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Effect of Temperature on Kinetics and Adsorption Profile of Endothermic Chemisorption Process: –Tm(III)–PAN Loaded PUF System

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Abstract: The sorption behavior of 3.18×10^{-6} mol l^{-1} solution of Tm(III) metal ions onto 7.25 mg l^{-1} of 1-(2-pyridylazo)-2-naphthol (PAN) loaded polyurethane foam (PUF) has been investigated at different temperatures i.e. 303 K, 313 K, and 323 K. The maximum equilibration time of sorption was 30 minutes from pH 7.5 buffer solution at all temperatures. The various rate parameters of adsorption process have been investigated. The diffusional activation energy (ΔE_{ads}) and activation entropy (ΔS_{ads}) of the system were found to be 22.1 ± 2.6 kJ mol^{-1} and 52.7 ± 6.2 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 value of ΔH and negative value of ΔG indicate that sorption is endothermic and spontaneous in nature, respectively. The adsorption isotherms such as Freundlich, Langmuir, and Dubinin–Radushkevich isotherm were tested experimentally at different temperatures. The changes in adsorption isotherm constants were discussed. The binding energy constant (b) of Langmuir isotherm increases with temperature. The differential heat of adsorption (ΔH_{diff}), entropy of adsorption (ΔS_{diff}) and adsorption free energy (ΔG_{ads}) at 313 K were determined and found to be 38 ± 2 kJ mol^{-1}, 249 ± 3 J mol^{-1} K^{-1} and -40.1 ± 1.1 kJ mol^{-1}, respectively. The stability of sorbed complex and mechanism involved in adsorption process has been discussed using different thermodynamic parameters and sorption free energy.

Keywords: Tm(III), 1-(2-pyridylazo)-2-naphthol, kinetics, thermodynamics, adsorption, chemisorption, polyurethane foam

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INTRODUCTION

Sorption is an effective and convenient separation technique of solute and solvent separation. The greatest advantage of sorption is the high distribution factor of the separation of small amount of substances from large volume of solution as compared to the other analytical techniques employed in analytical chemistry such as solvent extraction, ion exchange, co-precipitation, and solid phase extraction (1–6). Buchmeiser has reviewed developments in off line and on line preconcentration and quantification of separation techniques of rare earths (7). No universal adsorbent has yet been developed for any given purpose. Knowledge of adsorption properties of inorganic materials has become considerable importance in many fields.

PUF is a cheap and good sorbent for the separation and preconcentration of trace metal ions, reflects its potential in chemical analysis by improving the detection limit, increasing the sensitivity by several order of magnitude and enhancing the accuracy of the results. It is widely used for the preconcentration, separation, and selective collection of the desired analysts prior to instrumental analysis for quantitative and semi quantitative determinations. A number of reviewed have been published (8, 9). The sorption properties of PUF can be changed towards trace metal ions by impregnated foreign substances which may be suitable for one system but not for the others. The exact sorption mechanism of metal ions on PUF is not yet fully defined. They are changed according to the nature of the sorbent and aqueous chemistry of the metal ions.

In previous work, it was observed that the sorption behavior of metal ions onto PUF is predominantly endothermic chemisorption (10, 11). The presence of lone pair of electrons of nitrogen atom of isocyanate group and oxygen atom of ether group in the basic unit of PUF played an important role in the sorption of metal ions. The formation of micropore or macropore holes in three-dimensional structure of PU enables us to study the different kinetics parameters and equilibrium sorption behavior of trace metal ions. The pore classification of semi amorphous type material is not well defined, however, micropore diffusion differs in several respects from diffusion in macropore or in bulk fluids since the diffusing molecules never escapes from the force field of solids. Moreover, micropore diffusion is an activated process and can be related to the diffusional activation energy with temperature gradient (12). No work has yet been reported to highlight the variation of different adsorption isotherms and kinetics parameters with temperature of endothermic chemisorption process.

In the present study, the sorption properties of PAN loaded PUF has been investigated at different temperatures. Tm(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 thermodynamics, kinetics, and adsorption isotherm parameters/constants have been investigated at different temperatures. The relationship of different kinetic parameters and adsorption isotherm constants with temperature have been tested and discussed.

EXPERIMENTAL

Reagents

All the reagents used were of the analar grade. PAN from Fluka was used as such. Buffer solutions of pH l-10 having ionic strength of 0.1 M were prepared by mixing an appropriate volume of 0.2 M solutions of HCl and KCl, CH_3COOH, and CH_3COONa and H_3BO_3 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.

Radiotracer

The radiotracer of ^{170}Tm used was prepared by irradiating specpure thulium oxide (Tm_2O_3) in a 10 MW swimming pool-type research reactor (PARR-1) of this Institute at a neutron flux of 7×10^{13} n cm^{-2} 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 4 K series of 85 Canberra multichannel analyzer coupled with a 25 cm^3 Ge (Li) detector.

Polyurethane Foam Preparation

The foam plugs were prepared and washed as described elsewhere (10). The washed foam plugs were socked 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 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 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.

Procedure

Five ml buffer solution of known pH was taken in a glass culture tube with a polyethylene cap. A known concentration of radiotracer of ^{170}Tm(III) ions was added and mixed thoroughly. An aliquot of one ml was drawn to measure the initial activity for gross gamma counts (A_o). The remaining solution was shaken with PAN loaded PUF (~29 mg) for 30 minutes on a Stuart Scientific wrist-action shaker. After shaking, one ml (A_e) of aliquot was again withdrawn for assayed radiometrically on a Tennelec gross gamma counter equipped with a 30 cm^3 well type Na(Tl) crystal.

For temperature studies, the solution was taken in a culture tube and dipped in the Gallenkamp thermostirrer-100 model BKL 234, water bath at constant temperature for at least 30 minutes to attain the required 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.

The sorbed concentration of Tm(III) at equilibrium was calculated by the difference in the amount of europium in aliquot drawn before (A_o) and after shaking (A_e). The percentage sorption and distribution coefficient (K_d) were calculated as

$$\%\text{Adsorption} = \frac{A_o - A_e}{A_0} \times 100 \tag{1}$$

$$K_d = \frac{\text{amount of metal in PUF}}{\text{amount of metal in solution}} \times \frac{\text{volume of solution(V)}}{\text{weight of dry PUF (W)}} = (\text{mLg}^{-1}) \tag{2}$$

The % sorption and the distribution coefficient can be correlated as

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

All the experiments were performed at 25 ± 2°C or at temperature specified otherwise. The results are the average of at least triplicate independent measurements and precision in most cases is ±2%. The linear regression and slope analyses for the statistical data were carried out.

RESULTS AND DISCUSSION

Effect of pH

The effect of pH on the sorption of 3.18×10^{-6} mol l^{-1} solution of Tm(III) ions onto 7.25 mg l^{-1} of PAN loaded PUF with 30 minutes shaking time was investigated at ambient temperature and results are shown in Fig. 1. This figure shows that sorption is negligible upto pH 6 and after that the sorption increases and attains the maximum value at pH 7.5 and remains constant after that. Similarly the distribution coefficient (K_d) starts increasing from pH 6 and attains the maximum value at pH 7.5. On further increase in pH, the K_d value decreases and remains constant upto pH 10.

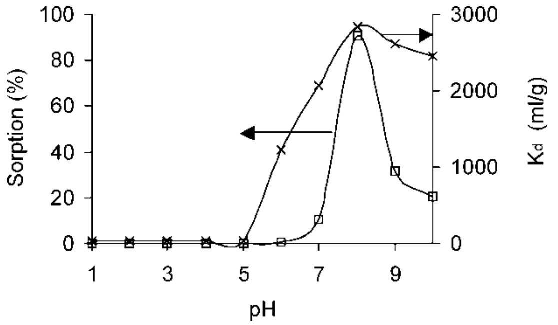

Figure 1. Effect of pH on the sorption of Tm(III) ions onto PAN loaded PUF.

However, the decrease in K_d value does not affect the percentage sorption. The sorption of Tm(III) ions from neutral or basic medium is due to the complexation of PAN and PUF with Tm(III) ions. Depending on the pH of the medium, the PAN exists in different chromophoric species with pH (13). In low pH range (<3), the cationic species of the type H_2PAN^+ is predominant, while the anionic species of PAN^- is predominant in basic medium (pH >10). The neutral species HPAN or HL, insoluble in aqueous solution and responsible for complex formation with metal ions exists in the pH range 3–10. The neutral form of HPAN (HL) has strong ability to dissociate the hydrogen atom of the hydroxyl group of naphthol as:

$$HL \rightleftharpoons H^+ + L^-$$

where L^- species form complexes with Tm(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 Tm(III) ions to neutralize its charge and simultaneously sorbed onto PUF to satisfy the stable coordination number 8, and subsequently increases the sorption of Tm(III) ions onto PAN loaded PUF as shown in Fig. 1.

Kinetic Studies

Maximum sorption can be attained by the maximum distribution of Tm(III) ions between solid phase and aqueous solution. The effect of agitation time on the sorption of 3.18×10^{-6} mol l^{-1} solution of Tm(III) ions onto PAN loaded PUF from borate buffer solution of pH 7.5 at different temperature 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 than remains constant.

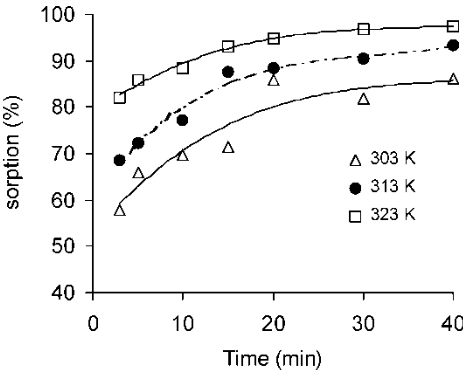

Figure 2. Effect of contact time of the sorption of Tm(III) ions onto PAN loaded PUF at different temperature.

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 of solute occurs by the following three steps model.

1. Transfer of solute from bulk to the outer surface or macropore region of the sorbent (PUF) via film diffusion.
2. Transfer of solute from macropore region to the micropore or interior region by diffusion with in the pore filled liquid via intra particle diffusion process.
3. Interaction of solute on the active sites of interior region.

The first two steps act in parallel and the rate of adsorption process will be controlled by the slowest step. Since, the third step is interaction of solute with active sites of PUF, the adsorption process is rapid and does not influence the overall kinetics of adsorption.

In order to distinguish the film diffusion or intra particle diffusion process, the Weber–Morris (14) equation was tested in the form:

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

where q_t is the amount of Tm(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, indicating intra particle diffusion process is predominant. The numerical value of k at different temperature is given in Table 1.

The intra particle diffusion equation derived by Reichenberg (15) given below was also tested:

$$F = 1 - \left(\frac{6}{\pi^2}\right)e^{-Bt} \tag{5}$$

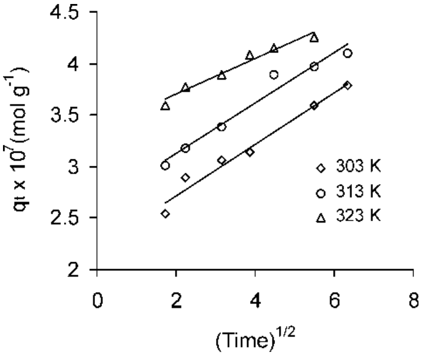

Figure 3. Plot for the rate constants of pore diffusion at different temperature of Tm(III) ions onto PAN loaded PUF.

where

$$F = \frac{q_t}{q_\infty} = \frac{\text{amount of metalions sorbed at time t}}{\text{amount of metalions sorbed at equilibrium}}$$

The values of Bt is the mathematical function of F and was calculated as;

$$Bt = -0.4977 - \ln(1 - F) \tag{6}$$

The obtained value of Bt corresponding to each value of F was verified from the Reichenberg table. The plots of Bt vs. time are straight lines for all temperatures as shown in Fig. 4. The straight lines indicate that the intraparticle diffusion process predominantly controls the kinetics of the sorption of the Tm(III) ions onto PAN imbedded PUF.

The overall rate sorption of solute particle into the pores of solid surface regardless of the mechanism used depends on the mass action process. There is a correlation between q, the number of Tm(III) ions adsorbed per unit area at a given pressure and temperature and time required to complete the adsorption process as shown by Lagergren (16) in the form:

$$q_t = q_\infty(1 - e^{-k_1 t}) \tag{7}$$

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

Temp (K)	$k \times 10^7$ $(\text{mol g}^{-1}\,\text{min}^{-1/2})$	k_1 (min^{-1})	ΔE_{ads} (kJ mol^{-1})	ΔS_{ads} $(\text{J mol}^{-1}\,\text{K}^{-1})$
303	(2.49 ± 0.02)	0.065 ± 0.007	22.1 ± 2.6	52.9 ± 6.2
313	(2.45 ± 0.02)	0.082 ± 0.008		52.7 ± 6.2
323	(1.80 ± 0.01)	0.112 ± 0.006		52.4 ± 6.1

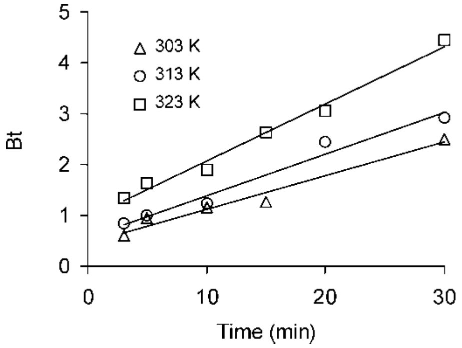

Figure 4. Reichenburg plot of the particle diffusion of Tm(III) ions onto PAN loaded PUF at different temperatures.

or

$$\ln(1 - F) = k_1 t \tag{8}$$

where $F = qt/q_\infty$, 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 a different temperature 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.

The relationship between rate constant (k_1) and temperature enables us to calculate the activation energy of adsorption (ΔE_{ads}). In this regard, Arrhenius

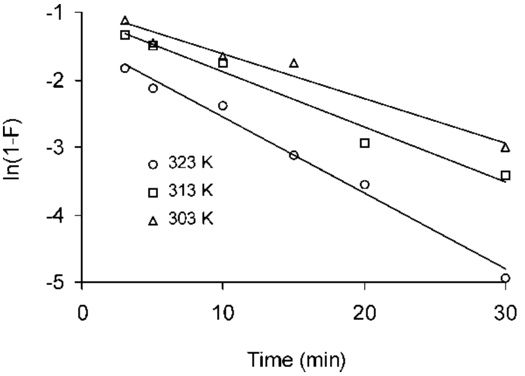

Figure 5. Plot of ln(I − F) vs. time for the estimation of adsorption rate constants of Tm(III) ions onto PAN loaded PUF.

equation was used in the form (17):

$$\ln k_1 = \ln D_o - \left(\frac{\Delta E_{ads}}{RT}\right) \tag{9}$$

The plot of ln k_1 vs. $1/T$ is a straight line as shown in Fig. 6. The numerical value of ΔE_{ads} was evaluated and given in Table 1. Moreover, the pre exponent constant D_o of sorption process is related to the entropy of activation (ΔS_a) of sorption and was determined by applying the equation proposed by Barrer et al. (18).

$$D_o = 2.72\left(\frac{KTd^2}{h}\right)\exp\left(\frac{\Delta S_a}{R}\right) \tag{10}$$

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 Å for micropore structure of semi solids (12).

The activation energy of adsorption in the range 20–50 kJ mol^{-1} corresponds to the intra particle diffusion process, which is lower than the chemical reaction in chemisorption (19). Table 1 clearly indicates that the activation energy is in the range of particle diffusion as predicted from Figs. 3 and 4. The low activation energy is mainly a result of the favorable thermodynamics and vice versa. The high value of activation entropy in Table 1 indicates that the mobility of Tm(III) ions in micropore region is set free from hydration shell and the adsorption rate is controlled by the strong complexation reaction between metal ions and active sites PAN loaded PUF (20).

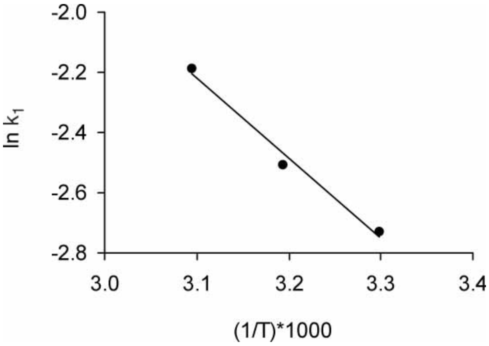

Figure 6. Arrheniues plot for the determination of activation energy of Tm(III) ions sorption onto PAN loaded PUF.

Thermodynamic Studies

The thermodynamic parameters of 3.18×10^{-6} mol l^{-1} solution of Tm(III) ions uptakes onto PAN loaded PUF have been evaluated using the following equation:

$$\ln K_c = \frac{-\Delta H}{R} + \frac{\Delta S}{RT} \tag{11}$$

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

The plot of ln K_c vs. $1/T$ is linear over the entire range of temperature (298–343 K). The numerical values of ΔH and ΔS are 58 ± 4 kJ mol^{-1} and 213 ± 12 J mol^{-1} K^{-1}, respectively, calculated from the slop and intercept of Fig. 7, respectively. The Gibb's free energy (ΔG) is determined from the following relationship:

$$\Delta G = \Delta H - T\Delta S \tag{12}$$

The numerical value of (ΔG) is −5.5 ± 1.6 kJ mol^{-1}. The negative value of ΔG indicates that sorption is spontaneous in nature. However, the positive value of ΔH and ΔS indicates that sorption of Tm(III) ions onto PAN loaded PUF is endothermic and stability of sorption is entropy driven. The high numerical values of enthalpy and entropy do not decipher any special bond formation but favors the chemisorption by involving the rapture of hydration shell formed around central metal atom in mother liquid and creation of new bond formation with active sites of sorbent surface as well as chelate effect of PAN complexing with central metal atom (21). Moreover, the − TΔS term is much greater than the ΔG and makes the ΔH

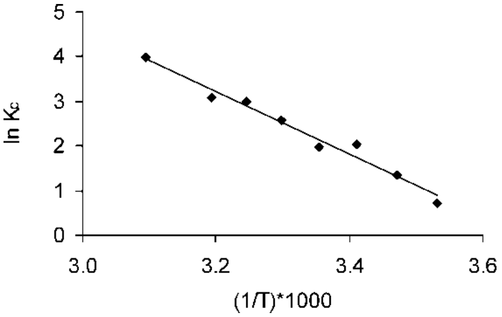

Figure 7. Van't Hoff plot of equilibrium constant (k_c) for the determination of thermodynamic parameters of Tm(III) ions sorption onto PAN loaded PUF.

term positive for endothermic chemisorption; correspond to net gain in the degree of freedom of sorbed species (21, 22).

Effect of Metal Ion Concentration

The effect of Tm(III) ions concentration sorption was examined from 3.18×10^{-6} mol l^{-1} to 3.36×10^{-4} mol l^{-1} solutions. The variation of sorption (%) with itself metal ion concentration using 30 minutes shaking time and 7.25 mg ml^{-1} of PAN loaded PUF at different temperatures is shown in Fig. 8. The decrease in the sorption with increase in initial Tm(III) ion concentration is due to the saturation of the active sites of PAN loaded PUF for bonding.

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

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. The Freundlich isotherm (23) is expressed as:

$$C_{ads} = K_F C_e^{1/n} \tag{13}$$

where C_{ads} is concentration of Tm(III) ions in solid phase in mol g^{-1} and C_e is the concentration of Tm(III) ions in aqueous solution in mol l^{-1} at equilibrium. The logarithmic linearization form of Freundlich isotherm facilitates to determine the isotherm constants K_F and $1/n$. The numerical values are given in Table 2 with standard deviation ±4.5%.

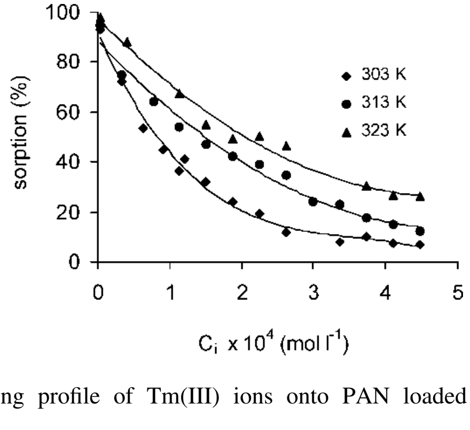

Figure 8. Loading profile of Tm(III) ions onto PAN loaded PUF at different temperatures.

Table 2. Freundlich, D-R, and Langmuir isotherms constants of Tm(III) metal ions at different temperatures at pH 7.5

Constants	Values 303 K	 313 K	 323 K
Freundlich isotherm			
$1/n$	0.46 ± 0.03	0.48 ± 0.03	0.47 ± 0.03
$K_F \times 10^4$ (mol g^{-1})	5.4 ± 0.3	8.6 ± 0.4	11.8 ± 0.5
r	0.989	0.986	0.995
D-R isotherm			
β (kJ^2 mol^{-2})	-0.0032 ± 0.00015	-0.0030 ± 0.00002	-0.0026 ± 0.00008
$X_m \times 10^5$ (mol g^{-1})	3.3 ± 0.3	6.2 ± 0.5	7.2 ± 0.3
E (kJ mol^{-1})	13.1 ± 0.3	12.9 ± 0.2	13.9 ± 0.3
r	0.990	0.997	0.998
Langmuir isotherm			
$Q \times 10^5$ (mol g^{-1})	0.83 ± 0.04	1.11 ± 0.05	1.43 ± 0.11
$b \times 10^{-4}$ (l mol^{-1})	5.11 ± 0.34	8.66 ± 1.02	13.0 ± 1.0
ΔG_{ads} (kJ mol^{-1})	-37.5 ± 1.0	-40.1 ± 1.1	-42.5 ± 1.3
r	0.993	0.990	0.978

The D-R isotherm based on the Polanyi potential theory of adsorption is successfully describe the adsorption isotherm of micropore adsorbent. The D-R isotherm (24) was tested in the form:

$$C_{ads} = X_m \exp(-\beta\varepsilon^2) \tag{14}$$

where constants, Polanyi potential $(\varepsilon) = -RT\ln(1 + (1/C_e))$, β is the net adsorbate–adsorbent activity coefficient, X_m is the maximum adsorption of D-R monolayer coverage, R is gas constant (8.3143 J mol^{-1} K^{-1}), C_{ads} and C_e are the same as described above. The natural logarithmic form of D-R isotherm give the values of β and X_m constants from the slope and intercept, respectively, are summarized in the Table 2. The sorption free energy $(E) = (-2\beta)^{-1/2}$ was evaluated for all three temperatures and presented in Table 2.

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. Moreover, the molecules cannot migrate across the surface of the adsorbent. The Langmuir isotherm (25) was written in the form:

$$C_{ads} = \frac{QbC_e}{1 + bC_e} \tag{15}$$

where C_{ads} and C_e are describe above, Q and b are the constants related to the sorption capacity (monolayer coverage) and sorption energy, respectively, were evaluated from the linear form of the Langmuir isotherm and given in the Table 2.

The equilibrium plot of C_{ads} vs. C_e at different temperature is shown in Fig. 9. This figure indicates that the data point of the sorption of Tm(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 the Langmuir model is reasonably satisfying the whole range of metal ions concentration under investigation.

Table 2 clearly indicates that the sorption affinity (1/n) constant of Freundlich isotherm is <1 and almost remains constant at all temperatures, encompassing the exponential distribution of active sites in their energy. The sorption capacities K_F, X_m, and Q of Freundlich, D-R and Langmuir isotherms respectively, are increased with temperatures. The Freundlich isotherm does not predict and saturation of the sorbent surface, thus infinite surface coverage is predicted mathematically. Therefore, high value sorption capacity of Freundlich isotherm was observed as shown in Table 2. This increase in sorption capacity with temperature is due to the formation of multi layer coverage of the sorbent. However, D-R and Langmuir isotherms are based on the monolayer coverage of the sorbent and have low and comparable sorption capacities. The slight increase in the sorption capacities with temperature may be due to the decrease in the potential energy barrier of activation energy (E_{ads}) of the sorption of adsorbate and active sites of adsorbent at higher temperature and supports the endothermic chemisorption (26).

The binding energy constant (b) of monolayer coverage of Langmuir isotherm increases with temperature, and high value of sorption free energy (E) of D-R monolayer coverage isotherm indicates the stability of the sorbed complex at higher temperature and endothermic type chemisorption. The large value of sorption energy constant (b) favours the adsorption

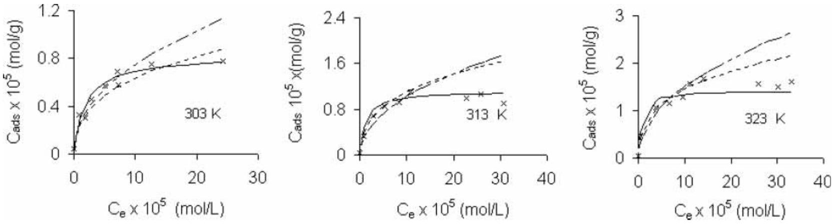

Figure 9. Adsorption isotherm of Tm(III) ions onto PAN loaded PUF at different temperatures. Symbols: × Experimental data, lines model fitting (solid, Langmuir; dotted, D-R; dashed, Freundlich).

process. The linear Van't Hoff relationship of adsorption coefficient (b) with temperature is related to the differential heat of adsorption (ΔH_{diff}) as (27, 28):

$$\ln b = \ln b' + \frac{-\Delta H_{diff}}{RT} \tag{16}$$

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 (ΔH_{diff}) was evaluated from the slope of the graph and found to be $38 \pm 2\,kJ\ mol^{-1}$. The positive value indicates the endothermic chemisorption. The differential heat of sorption (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 pre covered with adsorbate (29).

The magnitude and sign of net enthalpy change (ΔH) associated with adsorption process in aqueous solution comprise (21, 30):

$$\Delta H = \Delta H_{de} + \Delta H_c + \Delta H_{ads} \tag{17}$$

The stepwise enthalpy changes are defined as:

1. ΔH_{de} is the enthalpy change of dehydration, which will cause ΔH to be endothermic because energy is required to break the ion-water and water-water bonding of hydrated metal ions.
2. ΔH_c is the enthalpy change for complexation that will make ΔH more endothermic due to formation of metal complex.
3. ΔH_{ads} is the enthalpy change due to sorption of metal complexes and new bonds formation at the sorbent surface in chemisorption and thus makes ΔH more positive.

The differential enthalpy (ΔH_{diff}) change occurs at the surface of the sorbent and comprises:

$$\Delta H_{diff} = \Delta H_c + \Delta H_{ads} \tag{18}$$

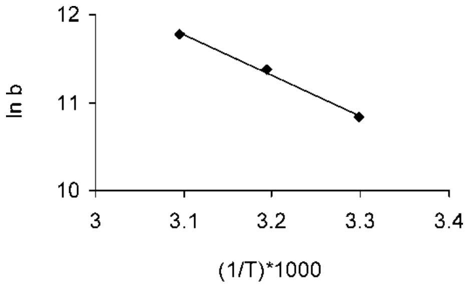

Figure 10. Van't Hoff plot of adsorption coefficient 'b' of Langmuir isotherm.

The low value of differential heat of adsorption ($38 \pm 2\,\mathrm{kJ\,mol^{-1}}$) as compared to the equilibrium heat of adsorption, reflecting the dominance of energetic heterogeneity of the solid surface, and decreasing contribution of electrostatic contributions to the energy of adsorption at monolayer surface coverage. The difference in the enthalpy ($20\,\mathrm{kJ\ mol^{-1}}$) 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.

The binding energy equilibrium constant of Langmuir isotherm is also related to the adsorption free energy as follows (31):

$$\Delta G_{ads} = -RT\ln(b\omega) \tag{19}$$

Where ω is the molal concentration of solvent, R, T, and b are described as above. The large negative value of ΔG_{ads} as shown in Table 2, indicating the high affinity of the Tm(III)-PAN complex onto PUF. The large negative value of ΔG_{ads} is also related to the micropore filling of the PUF with Tm(III)-PAN complexes as the pore width approaches adsorbate dimension. The more contact points of adsorbate in sorbent micropore will be more favorable adsorption free energy. The ΔG_{ads} term increases with monolayer sorption capacity (Q) of Langmuir isotherm for endothermic nature of sorption and vice versa is true for exothermic sorption (32).

The origin of ΔH_{diff} and ΔG_{ads} are the same (adsorption coefficient b) as those that correspond to the adsorption of metal ions at the surface of adsorbate. The differential entropy of adsorption (ΔS_{diff}) can be evaluated using following thermodynamic relationship:

$$\Delta G_{ads} = \Delta H_{diff} + \Delta S_{diff} \tag{20}$$

the numerical value of ΔS_{diff} is found to be $249 \pm 3\,\mathrm{J\ mol^{-1}\ K^{-1}}$. The high value of ΔS_{diff} indicates that during sorption, the metal ions are free from water molecules and there are no intra molecular forces acting between the metal ions. The sorption of Tm(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 ring formation in Tm(III)-PAN complex will lead the sorbed complex to be a more oriented and ordered structure which acts as an increase source of entropy (21, 33). Thus, the stability of metal complexes onto PUF is due to the loss in vibrational entropy mode and 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 use of PAN loaded PUF is very promising to remove / preconcentrate the Tm(III) ions from buffer solution of pH 7.5.

The kinetic studies at different temperatures indicate that the sorption is slow and occurs at micropore region of PUF. The intra particle diffusion process and peusdo first order models control the adsorption process. The low activation energy confirms the intra particle diffusion process and high values of activation entropy envisage the free form movement of metal ions in micropore region of adsorbent.

The thermodynamic calculation confirms the entropy driven endothermic nature of chemisorption. The high value of entropy is mainly due to the chelate effect of PAN-Tm(III) complex and formation of new chemical bonds with adsorbent rather than condensation of metal ions at the surface of sorbent.

The equilibrium adsorption process can be acceptably described by the Freundlich, D-R, and Langmuir isotherms at all temperatures. The sorption constant (1/n) and sorption free energy (E) of D-R, isotherms almost remain constant at all temperatures. The sorption capacities of sorption have been evaluated from the characteristic constants of isotherms for Tm(III) ions at different temperatures. The sorption capacities of all three isotherms increase with temperature and converted from multilayer to monolayer coverage as predicted for endothermic chemisorption. The binding energy sorption coefficient (b) of Langmuir isotherm, related to the differential heat of enthalpy (ΔH_{diff}) and sorption free energy (ΔG_{ads}), also increases with temperature. The low value of ΔH_{diff} and high negative value of ΔG_{ads} indicate that the accumulation of metal ions is based on the interaction of metal ions with sorbent and are very strong and spontaneous in nature with the active sites of PUF. The stability of chemisorption is entropy driven and chelate ring formation is the additional source of entropy.

REFERENCES

1. Prasada Rao, T. and Kala, R. (2004) On–line and off-line preconcentration of trace and ultratrace amounts of lanthanides. *Talanta*, 63 (4): 949–959.
2. El-Shahawi, M.S. and Nassif, H.A. (2003) Retention and thermodynamic characteristics of mercury(II) complexes onto polyurethane foams. *Anal. Chim. Acta*, 481: 29–39.
3. Rengan, K. and Sun, B.C. (2004) Sorption of Zn(II) and Cd(II) by chelating resins: comparison of three resins. *J. Radioanal. Nucl. Chem.*, 262 (1): 175–182.
4. Gao, J., Hu, G., Kang, J., and Bai, G. (1993) 1-(2pyridylazo)-2-naphthol (PAN) as extractant in solid-liquid extraction of some trivalent rare earth elements. *Talanta*, 40 (2): 195–200.
5. Sekine, T. and Hasegawa, Y. (1977) Applications of solvent extraction in analytical and inorganic chemistry. In *Solvent Extraction Chemistry*; Marcel Dekker, Inc.: New York, 363–649.
6. Kuznik, B. (1981) Solvent extraction of certain rare earth metal ions with 1-(2-pyridylazo)-2-naphthol (PAN). *J. Inorg. Nucl. Chem.*, 43 (12): 3363–3368.
7. Buchmeiser, M.R. (2001) Recent advances in the quantification of lanthanides. *Rev. Anal. Chem.*, 20 (3): 161–184.

8. 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, 363–400.
9. Saeed, M.M. and Rusheed, A. (1998) Analytical application of polyurethane foam in separation and preconcentration processes—A review. *Sci. Int.*, 10: 273–286.
10. Saeed, M.M. and Rusheed, A. (2002) Investigation of Tb(III) by 2-thenoyltrifluoroacetone supported onto polyurethane foam. *Radiochim. Acta*, 90 (1): 35–42.
11. Saeed, M.M., Ahmed, M., Chaudary, M.H., and Gaffar, A. (2003) Kinetics, thermodynamics, and sorption profile of Eu(III) and Tm(III) on 4-(2-pyridylazo) resorcinol (PAR) imbedded polyurethane foam. *Solvent Extr. Ion Exch.*, 21 (6): 881–898.
12. Ruthven, D.G. (2002) Adsorption (chemical engineering). In *Encyclopedia of Physical Science and Technology*, 3rd ed.; Meyers, R.A. (ed.), Academic Press: New York; Vol. 1, 251–271.
13. Anderson, R.G. and Nickless, G. (1967) Heterocyclic azo dystuffs in analytical chemistry: A review. *Analyst*, 92: 207–238.
14. Weber, W.J. and Morris, J.C. (1963) Kinetics of adsorption on carbon from solution. *J. Sanit. Eng. Div. ASCE*, 89 (SA2): 31–59.
15. Reichenberg, D. (1953) Properties of ion exchange resins in relation to their structure. III. Kinetics of exchange. *J. Am. Chem. Soc.*, 75 (2): 589–597.
16. Lagergren, S. (1898) Zur theorie der sogennanten adsorption geloster stoffe. *K. Seveska Vetenskapsaked Handle*, 24: 1–39.
17. Leenson, I.A. (1986) Thermodynamics and kinetics of chemical equilibrium in solution. *J. Chem. Edu.*, 63 (5): 437–440.
18. Barrer, R.M., Bartholomew, R.F., and Rees, L.V.C. (1963) Ion exchange in porous crystals part 1. Self- and exchange-diffusion of ions in chabazites. *J. Phys. Chem. Solids*, 24 (1): 51–62.
19. 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 (4): 613–620.
20. Vallet, V., Wahlgren, U., and Grenthe, I. (2003) Chelate effect and thermodynamics of metal complex formation in solution: A quantum chemical study. *J. Am. Chem. Soc.*, 125 (48): 14941–14950.
21. Choppin, G.R. and Morgenstern, A. (2000) Thermodynamics of solvent extraction. *Solvent Extr. Ion Exch.*, 18 (6): 1029–1049.
22. Thomas, J.M. (1961) The existence of endothermic adsorption. *J. Chem. Edu.*, 38 (3): 138–139.
23. Freundlich, H. (1926) *Colloid and Capillary Chemistry*; Methuen: London, 397.
24. Dubinin, M.M. and Radushkevich, L.V. (1947) The equation of the characteristic curve of activated charcoal. *Proc. Acad. Sci. USSR, Phys. Chem. Sect.*, 55: 331–333.
25. Langmuir, I. (1918) The adsorption of gases on plane surface of glass, mica and platinum. *J. Am. Chem. Soc.*, 40 (7): 1361–1403.
26. Oblad, A.G., Goyal, S.K., Ramakrishnan, R., and Sunder, S. (1978) Catalysis and catalysts. In *Encyclopedia of Chemical Processing and Design*; McKetta, J.J. and Cunningham, W.A. eds., Marcel Dekker, Inc.: New York; Vol. 6, 436–442.
27. Faust, S.D. and Aly, O.M. (1987) Elements of surface chemistry. In *Adsorption Processes for Water Treatment*; Butterworth Publs.: Boston, 1–22.
28. Yadava, K.P., Tyagi, B.S., and Singh, V.N. (1991) Effect of temperature on the removal of lead(II) by adsorption on china clay and wollastonite. *J. Chem. Tech. Biotechnol.*, 51 (1): 47–60.

29. Clark, A. (1970) Thermodynamics of adsorption. In *The Theory of Adsorption and Catalysis*; Academic Press: New York, 1–16.
30. El-Kamash, A.M., El-Sayed, A.A., and Aly, H.F. (2002) Thermodynamics of uranium extraction from nitric acid solution by TBP loaded on inert supporting material. *J. Radioanal. Nucl. Chem.*, 253 (3): 489–495.
31. Sabio, E., González-Martin, M.L., Ramiro, A., González, J.F., Bruque, J.M., Labajos-Broncano, L., and Encinar, J.M. (2001) Influence of the regeneration temperature on the phenols adsorption on activated carbon. *J. Colloid Interface Sci.*, 242 (1): 31–35.
32. Gimeno, O., Plucinski, P., Kolaczkowski, S.T., 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 (5): 1076–1086.
33. Cotton, F.A., Wilkinson, G., Murillo, C.A., and Bochmann, M. (1999) Some cross–cutting topics. In *Advance Inorganic Chemistry*, 6th ed.; John Wiley & Sons, Inc., 27–29.