Adsorption 7: 305–317, 2001

A Film-Pore-Surface Diffusion Model for the Adsorption of Acid Dyes on Activated Carbon

KEITH K.H. CHOY, JOHN F. PORTER AND GORDON MCKAY*
Department of Chemical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR, People's Republic of China
kemckayg@ust.hk

Received March 9, 2001; Revised August 13, 2001; Accepted September 19, 2001

Abstract. The sorption of acid dyes from aqueous effluents onto activated carbon has been studied. The effects of initial dye concentration and activated carbon mass on the rate of Acid Blue 80, Acid Red 114 and Acid Yellow 117 removal have been investigated. A three-resistance mass transport model based on film, pore and surface diffusion control has been applied to model the concentration decay curves. The model incorporates an effective diffusion coefficient D_{eff}, which is dependant on the equilibrium solid phase concentration or fractional surface coverage. The results of the film-pore-surface diffusion model are compared with the data obtained from the basic film-pore diffusion model. It has been found that the film-pore-surface diffusion model provides a major improvement over the data correlated by the film-pore diffusion model. Also, the relationship between surface diffusion and fractional surface coverage has been investigated for the adsorption of acid dyes on activated carbon.

Keywords: film-pore-surface diffusion, batch sorption, surface coverage, acid dyes, activated carbon

Introduction

Adsorption is now widely accepted as an effective purification method for the treatment of wastewater. The removal of colour by various adsorbents has been the subject of several recent research papers. Agricultural waste materials such as bagasse pith, sawdust, pine bark, maize cob, rice bran, rice hull, coconut husk fibres, nut shells, soybean and cotton seed hulls have been evaluated for their adsorption properties and these materials have been reported to adsorb different pollutants such as dyestuffs and other toxic pollutants (Okieimen et al., 1991; Marshall et al., 1993; Marshall and Johns, 1996). Sawdust waste (Asfour et al., 1985) and bagasse pith (McKay et al., 1987; Marshall and Champagne, 1995; Marshall and Johns, 1996; Al-Asheh et al., 2000) have also been reported as capable of adsorbing significant quantities dyestuffs from aqueous effluents. Palm fruit branch particles were used for the adsorption of basic dyes (Nassar et al., 1995).

The suitability of using peat as a natural adsorbent material for the removal of dyestuffs from simulated wastewater has been studied by McKay and Allen (1980) and adsorption isotherms of dyestuffs onto peat have been determined. The data obtained were correlated using equations based on the Langmuir and Freundlich models. The adsorption kinetics of dyestuffs onto peat have also been studied in an agitated batch adsorber based on an intraparticle diffusion process (McKay and Allen, 1980) and external mass transfer (McKay and Allen, 1980, 1981).

El-Geundi (1987) studied the suitability of using of hardwood (sawdust) as a natural adsorbent for the removal of basic dyestuffs from simulated wastewater. It was found that the maximum adsorption capacity of hardwood is higher than that of softwood. The kinetics of adsorption as well as the adsorption isotherms

---

*To whom correspondence should be addressed.

for removal of dyestuffs by hardwood (sawdust) were studied by Asfour (1985).

McKay et al. (1987) studied the adsorption isotherms of the dyestuffs onto bagasse pith and the experimental data were well correlated by the Langmuir, Freundlich and Redlich-Peterson isotherms. The adsorption kinetics of the dyestuffs onto bagasse pith have also been studied in an agitated batch adsorber (McKay et al., 1996; Al Duri et al., 1990). Several mathematical models have been developed describing the experimental results for batch adsorbers (McKay et al., 1988; Al Duri et al., 1990). Namasivayam and Kanchana (1992) used banana pith for decolourising wastewaters and waste orange peel has also been used for dye removal (Namasivayam and Arasi, 1996)

The feasibility of using maize cob waste as a natural adsorbent material for the removal of dyestuffs from simulated wastewater has been studied (El-Geundi, 1991). Adsorption isotherms have been determined for the adsorption of basic dyestuffs onto maize (El-Geundi, 1991). Maize cob waste was shown to possess an affinity for dyestuffs of such a magnitude as to make its use as an adsorbent a possible alternative to the use of the more expensive activated carbon. Waste red mud was successful for removing Congo Red dye from effluent (Namasivayam and Arasi, 1996).

A large number of equilibrium and kinetic studies on the adsorption of dyes using chitosan and its derivatives have been carried out (Maghami and Roberts, 1988; Seo et al., 1988). Also, the adsorption of the acid dyes on chitosan has been studied in column systems. Several mathematical models have been developed describing the experimental results (Yoshida et al., 1994, 1995). Adsorption isotherms of acid dyes and direct dyes on chitin have been studied by McKay et al. (1982, 1983).

The ability of Fuller's Earth to adsorb basic dyestuffs from aqueous solutions has been studied by McKay et al. (1985). The adsorption isotherms for the removal dyestuffs by Fuller's Earth have both been studied. The results indicated that Fuller's Earth has considerable potential as an adsorbent material for the removal of basic dyestuffs in a commercial system (McKay et al., 1985).

Wool waste discarded from wool manufacturing processes has been used as an adsorbent material for the removal of surfactants and dyestuffs from simulated wastewater (Perineau et al., 1983). The adsorption isotherms as well as the adsorption kinetics of the surfactants and dyestuffs have both been studied.

Activated carbon still remains the most widely used industrial adsorbent and has also been used for dye adsorption (McKay et al., 1998). The application of models to adsorption systems is important to predict the performance of adsorbers. Several models based on various mass transfer resistance have been developed and tested. These include pore diffusion (Furusawa and Smith, 1973; Fritz and Schlunder, 1981) and solid phase or homogeneous surface diffusion (Hand et al., 1983; Traegner and Suidan, 1988). Three resistance models have been developed and include one based on the macro/meso/micropore structure of activated carbon (Peel et al., 1981). In practice the adsorption process involves the various diffusion models acting together in different ways depending on experimental and process conditions.

Theory

The basic mass transport model is the well-established shrinking core pore diffusion model, only the main equations are summarized here as the derivation has been presented previously (McKay et al., 1996)

The main equations are:

(i) External mass transfer:

$$\dot{N}_t = k_f A(C_t - C_{e,t}) \tag{1}$$

(ii) Internal mass transfer:

$$\dot{N}_t = k_p \rho A(Y_{e,t} - \bar{Y}_t) \tag{2}$$

(iii) Material balance:

$$\dot{N}_t = \frac{-V dC_t}{dt} = \frac{W d\bar{Y}_t}{dt} \tag{3}$$

(iv) Pore diffusion rate:

$$\dot{N}_t = \frac{4\pi D_{\text{eff}} C_{e,t}}{1/r_f - 1/R} \tag{4}$$

(v) Velocity of the concentration front:

$$\dot{N}_t = -4\pi r_f^2 Y_{e,h} \rho_t \frac{dr_f}{dt} \tag{5}$$

(vi) Average concentration in the adsorbed phase:

$$Y_t = Y_{e,h}[1 - (r_f/R)]^3 \tag{6}$$

Solving the above set of equations for $C_{e,t}$ yields:

$$C_{e,t} = C_t + \left[\frac{V}{k_f A}\right]\left[\frac{dC_t}{dt}\right] \tag{7}$$

Using the system initial conditions, at $t = 0$

$$C_t = C_0 \tag{8}$$

$$C_{e,t} = 0 \tag{9}$$

$$N(0) = k_f A C_0 \tag{10}$$

$$k_f = \frac{-V}{AC_0}\left[\frac{dC_t}{dt}\right]_{t\to 0} \tag{11}$$

Initially, all the mass transfer resistance is in the boundary layer and $(dC)/(dt)_{t\to 0}$ approaches a straight line. In this study, equilibrium is described by the Langmuir formula (Langmuir, 1918), given by:

$$Y_e = \frac{K_L C_e}{1 + a_L C_e} \tag{12}$$

With the above conditions and the introduction of dimensionless parameters, the adsorption rate for a single particle can be expressed in terms of adsorbate concentration in the water phase ε, the absorbent phase η and the B_{iot} number B_i.

$$\frac{d\eta}{d\tau} = \frac{3(1 - C_h\eta)(1-\eta)^{1/3}}{1 - (1 - 1/B_i)(1-\eta)^{1/3}} \tag{13}$$

or the general type:

$$\frac{d\eta}{d\tau} = f(\eta)\varepsilon B_i \tag{14}$$

where

$$\tau = \frac{C_0}{\rho_t Y_{e,h}}\frac{D_p t}{R^2} \tag{15}$$

$$\eta = \frac{Y_t}{Y_{e,h}} \tag{16}$$

$$\varepsilon = \frac{C_t}{C_0} \tag{17}$$

$$B_i = \frac{k_f R}{D_p} \tag{18}$$

$$C_h = (Y_{e,h}W)/(C_0 V) \tag{19}$$

The set of equations is solved and the rate of adsorption is calculated as a function of ε, η and B_i; an analytical solution is available when $Y_{e,t}$ is assumed constant.

$$\tau = \frac{1}{6C_h}\left[\ln(|x^3 + a^3|)^{(2B-\frac{1}{a})}\right] + \ln\left[\left\{(|x+a|)^{\frac{3}{a}}\right\}\right] - \frac{1}{aC_h}\arctan\left[\frac{(2x-a)}{a\sqrt{3}}\right] \tag{20}$$

where $x = (1-\eta)^{1/3}$, $C_h = (Y_{e,h}W)/(C_0V)$, $B = 1 - 1/B_i$ and $a = [(1 - C_h)/C_h]^{1/3}$ The solution of this model results in the best fit values of k_f and D_{eff} being obtained for correlating the experimental data. Under the experimental conditions of constant agitation and constant particle size, k_f is constant. However, it is found that D_{eff} does vary, suggesting a mechanism involving surface and pore diffusion and a variable surface diffusivity.

For the case of both pore and surface diffusion being involved in the mass transfer process, D_{eff} is represented by:

$$D_{\text{eff}} = D_p + \rho_t D_s \frac{\partial Y}{\partial C} \tag{21}$$

It has been shown (McKay and Al Duri, 1988; Suzuki and Fujii, 1982) that the estimated effective diffusion coefficient was greater than the pore diffusivity D_p, due to surface migration on the pore wall. The authors also found surface diffusion is concentration dependent. Komiyama and Smith (1974) found that surface diffusion contributed 20 times as much as pore diffusion. Therefore, surface diffusion has an inevitable effect on the effective diffusivity defined by the "film-pore diffusion" model.

For the Langmuir isotherm, $\partial Y/\partial C$ becomes:

$$\frac{\partial Y}{\partial C} = \frac{\partial Y_e}{\partial C_e} = \frac{K_L}{(1 + a_L C_{e,t})^2} \tag{22}$$

hence D_{eff} can be expressed as:

$$D_{\text{eff}} = D_p + \rho_p D_s \frac{K_L}{(1 + a_L C_{e,t})^2} \tag{23}$$

Several workers (McKay and Al Duri, 1988; Do and Rice, 1987; Hu and Do, 1994; Do et al., 2000) have reported D_s as a function of the fractional surface coverage, $Y_{e,t}/Y_{\max}$. Therefore, the expression used for surface diffusivity, D_s, in the present work is:

$$D_s = \frac{D_{s,0}\exp\left(\frac{-E_{\text{act}}}{R'T}\right)}{\left(1 - \frac{Y_{e,t}}{Y_{e,\max}}\right)} \tag{24}$$

A detailed discussion on the correlation between D_s and $D_{s,0}$ has been given by Do et al. (2000).

In the earlier versions of the pore diffusion model (Spahn and Schlünder, 1975; McKay and Allen, 1984; Neretnieks, 1974), the diffusion coefficient, D_{eff}, was based on combining constant values of D_p and D_s. The cases in which this assumption is justified have been discussed in detail (Crittenden et al., 1985; Yeroshenkova et. al., 1983; Neogi and Ruckenstein, 1980; Whitaker, 1988; Cheung et al., 2000).

Since the present work has been performed isothermally, the relationship between D_s and $D_{s,0}$ is primarily dependent on surface coverage (McKay et al., 1988; Do et al., 2000). The relationship proposed by Higashi (1963) is:

$$D_s = \frac{D_{s,0}\exp\left(\frac{-E_{\text{act}}}{R'T}\right)}{(1-\theta)} \quad \text{where } \theta = Y_e/Y_{\max} \tag{25}$$

At constant temperature, Eq. (25) will be become:

$$D_s = \frac{D'_{s,0}}{(1-\theta)} \tag{26}$$

There is an anomaly at the monolayer, because as the surface coverage θ trend to 1, then D_s will become infinite. Darken (1948) have considered the relationship between the diffusivities in terms of chemical potential. The surface diffusion flux, J_s, is related to the chemical potential, μ, gradient by:

$$J_s = -LY_e\frac{d\mu}{dc} \tag{27}$$

At equilibrium, in an ideal solution, the chemical potential is related to the reference chemical potential, μ_0, as follows:

$$\mu = \mu_0 + RT\ln C_e \tag{28}$$

Combining Eqs. (27) and (28), the flux is:

$$J_s = -D_{s,0}\exp(-E/RT)Y_e\frac{d\ln C_e}{dc} \tag{29}$$

However, from Eq. (27):

$$D_{s,0} = \exp(-E/RT) = LRT \tag{30}$$

Then, we obtain Eq. (31):

$$D_s = D_{s,0}\exp(-E/RT)\frac{\partial\ln C_e}{\partial\ln Y_e} \tag{31}$$

Using the Langmuir isotherm from Eq. (12), $\partial\ln C_e/\partial\ln Y_e$ is obtained, and in terms of fractional coverage $\theta(=Y_e/Y_{\max})$; then Eq. (31) reduces to Eq. (25), i.e. the Higashi model. Yang et al. (1973) and Kapoor and Yang (1990) have developed modifications to Eq. (25). These papers incorporated expressions to represent activation energies for surface diffusion on first and second layers respectively.

A Microsoft Excel 2000 spreadsheet program was used to determine the value of external mass transfer coefficient and pore and surface diffusion coefficient by using the built-in function 'Solver' to minimize the Average Relative Error (ARE) where $C_{t,\exp}$ is the experimental dye concentration and $C_{t,\text{cal}}$ is the calculated dye concentration.

$$\text{ARE} = \frac{100}{n}\sum_{i=1}^{p}\left|\frac{C_{t,\text{cal}} - C_{t,\exp}}{C_{t,\exp}}\right|_i \tag{32}$$

Experimental

The design of the standard agitated batch adsorber has been described in previous papers (Furusawa and Smith, 1973; McKay et al., 1996; Cheung et al., 2000). In addition, the methodology for carrying out the kinetic mass transport studies in the agitated batch adsorber and the methodology for measuring the equilibrium isotherms have also been presented in these papers. Three systems have been studied, namely, the adsorption of Acid Blue 80 (Ciba Speciality Chemicals), Acid Red 114 (Sigma- Aldrich Chemical Co.) and Acid Yellow 117 (Ciba Speciality Chemicals) onto Activated Carbon, Type F400 (Chemviron Carbon). Acid dyes were selected because they are a major concern to industry. The dye concentrations in solution were all measured using a Varian Cary 1E UV/VIS spectrophotometer.

The effect of concentration of acid dye solution on the adsorption rate is studied in these experiments. A mass of 1.7 g of activated carbon (particle size between 500 and 710 μm) is agitated with 1.7 dm^3 aqueous solution containing single dyes in the batch system for 3 hours. The impeller speed is 400 rpm, the temperature is kept at 20 ± 2°C. A range of concentrations of acid dye solutions (75, 100, 150 and 200 mg/dm^3) is used to analyse the sorption of acid dyes onto activated carbon. The effect of activated carbon mass on the adsorption rate is also studied using the same conditions as above except the initial concentration of solution is set at 100 mg/dm^3 and a range of sorbent masses (0.4, 0.8, 1.2, 1.7 and 2.2 g) are used.

Results and Discussion

Equilibrium Isotherm

The equilibrium isotherms were measured by contacting the adsorbents with dye solutions for twenty-one days, which was sufficient to achieve equilibrium. The data are analyzed by Eq. (12) and the Langmuir constants K_L and a_L and the saturation monolayer capacity, $Y_{\max}$, $(= K_L/a_L)$ are shown in Table 1. The best-fit values of K_L and a_L were determined by linear regression and the correlation coefficients, R^2, are also shown in Table 1. The saturation capacities for Acid Blue 80, Acid Red 114 and Acid Yellow 117 on carbon are 112.3 mg/g, 103.5 mg/g and 155.8 mg/g respectively.

The experimental equilibrium points are shown in Fig. 1, together with the theoretical Langmuir isotherm plots shown by the solid lines. The three sets of data approximate reasonably well to a rectangular isotherm, which is a required assumption of the shrinking core model.

Table 1. Langmuir isotherm constants.

Single component system	K_L (dm^3 g^{-1})	a_L (dm^3 mg^{-1})	$Y_{\max}$ (mg g^{-1})	R^2
AB80	60.73	0.5408	112.3	0.9979
AR114	27.84	0.2689	103.5	0.9952
AY117	78.28	0.5023	155.8	0.9938

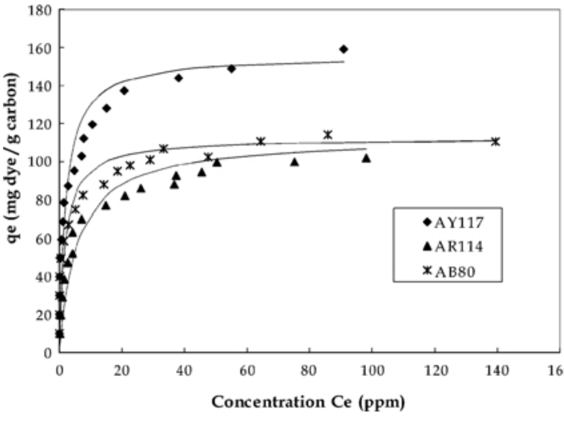

Figure 1. Langmuir isotherm plot for three acid dyes.

Mass Transfer Studies

In the previous paper (Cheung et al., 2000), a film-pore diffusion model was used to correlate the adsorption of acid dyes onto activated carbon. The film-pore diffusion model assumes that the equilibrium solid phase concentration $Y_{e,t}$ is constant, $Y_{e,t} = Y_{\max}$, for all system conditions and the effective diffusion coefficient D_{eff} is also constant because surface diffusion does not contribute to the diffusion process. The effect of initial dye concentration on the adsorption of AB80 on carbon by film-pore diffusion model is presented in Fig. 2 and the effect of adsorbent mass for the adsorption of AY117 on carbon is shown in Fig. 3. The film-pore diffusion model is based on the non-dimensionless time

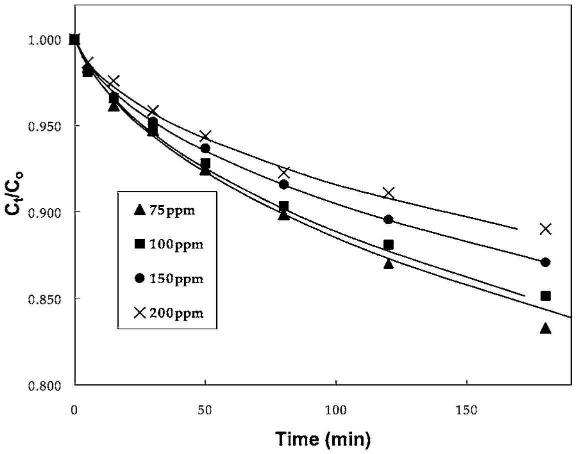

Figure 2. Effect of initial dye concentration (ppm) on the adsorption of Acid Blue 80 using the film-pore diffusion model.

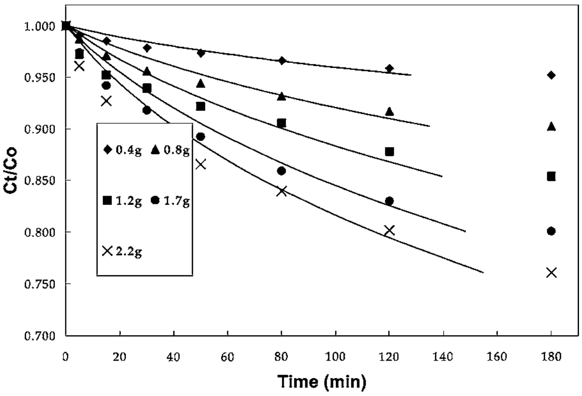

Figure 3. Effect of activated carbon mass on the adsorption of Acid Yellow 117 using the film-pore diffusion model.

method in Eq. (20) to determine the values of D_{eff} and k_f. From these two figures, it is found that the correlation between the experimental and theoretical data is not good using the film-pore diffusion model. It implies that the adsorption of acid dyes on activated carbon not only depends on pore diffusion but also involves surface diffusion. Therefore, an improved model—the film pore surface diffusion model—has been proposed in the present paper.

Film-Pore-Surface Diffusion Model

Two main improvements have been made in this model over the previous film-pore model (Cheung et al., 2000). The system is dominated by both pore and surface diffusion, so the effective diffusion coefficient D_{eff} is variable and the surface solid phase concentration is variable with time. Therefore, the equations in the model were solved to determine the single best fit k_f, D_p and $D'_{s,0}$ values for each of the three systems to correlate the experimental concentration versus time decay curves. The model has been compared with the previous models on the basis of the average relative error, ARE. Figures 4–9 present the effects of initial dye concentrations and adsorbent mass for the adsorption of three acid dyes on activated carbon where the plots of dimensionless liquid phase concentration, C_t/C_0, against time for each acid dye are shown. The correlation of the model results and experimental data are excellent for all different adsorbent mass and initial dye concentration variation for three acid dyes. The tables of best fit values for k_f, D_p and $D_{s,0}$ for each acid dye system with ARE values are given in Tables 2–4. A comparison of ARE values is also shown in Tables 2–4. This model provides a major improvement over the data correlated by the original film-pore diffusion model. A comparsion of the ARE values between film-pore and film-pore-surface diffusion models is shown in Table 5.

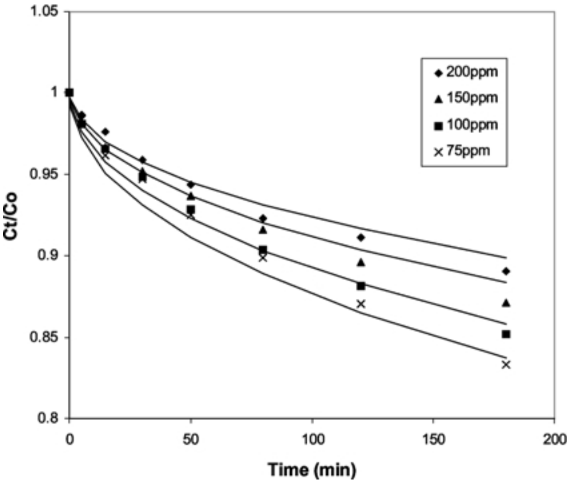

Figure 4. Sorption of AB80 onto activated carbon using film pore surface diffusion model (different initial dye concentration systems).

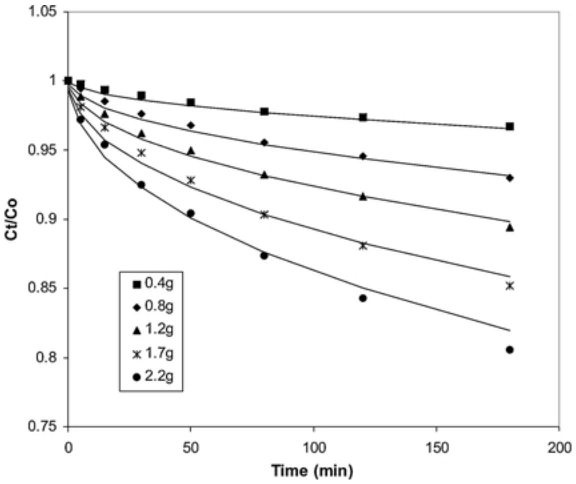

Figure 5. Sorption of AB80 onto activated carbon using film pore surface diffusion model (different carbon mass systems).

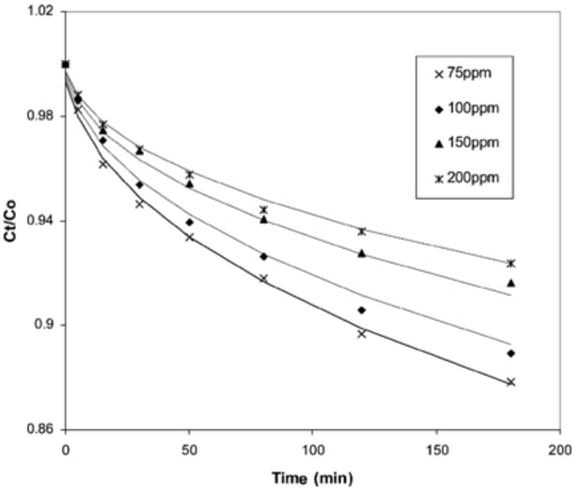

Figure 6. Sorption of AR114 onto activated carbon using film pore surface diffusion model (different initial dye concentration systems).

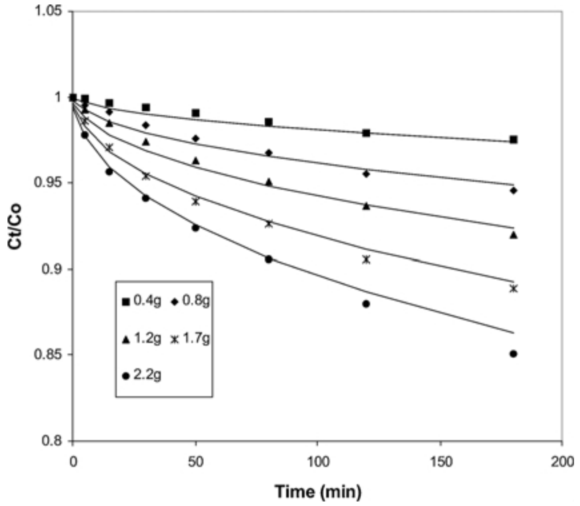

Figure 7. Sorption of AR114 onto activated carbon using film pore surface diffusion model (different carbon mass systems).

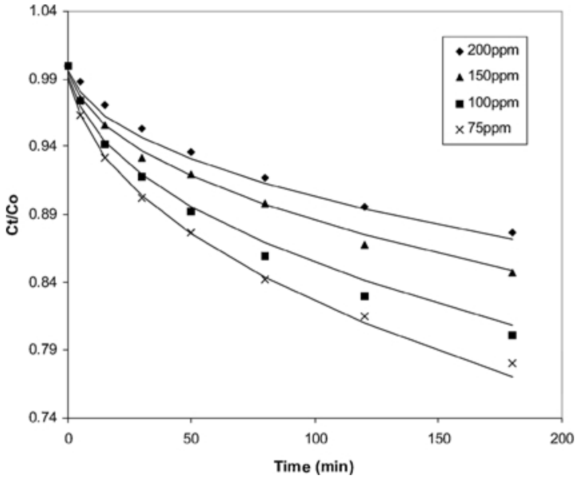

Figure 8. Sorption of AY117 onto activated carbon using film pore surface diffusion model (different initial dye concentration systems).

Relation Between Surface Diffusion and Fractional Surface Coverage

The effective diffusivity in pore diffusion models should be constant and equal to the pore diffusivity, which is also a function of molecular diffusivity, porosity and tortuosity, as defined in Eq. (33).

$$D_{\text{eff}} = D_p = D_M \varepsilon_p / \mu_{\text{tor}} \tag{33}$$

Table 2. Results of Acid Blue 80 on activated carbon by using the film pore surface diffusion model.

Carbon mass (g)	C_0 (mg/dm^3)	K_f (cm/s)	D_p (cm^2/s)	$D'_{s,0}$ (cm^2/s)	ARE
2.2	100				1.671
1.7	100				0.959
1.2	100				0.614
0.8	100				0.447
0.4	100	1.25E−04	4.73E−08	2.66E−11	0.462
1.7	200				0.574
1.7	150				0.833
1.7	100				0.959
1.7	75				1.183

Table 3. Results of Acid Red 114 on activated carbon by using the film pore surface diffusion model.

Carbon mass (g)	C_0 (mg/dm^3)	K_f (cm/s)	D_p (cm^2/s)	$D'_{s,0}$ (cm^2/s)	ARE
2.2	100				1.046
1.7	100				0.573
1.2	100				0.474
0.8	100				0.363
0.4	100	8.91E−05	3.38E−08	5.01E−09	0.329
1.7	200				0.201
1.7	150				0.612
1.7	100				0.573
1.7	75				0.799

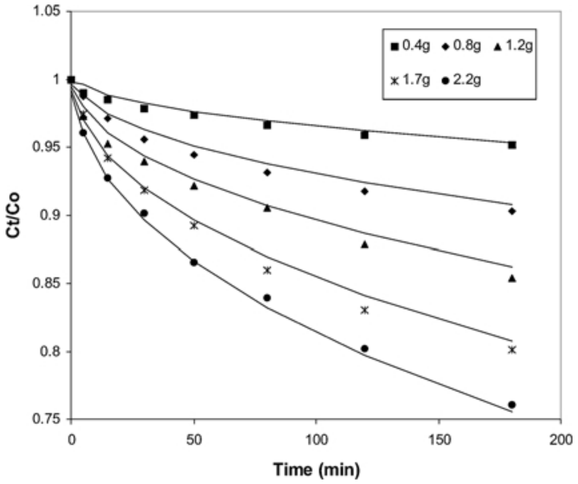

Figure 9. Sorption of AY117 onto activated carbon using film pore surface diffusion model (different carbon mass systems).

Table 4. Results of Acid Yellow 117 on activated carbon by using the film pore surface diffusion model.

Carbon mass (g)	C_0 (mg/dm^3)	K_f (cm/s)	D_p (cm^2/s)	$D'_{s,0}$ (cm^2/s)	ARE
2.2	100	6.12E−05	6.15E−08	3.24E−08	1.473
1.7	100				1.010
1.2	100				0.584
0.8	100				0.364
0.4	100				0.291
1.7	200				0.611
1.7	150				0.835
1.7	100				1.010
1.7	75				1.216

If surface diffusion is contributing to diffusion mass transfer, the mass transfer rate becomes:

$$N_t = D_p \frac{\partial C}{\partial r} + \rho_s D_s \frac{\partial Y}{\partial r} \tag{34}$$

Further development and analysis gives Eq. (35):

$$D_{\text{eff}} = D_p + \rho_s D_s \frac{\partial Y}{\partial C} \tag{35}$$

The best fit values of D_{eff} on a time dependent basis have been evaluated using the model presented in this paper. The gradients of the isotherm are defined by the surface tie line condition, $C_{e,t}$, $Y_{e,t}$ and are obtained by Langmuir isotherm. Therefore:

$$D_{\text{eff}} = D_p + \rho_s D_s \frac{K_L}{(1 + a_L C_{e,t})^2} \tag{23}$$

Based on optimizing Eq. (23) using Excel solver, the best fit constant single value for D_p is obtained and the surface concentration dependent D_s value can be obtained. Finally, Figs. 10–12 show D_s plotted against fractional surface coverage, for three acid dye experimental systems. The curves are correlated by the general Eq. (36) for AB80, AR114 and AY117.

$$D_{\text{eff}} = D_p + \rho_s \left(\frac{D'_{s0}}{1 - \theta} \right) \left(\frac{K_L}{(1 + a_L C_{e,t})^2} \right) \tag{36}$$

From Eq. (36), both pore and surface diffusion contribute to diffusion mass transfer, so the adsorption mass transfer rate is dependent on the magnitude of the pore and surface diffusivities. For the AB80 and AR114 systems, the value of D_p is much greater than

Table 5. Comparison of ARE values between film-pore and film-pore-surface diffusion models.

System	Carbon mass (g)	C_0 (mg/dm^3)	ARE values of film-pore diffusion model	ARE values of film-pore-surface diffusion model
Acid Blue 80 System	1.7	200	7.877	0.574
	1.7	150	8.362	0.833
	1.7	100	9.159	0.959
	1.7	75	7.659	1.183
Acid Blue 80 System	2.2	100	23.386	1.671
	1.7	100	9.159	0.959
	1.2	100	7.638	0.614
	0.8	100	15.377	0.447
	0.4	100	27.257	0.462
Acid Yellow 117 System	1.7	200	29.337	0.611
	1.7	150	36.845	0.835
	1.7	100	40.210	1.010
	1.7	75	70.551	1.216
Acid Yellow 117 System	2.2	100	46.913	1.473
	1.7	100	40.210	1.010
	1.2	100	61.847	0.584
	0.8	100	45.928	0.364
	0.4	100	64.817	0.291

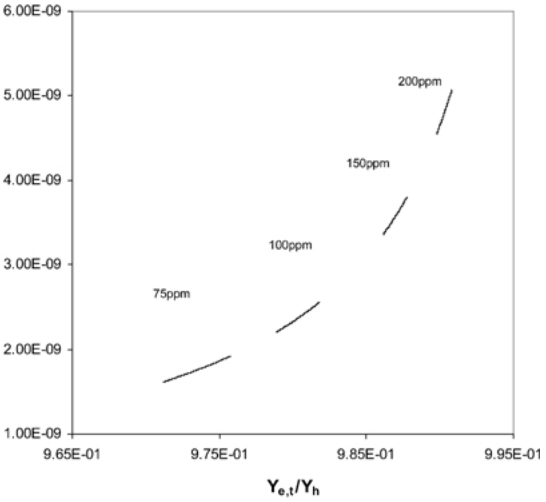

Figure 10. Surface diffusivity against surface coverage (Acid Blue 80 system).

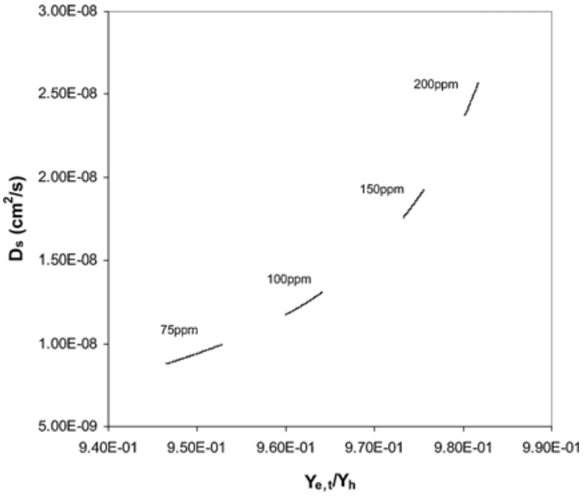

Figure 11. Surface diffusivity against surface coverage (Acid Red 114 system).

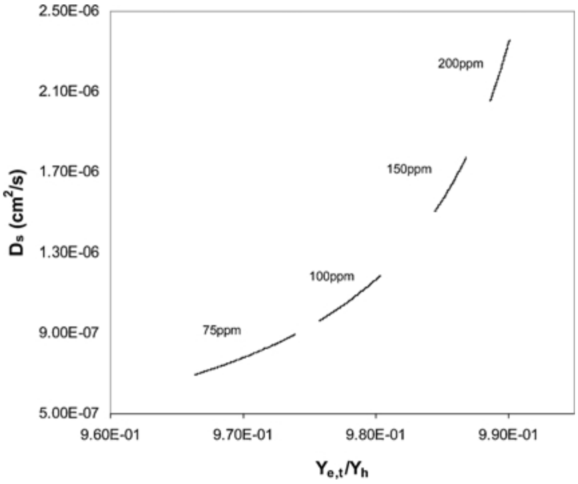

Figure 12. Surface diffusivity against surface coverage (Acid Yellow 117).

the value of D'_{s0}, it implies that pore diffusion is a main factor in the adsorption of AB80 and AR114 on carbon. For the AY117 system, the magnitude of D_p and D_{s0}, is quite similar, so the role of surface diffusion is as important as pore diffusion in the adsorption process of Acid Yellow 117 on activated carbon. It can also be proved by comparing the results between film-pore and film-pore-surface diffusion models. From Table 5, the correlation of the AY117 system is poorer than the AB80 system using film-pore diffusion model, it is because surface diffusion is involed in a higher contribution in the adsorption of AY117 on carbon. Hence, the film-pore-surface diffusion model provides the greatest improvement in fitting of the AY117 system.

New Model Validation

The incorporation of a solid surface diffusion component into a shrinking core film- pore diffusion model has to assess carefully. An additional surface diffusion resistance will have the effect of smearing or spreading the 'sharp' adsorbed dye concentration front, required by the assumptions of the shrinking core theory. This phenomenon tends to contravene the requirement of a sharp concentration front although it is not possible to quantify the extent of surface spreading. Therefore, the theoretical predictions, presented in the previous section, were based on a short contact time of three hours in which the relative contribution of surface diffusion adsorption will be small compared to the total amount of diffusion due to pore and surface. In which case, the effect of surface spreading should be small. In effect, the relative amounts of pore and surface adsorption can be compared by setting the surface diffusivity equal to zero. This was done in Figs. 13 and 14 and the amount of surface diffusion at three hours was calculated as 2% to 4% for the Acid Blue 80 system for C_0 from 75 mg/dm^3 to 200 mg/dm^3, and for the Acid Yellow 117 system as 14% to 6% for C_0 ranging from 75 mg/dm^3 to 200 mg/dm^3 respectively.

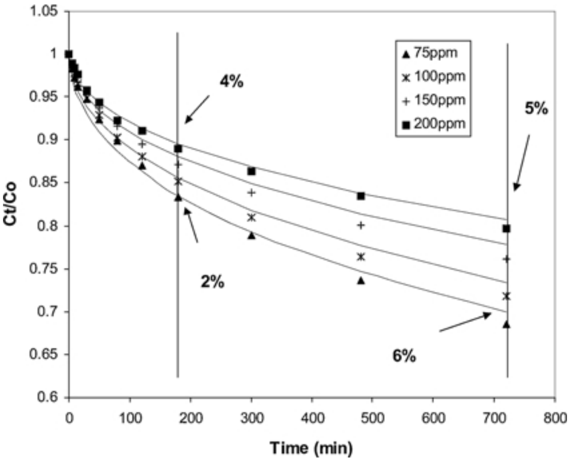

Figure 13. Sorption of AB80 onto activated carbon using film pore surface diffusion model (set $D'_{s,0} = 0$, different initial dye concentration systems).

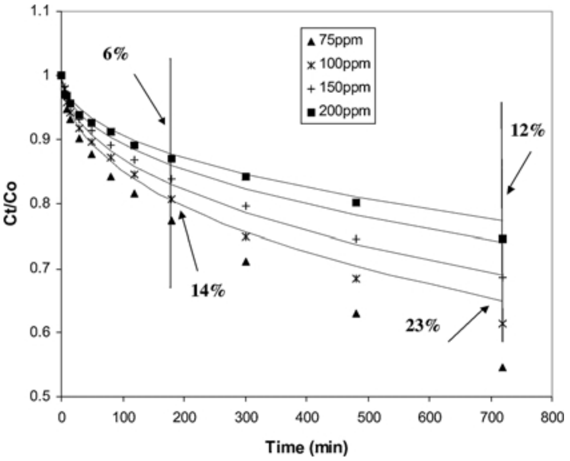

Figure 14. Sorption of AY117 onto activated carbon using film pore surface diffusion model (set $D'_{s,0} = 0$, different initial dye concentration systems).

To assess the quality of the model over a longer time period the experiments were conducted for 12 hours. After 12 hours, Figs. 13 and 14 show the fits for the film and pore mass transfer resistance model only. At twelve hours, Fig. 13 shows the contribution of surface diffusion is 6% to 5% for C_0 values from 75 mg/dm^3 to 200 mg/dm^3. In Fig. 14, at twelve hours the contribution of surface diffusion is 23% for a C_0 of 75 mg/dm^3 and 12% for a C_0 of 200 mg/dm^3.

The results of the three resistance model, including film, pore and surface diffusion mass transfer are shown in Figs. 15 and 16 for the adsorption of Acid Blue 80 and Acid Yellow 117 respectively onto activated carbon. Over the wide range of initial dye concentrations and carbon masses, the theoretical results are in good agreement with the experimental data points. Since constant D'_{s0} is used for the whole concentration and mass ranges involved for up to 12 hours, the assumptions of the sharp concentration front of the shrinking core model must not be significantly invalidated at these contribution levels of surface diffusion.

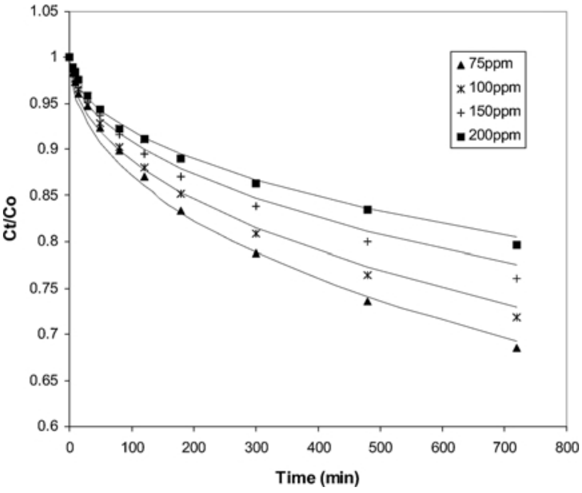

Figure 15. Sorption of AB80 onto activated carbon using film pore surface diffusion model (12 hours).

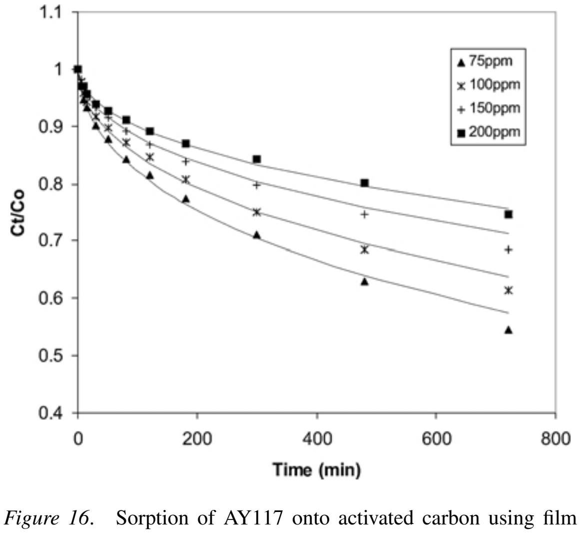

Figure 16. Sorption of AY117 onto activated carbon using film pore surface diffusion model (12 hours).

Conclusion

A new three-resistance model based on external mass transfer, pore and surface diffusion has been presented in the present paper. The model assumes that the adsorption process is predominantly dependent on both pore and surface diffusion, so the effective diffusion coefficient D_{eff} is variable and the equilibrium solid phase concentration is variable with time. An analytical solution is possible to obtain the effective diffusivity by minimizing the absolute relative error (ARE) of each individual data set. The results show that pore and surface diffusion are both involved in the mass transfer mechanism of acid dyes on activated carbon. The film-pore-surface diffusion model provides a major improvement over the basic film-pore diffusion model. Furthermore, the relation between surface diffusion and fractional surface coverage has been accurately correlated by equations incorporating the isotherm parameters.

Nomenclature

a_L	(dm^3 mg^{-1})	Langmuir isotherm constant
A	(m^2 g^{-1})	Surface area of adsorbent per unit mass of adsorbent
B_i	(dimensionless)	Biot number
C_t	(mol m^{-3})	Solute concentration in bulk phase
C_0	(mol m^{-3})	Initial concentration
C	(mg dm^{-3})	Liquid phase dye concentration
C_e	(mg dm^{-3})	Equilibrium liquid phase dye concentration
C_h	(mg dm^{-3})	Capacity factor in the pore diffusion model
D_{eff}	(m^2 s^{-1})	Effective diffusion coefficient
D_M	(m^2 s^{-1})	Molecular diffusivity
D_p	(m^2 s^{-1})	Effective pore diffusion coefficient
D_s	(m^2 s^{-1})	Effective surface diffusion coefficient
d_p	(m)	Adsorbent particle diameter
E_{act}	(J mol^{-1})	Activation energy
J_s	(m s^{-1})	Surface diffusion flux
k_f	(m s^{-1})	External film mass transfer coefficients
k_p	(m s^{-1})	Internal solid phase mass transfer coefficient
K_L	(dm^3 g^{-1})	Langmuir isotherm constant
W	(g)	Mass of adsorbent
$\dot{N}_t$	(g s^{-1})	Mass transfer rate
r_f	(m)	Radius of concentration front of adsorbate penetrating adsorbent
R'	(J mol^{-1} K^{-1})	Universal gas constant
R	(m)	Radius of adsorbent particle size
t	(s, min, h)	Time
T	(K)	Temperature
V	(dm^3)	Volume of liquid phase
Y	(mg g^{-1})	Concentration in solid phase
$\bar{Y}_t$	(mg g^{-1})	Mean equilibrium solid-phase concentration at fixed time
$Y_{e,h}$	(mg g^{-1})	Hypothetical equilibrium solid-phase concentration

Greek Letters

ε	(dimensionless)	Dimensionless liquid-phase concentration in the pore diffusion model
η	(dimensionless)	Dimensionless solid phase concentration
θ	(dimensionless)	Surface coverage
μ	(J mol^{-1})	Chemical potential
μ_{tor}	(dimensionless)	Tortuosity
ρ	(g cm^{-3})	Particle density of adsorbent
η	(dimensionless)	Dimensionless solid-phase concentration in the pore diffusion model
τ	(dimensionless)	Dimensionless time

Subscripts

0	Initial value
e	Equilibrium value
h	Hypothetical
t	Species time
T	Total value for the system
max	Maximum
exp	Predicted by experiment
cal	Predicted by calculation

References

Al-Asheh, S., F. Banat, R. Al-Omari, and Z. Duvnjak, "Predictions of Binary Sorption Isotherms for the Sorption of Heavy Metals by Pine Bark Using Single Isotherm Data," *Chemosphere*, **41**, 659–665 (2000).

Al Duri, B., G. McKay, and M.S. El Geundi, "Three-resistance Transport Model for Dye Adsorption Onto Bagasse Pith," *J. Envir. Eng.*, **116**, 487–502 (1990).

Asfour, H.M., M.M. Nassar, O.A. Fadali, and M.S. El-Geundi, "Colour Removal from Textile Effluents Using Hardwood Sawdust as an Adsorbent," *J. Chem. Technol. Biotechnol.*, **35**, 28–35 (1985).

Cheung, C.W., K.H. Choy, J.F. Porter, and G. McKay, "Combined Diffusion Model for Batch Adsorption," *Ads. Sci. Technol.*, 426–430 (2000).

Crittenden, J.C., P. Luft, D.W. Hand, J.L. Oravltz, S.W. Loper, and M. Arl, "Solid Pore Diffusion Model for Adsorption Systems," *Env. Sci. azTechnol.*, **19**, 1037–1043 (1985).

Darken, L.S., "Diffusion, Mobility and Their Interrelation Through Free Energy in Binary Metallic Systems," *Trans. AIME*, **175**, 184–201 (1948).

Do, H.D., I. Prasetyo, and D.D. Do, "Surface Diffusion of Hydrocabon in Activated Carbon," *Ads. Sci. Technol.*, 184–188 (2000).

Do, D.D. and R.G. Rice, "On the Relative Importance of Pore and Surface Diffusion in Non-equilibrium Adsorption Rate Processs," *Chem. Eng. Sci.*, **42**, 2269–2284 (1987).

El-Geundi, M.S., "Mass Transfer Processes During Colour Removal from Effluents Using Adsorption Techniques," Ph.D. Thesis, Minia University, Egypt, 1987.

El-Geundi, M.S. and M. Akl, "Colour Removal from Textile Effluents by Adsorption Techniques," *Water Research*, **25**, 271–273 (1991).

Fritz, W. and E.U. Schlünder, "Competitive Adsorption of Two Dissolved Organics Onto Activated Carbon-I," *Chem. Eng. Sci.*, **36**, 721–730 (1981).

Furusawa, T. and J.M. Smith, "Fluid-particle and Intraparticle Mass Transport Rates in Slurries," *Ind. Eng. Chem. Fundam.*, **12**, 197–203 (1973).

Hand, D.W., J.C. Crittenden, and W.E. Thacker, "User Orientated Batch Reactor Solutions to the Homogeneous Surface Diffusion Model," *J. Envir. Engng Div. Am. Soc. Civ. Engrs.*, **109**, 82–92 (1983).

Higashi, K., H. Ito, and J. Oishi, "Surface Diffusion Phenomena in Gasous Diffusion, (I). Surface Diffusion of Pure Gas," *J. Atom. Energy Soc. Japan*, **5**, 846–853 (1963).

Hu, X. and D.D. Do, "Effect of Surface Heterogeneity on the Adsorption Kinetics of Gases in Activated Carbon: Pore Size Distribution vs Energy Distribution," *Langmuir*, **10**(9), 3296–3302 (1994).

Kapoor, A. and R.T. Yang, "Surface Diffusion on Energetically Heterogeneous Surfaces—an Effective Medium Approximation Approach," *Chem. Eng. Sci.*, **31**, 129–135 (1990).

Komiyama, H. and J.M. Smith, "Surface Diffusion in Liquid Filled Pores," *AIChE J.*, **20**, 1110–1177 (1974).

Langmuir, I., "The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum," *J. Amer. Chem. Soc.*, **40**, 1361–1403 (1918).

Maghami, G.G. and G.A. Roberts, "Studies on the Adsorption of Anionic Dyes on Chitosan," *Makromol. Chem.*, **189**, 2239–2243 (1988).

Marshall, W.E. and E.T. Champagne, "Agricultural By-products as Adsorbents for Metal Ions in Laboratory Prepared Solutions and in Manufacturing Wastewater," *J. Env. Sci. Health Part A*, **A30**, 241–261 (1995).

Marshall, W.E., E.T. Champagne, and W.J. Evans, "Use of Rice Milling By-products (Hulls and Bran) to Remove Metal Ions from Aqueous Solutions," *J. Env. Sci. Health Part A*, **A28**, 1977–1992 (1993).

Marshall, W.E. and M.M. Johns, "Agricultural By-products as Metal Adsorbents: Sorption Properties and Resistance to Mechanical Abrasion," *J. Chem. Technol. Biotechnol.*, **66**, 192–198 (1996).

McKay, G. and S.J. Allen, "Surface Mass Transfer Processes Using Peat as an Adsorbent for Dyestuffs," *Canadian J. Chem. Eng.*, **58**, 521–526 (1980).

McKay, G. and S.J. Allen, "Pore Diffusion Model for Dye Adsorption Onto Peat in Batch Adsorbers," *Canadian J. Chem. Eng.*, **62**, 340–345 (1984).

McKay, G., S.J. Allen, I.F. McConvey, and M.S. Otterburn, "Transport Processes in the Sorption of Colored Ions by Peat Particles," *J. Coll. Interf. Sci.*, **80**, 323–339 (1981).

McKay, G., S.J. Allen, and L. Whitten, "The Production and Characterisation of Activated Carbons: A Review," *Dev. Chem. Eng. Mineral Process*, **6**(5), 231–261 (1998).

McKay, G., H.S. Blair, and J.R. Gardner, "Adsorption of Dyes on Chitin. I. Equilibrium Studies," *J. Appl. Poly. Sci.*, **27**, 3043–3057 (1982).

McKay, G., H.S. Blair, and J.R. Gardner, "The Adsorption of Dyes in Chitin. III. Intraparticle Diffusion Processes," *J. Appl. Poly. Sci.*, **28**, 1767–1778 (1983).

McKay, G., M. El Geundi, and M.M. Nassar, "Equilibrium Studies During the Removal of Dyestuffs from Aqueous Solutions Using Pith," *Water Research*, **21**, 1513–1520 (1987).

McKay, G., M. El Geundi, and M.M. Nassar, "Pore Diffusion During the Adsorption of Dyes Onto Bagasse Pith," *Trans. I ChemE.*, **74**, 277–288 (1996).

McKay, G., M.S. Otterburn, and J.A. Aga, "Fuller's Earth and Fired Clay as Adsorbents for Dyestuffs Equilibrium and Rate Studies," *Water Air Soil Pollut.*, **24**, 307–322 (1985).

Namasivayam, C. and D.J.S.E. Arasi, "Removal of Congo Red from Wastewater by Adsorption Onto Waste Red Mud," *Chemosphere*, **34**, 401–417 (1996).

Namasivayam, C. and N. Kanchana, "Waste Banana Pith as an Adsorbent for Colour Removal From Wastewaters," *Chemosphere*, **25**, 1691–1705 (1992).

Namasivayam, C., N. Muniasamy, K. Gayatri, M. Rani, and K. Ranganathan, "Removal of Dyes From Aqueous Solutions by Cellulosic Waste Orange Peel," *Bioresource Technol.*, **57**, 37–43 (1996).

Nassar, M.M., M.F. Hamoda, and G.H. Radwan, "Adsorption Equilbiria of Basic Dyestuff Onto Palm-fruit Branch Particles," *Wat. Sci. Technol.*, **32**, 27–32 (1995).

Neogi, P. and E. Ruckenstein, "Transport Phenoma in Solids With Bidispersed Pores," *AIChE J.*, **26**, 787–799 (1980).

Neretnieks, I., "Adsorption of Components Having a Saturation Isotherm," *Chem. Ing. Technol.*, **46**, 781–792 (1974).

Okieimen, F.E., E.U. Okundia, and D.E. Ogbeifun, "Sorption of Cadmium and Lead Ions on Modified Groundnut (Arachis Hypogea) Husks," *J. Chem. Technol. Biotechnol.*, **51**, 97–103 (1991).

Peel, R.G., A. Benedek, and C.M. Crowe, "A Branched Pore Kinetic Model for Activated Carbon Adsorption," *AIChE J.*, **27**(1), 26–31 (1981).

Perineau, F., J. Molinier, and A. Gaset, "Adsorption of Ionic Dyes on Wool Carbonizing Waste," *Water Research*, **17**, 559–567 (1983).

Seo, T., T. Kanbara, and T. Iijima, "Sorption of Methyl Orange by Chitosan Gels Having Hydrophobic Groups," *J. Appl. Polym. Sci.*, **36**, 1443–1451 (1988).

Spahn, H. and E.U. Schlünder, "The Scale-up of Activated Carbon Columns for Water Purification, Based on Results from Batch Test-I," *Chem. Eng. Sci.*, **30**, 529–537 (1975).

Suzuki, M. and T. Fujii, "Concentration Dependence of Surface Diffusion Coefficient of Propionic Acid in Activated Carbon," *AIChE J.*, **28**, 380–388 (1982).

Traegner, U.K. and M.T. Suidan, "Evaluation of Surface and Film Diffusion Coefficients for Carbon Adsorption," *Wat. Res.*, **23**(3), 267–273 (1988).

Whitaker, S., "Diffusion in Packed Beds of Porous Particles," *AIChE J.*, **34**, 679–688 (1988).

Yang, R.T., J.B. Fenn, and G.L. Haller, "Modification to the Higashi Model for Surface Diffusion," *AIChE. J.*, **19**, 1052–1054 (1973).

Yeroshenkova, G.V., S.A. Volkov, and K.I. Sakodynskii, "Effect of Packing Irregularities Along the Bed Length," *J. Chromatog.*, **262**, 19–24 (1983).

Yoshida, H., N. Kishimoto, and T. Kataoka, "Adsorption of Strong Acid on Polyaminated Highly Porous Chitosan: Equilibria," *Ind. Eng. Chem. Res.*, **33**, 854–859 (1994).

Yoshida, H., N. Kishimoto, and T. Kataoka, "Adsorption of Glutamic Acid on Polyaminated Highly Porous Chitosan; Equilibria," *Ind. Eng. Chem. Res.*, **34**, 347–355 (1995).