

EFFECT OF TEMPERATURE ON KINETICS AND SORPTION BEHAVIOUR OF TERBIUM (III) IONS ONTO 1-(2-PYRIDYLAZO)-2-NAPHTHOL LOADED POLYURETHANE FOAM

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The sorption behaviour of 9.8×10^{-6} mol l⁻¹ solution of Tb(III) metal ions onto 7.25 g l⁻¹ of 1-(2-pyridylazo)-2-naphthol (PAN) loaded polyurethane foam (PUF) at different temperatures has been investigated. The maximum equilibration time of sorption was found to be 30 minutes from pH 7.5 buffer solution at all temperatures. Different kinetic parameters of adsorption process have been determined. The diffusional activation energy (ΔE_{ads}) and activation entropy (ΔS^{\ddagger}) of the sorption of Tb(III) ions were found to be 32.2 ± 4.2 kJ mol⁻¹ and 86.2 ± 10.3 J mol⁻¹ K⁻¹, respectively. The thermodynamic parameters such as enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG) were calculated and interpreted. The positive values of ΔH and ΔS indicate that sorption is endothermic and entropy driven. The adsorption isotherms such as Freundlich, Langmuir and Dubinin – Radushkevich were tested experimentally at different temperatures. The changes in adsorption isotherms constants at different temperatures have been discussed. The differential enthalpy of adsorption (ΔH_{diff}), entropy of adsorption (ΔS_{diff}) and free energy of adsorption (ΔG_{diff}) were determined and found to be 54 ± 3 kJ mol⁻¹, 303 ± 4 J mol⁻¹ K⁻¹ and -40.9 ± 1.7 kJ mol⁻¹, respectively. The stability of sorbed complex and possible mechanism involved in adsorption process has been discussed using different thermodynamic parameters and adsorption isotherms.

Keywords : Temperature, Kinetics, Adsorption, Terbium (III), 1-(2-pyridylazo)-2-naphthol, Polyurethane foam

1. Introduction

In last two decades, the research has been focused on using low cost effective sorbent for metal ions adsorption and sorption behaviour of several natural and waste materials has been investigated. Some of the low cost materials include polyurethane foam, carbon, peat, clay zeolite, dead biomass, agriculture waste, fly ash, etc. [1-3]. Among these, polyurethane foam (PUF) represents a cheap and effective media for the separation and preconcentration of heavy and toxic metal ions reflects its potential in chemical analysis by improving the detection limit, increasing the sensitivity by several orders of magnitude and enhancing the accuracy of the results. A number of reviews have been published [4,5].

The unique adsorption properties of PUF result from its high surface area, fast flow rate, micro and macropore structure. Broad range of surface functional groups present in the basic unit of PUF that can coordinate bonds with many metal ions as in synergic solvent extraction system. The sorption

properties of PUF can be changed with respect to their chemical, physical and application point of view towards transition and heavy metal ions by impregnated foreign chelating reagents, which may be suitable for one system but not for others [6-11]. The formation of micropore and macropore holes in three dimensional structure of PUF enables us to study the different kinetics and equilibrium sorption behaviour of trace metal ions.

In previous study, it was observed that sorption of metal ions onto PUF is entropy driven endothermic chemisorption [6, 8,11]. In this study, the sorption behaviour of Tb(III) metal ions onto PAN loaded PUF has been carried out at different temperatures. Tb(III) metal ions has been selected because rare earths usually formed higher coordination number complexes than double to their charge. The in depth study of thermodynamic, kinetic and adsorption isotherms have been investigated. The relationship between different parameters / constants with temperatures have been tested and discussed.

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2. Experimental

2.1. Reagents

All the reagents used were of the Analar grade. PAN from Fluka was used as such. Buffer solutions of pH 1-10 having ionic strength of 0.1M were prepared by mixing an appropriate volume of 0.2 M solutions of HCl and KCl, CH₃COOH and CH₃COONa and H₃BO₃ and NaOH for buffers solutions of pH 1-2, 3-6 and 7-10 respectively. The stability of buffer solutions was checked on Metrohm 632 pH meter periodically.

2.2. Radiotracer

The radiotracer of ¹⁶⁰Tb used was prepared by irradiating 15 mg specpure terbium oxide (Tb₂O₃) in a 10 MW research reactor (PARR-1), PINSTECH for three hours at a neutron flux $7 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$. The irradiated metal oxide was dissolved in concentrated nitric acid, heated to dryness and diluted upto 25 ml with deionized water. The radionuclide purity of the tracer was checked on a 4K series of 85 Canberra multichannel analyzer coupled with a 25 cm³ Ge (Li) detector.

2.3. Polyurethane foam preparation

The cylindrical foam plugs were prepared and washed as described elsewhere [8]. The washed foam plugs were soaked in 0.1% PAN solution in acetone for 30 minutes. The excess amount of acetone was drained out and the PUF plugs were pressed between filter paper to remove the excess acetone solution. After that, the PAN loaded plugs were dried in an oven at 50 °C and were kept in airtight plastic bottle for further studies. The loaded concentration of PAN on PUF was dissolved in acetone and was found to be 5.38 mmol g⁻¹ against standard calibration curve of PAN in acetone. The absorbance was measured by Hitachi 220S spectrophotometer at λ_{max} 462 nm against acetone.

2.4. Procedure

Five ml buffer solution of known pH was taken in 25 x 150 mm Pyrex glass culture tube with a polyethylene cap. A known concentration of radio tracer of ¹⁶⁰Tb(III) ions was added and mixed thoroughly. An aliquot of one ml was drawn to measure the initial activity for gross gamma counts (A₀). The remaining solution was shaken with PAN loaded PUF (~29 mg) for 30 minutes on a Stuart

Scientific wrist-action shaker coupled with Gallenkamp thermostirrer-100 model BKL 234, water bath at constant temperature. The culture tube was so adjusted in water bath that about 70% of the total length of the culture tube remained immersed in the water bath for the optimum control of temperature. After shaking, one ml (A_e) of aliquot was again withdrawn for assayed radiometrically on a Tennelec gross gamma counter equipped with a 30 cm³ well type Na(Tl) crystal.

The adsorbed concentration of Tb(III) at equilibrium was calculated by the difference in the amount of terbium in aliquot drawn before (A₀) and after shaking (A_e). The net gamma activity of the $9.8 \times 10^{-6} \text{ mol l}^{-1}$ solution of Tb(III) ions was in the range of 55,000 – 60,000 cpm ml⁻¹. The percentage sorption and distribution coefficient (K_d) were calculated as:

$$\% \text{Adsorption} = \frac{A_0 - A_e}{A_0} \times 100 \quad (1)$$

$$K_d = \frac{\text{amount of metal in PUF}}{\text{amount of metal in solution}} \times \frac{\text{volume of solution (V)}}{\text{weight of dry PUF (W)}} \quad (2)$$

$$= (\text{mL g}^{-1})$$

The % sorption and the distribution coefficient can be correlated as

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

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 $\pm 2.5 \%$. The linear regression and slope analyses for the statistical data were carried out.

3. Results and Discussion

3.1. Effect of pH

The sorption of $9.8 \times 10^{-6} \text{ mol l}^{-1}$ solution of Tb(III) ions onto 7.25 g l⁻¹ of PAN loaded PUF with 30 minutes equilibration time was investigated at ambient temperature from aqueous solution of pH range 1 – 10. The results are shown in Fig. 1. This figure indicates that sorption is negligible upto pH 6.5 and after that the sorption increases and attains the maximum value at pH 7.5 and again

decreases at pH 8 and again slightly increases with pH 10. However, with unloaded PUF, there was a slight increase (pH >8) in the sorption of Tb(III) ions due to the hydrolysis metal ions which is predominant in basic medium. A similar trend in the distribution coefficient (K_d) is also observed with pH.

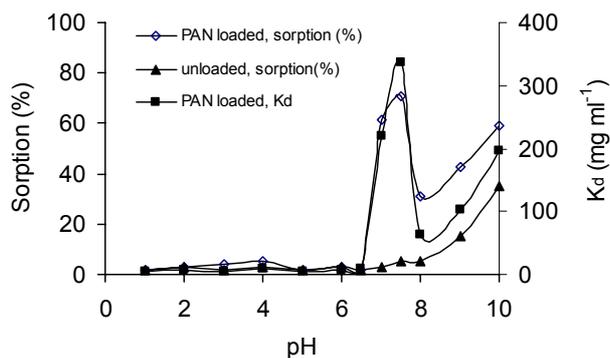


Figure 1 Effect of pH on the sorption of Tb(III) ions onto PAN loaded PUF.

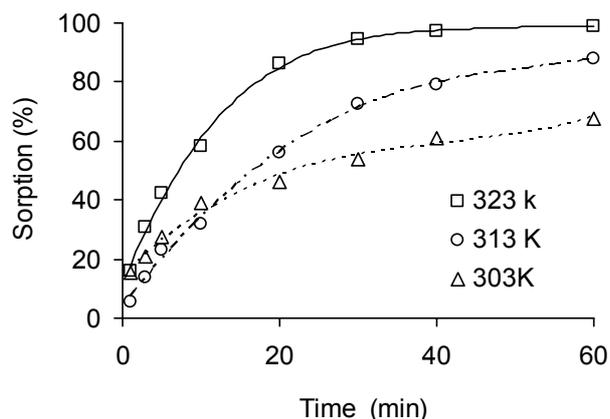


Figure 2. Effect of shaking time of the sorption of Tb(III) ions onto PAN loaded PUF at different temperatures.

The sorption of Tb(III) ions from neutral medium is due to the complexation of PAN and PUF with Tb(III) ions. PAN exists as neutral species in the pH range 3-10, which is insoluble in aqueous solution and responsible for complex formation with metal ions [12]. The neutral form of HPAN (HL) has strong ability to dissociate the hydrogen atom of the hydroxyl group of naphthol as:



where L^- species form complexes with Tb(III) ions. The concentration of anionic (L^-) species of PAN increases with pH and sufficient concentration of

anionic species are produced at pH 7.5 that interact with Tb(III) ions to neutralized its charge and simultaneously sorbed onto PUF to satisfy the stable coordination number (i.e. eight for rare earths), and subsequently increases the sorption of Tb(III) onto PAN loaded PUF in neutral aqueous medium as shown in Fig. 1.

3.2. Kinetic studies

The effect of agitation time on the sorption of $9.8 \times 10^{-6} \text{ mol l}^{-1}$ solution of Tb(III) ions onto PAN loaded PUF from borate buffer solution of pH 7.5 at different temperatures was investigated from 1–60 minutes shaking time as shown in Fig. 2. It is clear from the figure that sorption increases with temperature and shaking time, and attains the maximum equilibrium upto 30 minute shaking time and then remains constant.

The kinetic data treat the PUF sorbent as a porous medium and sorption depends upon the rate of diffusion of the adsorbate on the adsorbent. The arbitrary defined macropore and micropore structure of PUF, the rate of diffusion process depends on two transport processes act in parallel i.e. film diffusion and intra particle diffusion, respectively.

In order to distinguish the film diffusion or intra particle diffusion process, the Weber – Morris [13] equation was tested in the form:

$$q_t = k\sqrt{t} \tag{4}$$

where q_t is the amount of Tb(III) sorbed at time t , k is the adsorption rate. The plot of q_t vs $t^{1/2}$ is a straight line at all temperatures as shown in Fig. 3,

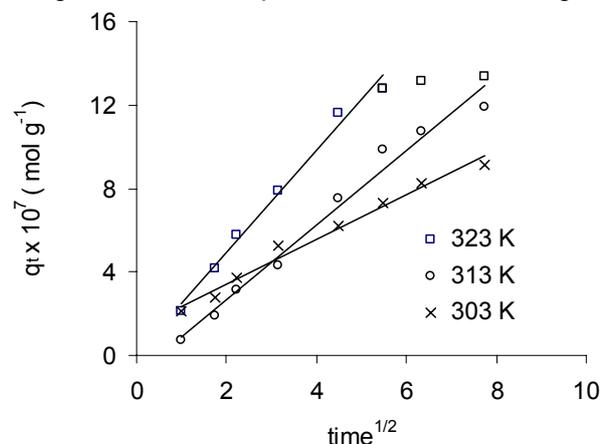


Figure 3. Weber-Morris plot of Tb(III) ions onto PAN loaded PUF at different temperatures.

Table 1. Different kinetic parameters of the sorption of Tb(III) ions onto PAN loaded PUF at pH 7.5.

Temperature (K)	$k \times 10^7$ (mol g ⁻¹ min ^{-1/2})	k_1 (min ⁻¹)	ΔE_{ads} (kJ mol ⁻¹)	ΔS^\ddagger (J mol ⁻¹ K ⁻¹)
303	(1.07 ± 0.06)	0.102 ± 0.003		86.4 ± 10.4
313	(1.79 ± 0.11)	0.057 ± 0.002	33.2 ± 4.2	86.2 ± 10.3
323	(2.44 ± 0.14)	0.045 ± 0.003		86.0 ± 10.3

indicating intra particle diffusion process is predominant. The numerical values of k at different temperatures are given in Table 1.

The intraparticle diffusion transport phenomenon was further verified using Reichenberg equation in the form as [14]:

$$Bt = -0.4977 - \ln(1 - F) \quad (5)$$

Where numerical value of Bt is the mathematical function (F) of q_t/q_e , can be calculated for each value F employing in above equation. The obtained values of Bt corresponding to each value of F was also verified from the Reichenberg table [14]. The plots of Bt vs time are straight lines passing through the origin for all temperatures as shown in Fig. 4. The straight lines indicate that the intraparticle diffusion process is predominant and controls the kinetics of the sorption of the Tb(III) ions onto PAN imbedded PUF.

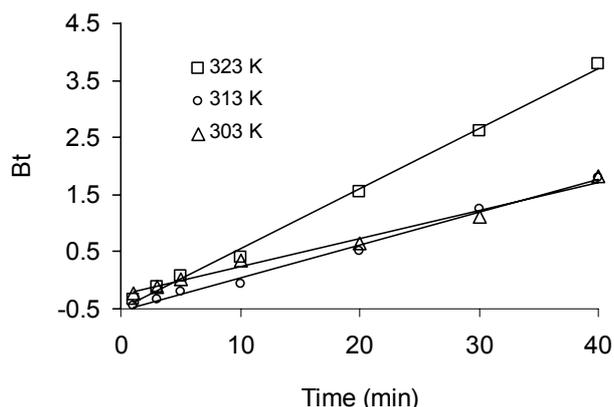


Figure 4. Reichenberg plot of Tb(III) ions onto PAN loaded PUF at different temperatures.

The overall rate of sorption of solute into the pores of solid surface regardless of the mechanism used depends on the mass action process. There is correlation between q , the

number of Tb(III) ions adsorbed per unit area at a given pressure and temperature, and time required to complete the adsorption process as shown by Lagergren [15] in the form :

$$q_t = q_\infty (1 - e^{-k_1 t}) \quad (6)$$

or

$$\ln(1 - F) = -k_1 t \quad (7)$$

where $F = q_t/q_\infty$, k_1 is the rate constant of sorption process. The plot of $\ln(1 - F)$ vs t is given in Fig. 5, indicating that the sorption is of first order reaction with respect to adsorbed concentration. The rate constants obtained at different temperatures are recorded in Table 1. This table indicates that sorption rate constants increased with temperature, may be due to the acceleration of some slow steps or due to the creation of some new energetically active sites on PUF.

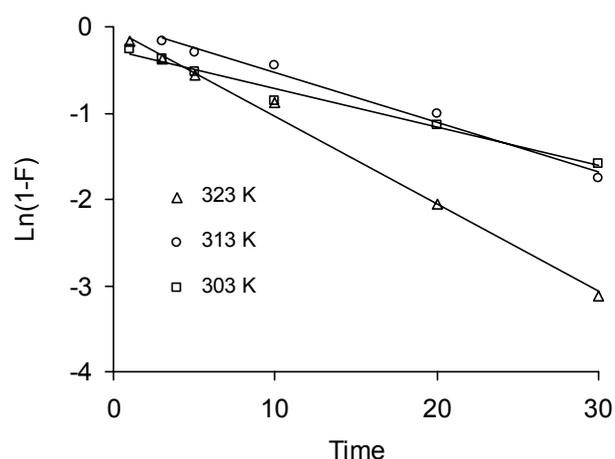


Figure 5. Plot of $\ln(1-F)$ vs time of Tb(III) ions onto PAN loaded PUF at different temperatures.

The relationship between rate constants (k_1) with temperature enables us to calculate the

activation energy of adsorption (ΔE_{ads}). In this regard, Arrhenius equation was used in the form :

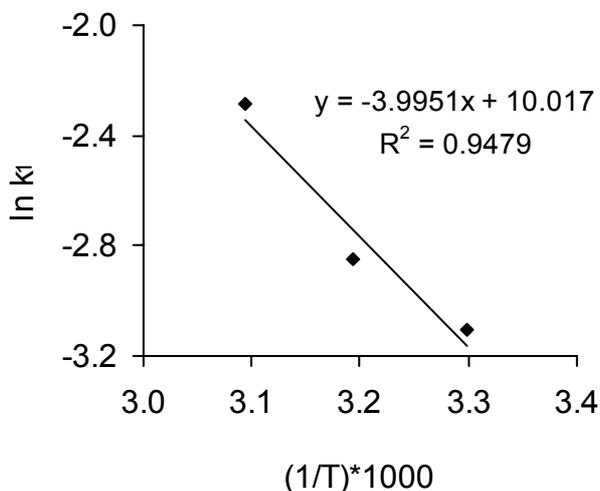


Figure 6. Arrhenius plot for the determination of activation energy of Tb(III) ions sorption onto PAN loaded PUF.

$$\ln k_1 = \ln D_0 - \left(\frac{\Delta E_{ads}}{RT} \right) \quad (8)$$

The plot of $\ln k_1$ vs $1/T$ is a straight line as shown in Fig. 6. The numerical value of ΔE_{ads} from slope of the graph was calculated and found to be $33.2 \pm 4.2 \text{ kJ mol}^{-1}$ and is given in Table 1. Moreover, the intercept of the graph gives the pre exponent constant D_0 of first order rate constant of sorption process and this can be related to the entropy of activation (ΔS^*) of sorption and was determined by applying the equation proposed by Barrer et al. [16].

$$D_0 = 2.72 \left(\frac{kT d^2}{h} \right) \exp \left(\frac{\Delta S^*}{R} \right) \quad (9)$$

where K is the Boltzman constant, T is the absolute temperature, h is the Plank's constant, R is the gas constant and d is the average distance between the successive positions on the process of diffusion, which is equivalent to the 20 \AA for micropore structure of semi solids [17].

The activation energy of adsorption is in the range $20\text{-}50 \text{ kJ mol}^{-1}$ corresponds to the diffusion process [18]. Table 1 clearly indicates that the activation energy is in the range of particle diffusion as predicted from Figs. 3 and 4. Moreover, the intraparticle diffusion process

follows the first order rate of sorption to controls the sorption process. The low activation energy is mainly result of the favourable thermodynamics and vice versa. The high numerical value of activation entropy of adsorption (ΔS_a) in Table 1 indicates that the mobility of Tb(III) ions in micropore region is controlled by the strong complexation reaction between metal ions and active sites of PAN loaded PUF [19].

3.3. Thermodynamic studies

The thermodynamic parameters of $9.8 \times 10^{-6} \text{ mol l}^{-1}$ solution of Tb(III) ions uptakes onto PAN loaded PUF have been evaluated using the following equation:

$$\ln K_c = \frac{-\Delta H}{R} + \frac{\Delta S}{RT} \quad (10)$$

where ΔH , ΔS , T are the enthalpy, entropy and temperature in Kelvin, respectively, R is gas constant ($8.3143 \text{ J mol}^{-1} \text{ K}^{-1}$) and K_c is the equilibrium constant depends on the fractional attainment (F_e) of metal ions at equilibrium as $K_c = F_e/(1-F_e)$.

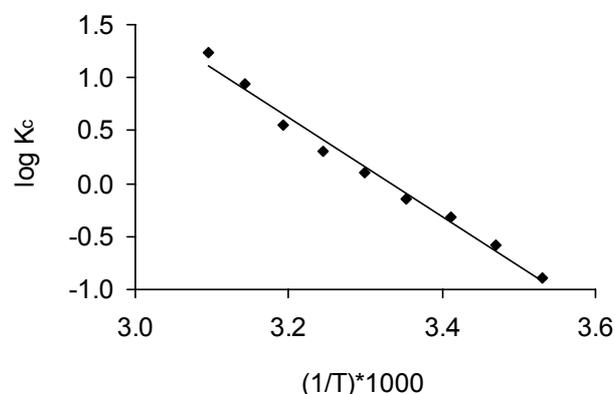


Fig. 7. Van't Hoff plot of equilibrium constant (K_c) for the determination of thermodynamic parameters of Tb(III) ions sorption onto PAN loaded PUF.

The plot of $\ln K_c$ vs $1/T$ is linear over the entire range of temperature ($298 - 343 \text{ K}$). The numerical values of ΔH and ΔS were calculated from the slope and intercept of Fig. 7, respectively. The Gibb's free energy (ΔG) is determined from the following relationship:

$$\Delta G = \Delta H - T\Delta S \quad (11)$$

The numerical value of ΔH and ΔS and ΔG are summarized in Table 2. The positive value of ΔH

Table 2. Thermodynamic parameters of Tb(III) metal ions at pH 7.5 onto PAN loaded PUF.

Temperature (K)	Distribution ratio (K_c)	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS ($\text{J mol}^{-1} \text{K}^{-1}$)	$-\Delta S$ (kJ mol^{-1})
283	0.129	4.8 ± 0.3			83.2 ± 3.7
288	0.267	3.2 ± 0.2			85.3 ± 3.7
293	0.476	1.8 ± 0.1			86.8 ± 3.8
298	0.725	0.80 ± 0.05	89 ± 4	296 ± 13	88.2 ± 3.9
303	1.288	-0.64 ± 0.04			89.7 ± 3.9
308	1.996	-1.8 ± 0.1			91.2 ± 4.0
313	3.599	-3.3 ± 0.2			92.7 ± 4.1
318	8.621	-5.7 ± 0.4			94.2 ± 4.1
323	17.344	-7.7 ± 0.5			95.7 ± 4.2

and ΔS indicate that sorption of Tb(III) ions on PAN loaded PUF is endothermic and stability of sorption is entropy driven. The high values of enthalpy and entropy envisage the chemisorption by involving the rupture of hydration shell (enthalpy effect) formed around central metal atom in mother liquid and creation of new bond formation (entropy effect) with active sites of sorbent surface as well as chelate effect of PAN complexing with central metal atom [20]. The change in the ΔG values from positive to negative with temperature as shown in table 2 indicates that at low temperature ($<298 \text{ K}$), the sorption is non spontaneous but at higher temperature ($>303 \text{ K}$), it becomes spontaneous. However, the $T\Delta S$ term in the entire range of temperature is negative and much higher than ΔG term and makes the ΔH term positive for endothermic chemisorption. Moreover, the stability of the sorbed complex corresponds to the net gain in the degree of freedom of the sorbed species [21].

3.4. Effect of metal ion concentration

The effect of Tb(III) ions concentration sorption was examined from $9.8 \times 10^{-6} \text{ mol l}^{-1}$ to $3.24 \times 10^{-4} \text{ mol l}^{-1}$ solutions. The variation of sorption (%) with initial metal ion concentration using 30 minutes shaking time and 7.25 g l^{-1} of PAN loaded PUF at different temperatures is shown in Fig. 8. The

decrease in the sorption with increase in initial Tb(III) ion concentration is due to the saturation of the active sites of PAN loaded PUF for bonding.

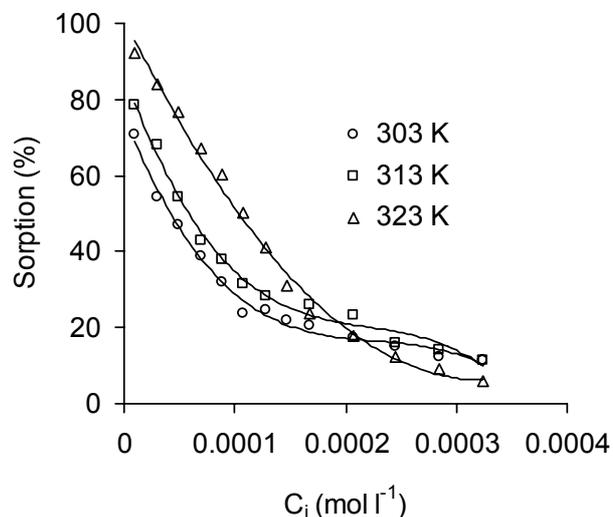


Figure 8. Loading profile of Tb(III) ions onto PAN loaded PUF at different temperatures.

The variations of sorption data with metal ion concentration at different temperatures are subjected to different adsorption isotherms namely Freundlich, Dubinin-Radushkevich (D-R) and Langmuir isotherms [22-24]. All these isotherms obey the data very well for all three temperatures.

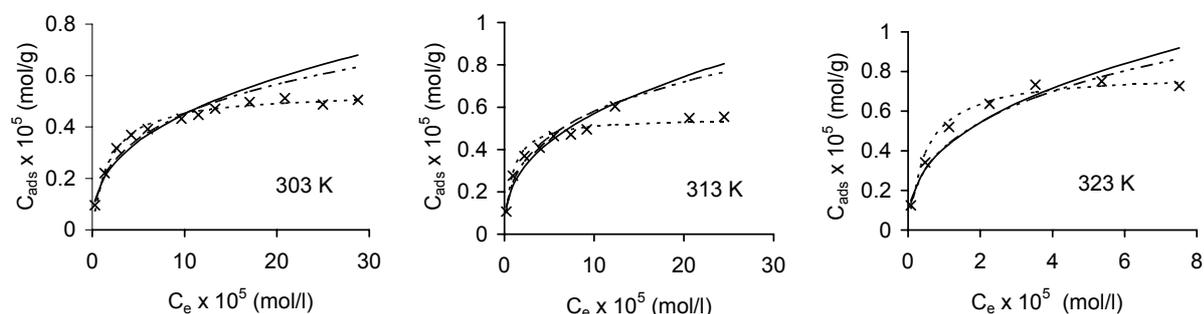


Figure 9. Adsorption isotherm of Tb(III) ions onto PAN loaded PUF at different temperatures. Symbols: x Experimental data, lines model fitting (solid, Langmuir; dotted, D-R; dashed, Freundlich).

The Freundlich isotherm usually fits the experimental data in low concentration range. In view of its empirical formulation it is frequently employed in connection with adsorption from solution. While the D-R isotherm based on the Polanyi potential theory of adsorption is successfully described the adsorption isotherm of micropore adsorbent and the Langmuir isotherm based on 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 migrate across the surface of the adsorbent. These isotherms are expressed as:

Freundlich isotherm

$$C_{\text{ads}} = K_F C_e^{1/n} \quad (12)$$

D-R isotherm

$$C_{\text{ads}} = X_m \exp(-\beta \epsilon^2) \quad (13)$$

Langmuir isotherm

$$C_{\text{ads}} = \frac{QbC_e}{1+bC_e} \quad (14)$$

where C_{ads} is concentration of Tb(III) ions in solid phase in mol g^{-1} and C_e is the concentration of Tb(III) ions in aqueous solution in mol l^{-1} at equilibrium. The Freundlich isotherm constants K_F and $1/n$ give a measure of the sorption capacity and adsorption intensity of the adsorbent respectively. The D-R isotherm constant X_m is the maximum adsorption of D-R monolayer coverage, β is the activity coefficient and related to the sorption free energy (E) = $(-2\beta)^{-1/2}$, Polanyi

potential (ϵ) = $-RT \ln(1+(1/C_e))$ and R is gas constant ($8.3143 \text{ J mol}^{-1} \text{ K}^{-1}$). While Q and b are the Langmuir constants related to the sorption capacity (monolayer coverage) and sorption energy, respectively. The linearization form of above mentioned isotherms facilitate to determine the numerical values of their isotherms constants that are summarized in Table 3.

The plot of C_{ads} vs C_e at different temperatures is shown in Fig. 9. This figure indicates that the data point of the sorption of Tb(III) ions onto PAN loaded PUF is strictly follows the adsorption isotherms models at all temperatures. The sorption of metal ions follows the Freundlich and D-R models more accurately at low metal ions concentration while Langmuir model is reasonably satisfy the whole range of metal ions concentration under investigation.

Table 3 clearly indicates that the sorption affinity ($1/n$) constant of Freundlich isotherm is <1 and almost remain constant at all temperatures, encompassing the exponential distribution of active sites in their energy. The sorption capacities C_m , X_m , and Q of Freundlich, D-R and Langmuir isotherms respectively, are increased with temperatures. The Freundlich isotherm does not predict the saturation of the sorbent surface, thus infinite surface coverage (multilayers) is predicted mathematically. Therefore, high value sorption capacity of Freundlich isotherm was observed as shown in Table 3. However, D-R and Langmuir isotherms are based on the monolayer coverage of the sorbent and have comparable low sorption capacities. The slight increase in the sorption capacities with temperature may be due to the decrease in the potential energy barrier of

Table 3. Freundlich, D-R, and Langmuir isotherms constants of Tb(III) metal ions at different temperatures at pH 7.5.

Constants	Values		
	303K	313K	323K
Freundlich isotherm			
1/n	0.39 ± 0.03	0.39 ± 0.03	0.40 ± 0.04
$K_F \times 10^4$ (mol g ⁻¹)	1.62 ± 0.06	2.01 ± 0.07	4.0 ± 0.2
r	0.976	0.977	0.970
D-R isotherm			
β (kJ ² mol ⁻²)	-0.0029 ± 0.0002	-0.00265 ± 0.00017	-0.0024 ± 0.0002
$X_m \times 10^5$ (mol g ⁻¹)	2.15 ± 0.25	2.58 ± 0.18	4.11 ± 0.05
E (kJ mol ⁻¹)	13.13 ± 0.91	13.73 ± 0.91	14.43 ± 0.05
r	0.987	0.985	0.982
Langmuir isotherm			
$Q \times 10^6$ (mol g ⁻¹)	5.37 ± 0.08	5.52 ± 0.15	7.93 ± 0.2
$b \times 10^{-4}$ (l mol ⁻¹)	5.3 ± 0.1	11.9 ± 0.5	20.1 ± 0.4
ΔG_{diff} (kJ mol ⁻¹)	-37.5 ± 0.7	-40.9 ± 1.7	-43.6 ± 0.9
r	0.999	0.995	0.998

activation energy (E_{ads}) of the sorption of adsorbate and active sites of adsorbent at higher temperature and supports the endothermic chemisorption [25].

The binding energy constant (b) of monolayer coverage of Langmuir isotherm increases with temperature and favour the adsorption process while the high value of sorption free energy (E) of D-R isotherm indicates the stability of the sorbed complex at higher temperature. The linear Arrhenius relationship of adsorption coefficient (b) with temperature is related to the differential enthalpy of adsorption (ΔH_{diff}) as [26,27]:

$$\ln b = \ln b' + \frac{-\Delta H_{\text{diff}}}{RT} \quad (15)$$

where R is the gas constant and pre exponential constant ' b ' is related to the entropy. The plot of $\ln b$ vs $1/T$ is a straight line as shown in Fig. 10. The numerical value of differential enthalpy of adsorption (ΔH_{diff}) was evaluated from the slope of the graph and found to be 54 ± 3 kJ mol⁻¹. The positive value indicates the endothermic chemisorption. The differential enthalpy of adsorption (ΔH_{diff}) is defined as the heat released or adsorbed upon adding a small increment of adsorbate to the surface of a solid. The value of ΔH_{diff} depends on the strength of the bond formed

upon adsorption and the degree to which a surface is precovered with adsorbate [28]. The low value of differential enthalpy of adsorption (54 ± 3 kJ mol⁻¹) as compared to the thermodynamic enthalpy of chemisorption reaction (89 ± 4 kJ mol⁻¹), is reflecting the dominance of energetic heterogeneity of the solid surface, and the decreasing contribution of electrostatic contributions to the energy of adsorption at monolayer surface coverage. The difference in the enthalpy (35 kJ mol⁻¹) can be attributed to the dehydration sub reaction of the metal ions in sorption process which is the slowest step and have more significant in endothermic chemisorption [29].

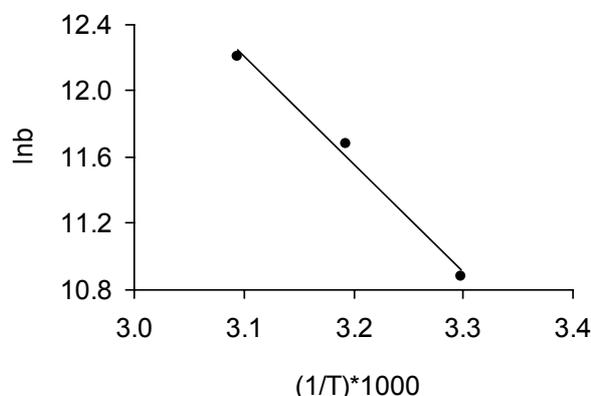


Figure 10. Arrhenius plot of adsorption coefficient ' b ' of Langmuir isotherm.

The binding energy equilibrium constant of Langmuir isotherm is also related to the differential free energy of adsorption (ΔG_{diff}) as follows [30] :

$$\Delta G_{\text{diff}} = -RT \ln(b\omega) \quad (16)$$

where ω is the molal concentration of solvent, R, T, and b are described as above. The large negative value of ΔG_{diff} as shown in Table 3 indicates the high affinity of the sorption of Tb(III) - PAN complex onto PUF and micropore filling of the PUF with Tb(III)-PAN complexes as the pore width approaches adsorbate dimension. The more contact points of adsorbate in sorbent, the more favourable will be the differential free energy of sorption

The origin of ΔH_{diff} and ΔG_{diff} are based on adsorption coefficient b of Langmuir isotherm that corresponds to the adsorption of metal ions at the surface of adsorbate. Therefore, the differential entropy of adsorption (ΔS_{diff}) can be evaluated using following relationship:

$$\Delta G_{\text{diff}} = \Delta H_{\text{diff}} - T\Delta S_{\text{diff}} \quad (17)$$

The numerical value of ΔS_{diff} is found to be $303 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1}$. The large increase in ΔS_{diff} values indicate that during sorption, the metal ions are set free from water molecules and there are not any intra molecular forces acting between the metal ions. The sorption of Tb(III) metal ions is taking place first to coordinate with the chelating reagent (PAN) and simultaneously fulfill its coordination number or geometric configuration by interacting with the active sites of the sorbent. The chelate effect in Tb(III)-PAN complex leads the sorbed complex to be more oriented and ordered structure which acts as an increased source of entropy [30,31]. The entropy effect not only leads to the stability of the sorbed complex but also partially cancels the unfavorable enthalpy change. Thus, the stability of metal complexes onto PUF is due to increase in configurational entropy mode that makes the sorbed complex more localized on a set of uniform energy sites of the sorbent as in the Langmuir isotherm.

Conclusion

The sorption of Tb(III) ions on PAN loaded PUF is temperature dependent and follows the adsorption process from aqueous solution of pH 7.5. The kinetic studies reveal the sorption is a

slow process and can be occurred at micropore region of the PUF. The intra particle diffusion and pseudo first order model control the adsorption phenomena. The low value of activation energy supports the intra particle diffusion process and the high value of activation entropy envisages the chemisorption phenomena with strong bonding between sorbed complex and sorbent.

The thermodynamic parameters confirm the entropy driven type chemisorption. The large value of entropy is attributed to the chelate effect of PAN - Tb(III) complex and new bond formation with sorbent rather than condensation of metal ions at the surface of sorbent.

The equilibrium data strongly followed by the Freundlich, D-R and Langmuir isotherms at all temperatures. The sorption constant $1/n$ correspond to surface heterogeneity and remain constant at all temperatures, indicates that 40% of the active sites of the sorbent have similar energy level for the sorption of solute. The sorption free energy (E) of D-R isotherm indicating the stability of adsorbed complex at higher temperature. The sorption coefficient 'b' of Langmuir isotherm increases with temperature and related to the differential enthalpy of adsorption (ΔH_{diff}) and differential free energy of adsorption (ΔG_{diff}). Moreover, the high negative value of ΔG_{diff} at all temperatures indicates that sorption process is highly spontaneous in nature as compared to the Gibb's free energy (ΔG). The overall stability of the chemisorption of Tb(III) ions onto PAN loaded PUF is entropy driven and chelate effect of the sorbed complex is not only cancelled the enthalpy effect of sorption but also act as an additional source of entropy gain.

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