

EQUILIBRIUM ADSORPTION BEHAVIORS AND KINETIC CHARACTERISTICS OF OXYMATRINE ON A SPHERICAL CELLULOSE ADSORBENT

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An investigation was conducted on the adsorption of oxymatrine (OMT) on a spherical cellulose adsorbent embedded with wattle bark tannin. The results showed that the adsorption of the OMT on the adsorbent was solution pH dependent and the adsorption process followed the Freundlich adsorption isotherm. The adsorption kinetics of the OMT on the adsorbent could be well described by the pseudo-second-order rate model. And, the adsorption capacity calculated by the pseudo-second-order rate model was close to the experimental data. Desorption and regeneration experiments showed that the OMT adsorbed on the adsorbent could be easily recovered by 50% methanol solution.

Keywords: Absorption Behaviors; Kinetics; Oxymatrine; Spherical Cellulose Adsorbent; Embedded

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INTRODUCTION

Oxymatrine (OMT) and matrine are two primary components of the dried root of *Sophora flavescens*, which is a widely used traditional Chinese herbal drug. These compounds possess strong biological activities and exhibit potentially useful pharmacological activities (Kinghorn et al. 1984), such as analgesic, antipyretic, anti-cancer, anti-inflammatory, and anti-virus properties, and are used in acute conditions such as colpitis, HBV, and other cases requiring anti-bacterial or anti-virus effects. Therefore it is important to develop efficient methods for the separation and determination of MT and OMT from Chinese herbs.

There have been a few reports on the separation of these two compounds, including pH-zone-refining counter-current chromatography (CCC) (Yang et al. 1998), high-performance liquid chromatography (HPLC) (Ma and Cao 2000), and thin-layer chromatography (TLC) (Li and Yang 1994). However, these methods lack quantitative precision, have relatively low efficiency, or take a rather long analysis time. For example, the separation capacity of classical HPLC is relatively low, limited by the column capacity, and the stationary phase may be affected by losses. Although CCC has been used to separate and purify a large amount of active components from traditional Chinese medicinal herbs and other natural products (Li et al. 2002), too much harmful solvent has to be used with the method. TLC is an inexpensive method, but the operational processes are fussy and tedious.

Compared with the other methods, adsorption-desorption is considered as an effective and economic method to separate and extract active constituents from Chinese traditional medicine. It has the advantages of lower generation of residues, easy adsorbate recovery, and the possibility to reuse adsorbent.

Cellulose is regarded as the most abundant and renewable biopolymer in nature, and is one of the promising raw materials available in terms of cost for the preparation of various functional materials (Zugenmaier, 2001; Saito and Isogai, 2005). It is nontoxic, biodegradable, and can be chemically modified to possess new functional groups with the aim of preparing new products having special properties. The applications of cellulose to use as an adsorbent have been well documented (Liu et al. 2002a,b; Lin et al. 2009). Therefore, much attention has been drawn to this biopolymer or its derivatives for sorption. Tannins, natural biomass containing multiple adjacent hydroxyl groups, can be used as an alternative, effective, and efficient adsorbent (Matsumura and Usuda 1998; Nakano et al. 2001; Sengil et al. 2009). However, tannin is a water-soluble compound, which restricts its practical application as an adsorbent. Therefore, great efforts have been made to overcome this disadvantage, mainly by immobilizing tannins onto various water-insoluble matrices such as agarose (Nakajima and Sakaguchi, 1987), viscose rayon fiber (Sakaguchi and Nakajima 1987), cellulose (Chibata et al. 1986), and other matrices (Nakajima and Sakaguchi 1990).

The present study describes the adsorption-desorption of OMT by cellulose adsorbent embedded with tannin. There have been few reports however of the use of a natural macromolecule adsorbent for adsorption of OMT. In order to improve the surface area, permeability, and hydraulic performance of the cellulose adsorbent, a spherical shape of the adsorbent was developed to further increase the adsorption efficiency (Liu et al. 2001, 2002).

EXPERIMENTAL

Materials

Masson pine bleached sulfate pulp cellulose was obtained from Nanping Paper industry Co., LTD, Fujian, China. Oxymatrine (98%) was purchased from Xi an Honson Biotechnology Co., Ltd. Other reagents were commercial products supplied by ShenHui Chemical Reagent LTD. Co. Deionised water was used throughout the work.

Preparation of Spherical Cellulose Adsorbent

Preparation of viscose fibre

20.0 g (dry basis) of Masson pine bleached sulfate pulp cellulose was immersed into 20.0% of NaOH solution at room temperature for 2 h. The excess alkali liquor was removed under reduced pressure, and the resulting mixture was aged at room temperature for 3.0 days to get optimum viscosity, which could be easily spheroidized. The alkali cellulose was put into a 500 mL three-mouth flask, and then 9.1 mL CS₂ was added into the flask, after stirring for 15min with mechanic agitation, 210 mL 6% of NaOH solution and 0.028g of sodium oleate (as surfactant) were added. The mixture was stirred for 3.0h at room temperature, and then the viscose fibre was obtained.

Embedded spherical cellulose adsorbent

30 g of alkali cellulose and 0.3 g of imbedding agent wattle bark tannin and 2.0 g of CaCO_3 were put into a three-mouth flask, then 120 mL of dispersed phase transformer oil was added after stirring for 10 minutes, and 30 mL of distilled water and 0.6 g of dispersant sodium oleate were added. The viscosity of the system was adjusted by gelatin, after dispersing uniformly under the stirring at 200 revolutions per min. The mixtures were slowly heated up to 60 °C and reacted for 1.5 h. After the reaction, the mixtures were allowed to cool to ambient temperature and moved out; then the upper oil phase was recovered and the lower phase containing cellulose beads was filtered. Dark brown spherical cellulose adsorbent was obtained. The product was washed with water and identified as the tannin-embedded spherical cellulose adsorbent.

Adsorption Experiment

Batch adsorption experiments were carried out by shaking 0.2 g of cellulose adsorbent with 25 mL OMT solution at the desired concentration and pH (adjusted with 1 mol/L NaOH or HCl solutions) in a conical flask for 2 h. After equilibrium, the flask contents were filtered to separate the sorbents from the solution, and the filtrate was analyzed for sorbate concentration by High Performance Liquid Chromatography (HPLC, HITACHI L-2000) method with Ultimate 5 μm XB-C18 (4.6 \times 250 mm) column and mobile phase of acetonitrile-dehydrated alcohol-ultrapure water (80:10:10) at a flow rate of 1.0 mL/min, and refractive index detector. The amount of OMT adsorbed by the cellulose adsorbents, $q_e(\text{mg/g})$, was obtained as follows,

$$q_e = (C_0 - C_e) \times V/W \quad (1)$$

where C_0 and C_e (mg/L) are the initial and final concentrations of OMT, respectively, V the volume of solution (L), and W is the weight of cellulose adsorbent (g).

The used adsorbent after adsorption was washed twice with 50% methanol followed by distilled water several times to remove adsorbed OMT. It was reused for further adsorption studies.

RESULTS AND DISCUSSION

Effect of pH on the Adsorption of OMT

In the adsorption process, the pH of the aqueous solution is a critical controlling parameter (Taty-Costodes et al. 2003). The pH value will determine the extent of ionization of OMT and the surface charge of the adsorbents, which will affect the interaction between the adsorbate and the adsorbent. The effect of the hydrogen ions concentrations on the adsorption of OMT on cellulose adsorbent was as shown in Fig. 1.

It can be seen that both the removal rate and adsorption capacity of OMT increased with increasing pH in the range of 1-6, and then decreased in the pH range of 6.0 to 10.0. These facts indicated that the adsorption of OMT onto cellulose adsorbent was highly pH-dependent, and strong acidity or alkaline nature of the solution was not beneficial to the adsorption. At very low pH (1.0), the surface of the sorbent was more

protonated (due to more H^+ ions), and the OMT existed mainly as positive ions. Thus, the chelating interaction of OMT with phenolic hydroxyls of adsorbent was suppressed, and the adsorption capacity was relatively lower. When the solution pH was higher, the availability of $-OH^-$ group increased, making more phenolic hydroxyls of the adsorbent ionized, which significantly promoted the chelating interaction of OMT, resulting in the obvious increase of adsorption capacity. However, when the solution pH was higher than the pK_a value (5.77) of the OMT (Gong et al. 2003), the OMT existed mainly as molecules in solution,

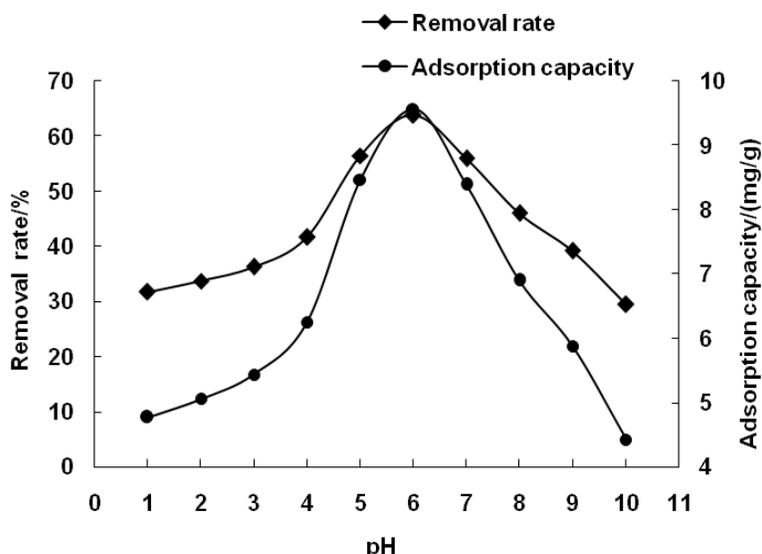


Fig. 1. Effect of pH on the adsorption. Sorption conditions: initial OMT concentration, 120mg/L; adsorption time, 2h; adsorbent usage, 0.2 g/25mL; room temperature

Adsorption Isotherm

Adsorption isotherms are important for the description of how molecules or ions of adsorbate interact with adsorbent surface sites. They are also critical in optimizing the use of adsorbent. Hence, the correlation of equilibrium data using either theoretical or empirical equations is essential for the adsorption interpretation and prediction of the extent of adsorption. In this study, the analysis of the adsorption isotherms of OMT was carried out by applying the Langmuir and Freundlich equations (Saucedo et al. 1993).

The Langmuir isotherm describes monolayer adsorption and is based on the assumption that all the adsorption sites are energetically identical and adsorption takes place on a structurally homogeneous adsorbent (Ünlü and Ersoz 2006). The Langmuir isotherm is given by Eq. 1,

$$\frac{C_e}{q_e} = \frac{1}{b \cdot Q_0} + \frac{C_e}{Q_0} \quad (1)$$

where, the C_e and q_e are the concentration (mg/L) and amount (mg/g) of OMT adsorbed at equilibrium, respectively. The coefficient b is a direct measure of the intensity of the adsorption process (L/mg), and Q_0 is a constant related to the area occupied by a

monolayer of the adsorbent, reflecting the maximum adsorption capacity (mg/g). From a plot of $1/q_e$ vs. $1/C_e$, the values of Q_0 and b can be obtained from its slope and intercept.

The Freundlich isotherm describes monomolecular layer coverage of adsorbent by the solutes (Al-Asheh et al 2000). It is an empirical isotherm model used for the adsorption on heterogeneous surfaces or surfaces supporting sites of varied affinities (Dabrowski 2001). The Freundlich isotherm model is formulated as,

$$q_e = KC_e^{1/n} \quad (2)$$

or

$$\lg q_e = \lg K + \frac{1}{n} \lg C_e \quad (3)$$

where K is a constant for the system relating to the bonding energy. The parameter K can be defined as the adsorption or distribution coefficient, and it represents the quantity of the adsorbate adsorbed on the adsorbents for a unit equilibrium concentration. The slope $1/n$ is a measure of the adsorption intensity.

Tables 1 and 2 show the results of Langmuir and Freundlich isotherm fits. Obviously, it could be observed that the data fit well to the classical Freundlich equation, rather than the Langmuir equation for the studied system, as reflected by the values of the coefficients of determination (R^2). Moreover, the calculated values of Q_0 in the Langmuir isotherm were higher than the actual value by a huge difference or reached negative values. The results meant that the adsorption isotherm of OMT onto cellulose adsorbent could not be described by Langmuir isotherm, implying an uneven distribution of the adsorption sites on the adsorbent surface, which is consistent with heterogeneous adsorption. This was because the cellulose adsorbents were constituted by the random combination of different monoflavonoid units corresponding to the structural heterogeneity of wattle bark tannins.

Table 1. Langmuir Parameters of Adsorption towards OMT

Temperature(°C)	Q_0 (mg/g)	b (L•mg ⁻¹)	R^2
30	-116.279	-0.0482	0.5588
40	-161.29	-0.033	0.2509
50	76.336	0.0552	0.8361
60	169.49	0.02592	0.6014

Table 2. Freundlich Adsorption Isotherm of OMT

Temperature (°C)	K	$1/n$	$q_e=KCe^{1/n}$	R^2
30	0.1110	1.0581	$q_e=0.111Ce^{1/1.0581}$	0.998
40	0.06557	1.0348	$q_e=0.06557Ce^{1/1.0348}$	0.996
50	0.002584	0.9215	$q_e=0.002584Ce^{1/0.9215}$	0.9973
60	0.006835	0.9634	$q_e=0.006835Ce^{1/0.9634}$	0.9989

Kinetic Study

Figure 2 describes the adsorption kinetic curves. A high adsorption rate was observed at the beginning of adsorption, and then the adsorption rate slowed down as the adsorption equilibrium was approached.

To examine the underlying mechanism of the adsorption process, Lagergren pseudo first- (Eq. (9)) and second-order (Eq. (10)) kinetic models were applied (Rengaraj et al. 2004):

$$\log (q_e - q_t) = \log q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where q_e (mg/g) and q_t (mg/g) are the adsorption capacity at equilibrium and time t (h), respectively, and k_1 (min^{-1}) and k_2 ($\text{mg}/(\text{g}\cdot\text{min})$) are pseudo first and second order rate constants of adsorption, respectively. The pseudo first-order model is consistent with an assumption that the rate of occupation of the adsorption sites is proportional to the number of unoccupied sites. The value of k_1 can be calculated from the slope of the linear plot of $\log (q_e - q_t)$ versus t .

The pseudo second-order kinetic model is based on a chemical reaction mechanism (Iftikhar et al. 2009). It is assumed that the adsorption rate is controlled by chemical adsorption through sharing or exchange of electrons between the adsorbent and adsorbate. The value of k_2 can be calculated from the slope of the linear plot of t/q_t versus t (Ozacara et al. 2008).

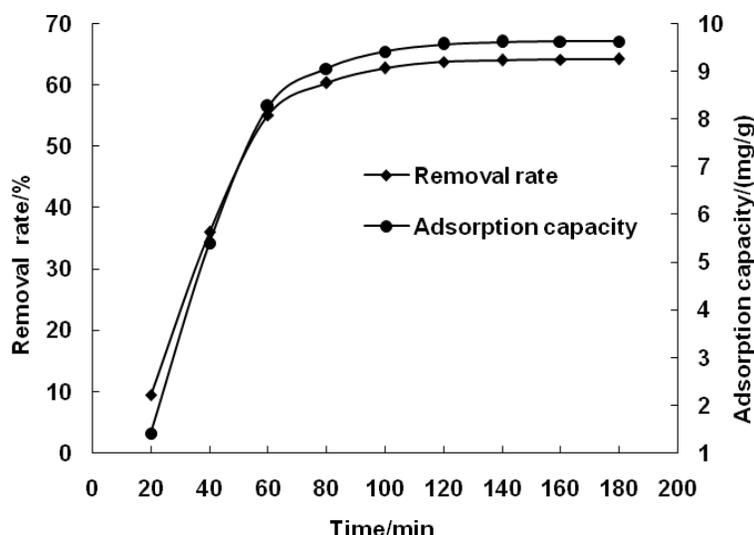


Fig. 2. Kinetics curve of the adsorption for OMT. Sorption conditions: pH value: 6; initial OMT concentration, 120 mg/L; adsorbent usage, 0.2 g/25mL; room temperature.

The pseudo first- and second- order kinetic curves are shown in Figs. 3 and 4, and the coefficients of determination (R^2) as well as the calculated kinetic parameters are given in Table 3. As shown in Table 3, although the correlation coefficient value of pseudo first-order kinetic curve was higher than 0.99, the experimental q_e values did not agree with the calculated ones, obtained from the linear plots (Table 3). This showed that the adsorption of OMT onto cellulose adsorbent was not a first-order reaction. However, the linear plots of t/q_t versus t (Fig.4) showed a good agreement between experimental and calculated q_e values (Table 3). The coefficients of determination for the second-order kinetic model were greater than 0.995, indicating the applicability of this kinetic equation and the second-order nature of the adsorption process of OMT on cellulose adsorbent.

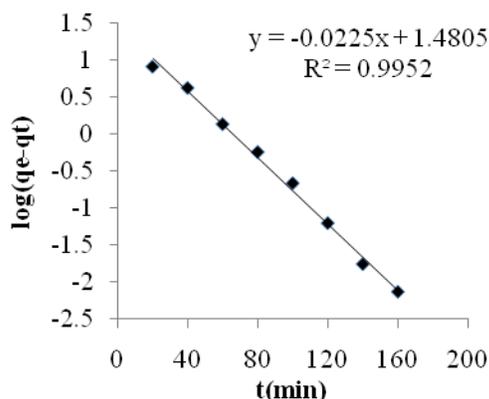


Fig. 3. Pseudo-first-order kinetic curves

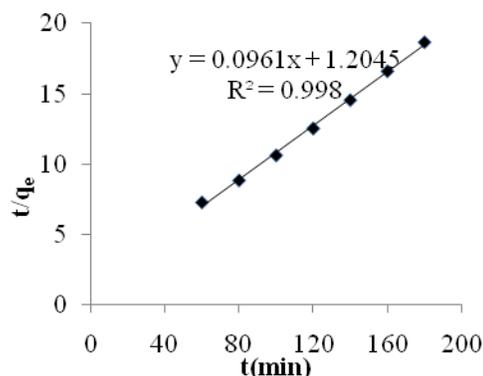


Fig. 4. Pseudo-second-order kinetic curves

Table 3. Dynamic Equations and Parameters

Dynamic equations		Dynamic parameters		R^2
		k_i	q_e	
Pseudo-first-order equation $\log(q_e - q_t) = \log q_e - k_i t$	$y = -0.0225x + 1.4805$	0.0225	50.59	0.9952
Pseudo-second-order equation $t/q_t = 1/(k_2 q_e^2) + t/q_e$	$y = 0.0961x + 1.2045$	0.007667	10.40	0.998

Desorption and Reproducibility

In order to study the stability and reproducibility of the adsorbents, three cycles of adsorption/elution/regeneration were performed, using 50% of methanol as eluent. The results are listed in Table 4. The results indicate that the adsorbents could be used many times without decreasing their adsorption capacities significantly.

Table 4. Reproducibility of Cellulose Adsorbent

Repeated times	Adsorption capacity(mg/g)	Desorption efficiency%
0	9.56	82.3
1	8.24	80.2
2	7.83	79.6
3	7.28	77.9

Sorption conditions: pH value: 6; initial OMT concentration, 120 mg/L; adsorption time, 2h; adsorbent usage, 0.2 g/25mL; 50% methanol as eluent; desorption time, 60 min; adsorption and desorption temperature, room temperature.

CONCLUSIONS

The adsorption ability of cellulose adsorbent embedded with wattle bark tannin was studied. The results showed that the static adsorption capacity of adsorbent towards the OMT could reach 9.56 mg/g, and the adsorption process was found to be pH value dependent. Moreover, the adsorption processes followed the Freundlich adsorption isotherm and chemical adsorption was predominant in the adsorption process. The adsorbent could be regenerated by using 50% methanol as eluent, and the regeneration showed good reproducibility.

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