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Adsorption behavior of L-tryptophan on ion exchange resin

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Abstract−A batch method was applied to investigate the adsorption behavior and mechanisms of L-tryptophan (L-trp) on ion exchange resins. HZ-001 and JK006 were proved to be ideal adsorbents due to their large loading capacity and favorable selective adsorption for L-trp. Langmuir, Freundlich, and Dubinin-Radushkevich equations were applied to simulate the experimental data to describe the adsorption process of L-trp onto HZ-001 and JK006. The maximum loading capacity (at pH 5.0, 30 °C), determined by the Langmuir and Dubinin-Radushkevich models, was close to each other (833 mg/g vs. 874 mg/g) for HZ-001, while discrepant (833 mg/g vs. 935 mg/g) for JK006. Three diffusion-controlled kinetic models were utilized to analyze the results in order to identify the adsorption mechanism. The adsorption kinetics of L-trp onto cation exchange resins was investigated under different experimental conditions, including initial solution pH, temperature, initial L-trp concentration, and adsorbent dosage. Moreover, the diffusion process of L-trp onto HZ-001 and JK006 was evaluated at different initial adsorbate concentrations. The thermodynamic parameters, obtained from the kinetic data, demonstrated that L-trp could be adsorbed spontaneously onto both resins.

Key words: Adsorption, L-trp, Ion Exchange Resin, Isotherms, Diffusion and Kinetics

INTRODUCTION

As an essential aromatic amino acid, L-trp has broad application in food additives, feed supplements, therapeutic agents, and precursors [1, 2]. L-trp is produced from the conversion of chemically synthesized precursors by enzymatic reactions and microbial fermentation from cheap carbon sources in industry [3,4]. With great genetic improvement of L-trp producers, L-trp was mainly produced by microbial fermentation. Further studies on the L-trp separation from the fermentation broth are necessary to reduce the production cost.

Due to the amphoteric character of amino acids, ion exchange technology has been widely utilized in the separation and recovery process during the industrial production of amino acids. Adsorbent resins are considered to be the most promising due to their chemical stability, low cost and reusage [5,6]. A cation resin can easily take up an amino acid at a pH value in which the amino acid is positively charged and can desorb it when the amino acid is negatively charged. The characteristics of adsorption behavior are generally inferred in terms of the equilibrium isotherm, adsorption kinetics and thermodynamics, with which a rational design and optimization of such ion exchange processes can be constructed [7-9]. In this study, seven cation resins were screened to obtain the most suitable resin for L-trp separation. Then the equilibrium and kinetics of L-trp adsorption were investigated to understand the adsorption behavior and mechanism.

THEORETICAL APPROACHES

1. Adsorption Isotherms

Adsorption equilibrium, which determines the maximum loading capacity of an adsorbent, is usually modeled by an isotherm describing the relationship between the amount adsorbed and that dissolved in liquid phase at equilibrium. Three models have been utilized to describe this relationship as introduced below:

The empirical model developed by Freundlich, which can be used for the non-ideal adsorption on heterogeneous surfaces, is given by:

$$q_e=k_fC_e^n \tag{1}$$

The Langmuir equation is given by:

$$q_e=\frac{q_m bC_e}{1+bC_e} \tag{2}$$

The Dubinin-Radushkevich (D-R) model is given by:

$$\mathrm{Ln}q_e=\mathrm{Ln}q_0-\beta\varepsilon^2 \tag{3}$$

where β is the activity coefficient and ε the Polanyi potential given by:

$$\varepsilon=\mathrm{RTLn}\left(1+\frac{1}{C_e}\right) \tag{4}$$

where R is the gas constant (kJ/mol K) and T the temperature (K)

2. Adsorption Kinetics

In addition to the loading capacity, adsorption rate is another important factor in the design of an adsorption system. A number of mechanisms that control the adsorption rate were described previ-

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ously [10-13], in which either the film diffusion or the internal diffusion is often considered to control the adsorption process due to the dominance of film resistance or intraparticle mass-transfer resistance compared with the non-limiting bulk diffusion and instantaneous uptake of adsorbate. The external diffusion model [14] can be expressed as:

$$\mathrm{Ln}\left(\frac{C_t}{C_0}\right) = -k_f\frac{A}{V}t \tag{5}$$

where A is the total interfacial area of the adsorbent (cm^2). Intraparticle diffusion was first introduced by Weber and Morris [15] in 1963 and the intraparticle diffusion, D, can be calculated from the following equation [16]:

$$-\mathrm{Ln}\left[1-\left(\frac{q_t}{q_e}\right)^2\right] = \frac{4\pi Dt}{6d^2} \tag{6}$$

In batch adsorption processes, the kinetics of adsorbate diffuse in porous adsorbent is usually described by [16,17]:

$$q_t = k_i t^{0.5} \tag{7}$$

where k_i is the intraparticle diffusion rate constant (mg/(g min$^{0.5}$)).

MATERIALS AND METHODS

1. Materials

Strong-acid cation ion-exchange resins used (Table 1) were spherical beads and commercially obtained in this study. The ionic forms and functional groups of all are Na$^+$ and sulfonic acid, respectively. The other characteristics are listed in Table 1. Before use, the resins were washed in distilled water for several times, and then immersed and washed with 1.5 M NaOH and 1.5 M HCl alternately. The resins were finally washed by double distilled water until the pH value was close to 7.0. L-trp (Sigma) was of analytical reagent grade and was used without further purification.

2. Experimental Methods

Batch experiments were carried out to study the ion-exchange equilibrium of L-trp onto resins. The resins were weighed and added to the solutions of thermal-equilibrium in each flask and were agitated in a thermostatic shaker at 150 rpm. Preliminary tests showed the adsorption process was completed in 2 hours. The amount of adsorption at equilibrium, q_e was obtained by:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{8}$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of solutes at the initial time and at equilibrium, respectively, v (L) is the volume of solution and w the mass of resin (g). Ion exchange rates were determined at the desired pH and temperature in an orbital shaker. L-trp solution was added to the flask and left to reach thermal equilibrium, and then the resin of known mass was promptly poured into the flask. Aliquots of the solution were taken out at the same intervals to determine q_t (mg/g) at time t:

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{9}$$

where C_t (mg/L) is the liquid-phase concentration of solute at the given time t.

The distribution constant of solute, k_d, was given by the following equation:

$$k_d = \frac{\text{amount of solute in resin}}{\text{amount of solute in solution}} \times \frac{V}{W} \tag{10}$$

Selective coefficient of different resins was obtained based on the distribution coefficient:

$$K_B^A = \frac{K_A}{K_B} \tag{11}$$

The amount of L-trp was measured by UV spectrometry at 280 nm and the concentration of L-phenylalanine (L-phe), L-tyrosine (L-tyr), and L-trp in the mixtures was determined by HPLC. Compounds were separated by a 250 mm×4.6 mm C_{18} reversed-phase column (Dalian, China). The mobile phase was a 6 : 94 (v/v) mixture of acetonitrile and water with an adjusted pH of 3.4. The flow rate and the detection wavelength were set at 1.0 mL/min and 215 nm, respectively.

RESULTS AND DISCUSSION

1. Adsorbent Selection

Seven cation exchange resins were selected to determine the adsorption capacity for L-trp. As shown in Table 1, the gel-type resins showed better adsorption performance than the macropore-type ones. This discrepancy may be attributed to the structural characteristics of the two types of resins. The high degree of cross-linking of macroporous adsorbent brings about large steric hindrance on the adsorption of L-trp cations. Moreover, the fixed functional groups in the gel-type resin are generally more than in macroporous adsorbent.

Table 1. Properties of each cation exchange resin[a] and equilibrium adsorption quantity (30 °C) of L-trp

Adsorbent	Constitutional type	Mean particle size (μm)	True density in wet state (g/ml)	Polymer matrix	Maximum operating temperature (°C)	Total exchange capacity (mM/g)	q_e (mg/g)
D008	Macropore	850	1.25-1.28	Polystyrene-DVB	120	≥4.3	616.4
SA-2	Gel	650	1.20-1.30	Polystyrene	100	≥4.5	736.2
JK006	Gel	782.5	1.25-1.29	Polystyrene	120	≥4.6	794.1
HD-8	Macropore	800	1.10-1.20	Polystyrene	130	≥4.0	576.4
HZ-001	Gel	110.5	1.24-1.28	Polystyrene-DVB	100	≥4.2	753.9
S-9	Macropore	770	1.17-1.25	Polystyrene-DVB	110	≥4.0	551.2
SR-1	Gel	780	1.18-1.25	Polystyrene-DVB	110	≥4.6	756.7

[a] Information provided by the manufacturer

Table 2. Distribution constant of L-trp, L-tyr and L-phe in each resin and selective coefficient between L-trp/L-tyr and L-trp/L-phe

Adsorbent	$K_{L\text{-}trp}$ (L/g)	$K_{L\text{-}tyr}$ (L/g)	$K_{L\text{-}Phe}$ (L/g)	$K_{L\text{-}trp/L\text{-}tyr}$	$K_{L\text{-}trp/L\text{-}phe}$
SA-2	5.99	1.29	2.00	4.63	2.99
JK006	10.12	1.44	1.95	7.01	5.20
HZ-001	9.74	1.29	1.83	7.53	5.32
SR1-1	7.93	1.16	1.62	6.85	4.89

Therefore, four gel-type resins were screened out for further study.

2. Selective Adsorption of L-trp

In L-trp fermentation, two main byproducts, L-phe and L-tyr, were found to have similar characters as L-trp. To separate L-trp from these two byproducts, preferential adsorption of L-trp is one of the key considerations for the selection of suitable cationic resin. As shown in Table 2, the distribution constant of L-tyr and L-phe in tested resins varied slightly, while that of L-trp showed a significant difference. The maximal selective coefficients of L-trp/L-tyr and L-trp/L-phe were obtained with HZ-001 resin, which was therefore chosen for further study.

3. Ion Exchange Equilibrium

The adsorption equilibrium of L-trp was studied by using two cationic resins, HZ-001 and JK006. The curves of isothermal adsorption of L-trp on HZ-001 and JK006 are shown in Fig. 1. The experimental data were fitted by several isotherm equations and the results are listed in Table 3. The constants q_0 in Langmuir model and D-R model represent the adsorption capacity (mg/g) of the resins and the values obtained from these two models are similar to each other. The essential characteristics of the Langmuir equation are described in terms of a dimensionless equilibrium parameter, R_L, which is defined as:

$$R_L=\frac{1}{1+bC_0} \tag{12}$$

For both adsorbents, the R_L values indicated favorable adsorption of L-trp. The exponent in the Freundlich equation always provides an indication of the adequacy and capacity between adsorbent and adsorbate. In most cases, beneficial adsorption is suggested by an n value between 1 and 10. So for both resins, favorable adsorption was obtained for L-trp. D-R model can be applied to distinguish physical and chemical adsorption of adsorbate onto adsorbent. The mean adsorption energy E, which indicates the adsorption type, is calculated by:

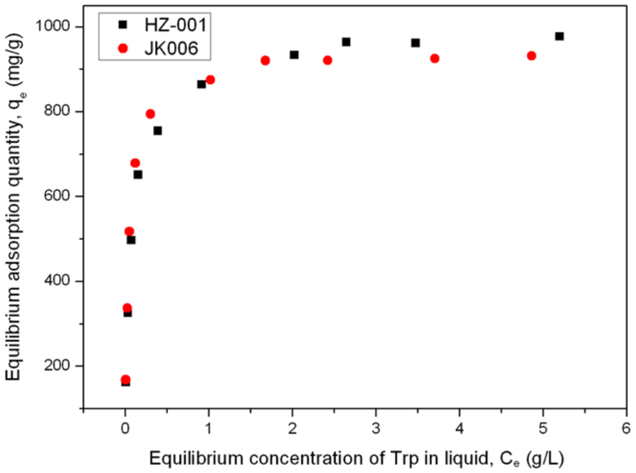

Fig. 1. Curves of isothermal adsorption of L-trp on HZ-001 and JK006.

Table 3. Isotherm parameters collected for L-trp adsorption onto adsorbent resins

Isotherm models	Adsorbent	
	HZ-001	JK006
Langmuir constants		
q_0	833.3	833.3
b	24.00	40.00
r^2	0.9842	0.9884
Freundlich constants		
k_f	748.2	807.6
n	4.196	4.378
r^2	0.8392	0.8281
D-R constants		
q_0	874.1	935.1
E	6.402	6.742
r^2	0.9940	0.9963

$$E=\frac{1}{-2\beta} \tag{13}$$

The E value was 6.402 for HZ-001 and 6.742 for JK006, which suggested that the adsorption process was a physical adsorption [17, 18]. Therefore, it was possible that the physical means such as electrostatic force played a significant role as an adsorption mechanism for the L-trp uptake in this work. Results obtained from aforementioned analyses showed that the adsorption isotherm was better correlated with the D-R model, while the Freundlich model resulted in the worst fit (Table 3).

4. Adsorption Kinetics

The adsorption rate of L-trp on ion exchange resin HZ-001 and JK006, which is affected by the interactions between adsorbent and adsorbate as well as by the operation conditions, was determined as follows.

4-1. Effect of pH on the Adsorption Kinetics

The adsorption of L-trp onto HZ-001 and JK006 at different pH is depicted in Fig. 2(a), (b). Amino acids are usually amphoteric and exist either as anions or as cations, depending upon the solution pH. In this study, the positively charged L-trp at a pH lower than 5.8 could be effectively adsorbed onto both resins and over 75% of that was adsorbed in the initial 30 minutes. The adsorption of L-trp on resins, however, would be harmed drastically at extremely low pH. For instance, the adsorbed L-trp on both resins decreased markedly at pH 1.0 (Fig. 2(a), (b)), which was attributed to the strong competition between hydrogen ions and the L-trp cations for the adsorption sites. Although more amino acid cations existed at low pH, the relative ionic fraction of the L-trp cations decreased because of the increase of hydrogen ions. Usually, the ionic fraction of amino acid cations enhances as pH increases, reaches to the peak value at

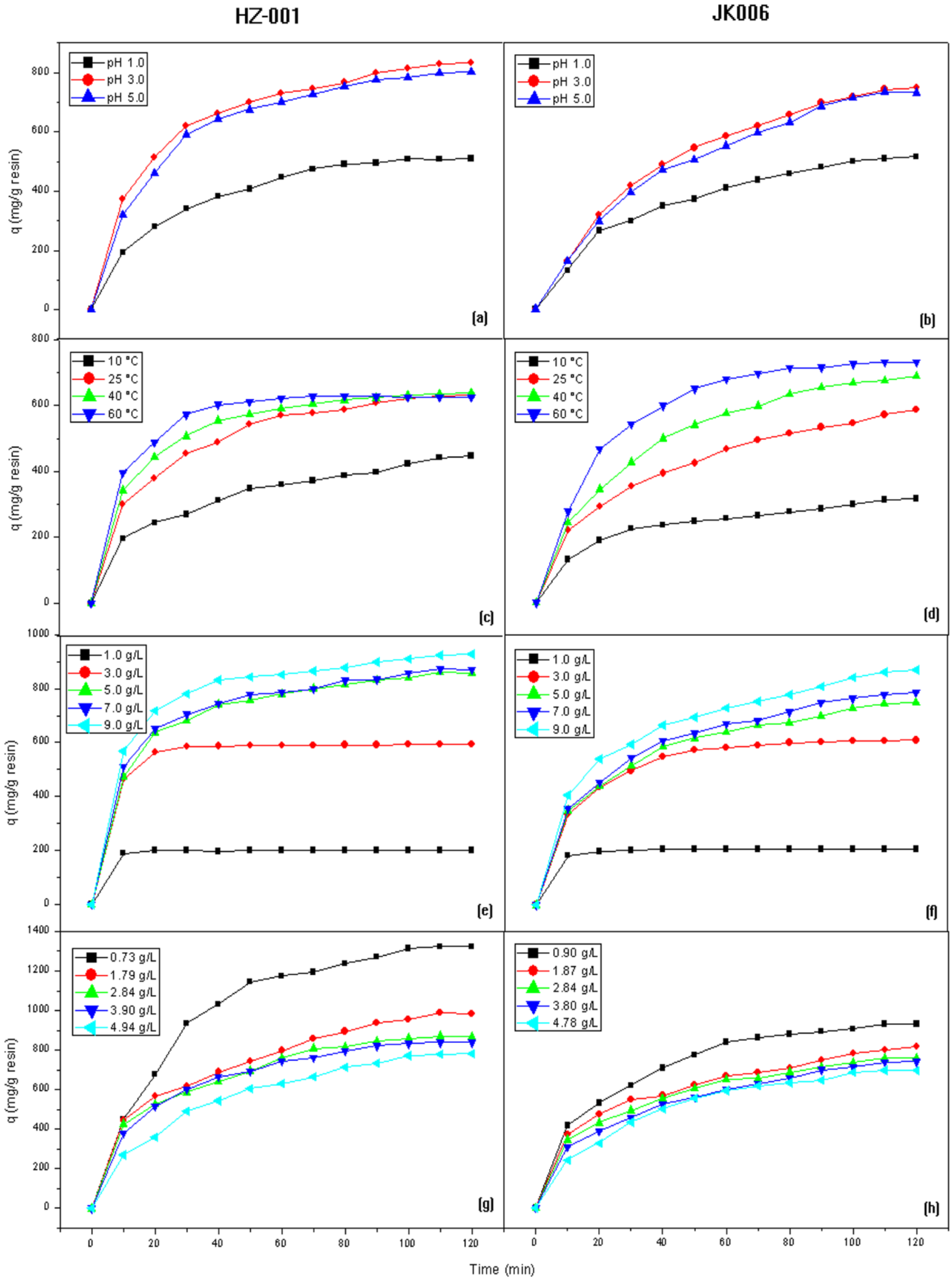

Fig. 2. Time-courses of L-trp adsorption onto HZ-001 and JK006 at different solution pH values (a), (b), different temperatures (c), (d), different initial concentrations of L-trp (e), (f) and different dosages of ion exchange resin (g), (h).

their isoelectric point, and then decreases sharply to zero at basic solutions [19]. A similar adsorption behavior was achieved at pH 3.0 and pH 5.0 because there is no significant difference in ionic fraction of L-trp cations with pH value increasing from 3.0 to 5.0.

Table 4. Diffusion kinetic parameters for the adsorption of L-trp on the adsorbent

Adsorbent	Parameters	External diffusion coefficients (cm/s)		Intraparticle diffusion coefficients (cm^2/s)		Adsorption rate [mg/(g min$^{0.5}$)]	
		10^3k_f	r^2	10^7D	r^2	k_i	r^2
HZ-001	pH value						
	1.0	2.858	0.977	8.395	0.931	58.07	0.995
	3.0	6.744	0.964	6.413	0.996	101.6	0.984
	5.0	6.477	0.929	6.178	0.973	97.78	0.985
	Temperature (°C)						
	10	2.286	0.982	4.314	0.991	37.42	0.959
	25	5.563	0.993	6.879	0.986	72.94	0.982
	40	6.553	0.930	7.113	0.989	76.42	0.952
	60	5.982	0.967	16.27	0.992	97.22	0.972
	Initial L-trp concentration (g/L)						
	1.0	26.86	0.825	37.37	0.922	47.41	0.941
	3.0	22.86	0.865	28.74	0.995	112.0	0.947
	5.0	7.353	0.993	13.76	0.973	108.3	0.960
	7.0	3.239	0.928	6.530	0.977	120.5	0.954
	9.0	2.210	0.895	5.597	0.930	147.3	0.973
	Resin dosage (g/L)						
	0.73	7.471	0.965	5.188	0.962	166.3	0.992
	1.79	4.006	0.987	4.781	0.984	111.7	0.975
	2.84	2.320	0.979	4.722	0.927	87.71	0.943
	3.90	5.413	0.887	5.655	0.987	83.47	0.926
	4.94	6.465	0.929	4.839	0.954	78.98	0.933
JK006	pH value						
	1.0	17.33	0.875	295.3	0.941	47.93	0.972
	3.0	33.34	0.938	198.8	0.976	69.28	0.975
	5.0	34.92	0.948	195.9	0.958	70.44	0.979
	Temperature (°C)						
	10	7.613	0.952	184.2	0.967	37.61	0.949
	25	23.63	0.923	248.5	0.982	51.38	0.976
	40	40.17	0.995	263.1	0.992	75.85	0.998
	60	57.49	0.973	447.3	0.987	90.83	0.985
	Initial L-trp concentration (g/L)						
	1.0	153.1	0.971	1400	0.989	46.88	0.953
	3.0	108.4	0.998	616.9	0.986	87.51	0.984
	5.0	32.29	0.984	248.5	0.968	91.60	0.989
	7.0	19.95	0.973	213.4	0.943	96.24	0.992
	9.0	13.65	0.952	233.9	0.987	106.0	0.981
	Resin dosage (g/L)						
	0.90	39.00	0.985	391.8	0.982	114.1	0.972
	1.87	28.18	0.958	400.5	0.936	96.05	0.997
	2.84	17.24	0.956	184.2	0.992	73.45	0.955
	3.80	22.08	0.961	187.1	0.977	73.32	0.984
	4.78	34.67	0.941	187.1	0.946	71.07	0.973

These results were consistent with previous work [19]. The loading capacity of resin JK006 for L-trp approached to that of resin HZ-001 (507.9 mg/g resin versus 510.1 mg/g resin) at pH 1.0, but was lower than that of HZ-001 when pH was adjusted to 3.0 and 5.0. For both resins, the external diffusion coefficients increased from pH 1.0 to 3.0, while remaining almost constant from pH 3.0 to 5.0. An opposite result was obtained in internal diffusion coefficients with pH value ranging from 1.0 to 3.0 (Table 4).

The adsorption rate parameter, k_i, was derived from the intraparticle diffusion model and the correlation coefficient indicated that the intraparticle diffusion model was valid for the diffusion of L-trp onto both resins (Table 4). The values of k_i for both resins increased when pH value increased from 1.0 to 3.0 and remained stable between pH 3.0 and 5.0, which was consistent with the trend of external coefficients. It was interesting to observe that the diffusion coefficients of HZ-001 were much smaller than those of JK006, while the diffusion rate constant, k_i, varied much less for the two resins. This may be attributed to the influence of the resin particle size on the diffusion kinetics. The mean particle diameter of HZ001 was much smaller than that of JK006 (110.5 μm vs 782.5 μm), resulting in larger specific surface areas for HZ001 which is beneficial for the quick adsorption for L-trp.

4-2. Effect of Temperature

The amounts of L-trp adsorbed by resins were determined at temperature from 10 °C to 60 °C. The results showed that L-trp adsorption was temperature-dependent. The amounts of L-trp adsorbed onto JK006 increased from 315.8 mg/g to 730.0 mg/g as the temperature changed from 10 °C to 60 °C. The amount of adsorbed L-trp onto HZ-001 went up when the temperature increased from 10 °C to 45 °C, and then decreased slightly as the temperature reached 60 °C (Fig. 2(c)). This indicated that temperature higher than 45 °C reduced the loading capacity of HZ-001. Meanwhile, the time required to arrive at equilibrium became shorter with the increase in temperature, which was due to the increasing diffusivity as shown in Table.

4-3. Effect of Adsorbate Concentration

Fig. 2(e), (f) shows the adsorption of L-trp onto resin HZ-001 and JK006 at different initial L-trp concentrations. When the initial concentration of L-trp changed from 1.0 g/L to 9.0 g/L, the adsorbed L-trp increased significantly from 201.2 mg/g to 948.4 mg/g for HZ-001 and from 206.5 mg/g to 870.8 mg/g for JK006. The equilibrium time is also dependent on the initial L-trp concentration. Although a larger loading capacity could be obtained with higher initial concentration of L-trp, the time required to achieve equilibrium was prolonged, which was attributed to the lower external and internal diffusivity at higher initial L-trp concentration (Table 4). Besides, it was found that quicker equilibrium could be reached for adsorbent HZ-001 than JK006 at each initial concentration. For both resins, k_f and D values varied inversely as the initial L-trp concentration increased from 1.0 g/L to 9.0 g/L. The external diffusion coefficient is related to the value of C_t/C_0 which is dependent on the initial adsorbate concentration. Since relatively more surface area and thus adsorption sites were available for L-trp cations at lower initial concentration, the fraction of adsorbed L-trp was much larger. The internal diffusivity D, which is determined by the ratio of q_t to q_e, is also dependent on the initial adsorbate concentration. Higher initial L-trp concentration, however, would result in a lower ratio of q_t and q_e, leading to the reduction of D value. The k_i value indicated that with the increase of the initial L-trp concentration, the adsorption rate enhanced for both resins. L-trp uptake vs. time monotonously increased until reached to saturation, indicating the possible monolayer coverage of L-trp cations on the surface of adsorbents.

4-4. Effect of the Adsorbent Dosage

The effect of resin dosage on the adsorption of L-trp was studied with an initial L-trp concentration of 5.0 g/L and the system was equilibrated for 120 min. It was found that the equilibrium concentration in solution decreased with the increase of resin dosage. This result was in expectation because greater surface area and more adsorption sites were provided by the increasing adsorbent dosage for a given initial solute concentration. The resin dosage should be optimized to achieve maximum loading capacity. As shown in Fig. 2(g), (h), with the increase of resins dosage, the adsorbed L-trp per gram resin decreased at equilibrium, indicating a reduction of the utilization efficiency of both resins. The optimal dosage of adsorbent per unit volume of solution in this investigation was 0.73 g/L for HZ-001 and 0.90 g/L for JK006, respectively. Due to the limited dosage range of adsorbents that has been tested, the loading capacity determined might be not the highest. The highest loading capacity was obtained corresponding to the saturation by adsorbate.

5. Diffusion Process and Thermodynamic Study of L-trp Adsorption

Mass transfer within the resin particles is complex because the transient process is controlled by various mechanisms in which film diffusion and intraparticle diffusion are expected to be the main rate-limited steps during the adsorption. For a micropore adsorbent, especially when the particle size is relatively large, the intraparticle mass-transfer resistance is often dominant compared with the external diffusion process. Understanding the diffusion process would benefit the optimization of the operation conditions. The biot number B_i (B_i=k_fd/D) can provide an estimation of the predominance of surface diffusion versus the external diffusion. The overall diffusion and adsorption are mainly controlled by intraparticle diffusion as the B_i value is higher than 100, otherwise, it will be controlled by external process. As shown in Table 5, the B_i values for HZ-001 at various initial L-trp concentrations were smaller than 100, indicating a predominance of external diffusion. In contrast to this, the Bi values for JK006 were greater than 100 between 3.0 and 5.0 g/L, which demonstrated that the intraparticle diffusion was the rate-determining step. This distinction might be attributed to the intraparticle resistance for large particle size (110.5 μm for HZ-001 and 782.5 μm for JK006).

Thermodynamic parameters were measured by the following equation [20-22]:

$$\mathrm{Ln}k_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{14}$$

where ΔS, R, ΔH and T were the entropy, gas constant, enthalpy and absolute temperature, respectively. Gibbs free energy (ΔG) was determined as the well-known equation:

$$\Delta G = \Delta H - T\Delta S \tag{15}$$

The adsorption of L-trp onto the resins was carried out at temper-

Table 5. Biot number for adsorbent at each initial L-trp concentration

Adsorbent	Initial L-trp concentration (g/L)	Biot number (B_i)
HZ-001	1.0	79.4
	3.0	87.9
	5.0	59.1
	7.0	54.8
	9.0	43.6
JK006	1.0	85.5
	3.0	137.5
	5.0	100.7
	7.0	73.2
	9.0	45.7

Table 6. Thermodynamic parameters for the adsorption of L-trp onto adsorbent

Adsorbent	Temperature (K)	ΔS (J/mol K)	ΔH (kJ/mol)	ΔG (kJ/mol)	Activation energy (kJ/mol)
HZ-001	283	136.158	2.541	−13.125	19.255
	298			−15.168	
	313			−17.209	
	333	44.443	−2.877	−17.677	
JK006	283	154.748	3.203	−11.764	13.020
	298			−14.085	
	313			−16.407	
	333			−19.502	

ature from 283 K to 333 K. As shown in Table 6, the positive value of entropy for adsorbent HZ-001 indicated that the adsorption was irreversible. The enthalpy, however, showed a different trend. The positive value indicated the adsorption of L-trp onto HZ-001 was endothermic from 283 K to 313 K, while an exothermic process occurred from 313 K to 333 K. The result proved that the adsorption of L-trp onto HZ-001 was temperature-dependent. An increment in temperature from 283 K to 313 K was beneficial for L-trp adsorption onto HZ-001, while an adverse effect on the adsorption process emerged from 313 K to 333 K. Results showed that the loading capacity increased from 446.2 mg/g to 637.7 mg/g as temperature increased from 298 K to 313 K, and then reduced to 627.2 mg/g at 333 K (Fig. 2(c)). The adsorption of L-trp onto JK006 was also an irreversible process since the entropy value was positive. Besides, the positive enthalpy value from 283 K to 333 K suggested an endothermic process. Consequently, an increment in temperature could lead to better performance for L-trp adsorption onto JK006. The data of Gibbs free energy for both resins demonstrated the spontaneous nature of adsorption. The activation energy (E_a) of adsorption of L-trp on both adsorbents was calculated by the following equation:

$$D_i = A\exp\left(\frac{-E_a}{RT}\right) \qquad (16)$$

where D_i is the intraparticle diffusion coefficient, A and E_a the frequency factor, apparent activation energy, respectively. Table 5 shows that the apparent activation energy for HZ-001 and JK006 was 19.3 kJ/mol and 13.0 kJ/mol, respectively.

CONCLUSIONS

Two cation exchange resins HZ-001 and JK006 were selected for the determination of adsorption kinetics and mechanisms of L-trp after investigating the loading capacity and selective adsorption of seven cation resins. Three adsorption isotherm models were applied to study the adsorption behavior, and the results indicated beneficial adsorption of both adsorbents for L-trp. Adsorption kinetics of L-trp on HZ-001 and JK006 were studied under different conditions including solution pH, temperature, initial L-trp concentration, and resin dosage. The results demonstrated that all of these factors had a great influence on the loading capacity, diffusivity, and adsorption rate. In addition, analyses showed that the adsorption of L-trp onto HZ-001 was determined by external diffusion while the rate-limiting step for L-trp adsorption on JK006 was internal diffusion with L-trp concentration between 3.0 and 5.0 g/L. Furthermore, the thermodynamic parameters (ΔG and ΔS) showed the adsorption of L-trp onto these two adsorbents were spontaneous and irreversible. The positive value of ΔH indicated an endothermic process for JK006 from 10 to 60 °C and for HZ-001 from 10 to 45 °C, while an exothermic process for HZ-001 from 45 to 60 °C.

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