2 equal to 0.985 (Fig. 6a) which supports the applicability of the Freundlich isotherm model in the present study. The numerical values of adsorption capacity (K) and intensity (n) were evaluated from the intercept and slope of the straight line, using a least-square fit program and were found to be $2.81 \times 10^{-4} \pm 6.387 \times 10^{-6}$ and 2.087 ± 0.084, respectively. The value of n ($1< n <10$) predicts the heterogeneous surface of the RH. The applicability of Freundlich isotherm in the present system is similar to earlier adsorption studies of thorium onto RH [46]; and lanthanum on bamboo charcoal [27].

The Freundlich adsorption isotherm capacity of RH for lanthanum ions was compared (39.08 mg/g) with reported values of adsorption capacities for different adsorbents and is given in Table 2. The calculated adsorption capacity of RH is less than that of reported value for magnetic alginate-chitosan gel beads for lanthanum ions. The adsorption capacity of RH can be compare with the reported value of adsorption capacity of biosorbent prepared from fish scales but it is higher than nanoporous aluminosilicates, aliquat-336 impregnated onto amberlite XAD-4, neem sawdust, orange peel, pineapple crown, corn style, prawn carapace, egg and crab shells reported in literature for lanthanum ions.

The Langmuir equation was applied in the following nonlinear and linearized forms [59] :

$$C_{Ads} = \frac{Q_m k_L C_{Eq}}{1 + k_L C_{Eq}} \tag{11}$$

$$\frac{C_{Eq}}{C_{Ads}} = \frac{1}{Q_m K_L} + \frac{C_{Eq}}{Q_m} \tag{12}$$

where Q_m is maximum adsorption capacity (mol/g), K_L is Langmuir affinity constant (dm^3/mol). The plot of C_{Eq}/C_{Ads} against C_{Eq} was a straight line (Fig. 6a), indicating the conformity of data to the Langmuir equation in the concentration range of 9.98×10^{-5} to 1.39×10^{-3} mol/L of lanthanum ions. Values of the constants Q_m and K_L calculated from the slope and intercept of the plot in Fig. 6a were $(1.046 \pm 0.105) \times 10^{-5}$ mol/g and 5347 ± 995 dm^3/mol respectively.

Dubinin-Radushkevich (D-R) isotherm model [60] was applied to experimental data to classify the physical or chemical adsorption of lanthanum ions onto RH. The D-R equation is:

$$C_{Ads} = C_m e^{-\beta\varepsilon^2} \tag{13}$$

where C_{Ads} is the amount of lanthanum adsorbed onto EH, C_m is the maximum amount of lanthanum that can be

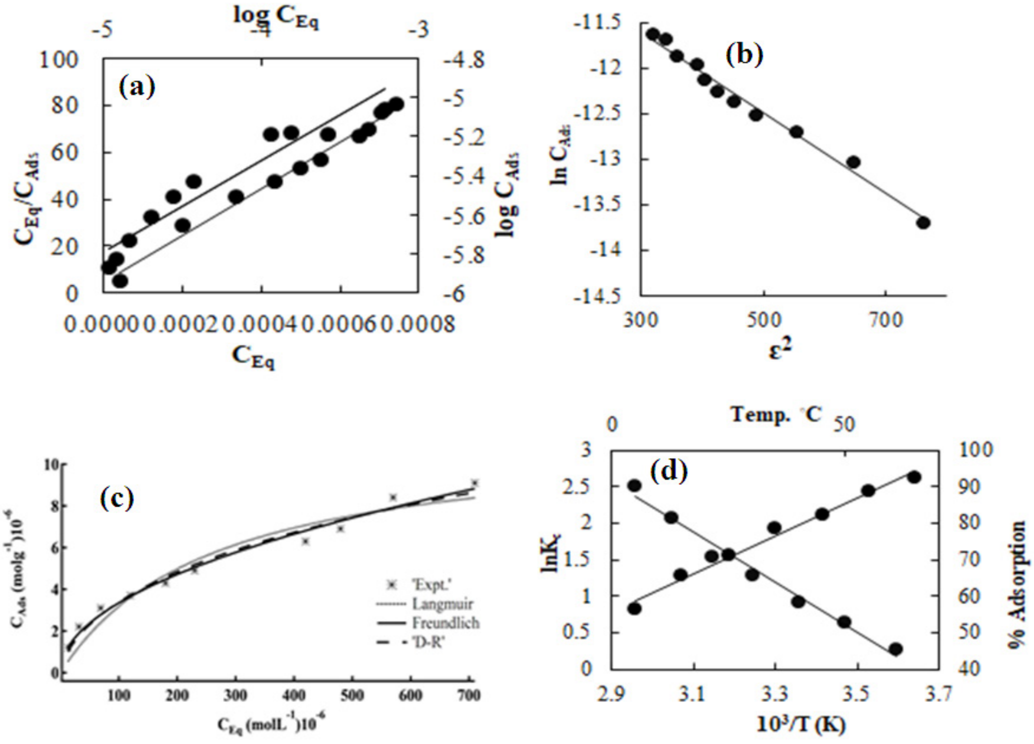

Fig. 6. (a) Linear plots of Freundlich, and Langmuir (b) Linear plot of D-R (c) Nonlinear plots of isotherms (d) Effect of temperature and Van't Hoff plot for the adsorption of lanthanum ions on rice husk.

Table 2
Adsorption capacities of lanthanum for different adsorbents

Adsorbent	Capacity mg g^{-1}	Ref.
Aliquat-336 impregnated onto Amberlite XAD-4	3.29	[22]
Magnitic alginate-chitosan gel beads	49.40	[25]
Nanoporousaluminosilicates	1.25	[26]
Biosorbent from fish scales	40.65	[57]
Neem sawdust	2.3	[58]
Orange peel	9.7	[58]
Pineapple crown	7.5	[58]
Corn style	10.5	[58]
Fish scales	23.1	[58]
Prawn carapace	7.9	[58]
Egg shell	8.6	[58]
Crab shell	8.5	[58]
Rice husk	39.08	Presents study

adsorbed onto RH under the optimized experimental conditions, β is a constant related to sorption energy, and ε (Polyanyi potential) = RT ln(1 + 1/C_{Eq}), where R is the gas constant in kJ/mol·K, T is the absolute temperature in K, and C_{Eq} is the equilibrium concentration of lanthanum in solution. The linearized form of D-R isotherm is

$$\ln C_{Ads} = \ln C_m - \beta\varepsilon^2 \tag{14}$$

When $\ln C_{Ads}$ is plotted against ε^2, a straight line was observed (Fig. 6b). The computed values of β and C_m from the slope and intercept of this straight line were – (4.30± 0.187) × 10^{-3} kJ^2/mol and (3.26 ± 0.017) × 10^{-5} mol/g, respectively. From the value of β the mean sorption energy (E) was calculated by using following expression:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{15}$$

which is the mean free energy of transfer of one mole of solute from infinity to the surface of RH. The numerical value of E computed from Eq. (15) is 10.78 ± 0.641 kJ/mol which is in the range for chemisorption interaction of lanthanum ions with RH based on ion exchange phenomena.

Wave Metrices IGOR Pro 6.1.2, software, was used for the calculation of isotherm parameters while using non-linear equations. Fig. 6c is the nonlinear plots of Freundlich, Langmuir and D-R isotherms, the isotherm constants from the nonlinear plots along with Chi-square "χ^2" values for nonlinear equations and correlation coefficient "R^2" values for linear equations are shown in Table 3.

3.3.6. Effect of temperature and thermodynamic parameters

The effect of temperature on the sorption of lanthanum ions onto RH was studied by conducting experiments in the range of 278.16–338.16 K under optimized experimental conditions. With the rise in temperature, adsorption of lanthanum increased (Fig. 6d). The linearized form of Van't Hoff Eq. (16) was used for the determination of thermodynamic parameters like change in adsorption enthalpy (ΔH) and change in entropy (ΔS).

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{16}$$

$$K_c = \frac{C_s}{C_e} \tag{17}$$

$$\Delta G = \Delta H - T\Delta S \tag{18}$$

where K_c is equilibrium constant, ΔS is entropy change for the process (kJ/mol), ΔH is enthalpy change for the process (kJ/mol), R is gas constant (kJ/mol.K), T is absolute temperature (K), ΔG is changes in Gibbs free energy, C_s is concentration of metal adsorbed onto the adsorbent at equilibrium (mol/ L) and C_e is concentration of metal in solution at equilibrium (mol/L).The values of ΔH and ΔS were calculated from slope and intercept of the plot of $\ln K_c$ vs $1/T$ which is a straight line (Fig. 6d) with slope equal to $-\Delta H/R$ and intercept equal to $\Delta S/R$. The determined values of ΔH, ΔS and ΔG have been reported in Table 4. The negative values of ΔG indicate the spontaneous process of lanthanum adsorption onto RH. The increase in the ΔG values with the rise in temperature indicated more favourable adsorption of lanthanum ions at higher temperatures. The endothermic nature of the lanthanum adsorption onto RH was confirmed by positive value of ΔH and the positive value of ΔS suggests the increased randomness at the solid-solution interface during the adsorption of lanthanum onto RH. Similar results were reported in literature [61].

3.3.7. Effect of diverse ions

The presence of various ions affects the adsorption efficiency of the adsorbent, may alter the environment and chemistry of adsorbing media for the metal of interest in solution. The adsorption of lanthanum ions was checked in the presence of high concentration of different ions to check their effect on adsorption under optimized conditions. All the anions were used as their sodium salts, whereas for cations the nitrate salts were used. The influence of common anions and cations was investigated for lanthanum removal under optimized experimental conditions. Table 5 reveals that NO_2^-, PO_4^{3-}, SO_4^{2-} and halides suppressed the adsorption of lanthanum whereas complexing agents like EDTA and CN^- reduced the lanthanum adsorption drastically from aqueous media.

3.4. Applicability of studies

In order to verify the applicability of the developed procedure on real samples, the removal of lanthanum was checked from ordinary tap water sample using the conditions of 0.0001 mol/L of HNO_3 solution, 25 min shaking time and adsorbent weight of 300 mg. The results are shown in Table 6 along with the determined composition of tap water sample. The data showed that the determined

Table 3
Determined adsorption isotherm parameters of lanthanum adsorption on rice husk

Isotherm	Experimental adsorption capacity = 9.11 × 10^{-6} (mol g^{-1})					
	Linear equation		R^2	Nonlinear equation		χ^2
Langmuir	Q_m (mol g^{-1})	*b* (Lmol^{-1})	0.926	Q_m (mol g^{-1})	*b* (L mol^{-1})	3.87 × 10^{-12}
	1.04 × 10^{-5}	5347		1.15 × 10^{-5}	3828	
Freundlich	K_f (mol g^{-1})	*N*	0.985	K_f (mol g^{-1})	*N*	9.46 × 10^{-13}
	2.81 × 10^{-4}	2.087		3.21 × 10^{-4}	2.018	
D-R	Q_m (mol g^{-1})	β (mol^2 j^{-2})	0.985	Q_m (mol g^{-1})	β (mol^2 j^{-2})	1.5 × 10^{-12}
	3.26 × 10^{-5}	4.3 × 10^{-3}		4.0 × 10^{-5}	4.8 × 10^{-3}	
	E = 10.78 kJ mol^{-1}			*E* = 10.16 kJ mol^{-1}		

Table 4
Determined thermodynamic parameters for adsorption of La^{+3} ions on rice husk

Temp K	10^3/T	C_{Ad} (mol L^{-1}) × 10^{-4}	C_{Eq} (mol L^{-1}) × 10^{-5}	K_c	lnK_c	Δ*H* (kJ mol^{-1})	Δ*S* (J K^{-1} mol^{-1})	Δ*G* (kJ mol^{-1})
278.16	3.595	1.689	13.049	1.295	0.258	28.563	104.065	−0.384
288.16	3.470	1.962	10.324	1.900	0.642		104.067	−1.425
298.16	3.354	2.140	8.542	2.505	0.918		104.069	−2.466
308.16	3.245	2.348	6.457	3.637	1.291		104.071	−3.508
318.16	3.143	2.470	5.242	4.712	1.550		104.072	−4.549
328.16	3.047	2.661	3.327	8.000	2.079		104.074	−5.590
338.16	2.957	2.771	2.231	12.419	2.519		104.076	−6.631

Table 5
Effect of diverse ions on lanthanum adsorption by rice husk

Cations	Concentration Mol L^{-1} × 10^{-3}	% Adsorption	Anions	Concentration Mol L^{-1} × 10^{-03}	% Adsorption
None	–	87.00	None	–	87.00
K^+	6.41	65.08	SO_4^{2-}	2.60	51.99
Cd^{2+}	0.445	68.19	CO_3^{2-}	4.16	71.49
Mg^{2+}	20.06	84.26	HCO_3^-	4.10	77.42
Cr^{6+}	0.962	82.02	PO_4^{3-}	2.63	27.77
Pb^{2+}	1.21	83.02	NO_3^-	4.03	87.29
Al^{3+}	9.27	62.50	NO_2^-	5.43	61.05
Na^+	10.09	83.00	Cl^-	7.05	55.94
Cu^{2+}	0.787	66.96	Br^-	3.13	42.05
Co^{2+}	0.848	73.81	I^-	1.97	46.15
Fe^{3+}	0.895	90.11	F^-	1.32	61.78
Ni^{2+}	0.852	76.08	S^{2-}	7.80	70.28
Zn^{2+}	0.765	82.32	CN^-	9.62	08.02
Mn^{2+}	4.55	71.42	EDTA	0.672	10.31

concentration of lanthanum in tap water sample was quite low; therefore, the removal efficiency of lanthanum was checked by spiking the sample with 13.863 mg/L of lanthanum ions. The data in Table 6 indicate that concentration of lanthanum was decreased by 78.83 % from the spiked tap water in a single step, however, by shaking the aliquot with the same weight of fresh RH removed the lanthanum up to 86.64% from the spiked tap water sample, indicating that RH has high potential to remove lanthanum from such matrices.

Table 6
Determined composition of tap water sample

Cations/anions	Concentration (mg/L)
Ca	31.52
Mg	12.90
Na	15.42
K	2.23
Fe	0.02
Mn	0.01
Zn	0.11
Cu	0.01
Pb	0.01
CO_3^{2-}	7.00
HCO_3^{2-}	140.00
Cl–	2.80
NO_3–	2.00
SO_4^{2-}	12.00
La	13.86*
La	2.93**
La	1.85***

* Concentration after spiking
** Concentration after decontamination
*** Concentration after two consecutive decontamination steps

4. Conclusions

From these studies following conclusion can be made:

- The abundantly available RH is an efficient adsorbent for the removal of lanthanum ions from aqueous solutions.
- The lanthanum was removed quantitatively within 25 min of time without any prior chemical treatment or time consuming adjustments.
- The data generated obeyed pseudo 2nd order kinetic model and obeyed the Freundlich, Langmuir, and Dubinin-Radushkevich isotherm equations.
- The adsorption process was found to be endothermic, spontaneous and favorable and occurs in the presence of a variety of anions and cations.
- The RH can be used for safe disposal of radioactive effluents and will provide an alternative solution to environmental damages caused by radio nuclides.

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