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Inferring the favorable adsorption level and the concurrent multi-stage process with the Freundlich constant

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Abstract

This paper proposes a method for inferring a favorable level for the adsorption isotherm curve with the Freundlich constant ($1/n$), explains that a favorable level is only a function of $1/n$, and then, five favorable levels are classified according to $1/n$ value. The adsorbent consumption ratio of the concurrent multi-stage to single-stage system was deduced in order to investigate the relationship between favorable level and the most suitable number of stages. Activated carbon (TGBAC) was prepared from Taiwan Giant Bamboo with steam activation. The isotherm equilibrium of the adsorption of three phenols (phenol, 3-CP, and 4-CP), two dyes (MB and BB 69), and tannic acid on TGBAC was obtained. According to the Freundlich constant ($1/n$), the adsorption of MB was inferred in a strongly favorable zone. The favorable zone for BB69, phenol, 3-CP, and 4-CP was determined. The tannic acid, the pseudo-linear zone and their most suitable number of stages were also determined. The $1/n$ values and favorable levels summarized from more than a hundred sources/studies indicate that the favorable levels of the adsorption of dyes and phenols on TGBAC are excellent. This paper proposes a simple method for inferring the favorable level and the most suitable number of stages for the concurrent multi-stage adsorption system.
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Keywords: Activated carbon; Multi-stage; Adsorption process; Freundlich equation; Favorable level

1. Introduction

The Freundlich equation has been described in several publications. Crittenden et al. adopted H. Freundlich, 1906 [1] and Suzuki adopted H. Freundlich, 1926 [2]. Although the name of the author in these two books was the same, H. Freundlich, were published 20 years apart. Salame and Bandosz adopted a different name, Z. F. Freunlich, 1907 [3]. These three books describe the same equation, but the publication date and name of the author are different. This equation has been used for a hundred years, but, at the same time, was subjected to many descriptions and questions, such as: (1) according to its exponential equation description, the amount of adsorbent would be infinite at an infinite concentration of adsorbate [4]. (2) It is believed that it does not meet the requirements of Henry's law at all at low concentration ranges, thus it is just suitable for medium and high concentration ranges [5]. (3) It is believed that it is not suitable

for describing wide adsorption ranges [4], and only suitable for the adsorption data of certain limited concentration ranges [5]. (4) It is believed that the assumption of heterogeneous surface on different adsorption sites with different energy of adsorption is impossible to obtain [6]. In spite of the above criticisms, the Freundlich equation is still one of the most used adsorption isotherm equilibriums and it is widely employed in adsorption engineering [2,5].

Some description of the Freundlich constant, $1/n$ reads "The expression is characterized by the heterogeneity factor, $1/n$ (Al-Duri and McKay, 1988; Moon and Lee, 1983)" [4]. "Mathematically it is characterized by the heterogeneity factor '$1/n$'" [6]. "$1/n$ (dimensionless) is the empirical parameter that represents the heterogeneity of the site energies" [3]. "$1/n$ is the Freundlich adsorption intensity parameter" [1]. The above descriptions reveal that $1/n$ can represent the heterogeneity factor, the heterogeneity of site energies, and the adsorption intensity. Though many studies suggest that "If adsorption is favorable, then $1/n < 1$", formally inferring the favorable level for an isotherm curve with the Freundlich constant, $1/n$, of the adsorption system has not been discussed.

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In this study, concurrent multi-stage adsorption system was analyzed using the Freundlich equation to determine the effect of the Freundlich constant $(1/n)$ in adsorbent consumption of a concurrent multi-stage adsorption system and to infer the favorable level and the most suitable number of stages. The isotherm equilibrium adsorptions of three phenols (phenol, 3-CP, and 4-CP), two dyes (MB and BB 69), and tannic acid on steam-activated Taiwan Giant Bamboo activated carbon (TGBAC) were studied to determine the favorable adsorption level and the most suitable number of stages according to the Freundlich constant $(1/n)$ and prove that TGBAC has a good adsorption capacity and a favorable level. Simple methods for inferring the favorable level and the most suitable number of stages are given.

2. Theory

2.1. Concurrent multi-stage adsorption process

Concurrent multi-stage adsorption is a combination of J batch in a stirred tank series. Its operation is shown in Fig. 1. The starting solution with mass m_{yi} (kg$_{solution}$) and concentration y_i (kg$_{solute}$/kg$_{solution}$) enters the first stirred tank and is stirred with an adsorbent mass m_{x1} (kg$_{adsorbent}$) and solute concentration x_0 (kg$_{solute}$/kg$_{adsorbent}$). It is stirred to reach equilibrium, and then separated. After separation, the solution with mass m_{y1} and concentration y_1 enters the second tank and after stirring it is separated again with an adsorbent mass m_{x2} and concentration mass x_0, and so on. The solution concentration leaving the Jth stirred tank is y_J, i.e., the final solution concentration is y_{fo}.

Suppose the solution mass in all the tanks is the same, then

$$m_y = m_{yi} = m_{y1} = m_{y2} = \ldots m_{y_{J-1}} = m_{y_f} \tag{1}$$

When any stage j ($j = 1, 2, 3, \ldots, J$) in the concurrent multi-stage adsorption process is selected for solute mass equilibrium, we obtain

$$m_y(y_{j-1} - y_j) = m_{xj}(x_j - x_0) \tag{2}$$

When the adsorbent is fresh, $x_0 = 0$, and its operation line is

$$y_j = \left(\frac{-m_{xj}}{m_y}\right)x_j + y_{j-1} \tag{3}$$

its slope and intercept are, respectively, $(-m_{xj}/m_y)$ and y_{j-1}.

When the adsorption equilibrium is according to the Freundlich isotherm equation, then

$$q_e = K_F C_e^{1/n} \tag{4}$$

when, in Eq. (4), the solute concentration C_e (g$_{solute}$/m$^3_{solution}$) in solution is replaced with y_j and solute concentration (adsorption amount) q_e (g$_{solute}$/kg$_{adsorbent}$) in the solid phase (adsorbent) is replaced with x_j, the Freundlich constant K_F ((g$_{solute}$/kg$_{adsorbent}$) (g$_{solute}$/m$^3_{solution}$)^n) in solution is replaced with K'_F ((kg$_{solute}$/kg$_{adsorbent}$) (kg$_{solute}$/m$^3_{solution}$)^n), then, ρ is the solution mass per unit volume of the solution (kg$_{solution}$/m$^3_{solution}$). Then the isotherm equilibrium at jth stage is

$$x_j = K'_F \rho^{1/n} y_j^{1/n} \tag{5}$$

When Eqs. (3) and (5) are combined, the adsorbent consumption at the jth stage is obtained as the following equation

$$m_{xj} = \frac{m_y(y_{j-1} - y_j)}{(K'_F \rho^{1/n} y_j^{1/n})} \tag{6}$$

When the total stage number is 1, i.e., single-stage, its y_{j-1} is influent solution concentration y_i, y_j, the effluent solution concentration is y_f, and the adsorbent consumption is m_{xs}. Substituting these notations into Eq. (6) gives

$$m_{xs} = \frac{m_y(y_i - y_f)}{(K'_F \rho^{1/n} y_f^{1/n})} \tag{7}$$

The adsorption consumptions of stage 1 and stage 2 of the concurrent two-stage adsorption process are, respectively,

$$m_{x1} = \frac{m_y(y_i - y_1)}{(K'_F \rho^{1/n} y_1^{1/n})} \tag{8}$$

$$m_{x2} = \frac{m_y(y_1 - y_f)}{(K'_F \rho^{1/n} y_f^{1/n})} \tag{9}$$

When $m_{x1} = m_{x2} = 1/2 m_{xd}$, Eqs. (8) and (9) can be combined into

$$m_{xd} = \frac{2m_y(y_i - y_f)}{(K'_F \rho^{1/n} y_1^{1/n}) + (K'_F \rho^{1/n} y_f^{1/n})} \tag{10}$$

For comparing the adsorbent consumption of the concurrent two-stage adsorption system with that of a single-stage system, let the solution concentrations of both effluents be equal, and Eq. (7) is divided by Eq. (10), which gives

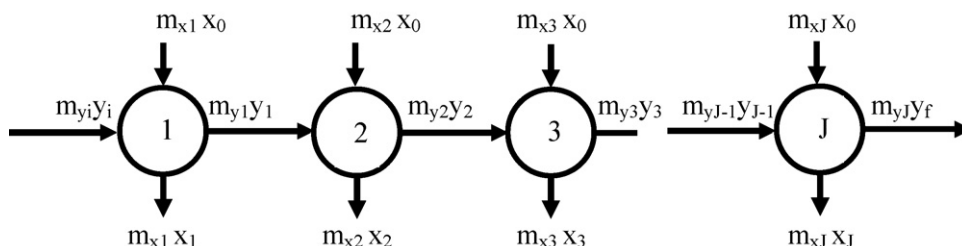$$\frac{m_{xs}}{m_{xd}} = \frac{(y_1^{1/n} + y_f^{1/n})}{2y_f^{1/n}} \tag{11}$$

Fig. 1. Concurrent multi-stage adsorption processes.

The middle solution concentration y_1 of the above two-stage system can be obtained by dividing Eq. (8) by Eq. (9) as shown in the following Eq. (12):

$$\frac{y_i - y_1}{y_1 - y_f} = \left(\frac{y_1}{y_f}\right)^{1/n} \tag{12}$$

Suppose $1/n$, solution influent and effluent concentrations y_i and y_f are known, then y_1 can be obtained by solving Eq. (12) using the numerical method. The y_1 value is then substituted into the equation to obtain the adsorbent consumption ratio, m_{xs}/m_{xd}, of a single-stage in the concurrent two-stage system.

Following the same steps, when $m_{xt} = 3m_{x1}$ and $m_{x1} = m_{x2} = m_{x3}$, the adsorbent consumption ratio, m_{xs}/m_{xt}, of both the single-stage and concurrent three-stage system can be expressed as

$$\frac{m_{xs}}{m_{xt}} = \frac{(y_1^{1/n} + y_2^{1/n} + y_f^{1/n})}{3y_f^{1/n}} \tag{13}$$

The middle concentration can be calculated from the following two equations

$$\frac{y_i - y_1}{y_1 - y_2} = \left(\frac{y_1}{y_2}\right)^{1/n} \tag{14}$$

$$\frac{y_i - y_1}{y_2 - y_f} = \left(\frac{y_1}{y_f}\right)^{1/n} \tag{15}$$

And so on, the adsorbent consumption ratio, m_{xs}/m_{xJ}, of the single-stage to the concurrent J-stage

$$\frac{m_{xs}}{m_{xJ}} = \frac{(y_1^{1/n} + y_2^{1/n} + \ldots + y_f^{1/n})}{Jy_f^{1/n}} \tag{16}$$

Assume solution concentration ratio (y_i/y_f), of influent to effluent is 100, and the adsorbent consumption ratios m_{xs}/m_{xd} and m_{xs}/m_{xt} are calculated according to Eqs. (11) and (13), and the results have been listed in Table 1. When the value of $1/n$ of adsorbent is 1, the adsorbent consumption of the single-stage system is 5.50 times that of the two-stage system, or 7.01 times that of the three-stage system; when $1/n$ is 0.1, the adsorbent consumption of the single-stage system is 1.23 times that of the two-stage system, or 1.30 times that of the three-stage system. This shows that when $1/n$ value is low, the saving in adsorbent consumption is not high; in contrast, when $1/n$ value is high,

Table 1
Adsorbent consumption ratio of single-stage to concurrent multi-stage process (at $y_i/y_f = 100$)

$1/n$	m_{xs}/m_{xd}	m_{xs}/m_{xt}	m_{xd}/m_{xt}	$m_{xs}/m_{x\infty}$	Zone
0.01	1.020	1.026	1.006	1.037	II
0.03	1.061	1.081	1.019	1.115	II
0.06	1.128	1.170	1.037	1.243	II
0.1	1.226	1.301	1.061	1.435	III
0.2	1.511	1.689	1.118	2.041	III
0.3	1.854	2.156	1.163	2.873	III
0.5	2.697	3.294	1.221	5.500	IV
0.6	3.188	3.949	1.238	7.458	IV
0.8	4.283	5.402	1.261	13.096	IV
1.0	5.50	7.007	1.274	21.50	IV

the saving is significant, proving that $1/n$ value is an important parameter for the process design of an adsorption system.

If the highest operation concentration of the adsorption system is C_{ref}, and its correspondent concentration is q_{ref}, then the Freundlich isotherm equation is expressed as

$$q_{ref} = K_F C_{ref}^{1/n} \tag{17}$$

When Eq. (4) is divided by Eq. (17), the following dimensionless equation is obtained:

$$\left(\frac{q_e}{q_{ref}}\right) = \left(\frac{C_e}{C_{ref}}\right)^{1/n} \tag{18}$$

For (C_e/C_{ref}) is plotted against (q_e/q_{ref}), the curves with various values of $1/n$ are shown in Fig. 2. The isotherm curve types (level of favorability) are compared in Table 2; when $1/n = 0.01$, the curve is pseudo-rectangular (pseudo-irreversible); when $1/n = 0.03$ and 0.06, fast rising (strongly favorable); $1/n = 0.2$ and 0.4, mildly rising (favorable); when $1/n = 0.6$ and 0.8, pseudo-linear (pseudo-linear); when $1/n = 1$, linear (linear); when $1/n = 0.8$, 1.5, and 3, upwards concave (unfavorable). The numbers I, II, III, IV, and V in the last column of Table 2 represent the favorability level of each $1/n$ value. The relationship between favorability level and optimum stage number of concurrent multi-stage process is also shown in Table 2 and will be discussed later.

Table 2
Freundlich favorable parameter, isotherm curve type and optimum stage number of concurrent multi-stage process

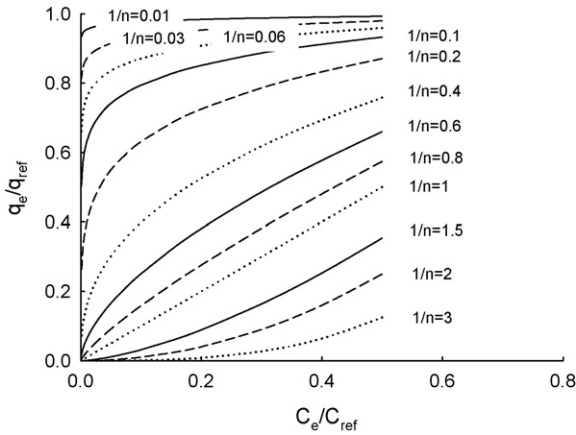| $1/n$	Isotherm curve type	Favorable level	Zone	Concurrent stages
$1/n < 0.01$	Pseudo-rectangular	Pseudo-irreversible	I	Single
$0.01 < 1/n < 0.1$	Hastily rise	Strong favorable	II	Single
$0.1 < 1/n < 0.5$	Mildly rise	Favorable	III	Two
$0.5 < 1/n < 1$	Pseudo-linear	Pseudo-linear	IV	Three
$1/n = 1$	Linear	Linear		>Three
$1/n > 1$	Concave up	Unfavorable	V	>Three

Fig. 2. Relationship between adsorption isotherm curves type and Freundlich constant (1/n).

2.2. Graphic method and infinite-stage adsorption

The adsorbent consumption at the *j*th stage of concurrent multi-stage system is

$$m_{xj} = m_y \left(\frac{1}{x_j} \right) (y_{j-1} - y_j) \tag{19}$$

for $1/x_j$ is plotted against y_j, the curve is shown in Fig. 3.

When it is single-stage adsorption,

$$\frac{m_{xs}}{m_y} = \left(\frac{1}{x_f} \right) (y_i - y_f) \tag{20}$$

Fig. 3 is shown that the adsorbent consumption per unit mass of solution, m_{xs}/m_y, is equal to the rectangular area IJKL.

When it is concurrent two-stage adsorption,

$$\frac{m_{xd}}{m_y} = \left(\frac{1}{x_1} \right) (y_i - y_1) + \left(\frac{1}{x_f} \right) (y_1 - y_f) \tag{21}$$

and m_{xd}/m_y values are equal to the sum of two rectangular IOPL and MNKP. Thus the adsorbent consumption of the concurrent
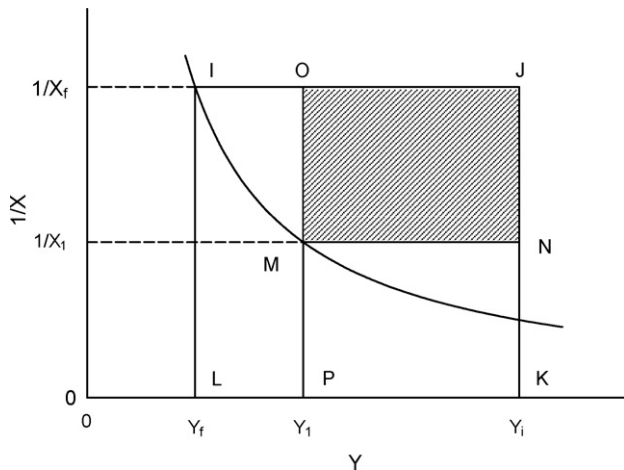

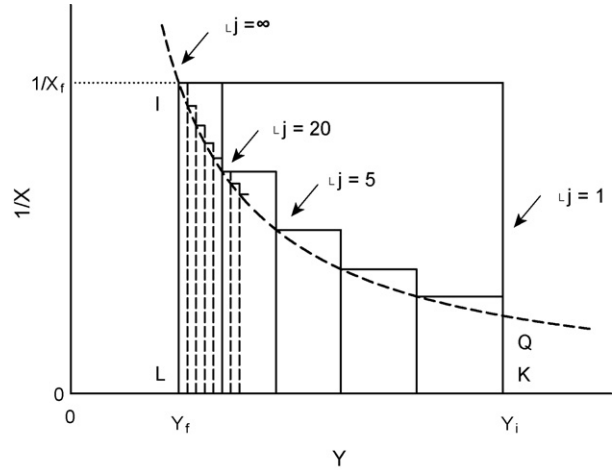Fig. 3. Graphical analysis of adsorbent consumption for a concurrent two-stage adsorption process.

Fig. 4. Graphical analysis of adsorbent consumption for the concurrent *j*-stage (*j* from 1 to ∞) adsorption processes.

two-stage system is rectangular OJNM, less than that of the single-stage system.

The total adsorbent mass m_{xj} in the concurrent *j*-stage system is

$$\frac{m_{xj}}{m_y} = \left(\frac{1}{x_1} \right) (y_i - y_1) + \left(\frac{1}{x_2} \right) (y_1 - y_2)$$

$$+ \ldots + \left(\frac{1}{x_f} \right) (y_{f-1} - y_f) \tag{22}$$

Fig. 4 shows that the total adsorbent mass m_{xj} decreases gradually with increased *j*-stages. When the number of stages approaches infinite, the adsorbent mass is equal to area IQKL, which can be obtained by integration as expressed in the following Eq. (23)

$$\frac{m_{x\infty}}{m_y} = \int_{yf}^{yi} \left(\frac{1}{x_j} \right) dy_j \tag{23}$$

when x_j is expressed with Freundlich isotherm Eq. (5) and is substituted into Eq. (23), after integration:

$$m_{x\infty} = m_y y_i^{1-(1/n)} \frac{1 - (y_i/y_f)^{1-(1/n)}}{(K'_F \rho^{1/n})[1 - (1/n)]} \tag{24}$$

The adsorption consumption ratio, $m_{xs}/m_{x\infty}$, of a single-stage to an infinite-stage system can be expressed as

$$\frac{m_{xs}}{m_{x\infty}} = \frac{[1 - (1/n)][1 - (y_f/y_i)]}{[(y_f/y_i)^{1/n}][1 - (y_f/y_i)^{1-(1/n)}]} \tag{25}$$

The effect of varying 1/n value on the adsorbent consumptions for 2, 3, and ∞-stage systems are shown in Fig. 5.

3. Materials and methods

3.1. Preparation of the activated carbons

Taiwan Giant Bamboo (TGB) grows massive in Taiwan. Its stem perimeter can reach up to 20 cm. In earlier times, it was widely used for building, for furniture, for tools, and for food.
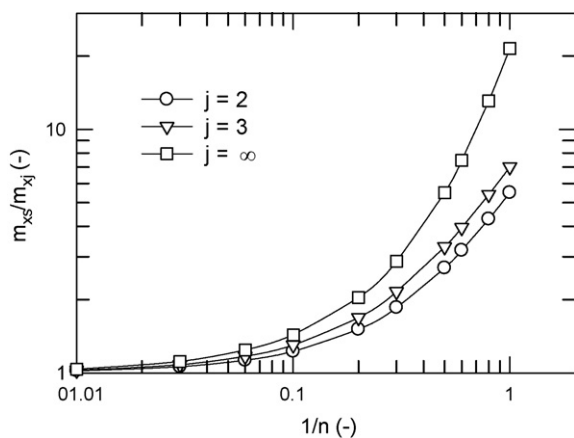
Fig. 5. The effect of $1/n$ value on the adsorbent consumption for 2-, 3-, and ∞-stage processes.

Fig. 6. Adsorption/desorption isotherms of N_2 at 77 K on steam-activated carbons derived from four plant materials (Carbons are: TGB (-●-), plum kernels (-○-), pine wood (-▽-), and corncob (-□-)).

Recently, it has only been used for food, the fully grown bamboo is not effectively utilized. Because of the low value of the bamboo, bamboo forests are being neglected, and the area under bamboo is dwindling, which is ecologically harmful in terms of water–soil conservation. Taiwan Giant Bamboo, being dense, is suitable for high quality activated carbon preparation. In this study, high performance Taiwan Giant Bamboo activated carbon was prepared by steam activation [7,8]. Pore structure and adsorption characteristics of activated carbon were investigated. Hopefully, the economic application of TBG can be enhanced, bamboos on hill slops can be preserved, and agriculture and forestry can be developed.

In this study, Taiwan Giant Bamboo was cut into approximately 2 cm pieces and steam-activated at 900 °C for 4 h to prepare the carbon, TGBAC. The steam activation is described in the literature [7,8]. The pore and physical properties of the activated carbon were measured as described in the same literature [7,8].

3.2. Procedures for adsorption experiments

Commercial-grade solutes, including basic blue 69 (BB69) and methylene blue (MB, M_W (molecular weight) = 284.3 g/mole), were used. The four solutes, phenol (M_W = 94 g/mole), 4-chlorophenol (4-CP, M_W = 128.5 g/mole), 3-chlorophenol (3-CP, M_W = 128.5 g/mole), and tannic acid (TA, M_W = 1701 g/mole) were reagent grade. The procedures for the adsorption equilibrium experiments were the same as those in previous study [8].
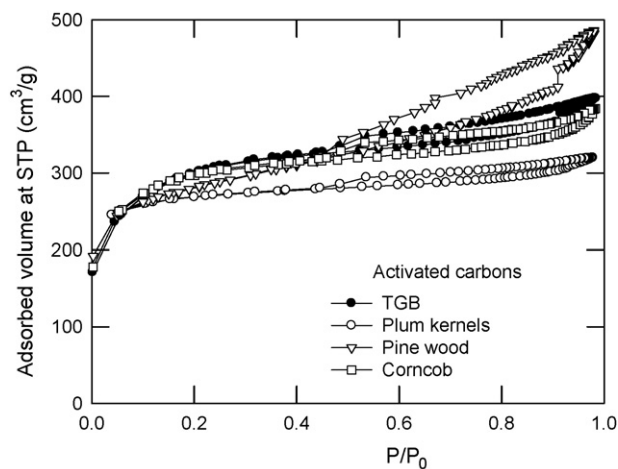
4. Results and discussion

4.1. Physical properties of activated carbon

Fig. 6 shows the adsorption/desorption isotherms of N_2 at 77 K onto the activated carbons prepared from four raw plant materials (TGB, plum kernels [7], pine wood [8], and corncob [9]). The adsorbed volumes of these four carbons were almost the same (from 171 to 192 cm^3/g) at P/P_0 approaching zero. Of these the pine wood hysteresis loop was the largest and its rising rate of adsorbed volume with increased P/P_0 was the highest. The rising rate of adsorbed volume with increased P/P_0 for plum kernels was the lowest, TGB and corncob were between the two. The hysteresis loop shape of the adsorption/desorption isotherm curve and the rising of the adsorbed volume were related to the raw material from which the activated carbon was prepared. The plum kernels, being hard, formed, mainly, micropore activated carbon, and the pine wood, being soft, formed, mainly, mesopore activated carbon. The pore and physical properties of the TGB studied in this work were between the two. The pore and physical properties of the activated carbons prepared from the four kinds of raw materials by steam activation, listed in Table 3, were compared in terms of specific surface area (S_p), total pore volume (V_{pore}), micropore volume (V_{micro}), mesopore volume (V_{meso}), and average pore diameter (D_p). Table 3 shows that the V_{micro} values of the four carbons were similar (from 0.360 to 0.392 cm^3/g); differences in V_{meso} were larger (from 0.117 to 0.389 cm^3/g); differences in D_p were also large (from

Table 3
Physical properties of the activated carbon prepared from various agricultural wastes

Source	S_P (m²/g)	V_{pore} (cm³/g)	V_{micro} (cm³/g)	V_{meso} (cm³/g)	D_p (nm)	Ref.
Taiwan Giant Bamboo	974	0.612	0.378	0.234	2.51	This work
Plum kernels	825	0.493	0.376	0.117	2.39	[7]
Pine wood	902	0.749	0.360	0.389	3.32	[8]
Corncob	943	0.592	0.392	0.200	2.51	[9]

2.39 to 3.72 nm). V_{meso} and D_p of TGBAC were, respectively, 0.234 cm^3/g and 2.51 nm. Literature reports good adsorption performance of the other three activated carbons, so, it could be inferred that TGBAC had good adsorption performance. However, previous studies showed that the adsorption performance of activated carbon prepared from bamboo was the worst. For example, the adsorption of chloroform on activated carbon obtained from five different raw materials was the least on the bamboo carbon [10]; of six kinds of raw materials the adsorption of MB, on bamboo dust was far less than on other raw materials [11]. In this work, adsorptions of three phenols (phenol, 4-CP, and 3-CP), two dyes (MB and BB69), and tannic acid on TGBAC were investigated to explain the concurrent multi-stage adsorption process, and to clarify performance of the bamboo carbon.

4.2. Adsorption equilibrium and isotherm equation

When an adsorbent comes into contact with the surrounding fluid of a certain composition, adsorption takes place and after the necessary time, the adsorbent and the surrounding fluid reach equilibrium [2].

Langmuir isotherm equation is defined as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{mon}} + \left(\frac{1}{q_{mon}}\right) C_e \qquad (26)$$

When C_e/q_e is plotted against C_e, a straight line is obtained with slope $1/q_{mon}$ and intercept $1/K_L q_{mon}$, from which the Langmuir constant (K_L) and the amount of adsorption corresponding to monolayer (q_{mon}) are obtained.

Take the logarithm of Freundlich isotherm Eq. (4), and plot $\ln q_e$ is against $\ln C_e$, then a straight line is obtained with slope $1/n$ and intercept $\ln K_F$, from which the Freundlich constant (K_F) and $(1/n)$ are obtained.

In order to compare the validity of two isotherm equations, a normalized standard deviation Δq_e (%) is calculated,

$$\Delta q_e (\%) = 100 \sqrt{\frac{\sum [(q_{e,\exp} - q_{e,\text{cal}})/q_{e,\exp}]^2}{N - 1}} \qquad (27)$$

where N is the number of data points.

The parameters obtained in the two isotherm equations, together with Δq_e, are listed in Table 4. It was found that the value of Δq_e with the Langmuir equation was larger

Table 4
Parameters in the Langmuir equation for adsorption of solute at 30 °C onto the activated carbon prepared from Taiwan Giant Bamboo

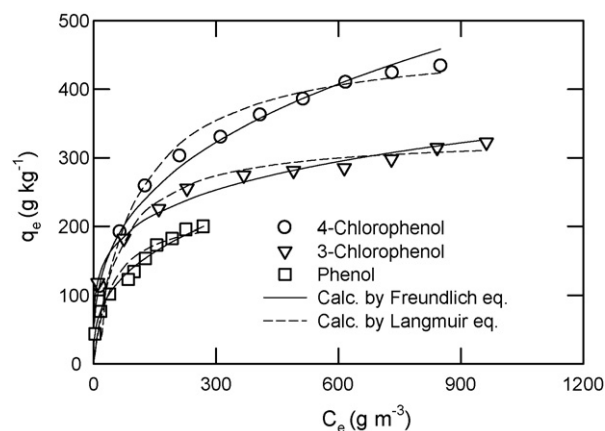| Solute	Langmuir eq.			Frundlich eq.		
	q_{mon} (g/kg)	K_L (m^2/g)	Δq %	$1/n$	K_F*	Δq %
MB	661	0.4927	2.74	0.0302	555.1	0.50
TA	934	0.0329	2.24	0.5438	31.75	3.33
BB69	1208	0.0413	10.38	0.1453	838.7	1.70
4-CP	474	0.0098	7.55	0.3378	46.97	2.93
3-CP	331	0.0157	9.03	0.2189	72.59	2.55
Phenol	223	0.0233	14.21	0.3446	29.06	3.22

* K_F: ((g/kg) (g/m^3)^n).

Fig. 7. Adsorption isotherm equilibrium of 3-CP, 4-CP, and phenol on steam-activated carbon derived from Taiwan Giant Bamboo.

(2.24–14.21%). Basically, Eq. (26) is intended for a homogeneous surface although it obeys Henry's law at very low concentrations. The poor fit of the isotherm data was probably due to the highly heterogeneous surface of steam-activated carbons. In contrast, the Freundlich fit was better ($\Delta q_e = 0.5$–3.33%). This equation is suitable for a highly heterogeneous surface, which often gives a good representation of adsorption data over a restricted range of concentrations [12].

Whenever the experimental results of the adsorption isotherm are discussed, the q_{mon} values of the Langmuir equation are frequently compared. Table 4 shows that the q_{mon} values of three phenols: phenol, 3-CP, and 4-CP were, respectively, 223, 331, and 474 g/kg. According to these values, it can be inferred that the adsorption performance of phenols on TGBAC was good. The q_{mon} values of two dyes: MB and BB69 were, respectively, 661 and 1208 g/kg, revealing also high adsorption of TGBAC on dyes. The K_F values of the Freundlich equation in Table 4 are seldom used for comparison. In real terms, it implies that the equilibrium adsorption at equilibrium concentration (C_e) equal to 1 is the "unit capacity factor" [3]. The K_F values of the adsorptions of two dyes: MB and BB69 were, respectively, 555 and 838 g/kg, which were compared with the reported values from literature in the following section.
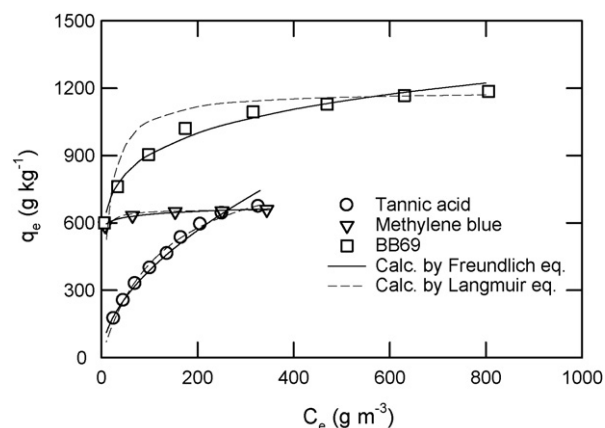

Fig. 8. Adsorption isotherm equilibrium of tannic acid, MB, and BB69 on steam-activated carbon derived from Taiwan Giant Bamboo.

4.3. Adsorption isotherm curve type and favorable parameter

Fig. 7 shows that the isotherm curve types of the three adsorbate (phenol, 4-CP, and 3-CP) equilibriums were similar.

However, Fig. 8 shows that the isotherm curve types of the three-adsorbate (tannic acid, MB, and BB69) equilibriums were quite different. The isotherm curve of the tannic acid rose mildly; that of MB the first rose rapidly, then approached a plateau; and that of BB69 was between the two. The curves in Figs. 7 and 8 are

Table 5
Freundlich favorable parameters of dyes from literature

Zone	Adsorbent	Adsorbate	$1/n$	K_F [*]	Ref.
II	AC < 106 μm	MB (pH 4)	0.077	183	[6]
	AC:180–250 μm	MB (pH 7)	0.056	178	
	PKSAC	BB9	0.096	194.9	[15]
	AC4	Basic dye	0.077	490	[16]
III	AC	Victoria blue	0.323	3.1	[17]
		Deorlene yellow	0.145	112	
		Disperse blue	0.200	2.8	
		Telon blue(AB25)	0.108	110	
	AC < 106 μm	MB (pH = 7)	0.103	185	[6]
	SAC	Bismark brown R (Cationic dye)	0.117	1003	[14]
	CSAC		0.101	598	
	CAC		0.326	54	
	ACC	Malachite green	0.411	1.19	[18]
	ACL		0.449	5.63	
	SDC(AC)	AY36	0.204	41.7	[19]
	RHC(AC)		0.435	2.1	
	CB-100(AC)	Acid orange 10	0.1293	3.20	[20]
	Sawdust (AC)	Direct blue 2B	0.199	201.8	[21]
		Direct green B	0.251	88.3	
	PAC(Merck)	BV3	0.469	17.1	[22]
		BV10	0.225	71.3	
	Coffee grounds (ACP)	BY2	0.391	2.04	[23]
	CC-15(AC)	AB80	0.15	179	[24]
	GAC	MG-400	0.123	77.8	[25]
	AC4	Acid dye	0.102	177	[26]
		Reactivate dye	0.204	71	
	GSPAC	Malachite green	0.195	128	[27]
	CPAC		0.129	143	
	K700$_{OX}$(AC)	MB	0.256	89.0	[28]
	Rice husk (AC)	Acid yellow 36	0.435	2.1 [**]	[29]
	CZ300	MB	0.111	284	[13]
	F100	MB	0.137	123	
	CZ300	Erythrosine red	0.150	262	
	F100	Erythrosine red	0.318	11	
	S800/30	MB	0.183	0.66 [**]	[30]
	ACA	MB	0.556	0.10	[31]
	ACH	MB	0.233	3.31	
	CS600	MB	0.147	40	[32]
	CP55		0.213	72	
	CS600$_{OX}$	MB	0.244	41	[33]
	CP55$_{OX}$		0.175	199	
	Commercial(ACC)	Acid blue	0.346	2.27	[23]
	Coffee grounds(ACP)	Basic yellow	0.391	2.04	[23]
	Commercial(ACC)		0.210	3.49	
IV	PAC(Merck)	Reactive black 5	0.589	5.75	[34]
	PAC(Merck)	BB1	0.511	23.8	[22]
		BR9	0.524	5.9	
	Coffee grounds (ACP)	AB25	0.714	2.27	[23]
	Activated carbon	BR9	0.935	0.88	[35]
	Activated slag	BR9	0.518	0.35	
V	Calgon F400	Basic blue 9	1.20	0.02	[36]
		Acid blue 29	3.59	37.1×10^{-6}	
		Acid red 91	1.86	0.04	

[*] K_F: $((g/kg)(g/m^3)^n)$.
[**] K_F: $((mmol/kg)(g/m^3)^n)$.

Table 6
Freundlich favorable parameters of phenols from literature

Zone	Adsorbent	Adsorbate	$1/n$	K_F[*]	Ref.
II	$t_A 4.0$	*o*-cresol	0.094	208.5	[8]
III	Calgon F-1400	Phenol	0.223	198.3	[37]
	GAC(oxic)	Phenol	0.18	83.5	[38]
	ACP(coffee grounds)	Phenol	0.370	1.07	[23]
	F400	Phenol	0.31	39	[39]
	CZ52942		0.24	96	
	APET carbons	Phenol (unbuffered)	0.230	2.2[**]	[40]
	$t_A 4.0$	Phenol	0.256	53.5	[8]
	Fir wood(steam AC)	Phenol	0.237	21.1	[12]
	Pistachio (steam AC)		0.187	87.3	
	SP207A	Phenol	0.245	0.95[**]	[41]
	Pica 103		0.436	0.77[**]	
	208C		0.278	1.21[**]	
	CZ300	Phenol	0.236	73	[13]
	F100		0.303	44	
	Sludge derived (AC)	Phenol	0.41	2.69	[42]
	BESTCHEM (AC)		0.38	15.65	
	ACA	Phenol	0.357	7.13	[31]
	ACH	Phenol	0.238	41.3	
	Coffee grounds(ACP)	Phenol	0.370	1.07	[23]
	Commercial(ACC)		0.140	2.41	
	Sigma-AC	Phenol	0.420	37.0	[43]
	F400		0.319	36.3	
	Activated 850/5	Phenol	0.263	1.12	[44]
	S800/30	Phenol	0.312	0.97[**]	[30]
	RGM1(GAC)	Phenol	0.396	0.851	[30]
	$t_A 4.0$	3-CP	0.265	95.6	[8]
	Calgon F-1400	4-CP	0.141	331.1	[37]
	SP207A	4-CP	0.202	1.46[**]	[41]
	Pica 103		0.398	1.73[**]	
	208C		0.259	2.12[**]	
	CAC	4-CP	0.378	9.11	[45]
	CSAC		0.320	9.21	
	RGM1(GAC)	4-CP	0.309	28.84	[46]
	Norit SA4(PAC)	2-CP	0.195	86.5	[47]
	Norit PKDA(GAC)		0.227	60.4	
	F-300	2-CP	0.41	51	[49]
		2-NP	0.26	101	
	Calgon F-1400	4-NP	0.138	254.1	[37]
	S800/30	4-NP	0.355	0.81[**]	[30]
	GAC(oxic)	Nitrophenol	0.15	87.0	[38]
		o-cresol	0.13	190.4	
IV	IIT carbon	Phenol	0.87	0.44	[49]
	F-300	Phenol	0.54	21	[48]
	WVA1100(AC)	Phenol	0.822	1.76	[3]
	UMC(AC)		0.788	2.53	
	GAC	Phenol	0.616	6.19	[50]
	RSCC	Phenol	0.769	15.5	[51]
	CAC	2,4,6-TCP	0.602	2.94	[45]
	CSAC		0.681	2.05	
	RGM1(GAC)	4-CP	0.534	3.034	[46]
		2,4-DCP	0.547	6.934	
		2,4,6-TCP	0.517	13.37	
	CWZ30 (PAC)	Phenol	0.683	70.2	[51]
V	Sorbonorite 4	Phenol	2.5	0.024	[49]
	Carbonised 485/30	Phenol	1.92	0.02	[44]
	E-Merck, (PAC)	Phenol	1.51	2.45	[52]

[*] K_F: $((g/kg) (g/m^3)^n)$.
[**] K_F: $((mmol/kg) (g/m^3)^n)$.

values of the Langmuir and Freundlich isotherm equations for comparing the suitability of the two isotherm equations.

Among the adsorptions of six adsorbates on TGBAC, according to $1/n$ value, the MB fell in the strong favorable zone (II); BB69, 4-CP, 3-CP, and phenol, were in the favorable zone (III); and the tannic acid was in pseudo-linear zone (IV).

In total, 53 adsorption systems were used for obtaining the isotherm equilibrium of dyes on activated carbon which were then analyzed with the Freundlich equation from literature; these have been listed in Table 5. Table 5 shows favorable level zones according to $1/n$ values of adsorption systems. Of these, 40 systems (75%) were in the favorable zone (III); 4 systems in the strongly favorable zone (II); 6 systems in the pseudo-linear zone (IV); and 3 systems in the unfavorable zone (V). In this study, MB was in the strongly favorable zone (II) and BB69 was in the favorable zone (III), which means that the isotherm curve types of these two adsorption systems were good. Compared with the K_F values in Table 5, the adsorption of MB on CZ300 was 284 g/kg, the highest [13], lower than the adsorption in this work, namely 555 g/kg. Of all the adsorption systems in Table 5, the K_F for the adsorption of Bismark brown R on SAC was the highest, namely 1003 g/kg [14], which were higher than the 838 g/kg in this work. From the comparison of the K_F values, it is clear that TGBAC had good adsorption performance with dyes.

Furthermore, the isotherm equilibriums of 58 adsorption systems for phenols on activated carbon have been listed in Table 6. Of these, 41 systems (71%) were in the favorable zone (III); 1 system in the strong favorable zone (II); 12 systems in the pseudo-linear zone (IV); and 4 systems in the unfavorable zone (V). The isotherm curve types of phenol, 3-CP, and 4-CP all were in the favorable zone (III).

4.4. Application to the concurrent multi-stage adsorption process

An increased number of stages in the concurrent multi-stage adsorption process decreased the adsorbent consumption. But, an increased number of stages increased the operation cost. The optimum number of stages has to be based on economic considerations. At y_i/y_f equal to 100, suppose that 20% reduction in adsorbent for each increased number of stages would be economically viable, then, based on this assumption, Table 1 shows that all m_{xs}/m_{xd} values were less than 1.2 for the strongly favorable zone (II), which implies that the single-stage operation was suit-

able. When all m_{xs}/m_{xd} values were larger than 1.2, and m_{xd}/m_{xt} was less than 1.2 for the favorable zone (III), the most suitable number of stages was two. When all m_{xd}/m_{xt} values were larger than 1.2 for the pseudo-linear zone (IV), the suitable number of stages were three or more. The adsorbent consumption ratio for concurrent ∞-stage system, $m_{xs}/m_{x\infty}$ listed in the second last column of Table 1 shows that the $m_{xs}/m_{x\infty}$ value in the pseudo-linear zone (IV) rapidly increased with increased $1/n$, indicating an ample adsorbent dose reduction according to the increased number of stages in this zone, and also that the adsorbate in the adsorbent cannot reach saturation with the concurrent multi-stage operation in zone (IV), unless more stages are used.

Middle concentrations (y_j/y_f) of concurrent two-stage and three-stage systems were calculated from Eqs. (12), (14) and (15), the total adsorbent consumption ratios (m_{xs}/m_{xd}) and (m_{xs}/m_{xt}) were calculated from Eqs. (11) and (13), assuming that the adsorbate concentration ratio of influent to effluent (y_i/y_f) is 100, and the results have been listed in Table 7. The adsorption of MB was the only one where the adsorbent consumption ratio (m_{xs}/m_{xd}) for the two-stage system was less than 1.2, meaning that adsorbent was fully consumed in a single-stage operation. For the other adsorption systems, where m_{xs}/m_{xd} was larger than 1.20, had to adopt two-stage or more stage operations. When the adsorbent consumption ratio (m_{xs}/m_{xt}) for the three-stage operation was larger than that for the two-stage (m_{xs}/m_{xd}) operation, the three-stage operation saved more adsorbent consumption. For the sake of comparison (m_{xs}/m_{xt}) was divided by (m_{xs}/m_{xd}) and (m_{xd}/m_{xt}) to obtain the adsorbent consumption ratio of the two-and three-stage operation. Table 7 shows that the values of (m_{xd}/m_{xt}) were less than 1.2 for the adsorption systems of BB69 and 3-CP, and those for 4-CP and phenol were approximately 1.20. These four adsorption systems were suitable for concurrent two-stage operation. The value of (m_{xd}/m_{xt}) was 1.34 for tannic acid, suitable for a three-stage operation. The relationship between optimum stage number of concurrent multi-stage process and favorability level zone is listed in Table 2, zone I and II being single stage, zone III being two stages, zone IV being three stages, and zone V being larger than three stages.

From Eq. (18), q_e/q_{ref} was plotted against C_e/C_{ref}. The resulting curves are shown in Fig. 9. Of the six adsorption systems in this study, the uppermost curves, belonging to the strong favorable zone (II), was for MB; only a single-stage adsorption process was needed. The four middle curves (BB69, 3-CP, 4-CP, and phenol) in Fig. 9 belong to the favorable zone (III), needing a concurrent two-stage adsorption process. The

Table 7

Middle concentrations and total adsorbent consumption ratios of concurrent two-, three-, and ∞-stage processes (at $y_i/y_f = 100$)

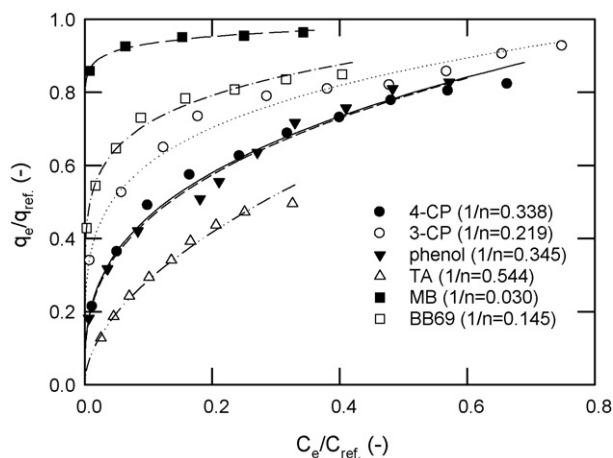| Matter	$1/n$	Two-stage		Three-stage				Stage
		y_1/y_f	m_{xs}/m_{xd}	y_1/y_f	y_2/y_f	m_{xs}/m_{xt}	m_{xd}/m_{xt}	Number
MB	0.0302	47.62	1.062	65.38	31.51	1.081	1.018	1
BB69	0.1453	37.75	1.347	59.21	23.54	1.464	1.087	2
3-CP	0.2189	32.50	1.571	55.25	19.59	1.775	1.130	2
4-CP	0.3378	25.77	1.998	48.88	14.77	2.401	1.202	2
Phenol	0.3446	25.44	2.025	48.50	14.52	2.441	1.205	2
TA	0.5438	18.02	2.909	38.35	9.49	3.888	1.337	3

Fig. 9. Dimensionless adsorption isotherms of six solutes on steam-activated carbon derived from Taiwan Giant Bamboo.

lowest curve, which belongs to the pseudo-linear (IV), in Fig. 9, was for tannic acid; a concurrent three-stage adsorption system was needed. Isotherm curve type can be employed to infer the required stage number of a concurrent multi-stage adsorption process. The Freundlich constant ($1/n$) can be utilized to completely describe isotherm curve type.

5. Conclusions

In this study, mass balance and the Freundlich equation of two phases liquid–solid were employed to deduce the middle concentrations and adsorbent consumption of single-, two-, and three-stage operations for the concurrent multi-stage adsorption process. A graphical method was used to explain and calculate a ∞-stage adsorption process. The Freundlich equation parameter $1/n$ was divided into five zones: $1/n < 0.01$, $0.01 < 1/n < 0.1$, $0.1 < 1/n < 0.5$, $0.5 < 1/n < 1$, and $1/n > 1$. Its favorable levels were called pseudo-irreversible, strongly favorable, favorable, pseudo-linear, and unfavorable. With the concentration ratio of influent to effluent for the adsorption process set at 100, the most suitable adsorption process for the pseudo-irreversible and strongly favorable zones was a single-stage operation; that for the favorable zone, a two-stage operation; that for the pseudo-linear zone, a three- or more than three-stage operation. In this study, activated carbon was prepared from Taiwan Giant Bamboo by 4 h steam activation at 900 °C. The BET surface area was 974 m^2/g. Isotherm equilibrium adsorptions of three phenols (phenol, 3-CP, and 4-CP), two dyes (MB and BB69), and tannic acid were studied. Isotherm curves derived from the Freundlich equation were well fitted to the data of the above adsorption systems. The favorable levels were: MB, strongly favorable zone; BB69, phenol, 3-CP, and 4-CP, favorable zone; and tannic acid, pseudo-linear zone. The values of the Freundlich favorable parameter ($1/n$) of 53 adsorptions of dyes and 58 adsorptions of phenols on activated carbon reported in literature were collected and their favorable levels were analyzed. The results revealed good isotherm curves for the adsorption systems in this study and proved the good adsorption performance of dyes and phenols on TGBAC.

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