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Equilibrium, Kinetics, and Thermodynamics Studies on the Recovery of Rhenium(VII) and Molybdenum(VI) from Industrial Wastewater by Chemically Modified Waste Paper Gel

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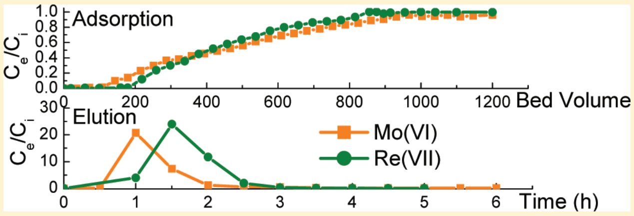
ABSTRACT: Waste paper was chemically modified with dimethylamine (DMA) to obtain a tertiary-amine-type gel, named WPD. By comparing with the adsorption of other coexisting metals, such as Pb(II), Ca(II), Zn(II), Mn(VII), and Ni(II), this novel gel exhibited selectivity only for Mo(VI) and Re(VII) with a remarkably high capacity 4.99 mol·kg^{-1} and 0.96 mol·kg^{-1}, respectively. The adsorption mechanism of Mo(VI) and Re(VII) on the WPD gel was proposed as the anion exchange process. In addition, both the adsorption behavior obeys the Langmuir model, and the endothermic adsorption process followed pseudosecond-order kinetics. Also, the effectiveness of recovery and separation of Mo(VI) and Re(VII) from industrial wastewater was also tested using a column packed with the WPD gel, and it showed highly encouraging results with respect to the stability of the gel and selectivity for the targeted metal ions in the presence of excess of other metal ions.



■ INTRODUCTION

Rhenium and molybdenum are important and strategic metals in human life and industry. Rhenium is a rare metal with special properties such as high melting point and is extensively used in metallurgy, medicine, defense, aviation, chemical, and petrochemical industries. It does not occur naturally, and no mineable ore has been found either. It is usually recovered from molybdenite concentrates through incinerating or direct reduction of the concentrates.[1] Taking into account the declining resource of rhenium and molybdenum against their ever-increasing applications as well as highly toxic of molybdenum and its compounds, efforts should be made for their recovery and recycle from rhenium-rich sources.

For this purpose, lots of methods are used to purify and separate these elements, such as chemical deposition, ion exchange, capillary electrophoresis, liquid chromatography, and solvent extraction. Among them, liquid−liquid extraction provides an effective and simple separation method.[2−5] However, it is often complicated by multistage cycles, extractant loss, and formation of stable emulsions. Thus, it is important to explore new separation techniques, which would be superior to the current separation processes and widely applied to recovery of rhenium and molybdenum.[6−10] From the viewpoint of low cost and green technology, exploration and development of a competent biomass material that can replace the use of a variety of petroleum-based ion exchange resins, chelating resins, and extraction solvents are still big challenges.

At present, the search for environmentally benign and cost-effective methods for rare metals recovery is in progress.[11−17] Waste recycled paper is one of the various cellulosic biomass wastes generated in voluminous amount in various fields.[18,19] It is much easier and consumes only a small amount of energy to incinerate the adsorption gel prepared from waste paper. This is the biggest advantage of the waste paper gel over commercially available ion exchange resins. To date, there has been very little work on waste paper for the purpose of separation and recovery of metal ions, though a wide variety of sorbents based on chemically modified cellulose have been investigated.[20−22] In the present work, we have synthesized waste printing paper and introduced an amine group to prepare an adsorption gel, which was investigated for recovery of rhenium and molybdenum from synthetic solution as well as industrial wastewater.

■ EXPERIMENTAL SECTION

Materials. Spent printing paper was used as the feed material for the adsorption gel. The main components of spent printing paper are cellulose and hemicellulose. The degree of cellulose is more than 90 %. Chloride salts of lead, calcium, zinc, manganese, and nickel were used to prepare test solutions of the respective metals. Rhenium and molybdenum stock solutions were prepared by dissolving NH_4ReO_4 and $(NH_4)_6Mo_7O_{24}·4H_2O$, respectively, in hydrochloric acid. All reagents were of analytical grade and were used without further purification.

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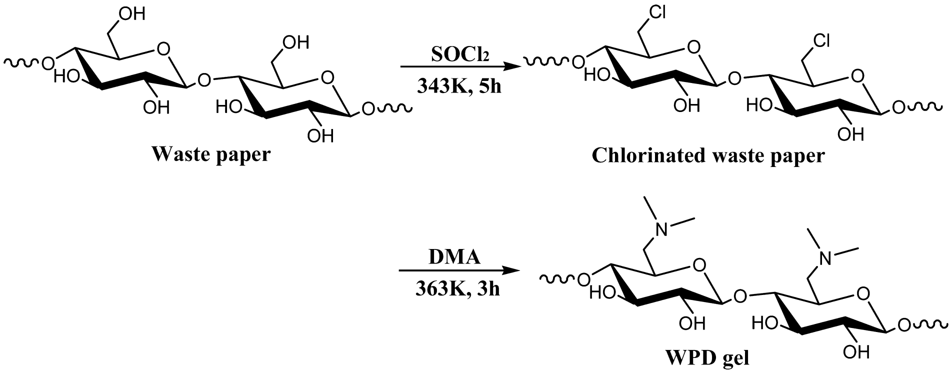
Scheme 1. Preparation of WPD Gel



Preparation of the Adsorption Gel. Waste printing paper was crushed, washed with soap and water, and treated with 20 % sodium hydroxide solution. The suspension was further washed until neutral pH, and the obtained product was dried. As shown in Scheme 1, the pretreated waste paper (abbreviated as WP) was chlorinated by treating with thionyl chloride in pyridine medium under a N_2-atmosphere at 343 K for 5 h. The chlorinated WP obtained was washed and dried. For the immobilization of amine groups, the chlorinated WP was treated with dimethylamine. The product was successively washed with dilute hydrochloric acid, dilute sodium chloride solution, and distilled water. It was dried and crushed to obtain (100 to 150) μm mesh sized black powder and named as waste paper modified with dimethylamine (WPD) gel. This powdered WPD gel was used for adsorption experiments.

Batch Adsorption Studies. All equilibrium adsorption experiments were individually conducted at 303 K for Mo(VI), Re(VII), Pb(II), Ca(II), Zn(II), Mn(VII), and Ni(II) ions. A sample of 10 mg of the WPD gel was mixed with 5 mL of adsorbate solution (20 mg·L^{-1}) at varying HCl concentration in a 25 mL flask. The flask was kept in a thermostatted shaker at a speed of 180 rpm for 24 h. Adsorption kinetics for metal ions were carried out by adding 10 mg of WPD gel in 5 mL of Mo(VI) or Re(VII) solution of concentration 20 mg·L^{-1} (prepared in 0.1 mol·L^{-1} hydrochloric acid) at varying temperatures. The percentage adsorption (%A) for each metal ion was calculated according to eq 1:

$$\%A = \frac{(C_i - C_e)}{C_i}\cdot 100 \tag{1}$$

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

Column Experiments: Loading Followed by Elution. A continuous-mode column experiment was carried out at 303 K using a transparent glass column of 0.8 cm inner diameter and 24.5 cm high. A sample of 100 mg of the WPD gel was packed into the column. Prior to passing the test solution, the column was conditioned by passing distilled water followed by 0.1 mol·L^{-1} hydrochloric acid solution for 24 h. Finally a test solution was fed at a constant flow rate of approximately 6 mL·h^{-1} through the column using a peristaltic pump. The effluent solution was collected at 1 h time intervals. To elute the adsorbed metal ions, the loaded column was first washed with water, and then 3 mol·L^{-1} hydrochloric acid was passed through the column at a same rate (6 mL·h^{-1}). The eluted solution was collected at 30 min time intervals for measuring the metal concentration.

Analyses. The pH of the solution was measured by S-3C model pH meter, while the concentrations of metal ions were measured by using a PE model atomic absorption spectrophotometer and a DV 2000 ICP (inductively coupled plasma) atomic emission spectrometer. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 5700 FTIR spectrophotometer. The reproducibility of every datum was confirmed by repeating the same experiment three times, and the average value was taken.

■ RESULTS AND DISCUSSION

Elemental Analysis. The FTIR spectrum of WP and WPD gel was shown in Figure 1a. Compared with the spectra of WP, the intensity of O−H peak of the WPD gel decreased in the region of (3650 to 3300) cm^{-1}. This change was attributed to the substitute of free hydroxyl groups in WP by dimethylamine groups. The peak at 1588 cm^{-1} ascribed to the C−N bonds was found to be intensified. It suggests grafted tertiary amine groups in the structure of the WPD gel.

To identify the degree of immobilization of the dimethylamine functional groups onto the gel, an elemental analysis was performed. The % composition of carbon, hydrogen, and nitrogen in the prepared functionalized gel was calculated according to the expected chemical structure of the gel as 50.79, 7.94, and 7.41, respectively. The extent of nitrogen was found to be 6.43 %, and hence the extent of modification was determined as 86.77 %. In addition, the functional group density in the WPD gel was calculated as 4.59 mol·kg^{-1}. For comparison, commercial cellulose was modified by dimethylamine, and the nitrogen content was found to be only 1.02 % in it with a functional group density of 0.73 mol·kg^{-1}. The difference in the extent of modification under identical experimental conditions is attributable to the difference in the structure of paper and commercial cellulose. Paper cellulose is highly amorphous and is easily chemically modified, whereas commercial cellulose is crystalline in nature, and consequently reagents cannot easily penetrate into the inner parts of the matrix.

Comparison of the Adsorption Behavior of the WP and WPD Gel. The adsorption behavior of the WP and the WPD gel for various metal ions at varying hydrochloric acid concentrations is shown in Figures 2a,b, respectively. As depicted in Figure 2a, WP exhibited 75 % adsorption of Mo(VI) at pH 6, which was further decreased with increasing HCl concentrationa. For Re(VII), WP exhibited almost no

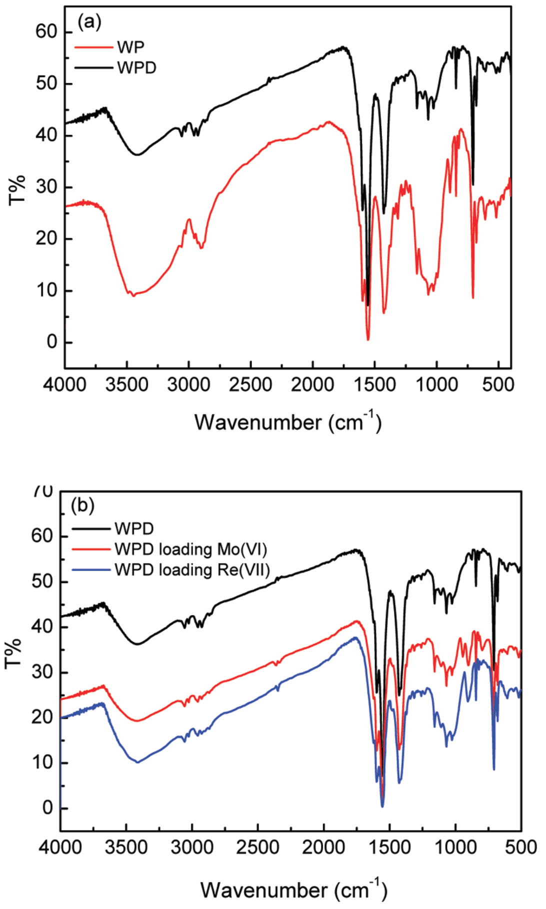


Figure 1. FTIR spectra of (a) WP and WPD gel and (b) WPD gel before and after the adsorption of metal ions.

adsorption due to its low affinity to hydroxyl groups. On the other hand, WPD gel (Figure 2b) showed very good affinity toward molybdenum and rhenium. Almost complete adsorption of Mo(VI) and Re(VII) was found to occur at a wide range of pH. In addition, Figure 2b showed that the adsorption of other coexisting base metal ions such as Pb(II), Ca(II), Zn(II), Mn(VII), and Ni(II) on the WPD gel decreased with increasing hydrochloric acid concentration. A sharp decrease was observed at an ambient condition of 0.1 mol·L^{-1} hydrochloric acid. This result indicates that Re(VII) and Mo(VI) can be selectively separated from other coexisting base metal ions using the WPD gel at an HCl concentration of 0.1 mol·L^{-1} and higher. Unlike the WPD gel, the WP gel exhibited a similar adsorption pattern for Mo(VI) and Pb(II) at lower HCl concentrations, for Mo(VI) and Zn(II) at higher HCl concentrations, indicating a very limited scope for mutual separation by using the WP. Moreover, the mean pK_a value of the WPD gel is 10.77. The adsorption ability is enhanced at a higher pH than the pK_a value.

To determine the effect of functional groups for metal ion adsorption and to infer adsorption mechanism, FTIR spectra of WPD gel before and after Mo(VI) as well as Re(VII) adsorption were analyzed. As shown in Figure 1b, the peak at 1550 cm^{-1} (corresponding to R_2NH) was found to diminish in the gel after Mo(VI) and Re(VII) adsorption. The appearance of two new peaks at 2350 cm^{-1} and 906 cm^{-1} (corresponding to R_3NH^+) indicates the adsorption process. The tertiary amine group of the WPD gel in hydrochloric acid medium is protonated as described by eq 2. Re(VII) should be stable, its dominant species being the perrhenate anion ReO_4^- at the experimental conditions. Hence, the adsorption of metal anion takes place according to the anion exchange reactions as expressed by eq 3 for Re(VII).

$$RN(CH_3)_2 + HCl \leftrightarrow RNH^+(CH_3)_2Cl^- \tag{2}$$

$$RNH^+(CH_3)_2Cl^- + ReO_4^- \leftrightarrow [RNH^+(CH_3)_2]^+ReO_4^- + Cl^- \tag{3}$$

The ionic state of molybdenum in aqueous solution has already been described in our previous work.[23] 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 of solution is higher than 2, as shown in Table 1. Hence, it is expressed by eq 4 as the anion exchange reaction.

$$nRNH^+(CH_3)_2Cl^- + H_ZMo_xO_y^{\,n-} \leftrightarrow [RNH^+(CH_3)_2]_n^{n+}\cdot H_ZMo_xO_y^{\,n-} + nCl^- \tag{4}$$

Kinetics of Adsorption of Mo(VI) and Re(VII) on the WPD Gel. The adsorption kinetics of Mo(VI) and Re(VII) on the WPD gel was studied at mild conditions (0.1 mol·L^{-1} HCl concentration), respectively. The kinetic data for Mo(VI) and

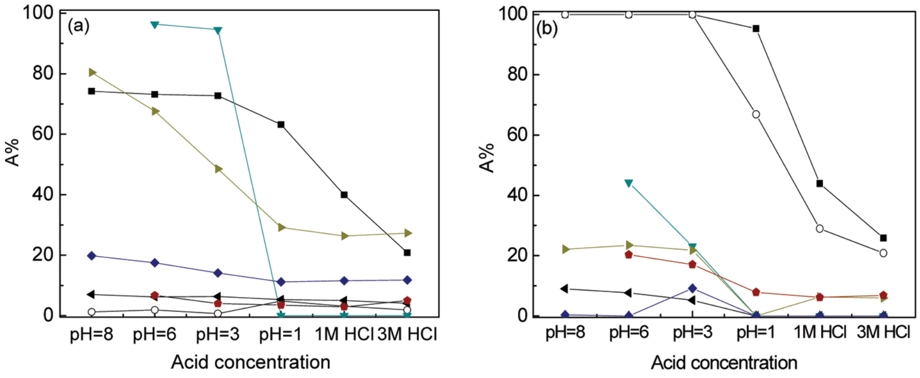


Figure 2. Adsorption of various metal ions on (a) WP and (b) WPD gels at varying hydrochloric acid concentrations. Initial concentration of metal ions = 20 mg·L^{-1}, solid-to-liquid ratio = 2 g·L^{-1}, temperature = 303 K, shaking time = 48 h. ■, Mo(VO); ○, Re(VII); ▼, Pb(II); ◀, Ca(II); ▶, Zn(II); ◆, Mn(VII); ⬟, Ni(II).

Table 1. Ionic State of Molybdenum in Aqueous Solution

acid concentration	ionic species of Mo(VI)
pH = 0−1	$H_6Mo_2O_8^{2+}$, $H_3MoO_4^{+}$, H_2MoO_4
pH = 1−2	H_2MoO_4, $H_3Mo_7O_{24}^{3-}$, $H_2Mo_7O_{24}^{4-}$
pH = 2−3	$H_3Mo_7O_{24}^{3-}$, $H_2Mo_7O_{24}^{4-}$, $HMo_7O_{24}^{5-}$
pH = 3−4	$H_3Mo_7O_{24}^{3-}$, $H_2Mo_7O_{24}^{4-}$, $HMo_7O_{24}^{5-}$, $Mo_8O_{26}^{4-}$
pH = 4−5	$H_3Mo_7O_{24}^{3-}$, $H_2Mo_7O_{24}^{4-}$, $HMo_7O_{24}^{5-}$
pH = 5−6	$H_2Mo_7O_{24}^{4-}$, $HMo_7O_{24}^{5-}$, $Mo_7O_{24}^{6-}$
pH > 6	MoO_4^{2-}

Re(VII) adsorption were analyzed in terms of various kinetics models, among which the pseudosecond-order rate law was found to be the best fit in terms of determination coefficient, as shown in Figure 3a,b, respectively. Ho's equation for a pseudosecond-order reaction is given as:

$$\frac{1}{C_t} - \frac{1}{C_i} = kt \tag{5}$$

where C_t and C_i stand for the concentration at time = t and initial concentration, respectively.

In addition, from the slopes of the straight lines, the rate constants for Mo(VI) adsorption were calculated as $(3.4 \cdot 10^{-1}$, $4.9 \cdot 10^{-1}$, $6.8 \cdot 10^{-1}$, $8.5 \cdot 10^{-1}$, and 1.35) $L \cdot mol^{-1} \cdot h^{-1}$ at (293, 298, 303, 318, and 323) K, respectively. In case of Re(VII), the rate constants were found to be $(3.6 \cdot 10^{-2}$, $5.9 \cdot 10^{-2}$, $9.6 \cdot 10^{-2}$, and $1.2 \cdot 10^{-1})$ $L \cdot mol^{-1} \cdot h^{-1}$ at (288, 303, 318, and 323) K, respectively. Furthermore, from the relationship between rate constant and temperature, the Arrhenius plot (Figure 3c) was depicted according to eq 6 from which the activation energy, E_a, was calculated as (49.69 and 26.02) $kJ \cdot mol^{-1}$ for Mo(VI) and Re(VII), respectively. Since chemical adsorption needs a higher activation energy,[24] the extent of calculated activation energy suggests that a chemisorption process is involved in the adsorption of both Mo(VI) and Re(VII) on the WPD gel prepared from biomass material. The Arrhenius plot which can be written as:

$$\ln k = -\frac{E_a}{RT} + B \tag{6}$$

where k, E_a, R, T, and B are the rate constant $L \cdot mol^{-1} \cdot h^{-1}$, activation energy $(kJ \cdot mol^{-1})$, universal gas constant $(J \cdot mol^{-1} \cdot K^{-1})$, temperature (K), and pre-exponential factor, respectively.

The adsorption thermodynamics of Mo(VI) and Re(VII) on the WPD gel was also studied at the earlier-mentioned temperatures, respectively. The change in enthalpy of the reactions, ΔH, can be determined according to eq 7:

$$\frac{\Delta \ln D}{\Delta(1/T)} = -\frac{\Delta H}{R} \tag{7}$$

where R is the gas constant and D is equilibrium distribution ratios of metal ions in the liquid−solid phase.

From the slope of the plot of ln$D$ versus $1/T$ (shown in Figure 3d), the enthalpy was calculated to be (15.16 and 25.14) $kJ \cdot mol^{-1}$ for Mo(VI) and Re(VII), respectively. The positive value of ΔH indicates the endothermic nature of the adsorption process of both Mo(VI) and Re(VII) onto the WPD gel. The result supports the view that the deduced endothermic process for kinetic studies is correct.

Adsorption Isotherms for Mo(VI) and Re(VII) on the WPD Gel. Adsorption isotherms are important for the description of how molecules or ions of adsorbate interact

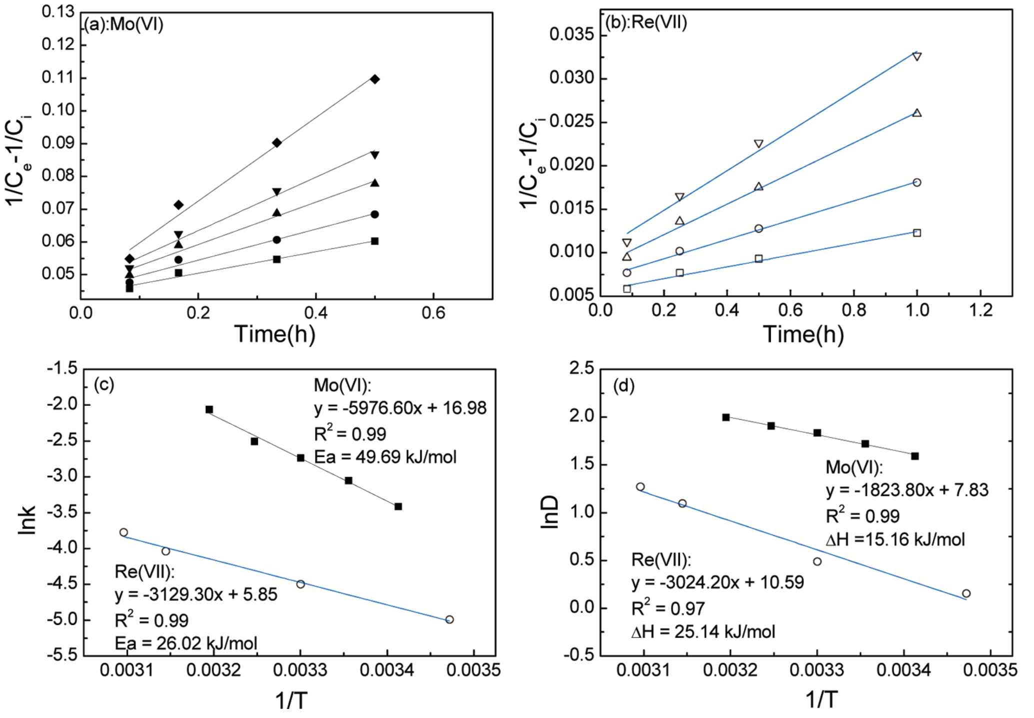


Figure 3. Pseudosecond order in case of (a) Mo(VI) and (b) Re(VII); (c) Arrhenius plot in the adsorption of Mo(VI) and Re(VII) on the WPD gel at various temperatures; (d) relationship between distribution ratio D and temperature. Initial concentration of metal ions = 20 $mg \cdot L^{-1}$ (prepared in 0.1 $mol \cdot L^{-1}$ HCl), solid-to-liquid ratio = 2 $g \cdot L^{-1}$. ■, 293 K, slope = 0.033, R^2 = 0.98; ●, 298 K, slope = 0.047, R^2 = 0.98; ▲, 303 K, slope = 0.065, R^2 = 0.98; ▼, 313 K, slope = 0.082, R^2 = 0.99; ◆, 323 K, slope = 0.127, R^2 = 0.98. □, 288 K, slope = 0.0068, R^2 = 0.98; ○, 303 K, slope = 0.011, R^2 = 0.99; △, 218 K, slope = 0.018, R^2 = 0.99; ▽, 323 K, slope = 0.023, R^2 = 0.99.

with sorbent surface sites and its degree of accumulation onto sorbent surface at constant temperature. Hence, the correlation of equilibrium data using either a theoretical or empirical equation is essential for the adsorption interpretation and prediction of the extent of adsorption. Four isotherm equations (eq 8 to 11) have been tested in the present study, namely, Langmuir, Freundlich, Temkin, and Dubinin−Radushkevich.[25−28]

$$\text{Langmuir isotherm: } q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \tag{8}$$

$$\text{Freundlich isotherm: } q_e = K_F {C_e}^{1/n} \tag{9}$$

$$\text{Temkin isotherm: } q_e = \frac{RT}{b} \ln(AC_e) \tag{10}$$

Dubinin−Radushkevich isotherm:

$$q_e = q_m \exp(-\beta \varepsilon^2) \tag{11}$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{12}$$

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

The linear forms of the Langmuir, Freundlich, Temkin, and Dubinin−Radushkevich isotherms can be expressed by eqs 13 to 16, respectively:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{q_{\max} K_L} \tag{13}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{14}$$

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e \tag{15}$$

$$\ln q_e = \ln q_m - \beta \left[RT \ln\left(1 + \frac{1}{C_e}\right)\right]^2 \tag{16}$$

The adsorption isotherm data for both Mo(VI) and Re(VII) onto WPD gel has been plotted in Figure 4a,b, respectively, from which isotherm constants have been tabulated in Table 2. It is clear that the Langmuir isotherm shows a better fit to adsorption data than the other isotherm equations both for molybdenum (r^2 = 0.94) and rhenium (r^2 = 0.98) when the adsorption data is directly simulated by origin nonlinear curve fit according to eqs 8 to 11. The linear regression equations for four isotherms (eqs 13 to 16) were also calculated and give the same result. The plot of C_e/q_e versus C_e is linear with a better determination coefficient (R^2) of 0.97 for molybdenum and 0.99 for rhenium. Especially, when the concentration of Mo(VI) remained in the solution is higher than 0.0002 mol·L^{-1}, a better determination coefficient (R^2) of 0.99 could be obtained. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogeneous distribution of active sites on the WPD gel surface, since the Langmuir equation assumes that the surface is homogeneous.[25] This situation may be explained based on the structure of WPD gel, containing the same surface reactive R_3NH^+ groups binding Mo(VI) or Re(VII) ions.

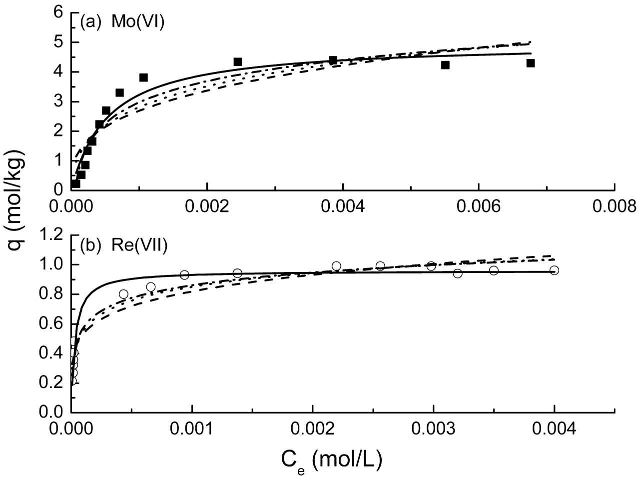


Figure 4. Adsorption isotherms for Mo(VI) and Re(VII) on the WPD gel. Solid-to-liquid ratio = 2 g·L^{-1}, temperature = 303 K, shaking time = 72 h. (a) ■, Experimental; —, Langmuir, R^2 = 0.9416; - - -, Freundlich, R^2 = 0.7773; — — —, Temkin, R^2 = 0.9020; ···, Dubinin−Radushkevich, R^2 = 0.8297. (b) ○, Experimental; —, Langmuir, R^2 = 0.9774; - - -, Freundlich, R^2 = 0.9258; — — —, Temkin, R^2 = 0.9677; ···, Dubinin−Radushkevich, R^2 = 0.9563.

Moreover, the maximum adsorption capacity was evaluated as 4.99 mol·kg^{-1} of WPD dry gel for molybdenum and 0.96 mol·kg^{-1} of WPD dry gel for rhenium. However, it was only 0.91 mol·kg^{-1} of dry gel for the WP gel for molybdenum and nonadsorption for rhenium at the same experimental conditions, which further indicates that the adsorption of Mo(VI) and Re(VII) on this gel is greatly enhanced after chemical modification. In addition, the value of K_L was about (1.82 and 39.69) L·mmol^{-1} for molybdenum and rhenium, respectively. An essential characteristic of the Langmuir isotherm can be expressed by a dimensionless separation factor (R_L) which is defined as:

$$R_L = \frac{1}{1 + K_L \cdot C_0} \tag{17}$$

where C_0 is the initial concentration of the metal ions (mol·L^{-1}). The significance of the 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.[29] The obtained values of R_L in the range (0.034 to 0.51 for Mo(VI) and 0.005 to 0.18 for Re(VII)) signify a highly favorable adsorption for different initial concentrations at the experimental conditions.

Column-Mode Adsorption and Elution. Since the WPD gel has shown a high adsorption capacity and selectivity for molybdenum and rhenium, column-mode adsorption−elution experiments were conducted to recover Mo(VI) and Re(VII). Different column experiments were conducted at a varying flow rate (e.g., (4, 6, 8, and 10) mL·h^{-1}). The loading capacity of the

Table 2. Langmuir, Freundlich, Temkin, and Dubinin−Radushkevich Isotherm Constants

		Mo(VI)		Re(VII)	
		nonlinear curve fit	linear fit	nonlinear curve fit	linear fit
Langmuir	q_{max} (mmol·g^{-1})	4.99	4.92	0.96	0.98
	K_L (L·mmol^{-1})	1.82	2.03	32.69	25.56
	r^2	0.94	0.97	0.98	0.99
Freundlich	K_F (L/g)	26.86	122.90	2.96	3.66
	n	3.07	1.75	5.37	4.61
	r^2	0.78	0.77	0.96	0.92
Temkin	A (L·g^{-1})	17.89	17.88	1042.18	998.86
	b·10^{-3}	2.44	2.44	20.33	20.33
	r^2	0.90	0.91	0.97	0.97
Dubinin−Radushkevich	q_m (mmol·g^{-1})	9.22	19.19	1.47	1.58
	β (mmol^2·J^{-2})	0.0039	0.0066	0.0018	0.0020
	r^2	0.83	0.84	0.96	0.95

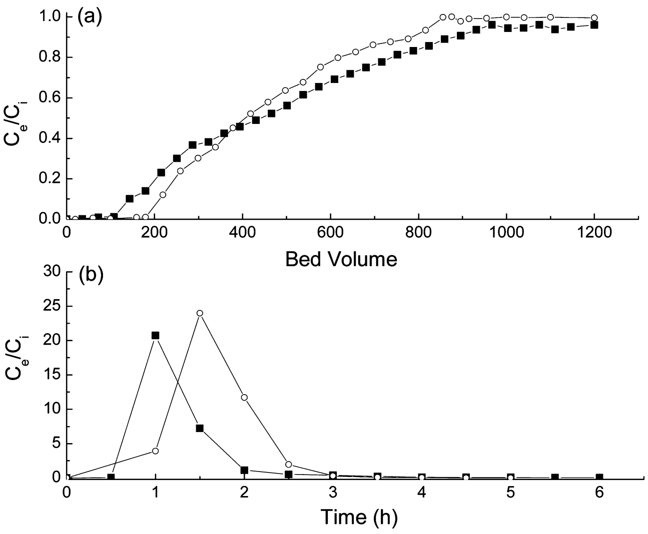


Figure 5. (a) Breakthrough profiles for Mo(VI) and Re(VII) on the WPD gel. Flow rate = 6 mL·h^{-1}, Mo(VI) = 50 ppm, Re = 20 ppm. (b) Elution profiles for loaded metals from the column. Eluent = 3 mol·L^{-1} HCl, flow rate = 6 mL·h^{-1}, weight of gel = 100 mg. ■, Mo(VI); ○, Re(VII).

gel was found to be the same for each flow rate. Figure 5a shows the breakthrough profiles of the tested metal ions at a flow rate of 6 mL·h^{-1} using a column packed with WPD gel under the conditions described in the figure legend. As can be seen from Figure 5a, both Mo(VI) and Re(VII) were adsorbed onto the WPD gel packed in the column. Complete saturation of the column was found to occur at 950 BV and 850 BV for Mo(VI) and Re(VII), respectively. However, from the analyses of these breakthrough curves, the maximum loading capacities of the WPD gel for Mo(VI) and Re(VII) were evaluated as (0.46 and 0.17) mol·kg^{-1} of the dry gel, respectively. Taking account of the amount of the gel packed in the column, the adsorption capacity of the gel for Mo(VI) and Re(VII) appears quite reasonable in comparison to the adsorption capacity obtained from batchwise tests ((4.99 and 0.96) mol·kg^{-1}). Such a low extent of adsorption capacity can be attributed to the channeling of the adsorbent column, low initial metal concentration in column-mode operation, the continuous flow of the solution, and competitive adsorption. Figure 5b shows the elution profiles of the loaded metal ions with hydrochloride acid solution. It reveals that both of the metals were eluted with high preconcentration factors such as 21 for Mo(VI) and nearly 25 for Re(VII). According to the area of the curves, about 99 % Mo(VI) and 99 % Re(VII) were eluted and recovered. It is clear that the % recovery of rare metals in this study is quite high, and it is probably due to the optimal affinity of the WPD gel for Mo(VI) and Re(VII).

To evaluate the durability of the adsorbent, six consecutive adsorption-elution cycle tests using the column packed with the WPD gel were also conducted. This would give an idea for recovering Mo(VI) and Re(VII) after its adsorption, as shown in Table 3. Furthermore, no change in the physical appearance of the gel was observed, and the phenomenon of swelling or shrinking was not apparent with repeated use. The high level of preconcentration and the recovery ability could be very useful for the treatment of rare metals in industrial wastewater as described in the following section.

Table 3. Performance of the WPD Gel in Consecutive Adsorption−Elution Cycles

adsorption %		absorbed (mg)	eluted (mg)	% recovery
Mo(VI)	cycle 1	4.35	4.31	99.08
	cycle 2	4.33	4.15	95.84
	cycle 3	4.45	4.54	102.01
	cycle 4	4.12	4.07	98.78
	cycle 5	4.37	4.20	96.11
	cycle 6	4.29	4.32	100.70
Re(VII)	cycle 1	3.07	3.15	102.61
	cycle 2	3.22	3.15	97.82
	cycle 3	3.13	3.10	99.04
	cycle 4	3.30	3.28	99.39
	cycle 5	3.11	2.98	95.82
	cycle 6	3.09	3.08	99.68

Recovery of Mo(VI) and Re(VII) from Industrial Wastewater. In connection to the recovery of Mo(VI) and Re(VII) by using the prepared gel, column adsorption as well as elution tests were carried out. In this experiment, industrial wastewater, collected from Yangjiazhangzi Economic Development Zone Management Committee, China, was used to get the essence of on-the-field use of the gel. The pH of the sample was 7.6, and it contained assorted metal ions in different concentrations as shown in Table 4. However, in our previous study, we have prepared an adsorption gel from astringent persimmon by chemical modification (APF gel) and success-

Table 4. Adsorptive Recovery of Mo(VI) and Re(VII) from Industrial Wastewater

		initial concentration	absorbed (mg)	eluted (mg)	% recovery
column 1 (100 mg APF)	Mo(VI)	145	7.25	7.11	98.07
	Re(VII)	450	0	0	0
	Ca(II)	900	0	0	0
	Ge(IV)	56	0	0	0
	Si(IV)	33	0	0	0
column 2 (100 mg WPD)	Mo(VI)	4	0.04	0.04	99.93
	Re(VII)	450	4.83	4.78	98.96
	Ca(II)	900	0	0	0
	Ge(IV)	56	0	0	0
	Si(IV)	33	0	0	0

fully applied for the selective removal and recovery of Mo(VI).[23] Therefore, we have performed two different column experiments, and the result has been shown in Table 4. The first column, which was loaded with APF gel, has selectively recovered almost all molybdenum from the industrial wastewater while the second, loaded with WPD gel, recovered rhenium from all other metal ions.

The results have been tabulated in Table 4. It is clear that about 98.07 % Mo(VI) using the APF gel was eluted and recovered, while the adsorption of rhenium, germanium, calcium, and silicon as observed is negligible. The results given in Table 4 also show that the absorbed amount of Re(VII) is 4.83 mg/100 mg of the WPD gel, and 98.96 % Re(VII) was recovered from the industrial wastewater. The recovery of rare metals in this study appears to be highly satisfactory, and it is perhaps due to the optimal affinity of the gel prepared in this study.

■ CONCLUSIONS

The modified waste paper gel was investigated for the adsorption of molybdenum and rhenium as well as some base metals from hydrochloric acid medium. It is concluded that Re(VII) and Mo(VI) can be selectively separated from other coexisting base metal ions using the WPD gel at HCl concentrations of 0.1 mol·L^{-1} and higher. The Langmuir adsorption model, endothermic adsorption process, and anion exchange reactions mechanism for Mo(VI) were obtained. Column adsorption and subsequent elution for different cycles revealed the enormous scope for recovery of Mo(VI) and Re(VII), which provides an effective approach to the recovery of molybdenum and rhenium by the WPD gel.

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■ REFERENCES

(1) Sutulov, A. *Molybdenum and rhenium recovery from porphyry coppers*; University of Concepcion: Concepcion, Chile, 1970.

(2) Jordanov, N.; Mareva, S.; Borisov, G.; Jordanov, B. Substituted ethan phosphonic acid esters as reagents for the separation of molybdenum from rhenium by solvent extraction. *Talanta* **1968**, *15*, 221−227.

(3) Karagiozov, L.; Vasilev, C. Separation of molybdenum and rhenium by extraction with mixtures of trioctylamine and Aliquat 336 followed by selective stripping. *Hydrometallurgy* **1979**, *4*, 51−55.

(4) Zhang, X.-X.; Zhou, Z.-X.; Ma, S.-J.; Shu, C. Solvent extraction of rhenium(VII) with crown ethers and some univalent cations. *Solvent Extr. Ion Exch.* **1993**, *11*, 585−601.

(5) Cao, Z.-F.; Zhong, H.; Qiu, Z.-H. Solvent extraction of rhenium from molybdenum in alkaline solution. *Hydrometallurgy* **2009**, *97*, 153−157.

(6) Park, K.-H.; Mohapatra, D.; Reddy, R. Selective recovery of molybdenum from spent HDS catalyst using oxidative soda ash leach/carbon adsorption method. *J. Hazard. Mater.* **2006**, *B138*, 311−316.

(7) Elwakeel, K.-Z.; Atia, A.-A.; Donia, A.-M. Removal of Mo(VI) as oxoanions from aqueous solutions using chemically modified magnetic chitosan resins. *Hydrometallurgy* **2009**, *97*, 21−28.

(8) Mashkani, S.-G.; Ghazvini, P.-T.-M.; Aligol, D.-A. Uptake of Re(VII) from aqueous solutions by Bacillus sp. GT-83-23. *Bioresour. Technol.* **2009**, *100*, 603−608.

(9) Valdés, H.; Romero, J.; Sanchez, J.; Bocquet, S.; Rios, G.-M.; Valenzuela, F. Characterization of chemical kinetics in membrane-based liquid−liquid extraction of molybdenum(VI) from aqueous solutions. *Chem. Eng. J.* **2009**, *151*, 333−341.

(10) Dodbiba, G.; Fujita, T.; Kikuchi, T.; Manjanna, J.; Matsuo, S.; Takahashi, H.; Tohji, K. Synthesis of iron-based adsorbents and their application in the adsorption of molybdenum ions in nitric acid solution. *Chem. Eng. J.* **2011**, *166*, 496−503.

(11) Nakano, Y.; Takeshita, K.; Tsutsumi, T. Adsorption mechanism of hexavalent chromium by redox within condensed-tannin gel. *Water Res.* **2001**, *5*, 496−500.

(12) Nakajima, A.; Baba, Y. Mechanism of hexavalent chromium adsorption by persimmon tannin gel. *Water Res.* **2004**, *38*, 2859−2864.

(13) Ahmaruzzaman, M.; Gayatri, S.-L. Activated tea waste as a potential low-cost adsorbent for the removal of *p*-nitrophenol from wastewater. *J. Chem. Eng. Data* **2010**, *55*, 4614−4623.

(14) Calero, M.; Blázquez, G.; Martin-Lara, M.-A. Kinetic modeling of the biosorption of lead(II) from aqueous solutions by solid waste resulting from the olive oil production. *J. Chem. Eng. Data* **2011**, *56*, 3053−3060.

(15) Liang, S.; Guo, X.-Y.; Feng, N.-C.; Tian, Q.-H. Application of orange peel xanthate for the adsorption of Pb^{2+} from aqueous solutions. *J. Hazard. Mater.* **2009**, *170*, 425−429.

(16) Eroglu, H.; Yapici, S.; Varoglu, E. An investigation of the biosorption of radioactive gallium-67 in an aqueous solution using rose residue. *J. Chem. Eng. Data* **2010**, *55*, 2848−2856.

(17) Wang, X.-S.; Lu, Z.-P.; Miao, H.-H.; He, W.; Shen, H.-L. Kinetics of Pb(II) adsorption on black carbon derived from wheat residue. *Chem. Eng. J.* **2011**, *166*, 986−993.

(18) Richardson, S.; Gorton, L. Characterisation of the substituent distribution in starch and cellulose derivatives. *Anal. Chim. Acta* **2003**, *497*, 27−65.

(19) Beolchini, F.; Fonti, V.; Ferella, F.; Veglio, F. Metal recovery from spent refinery catalysts by means of biotechnological strategies. *J. Hazard. Mater.* **2010**, *178*, 529−534.

(20) Uraki, Y.; Kubo, S.; Sano, Y. Preparation of activated carbon moldings from the mixture of waste newspaper and isolated lignins: mechanical strength of thin sheet and adsorption property. *J. Wood Sci.* **2002**, *48*, 521−526.

(21) Adhikari, C.-R.; Parajuli, D.; Kawakita, H.; Inoue, K.; Ohto, K.; Fujiwara, D. Adsorption behavior of iminodiacetic acid type of chelating gel prepared from waste paper. *Sep. Sci. Technol.* **2007**, *42*, 579−590.

(22) Adhikari, C.-R.; Parajuli, D.; Inoue, K.; Ohto, K.; Kawakita, H. Pre-concentration and separation of heavy metal ions by chemically modified waste paper gel. *Chemosphere* **2008**, *72*, 182−188.

(23) Xiong, Y.; Wang, H.-T.; Lou, Z.-N.; Shan, W.-J.; Xing, Z.-Q.; Deng, G.-C.; Wu, D.-B.; Fang, D.-W.; Biswas, B.-K. Selective adsorption of molybdenum(VI) from Mo−Re bearing effluent by chemically modified astringent persimmon. *J. Hazard. Mater.* **2011**, *186*, 1855−1861.

(24) Unuabonah, E.-I.; Adebowale, K.-O.; Olu-Owolabi, B.-I. Kinetic and thermodynamic studies of the adsorption of lead(II) ions onto phosphate-modified kaolinite clay. *J. Hazard. Mater.* **2007**, *144*, 386−395.

(25) Langmuir, I. The constitution and fundamental properties of solids and liquids. *J. Am. Chem. Soc.* **1916**, *38*, 2221−2295.

(26) Freundlich, H. Uber die adsorption in losungen. *Z. Phys. Chem.* **1906**, *57*, 385−470.

(27) Tempkin, M.-J.; Pyzhev, V. Kinetics of ammonia synthesis on promoted iron catalysts. *Acta Physicochim. URSS* **1940**, *12*, 217−222.

(28) Dubinin, M.-M.; Radushkevich, L.-V. Equation of the characteristic curve of activated charcoal proceedings of the academy of sciences. *Phys. Chem. Sect. USSR* **1947**, *55*, 331−333.

(29) Hall, K.-R.; Eagleton, L.-C.; Acrivos, A.; Vermeulen, T. Pore- and solid-diffusion kinetics infixed-bed adsorption under constant-pattern conditions. *Ind. Eng. Chem. Fundam.* **1966**, *5*, 212−223.