# 基于桔子皮废弃物从含铼废水中高效、高选择地提取钼

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摘要:以生物质废弃物桔子皮为原料,直接氨化后得到 OW-NH$_2$ 生物吸附剂,OW-NH$_2$ 对 Mo(Ⅵ)的吸附具有很高的选择性,对其他共存离子 Re(Ⅶ)、Pb(Ⅱ)、Fe(Ⅲ)、Zn(Ⅱ)、Mn(Ⅶ)、Ca(Ⅱ)和 Cu(Ⅱ)基本不吸附,尤其是对 Mo(Ⅵ)、Re(Ⅶ)的分离具有高选择性。红外光谱分析表明阴离子形式的 H$_3$Mo$_7$O$_{24}$$^{3-}$、H$_2$Mo$_7$O$_{24}$$^{4-}$、HMo$_7$O$_{24}$$^{5-}$、Mo$_8$O$_{26}$$^{4-}$、Mo$_7$O$_{26}$$^{6-}$ 和 MoO$_4$$^{2-}$ 与引入在纤维素上的 RNH$_3$$^+$发生离子缔合反应。OW-NH$_2$ 吸附 Mo(Ⅵ)的过程符合 Langmiur 吸附模型,最大吸附量为 1.71 mmol·g$^{-1}$。另外,OW-NH$_2$ 对工业实际料液的动态模拟实验的结果表明 Mo(Ⅵ)回收率可达 99%以上。

关键词:吸附;生物质废弃物;钼;铼

# Recovery of Mo(Ⅵ) from Re(Ⅶ)-Containing Wastewater by Chemically Modified Orange Waste: Competitiveness and Selectivity

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Abstract: New adsorption gel (OW-NH$_2$) was prepared by chemically immobilizing functional group of amine orange waste. For the system of Mo(Ⅵ) coexisted with Re(Ⅶ), Pb(Ⅱ), Fe(Ⅲ), Zn(Ⅱ), Mn(Ⅶ) Ca(Ⅱ) and Cu(Ⅱ), the gel exhibits selectivity only for Mo(Ⅵ). The maximum adsorption capacity for Mo(Ⅵ) is 1.71 mmol·g$^{-1}$, and the adsorption behavior obeys the Langmuir model. The adsorption mechanism of molybdenum anion could be explained as the anion exchange reactions. In addition, the excellent adsorption characteristics for Mo(Ⅵ) are confirmed by separation of Mo(Ⅵ) from Mo-Re containing industrial effluent.

Key words: adsorption; biomass; molybdenum; rhenium

## 0 Introduction

As an important and strategic metal in human life and industry, the demand of both molybdenum and rhenium is rising due to its widespread utilization. However, rhenium and molybdenum have similar chemical properties so that it is difficult to separate molybdenum and rhenium. Lots of methods are used to purify and separate them, such as chemical deposition, ion exchange, capillary electrophoresis, liquid chromatography and solvent extraction[1-7]. Among them, liquid-liquid extraction provides an effective and simple separation. However, it is often complicated by multi-stage cycles, extractant loss, high-cost and

formation of stable emulsions etc. Thus, it is important to develop new separation systems or methods.

At present, the search for environmentally benign and cost effective method for rare metals recovery is in progress[8-11]. Among materials searched, the orange waste was reported to be able to adsorb metals in aqueous systems[12-16]. The major component of orange waste is cellulose, pectin, hemicellulose and lignin in the form of carboxyl and hydroxyl, which have high affinity to metal ions. Although several studies have proposed using modified orange waste by common chemical modifications such as alkaline and acid treatment in relation to heavy metal adsorption from solution, the adsorption capacity and selectivity of orange waste gels prepared by these methods were not much improved. In the present work, we have synthesized orange waste and introduced amine group to prepare an adsorption gel for recovery of molybdenum from Re-containing wastewater.

# 1 Experimental

## 1.1 Materials

The orange waste was used as the feed material for the adsorption gels. Chloride salts of lead, iron, zinc, manganese calcium and copper were used to prepare test solutions of the respective metals. Rhenium and molybdenum stock solutions were prepared by dissolving $NH_4ReO_4$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, respectively, in hydrochloric acid. All reagents were of analytical grade and were used without further purification.

## 1.2 Preparation of the adsorption gels

Amine was chemically immobilized to obtain an amine type of orange waste gel. The orange waste was crushed and treated with 1% NaOH solution and ethanol at room temperature for 24 h in order to remove chlorophyll pigments and other low molecular weight compounds. The suspension was further washed till neutral (pH=7) and the obtained product (abbreviated as OW) was dried at 343 K for 3 h.

As shown in Scheme 1, the pretreated orange waste (OW) was chlorinated by treating with thionyl chloride in pyridine medium under a $N_2$-atmosphere at 353 K for 2.5 h. The chlorinated OW obtained was washed and dried. For the immobilization of amine groups, the chlorinated OW was treated with amine. The product was washed, dried and crushed to obtain 100~150 μm mesh sized powder, and denoted as OW-NH$_2$ gel.
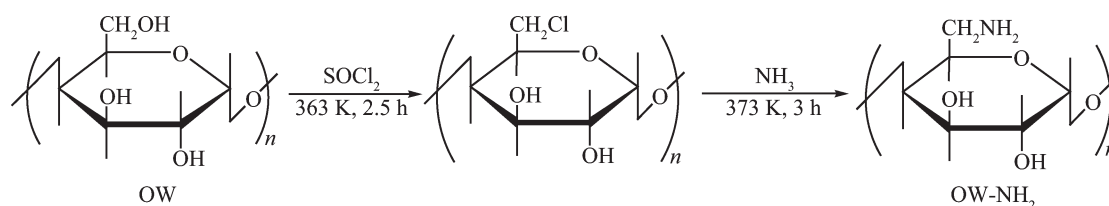
## 1.3 Batch adsorption studies

All equilibrium adsorption experiments were individually conducted at 303 K for Mo(VI), Re(VII), Pb(II), Fe(III), Zn(II), Mn(VII), Ca(II) and Cu(II) ions. 10 mg of the gel was mixed with 5 mL adsorbate solution (20 mg·L$^{-1}$) at various HCl concentrations in 25 mL flask. The flask was kept in a thermostatic shaker at a speed of 180 r·min$^{-1}$ for 24 h. Adsorption kinetics for metal ions were evaluated by taking 10 mg of gel in 5 mL Mo(VI) solution with concentration of 20 mg·L$^{-1}$ (prepared in 0.1 mol·L$^{-1}$ hydrochloric acid) at various temperatures. Percentage adsorption (A) for each metal ion was calculated according to Eq.(**1**):

$$A = \frac{C_i - C_e}{C_i} \times 100\% \qquad (1)$$

where $C_i$ is the initial concentration of the adsorbate and $C_e$ stands for the equilibrium concentration measured after adsorption on the gel.

## 1.4 Analyses

The pH value of the solution was measured by S-3C model pH meter, while the concentrations of metal ions were measured by using PE model atomic absorption spectrophotometer and a DV 2000 ICP (Inductively Coupled Plasma) atomic emission spectrometer.



Scheme 1　Preparation of orange waste gel

## 2 Results and discussion

### 2.1 Characterization of OW and OW-NH₂

The FTIR spectra of OW and OW-NH₂ gel are shown in Fig.1. Compared with the spectrum of OW, the intensity of O-H peak for the OW-NH₂ gel decreases at the region of 3 600~3 300 cm⁻¹. This change is attributed to the substitute of free hydroxyl groups in OW by amine group. The peak at 2 400 cm⁻¹ ascribed to the O-H bonds is disappeared. The composition (%) of carbon, hydrogen, and nitrogen in the prepared functionalized gel is 43.19, 5.94 and 1.68, respectively, while the composition(%) of nitrogen in the OW is 0.39. It also suggests the grafted amine group in the structure of the OW-NH₂ gel. The functional group density in the OW-NH₂ gel is 1.20 mol·kg⁻¹.
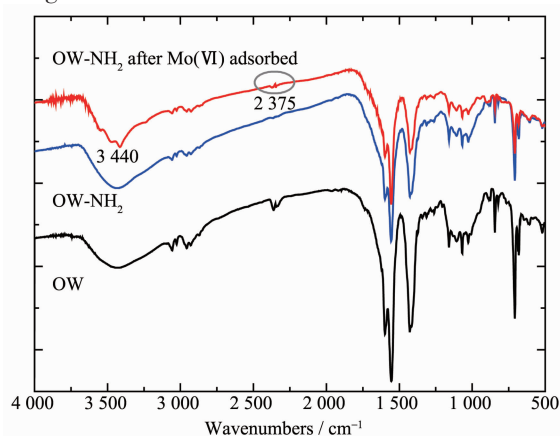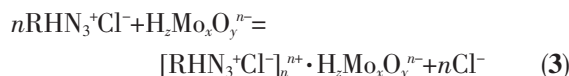


Fig.1　FTIR spectra of the OW-NH₂ gel before and after Mo(Ⅵ) adsorbed

### 2.2 Adsorption mechanism

As shown in Fig.1, the appearance of new peak at 2 375 cm⁻¹ (corresponding to $R_3NH^+$) indicates the adsorption process. The amine group of the OW-NH₂ gel in hydrochloric acid medium is protonated as described by Eq.(2). The ionic state of molybdenum in aqueous solution has already been described in our previous work[11]. Predominating ionic species of Mo(Ⅵ) such as $H_3Mo_7O_{24}^{3-}$, $H_2Mo_7O_{24}^{4-}$, $HMo_7O_{24}^{5-}$, $Mo_8O_{26}^{4-}$, $Mo_7O_{24}^{6-}$ and $MoO_4^{2-}$ are present in a molybdenum solution when the pH value of the solution is higher than 2. The adsorption mechanism of molybdenum anion could be explained as the anion exchange reaction. Hence, it is expressed by Eq.(3) as the anion exchange reaction.

$$RNH_2+HCl=RNH_3^+Cl^- \tag{2}$$

$$nRHN_3^+Cl^-+H_zMo_xO_y^{n-}=$$
$$[RHN_3^+Cl^-]_n^{n+}\cdot H_zMo_xO_y^{n-}+nCl^- \tag{3}$$

### 2.3 Adsorption behavior of the OW-NH₂ gel

The adsorption behavior of the OW-NH₂ gel for Mo(Ⅵ) along with other metal ions such as Re(Ⅶ), Cu(Ⅱ), Pb(Ⅱ), Fe(Ⅲ), Zn(Ⅱ) and Mn(Ⅶ) at various hydrochloric acid concentrations is shown in Fig.2.
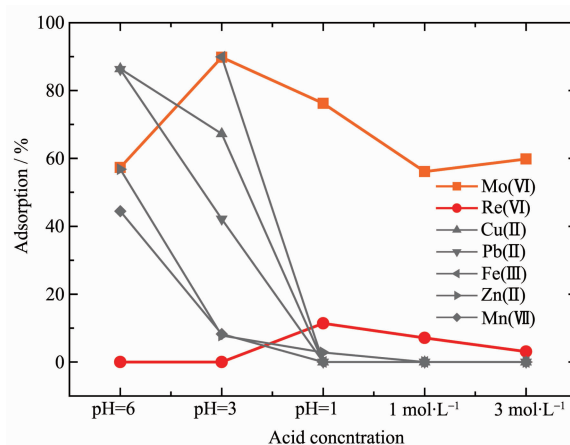


Fig.2　Adsorption behavior of the OW-NH₂ gel for various metal ions as a function of hydrochloric acid concentration; Initial concentration of metal ions= 20 mg·L⁻¹, solid-to-liquid ratio: 2 g:1 L, temperature: 303 K

The OW-NH₂ gel shows very good affinity towards molybdenum, and against for rhenium. A significant extent of adsorption of Mo(Ⅵ) over a wide range of hydrochloric acid concentration is achieved while the adsorption of Re(Ⅶ) is very low (0%~15%) under the studied condition. Fig.2 also shows that the adsorption of other metal ions such as Cu(Ⅱ), Pb(Ⅱ), Fe(Ⅲ), Zn(Ⅱ) and Mn(Ⅶ) decreases with the increase in hydrochloric acid concentration. A sharp decrease is observed at an ambient condition of 0.1 mol·L⁻¹ hydrochloric acid. This result indicates that Mo(Ⅵ) can be selectively separated from Re(Ⅶ) and other coexisting base metal ions using the modified orange waste gel at HCl concentration of 0.1 mol·L⁻¹ and higher.

The separation factor, $\beta_{Mo/Re}$, is the distribution ratio of two metal ions measured under the same condition, i.e. $\beta_{Mo/Re}=D_{Mo}/D_{Re}$, where $D_{Mo}$ and $D_{Re}$ are distribution of molybdenum and rhenium, respectively.

**Table 1　Separation factor ($\beta_{Mo/Re}$) for the OW-NH$_2$ gel under different acidic conditions**

|  | pH=6 | pH=3 | pH=1 | 1 mol·L$^{-1}$ | 3 mol·L$^{-1}$ |
|---|---|---|---|---|---|
| $D_{Mo}$ | 1.34 | 8.81 | 3.21 | 1.28 | 1.49 |
| $D_{Re}$ | 0.0001 | 0.0001 | 0.13 | 0.076 | 0.032 |
| $\beta_{Mo/Re}$ | 13436 | 88135 | 24.99 | 16.71 | 47.09 |

The $\beta_{Mo/Re}$ values obtained for the OW-NH$_2$ gel at various hydrochloric acid concentrations are given in Table 1. $\beta_{Mo/Re}$ values over a wide range of hydrochloric acid concentration are found to be much higher (16.71~13 436) for practical purposes. It means that the gel is highly effective for separating molybdenum from rhenium in the whole hydrochloric acid concentration range studied.

## 2.4　Adsorption isotherms

As the OW-NH$_2$ gel is found to be selective only for Mo(Ⅵ), test of adsorption isotherm should be carried out for Mo(Ⅵ) ion. The adsorption isotherm studies for Mo(Ⅵ) on the OW-NH$_2$ gel, was carried out taking various concentrations of individual metal solutions. The adsorption equilibrium data and the maximum adsorption capacity were analyzed in terms of the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. The maximum adsorption capacity is 1.71 mmol·g$^{-1}$ of OW-NH$_2$ dry gel for molybdenum. However, it is only 0.23 mmol·g$^{-1}$ of OW for molybdenum at the same experimental condition. It further indicates that the adsorption of Mo(Ⅵ) on the OW-NH$_2$ gel is greatly enhanced after chemical modification by amine group.

The linear forms of four isotherm equations have been tested in the present study, namely, Langmuir, Freundlich, Temkin and Dubinin-Radushkevich[17-20]. The adsorption isotherm data for Mo(Ⅵ) onto the OW-NH$_2$ gel have been plotted in Figs.3 (a~d), respectively, from which isotherm constants have been tabulated in Table 2. As seen from Fig.3, the plot of $C_e/q_e$ versus $C_e$ is linear with a better correlation
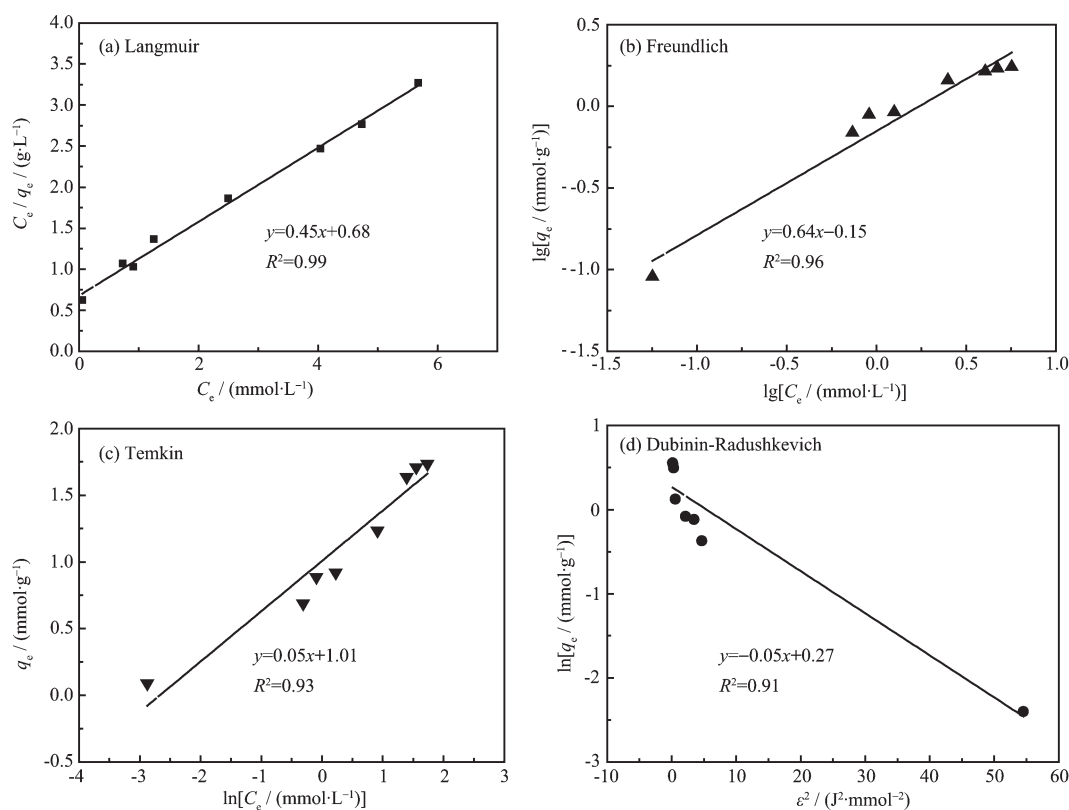
Fig.3　Adsorption isotherms for Mo(Ⅵ) on the OW-NH$_2$ gel. Initial concentration of metal ions: 20 mg·L$^{-1}$ (prepared in 0.1 mol·L$^{-1}$ HCl), solid-to-liquid ratio: 2 g·L$^{-1}$, temperature: 303 K

**Table 2　Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm constants**

| Isotherm model | Isotherm parameter | Value |
|---|---|---|
| Langmuir* | $q_{max}$ / (mmol·g$^{-1}$) | 2.22 |
| $\dfrac{C_e}{q_e}=\dfrac{C_e}{q_{max}}+\dfrac{1}{q_{max}K_L}$ (Type(I)) | $K_L$ / (L·mmol$^{-1}$) | 0.66 |
|  | $R^2$ | 0.99 |
| Freundlich | $K_F$ / (L·mmol$^{-1}$) | 0.71 |
| $\ln q_e=\ln K_F+\dfrac{1}{n}\ln C_e$ | $n$ | 1.56 |
|  | $R^2$ | 0.96 |
| Temkin | $A$ / (L·mmol$^{-1}$) | 14.3 |
| $q_e=\dfrac{RT}{b}\ln A+\dfrac{RT}{b}\ln C_e$ | $b$ | 0.48 |
|  | $R^2$ | 0.93 |
| Dubinin-Radushkevich | $q_m$ / (mmol·g$^{-1}$) | 1.31 |
| $\ln q_e=\ln q_m-\beta\varepsilon^2$ | $\beta$ / (mmol$^2$·J$^{-2}$) | 0.05 |
| $\varepsilon=RT\ln(1+\dfrac{1}{C_e})$ | $R^2$ | 0.91 |

*Note: $q_e$=the equilibrium amount of metal adsorbed on gel (mmol·g$^{-1}$), $C_e$=the concentration of the metal remained in the solution　(mmol·L$^{-1}$), $q_{max}$=the maximum loading capacity of the gel, $K_L$=the Langmuir constant related to the energy of adsorption　(L·mmol$^{-1}$), $K_F$=the Freundlich constant related to the adsorption capacity, $1/n$=the heterogeneity factor, $A$ and $b$=the Temkin constants, $q_m$=the Dubinin-Radushkevich monolayer capacity (mmol·g$^{-1}$) and $\beta$　(mmol$^2$·J$^{-2}$)=a constant with dimensions of energy and the Polanyi sorption potential $\varepsilon$, which is the amount of energy required to pull a adsorbed molecule from its sorption site.

**Table 3　Dimensionless separation factor values ($R_L$) for Mo(Ⅵ) on the OW-NH$_2$ gel**

| $C_0$ / (mmol·L$^{-1}$) | 0.06 | 0.74 | 0.91 | 1.26 | 2.50 | 4.03 | 4.73 | 5.68 |
|---|---|---|---|---|---|---|---|---|
| $R_L$ | 0.96 | 0.67 | 0.62 | 0.55 | 0.38 | 0.27 | 0.24 | 0.21 |

coefficient　($R^2$) of 0.99 for the OW-NH$_2$ gel. It could be concluded that the Langmuir isotherm shows a better fit to adsorption data than the other isotherm equations. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogenous distribution of active sites on the orange waste gel surface, since the Langmuir equation assumes that the surface is homogenous[17]. This situation may be explained based on the structure of the gel, containing the same surface reactive amine group binding molybdenum ions.

In addition, the value of $K_L$ was about 0.66 L·mmol$^{-1}$ for the OW-NH$_2$ gel. An essential characteristic of the Langmuir isotherm can be expressed by a dimensionless separation factor ($R_L$):

$$R_L=\frac{1}{1+K_L\cdot C_0} \tag{4}$$

where $C_0$ is the initial concentration of metal ions (mol·L$^{-1}$). The significance of separation factor is that if $R_L>1$, the adsorption is unfavorable; if $0<R_L<1$, the

adsorption is favorable; and if $R_L=0$, the adsorption is irreversible[21]. The obtained values of $R_L$ shown in Table 3 signify a highly favorable adsorption for different initial concentrations at the experimental conditions.

## 2.5　Removal and separation of Mo(Ⅵ) from two kinds of Re-containing industrial wastewaters

In this work, adsorption tests were conducted for the removal and separation of molybdenum from a real Re-containing industrial wastewater (MOW1). Several metal ions and some other elements were found to be present at various proportions of concentration. In thousands range: Fe (1 142 mg·L$^{-1}$) and Mo (1 231 mg·L$^{-1}$); in hundreds range: Re (500 mg·L$^{-1}$), Ge (280 mg·L$^{-1}$) and Ca (453 mg·L$^{-1}$); in the tenths range: Cu, K, Mg, Si, Na, Al, As, In. And the acid concentration of sample was 1.0 mol·L$^{-1}$. In order to know the affinity of the OW-NH$_2$ gel for the rare metals in the MOW1 mixture, solid-liquid ratio adsorption tests in static mode taking 10 mL of MOW1 with various mass

of the gel was carried out. The result in Fig.4(a) shows almost complete adso rption of Mo(Ⅵ) at solid-liquid ratio as less as 0.2 mg:1 mL. As explained earlier, the concentration of iron in sample MOW1 is several folds higher than that of any given metals but its adsorption as observed in Fig.4(a) is almost negligible. Despite the concept that many metal ions including rhenium, iron and copper form anionic chloro-complexes in acidic chloride medium while molybdenum as $MoO_2^{2+}$ cation, the selective adsorption of molybdenum over the dominating level of iron ion and rhenium ion is very interesting.
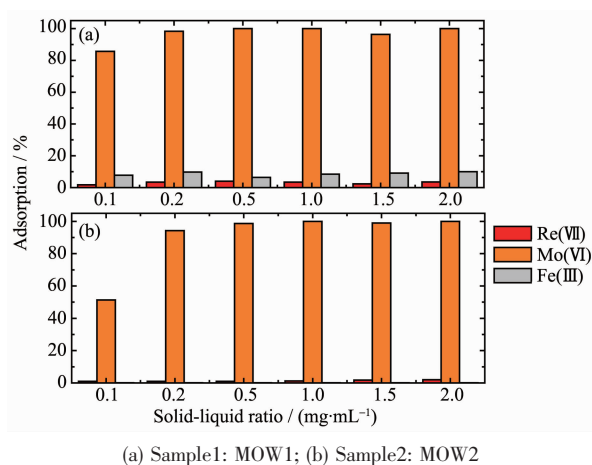


(a) Sample1: MOW1; (b) Sample2: MOW2

Fig.4　Solid-liquid ratio for the adsorption of molybdenum, rhenium and ions from two kinds of industrial wastewater on the OW-NH$_2$ gel

In addition, the other real industrial wastewater (MOW2) was treated by using the OW-NH$_2$ gel. Several metal ions and some other elements in the sample MOW2 were also found to be present at various proportions of concentration. In hundreds range: Mo (145 mg·L$^{-1}$), Re (450 mg·L$^{-1}$) and Ca (900 mg·L$^{-1}$); in the tenths range: Ge, K, Si, Na and so on, and the pH value of the sample was 7.6. The solid-liquid ratio adsorption tests in static mode taking 10 mL of MOW2 with various masses of the gel were carried out, as shown Fig.4(b). It is clear that almost complete adsorption of Mo(Ⅵ) at solid-liquid ratio as less as 0.5. Similarly, despite rhenium and molybdenum both form anionic chloro-complexes at this conditions, molybdenum in comparatively low concentration is selectively adsorbed over the dominating level of

rhenium ion.

On the other hand, the adsorption of other metal ions such as iron and rhenium, the concentration of which in MOW1 and/or MOW2 is also several folds of that of other metals, is also negligible, as shown in Table 4. It shows about 99.90% Mo(Ⅵ) is recovered and separated from the Re-containing industrial wastes effluent. Further, the selectivity pattern over other metal ions in smaller concentration range is basically the same. The recovery of molybdenum in this study appears highly satisfactory, and it is perhaps due to the optimal affinity of the gel prepared in this study.

Table 4　Adsorption and separation of Mo(Ⅵ) from the Re-containing industrial wastewaters (sample MOW1 and MOW2, solid-liquid ratio: 2 g:1 L)

| | Adsorption / % | | | | |
| --- | --- | --- | --- | --- | --- |
| | Fe | Mo | Re | Ge | Ca |
| MOW1 | 6.21 | 99.94 | 2.46 | 0.23 | 1.89 |
| MOW2 | 0 | 100 | 0.53 | 0.46 | 4.27 |

## 3　Conclusions

The modified waste orang gel was investigated for adsorption of molybdenum and rhenium as well as some base metals from hydrochloric acid medium. The results show that the gel exhibits selectivity only for molybdenum with a remarkably high adsorption capacity, that is 1.71 mmol·g$^{-1}$ dry gel. Langmuir adsorption model is fit best with the experimental data. This situation may be explained based on the structure of the gel, containing the same surface reactive amine group binding molybdenum ions. More importantly, rhenium and molybdenum, which has similar chemical behavior in aqueous solution and often finds together in industrial effluent, could be also separated by using the orange waste gel modified by amine.

**References:**

[1] Karagiozov L, Vasilev C. *Hydrometallurgy*, **1979,4**:51-55

[2] Blazy P, Jdid E A, Floreancig A, et al. *Sep. Sci. Technol.*, **1993,28**:2073-2096

[3] Yamini Y, Saleh A, Khajeh M. *Sep. Purif. Technol.*, **2008**, **61**:109-114

[4] Cao Z F, Zhong H, Qiu Z H. *Hydrometallurgy*, **2009**,**97**:153-157

[5] Ogata T, Takeshita K, Tsuda K, et al. *Sep. Purif. Technol.*, **2009**,**68**:288-290

[6] Elwakeel K Z, Atia A A, Donia A M. *Hydrometallurgy*, **2009**, **97**:21-28

[7] Mashkani S G, Ghazvini P T M, Aligol D A. *Bioresour. Technol.*, **2009**,**100**:603-608

[8] Minamisawa M, Minamisawa H, Yoshida S, et al. *Green Chem.*, **2005**,**7**:595-601

[9] Beolchini F, Fonti V, Ferella F, et al. *J. Hazard. Mater.*, **2010**,**178**:529-534

[10]Zamboulis D, Peleka E N, Lazaridis N K, et al. *J. Chem. Technol. Biotechnol.*, **2011**,**86**:335-344

[11]Xiong Y, Chen C B, Gu X J, et al. *Bioresour. Technol.*, **2011**,**102**:6857-6862

[12]Ajmal M, Rao R A K, Ahmad R, et al. *J. Hazard. Mater.*, **2000**,**B79**:117-131

[13]Pérez-Marín A B, Zapata V M, Ortuo J F. *J. Hazard. Mater.*, **2007**,**B139**:122-131

[14]Li X M, Tang Y R, Xuan Z X, et al. *Sep. Purif. Technol.*, **2007**,**55**:69-75

[15]Biswas B K, Inoue J, Kawakita H, et al. *J. Hazard. Mater.*, **2009**,**172**:721-728

[16]Feng N C, Guo X Y, Liang S, et al. *J. Hazard. Mater.*, **2011**, **185**:49-54

[17]Langmuir I. *J. Am. Chem. Soc.*, **1916**,**38**:2221-2295

[18]Freundlich H. *Z. Phys. Chem.*, **1906**,**57**:385-470

[19]Tempkin M J, Pyzhev V. *Acta Physicochim. URSS*, **1940**,**12**:217-222

[20]Dubinin M M, Radushkevich L V. *Phys. Chem. Sect. USSR*, **1947**,**55**:331-333

[21]Hall K R, Eagleton L C, Acrivos A, et al. *Ind. Eng. Chem. Fundam.*, **1966**,**5**:212-223