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# Kinetics, isotherm and thermodynamics for thorium ions adsorption from aqueous solutions by coal

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**ABSTRACT**

The adsorption of thorium ions on coal has been studied as a function of shaking time, nature of electrolytes ($HClO_4$, HCl, $H_2SO_4$ and $HNO_3$), dose of adsorbent, metal ion concentration and temperature. The radiotracer technique was applied to examine the distribution of thorium using a batch method. Maximum adsorption was found to be at 0.0001 mol $L^{-1}$ of $HNO_3$ solution, using 0.3 g of adsorbent for 4 mL of $4.310 \times 10^{-5}$ mol $L^{-1}$ thorium concentration with equilibration time of 20 min. The adsorption of thorium was decreased with the increase in the concentrations of all the mineral acids used. The kinetic data indicated an intraparticle diffusion process with sorption being pseudo-second-order. The determined rate constant $k_2$ was 13.699 g $mg^{-1}$ $min^{-1}$. The adsorption data obeyed the Langmuir, Freundlich and Dubinin–Radushkevich isotherm plots with correlation coefficients ($R^2$) of 0.999, 0.986 and 0.994, respectively, over the thorium concentration range of $4.310 \times 10^{-5}$ to $4.310 \times 10^{-4}$ mol $L^{-1}$. The characteristic Freundlich constants such as $1/n = 0.596$ and $K = 0.706$ m mol $g^{-1}$ whereas the Langmuir constants $Q = 4.609 \times 10^{-3}$ m mol $g^{-1}$ and $b = 17.021 \times 10^3$ $dm^3$ $mol^{-1}$ have been calculated for the adsorption system. The sorption mean free energy from the Dubinin–Radushkevich isotherm is 10 kJ $mol^{-1}$ indicating chemical sorption of ion-exchange mechanism. The uptake of thorium was increased with the rise in temperature (283-333 K). Thermodynamic quantities such as $\Delta H$, $\Delta G$ and $\Delta S$ have been computed and discussed for the system. Sorbent was characterized by using scanning electron microscopy and Fourier transform infrared spectroscopy before and after the adsorption of thorium. Effect of coexistent ions on the adsorption of thorium has also been investigated. By using the optimized parameters the removal of spiked thorium ions from tap water sample was found to be 81.0%.

*Keywords:* Coal; Thorium; Radiotracer; Removal; Kinetic; Coexistent ions

## 1. Introduction

The presence of radionuclides in aqueous wastes is of main environmental concern that attracted the attention of researchers in these days. The induction of thorium into the environment is through uranium mining and processing, extensive use of fertilizers, optics industry, reprocessing of nuclear fuel, radioactive wastes from nuclear power plants [1,2]. The inhaled/ingested thorium accumulates in liver, lungs, spleen and kidney causing cancer of these organs [3]. Therefore, there is a dire need to remove thorium ions from the effluents of the above mentioned industries for their safe disposal.

Various techniques are being used for the removal of thorium ions from aqueous media, those include coprecipitation [4], electrodialysis [5], ion exchangers [6,7], solvent extraction [8,9] and adsorption [10]. But these processes have the limitations of generation of large quantities of sludge, lack of selectivity, use of large amounts of toxic chemicals, etc. The adsorption process has been an edge over these with respect to its simplicity, ease of operation and cost-effectiveness.

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For adsorption of thorium from aqueous solutions, various researchers have investigated many adsorbents such as, PAN/zeolite composite [11], silica [12], gibbsite [13], $TiO_2$ [14,15], hematite [16], XAD-4 resin [17], diatomite [18], attapulgite [19], perlite [20], activated carbon [21], amberlite XAD [22], flux calcined diatomite [23], etc.

The present study deals with exploitation of the potentials of low-rank Pakistani coal for the removal of thorium ions from aqueous solution. The selected material is abundantly available as a low cost material even after its wide consumption as a fuel in power generation plants, brick kilns and various other mills. The coal possesses a granular structure, high surface area, highly oxygenated with many carboxyl and phenolic hydroxyl functional groups which are capable to adsorb the metal ions. Due to the presence of such properties, the coal seems to be a good candidate for adsorbent of thorium ions. The inexpensive coal has been used for the adsorption of copper [24], chromium [25] and lead [26] from aqueous solutions.

## 2. Materials and methods

### 2.1. Radiotracer preparation

The radiotracer of thorium used in this research was prepared by irradiating a known amount of spec-pure thorium nitrate from Johnson and Matthey in a 10 MW swimming pool type reactor (PARR-1) of PINSTECH for a specific time, at a neutron flux of $4.5 \times 10^{13}$ $cm^{-2}$ $s^{-1}$. After a proper cooling time, the sample was dissolved in hydrochloric acid and diluted to a fixed known volume with the help of water. The tracer purity of the radionuclide was checked on 4K series of 85 Canberra Multichannel analyzer coupled with a 25 $cm^3$ Ge(Li) detector.

### 2.2. Reagents

Low-rank Pakistani coal was collected from mines in the province of Punjab (Khoshab and Makerwal). The sample was ground and sieved to a particle size of about 500 µm. The coal powder was activated at 300°C in a muffle furnace for 4 h which enhance the basicity of adsorbent. The activated coal sample was treated with 2 M $H_2SO_4$ at room temperature for 2 h to increase its acidic behavior, remove the mineral components and improve the hydrophilicity of the surface. After acid treatment, the coal was washed thoroughly with deionized water until the neutral pH of the filtrate. The washed coal sample was dried at 60°C till constant weight and stored in plastic container.

### 2.3. Batch adsorption measurements

A known amount of coal was taken in a 4 mL of standard acid solution of required strength, along with a known aliquot of stock radiotracer solution in 16 mL culture tube with a screwed polyethylene cap. The contents were equilibrated on a mechanical shaker for 20 min, the contents were centrifuged and the supernatant solution was withdrawn. The radioactivities of the liquid phase were determined before and after equilibration with a well type NaI scintillation counter (Canberra Inc., USA) coupled with a counter scalar (Nuclear Chicago, USA). All the measurements were performed at room temperature (297 ± 1 K) unless otherwise specified and the reported values are the average of at least two measurements.

The amount of thorium ions adsorbed per unit mass of the adsorbent and percentage adsorption from the solution were calculated using the following expressions:

$$q_{e,\exp} = \frac{(C_{\text{ini}} - C_{\text{fin}})V}{m} \tag{1}$$

$$\%\ \text{adsorption} = \frac{A_{\text{initial}} - A_{\text{final}}}{A_{\text{initial}}} \times 100 \tag{2}$$

where $A_{\text{initial}}$ is the initial radioactivity of thorium ions in the solution and $A_{\text{final}}$ is the radioactivity of thorium ions in solution after equilibrium. $q_{e,\exp}$ is the equilibrium adsorption capacity (mg $g^{-1}$), $C_{\text{ini}}$ is the initial concentration of thorium ions in solution (mg $L^{-1}$), $C_{\text{fin}}$ is the equilibrium concentration of thorium ions in solution (mg $L^{-1}$), $V$ is the volume (L) and $m$ is the weight of the adsorbent (g).

## 3. Results and discussion

### 3.1. Characterization of adsorbent

The surface area of low-rank Pakistani coal sample was measured according to Brunauer–Emmett–Teller (BET) method by nitrogen adsorption at 77 K using Quanta chrome S1 BET surface area analyzer. Before nitrogen adsorption the sample was degassed for 2 h at final pressure of $133.32 \times 10^{-4}$ Pa. The bulk density, percentage porosity, pH and $pH_{zpc}$ of the adsorbent were determined by using the reported methods [27,28] and the results are summarized in Table 1.

#### 3.1.1. FTIR studies

The chemical modification of coal and thorium loaded coal was followed using Fourier transform infrared (FTIR) spectroscopy. The FTIR spectra of coal, activated coal and thorium loaded activated coal are shown in Fig. 1.

The adsorption band at 2,914 $cm^{-1}$ in coal attributed to C–H aliphatic alkane. A band at 1,736 $cm^{-1}$ due to C=O stretching

Table 1
Characteristics of coal

| Parameters | Value |
|---|---|
| Particle size, µm | 500 |
| Bulk density, g $mL^{-1}$ | 2 |
| BET surface area, $m^2$ $g^{-1}$ | 4.8 |
| Total pore volume, cc $g^{-1}$ | $4.8 \times 10^{-3}$ |
| Average pore diameter, nm | 4 |
| Porosity, % | 53 |
| Organic content, % | 81.6 |
| Ash content, % | 18.39 |
| pH | 5.0 |
| $pH_{zpc}$ | 3.1 |

of carboxylic group. A peak at 1,613 cm$^{-1}$ assigned to aromatic C=C or either C=O stretching. The peak at 1,439 cm$^{-1}$ is due to C–H stretching. The peak at 1,362 cm$^{-1}$ is due to S=O stretching of sulfonic group. The band at 1,211 cm$^{-1}$ is attributed to C–O stretching vibrations. The band at 1,027 cm$^{-1}$ originates from the C–O stretching vibration of –C–O–H group. Absorption bands at 430–470 and 516 cm$^{-1}$ are due to mineral components. In case of activated coal the band at 2,914, 1,613, 1,439, 1,027 and 908 cm$^{-1}$ disappeared. Peaks at 1,736, 1,362 and 1,211 cm$^{-1}$ shifted to 1,735, 1,365 and 1,217 cm$^{-1}$ with enhanced intensity, respectively.

Some bands in activated coal after adsorption show lower intensities and also show small differences in frequencies indicating the participation of these functional groups in the adsorption of Th by activated coal. The major changes are the bands at 1,735, 1,365 and 1,217 cm$^{-1}$ shifted to lower frequency region (1,731, 1,363 and 1,214 cm$^{-1}$) with reduction in intensity. This represents that the sulfonic and carboxylic groups are interacting with the thorium adsorption on low-rank Pakistani coal.

### *3.1.2. SEM studies*

The scanning electron microscopic (SEM) micrographs of coal and thorium adsorbed coal were recorded and are shown in Fig. 2. In the SEM image of the virgin coal the bright surface shows the rough and porous nature of the adsorbent, which may be responsible for the adsorption of thorium ions. The SEM micrograph of the thorium loaded coal clearly shows that the caves, pores and surface of coal were covered by thorium, resulting in the smoothness of the surface of adsorbent.

### *3.2. Influence of acid concentration*

The chemical contact plays a significant role in the adsorption process by affecting the surface charge of sorbent, the extent of ionization and speciation of the sorbate. Therefore, the adsorption characteristics of thorium was investigated in mineral acid solutions ($HNO_3$, HCl, $H_2SO_4$ and $HClO_4$) in the concentration range of 0.0001–1.0 mol L$^{-1}$ using 4.310 × 10$^{-5}$ mol L$^{-1}$ of thorium with 0.3 g of coal. The concentration of thorium and adsorbent dose of 0.3 g of coal was selected arbitrarily and the results are presented in Fig. 3.

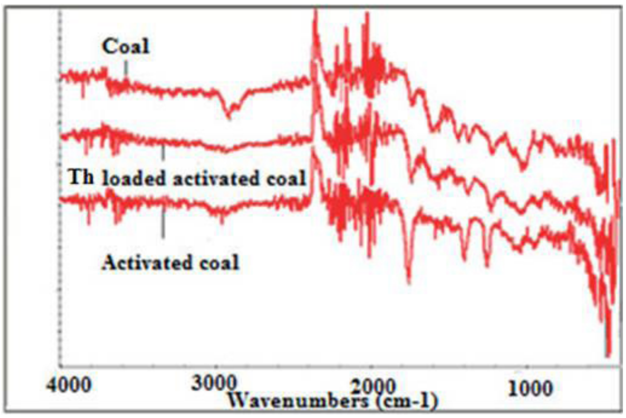

Fig. 1. FTIR spectra of coal, activated coal and thorium loaded activated coal.

Maximum removal of thorium ions was occurred at 0.0001 mol L$^{-1}$ acid concentration. With further increase in mineral acid concentration the adsorption of thorium was

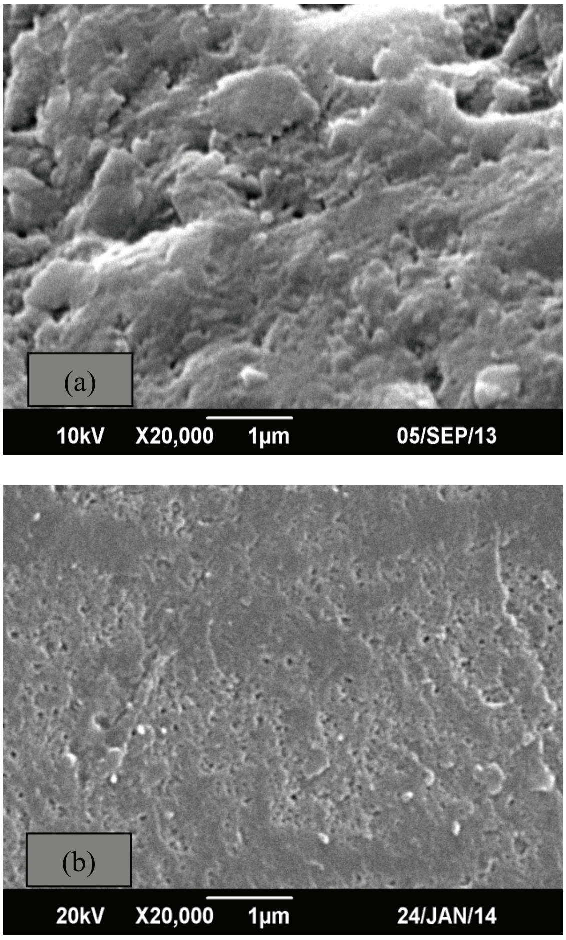

Fig. 2. SEM images of the coal before (a) and after (b) thorium adsorption.

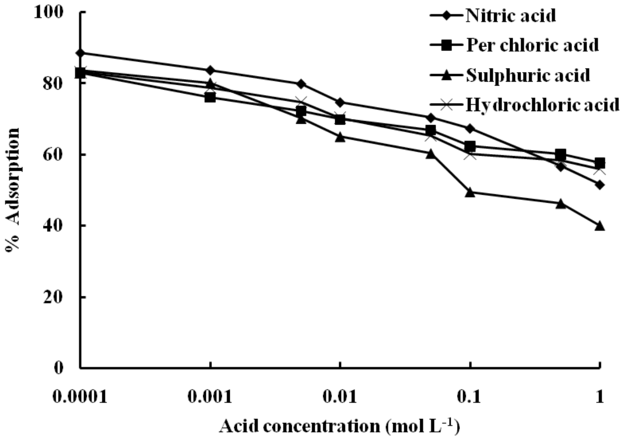

Fig. 3. Variation of adsorption of thorium ions on coal as a function of acid concentration.

started decreasing up to 1 mol L$^{-1}$. Similar trend was observed by all the acids used. At higher acid concentration, the adsorbent's surface was highly associated with the hydrogen ions as compared with positively charged thorium ions. At lower acid concentrations the surface of the adsorbent containing carboxyl, sulfonic groups would be exposed and possess negative charges which attract positively charged thorium ions resulting in greater adsorption.

Maximum adsorption of thorium ions at 0.0001 mol L$^{-1}$ acid concentration is in accordance with the concept of zero point charge (ZPC), which is 3.0 for the adsorbent used in the present work. Above the ZPC, the coal surface has a net negative charge which leads to electrostatic attraction of positively charged thorium ions.

The thorium ions adsorption on the coal surface is likely to be via ion-exchange mechanism according to the following relation:

$$m\left[\mathrm{Coal-OH}\right] \rightleftharpoons m\left[\mathrm{Coal-O}\right]^{-} + m\mathrm{H}^{+} \tag{3}$$

$$\mathrm{M}^{n+} + m\left[\mathrm{Coal-O}\right]^{-} \rightleftharpoons \mathrm{M}\left[\mathrm{Coal-}\right]_{m}^{(n-m)} \tag{4}$$

where [Coal–OH] is the activated coal surface; $\mathrm{M}^{n+}$ is the metal ions with $n$ + charge; $m\mathrm{H}^{+}$ is the number of protons released.

It was also observed that maximum adsorption of thorium ions has been occurred at 0.0001 mol L$^{-1}$ $HNO_3$ as compared with the other mineral acids; therefore, this acid concentration of $HNO_3$ was selected for all the subsequent experiments regarding the optimization of adsorption conditions for thorium ions on coal.

### 3.3. Effect of coal dose

Effect of the coal dose on Th(IV) removal was studied by varying the coal dose from 0.025 to 0.65 g using 4.310 × 10$^{-5}$ mol L$^{-1}$ of thorium solution at 0.0001 mol L$^{-1}$ of $HNO_3$ for time interval of 20 min. It is clear from Fig. 4, which is a plot of percentage sorption of thorium vs. coal dose that percentage sorption increases with an increase in the amount of coal. This is because by increasing the adsorbent dose, the number of active sites available for coal–thorium interaction is increased. It was observed that 0.3 g of coal was sufficient for the quantitative sorption of thorium solution used beyond which the percentage sorption was almost constant, therefore, this amount was considered to be sufficient and was used for all further investigations.

### 3.4. Effect of shaking time

The effect of shaking time on removal of Th(IV) was studied by varying the time from 1 to 30 min using 4.310 × 10$^{-5}$ mol L$^{-1}$ of thorium solution at 0.0001 mol L$^{-1}$ $HNO_3$ with 0.3 g of coal dose as shown in Fig. 5. Increase in percentage sorption with increase in contact time is due to more time required for Th(IV) ions to make complex with coal up to 20 min after this no considerable increment is observed because of unavailability of active sites. Finally, 20 min shaking time was considered for further investigation.

The adsorbate can be moved from the liquid medium to the surface binding sites of the adsorbent in different processes. The process may involve film or pore diffusion, external diffusion, surface diffusion and sorption on the pore surface. The overall sorption may involve one or several steps. The sorption data were applied to the Weber–Morris expression [29]:

$$q_t = K_{\mathrm{int}}\, t^{0.5} + C \tag{5}$$

where $q_t$ is the adsorbed concentration of thorium at time ($t$) (mg g$^{-1}$); $K_{\mathrm{int}}$ is the intraparticle diffusion rate constant.

The value of $K_{\mathrm{int}}$ was determined from the slope by plotting $q_t$ against $t^{0.5}$ (Fig. 6) and was found to be $4.8 \times 10^{-3}$ mg g$^{-1}$ min$^{-0.5}$.

Fig. 6 depicts that the adsorption of thorium ions was rapid up to 15 min and then slowed down up to 30 min, which is clear from two distinct slopes of 0.005 and 0.002 for the first 16 and 20–30 min, respectively.

To verify the adsorption process either through film diffusion or intraparticle diffusion mechanism the time

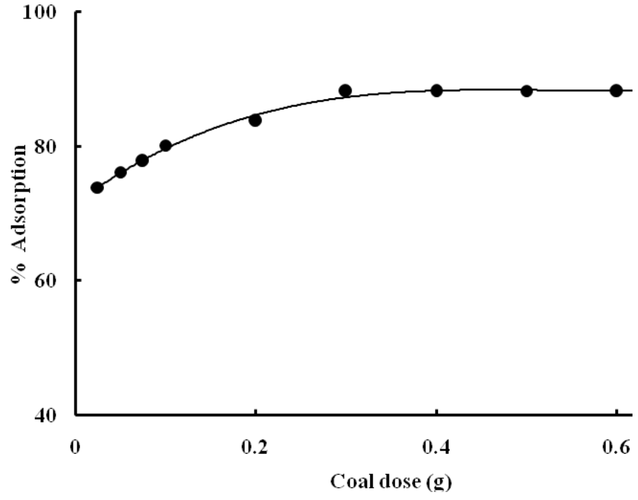

Fig. 4. Effect of coal dose on the adsorption of thorium.

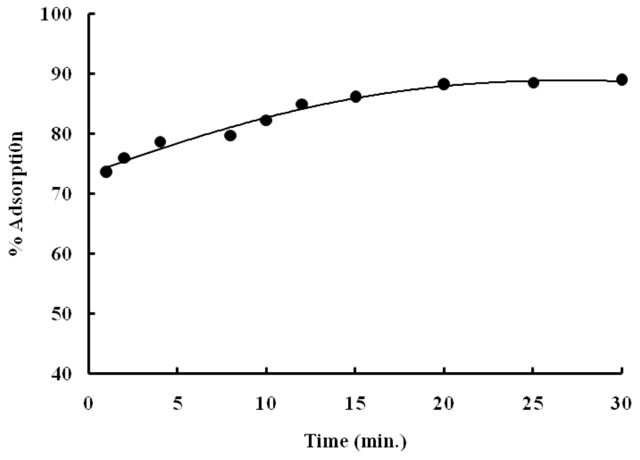

Fig. 5. Effect of shaking time on the adsorption of thorium on coal.

dependent adsorption data were also subjected to the Reichenberg [30] Eq. (6):

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

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

The value of $\beta_t$ is a mathematical function of $X$ that can be calculated for each value of $X$ by using Eq. (7):

$$\beta_t = -0.4977 \ln(1 - X) \qquad (7)$$

The plot of $\beta_t$ vs. time is a straight line (Fig. 7) with a correlation coefficient of 0.979 which indicates that the adsorption was controlled through film diffusion mechanism. It was also observed that the Reichenberg plot is not passing through origin indicating that the film diffusion is not the only mechanism involved during the adsorption of thorium ions on low-rank Pakistani coal.

The kinetic data of the adsorption of thorium ions on coal was subjected to the first-order Lagergren (Eq. (8)) and pseudo-second-order (Eq. (9)) rate expressions using the linearized form as:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303} t \qquad (8)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (9)$$

where $q_e$ is the amount of thorium adsorbed at equilibrium (mg g$^{-1}$), $q_t$ is the amount of thorium adsorbed at any time $t$ (min), $k_1$ is the rate constant of the first-order relationship (min$^{-1}$) and $k_2$ is the rate constant of the pseudo-second-order relationship (g mg$^{-1}$ min$^{-1}$).

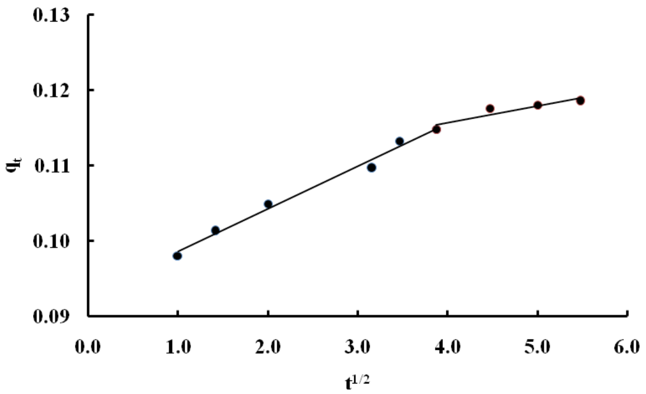

Fig. 6. Weber–Morris plot of thorium ions adsorption on coal.

The linear plots were obtained by plotting log($q_e$ − $q_t$) against $t$ and $t/q_t$ vs. $t$ with correlation coefficients ($R^2$) of 0.984 and 0.999, respectively, as shown in Fig. 8. The determined kinetic parameters and $\Delta q$ values for the first-order and pseudo-second-order models have been given in Table 2.

The quantitative comparison of the applicability of each model was made by a normalized standard deviation ($\Delta q$) calculated by employing Eq. (10) [31]:

$$\Delta q\,(\%) = \frac{100}{n-p} \sum_{i=1}^{n} \left[ \frac{\left(q_{e,\text{exp}} - q_{e,\text{calc}}\right)^2}{q_{e,\text{exp}}} \right] \qquad (10)$$

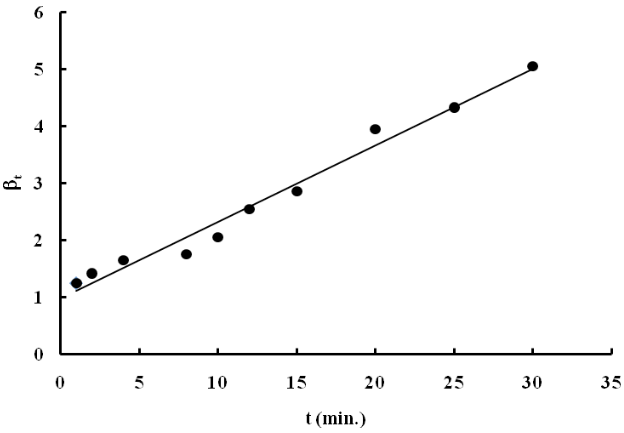

Fig. 7. Reichenberg plot of thorium adsorption on coal.

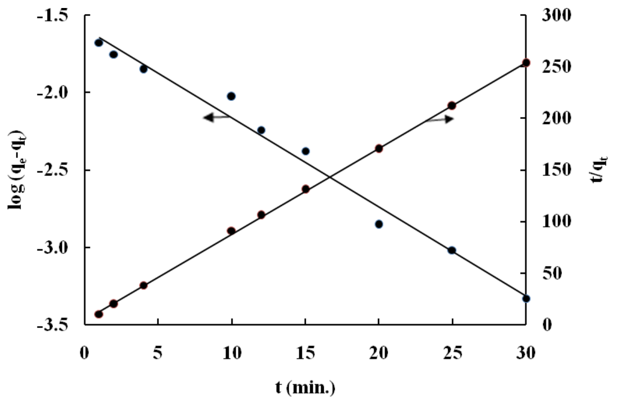

Fig. 8. Lagergren first-order and pseudo-second-order plots of thorium ions adsorption on coal.

Table 2
Kinetic data for the adsorption of thorium ions on coal

| Pseudo-first-order | | | | Pseudo-second-order | | | |
|---|---|---|---|---|---|---|---|
| $q_e$ (mg g$^{-1}$) | $k_1$ (min$^{-1}$) | $R^2$ | $\Delta q$ (%) | $q_e$ (mg g$^{-1}$) | $k_2$ (g mg$^{-1}$ min$^{-1}$) | $R^2$ | $\Delta q$ (%) |
| 0.027 | 0.134 | 0.979 | 6.989 | 0.120<br>0.119[a] | 13.699 | 0.999 | 0.155 |

[a] Experimentally calculated.

where $n$ is the number of data points; $p$ is the number of parameters in the equation; $q_{e,\exp}$ is the adsorbent capacity at the equilibrium experimental conditions; $q_{e,\text{calc}}$ is the calculated adsorbent capacity.

The $q_{e,\exp}$ is the experimentally determined adsorbed concentrations of thorium ions obtained from Eq. (1).

Because the $\Delta q$ represents the agreement between the calculated and experimental values, it provides a numerical measure to interpret the goodness of fit of a given mathematical model of the data. A model is considered to be more appropriate which have maximum correlation coefficient "$R^2$" and minimum "$\Delta q$" values.

The maximum higher $R^2$, minimum $\Delta q$ values and good correspondence between the calculated (0.120 mg Thg$^{-1}$) and the experimental (0.119 mg Th g$^{-1}$) values of sorption capacity confirm that the experimental kinetic data is better described by the pseudo-second-order rate expression.

### *3.5. Effect of initial thorium ion concentration*

The effect of initial thorium ion concentration on the efficiency of adsorption on coal was checked under the optimized conditions of contact time 20 min, adsorbent dose 0.3 g and the 0.0001 mol L$^{-1}$ of $HNO_3$. The initial concentration of thorium was varied from $4.310 \times 10^{-5}$ to $4.310 \times 10^{-4}$ mol L$^{-1}$ and the results are shown in Fig. 9.

The results in Fig. 9 show that with the increase in the initial concentration of thorium from $4.310 \times 10^{-5}$ to $4.310 \times 10^{-4}$ mol L$^{-1}$, the adsorption capacity of coal was increased from 0.112 to 0.814 mg g$^{-1}$. This could probably be due to an increase in the initial concentration of thorium ions provide a larger deriving force to overcome the total mass transfer resistance of thorium ions between the liquid and solid phases, leading to higher collisions between adsorbate and adsorbent surface [32].

### *3.5.1. Adsorption isotherms*

To describe the interactive behavior between the adsorbate and adsorbent, the experimental data of the thorium ions adsorption on low-rank Pakistani coal under the optimized parameters was subjected to various adsorption isotherm models such as Freundlich, Langmuir and Dubinin–Radushkevich.

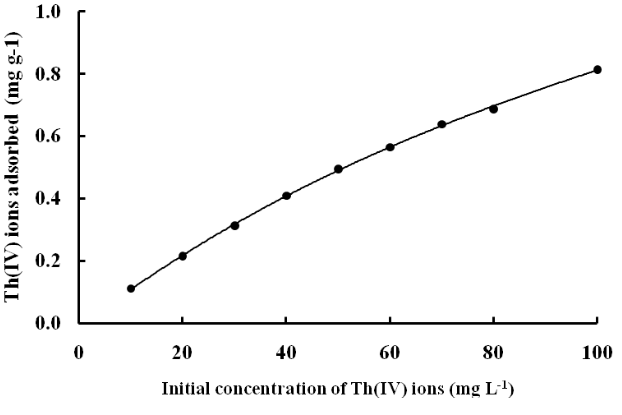

Fig. 9. Adsorption of thorium ions as a function of its own concentration on coal.

*3.5.1.1. Freundlich isotherm* Freundlich isotherm is the relationship between the adsorbed concentration of thorium ions per unit mass of the adsorbent ($C_{\text{ad}}$) and the concentration of metal at equilibrium ($C_e$) and is mathematically expressed as:

$$C_{\text{ad}} = KC_e^{\frac{1}{n}} \tag{11}$$

The logarithmic form of the above expression can be written as:

$$\log C_{\text{ad}} = \log K + \frac{1}{n}\log C_e \tag{12}$$

where $1/n$ and $K$ are Freundlich constants indicating the intensity of sorption and adsorbent capacity, respectively.

A plot of $\log C_{\text{ad}}$ vs. $\log C_e$ yields a straight line (Fig. 10) with a correlation coefficient "$R^2$" of 0.986 and the normalized standard deviation ($\Delta q$) value of 39.049. The linear plot supports the applicability of the Freundlich adsorption model in the present work.

The values of $1/n$ and $K$ were determined from the slope and intercept of the Freundlich isotherm plot and were found to be 0.596 and $7.05 \times 10^{-1}$ m mol g$^{-1}$, respectively. The fractional value of the adsorption affinity ($1/n$) is <1, indicates the extent of heterogeneity of the coal surface.

*3.5.1.2. Langmuir isotherm* According to the Langmuir adsorption isotherm all sites have equal affinity for the metal. The linear form of Langmuir adsorption isotherm may be written as:

$$\frac{C_e}{C_{\text{ad}}} = \frac{1}{Qb} + \frac{C_e}{Q} \tag{13}$$

where $C_{\text{ad}}$ is the concentration of thorium sorbed at equilibrium (mol g$^{-1}$); $C_e$ is the equilibrium concentration of thorium in solution (mol L$^{-1}$); $Q$ and $b$ are Langmuir isotherm constants.

A plot of $C_e/C_{\text{ad}}$ against $C_e$ gives a straight line (Fig. 11) with a correlation coefficient "$R^2$" of 0.999 and the normalized standard deviation ($\Delta q$) value of 0.001. This linear plot

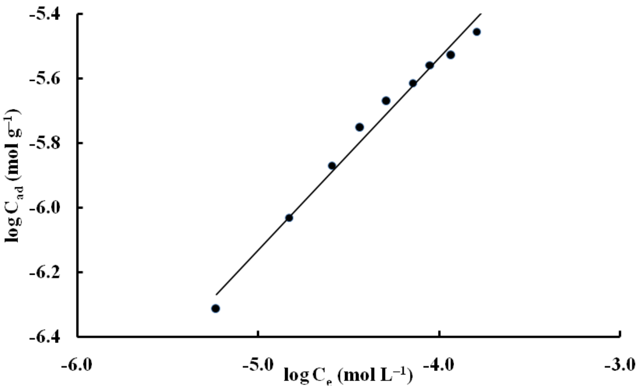

Fig. 10. Freundlich plot for the adsorption of thorium on coal.

supports the validity of the Langmuir model in the present work. The values of Langmuir constants $Q$ and $b$ calculated from the slope and intercept of the plot in Fig. 11 and were found to be $4.609 \times 10^{-3}$ mmol g$^{-1}$ and $17.021 \times 10^{3}$ dm$^{3}$ mol$^{-1}$, respectively. Conformation of the experimental data into the Langmuir isotherm model indicates the formation of monolayer coverage of thorium ion at the surface of coal.

The value of sorption capacity ($K_f$) calculated from Freundlich isotherm is greater than Langmuir. Langmuir isotherm reflects only the monolayer sorption while Freundlich isotherm assumes multilayer sorption of the coal resulting in the lower sorption capacity as compared with Freundlich adsorption isotherm.

*3.5.1.3. Influence of isotherm shape* One of the important parameters of the Langmuir isotherm model is the separation factor ($R_L$). This dimensionless parameter may be defined by the following Eq. (14) [32]:

$$R_L = \frac{1}{1 + K_L C_{\text{in}}} \tag{14}$$

where $K_L$ is the Langmuir constant related to adsorption energy (L mol$^{-1}$); $C_{\text{in}}$ is the initial concentration of thorium ion (mol L$^{-1}$).

The value of "$R_L$" indicates the favorability of the adsorption process. The $R_L$ value of $0 < R_L < 1$ indicates a favorable adsorption, $R_L = 0$ means irreversible, $R_L = 1$ means linear and $R_L > 1$ shows unfavorable adsorption process. In the present work, the calculated values of this dimensionless parameter $R_L$ are in the range of 0.120–0.577 which indicates the favorable adsorption of thorium ions on coal surface. This also confirms that the equilibrium isotherm can be better described by the Langmuir model and the adsorption process is monolayer on the coal surface.

*3.5.1.4. Dubinin–Radushkevich isotherm* The D-R isotherm was also applied in its linearized form to classify the chemical or physical adsorption.

$$C_{\text{ad}} = C_m \exp\left(-\beta\varepsilon^2\right) \tag{15}$$

where $C_{\text{ad}}$ is the amount of thorium sorbed on coal, $C_m$ is the maximum amount of thorium that can be sorbed on coal using the optimized experimental conditions, ε is Polanyi potential and β is a constant with a dimension of energy.

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{16}$$

where $R$ is the ideal gas constant; $T$ is the absolute temperature; $C_e$ is the equilibrium concentration of thorium in solution.

The linear form of D-R isotherm can be written as:

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

A straight line was obtained when $\ln C_{\text{ad}}$ is plotted against $\varepsilon^2$ (Fig. 12) with "$R^2$" value 0.994 and the $\Delta q$ value of 0.081, indicating that adsorption of thorium ions obeys the D-R equation.

From the linear plot value of β calculated was $5 \times 10^{-3}$ kJ$^2$ mol$^{-2}$. By substituting the value of β the mean sorption energy ($E_s$) was determined as:

$$E_s = \frac{1}{\left(-2\beta\right)^{\frac{1}{2}}} \tag{18}$$

The values of adsorption free energy ($E_s$) for physical sorption is in the range of 1–8 kJ mol$^{-1}$, and greater than 8 kJ mol$^{-1}$ for chemical sorption [33,34]. The determined value of $E_s$ from Eq. (15) was 10 kJ mol$^{-1}$, indicated chemical sorption or ion-exchange process.

*3.6. Influence of temperature*

The sorption of $8.621 \times 10^{-5}$ mol L$^{-1}$ of thorium ions on coal was carried out using optimized parameters at different temperatures varying from 283 to 333 K and the results are shown in Table 3. It was found that the thorium ions sorption was increased with the increase in temperature. The increased adsorption with the rise in temperature could be attributed to increased mobility of the thorium ions and their tendency to be adsorbed from aqueous solution.

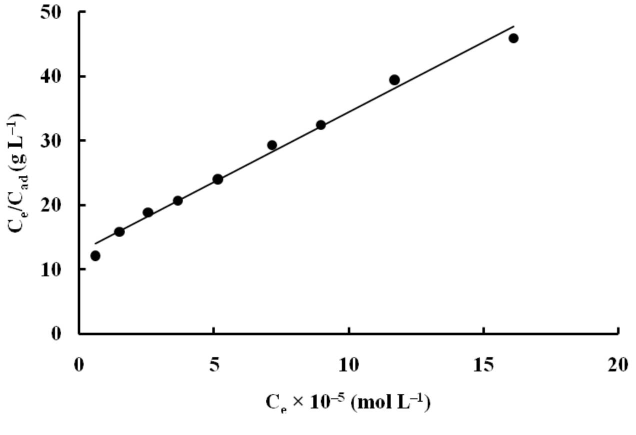

Fig. 11. Langmuir isotherm for the adsorption of thorium on coal.

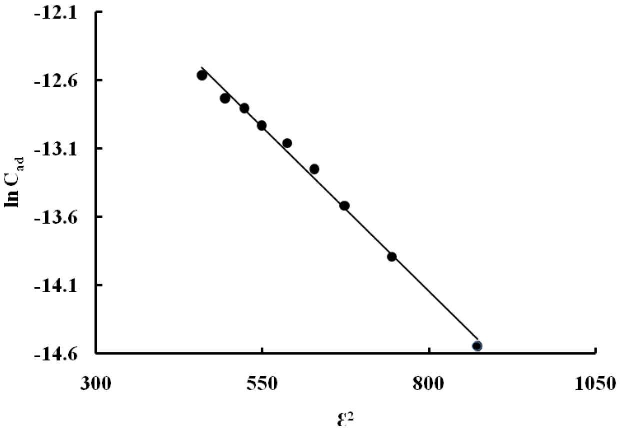

Fig. 12. D-R plot for the adsorption of thorium on coal.

Table 3
Adsorption of thorium ions on coal as a function of temperature

| Temperature (K) | $1/T \times 10^{-3}$ ($K^{-1}$) | Concentration adsorbed $\times 10^{-5}$ (mol $L^{-1}$) | Concentration in bulk $\times 10^{-5}$ (mol $L^{-1}$) | $K_c$ | ln$K_c$ |
|---|---|---|---|---|---|
| 283 | 3.534 | 5.153 | 3.468 | 1.486 | 0.396 |
| 293 | 3.413 | 6.451 | 2.170 | 2.972 | 1.089 |
| 299 | 3.344 | 7.082 | 1.539 | 4.601 | 1.526 |
| 303 | 3.300 | 7.320 | 1.301 | 5.627 | 1.728 |
| 313 | 3.195 | 7.760 | 0.861 | 9.010 | 2.198 |
| 323 | 3.096 | 8.177 | 0.444 | 18.399 | 2.912 |
| 333 | 3.003 | 8.492 | 0.129 | 65.892 | 4.188 |

Note: Dose of coal 0.3 g; shaking time 20 min; volume equilibrated 4 $cm^3$; concentration of $HNO_3$ 0.0001 mol $L^{-1}$; thorium ions concentration $8.621 \times 10^{-5}$ mol $L^{-1}$.

Van't Hoff plot [24,26] was used to find out ΔH and ΔS from the slope and intercept, respectively, by using the following expression:

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (19)$$

where ΔH, $K_c$, R, ΔS and T are enthalpy change, equilibrium constant, gas constant, change in entropy and absolute temperature for the sorption process, respectively.

The equilibrium constant ($K_c$) was determined by using the relationship:

$$K_c = \frac{C_{\text{eq.S}}}{C_{\text{eq.L}}} \quad (20)$$

where $C_{\text{eq.S}}$ is equilibrium concentration of thorium adsorbed on the coal (mg $L^{-1}$) and $C_{\text{eq.L}}$ is equilibrium concentration of thorium in solution (mg $L^{-1}$).

ΔG and ΔS for the specific sorption process have also been calculated using the expressions:

$$\Delta G = -RT \ln K_c \quad (21)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (22)$$

ΔS and ΔH were calculated by from the intercept and slope of the plot of ln$K_c$ against 1/T (Fig. 13). The determined values of ΔS, ΔG and ΔH have been presented in Table 4. The negative values of ΔG represent that the adsorption of thorium on coal is a spontaneous process. The increase in the numerical value of –ΔG with the rise in temperature indicates that the sorption process of thorium ions on coal is more favorable at higher temperatures. The positive values of enthalpy change represent the endothermic nature of the adsorption process. Since diffusion is an endothermic process, it was studied that increased solution temperature resulted in increased sorption of thorium ions. The positive value of ΔS indicates increase in the degree of freedom of the thorium ions.

### 3.7. Effect of coexistent ions

The presence of other cations and anions in the adsorptive phase may affect the environment and solution chemistry of the thorium ions, which influences the sorption efficiency of coal. Therefore, using the optimized parameters the sorption of $4.310 \times 10^{-5}$ mol $L^{-1}$ of thorium ions on coal was also studied in the presence of high concentrations of foreign ions. The anions were used as their sodium salts, while for cations the nitrate salts were used. The results are summarized in Table 5. The results show that adsorption efficiency of thorium ions on coal was almost constant in the presence of all the tested cations except antimony. On the other hand adsorption of thorium ions on coal was decreased up to 15% in the presence of cyanide, phosphate and fluoride anions.

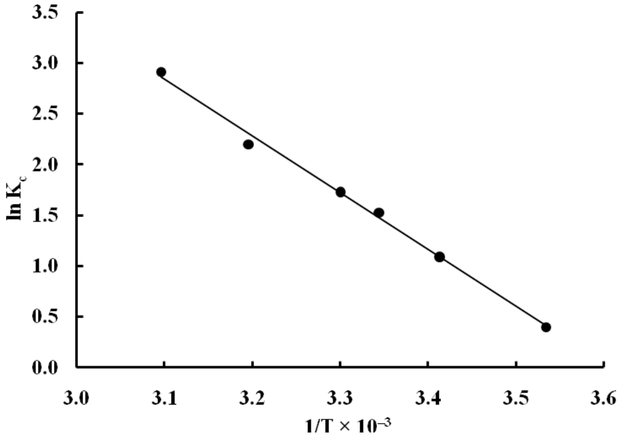

Fig. 13. Van't Hoff plot for the adsorption of thorium ions on coal.

Table 4
Thermodynamic parameters for adsorption of thorium ions on coal

| Temperature (K) | ΔG (kJ $mol^{-1}$) | ΔH (kJ $mol^{-1}$) | ΔS (J $K^{-1}$ $mol^{-1}$) |
|---|---|---|---|
| 283 | –0.932 | | |
| 293 | –2.654 | | |
| 299 | –3.794 | | |
| 303 | –4.352 | 46.517 | 0.168 |
| 313 | –5.721 | | |
| 323 | –7.821 | | |
| 333 | –11.595 | | |

Table 5
Effect of coions on the adsorption of $4.310 \times 10^{-5}$ mol $L^{-1}$ of thorium ions on coal

| Cation | Concentration (mol $L^{-1}$) | Adsorption (%) | Anion | Concentration (mol $L^{-1}$) | Adsorption (%) |
|---|---|---|---|---|---|
| No ion | – | 90 | No ion | – | 90 |
| Sodium | $2.176 \times 10^{-3}$ | 87 | Carbonate | $8.333 \times 10^{-4}$ | 86 |
| Potassium | $1.282 \times 10^{-3}$ | 87 | Bicarbonate | $8.197 \times 10^{-4}$ | 84 |
| Calcium | $1.250 \times 10^{-3}$ | 89 | Nitrate | $8.065 \times 10^{-4}$ | 99 |
| Magnesium | $2.058 \times 10^{-3}$ | 88 | Fluoride | $2.632 \times 10^{-3}$ | 75 |
| Copper | $7.868 \times 10^{-4}$ | 89 | Nitrite | $1.087 \times 10^{-3}$ | 84 |
| Iron | $8.954 \times 10^{-4}$ | 88 | Phosphate | $5.265 \times 10^{-4}$ | 78 |
| Lead | $2.413 \times 10^{-4}$ | 87 | Bromide | $6.258 \times 10^{-4}$ | 87 |
| Cobalt | $8.484 \times 10^{-4}$ | 81 | Cyanide | $1.923 \times 10^{-3}$ | 80 |
| Aluminum | $1.853 \times 10^{-3}$ | 87 | Perchlorate | $5.028 \times 10^{-4}$ | 93 |
| Nickel | $8.516 \times 10^{-4}$ | 88 | Borate | $8.502 \times 10^{-4}$ | 92 |
| Antimony | $4.107 \times 10^{-4}$ | 50 | Chloride | $1.410 \times 10^{-3}$ | 94 |
| Zinc | $7.648 \times 10^{-4}$ | 88 | Sulfide | $1.560 \times 10^{-3}$ | 84 |
| Cadmium | $4.448 \times 10^{-4}$ | 89 | Citrate | $8.475 \times 10^{-4}$ | 83 |
| Chromium | $9.616 \times 10^{-4}$ | 89 | Sulfate | $5.208 \times 10^{-4}$ | 89 |

This decrease in the sorption efficiency of thorium ions may be due to the competitor action of cations or the formation of stable complexes/compounds with anions for the active sites present on the surface of coal.

### *3.8. Application of the procedure*

In order to determine the applicability and efficiency of the developed procedure to a real sample, the removal of thorium ions was checked from the spiked tap water it was applied to the sorption of thorium in tap water sample. For this purpose 4 mL of tap water having 0.0001 mol $L^{-1}$ $HNO_3$ solution was spiked with $4.310 \times 10^{-5}$ mol $L^{-1}$ concentration of thorium ions and were equilibrated with 0.3 g of coal for 20 min. The percentage removal of thorium ions was found to be 81% in a single step, indicating that the low-rank Pakistani coal has good potential to remove the thorium ions from such matrices.

### *3.9. Recycling process*

To be useful in thorium ion recycling processes, adsorbed thorium ions should be easily desorbed under suitable conditions. Therefore, desorption experiments were carried out by using 1.0 M $HNO_3$ as the desorption agent. Thorium loaded coal was shaken with 1.0 mol $L^{-1}$ of $HNO_3$ for 25 min and the desorbed thorium was quantified in the liquid phase. It was observed that 86% of the adsorbed thorium was removed from the surface of the coal. This clearly shows that the coal can be reused for the sorption of thorium ions from aqueous solutions. It also indicates that the complexation of thorium ions with coal is reversible in acidic medium.

## 4. Conclusions

The present study reveals that the abundantly available, inexpensive low-rank Pakistani coal has great potential for the removal of thorium ions from aqueous media. Maximum adsorption (88%) of thorium ions was observed within 20 min from $1.0 \times 10^{-3}$ mol $L^{-1}$ of $HNO_3$ solution. The sorption of thorium on coal follows the pseudo-second-order rate expression ($R^2 = 0.999$) with intraparticle diffusion process. The adsorption capacity of coal for thorium ions calculated from Langmuir isotherm was found to be $4.609 \times 10^{-3}$ mmol $g^{-1}$. The sorption of thorium was increased with the increase in temperature. The thermodynamic parameters such as $\Delta G$ and $\Delta H$ represent spontaneity and endothermicity of thorium ion sorption on coal. The removal of thorium ions from spiked tap water sample indicates that the proposed method is efficient.

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