Film-pore diffusion models – analytical and numerical solutions

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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 and Acid Yellow 117 removal have been investigated. Three mass transport models based on film and pore diffusion control have been applied to model the experimental concentration decay curves. The models are compared on the basis of the solid phase loading capacity using various assumptions since the assignment of an appropriate solid phase loading has been the subject of several papers on this topic and no comparisons have been provided on the effectiveness of each approach. The equilibrium solid phase concentration is assumed: (i) incorporating a time dependant solid phase concentration $Y_{e,t}$, (ii) equal to the intersection point of the equilibrium isotherm and the operating line and (iii) the point on the equilibrium isotherm where the liquid phase concentration equals the initial concentration in the film-pore diffusion model.

Keywords: Film-pore diffusion, batch sorption, analytical method, numerical method, Acid Blue 80, Acid Yellow 117, activated carbon.

1. Introduction

World dye production rose more than 10% annually to 1 billion kg in 1994 (Marc, 1996). The value of dyes produced also rose more than 10% annually to US\$9.2 billion (56% textile dyes, 23.5% pigments, 14% dyes for paper and leather and 6.5% others). In the textile sector, an estimated 10-20% of dyes (active substances) used is lost in residual liquors through incomplete exhaustion and washing operations. For pigments the rate of loss is about 1-2%, and for paper and leather dyes, 10%. Effluent treatment processes for dye containing effluents are currently capable of removing about half the dyes lost in residual liquors. Therefore, about 400 tonnes daily, finds its way into the environment, primarily dissolved or suspended in water causing a major environmental impact. Colored organic substances generally impart only a small fraction of the total organic load in a waste water; however, their high degree of color is easily detectable and detracts from the aesthetic value of rivers, streams etc. and inhibits photosynthetic processes.

It has been widely recognized for over ten years that adsorption offers an effective means of color removal from liquid effluents and produces a high quality treated water for recycling and re-use. The design of an adsorption system requires a knowledge of the sorbent equilibrium capacity for the dyestuff and a knowledge of the kinetics or mass transport processes. There is vigorous and ongoing research for new adsorbents but activated carbon is still the most widely used adsorbent commercially.

A number of adsorption systems have been used to test for the removal of dyestuffs from wastewaters, such as peat (Poots et al., 1976 and Allen et al., 1987), wood (Poots et al., 1976 and McKay et al., 1986), lignite (Allen et al. 1988), banana pith

(Namasivayam et al. 1992), chrome sludge (Lee et al., 1996) and activated carbon (Walker and Weatherley, 2000 and Lin and Liu, 2000).

Activated carbon is still the most widely used adsorbent for the removal of colour (Allen, 1998). It also widely used in many applications as such as purification of motor vehicle exhaust emissions, wastewater treatment, solvent recovery and as a catalyst support. A large number of equilibrium studies on the adsorption of dyes using activated carbon and its derivatives have been carried out (McKay, 1983; Al Duri and McKay 1992; Gupta et al., 1990; Porter et al., 1999, Walker and Weatherley, 2000 and Choy et al., 2000).

In addition to adsorbent selection, based on capacity and adsorbent cost, the rate of removal of dye by an adsorbent is a crucial factor in designing the system. Different adsorbents have different pore structures and different surfaces, consequently adsorption rates may be controlled by pore, surface or external film diffusion or any combination of these transport resistances.

Several models have been reported in the literature based on diffusional mass transport models, such as the external film diffusion model (Furusawa and Smith, 1973; McKay and Allen, 1983 and Khare et al., 1987), the intraparticle diffusion model (Crank, 1979; Weber and Morris, 1962 and Low et al., 1995), the film-surface diffusion model (Mathews and Weber, 1976; Suidan et al., 1988, Miyahara et al., 1993 and Traegner and Suidan (199) and the film-pore diffusion model (Spahn and Schlunder, 1975; Crittenden et al., 1985; Yeroshenkova et al., 1983 and Whitaker, 1988). The model selected in this paper, for predicting concentration versus time decay curves, is based

on external film mass transport and pore diffusion. The purpose is to apply an easy to use analytical solution to the sorption of two acid dyes, namely, Acid Blue 80 and Acid Yellow 117, onto activated carbon. The limiting assumptions, particularly in relation to a pore diffusion mechanism only and selection of the most appropriate solid phase loading parameter used in the capacity factor, will be investigated.

2. Theoretical Background

Several models (Spahn and Schlunder, 1975; Neretnieks, 1974; McKay et al., 1997 and Chen et al., 2000) have been reported in the literature based on diffusional mass transport models. The model selected in this paper, for predicting concentration versus time decay curves, is based on external film mass transport and pore diffusion. The purpose is to apply an easy to use analytical solution to the sorption of two acid dyes, namely, Acid Blue 80 and Acid Yellow 117, onto activated carbon. The limiting assumptions, particularly in relation to a pore diffusion mechanism only and the selection of the solid phase loading parameter used in the capacity factor, will be investigated.

Spahn and Schlunder (1975) developed the film-pore diffusion model based on the unreacted shrinking core mass transfer model by Yagi and Kunii (Levenspiel, 1962). This model assumes that an external and internal mass transfer resistance controls the adsorption rate. Therefore, the adsorption reaction starts at the particle surface forming a reacted zone, which moves inwards with a defined velocity. During the entire reaction time there is an unreacted core, shrinking in size as adsorption proceeds. The mathematical model started with the following assumptions:

- (1) Equilibrium occurs between the pore liquid and particle interior – that is, the solution flow to the pores is much faster than its uptake at sorption sites.
- (2) Mass transfer in the pores is solely by molecular diffusion, i.e. it follows Fick's first law and is measured by the effective pore diffusion coefficient, D_{eff} .
- (3) Solute concentration in the pore liquid is very small, relative to that in the sorbed phase and can therefore be neglected.

The adsorbate concentration profile of carbon particle based on the film-pore diffusion model is shown in Figure 1. The concentration of the adsorbate decreases from the value of C_i at bulk to $C_{e,t}$ at the particle surface due to the external film resistance measured by the external mass transfer coefficient, k_f . Then, the value of $C_{e,t}$ drops further to zero at point r in the particle interior due to the internal resistance measured by D_{eff} . The reacted zone moves inwards in a well-defined concentration front with a variable velocity and at all times there is an unreacted core shrinking in size. Therefore, k_f and D_{eff} are the main parameters that describe the profile of a concentration decay curve.

Figure 1: Mass transport of sorbate and concentration profile of sorbent.

Isotherm Models

Equilibria experimental data can be accurately correlated using the following Langmuir equation (Langmuir, 1918):

$$Y_e = \frac{K_L C_e}{1 + a_L C_e} \quad (1)$$

Experimental External Mass Transport Coefficient

This model is based on the unreacted shrinking core model (Yagi et al., 1961 and Levenspiel, 1962). The mass transfer at the external surface of the carbon particles is given by

$$\dot{N}_t = k_f A (C_i - C_{e,t}) \quad (2)$$

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

The adsorption rate, $\dot{N}_t$, can then be obtained by the graphical method of plotting the liquid phase concentration, C_t , versus time curve in the batch system and determining the gradient. At time = 0, all the mass transfer resistance is restricted to the external layer of the particle. Hence, the external mass transfer resistance, k_f , was determined by using the initial mass transfer rate $\dot{N}(0)$ at time = 0.

$$k_f = \frac{-V}{AC_0} \left[\frac{dC_t}{dt} \right]_{t \rightarrow 0} \quad (4)$$

By substituting the value of k_f and the rate of change of liquid phase concentration

$\left[\frac{dC_t}{dt} \right]_t$ at different times into equation (2) and rearrangement, the equilibrium

concentrations ($C_{e,t}$ and $Y_{e,t}$) can then be expressed in terms of liquid and solid phase concentration (C_t and $\bar{Y}_t$).

$$C_{e,t} = C_i + \left[\frac{V}{k_f A} \right] \left[\frac{dC_i}{dt} \right]_t \quad (5)$$

Each value of $C_{e,t}$ can be plotted on the isotherm and the corresponding $Y_{e,t}$ can be obtained. The values of $C_{e,\infty}$ and $Y_{e,\infty}$ were determined by extending the operating line to cut the isotherm. The mass transfer rate from the external water phase is:

$$\dot{N}_t = k_f 4\pi R^2 (C_i - C_{e,t}) \quad (6)$$

According to the first Fick's law, the diffusion in the pore water is :

$$\dot{N}_t = \frac{4\pi D_{eff} C_{e,t}}{1/r - 1/R} \quad (7)$$

With the above assumptions this transfer rate can be calculated as quasi-stationary.

The velocity of the concentration front is obtained from the mass balance on a spherical element:

$$\dot{N}_t = -4\pi r^2 Y_{e,h} \rho \frac{dr}{dt} \quad (8)$$

The average concentration in the activated carbon is given by:

$$\bar{Y}_t = Y_{e,h} [1 - (r/R)^3] \quad (9)$$

$$\bar{Y}_t = \frac{(C_o - C_i)V}{W} \quad (10)$$

In order to solve the mass transfer equations in the film pore diffusion model, two different approaches, a numerical method and an analytical solution, were developed in this paper.

Numerical Method for Film Pore Diffusion Model

By substituting equation (9) in the solid phase/liquid mass balance equation (10), it becomes:

$$W[Y_{e,t}(1 - (r/R)^3)] = V(C_o - \lambda C_{e,t}) \quad (11)$$

$$\text{where } C_i = \left[1 + \frac{D_{eff} r}{k_f R(R-r)} \right] C_{e,t} \quad \text{and} \quad \lambda = 1 + \frac{D_{eff} r}{k_f R(R-r)} \quad (12)$$

In the numerical model, the tie lines are time-dependent values for $C_{e,t}$ therefore, $Y_{e,t}$ is a variable. The Langmuir equation has been used to relate the equilibrium concentrations, $Y_{e,t}$, on the solid phase surface:

$$Y_{e,t} = \frac{K_L C_{e,t}}{1 + a_L C_{e,t}} \quad (13)$$

and combining the mass balance equations (11) with (13), the following quadratic equation is obtained:

$$a_L \lambda C_{e,t}^2 + (\lambda + K_L R_m - a_L C_o) C_{e,t} - C_o = 0, \text{ where } R_m = (1 - (r/R)^3)(W/V) \quad (14)$$

Hence, $C_{e,t}$ can be calculated from eq.(15):

$$C_{e,t} = \frac{-(\lambda + K_L R_m - a_L C_o) + \sqrt{(\lambda + K_L R_m - a_L C_o)^2 + 4a_L \lambda C_o}}{2a_L \lambda} \quad (15)$$

Combining equations (8) (9) and (15), the rate equation becomes

$$\frac{\Delta r}{\Delta t} \cong \frac{dr}{dt} = \frac{D_{eff}(1 + a_L C_{e,t})R}{K_L r(r-R)\rho} \quad \text{or} \quad \Delta r = -\frac{D_{eff}(1 + a_L C_{e,t})R}{q_m a_L r(R-r)\rho_p} \cdot \Delta t \quad (16)$$

Since $C_{e,t}$ is known as a function of r , equations (11), (15) and (16) can be solved for a specified time by a numerical method. The solution scheme proposes that the shrinking core radius can be calculated by equation (17).

$$r^{L+1} = r^L + \Delta r^L \quad (17)$$

The shrinking core radius at $t = 0$, r^0 , is assumed to be the arithmetic mean radius between respective mesh sizes of the sorbent ($r^0 = d_p/2 = 3.025 \times 10^{-2}$ cm). The initial guess of the time interval ($t = 0$), Δt , between each data point and the Δr^0 in the numerical program are 0.2 s and -1×10^{-5} cm. Therefore, at time equal to t^l , the

shrinking core radius, r^I , the deta radius, Δr^I , and the concentration of solution on the surface, $(C_{e,t})^I$, can be calculated using equations (15), (16) and (17), respectively. The concentration of solution on the surface at any time t can be obtained by repeating the calculation of $(C_{e,t})^I$ and r^I and the initial condition of $C_{e,t}$ is equal to C_0 . Since the concentration of solution on the surface cannot be measured, equation (12) will be used to calculate the sorbate concentration, $(C_t)^I$, in solution. Hence, the optimum best-fit values k_f and D_{eff} were found by minimizing the difference between experimental and theoretical data of the concentration of solution, C_t , using the average relative error (ARE).

$$ARE = \frac{100}{n} \sum_{i=1}^n \left| \frac{C_{t,cal} - C_{t,exp}}{C_{t,exp}} \right|_i \quad (18)$$

Analytical Method for Film Pore Diffusion Model

The previous section introduced the use of a numerical method to determine the external mass transfer coefficient and the pore diffusion coefficient. The numerical method can provide an excellent correlation of experimental data where the adsorbent concentration in the carbon used $Y_{e,t}$ which is a function of $C_{e,t}$. However, the numerical solution of the film pore diffusion model is complex and it was used to solve the mass transfer equations by the more lengthy finite difference method. A relatively simple method, using an analytical solution, for the film-pore diffusion model is proposed in this section. The theoretical assumptions of the analytical film pore diffusion model are similar to the numerical film-pore diffusion model with one more assumption (4):

- (4) The solute concentration in the sorbed phase is independent of that in the pore liquid; therefore, adsorption is irreversible and $Y_{e,t}$ can be substituted by a

hypothetical equilibrium concentration, $Y_{e,h}$, which is constant for all $C_{e,t}$ values in the analytical method.

Therefore, in the analytical model, the solution has been developed by assuming that $Y_{e,t}$ is a constant and equal to $Y_{e,h}$. By introducing dimensionless parameters in the mass transfer equations (1) to (10), the adsorption rate for a single particle can be expressed in terms of adsorbate concentration in the water phase, ε , the adsorbent phase, η , and the Biot number, B_i .

$$\frac{d\eta}{d\tau} = \frac{3(1 - C_h\eta)(1 - \eta)^{1/3}}{1 - (1 - 1/B_i)(1 - \eta)^{1/3}} \quad \text{or} \quad \frac{d\eta}{d\tau} = f(\eta)\varepsilon Bi \quad (19)$$

The dimensionless parameters in equation (19) are defined as:

$$\eta = \frac{\bar{Y}_t}{Y_{e,h}}, \quad \tau = \frac{C_0}{\rho Y_{e,h}} \frac{d_p t}{R^2}, \quad B_i = \frac{k_f R}{D_p} \quad \text{and} \quad \varepsilon = \frac{C_t}{C_0} \quad (20)$$

Then equation (19) can be integrated into :

$$\tau = \frac{1}{6Ch} \left[\ln \left\{ \left(x^3 + a^3 \right) \right\}^{\frac{2B-1}{a}} \right] + \ln \left[\left\{ \left(x + a \right) \right\}^{\frac{3}{a}} \right] - \frac{1}{aCh} \arctan \left[\frac{(2x - a)}{a\sqrt{3}} \right] \quad (21)$$

where $x = (1 - \eta)^{1/3}$, $Ch = (Y_{e,h}M)/(C_0V)$, $B = 1 - 1/B_i$ and $a = [(1 - Ch)/Ch]^{1/3}$

The limits for this equation are: $x = 1$, $\tau = 0$, $\eta = 0$ and $x = x$, $\tau = \tau$, $\eta = \eta$.

These limits were inserted to give:

$$\tau = \frac{1}{6Ch} \left[\ln \left(\frac{x^3 + a^3}{1 + a^3} \right)^{\frac{2B-1}{a}} + \ln \left(\frac{x + a}{1 + a} \right)^{\frac{3}{a}} \right] + \frac{1}{a\sqrt{3}Ch} \left[\arctan \left[\frac{(2x - a)}{a\sqrt{3}} \right] - \arctan \left[\frac{2 - a}{a\sqrt{3}} \right] \right] \quad (22)$$

Therefore by converting dimensionless time, τ , into real time, t , it is possible to compare experimental and theoretical concentration decay curves.

Two Different Analytical Solutions

Considering equation (4), the differential term $\left[\frac{dC_t}{dt} \right]$ is not easily determined. This

has been approached by a number of methods:

- Spahn and Schlunder (1975) used graphical differentiation at various times to solve the equation, although the method is time consuming.
- McKay (1997) modified the solution by introducing the saturated isotherm constraint, i.e. all operating and tie lines terminated on the isotherm plateau. This approach is advantageous for minimizing computational time.
- McKay has also used $Y_{e,t} = \text{constant}$, for $Y_{e,\infty}$ that is the value of Y_t at the end of the system operating line.

Based on the above second and third solution methods, two analytical models have been developed using a different equilibrium solid phase concentration, $Y_{e,Ce}$ or Y_{e,C_0} . In the analytical model 1, the equilibrium solid phase concentration takes the intersection point of the equilibrium isotherm and the operating line. In the analytical model 2, the equilibrium solid phase concentration takes the point of the equilibrium isotherm where the liquid phase concentration equals the initial concentration. Figure 2 shows the equilibrium solid phase concentration of two models. Similarly, the best-fit values of k_f and D_{eff} in analytical model 1 and 2 can be found by minimizing the error (ARE) between the experimental time, t_{exp} and the calculated time from adsorption model, t_{cal} .

$$ARE = \frac{100}{n} \sum_{i=1}^n \left| \frac{t_{cal} - t_{exp}}{t_{exp}} \right|_i \quad (23)$$

Figure 2: Equilibrium solid phase concentration of model 1 and model 2.

3. Experimental materials and methods

Materials

Sorbent

The adsorbent used in the research is Activated Carbon type F400 supplied by the Filtrasorb Corporation. This carbon is described by the supplier as a generally effective water treatment activated carbon. Activated Carbon Filtrasorb 400 was crushed by using a hammer mill and washed by distilled water to remove fines. It was dried at 110 °C in an oven for 24 hours. Then, the dried activated carbon was sieved into several discrete particle size ranges. The 500 to 710 μm size range of activated carbon was used in this study. The carbon particles were assumed to be spheres having a diameter given by the arithmetic mean value between respective mesh sizes (average particle diameter, d_p , was 605 μm). The particle appeared irregularly shaped under a microscope but approximated more closely to spheres than to cylinders or parallel

pipes for the size ranges under investigation. The arithmetic mean diameter of the carbon particles will be used in the film-pore diffusion model to take into account the particle size distribution of sorbent in the modelling approach. Table 1 gives the physical properties of carbon F400.

Table 1: Physical properties of Activated Carbon Filtrasorb F400

Total surface (N ₂ BET method) (m ² g ⁻¹)	1150
Bed density, backwashed and drained (kg m ⁻³)	425 × 10 ³
Bulk density (g m ⁻³)	1.30
Porosity	0.38

Sorbates

Two dyes, namely Acid Blue 80 (AB80) and Acid Yellow 117 (AY117), were used in this study. Table 2 shows the color index number, molecular mass, dye content and the wavelengths at which maximum absorption of light occurs, λ_{max} . The dye structures are reported in our previous paper (Choy et al., 2000).

Table 2: Information regarding the Acid Dyes

Name of Dyes	Acid Blue 80	Acid Yellow 117
Color index number	61585	24820
Molecular Mass (g)	676	848
Dye Content (%)	60	60
λ_{max} (nm)	626	438

Experimental Method

Sorption Equilibrium Studies

A series of fixed volumes (0.050 dm³) of solutions with predetermined initial dye concentrations were prepared and brought into contact with predetermined masses (0.05 g) of carbon F400 (d_p = 500 to 710 μ m). The jars were sealed and agitated in the shaker bath (200 rev/min shaking rate) at constant temperature 20±2 °C for 21 days until equilibrium was reached. All samples were analyzed using a Varian Cary IE spectrophotometer.

Batch Control Time Studies

The batch kinetics experiments were used to investigate the influence of sorbent mass and initial liquid phase concentration on the adsorption rate. An adsorber vessel in a batch stirred tank configuration was used in all of the experiments. The design of the standard agitated batch adsorber has been described in previous papers (Furusawa et al., 1973 and McKay et al., 1996). The adsorber vessel was a 2 dm³ plastic beaker with 0.13 m internal diameter. It can hold a volume of 1.7 dm³ acid dye solution. A six bladed, flat plastic impeller was used to achieve complete mixing and the diameter of the impeller and the blade height were 0.065 m and 0.013 m respectively. A motor was used to drive the impeller using a 0.005 m diameter plastic shaft. The adsorption vessel was used to obtain kinetic data, and the following variable parameters were studied:

(a) Effect of Initial Concentration

The effect of concentration of acid dye solution on the adsorption rate was studied in these experiments. Activated carbon (1.7 g and particle size range between 500 and 710 μ m) was agitated with 1.7 dm³ aqueous solution containing single dye in the batch

system for 3 hours while the impeller speed was 400 rpm and the temperature was kept at 20 ± 2 °C. A range of concentrations of acid dye solutions (see Table 4) was used to analyse the sorption of acid dyes onto activated carbon. At time = 0 and at selected time intervals, 3 ml samples were extracted using a 10 ml syringe from the adsorption vessel. The concentration of the dyes samples were determined by the UV-spectrophotometer.

(b) Effect of Sorbent Mass

The effect of activated carbon mass on the adsorption rate was also studied using the same conditions as in (i) except the initial concentration of solution was set at 100 mg dm^{-3} and a range of sorbent masses (see Table 4) were used. Sampling, analysis and treatment of results were the same as previously described in (a).

4. Results and Discussion

The external mass transfer coefficient (k_f) and the effective diffusion coefficient (D_{eff}) have been determined for the sorption of Acid Blue 80 (AB80) and Acid Yellow 117 (AY117) onto activated carbon using the three model assumptions, one numerical and two analytical methods. The effects of changing liquid phase initial concentration and mass of adsorbent on the values of external mass transfer coefficient and effective diffusion coefficient have been studied. Finally, the relationship between the effective diffusion coefficient and the ratio of initial concentration to mass has been established and is useful for predicting the design of batch adsorbers for color removal.

Equilibrium Isotherm

The Langmuir equation was used to describe the equilibrium isotherms in this research

due to its high correlation factor. The Langmuir constants are determined by minimizing the difference between the experimental and theoretical data using the ARE method. The Langmuir constants of two acid dyes systems are shown in Table 3 and Figure 3 presents a comparison of the isotherms of the two acid dyes.

Table 3: Langmuir Sorption Isotherm Constants for AB80 and AY117 in Single Component Systems

Single Component System					
	K_L ($\text{dm}^3 \text{g}^{-1}$)	a_L ($\text{dm}^3 \text{mg}^{-1}$)	Y_{max} (mg g^{-1})	ARE	
AB80	60.73	0.5408	112.3	26.20	
AY117	78.28	0.5023	155.8	31.92

Figure 3: Langmuir Isotherm Plots for Acid Blue 80 and Acid Yellow 117 on Carbon.

Results of Numerical Method

In the numerical film pore diffusion model, the equilibrium solid phase concentration,

$Y_{e,t}$ is a variable with time and this is the main difference between the two analytical models, since these two models assume $Y_{e,t}$ is a constant for all $C_{e,t}$ values. Figures 4 and 5 show the theoretical curves and experimental data for the effect of carbon mass and dye concentration on Acid Blue 80 and Acid Yellow 117 adsorption systems. The correlation between experimental and theoretical results is excellent and the values k_f , D_s and ARE of the two dye systems are given in Table 4. The small values of ARE in the all systems indicate that the numerical model incorporating a time dependant $Y_{e,t}$ provides an excellent best correlation of experimental data..

The effective diffusivity in the pore diffusion model should be constant and equal to the pore diffusivity, which is also a function of molecular diffusivity, porosity and tortuosity, as defined in equation (24).

$$D_{eff} = D_p = D_M \varepsilon_p / \mu_{tor} \quad (24)$$

$$D_M = \frac{(7.4 \times 10^{-8}) \cdot (X \cdot M_B)^{0.5} \cdot T}{\mu \cdot V_m^{0.6}} \quad (25)$$

The molecular diffusivity, D_M , of the acid dyes was estimated using the Wilke-Chang expression (Wilke and Chang, 1995) as shown in equation (25). The molecular diffusivities of AB80 and AY117 are $4.67 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $3.75 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively. Hence, the tortuosity factor of the sorbent can be calculated from equation (24). The tortuosity factor of activated carbon for the two acid dye systems are 11.38 and 10.15. The tortuosity factors of activated carbon for AB80 and AY117 are very close. McKay and Al-Duri (1990) obtained a tortuosity of 6 for activated carbon with 0.79 porosity in three basic dye-carbon systems. The effective diffusivities for Basic Red 22 (BR22), Basic Blue 29 (BB29), Basic Yellow 21 (BY21) on carbon are 8.01×10^{-7} , 7.38×10^{-7} and $6.54 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, respectively and the values of external

mass transfer coefficients for BR22, BB29 and BY21 on carbon are 2.20×10^{-3} , 1.70×10^{-3} and $5.00 \times 10^{-3} \text{ cm s}^{-1}$, respectively. These values of external mass transfer coefficients and effective diffusion coefficients are of a similar order of magnitude to those obtained in the present systems for acid dye ions. It may imply the values of effective diffusion coefficient obtained from the numerical film pore diffusion model are reasonable.

Table 4: Predicted Results of Acid Dyes on Carbon using Numerical Model, Analytical Model 1 and Analytical Model 2.

Acid Blue 80										
Co (ppm)	50	75	100	150	200	100	100	100	100	100
Mass (g)	1.7	1.7	1.7	1.7	1.7	0.4	0.8	1.2	1.7	2.2
Results of Numerical Model										
$K_f (\text{cm s}^{-1})$	3.11×10^{-4}									
$D_{eff} (\text{cm}^2 \text{ s}^{-1})$	1.56×10^{-7}									
ARE	1.91	1.29	0.64	0.50	0.52	0.33	0.45	0.51	0.64	0.74
Results of Analytical Model 1										
$K_f (\text{cm s}^{-1})$	3.85×10^{-4}									
$D_{eff} (\text{cm}^2 \text{ s}^{-1})$	5.21×10^{-7}									
ARE	57.67	36.86	38.02	36.40	23.02	12.00	20.67	31.81	38.03	51.72
Results of Analytical Model 2										
$K_f (\text{cm s}^{-1})$	7.13×10^{-4}									
$D_{eff} (\text{cm}^2 \text{ s}^{-1})$	4.59×10^{-7}									
ARE	9.41	10.50	10.39	16.00	7.21	19.84	6.86	7.54	10.39	20.07
Acid Yellow 117										
Co (ppm)	50	75	100	150	200	100	100	100	100	100
Mass (g)	1.7	1.7	1.7	1.7	1.7	0.4	0.8	1.2	1.7	2.2
Results of Numerical Model										
$K_f (\text{cm s}^{-1})$	3.61×10^{-4}									
$D_{eff} (\text{cm}^2 \text{ s}^{-1})$	1.40×10^{-7}									
ARE	1.09	0.60	0.86	0.35	1.06	0.21	0.56	0.67	0.86	0.29
Results of Analytical Model 1										
$K_f (\text{cm s}^{-1})$	4.69×10^{-4}									
$D_{eff} (\text{cm}^2 \text{ s}^{-1})$	1.57×10^{-7}									
ARE	157.4	90.46	56.89	47.23	29.09	83.68	62.53	80.25	56.89	63.05
Results of Analytical Model 2										
$K_f (\text{cm s}^{-1})$	3.98×10^{-4}									
$D_{eff} (\text{cm}^2 \text{ s}^{-1})$	4.95×10^{-7}									
ARE	56.97	5.47	7.66	18.03	42.06	13.54	8.46	12.07	7.66	13.81

Figure 4: Sorption of Acid Blue 80 on activated carbon with different carbon mass systems (Numerical model, $D_{eff} = 1.56 \times 10^{-7}$).

Figure 5: Sorption of Acid Yellow 117 on activated carbon with different initial concentration systems (Numerical model, $D_{eff} = 1.40 \times 10^{-7}$).

Results of Analytical Model 1 (Constant Effective Diffusivity)

The film diffusion coefficient and effective diffusivity predicted by analytical model 1 are given in Table 4, while the plots of dimensionless liquid phase concentration, C_t/C_o , against time for Acid Blue 80 are shown in Figure 6. From the plots, we found that the correlation between the experimental data and predicted data is poor in both dye systems and especially bad for different carbon mass systems.

Figure 6: Sorption of Acid Blue 80 on activated carbon with different carbon mass systems (Analytical model 1, constant effective diffusivity).

Results of Analytical Model 2 (Constant Effective Diffusivity)

Another set of results predicted by analytical model 2 is listed in Table 4. The correlation values in model 2 are much better those obtained using the analytical model 1. It can be seen by the ARE values that analytical model 2 gives ARE values that are smaller in both dye systems. Figure 7 shows that analytical model 2 can be used in all concentrations and V/M ratios except $M = 0.4\text{g}$ for the system of Acid Blue 80 on activated carbon. Analytical model 2 can also be applied successfully for all V/M ratios except $M = 2.2\text{g}$ for Acid Yellow 117 on carbon in Figure 8. For the series of concentration systems, analytical model 2 only correlates well for the 75 and 100ppm systems but, overall, it still provides a great improvement in correlating the data when compared with the results of analytical model 1. To evaluate the importance of the film diffusion process in the mass transfer mechanism, the Biot number can be used since the Biot number represents the ratio of the rates of transport across the liquid layer to the rate of diffusion within the particle. The Biot number is equal to 47.02 for Acid Blue 80 and 243.2 for Acid Yellow 117. For $Bi \ll 1$, external mass transport resistance is the controlling mass transfer step, while for $Bi \gg 100$, pore diffusion is the predominant mass transfer controlling mechanism for the particular process. Biot numbers between 1 and 100 indicate that both mass transfer mechanisms are involved for the particular process (Suidan and Traegner, 1988). Therefore, the film-pore diffusion analytical model 2 is relevant to describe the mass transfer mechanism in the case of Acid Blue 80 but as significant for Acid Yellow 117.

Figure 7: Sorption of Acid Blue 80 on activated carbon with different carbon mass systems (Analytical model 2, constant effective diffusivity).

Figure 8: Sorption of Acid Yellow 117 on activated carbon with different carbon mass systems (Analytical model 2, constant effective diffusivity).

Results of Analytical Model 1 and Model 2 (Best Fit Individual Effective Diffusivity)

Analytical models 1 and 2 are used to obtain the individual effective diffusion coefficients for each dye-carbon experiment by the minimizing the ARE in equation (23). The film diffusion coefficient k_f , effective diffusion coefficient D_{eff} and Biot numbers are shown in Tables 5 and 6. For analytical model 1, Table 5 shows that increasing the initial concentration will decrease the effective diffusivity. Increasing the mass of sorbent will increase the diffusivity. Figure 9 shows that analytical model 1 with the individual effective diffusivity for each system can fit the data much better than the constant D_{eff} analytical model 1. Analytical model 2 provides a good correlation for Acid Blue 80 on carbon and it gives the same trend in effective diffusivity with analytical model 1. For the Acid Yellow 117 system, analytical model 2 can also fit the data very well, the plot is shown in Figure 10, the values of effective diffusivity in all V/M ratios are almost equal.

The deviations can be explained by the full expression for effective diffusivity.

$$D_{eff} = D_p + \rho D_s \frac{\partial Y}{\partial C} \quad (26)$$

where D_p is a pore diffusion coefficient, and D_s is the solid phase diffusion coefficient and $\partial Y / \partial C$ is the slope of the equilibrium isotherm. The pore diffusion coefficient, D_p is a constant. However, the solid phase diffusion coefficient, D_s , is a function of energy distribution, temperature and fractional surface coverage.

On the other hand, the inaccurate predictions by the two analytical models may be the cause of the variation of the equilibrium solid phase concentration, $Y_{e,t}$, of the carbon particle, since the analytical method can provide a good correlation of experimental data when all operating lines terminate on the saturation monolayer, i.e. $Y_{e,t} = Y_{e,h} =$

Y_{max} . However, when the operating lines do not terminate on the monolayer of equilibrium isotherm, the hypothetical equilibrium concentration must be assumed to be a certain value before calculation. Hence, the numerical model may be applied in the acid dye systems, not the analytical model, since the hypothetical equilibrium concentration is variable in the numerical model where $Y_{e,h} = Y_{e,t}$ is a function of the adsorbate liquid concentration, $C_{e,t}$, at the adsorbent surface.

Table 5: Analytical model 1 predicted results of Acid Blue 80 and Acid Yellow 117 on activated carbon where D_{eff} is variable

Sorbent Mass (g)	C_o (mg dm ⁻³)	Acid Blue 80 k_f (cm s ⁻¹) = 3.51×10 ⁻⁴			Acid Yellow 117 k_f (cm s ⁻¹) = 4.69×10 ⁻⁴		
		D_{eff} (cm ² s ⁻²)	Biot number	ARE	D_{eff} (cm ² s ⁻²)	Biot number	ARE
1.7	50	1.66×10 ⁻⁶	6.99	32.04	6.34×10 ⁻⁶	2.24	126.80
1.7	75	6.09×10 ⁻⁷	19.09	33.51	2.10×10 ⁻⁶	6.77	85.85
1.7	100	4.31×10 ⁻⁷	26.98	39.96	1.16×10 ⁻⁶	12.18	60.61
1.7	150	3.50×10 ⁻⁷	33.19	39.56	4.27E-07	33.17	52.26
1.7	200	2.92×10 ⁻⁷	39.77	25.69	2.59×10 ⁻⁷	54.83	17.65
0.4	100	2.59×10 ⁻⁷	44.95	11.81	6.52×10 ⁻⁷	21.74	94.19
0.8	100	3.20×10 ⁻⁷	36.36	22.25	7.70×10 ⁻⁷	18.42	69.09
1.2	100	3.61×10 ⁻⁷	32.26	34.27	8.51×10 ⁻⁷	16.66	87.07
1.7	100	4.31×10 ⁻⁷	26.98	39.96	1.16×10 ⁻⁶	12.18	60.61
2.2	100	6.20×10 ⁻⁷	18.76	47.42	1.12×10 ⁻⁶	12.62	67.08

Table 6: Analytical model 2 predicted results of Acid Blue 80 and Acid Yellow 117 on activated carbon where D_{eff} is variable

Sorbent Mass (g)	C_o (mg dm ⁻³)	Acid Blue 80 k_f (cm s ⁻¹) = 7.13×10 ⁻⁴			Acid Yellow 117 k_f (cm s ⁻¹) = 3.98×10 ⁻⁴		
		D_{eff} (cm ² s ⁻¹)	Biot number	ARE	D_{eff} (cm ² s ⁻¹)	Biot number	ARE
1.7	50	5.50×10 ⁻⁷	39.24	5.27	7.68×10 ⁻⁷	156.83	13.56
1.7	75	4.38×10 ⁻⁷	49.25	9.81	4.51×10 ⁻⁷	266.69	7.60
1.7	100	4.52×10 ⁻⁷	47.67	10.39	4.78×10 ⁻⁷	251.69	6.78
1.7	150	4.96×10 ⁻⁷	43.52	12.13	4.03×10 ⁻⁷	298.64	6.64
1.7	200	4.67×10 ⁻⁷	46.21	7.00	3.34×10 ⁻⁷	360.16	19.28
0.4	100	3.58×10 ⁻⁷	60.31	11.22	4.59×10 ⁻⁷	262.34	17.22
0.8	100	4.18×10 ⁻⁷	51.64	3.47	4.87×10 ⁻⁷	246.99	9.17
1.2	100	4.43×10 ⁻⁷	48.70	7.18	4.84×10 ⁻⁷	248.92	12.12
1.7	100	4.52×10 ⁻⁷	47.67	10.39	4.79×10 ⁻⁷	251.54	3.90
2.2	100	4.97×10 ⁻⁷	43.35	15.85	4.08×10 ⁻⁷	295.28	3.96

Figure 9: Sorption of Acid Blue 80 on activated carbon with different carbon mass systems (Analytical model 1, variable individual effective diffusivity).

Figure 10: Sorption of Acid Yellow 117 on activated carbon with different initial concentration systems (Analytical model 2, variable individual effective diffusivity).

Model Selection

To evaluate the mass transfer mechanism of activated carbon, in general, the two consecutive rate controlling steps of adsorption in a porous sorbent are: (a) external mass transfer across the liquid film measured by the external mass coefficient k_f , (b) intraparticle diffusion through the liquid-filled pores expressed by the effective pore diffusivity D_{eff} . The effective pore diffusivity, D_{eff} , is determined by minimizing the error between the model and the experimental data. Usually, the change of initial concentration and the change of volume to mass ratio will be used to evaluate the effective diffusivity. In these studies, the adsorption equilibrium is controlled by these two parameters at constant conditions of temperature, particle size and pH. If a constant D_{eff} can be obtained, the intraparticle diffusion should be the pore-diffusion. Since the pore diffusion is a constant, the effective diffusivity $D_{eff} = D_p = \text{constant}$. The pore diffusivity can be obtained from the molecular diffusion, D_m , porosity, ϵ_p , and tortuosity factor, μ (see equation (24)).

The numerical model incorporating a time dependent $Y_{e,t}$ in the pore diffusion model provides a better description of the true physical situation than the two analytical models as the two analytical models assume $Y_{e,h}$ is a constant value. By comparing the values of ARE in three models, see Table 4 to 6, the numerical model provides the best correlation of experimental data in both Acid Blue 80 and Acid Yellow 117 systems in the three diffusion models (both numerical and analytical models) using ONE (constant) effective diffusivity in different carbon mass and different initial dye concentration systems. Moreover, the tortuosity factors calculated from the numerical model effective diffusivities are very close for two acid dye systems. This means that pore diffusion dominates in the mass transfer mechanism for the sorption of acid dyes

on activated carbon.

In the constant D_{eff} film-pore diffusion analytical model, analytical model 2 provides a better correlation between experimental and theoretical data than analytical model 1. However, analytical model 2 can only perform quite well with constant mass transfer coefficient and constant diffusivity for the two dyes in the 0.4, 0.8 and 1.7g carbon mass systems. The correlation between the experimental data and predicted data by analytical model 2 is poor for different initial concentrations in the AY117 systems, while these plots have not been given in the paper.

In the best-fit variable individual D_{eff} analytical models 1 and 2, the correlation of curve fitting is better than in the case of the constant D_{eff} analytical model. Also, the correlation is good in both acid dyes systems. Increasing the initial concentration of solution decreases the pore diffusivities and increasing the carbon mass increases the pore diffusivities. This implies that the diffusivities at low initial concentration and high V/M ratio are considered to have a contribution from surface diffusion in the mass transfer process.

The average tortuosity factor for the two acid dye systems based on the analytical model 2 with an individual effective diffusivity is 3.88 and 3.01. The difference of tortuosity factor between AB80 and AY117 obtained from analytical model 2 is relatively greater than that obtained from numerical model. The possible reason may be due to the correlation of the two acid dye systems using the analytical model 2 is poorer than the numerical model. By comparing the values of ARE obtained from analytical model 2 and the numerical model, see Table 4, analytical model 2 provides

much larger values of ARE, 5 to 65 times larger, than those obtained from the numerical model for the two dyes in all systems. The values of effective diffusivity obtained by the two analytical models are greater than those obtained by the numerical model for the two acid dye systems. This may be due to the larger values of the hypothetical equilibrium solid phase concentration, which is assumed in both analytical models, therefore, the values of effective diffusivity are over-predicted by the two analytical models.

5. Conclusion

A two-resistance model based on external mass transfer and pore diffusion has been studied. The equilibrium solid phase concentration has been assumed as (i) incorporating a time dependent $Y_{e,t}$, (ii) equal to the intersection point of the equilibrium isotherm and the operating line and (iii) the point of the equilibrium isotherm where the liquid phase concentration equals the initial concentration in the film pore diffusion model. A time dependent solid phase concentration in the film pore diffusion model provides the best-fit correlation to the experimental data with constant effective diffusivity. These results show that pore diffusion dominates the mass transfer mechanism of acid dyes on activated carbon and that a time dependent solid phase capacity provides the best-fit model to the experimental data.

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Nomenclature

a_L	$\text{dm}^3 \text{mg}^{-1}$	Langmuir isotherm constant
A	$\text{m}^2 \text{g}^{-1}$	Surface area of adsorbent per unit mass of adsorbent
Bi	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 diffusional model
D_{eff}	$\text{m}^2 \text{s}^{-1}$	Effective diffusion coefficient
D_M	$\text{m}^2 \text{s}^{-1}$	Molecular diffusivity
D_p	$\text{m}^2 \text{s}^{-1}$	Effective pore diffusion coefficient
D_s	$\text{m}^2 \text{s}^{-1}$	Effective surface diffusion coefficient
d_p	m	Adsorbent particle diameter
k_f	m s^{-1}	External film mass transfer coefficients
K_L	$\text{dm}^3 \text{g}^{-1}$	Langmuir isotherm constant
W	g	Mass of adsorbent
N_t	gs^{-1}	Mass transfer rate
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}	Dye concentration in solid-phase
$\bar{Y}$	mg g^{-1}	Average dye concentration in solid-phase

Y_0	mg g^{-1}	Initial dye concentration in solid phase
Y_e	mg g^{-1}	Equilibrium dye concentration at solid phase
$Y_{e,h}$	mg g^{-1}	Hypothetical equilibrium solid-phase concentration
r	cm	Radial position within particle

Greek letters

ε	dimensionless	Dimensionless liquid-phase concentration in the pore diffusion model
ε_p	dimensionless	Porosity of the adsorbent
η	dimensionless	Dimensionless solid phase concentration
θ	dimensionless	Dimensionless time variable
μ	dimensionless	Tortuosity
ρ	g cm^{-3}	Particle density of adsorbent
τ	dimensionless	Dimensionless time

Subscripts

0	initial value
e	equilibrium value
t	species time
T	total value for the system
∞	infinite
exp	predicted by experiment
cal	predicted by calculation

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