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Ion Exchange Adsorption Kinetics of Miglitol by D001 Resins

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Abstract

In order to explore internal factors for adsorption kinetic effect of miglitol by D001 resin, a batch adsorption operation for miglitol kinetic adsorption at different concentrations, temperatures and vibrating rates was investigated in oscillator (SHZ-A), respectively. The different kinetic mathematical model, Webber-Morris kinetic equation, film diffusion coefficient equation and kinetic boundary model were all applied to discuss the adsorption process. The results showed that Type 1 pseudo-second order kinetic equation can be all used to describe miglitol adsorbed by D001 resin at different concentrations, temperatures and vibrating rates. Moreover, the total activation energy (Ea) can be calculated and its value is 9.7 kJ/mol, and then calculated values of the process film diffusion coefficient and pore diffusion coefficient, it may be inferred from these gotten values that the ion exchange process is all mainly controlled by film diffusion. Therefore, the results also suggest that the external adsorption factors such as solute concentration, temperature and vibrating rate for effect of mass transfer diffusion process control of miglitol onto D001 resin are relatively weak.

Keywords

Miglitol, Ion Exchange Adsorption, Kinetic Equation, Resins

1. Introduction

Miglitol ((2R, 3R, 4R, 5S)-1-(2-hydroxyethyl)-2-(hydroxymethyl) piperidine-3,4,5-triol, CAS No.72432-03-2) is a desoxynojirimycin derivative, also competitively inhibits glucoamylase and sucrase but has weak effects on pancreatic α-amylase, it is the first pseudomonosaccharide α-glucosidase inhibitor, smooths postprandial peak plasma glucose levels and thus can improve glycaemic control, Miglitol is generally well tolerated and is not associated with bodyweight gain or hypoglycaemia as monotherapy. Meanwhile, the drug is also systemically absorbed and not metabolised, also is rapidly excreted via the kidneys [1] [2] [3]. It was firstly developed by Bayer as drug for the treatment of type II (non-insulin-dependent) diabetes mellitus. Miglitol was authorized for marketing in Europe (trade name: Diastabol®), the United States (Glyset®) and in China, miglitol was also known as Otianpin® [4]. Nowadays, miglitol can be synthesized via different many ways, mainly including two types of chemical synthesis and chemical-biological synthesis. However, due to its many synthetic steps, complex craft and higher production cost for most of the chemical synthetic miglitol method, and it has been gradually replaced by chemical-biological method [5] [6]. The chemical-biological synthesis is still regarded as the more efficient industrial process. The reaction process is consisted of three-step synthesis, *i.e.* regioselective microbial oxidation and two step simple chemical reductive reactions. Two intermediates that containing amino group were formed in the process, *i.e.* N-hydroxyethyl-1-amino-1-deoxy-D-sorbitol and its corresponding L-sorbose derivative [7] [8]. As known that the synthesis substance generally possesses the higher purity product for the premise of the pharmaceutical application. As a rule, the synthesized miglitol is expected to establish the separation method of reaction mixture to remove the intermediates and other related compounds, and reaches the purpose of miglitol purification.

As known that adsorption of cation ion exchange resin is a suitable technology for the separation of N-substituted-1-desoxynojirimycin and miglitol [9] [10]. In our experiment, D001 resin as a separation medium has been appeared a good adsorption efficiency. That is a macroreticular strong-acidic cation ion exchange resin and applies widely in China. Up to now, due to the theory lack for miglitol separation, especially adsorption kinetics, the results of adsorption kinetics can conduct separation craft of substance and infer the efficiency of adsorption or separation for mixture. Therefore, it is very important to purify miglitol. In this study, the miglitol adsorption kinetics at different effect factors will be investigated by the selected D001 resin as adsorbent in batch adsorption, our results are not only for important scientific significance but also for wide reference in practical application.

2. Materials and Methods

2.1. Materials

The D001 resin (Na^+ form) was purchased from Sunresin Technol. Ltd., Xi'an, China. The chemical and physical properties of the resin are similar to those of Amberlite IR200 resins [11]. Drug-grade miglitol was obtained from Jinan Huifengda Chemical Ltd., Ji'nan, China. $KMnO_4$ and NaOH were used to aid the content determination of miglitol, and all other reagents in the experiment were of analytical grade. The constant temperature bath oscillator (SHZ-A) was used for adsorption process studies, The content of miglitol was determined at 610 nm by the double-beam UV-Vis spectrophotometer (TU-1900) [12]. The raw material was weighed by Electronic Analytical Balance (FA2004N).

2.2. Adsorption Kinetics Experiments

Fixed 200 mg resin into the different conical flasks (250 mL), miglitol was diluted by the distilled water and formed experimental set concentration solution. The adsorption process factors of different concentrations (4 mmol/L, 6 mmol/L, 8 mmol/L), different temperatures (30˚C, 40˚C, 50˚C) and different vibrating rates (80 rmp, 120 rmp, 160 rmp) were investigated in batch adsorption experiment, respectively. The adsorbed solutions were taken 1 mL by pipette at different time intervals and were measured by spectrophotometer at 610 nm. The process adsorption capacity at time t by D001 resins was as follows:

$$q_t = \frac{C_0V_0 - \left[C_nV_n + \sum_{i=1}^{n-1} C_iV_i\right]}{W} \tag{1}$$

where q_t (mmol/g) is the adsorption capacity of resin at time t, C_0 (mmol/L) and V_0 (L) are the initial concentration and volume of miglitol solution, C_n (mmol/L) and V_n (L) are the concentration and volume of remaining miglitol solution at time n, C_i (mmol/L) and V_i (L) correspond with the substance concentration and volume of the taken solution sample at time i, W is the weight of resin.

2.3. Batch Adsorption Kinetic Theoretical Background

2.3.1. The Pseudo-First Order Equation

The pseudo-first order equation for solid-liquid adsorption system was firstly proposed by Lagergren in 1989 [13]. The equation mathematical expression is given [14]:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_1\left(q_e - q_t\right) \tag{2}$$

where q_e (mmol/g) is the amount of adsorbate adsorbed at equilibrium, q_t (mmol/g) is the amount of adsorbate adsorbed at time t. k_1 (g/mmol·h) is rate constant for the Lagergren equation. Integrating Equation (2) with the following boundary condition:

1) $t = 0, q_t = 0$
2) $t = t, q_t = q_t$

The linear equation is obtained:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1 t}{2.303} \tag{3}$$

If $t \to 0$, the initial rate (h1) is [15]:

$$h_1 = k_1 q_e \tag{4}$$

As $k_1\left(q_e - q_t\right)$ cannot stand for total active site of adsorbent, and at the same time $\log q_e$ in Equation (3) is the adjustable parameter and often finds that its value is not equal to intercept value by linear regression with $\log\left(q_e - q_t\right)$ and

t. The values of $\log q_e$ must be intercept value if the equation is the first-order kinetic equation. Therefore, in order to distinguish the first-order equation, and the above Lagergren equation is also called the pseudo-first order equation. The pseudo-first order equation can only be used for estimating rate constant k_1 and not estimate q_e value.

2.3.2. The Pseudo-Second Order Equation

The pseudo-second order equation was firstly proposed by Ho and McKay [16] [17]. The pseudo-second order equation can be derived from chemical equations. The equation can be used for estimating q_e value. Its general mathematical expression is as follows:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_2\left(q_e - q_t\right)^2 \tag{5}$$

where k_2 ($\mathrm{g^2/mmol^2 \cdot h}$) is rate constant for the pseudo-second order equation.

Integrating Equation (5) with the following boundary condition:

1) $t = 0, q_t = 0$
2) $t = t, q_t = q_t$

The following equation can be gotten:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

If t → 0, the initial rate (h_2) is

$$h_2 = k_2 q_e^2 \tag{7}$$

The Equation (7) is substituted into Equation (6) and obtains Type 1 pseudo-second order equation, the equation can be written as:

$$\frac{t}{q_t} = \frac{1}{h_2} + \frac{t}{q_e} \tag{8}$$

By means of linear fitting with $\frac{t}{q_t}$ and t, the gotten results may use for calculating values of q_e and k_2, respectively.

In addition, the above pseudo-second order equation can also transform other four types of pseudo-second order equation by a series of transformation. These equations are separately as follows:

The Type 2 pseudo-second order equation is:

$$\frac{1}{q_t} = \frac{1}{h_2 t} + \frac{1}{q_e} \tag{9}$$

The Type 3 pseudo-second order equation is:

$$\frac{1}{t} = \frac{h_2}{q_t} - \frac{h_2}{q_e} \tag{10}$$

The Type 4 pseudo-second order equation is:

$$\frac{q_t}{t} = h_2 - \frac{h_2}{q_e} q_t \tag{11}$$

The Type 5 pseudo-second order equation is:

$$\frac{1}{\left(q_e - q_t\right)} = \frac{1}{q_e} + k_2 t \tag{12}$$

2.3.3. The Elovish Equation

The Elovish equation was generally applied to chemisorption kinetic analysis [18], and it was established by changes of adsorption capacity. The mathematical equation is expressed as:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = \alpha \exp\left(-\beta q_t\right) \tag{13}$$

where α (mmol/g·h) is initial adsorption rate, β (g/mmol) is desorption constant. As far as chemical adsorption is concerned, the β value is relate to adsorption activation energy and covering content of adsorbate onto adsorbent surface.

By assuming $\alpha\beta t \gg 1$, and Integrating Equation (13) with the following boundary condition:

1) $t = 0, q_t = 0$
2) $t = t, q_t = q_t$

The above Equation (13) can be transformed into the following equation:

$$q_t = \frac{1}{\beta}\ln\left(\alpha\beta\right) + \frac{1}{\beta}\ln t \tag{14}$$

The kinetic constant values of α and β can be estimated by linear fitting with q_t and t.

2.3.4. Mass Transfer Mechanism

As far as ion exchange adsorption process is concerned, it is very important to understand transfer direction and transfer rate of adsorbate for exploring mass transfer mechanism during adsorption process. The kinetic boundary model is widely applied to judge control step of mass transfer rate [19] [20]. The mass transfer process is divided into film diffusion, particle pore diffusion and chemical reaction according to mass transfer process, and the corresponding mathematical equations are established. These equations are as follows:

Film diffusion: $\ln\left(1 - F\right) = -kt$ (15)

Particle pore diffusion: $1 - 3\left(1 - F\right)^{2/3} + 2\left(1 - F\right) = kt$ (16)

Chemical reaction: $1 - \left(1 - F\right)^{1/3} = kt$ (17)

There into, k is mass transfer rate constant, F is called ion exchange degree, the corresponding equation is written as:

$$F = \frac{C_0 - C_t}{C_0 - C_e} \tag{18}$$

The established relationship between F and t from the kinetic boundary model may be used to judge main mass transfer process by correlation coefficient (R^2)

during ion exchange. The main mass transfer process corresponds with the slowest diffusion, and its process means the largest mass transfer resistance.

Meanwhile, there are different mass transfer rate constants with at different experimental temperatures. The corresponding activation energy (E_a) can be calculated by Arrhenius equation [21]. Its mathematical equation is:

$$k = A\exp\left(-E_a/RT\right) \tag{19}$$

where R is a ideal gas constant, A is a constant. Equation (19) can be rewritten to a linear form from which the activation energy can be calculated from the slope, the equation expression is:

$$\ln k = -\frac{E_a}{RT} + \ln A \tag{20}$$

The calculated value of E_a can also be used to determine ion exchange control step [22]. The ion exchange process is controlled by film diffusion at E_a < 16.0 kJ/mol. It is for particle pore diffusion at 21.0 kJ/mol < E_a < 38.0 kJ/mol, and at E_a > 50.0 kJ/mol, it belongs to chemical reaction control.

In addition, the activation entropy change value (ΔS^*) can be estimated by the following equation and the calculated value A by the above Arrhenius equation. The equation is defined as [23]:

$$A = \left(\frac{2.72d^2KT}{h}\right)\exp\left(\frac{\Delta S^*}{R}\right) \tag{21}$$

where K (1.38×10^{-23} J/K) is Boltzmann constant, h (6.62×10^{-34}) is Plank constant. d is for the average distance of the ion exchange active site, and its value is generally taken as 5×10^{-10} m, T is absolute zero degree , its value is set to 273 K.

3. Results and Discussion

3.1. Effect of Concentrations

The ion exchange process at different initial concentrations of miglitol solution onto resin D001 resin was investigated and was analysized by the kinetic adsorption mathematical models, and the results are shown in **Figures 1-3**. At the same time, the parameters are got by kinetic equation fitting and are given in **Table 1**. Comparing with **Figures 1-3**, and it shows that the ion exchange process is fitted better by Type 1 pseudo-second order kinetic equation. The experimental parameters from **Table 1** is further showed that the correlation coefficients are gotten from fitting pseudo-first order kinetic equation and pseudo-second order kinetic equation, and these values reach over 0.99. The parameters for k_1 and h_1 increase with enhancing the initial concentration solution of miglitol, and their change trends are closely related to the value of initial solution concentration and concentration difference between solution adsorbate and absorbent surface. Meanwhile, **Table 1** is also found that the experimental equilibrium adsorption capacity ($q_{e,exp}$) is not equal to the theoretical adsorption capacity($q_{e,exp}$) gotten from pseudo-first order kinetic equation. The result further proves the ion exchange process is not adapted to first-order kinetic equation. In addition, the

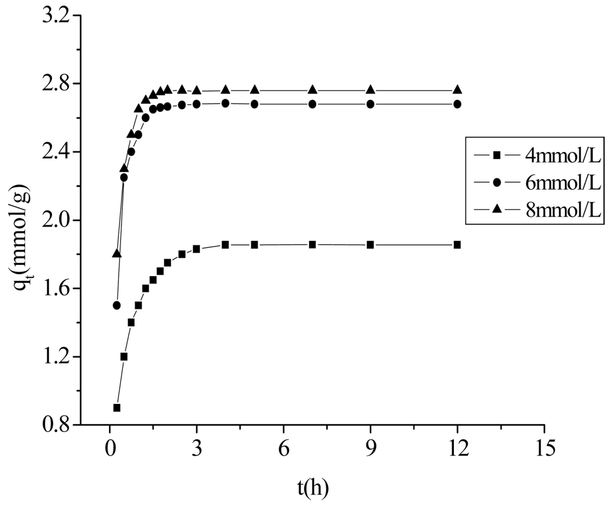


Figure 1. Dynamic process of miglitol at different concentrations adsorbed onto resin D001.

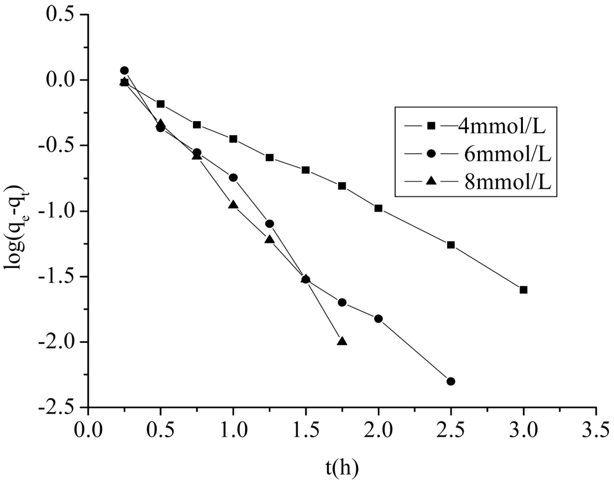
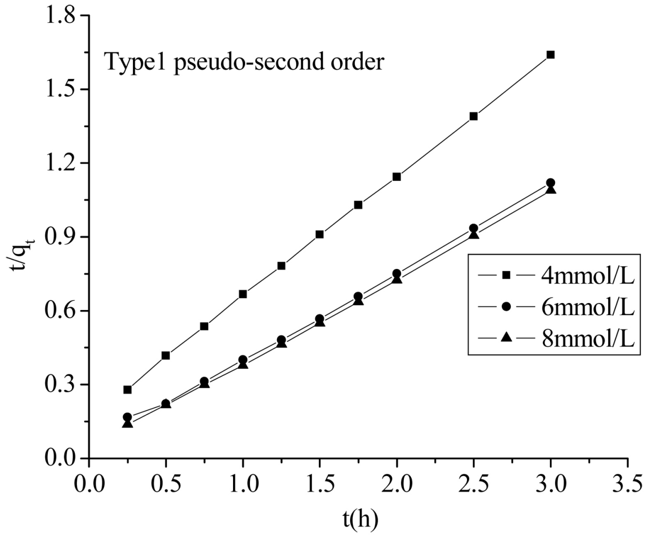
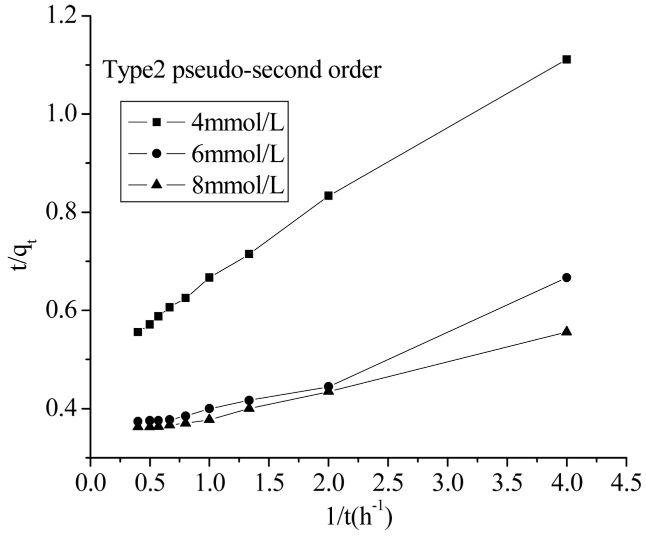


Figure 2. Fitting curves of the pseudo-first order kinetic model for miglitol adsorbed onto D001 resin.

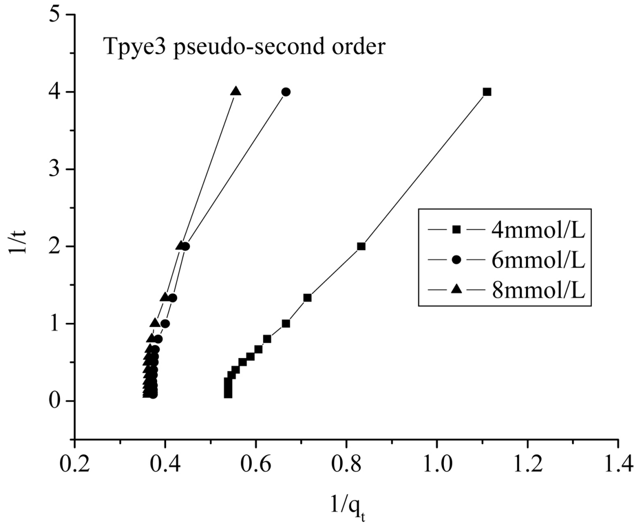
parameter values of k_2 and h_2 were calculated by Type 1 pseudo-second order kinetic equation vary with the same change trend for values of k_1 and h_1 in Table 1, their change trend is connected with the higher correlation coefficient gotten by the above two equations. In the meantime, the minimum difference between values of $q_{e,cal}$ and $q_{e,exp}$ is showed from Table 1, and it suggests that the ion exchange process can be described by Type 1 pseudo-second order kinetic equation. Moreover, as known that the pseudo-second order kinetic model corresponds with 5 mathematical equation types. Nevertheless, the results find that the parameter values and correlation coefficients gotten by these equations differs each other. It showed that different analysis method for ion exchange experimental data can be directly influenced with different type of pseudo-second order kinetic equation. It is very important to select an appropriate type of pseudo-second order kinetic equation for describing ion exchange process.


Type1 pseudo-second order
t/q_t
t(h)
1.8
1.5
1.2
0.9
0.6
0.3
0.0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4mmol/L
6mmol/L
8mmol/L

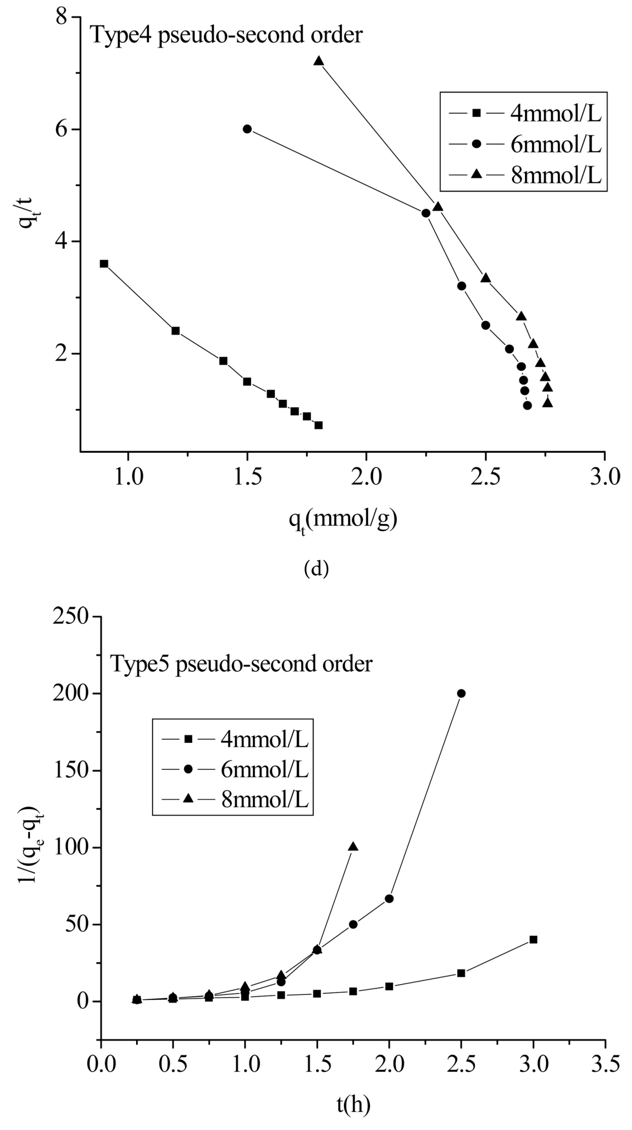
(a)


Type2 pseudo-second order
t/q_t
1/t(h^-1)
1.2
1.0
0.8
0.6
0.4
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
4mmol/L
6mmol/L
8mmol/L

(b)


Tpye3 pseudo-second order
1/t
1/q_t
5
4
3
2
1
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
4mmol/L
6mmol/L
8mmol/L

(c)



(d)

(e)

Figure 3. Fitting curves of the pseudo-second-order kinetic model for miglitol adsorbed onto D001 resin.

On the other hand, the ion exchange behavior is discussed at different initial concentrations for miglitol solution onto D001 resin by Webber-Morris particle pore diffusion model [24] [25]. It may be used to infer whether the mass transfer process is a internal pore diffusion process or not. The Webber-Morris pore diffusion mathematical equation is:

$$q_t = k_{id} t^{0.5} + C \tag{22}$$

where k_{id} (mmol/g·min$^{0.5}$) is internal diffusion rate constant. C is an intercept of the equation, its value is related to the boundary layer thickness of particle, the external mass transfer resistance is directly proportional to the size of the value.

Supposing substance diffusion process is only controlled by particle internal pore diffusion, at this time, the relationship between q_t and $t^{0.5}$ can present

Table 1. Kinetic fitting results of miglitol adsorbed onto D001 resin.

Kinetic models	Parameters	C_0 (mmol/L)		
		4	6	8
Pseudo-first order: $\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$	$q_{e,exp}$ (mmol/g)	1.86	2.68	2.76
	$q_{e,cal}$ (mmol/g)	1.29	1.69	2.13
	k_1 (g/mmol·h)	1.28	2.42	2.95
	h_1 (1/h)	1.64	4.09	6.28
	R^2	0.9980	0.9925	0.9967
Type-1 pseudo-second-order: $\frac{t}{q_t} = \frac{1}{h_2} + \frac{t}{q_e}$	$q_{e,exp}$ (mmol/g)	1.86	2.68	2.76
	$q_{e,cal}$ (mmol/g)	1.90	2.70	2.78
	k_2 (g^2/mmol^2·h)	2.48	5.49	7.05
	h_2 (1/h)	8.97	40.00	54.50
	R^2	0.9998	0.9999	0.9999
Type 2 pseudo-second-order: $\frac{1}{q_t} = \frac{1}{h_2 t} + \frac{1}{q_e}$	$q_{e,exp}$ (mmol/g)	1.86	2.68	2.76
	$q_{e,cal}$ (mmol/g)	2.00	2.94	2.94
	k_2 (g^2/mmol^2·h)	1.67	1.66	2.36
	h_2 (1/h)	6.67	14.32	20.45
	R^2	0.9974	0.9606	0.9778
Type 3 pseudo-second-order: $\frac{1}{t} = \frac{h_2}{q_t} - \frac{h_2}{q_e}$	$q_{e,exp}$ (mmol/g)	1.86	2.68	2.76
	$q_{e,cal}$ (mmol/g)	1.97	2.95	2.92
	k_2 (g^2/mmol^2·h)	1.68	1.49	2.28
	h_2 (1/h)	6.53	12.97	19.45
	R^2	0.9974	0.9606	0.9778
Type 4 pseudo-second-order: $\frac{q_t}{t} = h_2 - \frac{h_2}{q_e} q_t$	$q_{e,exp}$ (mmol/g)	1.86	2.68	2.76
	$q_{e,cal}$ (mmol/g)	1.97	2.90	2.92
	k_2 (g^2/mmol^2·h)	1.67	1.68	2.36
	h_2 (1/h)	6.52	14.13	20.12
	R^2	0.9961	0.9488	0.9901
Type 5 pseudo-second-order: $\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t$	$q_{e,exp}$ (mmol/g)	0.86	2.68	2.76
	k_2 (g^2/mmol^2·h)	11.79	73.72	53.03
	h_2 (1/h)	40.57	529.02	403.73
	R^2	0.8639	0.8459	0.8092
Elovich $q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t$	$q_{e,exp}$ (mmol/g)	1.86	2.68	2.76
	$q_{e,cal}$ (mmol/g)	2.03	2.93	2.84
	α (mmol/g·h)	16.68	71.32	96.25
	β (g/mmol)	2.50	2.08	2.00
	R^2	0.9959	0.9277	0.9747

the straight line through the origin, and C is equal to zero. Meanwhile, the corresponding pore diffusion coefficient (D_p, cm^2/min) can be calculated, the calculating equation expression is:

$$k_{id} = \frac{6q_e}{r_0}\sqrt{\frac{D_p}{\pi}} \tag{23}$$

where r_0 is the radius of particle, and the value is generally set to 0.05 cm.

The graph between q_t and $t^{0.5}$ at different initial concentrations about miglitol solution was plotted before reaching adsorption equilibrium. The results are shown in Figure 4. The parameters gotten by Webber-Morris equation fitting are presented in Table 2. It can be seen from Table 2 that the value of C is not for zero, and just their values for C increase with enhancing of solute concentration. It can make clear that the ion exchange process is not particle internal pore diffusion process, and further infer that the mass transfer process may be controlled by film diffusion or chemical reaction. Furthermore, the number of solute molecules for external layer of particle will increase with the augment of solute concentration, and then enhances mutual exclusive role for gay ions. It hinders migration of solute ions in the solution and leads to enlarge mass transfer resistance of the boundary layer, and the corresponding values C will increase. In addition, the solute concentration in particle pore will increase with the initial concentration of miglitol during ion exchange process if the mass transfer process is controlled by internal pore diffusion. As known that internal pore diffusion resistance will increase because the adding the numbers of solute ions lead to enhance charge repulsive interaction in particle pore, the corresponding D_p will decline.

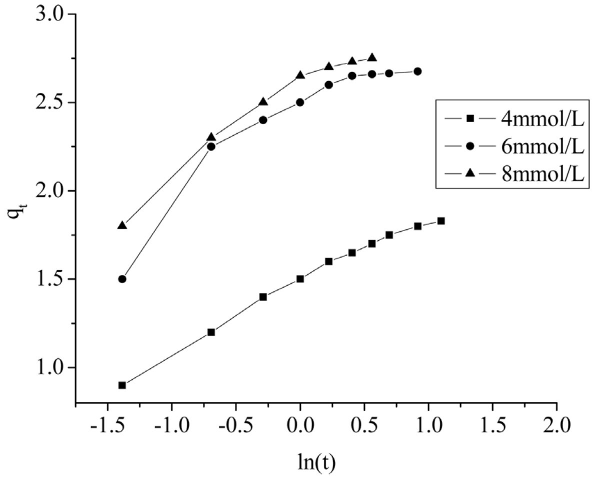


Figure 4. Fitting curves of the Elovich kinetic model for miglitol adsorbed onto D001 resin.

Table 2. Fitting parameters of the Webber-Morris kinetic model for miglitol adsorbed onto D001 resin.

C_0 (mmol/L)	k_{id} (mmol/g·min$^{0.5}$)	r_0 (cm)	$D_p \times 10^6$ (cm^2/min)	C (mmol/g)	R^2
4	0.09	0.05	0.50	0.700	0.9546
6	0.12	0.05	0.43	1.428	0.8545
8	0.14	0.05	0.50	1.434	0.9333

However, the calculating value D_p in **Table 2** is not the change trend of linear decline. It is mainly due to the internal diffusion coefficient greatly influenced by its own properties, and the homologous pore diffusion coefficients change a little. Therefore, it further proves that the adsorption process is not mainly controlled by internal pore diffusion.

Furthermore, the film diffusion coefficient can be calculated by film diffusion coefficient equation during ion exchange [26] [27] [28]. The equation is expressed as:

$$D_f = 0.23 \frac{r_0 \delta}{t_{1/2}} \frac{\bar{C}}{C_0} \tag{24}$$

where D_f (cm^2/min) is film diffusion coefficient, δ (cm) is a film thickness, the δ value is set to 10^{-3} cm for the spherical particle adsorbent. $t_{1/2}$ (min) is the corresponding time for reaching halfway of adsorption capacity in the total ion exchange process. $\bar{C}$ is the solute quantity adsorbed by adsorbent particles. C_0 is an initial concentration for miglitol solution.

The experimental ion exchange was discussed by Type 1 pseudo-second order kinetic equation and film diffusion coefficient, the related parameters results are shown in **Table 3**. As known that the ion exchange process is controlled by film diffusion when the D_f value is between from 10^{-6} cm^2/min to 10^{-8} cm^2/min, the ion exchange process is regarded as pore diffusion control at D_p value from 10^{-11} cm^2/min to 10^{-13} cm^2/min [29]. Combining with D_f value at 10^{-6} to 10^{-8} cm^2/min in **Table 3** and D_p value in **Table 2** and the diffusion coefficient magnitude corresponding with ion exchange process control principle, the ion exchange process at different concentrations for miglitol solution onto D001 resin is inferred as film diffusion control.

3.2. Effect of Temperature

The ion exchange process at different temperatures was investigated and the adsorption data gotten at the above experimental condition was analysed by the kinetic boundary model. The fitting result was obtained and the corresponding correlation coefficients were presented in **Table 4**. It is showed in **Table 4** that there is a higher correlation coefficient for the ion exchange process fitted by film diffusion equation of the kinetic boundary, and the fitted curve is seen as in **Figure 5**, and makes clear that the ion exchange process is mainly controlled by film diffusion, the conclusion is consistent with the mass diffusion behavior gotten at different concentrations. However, the fitting correlation coefficients in **Table 4**

Table 3. Film diffusion coefficients for miglitol at different initial concentrations.

C_0 (mmol/L)	$\bar{C}$ (mmol/L)	r_0 (cm)	$t_{1/2}$ (min)	$D_f \times 10^6$ (cm^2/min)
4	3.71	0.05	12.6	0.8
6	5.36	0.05	4.05	2.53
8	5.52	0.05	3.06	2.59

Table 4. Fitting correlation coefficients of the kinetic boundary model of miglitol adsorbed onto resin.

Temperature	Correlation coefficient (R^2)		
	$-\ln(1-F)$	$1-3(1-F)^{2/3}+2(1-F)$	$1-(1-F)^{1/3}$
30˚C	0.986	0.93	0.89
40˚C	0.97	0.92	0.898
50˚C	0.97	0.97	0.94

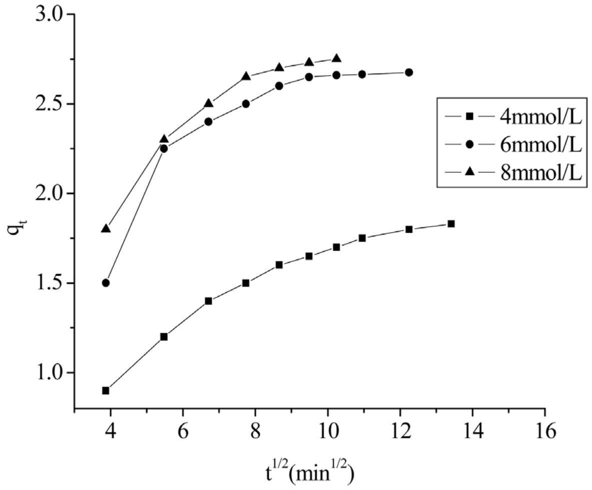


Figure 5. Plot of $t^{1/2}$ and q_t for miglitol at different initial concentrations.

for film diffusion and particle pore diffusion gradually come close each other with the increase experimental temperature. It can be concluded with increasing temperature that the mass transfer mechanism in ion exchange process is transferred gradually from film diffusion control to particle pore diffusion control. The main reason is that the mutual collision probability for solute molecules in particle pore and repulsion role of molecules each other all increase with the adding temperature, and hinders the external solute molecules to pass into the pore particle. The mass transfer resistance increases and leads to decrease for diffusion rate of solute molecules in particle pore. Therefore, the phenomenon in the whole ion exchange process emerges from film diffusion to the common control with particle pore diffusion and film diffusion.

In addition, the rate constant at different temperatures were obtained by the linear slope in **Figure 5**, and then the activation energy (Ea) can be calculated by Equation (20) and its value is 9.7 kJ/mol. Due to the activation energy of the ion exchange process is less than 16 kJ/mol, and it shows that the adsorption is controlled by the film diffusion. The conclusion is consistant with the gotten result from the kinetic boundary model. Meanwhile, the activation entropy change (ΔS^*) is counted for −78.7 J/mol·K.

Moreover, the ion exchange process is analysed further by Type 1 pseudo-second order kinetic Equation (8) and the gotten drawing and the corresponding parameters are shown in **Figure 6** and **Table 5**, respectively. It can be seen from **Figure 6** and **Table 5** that the curve between t/q_t and t is displayed the gradual increasing slope and has higher fitting degree by Equation (8) with the increase temperature. Their correlation coefficients reach over 0.99, and it finds that the difference between the theory adsorption capacity for D001 resins ($q_{e,cal}$) and the gotten experimental value ($q_{e,exp}$) is very small. This indicates that the Type 1 pseudo-second order kinetic equation can be used to describe the ion exchange process for miglitol onto D001 resin at different temperatures, and it is the same to the gotten results at different concentrations. The initial rate and the rate constant are all influenced obviously by experimental temperature. The initial rate h_2 declines apparently with the increase temperature and the rate constant reaches maximum at 40˚C. Meanwhile, the film diffusion constant is calculated by Equation (24) and shown in **Table 6**. It can be seen from **Table 6** that the film diffusion coefficients decrease obviously with the increase temperature and are unfavorable to the mass transfer during ion exchange. Moreover, the calculated film diffusion coefficient consists in the range of 10^{-6} to 10^{-8} cm^2/min, and the ion exchange process is regarded as the film diffusion control, its inference is consistent with the gotten conclusion by the kinetic boundary model.

3.3. Effect of Vibrating Rate

The adsorption process at different vibrating rate was discussed and analysed by

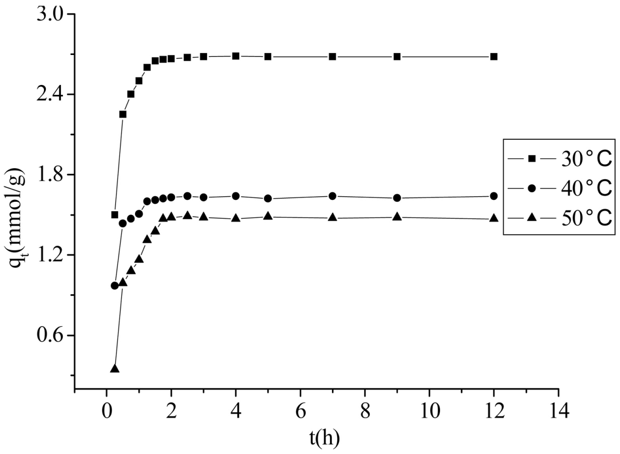


Figure 6. Effect of temperature on ion exchange process of miglitol adsorbed onto D001 resin.

Table 5. Fitting parameters of the pseudo-second-order kinetic model (Type 1) for miglitol adsorbed onto D001 resin.

Temperature (˚C)	$q_{e,cal}$ (mmol/g)	k_2 (g^2/mmol^2·h)	h_2 (1/h)	R^2	$q_{e,exp}$ (mmol/g)
30	2.70	5.49	40.00	0.9999	2.68
40	1.65	9.69	26.30	0.9999	1.64
50	1.52	2.80	6.49	0.9983	1.48

Table 6. Film diffusion coefficients at different temperatures for miglitol adsorbed onto D001 resin.

Temperature (˚C)	C_0 (mmol/L)	$\bar{C}$ (mmol/L)	r_0 (cm)	$t_{1/2}$ (min)	$D_f \times 10^6$ (cm^2/min)
30	6	5.36	0.05	4.05	2.53
40	6	3.28	0.05	3.76	1.68
50	6	2.96	0.05	14.00	0.40

Type 1 pseudo-second order kinetic equation, the gotten process parameters were shown in Table 7. It is seen from Table 7 that their correlation coefficients all reach higher value and are over 0.99, and it indicates that the ion exchange process at different stirring rates can be used to be described by Type 1 pseudo-second order kinetic equation. It is further analysed for Table 7 and found that the values of initial rate h_2 and rate constant k_2 all gradually increase with the boosting vibrating rate, and also affects mass transfer distinctly.

The film diffusion coefficient Equation (24) was used to calculate film diffusion coefficients in the experimental conditions, and was presented in Table 8. It is observed from Table 8 that the diffusion coefficients all present increase trend with the enhancing the vibrating rate, and the change trend is consistent with the above value changes of k_2 and h_2. At the same time, the calculated film diffusion coefficients is also existed in 10^{-6} and 10^{-8} cm^2/min, and the ion exchange process at different vibrating rates are regarded as film diffusion control too. The main reason is due to the selected adsorption resin D001 that belongs to a macroporous resin, and there is relatively weak adsorption resistance into the macroporous resin, ion exchange rate appears very fast and leads to complete the ion exchange very quickly within a very short time. The above a series of analysis can be concluded that the external adsorption factors such as solute concentration, temperature and vibrating rate for effect of mass transfer diffusion process control of miglitol onto D001 resin is relatively weak.

4. Conclusion

In the present work, a batch adsorption operation at the different influence factors for concentrations, temperatures and vibrating rate in the constant temperature bath oscillator (SHZ-A) has been performed for miglitol adsorption by resin D001. The experimental results showed that Type 1 pseudo-second order kinetic equation can be all used to describe miglitol adsorbed by D001 resin at different concentrations, temperatures and vibrating rates. Moreover, Webber-Morris kinetic equation, film diffusion coefficient equation and kinetic boundary model were also applied to discuss the adsorption process, and then calculated values of the process film diffusion coefficient and pore diffusion coefficient, the total activation energy (E_a) can be calculated and its value is 9.7 kJ/mol. The ion exchange process is all mainly controlled by film diffusion. The external adsorption factors such as solute concentration, temperature and vibrating rate for effect of mass

Table 7. Fitting parameters of the Type-1 pseudo-second-order kinetic model for miglitol adsorbed onto resin D001.

Vibrating rate (rmp)	$q_{e,cal}$ (mmol/g)	k_2 ($g^2/mmol^2 \cdot h$)	h_2 (1/h)	R^2	$q_{e,exp}$ (mmol/g)
80	2.94	0.39	3.4	0.9963	2.68
120	2.70	5.49	40.0	0.9999	2.68
160	2.70	5.97	43.5	0.9999	2.68

Table 8. Film diffusion coefficients at different vibrating rates.

Vibrating rate (rmp)	C_0 (mmol/L)	$\bar{C}$ (mol/L)	r_0 (cm)	$t_{1/2}$ (min)	$D_f \times 10^6$ (cm^2/min)
80	6	5.36	0.05	51.16	0.20
120	6	5.36	0.05	4.05	2.53
160	6	5.36	0.05	3.73	2.74

transfer diffusion process control of miglitol onto D001 resin is relatively weak.

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Nomenclature

q_t	[mmol/g]	adsorption capacity of resin at time t
C_0	[mmol/L]	initial concentration
V_0	[L]	initial solution volume
C_n	[mmol/L]	remaining solution concentration
V_n	[L]	remaining volume
C_i	[mmol/L]	taken solution sample concentration
V_i	[L]	taken solution sample volume
W	[g]	resin weight
q_e	[mmol/g]	equilibrium adsorption capacity for adsorbent
q_t	[mmol/g]	adsorption capacity for adsorbent at time t
k_1	[g/mmol·h]	rate constant for the Lagergren equation
k_2	[$g^2/mmol^2 \cdot h$]	rate constant for the pseudo-second order equation
h_1	[1/h]	initial rate of pseudo-first order equation
h_2	[1/h]	initial rate of pseudo-second order equation
α	[mmol/g·h]	initial adsorption rate of Elovish equation
β	[g/mmol]	desorption constant
F	[%]	ion exchange degree
R^2		correlation coefficient
E_a	[kJ/mol]	activation energy
ΔS^*	[J/mol·K]	activation entropy change
K	[J/K]	Boltzmann constant
h		Plank constant
k_{id}	[$mmol/g \cdot min^{0.5}$]	internal diffusion rate constant
C		intercept
r_0	[cm]	particle radius
D_p	[cm^2/min]	pore diffusion coefficient
D_f	[cm^2/min]	film diffusion coefficient
δ	[cm]	film thickness
$t_{1/2}$	[min]	time for reaching halfway of adsorption capacity
$\bar{C}$	[mmol/L]	solute quantity adsorbed by adsorbent particles
Subscripts		
cal	calculated	
exp	experimental	