D301 树脂吸附铼(Ⅶ)的研究

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摘要：本文研究了 D301 树脂对铼(Ⅶ)的吸附性能，结果表明在 T=298 K，pH=2.7 的 HAc-NaAc 缓冲溶液中静态饱和吸附容量为 715 mg·g^{-1}；0.5~5.0 mol·L^{-1} HCl 溶液可以不同程度地解吸树脂上的铼，其中 4.0 mol·L^{-1} HCl 作为解吸剂时，一次解吸率可达 100%。反应开始阶段的表观吸附速率常数 $k_{298\ K}$=7.2×10^{-5} s^{-1}；等温吸附服从 Freundlich 经验式；吸附反应的 ΔH=−4.4 kJ·mol^{-1}；吸附物中树脂功能基与 Re(Ⅶ)的物质的量比约为 1:1。并用化学法和红外光谱探讨了吸附机理。

关键词：D301 树脂；铼；吸附
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Adsorption of Rhenium(Ⅶ) with D301 Resin

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Abstract: The adsorption properties of D301 resin (D301R) for Re(Ⅶ) were investigated. The statically saturated adsorption capacity is 715 mg·g^{-1} at 298 K in HAc-NaAc medium at pH 2.7. Re(Ⅶ) adsorbed on D301R can be eluted by 0.5~5.0 mol·L^{-1} HCl and the elution percentage is as high as 100% in 4.0 mol·L^{-1} HCl solution. The apparent adsorption rate constant of D301R for Re(Ⅶ) at the initial stage is $k_{298\ K}$=7.2×10^{-5} s^{-1}. The adsorption behavior obeys the Freundlich empirical formula. The thermodynamic adsorption parameter, enthalpy change ΔH is −4.4 kJ·mol^{-1}. The molar ratio of the functional group of D301R to Re(Ⅶ) is about 1:1. The adsorption mechanism of D301R for Re(Ⅶ) was examined by using chemical method and IR spectrometry.

Key words: D301 resin; rhenium; adsorption

Rhenium is a kind of valuable metal with high melting point and plays an important role in many fields such as chemical industry, metallurgy, spaceflight, national defense and other fields. However, it always exists in molybdenite rather than individual mineral in nature. In recent years, rhenium is always in short supply on the world market. Thus, the recovery of rhenium from molybdenite and wastewater makes an interesting task. There are various methods to recover rhenium like precipitation[1], extraction[2~7] and ion exchange on polymeric materials[8~16] about which much attention has been paid to the synthesis, characterization and adsorption property due to the advantages such as high adsorption capacity, easy regeneration and convenient operation, etc. In some papers, strong base resin which have a quaternary amine functional group like IRA400, D296, AV-17, D201×7 and Dowex-1 were used to concentrate rhenium from the aqueous effectively. Unfortunately, the elution of rhenium from these ion exchangers are always accomplished with

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thiocyanate or with $HClO_4$ or HNO_3. Recently, weak base resin also displays a good exchange capacity for rhenium and what's more, it is possible to desorb perrhenate ions with aqueous ammonia. Therefore, the present paper aims at studying the adsorption behavior of D301 resin which is a weak base resin containing a functional group of $[N(CH_3)_2]$ for rhenium(Ⅶ). The adsorption capacity is good and elution can be achieved by hydrochloric acid. The basic adsorption parameters are also determined. The experimental results may provide a basis for the further studying of concentrating rhenium in hydrometallurgy.

1 Experimental

1.1 Materials and instruments

D301R: D301 resin (provided by Nankai university, activated before use). The aqueous stock rhenium(Ⅶ) solution of 1.0 $mg\cdot mL^{-1}$ was obtained by dissolving 1.000 0 g rhenium powder (99.99%) in 10 mL concentrated hydrochloric acid and by adding 30% hydrogen peroxide until it was decomposed completely, and then diluted to 1 L solution. The aqueous stock molybdenum(Ⅵ) solution of 1.0 $mg\cdot mL^{-1}$ was prepared by dissolving 1.840 3 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ into 1 L purified water. Buffer solution with pH 2.7~6.0 were prepared from 1.0 $mol\cdot L^{-1}$ sodium acetate-acetic (NaAc-HAc), other reagents were of A.R. grade.

UV-2401PC ultraviolet-visible spectrophotometer, SartoriusPB-20 pH meter, SHZ-B temperature constant shaking machine, AVATAR330 FTIR, Elemental Analyzer EA 1110.

1.2 Experimental method

1.2.1 Adsorption equilibrium experiment

A desired amount of treated resin was pre-swollen in a desired volume of buffer solution for 24 h before adding a required amount of standard Re(Ⅶ) solution and shaken at constant temperature until adsorption equilibrium arrived. The concentration of Re(Ⅶ) in the aqueous phase was determined by the reagent of NH_4SCN at 390 nm[17]. The adsorption capacity (Q), distribution coefficient(D) and separating coefficient(β) were calculated with the following formulas:

$$Q=\frac{(c_0-c_e)\cdot V}{W}$$

$$D=\frac{Q}{c_e}$$

$$\beta_{Re/Mo}=\frac{D_{Re}}{D_{Mo}}$$

where c_0 is initial concentration ($mg\cdot mL^{-1}$), c_e is equilibrium concentration ($mg\cdot mL^{-1}$), V is total volume of solution (mL), W is resin weight (g).

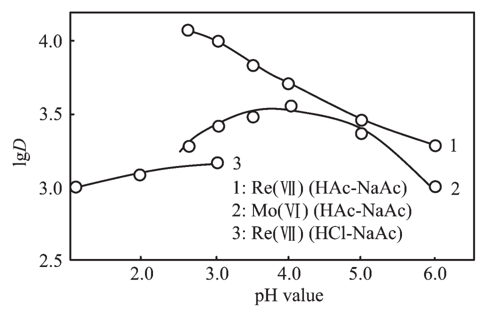
1.2.2 Elution test

According to 1.2.1, the adsorption capacity of the desired amount resin for Re(Ⅶ) was determined and the resin separated from aqueous phase was washed three times with pH 2.7 buffer solution. Then it was shaken with eluant until equilibrium was reached and the percentage of elution was obtained.

2 Results and discussion

2.1 Effect of pH on distribution coefficient

The test was carried out according to the above-mentioned method. The effect of pH on the adsorption behavior of D301R for Re(Ⅶ) was shown in Fig.1. The results demonstrate that the distribution coefficient decreases with the increase of pH in HAc-NaAc system. And it is also influenced by buffer system. The value of lg$D$ is 4.09 at pH 2.7 in HAc-NaAc system while it is only 3.15 in HCl-NaAc system. This may be explained by the fact that Cl^- existing in solution competes against ReO_4^-. At the same time, the experiment of the adsorption for Mo(Ⅵ) was conducted individually. From Fig.1, it can be found out that the distribution coefficient of Mo(Ⅵ) reaches a maximum around pH 4.0 before decreasing gradually. So the separating coefficient between Re(Ⅶ) and Mo(Ⅵ) is $\beta_{Re/Mo}$=6.9 at pH 2.7, which indicates that Re(Ⅶ) and Mo(Ⅵ) can be separated

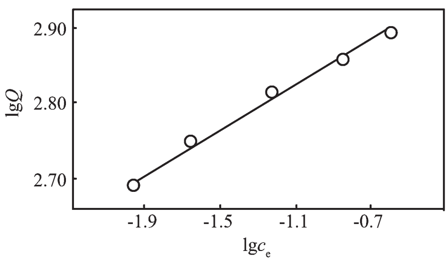


Resin 10.0 mg, c_0=7.0/30.0 ($mg\cdot mL^{-1}$), T=298 K

Fig.1 Effect of pH on distribution coefficient to a certain degree. Therefore, all further tests were conducted at pH 2.7 in HAc-NaAc system.

2.2 Isotherm adsorption curve

10.0, 15.0, 20.0, 25.0, 30.0 mg of the resin were weighed and put into conical flasks individually. The other experimental conditions are shown in Fig.2. When the adsorption equilibrium arrived, equilibrium concentration c_e ($mg \cdot mL^{-1}$) was determined and its corresponding adsorption capacity Q ($mg \cdot g^{-1}$) was calculated. The experimental data are regressed by the Freundlich equation $Q=ac_e^{1/b}$, i.e., $\lg Q=(1/b)\lg c_e+\lg a$, which is the empirical relationship whereby it is assumed that the adsorption energy of a metal binding to a site on an absorbent depends on whether or not the adjacent sites are already occupied, where b and a are Freundlich constants. The regression equation at 298 K is $\lg Q = 0.15\lg c_e+2.99$ with a correlation coefficient 0.995. So, b is equal to 6.7 and a is 977.2. A value of b between 2 and 10 indicates easy adsorption of D301R for Re(Ⅶ) from aqueous medium[18].



c_0=15.0/30.0 ($mg \cdot mL^{-1}$), pH=2.7, T=298 K

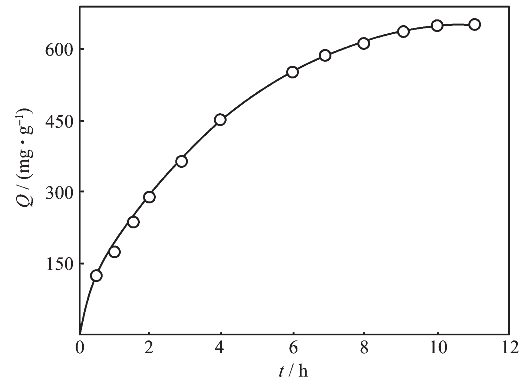
Fig.2 Freundlich isotherm curve

2.3 Determination of adsorption rate constant

According to the experimental condition shown as Fig.3, small samples of clear solution was taken out at intervals for the determination of residual concentration, after the remanent kept constant and volume was corrected, a series of data was obtained. When the adsorption amount is half of that at equilibrium, the required time is $t_{1/2}$=2.5 h. According to Brykina method[19]

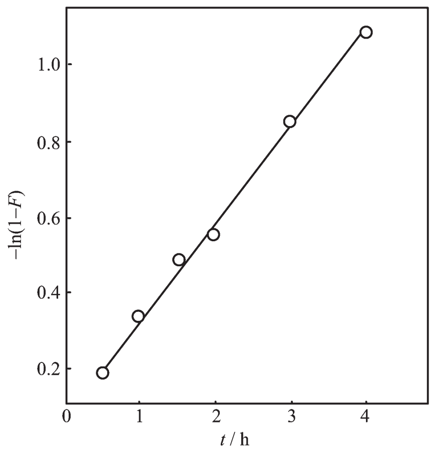
$$-\ln(1-F)=kt$$

where $F=Q_t/Q_\infty$, Q_t and Q_∞ are the adsorption amounts at certain time and at equilibrium, respectively. The experimental results are accorded with the equation and a straight line is obtained by plotting $-\ln(1-F)$ against t during the first 4 h. Therefore, the adsorption rate constant calculated from the slope of the straight line is $k_{298\,K}=7.2\times10^{-5}\ s^{-1}$ at the initial stage.



Resin 10.0 mg, c_0=10.0/50.0 ($mg \cdot mL^{-1}$), pH=2.7, T=298 K

Fig.3 Adsorption capacity Q in different adsorption time



Resin 10.0 mg, c_0=10.0/50.0 ($mg \cdot mL^{-1}$), pH=2.7, T=298 K

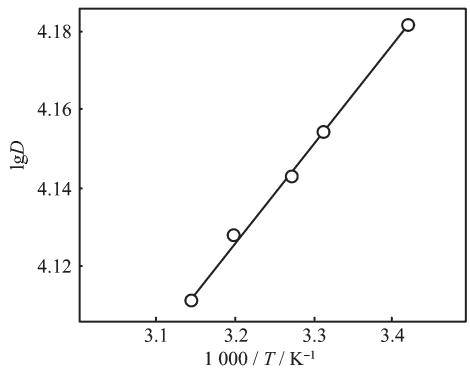
Fig.4 Determination of adsorption rate constant

2.4 Effect of temperature on distribution coefficient and determination of thermodynamic parameter

Under the experimental condition shown in Fig.5, distribution coefficient of Re(Ⅶ) on the resin during the range of temperature from 291 K to 318 K was measured. A straight line was obtained by plotting $\lg D$ against $1/T$ with a correlation coefficient 0.990. The result obviously indicates that it is unfavorable for the adsorption with the increase of the temperature, namely, the adsorption ability of the resin weakens as the temperature of the solution rises. According to

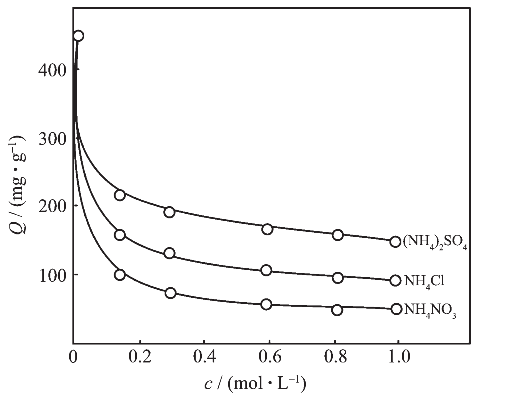
$$\lg D=-\Delta H/(2.30RT)+\text{constant}$$

ΔH can be calculated to be $-4.4\ kJ \cdot mol^{-1}$ from the slope of the line. The negative value of ΔH indicates the exothermic nature of the process[20].



Resin 10.0 mg, c_0=9.0/30.0 (mg·mL^{-1}), pH=2.7

Fig.5 Effect of temperature on distribution coefficient



Resin 10.0 mg, c_0=5.0/30.0 (mg·mL^{-1}), pH=2.7, T=298 K

Fig.6 Effect of anion on the adsorption of D301 for Re(Ⅶ)

2.5 Effect of anion on the adsorption of D301R for Re(Ⅶ)

The effect of anion on the adsorption of D301R for Re(Ⅶ) was conducted by adding different amount of NH_4Cl, NH_4NO_3 and $(NH_4)_2SO_4$ to the solution. The results shown in Fig.6 illustrates that the adsorption capacity drops with the increase of the anion of the solution (i.e., the increase of NH_4Cl, NH_4NO_3 and $(NH_4)_2SO_4$ concentration) and the order of different anion on the adsorption for Re(Ⅶ) is NO_3^->Cl^->SO_4^{2-}.

2.6 Determination of the molar ratio

2.6.1 Saturated method

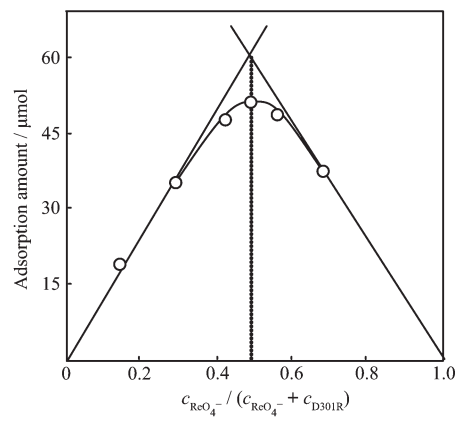
Under the experimental condition of T=298 K, c_0=10.0/30.0 (mg·mL^{-1}), the experiment was performed by using the above-mentioned method. The adsorption capacity of the resin for Re(Ⅶ) is 715 mg·g^{-1} resin. The amount of functional group and the capacity of the resin for Re(Ⅶ) are calculated in Table 1, which indicates that the molar ratio of the functional group to Re(Ⅶ) is approximately 1:1.

Table 1 Molar ratio of D301R functional group to Re(Ⅶ)

Functional group capacity of D301R / (mmol FG·g^{-1})	Adsorption capacity of D301R / (mmol Re(Ⅶ)·g^{-1})	Molar ratio FG/Re(Ⅶ)
4.05	3.84	1.05:1

2.6.2 Equimolar method

Six parts of different amount of resin were accurately weighed and added into the conical flasks, then mixed with different amount of Re(Ⅶ). The total amount of D301R and Re(Ⅶ) was kept at 120.0 μmol whatever the molar ratio may be. That was carried out with the same method mentioned before. The adsorption amount vs $c_{ReO_4^-}/(c_{ReO_4^-}+c_{D301R})$ yields a curve shown in Fig.7. The expected adsorption amount reaches the maximum as the molar fraction of Re(Ⅶ) is 0.49 shown on the abscissa. It means that the molar ratio of functional group to Re(Ⅶ) is about 1:1, which is in agreement with the conclusion of the saturated method.



T=298 K, pH=2.7

Fig.7 Equimolar series method

2.6.3 Analysis of infrared spectra

In order to examine the mechanism of the adsorption, we compared the spectra of the resin before and after Re(Ⅶ) adsorbed. It is easy to discover that the new peak 940.8 cm^{-1} and 902.5 cm^{-1} which are the characteristic adsorption peaks of the bond Re-O[21] has formed, while there is little change on the other adsorption peaks. It means that ReO_4^- might be adsorbed by ion exchange mechanism under the present experimental condition.

2.7 Elution and regeneration of resin

When HCl is used as an eluant, the percentages of elution varies from 0.5 mol·L^{-1} to 5.0 mol·L^{-1} HCl and reaches 100% in 4.0 mol·L^{-1} HCl solution as listed in Table 2. So, Re(Ⅶ) adsorbed on the resin can be recovered quantitatively. In order to examine the practical value of HCl as an eluant, the elution rate of 4.0 mol·L^{-1} HCl was determined and the results showed that $t_{1/2}'$ was equal to 5 minutes, which was the time required to reach 50% of elution.

Table 2 Elution test of Re(Ⅶ)

Concentration of HCl / (mol·L^{-1})	Adsorption capacity of D301R / (mg Re(Ⅶ)/10.0 mg)	Elution amount / mg	Elution percentage / %
0.5	7.15	5.35	74.8
1.0	7.15	5.74	80.3
2.0	7.13	6.13	85.9
3.0	7.16	6.61	92.3
4.0	7.17	7.17	100.0
5.0	7.14	6.91	96.8

Three tests of regeneration were also carried out and showed no change in the adsorption capacity of D301R, which therefore allows the resin to be regenerated and reused effectively.

3 Conclusion

(1) Rhenium(Ⅶ) can be optimally adsorbed on D301R in the HAc-NaAc system at pH 2.7. The statically saturated adsorption capacity is 715 mg·g^{-1} resin at 298 K. The Re(Ⅶ) adsorbed on D301R can be eluted by using 4.0 mol·L^{-1} HCl quantitatively. The resin can be regenerated and reused without apparent decrease in adsorption capacity.

(2) Under the experimental conditions, the apparent adsorption rate constant at the initial stage is $k_{298\,K}=7.2\times10^{-5}$ s^{-1}. The adsorption behavior of D301R for Re(Ⅶ) obeys the Freundlich empirical formula. The thermodynamic adsorption parameter is $\Delta H=-4.4$ kJ·mol^{-1}. The adsorption mechanism of D301R for Re(Ⅶ) was examined by using chemical method and IR spectrometry.

References:

[1] Petrov D G, Troshkina I D, Chekmarev A M, et al. *Russian J. Appl. Chem.*, **2001**,**74**(6):954~957

[2] YU Shu-Qiu(于淑秋), YU Ke-Ning(喻克宁), AN Zhen-Tao(安震涛), et al. *Chinese J. Rare Metals*(*Xiyou Jinshu*), **1987**,**11**(6):401~405

[3] WANG Xiao-Lin(汪小琳), LIU Yi-Nong(刘亦农), XIONG Zong-Hua(熊宗华). *Chemical Reagents*(*Huaxue Shiji*), **1995**, **17**(3):143~145

[4] Vartak S V, Shinde V M. *Talanta*, **1996**,**43**(9):1465~1470

[5] Koshima H, Onishi H. *Fresenius' J. Anal. Chem.*, **1990**,**232**: 287~291

[6] Gai H F, Shen J L, Hughes M A. *Hydrometallurgy*, **1990**,**25**(3): 293~304

[7] FANG Da-Wei(房大维), WANG Shu-Kun(王淑坤), LIU Xing-Zhi(刘兴芝), et al. *Chinese J. Process Engineering*(*Guocheng Gongcheng Xuebao*), **2005**,**5**(1):29~31

[8] Fisher S A, Meloche V W. *Anal. Chem.*, **1952**,**24**(7):1100~1106

[9] QIN Yu-Nan(秦玉楠). *China Molybdenum Industry*(*Zhongguo Muye*), **1998**,**22**(5):39~41

[10]HE Huan-Jie(何焕杰), WANG Xiu-Shan(王秀山), YANG Zi-Chao(杨子超), et al. *Ion Exchange and Adsorption*(*Lizi Jiaohuan Yu Xifu*), **1989**,**5**(6):407~412

[11]Sadykov I I, Salimov M I, Usmanova M M, et al. *J. Anal. Chem.*, **2001**,**56**(6):534~537

[12]Lan X, Liang S, Song Y. *Hydrometallurgy*, **2006**,**82**(3~4):133~136

[13]Lukić D M, Vučina J L, Milonjić S K. *J. Serb. Chem. Soc.*, **2008**,**73**(3):333~339

[14]Kholmogorov A G, Kononova O N, Kachin S V, et al. *Hydrometallurgy*, **1999**,**51**(1):19~35

[15]LIU Zhi-Rong(刘峙嵘), LIU Xin-Pin(刘欣萍), PENG Xue-Jiao(彭雪娇), et al. *Chinese J. Rare Metals*(*Xiyou Jinshu*),

2002,**26**(3):221~224

[16]LIU Zhi-Rong(刘峙嵘), LIU Xin-Pin(刘欣萍), LIU Jian-Qiang(刘健强), et al. *Hydrometallurgy of China*(*Shifa Yejin*), **2002**,**21**(2):70~75

[17]LIU Zhi-Rong(刘峙嵘), LI Chuan-Mao(李传茂), GUO Jin-Yong(郭锦勇). *Hydrometallurgy of China*(*Shifa Yejin*), **2000**, **19**(4):12~20

[18]Kitagawa H(北川浩), Suzuki K(铃木谦一郎), Translated by LU Zheng-Li(鹿政理). *Adsorption Basis and Design*(吸附的基础与设计). Beijing: Chemical Industry Press, **1983**.33~36

[19]Brykina G D, Marchak T V, Krysina L S, et al. *Zh. Anal. Khim.*, **1980**,**35**(12):2294~2299

[20]Gode F, Pehlivan E. *J. Hazard. Mater.*, **2003**,**B100**:231~243

[21]Magee R J, Al-Kayssi M. *Anal. Chim. Acta*, **1962**,**27**:469~473