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Selective Removal of Al(III) from Rare Earth Solutions Using Peas-based Activated Carbon

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ABSTRACT. Efficiently removing Al(III) from rare earth is very significant because even trace amount of Al(III) can cause serious harm to the rare earth materials. In this paper, a nitrogen-containing activated carbon, AC-P700, was synthesized using peas as raw materials. The AC-P700 was characterized by surface area analyzer, FT-IR, and XPS methods. The adsorption and recognition properties of AC-P700 towards Al(III) were investigated, and the recognition mechanism was also analyzed. The BET special surface area of AC-P700 was 1277.1 $m^2 \cdot g^{-1}$, and the average pore diameter was 1.90 nm. The AC-P700 possesses strong adsorption affinity and excellent recognition selectivity towards Al(III). The adsorption capacity for Al(III) could reach to 0.53 $mmol \cdot g^{-1}$, and relative selectivity coefficients relative to La(III) and Ce(III) is 9.6 and 8.7, respectively. Besides, AC-P700 possesses better regeneration ability and reusability.

Key words: Activated carbon, Recognition, Selectivity, Al(III), Peas

INTRODUCTION

Rare earth elements (REEs) have been widely applied in optical, electronics, magnetism, catalysis, metallurgy, the ceramic industry, and etc.[1–3] However, even trace amount of non-rare earth impurities will cause serious harm to the performances of rare earth material.[4–6] For example, the relative brightness of La_2O_2S cathode material could be reduced by 10.3% due to 0.06% of Al impurity doping. Efficiently removing non-rare earth impurities is very significant and has attracted more and more attentions. Some related studies have been researched.[4–7] Solvent extraction method, extraction-elution resin (solvent impregnated resin), precipitation with oxalic acid, and ionic imprinted polymer solid phase extraction method are mainly used. However, a large amount of organic phase was consumed in solvent extraction method, and secondary pollution for the environment is inevitable. The adsorption capacity and separating efficiency of extraction-elution resin is low. The precipitation with oxalic acid is of high cost. The ionic imprinted polymer is very difficult to realize industrialization. So, seeking for an effective and easy separation material or method is very necessary.

Porous activated carbons have been widely used as adsorbents due to their developed pore structure and high specific surface.[8–11] Furthermore, surface functional groups also have important contribution to the adsorption properties of activated carbons. The abundant surface functional groups can improve the adsorption properties markedly. For metal ions, nitrogen-containing groups are usually considered because of the coordination ability of N towards most metal ions. Surface modification with nitrogen-containing chemical reagents[12–14] and direct preparation using nitrogen-containing biomass or polymers as precursor[15–23] are effective pathways to introduce nitrogen-containing groups into carbon matrix. The latter method is more commonly used to prepare porous nitrogen-containing activated carbons.

In this work, nitrogen-containing porous activated carbons, AC-P700, were synthesized using peas (*Pisum sativum L.*) as raw materials carbonized at 700 °C. The pore structure was determined, and the surface chemical groups of resultant porous activated carbon were characterized. Its adsorption and recognition properties for Al(III) were investigated, and recognition mechanism was also analyzed.

EXPERIMENTAL

Preparation of AC-P700

Firstly, the dry peas were pulverized and sieved. Then, 10 g of peas powders (100-125 μm) were soaked in 100 mL of KOH aqueous solution with concentration of 20 $g \cdot L^{-1}$ for 24 h. After filtrated, the resultant solid was carbonized in charcoal furnace at 700 °C for 2 h with heating rate of

3 °C·min^{-1} and N_2 flow of 50 mL·min^{-1}. Finally, the resultant samples were washed with distilled water until neutral and then dried at 80 °C for 24 h in a vacuum oven.

Characterizations

Fourier transform infrared (FTIR) spectra of the samples were measured on the Nicolet FT-IR 4800S (Shimadzu, Japan) spectrometer using the conventional KBr pellet method. Nitrogen adsorption-desorption isotherm was measured with the surface area analyzer (Beijing JWGB BF-JW132F) by nitrogen absorption at 77 K using the Brunauer-Emmett-Teller (BET) method. The X-ray photoelectron spectroscopy (XPS) was measured with the ESCALAB 250 (Thermo Electron).

Batch Adsorption of AC-P700 toward Al(III)

Kinetic adsorption curve. About 0.05 g of AC-P700 was introduced into a conical flask directly. 25 mL of Al(III) aqueous solution with initial concentration (C_0) of 3.7 mmol·L^{-1} and pH of 3 was then added into the conical flask. This conical flask was placed in a shaker at 25 °C. At different times, the concentrations (C_t) of Al(III) solution were determined by inductive coupled plasma emission spectrometer. The adsorption capacity (Q, mmol·g^{-1}) was calculated by Eq. 1. This procedure was repeated three times.

$$Q = \frac{V(C_0 - C_t)}{m} \tag{1}$$

where V is the volume of the solution (L); m is the weight of absorbent (g).

Selectivity experiments. The mixed solution of Al(III) and REE(III) was prepared, and the batch adsorption experiments under different ion concentrations were performed. After adsorption reached equilibrium, the concentrations of Al(III) and REE(III) in the remaining solutions were determined by inductive coupled plasma emission spectrometer. Distribution coefficients (K_d) of Al(III) and REE(III) were calculated by Eq. 2.

$$K_d = \frac{Q_e}{C_e} \tag{2}$$

Selectivity coefficient (k) of AC-P700 towards Al(III) with respect to the competitor species REE(III) can be obtained by Eq. 3.

$$k = \frac{K_d(Al^{3+})}{K_d(REE^{3+})} \tag{3}$$

Dynamics adsorption and elution experiment

2.1354 g of AC-P700 was filled in a glass column with 10 ml of bed volume (BV). The Al(III)/La(III) mixture solution (pH of 3, and the initial concentrations of 0.37 mmol·L^{-1} and 0.72 mmol·L^{-1}, respectively) was allowed to flow gradually through the column at a rate of 5 BV·h^{-1}. 1 BV of effluent was collected and the concentrations of every ion were determined. Then the dynamics adsorption curve was plotted.

Elution experiment was performed using hydrochloric acid solution with concentration of 2 mol·L^{-1} as eluting agent, and the flow rate of the eluting agent was controlled at 1 BV·h^{-1}. The eluent with one bed volume was collected and the concentration of every ion was determined, and the elution curve was plotted.

Adsorption-Desorption Experiment

The reusability is an important factor for a good absorption material. Desorption of the adsorbed Al(III) from the AC-P700 also studied by batch experimental using 2 mol·L^{-1} of hydrochloric acid solution as eluent. In order to test the reusability of AC-P700, Al(III) adsorption-desorption procedure was repeated ten times.

RESULTS AND DISCUSSION

Characterization of AC-P700

The FTIR spectrum of AC-P700 is shown in *Fig*. 1.

In the spectrum of peas, the peak at 2925 cm^{-1} is assigned to the characteristic absorption of the -CH_3 and -CH_2- group. The peaks at 1721, 1399, 1170 cm^{-1} are assigned to the characteristic absorption of the -C=O and -CHO group. The peak at 1652 cm^{-1} is assigned to the characteristic absorption of the -NH- group. In the spectrum of AC-P700, the peak at 1674 cm^{-1} is assigned to the characteristic

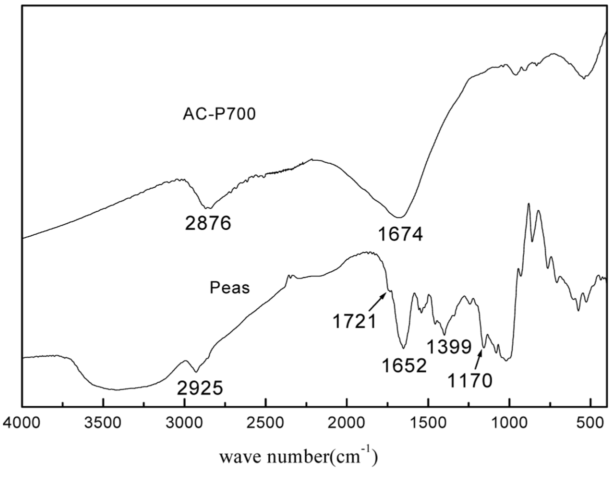

***Figure* 1.** FTIR spectra of peas and AC-P700.

***Table* 1.** The type and amount of surface functional groups of AC-P700

Group	-COO$^-$	-C=O	-OH	-NH-
Amount (mmol·g^{-1})	0.05	0.04	0.05	4.3

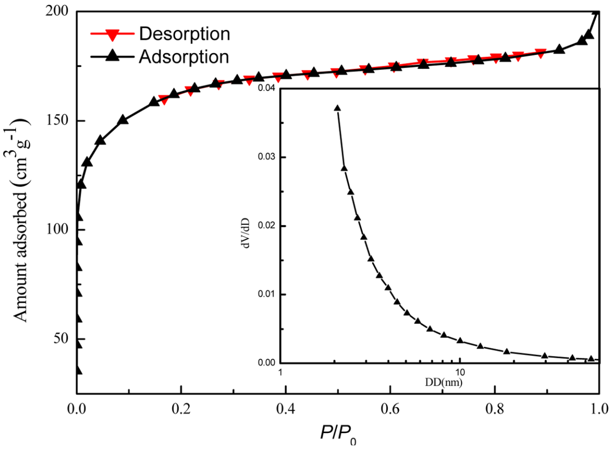

***Figure* 2.** N_2 adsorption-desorption isotherms and pore size distribution curves.

***Table* 2.** The pore structure parameters of AC-P700

S_{BET} (m^2·g^{-1})	Pore size (nm)	V_{Micro} (cm^3·g^{-1})	V_{total} (cm^3·g^{-1})
1277.1	1.90	0.365	0.424

absorption of the -NH- group. This indicates that AC-P700 still retains a certain amount of amine groups after carbonization. This is according with the result of Boehm titration (*Table* 1). These amine groups can coordinate with the metal ions.

The N_2 adsorption-desorption isotherms and pore size distribution curve are shown in *Fig*. 2. The pore properties of AC-P700 are listed in *Table* 2.

The N_2 adsorption-desorption isotherm gives steep type I isotherm with a small hysteresis loop of type H_4 according to the IUPAC classification.[24] The adsorption of N_2 increases rapidly at low relative pressure ($P/P_0<0.10$) and then approaches a plateau. It can be also seen that the N_2 adsorption and desorption curve is almost overlapped. These indicate that a large amount of micropores with a highly narrow pore size distribution were developed, and this is accord with sharp pore size distribution curve. The average pores size of AC-P700 is 1.90 nm, and the $V_{micropore}$ accounts for 86.1% of V_{total}. These indicate again that there were a large amount of micropores in AC-P700.

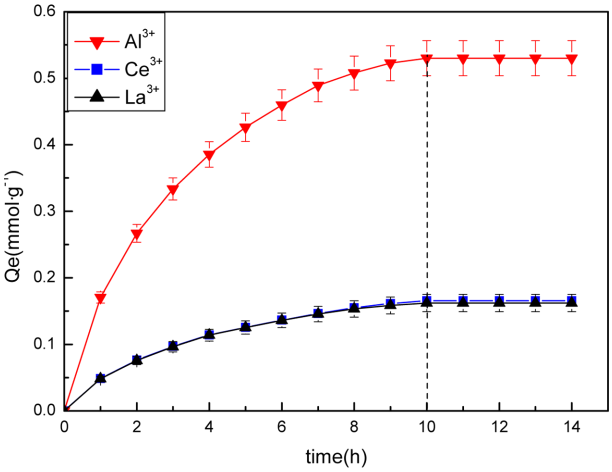

***Figure* 3.** Kinetic adsorption curves of AC-P700 for Al(III), Ce(III), and La(III). (Temperature: 25 °C, pH = 3)

Adsorption Properties of AC-P700 towards Al(III)

The kinetic adsorption curves are shown in *Fig*. 3.

The adsorption towards the Al(III) and REE(III) ions reached to equilibrium within 10 h. The saturated adsorption capacity of AC-P700 for Al(III), La(III), and Ce(III) is 0.53 mmol·g^{-1}, 0.16 mmol·g^{-1}, and 0.17 mmol·g^{-1}, respectively. It was implied that AC-P700 possesses very strong adsorption ability for Al(III) and REE(III) ion. The reason is that the AC-P700 has developed pore structure and abundant surface functional groups, and Al(III) and REE(III) ion could quickly pass the pore and combine with the action site (mainly amino groups).

Adsorption Selectivity

Competitive adsorptions of AC-P700 towards Al(III)/La(III)/Ce(III) ternary mixtures were researched by batch method to research the recognition selectivity. *Table* 3 summarizes the data of the distribution coefficients K_d and selectivity coefficients k.

It can be seen that the AC-P700 has excellent recognition selectivity towards Al(III). The high selectivity of AC-P700 towards Al(III) relative to REE(III) could be

***Table* 3.** Distribution coefficient and selectivity coefficient data of AC-P700

Initial concentration (mg·L^{-1})		K_d (L·g^{-1})				
Al(III)	REE(III)	Al(III)	La(III)	Ce(III)	k(Al/La)	k(Al/Ce)
10	100	0.096	0.010	0.011	9.6	8.7
100	100	0.088	0.009	0.010	9.8	8.8

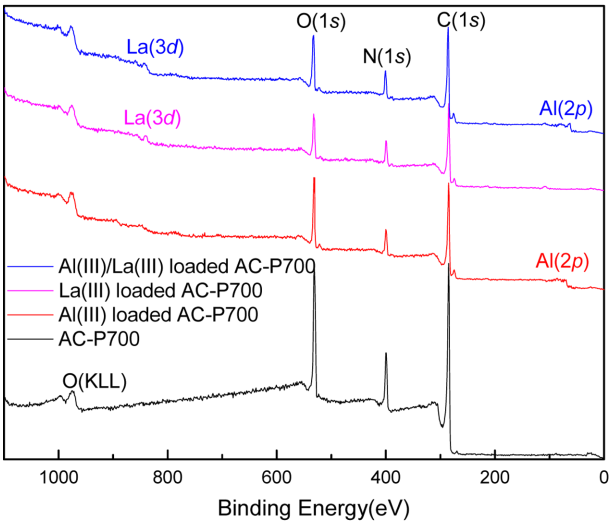

***Figure* 4.** The XPS spectra of AC-P700 before and after adsorbing Al, La, and Al/La.

explained through analyzing the adsorption driving force.

In order to analyze the adsorption and recognition selectivity mechanism, XPS method was further used to study the surface chemical compositions and oxidation states of metal ions. The XPS spectra of AC-P700 before and after adsorbing Al, La, and Al/La are shown in *Fig*. 4, and detailed deconvolution XPS spectra of every element are shown in *Fig*. 5 and *Fig*. 6, respectively.

The signal of metal ion was observed in the XPS spectra of metal ion-loaded AC-P700, and this indicates that the adsorption of AC-P700 towards metal ions was carried out.

Some important laws can be also found from *Fig*. 5 and *Fig*. 6. Firstly, the binding energy of C and O has almost no change, and this indicates that C and O did not coordinate with metal ions. Secondly, the new signal of N (~399 eV, ~401 eV), Al (71.82 eV, 71.05 eV), and La (850.12 eV, 832.36 eV) was observed in spectra of single metal ion-loaded AC-P700 (Al(III) loaded AC-P700 and La(III) loaded AC-P700). The binding energy of N was increased, and that of Al and La was decreased. These indicate that coordination bonds (N→Al, N→La) were formed between the lone pair electrons of N and unoccupied orbital of metal ions. The outer electrons migration of N makes N having higher valence state, so the binding energy was increased. Lastly, the new signal of N and Al was also observed in spectra of double metal ion-loaded AC-P700 (Al(III)/La(III) loaded AC-P700), but the new signal of La was not observed. This indicates that the N atoms only coordinate with Al and no coordinate with La when Al and La exists simultaneously due to the special electronic structure of

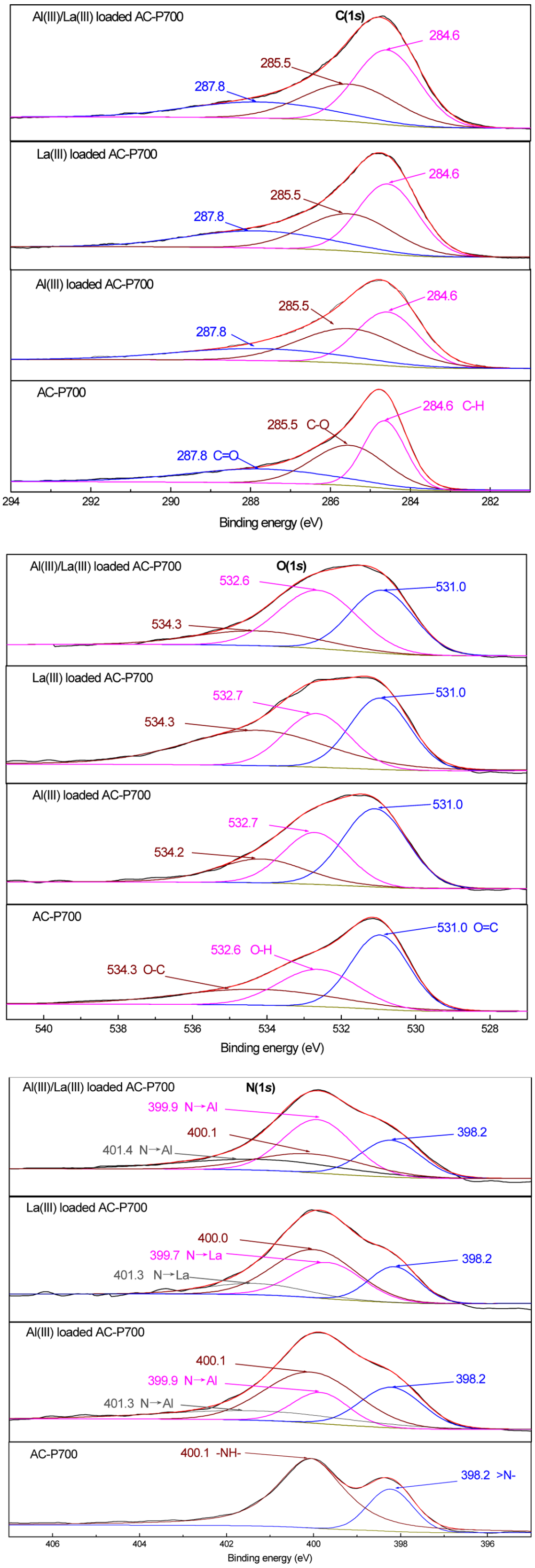

***Figure* 5.** Deconvolution XPS spectra of C, O, and N in AC-P700.

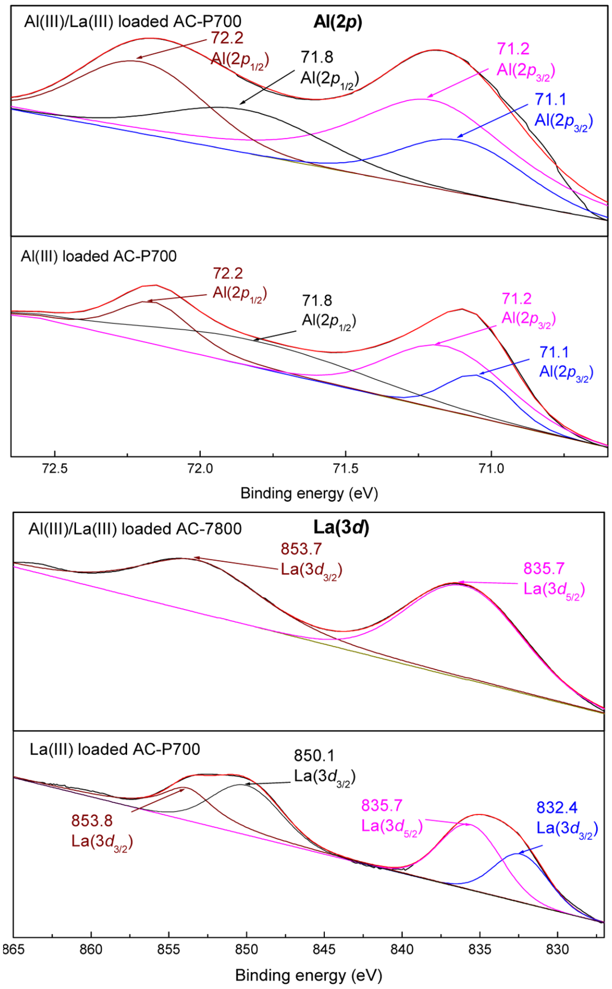

***Figure* 6.** Deconvolution XPS spectra of Al and La.

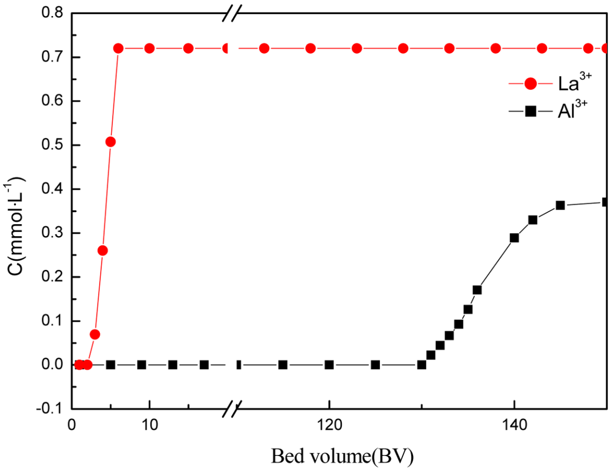

***Figure* 7.** Dynamic adsorption curve of AC-P700 towards mixture of Al(III) and La(III) Temperature: 25 °C; pH = 3.

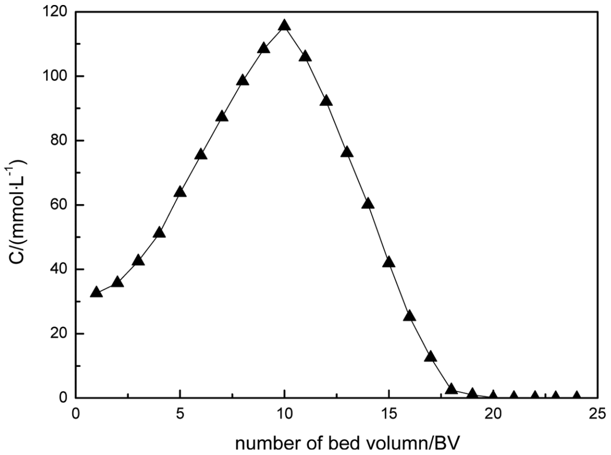

***Figure* 8.** Dynamic elution curve.

La. The special electronic structure results in the weaker coordinating ability and the larger coordination number (mainly 6, 8, 9, 12), and the La adsorbed by means of coordination could be easily replaced by Al with stronger coordinating ability. Based on the above analysis, it can be seen that AC-P700 could selectively adsorb Al(III) from Al(III)/La(III) mixture solution, namely AC-P700 has excellent recognition selectivity towards Al(III).

In order to demonstrate further the selectivity and practical application value of AC-P700, the Al(III)/La(III) mixture solution (pH of 3, and the initial concentrations of 0.37 mmol·L^{-1} and 0.72 mmol·L^{-1}, respectively) were treated using AC-P700 column with upstream flows. The dynamic adsorption curve is shown in *Fig*. 7.

The leaking bed volume is 130 BV for Al(III) and 3 BV for La(III). This indicates that Al(III) can be recognized better by AC-P700 and AC-P700 can selectively remove Al(III) from La(III) solution. In the total 130 BV (1300 mL) of effluent, the Al(III) was not determined and the concentration of La(III) was 0.71 mmol·L^{-1}. This confirms again that AC-P700 has excellent selectivity towards Al(III), and highly pure La(III) solution could be obtained.

Good desorption performance of an adsorbent is important for its potential practical applications. Relative to the metal ions, H$^+$ has more strong interaction with amino nitrogen, and H$^+$ could destroy the coordination between N and metal ions. So, 2 mol·L^{-1} of hydrochloric acid was used as the eluent. *Fig*. 8 gives the elution curve of Al(III) and La(III) from the exhausted AC-P700.

It can be seen that the shape of Al(III) desorption curve is cuspate and without tailing, and it shows fine elution result. The calculation results show that within 18 bed volumes, Al(III) is eluted with a desorption ratio of 99.57%. This fact reveals fully that AC-P700 has outstanding elution property and excellent reusing property.

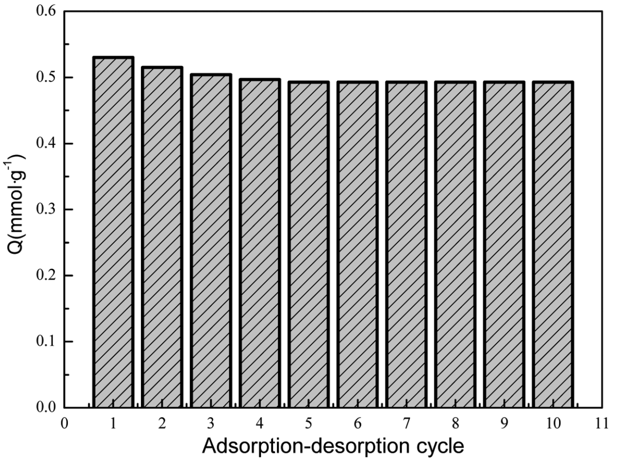

***Figure* 9.** Adsorption-desorption cycle of AC-P700.

Desorption and Reusability

The exhausted AC-P700 was regenerated using hydrochloric acid as the eluent. In order to show the reusability of the AC-P700, adsorption-desorption cycle was repeated 10 times by using the same carbon material. Adsorption-desorption cycle is shown in *Fig*. 9.

The result clearly shows that the AC-P700 could be used repeatedly without loosing significantly adsorption capacity.

CONCLUSION

High-performance nitrogen-containing porous activated carbon, AC-P700, was synthesized successfully by peas carbonized at 700 °C. The BET special surface area could be reached 1277.1 $m^2·g^{-1}$, and the pore size was 1.90 nm. The AC-P700 possesses strong adsorption affinity and excellent recognition selectivity towards Al(III) due to its developed pore structure and nitrogen-containing chemical groups. The adsorption capacity for Al(III) could reach to 0.53 mmol·g^{-1}, and relative selectivity coefficients relative to La(III) and Ce(III) is 9.6 and 8.7, respectively. Besides, AC-P700 was regenerated easily using diluted hydrochloric acid solution as eluent and AC-P700 possesses better reusability. On the basis of the results obtained in this study, it is obvious that comparing to traditional solvent extraction and extraction-elution resin, the porous activated carbon AC-P700 can selectively adsorb and effectively remove trace amount of Al(III) from La(III) and Ce(III) solution.

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