MULTICOMPONENT MASS TRANSFER DIFFUSION MODEL FOR THE ADSORPTION OF ACID DYES ON ACTIVATED CARBON

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Abstract

- The ability of activated carbon to adsorb two acid dyes, namely, Acid Blue 80 (AB80) and Acid Yellow (AY117) from wastewater has been studied in equilibrium and batch kinetic systems.
- A two resistance mass transport model based on film and surface diffusion control, Homogeneous Surface Diffusion Model (HSDM), has been applied to model the concentration decay curves in single component system.
- 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.
- A multicomponent HSDM was developed to predict the binary component system decay curves from the single component HSDM and the IAST-RP model.

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Introduction

- Activated carbons are known to have extremely high surfaces areas (McKay, 1983).
- In addition, the adsorption capacity of acid dyes on activated carbon is relatively higher than that of several other adsorbents (Choy, 2001).
- Batch kinetic adsorption is an effective contacting operation which can provide a high degree of pollutant removal from effluents.

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Introduction

Previous Work

- Mathews and Weber (1976) developed a solid-phase, homogeneous surface diffusion model (HSDM), using the finite difference solution method for any arbitrary isotherm in batch adsorption system.
- The HSDM has been successfully extended to batch kinetic adsorption systems on activated carbon in single component system. (Suidan et al., 1988; Miyahara and Okazaki, 1993; Traegner and Suidan, 1996; Axe et al., 1997; Trivedi et al., 2000 and McKay, 2001).

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Introduction

Present Work

- The semi-analytical solution method using the Redlich-Peterson (RP) equation has been applied to the acid dye batch kinetic adsorption system on activated carbon.
- A multicomponent HSDM for acid dye/carbon adsorption has been developed based on the ideal adsorbed solution theory (IAST) and the homogeneous surface diffusion model (HSDM) to predict the concentration versus time decay curves.

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Mathematical Model

- The basic steps in this model include:
 - the effect of external mass transfer
 - unsteady-state surface diffusion in the particle
 - a non-linear adsorption isotherm

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Mathematical Model

The assumptions of Multicomponent HSDM are as follows:

- The liquid film transport resistance occurs at the outer surface of the particle.
- The adsorbent particle is assumed to be a homogeneous solid in which the adsorbate is transported by surface diffusion;
- Pore diffusion makes a negligible contribution to mass transport.

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Model Equations

The concentration of solute inside the typical particle at distance r from the centre and at time t is defined by $q_j(r, t)$ and the variation of q_j with distance and time is governed by the diffusion equation for each component j :

(1)

A dimensionless variables are applied by defining $\phi_j \equiv X_j q_j$, and in equation (1) to form equation (2) with the following boundary conditions (3) and (4).

(2)

(3)

(4)

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Model Equations

The material balance equation for the multicomponent system and the rate of change of solid phase concentration of each component j are:

(5)

(6)

(7)

The mathematical problem presented by the model requires the simultaneous solution of equations (2) to (7). The starting point is a semi-analytical solution of equation (8), previously only applied to single component systems, that satisfies the boundary conditions in equations (3) and (4).

(8)

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Model Equations

By considering a short time interval, $\tau_0, \tau_1, \tau_2, \dots, \tau_n$, in the integration of equation (8) for j component and it is assumed that the time intervals are sufficiently short that is effectively constant in each interval to solve equation (8) by a numerical method. Also, equation (7) becomes:

(9)

The IAST with the Redlich-Peterson equation is used to determine the pair of liquid phase concentrations, $C_{s,1}$ and $C_{s,2}$, from the corresponding pair of solid phase concentrations, $q_{s,1}$ and $q_{s,2}$, at the surface of the carbon particle in the binary component.

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Model Equations

The IAS theory dictates that the spreading pressure should be constant for each component in a given system ()

$$(10) \qquad (11)$$

For a given pair of $q_{e,1}$ and $q_{e,2}$, the values of s_1 , s_2 and q_T can be calculated.

$$(12)$$

To calculate the spreading pressure, numerical computer integration is used to solve the equation (13).

$$(13)$$

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Model Equations

For a given (guess values) pair of $q_{e,1}$ and $q_{e,2}$, the values of S_1 , S_2 and q_T can be calculated. Combining the Redlich-Peterson equation (14) and equation (12) gives equation (15).

$$(14) \qquad (15)$$

A numerical computer program is used to optimize the value of until the spreading pressures of component 1 and 2 are equal. Hence, the value of $C_{e,1}$ and $C_{e,2}$ can be calculated from the and by equations (16) and (17) while and . Consequently:

$$(16) \qquad (17)$$

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Materials

Adsorbent

- The adsorbent used in this study is Filtrasorb 400 granular activated carbon (GAC) supplied by Chemviron Ltd.
- The GAC was washed in deionised water, dried and sieved to obtain certain size ranges: 355-500, 500-710 and 710-1000 microns.

Figure 1: Molecular Structure of Acid Blue 80

Adsorbate

The adsorbate used in the experiments is Acid Blue 80 (AB80) and Acid Yellow 117 (AY117) supplied by Ciba Specialty Chemicals.

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Batch Kinetic Experimental System

An adsorber vessel in a standard batch stirred tank configuration is used in the batch experiments.

- The impeller speed is 400 rpm.
- The temperature is kept at $20 \pm 2^\circ\text{C}$.
- Volume of dye solution is 1.7dm^3 .
- Experimental contact time is 48hrs.

The influence of initial dye concentration and carbon mass on (500-710 μm) the adsorption rate has been investigated.

- Different carbon masses: 0.4, 0.8, 1.2, 1.7 & 2.2g
- Different initial dye concentrations: 50, 75, 100, 150 & 200 ppm.

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Figure 2: Standard Tank Configuration for Batch Kinetic Studies

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Results and Discussion

Equilibrium Isotherm Studies

The equilibrium isotherms were measured for Acid Blue 80 (AB80) and Acid Yellow 117 (AY117) on Activated Carbon F400. The Redlich-Peterson isotherm is used to relate equilibrium concentrations between liquid phase and solid phase loading. The isotherm parameters of K_R , a_R and β for two acid dyes are shown in Table 1.

R-P equation :

Table 1: Redlich-Peterson Isotherm Constants for AB80 and AY117 in Single Component System

	AB80	AB80
K_R (dm ³ /g)	28.32	55.40
a_R (dm ³ /mmole) ^β	103.6	200.2
β	0.965	0.910
SSE Value (10 ⁻⁴)	1.088	1.191

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Figure 3: Redlich-Peterson Isotherm Plots for Two Acid Dyes in Single Component Systems

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Figure 4: Redlich-Peterson Isotherm Plots for Two Acid Dyes in Binary Component Systems

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Results and Discussion

Batch Kinetic Studies

- The effects of initial solute concentration and adsorbent mass have been studied on the diffusion processes for the multicomponent HSDM.
- The HSDM was used to correlate two acid dyes (AB80 & AY117) in the single component system in order to determine the relation between the single component and multicomponent systems.
- A comparison of the theoretical and experimental data for the AY117 in AB80+AY117 binary systems with different carbon masses is illustrated in Figure 5 and Figure 6.

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Figure 5: Effect of Activated Carbon Mass on the Adsorption of AB80 in AB80+AY117 using Multicomponent HSDM (IAS-RP)

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Figure 6: Effect of Initial Dye Concentrations on the Adsorption of AY117 in AB80+AY117 using Multicomponent HSDM (IAS-RP)

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Batch Kinetic Studies (Results and Discussion)

- Single component external mass transfer coefficient, $k_{f,1}$ and $k_{f,2}$, are used in the multicomponent HSDM model. It was found that there is some deviation in the first 30 minutes for the two binary component systems.
- The results indicate that the values of the external mass transfer coefficient in the multicomponent system are slightly different to those of the single component system.
- The $D_{s,i}$ and SSE values for the AB80+AY117 binary system with different carbon masses and different initial concentrations are shown in Table 2.
- It was found that parameters $D_{s,1}$ and $D_{s,2}$ are almost constant for different carbon mass systems while the surface diffusion coefficients are strongly dependent on the initial dye concentration of each system.

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Table 2: External Mass Transfer and Solid-phase Diffusion Coefficients for the Adsorption of AB80+AY117 on Activated Carbon using the Multicomponent HSDM (IAS-RP).

Carbon Mass (g)	Initial Dye Conc. C_o (mg/dm ³)		AB80 $k_{f,1} = 2.94 \times 10^{-4}$ cm/s	AY117 $k_{f,2} = 5.04 \times 10^{-4}$ cm/s	SSE (AB80+AY117) (10 ⁻⁶)
	AB80	AY117	$D_{s,1}$ (cm ² /s)	$D_{s,2}$ (cm ² /s)	
1.7	25	25	8.00×10^{-11}	6.04×10^{-11}	1.483
1.7	37.5	37.5	1.20×10^{-10}	9.04×10^{-11}	5.110
1.7	50	50	1.51×10^{-10}	1.18×10^{-10}	5.184
1.7	75	75	2.15×10^{-10}	1.69×10^{-10}	6.394
1.7	100	100	2.70×10^{-10}	2.04×10^{-10}	26.712
0.4	50	50	1.43×10^{-10}	1.26×10^{-10}	1.612
0.8	50	50	1.49×10^{-10}	1.23×10^{-10}	1.611
1.2	50	50	1.48×10^{-10}	1.22×10^{-10}	4.495
1.7	50	50	1.51×10^{-10}	1.18×10^{-10}	5.184
2.2	50	50	1.45×10^{-10}	1.20×10^{-10}	9.986

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Batch Kinetic Studies (Results and Discussion)

- For the AB80+AY117 system, the D_s values of AB80 in the single component system are smaller than the $D_{s,1}$ values of AB80 in the AB80+AY117 binary system while the $D_{s,2}$ values of AY117 produce an opposite trend, the D_s values of AY117 in the single component system are greater than the $D_{s,2}$ values of AY117 in the AB80+AY117 binary system.

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Batch Kinetic Studies (Results and Discussion)

- A Higashi expression (Higashi and Oishi, 1963) has been used to correlate the relationship between the multicomponent surface diffusivities, $D_{s,1}$ and $D_{s,2}$, and the fractional coverage, θ_A and θ_B , of the acid dyes in the binary adsorption system. The expressions are shown in equations 18 and 19 and the plots are shown in Figure 6:

$$D_{s,1} = D_1 \theta_A + D_2 \theta_B \quad (18)$$

$$D_{s,2} = D_1 \theta_A + D_2 \theta_B \quad (19)$$

where D_1 and D_2 are the self-diffusivities for components 1 and 2 in the mixture.

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Batch Kinetic Studies (Results and Discussion)

- It was found that the surface diffusivities are linearly proportion to the fractional coverage expressions and are similar in trend with the findings in the single component HSDM (see Figure 6 and Table 3).

Table 3: Slope and y-Intercept Values of the Correlated Lines in the Plots of the Surface Diffusivity against Fractional Coverage Expression

Dye	System	Slope	y-intercept
Acid Blue 80	AB80 (single)	2.646×10^{-9}	2.686×10^{-9}
	AB80+AY117	1.449×10^{-10}	1.524×10^{-10}
Acid Yellow 117	AY117 (single)	2.702×10^{-9}	2.896×10^{-9}
	AB80+AY117	2.525×10^{-9}	2.566×10^{-9}

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Figure 6: The Plots of Surface Diffusivity against Fractional Coverage

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Conclusions

For the Equilibrium Isotherm Studies:

- The Redlich-Peterson isotherm equation was found to provide the good correlation for the sorption of the two acid dyes, AB80 and AY117, on activated carbon.

For the Batch Kinetic Studies:

- A Multicomponent HSDM was developed by incorporating the HSDM with the IAST model using the Redlich-Peterson isotherm equation.
- The Multicomponent HSDM described the experimental data with a high degree of accuracy for a wide range of carbon mass and initial dye concentration systems.
- The multicomponent surface diffusivities were found to be strongly dependent on the effect of initial dye concentration.
- They are linearly proportion to the fractional coverage expressions and are similar in trend with the findings in the single component HSDM.

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