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Removal of ^{99}Tc from low level radioactive liquid waste using commercial anion exchanger resin

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ABSTRACT

Technetium exists as pertechnate (TcO_4^-) ion under oxidizing condition. It is found in almost all streams originating from reprocessing plant. The presence of ^{99}Tc results substantial operating problems in waste management practices due to the long half life (2.1 × 10^5 year with beta energy 0.297 MeV). Intermediate level radioactive liquid waste (ILW) generated at different steps of PUREX process is made alkaline using carbonates in order to facilitate its storage in carbon steel tank and to avoid precipitation in tank. Major radionuclides present in the waste are ^{137}Cs, ^{90}Sr, ^{106}Ru and ^{99}Tc. The waste also contains ^{125}Sb and alpha emitting radionuclides in trace concentration. The waste is being treated by ion exchange process using resorcinol formaldehyde (RF) resin for removal of ^{137}Cs and ^{90}Sr. During pH adjustment of the waste stream, alpha radionuclides as well as ^{90}Sr gets precipitated as corresponding hydroxide along with uranium and iron present in the waste. The conditioned waste was treated using RF resin. The effluent of the IX process is low active in nature. The activity of the IX column effluent is mainly due to ^{106}Ru and ^{99}Tc. Commercially available anion exchange resin Indion -GS300 was used for removal of ^{99}Tc in the present study. The performance of this anion exchanger resin material was evaluated for removal of ^{99}Tc from the radioactive liquid waste. Various parameters like effect of pH, effect of total dissolved salt content, column performance etc. were studied. The sorption behaviour was examined using various isotherms like Langmuir, Dubenin – Raduskevich and Freundlich. Thermodynamic parameters such as ΔG, ΔH and ΔS were also evaluated. Elution of 90% of loaded ^{99}Tc from the loaded anion exchanger column was possible using concentrated nitric acid.

Keywords: Technetium-99; Anion exchange resin; Tetra phenyl arsonium chloride; Langmuir; Dubenin radushkevitch; Free energy

1. Introduction

Technetium-99 is one of the fission product obtained during fission reaction in power reactor with a fission yield of about 6.13% [1]. Among the long lived fissions products, ^{99}Tc is an important beta emitting nuclide of concern from the nuclear waste management point of view ($t_{1/2} = 2.11 \times 10^5$ *y*, $E_{\beta\text{-max}} = 295.5$ keV) [2]. During reprocessing of the spent fuel from power reactor, ^{99}Tc reports in the radioactive liquid waste as pertechnate anion (TcO_4^-). To reduce radioactive discharge into the environment it is very much essential to separate the technetium from the radioactive liquid waste.

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Reprocessing of the spent fuel from reactor generates broadly two categories of radioactive liquid waste stream viz high level liquid waste (HLW) and intermediate level radioactive liquid waste (ILW). Concentrate of the aqueous raffinate of the coextraction cycle in PUREX process is referred to as HLW. HLW in acidic conditions is stored in stainless steel tanks for its subsequent treatments viz. actinide partitioning or vitrification [3–6]. The waste is concentrated prior to its vitrification. During concentration process, nitric acid is recovered through fractionator and subsequently the off gases are condensed to collect the condensate stream. The condensates as well as recovered acid are categorised as ILW. Major source of ILW, however is the second cycle raffinate of PUREX process. ILW is having activity in the range of mill curies per litre. All the streams are acidic in nature. These streams are neutralised by alkali. During the process large amount of salts are getting introduced in the waste. The ILW contains ^{137}Cs, ^{90}Sr, ^{106}Ru and ^{99}Tc as major radionuclides. ^{137}Cs and ^{90}Sr are removed from such waste by IX process using Resorcinol formaldehyde imino diacetic acid (RF – IDA) polycondensate resin [7,8]. The effluent obtained from the RF – IDA resin is low active in nature and contains ^{106}Ru and ^{99}Tc as major radionuclides along with trace concentration of ^{137}Cs and ^{90}Sr. This low active liquid waste is treated by chemical co-precipitation to remove the radionuclides prior to discharge into the environment. Copper ferrocyanide and barium sulphate precipitation are being adopted for removal of ^{137}Cs and ^{90}Sr [9]. Nickel sulphide precipitation is suitable for removal of ^{106}Ru [10]. However presence of ^{99}Tc puts limit on chemical treatment method for treatment of LLW. ^{99}Tc is present in the LLW as anionic species. Use of commercial anion exchanger for separation of ^{99}Tc has been reported [11,12]. Present study was focused on use of commercial anion exchanger resin Indion -GS300 supplied by M/s. Ion exchange India Ltd., for separation of ^{99}Tc from the radioactive liquid waste and the chemical treatment feasibility of the subsequent liquid waste stream. Various experimental parameters were studied to evaluate the performance of the resin material. The K_d value of the resin was evaluated as a function of pH, salt concentration, temperature and TcO_4^- ion concentration. The sorption behavior was examined with various isotherms like Langmuir, Dubinin – Radushkevich and Freundlich to understand the sorption mechanism. The thermodynamic parameters such as ΔG, ΔH and ΔS were also evaluated.

2. Experimental

2.1. Reagents

Commercially available anion exchanger resin (Indion -GS300) of strong base quaternary ammonium functionality in chloride form with the bead size of 0.5–1.0 mm supplied by M/s. Ion Exchange India Ltd., was used for the study. Tetra phenyl Arsonium Chloride—AR grade of ALDRICH make was used.

2.2. Preparation of ^{99}Tc solution

The ^{99}Tc required for the study was separated from the low level radioactive liquid waste using anion exchanger resin [13]. The effluent obtained after the removal of Cs from Intermediate level radioactive liquid waste using resorcinol formaldehyde resin was low active in nature. The major radionuclides present in this waste are ^{99}Tc and ^{106}Ru. This solution was used for separation of ^{99}Tc in pure form. Initial washing was performed with 1M nitric acid to elute ^{106}Ru [14]. Further washing with 8 M nitric acid eluted Tc. Both the eluents were collected separately. The 8 M nitric acid was destroyed by using formic acid [15]. The absence of gamma emitting isotopes was confirmed by making use of HPGe based multichannel analyser gamma spectroscopic system. The ^{99}Tc activity was monitored by its gross beta measurement using G.M. Counter of make NUCLEONIX, India. Presence of ^{99}Tc was confirmed by its gross beta cut – off through Al - absorber of thickness 100 mg/cm^2 (95%) [16]. This solution was used for the experimental work.

2.3. Determination K_d value

0.1 gm of the anion exchanger resin was equilibrated with 10 ml of the ^{99}Tc solution in PVC bottles at pH 11.0 for one hour using continuous magnetic stirrer. The initial and final activity was monitored using Geiger—Muller counter.

The K_d value was calculated as follows:

$$K_d = \frac{C_i - C_f}{C_f} \times \frac{V}{W} \text{(ml/gm)} \qquad (1)$$

where, C_i and C_f are the initial and final Gross beta/gamma activity, V is the volume (ml) of the liquid waste and W is weight (g) of the resin material. Effect of various parameters like pH, ionic concentration and time on K_d value was studied.

2.4. Column performance

In order to evaluate the column performance of the resin material, 5 ml of anion exchange resin in 25 ml capacity glass burette was used. The IX effluent waste was passed over the column with a flow rate of 5 bed volume per hour (25 ml/hr). The technetium content in the column feed as well as effluent waste was analysed using Tetraphenyl arsonium chloride precipitation method as per the standard procedure [17]. The column effluent samples were also checked for other radioisotopes. The ^{99}Tc loaded column was eluted with concentrated nitric acid. In order to see the reuse of the eluted column, fresh waste was passed over the eluted column under similar conditions. The effluent of the column was analysed for ^{99}Tc.

2.5. Kinetics

In order to study the kinetics part of the anion exchanger material, the resin was equilibrated with ^{99}Tc solution for varying time interval and fraction of ^{99}Tc sorbed on the resin was plotted as a function of time.

2.6. Sorption isotherm

0.1 gm of the anion exchange resin was equilibrated with 10 ml of ^{99}Tc solution at pH 1.0 for a period of two hours. The concentration of ^{99}Tc was varied from 4.54×10^{-5} to 2.70×10^{-4} mol/l. The sorption data was treated by various sorption isotherms like Langmuir, Dubinin – Raduskevich and Freundlich.

3. Results and discussion

The properties of the IX effluent waste indicated in Table 1 shows that the waste contains ^{99}Tc and ^{106}Ru in appreciable concentration.

The K_d value of the anion exchanger for ^{99}Tc varied from 4000–3000 at pH range of 1–13. Fig. 1 shows that K_d value is not getting affected significantly by change in pH of the solution. The radioactive low level liquid waste contains high concentrations of salt mainly in the form of sodium nitrate, hence effect of salt concentration on K_d value for ^{99}Tc was evaluated. It was observed that the K_d value decreases with increase in salt content (Fig. 2). However even the K_d value obtained with 25% (w/v) of salt content is sufficient for column mode of operation to get desired decontamination of ^{99}Tc.

Table 1
Radiochemical properties of IX effluent waste stream

Properties	Regenerant waste
pH	12.5
Total Solid, % w/v	16.5
Gross beta, mCi/l	0.40
^{137}Cs, mCi/l	3.00×10^{-3}
^{106}Ru, mCi/l	0.10
^{99}Tc, mCi/l	0.29

Column performance shown in Fig. 3 indicated an initial DF of 280, which gradually decreased to 1.85 at 175 bed volume and remained constant upto 250 bed volumes. The results of reuse of the eluted column showed similar observations.

Almost 90% of the loaded activity was recovered by elution with 25 bed volume of concentrated nitric acid. The ^{99}Tc in the eluent was confirmed by its beta count cut off in GM counter using Al absorber of thickness 0.4 mm of ^{106}Ru (about 1% total activity)

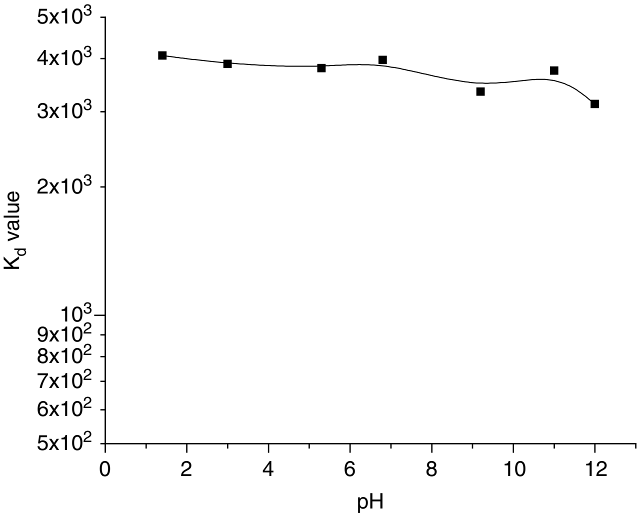

Fig. 1. Effect of pH on K_d value for sorption of ^{99}Tc on anion exchanger.

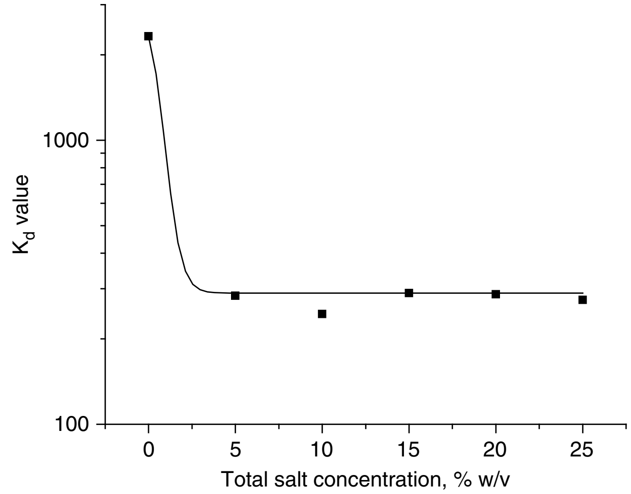

Fig. 2. Effect of salt concentration on K_d value for sorption of ^{99}Tc on anion exchanger.

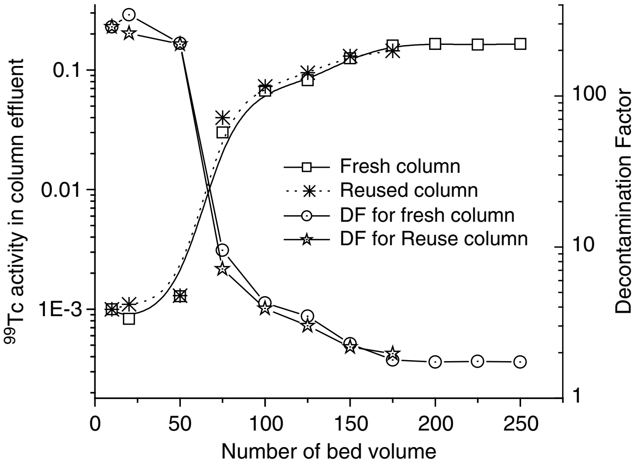

Fig. 3. Column performance of anion exchange resin for sorption of ^{99}Tc on anion exchanger.

(100 mg/cm^2). The eluent also contains small amounts and traces of ^{137}Cs.

3.1. Kinetics

The kinetics data as shown in Fig. 4 indicates a high initial rate of removal followed by slower subsequent removal rate that gradually approached an equilibrium condition with in two hours.

3.2. Adsorption isotherms

The effect of pH on K_d value was not appreciable and the solution of ^{99}Tc obtained was acidic in nature, hence the studies were performed at pH 1.

The sorption studies of ^{99}Tc with the anion exchanger resin was conducted by varying the concentration and the sorption data were tested with different types of isotherms such as Langmuir, Dubenin – Radushkevich (D-R) and Freundlich isotherms.

3.3. Langmuir adsorption isotherm

The Langmuir isotherm model has been successfully applied to many adsorption processes and it is most common model for the adsorption of solute from a liquid solution. Though Langmuir adsorption isotherm was developed for the sorption of gases on the solid surface, it could also be applied for the liquid phase. The Langmuir adsorption isotherm in the liquid phase can be represented by the following equation [18,19]:

$$\frac{C_e}{q_e} = \frac{1}{q_o b} + \frac{C_e}{q_o} \tag{2}$$

where, C_e is the equilibrium concentration of metal ions in the aqueous phase; q_e is the amount of metal ions sorbed on the solid phase at equilibrium; q_0 and b are the Langmuir constant related to the sorption capacity of the metal ions and energy of adsorption respectively. C_e/q_e was plotted against C_e over the concentration range of ^{99}Tc investigated (Fig. 5). From the slope and intercept of the plot the values of q_0 and b were evaluated as given in Table 2.

The Langmuir model is developed to represent chemisorption on a set of well defined localized adsorption sites having sorption energies independent of surface coverage and no interaction between adsorbed

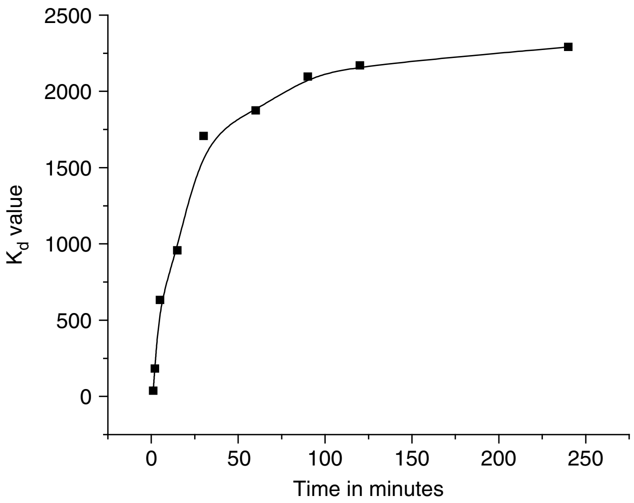

Fig. 4. Effect of contact time on K_d value sorption of ^{99}Tc on anion exchanger.

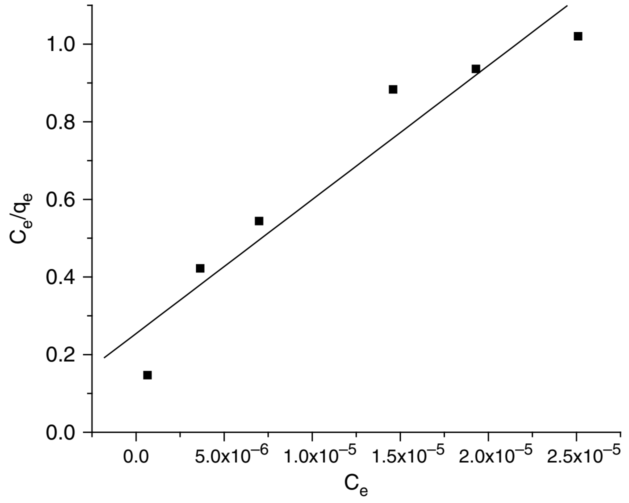

Fig. 5. Langmuir sorption isotherm for sorption of ^{99}Tc on anion exchanger.

Table 2
Adsorption isotherm parameters for sorption of ^{99}Tc on anion exchanger

Langmuir isotherm	D-R isotherm	Freundlich isotherm
$q_0 = 2.89 \times 10^{-5}$ mol/g	$\beta = -3.397 \times 10^{-9}$ mol^2/KJ^2	$1/n = 0.4615$
$b = 1.359 \times 10^5$ dm^3/mol	$E = 12.130$ KJ/mol	$K_f = 3.03 \times 10^{-3}$ mol/g
$R = 0.959$	$X_m = 11.91$ mol/g	$R = 0.9950$
	$R = 0.998$	

molecules. Maximum sorption capacity q_0 represents monolayer coverage of sorbent with sorbate and b represents enthalpy of sorption and should vary with temperature.

3.4. Dubinin–Radushkevich (D-R) isotherm

D-R isotherm is significant within an adsorption 'space' close to sorbent surface [20]. If the surface is heterogeneous and an approximation to a Langmuir isotherm is chosen as a local isotherm for all sites that are energetically equivalent then the quantity $\beta^{1/2}$ can be related to the mean sorption energy, E which is the free energy of the transfer of ^{99}Tc from infinity to the surface of sorbent. The difference in the free energy between the adsorbed phase and saturated liquid sorbate is referred as adsorption potential which was first put forward by Polanyi and later developed by Dubinin and his coworkers [21]. The linearised form of D-R isotherm is given by following equation:

$$\text{In } q_e = \text{In } X_m - \beta\varepsilon^2 \tag{3}$$

where, X_m is the maximum sorption capacity and β is the activity coefficient related to mean sorption energy and ε, the Polanyi potential is given by the equation:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{4}$$

where, R is gas constant in kJ/mole and T is temperature in Kelvin.

The saturation limit (X_m) may represent the total specific micropore volume of the sorbent. The sorption space in the vicinity of a solid surface is characterized by a series of equipotential surfaces having same sorption potential. This sorption potential is independent of the temperature but varies according to the nature of sorbent and sorbate. The plot of ln q_e versus ε^2 is given in Fig. 6. From slope and intercept values of the plot, the values of β and of X_m have been estimated as given in Table 2. The mean sorption energy (E) is the free energy change when one mole of the ion is transferred to the surface of the solid from infinity in solution and can be calculated by using the following relationship. The value of E was estimated and listed in Table 2 [22]:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{5}$$

3.5. Freundlich sorption isotherm

The sorption data were also tested on the following linearised form of Freundlich sorption isotherm:

$$\log\left(\frac{x}{m}\right) = \log K_f + \frac{1}{n}\log C_e \tag{6}$$

A linear plot is obtained when log (x/m) was plotted against log C_e over the concentration range investigated (Fig. 7). From the slope and intercept of straight portion of the plot the values of Freundlich parameter, i.e., $1/n$ and K_f are computed and given in Table 2. These values signify the sorption intensity and capacity respectively. The Freundlich sorption isotherm, one of the most widely used mathematical descriptions usually fits the experimental data over a wide range of concentration.

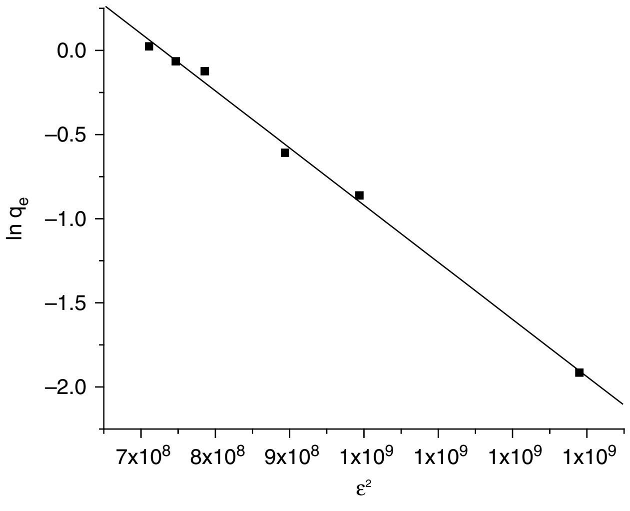

Fig. 6. D-R sorption isotherm for sorption of ^{99}Tc on anion exchanger.

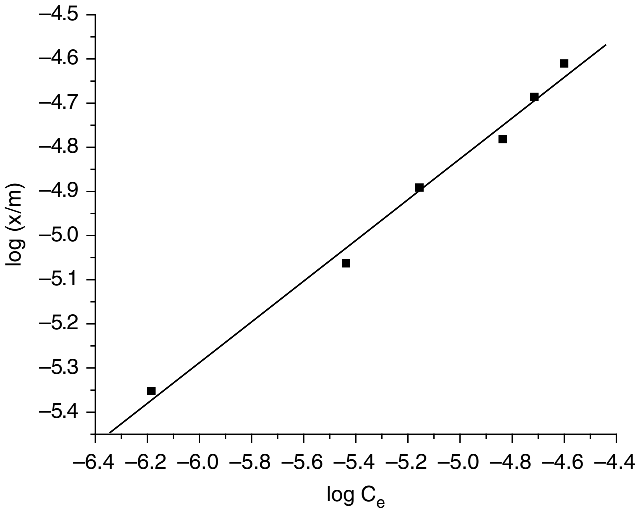

Fig. 7. Freundlich sorption isotherm for sorption of ^{99}Tc on anion exchanger.

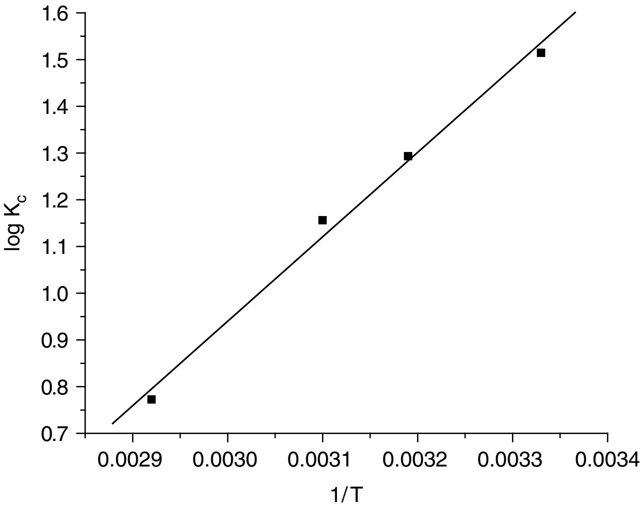

Fig. 8. Vant Hoff plot for sorption of ^{99}Tc on anion exchanger.

It can be seen from all the data that the Freundlich sorption constant ($1/n$) is less than unity. This has physicochemical significance with reference to the qualitative characteristics of the isotherms as well as to the interaction of metal ion species and sorbent surface. It also indicates an increased tendency for sorption with increasing solid phase concentration.

Although the Freundlich and Langmuir constants K_f and q_0 have different meanings, they led to the same conclusion about the correlation of the experimental data with the sorption model. The basic difference between K_f and q_0 is that Langmuir isotherm assumes adsorption free energy independent of both the surface coverage and the formation of monolayer and the solid surface reaches saturation, while the Freundlich isotherm does not predict saturation of the solid surface by the adsorbate and therefore the surface coverage being mathematically unlimited. In conclusion, q_0 is the monolayer sorption capacity while K_f is the relative adsorption capacity or sorption power.

3.6. Thermodynamic studies

According to the adsorption theory, adsorption decreases with increase in temperature. However at higher temperature increasing molecular motion and decreasing viscosity of the solution leading to increase in adsorption has been reported in case of activated carbon [23].

The influence of temperature variation was examined on the sorption of strontium at temperature 27, 40, 50 and 70°C. The plot of log K_c versus $1/T$ is shown in Fig. 8. The value of K_c, the equilibrium constant can be worked at each temperature using the following relationship:

$$K_c = \frac{F_e}{1 - F_e} \tag{7}$$

where, F_e is the fraction sorbed at equilibrium and is given by:

$$F_e = \frac{A_i - F_i}{A_i} \tag{8}$$

where A_i and F_i are initial and final concentration of the adsorbing species.

The equations given below were used to evaluate the values of Gibb's free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS):

$$\begin{aligned} \Delta G &= -RT \ln K_c \\ \Delta G &= \Delta H - T\Delta S \\ -2.303\, RT \log K_c &= \Delta H - T\Delta S \end{aligned} \tag{9}$$

$$\log K_c = \frac{-\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \tag{10}$$

From the slope and intercept of the Van't Hoff plot in Fig. 4, the values ΔH, ΔS and from Eq. (10) ΔG, were computed as given in Table 3. The negative value of ΔG confirms the feasibility of the process and the spontaneous nature of sorption. The value of ΔH was found to be negative and hence the process is exothermic.

Table 3
Thermodynamic parameters for sorption of ^{99}Tc on anion exchanger

Temperautre (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol-K)
300	–8.69	–34.596	85.78

4. Conclusions

Low Level radioactive can be effectively decontaminated with respect to ^{99}Tc using anion exchanger resin column even in presence of high concentration of anionic species at a wide pH range of 1–13. 90% of the loaded ^{99}Tc activity from the column can be eluted with concentrated nitric acid and eluted column can be reused for fresh waste loading. Kinetics of the sorption process was found to be relatively fast. 95% removal was attained with in one hour time period. The sorption was following the Freundlich sorption isotherm model. The negative value of ΔG confirms the feasibility of the process and the spontaneous nature of the sorption and shows the exothermic nature.

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