SEPARATION OF Re AND Mo BY ADSORPTION OF ACTIVE CARBON [1]

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ABSTRACT

Separation of Re and Mo by adsorption of active carbon has been studied. The results show that Re and Mo can be separated effectively by adjusting the pH value. As pH > 8.2, the coefficient of separation $S_{Re/Mo}$ > 3.042. The adsorption isotherm for Re conforms to the Freundlich formula.

Key words: active carbon adsorption rhenium

1 INTRODUCTION

Adsorption of active carbon has been widely used in industry and other fields. The adsorption by active carbon of Re has also been reported abroad[1-3]. Because active carbon has a fluffy structure, a great surface area and a strong adsorption ability, it does not contaminate the environment as solvent extraction for separating Re and Mo does, and the cost is cheaper and the separation efficiency higher compared with ion-exchange methods. Therefore the separation of Re and Mo by adsorption of active carbon was studied in this project.

2 EXPERIMENTAL

A spectrophotometer 721, accurate pH meter PHS−2C and super thermostat LB801 were used. The granularities of two kinds of active carbon (analytically pure) were 0.8 ~ 1.4 mm and 1.4 ~ 1.8 mm respectively. The purity of ammonium perrhenate was 99.99%, and of rhenium powder 99.99%, and the ammonium molybdenate was analytically pure. The static-adsorption solution containing 0.1 wt.−% Re was made of either NH_4ReO_4 or $(NH_4)_2MoO_4$. The pH values were adjusted by aqueous ammonia or sulphuricacid.

The contents of Re and Mo were analyzed by Thiourea and EDTA[4] respectively. The amount of Re adsorbed, the absorption rate, the distribution ratio and the separation coefficient were determined by a static adsorption method. 2 gram of active carbon was put into a 100 mL conical bottle and then 25 mL adsorption solution was added. Each experiment was carried out at 25℃ and lasted for 40 h. In order to determine the influences of temperature and granularity of the active carbon on adsorption rate, the conical bottle was declinely set on the water surface of a thermostat and it was rotated at intervals.

After experimenting, the amount of Re adsorbed (a), the absorption rate (b), the distribution ratio(D_{Re}) and the separation coefficient ($S_{Re/Mo}$) were calculated respectively by using equations (1) ~ (2). The results were listed in Table 1 and Table 2.

$$a = ([Re]_1 - [Re]_2) V / W \qquad (1)$$

$$b = \{([Re]_1 - [Re]_2) / [Re]_1\} \% \qquad (2)$$

$$D_{Re} = ([Re]_1 - [Re]_2) V / ([Re]_2 W) \qquad (3)$$

$$S_{Re/Mo} = D_{Re} / D_{Mo} \qquad (4)$$

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where $[Re]_1$— concentration of Re in solution before adsorption;

$[Re]_2$— concentration of Re in solution after adsorption;

V— volume of solution;

W— weight of active carbon

3 DISCUSSIONS

3.1 *Adsorption Amount of* Re *at Constant Temperature*

As shown in Fig. 1, the adsorption amounts, lg a, have a linear relation to the equilibrium concentration of Re, lg c. It conforms to the Freundlich formula of adsorption isotherms, lg $a = 0.69 + 0.8 \cdot \lg c$ (where c is equivalent to $[Re]_2$, and $c = 0.005 \sim 0.017{,}6$ mol / L).

In the process of production, higher Re concentrations make for efficient uses of active carbon.

Table 1 Adsorption amounts of Re (25℃, pH = 10)

$[Re]_1$ mg · mL^{-1}	1	2	3	4	5	6
$[Re]_2$ mol · L^{-1}	0.0016	0.005.0	0.008.1	0.011.2	0.014.1	0.017.6
lg$[Re]_2$	−2.80	−2.30	−2.09	−1.95	1.85	−1.75
a m mol · g^{-1}	0.047	0.072	0.101	0.128	0.160	0.183
lg a	−1.33	−1.14	−1.00	−0.89	−0.80	−0.74

Table 2 Iufluence of acidity (pH) on separation of Mo and Re (25 ℃)

pH	$[Re]_2$ mg · mL^{-1}	$[Mo]_2$ mg · mL^{-1}	b / % Re	b / % Mo	D_{Re}	D_{Mo}	$S_{Re/Mo}$
2.0	0.026	1.72	96.6	84.0	352.9	65.8	5.4
4.2	0.056	4.79	92.6	55.5	157.1	15.6	10.1
5.2	0.059	5.95	92.2	44.8	148.5	10.1	14.7
8.2	0.030	10.69	96.1	0.7	304.2	0.1	3042.0
9.0	0.053	10.78	93.0	−0.001	166.7		
10.0	0.095	10.91	87.5	−0.013	87.5		
10.6	0.128	10.96	83.2	−0.018	61.7		

3.2 *Influence of Temperature on Adsorption Rate of* Re

As shown in Table 3, the adsorption rate (b) decreases gradually with increasing temperature (T). This proves that adsorption by active carbon of Re may be a physical process. In production, it is beneficial to decrease the temperature for raising the adsorption rate and increasing the efficiency of active carbon.

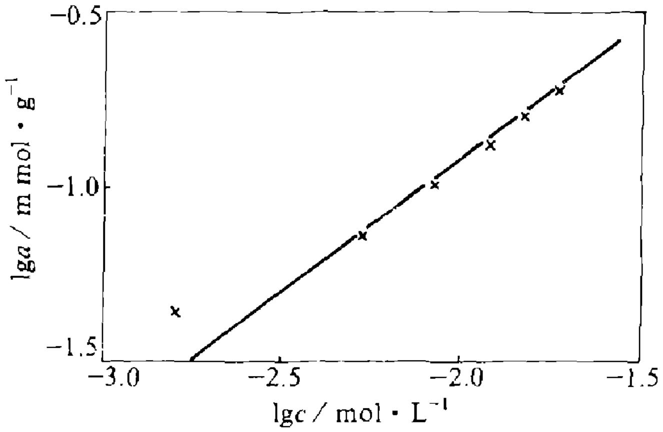

Fig. 1 Adsorption isotherm of Re at constant(T)

Table 3 The influence of T on b

No	1	2	3	4	5	6
T / ℃	20.0	30.0	40.0	50.0	60.0	70.0
$[Re]_2$ / mg · mL^{-1}	0.15	0.17	0.19	0.20	0.21	0.23
b / %	72.0	68.5	64.8	63.0	61.1	57.4

3.3 *Influences of Granularity of Active Carbon and* Mo on Adsorption Rate of Re

The exterior surface of active carbon is not regular, and its fluffy inner structure is not uniform. In the cases of different granularities, the same weights of active carbon do not have the same adsorption surface, and so different adsorption rates as well. As shown in Table 4, when the granularity of carbon different the adsorption rate (b) may be different, in spite of the temperature, time and acidity being held constant and the small granularity of active carbon (0.8 ~ 1.4 mm) has a higher adsorption rate than that of the large one (0.4 ~ 1.8 mm).

It can be also seen from Table 4 that the

Table 4 The adsorption rates of Re under different granularities of carbon concentration of Mo

Time / min	dia. 0.8 ~ 1.4		dia. 1.4 ~ 1.8
	$C_{Mo} = 0$	$C_{Mo} = 11$ mg / mL	$C_{Mo} = 0$
20	53.5	67.7	45.8
30	56.5	73.1	55.1
40	59.0	74.6	55.2

presence of Mo increases the adsorption of Re. The reason may be that the interaction between NH_4ReO_4 and $(NH_4)_2MoO_4$ increases the activity of NH_4ReO_4.

3.4 *The Influence of Acidity on the Separation of* Mo *and* Re

If the acidity is adjusted by aqueous ammonia or sulphuricacid, the moleculae structure of NH_4ReO_4 in the solution consisting of NH_4ReO_4 and $(NH_4)_2MoO_4$ does not change. Thus, the adsorption efficiency for Re changes slightly. As shown in Table 2, whether the solution is acidic (pH = 2.0 ~ 5.2) or basic (pH = 8.2 ~ 10.6), the adsorption rates for Re are higher than 80%. Ammonium molybdenate exists as large moleculae of $(NH_4)_6Mo_7O_{24}$, and as the acidity of the solution varies greatly, its molecular structure also changes. Under acidic conditions, formation of $(NH_4)_6Mo_7O_{24}$ does not change[6]. In changing the acidity of the solution, it was found that solutions containing Mo consumed much more aqueous ammonia than did those without molybdenum, proving that NH_4OH and $(NH_4)_6Mo_7O_{24}$ become $(NH_4)_2MoO_4$. According to the theory of molecular structure, the larger the molecule, the more electrons it contains, the greater it deforms and the easier it can be adsorbed[6]. Thus, under basic conditions (pH = 8.2 ~ 10.6), molybdenum was only slightly adsorbed (below 0.7%). If the pH value was 2.0 ~ 5.2, molybdenum was strongly adsorbed (44.8 ~ 84.0%).

It is also found from Table 2 that the separation coefficient between Re and Mo is above 3,000 when the pH value is equal to 8.2. This is much higher than the separation coefficient obtained by the the ion-exchange method[7]. When the pH value is above 9, the adsorption for Mo takes on a negative value. This is very useful for the separation of Re and Mo.

In order to prove the above point, a leach solution of roasted molybdenite ash with pH 9 ~ 10 was used to separate Re and Mo by the adsorption of active carbon. The original solution and the solution passing through the active carbon were both analyzed. However it was found that the concentration of Mo did not change at all. That means Mo was not adsorbed from the leach solution. As a matter of fact, the substance adsorbed by active carbon was verified by X-ray analysis to be NH_4ReO_4, and Mo was not found by spectrum analysis in crystallized NH_4ReO_4 either.

4 CONCLUSIONS

(1) Active carbon can effectively adsorb Re and separate Re from Mo. The adsorption rate for Re can reach 96.1%, $S_{Re-Mo} > 3{,}000$;

(2) At 25℃, pH = 10, the adsorption isotherm of active carbon for Re confirms to the Freundlich formula: $\lg a = 0.69 + 0.8 \cdot \lg c$;

(3) The adsorption rate for Re decreased from 72% to 57.4% when temperature increased from 20℃ to 70℃. This shows that adsorption at normal temperature is suitable;

(4) The adsorption rate of smaller granularity (0.8 ~ 1.4 mm) is higher than that for a bigger one (1.4 ~ 1.8 mm);

(5) Having Mo present in the adsorption solution, the adsorption rate of Re increases about 15%.

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