Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Retention, Thermodynamics and Adsorption Profile of Th(IV) Ions onto 1-(2-Pyridylazo)-2-Naphthol (PAN) Loaded Polyurethane Foam from Acetate Media and its Separation from Rare Earths

Muhammad Mufazzal Saeed[a]
[a] Chemistry Division, Pakistan Institute of Nuclear Science and Technology, Islamabad, Pakistan

To cite this Article Saeed, Muhammad Mufazzal(2008) 'Retention, Thermodynamics and Adsorption Profile of Th(IV) Ions onto 1-(2-Pyridylazo)-2-Naphthol (PAN) Loaded Polyurethane Foam from Acetate Media and its Separation from Rare Earths', Separation Science and Technology, 43: 4, 923 — 943

To link to this Article: DOI: 10.1080/01496390701870671

URL: http://dx.doi.org/10.1080/01496390701870671

Separation Science and Technology, 43: 923–943, 2008

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390701870671

Retention, Thermodynamics and Adsorption Profile of Th(IV) Ions onto 1-(2-Pyridylazo)-2-Naphthol (PAN) Loaded Polyurethane Foam from Acetate Media and its Separation from Rare Earths

Muhammad Mufazzal Saeed

Chemistry Division, Pakistan Institute of Nuclear Science and
Technology, Islamabad, Pakistan

Abstract: The sorption behavior of 2.7×10^{-5} M solution of Th(IV) ions on 1-(2-pyridylazo)-2-naphthol (PAN) loaded polyurethane foam (PUF) has been investigated. The quantitative sorption was occurred from pH 6 to 9 from acetate buffer solutions. The sorption conditions were optimized with respect to pH, shaking time, and weight of sorbent. The sorption data followed the Freundlich, Langmuir, and Dubinin-Radushkevich (D-R) isotherms very successfully at low metal ions concentration. The Freundlich isotherm constant ($1/n$) is estimated to be 0.22 ± 0.01, and reflects the surface heterogeneity of the sorbent. The Langmuir isotherm gives the maximum monolayer coverage is to be 8.61×10^{-6} mol g^{-1}. The sorption free energy of the D-R isotherm was 17.85 ± 0.33 kJ mol^{-1}, suggesting chemisorption involving chemical bonding was responsible for the adsorption process. The numerical values of thermodynamic parameters such as enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) indicate that sorption is endothermic, entropy driven, and spontaneous in nature. The adsorption free energy (ΔG_{ads}) and effective free energy (ΔG_{eff}) are also evaluated and discussed. The effect of different anions on the sorption of Th(IV) ions onto PAN loaded PUF was studied. The possible sorption mechanism on the basis of experimental finding was discussed. A new

Received 5 June 2007, Accepted 4 November 2007
Address correspondence to Muhammad Mufazzal Saeed, Chemistry Division, Pakistan Institute of Nuclear Science and Technology, P. O. Nilore, Islamabad, Pakistan. E-mail: mufazzal@pinstech.org.pk

separation procedure of Th(IV) from synthetic rare earth mixture using batch, column chromatography, and squeezing techniques were reported.

Keywords: Thorium, polyurethane foam, 1-(2-pyridylazo)-2-naphthol, adsoprtion, preconcentration, rare earths separation process

INTRODUCTION

Thorium is a naturally occurring radioactive element widely distributed over the earth crust. The main source of thorium is the monazite. It gets importance not only due to industrial applications but also in energy and environmental problems (1). Thorium and rare earths elements coexist in their minerals and in waste water. There are large stocks of thorium bearing residue in different countries. The separation of thorium from rare earths is difficult and limited, because rare earth compounds show the similar properties of thorium. The determination of thorium is significance. Different methods have been described for the effective separation and preconcentration of thorium based on ion exchange (2, 3), solvent extraction (4, 5), co-precipitation (6), and solid phase extraction (7, 8) are among them.

Solid phase extraction technique is recognized as the fast and reliable approach for quantitative metal ions separation and preconcentration. The physically impregnated organic reagents on solid support also found effective for this purpose because they have high distribution ratio of separation (9–11). Different factors influencing the sorption may be varied the systematically to reveal their part in mechanism.

Polyurethane foam (PUF) is a synthetic porous semi solid and has been widely used to separate a wide range of inorganic and organic compounds (12–14). It is an inexpensive solid extractor and effective sorbent for the removal of trace metal ions from aqueous solution. The foam sorbent gives unique advantage over conventional granular solid support in rapid, versatile, and effective separation of different species from fluid samples. The presence of electron donor atoms i.e., nitrogen and oxygen atoms s in the basic structure of PUF enables it to act as a solid neutral ligand in complex formation with metal ions. The three-dimensional structure of foam is heterogeneous in surface structure and in surface energy distribution and hence, metal ions preferentially adsorb on low energy sites. The separation of Th(IV) ions from aqueous solution onto bis (2-ethylhexyl) phosphoric acid loaded PUF (15), reversed phase chromatography separation of Th(IV) in rock samples with TBP loaded PUF (16), extraction chromatography of Th(IV) ions with PMBP–loaded PUF cylinder (17), and ^{234}Th separation with trioctylamine impregnated PUF (18) were reported in literature. A number of different mechanisms such as ion exchange, solvent extraction, ligand addition, ion association, surface sorption etc., have been reported by different workers depending upon the nature of the chemical species sorbed and conditions of sorption (14).

1-(2-Pyridylazo)-2-naphthol (PAN) is heterocyclic azo dystuffs, reacts with many metal ions, and found significant analytical uses. This reagent is least reactive with actinides due to formation of unsaturated complexes (19). The present work is focused to develop a simple and low cast procedure for the separation of Th(IV) ions from its associated metal ions in naturally occurring samples solution by employing the PAN immobilized on PUF. Different sorption parameters of Th(IV) ions onto PAN loaded PUF have been critically investigated. The kinetic and thermodynamic characteristics of sorption are discussed. The conformity of different adsorption models and nature of sorption mechanism has been discussed based on these observations.

EXPERIMENTAL

Reagents

All the reagents used were of the Analar grade. PAN from Fluka was used as such. Buffer solutions of pH 1–2 having ionic strength of 0.1 M were prepared by mixing an appropriate volume of 0.1 M solutions of HCl and KCl, and buffer solutions of pH 3–6 were made by mixing an appropriate volume of 0.1 M solutions of CH_3COOH and CH_3COONa. The buffer solutions of pH 7–10 were prepared by mixing an appropriate volume of CH_3COONa and NaOH, and H_3BO_3 and NaOH. The stability of the buffer solutions was checked on a Metrohm 632 pH meter periodically. The stock solution of Th(IV) ($1000\,\mathrm{mg\,L^{-1}}$) was prepared from $Th(NO)_4 \cdot 5H_2O$ (Merck) in water. The concentrated HNO_3 (~1 ml) was added in 250 ml of stock solution to suppress the hydrolysis. The 0.1% solution of Arsenazo III (Aldrich) was prepared in water. The concentration of Th(IV) ions in aqueous solution was determined using Th-Arsenazo-III complex in 0.1 M HCl (20) on SpectroScan 80 D spectrophotometer at 665 nm against a reagent blank.

Polyurethane Foam Preparation

The foam plugs were prepared and washed as described elsewhere (21). The washed foam plugs were socked in 0.1% PAN solution in ethanol for 30 minutes. The excess amount of ethanol was drained out and the PUF plugs were pressed between filter paper to remove the excess ethanol solution. After that, the PAN loaded plugs were dried in an oven at 50°C and were kept in an airtight plastic bottle for further studies. The loaded concentration of PAN on PUF was dissolved in acetone and was found to be $5.38\,\mathrm{mmol\,g^{-1}}$ against standard calibration curve of PAN in acetone. The absorbance was measured by SpectroScan 80 D spectrophotometer at λ_{max} 465 nm against acetone.

Procedure

Six ml buffer solution of known pH was taken in 25 × 150 mm Pyrex glass culture tube with a polyethylene cap. A known concentration of Th(IV) ions were added and mixed thoroughly. An aliquot of two ml was drawn to measure the initial concentration (A_o) of Th(IV) ions. The remaining solution was shaken with PAN loaded PUF (~29 mg) for 30 minutes or as specified on a Stuart Scientific wrist-action shaker. After shaking, two ml (A_e) of aliquot was again withdrawn for assayed spectrophotometrically.

The adsorbed concentration of Th(IV) at equilibrium was calculated by the difference in the amount of thorium Arsenazo-III complex absorbance of the aliquots drawn before (A_o) and after shaking (A_e). The percentage adsorption and distribution coefficient (K_d) were calculated as:

$$\%\text{Adsorption} = \frac{A_o - A_e}{A_o} \times 100 \tag{1}$$

$$K_d = \frac{\%\text{Adsorption}}{100 - \%\text{Adsorption}} \times \frac{\text{Volume of solution (V)}}{\text{Weight of PUF (W)}} = \text{ml g}^{-1} \tag{2}$$

The % adsorption and the distribution coefficient (K_d) can be correlated as

$$\%\text{Adsorption} = \frac{100K_d}{K_d + V/W} \tag{3}$$

All the experiments were performed at ambient temperature or at temperature specified otherwise. The results are the average of at least triplicate independent measurements and precision in most cases is ±2.5%. The linear regression and slope analyses for the statistical data were carried out.

RESULTS AND DISCUSSION

The sorption of 2.7×10^{-5} M solution of Th(IV) ions on PAN loaded PUF was carried out from aqueous solution of pH 1–10. The variation of percent sorption and distribution coefficient (K_d) with 30 minute shaking time is shown in Fig. 1. This figure shows that the sorption was quantitative at pH 6 and remains constant upto pH 10 in acetate buffer solutions. However, in standard borate buffer solutions, the sorption is negligibly small due to the masking effect of borate ions. A similar trend in distribution coefficient of the sorption behavior of Th(IV) ions in acetate and borate medium are observed as shown in Fig. 1.

The change of the orange red color of sorbed PAN on PUF to red violet indicates that sorption of Th(IV) ions from neutral medium is due to the complexation of PAN and PUF with Th(IV) ions. PAN shows hypsochromic and bathochromic shifts on protonation and ionization, respectively, as a function

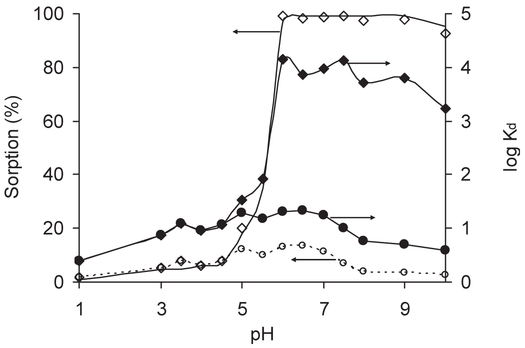


Figure 1. Effect of pH on the sorption of 2.7 × 10^{-5} M solution of Th(IV) ions onto PAN loaded PUF. (Symbols; Circle: borate buffer solutions; Square: acetate buffer solutions.)

of pH (19). The neutral species of PAN exists in the pH range 3–10, which is water insoluble and responsible for complex formation with metal ions. The neutral form of HPAN (HL) has strong tendency to dissociate the hydrogen atom of the hydroxal group of naphthol in neutral or basic medium as:

$$\mathrm{HL} \rightleftharpoons \mathrm{H}^+ + \mathrm{L}^-$$

where the anionic species (L^-) interact with Th(IV) ions. The concentration of anionic species are pH dependant and at pH 6, the sufficient amount is produced that interacts with 2.7 × 10^{-5} M solution of Th(IV) ions to neutralize its charge and sorbed onto PUF to satisfy the stable coordination number of central metal ions quantitatively from acetate aqueous medium as shown in Fig. 1.

Effect of Shaking Time

The effect of shaking time from 5 to 30 min at an interval of 5 min on the retention of 2.7 × 10^{-5} M solution of Th(IV) ions onto PAN loaded PUF under the optimum pH 6.5 was varied. The sorption is very fast and attains the equilibrium within 10 min shaking time as shown in Fig. 2. Thus, a shaking time of 10 minutes was adopted for maximum adsorption in the subsequent work.

Effect of Adsorbent

The effect of weight of the sorbent on the sorption of 2.7 × 10^{-5} M solution of Th(IV) ions was studied in the range of 1–14 mg ml^{-1} of PAN loaded PUF at pH 6.5 with 10 min shaking time. The variation of percent sorption and

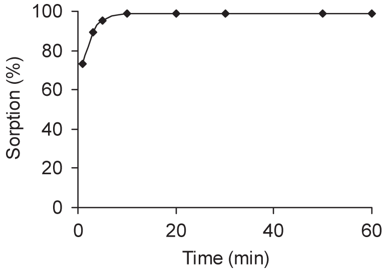


Figure 2. Effect of shaking time on the percentage sorption of 2.7 × 10^{-5} M solution of Th(IV) ions onto PAN loaded PUF at pH 6.5.

distribution coefficient (K_d) is presented in Fig. 3. This figure shows that sorption increases with increase in weight of sorbent and attains the maximum value ~100% at 7 mg ml^{-1} of sorbent and remains constant on further increase in sorbent weight. But the distribution coefficient (K_d) first increases and attains the max value $10^{4.2}$ upto 7 mg ml^{-1} of sorbent. The further decreases in the K_d value is due to the dominator effect of the sorbent weight. The increase in sorption with sorbent weight upto 7 mg ml^{-1} may be due to an increases in the sorption sites and pore volume available of the sorbent are sufficient to accommodate all Th(IV) ions present in aqueous solution.

Effect of Foreign Ions

The sensitivity of PAN loaded PUF for the preconcentration of Th(IV) ions under the optimum conditions was evaluated. The presence of different foreign ions in the sorptive medium may change environment around the central metal ion and subsequently its solution chemistry and sorption behavior. The sorption of Th(IV) was measured in the presence of different

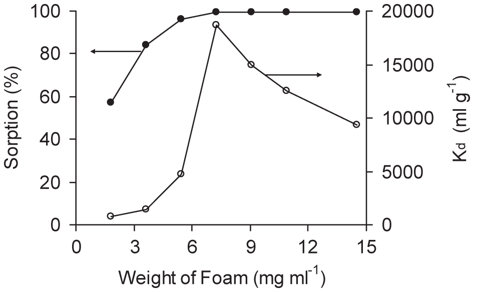


Figure 3. Variation of percentage sorption and distribution coefficient of 2.7 × 10^{-5} M solution of Th(IV) ions with weight of PAN loaded PUF at pH 6.5.

anions of sodium or potassium salts. The pH of the solution was adjusted with dilute NaOH or CH_3COOH solution as per requirement. The results are tabulated in Table 1. This table indicates that on addition of different electrolytes, the sorption was masked in the presence of citrate, EDTA, cyanide, oxalate, phosphate, ascorbate, and tartrate anions due to the formation of more stable metal complexes than Th(IV)-PAN complex. Moreover, borate, chromate, and molybdate readily alloy with thorium and decrease the percent sorption (1). Therefore, these anions should not be present in the sorption process of Th(IV) metal ions. The other anions as shown in Table 1, do not interfere in the adsorption process of Th(IV) metal ions. However, acetate anions showed little interference and hence acetate solutions provided the best media for the studies of the sorption process onto PAN loaded PUF.

Desorption Studies

In order to study the elution/desorption behavior of Th(IV)-PAN complex on PUF, the sorbed Th(IV) ions onto PAN loaded PUF plugs were shaken in different organic solvents and acids concentrations. The liquid phase was

Table 1. Effect of different anions on the sorption of 2.7×10^{-5} M solution of Th(IV) ions onto PAN loaded PUF from pH 6.5 acetate buffer solution, shaking time 10 min

Anions	Concentration (mol L^{-1})	Adsorption (%)	K_d (ml g^{-1})
None	2.70×10^{-5}	99.83	84137
Chloride	1.34×10^{-1}	99.42	23908
Sulphate	7.04×10^{-2}	98.47	8879
KSCN	1.03×10^{-1}	98.47	8879
Bromide	9.71×10^{-2}	95.44	2893
Fluoride	2.38×10^{-1}	91.41	1469
Sulphite	7.93×10^{-2}	89.39	1162
Perchlorate	8.16×10^{-2}	88.80	1093
Chromate	6.17×10^{-2}	75.26	419
Molybdate	4.13×10^{-2}	<47	125
Borate	1.62×10^{-1}	<16	27
Citrate	3.40×10^{-2}	<15	24
EDTA	2.69×10^{-2}	<10	15
Cyanide	1.53×10^{-1}	<9	13
Oxalate	7.46×10^{-2}	<9	12
Phosphate	6.09×10^{-2}	<4	5
Ascorbate	5.67×10^{-2}	<1	2
Tartrate	5.26×10^{-2}	<1	<1

heated to dryness and then treated with concentrated HNO_3 solution. The final residue was dissolved in 0.1 M HCl solution and assayed spectrophotometrically for thorium concentration using Arsenazo III as chromogenic reagent. The results of desorption are given in Table 2. This table indicates that Th-PAN complex does not get eluted in organic solvents or even desorbs in borate buffer solution of pH 7. This indicates that Th(IV) ions not only form strong complexes with PAN but PUF also plays an important role in the sorption process that is hindered in the elution of the sorbed Th(IV)-PAN complexes. Moreover, desorption of Th(IV) ions are quantitative in acidic medium due to the decomposition of the Th-PAN-PUF complex. The 1.0 M HCl solution is the most effective for desorption.

Adsorption Isotherm

The sorption of Th(IV) ions from bulk aqueous solution onto PAN loaded PUF can be explained in the form of its diffusion and thermodynamic behavior. The sorption of Th(IV) ions on PAN loaded foam is very fast and $>95\%$ of Th(IV) ions are sorbed within 5 min shaking time as described earlier. This indicates that film diffusion i.e., diffusion of the solute through hypothetical film of hydrodynamic boundary layer takes place in the sorption processes. The film diffusion sorption is related to the concentration gradient and considered to be very fast and generally occurs at the macropores of the sorbent. The variation of sorption with increase in Th(IV) ions was examined over the 10-fold concentration in the range 2.7×10^{-5} to 2.1×10^{-4} M under

Table 2. Desorption behavior of Th(IV) ions from PAN loaded PUF in different organic and aqueous solutions

Medium	Percent desorption
Ethanol	<5
Acetone	<5
Chloroform	<5
Benzene	<5
pH 4, acetate buffer	<2
pH 7.5, borate buffer	<4
0.5 M HNO_3	80
1.0 M HNO_3	91
2.0 M HNO_3	93
0.5 M HCl	92
1.0 M HCl	100
2.0 M HCl	98

optimum conditions of pH, shaking time, and weight of foam is shown in Fig. 4. This figure indicates that sorption increases with equilibrium metal ions concentration and then remains constant due to the saturation of the active sites of the sorbent. The similar trend is observed in sorption with initial concentration of Th(IV) metal ions. This non-linear behavior of both the curves is the characteristic feature of the Freundlich adsorption isotherm and can be described on thermodynamic behavior. The equilibrium data were subjected to test the most commonly used mathematical expressions of classical adsorption isotherms (21) i.e., Freundlich isotherm, Langmuir isotherm, and Dubinin-Radushkevich (D-R).

The Freundlich isotherm usually fits the experimental data in low concentration range and represent the adsorption model with multi-layer coverage. In view of its empirical formulation, it is frequently employed in connection with adsorption from aqueous solution. The linear form of the Freundlich isotherm is expressed as:

$$\log C_{ads} = \log K_F + \frac{1}{n} \log C_e$$

where C_{ads} is the concentration of Th(IV) ions in solid phase in mol g^{-1}, and C_e is the concentration in aqueous solution in mol l^{-1}, K_F and $1/n$ are the characteristic constants. The plot of log C_{ads} vs log C_e is a straight line as shown in Fig. 5. The numerical values of K_F and $1/n$ are evaluated from intercept and slope respectively, of the plot are given in Table 3. The high or infinite surface coverage (K_F) is predicted mathematically indicating a submonolayer sorption of the sorbate on the surface of the sorbent. The $1/n$ value indicates the energy and intensity of the sorption as well as distribution

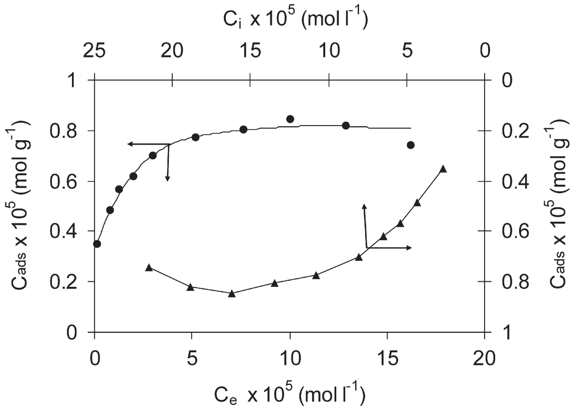


Figure 4. The equilibrium adsorption profile of Th(IV) ions with aqueous concentration of Th(IV) onto PAN loaded PUF at pH 6.5. (Symbols: C_e = equilibrium metal ion concentration; C_i = initial metal ions concentration.)

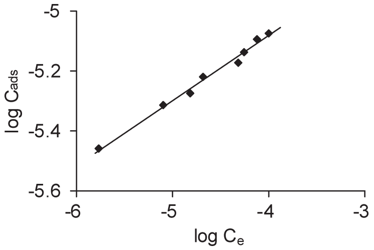


Figure 5. Freundlich adsorption isotherm of Th(IV) ions onto PAN loaded PUF at pH 6.5.

of active sites. The low value (<1) of $1/n$ clearly corresponds to heterogeneous surface with an exponential distribution of active sites of the sorbent.

The Langmuir model was originally developed to represent chemisorption on a set of well-defined, localized monolayer coverage of sorption i.e., sorption occurs on definite sites, all sites are identical in energy, and accommodate only one molecule and these molecules cannot move across the surface of the adsorbent. The familiar form of Langmuir isotherm based on the kinetic consideration is expressed as:

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q}$$

where C_{ads} and C_e are same as described previously, Q is the constant related to maximum amount of solute adsorbed, and "b" is the constant related to the binding energy of solute.

Table 3. Freundlich, Langmuir, and D-R isotherms constants of Th(IV) ions onto PAN loaded PUF at pH 6.5

Constants	Values
Freundlich isotherm	
$1/n$	0.22 ± 0.01
$K_F \times 10^5$ (mol g^{-1})	6.09 ± 0.55
r	0.9951
Langmuir isotherm	
$Q \times 10^6$ (mol g^{-1})	8.61 ± 0.25
$b \times 10^{-5}$ (l mol^{-1})	1.5 ± 0.4
r	0.9958
D-R isotherm	
β (kJ^2 mol^{-2})	-0.00157 ± 0.0005
$X_m \times 10^5$ (mol g^{-1})	1.86 ± 0.08
E (kJ mol^{-1})	17.85 ± 0.33
r	0.9959

The graphic presentation of C_e/C_{ads} against C_e is shown in Fig. 6. The model parameters of Q and b are obtained from the slope and intercept, respectively, of straight line of the graph and are given in Table 3. The value of Q corresponding to the monolayer coverage and is independent of temperature, while the sorption coefficient "b" is related to the enthalpy of adsorption and should vary with temperature.

The D-R isotherm postulates on "adsorption space" close to the adsorbent's surface where adsorption occurs and relates pore filling to the free energy of adsorption. This model features the heterogeneous surface of the adsorbent as in Freundlich isotherm (22). In order to distinguish between physical and chemical adsorption, the data were applied to D-R isotherm in the linear form as:

$$\ln C_{ads} = \ln X_m - \beta\varepsilon^2$$

where C_{ads} is concentration of Th(IV) ions in solid phase in mol g^{-1}, X_m is the maximum adsorption of D-R monolayer coverage, β is the activity coefficient with dimension of energy and Polanyi potential $(\varepsilon) = -RT\ln(1 + (1/C_e))$ where R is gas constant (8.3143 J mol^{-1} K^{-1}) and T is the temperature in Kelvin.

The plot of ln C_{ads} vs ε^2 shown in Fig. 7 is a straight line. The computed values of β and X_m from the slope and the intercept are given in Table 3. If the surface is heterogeneous and an approximation to a Langmuir isotherm is chosen as a local isotherm for all sites that are energetically equal then the activity coefficient (β) constant can be related to the mean sorption free energy $(E) = (-2\beta)^{-1/2}$. The numerical value of sorption free energy (E) is given in Table 3. The high value (>8 kJ mol^{-1}) of sorption free energy indicates that the chemisorption phenomenon is predominant and reflects strong bonding that may be due to the effective role played by the PUF in the sorption process.

The sorption capacity (Q) derived form Langmuir isotherm corresponds to the monolayer coverage and is much lower than the sorption capacity (K_F) derived from the Freundlich isotherm that indicates the sub-monolayer surface coverage. The sorption capacity (K_F) is generally used in the description of the real system. The numerical value of maximum sorption capacity

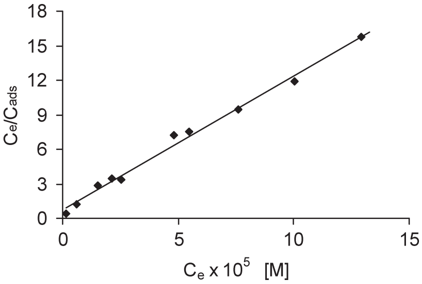


Figure 6. Langmuir adsorption isotherm of Th(IV) ions onto PAN loaded PUF at pH 6.5.

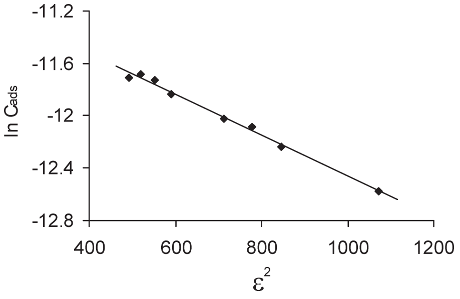


Figure 7. Dubinin-Radushkevich adsorption isotherm of Th(IV) ions onto PAN loaded PUF at pH 6.5.

$(6.09 \pm 0.55) \times 10^{-2}$ mmol g^{-1} is closed to the reported values of different sorbents used for the sorption of thorium (7, 9, 11).

Effect of Temperature on Sorption Equilibrium

The effect of temperature of the sorption of 2.7×10^{-5} M solution of Th(IV) ions under optimum conditions of pH, shaking time and weight of foam was studied. Different thermodynamic parameters were computed using Van't Haff equation in the form:

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

and

$$\Delta G = -RT \ln K_c$$

where ΔH, ΔS, ΔG, and T are the enthalpy, entropy, Gibbs free energy, and temperature in Kelvin, respectively. The values of equilibrium ratio (K_c), was calculated at each temperature using the relationship $K_c = F_e/(1 - F_e)$, where F_e is the fraction of Th(IV) ions adsorbed at equilibrium.

The plot of log K_c vs $1/T$ is a straight line as shown in Fig. 8 with correlation coefficient $r = 0.9917$. The numerical values of ΔH, ΔS are computed from the slope and intercept of the graph are given in Table 4. The negative value of Gibbs free energy as shown in Table 4 indicates the spontaneous nature of sorption from bulk or aqueous phase, while positive values of ΔH reflects the endothermic sorption behavior.

The large increase in entropy favors the stability of the sorbed complex via covalent interaction type chemisorption. The main source of this entropy gain may be due to the rupturing of the hydration zone formed around a central metal atom in mother liquid to a great extent and direct interaction of Th(IV)-PAN complex with sorbent that results in net positive entropy effect.

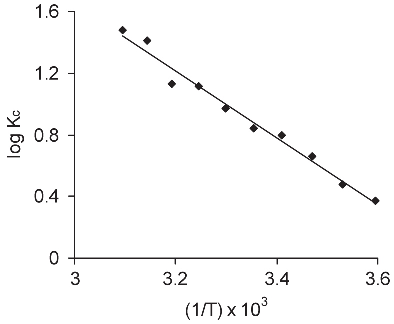


Figure 8. Variation of equilibrium ratio (K_c) with temperature for the adsorption of Th(IV) ions onto PAN loaded PUF at pH 6.5.

The numerical value of $-T\Delta S$ term is 46.6 ± 1.9 which is greater than ΔH (Table 4) also supports the entropy driven sorption due to decrease in the randomness of the system that results in the positive entropy change (23, 24a).

The adsorption free energy (ΔG_{ads}) related to the micropore filling of the sorbent as the pore width approaches adsorbate dimensions has been evaluated using the following relationship (25):

$$\Delta G_{ads} = -RT \ln(b\omega)$$

where ω is the molal concentration of solvent and b is the Langmuir constant. The large negative value of ΔG_{ads} indicates the strong affinity of Th(IV)-PAN sorption onto PUF is related to pore filling of the sorbent that is energetically

Table 4. Thermodynamic and stability constants of the sorption of Th(IV) ions onto PAN loaded PUF at pH 6.5

Constants	Values
Thermodynamic parameters	
ΔH (kJ mol^{-1})	42 ± 2
ΔS (J mol^{-1} K^{-1})	156 ± 6
$-T\Delta S$ (kJ mol^{-1})	46.6 ± 1.9
ΔG (kJ mol^{-1})	−5.1 ± 0.3
ΔG_{ads} (kJ mol^{-1})	−39.5 ± 0.6
ΔG_{eff} (kJ mol^{-1})	−34.4 ± 0.7
Scatchard plot constants	
log K_1	5.81 ± 0.02
n_1 (mol g^{-1})	(1.5 ± 0.1) × 10^{-3}
r	0.993
log K_2	5.04 ± 0.04
n_2 (mol g^{-1})	(2.1 ± 0.2) × 10^{-3}
r	0.982

homogenous and close to the size of Th(IV)-PAN complex. The numerical values of Gibbs free energy (ΔG) and adsorption free energy (ΔG_{ads}) are similar to the reported values in the literature (26). The difference between ΔG_{ads} and ΔG is called as effective Gibbs free energy (ΔG_{eff}) and is given in Table 4. The ΔG_{eff} is the surface phase (PUF) sorption related to the finite region of space within which the concentration of the adsorbate is uniform and different from that of bulk or aqueous phase.

Sorption Mechanism

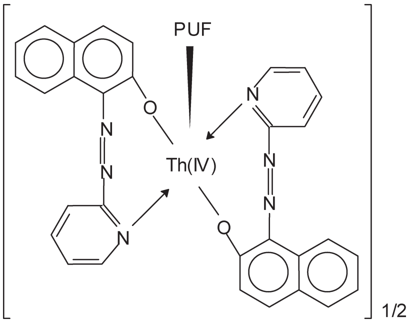
Thorium is a hard acid with a small ionic radius (0.095 nm). It has a strong tendency to coordinate electron donor (O, N donor) ligands and expand its coordination number upto 10 (1). It interacts with organic compounds and form chelate type complexes very readily analogous to solvent extraction process such as $Th(TTA)_4 \cdot 2S$ and $[Th(oxalate)_4 \cdot 2H_2O]^{-4}$, where HTTA is 2-thenoyltrifluroacetone and S is neutral donor ligand. PAN is a bidentate chelating reagent and interacts with many metal ions (5, 24b). Only in one report, the organometallic compound of thorium with PAN of the type $Th(PAN)_4 \cdot 2HPAN$ has been reported (27).

In the present system, Th(IV) ions interact with PAN from acetate medium and sorbed on PUF as reddish violet complex. The desorption data (Table 2) indicates that Th(IV) ions were strongly sorbed onto PAN loaded PUF and does not elute in any polar or non polar organic solvents. Similarly, the solvent extraction studies of the Th(IV) ions from 0.1 M sodium acetate (pH 7.4) aqueous solution in chloroform, benzene, chlorobenzene, and 1-butanol containing 0.05 M PAN gives the percentage extraction <5 indicates that $Th(PAN)_4$ complex is highly unstable and does not extract in any polar or non polar solvents. These observations reflect that PUF plays an active role in the adsorption process and Th(IV)-PAN complex is strongly bounded to the active sites of the PUF. The polyurethane foam has the strong tendency to act as a neutral donor ligand to satisfy the stable coordination number of the central metal atom. The basic unit of PUF consist of an amide group from isocyanate and an ether group from polyol. The nitrogen atom of the amide group and oxygen atom of the ether group are hard base donor atoms and have the strong tendency to donate the lone pair of electrons to the thorium ions and stabilize the Th-PAN complex by expanding the coordination number of Th(IV) ions from 8 to 10. The overall sorption mechanism of Th(IV) ions is as follow:

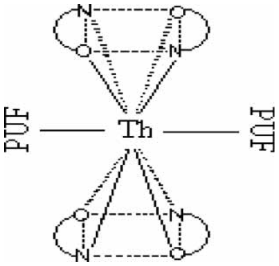
$$\mathrm{HPAN} + \overline{\mathrm{Site}_{(foam)}} \xrightleftharpoons{\text{acetone}} \overline{\mathrm{HPAN} \cdot \mathrm{Site}_{(foam)}}$$

$$\mathrm{Th}^{+4} + \overline{4\mathrm{HPAN} \cdot \mathrm{Site}_{(foam)}} \xrightleftharpoons{\substack{\text{aqueous}\\ \text{solution}}} \overline{\mathrm{Th(PAN)_4} \cdot \mathrm{Site}_{(foam)}} + 4\mathrm{H}^{+}$$

The four molecules of PAN neutralize the charge of the Th(IV) ions and two active sites of PUF can interact and make the sorbed complex coordinately saturated and stable. In previous studies (26), it was observed that in endothermic chemisorption of metal ions the expansion of the coordination number double to their charge is thermodynamically stable (usually occurred). Similarly, in this system the higher coordination number of ten makes the sorbed complex to be stable and more oriented with tricapped square antiprism geometry. The possible complex structure is as follows:



and the overall structure of tricapped square antiprism can be viewed as:



The thermodynamic values support the stability of the sorbed complexes of Th(IV) ions onto PAN loaded PUF. The positive value of ΔH indicates the endothermic chemisorption and expansion of the coordination number of the central metal ions by new bond formation with active sites of PUF. The high positive value of entropy reflects that the sorbed complex is more oriented as compared to the hydrated state of thorium ions in aqueous solution. The chelate effect of PAN also contributes to the stability of the sorbed complex by decreasing the randomness of the complex that results in a positive value of entropy change. Moreover, the formation of four chelate rings of PAN in Th-PAN-PUF complex not only enhanced the stability of the sorbed complex but also cancelled the unfavorable enthalpy change. The high value of sorption free energy (E) of D-R isotherm supports the strong bonding between the metal ions and active sites of the

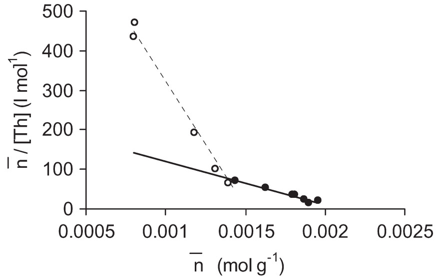


Figure 9. Scatchard plot of the Th(IV) binding on PAN loaded PUF at pH 6.5.

sorbent. The $-T\Delta H$ term is greater than ΔH term indicates that Gibbs free energy ($\Delta G = \Delta H - T\Delta S$) is negative and sorption is spontaneous in nature. The overall endothermic chemisorption mechanism is ligand addition and stability of the sorbed complex is entropy driven (23).

The stability of the sorbed complex entirely depends upon the nature and interaction of the active sites of PUF i.e., the nitrogen atom of the amide group and the oxygen atom of the ether group present in the basic units of PUF. In this regard, the Scatchard equation has been tested to evaluate the stability of the active sites (28). This equation is successfully used in biosciences to analyze the data of extraction and sorption of metal ions on organic sorbents that have two independent sorption sites. The stability constants of sorption can be obtained if the Scatchard equation is written in the form:

$$\frac{\bar{n}}{[\mathrm{Th}]} = K(n_1 - \bar{n})$$

where $\bar{n}$ = weight of Th(IV) bound to foam (g)/weight of foam (g); K = stability constant of the Th(IV) ions on PUF; n_1 = maximum concentration of Th(IV) ions sorbed by all sites on PAN loaded PUF; [Th] = equilibrium concentration of Th(IV) ions in solution (M).

The plot of $\bar{n}$/Th(IV) vs $\bar{n}$ is shown in Fig. 9. The resultant curve can be resolved into linear portions indicating the presence of two different sites of PUF. The stability constants log K_1 and log K_2 of the sorbed species derived from the respective slopes and the n_1 and n_2 parameter were given in Table 4. The high values of stability constants reflect that both bonding sites of PUF are highly active towards the sorption of Th(PAN)$_4$ complex on PUF. However, this equation involves only macroscopic parameters and does not give any special type of bonding or molecular configuration (29).

Application

Figure 1 clearly indicates that maximum sorption (>99%) of Th(IV) ions onto PAN loaded PUF in acetate medium starts from pH 6 and remains constant with increase in pH. Moreover, in previous studies (26, 30), it was observed that rare earths adsorbed onto PAN loaded PUF from borate medium at pH 7. The pH range 6 to 7 is quite stable and sorption of rare earths is negligible. This range is useful to separate the Th(IV) ions from its associated rare earths present in ores such as monazite. The sorption of Th(IV) ions in the presence of Eu(III) ions was carried out using a batch shaking technique from acetate medium at pH 6.5 onto PAN loaded PUF. The foam plugs were separated, washed, and desorbed/eluted in 1 M HCl aqueous solution and assayed spectrophotometrically using the Arsenazo III method as chromogenic reagent. The results are shown in Table 5. The table indicates the clear separation of Th(IV) ions from Eu(III) ions while sorption and desorption of Th(IV) ions are quantitative. The high value of Th(IV) ions is due to the slight interference of Eu(III)-Arsenazo-III complex.

Similarly, the separation of Th(IV) ions from a mixture of rare earths was also carried out by column chromatography. The 25 ml of pH 6.5 buffer solution containing Th(IV) and rare earths ions are passed through a PAN loaded PUF column (100 mm h × 10 mm ϕ) at flow rate 1 ml/min. The thorium loaded column was washed with 10 ml of pH 6.5 buffer solution. The sorbed Th(IV) ions on column was eluted with 25 ml of 1 M HCl at flow rate 1 ml/min. Both effluent and eluant were assayed on ICP-OES. The results are summarized in the first step (column 1) of Table 5. This indicates that 20% of Th(IV) ions were left in the effluent. The method was repeated and the effluent and washing of the first column was passed through the second column of PAN loaded PUF. The second column was washed with 10 ml of pH 6.5 buffer solution. The effluent and washing were combined for thorium determination. The sorbed concentration of Th(IV) ions were eluted with 10 ml of 1 M HCl aqueous solution and combined the eluent of both columns. The concentration of Th(IV) ions in effluent and eluent were determined on ICP-OES. The results are given in Table 5. The results indicate the complete separation of Th(IV) ions from rare earths mixture which was easily achieved after passing the effluent from two PAN loaded PUF columns.

The separation of Th(IV) ions from rare earths using the squeezing method was also carried out. The 50 ml buffer solution of pH 6.5 containing Th(IV) ions and rare earths mixture was taken in 250 ml beaker. The PAN loaded PUF disc (10 mm h × 25 mm ϕ) was added in the solution and squeezed with a glass plunger for 30 minutes. The PUF disc was removed, washed, and squeezed (desorption) in 50 ml of 1 M HCL solution for 15 minutes. The effluent and eluent were assayed on ICP-OES for Th(IV) ions. The results are shown in Table 5, indicating that Th(IV) ions are quantitatively separated from rare earths mixture. Moreover, the squeezing method of the sorption of Th(IV) ions onto PAN loaded PUF is the most effective and easy procedure for the separation of Th(IV) ions from rare earths.

Table 5. Analysis of Th(IV) in synthetic mixture of rare earths

		First step		Second step		
Sr. no	Mixture composition (μg ml^{-1} added)	Th in effluent (μg ml^{-1})	Th in eluent (1 M HCl) (μg ml^{-1})	Th in effluent (μg ml^{-1})	Th in eluent (1 M HCl) (μg ml^{-1})	Total thorium recovery (μg ml^{-1}) (%)
1.	Batch shaking Eu(6), Th(6)	ND	6.2 ± 0.5	—	—	6.2 ± 0.5 (101%)
2.	Column chromatography Ce(20), Nd(20), Eu(20), Dy(20), Er(22), Lu(24), Tb(10), Tm(15), Th(12)	3.4 ± 0.3	9.2 ± 0.2	ND	11.8 ± 0.2	11.8 ± 0.2 (98%)
3.	Squeezing method Ce(20), Nd(20), Eu(20), Dy(20), Er(22), Lu(24), Tb(10), Tm(15), Th(12)	ND (After 30 min squeezing)	11.9 ± 0.2	—	—	11.9 ± 0.2 (99%)

ND = Not detected.

CONCLUSION

PUF is prone to be an excellent amorphous material for the separation and preconcentration of trace metal ions at low level. The presence of neutral donor ligands in the basic structure of PUF fiber allows the metal ions separation which is not possible in any other system. The PAN loaded PUF sorbed the Th(IV) ions quantitatively from acetate medium. The sorbent appears promising for a number of industrial applications and as well as separation of thorium from its associated rare earths in a single stage operation from a solution of pH 6.5. An accurate control of pH of the solution is important. The purity of thorium can be obtained by eluting the sorbed Th(IV)-PAN complex with mineral acids.

Kinetic data reflects the film diffusion process involved in adsorption. The equilibrium adsorption process follows the classical adsorption isotherms i.e., Freundlich, Langmuir, and D-R isotherms. The maximum sorption capacities constants of Freundlich and D-R isotherms are very close to the sorption capacity constant of the Langmuir isotherm which is related to the mono layer coverage of the sorbent. The value of sorption free energy (E) gives an idea of chemisorption involving strong bonding. The binding energy constant “b” is related to the adsorption free energy (ΔG_{ads}). The high negative value forecast the strong interaction of the Th(IV)-PAN complex with sorbent.

The thermodynamic parameters confirm the entropy driven endothermic nature of chemisorption. The high value of entropy is due to the chelate effect of Th(IV)-PAN complex which counteracts the enthalpy effect. The negative value of Gibbs free energy (ΔG) indicates the spontaneous nature of sorption. The sorption mechanism is ligand addition and direct interaction of the active sites of PUF with the expansion of the coordination number of central metal atoms has been postulated on the basis of experimental data and theoretical model.

ACKNOWLEDGMENT

The author thanks the Central Analytical Facility Division for their help in ICP-OES measurements. Special thanks are due to Mr. Munawar Hussain Chaudary for his valuable suggestions and help.

REFERENCES

1. Katzin, L.I. (1981) Thorium and thorium compounds. In *Kirk-Othmer Encyclopedia for Chemical Technology*, 3rd edn.; Grayson, M. (ed.); Wiley: New York, Vol. 22, pp. 989–1002.
2. Korkisch, J. and Arrheius, G. (1964) Separation of uranium, thorium and the rare earth elements by anion exchange. *Anal. Chem.*, 36: 850–854.

3. Aly, H.M. and Kamar, E.M. (2003) Kinetic studies of some actinide ions exchange on AI-13-phosphatoantimonic acid. *Solvent Extr. Ion Exch.*, 21: 613–620.
4. Meera, R. and Reddy, M.L. P. (2004) Para substituted 1-phenyl-3-methyl-4-aroyl-5-pyrazolones as chelating agents for the synergistic extraction of Thorium(IV) and Uranium(VI) in the presence of various crown ethers. *Solvent Extr. Ion Exch.*, 22: 761–789.
5. Sekine, T. and Hasegawa, Y. (1977) *Solvent Extraction Chemistry, Chapter 7*; Marcel Dekker Inc.: New York, pp. 535–539.
6. Lieser, K.H. and Medert, K. (1995) Coprecipitation of Th with $SrSO_4$ and uptake of Th by $SrSO_4$. *Radiochim. Acta*, 68: 191–195.
7. Büyüktiryaki, S., Say, R., Ersöz, A., Birlik, E., and Denizli, A. (2005) Selective preconcentration of thorium in the presence of UO^{+2}, Ce^{+3} and La^{3+} using Th(IV)-imprinted polymer. *Talanta*, 67: 640–645.
8. Weijuan, L. and Zuyi, T. (2002) Comparative study on Th(IV) sorption on alumina and silica from aqueous solution. *J. Radioanal. Nucl. Chem.*, 254: 187–192.
9. Raju, C.S. K. and Subramanian, M.S. (2005) DAPPA grafted polymer: an efficient solid phase extractant for U(VI), Th(IV) and La(III) from acidic waste streams and environmental samples. *Talanta*, 67: 81–89.
10. Maheswari, M.A. and Subramanian, M.S. (2004) Selective enrichment of U(VI), Th(IV) and LA(III) from high acidic streams using a new chelating ion-exchange polymeric matrix. *Talanta*, 64: 202–209.
11. Erdogan, S., Merdivan, M., Hamamci, C., Akba, O., and Baysal, A. (2004) Polymeric supported humic acid for separation and preconcentration of thorium(IV). *Anal. Letts.*, 37: 2565–2575.
12. El-Shahawi, M.S., Othman, M.A., Nassef, H.M., and Abdel-Fadeel, M.A. (2005) An investigation into the retention profile and kinetics of sorption of the ternary complex ions association of uranyl ions with crown ether and picric acid by the polyurethane foams. *Anal. Chim. Acta*, 536: 227–235.
13. Katragadda, S., Gesser, H.D., and Chow, A. (1997) Extraction of uranium from aqueous solution by phosphonic acid–imbedded polyurethane foam. *Talanta*, 44: 1865–1871.
14. Palágyi, S. and Braun, T. (1992) Separation and preconcentration of trace elements and inorganic species on solid polyurethane foam sorbent. In *Preconcentration Techniques for Trace Elements*; Alfassi, Z.B. and Wai, C.M. (eds.); CRC Press: Boca Raton, pp. 363–400.
15. Xie, C. (1982) Enrichment with impregnated polyurethane foam and spectrophotometric determination of trace thorium in natural water. *Huaxue Xuebao*, 40: 605–610.
16. Xie, C. and Huang, L. (1986) Reversed phase foam chromatography separation and spectrophotometric determination of trace uranium and thorium. *Yankuang Ceshi*, 5: 31–35.
17. Yu, Y. and Tang, J. (1983) Study on extraction of thorium with PMBP-loaded polyurethane. *He Huaxue Yu Fangshe Huaxue*, 5: 314–318.
18. Grudpan, K. and Moebius, S. (1985) Thorium-233 and thorium-234 production and use as thorium tracers. *Chem.–Ztg.*, 109: 109–111.
19. Anderson, R.G. and Nickless, G. (1967) Heterocyclic azo dyestuffs in analytical chemistry. *Analyst*, 92: 207–238.
20. Savvin, S.B. (1961) Analytical use of Arsenazo III; determination of thorium, zirconium, uranium and rare earths elements. *Talanta*, 8: 673–685.

21. Saeed, M.M. and Ahmed, M. (2004) Retention, kinetics and thermodynamics profile of cadmium adsorption from iodide medium onto polyurethane foam and its separation from bulk zinc. *Anal. Chim. Acta*, 525: 289–297.
22. Cerofolini, G.F. and Re, N. (1993) The mathematical theory of adsorption on non-ideal surfaces. *Rivista Del Nuovo Cimento*, 16 (7): 1–64.
23. Choppin, G.R. and Morgenstern, A. (2000) Thermodynamics of solvent extraction. *Solvent Extr. Ion Exch.*, 18: 1029–1049.
24. Cotton, F.A., Wilkinson, G., Murillo, C.A., and Bochmann, M. (1999) *Advance Inorganic Chemistry*, 6th edn.; John Wiley & Sons, Inc., (a) pp. 27–29, (b) pp. 1143–1144.
25. Gimeno, O., Plucinski, P.T., Kolaczkowski, S., Rivas, F.J., and Alvarez, P.M. (2003) Removal of the herbicide MCPA by commercial activated carbons: equilibrium, kinetics, and reversibility. *Ind. Eng. Chem. Res.*, 42: 1076–1086.
26. Saeed, M.M. and Ahmed, M. (2006) Effect of temperature on kinetics and adsorption profile of endothermic chemisorption process: -Tm(III)-PAN loaded PUF system. *Sep. Sci. Technol.*, 41: 705–722.
27. Mohanta, H. and Sahoo, K. (1994) Multidentate azo dye complexeses of dioxouranium(VI), thorium(IV) and cerium(III). *Asian J. Chem.*, 6: 454–459.
28. Saeed, M.M., Ahmed, M., and Ghaffar, A. (2003) Adsorption behavior of Hg(II) from acetate medium onto PAR-imbedded polyurethane foam. *Ads. Sci. Technol.*, 21: 67–80.
29. Sposito, G. (1981) Trace metals in contaminated waters. *Environ. Sci. Technol.*, 15: 396–403.
30. Saeed, M.M. and Ahmed, R. (2006) Temperature effected sorption of europium(III) onto 1-(2-pyridylazo)-2-naphthol impregnated polyurethane foam. *J. Radioanal. Nucl. Chem.*, 267: 147–153.