Adsorption of Dyes on Chitin. I. Equilibrium Studies

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Synopsis

Equilibrium isotherms have been studied for the adsorption of four dyestuffs, namely, Acid Blue 25, Acid Blue 158, Mordant Yellow 5, and Direct Red 84, onto chitin. Langmuir and Freundlich constants have been determined and the effects of chitin particle size and solution temperature have been investigated. Theoretical isotherms have been compared with experimental data and good agreement was obtained using a composite isotherm of the general form: $Y_e = iC_e/(1 + jC_e^m)$, where i, j, and m are constants.

INTRODUCTION

Chitin has been studied as an adsorption substrate in a variety of application fields all dealing with effluent treatment. Lord,[1] in one of the earlier studies, examined the adsorption of DDT and its analogs and in 1955 Hackman[2] investigated the adsorption of proteins. Giles et al.[3–6] reported on the adsorption of aromatic anionic species, sulfonated azo dyes, and inorganic and organic acids between 1955 and 1958. Apparently no more major studies were undertaken until 1969 when Takeda and Tomida[7] used chitin as a substrate in thin-layer chromatography for the separation of phenols and amino acids. Akagae and Allan[8] showed that chitin could be used in combination with alum to clarify paper mill wastewater and Iwata and Nakabayashi[9] used chitin to decolorize tea and other beverage solutions. Muzzarelli and Isolatti[10] reported on the removal of methyl mercury acetate in 1971 and most of the subsequent adsorption studies dealt with metal ion removal.[11–22] The most notable studies on solutes other than metal ions were those of Takeda and Tomida[23] on nucleic acid separation, Safronov et al.[24] on petroleum products' removal from wastewater, and Shinagawa et al.[25,26] on dye removal using a combination of deacetylated chitin, activated carbon, and cellulose as an adsorbent system.

The aim of the present work is to study in detail the adsorption of four dyestuffs on chitin to determine the kinetics, mechanisms, and equilibria processes involved. A study of such processes will enable the design of dyehouse effluent plant to be undertaken using chitin as an adsorbent. The dyestuffs studied include a direct, a mordant, an acid, and a premetallized acid dyestuff. Two basic dyestuffs were tested in preliminary studies but no significant uptake was achieved.

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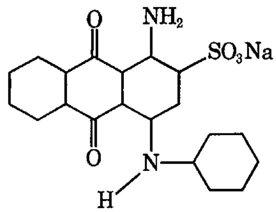
EXPERIMENTAL

Materials

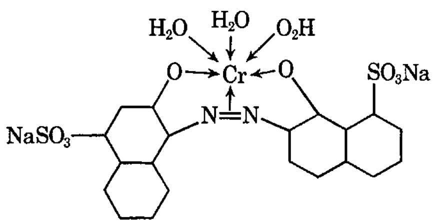
The chitin, as supplied by Sigma Ltd., was sieved into discrete particle size ranges.

The dyes used in the adsorption experiments are shown and they were used as the commercial salts.

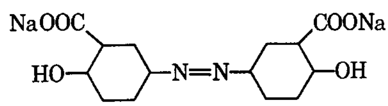
Teflon Blue ANL (Acid Blue 25) as supplied by Bayer:



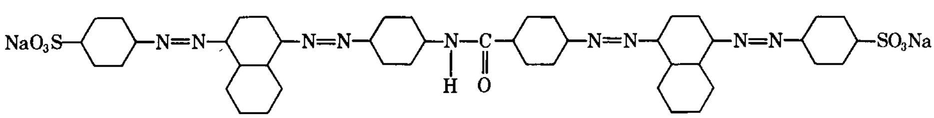
Neolan Blue 2G (Acid Blue 158) as supplied by Ciba-Geigy:



Eriochrome Flavine A (Mordant Yellow 5) as supplied by Ciba-Geigy:



Solophenyl Brown 3RL (Direct Red 84) as supplied by Ciba-Geigy:



METHOD

The equilibrium isotherms were determined by contacting a constant mass of chitin of constant particle size range with a range of different concentrations of dye solution. The chitin and 0.050 dm^3 dye solution were agitated in a Griffin constant temperature shaker-bath for a period of five days. The dye concentrations were measured using a Perkin-Elmer model 5505 spectrophotometer at a wavelength, λ_{max} (corresponding to the maximum wavelength of absorbance). These wavelengths were determined for each dyestuff and are shown in Table

TABLE I
Wavelengths for Four Dyestuffs

Dye	λ_{max} (nm)
Acid Blue 25	600
Acid Blue 158	592
Mordant Yellow 5	360
Direct Red 84	460

I. Isotherms were undertaken to study the effect of adsorbent particle size and dye solution temperature.

DISCUSSION AND RESULTS

General

In two-component systems, a single curve can be drawn of the solute concentration in the solid phase, Y_e, as a function of the solute concentration in the fluid phase, C_e. Each usually holds at one specific temperature and hence is called an isotherm.

Positive adsorption in a solid–liquid system results in the removal of solutes from solution and their concentration at the surface of the solid, to such a time as the concentrations of the solute remaining in solution are in dynamic equilibrium with that at the surface. At this position of equilibrium, there is a defined distribution of solute between the liquid and solid phases which is generally expressed by one or more of a series of isotherms.

Figure 1 shows curves of Y_e vs. C_e for the adsorption of each of the four dyes on chitin. A constant particle size range of 500–710 μm was used and a temperature of 20°C was maintained. The acidic dyes both show a strong affinity for chitin; Acid Blue 25 being adsorbed to a monolayer capacity of 190 mg/g and the metallic Acid Blue 158 having a saturation adsorption capacity of 222 mg/g.

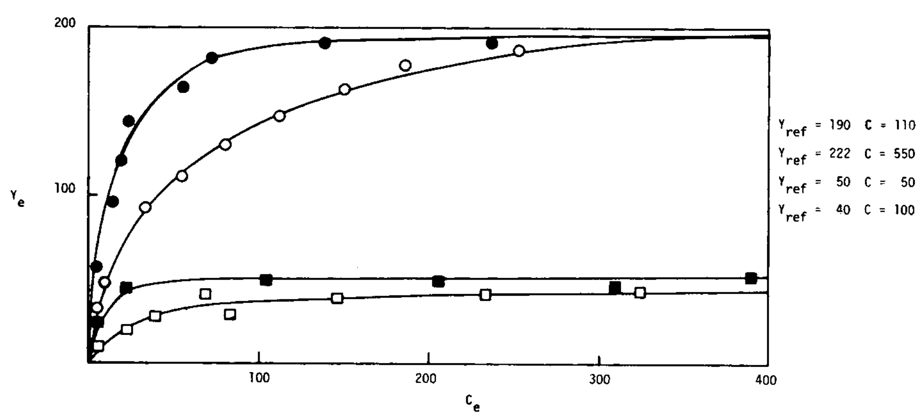


Fig. 1. Adsorption of dyes on chitin: (●) Acid Blue 25, (○) Acid Blue 158, (■) Mordant Yellow 5, (□) Direct Red 84, T = 20°C, d_p = 605 μm.

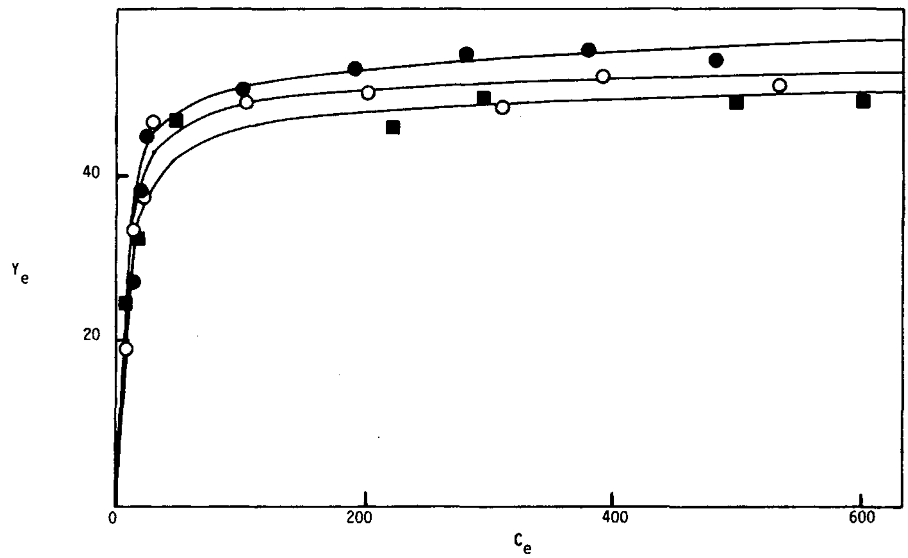


Fig. 2. Effect of particle size for the adsorption of Mordant Yellow 5 on chitin: (●) 850–1000 μm, (○) 500–710 μm, (■) 250–355 μm, T = 20°C.

Mordant Yellow 5 and Direct Red 84 have lower saturation capacities, namely, 50 and 40 mg/g, respectively. Many other factors will affect the degree of adsorption, the fraction of colored ions in the commercial salt, the molecular volume of dye and its planarity, the chelating ability of the chitin–dye system, and the dimerization ability of the dye.

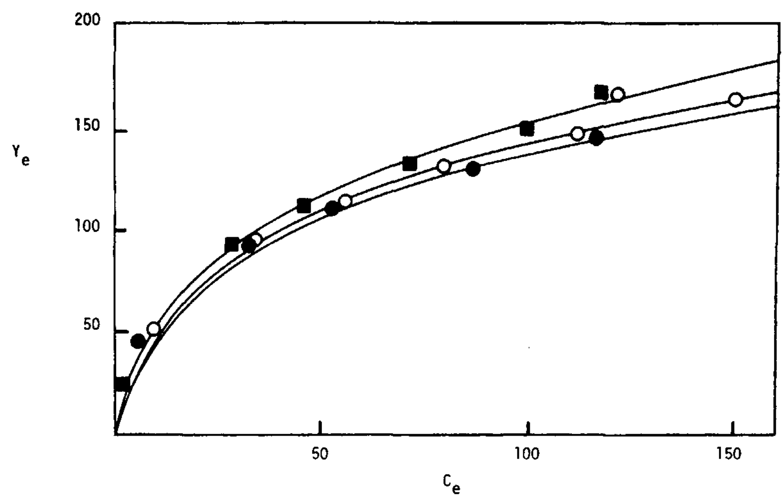


Fig. 3. Effect of particle size for the adsorption of Acid Blue 158 on chitin: (■) 250–355 μm, (○) 500–710 μm, (●) 850–1000 μm, T = 20°C.

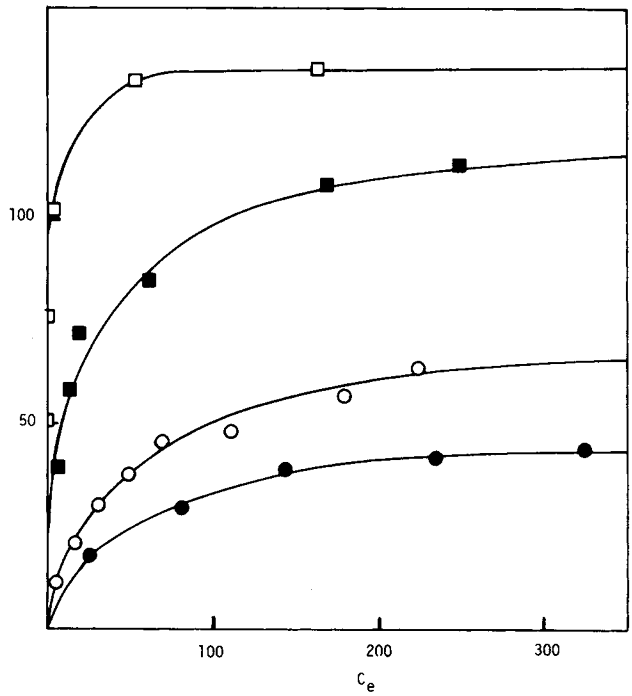


Fig. 4. Effect of temperature for the adsorption of Direct Red 84 on chitin. d_p = 605 μm. *T*: (□) 60°C, (■) 40°C, (○) 30°C, (●) 20°C.

The influence of adsorbent particle size is shown in Figures 2 and 3 indicating chitin particle size has little or no influence on its ability to adsorb Mordant Yellow 5 and Acid Blue 158. Acid Blue 25 was similar showing that these three dyes could completely penetrate the internal pore structure of chitin and saturate the particle. In the case of the large Direct Red 84 dye molecule, a particle size effect was observed and is illustrated in the Langmuir isotherm plot shown later. Such an effect is probably due to the inability of the large molecule to penetrate all the internal pore structure of the chitin and a similar phenomenon was reported previously McKay et al.[27] and McKay and Poots,[28] for the adsorption of certain dyes on peat and wood particles.

The effect of temperature on the adsorption of Direct Red 84 and Acid Blue 158 on chitin is shown in Figures 4 and 5, respectively. The results show two completely different effects. In the adsorption of Acid Blue 158, the adsorption capacity decreases with increasing temperature, decreasing from over 222 mg/g at 20°C to 106 mg/g at 80°C. This phenomenon is quite common and is due to the enhanced magnitude of the reverse (or desorption) step in the mechanism as the temperature increases. The bonds formed between chitin and dye must be quite reversible in this case. A similar increase in the rate of the reverse step was observed with Acid Blue 25. The capacity of chitin for Direct Red increases from 40 mg/g at 20°C to 135 mg/g at 60°C. Consequently, increasing the temperature must increase the mobility of the large dye ion. Furthermore, increasing the temperature may produce a swelling effect within the internal structure of

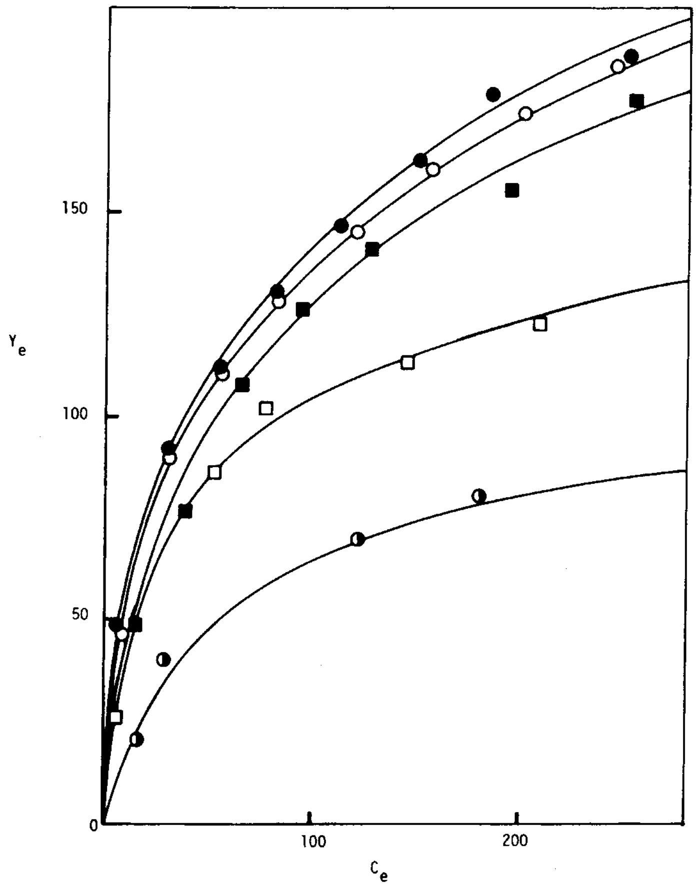


Fig. 5. Effect of temperature for the adsorption of Acid Blue 158 on chitin. d_p = 605 μm. *T*: (●) 20°C, (○) 30°C, (■) 40°C, (□) 60°C, (◑) 80°C.

the chitin enabling the large dyes to penetrate further. Temperature data for Mordant Yellow 5 were quite complex and did not show a major change with temperature; this latter system is still under investigation.

Langmuir Isotherm

The Langmuir isotherm[29] is valid for monolayer adsorption on a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption on the surface and no transmigration of adsorbate in the plane of the surface. The Langmuir expression is represented by the following equation:

$$Y_e = QbC_e/(1 + bC_e) \tag{1}$$

Equations (2) and (3) represent linear forms which are convenient for plotting and determining the Langmuir constants.[30]

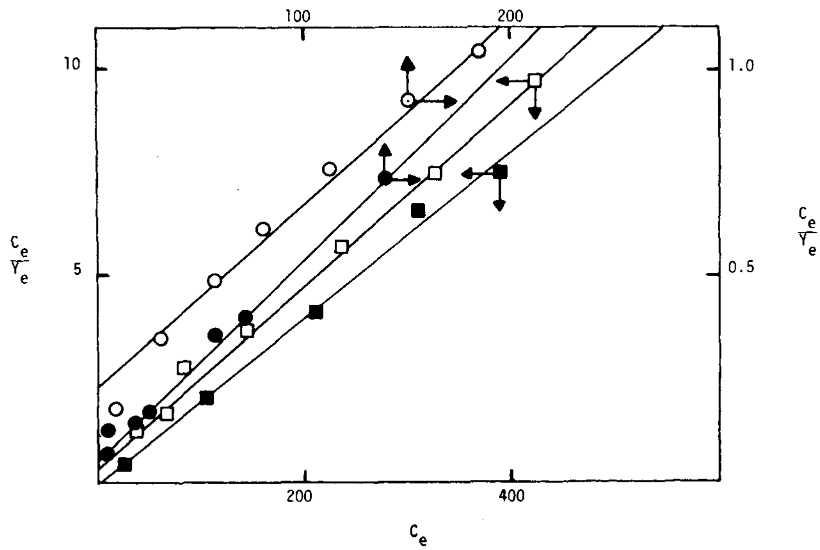


Fig. 6. Langmuir plots for the four dyes on chitin (500–710 μm): (●) Acid Blue 25, (○) Acid Blue 158, (■) Mordant Yellow 5, (□) Direct Red 84, $T = 20°C$.

$$1/Y_e = 1/QbC_e + 1/Q \tag{2}$$

A plot of $1/Y_e$ vs. C_e yields Q and b.

$$C_e/Y_e = 1/Q_b + C_e/Q \tag{3}$$

A plot of C_e/Y_e vs. C_e yields Q and b. Figures 6 and 7 show plots of eq. (3) and Table II lists the isotherm constants for the four dyes using various adsorbent particle size ranges and various temperatures.

In eq. (1) Q represents the monolayer coverage of the adsorbent particle in terms of mg dye/g chitin and is related to the Langmuir equilibrium constant, K_L, by eq. (4):

$$K_L = Qb \tag{4}$$

and the form of eq. (1) thus becomes:

$$Y_e = \frac{K_L C_e}{1 + (K_L/Q \cdot C_e)} \tag{5}$$

The equilibrium constant, K_L, may be used to determine the enthalpy of adsorption, ΔH, using the Clausius–Clapeyron equation.

$$K_L = A \exp(-\Delta H/RT) \tag{6}$$

Figure 8 shows a plot of log K_L vs. $1/T°K$ for a chitin particle size range of 500–710 μm, and the enthalpies of adsorption for Acid Blue 25, Acid Blue 158, Mordant Yellow 5, and Direct Red 84 are −19.1, −19.9, −23.8, and an apparent value of +55.5 kJ/mol respectively. The negative values indicate that heat is liberated during the adsorption process and a positive value that heat is ab-

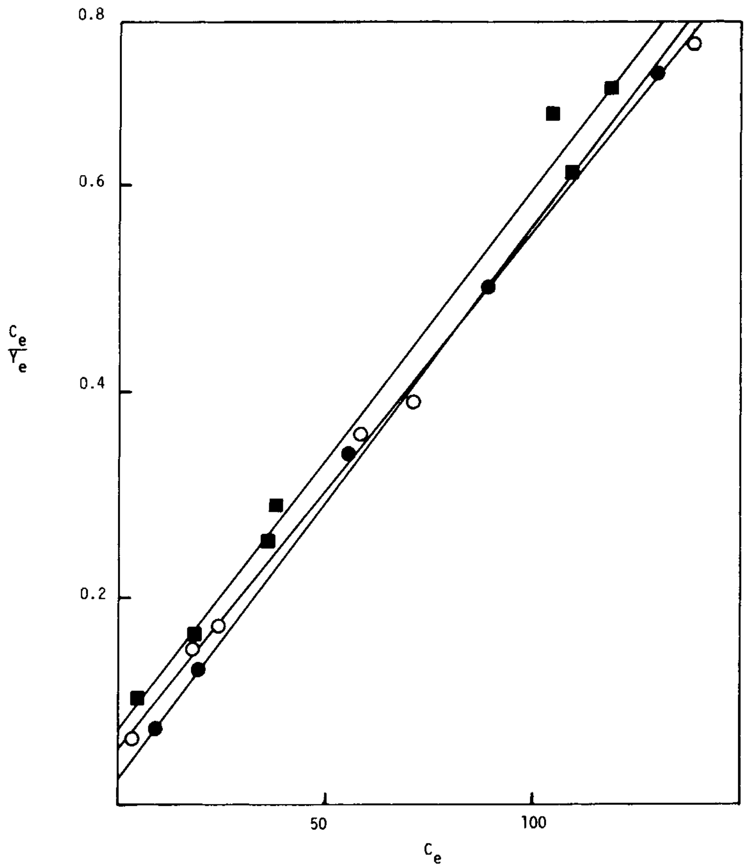


Fig. 7. Effect of particle size on Langmuir isotherms for adsorption of Acid Blue 25 on chitin: (■) 250–355 μm, (●) 500–710 μm, (○) 1.10–1.18 μm.

stracted from the surroundings. However, the high positive value obtained for Direct Red 84 may be largely influenced by the geometric factors, discussed previously, enabling chitin to adsorb more dye.

Freundlich Isotherm

The Freundlich equation[31] is used for heterogeneous surface energies in which the energy term, Q, in the Langmuir equation varies as a function of the surface coverage, Y_e, strictly due to variations in the heat of adsorption. The Freundlich equation has the general form,

$$Y_e = PC_e^{1/n} \tag{7}$$

A logarithmic plot linearizes eq. (5).

$$\log Y_e = \log P + (1/n) \log C_e \tag{8}$$

Figures 9 and 10 show typical Freundlich plots and the constants P and n are

TABLE II
Langmuir Constants from Eqs. (1) and (5)

Dye	Particle diameter (μm)	Temp (°C)	Langmuir K_L (dm^3/g)	Constants Q (mg/g)	b (dm^3/mg)
AB 25	302	20	14.3	188	0.076
	605	20	22.8	186	0.123
	925	20	28.6	200	0.143
	605	30	18.9	204	0.092
	605	40	11.1	220	0.050
	605	60	9.1	260	0.035
	605	80	0.89	287	0.003
AB 158	302	20	5.71	222	0.026
	605	20	5.6	226	0.024
	925	20	4.17	217	0.019
	605	30	4.76	208	0.023
	605	40	4.76	185	0.026
	605	60	5.00	143	0.035
	605	80	1.82	106	0.017
MY 5	302	20	8.00	61	0.132
	605	20	16.7	51	0.328
	925	20	10.0	66	0.151
	605	30	50.0	39	1.29
	605	40	10.0	35	0.283
	605	60	5.0	38	0.132
DR 84	302	20	1.25	60	0.021
	605	20	3.03	46	0.068
	925	20	0.50	42	0.012
	605	30	1.74	72	0.024
	605	40	7.14	121	0.059

listed in Table III. Data for the adsorption of Mordant Yellow 5 could not be correlated by the Freundlich isotherm very accurately.

The magnitude of the exponent n gives an indication of the favorability and capacity of the adsorbent/adsorbate system. Values of $n > 1$ represent favorable adsorption conditions according to Treybal.[32] In all cases the exponent is $1 < n < 10$ showing beneficial adsorption.

General Isotherm

A general isotherm incorporating the features of the Langmuir and Freundlich expressions has been postulated by Weber and Matthews[33] and is represented by the following equation:

$$Y_e = iC_e/[1 + j(C_e)^m] \tag{9}$$

For practical design purposes in a system operating over a wide range of conditions an "intermediate" isotherm is often a more realistic representation of the system.

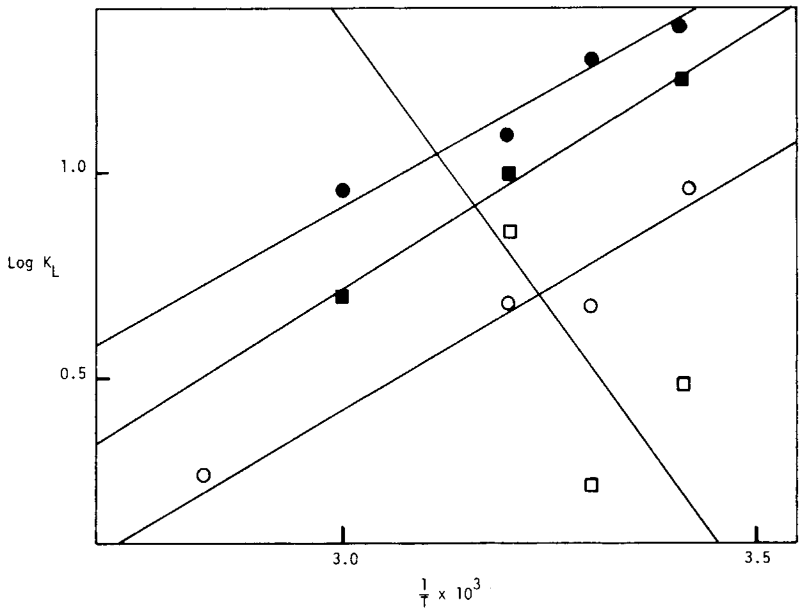


Fig. 8. Log K_L vs. reciprocal temperature: (●) Acid Blue 25, (○) Acid Blue 158, (■) Mordant Yellow 5, (□) Direct Red 84.

Figures 6 and 9 show that the adsorption data agree very well with the Langmuir isotherm and fairly well with the Freundlich but over the whole concentration range variations are observed. The adsorption of Acid Blue 25 is considered in Figure 11 comparing experimental plots with three theoretical iso-

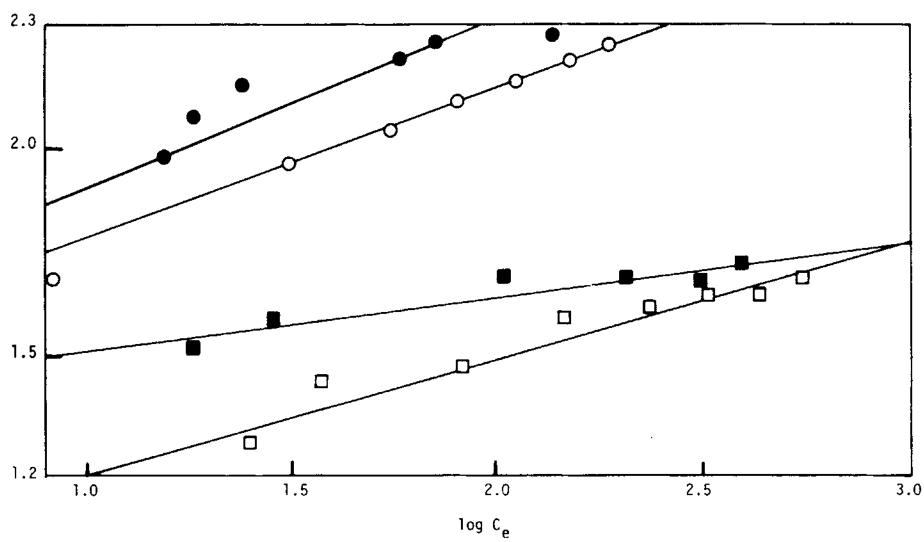


Fig. 9. Freundlich analysis for the adsorption of four dyes on chitin (500–710 μm): (●) Acid Blue 25, (○) Acid Blue 158, (■) Mordant Yellow 5, (□) Direct Red 84.

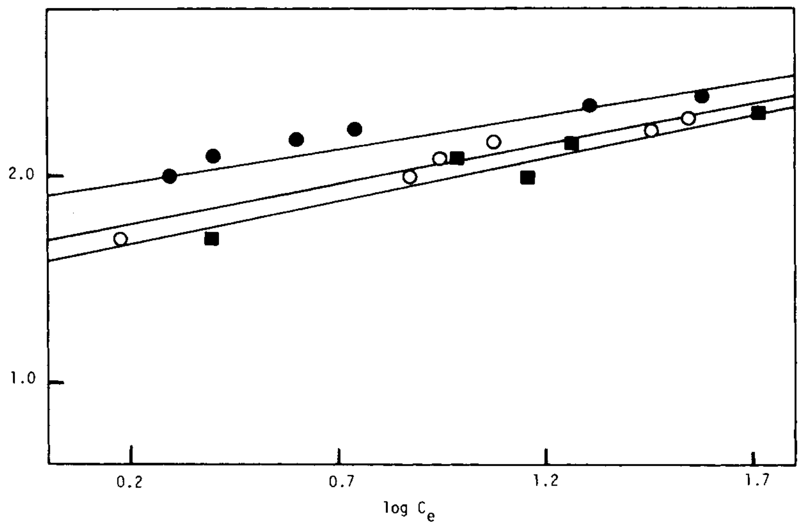


Fig. 10. Effect of particle size on the Freundlich isotherm for the adsorption of Acid Blue 25 on chitin: (●) 150–250 μm, (○) 500–710 μm, (■) 250–355 μm.

therms. The weaknesses of the Langmuir and Freundlich isotherms are highlighted approaching and at monolayer coverage; the composite isotherm is in good agreement with experimental points at high concentrations.

Other types of isotherm expressions are given by Perry.[34]

Effect of Isotherm Shape

The effect of isotherm shape has been considered by Weber and Chakravorti[35] with a view to predicting if an adsorption system is "favorable" or "unfavorable." The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor "r" which is defined by the following relationship given by Hall et al.[36]:

$$r = 1/(1 + bC_0) \tag{10}$$

The parameter indicates the isotherm shape according to Table IV.

These values of r are represented graphically in Figure 12 on a dimensionless or fractional scale. The relationship between the parameters and the Langmuir isotherm are outlined.

$$q = x/[r(1 - x) + x] \tag{11}$$

or

$$r = x(1 - q)/q(1 - x) \tag{12}$$

where

$$x = C_e/C_{\text{ref}} \tag{13}$$

TABLE III
Freundlich Constants from Eq. (7)

Dye	Particle diameter (μm)	Temp (°C)	Freundlich constants [P mg (mg dm^{-3})$^{1/n}$/g]	n
AB 25	302	20	24.0	2.24
	605	20	31.6	2.44
	925	20	57.5	5.00
	605	30	49.8	3.44
	605	40	52.5	3.81
	605	60	17.2	2.26
	605	80	23.4	3.81
AB 158	302	20	24.3	2.56
	605	20	24.8	2.71
	925	20	27.4	2.80
	605	30	28.2	2.87
	605	40	28.3	3.06
	605	60	33.3	4.06
	605	80	21.4	4.00
MY 5	302	20	45.2	150.00
	605	20	32.0	10.0
	925	20	—	—
	605	30	—	—
	605	40	—	—
	605	60	—	—
DR 84	302	20	28.2	2.90
	605	20	39.8	3.60
	925	20	15.2	4.80
	605	30	12.6	2.32
	605	40	28.5	3.95

and

$$q = Y_e/Y_{\text{ref}} \tag{14}$$

For single-solute adsorption, C_{ref}, is usually the highest fluid-phase concentration encountered and Y_{ref} is the equilibrium solid-phase concentration coexisting with C_{ref}. Substituting eqs. (13) and (14) into eq. (12) yields,

$$r = C_e(Y_{\text{ref}} - Y_e)/Y_e(C_{\text{ref}} - C_e) \tag{15}$$

Substituting for Y_e from eq. (3):

$$r = \left[\frac{C_e}{Y_e}\right]\left[\frac{Y_{\text{ref}} - Q_bC_e/(1 + bC_e)}{C_{\text{ref}} - C_e}\right] \tag{16}$$

$$r = [1 + bC_e]\left[\frac{C_{\text{ref}}/(1 + bC_{\text{ref}}) - C_e/(1 + bC_e)}{C_{\text{ref}} - C_e}\right] \tag{17}$$

$$r = \left[\frac{1}{1 + bC_{\text{ref}}}\right]\left[\frac{C_{\text{ref}}(1 + bC_e) - C_e(1 + bC_{\text{ref}})}{C_{\text{ref}} - C_e}\right] \tag{18}$$

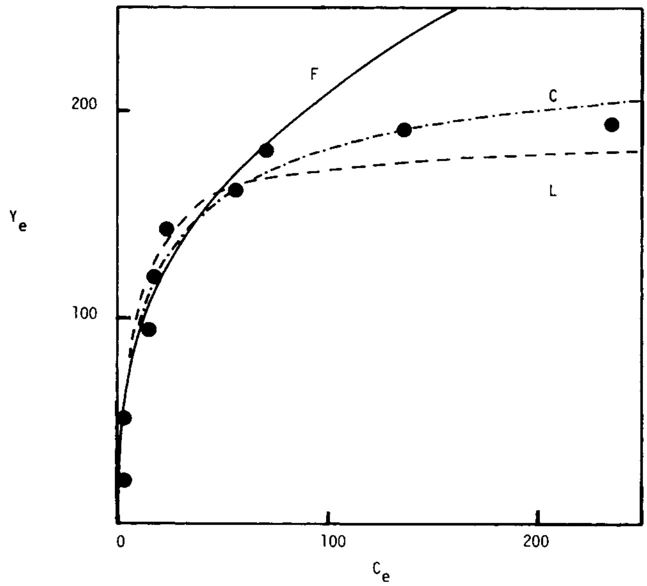


Fig. 11. Comparison of theoretical isotherms with experimental data for Acid Blue 25 on chitin (500–710 μm) at 20°C: F = Freundlich, $Y_e = 32C_e^{0.41}$; L = Langmuir, $Y_e = 23C_e/(1 + 0.12C_e)$; C = Composite, $Y_e = 20C_e/(1 + 0.16C_e^{0.90})$.

$$r = \left[\frac{1}{1 + bC_{\text{ref}}}\right] \tag{19}$$

Since C_{ref} is the highest fluid-phase concentration encountered, i.e., $C_{\text{ref}} \equiv C_0$, then eq. (19) is the same as eq. (10).

CONCLUSION

The ability to chitin to adsorb four dyestuffs has been studied. The adsorption capacities at 20°C of the dyes were 186, 222, 51, and 46 mg/g chitin (500–710 μm) for Acid Blue 25, Acid Blue 158, Mordant Yellow 5, and Direct Red 84, respectively. Langmuir and Freundlich isotherms could be correlated to the data over limited concentration ranges although a composite equation provided the best data fit as given by eq. (9). All isotherms were shown to be "favorable" and the

TABLE IV
Effect of Separation Factor on Isotherm Shape

Separation Factor "r"	Type of isotherm
$r > 1$	Unfavorable
$r = 1$	Linear
$0 < r < 1$	Favorable
$r = 0$	Irreversible

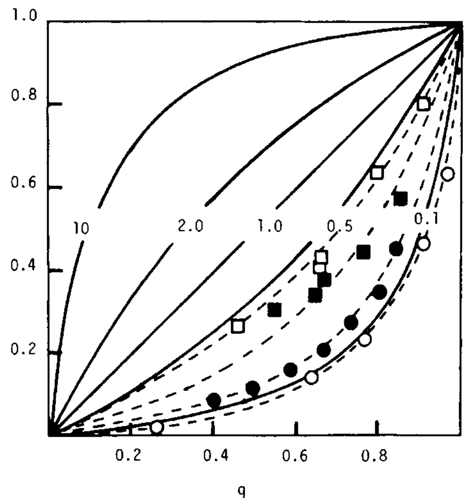


Fig. 12. Dimensionless concentration isotherms as functions of the separation factor, on linear coordinates: (○) Acid Blue 158, (●) Acid Blue 25, (■) Mordant Yellow 5, (□) Direct Red 84.

effect of chitin particle size was significant only for Direct Red 84. The influence of temperature was studied and enthalpies of adsorption were determined.

NOMENCLATURE

A	pre-exponential factor in Clausius–Clapeyron equation
b	constant related to the energy of adsorption (dm^{-3}/g)
C_e	dye concentration in solution at equilibrium ($mg\ dm^{-3}$)
C_0	initial dye concentration in solution ($mg\ dm^{-3}$)
C_{ref}	maximum fluid-phase dye concentration ($mg\ dm^{-3}$)
ΔH	enthalpy of adsorption (kJ/mol)
i	isotherm constant in eq. (7)
j	isotherm constant in eq. (7)
m	isotherm constant in eq. (7)
n	adsorption intensity
P	measure of adsorption capacity [$mg\ (mg\ dm^{-3})^{1/n}/g$]
q	dimensionless solid-phase concentration at equilibrium
Q	dye concentration on chitin at monolayer coverage (mg/g)
r	dimensionless constant separation factor
x	dimensionless liquid-phase concentration at equilibrium
Y_e	dye concentration on chitin at equilibrium (mg/g)
Y_{ref}	maximum solid-phase dye concentration (mg/g)

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