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Langmuir Isotherm Models Applied to the Multicomponent Sorption of Acid Dyes from Effluent onto Activated Carbon

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The adsorption of three acidic dyes, Acid Blue 80 (AB80), Acid Red 114 (AR114), and Acid Yellow 117 (AY117) onto activated carbon, Filtrasorb 400, has been studied. Three single-component and three binary, AB80 + AR114, AB80 + AY117, and AR114 + AY117, isotherms were determined. Four models for predicting the multicomponent equilibrium sorption isotherms have been compared in order to determine which is the best fit model to predict or correlate binary adsorption data. These were an extended Langmuir isotherm, a simplified model based on single-component equilibrium factors, a modified extended Langmuir isotherm with a constant interaction factor, and a modified extended Langmuir isotherm incorporating a surface coverage dependent interaction factor.

Introduction

The removal of dyes from effluents is significant to many industries on an environmental basis, as the legal standards for the quality of effluent discharges are becoming increasingly stringent. Many companies are looking at tertiary treatment processes to remove organic from their effluents. Adsorption, as a treatment process, has attracted considerable attention in this respect, since a well-designed adsorption system can produce an effluent with virtually no dyestuffs present. Adsorption is a physiochemical wastewater treatment process in which dissolved molecules are attached to the surface of an adsorbent by physical/chemical forces. In addition, because adsorption is sometimes reversible, the regeneration of the adsorbent with resultant economy of operation is also possible.

Several studies, as shown in Table 1, have been undertaken to assess the ability of various adsorbents to remove dyestuffs from aqueous effluents. Investigations have been undertaken to determine whether commercially available materials hold promise in the treatment of wastewater. Using activated carbon as a reference, some of the materials investigated included minerals, industrial byproducts, proteinaceous materials, and conventional water-treatment agents. It was concluded that although no cheap, commercially available solid is likely to remove all contaminants found in secondary effluents, these materials can be expected to make contributions to water purification through the removal of specific contaminants. Several of the alternatives which have been investigated are activated silica, activated alumina, peat, and wood.

A number of adsorption systems used for the removal of dyestuffs are presented in Table 1. The adsorption saturation capacities are also given where the data are available.

Although considerable information has been accumulated for the adsorption of single-component dyes by various adsorbents, many industrial situations still result in companies discharging effluents which contain several dye components. Experimental data on multicomponent sorption systems are still very limited in the literature. Data on binary mixtures have been reported (Amiot, 1934; El Dib et al., 1978; McKay et al., 1989) for the adsorption of hydrocarbon mixtures onto activated carbon. Studies on multicomponent adsorption (Hill, 1949; Young et al., 1962) formed the basis of the thermodynamic model (Myers et al., 1965) which provided an expression analogous to Raoult's law for gas/liquid systems which was applicable to the prediction of multicomponent sorption equilibria. This ideal adsorbed solute (IAS) theory requires time-consuming graphical solutions or extensive computational methods, although simplifying assumptions have made solutions to the IAS theory easier. The Freundlich isotherm was incorporated into the IAS theory (Radke et al., 1972; Fritz et al., 1981) and tested for bisolute systems. A modified Langmuir approach (Butler et al., 1930; Jain et al., 1973) has also been developed and applied to bisolute systems. These previous theories are applied to the binary acid dye/carbon systems in the present paper. All the theories require the bisolute equilibrium isotherms to be determined for confirmation of the fractional sorbent coverage.

Acid dyes were selected for this study because they are widely used throughout industry and are known to be difficult to remove by many sorbents. The present paper reports the sorption equilibrium data of three acidic dyestuffs—Acid Blue 80 (Polar Blue RAWL), Acid Red 114 (Polar Red), and Acid Yellow 117 (Polar Yellow GN 400%)—onto activated carbon. In addition, the three possible bisolute isotherms are also analyzed in this paper. A comprehensive isotherm analysis was carried out for the sorption of each acid dye onto activated carbon in each system. On the basis of the Langmuir isotherm results for single-component systems, a number of models have been tested to predict the multicomponent equilibrium isotherms. The approaches used include those based on thermodynamic theory as well as correlative and empirical methods.

Experimental Materials

Adsorbent. The adsorbent used in the research is activated carbon type F400 supplied by the Filtrasorb

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10.1021/je9902894 CCC: $19.00

Table 1. Materials Used as Adsorbents for Dyestuffs

adsorbent	dyestuff	capacity/mg·g^{-1}	ref
activated carbon	Basic Red 22	708	McKay et al. (1987)
	Basic Yellow 21	628	McKay et al. (1987)
	Basic Blue 69	871	McKay et al. (1987)
peat	Acid Blue 25	13.0	Poots et al. (1976)
	Basic Blue 3	390	Allen et al. (1987)
	Basic Yellow 21	300	Allen et al. (1987)
	Basic Red 22	240	Allen et al. (1987)
silica	Basic Blue 69	25.0	McKay et al. (1978)
	Acid Blue 25	<5.0	McKay et al. (1978)
banana pith	Acid Violet	13.1	Namasivayam et al. (1992)
wood	Acid Blue 25	8.3	Poots et al. (1976)
	Saffranine (BR)	100	McKay et al. (1986)
	Foron Brill (DispR)	12	McKay et al. (1986)
	Methylene Blue (BB)	84	McKay et al. (1986)
	Sandolan Blue (AB)	15	McKay et al. (1986)
bagasse pith	Acid Blue 25	21.7	McKay et al. (1997)
	Acid Red 114	22.9	McKay et al. (1997)
	Basic Blue 69	155	McKay et al. (1997)
	Basic Red 22	77.6	McKay et al. (1997)
lignite	Basic Red 22	235	Allen et al. (1988)
	Basic Yellow 21	390	Allen et al. (1988)
biogas residual slurry	Acid Brilliant Blue	13.7	Yamuna et al. (1992)
	Direct Red	12.3	Namasivayam et al (1995)
orange peel	Congo Red (DirR)	22.4	Namasivayam et al. (1996)
	Procion Orange	1.33	Namasivayam et al. (1996)
	Rhodamine B	3.23	Namasivayam et al. (1996)
carbon	Victoria Blue	5.5	McKay et al. (1982)
	Deorlene Yellow	200	McKay et al. (1982)
	Disperse Blue 7	25	McKay et al. (1982)
	Telon Blue (AB25)	175	McKay et al. (1982)
	Basic Blue 69	840	McKay et al. (1985)
	Basic Yellow 21	600	McKay et al. (1988)
	Basic Red 22	550	McKay et al. (1988)
red mud	Congo Red	4.05	Namasivayam et al. (1996)
chitin	Acid Blue 25	190	McKay et al. (1983)
	Acid Blue 158	200	McKay et al. (1983)
	Mordant Yellow 5	50	McKay et al. (1983)
	Direct Red 84	40	McKay et al. (1983)
carbonized spent bleaching earth	Basic Blue 3	102.6	Low et al. (1996)
	Methylene Blue	94.5	Low et al. (1996)
sulfonated coal	Basic Blue 9	113.3	Atul et al. (1996)
	Basic Violet 10	66.7	Atul et al. (1996)
cotton waste	Safranine (BR)	73	McKay et al. (1986)
	Congo Red (DirR)	45	McKay et al. (1986)
	Methylene Blue (BB)	24	McKay et al. (1986)
bentonite	Safranine (BR)	120	McKay et al. (1986)
	Congo Red (DirR)	50	McKay et al. (1986)
	Foron Brill (DispR)	26	McKay et al. (1986)
	Methylene Blue (BB)	150	McKay et al. (1986)
	Sandolan Blue (AB)	20	McKay et al. (1986)
	Foron Blue (DispB)	40	McKay et al. (1986)
Fuller's earth	Acid Blue 25	220	McKay et al. (1985)
	Basic Blue 69	1200	McKay et al. (1985)
chrome sludge	Acid Blue 29	58.8	Lee et al. (1996)
	Basic Blue 3	38.5	Lee et al. (1996)
	Acid Blue 25	32.3	Lee et al. (1996)
	Reactive Yellow 2	41.7	Lee et al. (1996)
	Basic Blue 3	0.18	Lee et al. (1996)
	Methylene Blue	0.51	Lee et al. (1996)

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 with distilled water to remove fines. It was dried at 110 °C in an oven for 24 h. Then, the dried activated carbon was sieved into several discrete particle size ranges. The 500 to 710 μm size range activated carbon was used in this study. Table 2 gives the physical properties of carbon F400.

Sorbates. Three dyes, namely Acid Red 114(AR114), Acid Blue 80(AB80), and Acid Yellow 117(AY117), were used in these studies as three single-component and three equimass binary systems. Some information about the three acid dyes, which are used to measure and prepare the dye concentration, is shown in Table 3. They are color

Table 2. Physical Properties of Activated Carbon Filtrasorb F400

total surface area (N_2 BET method)/(m^2 kg^{-1})	(1.05−1.2) × 10^6
bed density, backwashed and drained/(kg m^{-3})	425 × 10^3
bulk density/(kg m^{-3})	1300−1400
pore volume/(m^3 kg^{-1})	0.90 × 10^{-3}
iodine number	1000−1100
Methylene Blue number	260−300

Table 3. Information on the Acid Dyes

	Acid Blue 80	Acid Red 114	Acid Yellow 117
color index number	61585	23635	24820
molecular mass/g	676	830	848
λ/nm	626	522	438

Table 4. Constants for Calculations of Dye Concentrations in Mixtures from Optical Density Values

name of dye	λ/nm	constants		
Acid Blue 80 (1)	626	k_{11}	k_{12}	k_{13}
		0.0493	0.0010	0.0002
Acid Red 114 (2)	522	k_{21}	k_{22}	k_{23}
		0.0007	0.0677	0.0211
Acid Yellow 117 (3)	438	k_{31}	k_{32}	k_{33}
		0.0043	0.0011	0.0744

index number, molecular masses, and the wavelengths at which the maximum absorption of light occurs, λ.

Experimental Methods

A series of fixed volumes (0.050 dm^3) of solutions with predetermined initial dye concentrations were prepared and brought into contact with predetermined masses (0.05 g) of carbon F400 (particle diameter $d_p = 500$ to 710 μm). The jars were sealed and agitated in the shaker bath until equilibrium was reached. For the binary systems, all solutions were prepared with solutions of equal mass concentrations; for example, $C_{0,1} = C_{0,2}$ for a binary system comprising components 1 and 2. Mass concentrations for dyestuffs are usually used in industrial practice, and this approach has been adopted in the present study. The ratios were the same fixed constant values in every experiment.

Finally, 0.05 g of activated carbon was added to each of the solutions, and the mixture was swirled gently to ensure the activated carbon was both wetted and in contact with the dye solution. The bottles were agitated in a Grant shaking water bath at 20 ± 2 °C at 200 rpm for 21 days.

Analysis. Each sample taken was analyzed using a Varian Cary 1E spectrophotometer by measuring the optical densities of its components at their respective maximum adsorbance wavelengths, which were determined by performing absorbance−wavelength scans for each dye. These are (600, 522, and 438) nm for Acid Blue 80, Acid Red 114, and Acid Yellow 117, respectively.

Calibration for cross-interference was carried out as previously described by Al Duri and McKay (1999). Dye concentrations were calculated as follows. For a bisolute system of components A and B measured at λ_1 and λ_2, respectively, to give optical densities of d_1 and d_2:

$$C_A = \frac{k_{B2}d_1 - k_{B1}d_2}{k_{A1}k_{B2} - k_{A2}k_{B1}} \tag{1}$$

$$C_B = \frac{k_{A1}d_2 - k_{A2}d_1}{k_{A1}k_{B2} - k_{A2}k_{B1}} \tag{2}$$

where k_{A1}, k_{B1}, k_{A2}, and k_{B2} are the calibration constants for components A and B at the two wavelengths λ_1 and λ_2, respectively.

The optical density values for three dyes at three different wavelengths are shown in Table 4.

Finally, the results were used to obtain the carbon loading q by material balance:

$$\text{When } C = C_e\text{, then } q = q_e$$

$$\text{When } C = C_0\text{, then } q = q_0$$

The equilibrium study mass balances are defined by

$$(C_0 - C_e)V = (q_e - q_0)m \tag{3}$$

where C_0 = initial concentration of acid dyes in the solution, C_e = equilibrium concentration of acid dyes in the solution, q_e = amount of acid dye sorbed by the sorption per unit of mass, q_0 = initial amount of dye sorbed by the sorption per unit of mass, m = mass of the carbon used, and V = sample volume.

Table 5. Single-Component Equilibrium Results

C_0	C_e/mg·dm^{-3}			C_0	C_e/mg·dm^{-3}		
mg·dm^{-3}	AB80	AR114	AY117	mg·dm^{-3}	AB80	AR114	AY117
10	0.001	0.201	0.001	100	14.25	20.97	4.787
20	0.030	0.460	0.012	110	18.63	26.05	7.137
30	0.096	0.961	0.050	120	22.56	36.68	7.816
40	0.194	1.585	0.103	130	29.00	37.31	10.54
50	0.486	2.676	0.198	140	33.26	45.48	15.12
60	1.405	4.186	0.705	150	47.57	50.32	20.76
70	2.908	4.186	1.194	175	64.33	75.13	38.11
80	5.074	7.096	1.464	200	85.83	98.10	55.05
90	7.590	14.82	2.793	250	139.4	147.6	90.83

Table 6. Binary Component Equilibrium Results

	C_e (mg·dm^{-3})					
	AB80 + AR114		AB80 + AY117		AR14 + AY117	
C_0 (mg·dm^{-3})	AB80	AR114	AB80	AY117	AR114	AY117
25	0.477	0.957	0.200	0.190	0.700	0.500
30	0.684	1.146	0.400	0.380	1.100	1.200
35	0.945	1.492	0.887	0.875	1.553	2.413
40	1.146	1.814	1.338	1.190	2.166	3.868
45	1.935	2.912	2.489	2.315	3.200	5.228
50	3.382	4.762	3.967	3.377	5.339	7.713
55	5.287	7.379	6.382	5.671	7.740	10.17
60	6.806	9.471	8.500	7.467	9.841	12.64
70	11.30	14.60	14.41	12.41	13.42	16.76
75	14.23	18.06	17.32	14.89	16.67	19.04
87.5	24.43	28.70	25.37	24.47	19.30	21.99
100	31.67	37.11	34.98	34.19	27.50	30.97
125	54.37	61.39	57.27	54.34	34.41	38.95

Experimental Results

The single-component equilibrium liquid-phase concentrations are presented in Table 5, and the binary data are presented in Table 6. The solid-phase concentrations, q_e, are calculated using the mass balance equation (eq 3).

Theoretical Analysis

Multicomponent equilibrium studies have passed through many stages of development since the beginning of this century, when none of the multicomponent equilibrium studies dealt with competitive adsorption and only a few were concerned with the selectivity of adsorption processes. Extensions of several common isotherms were used to model the experimental data, namely, the extended Langmuir equation, the Jain and Snoeyink modified extended Langmuir model, the P-factor, and the interaction factor. Two of these are predictive in nature (extended Langmuir equation and Jain and Snoeyink modified extended Langmuir model); the remainder are correlative.

Extended Langmuir Equation. Butler and Ockrent (1930) were the first to develop the Langmuir model for competitive adsorption. This model assumed (i) a homogeneous surface with respect to the energy of adsorption, (ii) no interaction between adsorbed species, and (iii) that all adsorption sites are equally available to all adsorbed species.

$$q_{e,i} = \frac{K^\circ_{L,i}C_{e,i}}{1 + \sum a^\circ_{L,i}C_{e,i}} \tag{4}$$

For example, using components 1 and 2

$$q_{\mathrm{e},1} = \frac{K^{\circ}_{\mathrm{L},1}C_{\mathrm{e},1}}{1 + a^{\circ}_{\mathrm{L},1}C_{\mathrm{e},1} + a^{\circ}_{\mathrm{L},2}C_{\mathrm{e},2}} \tag{5}$$

$$q_{\mathrm{e},2} = \frac{K^{\circ}_{\mathrm{L},2}C_{\mathrm{e},2}}{1 + a^{\circ}_{\mathrm{L},1}C_{\mathrm{e},1} + a^{\circ}_{\mathrm{L},2}C_{\mathrm{e},2}} \tag{6}$$

where K_{L} and a_{L} are the Langmuir isotherm constants.

Jain and Snoeyink Modified Extended Langmuir Model. Jain and Snoeyink (1973) investigated competitive sorption on activated carbon from aqueous bicomponent solutions of organic sorbates and developed a model that predicts sorption equilibria in such nonideal systems. According to Jain and Snoeyink, the Langmuir theory for binary sorbate systems is based on sorption without competition. Therefore, to account for competition in the Langmuir theory, the Jain−Snoeyink (JS) model proposed to add an additional term to the extended Langmuir equation.

$$q_{\mathrm{e},1} = \frac{(Q^{\circ}_{\mathrm{m},1} - Q^{\circ}_{\mathrm{m},2})a^{\circ}_{\mathrm{L},1}C_{\mathrm{e},1}}{1 + a^{\circ}_{\mathrm{L},1}C_{\mathrm{e},1}} + \frac{Q^{\circ}_{\mathrm{m},2}a^{\circ}_{\mathrm{L},1}C_{\mathrm{e},1}}{1 + a^{\circ}_{\mathrm{L},1}C_{\mathrm{e},1} + a^{\circ}_{\mathrm{L},2}C_{\mathrm{e},2}} \tag{7}$$

$$q_{\mathrm{e},2} = \frac{Q^{\circ}_{\mathrm{m},2}a^{\circ}_{\mathrm{L},2}C_{\mathrm{e},2}}{1 + a^{\circ}_{\mathrm{L},1}C_{\mathrm{e},1} + a^{\circ}_{\mathrm{L},2}C_{\mathrm{e},2}} \tag{8}$$

where Q°_{m} is the monolayer saturation capacity for the Langmuir isotherm.

The first term on the right-hand side of eq 7 refers to the amount of species 1 adsorbed without competition with 2, while the second term gives the amount of species 1 adsorbed in competition with 2, as described by applying the competition to the Langmuir model. The additional term of eq 7 is the Langmuir expression for the number of molecules of solute 1 which are sorbed without competition on the surface, and the term is proportional to $(Q_{\mathrm{m},1} - Q_{\mathrm{m},2})$, where $Q_{\mathrm{m},1} > Q_{\mathrm{m},2}$. By eq 8, the number of molecules of solute 2 sorbed on the sorbent surface (proportional to $Q_{\mathrm{m},2}$ and in competition with solute 1) can be calculated from the extended Langmuir equation.

P-Factor. This method is another correlative technique that has been developed (McKay and Al Duri, 1987) and applied to dye/carbon systems. It is an easy-to-use method based on introducing a "lumped" capacity factor P_i.

$$P_i = \frac{(K_{\mathrm{L},i}/a_{\mathrm{L},i})_{\mathrm{singlesolute}}}{(K_{\mathrm{L},i}/a_{\mathrm{L},i})_{\mathrm{multisolute}}} \tag{9}$$

where $(K_{\mathrm{L},i}/a_{\mathrm{L},i})$ is the sorbent monolayer capacity for component i in a multisolute system while $(K_{\mathrm{L},i}/a_{\mathrm{L},i})$ is that in the single-solute system. This model assumes a Langmuir isotherm; hence, for each component i, the multicomponent isotherm equation is described as

$$q_{\mathrm{e},i,\mathrm{multi}} = \frac{1}{P_i}\,\frac{K^{\circ}_{\mathrm{L},i}C_{\mathrm{e},i,\mathrm{multi}}}{1 + a^{\circ}_{\mathrm{L},i}C_{\mathrm{e},i,\mathrm{multi}}} \tag{10}$$

Interaction Factor. The interaction factor is a correlative method based on combining single-component and multicomponent data to produce correlative factors. These factors are back-substituted in the extended isotherm formulas to produce generalized multicomponent isotherms. It assumes that the value of the interaction factor cannot have a negative value.

Sorbent−sorbate interactions and competition will change the diffusivity of each component and alter its sorption energy, leading to changes in sorption capacities, which appear difficult to predict. Different interactions in solution and on the surface of the sorbent lead to a different loading; to incorporate these effects into a correlative model, an interaction term η has been introduced. In 1957, Schay was the first to propose the interaction factor η_i for the ith component in a system of N components. η is specific to each component i and is a function of all other components in solution.

The calculation of the interaction factor is based on minimizing the hybrid fractional error function (HYBRID). It also includes the number of degrees of freedom of the system—the number of data points n minus the number of parameters p of the isotherm equation—as a divisor.

$$\frac{100}{n - p}\sum_{i=1}^{n}\left[\frac{(q_{\mathrm{e,meas}} - q_{\mathrm{e,calc}})^2}{q_{\mathrm{e,meas}}}\right]_i \tag{11}$$

Yon and Turnock (1971) incorporated η in their systems of gases adsorbing on molecular sieves, and successful results were obtained. Incorporating this approach with the Langmuir isotherm, Mathews (1975) presented the following:

$$q_{\mathrm{e},i} = \frac{K_i(C_{\mathrm{e},i}/\eta_i)}{1 + \sum_{j=1}^{n} a_j(C_{\mathrm{e},j}/\eta_j)} \tag{12}$$

Seidel (1988) applied eq 11 for binary mixtures of phenol and indol on activated carbon. McKay and Al Duri (1989) and Al-Duri and McKay (1991) adopted this approach with dye/carbon and dye/pith systems, respectively, and obtained a significant improvement to the Extended Langmuir Equation. Although it has given good results for systems whose components have similar sorbent affinities, this model has not been widely applied because, first, the interaction factor η does not have a strong theoretical foundation and, second, eq 12 does not include the constant K for other components. K refers to the sorbent capacity and adsorption energy. This implies that η is deficient in including the adsorption constants of other components and hence neglects their presence to some extent. However, to date it is one of the "simpler" and relatively more accurate approaches.

Results and Discussion

Three bisolute equilibrium isotherms have been determined for the sorption of Acid Blue 80 (AB80), Acid Red 114 (AR114), and Acid Yellow 117 (AY117) onto activated carbon. This present paper is concerned with the use of the Langmuir equation for predicting and correlating multicomponent equilibrium isotherm data. In all cases, a linear transform method (LTFM) was used to find the Langmuir constants. The Langmuir constants K_{L} and a_{L} can be determined from a linearized form of Langmuir eq 13, represented by eq 14.

$$q_{\mathrm{e}} = \frac{K_{\mathrm{L}}C_{\mathrm{e}}}{1 + a_{\mathrm{L}}C_{\mathrm{e}}} \tag{13}$$

$$\frac{C_{\mathrm{e}}}{q_{\mathrm{e}}} = \frac{a_{\mathrm{L}}}{K_{\mathrm{L}}}C_{\mathrm{e}} + \frac{1}{K_{\mathrm{L}}} \tag{14}$$

The linear correlation coefficient for the Langmuir isotherms was >0.9840, as shown in Table 7. Consequently, it was decided to see if a simple method based on the

Table 7. Langmuir Sorption Isotherm Constants for AB80, AR114, and AY117 in Single and Binary Systems

	K_L/dm^3·g^{-1}	a_L/dm^3·mg^{-1}	Q_0/mg·g^{-1}	R^2
		Single Component System		
AB80	60.73	0.541	112.3	0.9979
AR114	27.84	0.269	103.5	0.9952
AY117	78.28	0.502	155.8	0.9938
		AB80 + AR114 System		
AB80	32.81	0.507	64.75	0.9965
AR114	45.27	0.638	70.97	0.9979
		AB80 + AY117 System		
AB80	54.16	0.809	66.98	0.9940
AY117	58.51	0.844	69.35	0.9940
		AR114 + AY117 System		
AR114	32.89	0.477	68.94	0.9845
AY117	27.88	0.440	63.34	0.9854

Langmuir isotherm equation could be used to predict or correlate single-component and multicomponent isotherms. Fixed different multicomponent isotherm equations based on the Langmuir isotherm were used to attempt to predict the multicomponent acid dye systems:

A. the extended Langmuir equation

B. the Jain and Snoeyink modified extended Langmuir model

C. the P−factor model

D. the extended Langmuir-based constant interaction factor

A. Extended Langmuir Equation. The extended Langmuir equation, using the LTFM constants as an example, is

$$q_{e,i} = \frac{K^{\circ}_{L,i} C_{e,i}}{1 + \sum a^{\circ}_{L,i} C_{e,i}} \tag{4}$$

Therefore, for the AB80−AR114 binary system, substituting the appropriate parameter values from Table 7, the extended Langmuir equation becomes

$$q_{AB80} = \frac{60.73 C_{AB80}}{1 + 0.541 C_{AB80} + 0.269 C_{AR114}} \tag{15}$$

$$q_{AR114} = \frac{27.84 C_{AR114}}{1 + 0.541 C_{AB80} + 0.269 C_{AR114}} \tag{16}$$

Figure 2 shows the extended Langmuir plots applicable to dilute solutions for the sorption of Acid Blue 80 in the two binary systems—namely Acid Blue 80 plus Acid Red 114 (AB80 + AR114) and Acid Blue 80 plus Acid Red 114 (AB80 + AR114). In the cases of Acid Blue 80 in the AB80 + AR114 binary system, the best fit model to the experimental data (diamonds) is obtained from the LTFM constants (solid line). For the other case of Acid Blue 80 in the AB80 + AY117 binary system using the LTFM (triangles and broken line), the correlation between the theoretical and experimental data is quite good.

The single-component isotherms for Acid Blue 80 and Acid Yellow 117 have monolayer saturation capacities of 112.3 mg/g and 155.8 mg/g, respectively—a sizable difference. It is possible that competition and interaction between these two acid dyes would be significant and affect each component to a different extent. The extended Langmuir isotherm is based on the same basic assumptions as those for the single-component Langmuir isotherm—namely, that the energy of adsorption between the specific adsorbing species and the surface site is constant and equal for each site, there is no interaction between components, and there is equal competition between species for adsorption sites. Therefore, if interaction and competition are occurring, the extended Langmuir isotherm will not be suitable for representing this system.

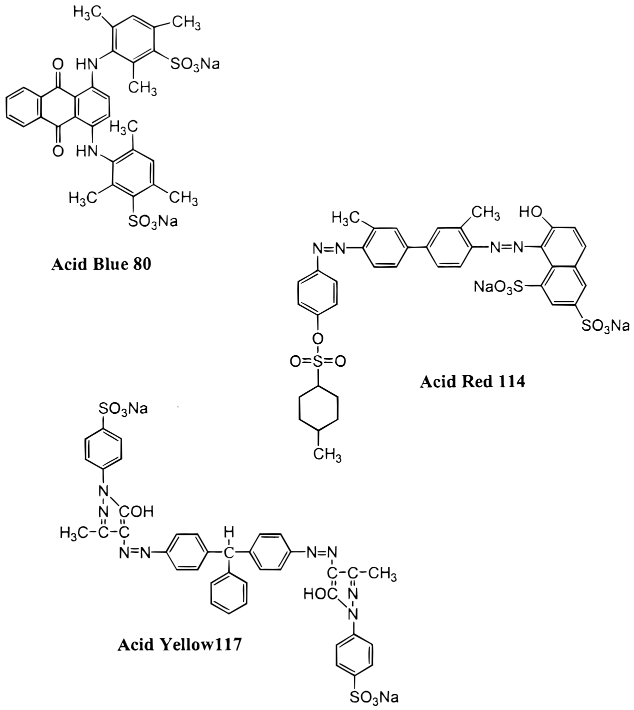

Figure 1. Structures of the three acid dyes.

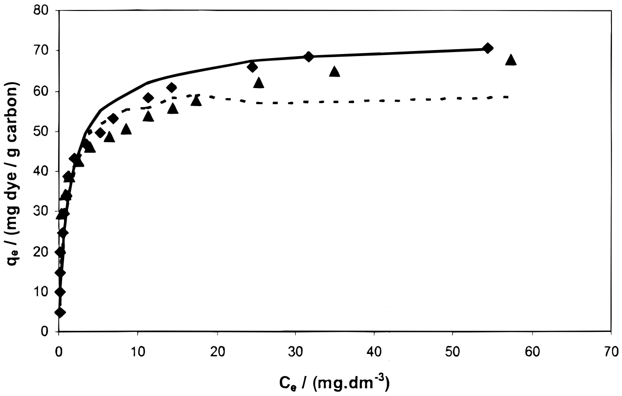

Figure 2. Extended Langmuir analysis for Acid Blue 80 in the binary system: ♦, (AB80 + AR114) experimental; ▲, (AB80 + AY117) experimental; —, (AB80 + AR114) calculated; ---, (AB80 + AY117) calculated.

The correlation between the experimental data and that predicted by the LTFM-based extended Langmuir isotherm for Acid Blue 80 in the AB80 + AR114 binary system is good. In Table 7, the monolayer capacities, Q_0, for the single-component data are 112.3 and 103.0 mg/g for Acid Blue 80 and Acid Red 114, respectively, using the LTFM constants. This similarity is also confirmed by the Q_0 values for the binary monolayer capacities shown in Table 7 as 64.7 mg/g for AB80 and 71.0 mg/g for AR114 in the AB80 + AR114 binary system, again using LTFM constants. Even if there are some competitive and interactive processes, they will be of a similar relative order of magnitude for the two species. This is confirmed in the following *P*-factor analysis for AB80 and AR114 in the binary system

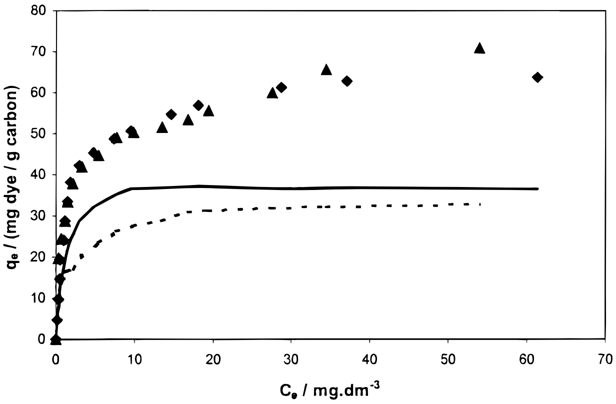

Figure 3. Extended Langmuir analysis for Acid Red 114 in the binary system: ◆, (AB80 + AR114) experimental; ▲, (AR114 + AY117) experimental; —, (AB80 + AR114) calculated; ---, (AR114 + AY117) calculated.

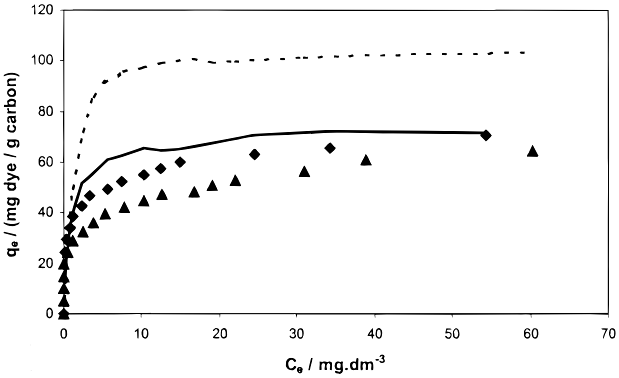

Figure 4. Extended Langmuir analysis for Acid Yellow 117 in the binary system: ◆, (AB80 + AY117) experimental; ▲, (AR114 + AY117) experimental; —, (AB80 + AY117) calculated; ---, (AR114 + AY117) calculated.

(AB80 + AR114), where the *P*-factor values are 1.734 and 1.459, respectively; that is, they are quite similar in value.

Figure 3 shows the correlation between experimental data and predicted data for the sorption of AR114 in two binary systems AR114 with AB80 and AR114 with AY117. The monolayer capacities, Q_0, for the single-component data are 112.3 mg/g, 103.0 mg/g, and 155.8 mg/g for AB80, AR114, and AY117, respectively, using the LTFM constants. The extended Langmuir model gives a very poor fit for AR114 in both AR114 + AB80 and AR114 + AY117 systems. It indicates that interaction and competition between these two species are significant. The correlation between data in Figure 3 for AR114 in the AR114 + AB80 system is not as good as would have been expected on the basis of the correlation observed in Figure 2 for AB80 in AR114 + AB80. The difference between theoretical data from the extended Langmuir equation and the experimental data is greater than a factor of 2 in most cases.

Similarly, Figure 4 shows the comparison between experimental data and predicted data for the sorption of AY117 in the two binary systems AY117 with AB80 and AY117 with AR114. The correlation between data in Figure 4 is very poor in both the AY117 + AB80 and the AY117 + AR114 binary systems. It is likely that competitive and interactive processes between the two acid dyes occur in these two binary systems.

The application of the extended Langmuir isotherm to the prediction of multicomponent acid dye sorption equilibria results in poor agreement between the predicted data and the experimental data. This is due to the basic assumptions of the Langmuir model, which are constant energy of sorption, no interaction, and equal independent competition between species. Some reasonable agreement was observed between predicted and experimental data when the sorption capacities of the species were almost the same, such as for the case of Acid Blue 80 in the AB80 + AR114 binary system.

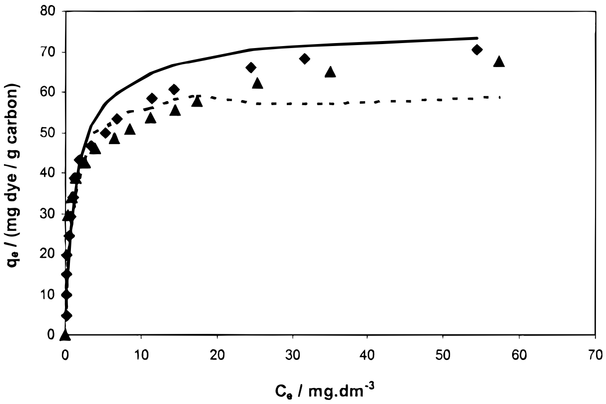

Figure 5. Jain and Snoeyink modified extended Langmuir analysis for Acid Blue 80 in the binary system: ◆, (AB80 + AR114) experimental; ▲, (AB80 + AY117) experimental; —, (AB80 + AR114) calculated; ---, (AB80 + AY117) calculated.

B. Jain and Snoeyink Modified Extended Langmuir Model. In 1973, the extended Langmuir equation was improved and modified by Jain and Snoeyink, who assumed that a portion of adsorption takes place without competition because not all adsorption sites are available to all species. This was attributed to the chemical nature of sites and adsorbates or the relatively large molecular size of the latter. The number of sites with noncompetitive adsorption is given by the difference between the maximum loading of the species, that is, $Q_{m,1} - Q_{m,2}$. The model is described by

$$q_{e,1} = \frac{(Q^{\circ}_{m,1} - Q^{\circ}_{m,2})a^{\circ}_{L,1}C_{e,1}}{1 + a^{\circ}_{L,1}C_{e,1}} + \frac{Q^{\circ}_{m,2}a^{\circ}_{L,1}C_{e,1}}{1 + a^{\circ}_{L,1}C_{e,1} + a^{\circ}_{L,2}C_{e,2}} \quad (7)$$

$$q_{e,2} = \frac{Q^{\circ}_{m,2}a^{\circ}_{L,2}C_{e,2}}{1 + a^{\circ}_{L,1}C_{e,1} + a^{\circ}_{L,2}C_{e,2}} \quad (8)$$

Figures 5−7 show the comparison between experimental data and predictions based on the Jain and Snoeyink modified extended Langmuir model. Figure 5 shows the agreement between the model prediction and the experimental points for Acid Blue 80 in two binary systems, AB80 + AR114 and AB80 + AY117. In all cases of AB80 binary systems, comparing with the extended Langmuir equation results, the best fit between the experimental and theoretical data became worse. Figures 6 and 7 show the predictions for AR114 and AY117 in different binary dye systems; similarly, the correlations between the prediction data and experimental data are fairly poor. The Jain and Snoeyink modified extended Langmuir model does not provide an improvement over the data predicted by the extended Langmuir isotherm equation in all cases of multicomponent dye systems. Overall, the Jain and Snoeyink modified extended Langmuir model cannot be used to predict multicomponent acid dye sorption on activated carbon.

C. P-Factor. The *P*-factor is a simplified approach that may be adopted to compare and correlate single-component sorption isotherms with those of the multicomponent

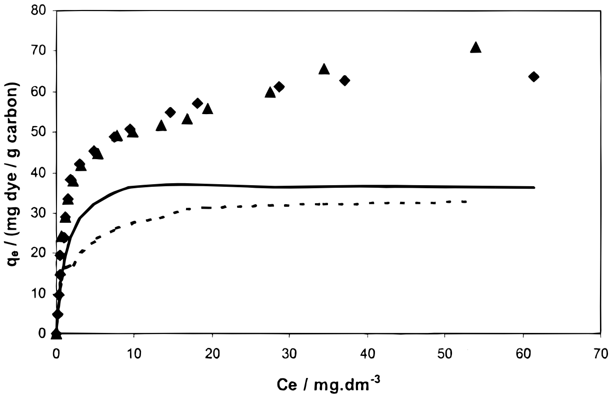

Figure 6. Jain and Snoeyink modified extended Langmuir analysis for Acid Red 114 in the binary system: ♦, (AB80 + AR114) experimental; ▲, (AR114 + AY117) experimental; —, (AB80 + AR114) calculated; ---, (AR114 + AY117) calculated.

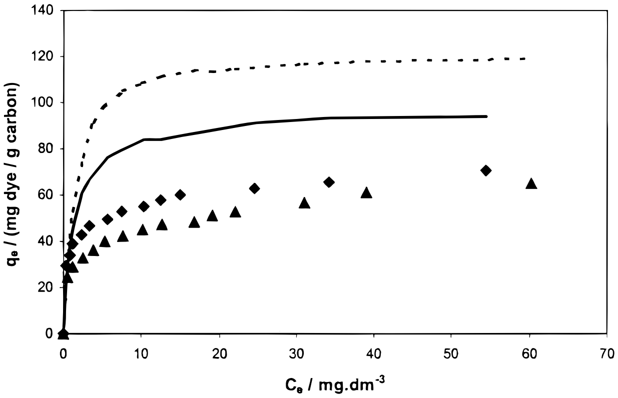

Figure 7. Jain and Snoeyink modified extended Langmuir analysis for Acid Yellow 117 in the binary system: ♦, (AB80 + AY117) experimental; ▲, (AR114 + AY117) experimental; —, (AB80 + AY117) calculated; ---, (AR114 + AY117) calculated.

systems. The results presented in Table 7 show that the Langmuir equation correlates all the single-solute and multisolute data over a wide concentration range, since each set of data has a correlation coefficient > 0.9840. Consequently, it was decided to use the *P*-factor to correlate single-component and multicomponent isotherms using the Langmuir constants K_L and a_L. The constant K_L represents the ratio of kinetic parameters, and a_L is linked to the thermodynamic properties of the system through the enthalpy of adsorption. Therefore, it was decided to use the ratio K_L/a_L (McKay et al., 1987) for this correlation. These ratios are the Q_0 values shown in Table 7. The method involved modifying the single-component solid-phase concentration Q_i and correlating it with the $Q_{i,\mathrm{mixture}}$ values of the mixtures. The capacity factor was converted to a dimensionless form by expressing it as a capacity ratio, the *P*-factor, as shown in the following equation:

$$P_i = \frac{(K_{L,i}/a_{L,i})_{\mathrm{singlesolute}}}{(K_{L,i}/a_{L,i})_{\mathrm{multisolute}}} = \frac{(Q_{O,i})_{\mathrm{singlesolute}}}{(Q_{O,i})_{\mathrm{multisolute}}} \tag{9}$$

The capacity factors (*P*) for different acid dye systems are shown in Table 8. All the C_e values for the pure single-component systems were divided by the appropriate *P* values and plotted on the experimental isotherm for that particular system.

The predictions of isotherms for three acid dyes in the binary systems using the *P*-factor are shown in Figures 8−10.

Table 8. Correlation Factors (*P*) for Various Acid Dye Systems

acid dye	system	correlation factor (*P*) by LTFM	correlation factor (*P*) by HYBRID
Acid Blue 80	AB80	1.000	1.000
Acid Red 114	AR114	1.000	1.000
Acid Yellow 117	AY117	1.000	1.000
Acid Blue 80	AB80 + AR114	1.734	1.465
Acid Red 114	AB80 + AR114	1.459	1.551
Acid Blue 80	AB80 + AY117	1.676	1.658
Acid Yellow 117	AB80 + AY117	2.247	2.020
Acid Red 114	AR114 + AY117	1.502	1.603
Acid Yellow 117	AR114 + AY117	2.461	2.200

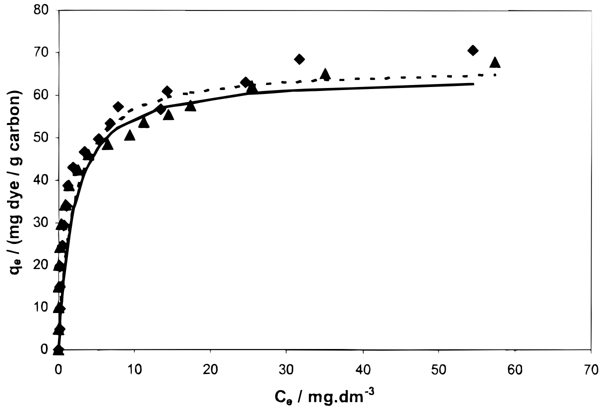

Figure 8. Prediction of isotherms for Acid Blue 80 in acid dye mixtures using the *P*-factor: ♦, (AB80 + AR114) experimental; ▲, (AB80 + AY117) experimental; —, (AB80 + AR114) calculated; ---, (AB80 + AY117) calculated.

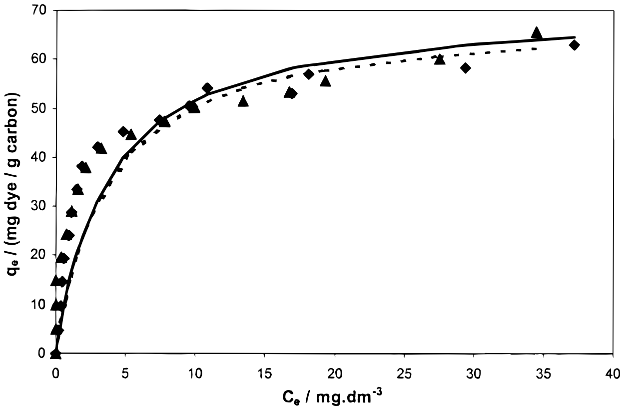

Figure 9. Prediction of isotherms for Acid Red 114 in acid dye mixtures using the *P*-factor: ♦, (AB80 + AR114) experimental; ▲, (AR114 + AY117) experimental; —, (AB80 + AR114) calculated; ---, (AR114 + AY117) calculated.

Figure 8 shows the curves predicted by the *P*-factor correlation with the experimental data points for the sorption of Acid Blue 80 in the two binary systems AB80 + AR114 and AB80 + AY117. The agreement between the predicted AB80 concentration (solid line) and the experimental data (diamonds) in AB80 + AR114 binary system is good. The correlation between experimental and theoretical data in the AB80 + AY117 (broken line and triangles) binary system is also good. The differences in the curves are probably due to the relative competition between the acid dyes, and a contact time study would help confirm if this was the cause.

The curves predicted by the *P*-factor correlation with the experimental data points for the sorption of Acid Red 114 in the two binary systems are shown in Figure 9. Again,

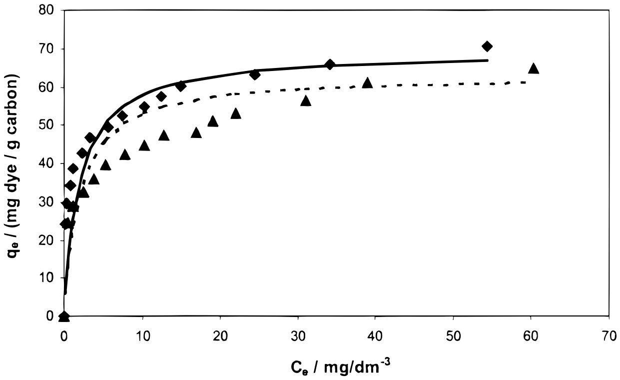

Figure 10. Prediction of isotherms for Acid Yellow 117 in acid dye mixtures using the *P*-factor: ◆, (AB80 + AY117) experimental; ▲, (AR114 + AY117) experimental; —, (AB80 + AY117) calculated; ---, (AR114 + AY117) calculated.

the agreement between the predicted concentrations (line) and the experimental data (points) in the two binary systems is reasonable, but it provides a major improvement over the data predicted by the extended Langmuir isotherm equation for the AR114 binary systems (Figure 3).

Figure 10 shows the correlation for the sorption of Acid Yellow 117 in the two binary systems with two different error analysis methods. The agreement between the experimental points and the curves predicted by the *P*-factor models is good in both binary systems. In the high-concentration range, the sorption capacities from the experimental data and the curves predicted by the *P*-factor model are almost identical.

The *P*-factor model uses basic thermodynamic parameters characteristic of each system's Langmuir equilibrium isotherm and is based on sorption capacity. The model's predictions provided good agreement for six acid dye sorption systems. The model cannot account for all the competitions and interactions which may influence relative sorption rates, resulting in some deviations of the predicted data from the experimental points. The *P*-factor is a single "lumped" correction factor, whereas it is likely that interaction and competitive effects will have a dependence on the following:

1. the relative concentrations of the dyes, which vary throughout the adsorption isotherm;
2. the extent of surface coverage of the adsorbent;
3. the relative rates of each dye component to reach equilibrium;
4. changes in affinity and interactions throughout the equilibrium isotherm.

Overall, it provides a major improvement over the data predicted by the extended Langmuir isotherm equation.

D. Constant Interaction Factor η Method. Multicomponent sorption systems generally involve sorbent−sorbent interaction and competition. The sorbent−sorbent affinity changes due to equilibrium readjustment in the system. To incorporate these effects into a correlative model, an interaction term η has been introduced. This term is estimated on the basis of minimizing the HYBRID error function. The theoretical curves generated by this model are based on using the extended Langmuir equation and incorporating the constant interaction factor, η, as shown in eq 11.

$$q_{e,i} = \frac{K^{\circ}_{L,i}(C_{e,i}/\eta)}{1 + \sum_{j=1}^{n} a^{\circ}_{L,j}(C_{e,j}/\eta)} \tag{12}$$

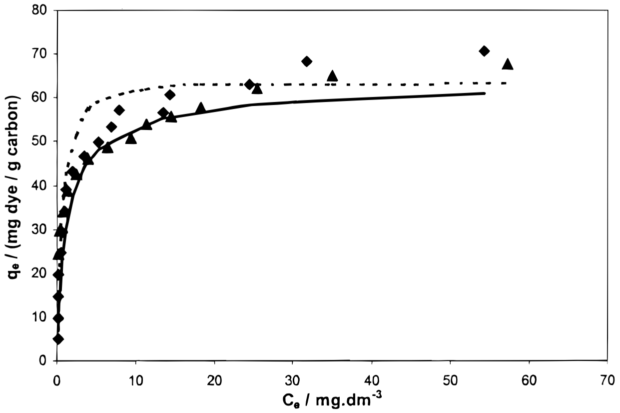

Figure 11. Interaction factor, η, analysis for Acid Blue 80 in acid dye mixtures: ◆, (AB80 + AR114) experimental; ▲, (AB80 + AY117) experimental; —, (AB80 + AR114) calculated; ---, (AB80 + AY117) calculated.

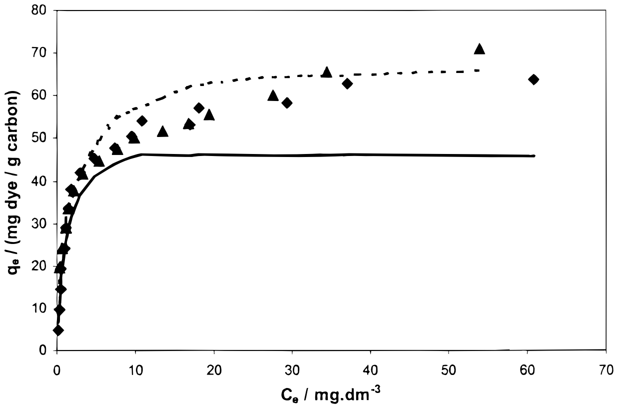

Figure 12. Interaction Factor, η, analysis for Acid Red 114 in acid dye mixtures: ◆, (AB80 + AR114) experimental; ▲, (AR114 + AY117) experimental; —, (AB80 + AR114) calculated; ---, (AR114 + AY117) calculated.

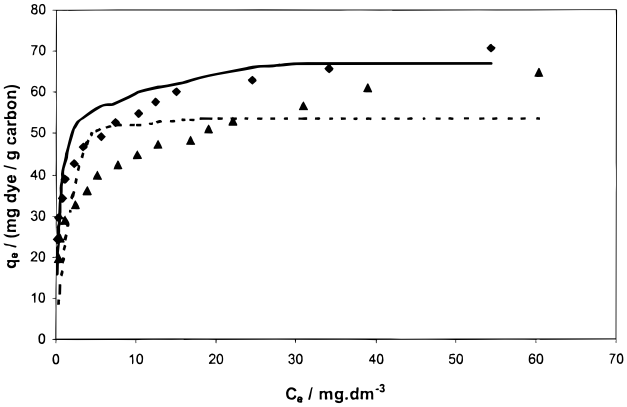

Figure 13. Interaction Factor, η, analysis for Acid Yellow 117 in acid dye mixtures: ◆, (AB80 + AY117) experimental; ▲, (AR114 + AY117) experimental; —, (AB80 + AY117) calculated; ---, (AR114 + AY117) calculated.

In the present approach η is assumed constant and specific to each dye in each multicomponent system. Figures 11−13 show the comparison between experiment and predictions based on the interaction factors for the multicomponent systems. Table 9 gives a list of the interaction factors for each dye in different multicomponent systems.

The corresponding values of η_i are substituted into eq 12 for the number of components in the system. The HYBRID error between the values predicted by the equa-

Table 9. Interaction Factors (η_i) Based on the η Factor Analysis for Different Multicomponent Systems

	interaction factor (η_i)		
system	Acid Blue 80	Acid Red 114	Acid Yellow 117
AB80 + AR114	0.9762	0.6809	
AB80 + AY117	0.6050		0.8228
AR114 + AY117		0.5461	2.1228

tion and the experimental data points is then minimized by varying the η_i values to give a maximum correlation coefficient for all components.

Figure 13 compares the theoretically predicted points and the best fit experimental curves for the two Acid Yellow 117 binary systems. The experimental points for Acid Yellow 117 in the AY117 + AB80 binary system (diamonds) show reasonably good agreement with the theoretical curve (solid line) which has been predicted by the interaction factor expression using LTFM constants. However, AY117 in the AY117 + AR114 binary system (broken line and triangles) shows poor correlation that deviates along the sorption capacity but provides a major improvement when compared to the results predicted by the extended Langmuir equation. Figure 12 compares the theoretical model data points with the experimental curves for Acid Red 114 in the two binary systems. The agreement between the experimental and theoretical data is good at low concentrations and is fairly poor at high concentrations, but this model provides a major improvement over the data predicted by the extended Langmuir isotherm equation.

Figure 11 shows the agreement between the experimental data points and the theoretical curves for Acid Blue 80 in the binary systems. As shown in Figure 11, the agreement between the model prediction and the experimental points is reasonable. Overall, the prediction by the interaction factor model is as successful as the *P*-factor model. It provides a great improvement on the Acid Red 114 and Acid Yellow 117 binary systems compared with the extended Langmuir model and the Jain and Snoeyink modified extended Langmuir model.

The concept of such an interaction factor was proposed by Schay et al. (1957) and was used with limited success by McKay and Al Duri (1987) for the sorption of basic dyes on carbon for metal ion sorption on peat. On the basis of these references and comparing them with the present results, it is not surprising that the application of the interaction factor to the present system under investigation does not provide a satisfactory correlation of experimental data. The reasons are summarized:

1. The solutes have different molecular size.
2. It is possible that dye micelles or dye aggregates may exist in solution.
3. The solutes are electrolytes, and therefore the system is nonideal; it may require activity coefficients to better describe the species.
4. The saturation capacities of each acid dye onto activated carbon in single-solute systems are different, AY117 being adsorbed to a greater capacity, which can be attributed in part to the different interaction forces of the dyes.
5. Although solute concentrations are relatively low, a 20-fold range of concentrations has been used and extends well beyond the range of applicability of Henry's law. Equilibrium saturation is also achieved. These two factors indicate the likely nonideality of the system.

Mechanism of Adsorption. The detailed mechanism of adsorption of acid dyes onto activated carbon F400 is difficult to predict due to the array of chemical groups in the dye molecules. Since the carbon is acid washed in solution, it will lose some residual hydrogens into solution, giving the carbon surface a negative ζ potential. McKay and Al Duri (1991) studied the adsorption of three basic dyes onto this carbon and found the sorption capacities, Q_0, to be 448, 500, and 680 mg/g for Basic Blue 3, Basic Red 22, and Basic Blue 69, respectively. The capacities of the acid dyes in the present work are significantly lower, ranging from 103 to 156 mg/g. The basic dyes will form molecules with a positive charge density in solution and will be attracted to the negatively charged surface, whereas the acid dyes will form molecules with a negative charge density in solution (loss of sodium ions) and will undergo some degree of repulsion from the charged sites on the activated carbon.

Table 10. HYBRID Error Function Values for Different Multicomponent Isotherm Equations Using LTFM Single-Component Langmuir Parameters

	extended Langmuir model	Jain and Snoeyink model	*P*-factor	constant interaction factor
	AB80 + AR114 Binary System			
AB80	70.016	83.135	234.20	108.33
AR114	533.59	533.59	232.29	136.85
	AB80 + AY117 Binary System			
AB80	95.189	95.189	274.27	161.33
AY117	168.51	1073.0	286.70	98.071
	AR114 + AY117 Binary System			
AR114	1184.8	1184.8	215.92	58.312
AY117	5102.5	7643.0	131.28	217.84

There is very limited information in the literature on the adsorption capacity of acid dyes. Allen (1995) reported the adsorption capacity of Acid Blue 25 on a range of adsorbents as 83, 36, 23, 54, 99, 96, and 22 mg/g on carbon, Fuller's earth, silica, wood, peat, alumina, and pith, respectively, the unspecified carbon having one of the highest capacities for the acid dye.

The relative differences in the adsorption capacities on a molar or mass basis, AY117 > AB80 > AR114, are more difficult to explain. In the case of Acid Red 114, the two negative charges on the dye are closest together, thus giving a high negative density at a localized point on the dye molecule. This could result in maximum repulsion from the surface of the carbon. Distinguishing between the capacities of AY117 and AB80 needs more detailed consideration and may involve molecular size and individual chemical group participation in the adsorption process. Since the molecular volume of AB80 is smaller but the molar adsorption capacity of AY117 is greater, then molecular volume is not the sorption capacity determining factor. It is known that benzene adsorbs onto activated carbon, and therfore, the benzene rings could be the bonding species. The three rings in the center of AY117, away from the negative charges of the SO_3 groups, could be responsible for the higher uptake of AY117.

Conclusions

Several methods based on the Langmuir isotherm equation were used to determine a "best fit" model based on the single-component data to predict multicomponent system performance. It was found that the *P*-factor and the interaction factor are better methods to predict and correlate the experimental data. Table 10 shows the values of the HYBRID error function for different multicomponent isotherm equations. The smaller value of the HYBRID error means that the model gives better correlation between experimental and theoretical data. The model based on applying a constant interaction factor, η, correlates binary acid dye experimental isotherm data best.

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