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Modeling of Mass Transfer Controlled Adsorption Rate Based on the Langmuir Adsorption Isotherm

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ABSTRACT

Adsorption techniques are extensively used in bulk separations, purifications, and physiochemical parameter determinations. Generally, the adsorption models are described for equilibrium conditions. This study investigates the development of a mathematical model which describes the rate of adsorption under the conditions when the dynamic mass transfer is the controlling step. The underlying assumption is that the equilibrium isotherms can be used to describe the adsorption phenomena. A mathematical model for the external mass transfer controlled adsorption rate based on the Langmuir adsorption isotherm was developed and validated using data reported in literature using different adsorbents and adsorbates. In addition, using Freundlich adsorption isotherm, mathematical models for zero, one-half, and first-order were obtained. The various relevant parameters, namely the adsorption capacity, the adsorption energy, and the mass transfer coefficients were evaluated and the extension of the model to energetically heterogeneous surfaces is discussed. In addition, the results obtained from the Langmuir isotherm-based model were compared against the results derived from the mass transfer controlled rate equation based on the Freundlich isotherm.

Key Words. Langmuir; Adsorption; Kinetics; Mass transfer; Modeling

INTRODUCTION

The simulation of adsorption processes involves the consideration of equilibrium and the rate of adsorption. Lagergren (1) proposed a first-order kinetic rate equation based on surface reaction as shown by the following

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relationship:

$$\log(q_e - q) = \log q_e - \frac{K}{2.303} t \quad (1)$$

where q is the amount of sorbate adsorbed per unit gram of adsorbent at time t, and the subscript e represents equilibrium. Although the kinetics of adsorption is not necessarily of the first order, one can follow the methodology used by Lagergren to develop the models for other reaction orders. For cases when adsorption is pore-diffusion-dependent, Weber and Morris (2) proposed that the concentration remaining in the solution after adsorption at time t is proportional to $t^{0.5}$.

The overall rate of adsorption for mass transfer controlled situations was first described by McCay et al. (3). Their model, based on the Freundlich isotherm ($q = k_f C_e^n$) for the case of $n = 1$, gives the following expression of dynamic concentration C_t:

$$C_t = C_0 \left(\frac{1}{1 + m_s k_f} + \frac{m_s k_f}{1 + m_s k_f} e^{-\left(\frac{1+m_s k_f}{m_s k_f}\right) k_m A_m t} \right) \quad (2)$$

where C_t is the concentration of sorbate at time t, C_0 is the initial concentration of the sorbate, m_s is the loading of the sorbent, k_m is the mass transfer coefficient, and A_m is the surface area, which is directly proportional to the number of available sites.

The above-discussed relationships have been used by many researchers to quantify their process kinetics. Pandey et al. (4) determined the rate kinetics of Cu (II) adsorption onto fly ash. Similar studies were conducted by Vishwakarma et al. (5) during their investigation of Ni (II) adsorption on fly ash. These studies concluded that the mass transfer from the bulk to the particle surface was the main rate-determining step. Although in the above studies Eq. (2) was used to fit the kinetic data, the equilibrium data itself were observed to behave more closely according to the Langmuir isotherm. Thus, we believe that the McKay et al. model is not suitable to explain the data reported by Vishwakarma et al. (5). Therefore, there is a need to develop a model for predicting the dynamic concentration under mass transfer controlled conditions for systems that follow Langmuir adsorption isotherm.

In general, two simplified models are used in simulating the rate of adsorption: (*a*) equilibrium and (*b*) diffusion limiting (6). The aim of this paper is to use the Langmuir isotherm to develop a model to enable us to predict the dynamic concentration for mass-transfer-dependent adsorption kinetics, assuming the surface reaction is extremely fast and is thus constantly in equilibrium, with the solute contacting the adsorbent. The data published in the literature are then used to estimate the constants, adsorption energy (a), and adsorption capacity (b) from the model developed.

The carbon adsorbents used commonly have heterogeneous surfaces. As such, a new model or an extension of an existing model needs to be developed for such surfaces. Rudzinski and Aharoni (7) developed a procedure for developing equations for simultaneous description of equilibria and kinetics of adsorption on an energetically heterogeneous surface based on the statistical theory of rate of interfacial transport. This paper provides a much-simplified strategy for the extension of the model developed for heterogeneous surfaces.

MATHEMATICAL MODEL DEVELOPMENT

The overall approach in this study is to equate the rate of external mass transfer to the rate of adsorption given by the Langmuir adsorption curve. Thus, the inherent assumption in this investigation is that the adsorption equilibrium is reached instantaneously.

The Langmuir isotherm is given by

$$\frac{1}{q_e} = \frac{1}{b} + \frac{1}{abC_e} \tag{3}$$

The equilibrium adsorption (mg/g) is defined as the ratio of the amount adsorbed (x) to the mass of adsorbent (m). Hence,

$$q_e = \frac{x}{m} = \frac{(C_0 - C_t)\cdot V}{m_s \cdot V} = \frac{(C_0 - C_t)}{m_s} \tag{4}$$

where C_0 and C_t are the initial and dynamic sorbate concentrations, respectively, m_s, is the dosing of adsorbate, and V is the volume of the fluid phase. The rate of mass transfer is given by

$$\frac{dC_t}{dt} = -k_m A_m (C_t - C_e) \tag{5}$$

where k_m and A_m are the mass transfer coefficient and the area of mass transfer, respectively. Eqs. (3) and (4) are used to solve for the equilibrium concentration, C_e

$$C_e = \frac{C_0 - C_t}{a[C_t + (bm_s - C_0)]} \tag{6}$$

and substituting C_e from Eq. (6) into Eq. (5) results in the following differential equation:

$$\frac{dC_t}{dt} = -k_m A_m \left[\frac{aC_t^2 + (a\alpha + 1)C_t - C_0}{aC_t + a\alpha} \right] \tag{7}$$

where

$$\alpha = bm_s - C_0. \tag{8}$$

On arranging and integrating equation (7) (Appendix) the following expression is obtained for the initial condition, $t = 0$ and $C = C_0$;

$$\left(\frac{aC_t^2 + (a\alpha + 1)C_t - C_0}{aC_0^2 + a\alpha C_0}\right)^{1/2a} \times \left(\frac{\dfrac{2aC_t + (a\alpha + 1) - \sqrt{-q}}{2aC_0 + (a\alpha + 1) - \sqrt{-q}}}{\dfrac{2aC_t + (a\alpha + 1) + \sqrt{-q}}{2aC_0 + (a\alpha + 1) + \sqrt{-q}}}\right)^{\frac{a\alpha-1}{2a}\cdot\frac{1}{\sqrt{-q}}} = e^{-k_m A_m t/a} \tag{9}$$

where

$$q = -[4aC_0 + (a\alpha + 1)^2]. \tag{10}$$

Equation (9) is the rate equation for adsorption based on the Langmuir isotherm.

The Freundlich isotherm is given by the following expression:

$$q_e = k_f C_e^n \tag{11}$$

Using the approach described above, the rate equation based on the Freundlich isotherm for any value of exponent n yields the following equation:

$$\int_{C_0}^{C} \frac{dC}{(k_f m_s)^{1/n} C - (C_0 - C)^{1/n}} = -\frac{k_m A_m}{(k_f m_s)^{1/n}} t \tag{12}$$

The dynamic concentration expressions for the various values of n (0, 0.5, 1, and 2) were derived (Table 1). For values of n other than those mentioned above, the solution to Eq. (12) is obtained numerically. The Langmuir isotherm can be rewritten as

$$q_e = \frac{abC_e}{1 + aC_e} \tag{3a}$$

Because Eq. (3a) is a shifting-order expression (zero to first-order), it can be used conveniently to express the Freundlich isotherm [Eq. (11)] for the n values ranging from 0 to 1. Therefore, only one equation [Eq. (9)] can be used to model the data obtained from high (corresponding to $n = 0$) to intermediate ($n = 0.5$) and low ($n = 1$) concentrations of adsorbate.

SOURCE OF DATA

The kinetic data for the validation of the proposed model were collected from various sources. Data were obtained so as to enable the study of the adsorption of both electrolytic and nonelectrolytic sorbates on a variety of ad-

TABLE 1
A Comparison of the Models Based on Linear, Langmuir, and Freundlich ($n = 0$, 0.5, and 1)

Linear	$C = C_0\left(\frac{1}{1 + m_s k_f} + \frac{m_s k_f}{1 + m_s k_f} e^{-\left(\frac{1 + m_s k_f}{m_s k_f}\right) k_m A_m t}\right)$
Freundlich ($n = 1$)	$C = C_0\left(\frac{1}{1 + m_s k_f} + \frac{m_s k_f}{1 + m_s k_f} e^{-\left(\frac{1 + m_s k_f}{m_s k_f}\right) k_m A_m t}\right)$
Langmuir	$\left(\frac{aC^2 + (a\alpha + 1)C - C_0}{aC_0^2 + a\alpha C_0}\right)^{1/2a}\left(\frac{\frac{2aC + (a\alpha + 1) - \sqrt{-q}}{2aC_0 + (a\alpha + 1) - \sqrt{-q}}}{\frac{2aC + (a\alpha + 1) + \sqrt{-q}}{2aC_0 + (a\alpha + 1) + \sqrt{-q}}}\right)^{\frac{a\alpha - 1}{2a}\cdot\frac{1}{\sqrt{-q}}} = e^{-k_m A_m t}$
Freundlich ($n = 0.5$)	$\frac{\text{arcTan}h\left(\frac{C_0 - C}{k_f b m_s \sqrt{C}}\right)}{k_f b m_s \sqrt{C}} = -\frac{k_m A_m}{(k_f b m_s)^2} t$
Freundlich ($n = 2$)	$2(C_0 - C)^{0.5} + 2(k_f m_s)^{0.5} C \ln[(k_f m_s)^{0.5} C - (C_0 - C)^{0.5}] - 2(k_f m_s)^{0.5} C_0 \ln[(k_f m_s)^{0.5} C_0)] = -\frac{k_m A_m}{(k_f m_s)^{0.5}} t$

sorbents, namely activated carbon (AC) and fly ash. Adsorption of various concentrations of benzaldehyde and nitro-4-phenol were obtained from the work done by Zhou and GuyMartin (8). Adsorption studies of nickel, copper, chromium, and cadmium performed by Kannan (9), Pandey et al. (4, 10), and Yadava et al. (11), respectively, were used to obtain the various constants such as the mass transfer coefficients, adsorption energy, and adsorption capacity. The experimental data were used to fit the rate equations derived from Langmuir [Eq. (9)] and Freundlich [Eq. (2)] isotherms.

RESULTS AND DISCUSSION

To estimate the constants of Langmuir and Freundlich adsorption isotherms, three equilibrium concentration data sets were used (Figs. 1 and 2). The various equilibrium constants are reported in Table 2. The analysis for calculating the equilibrium data requires the use of at least three and preferably five experimental observations made under equilibrium conditions. In addition, the dynamic concentration data are often disregarded. The purpose of the model presented in this paper is to show that the data from a single experiment can be used to estimate constants associated with adsorption

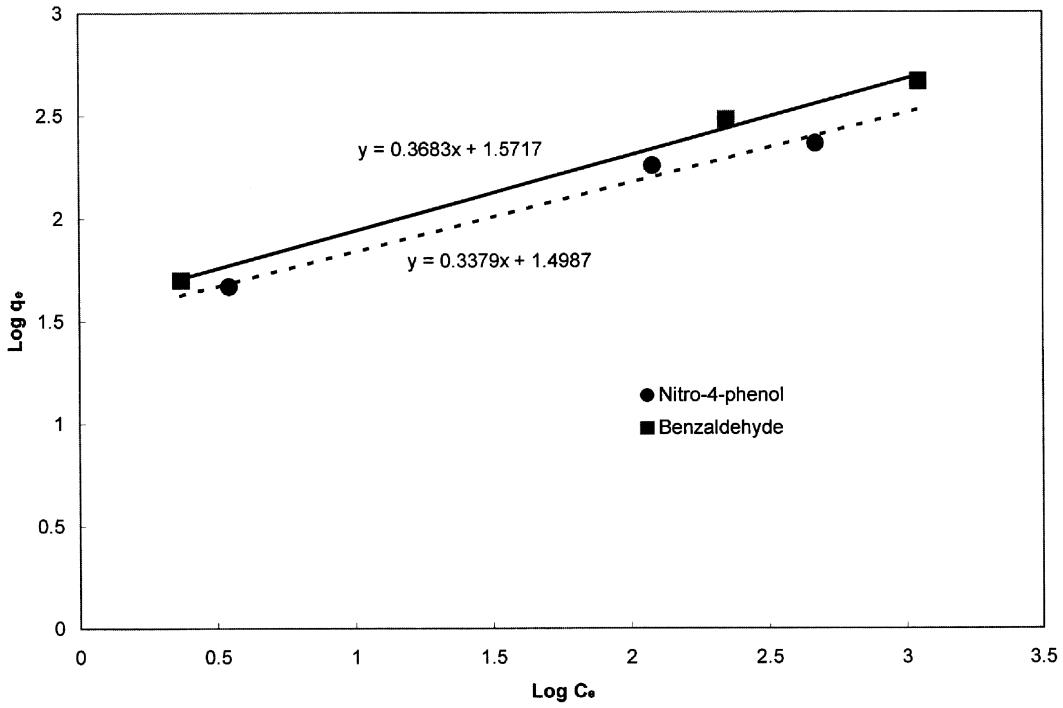


FIG. 1 Freundlich isotherms for adsorption of benzaldehyde and nitro-4-phenol. Experimental data were obtained from reference.

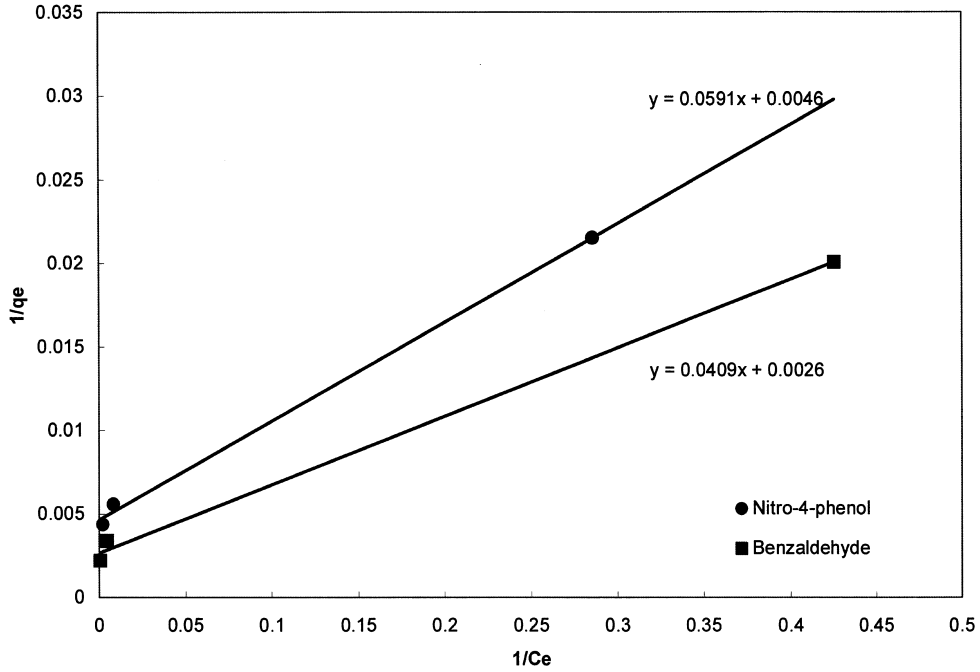


FIG. 2 Langmuir isotherms for adsorption of benzaldehyde and nitro-4-phenol. Experimental data were obtained from reference.

TABLE 2
Equilibrium Constants for Langmuir and Freundlich Isotherms

	Langmuir			Freundlich		
	a (L/g)	b (mg/g)	r^2	k_f (L/g)	n	r^2
Benzaldehyde	0.0636	384.6	0.9974	4.81	0.37	0.9948
Nitro-4-phenol	0.0778	217.4	0.9980	4.48	0.34	0.9833

Experimental data were obtained from reference 8.

isotherms. An important observation we make from data in Fig. 2 is the possibility that the plot of $1/q_e$ vs. $1/C_e$ is not necessarily linear. This observation will be used later to explain the heterogeneous nature of activated carbon.

The model developed in this paper [Eq. (9)] was used to obtain the Langmuir constants of adsorption of benzaldehyde and nitro-4-phenol on AC and copper, chromium, cadmium, and nickel on fly ash (Table 3). In addition, quantitative data on the mass transfer constants were also generated. Because the value of the coefficient of regression, r^2, is fairly high for the data processed, a great level of confidence can be placed on the approach described by the model [Eq. (9)]. The constants obtained were used to generate concentration versus time profiles (Figs. 3–5) and they were compared with the actual experimental data. There is a very good match between the two sets of data (predicted and experimental). According to the regression analysis, as compared to the adsorption of organic compounds, the model developed more ac-

TABLE 3
Estimated Langmuir Constants and Mass Transfer Coefficients [Eq. (9)]

Sorbent	Adsorbate	Initial concentration (mg/L)	m_s (g/L)	a (L/g)	b (mg/g)	$k_m A_m$ (L/h)	r^2
AC	Benzaldehyde	52.5	1.0	0.5796	91.51	1.5667	0.9937
AC	Benzaldehyde	522.5	1.0	0.8361	306.24	1.3771	0.9962
AC	Benzaldehyde	1568.0	1.0	0.0337	473.34	2.0176	0.9753
AC	Nitro-4-phenol	50.0	1.0	0.5265	75.18	1.6873	0.9941
AC	Nitro-4-phenol	300.0	1.0	0.5125	190.45	1.0892	0.9999
AC	Nitro-4-phenol	700.0	1.0	0.4985	231.68	1.3747	0.9965
Fly ash	Copper	12.0	20.0	1.5031	1.1413	0.5280	0.9967
Fly ash	Chromium	500.0	20.0	4.0985	0.0002	0.3997	1.0000
Fly ash	Cadmium	500.0	20.0	1.9893	0.0001	0.3997	1.0000
Fly ash	Nickel	500.0	7.5	2.0747	1.3788	0.1162	0.9961

Experimental data were obtained from references 4, 8–11.

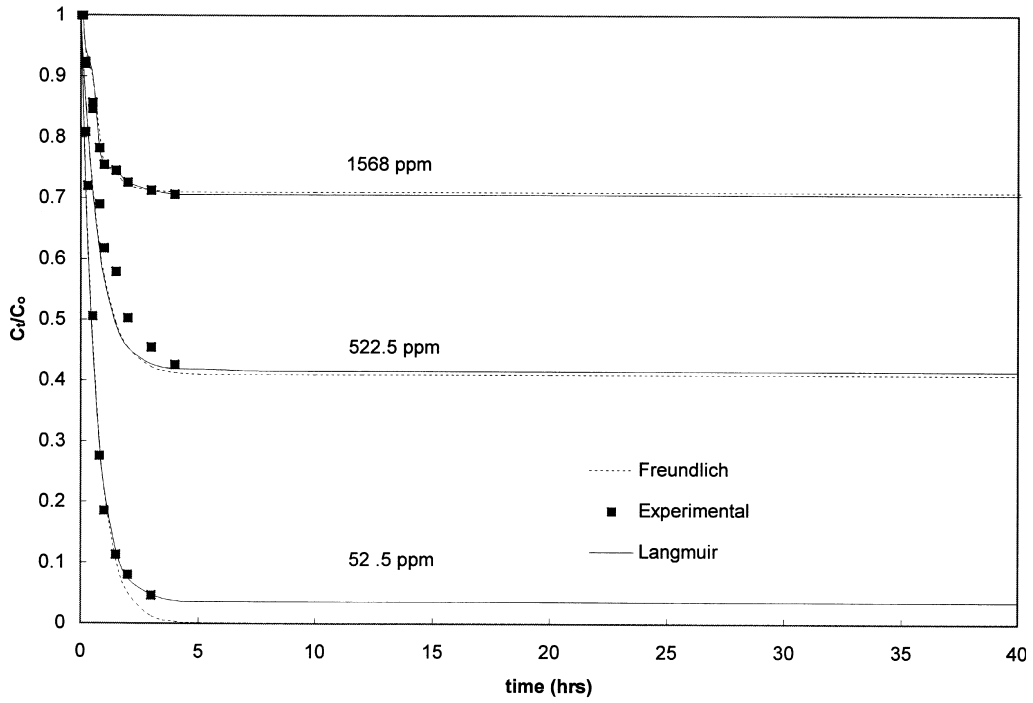


FIG. 3 Adsorption of benzaldehyde on activated carbon. Experimental data were obtained from reference.

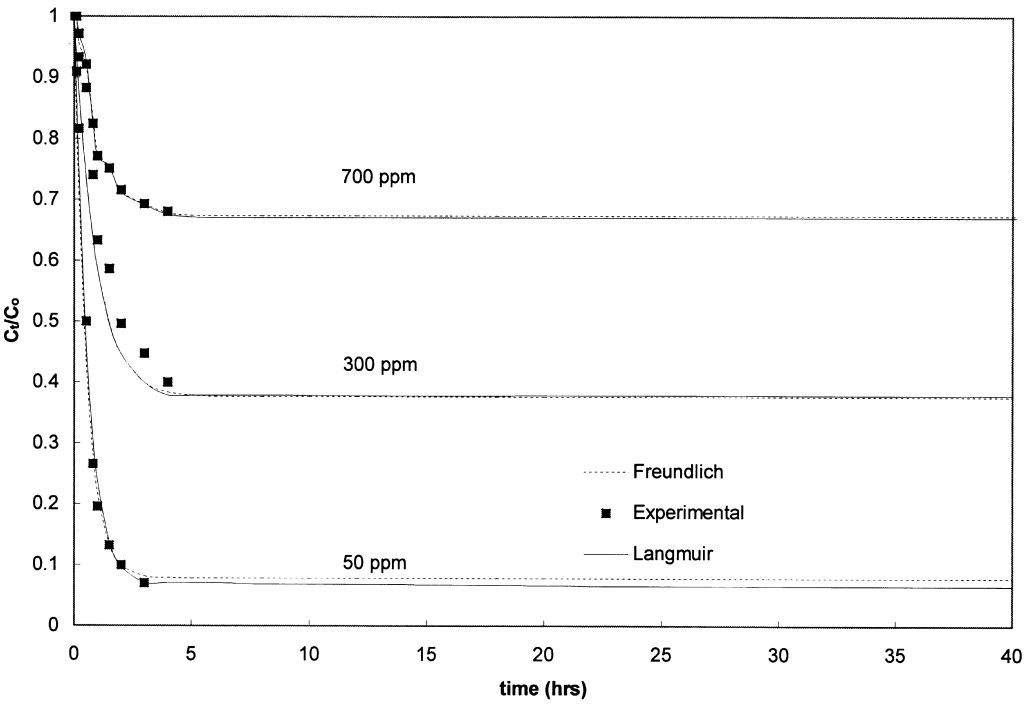
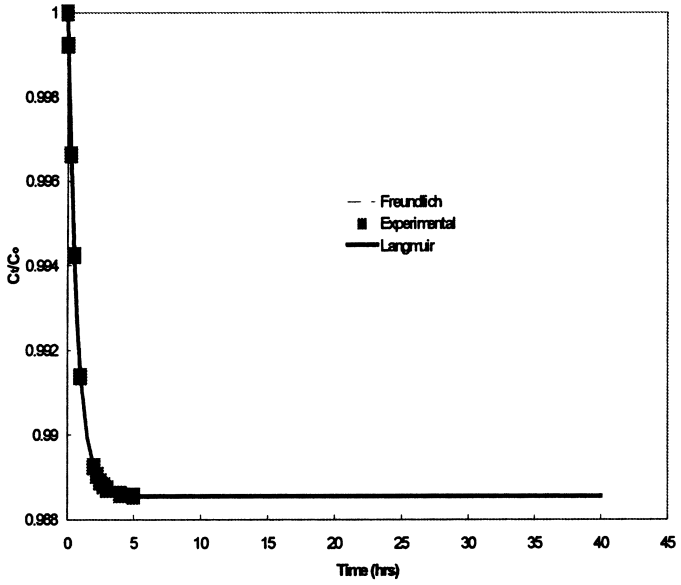
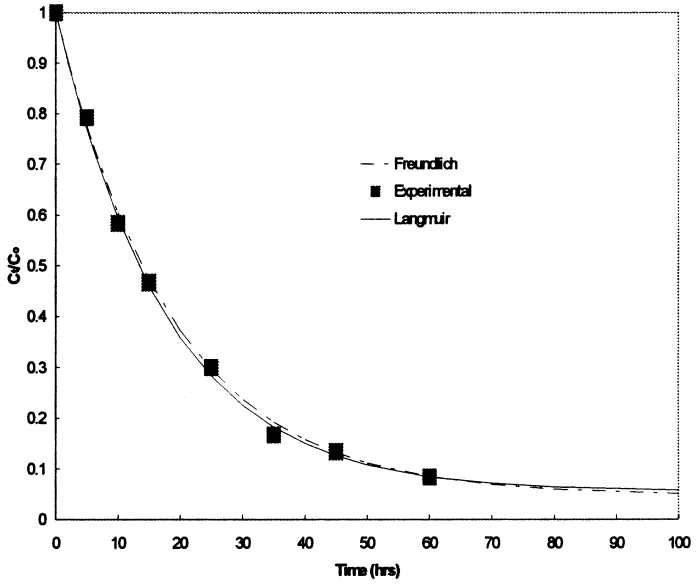


FIG. 4 Adsorption of nitro-4-phenol on activated carbon. Experimental data were obtained from reference.



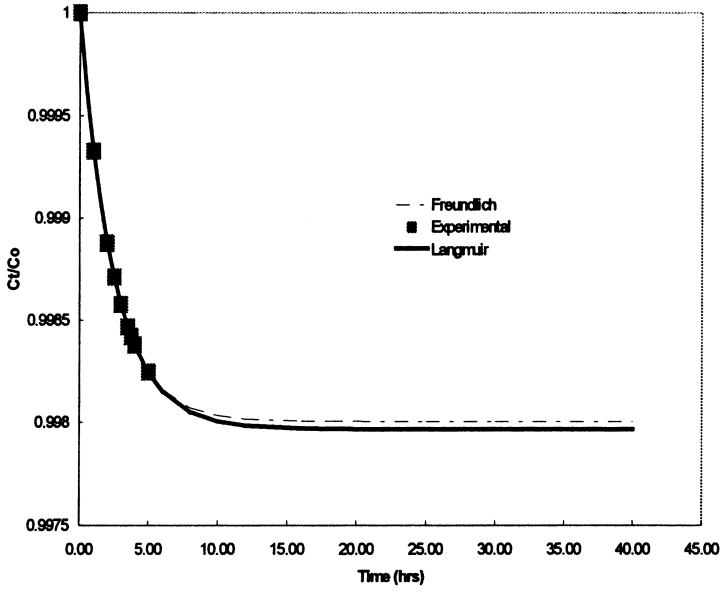
a



b

FIG. 5 Adsorption of (a) chromium, (b) copper, (c) cadmium, and (d) nickel onto fly ash. Experimental data were obtained from (a) reference 10, (b) reference 4, (c) reference 11, and (d) reference 9.

(continued)



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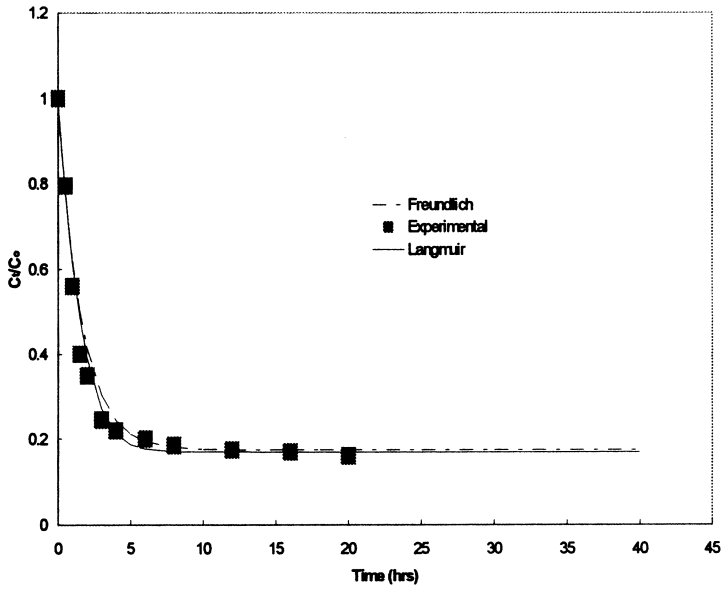

d

FIG. 5 Continued

curately describes the metal ion adsorption. A comparison of the mass transfer coefficients shows that higher values are obtained for the case when organic adsorbates were used in relation to metal ions. Metal ion adsorption is expected to occur at a faster rate than rates at which organic compound adsorption takes place because of higher diffusivity values of metal ions in relation to the corresponding mass diffusivity of the larger organic molecules. In

addition, relative to the organic molecules, the strong electrostatic interactions present in metal ions (including hydrated metal ions) could result in rapid movement of metal ions to the sorbent surface. Hence, equilibrium is reached rather quickly. Therefore, the process appears to be mass-transport-limited for metal ion adsorption and hence metal ion adsorption is more accurately described by the model. The constants, a and b, were found to be concentration-dependent, indicating a heterogeneous surface. For this reason, Fig. 2 indicates the convex nature of the relationship between the two axes. For benzaldehyde adsorption, the adsorption energy (a) is found to decrease with concentration according to the empirical relationship $a = 0.8934e^{-0.0028C_e}$, whereas the maximum adsorption capacity is found to increase with the concentration according to the following empirical relationship $b = 70.086C_e^{0.2728}$. The variation of constants can be explained by the distribution of energy sites. In the analysis presented for the model, homogeneous surface was assumed. However, in most practical cases, especially for activated carbon, there is a distribution of homotattic sites (12, 13). In the case studied for evaluating the model, an exponential distribution of adsorption potential was found to apply best. The adsorption energy decreased according to the empirical equation $a = 0.5300e^{-0.0001C_e}$ for nitro-4-phenol, whereas the maximum adsorption capacity increased with concentration according to the relationship $b = 85.701C_e^{0.1705}$. The explanation for the concentration dependence of adsorption capacity is provided below.

The adsorption capacity is a measure of maximum possible adsorption per unit mass of sorbent. This capacity is expected to be constant, because it is the value of monolayer capacity for a given component. However, in practice it was found to vary with concentration. This suggests a multilayer adsorption possibility. The other reason for this behavior can be attributed to the fact that at lower concentration, the maximum possible adsorption capacity cannot be extrapolated effectively from the data. The authors believe that this gives rise to a "pseudo-maximum." The Langmuir isotherm is essentially applicable to a monolayer, homogeneous surface. Figure 6 shows the relationship between $1/C_e$ vs. $1/\theta$ for a heterogeneous surface where the adsorption potential, a, for each type of site decreases exponentially and the sites are uniformly distributed. The data in Fig. 6 can be interpreted in the following way. The curve assumes a linear behavior at high concentrations of the solute and results in an intercept corresponding to 1. However, if a straight line approximation were to be made at lower concentrations, the intercept would be significantly greater than 1, indicating that the capacity is less than the actual capacity. These observations can be explained as follows. Let b' and b be the observed and actual capacities, respectively, then we can express the data in Fig. 6 as

$$\frac{1}{\theta} = \frac{b}{q} = \frac{1}{a}\cdot\frac{1}{C_e} + \frac{b}{b'}$$

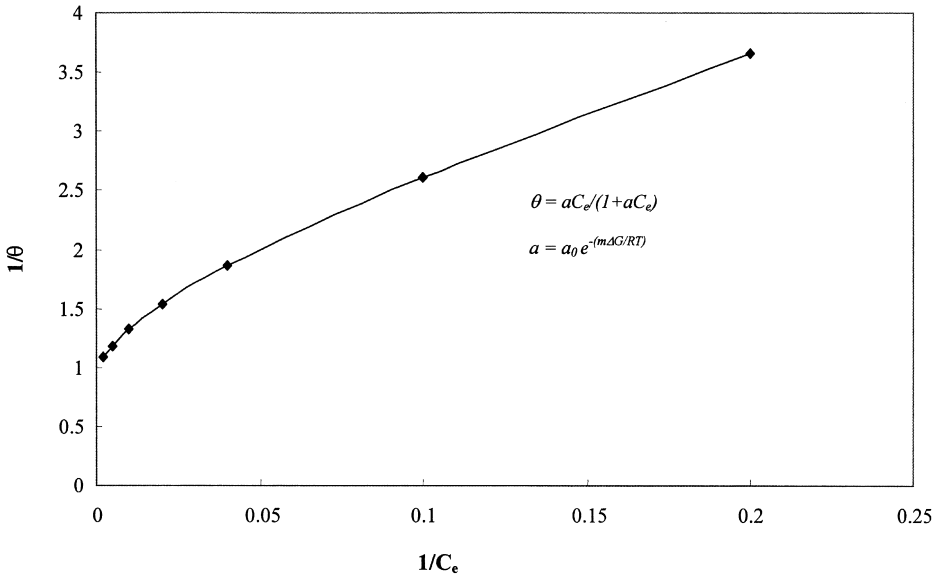

FIG. 6 Effect of heterogeneous surface on *a* and *b*.

Compare the above expression with the Langmuir equation:

$$\frac{1}{\theta} = \frac{1}{a}\cdot\frac{1}{C_e} + 1$$

Thus, the cases where the intercept is greater than 1 indicate that b' is less than 1, and this is referred to as the pseudo-maximum (i.e., the observed maximum). This pseudo-maximum may not always occur. In the cases studied, a power function appears to best explain the dependence of the pseudo-maxima on the concentration of the adsorbate.

The slope of the line in Fig. 6 varies with concentration. Thus, if there were multiple sites with different adsorption energies, both the *a* and *b* values would appear to vary with concentration. The model developed in the paper was for monolayer, homogeneous adsorption cases. However, it can be extended for heterogeneous surfaces, too. The concentration dependence of the adsorption potential observed in the present model can be explained using isotherms of heterogeneous surfaces such as the Jovanovic–Freundlich, Langmuir–Freundlich, Fowler–Guggenheim/Langmuir–Freundlich, and extensions of these models. For the Jovanovic–Freundlich model, the *a* value is expressed as a function of $e^{-\alpha C}$ (similar to the empirical fit in the paper), where α is a sole function of temperature and describes the adsorbate–adsorbent interactions.

Although the exponent *n*, according to the traditional analysis for Freundlich isotherm generation (Table 2 and Fig. 2) involving adsorbate uptake and equilibrium concentration values, was found to be between 0.34 and 0.37,

TABLE 4
Estimated Freundlich Constants (assuming $n = 1$) and Mass Transfer Coefficients [Eq. (2)]

Adsorbent	Adsorbate	Initial concentration (mg/L)	m_s (mg/L)	k_f (L/g)	$k_m A_m$ (L/hr)	r^2
AC	Benzaldehyde	52.5	1.0	1716	1.4983	0.9725
AC	Benzaldehyde	522.5	1.0	1.440	0.7582	0.9943
AC	Benzaldehyde	1568.0	1.0	0.406	0.6453	0.9693
AC	Nitro-4-phenol	50.0	1.0	11.752	1.7360	0.9903
AC	Nitro-4-phenol	300.0	1.0	1.659	0.6805	0.9994
AC	Nitro-4-phenol	700.0	1.0	0.562	0.4599	0.9960
Fly ash	Copper	12.0	20.0	1.0229	0.0511	0.9961
Fly ash	Chromium	500.0	20.0	0.0006	0.0161	1.0000
Fly ash	Cadmium	500.0	20.0	0.0001	0.0008	0.9998
Fly ash	Nickel	500.0	7.5	0.6305	0.5102	0.9740

the corresponding external mass transfer controlled model [Eq. (2)] was used in this study (which assumes $n = 1$). Note that the form of the Freundlich isotherm for $n = 1$ is equivalent to the linear isotherm and Langmuir isotherm for very low concentrations ($1 \gg aC_e$). Thus, we believe that this model is not a good representation of the experimentally obtained results (Table 4).

The data obtained show a high value of regression coefficient. The constant, k_f, is found to be dependent upon the adsorbate concentration. For example, $k_f = 5883.9C_e^{-1.4292}$ for benzaldehyde adsorption and $k_f = 1050C_e^{-1.1428}$ for nitro-4-phenol adsorption on AC. Compared to the organic adsorbates, higher values of the correlation coefficient were obtained for metal ion adsorbates, an observation that is also consistent with the results from the data obtained from the Langmuir adsorption analysis (Table 3). The mass transfer coefficients were again found to be much lower for metal ion adsorption than for organic compound adsorption. Thus, it appears that metal ion adsorption is rapid and is characterized by mass transfer limitations. The adsorption constant obtained, k_f, was used to generate dynamic concentration profiles (Figs. 3–5). A good match exists between the experimental data and the data obtained from the model. However, when the data generated from Langmuir and Freundlich isotherm-based models [Eqs. (9) and (2), respectively] are compared with experimental data, it clearly appears that the Langmuir adsorption model conforms to the experimental data more closely.

The model developed in this study is applicable when the mass transfer rate is significantly lower than the corresponding adsorption rate. The following section compares the rate constants obtained for adsorption-controlled and mass-transfer-controlled mechanisms. The first-order rate constants (based on surface reactions calculated by the use of the equation provided by Lagergren

[Eq. (1)] are 4.15, 1.38, 1.40, and 0.98 L/h for copper, chromium, cadmium, and nickel, respectively. The above values of the adsorption rate constants for metal are approximately 8–10 times as high as the mass transfer rate constants ($k_m A_m$) obtained from the model presented in this paper. The r^2 values obtained on fitting the Lagergren's equation to the experimental data for metal ions ranged from 0.9099 to 0.9324. In addition, the distribution of errors between the predicted value and the experimental value was not random when the Lagergren's equation was used. However, the mass transfer rate constants and the surface reaction rate constants for the adsorption of organic compounds on activated carbon were of comparable orders [e.g., 0.908 using Eq. (1) and 1.08 using Eq. (9) for the adsorption of 700 mg/L of nitro-4-phenol onto activated carbon]. However, linearization of the data was not achieved upon log transformation, indicating the unsuitability of the first-order kinetic model.

Langmuir isotherm provides a more complete description of equilibrium adsorption as compared to linear isotherm (which is a simplified case and is valid for low concentrations only) and the Freundlich isotherm (which is semiempirical). As a result, the C_t/C_0 value (for a given time, t) remains constant irrespective of concentration for the model based on Freundlich isotherm with $n = 1$, which is true at low concentrations and changes at higher concentrations.

Note that the Langmuir isotherm can explain both types of mechanisms: first-order and zero-order. The following is an explanation of the limiting cases (zero- and first-order). The zero-order adsorption kinetics are obtained when $C_e \gg 1$ or $a \gg 1$, while the product aC_e remains finite. However, the former condition has no experimental bearing on adsorption kinetics because both the initial and the dynamic concentrations are too large, and the amount adsorbed relative to the bulk concentration is negligible. In the latter case, for the product aC_e to be finite, the equilibrium concentration, C_e, must be close to zero. Applying the above condition to Eqs. (5) and (12) yields the same equation, i.e.,

$$C_t = C_0 e^{-k_m A_m t}$$

The first-order adsorption kinetics are obtained when abC_e is finite and aC_e/b tends to zero. The integration of Eq. (5) yields the same form obtained by McCay et al. (3) [Eq. (2)]. The k_f in Eq. (2) is replaced by the product of the constants in the Langmuir isotherm, a and b.

Thus, the model based on Langmuir isotherm [Eq. (9)] provides better predictions over a wide range of concentration (as seen in Fig. 7). In addition, the Freundlich isotherm yields an expression that cannot be solved analytically and therefore it is difficult to use. The derivation arrived in this paper is found to be helpful for homogeneous cases and its possible extension to heteroge-

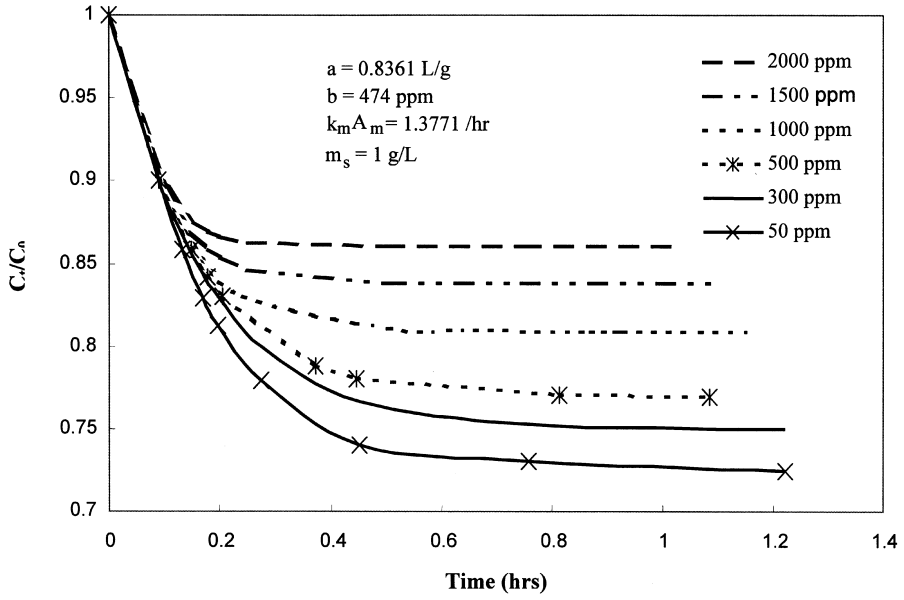

FIG. 7 Predicted effect of initial concentration on adsorption dynamics using Eq. (9).

neous cases has also been discussed. The model developed in this study based on the Langmuir isotherm can be used more conveniently to predict the dynamic concentration of adsorbate than the model developed previously using the Freundlich adsorption isotherm.

CONCLUSIONS

A new model that describes the dynamic concentration of adsorbate for external mass transfer limited case for Langmuir isotherm was developed. The model can be used to estimate the various constants of adsorption isotherm using only one set of concentration vs. time data with a reasonably high degree of accuracy. On the basis of the regression coefficient data obtained for concentration vs. time data, the model appears to predict dynamic concentration vs. time data more accurately for metal ion adsorption compared to the adsorption of organic compounds. The data show that the model prediction is more reliable when the mass transfer coefficient involved is low (or the rate of adsorption is high). Predictions for the external mass transfer limited case using the Freundlich adsorption isotherm [Eq. (2)] compare well with experimental data with high r^2 values (greater than 0.97). However, the model developed in this paper is more complete. The constants of adsorption are concentration-dependent. For the Langmuir adsorption isotherm, adsorption potential, *a*, and the maximum adsorption capacity, *b*, are found to respectively decrease and increase with adsorbate concentration. This concentration

is explained in terms of energy distribution associated with adsorption. The constant, k_f, associated with the Freundlich isotherm decreases with concentration and the explanation offered for this behavior also lies in considering the energy distribution of adsorption.

APPENDIX

Substitution of Eq. (4) in the differential Eq. (1) leads to the following expression:

$$\frac{dC_t}{dt} = -\frac{k_m A_m}{a} \qquad \frac{AC_t^2 + (a\alpha + 1)C_t - C_0}{C_t + \alpha}$$

Integrating between $t = 0$ and t, and C_0 and C_t, gives us

$$\int_{C_0}^{C_t} \frac{C_t + \alpha}{AC_t^2 + (a\alpha + 1)C_t - C_0} = -\frac{k_m A_m}{a} t$$

Let

$$\chi = C_t$$

The above integral is solved by using the following identities (14):

$$\int \frac{d\chi}{x} = \frac{1}{\sqrt{-q}} \ln \frac{2C\chi + b - \sqrt{-q}}{2C\chi + b + \sqrt{q}}$$

and

$$\int \frac{\chi d\chi}{x} = \frac{1}{2C} \ln x - \frac{b}{2C} \int \frac{d\chi}{x}$$

where $x = C\chi^2 + b\chi + a$ and $q = 4AC - b^2$

The result is given by Eq. (9).

NOMENCLATURE

a	adsorption energy, L/g
A_m	surface area, m^2
b	adsorption capacity, mg/g
C	concentration, mg/L
k_f	proportionality constant, $(L/g)(mg/L)^{-n}$
k_m	mass transfer coefficient, L/m^2-h
m_s	adsorbent loading, g/L
q	uptake, mg/g
t	time, h

Subscripts

e equilibrium
0 initial
t time

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