Asian Journal of Chemistry; Vol. 25, No. 5 (2013), 2857-2860

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.14096

Adsorption Studies of Cu(II) onto Total Polysaccharide Extracted from Astragals

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(*Received*: 23 May 2012; *Accepted*: 26 November 2012) AJC-12469

The adsorption studies of Cu(II) onto total polysaccharide extracted from astragals were carried out at different temperatures. The adsorption data could be fitted by Langmuir isotherm and Freundlich isotherm. It was noted that increase of temperature would result in a higher Cu(II) loading per unit weight of total polysaccharide. The thermodynamic parameters such as ΔH, ΔG and ΔS were also determined.

Key Words: Total polysaccharide, Copper, Adsorption, Thermodynamics, Dynamics.

INTRODUCTION

Polysaccharides extracted from different traditional Chinese medicines belong to macromolecular materials, which have various biological activities. Polysaccharides contain lots of polar functional groups including hydroxyl groups and amino groups, which combined with most metallic ions easily. In recent years, a number of studies reported the adsorption characteristic of polysaccharides extracted from different origins[1], including chitin[2], beet polysaccharides[3,4], tea polysaccharides[5] and so on. Most of the works have shown that polysaccharides could act as the good sorbents for trace elements. The trace elements adsorbed onto polysaccharides have better pesticide effects or new physiological activity[4] when compared with the single polysaccharides or single trace elements[6]. Therefore, these compounds are expected to be served as supplements of essential trace element[7] and they also have a very broad application prospect in the medicine field. However, the research concerned about the adsorption characteristics of metal ions onto the polysaccharides extracted from traditional Chinese medicines were seldom reported.

Total polysaccharide extracted from astragals (TPA) has many beneficial effects on living beings, such as the enhancement of resistance, the protection of cardiovascular system, the promotion of immunity and the bidirectional adjustment of blood sugar[8].

Copper is required in the formation of hemoglobin, red blood cells as well as bones, while it is also necessary for many redox enzymes. Therefore,it plays an important role in the maintenance of normal vital activities for living bodies. The harmful reaction will appear when it is deficient in the human body.

Adsorption studies facilitate to obtain the adsorption process information of TPA. In this work, Cu(II) was chosen as a research object to investigate the adsorption process of metal ions onto TPA at different temperature conditions. The experimental results were analyzed by using the Langmuir and Freundlich isotherms. The thermodynamic parameters such as ΔH, ΔG and ΔS were determined. The results would provide reliable scientific references for the new product development and research.

EXPERIMENTAL

AA-670 atomic adsorption spectrophotometer (Shimadzu, Japan) was utilized to detect the content of trace element. Shanghai Shogun. Ultra filtration centrifuge of Am icon Ultra-4 (MILLIPORE, cut-off molecular mass10K), PCR3000 Nanoparticle size analyzer (Malvern, British), PHs-2 PH-meter (Optoelectronic Technology Co., Ltd, China) and self-made electromagnetism oscillator were also used in this study.

The stock solution of Cu(II) (1 mg mL^{-1}) was prepared in double distilled water by using copper sulphate. All working solutions were prepared by diluting the stock solution with distilled water. All of the reagents used in this study are analytical grade.

Total polysaccharide extracted from Mongolia astragals[9] are faint yellow flocculent solid, which dissolves in water easily and does not dissolve in organic solvent, such as ethyl alcohol, acetone and ethyl ether. Viscosity-average molecular weight of them is 13.6×10^4. The average particle size of TPA determined by using Malvern nanoparticle size analyzer was 399.1 and 1608.1 nm, respectively. The results showed that TPA extracted from Mongolia Astragals was non-homogeneous polysaccharides.

Adsorption studies: Batch adsorption experiments were performed at an ordinary temperature on electromagnetism oscillator by using 150 mL capped conical flasks. 0.15 g of TPA was thoroughly mixed into 50 mL of Cu(II) solution. The pH was adjusted with diluted HCl or NaOH to (5.77). After shaking the flasks for 4 h, the reaction mixtures were filtered through a 10 K ultra-membrane filter to remove TPA. The Cu(II) concentration in filtrates was analyzed by atomic adsorption spectrophotometer and the amount of Cu(II) retained was calculated from the difference between the initial amount and the equilibrium concentration.

The amount of metal ion absorbed (Q_e (mg g^{-1})) is calculated according to the following formula[10]:

$$Q_e = \frac{(C_0 - C_e) \times V}{W} \quad (1)$$

where C_0 is the initial Cu(II) concentration (mg L^{-1}) and C_e is the equilibrium Cu(II) concentration (mg L^{-1}). V is the volume of adsorption solution (L) and W is the quality of TPA (g).

Detection method: For atomic absorption spectrophotometer detection, air-acetylene flame was used. Air flow was 10 L min^{-1} and acetylene gas current capacity was 1.8 L min^{-1}. Burner height was set as 7 mm. Copper lamp electric current was 3 mA and wave length was 324.8 nm. The slit width was fit as 0.5 nm.

RESULTS AND DISCUSSION

The equilibrium adsorption isotherm is fundamentally important in the design of adsorption systems. Moreover, the parameters described by adsorption isotherm could express the affinity of the sorbent exactly. Equilibrium relationships between sorbent and sorbate are described by adsorption isotherms. In order to investigate the adsorption isotherm, two equilibrium models were analyzed,which included the Langmuir isotherm and the Freundlich isotherm[11].

Adsorption isotherms of Cu(II) onto TPA: Adsorption isotherms of Cu(II) at various temperatures are shown in Fig. 1. The figure showed that the isotherms can be attributed to L1-type, which is defined by Giloes classification. The L-type isotherms are characterized by high initial slope value decreases when the equilibrium concentration increases. These isotherms demonstrate the high affinity of TPA for the retention of Cu(II) even at low concentration. In addition, the reduction of the number of available surface functional groups results in the increment of Cu(II) concentration[12], which also supports the judgment of the high affinity of TPA.

Langmuir isotherm: The Langmuir isotherm has been successfully applied to many typical adsorption processes and is the most widely used adsorption isotherm for the adsorption of a solute from a liquid solution. A basic assumption of the Langmuir theory is that the adsorbed layer is the single molecule in thickness and that all binding sites are the same, resulting in equal adsorption energy. It is then assumed that once a metal ion occupies a binding site, no further adsorption can occur at this site. The adsorption data were analyzed according to the linear formula of the Langmuir isotherm:

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \quad (2)$$

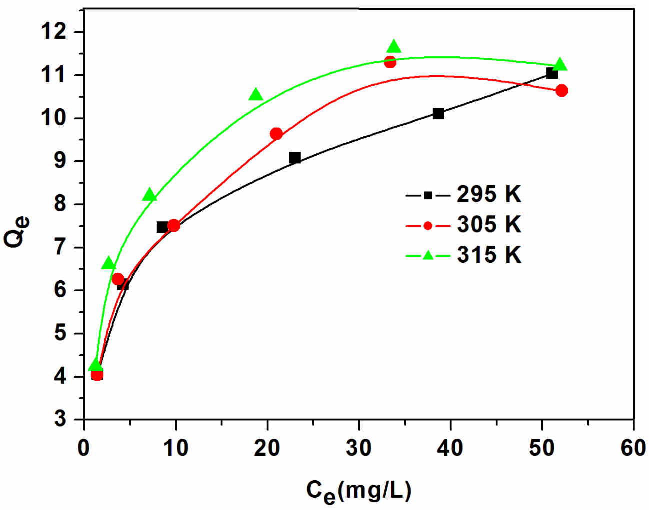

Fig. 1. Adsorption isotherms of Cu(II) onto TPA at different temperatures (pH = 5.77, CTPA = 3 g L^{-1})

where Q_m is the saturated monolayer adsorption capacity (mg g^{-1}); b is Langmuir equilibrium constant (L mg^{-1}), which showed that adsorption capacity of metal ions onto adsorbent. A plot of C_e/Q_e *versus* C_e indicated a straight line of slope $1/Q_m$ and an intercept of 1/b.

The Langmuir parameters, Q_m and b, for different temperatures have been calculated from eqn. 2 and the results are shown in Table-1. The adsorption process conforms the Langmuir isotherm and characterized with high correlation coefficient (R^2 > 0.993). It is clear that monolayer coverage for each temperature increased as the temperature rose. The value of Q_m obtained at 315 K appears to be higher when compared with the uptakes obtained at other temperatures.

TABLE-1
ADSORPTION CONSTANTS OF Cu(II) ONTO TPA

Temp. (K)	Langmuir constants			Freundlich constants		
	Q_m (mg g^{-1})	b (L mg^{-1})	R^2	K_f	n	R^2
295	11.5	0.241	0.9941	3.94	3.75	0.9801
305	11.6	0.294	0.9933	3.99	3.61	0.9539
315	11.9	0.429	0.998	4.64	3.93	0.9262

The shape of isotherm curve can be utilized to predict whether the adsorption system is 'favorable' or 'unfavorable' in fixed-bed systems as well as in batch processes. According to Hall's report[13], the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L[14], which is defined by the following relationship:

$$R_L = \frac{1}{1 + b \times c_0} \quad (3)$$

where R_L is a dimensionless separation factor and indicates the shape of the isotherm accordingly, which was indicated in Table-2.

The values of R_L at different temperatures are shown in Fig. 2. All R_L values indicate that adsorption of Cu(II) onto TPA are favorable at all concentrations and temperatures. The R_L values illustrate that adsorption is more favorable for

TABLE-2
THERMODYNAMIC PARAMETERS OF Cu(II) ONTO TPA

Values of R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

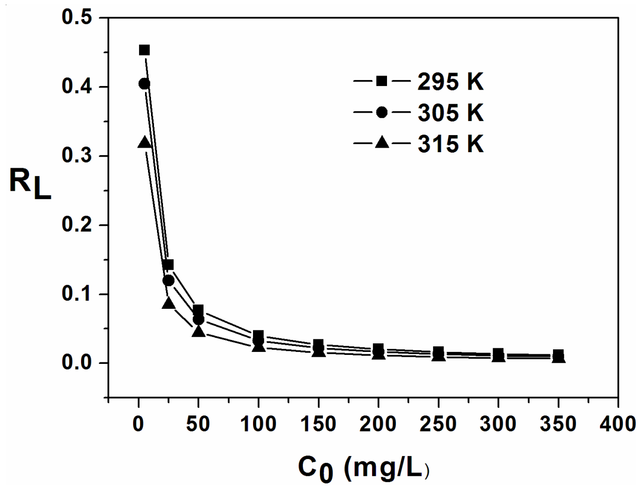

Fig. 2. Relationship between R_L and the initial concentration of Cu(II)

the higher initial Cu(II) concentrations and temperatures. Referring to Fig. 2, it is obvious that TPA is a good sorbent for Cu(II).

The ultimate adsorption capacity at high concentrations can be used to estimate the specific surface area (S) of TPA by using the following equation[15].

$$S = \frac{Q_m NA}{M} \quad (4)$$

where S is the specific surface area (m^2/g); N is Avogadro number (6.02×10^{23}); A is the cross sectional area of Cu(II) (1.58 $Å^2$); M is molecular weight of copper (63.5). Therefore, the maximum specific surface area of TPA towards Cu^{2+} binding is 1.72 m^2/g.

Freundlich isotherm: The Freundlich isotherm predicts that more Cu(II) binding to the adsorbent will increase as long as there is an increase of the Cu(II) concentration in the liquid. The adsorption data were analyzed according to the linear formula of the Freundlich isotherm:

$$\ln Q = \ln K_f + \frac{1}{n}\ln c \quad (5)$$

K_f is the capacity parameter. If K_f was high, this circumstance indicates the adsorption ability of adsorbent was better. If n was larger than 1, this situation demonstrates the degree of nonlinear of adsorption isotherms, otherwise n = 1 will attribute to the ideal linear adsorption isotherms.

This isotherm is another form of the Langmuir approach for characterization of the adsorption on an "amorphous" surface. The calculated amount of adsorption is in consideration of adsorption on all sites and each site has bond energy. The Freundlich isotherm describes reversible adsorption and is not restricted to the formation of the monolayer.

The Freundlich parameters, K_f and n, for different temperatures have been calculated from eqn. 5 and the results are given in Table-1. Analysis of the data shows that the Freundlich isotherm provides a good description of the data ($R^2 > 0.92$). As shown in Table-1, K_f increased from 3.94-4.64 and n increased from 3.75-3.93 as the temperature rose. The results further indicated that the adsorption capability of TPA enhanced when the temperature increased and displayed more and more obvious nonlinear characteristics.

The Langmuir isotherm exhibits extremely higher correlated coefficients and provides considerably better fits to the experimental data than the Freundlich isotherm. The Freundlich isotherms were developed to describe heterogeneous surface isotherms. In this case, there is a continuously varying energy of adsorption as the most actively energetic sites are occupied firstly and the surface is continually occupied until the lowest energy sites are filled at the end of the adsorption process. The main characteristic of the Langmuir equation is that it was based on the assumption that all sites have equal adsorption energy.

Thermodynamic parameters of Cu(II) onto TPA: Thermodynamic parameters such as enthalpy change (ΔH), Gibbs free energy (ΔG) and entropy change (ΔS) of Cu(II) onto TPA are calculated by using the following equations[12]:

$$\ln b = K - \frac{\Delta H}{RT} \quad (6)$$

$$\Delta G = -RT\ln(b) \quad (7)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (8)$$

where K is the constant, b is the Langmuir constant ($L\ mol^{-1}$), T is the absolute temperature, R is the gas constant, ΔH is the enthalpy change ($kJ\ mol^{-1}$), ΔG is the Gibbs free energy ($kJ\ mol^{-1}$) and ΔS is the entropy change ($J\ mol^{-1}\ K^{-1}$). Then, ΔH, ΔG and ΔS were calculated from the slope and intercept of the Van't Hoff plot (Fig. 3), respectively. The results were shown in Table-3.

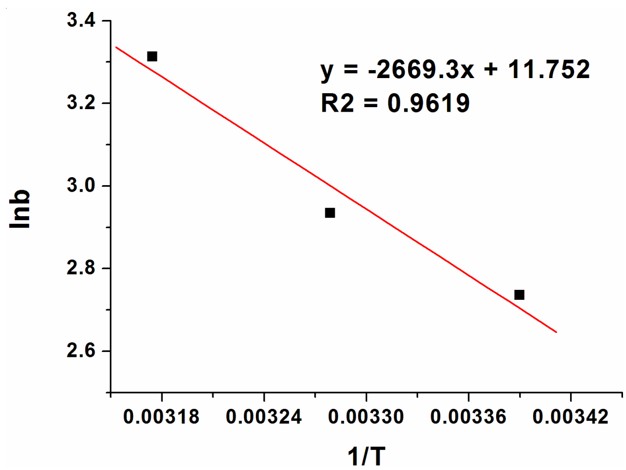

Fig. 3. Van't Hoff plot

TABLE-3
THERMODYNAMIC PARAMETERS OF Cu(II) ONTO TPA

Temp. (K)	ΔH ($kJ\ mol^{-1}$)	ΔG ($kJ\ mol^{-1}$)	ΔS ($J\ mol^{-1}\ K^{-1}$)
295	22.2	-6.71	98.0
305	22.2	-7.44	97.2
315	22.2	-8.68	98.0

The values of thermodynamic parameters demonstrated a spontaneous and favorable adsorption process. A positive value of ΔH indicated the endothermic nature of adsorption of Cu(II) onto TPA. In addition, ΔH < 40 kJ mol^{-1} also indicated that the adsorption of Cu(II) onto TPA was controlled by physical mechanisms rather than chemical mechanism.

The negative value and the increment in the negative direction of ΔG indicated the spontaneous interaction without requiring large activation energy of adsorption. Usually, the physical adsorption ΔG was less than the chemical adsorption ΔG. The former was -20~0 kJ mol^{-1} while the latter was -400 ~ -80 kJ mol^{-1}. This also showed that the adsorption of Cu(II) onto TPA was physical adsorption and the process could occur spontaneously in the experimental temperature. These results are correlated with the separation factor R_L of the Langmuir isotherm.

The positive value of ΔS showed the random increase during the adsorption of Cu(II) onto TPA. Normally, adsorption of gases leads to a decrease in entropy due to orderly arrangement of the gas molecules on a solid surface. However, the same way may not be true for the complicated system of adsorption of Cu(II) from solution onto TPA.

Conclusion

Total polysaccharide extracted from astragals could adsorb Cu(II) from aqueous solutions effectively. It was noted that an increase in the temperature resulted in a higher Cu(II) loading per unit weight of TPA. The experimental results were analyzed by using the Langmuir isotherm and Freundlich isotherm. The correlation coefficients for fitting the Langmuir equations were better than the coefficients for the Freundlich equation. The thermodynamic parameters of Cu(II) on TPA showed that the process was a spontaneous and favorable adsorption process. The adsorption of Cu(II) on TPA was controlled by physical mechanisms rather than chemical mechanism.

ACKNOWLEDGEMENTS

The authors are grateful to Natural Science Foundation Committee of China (NSFC 81000666) and the Ministry of Science and Technology (2009ZX09310-004) for their financial support.

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