# Adsorption and desorption characteristics of N235 levextrel resin for the dilute HCl Solution

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**Abstract:** The low concentration of hydrochloric acid produced during the separation process of rare earth no saponification extraction is best available for recycling. The adsorption and desorption characteristics of N235 resin on dilute HCl solution were investigated by static adsorption method and dynamic adsorption method. The adsorption equilibrium constant, the saturated adsorption capacity of resin and its relationship with the initial HCl concentration were obtained by static adsorption experiment. The results of dynamic adsorption showed that the adsorption flow rate, the resin column height, the HCl concentration, the chloride concentration in the solution, the downstream flow/countercurrent mode would affect the resin equilibrium adsorption capacity; Besides, the maximum concentration of HCl solution obtained by the adsorption and desorption of N235 resin on dilute HCl solution is equal to the initial concentration of adsorbate, and has obvious "memory effect",and with the method of alkali absorption can reach the enrichment of hydrochloric acid at extreme dilute solution.

## Introduction

Solvent extraction is the main method of rare earth separation, the phosphine 2-ethylhexyl phosphate 2-ethyl hexyl ester (HEH/EHP) or (2-ethylhexyl) di-phosphate ester (HDEHP) is commonly used as extractant. In order to improve the extraction capacity and stable extraction ratio, people usually using alkali (such as ammonia, sodium hydroxide, lime, etc.) for extraction agent saponification, but this process would produce salinity wastewater which would pollute the environment[1]. Some innovative researches are continuing on the issue of acidic wastewater or high salt wastewater during the process of rare earth extraction. Huang xiaowei et al[2,3] .have comthe HEH/EHP with HDEHP on synergistic extraction and made full use of their respective advantages, which enhanced the extraction capacity under the HEH/EHP acid condition and the HDEHP stripping rate, solved the ammonia nitrogen wastewater problem which produced in the process of the rare earth

extraction and separation. This technology have been successfully applied to practical production. Subsequently the new technology of using magnesium bicarbonate solution as a liquid saponification agent and precipitant on rare earth extraction and separation process[4], and recycling use of magnesium to avoid the discharge of high concentrations of magnesium salt wastewater, which helped to eliminate acid waste water pollution from the source. Using buffer solution to adjust the acid during the extraction process is a meaningful task[5], but the reagent can not be recycled.Yang youming etal. based on the strong alkaline amine extractant Trioctylamine(N235) has a strong extraction capacity of HCl, put forward a system of P507-N235 double solvent extraction system which can make the hydrogen ions released during the extraction process of the rare earth with the acidic phosphine extractant    not enter the aqueous phase and remain in the organic phase,and through a lot of experiments verified that the system does not need saponification, has a good extraction and separation effect on rare earth ions, besides the composite organic phase

structure is stable and can be recycled[6,7,8], organic phase before recycling can strip the acid in the N235 by water, and this method has a good industrial application prospects. But the concentration of hydrochloric acid gained by stripping is quite light [9], and it is difficult to be reused in the process of the rare earth extraction and separation.

Many disposal methods for HCl wastewater have been established: the evaporation concentration method avoided the emission of waste acid [10], but it has high equipment investment and energy consumption; the HCl acid analytical method[11] can obtain high-purity HCl,but it is only applicable for 28%–32% of waste hydrochloric acid[12];the electrolytic method can attain cyclic utilization of resources, but it has high electricity consumption[13]; and the diffusion dialysis method can separate HCl from HCl-bearing wastewater at low energy consumption and operation cost, but it has high equipment investment, low daily processing capacity per unit membrane area [14]， Tang Jianjun et al. [15] studied the feasibility of recovering hydrochloric acid from rare earth chloride solution by vacuum membrane distillation. It was proved that vacuum distillation could recover up to 80% of free hydrochloric acid in rare earth chloride solution, but not dilute hydrochloric acid ,especially the dilute hydrochloric acid solution.

Levextrel resin, environment-friendly, low cost, high selectivity, is a new convenient and efficient separation resin[16]。 we synthesized the N235 into the levextrel resin which can adsorption of dilute HCl solution and not easy to flow away.The HCl adsorption/desorption law of N235 levextrel resin was discussed in this paper, expect to solve the problem of saponification or acidic wastewater during the process of rare earth extraction.

## Experiment

### Experimental reagents

The experimental reagents include concentrated HCl acid (HR), lanthanum chloride solution (99.99%), and N235 levextrel resin (20–40 meshes).

### Experimental instruments
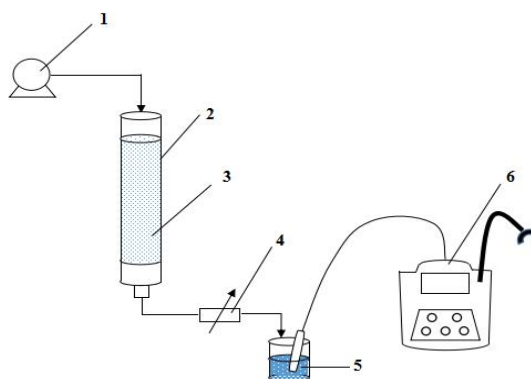
The main experimental apparatus is shown in Fig. 1.



Fig.1 Main experimental apparatus

1- YZ15 peristaltic pump; 2- Φ30 mm*1000-mm organic glass column (homemade); 3- N235 resin; 4- stop valve; 5- effluent; 6- ST3100 pH agent

### Experimental method

### Static experiment

An HCl solution of pH=2.13 with a certain amount of concentrated HCl acid and deionized water was prepared. Next, 100 ml of the prepared HCl solution and a certain amount of levextrel resin were placed in a 500-ml beaker, which was vibrated for 2 h under 40 °C. Some filtrate was collected for pH test.

The complex $n_{N235}$: $n_{HCl}$ =1:1 is often produced during HCl extraction of N235 levextrel resin[16], thus:
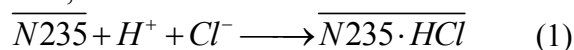
$$\overline{N235} + H^+ + Cl^- \longrightarrow \overline{N235 \cdot HCl} \qquad (1)$$

$$K = \frac{[\overline{N235 \cdot HCl}]}{[\overline{N235}] \cdot [H^+][Cl^-]} \qquad (2)$$

where *K* is a chemical reaction constant and the rest are concentrations in mol/L or mol/Kg.

## Dynamic experiment

### Adsorption elution curve

A certain amount of N235 resin column was taken, and a certain concentration of HCl acid solution was prepared. The peristaltic pump and the stop valve were opened to ensure that the raw material solution will pass through the ion exchange column at a constant flow rate. A beaker was placed at an outlet and every 100 ml of sample was collected to test the acid concentration; data were recorded. The equilibrium adsorption of the resin was achieved when the acid concentration of the effluent was equal to that of the raw material solution. The experiment and test were stopped, and the concentration of the effluent was calculated. The HCl adsorption elution curve of N235 resin was drawn.

### Desorption elution curve

After achieving the equilibrium adsorption of resin through the above operations, the stop valve was opened for half an hour to eliminate water. The raw material solution was changed by deionized water. The peristaltic pump was opened to ensure that the deionized water will pass through the ion exchange column at a constant flow rate. A beaker was placed in an outlet, and every 100 ml of sample was collected to test the acid concentration; data were recorded. When the acid concentration of the effluent was 0.2% lower than that of the raw material solution, the desorption of resin was considered complete; the experiment was then stopped, and the HCl desorption elution curve of N235 resin was drawn.

## Results and discussion

### Influencing factors of the adsorption process of resin

### Influence of the adsorption solution flow rate on the adsorption effect of resin

A cocurrent adsorption experiment was conducted with 15 g of resin, raw material solution pH of 1.76, and under two flow rates (14.5 and 3.5 ml/min). The pH test was conducted for every 100 ml of sample. The experiment was stopped after the resin equilibrium adsorption was achieved, and data were organized to draw the adsorption elution curve. The experimental results are shown in Fig. 2.

Fig. 2 shows that the higher flow rate results in the early achievement of resin equilibrium adsorption. The equilibrium adsorption was achieved at 500 ml of effluent under a flow rate of 14.5 ml/min, and the resin equilibrium adsorption capacity was 0.3041 mol/kg. The equilibrium adsorption was achieved at 900 ml of effluent under a flow rate of 3.5 ml/min, and the resin equilibrium adsorption capacity was 0.5192 mol/kg.
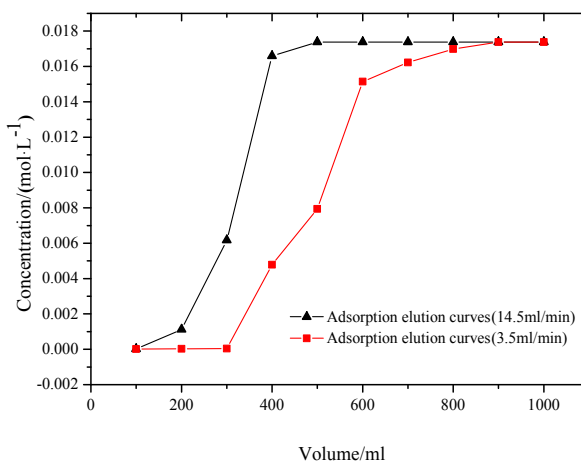
Fig.2 Adsorption elution curves under different adsorption solution flow rates

Therefore, the flow rate is negatively correlated with the adsorption capacity of resin. At similar conditions, the adsorption capacity of resin under a flow rate of 3.5 ml/min was 70.72% higher than that under 14.5 ml/min. Thus, a higher flow rate can shorten the interaction time between the resin and the solution, deteriorate diffusion effect, and decrease the resin equilibrium adsorption capacity.

**Influence of the adsorption solution concentration on the adsorption effect of resin**

A cocurrent adsorption experiment was conducted with 15 g of resin, under a flow rate of 14.5 ml/min, and at different pH conditions (1.76 and 2.71). The pH test was conducted for every 100 ml of sample; the experiment was stopped after the equilibrium adsorption of resin, and data were organized to draw the adsorption elution curve. The experimental results are shown in Fig. 3.
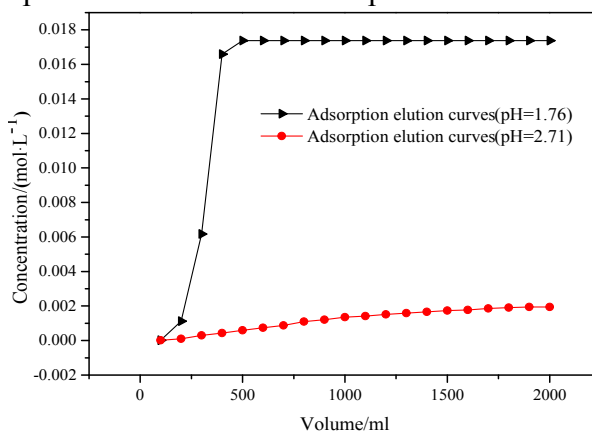


Fig.3 Adsorption elution curves under different pH conditions

Fig. 3 shows that the higher acid concentration of the adsorption solution can accelerate the achievement of the resin adsorption equilibrium. The equilibrium adsorption was achieved at 500 ml of effluent when pH=1.76. However, at pH=2.71, the equilibrium adsorption was not achieved until the amount of effluent reached 1800 ml, and the adsorption capacity of resin was 0.0996 mol/kg. In addition, a higher acid concentration could increase the resin equilibrium adsorption capacity. The equilibrium adsorption capacity of resin increased by 205.4% when pH decreased from 2.71 to 1.76, indicating the significant influence of pH on the adsorption effect of resin. The reason was that a higher acid concentration of adsorption solution meant a higher concentration of $H^+$ and $Cl^-$, thereby creating an environment conducive for adsorption reaction.

**Influence of rare-earth chloride concentration on the adsorption effect of resin**

Cocurrent adsorption experiments with and without lanthanum chloride (0.0621 mol/L) were conducted with 15 g of resin, pH=1.76, and flow rate of 14.5 ml/min. The pH test was conducted for every 100 ml of sample; the experiment was stopped after the equilibrium adsorption of resin was achieved. The experimental results are shown in Fig. 4.
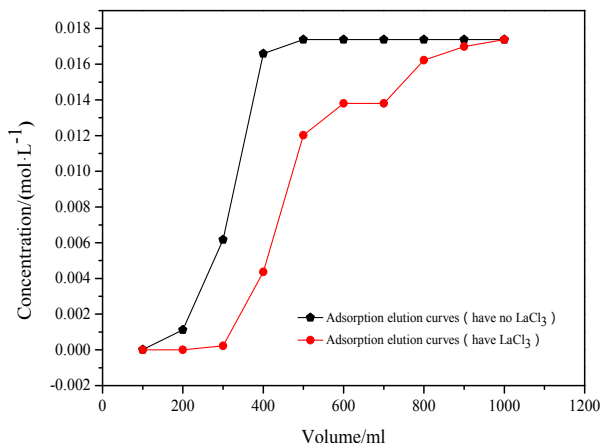
Fig.4 Adsorption elution curves with/without lanthanum chloride

According to the experimental results, the existence of rare-earth chloride will delay the achievement of the adsorption equilibrium of resin. The equilibrium adsorption was achieved at 500 ml of effluent when no lanthanum chloride was added into the adsorption solution; however, when lanthanum chloride was added, equilibrium adsorption was delayed to 1,000 ml of effluent. The adsorption capacity of resin was 0.5265 mol/kg. However, when lanthanum chloride was added, the adsorption capacity of resin (0.0621 mol/L) was 73.1% higher than that without lanthanum chloride.

This observation is attributed to the ability of lanthanum chloride to increase $Cl^-$ concentration in the water phase. According to Eq. 1, the higher $Cl^-$ concentration in the water phase is conducive for adsorption reaction, thus increasing the equilibrium adsorption capacity of resin.

**Influence of adsorption mode on the adsorption effect of resin**

Cocurrent and countercurrent adsorption experiments were performed with 15 g of resin, pH=2.71, and under a flow rate of 14.5 ml/min. The pH test was conducted for every 100 ml of sample; the experiment was stopped after the equilibrium adsorption of resin was achieved. Experimental results are shown in Fig. 5.
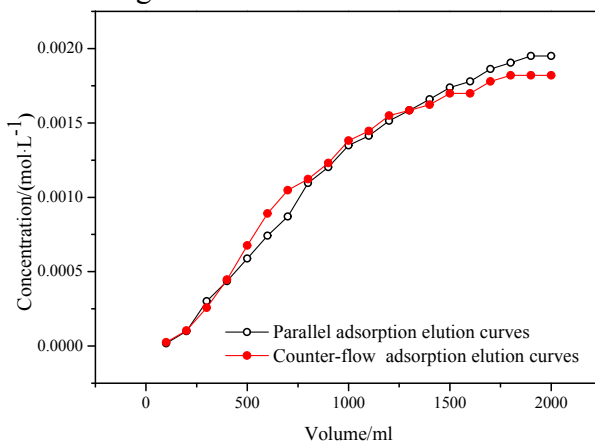

Fig.5. Adsorption elution curves under different adsorption modes

Results showed that the elution curves under parallel adsorption and counterflow adsorption are similar. The adsorption capacity of resin under the counterflow adsorption was 0.1046 mol/kg, which is 5% higher than that under parallel adsorption. Some fixed channels exist in the resin. During the parallel adsorption, the adsorption liquid exhibited only the effect of gravity and flows downward naturally from the resin, resulting in inadequate adsorption. During the counterflow adsorption, the adsorption solution exhibited the effect of gravity and an upward thrust, increasing the turbulence of the adsorption flow. Thus, the adsorption solution interacts with the resin more adequately, obtaining better adsorption effect.

**Influence of the aspect ratio of resin column on the adsorption effect of resin**

A cocurrent adsorption experiment was carried out under pH=1.76, flow rate of 14.5 ml/min, and 160 g of resin column. The pH test was conducted for every 500 ml of sample. The experimental results were compared with those using 15 g of resin. The results are shown in Fig. 6.
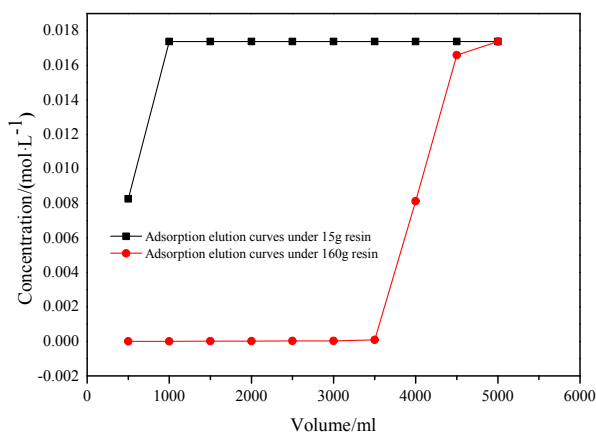
Fig.6 Adsorption elution curves under different aspect ratios of resin column

According to the experimental results, the higher resin dosage will delay the adsorption equilibrium. The adsorption equilibrium was achieved at 500 ml of effluent with 15 g of resin; however, with 160 g of resin, the adsorption equilibrium was delayed to 5,000 ml of effluent, and the adsorption capacity of resin was 0.4109 mol/kg. A higher resin dosage resulted in the higher adsorption capacity of resin. The adsorption capacity using 160 g of resin was 35.1% higher than that using 15 g of resin; this is because the higher resin dosage increases the height of the resin column, which increases interaction time of the resin with HCl, creating an environment conducive to an adequate HCl adsorption of resin, and thus delaying the adsorption equilibrium. Meanwhile, the diameter of the resin column was fixed and a taller column could reduce the proportion of invalid adsorption region, increasing the adsorption capacity of resin.

**Influencing factors of resin desorption process**

**Influence of the adsorption solution concentration on adsorption and desorption elution curves**

Four adsorption/desorption experiments were carried out with 10 g of resin and under a flow rate of 20 ml/min; the pH values were 3, 2.6, 2.2, and 1.8.In the experiments, the pH tests were conducted for every 100 ml of sample. The adsorption continued after 20 test points to ensure adsorption equilibrium. Next, the desorption experiments were implemented. The first test point was 10 ml, and then pH test was conducted for every 100 ml of sample. A total of 21 data were recorded. Results are shown in Fig. 7.
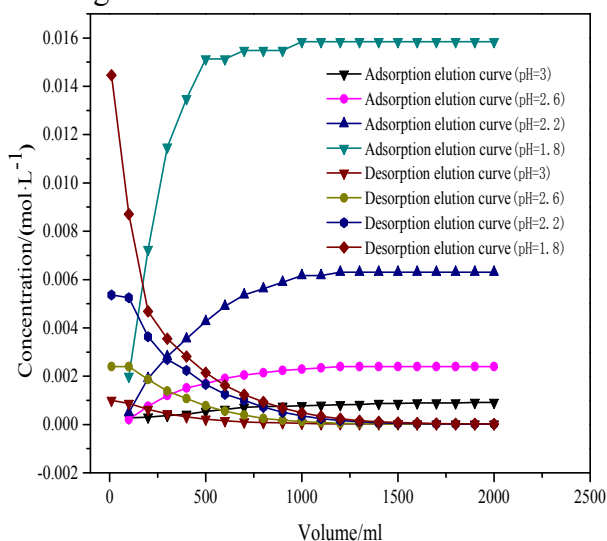


Fig.7 Influence of pH on the adsorption and desorption elution curves

Fig. 7 shows that:The HCl adsorption and desorption elution curves of the N235 resin were symmetric about the x-axis, indicating that the concentration of the adsorption effluent increased quickly initially and then equilibrated slowly, whereas the concentration of desorption effluent dropped dramatically and then equilibrated gradually. This observation reflects that HCl desorption of N235 resin is the inverse process of adsorption and that the HCl desorption is easy and complete.

The peak concentration of desorption effluent was close to the initial concentration of the adsorption effluent, indicating that the concentration of HCl desorption effluent in N235 resin exhibits a "memory effect".The adsorption and desorption elution curves of the same adsorption solution had one point of intersection. The higher the adsorption solution concentration, the higher the vertical coordinate (concentration) of this point of intersection, which is close to half concentration of the adsorption solution. Therefore, this point can be called as the "half-declining point" of desorption effluent concentration. The horizontal coordinate of this "half-declining point" was negatively correlated with the adsorption solution concentration, indicating that it took a shorter time (volume) for desorption effluent to reach the "half-declining point" when the adsorption solution concentration was higher. In other words, the higher the adsorption solution concentration, the quicker the concentration reduction during desorption will be.

**Influence of the aspect ratio of resin column on the adsorption and desorption elution curves**

Three adsorption/desorption experiments were carried out under a flow rate of 20 ml/min and pH=1.8, in which the resin dosages were 10, 20, and 40 g. The pH test was conducted for every 100 ml of sample until the achievement of the resin adsorption equilibrium. Next, desorption experiments were performed. Results are presented in Fig. 8.
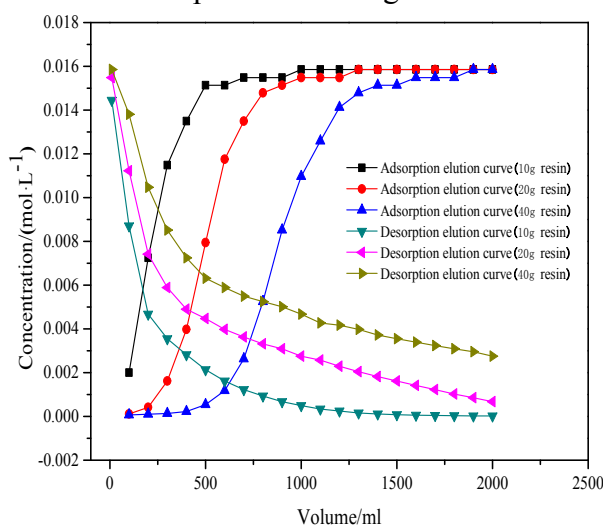


Fig.8 Adsorption and desorption elution curves under different resin dosages

Fig. 8 shows that:With the increase of resin dosage, the symmetry of adsorption and desorption elution curves about the x-axis still existed, but was weakened to some extent. The maximum concentration of desorption effluent was still equal to or slightly lower than the initial concentration of the adsorption solution. The "memory effect" of the desorption effluent concentration exists. With the increase of resin dosage, the horizontal axis of the "half-declining point" increased, and it took a longer time for desorption effluent to reach this point. In other words, the higher resin dosage would slow down the concentration reduction of the desorption effluent.The highest concentration of desorption effluent was close to the initial concentration of the adsorption solution.

**The effect of chloride concentration on desorption and adsorption outflow curve**

Pack with 50g resin and control the flow rate at 20ml/min. The concentration of HCl in the liquid was 0.050175mol/L, and the $LaCl_3$ in adsorption and desorption experiments was $2.63\times10^{-3}$, $9.805\times10^{-3}$, $2.678\times10^{-3}$mol/L, respectively. Each test of the pH was every 50ml until the adsorption process arrive a balance, while the desorption experiments set the first point at 5ml, then test the pH at every 50ml until the pH remains the same. The result are shown in Fig. 9.
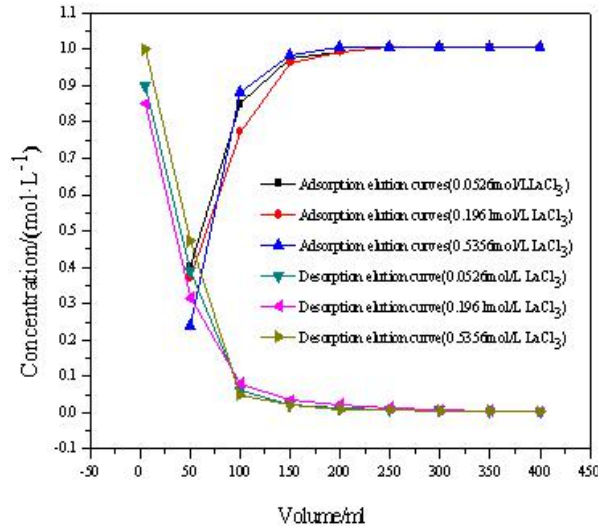
Fig. 9 Adsorption and desorption outflow curve at different lanthanum chloride concentration

It can be seen from Fig. 9 that with the concentration increase of lanthanum chloride in the solution, the X-axis symmetry characteristic of the adsorption and desorption effluent curve still exists and didn't change. The highest concentration of desorption solution exists a "memory effect" phenomenon can still equal or slightly smaller than the adsorption liquid, which indicates that change the concentration of chloride (salt) solution can't increase the concentration of hydrochloric acid, but with the increase of the concentration of lanthanum chloride, the resin can reach a adsorption- desorption balance more quickly.

**Adsorption equilibrium constant of N235 resin and acid concentration of desorption effluent**

**Saturated adsorption capacity of N235 resin**

Accurate 20 g of resin was placed in 1–8[#] 500 ml beakers in which 250-ml HCL solutions of different concentrations (1.426, 2.202, 2.852, 3.55, 3.959, 4.909, 6.126, and 6.908 mol/L) were added. Six hours of soaking adsorption was conducted at room temperature. The solution was filtered and the HCl concentration of the filtrate was determined. The adsorption capacity of resin could be deduced from:

$$c_n = \frac{(c_0 - c_e)*v}{m}*1000 \qquad (3)$$

where $c_n$ is adsorption capacity of resin (mol/kg); $c_o$ is the initial HCl concentration (mol/L), $c_e$ is the HCl equilibrium concentration (mol/L), $v$ is the volume (L), and $m$ is the resin mass (g).

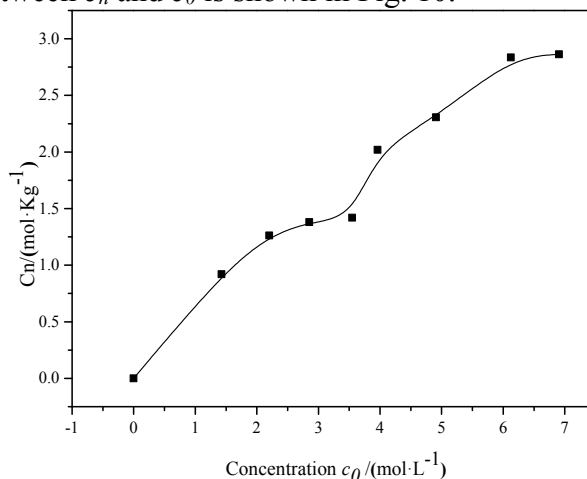The relation curve between $c_n$ and $c_0$ is shown in Fig. 10.



Fig.10elation curve between $c_n$ and $c_0$

Fig. 10 shows a positive relationship between $c_n$ and $c_0$ as well as two platforms. $c_n$ achieves

the first stability when $c_0$=3.55 mol/L, reaching 1.42 mol/kg. $c_n$ achieves the first stability when $c_0$=6.126 mol/L, reaching 2.84 mol/kg. These results are similar with reference literature [17].When $c_0$ was within the pH range, the saturated adsorption capacity of N235 resin was 1.42 mol/kg.

When the initial HCl concentration is in the pH range, the saturated adsorption capacity of N235 resin was 1.42 mol/kg.

**Adsorption equilibrium coefficient of N235 resin (K)**

Accurate 100 ml of HCl solution (pH =2.13) was placed in beakers with 0.2, 0.4, 0.6, 0.8, and 1.0 g N235 resin. The mixtures were stirred for 2 h under 40 °C for static adsorption experiments.

The above experimental data were analyzed according to Eq. 2, and *K* was calculated. The relation curve of lgk and resin dosage (m (g)) is shown in Fig. 11.
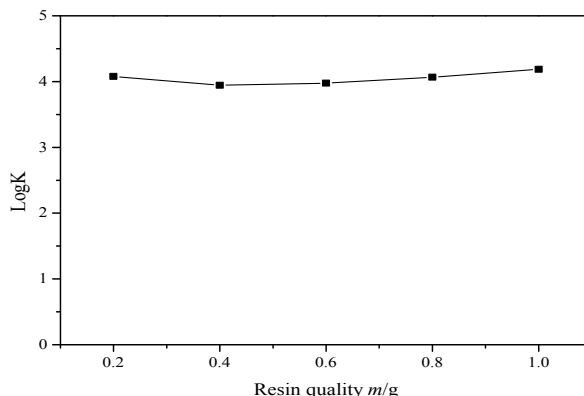


Fig.11 Relation curve of lgk and resin dosage

Fig. 11 shows that lgk fluctuated in a small range with resin dosage, averaging at lgk=4, $k$=1×10$^4$. Therefore, *K* was considerably higher than 1, and the adsorption was extremely easy. Under similar conditions, the adsorption process is priori to desorption process.

**Relationship between HCl concentration of desorption effluent and initial HCl concentration of the adsorption solution**

According to Eq. 2,

$Cn = K \cdot [N235] \cdot [H^+] \cdot [Cl^-]$       (4)

When the HCl concentration of adsorption effluent reaches the initial HCl concentration of the adsorption solution ($[H^+]_0$, $[Cl^-]_0$), HCl concentration on N235 resin reaches the peak ($C_{nmax}$),

$Cnmax = K \cdot [N235] \cdot [H^+]_0 \cdot [Cl^-]_0$     (5)

If the desorption equilibrium constant is *K'*, HCl concentration in desorption effluent ($[H^+]_{desorption}$, $[Cl^-]_{desorption}$) is:

$K' = [N235] \cdot [H^+]_{desorption} \cdot [Cl^-]_{desorption}/ Cn$     (6)

$[H^+]_{desorption} \cdot [Cl^-]_{desorption}= K' \cdot Cn/[N235]$     (7)

Since $K'*K$=1, when no ion is added in the desorption effluent, $[H^+]_{desorption\ max}$ corresponding to $C_{nmax}$ could be calculated by combining Eq. 5，Eq. 6 and Eq. 7:

$[H^+]_{desorption\ max} = [H^+]_0$       (8)

Eq. 8 reveals that $[H^+]_{desorption\ max} \leq C_{n\ max}$, which has been proven by the above experimental results. This means that even if the diameter ratio of adsorption desorption column is increased, the maximum concentration of hydrochloric acid in pure water desorption will not exceed the initial concentration of the adsorbed solution.

**Preparation of concentrated ammonium chloride solution by ammonia desorption**

The former result has been confirmed that the water desorption can't reach the purpose of concentrating the dilute hydrochloric acid, so instead by the ammonium water as a desorption reagent to reach the effect of neutralize the absorbed hydrochloric acid and the enrichment of extremely dilute hydrochloric acid.

Pack with 20 grams resin, and confecting the concentration of hydrochloric acid solution at

0.13, 0.23, 0.36mol/L respectively, and through the downstream adsorption method at a 10 ml/min flow rate. When the effluent concentration of hydrochloric acid was equal to the adsorption solution, which can consider the absorption-desorption had reached a balance, close the peristaltic pump and wait until the solution has been exhausted. Then using the concentration of ammonium water at 0.27mol/L to desorb by downstream method at 5ml/min flow rate, and collect 15ml of the front desorption solution, and the test shows that the concentration of chloride ions is 0.24, 0.41, 0.60mol/L respectively.

It can be seen that the concentration of chloride ions in desorption solution by using the ammonium water was much higher than other desorption solutions. That's because the ammonia water has a multi-effect on neutralizing hydrochloric acid and desorption of hydrochloric acid in the resin. When the concentration of hydrochloric acid in the adsorption solution was 0.13mol/L, which less than the desorption solution of ammonia water (0.27mol/L), because the hydrochloric acid in the resin is insufficient for ammonia, and the ammonia water neutralized the hydrochloric acid produced a certain amount of water, so the concentration of chloride ions in the desorption solution was 0.24mol/L, which higher than the absorption solution (0.13mol/L), and more or less to the desorption solution(0.27mol/L)，    When the concentration of hydrochloric acid in the adsorption solution was 0.23mol/L, which close to the desorption reagent of ammonia water (0.27mol/L), because the effect of neutralization by ammonia water and water desorption hydrochloric acid, so the concentration of chloride ions in the desorption solution was 0.41mol/L, which higher than ammonia water (0.27mol/L) but less than the sum concentration of ammonia water and hydrochloric acid(0.5mol/L). When the concentration of hydrochloric acid in the adsorption solution was 0.36mol/L, which higher than ammonia water (0.27mol/L), the effect of neutralization and water desorption had become more obvious, so the concentration of chloride ions in the desorption solution (0.60mol/L) was close to the sum concentration of ammonia water and hydrochloric acid (0.63mol/L). So the result shows that the extremely dilute hydrochloric acid can be enriched and disposed by adsorption with N235 resin and then desorbed with ammonia water.

## Conclusions

1. N235 levextrel resin has a strong adsorption capacity of dilute hydrochloric acid, the adsorption equilibrium coefficient $k=10^4$, the adsorption capacity increases along with the increase of the acidity of the adsorbed liquid and the concentration of chloride ion, decreases along with the flow rate, and increases along with the column height to diameter ratio grow, while the downstream/upstream flow method has little influence on the adsorption capacity.

2. N235 resin receive the maximum concentration of the desorption solution HCl through adsorption - desorption method of dilute HCl is equal with the initial concentration of the adsorption solution, which indicated that N235 resin has a "memory effect" on the adsorption-desorption of dilute hydrochloric acid, even change the column diameter ratio can not achieve the purpose of concentration the hydrochloric acid.

3. The adsorption capacity of resin usually exists two platforms. When the initial concentration of HCl has reached 3.55 mol/L, the resin adsorption capacity tends to be flatten, reaching 1.42 mol/Kg. When the initial concentration of HCl has reached 6.126 mol/L, the adsorption capacity of resin tends be flatten for the second time, reaching 2.84 mol/Kg.

4. The extremely dilute hydrochloric acid, which produced in the extraction process of rare earth can be enriched and disposed by adsorption with N235 resin and then desorbed with ammonia water. And this research can be used for the no saponification extraction separation process of rare earth.

## Acknowledgements

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