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Adsorption and desorption of phenylalanine and tryptophane on a nonionic polymeric sorbent

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Abstract−Adsorption equilibrium of two amino acids - Phenylalanine (Phe) and Tryptophane (Trp) - onto nonionic polymeric sorbent, SP850 was studied under various pH values and temperatures. Adsorption equilibrium data of two amino acids on SP850 were fitted well with the Langmuir and Freundlich equations. Thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were evaluated by applying the Van't Hoff equation. Besides, adsorption kinetic of Phe was also investigated. Adsorption kinetic data were analyzed using the models of pseudo-first-order, pseudo-second-order and intraparticle diffusion. The results indicated that the pseudo-second-order model was more successful in simulating the adsorption kinetic data and the adsorption rate was mainly controlled by the diffusion rate in adsorption process. On the other hand, desorption studies were conducted by employing different organic solvents such as isopropyl alcohol (IPA), ethanol, and methanol. It was found that IPA was the best material for desorbing amino acid on the polymeric sorbent.

Key words: Adsorption, Desorption, Amino Acids, Nonionic Polymeric Sorbent

INTRODUCTION

Amino acids are widely used in many fields, such as food, chemical, pharmaceutical, and medicine cosmetic industries. Two essential amino acids for humans are Phe and Trp. Separation technologies of amino acids from fermentation broths have been investigated for the past two decades. There are some studies reported in the literature for amino acid adsorption on various adsorbents such as activated carbon, silica, ion exchange, mesoporous materials and polymeric resins, etc. [Dutta et al., 1997; Kubota et al., 1996; Titus et al., 2003; Melis et al., 1996; Vinu et al., 2006]. Among these sorbents, although polymeric resins have lower adsorption capacities than ion exchange and activated carbons, they are more attractive because of their regeneration characteristics and selectivity [Doulia et al., 2001; Yang et al., 2003; Ramos et al., 2004; Lee et al., 2004]. Unlike activated carbon, polymeric sorbents typically have uniform surface chemistry and can be synthesized with a controlled pore structure. Such uniformity of property can reduce adsorption heterogeneity so that it allows regeneration under milder conditions [Grzegorczyk and Carta, 1996]. Regeneration of polymeric sorbents can be applied by using organic solvents, bases and acids, steam, supercritical fluids, or microware irradiation. Of these methods, organic solvents are chosen as an effective desorbate with high purity [Lee et al., 2004].

There are many regeneration techniques such as thermal, acid, base, and solvent regeneration. The selection of a certain regeneration method depends upon the physical and chemical characteristics of both the adsorbent and adsorbate. For nonionic polymeric adsorbents, the solvent regeneration technique has been known to be superior to other methods, as the attractive forces binding the solute to the resin surface are physical nature. The solvent regeneration of polymeric adsorbent is particularly effective when adsorbed components are very soluble in the solvent and solvating force is much greater than the physical adsorptive force holding the adsorbate onto the resin. Most solvents are adsorbed by polymeric adsorbents and in many cases they penetrate the gel phase of the polymeric matrix. This results in the solvent displacement of the component adsorbed in the resin. In this study, IPA, ethanol, and methanol were used as a desorbate for amino acids.

In this study, the adsorption equilibrium of Phe and Trp onto SP850 was focused on the effect of pH and temperature. The isotherm data were fitted by Langmuir and Freundlich equations. In addition, the adsorption kinetic of Phe was also investigated at different initial concentrations. The kinetic data were then examined by employing the models of pseudo-first-order, pseudo-second-order and intraparticle diffusion. Finally, desorption of Phe adsorbed on SP850 was carried out with different kinds of alcohols such as IPA, ethanol and methanol.

EXPERIMENTAL

1. Materials

The nonionic polymeric adsorbent used, SP850 (Bizubishi Chemical Co., Japan), is macro reticular and spherical polystyrene resin cross-linked with divinyl benzene (DVB). The physical properties and chemical structure of SP850 are shown in Table 1 and Fig. 1. The water content of resin particles was determined from the weight loss of samples which was dried in a vacuum oven at 80 °C for 48 h. Prior to the experiments, the adsorbent was leached with isopropyl alcohol (IPA) to wet internal pores.

Phe and Trp were used as typical amphoteric compounds (Table

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Table 1. Properties of SP850

Properties	Values	Unit
Particle diameter	382	μm
Particle density	457	kg/m^3
Moisture content^a	52	%
Surface area^a	1,000	m^2/s
Average pore diameter^a	38.1	Å
Pore volume^a	0.59	ml/g

^{a}From the manufacturer's report

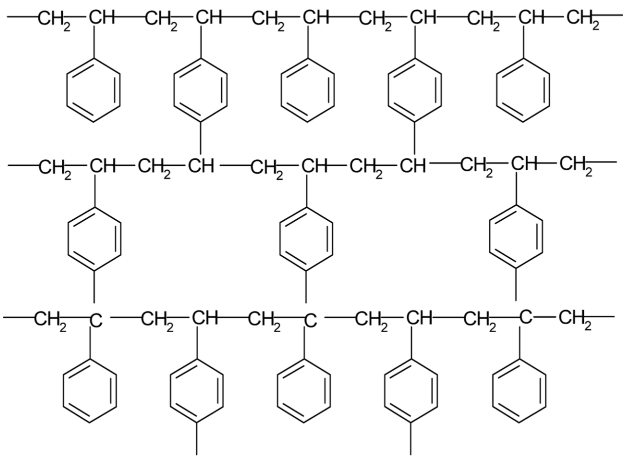
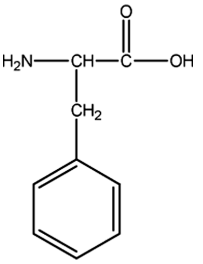
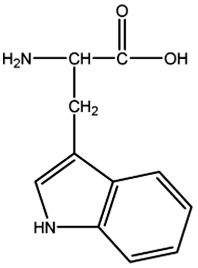


Fig. 1. Chemical structure of SP850.

Table 2. Properties of model compounds

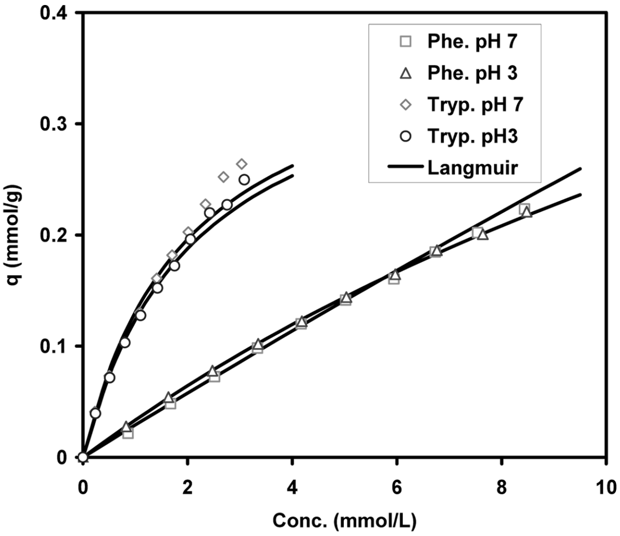
Compound	Chemical formula	Molar weight (MW)	pK$_a$	logP
Phenylalanine (Phe)		165.2	2.11	−1.43
$C_9H_{11}NO_2$			9.13	
Tryptophane (Trp)		204.23	2.43	−1.04
$C_{11}H_{12}N_2O_2$			9.44	

2). They exist both as anions and cations, depending on the solution of pH. Phe and Trp have isoelectric points of 5.5 and 5.9, respectively. IPA, ethanol and methanol were employed as organic desorbates in this study.

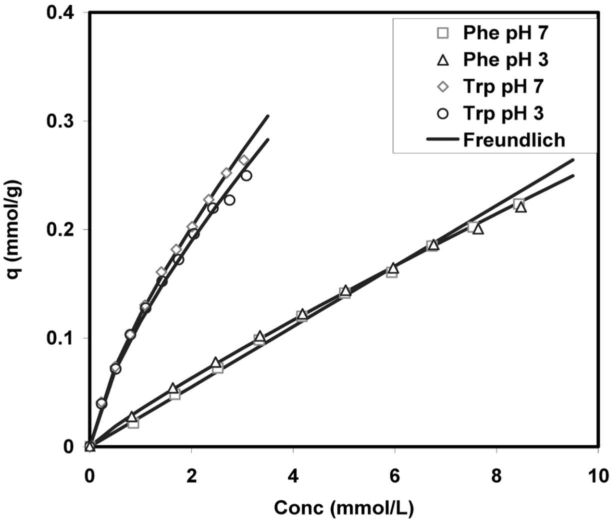
2. Methodology

Equilibrium experiments were carried out at different values of pH and temperatures. In the study on the effect of pH, a predetermined amount of adsorbent with adsorbate solution of 1-10 mmolL^{-1} for Phe and 0.5-5 mmolL^{-1} for Trp was allocated in an incubator and shaken at a constant temperature of 298.15 K for 24 hours. Similarly, when varying with different temperatures, the sample solutions were treated at pH 7 and shaken for 24 hours. After reaching the equilibrium, the excess of adsorbate left in the solution was analyzed by ultraviolet spectrometry. The adsorption capacity of resin was then evaluated from the material balance.

Dynamic adsorption and desorption experiments were conducted in a batch at room temperature of pH 7. The concentration of samples at different time intervals was analyzed using Shimadzu UV-1700. The effect of IPA, ethanol and methanol on desorption of Phe from SP850 was investigated at 298.15 K with the same 10% aqueous solution of alcohol. The desorption of Phe from SP850 was then performed using 5%, 10%, 20% aqueous solution of IPA to check the effect of concentration of IPA.



(a) Langmuir isotherm model



(b) Freundlich isotherm model

Fig. 2. Comparison of isotherm models for adsorption of Phe and Trp on SP850 in terms of pH at 298.15 K.

Table 3. Single-component adsorption isotherms used in this study

Name	Model equations	Parameters
Langmuir	$q=\frac{q_m bC}{1+bC}$	q_m, b
Freundlich	$q=k_F C^{1/n}$	k_F, n

RESULTS AND DISCUSSION

Adsorption isotherms play an important role in predicting modeling procedures for analysis and designing of adsorption systems. Adsorption onto synthesis sorbents is generally driven by the dispersed force between the adsorbate and the resin. Thus, the adsorption capacity depends on the property of the sorbents. Besides, the adsorption capacity is also influenced by other factors such as temperature and pH of the solution [Lee and Moon, 1999].

1. Effect of pH

Fig. 2 shows the adsorption isotherms for Phe and Trp on SP850 at 298.15 K and different pH (pH 3 and pH 7). As can be seen in Fig. 2 and Table 2, the adsorption capacity of Trp was higher than Phe due to their hydrophobicity. The hydrophobic character was measured by the octanol-water partition coefficient, P [Leo et al., 1971]. The higher value P means greater hydrophobicity. On the other hand, the effect of pH on the adsorption of Phe and Trp was marginal as the hydrophobic interactions with the adsorbent's surface were partially hindered by the neutral charges of amino acids [Grzegorczyk and Carta, 1996; Iskandarani and Pietrzyk, 1981]. The experimental data were fitted well with Langmuir and Freundlich isotherm equations (Table 3). The determined parameters of Langmuir and Freundlich isotherms are given in Table 4.

2. Effect of Temperature

Fig. 3 and Fig. 4 show the temperature effect on the adsorption of Phe and Trp on SP850. The experimental data of Phe adsorption were fitted well with both Langmuir and Freundlich equations. The Trp adsorption data matched the Freundlich equation better than the Langmuir equation at high concentration. It was found that the adsorption capacity and the Langmuir constant decreased with an increase in temperature for both of Phe and Trp [Diez et al., 1998; Grzegorczyk and Carta, 1996]. The magnitude of Langmuir constant is largely determined by the heat of adsorption. The values of b decreased, suggesting a low heat of adsorption with increasing temperature. The heat of adsorption was largest at 283.15 K in these

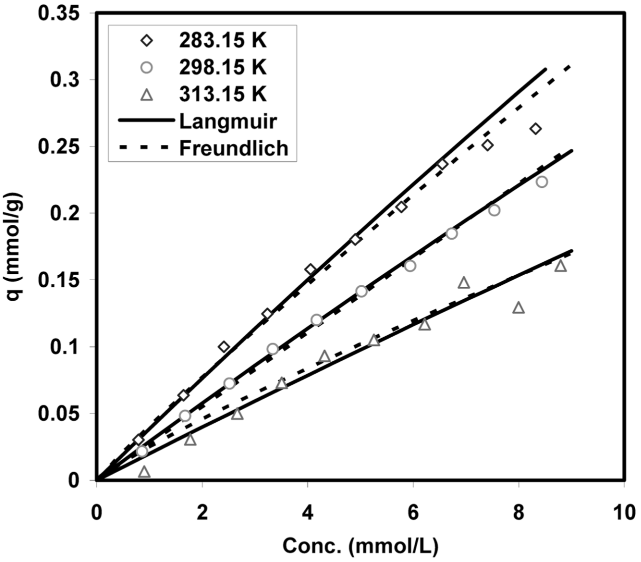


Fig. 3. Adsorption isotherm of Phe on SP850 at different temperatures.

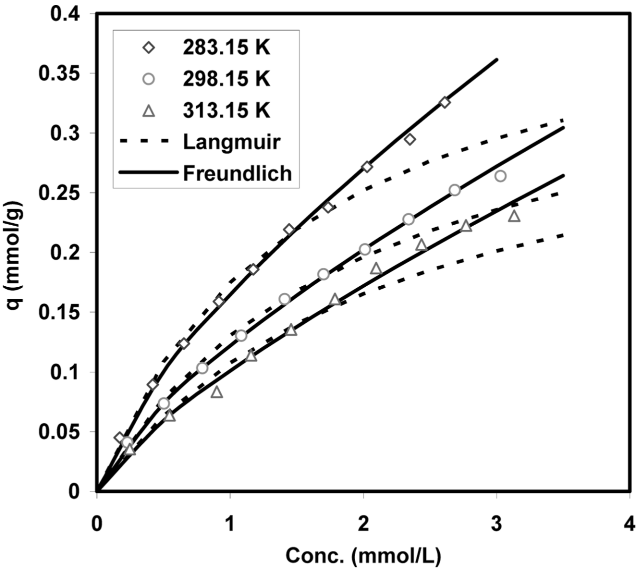


Fig. 4. Adsorption isotherm of Trp on SP850 at different temperatures.

Table 4. Adsorption isotherm parameters of Phe and Trp on SP850 at 298.15 K

Isotherm type			Langmuir			Fruendlich		
Adsorbate	pH	Temp. (K)	q_m	b	R^2	k_F	n	R^2
Phe	7	283.15	4.515	0.009	0.998	0.040	1.077	0.993
		298.15	3.877	0.008	0.999	0.032	1.092	0.995
		313.15	3.331	0.006	0.966	0.025	1.149	0.968
	3	298.15	0.813	0.043	1.000	0.034	1.135	0.999
Trp	7	283.15	0.630	0.454	0.996	0.164	1.396	0.999
		298.15	0.607	0.282	0.999	0.122	1.368	0.999
		313.15	0.553	0.183	0.997	0.101	1.301	0.994
	3	298.15	0.389	0.465	0.998	0.115	1.396	0.997

Table 5. Thermodynamic values of Phe and Trp adsorption on SP850

Amino acids	Temp. (K)	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	ΔS (J $mol^{-1}K^{-1}$)
Phe	283.15	−8.636	−5.108	−12.460
	298.15	−8.636	−4.921	−12.460
	313.15	−8.636	−4.734	−12.460
Trp	283.15	−22.315	−14.401	−27.948
	298.15	−22.315	−13.982	−27.948
	313.15	−22.315	−13.563	−27.948

cases, revealing strong adsorption at low temperature. According to Table 4, the adsorption rate (b) decreased with a rise of temperature with the decrease in k_F. The values of $0.1<1/n<1.0$ show that the adsorption of Phe and Trp on SP850 is favorable [Raji and Anirudhan, 1998; Kalavathy et al., 2005].

Temperature dependence is associated with various thermodynamic parameters. The Gibbs free energy (ΔG) is evaluated by Eq. (1) [Lee et al., 2004],

$$\Delta G = -RT \ln b \tag{1}$$

where, $R=8.314\ Jmol^{-1}K^{-1}$ is the gas constant. According to thermodynamic aspect, the change of Gibbs free energy is also related to the entropy change and heat adsorption at a constant temperature:

$$\Delta G = \Delta H - T\Delta S \tag{2}$$

From Eq. (1) and Eq. (2), the Van't Hoff equation is:

$$\ln b = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{3}$$

The enthalpy (ΔH) and entropy (ΔS) of adsorption were derived from the slope and intercept of the line from Eq. (3), respectively. The values of ΔG were obtained from Eq. (2) according to different temperatures. These values are reported in Table 5. As ΔG is negative, the adsorption of Phe and Trp on SP850 is considered to be spontaneous and thermodynamically favorable. The more negative values of ΔG imply a greater driving force to the adsorption process. An increase in temperature led to a decrease of ΔG and the spontaneity which could result in lower driving force and lesser adsorption capacity at higher temperature. The negative value of ΔH implies that the adsorption process is exothermic in nature [Kalavathy et al., 2005].

3. Adsorption Kinetics

The adsorption kinetic experiments were carried out at 298.15 K of pH 7. The kinetic data were analyzed with different kinetic models such as the pseudo-first-order, the pseudo-second-order and the intraparticle diffusion models [Ho and McKay, 1999; Hamadi et al., 2001; Sun and Yang, 2003; Kalavathy et al., 2005].

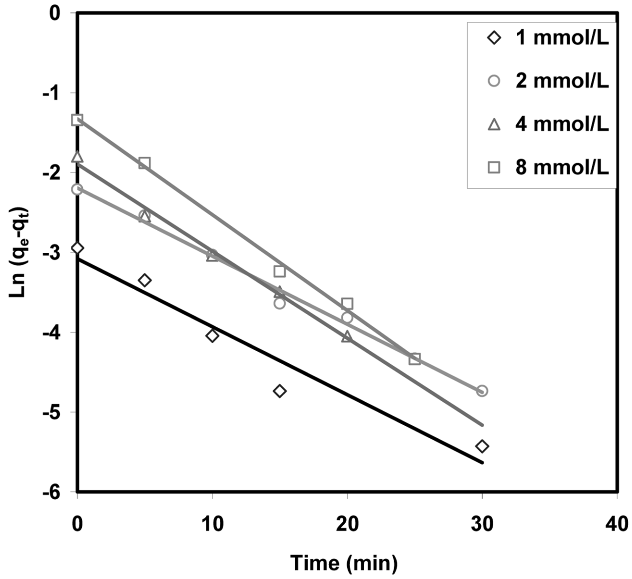


Fig. 5. Pseudo-first-order kinetic for adsorption of Phe on SP850 at pH 7 and 298.15 K.

4. The Pseudo-first-order Model

The kinetic data were treated with the pseudo-first-order model given by Kalavathy et al. [2005],

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

The first-order rate constant k_1 can be obtained from the plot of $\ln(q_e - q_t)$ versus time (Fig. 5). The values of predicted q_e (pre) and experimental q_e (exp) equilibrium capacity, the correlation coefficients R^2, and k_1 are shown in Table 6. An increase in initial concentration led to an increase in the adsorption capacity of Phe on SP850 and the value of k_1.

5. The Pseudo-second-order Model

The adsorption kinetic data were tested by using the pseudo-second-order model [Kalavathy et al., 2005; Ho et al., 1999]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \tag{5}$$

where k_2 (g $mmol^{-1}min^{-1}$) is the second-order rate constant determined from the plot of t/q_t versus t (Fig. 6 and Table 6). The second-order rate constants were used to calculate the initial sorption rate h:

$$h = k_2 q_e^2 \tag{6}$$

In this model, q_e (exp) matched very well with the predicted values,

Table 6. Adsorption rate constant for different initial concentrations of Phe

C_o (mmol/L)	q_e (Exp)	Pseudo-first-order				Pseudo-second-order				
		q_e (Pre)	k_1	R^2	E (%)	q_e (Pre)	k_2	R^2	h	E (%)
1	0.053	0.049	0.082	0.992	6.084	0.054	6.079	0.992	0.018	4.004
2	0.110	0.112	0.085	0.992		0.114	2.549	0.994	0.033	
4	0.165	0.142	0.102	0.995		0.172	1.987	0.997	0.059	
8	0.262	0.265	0.120	0.973		0.273	1.215	0.997	0.090	

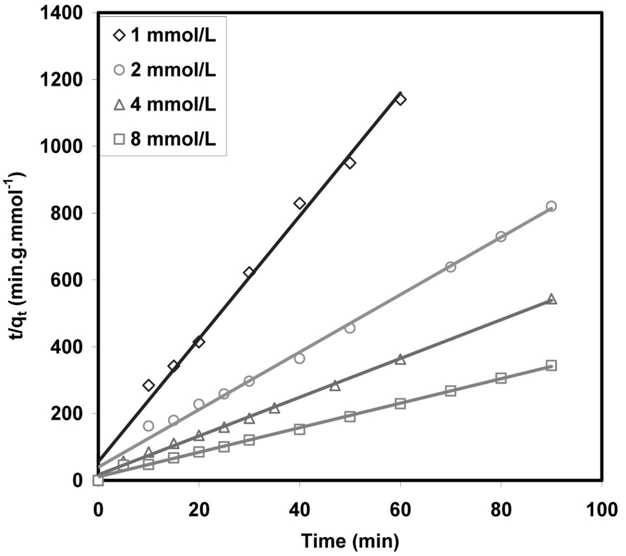


Fig. 6. Pseudo-second-order kinetic for adsorption of Phe on SP850 at pH 7 and 298.15 K.

q_e (pre). Thus, the initial sorption rate increased and the second-order rate constant decreased with an increased initial adsorbate concentration. In order to quantitatively apply the first-order and second-order models in fitting to data, a standard deviation, Δq, was calculated:

$$\Delta q(\%) = 100\sqrt{\frac{\sum[(q_{exp} - q_{cal})/q_{exp}]^2}{n-1}} \tag{7}$$

The standard deviation and regression coefficient showed that the experimental data followed the second-order model better than that of the first-order model (Table 6). We found that adsorption kinetics of Phe obeys the pseudo-second-order model.

6. The Intraparticle Diffusion Model

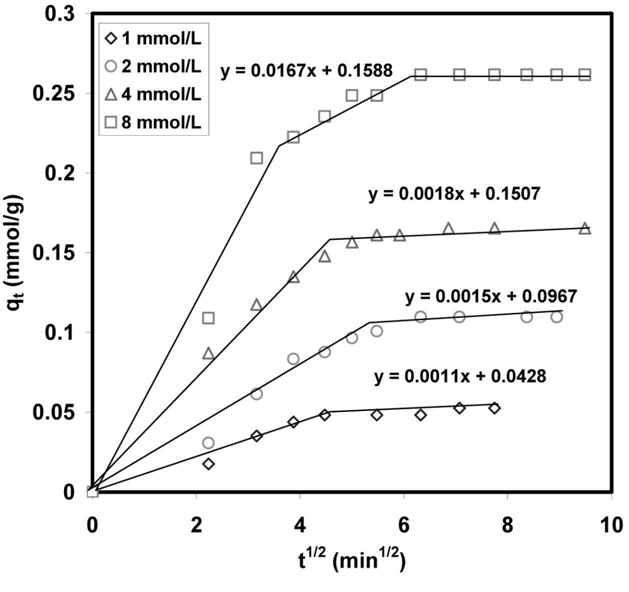


Fig. 7. Intraparticle diffusion plot for the adsorption of Phe on SP850.

Table 7. Intraparticle diffusion rate parameter and effective diffusion coefficient at different initial concentrations of Phe

C_o (mmolL^{-1})	$k_{id}\times 10^{-3}$ (mmolg^{-1}min$^{-1/2}$)	$D_{eff}\times 10^{-11}$ (m^{2}s^{-1})
1	1.1	0.424
2	1.5	0.486
4	1.8	0.562
8	16.7	0.695

In addition to analyzing the kinetic adsorption by the pseudo-first-order and the pseudo-second-order models, it was analyzed by the intraparticle diffusion model obtained from the assumption that all the resins are spherical, with uniform size and density. The relationship between the adsorption capacity q_t at time t and $t^{1/2}$ is shown by Al-Ghouti et al. [2005] and Kalavathy et al. [2005]:

$$q_t = x_i + k_{id}t^{1/2} \tag{8}$$

where k_{id} is the intraparticle diffusion constant (mmolg^{-1}min$^{-1/2}$) and x_i is the intercept of the line which is proportional to the boundary layer thickness. Fig. 7 shows a plot of q_t versus $t^{1/2}$. There are two or more regions in the plot, which indicates that two or more steps occur in the adsorption processes. The initial region relates to the film diffusion (i.e., the external surface adsorption). The second one suggests the intraparticle diffusion. In the third region, the intraparticle diffusion starts to slow down due to the extremely low adsorbate concentration [Sun and Yang, 2003]. The values of k_{id} were obtained from the slop of the second region of the plot (Fig. 7 and Table 7). With an increase in the initial concentration of adsorbate, the value of k_{id} increased rapidly. In addition, the larger intercept of the plot reflects the boundary layer diffusion effect.

On the other hand, the intraparticle diffusion coefficient (D_{eff}) derived from Fick's law, was given by

$$F = \frac{q_t}{q_e} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{\exp(-n^2B_t)}{n^2} \tag{9}$$

$$B_t = \frac{\pi^2 D_{eff}}{r^2} \tag{10}$$

where D_{eff} (m^{2}s^{-1}) is the effective diffusion coefficient and r (m) is the particle radius. At sufficiently high values of F, only one term of the series represented by Eq. (11) needs to be used [Reichenberg, 1952]:

$$F = \frac{q_t}{q_e} = 1 - \frac{6}{\pi^2}\exp(-B_t) \tag{11}$$

For the lower range of values of F, Eq. (9) may be transformed:

$$F = \frac{6}{\pi^{3/2}}\sqrt{B_t} - \frac{3}{\pi^2}B_t \tag{12}$$

According to Reichenberg, Eq. (12) was used for values of F from 0 to 0.85 and Eq. (11) for values from 0.86 to 1. The values of B_t were then plotted against the experimental values of time, based on the values of F (Fig. 8). The determined values of D_{eff} are listed in Table 7. The values were in the range of 0.424-0.695×10^{-11} m^{2}s^{-1}. As increasing in the concentration of adsorbate, the effective diffusion coefficient D_{eff} increased.

7. Desorption

Fig. 9 indicates the desorption breakthrough curves to examine

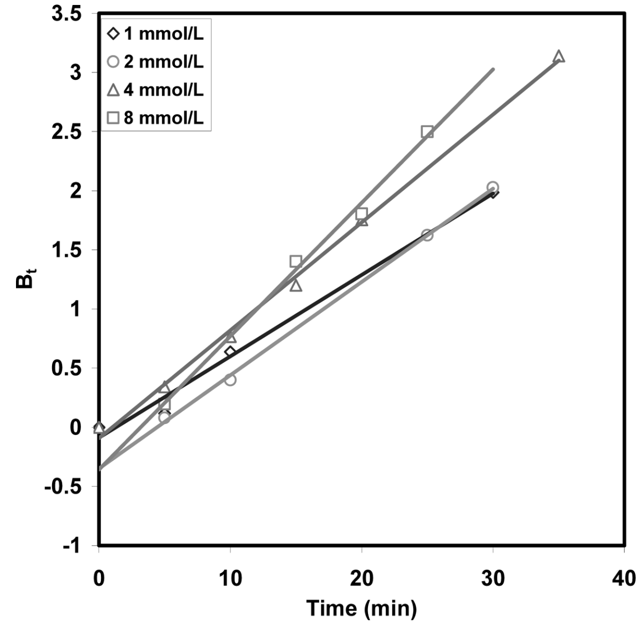


Fig. 8. B_t versus t plot for the adsorption of Phe on SP850.

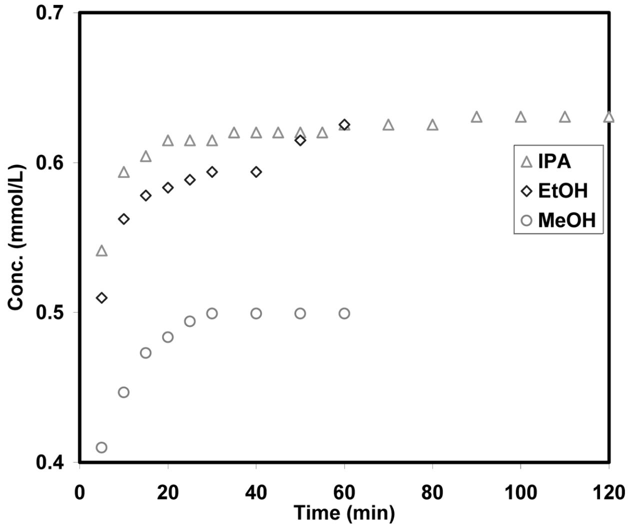


Fig. 9. Effect of alcohols on desorption of Phe on SP850 at pH 7 and 298.15 K.

the effect of IPA, ethanol and methanol on the desorption of Phe from SP850 at 298.15 K with the 10% aqueous solution of alcohol. As can be seen in Fig. 9, IPA is the best material to replace amino acids. The effect of IPA on desorption is better than that of ethanol and methanol because the adsorption affinity of IPA is very high.

In case of IPA, it was observed that desorption occurs more quickly when the concentration in the regeneration solution increases. Fig. 10 shows that the higher the concentration of IPA, the better removal efficiency was. However, the IPA concentration should be less than 20% to prevent the breakage of the structure of amino acids. Furthermore, an excess amount of IPA may present problems in further separation of amino acids from the mixture [Lee et al., 1997]. If the excess amount of IPA does not cause any trouble in the further process to separate amino acids from the mixture with IPA, a higher concentration of IPA can be used to perform the regeneration step more effectively.

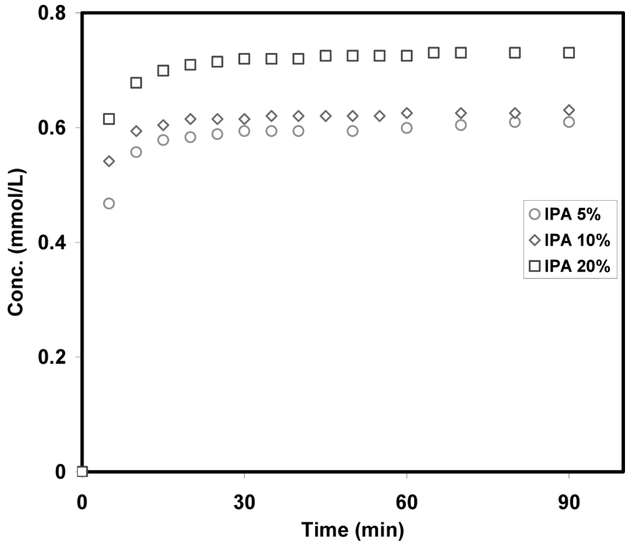


Fig. 10. Effect of IPA concentration on desorption of Phe on SP850 at pH 7 and 298.15.K.

CONCLUSIONS

As a separation and purification method for amino acids dissolved in aqueous solutions, the adsorption and desorption behaviors of amino acids on a nonionic polymeric adsorbent, SP850, were investigated in batch experiment under various operating conditions such as pH, temperature and concentration. Contrary to our expectation, the effect of pH to adsorption capacity was insignificant for both of Phe and Trp. The pure component adsorption equilibrium data of amino acids were fitted well with Langmuir and Freundlich equations. It was found that the adsorption capacity and the Langmuir constant decreased with an increase in temperature. Furthermore, the values of ΔG and ΔH were obtained from Van't Hoff equation indicated that adsorption is more spontaneous and exothermic when decreasing in temperature. Adsorption kinetic followed the pseudo-second-order model better than pseudo-first-order model in all cases. On the other hand, the desorption of amino acids from the resin using IPA, ethanol, and methanol was investigated. IPA was more effective than ethanol and methanol due to its higher affinity to a nonionic polymeric sorbent.

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REFERENCES

Al-Ghouti, M., Khraisheh, M. A. M., Ahmad, M. N. M. and Allen, S., "Thermodynamic behaviour and the effect of temperature on the removal of dyes from aqueous solution using modified diatomite: A kinetic study," *Journal of Colloid and Interface Science*, **287**, 6 (2005).

Diez, S., Leitgo, A., Ferreira, L. and Rodrigues, A., "Adsorption of phenylalanine onto polymeric resins: equilibrium, kinetics and operation of a parametric pumping unit," *Separation and Purification Technology*, **13**, 25 (1998).

Doulia, D., Rigas, F. and Gimouhopoulos, C., "Removal of amino acids from water by adsorption on polystyrene resins," *J. Chem. Technol. Biotechnol.*, **76**, 83 (2001).

Dutta, M., Baruah, R. and Dutta, N. N., "Adsorption of 6-aminopenicillanic acid on activated carbon," *Separation and Purification Technology*, **12**, 99 (1997).

Grzegorczyk, D. S. and Carta, G., "Adsorption of amino acids on porous polymeric adsorbents - I. Equilibrium," *Chemical Engineering Science*, **51**(5), 807 (1996).

Hamadi, N. K., Chen, X. D., Farid, M. M. and Lu, M. G. Q., "Adsorption kinetics for the removal of chromium(VI) from aqueous solution by adsorbents derived from used tyres and sawdust," *Chemical Engineering Journal*, **84**, 95 (2001).

Ho, Y. S. and McKay, G., "A kinetic study of dye sorption by biosorbent waste product pith," *Resources, Conservation and Recycling*, **25**, 171 (1999).

Iskandaranl, L. and Pietrzyk, D. J., "Liquid chromatographic separation of amino acids, peptides, and derivatives on a porous polystyrene-divinylbenzene copolymer," *Anal. Chem.*, **53**, 489 (1981).

Kalavathy, M. H., Karthikeyan, T., Rajgopal, S. and Miranda, L. R., "Kinetic and isotherm studies of Cu(II) adsorption onto H_3PO_4 - activated rubber wood sawdust," *Journal of Colloid and Interface Science*, **292**, 354 (2005).

Kubota, L. T., Gambero, A., Santos, A. S. and Granjeiro, J. M., "Study of the adsorption of some amino acids by silica chemically modified with aminobenzenesulfonic and phosphate groups," *Journal of Colloid and Interface Science*, **183**, 453 (1996).

Lee, J. W. and Moon, H., "Effect of pH on adsorption of cephalosporin C by a nonionic polymeric sorbent," *Adsorption*, **5**, 381 (1999).

Lee, J. W., Park, H. C. and Moon, H., "Adsorption and desorption of cephalosporin C on nonionic polymeric sorbents," *Separation and Purification Technology*, **12**, 1 (1997).

Lee, J. W., Shim, W. G., Yang, W. C. and Moon, H., "Adsorption equilibrium of amino acids and antibiotics on non-ionic polymeric sorbents," *J. Chem. Technol. Biotechnol.*, **79**, 413 (2004).

Leo, A., Hansch, C. and Elkins, D., "Partition coefficients and their uses," *Chemical Reviews*, **71**, 6 (1971).

Melis, S., Markos, J. and Cao, G., "Ion-exchange equilibria of amino acids on a strong acid resin," *Ind. Eng. Chem. Res.*, **35**, 1912 (1996).

Raji, C. and Anirudhan, T. S., "Batch Cr(VI) removal by polyacrylamide-grafted sawdust: kinetics and thermodynamics," *Wat. Res.*, **32**(12), 3772 (1998).

Ramos, A. M., Otero, M. and Rodrigues, A. E., "Recovery of vitamin B12 and cephalosporin-C from aqueous solutions by adsorption on non-ionic polymeric adsorbents," *Separation and Purification Technology*, **38**, 85 (2004).

Reichenberg, D., "Properties of ion-exchange resins in relation to their structure. III. Kinetics of exchange," *J. Am. Soc.*, **75**, 589 (1953).

Sun, Q. and Yang, L., "The adsorption of basic dyes from aqueous solution on modified peat-resin particle," *Water Research*, **37**, 1535 (2003).

Titus, E., Kalkar, A. K. and Gaikar, V. G., "Equilibrium studies of adsorption of amino acids on NaZSM-5 zeolite," *Colloids and Surfaces, A: Physicochem. Eng. Aspects*, **223**, 55 (2003).

Vinu, A., Hossain, K. Z., Kumar, G. S. and Ariga, K., "Adsorption of L-histidine over mesoporous carbon molecular sieves," *Carbon*, **44**, 530 (2006).

Yang, W. C., Shim, W. G., Lee, J. W. and Moon, H., "Adsorption and desorption dynamics of amino acids in a nonionic polymeric sorbent XAD-16 column," *Korean J. Chem. Eng.*, **20**, 922 (2003).