

# Equilibrium and kinetics study of Gd(III) and U(VI) adsorption from aqueous solutions by modified Sorrel's cement

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**Abstract** Modified Sorrel's cement was prepared by the addition of ferric chloride. The modified cement (MF5) was analyzed and characterized by different methods. Adsorption of Gd(III) and U(VI) ions in carbonate solution has been studied separately as a function of pH, contact time, adsorbent weight, carbonate concentration, concentration of Gd(III) and U(VI) and temperature. From equilibrium data obtained, the values of  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  were found to equal  $-30.9 \text{ kJ} \cdot \text{mol}^{-1}$ ,  $-85.4 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ , and  $-5.4 \text{ kJ} \cdot \text{mol}^{-1}$ , respectively, for Gd(III) and  $18.9 \text{ kJ} \cdot \text{mol}^{-1}$ ,  $67.8 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$  and  $-1.3 \text{ kJ} \cdot \text{mol}^{-1}$ , respectively, for U(VI). The equilibrium data obtained have been found to fit both Langmuir and Freundlich adsorption isotherms. The batch kinetic of Gd(III) and U(VI) on modified Sorrel's cement (MF5) with the thermodynamic parameters from carbonate solution were studied to explain the mechanistic aspects of the adsorption process. Several kinetic models were used to test the experimental rate data and to examine the controlling mechanism of the adsorption process. Various parameters such as effective diffusion coefficient and activation energy of activation were evaluated. The adsorption of Gd(III) and U(VI) on the MF5 adsorbent follows first-order reversible kinetics. The forward and backward constants for adsorption,

$k_1$  and  $k_2$  have been calculated at different temperatures between 10 and 60°C. From kinetic study, the values of  $\Delta H^*$  and  $\Delta S^*$  were calculated for Gd(III) and U(VI) at 25°C. It is found that  $\Delta H^*$  equals  $-14.8 \text{ kJmol}^{-1}$  and  $7.2 \text{ kJmol}^{-1}$  for Gd(III) and U(VI), respectively, while  $\Delta S^*$  were found equal  $-95.7 \text{ Jmol}^{-1}\text{K}^{-1}$  and  $-70.5 \text{ Jmol}^{-1}\text{K}^{-1}$  for Gd(III) and U(VI), respectively. The study showed that the pore diffusion is the rate limiting for Gd(III) and (VI).

**Keywords** Adsorption · equilibrium · Kinetics · Gd(III) · U(VI) · modified cement

## 1 Introduction

One of the most important practical methods for treatment of radioactive waste is adsorption (Abbasi and Streat, 1994; Kim et al., 1995; Tsuji et al., 1993; Srinivasan et al., 1988; Guin and Saha, 2002; Hasany and Saeed, 1992; Rengaraj and Moon, 2002). Cost effective alternative technologies or adsorbents for radioactive metal ions from "wastewater" or treatment are always needed. At low concentration, removal of such pollutants is more effectively implemented by ion exchange or adsorption on solid adsorbent (Tsuji et al., 1993).

Adsorption on cement is a promising technique for this purpose (Johnson et al., 2000). There are four different forms of Sorrel's cement designated as F2, F3, F5 and F9. The numbers stand for the ratio of moles of  $\text{Mg}(\text{OH})_2$  to  $\text{MgCl}_2$  in the formula

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for each form, as follows:  $2\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 4\text{H}_2\text{O}$  (F2);  $3\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 8\text{H}_2\text{O}$  (F3);  $5\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 5\text{H}_2\text{O}$  (F5); and  $9\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot \text{H}_2\text{O}$  (F9) (Sorrel, 1867; Demediuk et al., 1955; Cole and Demediuk, X-ray, 1955). Forms 3 and 5 are the only stable compositions at room conditions (Ball, 1977). Using magnesium hydroxide in the form of magnesium oxychloride cement the affinity for arsenic sorption was retained and the material was much more resistant to carbonate attack (Moore et al., 2002).

To understand the theoretical aspects of adsorbent or ion exchange separations, it is essential to study the thermodynamics and kinetics behaviors of their adsorption process (Rawat and Thind, 1976). Within these merits, a number of theoretical studies based on diffusion and other mechanisms have been reported (Rawat and Saladavo, 1953; Nachod and Wood, 1945; Helfferich and Plesset, 1958; Saraswat et al., 1981) and tested by several workers using both organic and inorganic exchangers (Rawat and Saladavo, 1953; Nachod and Wood, 1945).

In this contribution, F5 Sorrel's cement was modified by the addition of ferric chloride. The produced material (MF5) was characterized and equilibrium parameters of MF5 for adsorption of Gd(III) and U(VI) from aqueous carbonate solutions was investigated. The parameters that influence adsorption such as contact time, pH and adsorbent weight were investigated. The results obtained are discussed in terms of different adsorption models. Further, the batch kinetics of adsorption of Gd(III) and U(VI) by the MF5 were studied. The forward and backward constants,  $k_1$  and  $k_2$  have been calculated at different temperatures between 10 and 60°C for Gd(III) and U(VI). From the experimental results, the values of  $\Delta H^*$  and  $\Delta S^*$  were calculated for Gd(III) and U(VI) at 25°C and discussed.

## 2 Experimental

### 2.1 Chemical

All the chemicals used were of analytical grade products and obtained from BDH, England.

### 2.2 Preparation of A modified Sorrel's cement (MF5) adsorbent

Sorrel's cement adsorbent F5 was as reported in literature (Sorrel, 1867; Demediuk et al., 1955; Cole and

Demediuk, X-ray, 1955). In this respect, F5 was prepared by dissolving 1M  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and 5M MgO was added. The mixture left for 3 days at 75°C.

The modified Sorrel's cement (MF5) was prepared by dissolving 1M  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and 1M  $\text{FeCl}_3$  in 100 ml deionized water. To this solution, 5M MgO was added, and the slurry was thoroughly mixed and poured in circular plastic dishes (10 mm in diameter  $\times$  3 mm high) and left for 3 days at 75°C to cure. The prepared materials were grinded to fine particles of 21  $\mu\text{m}$  and  $0.5 \times 10^{-5}$  m radius as measured by scanning electron microscopy SEM image.

### 2.3 Adsorbent analysis

The morphology of MF5 was evaluated by scanning electron microscopy (SEM) using a Joel JSM-6300 scanning electron microscope. Energy dispersive spectroscopy (EDS) was used to analyze the chemical composition of the adsorbent. The crystallinity and structure of adsorbent was determined by X-ray diffraction (XRD) using a Bruker D8 advance X-ray diffraction System equipped with a Kevex model 2005-212 detectors.

Thermal analysis was carried out using a Shimadzu thermogravimetric analyzer, TGA, at a heating rate of 20°C. The surface area of the adsorbent (MF5 powder) was measured by a Quantachrome Corporation NOVA3200, Version 6.08, gas analyzer and found equals 93.88  $\text{m}^2/\text{g}$ .

### 2.4 Adsorbent stability in acids and bases

Both strong acid and alkaline solutions were added to known weight of the adsorbent. The solutions were filtered through filter paper. The solid residues were dried and weighed. The amount of material released from the adsorbent was measured from the difference in the weight.

### 2.5 $\text{OH}^-$ Capacity of MF5

The adsorbent (MF5) was characterized by potentiometric titration to determine the acid-base behavior at ionic strength of 0.1 M. In this concern, 0.02 g of investigated sample was taken in 25 ml water by stirring for about 15 min. using magnetic stirrer. Then 12.5 ml of 0.1 M  $\text{NaClO}_4$  were added and the sample titrated with 0.1 M HCl. The pH of the solution reached equilibrium

within 5–10 minutes after each addition of the acid, at this time the pH reading was taken. The end point was determined from the maxima of the first derivative of the titration curve.

## 2.6 Adsorption experiments

Aliquots of the stock solution were used to prepare working solutions. A stock solution of 0.1 g/l Gd(III) and 1 g/l U(VI) in 0.01 M  $\text{Na}_2\text{CO}_3$  were prepared. The solution was diluted as required to obtain standard solutions containing 5–25 mg/l Gd(III) and 25–400 mg/l U(VI). Adsorption experiments were performed with 10 ml of solution in 25 ml polypropylene bottles. 0.03 g and 0.1 g MF5 were added to each solution for Gd(III) and U(VI), respectively. The mixtures were placed on a shaker set at 100 rpm. After 90 min, the samples were filtered and the filtrate was analyzed spectrophotometrically (Marczenko, 1976) to determine Gd(III) and U(VI) content. For investigation of the effects of pH, adsorbent weight, contact time and temperature, 25 mg/l ( $2 \times 10^{-4}$  M) of Gd(III) and 50 mg/l ( $1.1 \times 10^{-3}$  M) U(VI) with 0.03 g and 0.1 g of MF5 were used for Gd(III) and U(VI), respectively. Gd(III) and U(VI) solution was adjusted to a desired pH by using 0.1 N HCl or dilute NaOH solutions.

The loading capacity of adsorbent for Gd(III) and U(VI) were studied by repeating the adsorption step with the same adsorbent weight and volume of the solution until the adsorbent is saturated with elements. In this concern, 0.15 g of adsorbent was shaken with 50 ml of the solution containing 25 mg/l Gd(III) in 0.01 M carbonate medium. Also, 50 ml of the aqueous solution containing 50 mg/l U(VI) in carbonate solution was shaken with 0.5 g of MF5. The two phases were separated, Gd(III) and U(VI) concentration were determined and the same adsorbent was used again for the removal with fresh Gd(III) and U(VI) solution.

## 2.7 Kinetic experiments

In kinetic investigations, Gd(III) and U(VI) varied in the range 5–25 mg/l and 50–400 mg/l, respectively, when studying the effect of their concentrations. Thermodynamic study were carried out at 0.01 M carbonate solution containing 25 mg/l Gd(III) or 50 mg/l U(VI) at different temperatures (10–60°C) in thermostat water bath. For this purpose, a known amount of adsorbent, 0.15 g and 0.5 g, were added to 50 ml of Gd(III) and

U(VI) solutions, respectively. At different time intervals, the solutions were analyzed to determine the uptake of Gd(III) and U(VI).

## 3 Results and Discussion

Preliminary investigation on the use of Sorrel's cement (F5) as adsorbent from aqueous solution showed the formation of slight dispersed emulsion as well as low adsorption capacity. Therefore, the prepared adsorbent was modified by the addition of ferric chloride to the matrix to give the modified form (MF5), under investigations.

### 3.1 Adsorbent characterization

Elemental analysis of the prepared adsorbent is given in Table 1. Based on this analysis, a proposed chemical formula for this adsorbent is,  $5\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 2[\text{Fe}(\text{OH})\text{Cl}_2] \cdot 3\text{H}_2\text{O}$ . The amount of water in this formula was obtained from thermal analysis. Further, the prepared material was showed good thermal stability up to 500°C.

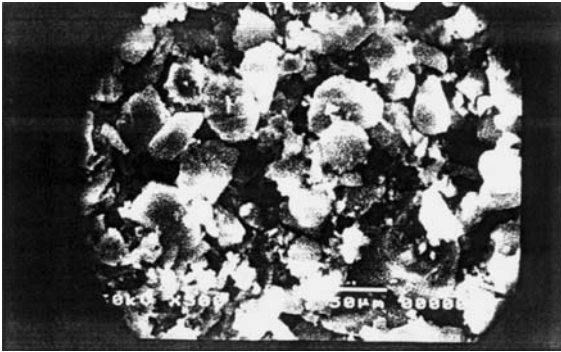
**Table 1** Percentage of elemental concentrations (%) in adsorbent sample by EDS:

Element	Element, %	
	Experimental	Proposed formula*
O	34.15	34.1
Mg	20.98	20.0
Cl	29.33	29.3
Fe	13.40	15.8
Total %	97.86	99.2

\*Chemical formula proposed  $(5\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 2[\text{Fe}(\text{OH})\text{Cl}_2] \cdot 3\text{H}_2\text{O})$ .

The scanning electron microscopy SEM image of the surface of MF5 used in adsorption experiments is shown in Fig. 1. It clears several different crystal structures. Beaudoin et al. (1997) reported the presence of different phases and crystal structures in F5. The average particle size and the radius were found 21  $\mu\text{m}$  and  $1.05 \times 10^{-5}$  m, respectively.

The X-ray diffraction (XRD) pattern of MF5 is given in Fig. 2. and indicates that the material is not highly crystallized and has some resemblances to iron oxide compounds. Peaks at  $2\theta^\circ$  equal to 30.2, 31.1, 33.8, and 62.8 are typical for  $\text{Fe}_2\text{O}_3$  and  $2\theta^\circ$  equal to 21.2,



**Fig. 1** Scanning electron microscope image of modified Sorrel's cement (MF5)

33.2, 36.7, and 53.2 are typical for FeO(OH). However, several major peaks for both of these compounds are not present on the pattern. Both 3:1 and 5:1 Sorrel's cement are characterized by large peaks at  $2\theta^\circ$  equal 11, 37, 43, and 62.5 (D. Dehua et al., 1996).

The ability of adsorbent to remain stable under continued exposure to different solutions containing defined weight of MF5 and having pH values from acidic to alkaline solutions is of great importance. In nitric acid medium higher than 0.1 M, the stability of MF5 is very low (~80% weight loss). But the stability of MF5 in HCl and H<sub>2</sub>SO<sub>4</sub> in the concentration higher than 0.05 M was also very low (~82% weight loss). The dissolution of adsorbent in NaOH in the range (0.5–2 M) was about (0.2% weight loss). The MF5 presented good stability in neutral and alkaline medium with no noticeable loss of weight was found (less than 0.5% in the pH range 4–11).

To assess the acid-base behavior of the MF5 adsorbent, the hydroxyl groups in adsorbent were determined. In this concern, direct titration for the sample was performed and the hydroxyl groups capacities

was determined from the maxima of the first derivatives of the titration curve (Stevenson, 1982). The number of hydroxyl groups is determined from the maximum of the first derivative, and found to contain 0.25 meq · OH<sup>-1</sup>/g.

### 3.2 Equilibrium investigation

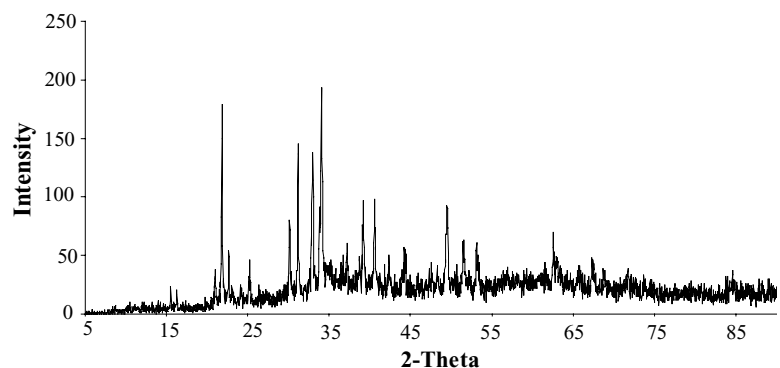
Unless otherwise stated, the concentrations of Gd(III) and U(VI) in solution were 25 mg/l and 50 mg/l, respectively. The equilibrium parameters of MF5 for adsorption of Gd(III) and U(VI) from dilute carbonate solution (0.01 M) comparable with natural water were studied. The main factors affecting the adsorption are, pH, adsorbent weight, contact time, carbonate concentration, the initial metal ion concentration and temperature.

MF5 are effective for removal of Gd(III) and U(VI) over the pH range 4–11. In all cases the equilibrium pH was found to equal 9.4–9.8. For comparison, a blank adsorption was studied for the two elements to exclude possible precipitation or adsorption of elements by the glass container in the pH range studied. Within the concentration range of the elements under study, it is found that there are no precipitation or adsorption on the glass vessels.

The adsorbent weight was varied from 0.03 to 0.3 g/10 ml and equilibrated for 2 h. The experimental results revealed that Gd(III) and U(VI) removal efficiency increases to reach value of 98% using 0.03 g/10 ml and 0.1 g/10 ml weight of adsorbent for Gd(III) and U(VI), respectively. Further increase in the weight of the adsorbent has no effect on removal percentage (Rengaraj et al., 1999; Rengaraj et al. 2000).

The effect of contact time of removal of two metal ions from carbonate solution by MF5 was studied. The removal efficiency increases with time and attains

**Fig. 2** X-ray diffraction (XRD) pattern for MF5 adsorbent used in this work



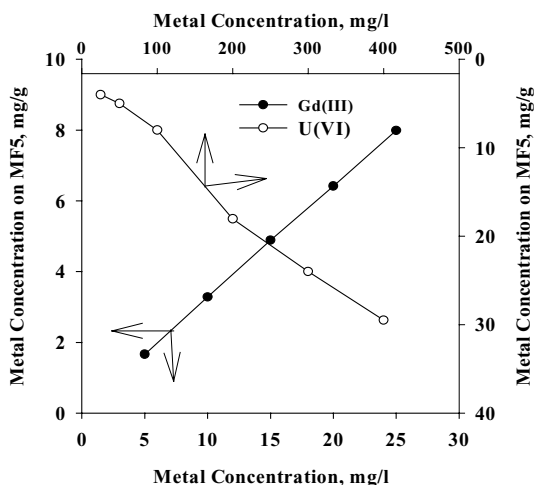
equilibrium within 60 min for Gd(III) but 150 min. for U(VI).

The effect of carbonate concentration within the range from 0.005–0.1 M was investigated. Table 2 is found that the maximum removal of Gd(III) and U(VI) was achieved at low carbonate concentration (0.005–0.03M). Higher carbonate concentration decreased the percent removal of both metal ions. The increase of carbonate concentration causes a decrease of adsorption capacity of Gd(III) and U(VI) can be related to the possible formation of non-adsorbed high carbonate complexes of the investigated metal ions.

**Table 2** Effect of carbonate concentration on the adsorption of 25 mg/l Gd(III) and 50 mg/l

Na <sub>2</sub> CO <sub>3</sub> Concentration, M	Amount adsorbent (%)	
	Gd(III)	U(VI)
0.005	98	98
0.010	98	99
0.020	97	95
0.030	92	91
0.050	84	86
0.070	73	78
0.100	55	60

The role of Gd(III) and U(VI) concentration on the adsorption were studied using MF5 within the range 5 mg/l–25 mg/l for Gd(III) and 25 mg/l–400 mg/l for



**Fig. 3** Effect of initial Gd(III) and U(VI) concentration on its concentration in the solid phase when adsorbed with MF5. pH = 9.5 Contact time = 2 hr MF5 weight for GD(III) = 0.03g/10 ml MF5 weight for GD(III) = 0.03g/10 ml MF5 weight for U(VI) = 0.1g/10 ml

U(VI). The results obtained are represented in Fig. 3. as a relation between the concentrations of the metal ions in the solution and in MF5 adsorbent. From this figure, it is clear that the concentration of U(VI) in the adsorbent increase with increasing their initial concentration in solution up to a concentration of 400 mg/l. In case of Gd(III), the amount of Gd(III) adsorbed increased up to 25 mg/l after which Gd(III) was precipitated.

The maximum loading capacity of adsorbent for Gd(III) and U(VI) was found to be 65.7 mg/g and 26.0 mg/g for Gd(III) and U(VI), respectively.

Based on the aforementioned results, the adsorption of 25 mg/l Gd(III) and 50 mg/l U(VI) on F5 was investigated and compared with that of MF5 under comparable condition as function of time, Table 3. In case of Gd(III), it is found that MF5 has faster and higher adsorption ability than F5. In this respect equilibrium uptake was reached after 15 min. for MF5 whereby the equilibrium adsorption of Gd(III) was reached after more than 30 min. for F5. Further the maximum adsorption percent of Gd(III) for F5 was around 80% whereby for MF5 is 92%. In case of U(VI), MF5 showed higher adsorption percent than that of F5 as given in Table 3.

**Table 3** Comparison between Sorrel’s cement (F5) and modified F5 (MF5)

Time, min.	Amount adsorbed (%)			
	Gd(III)		U(VI)	
	F5	MF5	F5	MF5
1	30	65	9	11
3	40	79	11	18
5	55	84	24	29
7	60	86	27	36
10	68	88	34	47
15	72	92	40	53
30	80	93	47	61
60	82	92	55	78
90	83	93	62	83
120	80	91	69	90
150	82	92	79	97
180	81	91	80	99

The effect of temperature on the adsorption of Gd(III) and U(VI) from 0.01 M carbonate solution was studied at temperature values of 10, 25, 40, 50 and 60°C. The equilibrium constant values,  $K_c$ , were evaluated in the respective temperature degrees according to equation (1) based on the linearity between  $q_e$  and

$C_e$  within the investigated temperatures, 10–60°C.

$$K_c = q_e/C_e \quad (1)$$

where  $q_e$  is the equilibrium concentration of Gd(III) or U(VI) on the adsorbent,  $C_e$  is the equilibrium concentration of Gd(III) or U(VI) in solution. The temperature effect on the metal adsorption could be evaluated in terms of their thermodynamic values calculated from the following relations:

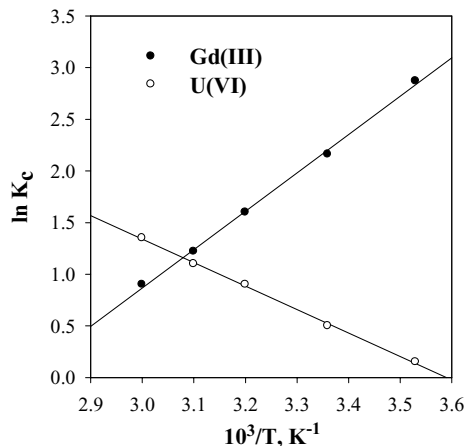
$$\Delta G = -RT \ln K_c \quad (2)$$

Where  $\Delta G$  is the free energy change,  $R$  is the gas constant ( $8.314 \text{ Jk}^{-1} \text{ mol}^{-1}$ ) and  $T$  is the absolute temperature.

$$\ln K_c = -\Delta H/RT + (\Delta S)/R \quad (3)$$

$$\Delta S = (\Delta H - \Delta G)/T \quad (4)$$

Where  $\Delta H$  is enthalpy change and  $\Delta S$  is entropy change.  $\ln K_c$ , for adsorption of Gd(III) and U(VI) at different temperatures were calculated and given as a relation between  $\ln K_c$  vs  $1/T$ , Fig. 4. A straight lines with negative slope for U(VI) and positive slope for Gd(III).  $\Delta G$  for both metals were calculated from this figure at  $298 \text{ K}^{-1}$  and found to equal  $-5.4 \text{ KJ} \cdot \text{mol}^{-1}$  and  $-1.3 \text{ KJ} \cdot \text{mol}^{-1}$  for Gd(III) and U(VI), respectively.



**Fig. 4** Effect of temperature on the equilibrium constant of adsorption 25 mg/l Gd(III) and 50 mg/l U(VI) from 0.01 M carbonate solution. pH = 9.5 Contact time = 2 hr MF5 weight for Gd(III) and 50 mg/l U(VI) = 0.1g/10 ml

The values of  $\Delta H$  and  $\Delta S$  for Gd(III) and U(VI) were calculated on the basis of the slope and intercept of the plot shown in Fig. 4. The values of  $\Delta H$  and  $\Delta S$

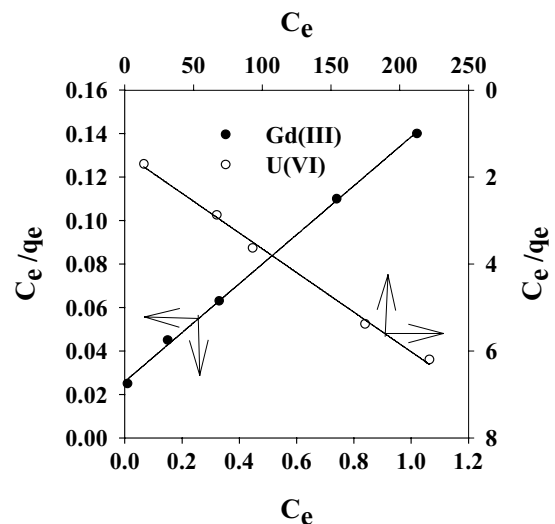
for Gd(III) were found to equal  $-30.9 \text{ kJ} \cdot \text{mol}^{-1}$  and  $-85.4 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$ , respectively. The negative  $\Delta H$  value indicates the exothermic character of Gd(III) adsorption while the negative  $\Delta S$  value indicates the decrease in the randomness of the system as a result of adsorption. The values of  $\Delta H$  and  $\Delta S$  for U(VI) were found to equal  $18.9 \text{ kJ} \cdot \text{mol}^{-1}$  and  $67.8 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$  respectively. The positive  $\Delta H$  value indicates the endothermic character of U(VI) adsorption process while the positive  $\Delta S$  value indicates the increase of the randomness of the system with U(VI) adsorption.

### 3.3 Adsorption isotherm

The investigated equilibrium removal of metal ions studied can be mathematically expressed in terms of the adsorption isotherms. The adsorption data are commonly fitted to the Langmuir or the Freundlich model at 25°C. The Langmuir equation was applied to the adsorption equilibrium for MF5, using the expression,

$$(C_e/q_e) = 1/(Q_o b) + C_e/Q_o \quad (5)$$

where  $C_e$  is the equilibrium concentration (mg/l),  $q_e$  is the amount adsorbed at equilibrium (mg/g), and  $Q_o$  is the Langmuir constant related to monolayer adsorption capacity. The linear plots of  $C_e/q_e$  vs  $C_e$  show that the adsorption obeys the Langmuir model, Fig. 5.  $Q_o$  determined from the Langmuir plot, were 8.72 mg/g and 45.70 mg/g for Gd(III) and U(VI), respectively, Fig. 5.

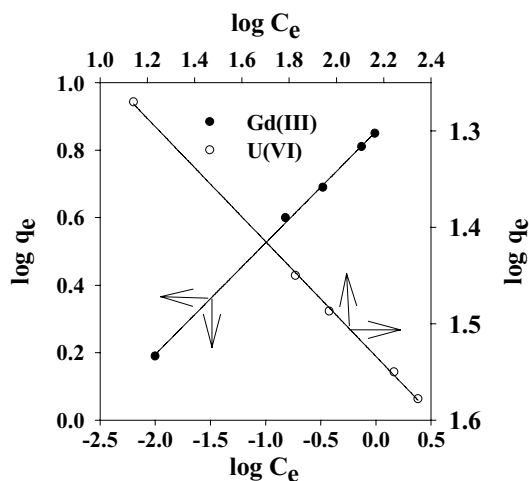


**Fig. 5** The Langmuir adsorption isotherm for Gd(III) and U(VI) on the MF5

The Freundlich adsorption isotherm was also applied for the adsorption of the same metal ions by the MF5. The experimental results obtained for the adsorption of metal ions on the MF5 at room temperature ( $25 \pm 1^\circ\text{C}$ ) under optimum conditions of contact time and weight adsorbent was found to obey the Freundlich adsorption isotherm (Glasstone, 1946).

$$\log q_e = \log k + 1/n \log C_e \text{ (Linear form)} \quad (6)$$

where  $\log q_e$  is the amount of metal ions removed per unit weight of adsorbent ( $\text{mg} \cdot \text{g}^{-1}$ ) and  $C_e$  is the concentration of U(VI) at equilibrium.  $n$  is constant representing the intensity of adsorption. The data obtained in this study fit to the Freundlich adsorption isotherm as shown in Fig. 6.



**Fig. 6** The Freundlich adsorption isotherm for Gd(III) and U(VI) on MF5

The plot of  $\log q_e$  vs  $\log C_e$  for various initial concentrations of metal ions, Fig. 6, is found to be linear, indicating the applicability of classical adsorption isotherm to the adsorbate-adsorbent system. Adsorption intensity ( $n$ ) for Gd(III) and U(VI) is found to be 3 and 3.9, respectively, for MF5. The value of  $n$  lies between 1 and 10, indicating favorable adsorption (Mckay et al., 1982).

In case of Gd(III), the correlation coefficient for Langmuir and Freundlich isotherms were found to equal 0.999 and 0.988, respectively. The values obtained from these correlation coefficients indicates that the isotherms are best fit with the Langmuir isotherm. In the case of U(VI) the correlation coefficient for Langmuir and Freundlich adsorption isotherms were found to equal 0.9830 and 0.9874, respectively. While the ad-

sorption obtained can fit both Langmuir and Freundlich isotherms, it is to be mentioned that the Freundlich adsorption isotherm is more favored based on the correlation coefficient obtained from the analysis of the data.

### 3.4 Kinetics investigation

It is well recognized that the characteristic of adsorbent surface is a critical factor that affects the adsorption rate parameters and diffusion resistance plays an important role in the over all transport of solute. To describe the changes in the adsorption of studied ions with time, several kinetic models were tested. Our hypothesis was that the uptake of each metal ion removal from the solution by the adsorbent followed a pseudo-first order mechanism. The order for the adsorption process of Gd(III) and U(VI) on MF5 surface has been examined by Lagergren first order rate expression (Lagergren, 1898) by plotting  $\log (q_e - q_t)$  against time,

$$\log(q_e - q_t) = \log q_e - (K/2.303)t \quad (7)$$

where  $q_e$  and  $q_t$  are the amounts of metal ions adsorbed at equilibrium and at time  $t$ , respectively, and  $K$  is the overall rate constant.

The adsorption kinetics describes the solute uptake rate that in turn governs the residence time of adsorption process. The adsorption of metal ions from an aqueous solution follows reversible first order kinetics, when a single species is considered to adsorb on a heterogeneous surface. The heterogeneous equilibrium between the metal ions and adsorbent may be expressed as



where  $M$  is Gd(III) or U(VI). The overall adsorption constant,  $K$ , and forward adsorption rate constant,  $k_1$ , and the backward adsorption rate constant,  $k_2$ , can be calculated by using the following equations:

$$K = k_1(1 + 1/K_c) = k_1 + k_2 \quad (9)$$

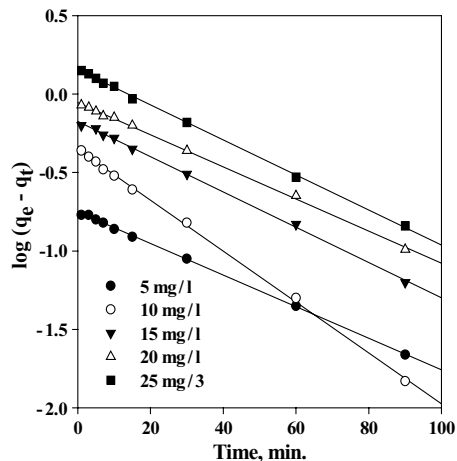
and

$$K_c = k_1/k_2 = q_e/C_e \quad (10)$$

Where  $q_e$  is the equilibrium concentration of metal ions on studied adsorbent,  $C_e$  is the equilibrium concentration of metal ions studied in solution and  $K_c$  is the

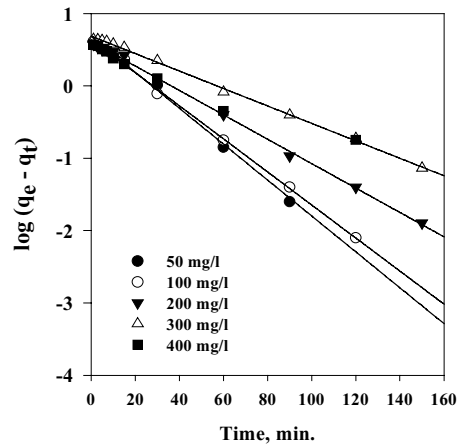
equilibrium constant. The values of  $K_c$ ,  $k_1$ ,  $k_2$  can be determined by using Eqs. (9) and (10).

The effect of Gd(III) and U(VI) concentrations were studied at concentrations within the range 5–25 mg/l for Gd(III) at 25°C and 50–400 mg/l U(VI) for U(VI) at 60°C and pH = 9.5. The first order plots of the obtained results are shown in Figs. 7 and 8. The different values of the rate constants  $K$  were calculated from the slope of these straight lines and are listed in Table 4. These data show that the values of  $K$  slightly decreases with increasing U(VI) concentration while there is almost no effect noticed in the case of Gd(III).



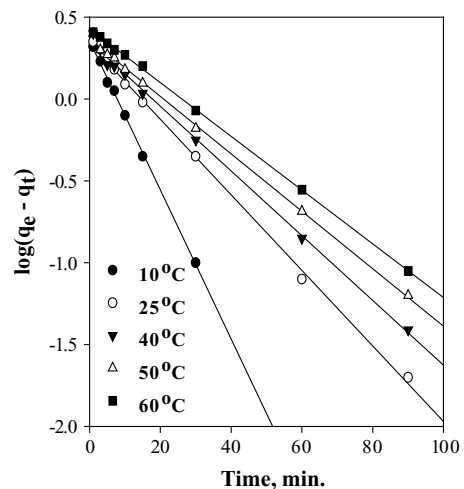
**Fig. 7** First order plots for the adsorption of Gd(III) by MF5 in carbonate at different Gd(III) concentrations

The effect of temperature on the kinetics of 25 mg/l Gd(III) and 50 mg/l U(VI) adsorption on MF5 from 0.01 M carbonate solution at pH = 9.5 has been examined at different temperatures from 10 to 60°C. The values of  $K$  were calculated from the slopes of the straight lines shown in Figs. 9 and 10, and listed in Table 5. The overall rate constant gradually decreases for rise in temperature from 10 to 60°C for Gd(III) while it is gradually increases for rise in temperature from 10 to



**Fig. 8** First order plots for the adsorption of U(VI) by MF5 in carbonate solution at different U(VI) concentrations

60°C for U(VI). Using the kinetic equations (9) and (10), the forward ( $k_1$ ) and backward rate ( $k_2$ ) constants were calculated and given in Table 5.



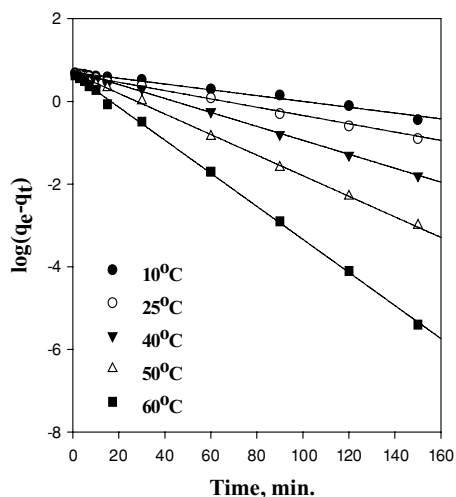
**Fig. 9** First order plots for the adsorption of Gd(III) by MF5 in carbonate solution at different temperatures

From Table 5, it could be seen that the forward rate constants for adsorption of Gd(III) and

**Table 4** Effect of Gd(III) and U(VI) concentration on the rate of adsorption

Gd(III) concentration, mg/l	Rate constant (K), $\times 10^2 \text{ min.}^{-1}$	U(VI) concentration, mg/l	Rate constant (K), $\times 10^2 \text{ min.}^{-1}$
5	1.01	50	2.5
10	1.62	100	2.3
15	1.12	200	1.7
20	1.02	300	1.2
25	2.00	400	1.1





**Fig. 10** First order plots for the adsorption of U(VI) by MF5 in carbonate solution at different temperatures

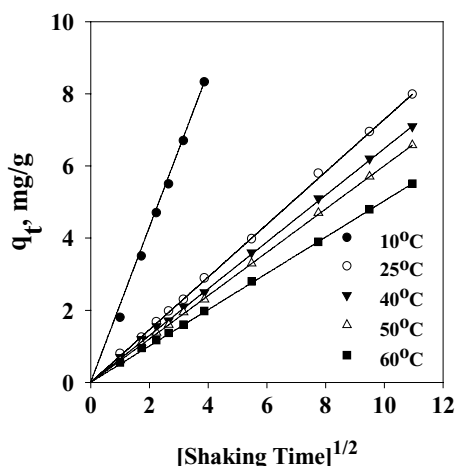
U(VI) were much higher than the back ward rate constants for de-sorption process (Srinivasan et al., 1988). The results imply that de-sorption hardly takes place.

Other models are also tested because of the Lagergren equation cannot give definite mechanism. It is also known that intensive stirring of the adsorptive system may cause the rate limiting mechanism to shift to interparticle diffusion of the solute adsorbed from the solution into the adsorbent pores could be a limiting step. In this study, two models namely those of Weber and Morris model and that suggested by Helfferich (Helfferich, 1962) were also used. The amount of Gd(III) and U(VI) at time  $t$  is plotted against  $t^{1/2}$  in Fig. 11 and 12 according to the Weber and Morris (Weber et al., 1963) equation:

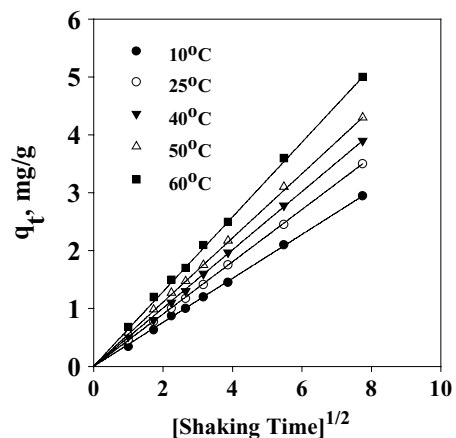
$$q_t = k_d t^{1/2} \tag{11}$$

**Table 5** Rate constants for the adsorption of 25 mg/l Gd(III) and 50 mg/l U(VI) with MF5

Temperatures, °C	Overall rate constant K, $\times 10^2 \text{ min.}^{-1}$		Forward rate constant $k_1$ , $\times 10^2 \text{ min.}^{-1}$		Backward rate constant $k_2$ , $\times 10^2 \text{ min.}^{-1}$	
	Gd(III)	U(VI)	Gd(III)	U(VI)	Gd(III)	U(VI)
10	4.6	1.6	4.35	0.85	0.25	0.75
25	2.3	2.4	2.00	1.4	0.26	1.0
40	2.0	3.8	1.60	2.5	0.40	1.2
50	1.81	5.7	1.40	4.4	0.41	1.3
60	1.62	9.2	1.20	9.0	0.42	0.2



**Fig. 11** Morris-Weber plots for kinetic modelling of Gd(III) adsorbed onto MF5



**Fig. 12** Morris-Weber plots for kinetic modelling of Gd(VI) adsorbed onto MF5

The slope of the straight line of  $q_t$  vs  $t^{1/2}$  yields the value of  $k_d$ , the rate constant of interparticle transport. The plots are linear and pass through the origin. It was found that the data fit into the Weber and Morris equation. This may indicate that particle diffusion

mechanism is operating and control the kinetics of metal ions adsorption.

Kinetic data were also analyzed by the procedure given by Helfferich (Helfferich, 1962). Various parameters were calculated by Boyd et al. (Boyd et al., 1947).

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp[-n^2 Bt] \quad (12)$$

and

$$B = \pi^2 D_i / r_o^2 \quad (13)$$

where  $F$  is the fractional attainment of adsorption at time  $t$  ( $F = q_t/q_e$ ),  $B$  is a mathematical function (the slope of  $Bt$  vs  $t$  plots),  $D_i$  is a self-diffusion coefficient of the ions,  $n$  is an integer number, refers to the radius of the particles.

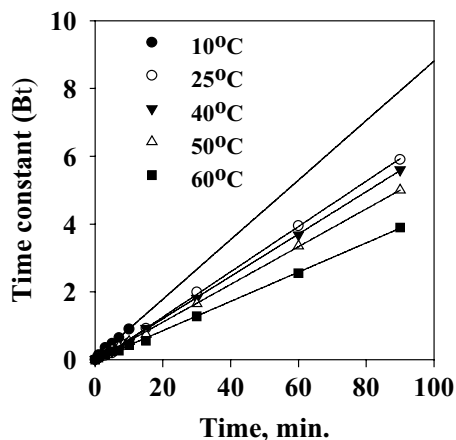
$Bt$  values for the observed values of  $F$  were obtained from Reichenberg's table by using the equation (14) derived by Reichenberg (Reichenberg, 1953):

$$Bt = 2\pi - \pi^2 F(t)/3 - 2\pi[1 - (\pi/3)F(t)]^{1/2} \quad (14)$$

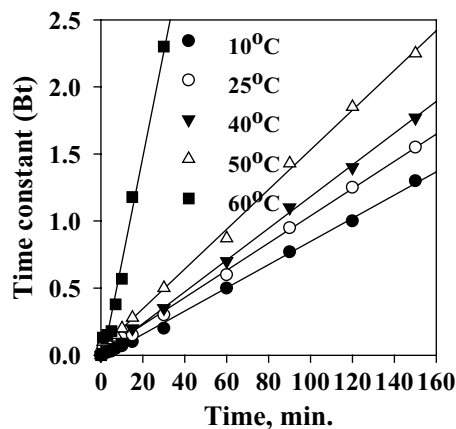
Figures 13 and 14 depict the  $Bt$  versus time plots for Gd(III) and U(VI) at different temperatures. The linearity test of  $Bt$  test versus time plots is employed to distinguish between the film and particle diffusion controlled rates of adsorption process. The plots are linear and pass through the origin, indicating the adsorption process to be particle diffusion at all studied temperatures. The value of  $D_i$  calculated at 10, 25, 40, 50 and 60°C are presented in Table 6.

If film diffusion is to be the rate determining step in the adsorption of ions on the adsorbent surface, the value of diffusion coefficient ( $D_i$ ) should be in the range  $10^{-6}$ – $10^{-8}$   $\text{cm}^2/\text{s}$ , while If pore diffusion is the rate limiting, the diffusion coefficient ( $D_i$ ) should be in the range  $10^{-11}$ – $10^{-13}$   $\text{cm}^2/\text{s}$  (Michelson, 1975).

Plotting of  $\ln D_i$  versus  $1/T$  gave straight line as shown in Fig. 15 enables the calculation of the energy



**Fig. 13** Time constant ( $Bt$ ) versus time of Gd(III) at different temperatures



**Fig. 14** Time constant ( $Bt$ ) versus time of U(VI) at different temperatures

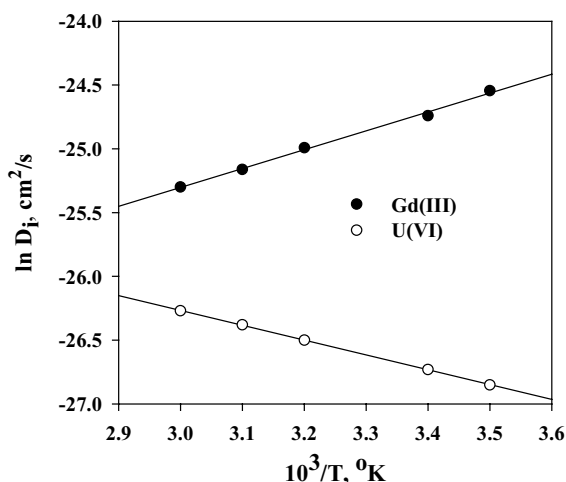
of activation ( $E_a$ ) from Arrhenius equation:

$$D_i = D_o e^{-E_a/RT} \quad (15)$$

The entropy of activation  $\Delta S^*$  can be calculated from  $D_o$  by substituting in the equation proposed by

**Table 6** Diffusivity of Gd(III) and U(VI) adsorbed onto MF5

Temperature, °C	Diffusion Coefficient, $D_i$ , $\times 10^{11}$ $\text{cm}^2/\text{s}$	Diffusion Coefficient, $D_i$ , $\times 10^{12}$ $\text{cm}^2/\text{s}$
	Gd(III)	U(VI)
10	2.19	2.18
25	1.80	2.46
40	1.40	3.10
50	1.18	3.49
60	1.03	3.90



**Fig. 15** Arrhenius diagram of Gd(III) and U(VI) adsorbed on MF5

Barrer et al. (1961):

$$D_o = 2.72(KT d_2/h) \exp^{\Delta S^*/R} \quad (16)$$

where  $K$  is Boltzmann constant,  $T$  is 273°K,  $d$  is the average distance between two successive particles in the process of diffusion which was taken as 0.5 mm, and  $h$  is Plank's constant.

The heat of activation of the adsorption,  $\Delta H$ , was calculated from the following equation (Flett, 1983):

$$\Delta H^* = E_a - RT \quad (17)$$

The energies of activation,  $E_a$ , for Gd(III) and U(VI) were calculated from the slope of straight lines in Fig. 15.  $E_a$  values are  $-12.3 \text{ kJ} \cdot \text{mol}^{-1}$  and  $9.7 \text{ kJ} \cdot \text{mol}^{-1}$  for Gd(III) and U(VI), respectively. Since the chemical controlled reaction has activation energy above 20.9 kJ/mole, whereas in the diffusion controlled processes it has lower values (Laidler, 1975). Therefore, the adsorption of Gd(III) and U(VI) are diffusion controlled.

The values of  $\Delta H^*$  were calculated from equation 17, and found to equal  $-14.80 \text{ kJ mol}^{-1}$  and  $7.2 \text{ kJ mol}^{-1}$  for Gd(III) and U(VI), alternatively. The enthalpy of activation is a mean of the height of energy barrier which must be overcome to attain the transition state, i.e., the larger value of  $\Delta H^*$ , the slower the adsorption (Esenonm, 1981). Since the value of  $\Delta H^*$  for adsorption of U(VI) is positive and much higher than of Gd(III), therefore the height of the energy barrier which has to be overcome the activated state of U(VI) is very high. Further the calculated  $\Delta S^*$  val-

ues for Gd(III) and U(VI) were found to equal  $-95.7 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $-70.5 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively. The negative values of entropy of activation obtained for the adsorption of both metal ions normally reflect that no significant change occurs in the internal structure of adsorbent during the adsorption of ions (Mohan and Singh, 2002).

#### 4 Conclusion

A modified Sorrel's cement (MF5) was prepared and characterised. MF5 can be effectively used as an adsorbent for removal of Gd(III) and U(VI) from dilute carbonate solutions. This adsorbent is stable at pH higher than 4. The adsorption of Gd(III) and U(VI) increases with decreasing of carbonate concentration, and weight of adsorbent. Decreasing the temperatures increased Gd(III) adsorption and decreased the adsorption of U(VI). The maximum loading capacity of adsorbent for Gd(III) and U(VI) was found to equal 65.7 mg/g and 26.0 mg/g for Gd(III) and U(VI), respectively. The adsorption equilibrium process of Gd(III) and U(VI) obeyed the Langmuir and Freundlich adsorption isotherms. The values of  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  for Gd(III) were found to equal  $-30.9 \text{ kJ} \cdot \text{mol}^{-1}$ ,  $-85.4 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$ , and  $-5.4 \text{ kJ} \cdot \text{mol}^{-1}$ , respectively. While the values of  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  for U(VI) were found to equal  $18.9 \text{ kJ} \cdot \text{mol}^{-1}$ ,  $67.8 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$  and  $-1.3 \text{ kJ} \cdot \text{mol}^{-1}$ , respectively.

The kinetics of adsorption of Gd(III) and U(VI) by the MF5 follow first-order reversible kinetics. The forward and backward constants,  $k_1$  and  $k_2$  have been calculated at different temperatures for Gd(III) and U(VI). This study showed that the particle diffusion is the rate limiting step for Gd(III) and (VI). The results also demonstrate that particle diffusion mechanism plays a significant role in the adsorption. The values of  $\Delta H^*$  and  $\Delta S^*$  were calculated for Gd(III) and U(VI) at 25°C. The values of  $\Delta H^*$  were found to equal  $-14.8 \text{ kJ mol}^{-1}$  and  $7.2 \text{ kJ mol}^{-1}$  for Gd(III) and U(VI), respectively, while  $\Delta S^*$  were found to equal  $-95.7 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $-70.5 \text{ J mol}^{-1} \text{ K}^{-1}$  for Gd(III) and U(VI), respectively.

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