Research Article

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Adsorption of L- α -glycerophosphocholine on ion-exchange resin: Equilibrium, kinetic, and thermodynamic studies

<https://doi.org/10.1515/gps-2020-0032>

received February 14, 2020; accepted April 19, 2020

Abstract: The adsorption of L- α -glycerophosphocholine (GPC) by cation-exchange resin 001 $\times$ 7 was studied in a batch system. The adsorbent dosage, shaking speed, and adsorption temperature were investigated. An adsorption efficiency of more than 99.4% was obtained under optimal conditions. The kinetic data evaluated by the pseudo-second-order kinetic model fitted the experimental data better than those evaluated by the pseudo-first-order model. The rate constant k_2 increased when the temperature increased, indicating the adsorption was endothermic in nature. The Langmuir and Freundlich isotherm models were used to analyze the adsorption equilibrium data, and it was found that the experimental data well fitted the Langmuir isotherm model. The thermodynamic parameters, enthalpy change (ΔG^0), free energy change (ΔH^0), and entropy change (ΔS^0), were calculated. The value of ΔG^0 was found to be in the range of -5.09 to -14.20 kJ mol $^{-1}$, indicating that the adsorption was spontaneous and basically physisorption, and the positive values of ΔH^0 and ΔS^0 exhibited that the adsorption was endothermic and the randomness of the system increased during the adsorption.

Keywords: L- α -glycerophosphocholine, cation-exchange resin, adsorption, isotherms, kinetics

1 Introduction

Ion-exchange resin is a spherical polymer compound with different functional groups [1], which are connected with the insoluble three-dimensional spatial network backbone. It has received significant attention because of its high adsorption speed, high mechanical strength, better stability, and reutilization. In the past few years, ion-exchange resins have been studied extensively and have been proven to be most effective in the process of separation, purification, and other biomedical applications [1,2]. Zhang et al. [3] selected D101 from nine different kinds of macroporous resins to purify flavonoids, and results showed that the recovery of flavonoids can be above 93% under optimum conditions. Shi et al. [4] proved that three weakly basic anion-exchange resins: D301, D314, and D354, can be efficiently used for the removal of hexavalent chromium from aqueous solutions. Ion-exchange resins can be widely used in water treatment, environmental protection, food processing, pharmaceutical, petrochemical, and other fields.

L- α -Glycerophosphocholine (GPC, for short) is widespread in all our cells, and it is important for our mental focus, attention, and other higher mental functions, so it is widely used in cosmetics, pharmaceutical field, and other applications [5–7]. Compared with the biological extraction method and the chemical synthesis method, hydrolysis of natural lecithin is the perfect method for preparing GPC, because, due to the natural origin, the product is more credible [8–10]. However, many studies used the solution of tetrabutylammonium hydroxide [11] or sodium methoxide [12] as a catalyst, and the catalyst is difficult to separate, so the purification of GPC is the most complicated step for its pharmaceutical application.

GPC contains many hydroxyl groups and can easily dissolve in aqueous solutions or alcohols. It can also be purified by an ion-exchange resin [1,13]. Resin 001 $\times$ 7 is one of the strong-acidic cation-exchange resins, and its adsorption capacity is equivalent to that of Amberlite

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IR-120 [1]. In this study, the 001×7 resin was chosen as a potential adsorbent for adsorbing GPC. Factors influencing the adsorption effect, adsorbent dosage, shaking speed, GPC concentration, and adsorption temperature, were evaluated thoroughly. The adsorption kinetics was determined using pseudo-first-order and pseudo-second-order models, and the equilibrium isotherm was fitted by Langmuir and Freundlich adsorption isotherm models. This preliminary study can provide theoretical basis and technical support for further separation investigations [1].

2 Materials and methods

2.1 Materials

GPC was purchased from Shanghai Yi Yao Fine Chemical Plant (Shanghai, P. R. China) and stored under airtight and light-free conditions until use. The resin 001×7 was obtained from Sunresin New Materials Co., Ltd (Xi'an, P. R. China); it was treated according to the manufacturer's instructions and then washed with anhydrous methanol several times to remove the residual water in it, and finally, the resin was kept in anhydrous methanol at normal temperature. Hydrochloric acid, ammonia, *n*-propanol, methanol, and chloroform were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, P. R. China). All chemicals used were of analytical grade.

2.2 Adsorption experiments

The adsorption experiments were performed in stoppered conical flasks in a water bath shaker, the cation-exchange resin 001×7 was chosen as a potential adsorbent, and solution of GPC was prepared in anhydrous methanol. The experiments were conducted with different resin amounts (wet-based weight) between 0.15 and 0.30 g mL^{-1} to optimize the solid/liquid ratio [14], and the effect of shaking speed on the adsorption process was investigated in the range of 120 – 240 rpm. The temperature was investigated from 20 to 40°C . During the experiments, the samples were drawn from the solution at predetermined time intervals before the adsorption equilibrium was achieved. All experiments were carried out in triplicate to minimize the random error.

2.3 Analytical method

High-performance liquid chromatography (HPLC) and thin-layer chromatography (TLC) determination methods were established and compared. The results showed that the minimum detection limit of HPLC was a bit lower than that of TLC; that is, the HPLC method is slightly more sensitive than the TLC method. However, the scanned data of TLC within 10 h after spotting were similar to those of HPLC; at the same time, the TLC is a simple, fast, and low-cost method, and it can detect more samples at the same time, so the TLC method is used in the experiments. The samples were treated by centrifugation at $10,000$ rpm for 5 min, then a certain amount of each sample (including the GPC solution before adsorption) was spotted on the TLC plate and developed in the solvent system of *n*-propanol: ammonia (5 mol L^{-1}) = $13:7$. The developed plate was detected in an iodine chamber after drying. Some yellow spots appeared on the white background after a period of time. Finally, the spots were quantified by densitometric scanning with a Shimadzu Dual-Wavelength TLC Scanner CS-930. The amount of GPC adsorbed, q_e , was computed by the following expression:

$$q_e = \frac{c_0 - c_e}{m} V, \quad (1)$$

where c_0 and c_e (mg L^{-1}) are the concentration of GPC solution before and after adsorption, V is the volume of GPC solution (L), and m is the mass of wet cation-exchange resin (g). The adsorption efficiency of GPC was calculated by the following equation [15]:

$$\text{Adsorption efficiency \%} = \frac{c_0 - c_e}{c_0} \times 100\%. \quad (2)$$

3 Results and discussion

3.1 Effect of adsorbent dosage

The effect of adsorbent dosage on adsorption of GPC on the resin 001×7 was studied by varying the amount of resin in the medium from 0.15 to 0.30 g mL^{-1} under the following conditions: GPC initial concentration, $7,450 \text{ mg L}^{-1}$; adsorption temperature, 25°C ; shaking speed, 120 rpm; and contact time, 2 h. The results are presented in Figure 1. The adsorption efficiency for GPC increased proportionally with an increase in the amount of resin. It increased from 82% to 98% when the adsorbent dosage increased from 0.15 to 0.20 g mL^{-1} ,

Figure 1: Effect of resin dosage on the adsorption efficiency for GPC by resin 001 $\times$ 7.

because when the adsorbent dosage increased, the surface area of the resin and its available adsorption sites for GPC molecules increased, consequently resulting in better adsorption [16,17]. But no obvious change was observed above the adsorbent dosage of 0.20 g mL^{-1} , so in the subsequent experiments, the appropriate adsorbent dosage was 0.20 g mL^{-1} .

3.2 Effect of shaking speed

The shaking speed is also one of the most important parameters which would affect the distribution of the adsorbate ions. The dependence of GPC adsorption on shaking speed was studied by varying the shaking speed

Figure 2: Effect of shaking speed on the adsorption efficiency for GPC by 001 $\times$ 7 cation-exchange resin.

(120, 160, 200, and 240 rpm), while the other factors such as the initial GPC concentration, adsorption temperature, and contact time remained constant. The results are shown in Figure 2. It was apparent that when the shaking speed increased from 120 to 240 rpm, the adsorption efficiency for GPC increased from 42% to 58% in the initial 10 min. This is because the uniformity of the system increased and the film resistance to mass transfer decreased [18]. But the final results did not change significantly in the experimental shaking speed. As clarified by Dotto and Pinto [19], there was usually a slight change in adsorption behavior when the shaking speed was between 100 and 200 rpm.

3.3 Effect of adsorption temperature

To determine the dependence of GPC adsorption on temperature, experiments were performed in the temperature range of 20 to 40°C . A shaking speed of 120 rpm was selected, and the other parameters remained constant. The results are shown in Figure 3.

Figure 3: Effect of temperature on the adsorption efficiency for GPC by 001 $\times$ 7 cation-exchange resin.

It could be found that the adsorption process reached equilibrium state quickly (30 min) when the temperature was above 30°C . The amount of GPC adsorbed on the resin increased when the adsorption temperature changed from 20 to 40°C , indicating that the adsorption of GPC on the resin 001 $\times$ 7 was favored at higher temperature. This may be a result that the higher temperature increased the mobility of GPC molecules

which can provide an extra driving force for GPC molecules to transfer from the aqueous to solid phases [20,21].

3.4 Adsorption kinetic studies

In order to examine the controlling mechanism of adsorption and to control the process efficiently, the kinetic studies were very necessary. The adsorption kinetics could provide important information for studying the mechanism [22] and selecting optimum operation conditions [23]. The kinetics of GPC adsorption on the resin 001 $\times$ 7 was examined with two familiar kinetic models: the pseudo-first-order and pseudo-second-order reaction kinetic models. The pseudo-first-order reaction kinetic model of Lagergren was widely used, and the simple linear equation is given below [24,25]:

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

where q_e and q_t are the amounts of GPC adsorbed at equilibrium and at time t (mg g^{-1}) and k_1 is the pseudo-first-order rate constant (min^{-1}).

Plots of $\ln(q_e - q_t)$ against t were used to determine the rate constants k_1 and correlation coefficients R^2 for different adsorbent dosages and temperatures (Figure 4).

In addition, the pseudo-second-order kinetic equation is expressed as [24,25]:

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

where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the pseudo-second-order rate constant.

Similar to the pseudo-first-order reaction kinetic model, q_e and the rate constant k_2 can be obtained from the slope and intercepts of plots t/q_t versus t (Figure 5).

The calculated adsorbed amounts of GPC at equilibrium ($q_{e,\text{cal}}$), rate constant (k_1 , k_2), and the correlation coefficient (R^2) for both pseudo-first-order and pseudo-second-order reaction kinetic models are listed in Table 1. The values of $q_{e,\text{cal}}$ from the pseudo-first-order reaction kinetic model were significantly different from the experimental values ($q_{e,\text{exp}}$), and the correlation coefficients (R^2), in the range of 0.6081–0.9773, were also lower, implying that the pseudo-first-order kinetic model was not suitable for this sorption system. While for the pseudo-second-order equation, the $q_{e,\text{cal}}$ values agreed well with the experimental values $q_{e,\text{exp}}$, and the correlation coefficients were all greater than 0.99 at different adsorbent dosages and temperatures.

On the other hand, the plots in Figure 5 show better linearity than those in Figure 4. Both facts suggest that

Figure 4: Pseudo-first-order plots of GPC adsorption on resin 001 $\times$ 7 at different (a) adsorbent dosages and (b) temperatures.

the adsorption of GPC by the resin 001 $\times$ 7 followed the pseudo-second-order kinetic model. The values of k_2 increased from 0.0071 to $0.2971 \text{ g mg}^{-1} \text{min}^{-1}$ as the temperature increased from 20 to 40°C , showing that the GPC adsorption on the resin 001 $\times$ 7 was an endothermic process.

3.5 Adsorption isotherms

In general, the adsorption isotherms are important to estimate the mechanism of the process [26,27]. The experimental data for GPC adsorption isotherms at different temperatures are shown in Figure 6. The adsorption capacity for GPC increased when the initial concentration increased; however, the higher adsorption efficiency was obtained at the lower concentration. This can be because the number of active sites on the per-unit surface area of resin reduced at higher GPC concentration.

Figure 5: Pseudo-second-order plots of GPC adsorption on resin 001 × 7 at different (a) adsorbent dosages and (b) temperatures.

Analysis of equilibrium data is important to compare different sorbents and to optimize an operating procedure [28,29]. The equilibrium data obtained in the experiments were analyzed with well-known adsorption models such as Langmuir and Freundlich models [18,30].

Figure 6: Plots of c_e against q_e for the GPC adsorption on resin 001 × 7 at different temperatures.

The Langmuir isotherm model (equation (5)) supposes that the adsorption arises on a homogeneous surface and there is no lateral interaction between the adsorbed molecules. The Freundlich isotherm (equation (6)) is usually used to analyze the adsorption on a heterogeneous surface. The linear form of them is expressed by the following equations:

$$\frac{c_e}{q_e} = \frac{1}{q_{\max} b} + \frac{c_e}{q_{\max}} \tag{5}$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln c_e, \tag{6}$$

where c_e is the concentration of GPC at equilibrium in solution (mg L^{-1}); $q_{\max}$ is the maximum adsorption capacity of adsorbent (mg g^{-1}); b is the adsorption energy coefficient (L mg^{-1}); and K_f (mg g^{-1}) and n are the Freundlich constants, respectively.

Table 1: Kinetic parameters for the adsorption of GPC on resin 001 × 7 based on the pseudo-first-order and pseudo-second-order kinetic equations at different adsorbent dosages and temperatures

Adsorbent dosage (g mL^{-1})	Temperature ($^{\circ}\text{C}$)	$q_{e,\text{exp}}$ (mg g^{-1})	Pseudo-first-order			Pseudo-second-order		
			$q_{e,\text{cal}}$ (mg g^{-1})	k_1 (min^{-1})	R^2	$q_{e,\text{cal}}$ (mg g^{-1})	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2
0.15		40.82	63.78	0.0680	0.9259	43.86	0.0028	0.9931
0.20		36.86	44.16	0.0632	0.8650	38.46	0.0049	0.9976
0.25		29.83	19.29	0.0635	0.9773	30.86	0.0093	0.9983
0.30		24.86	10.66	0.0740	0.8612	25.13	0.0354	0.9998
	20	23.31	8.87	0.0416	0.6587	27.17	0.0071	0.9903
	25	28.65	20.01	0.0557	0.8707	30.21	0.0077	0.9906
	30	29.82	10.89	0.0568	0.8261	29.94	0.0252	0.9991
	35	29.83	6.25	0.0600	0.7318	29.85	0.0719	0.9999
	40	29.83	3.01	0.0598	0.6081	29.76	0.2971	0.9999

Linear plots of the two models of GPC adsorption on the resin 001 $\times$ 7 are shown in Figures 7 and 8. The plots in Figure 7 show better linearity than those in Figure 8. The isotherm constants for adsorption of GPC on the resin 001 $\times$ 7 at different temperatures are shown in Table 2. The detailed analysis of the correlation coefficient R^2 values showed that the Langmuir model (0.9993–0.9999) fit the experimental data better than the Freundlich model (0.8233–0.9230) at different temperatures. From Table 2, it is also clear that the $q_{\max}$ increased when the temperature increased, once again indicating the adsorption was an endothermic process.

Figure 7: Langmuir isotherm plots for the adsorption of GPC on resin 001 $\times$ 7 at different temperatures.

Figure 8: Freundlich isotherm plots for the adsorption of GPC on resin 001 $\times$ 7 at different temperatures.

The essential features of the Langmuir isotherm are expressed by a dimensionless constant separation factor R_L , and it can be expressed as follows [31,32]:

$$R_L = \frac{1}{1 + bc_0}, \quad (7)$$

where c_0 is the initial concentration of GPC (mg L^{-1}) and b is the Langmuir adsorption energy constant (L mg^{-1}). The value of R_L indicates the shape of isotherm to be either irreversible ($R_L = 0$) or favorable ($0 < R_L < 1$) or linear ($R_L = 1$) or unfavorable ($R_L > 1$) [33–35]. The results showed that the R_L values (listed in Table 2) were all in the range of 0–1 at 20–35°C, indicating that the cation-exchange resin 001 $\times$ 7 is favorable for adsorption of GPC under the studied conditions [33].

3.6 Thermodynamic parameters

In order to evaluate the adsorption process better, the thermodynamic parameters, standard free energy change ΔG^0 , standard enthalpy change ΔH^0 , and standard entropy change ΔS^0 , were also obtained. They were calculated by using the following equations [36]:

$$K_c = \frac{c_{Ae}}{c_{Se}} \quad (8)$$

$$\Delta G^0 = -RT \ln K_c \quad (9)$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}, \quad (10)$$

where K_c is the equilibrium constant, and c_{Se} and c_{Ae} are the equilibrium concentration of GPC on resin and in solution (mg L^{-1}), respectively.

The values of ΔH^0 and ΔS^0 can be obtained from the slope and intercept of the plot of $\ln K_c$ versus $1/T$ (Figure 9). All the thermodynamic parameters were calculated and are tabulated in Table 3. The values of ΔG^0 were negative at all experiment temperatures, indicating that the adsorption process was spontaneous. According to Crini and Badot [37], the more negative value of ΔG^0 at higher temperature implies a greater driving force for adsorption; therefore, the adsorption is more favorable at higher temperature. The ΔG^0 for physical adsorption is between -20 and 0 kJ mol^{-1} usually, and for chemical adsorption, it is between -400 and -80 kJ mol^{-1} [36]. The ΔG^0 for GPC adsorption was between -5.09 and $-14.20 \text{ kJ mol}^{-1}$, so it was basically physisorption. The value of ΔH^0 was positive, exhibiting that the adsorption was endothermic, and it was anticipated that the uptake of GPC from solution increased when the solution temperature increased. The positive values of ΔS^0 indicated that the randomness at the interface of resin and solution increased during the adsorption.

Table 2: Adsorption isotherm constants for GPC adsorption on resin 001 $\times$ 7

Temperature ($^{\circ}\text{C}$)	Langmuir				Freundlich		
	$q_{\max}$ (mg g^{-1})	b (L mg^{-1})	R^2	R_L^a	K_F	n	R^2
20	29.15	0.0129	0.9993	0.0148	15.15	13.25	0.8233
25	31.85	0.0760	0.9999	0.0026	19.76	16.98	0.8278
30	37.88	0.0379	0.9999	0.0051	18.21	10.92	0.9230
35	43.29	0.0342	0.9999	0.0057	17.29	8.44	0.9011

^a Initial concentration (C_0): 5,144 mg L^{-1} .

Figure 9: Variation of equilibrium constant (K_c) as a function of temperature.**Table 3:** Thermodynamic parameters for the adsorption of GPC on resin 001 $\times$ 7

Temperature ($^{\circ}\text{C}$)	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 ($\text{J K}^{-1} \text{mol}^{-1}$)
20	-5.09	129.70	460.01
25	-7.89		
30	-10.57		
35	-12.62		
40	-14.20		

4 Conclusion

This preliminary study showed that the resin 001 $\times$ 7 can be used as a potential adsorbent for adsorbing GPC. The optimum conditions for maximum adsorption of GPC were found to be as follows: adsorbent dosage, 0.20 g mL^{-1} ; GPC initial concentration, 7,450 mg L^{-1} ; adsorption temperature, 25 $^{\circ}\text{C}$; and shaking speed, 160 rpm. The kinetics of GPC adsorption obeyed the pseudo-second-order kinetic model, and the adsorption was an endothermic process because the

rate constant k_2 increased when the temperature increased. The adsorption data fitted the Langmuir model better than the Freundlich model. The values of ΔG^0 , ΔH^0 , and ΔS^0 were calculated to predict the kinetic aspects of GPC adsorption. The negative values of ΔG^0 at the experimental temperatures indicated that the adsorption was spontaneous, and the positive values of ΔH^0 and ΔS^0 exhibited that the adsorption was endothermic and the randomness increased during the adsorption.

Acknowledgments: This study was funded by the National Natural Science Foundation of China (grant no. 21663033 and 21763030), the Yulin City Industry University Research Cooperation Project (grant no. 2016CXY-05-01), and the Startup Foundation for Advanced Talents of Yulin University (award no. 16GK10).

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