Adsorption Behavior of MWAR Toward Gd(III) in Aqueous Solution

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ABSTRACT: *Adsorption and desorption behavior of Gd(III) ion on macroporous weak acid resin (MWAR) had been investigated. The influence of operational conditions such as contact time, initial concentration of Gd(III) ion, initial pH of solution and temperature on the adsorption of Gd(III) ion had been examined. Experimental data were exploited for kinetic and thermodynamic evaluations related to the adsorption processes. Adsorption isotherms were attempted to be obtained the model parameters at different temperature and to be fitted better to Langmuir model than to Freundlich model within the studied concentration range. The maximum adsorption capacity of Gd(III) ion on MWAR was 384 mg/g at 298 K, calculated from Langmuir model. The apparent activation energy was $E_a = 18.0$ kJ/mol and adsorption rate constant was $k_{298} = 1.22 \times 10^{-5}$ s^{-1}, respectively. Thermodynamic parameters such as changes in the enthalpy (ΔH), entropy (ΔS) and Gibb's free energy (ΔG) indicated that Gd(III) ion adsorption by MWAR was an endothermic and spontaneous process in nature, and more favorable adsorption was obversed when the ambient temperature was high Gd(III) can be eluted with the composition of 0.5mol/L HCl and 0.5 mol/L NaCl solution.*

KEY WORDS: *Macroporous weak acid resin (MWAR), Gd(III), Thermodynamics, Kinetics, Adsorption.*

INTRODUCTION

Gadolinium, a soft silvery metallic element, is found in the lanthanide series of inner transition metals of the periodic table. Lanthanide series have gained a great attention owing to their unique properties and wide range of applications, especially used in metallurgy, ceramic industry and nuclear fuel control. For example, gadolinium oxide, one of its largest uses in nuclear power reactors is as shielding and fluxing devices [1]. Gd(III) ion, known as fission product, can leak to the environment and cause risks. Consequently, it is considered as hazardous material [2].

In recent years, there is a constant demand for more selective resins for the recovery of either toxic or valuable metals from liquids [3-10] Different techniques have been applied for group separation and preconcentration of REEs, off-line techniques including batch experiments, solid phase extraction (SPE) and counter current chromatography (CCC), as well as on-line methods using

Table 1: General description and properties of resin.

Resins	Functional group	Structure	Chemical composition	Average pore diameter (nm)	Surface area (m^2/g)	Capacity (mmol/g)	Thermal stability (°C)
MWAR	-COOH	macro porous	crylic acid	10.3	4.8	8.0	<100

SPE chromatographic units, cloud-point and liquid/liquid extraction. Various agents such as iminodiacetates, 8-hydroxyquinoline, resins, along with organophosphates have been used in these techniques [11]. Amongst those materials, resins were studied as available material in industrial wastewater treatment in China because of their high removal efficiency, `feasibility in application, as well as the potential to extract toxic or valuable metals from the waste steams. Macroporous weak acid resin (MWAR) is a polymeric material containing a functional group (-COOH), and it could be adopted to the adsorption of metal ions from aqueous solutions.

In this work, the removal of Gd(III) from aqueous solutions using batch and column adsorption method has been investigated by MWAR. Some factors to affect the adsorption, such as contact time, initial pH of solution, initial concentration of Gd(III) and temperature, were examined. Kinetics and isotherm adsorption experiments were carried out. Thermodynamic parameters of adsorption for Gd(III) were calculated. The Thomas model was applied to experimental data obtained f rom column adsorption experiments. The experimental results may provide a path for the removal of Gd(III) from aqueous solutions in the environmental protection and the preconcentration and recovery of Gd(III) in hydrometallurgical processes.

EXPERIMENTAL SECTION
Apparatus
The Gd(III) was determined with Shimadzu UV-2550 UV-vis spectrophotometer. Mettler toledo delta 320 pH meter was used for measuring pH of solutions. The sample was shaken in the DSHZ-300A and the THZ-C-1 temperature constant shaking machine. The water used in the present work was purified using Molresearch analysis-type ultra-pure water machine.

Materials
Macroporous weak acid resin was supplied by Nankai University and the properties were shown in Table 1. Standard solutions of metal ions were prepared from

gadolinium nitrate (AR). HAc-NaAc buffer solution with pH 4.50–6.70 and $C_6H_{15}O_3N$-HNO_3 buffer solutions with pH 7.20 were prepared from the NaAc, HAc, $C_6H_{15}O_3N$ and HNO_3 solutions. The chromophoric reagent of 0.1% arsenazo-I solution was obtained by dissolving 0.1000g arsenazo-I powder into 100mL purified water. All other chemicals were of analytical grade and purified water was used throughout.

Adsorption experiments
Experiments are run in a certain range of pH, temperature, contact time as well as adsorption isotherms. The operation for the removal of Gd(III) was carried out in batch vessels and glass columns.

Batch experiments were performed under kinetic and equilibrium conditions. A desired amount of treated MWAR was weighed and added into a conical flask, in which a desired volume of buffer solution with pH 6.70 was added. After 24 h, a required amount of standard solution of Gd(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 Gd(III) were similarly measured.

Continuous packed bed studies were performed in a fixed bed mini glass column (Φ3 mm×30 cm) with resin and filled with Gd(III) solution. At the bottom of the column, a stainless sieve was attached followed by a layer of cotton wool. The particles were dropped in from the top of the column. Time taken by the particles to travel a distance in vertical direction was noted. The Gd(III) solutions at the outlet of the column were collected at regular time intervals and the concentration of Gd(III) was measured using a UV-visible spectrophotometer at 575 nm. All the experiments were carried out at room temperature.

Analytical method
A solution containing lower than 75μg of Gd(III)

was accurately added into a 25mL colorimetric tube, and then 1.0mL of 0.1% arsenazo-I solution and 10mL pH 7.20 $C_6H_{15}O_3N$-HNO_3 buffer solution were added, after the addition of redistill water to the mark of colorimetric tube, the absorbency was determined in a 1cm colorimetric vessel at wavelength of 575nm and compared with blank test. The adsorption amount (Q, mg/g) and distribution coefficient (D, mL/g) were calculated with the following formulas:

$$Q = \frac{C_o - C_e}{W} V \qquad (1)$$

$$D = \frac{C_o - C_e}{W \cdot C_e} V \qquad (2)$$

where C_o is initial concentration (mg/mL), C_e is equilibrium concentration (mg/mL), V is solution volume (mL), W is MWAR weight (g)

RESULTS AND DISCUSSION

Influence of pH on the distribution coefficient for Gd(III)

The initial pH of solution significantly affected the adsorption capacity of adsorbent. The influence of pH on the adsorption behavior of MWAR for Gd(III), illustrated in Fig. 1, shows that the uptake of Gd(III) ion as a function of hydrogen ion concentration was in the range of pH 4.50–6.70 for an initial concentration of Gd(III) 10.0mg/30.0mL at 298K, 100 rpm. It can be easily seen that the adsorption capacity for Gd(III) was the highest when pH was 6.70 in the HAc-NaAc medium and decreased by either raising or lowering pH under the experimental conditions. At lower pH values, the Gd(III) ion uptake was inhibited in the acidic medium and this can be attributed to the presence of H^+ ion competing with the Gd(III) ion for the adsorption sites. Contrarily, the Gd(III) ion was prone to deposit at higher pH values [12]. Therefore, all the following experiments were performed at pH 6.70 in the HAc-NaAc system.

Determination of adsorption rate constant and apparent activation energy

The adsorption kinetics was determined according to the following procedure: 30mL mixture solution of the buffer and Gd(III) solution (10.0mg/30.0mL) was shaken with 15.0 mg of MWAR at 288K–308K. At predetermined
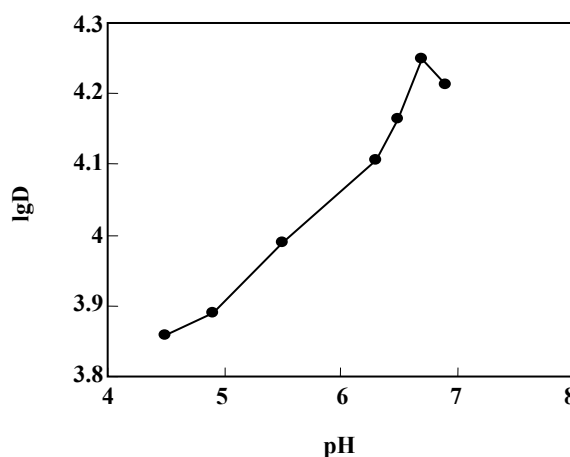

Fig. 1: Influence of pH on the distribution coefficient of Gd(III) Resin 15.0 mg, $[Gd^{3+}]_0$ =10 mg/30.0 mL, T=298K, 100 rpm.

intervals, aliquots of 0.2mL solution were taken out for analysis and the concentration of Gd(III) was determined. After the remains kept constant and volume was corrected, a series of data were obtained as shown in Fig. 2. It can be seen that an increase of the temperature deals induced an increase in the uptake of Gd(III) adsorption. It meant that the adsorption process was an endothermic process. The adsorption capacity of Gd(III) ions calculated from Fig. 2 was 379 mg/g MWAR at 298K. Further, the loading half time $t_{1/2}$ was 7h and the equilibrium time t was 30h.
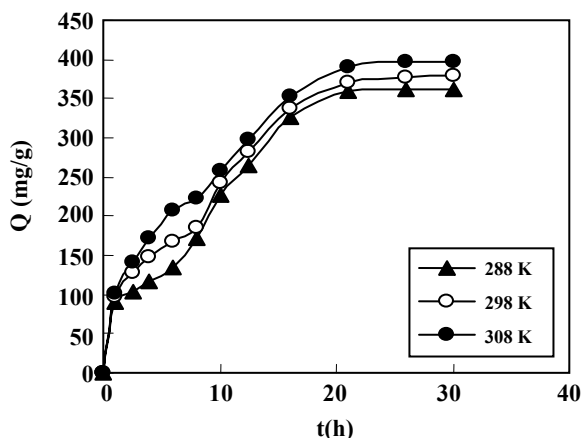
According to the *Brykina* method [13], the adsorption rate constant *k* can be calculated from:

$$-\ln(1-F) = kt \qquad (3)$$

where F is the fractional attainment of equilibrium (F=Q_t/Q_e), Q_t (mg/g) and Q_e (mg/g) are the adsorption amounts at certain time and at equilibrium time, respectively. The experimental results accorded with the equation and a straight line was obtained by plotting –ln(1–F) vs t as shown in Fig. 3. Therefore, the adsorption rate constant can be found from the slope of the straight line, which is $k_{298} = 1.22 \times 10^{-5} s^{-1}$. The correlation coefficient (R^2=0.9986) was obtained via linear fitting. The other results were listed in Table 2. According to the *Boyd* equation, it can be deduced from the linear relationship of –ln(1–F) vs t that the liquid film spreading was the predominating step of the adsorption process [14].

Table 2: Adsorption rate constants (k) and correlation coefficient (R²) for the adsorption of Gd(III) with MWAR.

T (K)	288	298	308
k ($\times 10^{-5} s^{-1}$)	0.97	1.22	2.07
R^2	0.9966	0.9986	0.9979

Fig. 2: Adsorption kinetics and capacity Q at different times and different temperatures Resin 15.0mg, [Gd³⁺]₀=10.0mg/30.0mL, pH=6.70, 100 rpm.

Fig. 3: Determination of adsorption rate constant Resin 15.0mg, [Gd³⁺]₀=10.0mg/30.0mL, pH=6.70, 100 rpm.
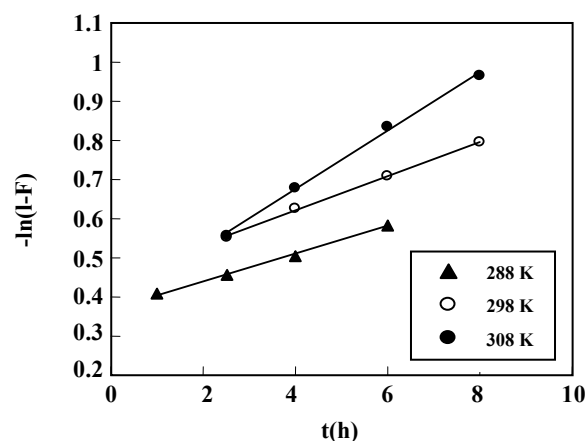
According to the *Arrhenius* equation:

$$\lg k = -\frac{E_a}{2.303RT} + \lg A \tag{4}$$

where E_a is the *Arrhenius* activation energy for the adsorption process indicating the minimum energy that reactants must have for the reaction to proceed, A is the *Arrhenius* factor, R is the gas constant (8.314 J/(mol·K)), k is the adsorption rate constant and T is the solution temperature. E_a and A values can be estimated from slope and intercept value of this plot lgk vs 1/T, respectively. The slope of straight line was $K_{slope}= -0.9407$. The correlation coefficient of the straight line $R^2 = 0.9864$ was achieved. The apparent activation energy E_a was 18.0 kJ/mol, which could be considered as a low energy barrier in this study. It can be deduced that the adsorption speed accelerated when the temperature rose within the scope of experimental temperature [15].

Isotherm adsorption curve

In order to perform the further characterization of the adsorption behavior of Gd(III) on MWAR, the equilibrium adsorption isotherms on MWAR at different temperatures were obtained for Gd(III). Therefore, the correlation of equilibrium data by either theoretical or

empirical equations was essential to the practical design and operation of adsorption systems[16,17]. The *Langmuir* and *Freundlich* equations are used to reveal the linearity fitting and to describe how solutes interact with the resins. For isotherm models, four parts of 15.0mg MWAR and the initial concentration of $[Gd^{3+}]_o = 4.0mg/30.0mL - 8.0mg/30.0mL$ were shaken until equilibrium at pH 6.70, 100 rpm.

Freundlich isotherm:

$$\lg Q = \frac{1}{n}\lg C_e + \lg a \tag{5}$$

Langmuir isotherm:

$$\frac{C_e}{Q} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \tag{6}$$

where Q is the equilibrium Gd(III) ions concentration on the adsorbent (mg/g); C_e is the equilibrium Cd(II) ions concentration in solution (mg/mL); a is the *Freundlich* constant; and n is an empirical constant related to the magnitude of the adsorption driving force; Q_m is the monolayer capacity of the adsorbent (mg/g) and b is the *Langmuir* constant which reflects quantitatively the affinity between the MWAR and Gd(III) ions. The plots

Table 3: Isotherm constants for the adsorption of Gd (III) on MWAR at various temperatures.

T (K)	Langmuir			Freundlich		
	Q_m (mg/g)	b	R_L	Q (mg/g)	n	R_F
288	357	46.7	0.9977	329	4.26	0.9892
298	384	86.8	0.9976	368	7.37	0.9870
308	416	120.2	0.9923	390	6.25	0.9990

of $\lg C_e$ versus $\lg Q$ (*Freundlich*) to generate a and n from the intercept and the slope, respectively obtained by plotting C_e/Q versus C_e (*Langmuir*) for the adsorption of Gd(III) ions onto resin give a straight line.

It is used to analyze batch equilibrium data by plotting C_e/Q vs C_e, which yields a linear plot if the data conform to the Langmuir isotherm. According to the experiment data, plotting of C_e/Q vs C_e gave a straight line and the correlation coefficient R^2 were high as shown in Table 3. This was indicative of applicability of the proposed model for the process undertaken. In other words, the *Langmuir*-type adsorption isotherm was suitable for equilibrium studies.

The plot of $\lg Q$ vs $\lg C_e$ for various initial concentrations of Gd(III) was found to be linear, indicating the applicability of the classical adsorption isotherm to this adsorbate-adsorbent system. The fit of the data to *Freundlich* isotherm in table 3 indicated that the adsorption process was not restricted to one specific class of sites and assumed surface heterogeneity [2]. The fact that the value of n was between 2 and 10 indicated that Gd(III) ion was easily adsorbed [16]. It was evident from these data that the adsorption of Gd(III) ions onto resin fitted well to Langmuir the isotherm model than that of the Freundlich isotherm models, as indicated by the R^2 values and Q_m.

The influence of adsorption temperature and the determination of thermodynamic parameters

The influence of temperature on the adsorption characteristics of Gd(III) was investigated by determining the adsorption isotherms at 288K, 298K, and 308K. Thermodynamic parameters of adsorption have been determined by using classical thermodynamic equations under the conditions of 15.0mg MWAR and $[Gd^{3+}]$ =10mg/30mL at pH 6.70, 100 rpm. There are three important thermodynamic parameters, i.e. enthalpy ΔH, entropy ΔS and Gibb's free energy ΔG, respectively.

The slope and intercept of $\lg D$ vs $1/T$ was used for the ΔH and ΔS. The linear equation was $y = -0.6837x + 5.7620$ and the correlation coefficient 0.9997. The slope of straight line was $K_{slope} = -0.4744 \times 10^3$.

According to the equation:

$$\lg D = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \tag{7}$$

where $\Delta H = -K_{slope} \times 2.303R = 0.4744 \times 10^3 \times 2.303 \times 8.31 = 9.08$ (kJ/mol).

The calculation results are listed in Table 4 along with the Gibb's free energy calculated by using equation given below:

$$\Delta G = \Delta H - T\Delta S \tag{8}$$

ΔG values were negative, indicating that the adsorption process led to a decrease in *Gibb's* free energy and confirming the feasibility of the adsorption process and the spontaneous nature of the adsorption process under the experimental conditions. The positive values of ΔS referred to the increased randomness at the solid-solution interface. The positive values of ΔH indicated that the adsorption process was an endothermic process.

Elution tests

15.0 mg MWAR was added into a mixed solution composed of pH 6.70 buffer solution and desired amount of Gd(III) solution. After equilibrium reached, the concentration of Gd(III) in the aqueous phase was determined, and the adsorption capacity of the MWAR for Gd(III) was obtained.

Then, the MWAR separated from aqueous phase was washed three times with pH 6.70 buffer solution. The MWAR adsorbed Gd(III) was shaken with 30.0mL the composition of HCl-NaCl eluant. After equilibrium reached, the concentration of Gd(III) in aqueous phase was determined and then the percentage of elution for Gd(III) was obtained. The results listed in Table 5

Table 4: Thermodynamic parameters for Gd(III) on MWA.

ΔH (kJ/mol)	ΔS (J/(K·mol))	ΔG (kJ/mol)		
		T = 288K	T = 298K	T = 308K
9.08	102	− 20.2	−21.2	−22.2

Table 5: The elution test of Gd(III) ion.

Composition of HCl-NaCl (mol/L)	Elution amount (mg)	Elution percentage (%)
0.5 mol/L HCl - 0.5 mol/L NaCl	3.94	99.1
0.5 mol/L HCl - 1.0 mol/L NaCl	3.66	96.1
0.25 mol/L HCl - 0.50 mol/L NaCl	3.78	97.2
0.75mol/L HCl - 0.25 mol/L NaCl	3.76	97.1
0.5 mol/L HCl	3.84	98.0

showed that the percentage of elution for Gd(III) was different when the composition of HCl-NaCl was changed. It was evident from data that the maximum percentages of elution for Gd(III) was obtained by using the 0.5 mol/L HCl and 0.5 mol/L NaCl solution as an eluant.

Dynamic adsorption and desorption

Dynamic adsorption curve

The performance of packed beds is described through the concept of the breakthrough curve. The breakthrough curve shows the loading behaviour of Gd(III) to be removed from solution in a fixed bed and is usually expressed in terms of adsorbed Gd(III) concentration (C_{ad} = inlet Gd(III) concentration (C_o) - outlet Gd(III) concentration (C_e)) or normalized concentration defined as the ratio of effluent Gd(III) concentration to inlet Gd(III) concentration (C_e/C_o) as a function of time or volume of effluent for a given bed height [18]. The area under the breakthrough curve obtained by integrating the adsorbed concentration (C_{ad}; mg/mL) vs the throughput volume (V; mL) plot can be used to find the total adsorbed Gd(III) quantity (maximum column capacity). Total adsorbed Gd(III) quantity (Q; mg/g) in the column for a given feed concentration and flow rate is calculated from Eq.(9):

$$Q = \int_0^v \frac{\left(C_o - C_e\right)}{m} dV \qquad (9)$$

where m (g) is the mass of the adsorbent. The capacity value Q was obtained by graphical integration as 321 mg/g. Successful design of a column adsorption

process requires prediction of the concentration vs time profile or breakthrough curve for the effluent. The maximum sorption capacity of MWAR is also in design. Traditionally, the Thomas model is used to fulfill the purpose. The model has the following form [19]:

$$\frac{C_e}{C_o} = \frac{1}{1 + \exp\left[K_T\left(Qm - C_o\right)/\theta\right]} \qquad (10)$$

Where K_T (mL/(min·mg)) is the Thomas rate constant and θ (mL/min) is the volumetric flow rate. The linearized form of the Thomas model is as follows:

$$\ln\left(\frac{C_o}{C_e} - 1\right) = \frac{K_T Qm}{\theta} - \frac{K_T C_o}{\theta} V \qquad (11)$$

The kinetic coefficient K_T and the adsorption capacity of the bed Q can be determined from a plot of ln[(C_o/C_e)−1] vs t at a certain flow rate as shown in Fig. 4. The Thomas equation coefficients for Gd(III) adsorption were K_T = 1.47×10⁻² mL/(min·mg) and Q = 330 mg/g. The theoretical predictions based on the model parameters were compared with the observed data as shown in Fig. 5.

Dynamic desorption curve

Efficient elution of adsorbed solute from MWAR in column was essential to ensure the reuse of MWAR for repeated adsorption/desorption cycles. With respect to the stripping of Gd(III) from MWAR, the 0.5mol/L HCl and 0.5 mol/L NaCl eluant was employed. Desorption curve was plotted as the effluent concentration (C_e) vs elution
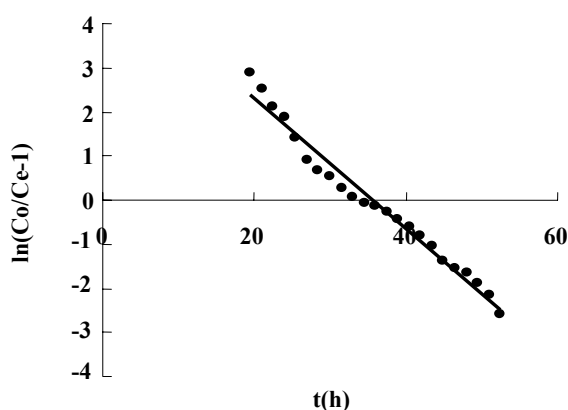
Fig. 4: Plot of ln [(C$_o$/C$_e$) −1] vs t Resin 300mg, pH=6.70, C$_o$=0.167 mg/mL, flow rate = 0.50 mL/min.
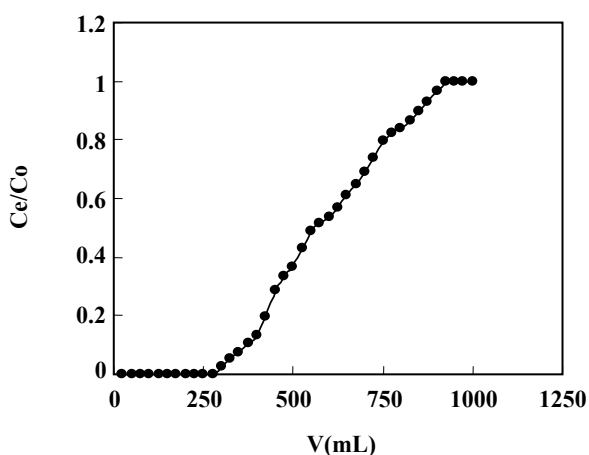

Fig. 5: Breakthrough Curve for adsorption of Gd(III) Resin 300mg, pH=6.70, C$_o$=0.167 mg/mL, flow rate = 0.50 mL/min.
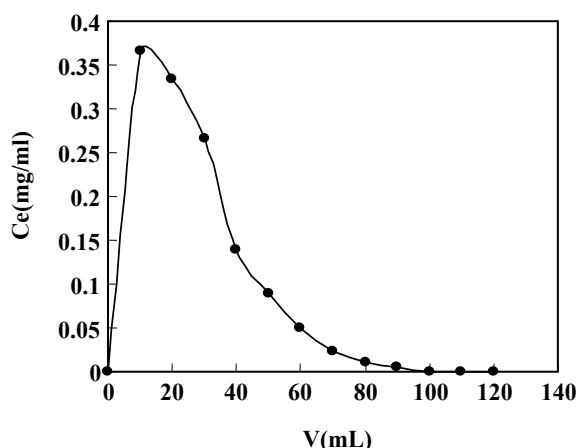

Fig. 6: Dynamic desorption curve Resin 300mg, flow rate=0.40mL/min, T=298K.

volume from the column at a certain flow rate. It can be seen from Fig. 6 that the adsorption flow rate was low so that the volume of elution was small which helped in easy handling, and high in concentration for economical recovery of Gd(III). It was observed that the total volume of eluent was 60 mL and the desorption process took 2.5 h, after which further desorption was negligible. Therefore, the 0.5mol/L HCl and 0.5 mol/L NaCl eluant could help in easy handling and removing of Gd(III).

CONCLUSIONS

Gd(III) can be optimally adsorbed on MWAR in HAc-NaAc medium at pH 6.70. The statically saturated adsorption capacity of Gd(III) was 384 mg/g MWAR at 298K. The adsorption behaviour of MWAR for Gd(III) obeyed the *Langmuir* isotherm and *Freundlich* isotherm. The adsorption rate constant was k$_{298}$ = 1.22 × 10^{-5}s^{-1} and the apparent activation energy was E$_a$ =18.0 kJ/mol. Thermodynamic parameters, ΔS, ΔH and ΔG, on the adsorption for Gd(III) indicated that the adsorption process was spontaneous and endothermic. The Gd(III) adsorbed on MWAR can be eluted by using 0.5mol/L HCl and 0.5 mol/L NaCl solution as an eluant.

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