Characters of Kinetic and Equilibrium of Adsorption of Eu(III) by an Cation Exchange Resin

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ABSTRACT: *The sorption and desorption behaviors of Eu(III) from aqueous solutions with cation exchange resins containing carboxyl groups (D155 resin) were studied in terms of varied Eu(III) concentration, adsorbent dosage, pH, contact time and temperature. Batch shaking sorption experiments were carried out to evaluate the performance of D155 resin in the removal of Eu(III) from aqueous solutions. The loading of Eu(III) ions onto D155 resin was found to increase significantly with the initial Eu(III) concentration increasing. The sorption was strongly dependent on pH of the medium with enhanced sorption as the pH changes from 4.00 to 6.40. The concentration of Eu(III) in aqueous solution was determined by UV–visible spectrophotometer. The adsorption kinetics, tested with Lagergren-first-order model and pseudo-second-order model, showed better agreement with Lagergren-first-order kinetics. The suitability of the Freundlich and Langmuir adsorption models was also investigated for europium–sorbent system. The thermodynamic parameters such as ΔG, which were all negative, indicated that the adsorption of Eu(III) ions onto D155 resin was spontaneous and the positive value of ΔH showed that the adsorption was endothermic in nature. Eu(III) ions can be eluted by using the 0.5mol/L HCl solution. The surface characteristic of Eu(III) on D155 resin before and after adsorption was shown using IR spectroscopic technique. Therefore, it has a good potential of the removal of Eu(III) from aqueous solutions.*

KEY WORDS: *Cation exchange resin (D155 resin), Europium(III), Kinetics, Thermodynamic, Equilibrium*.

INTRODUCTION

The safety of nuclear waste repositories and the assessment of radionuclide mobility in the environment have become a subject for various studies. Adsorption behavior of radionuclides on resins is a major process controlling the physicochemical behavior of radionuclides in the environment. Therefore, the knowledge of radionuclide adsorption is of great importance in the management of radioactive wastes containing long-lived lanthanides. Eu(III) is a trivalent lanthanide and a chemical homologue of trivalent actinides as both trivalent lanthanides and actinides exhibit similar adsorption properties. Europium oxide is used in fluorescence powder. Now Y_2O_2S: Eu^{3+} is the best fluorescence powder with the numerous merits: such as light-emitting efficiency, coating stability, cost recovery. In addition, to improve the luminous efficiency and

Table1: The physical-chemical properties of D155 resin.

Trade name	Moisture content (%)	Exchange capacity (mmol/g) $\geq$	True wet density (g/mL)	Bead size (mm)
D155 resin	40-50	9.5	0.70-0.78	0.3-1.2

technology it is being widely used. Europium oxide has also been used in stimulated emission fluorescence powder of new medical diagnostic X-ray system in recent years. Moreover, it can also be applied in magnetic bubble storage devices, in the manufacture of tinted lenses and optical filters and in the atomic reactor control materials, shielding materials and structural materials.

Solvent extraction and ion-exchange resin [1,2] are two of the most common methodologies for the preconcentration and separation of trace elements from various matrices. Solvent extraction is inefficient due to the requirement of large volume of solvent which may cause health problem. In addition, solvent extraction procedures are usually time-consuming and labor-intensive. Ion exchange resins have been used in the chemical analysis for over 50 years. They are solid and suitably insolubilized high molecular weight polyelectrolytes which can exchange their mobile ions for ions of equal charge from the surrounding medium. As a result, the ion exchange is reversible and stoichiometric with the displacement of one ionic species by another on the exchanger. Therefore, based on a number of scientific and economical considerations, the method of ion exchange resins for the recovery of valuable species or for the removal of toxic species has been well established [3]. Most of the papers related to the separation and enrichment of metal ions (including europium) used such methods as co-precipitation [4], solvent extraction [5], electroanalytical techniques [6], and solid phase extraction [7]. Various adsorbents including TiO_2 [8], N,N,N',N'-tetraoctyl diglycolamide [9], zeolites [10], chelating resins [11], hydrous metal-oxides [12], montmorillonite [13] and extraction chromatographic resin [14] were used in extraction of europium ions from various media. D155 cation-exchange carboxylic resins which have carboxylic groups as an exchange site are produced by means of the co-polymerization of methyl methacrylate with DVB and followed by hydrolysis. However, carboxyl, sulphate groups have been identified as the main metal-sequestering sites [15]. It has not only protons that can exchange with cation, but also oxygen

atoms that can coordinate directly with metal ions. The extraction studies for traces metal ions on macroporous weak acidic polyacrylic resins have been performed by various authors [16]. According to our literature survey, the research has scarcely been found on the use of D155 cation-exchange carboxylic resins for europium preconcentration.

The study of Eu(III) adsorption onto D155 resin is helpful and essential for the evaluation of trivalent lanthanides physicochemical behavior. In this work, the adsorption of Eu(III) from aqueous solutions using batch adsorption method was investigated with D155 cation-exchange carboxylic resins. Some factors affecting adsorption, such as contact time, initial pH of solution, initial concentration of Eu(III) and temperature were examined. Kinetics and isotherm adsorption experiments were carried out. Thermodynamic parameters of adsorption for Eu(III) ion were calculated. The experimental results may provide a new way for the adsorption of Eu(III) from aqueous solutions in the hydrometallurgical processes.

EXPERIMENTAL SECTION
Materials and Instruments

D155 resin was provided by Tianjin Nankai Hecheng S&T Co., Ltd, activated before use; It's physical–chemical properties were given in Table.1. Stock solution of Eu(III) was prepared by dissolving 1.0000g europium with a purity of 99.99% and 8mL concentrated HCl in purified water. Buffer solution (HAc ~ NaAc) with pH 4.00-6.40 and $C_6H_{15}O_3N$-HNO_3 buffer solutions with pH 7.20 were prepared from HAc, NaAc, $C_6H_{15}O_3N$ and HNO_3 solutions. The chromophoric reagent of 0.1% arsenazo-I solution was obtained by dissolving 0.1000g arsenazo-I into 100mL purified water. All other chemicals were of analytical grade.

Eu(III) was determined with Shimadzu UV-2550 UV-vis spectrophotometer. Mettler toledo delta 320 pH meter was used for measuring pH. The sample was shaken in the DSHZ - 300A temperature constant shaking machine.

A solution containing lower than 75μg of Eu(III) was accurately added into a 25mL colorimetric tube, and then 1mL 0.1% arsenazo-I solution and 10mL, pH 7.20 $C_6H_{15}O_3N$-HNO_3 buffer solutions were added, after addition of deionized water to the mark of colorimetric tube, the absorbency was determined in a 1cm colorimetric vessel at wavelength of 573nm and compared with blank test. The adsorption capacity (Q) of Eu(III) ions was calculated with the following formula:

$$Q = \frac{C_o - C_e}{W} V \tag{1}$$

The distribution coefficient (D) of Eu(III) ions between the aqueous phase and the solid phase can be directly obtained using:

$$D = \frac{C_o - C_e}{C_e} \times \frac{V}{W} \tag{2}$$

where C_o (mg/mL) and C_e (mg/mL) are the initial and equilibrium Eu(III) concentrations, respectively, V/W is the ratio of the volume of metal solution (mL) to the amount of D155 resin (g) in a batch.

Batch experiments

Batch experiments were performed under kinetic and equilibrium conditions. A desired amount of treated D155 resin was weighed and added into a conical flask, in which a desired volume of buffer solution was added. After 24 h, a required amount of standard solution of Eu(III) was put in. The flask was shaken in a shaker at constant temperature. The upper layer of clear solution was taken for analysis until adsorption equilibrium reached. The procedure of kinetic tests was identical to that of the equilibrium tests. The aqueous samples were taken at preset time intervals and the concentrations of Eu(III) were similarly measured.

RESULTS AND DISCUSSIONS
Effect of pH

The pH of aqueous solution has been identified as the most important variable governing the adsorption capacity of adsorbent. The influence of pH on the adsorption behavior of D155 resin for Eu(III) was illustrated in Fig.1 that the uptake of Eu(III) ion as a function of hydrogen ion concentration was in the range of pH 4.00–6.40 for an initial concentration of Eu(III) 10.0mg/ 30.0mL at 298K, 100 r/min. It can be easily seen
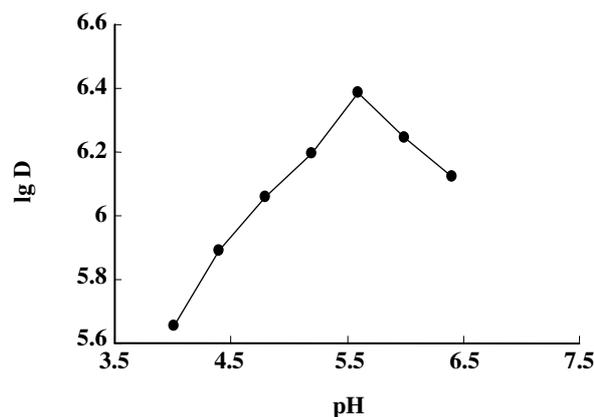

Fig. 1: Effect of pH Resin 15.0 mg, C_0 =10 mg/30.0 mL, T=298K, 100 r/min.

that the adsorption capacity for Eu(III) was the highest when pH value was 5.59 in the HAc-NaAc medium and decreased by either raising or lowering pH under the experimental conditions. At lower pH values, the Eu(III) ion uptake was inhibited in the acidic medium and this can be attributed to the presence of H^+ ion competing with the Eu(III) ion for the adsorption sites. Contrarily, the Eu(III) ion was prone to deposit at higher pH values [17]. Therefore, all the following experiments were performed at pH 5.59 in the HAc-NaAc system.

Effect of resin dosage

It may be concluded that the sorption capacity increases but ion exchange density decreases by increasing the ion exchanger dosage. The percentage metal removal was higher at the beginning due to large number of resin exchange sites available for the sorption of the metal. The decrease in ion exchange density can be attributed to some of the ion exchange remains unsaturated during the sorption process; whereas the number of available ion exchange sites increases by an increase of sorbent (Fig.2) and the sorption capacity increases [18]. The equilibrium concentration increases with increasing sorbent doses for a given initial Eu(III) concentration, because increasing sorbent doses provide a greater surface area or ion exchange sites for a fixed initial solute concentration [18-20].

Effect of initial Eu(III) concentration

A higher initial concentration provides an important driving force to overcome mass transfer resistances of the Eu(III) between the aqueous and solid phases, thus

increases the uptake. In addition, increasing initial Eu(III) concentration increases the number of collisions between Eu(III) ions and sorbent, which enhances the adsorption process. The effect of initial Eu(III) concentration on the adsorption capacity of D155 resin was investigated between 0.10g/L and 0.37g/L at different temperatures and was illustrated in Fig. 3. The effect of initial Eu(III) concentration on the adsorption capacity was found to be of considerable significant for all temperatures studied. The equilibrium Eu(III) uptake was enhanced notably as the initial concentration of Eu(III) increased and almost no saturation was observed at higher concentrations. At 288K, when the initial Eu(III) concentration increased from 0.10g/L to 0.37g/L, the uptake capacity of D155 resin increased from 200 to 327 mg/g. At 0.37mg/mL initial Eu(III) concentration, with the change of temperature from 288K to 308K, the uptake capacity increased from 327 to 345 mg/g.

Effect of contact time and temperature

The influence of contact time on the adsorption of Eu(III) ions onto D155 resin (Fig.4) was investigated at various temperatures, i.e. 288K, 298K, 308K. It is easily seen that the amount of adsorption increased with increasing contact time. In the first 6h the adsorption capacity increased rapidly, after 7h they increased slowly and the maximum adsorption was observed after 11h, beyond which there was almost no further increase in the adsorption. Therefore, this interaction time could be very well taken as equivalent to the equilibrium time. Meanwhile, the equilibrium adsorption capacity of Eu(III) ions onto D155 resin was found to increase with increasing temperature, indicating that the adsorption of Eu(III) ions onto the adsorbent was favored at higher temperatures. This effect suggests that an explanation of the adsorption mechanism associated with the removal of Eu(III) ions onto D155 resin involves a temperature dependent process.

Adsorption kinetic model

Several kinetic models are available to examine the controlling mechanism of adsorption from a liquid phase on D155 resin and to interpret the experimental data obtained. The kinetics of adsorption can be described by the Lagergren-first-order rate expression [21, 22] that is given by Eq.(3).
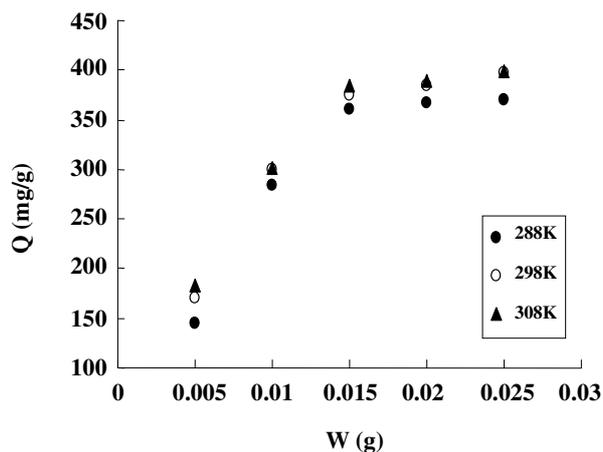
Fig. 2: Effect of resin dosage C₀ =10.0 mg/30.0 mL, T=298K, 100 r/min.
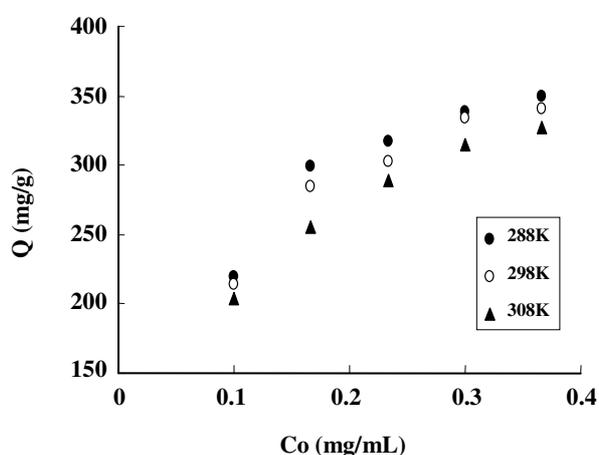
Fig. 3: Effect of initial Eu(III) concentration Resin 15.0 mg, C₀ =0.10 0.37mg/mL, T=288K, 298K, 308K.
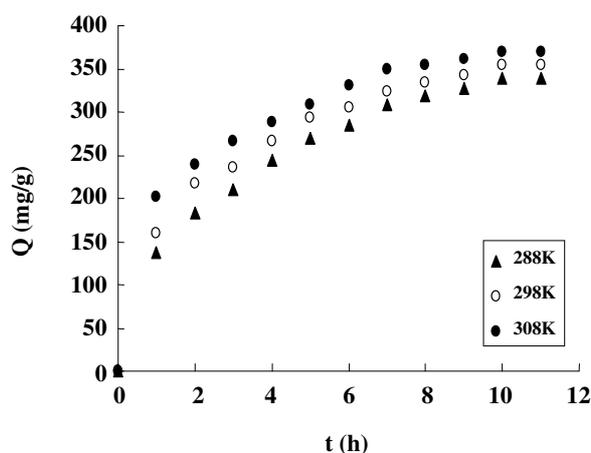
Fig. 4; Effect of contact time and temperature Resin=15.0 mg, C₀ =10.0 mg/30.0 mL, pH=5.59, 100 r/min.

Table 2: Comparison of Lagergren-first-order and pseudo-second-order kinetics models of D155 resin adsorption.

T (K)	Lagergren-first-order		Pseudo-second-order	
	k_1' (h^{-1})	R_1^2	k_2 (g/(mg·h))	R_2^2
288	0.2799	0.9957	0.0025	0.9814
298	0.2857	0.9897	0.0025	0.9352
308	0.2897	0.9820	000024	0.9707

$$lg\left(Q_l - Q_t\right) = \log Q_l \frac{k_1}{2.303} t \qquad (3)$$

The pseudo-second-order kinetic model equation [23–25] is given as:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_2^2} + \frac{t}{Q_2} \qquad (4)$$

where Q_e and Q_t are the amounts of Eu(III) ions adsorbed on the adsorbent at equilibrium and at various times t (mg/g); Q_1 and Q_2 are the calculated adsorption capacity of the Lagergren-first-order model and the pseudo-second-order model (mg/g), respectively; k_1 and k_2 are the rate constant of the Lagergren-first-order model (h^{-1}) and the pseudo-second-order model (g/(mg·h)).

The Lagergren-first-order model could be converted as follows:

$$-ln\left(1 - \frac{Q_t}{Q_e}\right) = k_1' t \qquad (5)$$

Namely Boyd G. E. [26] equation:

$$-ln\left(1 - F\right) = k_1' t \qquad (6)$$

where F is the fractional attainment of equilibrium (F = Q_t/Q_e). A linear plot of -ln(1 - F) vs t with zero intercept would suggest that the kinetics of the adsorption process is controlled by diffusion through the liquid film surrounding the solid adsorbents.

The fitting validity of these models is traditionally checked by the linear plots of $ln(Q_e - Q_t)$ vs t, and t/Q_t vs t, respectively. From the slope and intersection of the straight line obtained, the corresponding constant values for the Lagergren-first-order and pseudo-second-order kinetic models, for each temperature studied, provide the respective kinetic constants, k_1', k_2, R_1^2, R_2^2 parameters.

The correlation coefficient (R_1^2) for the Lagergren-first-order equation was better than the correlation coefficient

(R_2^2) for the pseudo-second-order equation, ranging from 0.9820 to 0.9957 and 0.9352 to 0.9814, respectively (Table.2). Thus, good linearity of the Lagergren-first - order plots was revealed that the interactions would follow the first order kinetics. This meant that the Lagergren-first-order kinetic model can describe the Eu(III)/D155 resin adsorption system studied in our work [27].

Sorption Isotherms

A sorption isotherm describes the relationship between the capacity of adsorbate that is adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium. Several two or three parameter models have been published in the literature to describe experimental data of sorption isotherms. The *Langmuir* [28] and *Freundlich* [29] models are the most frequently used models.

Langmuir isotherm

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \qquad (7)$$

Freundlich isotherm

$$lg Q_e = lg K_F + \frac{1}{n} lg C_e \qquad (8)$$

where Q_e is the equilibrium Eu(III) ions concentration on the adsorbent (mg/g), C_e is the equilibrium Eu(III) ions concentration in solution (mg/mL), Q_m is the monolayer capacity of the adsorbent (mg/g) and K_L is the Langmuir constant and related to the free energy of adsorption; K_F is Freundlich constant and n (dimensionless) is the heterogeneity factor. The plots of C_e/Q_e vs C_e (Langmuir) for the adsorption of Eu(III) ions onto D155 resin give a straight line of slope $1/Q_m$ and intercept $1/Q_m K_L$; by plotting $lg C_e$ vs $lg Q_e$ (Freundlich) to generate K_F and n from the intercept and the slope,

Table 3: Isotherm constants for the adsorption of Eu(III) on D155 resin at various temperatures.

T (K)	Langmuir			Freundlich		
	Q_m (mg/g)	K_L (mL/mg)	R_L	n	K_F (mg/g)	R_F
288	345	145	0.9972	1.48	227	0.9881
298	357	140	0.9982	1.76	283	0.9817
308	370	270	0.9991	1.52	389	0.9849

Table 4: Thermodynamic parameters for Eu(III) on D155 resin.

ΔH (kJ/mol)	ΔS (J/(K·mol))	ΔG (kJ/mol)		
		T = 288K	T = 298K	T = 308K
31.1	190	− 23.5	− 25.5	− 27.4

respectively. One of the Freundlich constants K_F indicates the adsorption capacity of the adsorbent [30]. The other Freundlich constants n is a measure of the deviation from linearity of the adsorption. The numerical values of n at equilibrium lay between 1.48 and 1.76, indicating that Eu(III) ions was favorably adsorbed by D155 resin at all the studied temperatures [31].

The Langmuir and Freundlich parameters for the adsorption of Eu(III) ions are being listed in Table.3. It is evident from these data that the adsorption of Eu(III) ions onto D155 resin is fitted well to the Langmuir isotherm model than that of the Freundlich isotherm models, as indicated by the R^2 values and the adsorption capacity values in Table.3. The Langmuir model is the best-known isotherm for describing adsorption from aqueous solution. The Langmuir model assumes that there is no interaction between the adsorbate molecules. The adsorption is localized in a monolayer. The maximum adsorption capacity (Q_m) of adsorbent calculated from Langmuir isotherm equation defines the total capacity of the adsorbent for Eu(III) ions. The adsorption capacity increased with an increase in the temperature. The highest value of Q_m obtained at 308K is 370 mg/g.

In any adsorption procedure, both energy and entropy considerations should be taken into account in order to determine which process will take place spontaneously. Values of thermodynamic parameters are the actual indicators for practical application of a process. The amounts of Eu(III) ions adsorbed at equilibrium at different temperatures, which are 288K, 298K and 308K, have been examined to obtain thermodynamic parameters for the adsorption system.

Because K_L is the Langmuir constant and its dependence with temperature can be used to predict

thermodynamic parameters, such as changes in the Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) associated to the adsorption process and were determined by using following equations:

$$\Delta G = -RT \ln K_L \tag{9}$$

$$\ln K_L = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{10}$$

where R is the gas constant and T is the absolute temperature as mentioned in Arrhenius equation. The plot of $\ln K_L$ vs 1/T gives the straight line from which ΔH and ΔS was calculated from the slope and intercept of the linearised form. Table.4 shows the values of thermodynamic parameters of Eu(III) ions adsorption onto D155 resin. The negative value of ΔG confirms the spontaneity of the adsorption process with increasing temperature and the positive value of ΔH suggests that the adsorption is endothermic in nature. Although there are no certain criteria related to the ΔH values that define the adsorption type, the heat of adsorption values between 5.0 and 100 kcal/mol (20.9–418.4 kJ/mol), which are heats of chemical reactions, are frequently assumed as the comparable values for the chemical adsorption process. In addition, the values of ΔS were found to be positive due to the exchange of the metal ions with more mobile ions present on the exchanger, which would cause increase in the entropy, during the adsorption process [32].

Elution

15.0 mg D155 resin was added into a mixed solution composed of pH 5.59 buffer solution and desired amount of Eu(III) solution. After equilibrium reached, the concentration of Eu(III) in the aqueous phase was

Table 5 The elution test of Eu(III) ions:

Concentration of HCl (mol/L)	0.5	1.0	2.0	3.0
Elution percentage (%)	100	99.35	98.23	96.15

Fig. 5: Infrared spectra.

adsorption. Therefore, the functional groups of D155 resin, C=O, C-OH and Eu(III) are supposed to form chemical bonds. To identify the possibility of Eu(III) bonding to resin, IR spectra were obtained for D155 resin before and after Eu(III) adsorption, as shown in Fig.5. In general, it is observed that there are significant changes in the IR spectra of D155 resin before and after Eu(III) adsorption. It should be noticed that the band at $3429cm^{-1}$ is stretching vibrations of the surface hydroxyl groups, $1713cm^{-1}$ and $1539cm^{-1}$ is an indication of C=O. The bands at $1405cm^{-1}$ and $1415cm^{-1}$ assigned to the peak of the bond C-OH [33]. It was found that the characteristic absorption peak of the bond C=O ($1713cm^{-1}$) weakened after Eu(III) adsorption, and the new peak $1539cm^{-1}$ formed. The characteristic peak of the bond C-OH shifts from $1405cm^{-1}$ to $1415cm^{-1}$. These results show that there are coordination bonds between oxygen atoms and Eu(III) and that H of C-OH has been exchanged with the formation of a complex compound. These results revealed that the C=O groups participate in the adsorption process.

CONCLUSIONS

On the base of the experimental results, it is possible to conclude that:

• The D155 resin containing carboxylic group has very good potential for utilization as an adsorbent for Eu(III) from aqueous medium.

• Variables, such as pH, contact time, and temperature can affect the sorption behavior. Maximum Eu(III) recovery was obtained at pH 5.59, 298K.

• The kinetics of adsorption of Eu(III) on D155 resin are complex and while the results were tested with models based on the Lagergren-first-order, pseudo-second-order, close conformity could be obtained with Lagergren-first-order mechanism.

• It is evident from the experimental data that the adsorption of Eu(III) ions is fitted well to the Langmuir isotherm model than that of the Freundlich isotherm models and the adsorption coefficients agree well with the conditions supporting favourable adsorption.

determined, and the adsorption capacity of D155 resin for Eu(III) was obtained.

Then, the D155 resin separated from aqueous phase was washed three times with pH 5.59 buffer solution. The D155 resin adsorbed Eu(III) was shaken with 30.0mL HCl eluant. After equilibrium reached, the concentration of Eu(III) in aqueous phase was determined and then the percentage of elution for Eu(III) was obtained. The results listed in Table.5 showed that the percentage of elution for Eu(III) was different when the concentration of HCl is changed. It was evident from data that the maximum percentages of elution for Eu(III) was obtained by using the 0.5mol/L HCl solution as an eluant.

Infrared spectra analysis

From the results above, it can be deduced that the adsorption of Eu(III) by D155 resin belongs to a chemical

• The adsorption process is endothermal and spontaneous at ambient higher temperatures.

• Involvement of various functional groups (C=O, -OH) is indicated by the observed IR spectral changes after adsorption. The results show that D155 resin is the effective adsorbent for the removal of Eu(III) ions.

Nomenclature

Q	Adsorption capacity, mg/g
D	Distribution coefficient
C_o	Initial Eu(III) ions concentration, mg/mL
C_e	Equilibrium Eu(III) ions concentration, mg/mL
V	Volume of metal solution, mL
W	Amount of D155 resin in the batch, g
Q_e	Adsorption capacity at equilibrium time, mg/g
Q_t	Adsorption capacity at various times, mg/g
Q_1	Calculated adsorption capacity of Lagergren-first-order model, mg/g
Q_2	Calculated adsorption capacity of pseudo-second-order model, mg/g
k_1	Lagergren-first-order rate constant, min^{-1}
k_2	Pseudo-second-order rate constant, g/(mg·min)
K_F	Freundlich constant, mg/g
K_L	Langmuir constant, mL/mg
R^2	Correlation coefficient

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