

# Thermodynamic and Sorption Behavior of U(VI) and Th(IV) on Unsaturated Polyester–Styrene Polymeric Beads

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Received 27 September 2004; accepted 11 May 2005

DOI 10.1002/app.23307

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The sorption behavior of Th(IV) and U(VI) species on two batch molds of radiation-induced polymerized unsaturated polyester beads containing 40 wt % styrene was investigated. The distribution coefficients of both ions on the polymeric sorbents were evaluated at 30°C using  $10^{-4}$  M solution and found to be 271.9 and 469.8 mL/g on the first mold and 296 and 1189.2 mL/g on the second mold for Th(VI) and U(IV), respectively. Testing the sorption data using different theories provided evidence that the sorption data accurately fit the Langmuir, Freundlich, and D-R isotherms, indicating chemisorption occurred and that  $E$ , the

mean sorption energy of thorium and uranium on the different molds of unsaturated polyester–styrene, was between 8.304 and 13.92 kJ/mol, reflecting the nature of the ion exchange. The thermodynamics of sorption were considered in order to evaluate  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$ . The data showed that the sorption process was spontaneous and exothermic. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4098–4106, 2006

**Key words:** waste; polyesters; polystyrene; adsorption; thermodynamics

## INTRODUCTION

When uranium is used in a reactor during the front end of the nuclear fuel cycle, significant quantities of radioactive wastes are created.<sup>1–5</sup> Therefore, the removal of these fission products and their subsequent treatment and disposal are major issues. U-233, U-234, and Th-234 are among the actinoids produced in the back end of the cycle. Knowing the characteristics of these elements<sup>6–11</sup> will assist in their extraction and removal for various purposes.

Synthetic inorganic ion exchangers have been developed for use in the nuclear fuel cycle in recent years mainly because of their greater power to withstand higher radiation doses and temperatures than the commonly used organic-based resins.<sup>12–16</sup> In addition, they sometimes exhibit highly specific properties that might permit improved separations under ordinary conditions.

However, different organic materials are used in the treatment of radioactive wastes. Many thermoplastics such as bitumen, polystyrene, polyethylene, and poly(methyl methacrylate) are used in the solidification of low and medium radioactive wastes. In addition, other thermosetting organic materials that are resistant to heat, radiation, mechanical shocks, and chem-

ical attack have been utilized for the same task. In the field of ion exchange, many organic ion exchangers are well known for this purpose because of their uniformity, chemical stability, and control of their ion exchange properties through synthetic methods and have been characterized as having higher capacities than the corresponding inorganic materials.<sup>17–19</sup> Regarding this, the present study introduces a well-defined thermosetting ion exchanger that is based on unsaturated polyester–styrene spheres that are not only economically feasible but also have high chemical and radiation resistance as well as enhanced physical characteristics for studying the sorption behavior of U(VI) and Th(IV) from nitrate media.

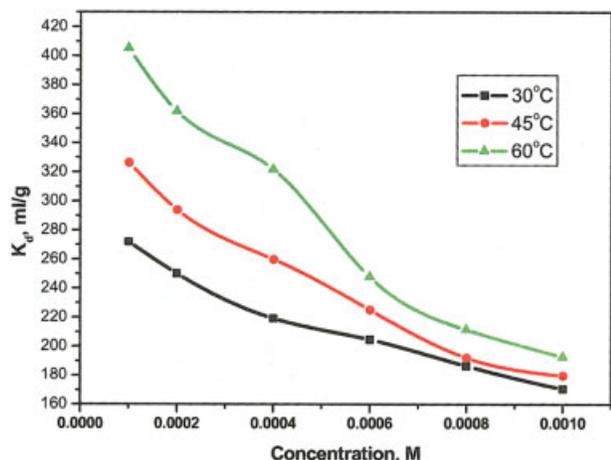
## EXPERIMENTAL

All the reagents used in this investigation were of Analar or equivalent grade, and all the solutions were made in doubly distilled deionized water. Arsenazo III, uranyl nitrate, and thorium nitrate were specifications-pure chemicals supplied by Sigma-Aldrich Chemical Company. (St. Louis, MO). Other chemicals were supplied by Kuraray Company (Tokyo, Japan) and used without further purification.

## Preparation

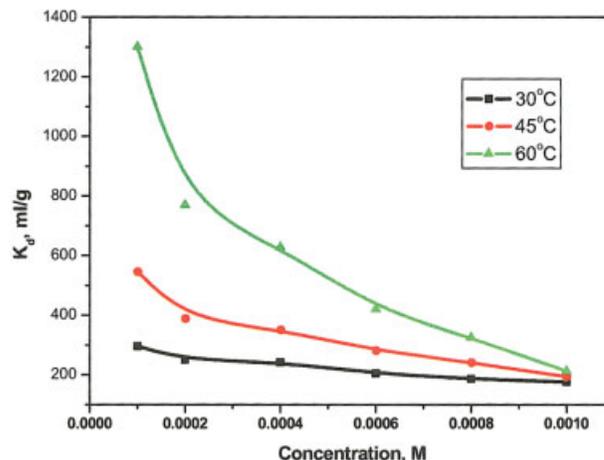
Two batch molds of unsaturated polyester–styrene beads were prepared using induced irradiation polymerization at 50 kGy with different compositions. The

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**Figure 1** Distribution coefficient of Th(IV) ions on polymeric mold I at different concentrations and temperatures.

beads were mainly prepared by dispersion polymerization based on agitation of radiation-cured unsaturated polyester containing 40 wt % styrene monomer within, immiscible, viscous, and noncured polymeric solution, with irradiation (hydroxyl propyl methyl cellulose, HPMC, or urea formaldehyde, UF). HPMC and UF act as dispersant matrices, whereas poly(vinyl alcohol) works as an emulsifier, so irradiation of the batches with 50 kGy would yield solid spheres in the size range of 20–200  $\mu\text{m}$ , depending on the preparation conditions. In this study, the preparation process was optimized so as to obtain 150  $\mu\text{m}$  of polymeric beads to be used in the sorption process. The first batch consisted of unsaturated polyester (40 wt % styrene), poly(vinyl alcohol) solution (8 vol % in  $\text{H}_2\text{O}$ ), and hydroxypropylmethyl cellulose solution (2 vol % in  $\text{H}_2\text{O}$ ) as 60, 5, and 35 wt %. The second mold consisted of unsaturated polyester (40 wt % styrene) and urea formaldehyde resin in a 1:1 wt ratio; the

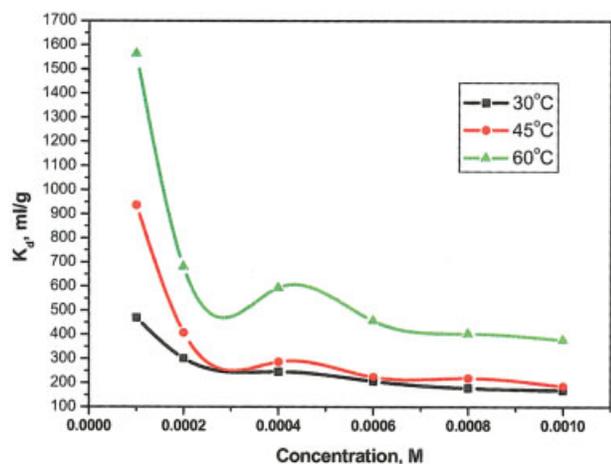


**Figure 3** Distribution coefficient of Th(IV) ions on polymeric mold II at different concentrations and temperatures.

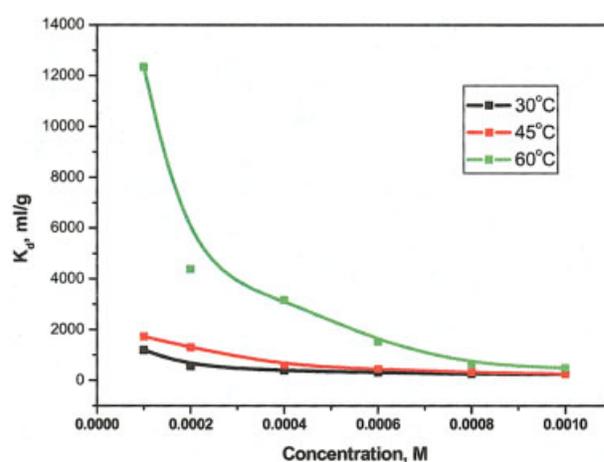
formaldehyde resin was prepared using urea and formaldehyde as precursors in a cold polymeric reaction. The preparation processes were described in detail previously.<sup>20</sup>

### Procedure

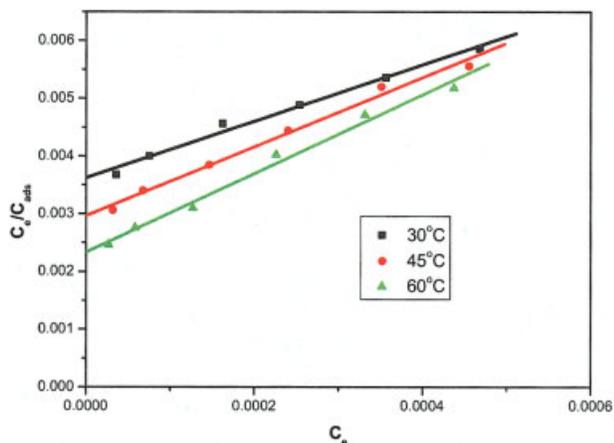
A batch technique was used to study the applicability of the compositions of the prepared polymeric molds for adsorbing U(VI) and Th(IV) ions and their corresponding complexes at pH 2.3. First, 0.1 g of the unsaturated polyester-styrene beads of molds I and II was mixed with 15 mL of  $10^{-4}$  M uranyl nitrate and thorium nitrate solutions and shaken in a shaker thermostat at  $30^\circ\text{C} \pm 1^\circ\text{C}$ . After 24 h, 1 mL of the supernatant liquid was taken for analysis using the Arsenazo III method.<sup>21</sup> Th(IV) and U(VI) were acidified using a 1:1 ratio of 3M HCl and 3M  $\text{HNO}_3$ , and excess 0.05% Arsenazo III (2:1) was then added. The intensity



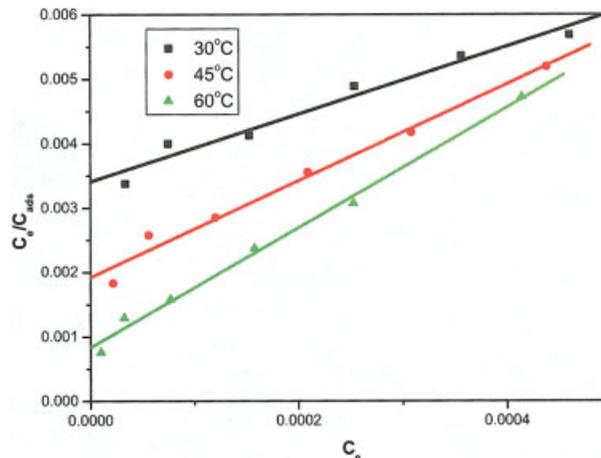
**Figure 2** Distribution coefficient of U(VI) ions on polymeric mold I at different concentrations and temperatures.



**Figure 4** Distribution coefficient of U(VI) ions on polymeric mold II at different concentrations and temperatures.



**Figure 5** Langmuir plots of Th(IV) ions on polymeric mold I at different reaction temperatures.



**Figure 7** Langmuir plots of Th(IV) ions on polymeric mold II at different reaction temperatures.

of the stable complexes of Th(IV) and U(VI) with Arsenazo III was measured as 655 and 665 nm, respectively, using a JASCO UV-visible spectrophotometer (UK). The amount taken up by the solid as percent

sorption and distribution coefficient,  $K_d$ , a value between the solid and aqueous phases, was determined according to the following equations:

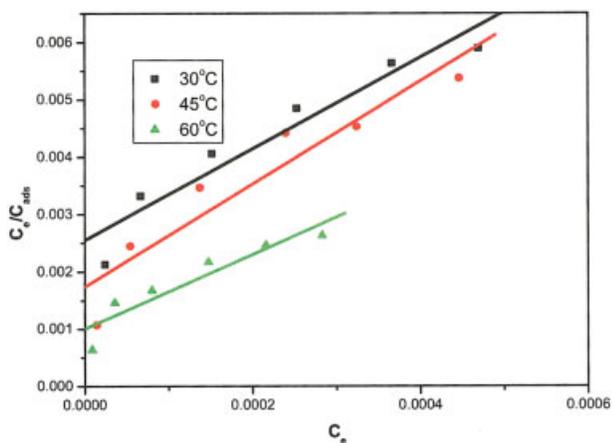
$$\% \text{ Sorption} = \frac{A_i - A_f}{A_i} * 100 \quad (1)$$

$$K_d = \frac{\text{Amount of metal in exchange phase}}{\text{Amount of metal in solution}} * \frac{\text{Volume of solution } (v)}{\text{Weight of dry exchanger } (m)} \quad (2)$$

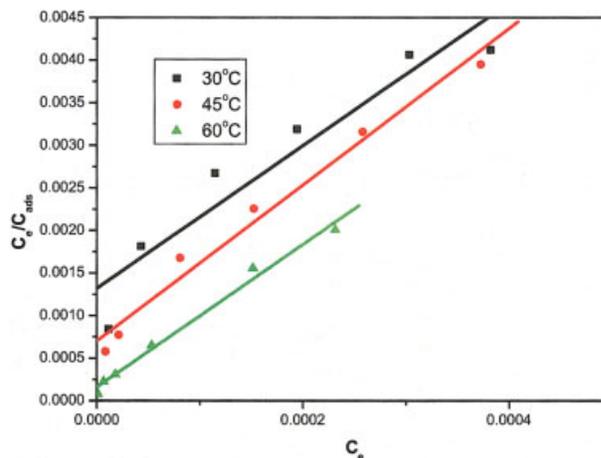
where  $A_i$  and  $A_f$  are the initial and final absorbance values of the working solution before and after equilibrium, respectively. Percent sorption and  $K_d$  (mL/g) were correlated by the following equation:

$$\% \text{ Sorption} = \frac{100 * K_d}{K_d + v/m} \quad (3)$$

All experiments were carried out at least in triplicate at  $30^\circ\text{C} \pm 1^\circ\text{C}$  unless specified otherwise, and the results are reported as the average of at least three independent measurements. In most cases precession was 3%. Linear regression was performed in order to evaluate statistical variation, and the correlation coefficients were found to lie in the range of 0.9829–0.9945, close to unity.



**Figure 6** Langmuir plots of U(VI) ions on polymeric mold I at different reaction temperatures.



**Figure 8** Langmuir plots of U(VI) ions on polymeric mold II at different reaction temperatures.

TABLE I  
Langmuir Constants for Sorption of Th(IV) and U(VI) on Different Polymeric Molds

Langmuir Constants	Temperature (K)	Mold I		Mold II	
		Th(IV)	U(VI)	Th(IV)	U(VI)
$Q$ ( $\mu\text{mol/g}$ )	303	204.2304	125.7745	190.7247	119.3471
	318	166.7776	111.5667	133.5251	108.8767
	333	146.4287	154.3431	107.6777	119.3111
$b$ (L/mol)	303	$1.35 \times 10^3$	$3.12 \times 10^3$	$1.54 \times 10^3$	$6.35 \times 10^3$
	318	$2.02 \times 10^3$	$5.15 \times 10^3$	$3.88 \times 10^3$	$1.31 \times 10^4$
	333	$2.92 \times 10^3$	$6.41 \times 10^3$	$1.10 \times 10^4$	$5.21 \times 10^4$

## RESULTS AND DISCUSSION

### Sorption of U(VI) and Th(IV)

Sorption of U(VI) and Th(IV) ions onto unsaturated polyester molds was investigated in an acidic nitrate medium whose pH was 2.3. On the first mold, equilibrium was attained within 18 min, corresponding to 64.45% and 75.8% sorption of Th(IV) and U(VI), respectively; whereas on the second mold, equilibrium was reached after 23 min, corresponding to 66.37% and 88.8% sorption of Th(IV) and U(VI), respectively. For the sorption determination,  $10^{-4}$  M thorium nitrate and uranyl nitrate solutions were used at  $30^\circ\text{C}$ , a temperature that remained constant beyond the equilibrium time. In a previous study,<sup>22</sup> quantitative extraction of Th(IV) and U(VI) was reported to occur within 2–3 h. Therefore, in further experiments, an equilibration time of 18–23 min was used.

In the present study, the volume of waste solution to the weight of the adsorbent, v/m was set as 150 mL/g in prediction of the adsorption and thermodynamic models. However, the sorption of Th(IV) and U(VI) was investigated on varying amounts of solid sorbent containing  $10^{-4}$  M uranium and thorium nitrate solutions at a pH of 2.3 and using a shaking time of 18–23 min. It was found that the percent sorption

increased with increases in the amount of unsaturated polyester of either composition, becoming almost 60 mg/5 cm<sup>3</sup>, which corresponded to a v/m of 83.33 mL/g, indicating 98% sorption that remained constant beyond this weight. Therefore, during the recovery of both these ions from nitrate media, it is recommended that about 60–62 mg/5 cm<sup>3</sup> be used. This trend in sorption of Th(IV) and U(VI) with varying amounts of unsaturated polyester was observed for sorption of palladium thiocyanate complex on polyurethane foam.<sup>23</sup>

Sorption of Th(IV) and U(VI) ions was studied as a function of their concentrations from nitric acid solutions employing a shaking time of 23 min. The concentrations varied from 0.0001 to 0.001 M. Figures 1–4 illustrate the  $K_d$  values as a function of the specified ions concentrations. The  $K_d$  increased with decreasing concentrations of both ions; in other words, these values increase as dilution of the ions proceeded. However, the distribution coefficients of both ions increased with increasing reaction temperature. Therefore, it is recommended that sorption of both ions be carried out at relatively higher reaction temperatures. The distribution coefficients of sorption of uranyl ionic species were higher than those of thorium species on the same mold. This may be attributed to the differ-

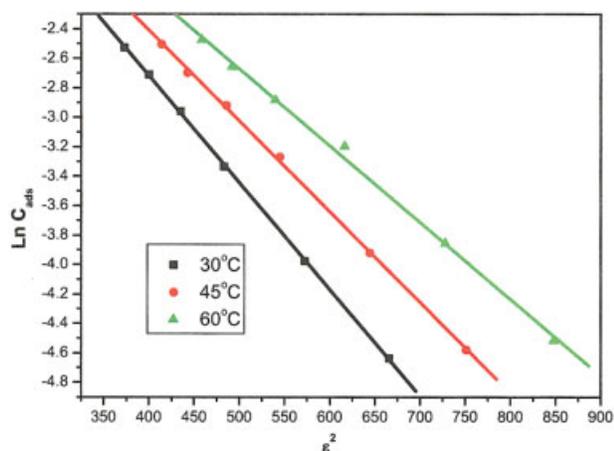


Figure 9 D-R isotherms of Th(IV) ions on polymeric mold I at different reaction temperatures.

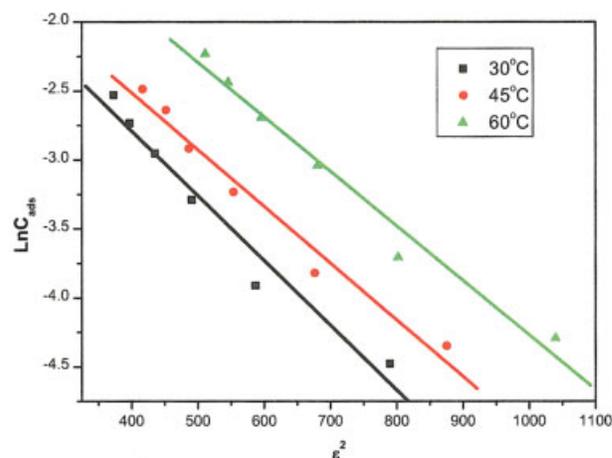
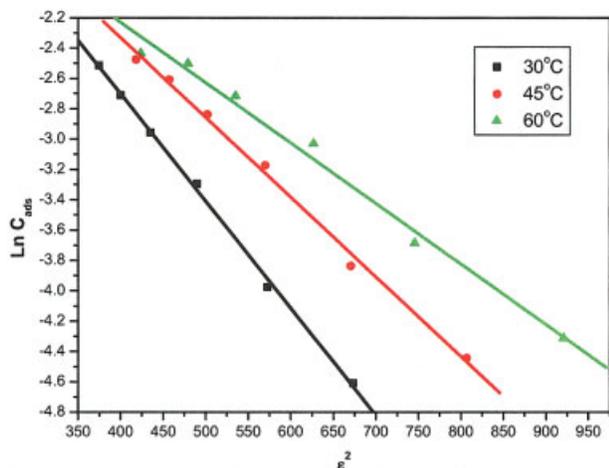


Figure 10 D-R isotherms of U(VI) ions on polymeric mold I at different reaction temperatures.



**Figure 11** D-R isotherms of Th(IV) ions on polymeric mold II at different reaction temperatures.

ence in charge of the acting ions. Using  $10^{-4}$  M solutions at 30°C, selectivity decreased in the following order: U(VI) mold II (1189.2 mL/g) > U(VI) mold I (469.8 mL/g) > Th(IV) mold II (296 mL/g) > Th(IV) mold I (271.9 mL/g).

### Sorption isotherms

The data from sorption were tested and subjected to three types of isotherms: the Dubinin–Radushkevich (D-R), Freundlich, and Langmuir isotherms. The latter can be examined using the linear form:

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \quad (4)$$

where  $C_e$  and  $C_{ads}$  are the concentrations of Th(IV) and U(VI), respectively, in solution at equilibrium (M) and sorbed onto the exchanging molds (mol/L), and  $Q$  and  $b$  are the Langmuir constants related to sorption capacity and sorption energy, respectively. Figures 5–8 show the testing of the sorption data with the Langmuir approach; linear plots were obtained over the entire concentration range of U(VI) and Th(IV) ions investigated. The data obtained were linearly fit using a fitting package supported by Microcal Origin software, version 7 (Cambridge, UK). The linearity of the plots suggested that chemisorption was predominant on a group of well-defined localized sorption sites having the same sorption energies independent of surface coverage and no lateral interaction between the adsorbate molecules. The Langmuir constants are represented in Table I. The sorption capacity,  $Q$ , was observed to be highest when the first polymeric mold was used for sorption of Th(IV) species. On both molds, monolayer coverage in adsorption of Th(IV) ions was greater than that of U(VI) ions. This reflected the highest monolayer capacity for coverage of the

adsorbent surface by adsorbate species that may be attributed to a chemical interaction between the sorbent and the sorbate, postulating that no bilateral interaction between the sorbate species was taking place,<sup>24</sup> which was confirmed from the thermodynamic data as well as the values of the affinity constant,  $b$ , which is a function of the enthalpy of sorption and should vary. These data were in the same order of magnitude as that reported for Pb(II) sorption onto TAC-loaded foams,<sup>25</sup> that is,  $Q = 181 \mu\text{mol/g}$  and  $b = 2.01E \pm 0.07 \text{ L/mol}$ .

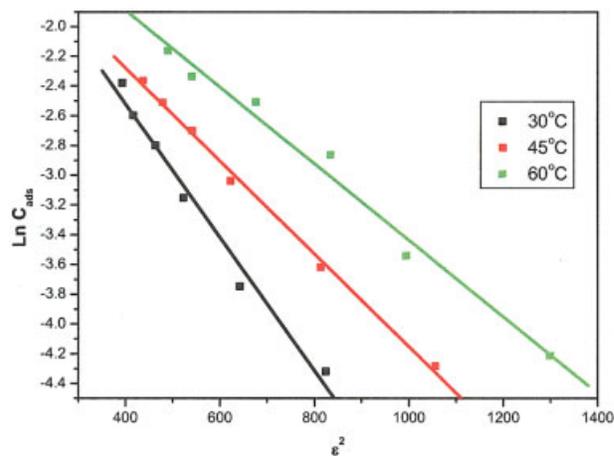
The sorption data were conducted to the D-R model<sup>26–28</sup> and are represented in Figures 9–12. The D-R equation was examined in the following linear form:

$$\ln C_{ads} = \ln X_m - \beta \varepsilon^2 \quad (5)$$

where  $X_m$  is the maximum sorption capacity,  $\beta$  is the activity coefficient related to the mean sorption energy,  $E$ , and  $\varepsilon$  is Polanyi's potential, which is equal to

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (6)$$

where  $R$  is the general gas constant and  $T$  is the absolute temperature. The plots made clear that the D-R theory could be applied to the sorption of uranium and thorium ionic species onto the two specified polymeric molds. The sorption process was obeyed over the whole concentration range, indicating that the surface was heterogeneous. Approximation of a Langmuir isotherm was chosen as a local isotherm for all sites that were energetically equivalent, and the sorption space in the vicinity of the solid surface was characterized by equipotential surfaces having the same sorption potential.<sup>27,29</sup> The D-R constants were estimated and are represented in Table II. The sorption capacity increased with an increasing reaction temperature, reflecting the endothermic nature of the sorption process. The maximum sorption capacity of



**Figure 12** D-R isotherms of U(VI) ions on polymeric mold II at different reaction temperatures.

TABLE II  
Dubinin–Radushkevich Constants for Sorption of Th(IV) and U(VI) on Different Polymeric Molds

D-R Constants	Temperature (K)	Mold I		Mold II	
		Th (IV)	U(VI)	Th (IV)	U(VI)
$X_m$ (mmol/g)	303	0.40312	1.19995	1.133885	0.48241
	318	0.41935	1.049349	0.795456	0.354992
	333	0.732904	0.93824	0.531815	0.424599
$\beta$ (mol <sup>2</sup> /kJ <sup>2</sup> )	303	-0.00725	-0.0047	-0.00707	-0.00448
	318	-0.00615	-0.00411	-0.00525	-0.00312
	333	-0.00521	-0.00396	-0.00399	-0.00258
$E$ (kJ/mol)	303	8.304548	10.31421	8.409599	10.56443
	318	9.016696	11.02971	9.759001	12.65924
	333	9.796392	11.23666	11.19434	13.92115

uranium was greater on the first mold than on the second mold, increasing their saturation limit, which represents the total specific micropore volume of the sorbent at the expense of the mean sorption energy,  $E$ . Sorption capacity,  $X_m$ , was complexed so that it was affected by the sorbent, sorbed ion, pH, and reaction temperature. The estimated D-R constants were comparable to those obtained for sorption of Zn(II)-SCN onto PUF ( $X_m = 494 \mu\text{mol/g}$ ,  $\beta = -0.0028 \text{ mol}^2/\text{kJ}^2$ , and  $E = 13.2 \text{ kJ/mol}$ )<sup>29</sup> and of Hg(II)-SCN onto PUF ( $X_m = 390 \mu\text{mol/g}$ ,  $\beta = -0.0033 \text{ mol}^2/\text{kJ}^2$ , and  $E = 12.4 \text{ kJ/mol}$ ). The free sorption energy of transferring 1 mol of the U(VI) and Th(IV) ionic species from infinity to the surface of the different sorbents increased with an increasing reaction temperature and was in the range of 8.304–13.92, which is characteristic of ion exchange.<sup>30</sup>

The sorption data of the U(VI) and Th(IV) species, are represented in Figures 13–16, were tested according to the Freundlich approach using the following linear form equation:

$$\log C_{\text{ads}} = \log C_m + 1/n \log C_e \quad (7)$$

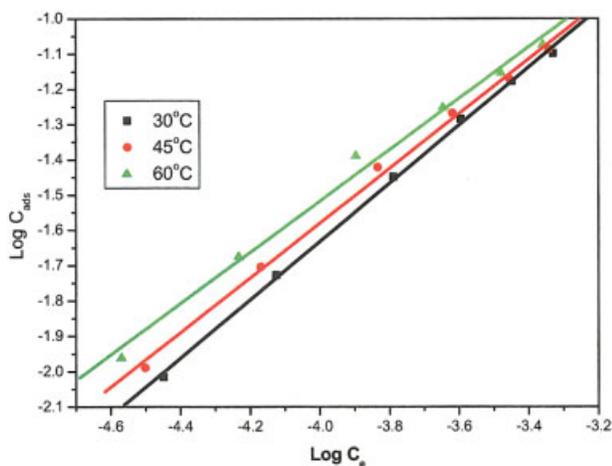


Figure 13 Freundlich isotherms of Th(IV) ions on polymeric mold I at different reaction temperatures.

where  $1/n$  and  $C_m$  are the sorption intensity and capacity, respectively, encompassing the surface heterogeneity and exponential distribution of both the active sites and their energies<sup>29</sup> for multilayer sorption on the surface of the solid. The Freundlich constants were

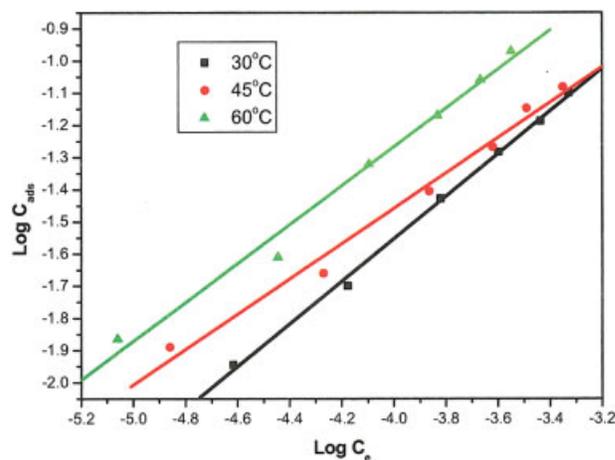


Figure 14 Freundlich isotherms of U(VI) ions on polymeric mold I at different reaction temperatures.

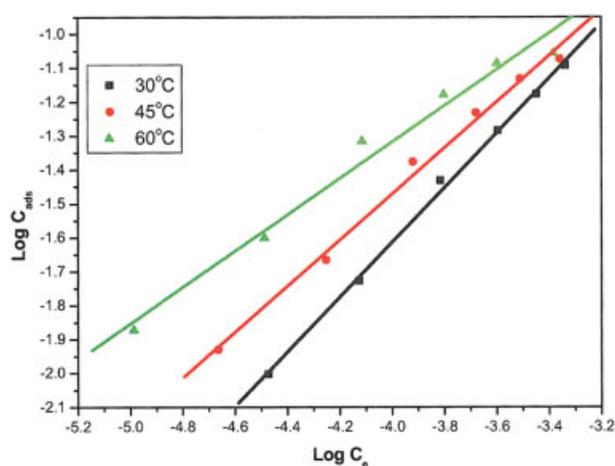
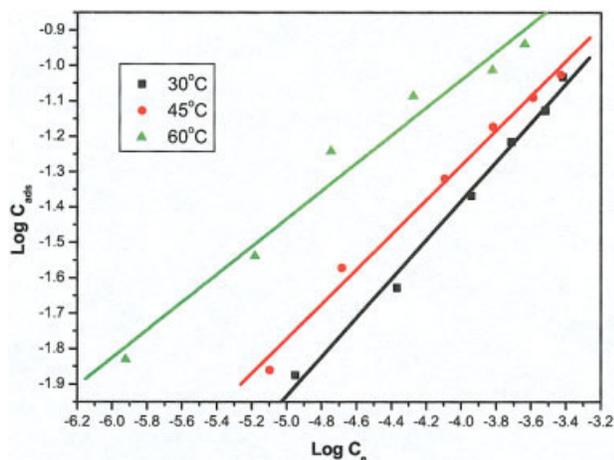


Figure 15 Freundlich isotherms of Th(IV) ions on polymeric mold II at different reaction temperatures.

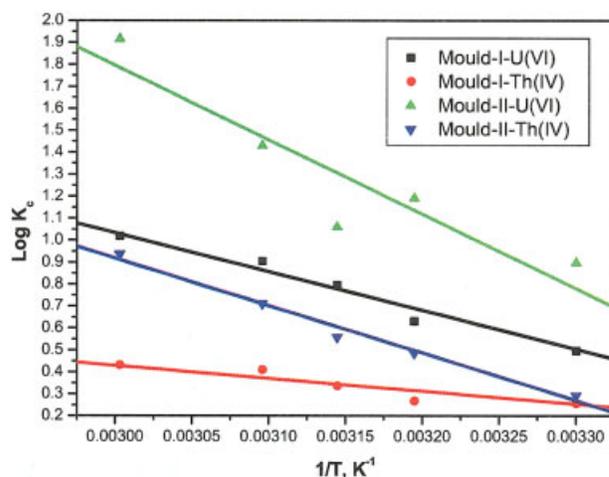


**Figure 16** Freundlich isotherms of U(VI) ions on polymeric mold II at different reaction temperatures.

estimated based on Figures 13–16 and are shown in Table III. Figures 13–16 indicate there was good evidence for satisfaction of the Freundlich model. The sorption capacity obtained when using the Freundlich model to test the sorption isotherms was greater than that obtained using other models. This can be ascribed to these isotherms not predicting any saturation of the sorbent by sorbate; thus, infinite surface coverage is predicted mathematically, indicating multilayer sorption on the surface. The obtained values were comparable to those of  $C_m = 3.86$  mmol/g and  $1/n = 0.44$  evaluated for Hg(II)-SCN sorption on PUF.<sup>29</sup> The intensity of sorption of Th(IV) and U(VI) species was generally a fraction at all temperatures. The values for  $1/n < 1$  indicated that sorption capacity was only slightly suppressed at lower equilibrium concentrations.

### Thermodynamic studies

Variation in the sorption of Th(IV) and U(VI) ions on unsaturated polyester–styrene beads from 1M HNO<sub>3</sub> after 23 min going from 30°C to 60°C of equilibrium was studied. Figure 17 shows this behavior in the temperature range of 30°C–60°C. The changes in the



**Figure 17** Influence of temperature on sorption of Th(IV) and U(VI) ions onto different polyester–styrene molds.

enthalpy, entropy, and free energy of the system were calculated using the following equations<sup>30</sup>:

$$\log K_c = \frac{-\Delta H}{2.303 RT} + \frac{\Delta S}{2.303R} \quad (8)$$

$$\Delta G = -RT \ln K_c \quad (9)$$

where  $K_c$  is the equilibrium constant (the ratio of the equilibrium concentration in solution to that in the solid phase). From the slope and intercept in Figure 17, when a plot between  $\log K_c$  and  $1/T$  was constructed on the basis of eq. (8),  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  were evaluated and are summarized in Table IV. The change in free energy of the system also was computed directly on the basis of eq. (9) from different concentrations of thorium nitrate and uranyl nitrate at different reaction temperatures using the two polymeric molds. The results, shown in Tables V and VI, indicate that the different free energies calculated on the basis of eqs. (8) and (9) were comparable at the different reaction temperatures when 0.0001M of both thorium and uranyl salt solutions were used. Generally, the values of  $\Delta G$  were negative indicating the

**TABLE III**  
Freundlich Constants for Sorption of Th(IV) and U(VI) on Different Polymeric Molds

Freundlich Constants	Temperature (K)	Mold I		Mold II	
		Th(IV)	U(VI)	Th(IV)	U(VI)
$1/n$	303	0.82389	0.66153	0.80585	0.55055
	318	0.77447	0.54827	0.67801	0.48972
	333	0.72654	0.60468	0.53491	0.39242
$C_m$ (mmol/g)	303	2.059453	1.607445	2.011253	1.427237
	318	1.934339	1.376632	1.714517	1.341963
	333	1.828729	1.649316	1.428415	1.258332

**TABLE IV**  
**Thermodynamic Parameters for Sorption of Th(IV) and U(VI) on Different Polymeric Molds**

Thermodynamic parameter	Mold I		Mold II	
	Th(IV)	U(VI)	Th(IV)	U(VI)
$\Delta H$ (kJ/mol)	11.15381	33.72632	41.25129	64.7024
$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )	41.68639	120.9579	141.3588	228.5039
$\Delta G_{303}$ (kJ/mol)	-1.47717	-2.92391	-1.58041	-4.53428
$\Delta G_{318}$ (kJ/mol)	-2.10246	-4.73828	-3.70079	-7.96184
$\Delta G_{333}$ (kJ/mol)	-2.72776	-6.55265	-5.82117	-11.3894

spontaneous nature of the sorption process at the selected concentrations; for the uranyl species the sorption process was more spontaneous than that of the tetravalent thorium species. This behavior was in agreement with the distribution coefficients results. The obtained data were quite close to those reported earlier for Co(II)<sup>31</sup> and Pd(II)<sup>32</sup> on PUF in the presence of thiocyanate ions. The  $\Delta G$  values went in a negative direction on dilution of the solution and when the reaction temperature was raised. This could be attributed to the endothermic behavior of the sorption process, as  $\Delta H$  values are positive. The computed  $\Delta H$  values, U(VI) mold II (64.7 kJ/mol) > Th(IV) mold II (41.25 kJ/mol) > U(VI) mold I (33.72 kJ/mol) > Th(IV) mold I (11.15 kJ/mol), were on the same order of magnitude as those reported for silver sorption on ceric tungstate ( $\Delta H = 34.7$  kJ/mol),<sup>33</sup> phosphate sorption on zirconium oxide ( $\Delta H = 25$  kJ/mol),<sup>34</sup> and silver sorption from manganese dioxide from nitric and perchloric acid solutions ( $\Delta H = 39.8$  and 43.5 kJ/mol, respectively).<sup>35</sup>

### Sorption mechanism

Taking into consideration the presence of different ionic species of uranium and thorium, hexavalent uranyl ions and tetravalent thorium ions exist and are responsible for the adsorption of both ions on the surface of the unsaturated polyester-styrene beads. The main uranyl nitrate species solutions expected in the adsorption of U(VI) on the various polymeric materials, in addition to the hydroxyl and nitrate anions, were  $[\text{UO}_2]^{2+}$ ,  $[\text{UO}_2\text{NO}_3]^+$ ,  $[(\text{UO}_2)_2(\text{OH})_2]^{2+}$ ,  $[\text{UO}_2\text{OH}]^+$ , and  $[(\text{UO}_2)_3(\text{OH})]^{5+}$ . When thorium nitrate was used,  $[\text{Th}]^{4+}$ ,  $[\text{Th}(\text{OH})]^{3+}$ ,  $[\text{ThNO}_3]^{3+}$ , and  $[\text{Th}(\text{OH})_2]^{2+}$  were coexistent at ambient pH (2.5) and were expected to be responsible for the sorption of uranium and thorium onto the different polymeric beads.<sup>36</sup> The sorption data accurately fit the Langmuir, Freundlich, and D-R isotherms, indicating that chemisorption occurred. The values of  $E$ , the mean sorption energy of thorium and uranium on the different molds of unsaturated polyester-styrene, were 8.304 and 13.92 kJ/mol, reflecting their ion exchange nature,<sup>30</sup> which stemmed from the unsaturated polyester-styrene resin beads being based on orthophthalic acid, maleic acid, and propylene glycol. Upon irradiation polymerization, some of the hydroxyl and carboxylic groups were involved in the polymerization process and crosslinked with the styrene monomers, so that a great number of the hydroxyl and carboxylic groups, which can act as ion exchange groups, especially in acidic media, remained free. The positive values of  $\Delta H$  and the negative values of  $\Delta G$  clearly showed the endothermic and spontaneous nature of the chemi-

**TABLE V**  
**Thermodynamic Parameters for Sorption of Th(IV) and U(VI) on Mold I**

Concentration [M]	U(VI)			Th(IV)		
	30°C	45°C	60°C	30°C	45°C	60°C
0.0001	-2.87622	-4.84132	-6.4945	-1.49876	-2.05387	-2.75367
0.0002	-1.75559	-2.65248	-4.1981	-1.28684	-1.77725	-2.43871
0.0004	-1.24715	-1.7313	-3.82077	-0.95651	-1.45257	-2.11491
0.0006	-0.80277	-1.08632	-3.10096	-0.78212	-1.07199	-1.39065
0.0008	-0.42422	-1.02251	-2.75367	-0.5483	-0.6537	-0.95396
0.001	-0.30974	-0.57331	-2.57374	-0.32289	-0.47718	-0.69578

**TABLE VI**  
**Thermodynamic Parameters for Sorption of Th(IV) and U(VI) on Mold II**

Concentration [M]	U(VI)			Th(IV)		
	30°C	45°C	60°C	30°C	45°C	60°C
0.0001	-5.21582	-6.4572	-12.2115	-1.71258	-3.40827	-5.98011
0.0002	-3.27736	-5.69935	-9.35135	-1.28899	-2.51015	-4.52754
0.0004	-2.29981	-3.64866	-8.45809	-1.20974	-2.24013	-3.96613
0.0006	-1.8573	-2.86383	-6.43942	-0.78212	-1.65992	-2.85139
0.0008	-1.24715	-1.97223	-4.02345	-0.54932	-1.23832	-2.13793
0.001	-1.21188	-1.38331	-3.32189	-0.39987	-0.65907	-0.9551

sorption. On the other hand, the positive values of  $\Delta S$  favored a slower sorption of uranium and thorium species on the active sites of the sorbent. This conclusion is in agreement with the fact that U(VI) and Th(IV) sorption is attained within about 23 min of equilibrium. This can further be explained on the basis of the high energy of sorption sites for both ions provided by an increase in temperature may cause stable interaction between the sorption sites and the metal ions, subsequently causing a higher sorption at higher temperatures. The endothermic nature of sorption may be interpreted in terms of salvation-type bond formation between metal ions and the surface of the solids on the basis of hydrogen and/or ionic bonding comprising ion exchange or ion association interaction.<sup>37,38</sup> The data obeying Langmuir and D-R isotherms refers to the transfer of U(VI) and Th(IV) ions from aqueous solution to the surface by adsorption rather than absorption, and the bond formation between metal ions and unsaturated polyester-styrene may be chemical in nature. The sorption capacity of Th(IV) and U(VI) ions onto the polymeric materials was different for all three sorption isotherms but was on the same order of magnitude. Difference in sorption capacity can be interpreted in terms of the assumptions taken into consideration while deriving these sorption models.

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