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Thermodynamic study of yttrium extraction from aqueous solution by ion exchange method

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Abstract
The study of thermodynamics plays an essential role in the analysis of the ion exchange process. In the present study extraction of yttrium(III) from aqueous solution was investigated using Dowex 50W X8 resin. The amount of gibbs free energy changes (ΔG^o) was always positive and the amount of entalphy changes (ΔH^o) was equal to 12.42 kJ/mol, which showed that the process of ion exchange of yttrium(III) from acidic aqueous solution is non-spontaneous and endotermic reaction.

Keywords: Thermodynamic, Aqueous Solution, Ion Exchange, Yttrium Extraction, Dowex 50W X8

Introduction
According to the international union of pure and applied chemistry (IUPAC), rare earth elements are a collection of seventeen chemical elements are a periodic table, including the fifteen lanthanides, yttrium, and scandium [1]. One of these rare elements is yttrium, which has the atomic number 39. Lasers, fluorescent lumps, monitors, and radio frequencies are all made from yttrium. The ion exchange method is more efficient than other methods in the process of extracting low-grade metals from aqueous solution [2]. Most previous research on yttrium extraction has been related to its recycling from fluoresent lamps or its separation from leaching solution. The study of thermodynamics plays an essential role in the analysis of the ion exchange process. In 2019, Hamid et al [3], They prepared the feed solution using $YCl_3.6H_2O$ and sulfuric acid (pH=1.5). Thermodynamics experiments with 0.1 gr resin (purolite C100),50 mL of solution, contac time of 24 hours, rotation speed of 130 rpm, and initial concentration of 500 mg/L yttrium in the temperature range of 298-328°K, performed by them. The results showed that values of ΔG^o, ΔH^o, and ΔS^o were all negative, where indicated that the process was spontaneous and exothermic. In 2021, Zhou et al [4], investigated the adsorption of yttrium from aqueous solution by montmorillonite (Mt). Thermodynamics study eas performed by them, whit 0.5 gr modified Mt, 25 ml of rare earth solution with certain concentration, and varios temperatures (283-323°K). The results showed, adsorption of Y^{3+} on modified Mt is spontaneous endothermic process in the measured temperature range.

Experimental
The thermodynamics parameters of ion exchange were determined using thermodynamic equations at the condition of 0.16 gr resin (Dowex 50W X8 H^+ form 100-200 mesh) and 50 mL 0.6 M sulfuric acid solution contaning 50 mg/L yttrium in the temperature range of 288-328°K. The feed solution was prepared from H_2SO_4 (95-97%) and $Y(NO_3)_3.6H_2O$ (purity 99.8%). The experiments were performed with a contact time of 72 hours and a rotation speed of 150 rpm. Resin preparation was used 0.1M HNO_3 solution. For each experiment, 0.16 gr of resin was contacted with 10 mL of 0.1M HNO_3 solution for 24 hours and then filtered, and used after drying. The specification of Dowex 50W X8 resin are listed in Table1.

Table 1. Specification of Dowex 50W X8 [5]

Resin propertis	
Exchange cation	H^+
Matrix	Styrene-divinylbenzene (gel)
Matrix active group	Sulfonic acid functional group
Cross-linkage	8%
Capacity	1.7 meq/mL
Particle Size	100-200 mesh
Moisture	50-58%
Density	800Kg/m^3

Results and discussion
The temperature of the ion exchange is important for energy dependent mechanism in metals ion exchange by resin. For an increase in temperature from 288K to 328K, an increase in the ion exchange of Y(III) was observed (Fig1).

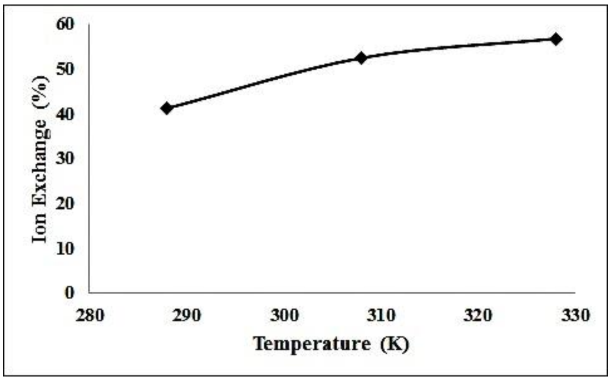

Figure 1. The effect of temperature on ion exchange perecentage (0.6 mol/L H_2SO_4, 0.16 gr resin, 50 mL solution, contact time 72 hr, initial concentration of Y 50 mg/L)

Meena et al [6]. reported tht the increase in ion exchange with temperature may be either attributed to the increase in the number of charged functional group available for ion exchange on the exchanger or owing to the decrease in the boundary layer thickness surrounding the exchanger , so that the mass transfer resistance of exchangeable ions in the boundary layer was decreased. The thermodynamic parameters, changes in the gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) values were calculated by using the Van't Hoff equation [7]:

$$\ln(K_d) = \frac{\Delta S°}{R} - \frac{\Delta H°}{R} \cdot \frac{1}{T} \quad (1)$$

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \quad (2)$$

Where K_d is the distribution coefficient,C_0 is initial concentration (mg/L), C_e is equilibrium concenteration (mg/L), V is volume of solution (L), M is the amount of exchanger (gr), R is the constant gas (8.314 Kj/mol.°K), and T is absolute temperature (°K). A linear plot was obtained by plotting ln (K_d) vs 1/T as shown in Figure 2.

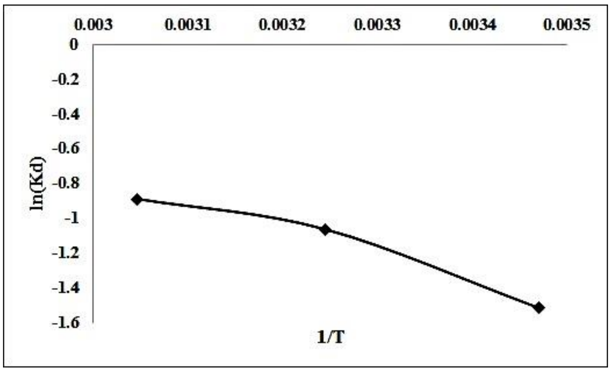

Figure 2. Relationship between ln(K_d) and 1/T (0.6 mol/L H_2SO_4, 0.16 gr resin, 50 mL solution, contact time 72 hr, initial concentration of Y 50 mg/L)

R^2 is 0.9551. ΔH°, ΔS° obtained from slope and intercept respectively. ΔG° can be calculated from the following equation 3 and equation 4 [6]. The values of ΔG°, ΔH°, and ΔS° listed in the Table 2.

$$\Delta G° = -RT\ln(K_d) \quad (3)$$

$$\Delta G° = \Delta H - T\Delta S \quad (4)$$

Table 2. Results of thermodynamic study in the ion exchange process of yttrium

T(°K)	Ln K_d	ΔH° (kJ/mol)	ΔS° (kJ/mol.°K)	ΔG° (kJ/mol)
288	-1.515			3.542
308	-1.063	12.426	0.0308	2.925
328	-0.888			2.309

Conclusions

The process of ion exchange of yttrium from aqueous solution was performed by Dowex 50W X8 resin .The positive ΔH° suggests the endothermic nature of ion exchange behavior among 288-328°K and a large amount of heat is consumed to transfer the Y^{3+} from aqueous into solid phase. The rare earth ions must give up a larger proportion of the hydration water so as to enter the smaller cavities. The positive value of ΔS° reflected the affinity of Exchanger particles toward Y(III). The gibbs free energy changes have always been positive, indicating that the ion exchange process is non-spontaneous. Although observed, with increasing temperature, the amount of gibbs free energy decreases, this means that the increasing temperature causes the process to gradually tend to be spontaneous.

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