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Separation of macro amounts of tungsten and molybdenum by ion exchange with D309 resin

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Abstract: Based on the difference in tendency to polymerize between tungsten and molybdenum, a new method using D309 resin was propounded. The batch tests indicate that the optimum pH value and contact time for the separation are 7.0 and 4 h respectively, the maxium separation factor of W and Mo is 9.29. And the experimental resules show that isothermal absorbing tungsten and molybdenum belongs to Langmuir model and Freundlich model respectively, and the absorbing kinetics for tungsten is controlled by intra-particle diffusion. With a solution containing 70 g/L WO_3 and 28.97 g/L Mo, the effluent with a mass ratio of Mo to WO_3 of 76 and the eluate with a mass ratio of WO_3 to Mo of 53.33 are obtained after column test.

Key words: high concentrated tungstate and molybdenum solution; ion exchange; batch tests; column tests

1 Introduction

Nowsday, tungsten and molybdenum are widely applied to many hi-tech industrial products. However, there is a great challenge for separating tungsten and molybdenum effectively because they have many similar properties [1,2]. There are many methods for separating tungsten and molybdenum, such as precipitation [3], solvent extraction [4], and ion exchange [5,6]. Most of these methods are based on the different affinities of tungsten and molybdenum towards sulfur [7], which more easily makes MoO_4^- transform into MoS_4^{2-} by sulfurizing agents, while tungsten still exists in the form of WO_4^{2-}. For example, the current technology for deep removal of molybdenum from tungstate solution is based on adsorbing MoS_4^{2-} by copper compounds, which has been widely applied in China. However, when the Mo to W molar ratio is more than 1/20, a worse result will be obtained [8]. The scheelite ($CaWO_4$) gradually became the main resource because of great consumption of wolframite ($FeWO_4$, $MnWO_4$), and the scheelite includes more Mo than wolframite, which results in feed solutions containing plenty of tungsten and molybdenum, and can obviously add the difficulty for separating tungsten and molybdenum [9,10].

Except for the different affinities of tungsten and molybdenum towards sulfur, the different tendencies to polymerize between tungsten and molybdenum are also used to separate tungsten and molybdenum [11]. According to Refs. [12,13], WO_4^{2-} and MoO_4^{2-} can form isopolytungstate and isopolymolybdate respectively: $7H^+ + 6MO_4^{2-} = HM_6O_{21}^{5-} + 3H_2O$, where M represents W or Mo. ZHANG et al [14] studied the thermodynamic analysis for separation of tungsten and molybdenum in W−Mo−H_2O system and concluded that the polymeric degree of tungsten is significantly higher than that of molybdenum in the pH range of 6.5−7.5, which indicates that the polymeric ability of monotungstate is stronger. Compared with the monomeric anions, heteropoly anions have higher affinity to some anion adsorbents. Taking the large-size heteropoly anions with slow diffusion rate in the adsorbent interior into account, macroporous resins are considered to be more suitable.

Among these methods, it has been illustrated that ion exchange has a great potention because this method has many advantages, such as, shorter flow process, higher recovery and less pollution. According to reports, an extractant of N1923 with primary amine can get better result in selective extraction of tungsten from sodium molybdate solution [15]. So, D309 resin with primary amine is selected in the present experiment.

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This study mainly focuses on the effective separation from a solution with high concentration of tungsten and molybdenum by ion exchange with D309 resin, and the adsorption behavior and the rate controlling steps were also studied.

2 Experimental

Initial solutions were synthesized by Na_2WO_4 (AR) and Na_2MoO_4 (AR). The D309 resin was used as adsorbent with the main characteristics listed in Table 1.

Prior to testing, the D309 resin was firstly soaked in water for 24 h, and then soaked in 4% NaOH (0.04 g/mL) for 12 h. After rinsing with distilled water, the resin was activated with 4% HCl (v/v) for 12 h.

Batch tests were carried out in the constant temperature oscillator using a 100 mL conical flask. Flask containing 50 mL solution (70 g/L WO_3 and 28.97 g/L) was shaken for 4 h after putting 10 mL resin into. Then the loaded resin was rinsed with distilled water.

In adsorption isotherm tests, 4.0 mL of D309 resin was mixed with 50 mL solutions containing different initial concentrations, in which the concentrations of WO_3 ranged from 10 to 80 g/L and the increment was 10 g/L, accordingly the concentrations of Mo ranged from 4.14 to 33.10 g/L and the increment was 4.14 g/L. In all cases, the pH of the solution was maintained at 7.0 and all samples were stirred for 4 h at ambient temperature.

For adsorption kinetics tests, 2.0 mL of D309 resin (particle size 0.6−1.0 mm) was stirred in 500 mL solution (pH=7.0) containing 70 g/L WO_3 and 28.97 g/L Mo at 30, 45 and 60 °C respectively. The WO_3 and Mo concentrations could be regarded as constants during the reaction process because the adsorbed metals contents were less than 1.5%. After the desired contact time, the resin was rapidly separated from the solution and then washed with distilled water. The adsorption rate of WO_4^{2-} ions was calculated according to the following equation:

$$\eta = \frac{m_t}{m_e} \times 100\% \tag{1}$$

where m_t is adsorption amount at time t; m_e is the equilibrium adsorption amount.

In column tests, 287 mL of D309 resin was wet-packed into the glass column (20 mm in diameter, 900 mm in height) with solution containing 70 g/L WO_3 and 28.97 g/L Mo, keeping a flow rate of 66.88 mL/h by upstream flow, which is much closer to plugflow [16]. Then the loaded resin was rinsed with distilled water, and desorbed using 1 mol/L NaOH solution with a linear flow rate of 10.45 mm/min.

All samples were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-OES). The adsorption rate and separation factor of tungsten and molybdenum were calculated as follows:

$$Q = \frac{(C_0 - C)\,V}{\overline{V}} \tag{2}$$

$$\alpha_{Mo}^{WO_3} = \frac{\lambda(WO_3)}{\lambda(Mo)} \tag{3}$$

$$\lambda(WO_3) = \overline{C(WO_3)} / C(WO_3) \tag{4}$$

$$\lambda(Mo) = \overline{C(Mo)} / C(Mo) \tag{5}$$

where C_0 is initial concentration; C is instantaneous concentration; V is solution volume; $\overline{V}$ is resin volume; λ is distribution ratio; $\alpha_{Mo}^{WO_3}$ is separation coefficient of WO_3 and Mo; $\overline{C}$ is concentrations in resin; C is concentration in solution.

3 Results and discussion

3.1 Batch tests

3.1.1 Effect of pH value

pH directly affectes the existing forms of tungsten and molybdenum. The experimental results are shown in Fig. 1. From Fig. 1, as pH of solution decreases from 10 to 8.0, the absorption quantity of W exceeds a little that of Mo. So the separation factor is low. The reason is that W and Mo do not polymerize within this pH range [14]. While as pH decreases to 7.0, the adsorbed amount of WO_3 increases rapidly, meanwhile the adsorption quantity of Mo changes slightly. The reason is that tungsten is transformed into $HW_6O_{21}^{5-}$, while dominant form of molybdenum is still monoions. D309 resin prefers to absorb the isopolytungstate than to absorb molybdate, so the separation factor significantly increases to 9.29. Continuing to lower pH value, tungsten and molybdenum are both present in the form of anionic polymerizations. The comparable adsorption capacities result in the small separation factor. As a conclusion, pH=7.0 should be selected in the following experiments.

Table 1 Characteristics of D309 ion exchange resin (obtained from manufacturer)

Polymer matrix	Functional group	Ionic form	Structure	Volume exchange capacity/ (mmol·L^{-1})	Water content/%	Visual density in wet state/ (g·mL^{-1})	True density in wet state/ (g·mL^{-1})
Polystyrene DVB	—CH_2NH_2	H^+	Macroporous	≥1.5	60−70	0.65−0.72	1.03−1.06

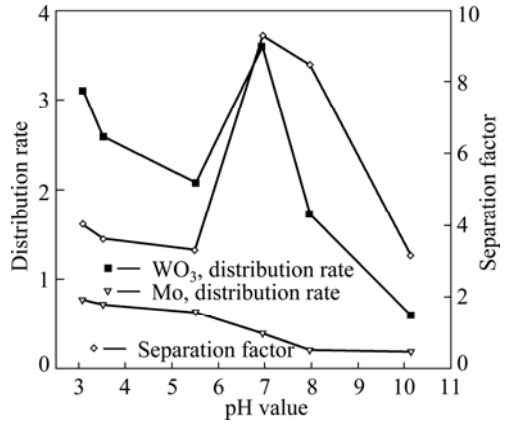

Fig. 1 Effect of pH value of solution on separation of tumgsten and molybdenum

3.1.2 Effect of contact time

The influence of contact time on adsorption rate was studied and the results are shown in Fig. 2.

It can be seen from Fig. 2, the adsorption rate of molybdenum rises rapidly within 1 h. The shorter equilibrium time attributes to the fast diffusion rate of the small-size MoO_4^{2-} and a large number of available vacant adsorptive sites. Whereas, the equilibrium time for adsorbing tungsten on D309 resin is 4 h, due to the slow diffusion rate of the large-size heteropoly anions. So, the optimum contact time for the separation of tungsten and molybdenum is 4 h.

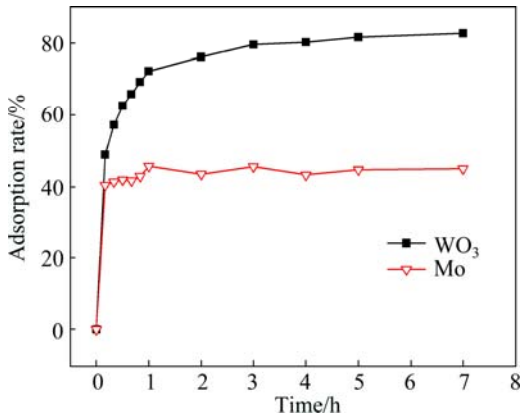

Fig. 2 Effect of contact time on separation of tungsten and molybdenum

3.2 Adsorption isotherm of D309 resin for absorbing tungsten and molybdenum

In the ion exchange process, the adsorption isotherm may reflect the ions equilibrium distribution between liquid and resin at a ceitain temperature. The adsorption data of binary system were simulated with multi-component models in the present study, which are all extended or modified from mono-component models mentioned earlier. For the sake of simplicity, in this research, Henry model, Langmuir model and Freundlich model were used to describe the equilibrium isotherm data. The mathematical expressions of the three models are described as follows:

$$\text{Henry model: } Q_e=K_HC_e \tag{6}$$

$$\text{Freundlic model: } \ln Q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{7}$$

$$\text{Langmuir model: } \frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \tag{8}$$

where K_H is Henry model constant; Q_e is equilibrium loading capacity of resin; C_e represents equilibrium concentration of solution; K_F and n are Freundlich model constants relative to the sorption capacity and sorption intensity, respectively; Q_m is saturated loading capacity; b is affinity parameter or Langmuir sorption constant.

These experiments were carried out as explained above and the result is shown in Fig. 3. Fitting the experimental results by above models respectively, the model with the largest correlation coefficient is the corresponding adsorption isotherm model.

As shown in Fig. 4, the adsorption of molybdenum belongs to Freundlic model: $\ln Q=1.08\ln C+0.58$. The Freundlich constant, K_F, can be taken as a relative indicator of the adsorption capacity [16]. The $1/n$ value indicates the relative distribution of energy sites and

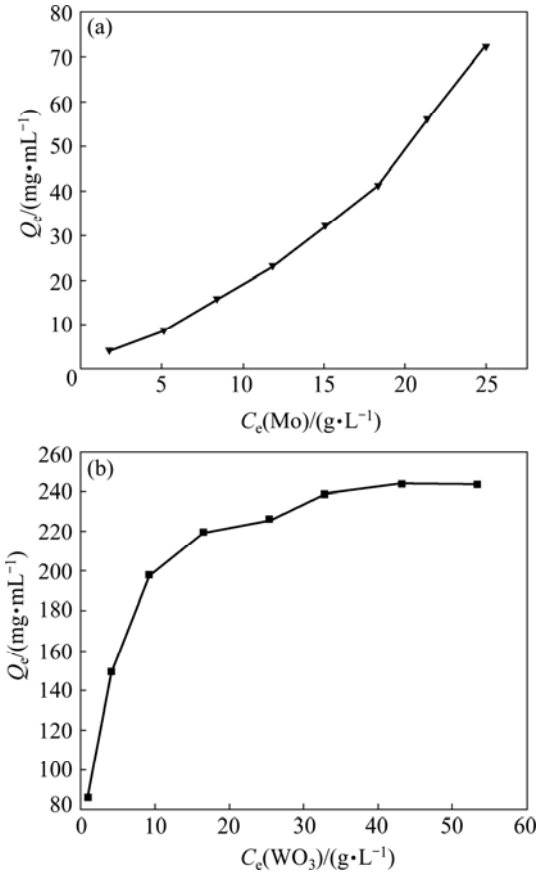

Fig. 3 Relationship between equilibrium concentration of Mo (a), WO_3 (b) and equilibrium loading capacity

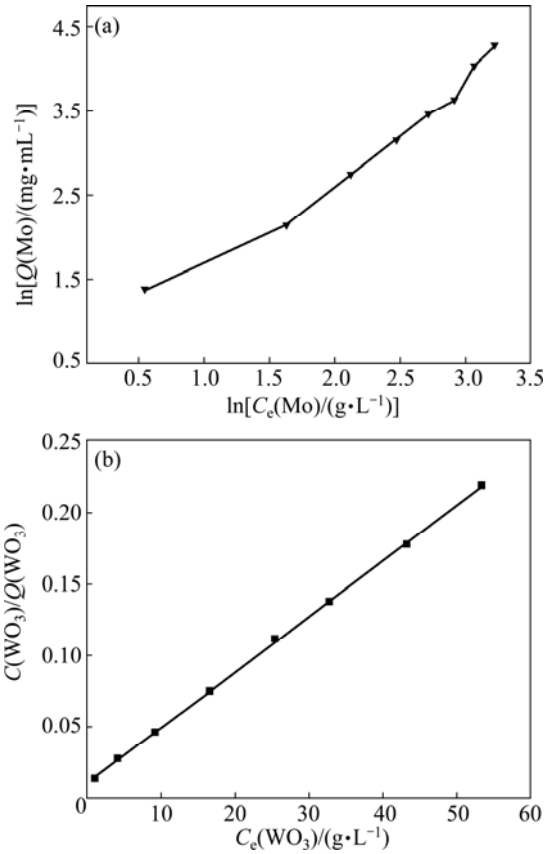

Fig. 4 Fitting curves by Freundlich model for Mo (a) and Langmuir model for WO_3 (b)

depends on the nature and intensity of the adsorption process [17]. On the other hand, in view of R^2 values, the Langmuir model exhibits a good fit to the experimental data of tungsten, indicating that the adsorption of tungsten may belong to Langmuir model.

3.3 Adsorption kinetics of D309 resin

Macroporous ion exchange resins have porous structure having many micro-pores and macro-pores [18]. Hence, the ion exchange process occurs on the surface of the resin particles and the internal micro-particles simultaneously. So the control step in ion exchange always includes film diffusion (FDC), intra-particle diffusion (PDC) and chemical reaction. The mathematical expressions of the three models are described as follows:

Film diffusion: $F=kt$

Intra-particle diffusion: $1-3(1-F)^{2/3}+2(1-F)=kt$

Chemical reaction: $1-(1-F)^{1/3}=kt$

where F is adsorption rate; t is time; k is the apparent rate constant.

It can be seen from Fig. 5 that the reaction rate increases with the increase of reaction temperature. The experimental data were fitted by the each model introduced above. Only PDC model is suitable and the fitting curves are shown in Fig. 6.

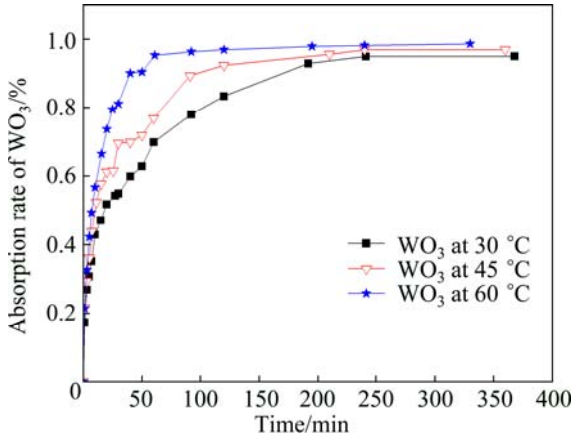

Fig. 5 Adsorption curves under different temperatures

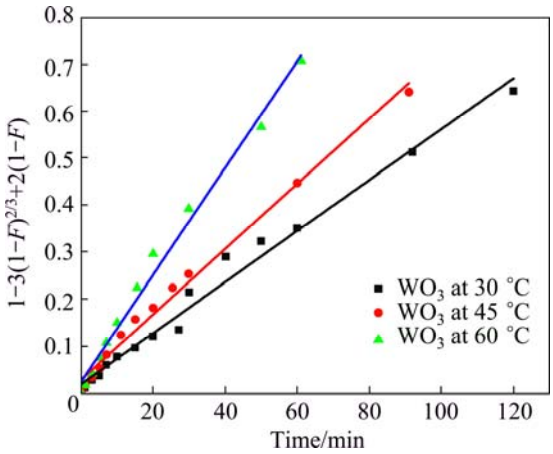

Fig. 6 Fitting curves by PDC model

As shown in Fig. 6, $1-3(1-F)^{2/3}+2(1-F)$ and t have a good linear relationship at different temperatures. Adsorption of tungsten onto D309 resin belongs to intra-particle diffusion control model. On the other hand, adsorption of molybdenum onto D309 resin reaches equilibrium quickly, so the useful experimental data are not obtained, but it can be concluded that D309 resin adsorbs molybdenum more easily than tungsten.

Based on the fitting line slope obtained from Fig. 6, the apparent rate constants k for the resin adsorption for tungsten under various temperatures are calulated. At 30, 45, and 60 °C, the apparent rate constants are 5.44×10^{-3}, 6.93×10^{-3} and 1.14×10^{-2} respectively. According to the Arrhenius formula: $\ln k=-E/(RT)+B$, apparent activation energy can be calculated to be 20.56 kJ/mol.

3.4 Column tests

3.4.1 Loading test

In loading tests, the breakthrough point takes place when the concentrations of tungsten and molybdenum in effluent begin to increase predominantly.

Figure 7 illustrates the loading curves of tungsten and molybdenum on D309 resin. It can be seen that the breakthrough volume of molybdenum is 500 mL, while almost no tungsten presents in the effluent until the volume of liquid reaches 1070 mL. The solution mainly containing molybdenum and trace tungsten can be obtained from the effluent from 500 mL to 1070 mL, whose mass ratio of Mo to WO_3 reaches 76 in contrast with the initial ratio of 0.414. The removal rate of tungsten reaches 95.14%. It can be concluded that D309 resin is suitable for the high-concentration solution.

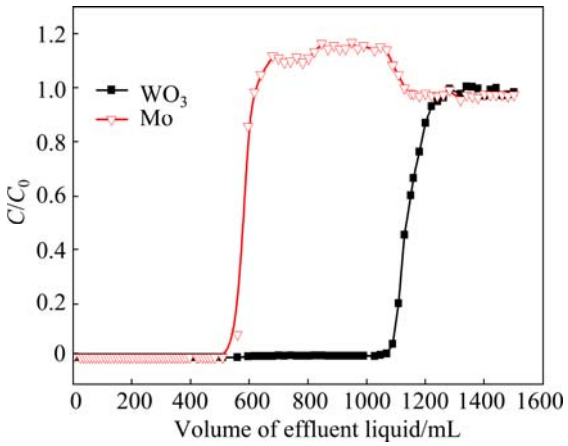

Fig. 7 Loading curves

3.4.2 Stripping test

The D309 resin is weak base anion exchange resin with primary amine group (—CH_2NH_2), which implies that the loaded resin can be desorbed by NaOH solution easily.

As shown in Fig. 8, the eluate from 683 mL to 1273 mL has a mass ratio of WO_3 to Mo 53.33 while the ratio of 2.41 in the initial solution. The saturated adsorption capacities of WO_3 and Mo for the collected effluents are 289.40 mg/mL and 41.68 mg/mL respectively. The removal rate of molybdenum is 85.60%.

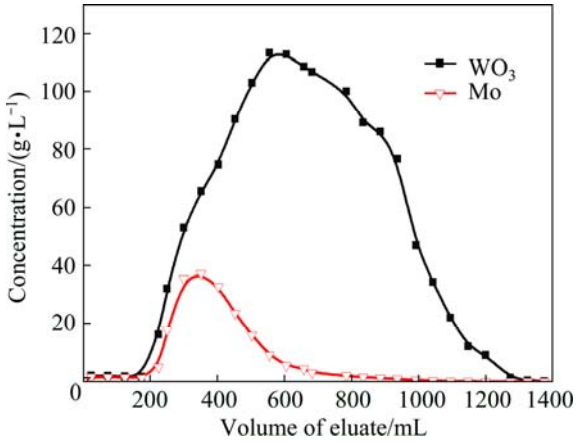

Fig. 8 Stripping curves for loaded D309 resin

4 Conclusions

1) Batch tests indicate that the optimum pH value for the separation is 7.0 and the optimum contact time is 4 h. In this case, the separation factor of W and Mo reachs 9.29.

2) The D309 resin absorbing tungsten and molybdenum belongs to Langmuir model and Freundlich model respectively, and the absorbing process for tungsten is controlled by intra-particle diffusion.

3) The column tests with a solution containing 70 g/L WO_3 and 28.97 g/L Mo show that the effluent with a mass ratio of Mo to WO_3 of 76 and the eluate with a mass ratio of WO_3 to Mo of 53.33 can be obtained.

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利用 D309 树脂离子交换分离宏量钨和钼

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摘　要：基于钨、钼在水溶液中聚合能力的差异，提出一种利用 D309 树脂离子交换分离钨、钼的新方法。静态实验表明，分离钨、钼的最佳 pH 值为 7.0，最佳接触时间为 4 h，钨、钼分离系数达到 9.29。等温吸附过程研究表明，D309 树脂对钨、钼的吸附分别属于 Langmuir 模型和 Freundlich 模型。吸附动力学研究表明，D309 树脂对钨的吸附属于内扩散控制。对于含 70 g/L WO_3 和 28.97 g/L Mo 的料液，经动态吸附分离钨、钼后，所得流出液中 Mo 与 WO_3 的质量比达 76，所得解吸液中 WO_3 与 Mo 的质量比达 53.33。

关键词：高浓度钨钼溶液；离子交换；静态实验；动态实验

(Edited by Hua YANG)