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Fixed-bed Adsorption of Food-Related Phenolic Acids on Charcoal in Single Solute System

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Abstract

Fixed-bed adsorption was adapted to separate phenolic acids from diluted phenolic solution. Break-through curve was obtained by nonlinear curve fitting method, and breakpoint, saturation time, and mass transfer coeffi-cient were calculated. Break point and saturation time were reached slower with *p*-coumaric acid than ferulic acid. The *p*-coumaric acid, having small molecular weight, is supposedly traveled longer pathway in charcoal than ferulic acid. Fixed-bed adsorption with gallic acid having more hydroxyl functional group than other phenolic acids showed slowest break point arrival and the largest saturation time. This fact means that there was bigger electrostatic affinity between gallic acid and charcoal than between other phenolic acids and charcoal.

Key words: phenolic acid, fixed-bed adsorption, breakthrough curve, mass transfer, nonlinear curve fitting

INTRODUCTION

Phenolic compounds presented in many plants are directly related to the characteristics of food such as taste, palatability, nutritional value, toxic effects, and microbial decomposition (1-4). The presence of phenolic compounds in tap water causes increases of COD and BOD, and/or the formation of chlorophenol, a toxic compound, which causes bad odor and vomiting (5). Nowadays, many researchers are interested in these compounds because of their abilities of recovering or removing metal ions (6-9) and their effects of anti-cancer, anti-mutation and of inhibition against binding between HIV and CD4 proteins (10,11). Therefore, these phenolic compounds are needed to be removed or recovered as harmful or useful materials.

The adsorption process is one of the efficient separation processes to separate these compounds in water. Fixed-bed adsorption has been an important unit operation for purification and separation of gas or liquid mixtures.

Adsorption of single solute phenolic acids in fixed-bed was studied using a model system. In order to compose the model system, *p*-coumaric acid, gallic acid, and ferulic acid were selected as phenolic compounds, which are widely distributed in plant-food materials.

In fixed-bed adsorption, break-point time and saturation time are very important parameters to decide the changing time of the adsorbent or the stopping time for adsorption.

Therefore, the objective of this study is to investigate the adsorption properties such as breakthrough curve, saturation time, and mass transfer coefficient with the changes of time and bed length (12). These results can be used as back-ground data to design a fixed-bed adsorption process.

MATERIALS AND METHODS

Preparation of adsorbent

According to the method of Lee et al., (13), charcoal was screened to 16~20 mesh, boiled for 4 hours, washed 5 times with deionized water, and then dried for 48 hours at 105°C. The charcoal was kept in a desiccator to prevent adsorption of moisture from air.

Reagents

Phenolic acids, which are basic materials in phenolic compounds, were used as adsorbates. *p*-Coumaric acid, gallic acid and ferulic acid, which are distributed widely in plant food materials such as chestnut, peanut, persimmon, etc., were selected in model system. The selected phenolic acids had over 99% purity. Acetonitrile

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and bis-trimethylsilic acetamide and acetonitrile were used for TMS (trimethylsilylation) and p-hydorxy benzoic acid was used as an internal standard in analysing phenolic acids. All reagents were purchased from Sigma (Sigma Co. St. Louis, Mo, USA).

Physical properties of charcoal

Specific surface area of charcoal was measured by N_2 gas adsorption method (Accusorb 2100E, Micrometrics Co., U.S.A). Charcoal was put in a flask for 24 hours under vacuum at 100~120°C before measuring specific surface area. After weighing the sample flask, adsorption and desorption were conducted by increasing relative pressure of saturated N_2 vapor pressure at 77.4 KPa. Porosimeter (Poresize 9320, Micrometrics Co., USA) was used to measure other physical properties of charcoal such as total pore area, average pore diameter, bulk density, apparent density, and porosity.

Analysis of phenolic acids

Phenolic acids were analyzed by the method of Hobert and Senter (14). Phenolic acids in 10 ml effluent solution were re-extracted with ethyl acetate and 5 ml re-extracts were dried under vacuum. The dried phenolic acids were dissolved in 100 μl acetonitrile and added with 50 μl BSA (N,O-bis-trimethysilyl acetamide) reagent and 25 μl p-hydroxy benzoic acid as internal standard. After TMS (trimethylsilylation) for 5 minutes at 90°C, the phenolic acids of the sample were analyzed by gas chromatography (Pye Unicam Series 304, Philips, England) equipped with a flame ionization detector. Glass column packed with SE-30 (Shimadzu Co., Japan) was 4 mm I. D. and 1.5 m length and SE-30 was 60~80 mesh. The oven temperature was programmed from 180°C to 240°C, with increasing 2°C/min. The injector and detector temperatures were 260°C and 270°C, respectively. The flow rate of N_2 carrier gas was 30 ml/min.

Experimental apparatus for adsorption

The adsorption apparatus (Fig. 1) had a storage tank with a by-pass to maintain constant hydrostatic pressure. Overflow solution was recycled to storage tank by a circulation pump. Water was circulated into jacket glass columns of fixed-bed to keep temperature constant at 25°C. Discharge amount of fluid was fixed to 10 ml/min. The changes of discharging fluid depending on bed length were controlled with storage tank height. The adsorption column was 50 cm (height) × 0.6 cm (inner diameter) in size.

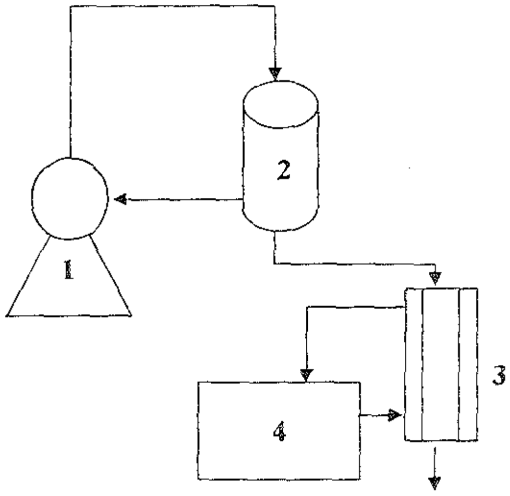

Fig. 1. Schematic diagram for adsorption in fixed-bed.
1. Circulation pump 2. Storage tank
3. Fixed-bed 4. Water bath

Rate of mass transfer

Equations for mass transfer in fixed-bed adsorption are obtained by making a solute material balance for a section dL of the bed in Fig. 2. The change in superficial velocity is neglected. Material balance was followed (12).

$$\varepsilon dL\frac{\partial C}{\partial t}+(1-\varepsilon)dL\rho_p\frac{\partial W}{\partial t}=u_oC-u_o(C+dc)$$

The term ε is the external void fraction of bed, and solute dissolved in the pore fluid is included with the particle fraction $1-\varepsilon$. Superficial velocity of fluid is u_0. The concentration C^* is the value that would be in equilibrium with average concentration W in the solid.

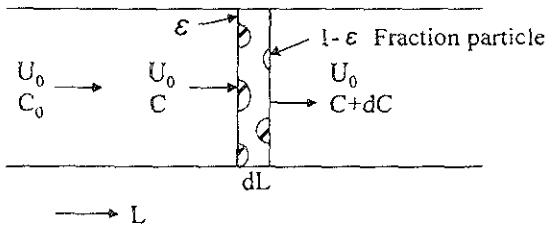

Fig. 2. Schematic diagram for mass balance in a section of a fixed-bed.
C: concentration of adsorbate in fluid
C_0: initial concentration of fluid
ε: external void fraction of bed
K_c: overall mass-transfer coefficient
L: total bed length

Neglect accumulated amounts in external void fraction.

$$\rho_p(1-\varepsilon)\frac{\partial W}{\partial t}=-u_0\frac{\partial C}{\partial L}=K_c a(C-C^*) \qquad (1)$$

The initial shape of the concentration profile is obtained by integration of Eq. 1

$$\ln\frac{C}{C_0}=-\frac{K_c aL}{u_0} \qquad (2)$$

The saturation time of the first portion of the bed, t_1 is the value of equilibrium capacity divided by the initial transfer rate.

$$t_1=\frac{W_{sat}\rho_p(1-\varepsilon)}{K_c aC_0} \qquad (3)$$

The terms that are not mentioned in the above equations are as follows:

a: external surface area pre unit volume
C: concentration of adsorbate in fluid
C_0: initial concentration of fluid
C^*: concentration of adsorbate in fluid in equilibrium with concentration is solid
ε: external void fraction of bed
$1-\varepsilon$: particle fraction
K_c: overall mass-transfer coefficient
L: total bed length
M: molecular weight
ρ_p: density of particle
t: time
u_0: superficial velocity
W: adsorbate loading
W_{sat}: adsorbate loading at equilibrium with the fluid

RESULTS AND DISCUSSION

Physical properties of charcoal

Nitrogen gas and mercury were commonly used as adsorbates in measuring physical properties of the adsorbent. The porosity of charcoal as measured using mercury was 26.02% which was the most effective factor in adsorption and the bulk density which was used to calculate breakthrough point was 0.81 g/ml. Other physical properties were presented in Table 1.

Monolayer adsorption and desorption curve using nitrogen gas as adsorbate were shown at Fig. 3. The charcoal used in this study was so porous that it had favorable or strongly favorable adsorption characteristic. Hysterisis like a crescent moon shape happened between adsorption and desorption curves, which means there is a little difference between amounts of adsorption and desorption because of little ink bottle phenomena. Ink bottle phenomena means that the exit size of pore on charcoal too narrow to desorb adsorbates. BET specific surface area calculated from nitrogen gas adsorption and desorption was 1,040 m^2/g cat.

Table 1. Physical properties of charcoal carbon as measured using porosimeter

Parameter	Value
Total intrusion volume	0.32 ml/g
Total pore area	25.22 m^2/g
Average pore diameter	490 Å
Median pore diameter	97 Å
Apparent(skeletal) density	1.09 g/ml
Bulk density	0.81 g/ml
Porosity	26.02 %

Breakthrough curve in single solute system

Breakthrough curve is generally used in explaining the relationship between adsorbate concentration and time for fluid leaving the bed. At starting point of adsorption, exit concentration is practically zero. When the concentration of adsorbate on adsorbent reaches some limiting value or break point, the flow is stopped or diverted into a fresh adsorbent bed. The break point is often taken as a relative exit concentration of C/C_0=0.05 or 0.10. If adsorption continued beyond the break-point, the concentration would rise rapidly to about C/C_0=0.5 and then slowly approach to C/C_0=1.0.

When feed fluid streams plug flow in a ideal adsorption without axial dispersion and vertical dispersion, breakthrough curve is S-shaped curve and it is nearly symmetrical at C/C_0=0.5. But it is hard to find symmetrical curve in real situation.

Breakthrough curve was obtained by nonlinear curve

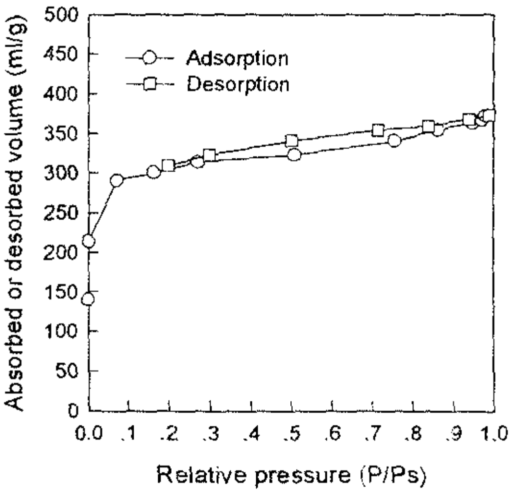

Fig. 3. Adsorption and desorption isotherm of N_2 on charcoal.

fitting method. In order to know breakthrough curve changes which depend on variation of fixed-bed length, adsorption experiments were conducted at 7 cm, 14 cm, and 21 cm bed length, then exit flow rate was maintained at 10 cm^3/min. Phenolic acids at 100 ppm concentration were fed from top toward bottom of the column.

Mass-transfer coefficient can be calculated from the equation (2). Saturation time was estimated from predicted breaktrough curve because it passed too fast to be detected at saturation point. Saturation time and break-point time were decided at $C/C_0=1$ and $C/C_0=0.05$, respectively from the equation (3). Break-point was commonly decided at $C/C_0=0.05$ in fixed-bed adsorption process.

Fig. 4 shows the breakthrough curve of *p*-coumaric acid. Eluent concentration was increased with time and changed moderately with bed length. These trends were commonly found in gallic and ferulic acid adsorption in Fig. 5 and 6. Prediction lines of *p*-coumaric acid had over 0.96 correlation coefficients. Gallic and ferulic acid had over 0.92 and 0.74, respectively. Eluent concentration changes of ferulic acid was so rapid to detect in short bed length that correlation coefficient showed poor value. The shapes of prediction lines for phenolic acids adsorption showed almost straight line in 7 cm-bed length but changed close to log curve in longer bed length. As increasing the bed length, the first elution time of phenolic acids was more late. These shapes of breakthrough curves and the late first elution time depending on increasing bed length are found commonly in fixed-bed adsorption process (15).

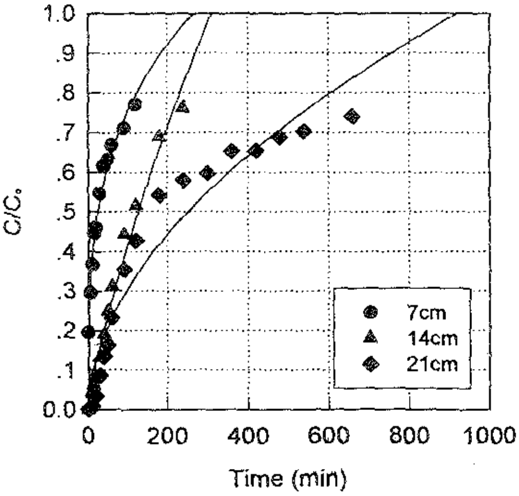

Fig. 4. Breakthrough curve fitting of *p*-coumaric acid at various bed length.
C: concentration of adsorbate in fluid
C_0: initial concentration of fluid

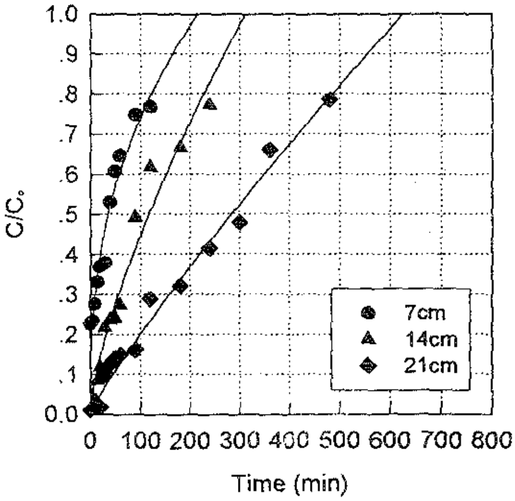

Fig. 5. Breakthrough curve fitting of gallic acid at various bed length.
C: concentration of adsorbate in fluid
C_0: initial concentration of fluid

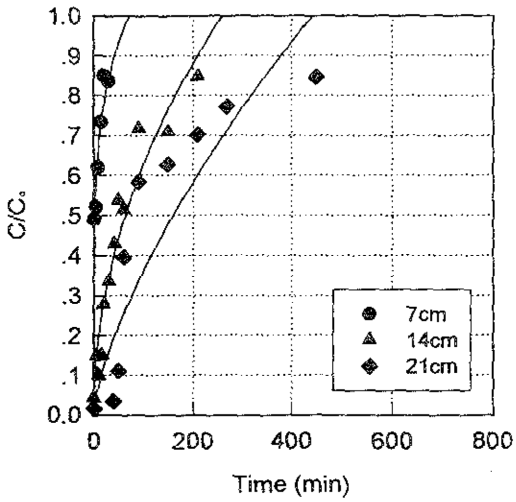

Fig. 6. Breakthrough curve fitting of ferulic acid at various bed length.
C: concentration of adsorbate in fluid
C_0: initial concentration of fluid

Saturation time, break-point time, and mass transfer coefficient are shown in Table 2. Ferulic acid showed the fastest saturation, break point time, and the highest mass transfer coefficient among the tested phenolic acids. *p*-Coumaric acid ranked next to ferulic acid and gallic acid was the last. These results were caused by the molecular weight and electric affinity of the molecule. *p*-Coumaric and ferulic acid, having the same number of hydoxyl functional group, had the same electric affinity on charcoal, however *p*-coumaric acid had slower break point and saturation time than ferulic acid.

The reason was that *p*-coumaric acid, having a small

Table 2. Values of t_1, break point and K_c calculated by regression equation in single solute system

Phenolic acid	Bed height (cm)	Value (min)		Overall mass	
		t_1	Break point ($C/C_0=0.05$)	K_c ($C/C_0=0.5$)	K_c ($C/C_0=1$)
p-Coumaric acid	7	2.65E+2	8.48E-3	2.75E-5	3.62E-8
	14	3.09E+2	3.28E+0	5.30E-6	3.18E-8
	21	9.22E+2	6.31E+0	2.66E-6	1.04E-8
Gallic acid	7	2.16E+2	9.78E-2	1.83E-5	4.45E-8
	14	3.11E+2	4.54E+0	5.68E-6	3.08E-8
	21	6.26E+2	20.5E+0	2.35E-6	1.54E-8
Ferulic acid	7	7.11E+1	2.06E+5	3.05E-4	1.35E-7
	14	2.60E+2	5.71E-1	1.05E-5	3.70E-8
	21	4.43E+2	5.46E+0	4.16E-6	2.17E-8

t_1 : staturation time C_0 : initial concentration of adsorbate
C : concentration of adsorbate K_c : mass transfer coefficient

molecular weight, traveled longer pathway into charcoal than ferulic acid. Gallic acid having more hydroxyl funtional group than other phenolic acids showed longest break point and saturation time. It means that there is bigger electric affinity between gallic acid and charcoal than between other phenolic acids and charcoal. The results discussed above can be explained from the study of Streat et al. (16) who mentioned adsorbates of different molecular size will be sorbed to varying extent depending on the availability of pores of appropriate size and the study of Kim (17) who mentioned the affinity of adsorbates on charcoal.

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