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ADSORPTION BEHAVIOR OF GADOLINIUM(III) FROM AQUEOUS SOLUTION BY D418 RESIN

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Abstract

Adsorption, desorption, and kinetics behavior of Gd(III) ion on chelating resin were investigated in this paper. Batch adsorption studies were carried out with different pH, contact time, and temperature. The adsorption of Gd(III) follows the Langmuir model better than the Freundlich model. The apparent activation energy E_a and adsorption rate constant are k_{308} 4.16 kJ/mol and 6.01×10^{-5} s^{-1}, respectively. Thermodynamic parameters such as ΔH, ΔS and ΔG indicated that Gd(III) ion adsorption by D418 resin was an endothermic and spontaneous process in nature. Column adsorption experiments indicated the maximum dynamically adsorption capacity of 281mg/g for Gd(III). The desorption rate of Gd(III) was 98.3% when the elution agent is 2.0 mol/L HCl solution and the chelating resin can be regenerated and reused. Analysis of IR spectroscopy for D418 resin before and after adsorption of Gd(III) ions and after desorption indicated the attendance of coordination and good regenerative ability of resin. Thermo gravimetric analysis for D418 resin before and after adsorption of Gd(III) ions proved the adsorption of Gd(III) ions.

Keywords: adsorption, desorption, D418 resin, gadolinium

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1. Introduction

The development of new technology makes higher demands on various functional materials. Rare earth elements and their chemical compounds have their peculiar optical, electric, magnetic, acoustic, thermal, mechanical properties and mutual transformations among them. Therefore, they play special significant role and occupy very important position in the science and technology of modern materials (Alexandratos, 2000; Awual et al., 2013a; Chen and Zhao, 2003). Gadolinium, a soft silvery metallic element, is found in the lanthanide series of inner transition metals of the periodic table. Gadolinium oxide, one of its largest uses in nuclear power reactors is as shielding and fluxing devices. Gd(III) ion, known as fission product, can leak to the environment and cause risks. Consequently, it is considered as hazardous material (El-Sofany, 2008; Junk et al., 1974).

For years, many methods have been developed to remove rare earth metals from the effluents. Several techniques, such as ion exchange, chemical precipitation, membrane separation, and extraction chromatography have been reported for the adsorption and separation of rare earth elements from aqueous solution (Awual et al., 2013b; Kondo and Kamio, 2002; Liang et al., 2008; Matlock et al., 2002). Various

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materials such as bamboo charcoal, zeolite, polystyrene beads and resins have been used in these techniques (Awual et al., 2013c; Khalil et al., 2016; Xiong et al., 2014). Amongst those, resins were studied as available material in industrial wastewater because of their high removal efficiency, feasibility in application, as well as the potential to extract toxic or valuable metals from the waste water (Li et al., 2016; Lin et al., 2018; Shen et al., 2016). D418 resin, as a typical ion exchange resin, possesses the advantages of polymeric adsorbents, such as the relatively low cost and effectiveness in removing metal ions. D418 chelating resin is a polymeric microporous material which contains aminophosphonic function group of [-$NHCH_2PO_3Na_2$]. It could be adopted to the adsorption of metal ions from aqueous solutions.

In this work, study of the adsorption of Gd(III) on D418 resin is carried out in the form of batch and column methods. Some factors to affect the adsorption, such as contact time, initial pH of solution, and temperature were examined. Kinetics and isotherm adsorption experiments were carried out, and thermodynamic parameters of adsorption for Gd(III) were calculated. The experimental results present a path for the removal of Gd(III) in the environmental protection.

2. Experimental

2.1. Materials

The chelating resin (D418) was provided by Nankai University, China and the properties are shown in Table1. The standard solutions of Gd(III) ion was prepared from Gd_2O_3 (AR). HOAc-NaAc buffer solution with pH 4.50-6.50 and $C_6H_{15}NO_3$-HNO_3 buffer solutions with pH 7.20 were prepared from acetic acid (HOAc), sodium acetate (NaAc), triethanolamine ($C_6H_{15}NO_3$) and Nitric acid (HNO_3) solutions. The chromophoric reagent of 0.1% arsenazo-I solution was obtained by dissolving 0.1000 g arsenazo-I powder into 100 mL purified water. All other reagents were of AR grade.

Table 1. General description and properties of D418 resin

Items	***Properties***
Functional group	-$NHCH_2PO_3Na_2$
Specific surface area (m^2/g)	400-440
Pore diameter (Å)	8.0-9.0
Pore volume (mL/g)	1.0-1.1
Mass capacity (mmol/g)	≥14
Moisture (%)	50-60
Wet apparent density (g/mL)	0.70-0.80
True wet density (g/mL)	1.10-1.18
Particle size (≥95%)	0.4-1.25mm
Whole bead after osmotic attrition	≥95

2.2. Apparatus

The Gd(III) ion was determined with Shimadzu UV-2550 UV-visiable 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 ultrapure water machine. The IR spectra were recorded on a Nicolet 380 FT-IR spectrometer. Thermo gravimetric analysis was performed on Mettler Toledo TGA/DSC1 STARe.

2.3. Adsorption experiments

Experiments were run in a certain range of pH, temperature, contact time and adsorption isotherms. The operations for the adsorption and desorption of Gd(III) were carried out in batch vessels and glass columns.

Batch experiments were performed under kinetics and equilibrium conditions. A desired amount of treated D418 resin was weighed and added into a conical flask, followed by the addition of a desired volume of buffer solution with pH 5.5. After 24h, a required amount of standard solution of Gd(III) was put in. The flasks were 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.

In the column experiments, continuous packed bed studies were performed in a fixed bed mini glass column of 0.3 cm inner diameter with resin and filled with Gd((III) solution. The Gd(III) ion solution was fed from the top at a fixed flow rate. The Gd(III) solutions at the outlet of the column were collected at regular time intervals and the concentrations of Gd(III) were measured till the outlet and inlet concentrations became equal.

2.4. Desorption experiments

Desorption experiments were performed immediately following the completion of the adsorption experiments.

Batch desorption: at the end of adsorption experiments, the exhausted resins were separated from the aqueous solution by filtration, washed by deionized water and were stirred with eluent solutions of various concentrations, oscillating to balance at constant temperature. After equilibrium reached, the concentration of Gd(III) in aqueous phase was determined and then the percentage of elution for Gd(III) was calculated.

Column desorption: after equilibrium was reached, D418 resins which were separated from the aqueous solution was washed five times with optimal pH HOAc-NaAc buffer solution. Then column desorption experiments carried on by use the preferred desorption conditions obtained in the batch desorption experiments. The samples in the outlet were taken at the preset volume intervals and the concentrations of Gd(III) were determined, until the concentration of Gd(III) in the effluent is zero.

2.5. Analytical method

A solution containing lower than 75μg/mg of Gd(III) was added into a 25 mL colorimetric tube, and then 1.0 mL of 0.1% arsenazo-I solution and 10 mL pH 7.20 $C_6H_{15}NO_3$-HNO_3 buffer solution were added, after the addition of purified water to the mark of the colorimetric tube, the absorbance was determined in an 1 cm colorimetric vessel at wavelength of 575 nm and compared with blank test. The adsorption capacity (Q, mg/g) and distribution coefficient (D, mL/g) were calculated with the following formulas Eq. (1) and Eq. (2) (Chen et al., 2014):

$$Q = (C_0 \quad C_e)V / m \tag{1}$$

$$D = Q / C_e \tag{2}$$

where: C_0 is initial concentration in solution (mg/mL); C_e is equilibrium concentration in solution (mg/mL); V is solution volume of solution(mL); m is resin dry mass (g).

3. Results and discussion

3.1. Influence of pH on the distribution coefficient of Gd(III)

The pH of solution has been identified as the most important variable governing the adsorption capacity. The influence of pH on the sorption behaviors of D418 resin for Gd(III) is shown in Fig. 1. It can be easily seen that the distribution coefficient for Gd(III) was the highest when the pH was 5.5 in the HOAc-NaAc medium and decreased by either raising or lowing pH under the experimental conditions.

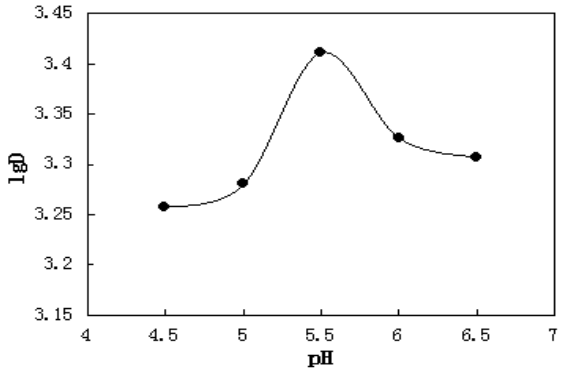


Fig. 1. Influence of pH on the distribution coefficient D (resin 15.0 mg, 298 K, 100rpm, C_0=10.0 mg/30.0 mL)

At lower pH values, the Gd(III) ion uptake was inhibited in the acidic medium and it can be attributed to the presence of H^+ ion competing with the Gd(III) ion for the adsorption sites. Due to the Gd(III) ion was prone to deposit beyond pH 5.5, the adsorption of Gd(III) ions is reduced. Therefore, we chose the HOAc-NaAc system at pH 5.5 for experiments.

3.2. Determination of adsorption rate constant and apparent activation energy

The influence of contact time on the adsorption of Gd(III) onto D418 resins (Fig. 2(a)) was investigated at 288, 298 and 308 K. It is easily seen that the amount of adsorption increased with increasing contact time and the maximum adsorption was observed after 45 h, beyond which there was almost no further increase in the adsorption. In addition, the maximum adsorption capacities increased with increase in the temperatures.

Adsorption kinetics curves were obtained for Gd(III) on D418 resins. The kinetics of adsorption can be described by the liquid film diffusion model (Xiong, 2015), using the Brykina method (Eq. 3) (Brykina et al., 1980):

$$ln(1 - F) = kt \tag{3}$$

where: F is the fractional attainment of equilibrium ($F = Q_t/Q_e$); Q_e and Q_t are the amounts of Gd(III) adsorbed on the adsorbent at equilibrium (mg/mL) and at any time t, respectively; k is the adsorption rate constant.

The experimental results accorded with the equation and a straight line was obtained by plotting *-ln(1-F) vs. t*. The results are 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 might be the predominating step of the adsorption process (Boyd et al., 1947). Also the results show that the sorption rate constant k increases with temperature, from which we may infer that the sorption reaction is endothermic (Xiong et al., 2013).

Table 2. Adsorption rate constants

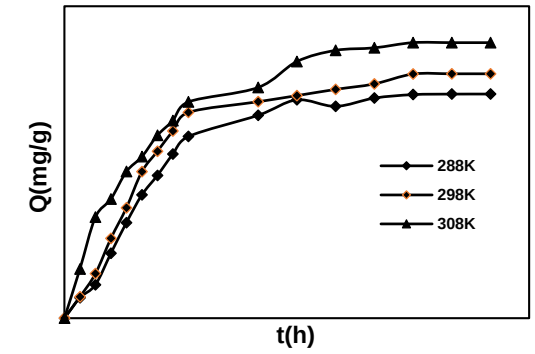
T(K)	***Linearity relation of-ln (1-F) and t***	***k × 10^{-5} (s^{-1})***	***R^2***
288	y=0.1934x-0.1761	5.37	0.993
298	y=0.2093x-0.1457	5.66	0.992
308	y=0.2165x-0.0857	6.01	0.996

According to the Arrhenius equation (Eq. 4):

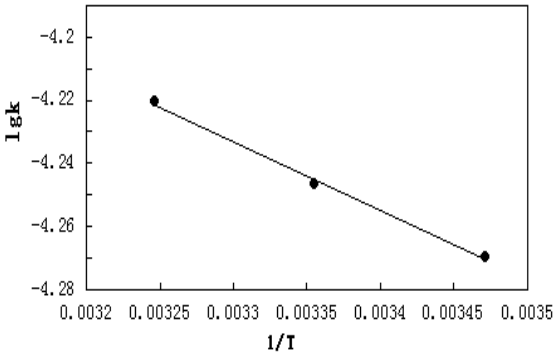
$$lg\, k = \frac{Ea}{2.303RT} + lg\, A \tag{4}$$

where: *Ea* is the *Arrhenius* activation energy for the adsorption process indicating the minimum energy that reactants must have for the reaction to proceed (kJ/mol), *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 temperature.

As can be observed in Fig. 2(b), the coefficient of determination of the straight line R^2 = 0.997 was achieved. The activation energy Ea was 4.16kJ/mol, which could be considered as a low energy barrier in this study (Balan et al., 2017).



(a)



(b)

Fig. 2. (a) Adsorption kinetics and capacity *Q* at different times and different temperatures and (b) relationship between lgk and 1/T (resin 15.0 mg, pH=5.5, 100 rpm, C_0= 10.0 mg/30.0 mL)

3.3. Adsorption isotherms

In order to perform the further characterization of the adsorption behavior of Gd(III) on D418, the equilibrium adsorption isotherms on D418 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. The Langmuir and Freundlich isotherm models (Jaafarzadeh et al., 2014) are used to reveal the linearity fitting and to describe how solutes interact with the resins.

The Langmuir isotherm is governed by the following relationship (Eq. 5) (Langmuir, 1918):

$$\frac{C_e}{Q_e} = \frac{1}{Q_0 K_L} + \frac{C_e}{Q_0} \quad (5)$$

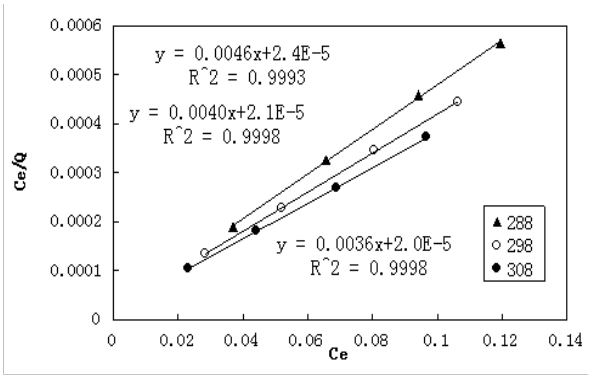
where Q_e is the equilibrium Gd(III) ions adsorption capacity (mg/g), C_e is the equilibrium Gd(III) ions concentration in solution (mg/mL), Q_0 is the maximum adsorption capacity corresponding to complete monolayer coverage (mg/g), K_L is the Langmuir constant and related to the free energy of adsorption.

The Freundlich isotherm model assumes heterogeneous surface energies in which energy term in Langmuir equation varies as a function of surface coverage. The Freundlich isotherm equation is used in the general form, as Eq. (6) (Freundlich, 1906):

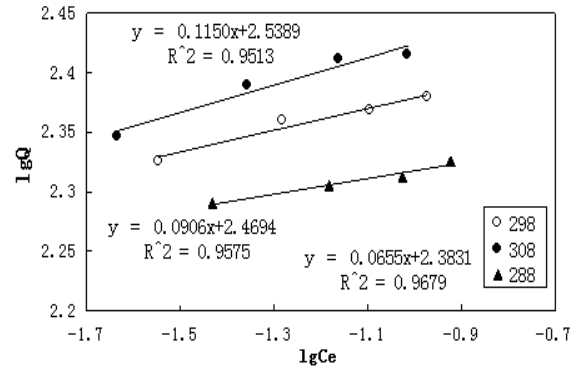
$$\lg Q_e = \frac{1}{n}\lg C_e + \lg K_F \quad (6)$$

where K_F and n are the Freundlich isotherm constants related to adsorption capacity and intensity of adsorption, respectively.

The isotherm constants of all the previous equations are very useful parameters for predicting adsorption capacities and also for incorporating into mass transfer relationships to predict the design of batch reactors. According to the results that show in Fig. 3, higher R^2 values (R^2_{288K} = 0.9993, R^2_{298K} = 0.9998, R^2_{308K} = 0.9998) were obtained from Langmuir model for Gd(III) than from the Freundlich model ($R^2_{288\ K}$ = 0.9679, $R^2_{298\ K}$ = 0.9575, $R^2_{308\ K}$ = 0.9513). It is evident that the adsorption of Gd(III) ion onto D418 resin is fitted better to the Langmuir isotherm model than that of the Freundlich isotherm models. This indicates that the adsorption of Gd(III) ions by D418 resin is monolayer-type.



(a)



(b)

Fig. 3. (a) Langmuir isotherm and (b) Freundlich isotherm curves of Gd(III)

3.4. Thermodynamic parameters

In any adsorption procedure, both energy and entropy considerations should be taken into account in order to conclude whether the process is spontaneous or not.

The amounts of Gd(III) adsorbed at equilibrium at 288, 298 and 308K have been examined to obtain thermodynamic parameters for the adsorption system. Thermodynamic parameters of adsorption have been determined by using classical thermodynamic equations under the conditions of 15.0mg D418 resin and C_0=10.0mg/30.0 mL at pH 5.5, 100 rpm.

Thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) can be estimated using equilibrium constants changing with temperature. The slope and intercept of lgD *vs.* 1/T was used for the calculation of ΔH and ΔS using the Eq. (7) (Ünlü and Ersoz, 2006):

$$lg\, D = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \quad (7)$$

Gibbs free energy ΔG calculated by using equation given below (Eq. 8):

$$\Delta G = \Delta H - T\Delta S \quad (8)$$

where R is the gas constant and T is the absolute temperature.

The linear equation was y = -0.978x + 6.934, the correlation coefficient of the straight line R^2= 0.9765 was achieved. ΔH and ΔS values can be estimated from slope and intercept value of this plot lgD *vs*. 1/T and the ΔG values at different temperatures were calculated using the Eq. (8), respectively. The values of ΔS, ΔH and ΔG are ΔH 18.7 kJ/mol; ΔS 132.8 J/(K·mol); and ΔG (–)19.5 kJ/mol for 288K, (–)20.9 kJ/mol for 298K, and (–) 22.2 kJ/mol for 308K.

The values of ΔG were negative, and confirm that the spontaneity of the adsorption process with increasing temperature. The positive value of ΔH suggests that the adsorption is endothermic in nature. In addition, the values of ΔS were found to be positive due to the exchange of Gd(III) ions with more mobile ions (-$NHCH_2PO_3Na_2$) present on the exchanger, which would cause increase in the entropy, during the adsorption process.

3.5. Elution and regeneration tests

Efficient elution is essential to ensure of adsorbed solute from resin is the reuse of resin for repeated adsorption-desorption cycles.

After adsorption equilibrium reached, the D418 resin separated from aqueous phase was washed three times with pH 6.5 buffer solution. 30.0mL HCl solution with various concentrations were added into the flasks respectively as eluents followed by shaking the flasks. After equilibrium was reached, the concentration of Gd(III) in aqueous phase was determined and then the percentage of elution for Gd(III) was obtained. The percentages of elution are 88.7%, 93.9%, 98.3% and 96.5% for 1.0, 1.5, 2.0 and 3.0mol/L HCl concentration respectively.

The experimental results of elution show that 2.0 mol/L HCl is the most efficient. In order to show the reusability of the adsorbent, adsorption-desorption cycle of metal ion was repeated six times by using the same beads. The adsorption capacities for the D418 resin did not noticeably change during the repeated adsorption-desorption operations. These results show that the D418 resin has good regeneration ability.

3.6. Dynamic adsorption and desorption

3.6.1. Dynamic adsorption curve

The performance of packed beds is described through the concept of the breakthrough curve. The breakthrough curve shows the dynamic adsorption capacity of Gd(III) adsorbed on D418 resin and is usually expressed in terms of adsorbed Gd(III) concentration [C_{ad} = inlet Gd(III) concentration (C_0) - 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_0) as a function of time or volume of effluent for a given bed height (Xiao et al., 2009). 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 using Eq. (9):

$$Q = \int_0^v \frac{C_0 - C_e}{m} dV \quad (9)$$

where m (g) is the mass of the adsorbent. The capacity value Q was obtained by graphical integration as 281 mg/g. Traditionally, the Thomas model is used to fulfill the purpose. The model has the following form (Eq. 10)(Min Min et al., 2017):

$$C_e / C_0 = \frac{1}{1 + exp[K_T(Qm - C_0 V)/\theta]} \quad (10)$$

where K_T [mL/(min·mg)] is the Thomas rate constant; and θ (mL/min), the volumetric flow rate. The linearized form of the Thomas model is (Eq. 11):

$$ln(C_0/C_e - 1) = K_T Qm/\theta - K_T C_0 V/\theta \quad (11)$$

The dynamic coefficient K_T and the adsorption capacity of the bed Q can be determined from the curve of $ln(C_o/C_e\text{-}1)$ *vs*. t at a certain flow rate as shown in Fig. 4. (a) The outlet time t is obtained from V/θ. Thomas equation coefficients for Gd(III) adsorption were K_T = 7.8×10^{-3} mL/(min·mg) and Q=273mg/g. The theoretical predictions based on the model parameters were compared with the observed data as shown in Fig. 4. (b) Therefore, it can be concluded that the experimental data fitted well to the Thomas model, which shows that the external and internal diffusion isn't the limiting step.

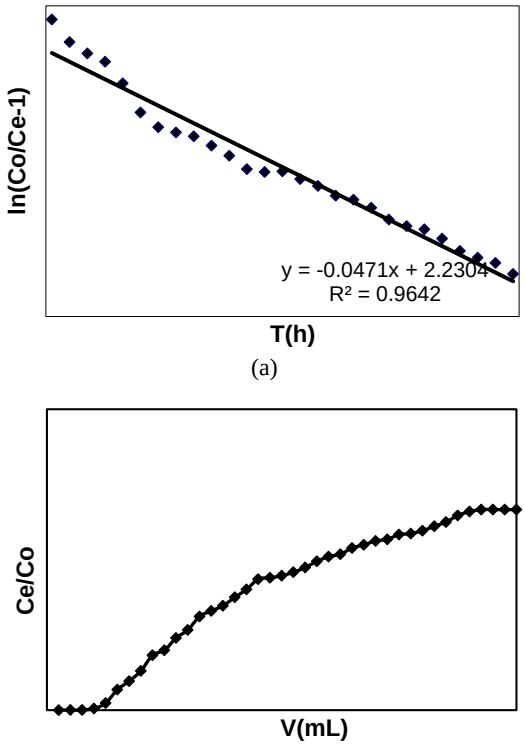


Fig. 4. (a) Plot of $\ln(C_0/C_e\text{-}1)$ *vs* t and (b) Breakthrough curve for adsorption of Gd(III) (resin 150 mg, pH = 5.5, C_0= 0.20 mg/mL, flow rate = 0.139 mL/min)

3.6.2. Dynamic desorption curve

Efficient elution of adsorbed solute from D418 in column was essential to ensure the Recycling performance of D418. With respect to the separate Gd(III) from D418, using 2mol/L HCL as eluent. Desorption curve was plotted as the effluent concentration (C_e) *vs* elution volume from the column at 0.278mL/min flow rate. It can be seen from Fig. 5 that the adsorption flow rate (0.278mL/min) was low so that the volume of elution was small which helped in easy handling, and high in concentration for economic recovery of Gd(III). It was observed that the total volume of eluent was 175 mL and after which further desorption was negligible. Therefore, the 2.0mol/L HCl eluant could help in easy handling and removing of Gd(III).

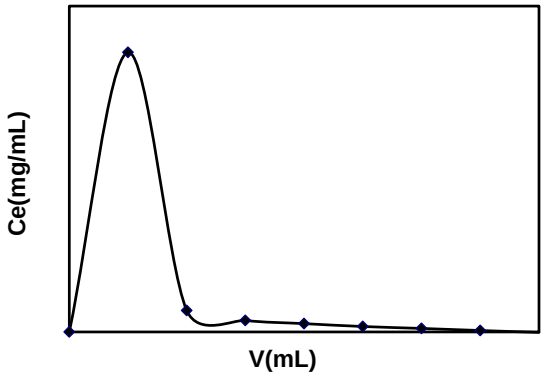


Fig. 5. Dynamic desorption curve (flow rate = 0.278mL/min)

3.7. Infrared spectra analysis

The FTIR spectral analysis is important to identify some characteristic functional groups which are responsible of adsorbing metal ion. From the above results, it can be deduced that the adsorption of Gd(III) ion by D418 resin belongs to a chemical adsorption. Therefore, in the functional groups of D418 resin, N-H, P=O, P-OH and Gd(III) are supposed to form chemical bonds. Fig. 6 shows typical FTIR spectra for D418 resin before and after the adsorption of Gd(III) ions and after desorption. It should be noticed that the characteristic adsorption peaks of N-H shift from 3420cm^{-1} to 3411cm^{-1}. P=O characteristic adsorption peaks shift from 1175cm^{-1} to 1168cm^{-1}.

These results suggest that the formation of the coordination of the oxygen and Gd(III) weakens the stretch contraction vibration and causes the peak to shift to the lower frequency. The peak shifted from 928cm^{-1} to 918cm^{-1} indicates that H of P-OH has been replaced. The infrared spectra of resin that before adsorption and after desorption are basically the same, indicating that D418 resin can regeneration effectively after eluted with HCl.

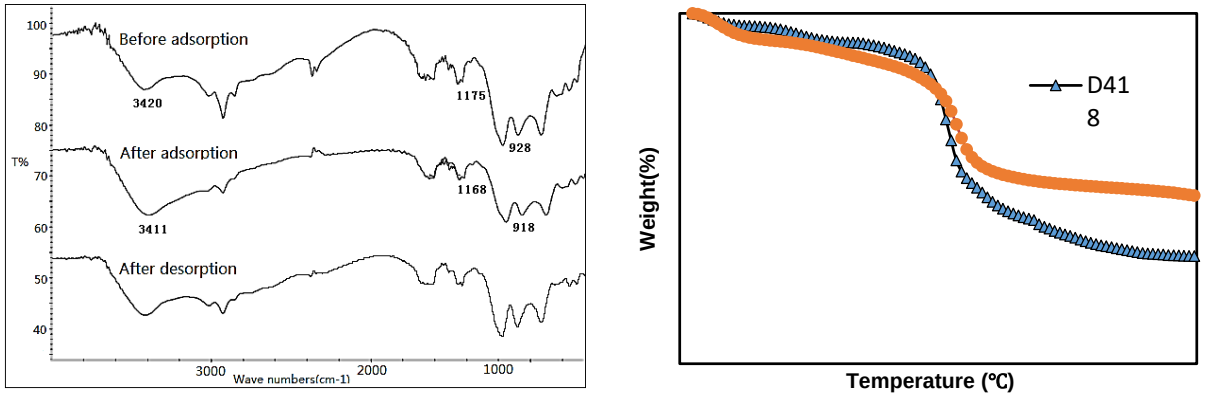


Fig. 6. (a) FTIR spectra and (b) TGA of D418 resin before and after being loaded Gd(III)

3.8. Thermo gravimetric analysis

TGA were carried out at a heating rates 20°C/min under nitrogen (flow rate, 20 mL/min). In the present work, according to the TGA curves, the residue of D418 resin before and after Gd(III) ion adsorption is about 30.7wt.% and 48.1wt.%, respectively. The difference of residue (17.4 wt.%) is the weight of adsorptive Gd(III) ion, and it approaches the experimental value (16.9 wt.%), which can be calculated from the maximum adsorption capacity (281 mg/g). These results prove the adsorption of Gd(III) ion on D418 resin.

4. Conclusions

Gd(III) can be optimally adsorbed on D418 resin in pH 5.5 HOAc-NaAc system. At 298K, the dynamic saturated adsorption capacity of Gd(III) is 281mg/g. The dynamic adsorption curve of D418 resin for Gd(III) obeys the Langmuir isotherm.

The analysis of the thermodynamic parameters (ΔS, ΔH and ΔS) of Gd(III) adsorption showed that the adsorption process was spontaneous and endothermic. The Gd(III) adsorbed on D418 resin can be effectively eluted by using 2.0mol/L HCl solution. FTIR and TGA of D418 resin adsorbed Gd(III) show that the functional group of resin is coordinated with Gd(III) to form coordination compound. D418 resin has very good potential for utilization as an adsorbent for Gd(III) from aqueous medium.

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