Adsorption of Dyestuffs onto Chitin. External Mass Transfer Processes

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Synopsis

The effect of several variables on the adsorption rate of four dyestuffs onto chitin was studied. A model is proposed enabling the film mass transfer coefficients to be determined. The coefficients were independent of initial dye concentration, chitin mass, chitin particle size, and temperature; a slight dependence with agitation was obtained. The film mass transfer coefficients at 400 rpm were 2.8×10^{-3}, 2.9×10^{-3}, 3.9×10^{-3}, and 0.9×10^{-3} cm/s for Acid Blue 25, Acid Blue 158, Mordant Yellow 5, and Direct Red 85, respectively.

INTRODUCTION

The equilibrium isotherms for the adsorption of certain dyes on chitin have been reported in part I of this article,[1] and the data are useful in predicting the capacity of dye adsorption systems using chitin. The aim of the present contribution is to study the kinetics of the adsorption of dyes onto chitin.

The kinetics of adsorption processes are concerned with force fields between sites and molecules (atoms, ions, etc.) and form an important area of surface chemistry. The effective rate of adsorption is determined by one or more of several steps. Individual steps in the "transport mechanism" can be classified into the following groups: (a) the degree of mixing produced by the contacting equipment; (b) mass transfer from the bulk liquid phase to the external surfaces of the chitin particles; (c) reaction at the phase boundaries, although this process is usually considered as very fast and neglected in the resistance steps; (d) pore diffusion in the fluid phase, within the particles; and (e) diffusion in the adsorbed state, usually designated as particle phase diffusion, intraparticle diffusion, or homogeneous solid phase diffusion.

In general, systems with high total solute concentrations are more likely to have their mass transfer rates controlled by particle phase diffusion (e), and systems with low fluid phase concentrations are more likely to be controlled by fluid side effects (a, b, and c). Mechanism b, c, d and b, c, e occur in series; and in some systems, the two mechanisms both occur in parallel, and the slower of the two is rate controlling.

The modeling of two resistance adsorption processes to obtain design data is complex, and consequently the aim of the present report is to study the fluid phase mass transfer processes for the adsorption of dyes onto chitin.

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EXPERIMENTAL

Details of the materials and techniques used were given in Part I. Certain design details of the batch adsorber used in the kinetic studies have been reported previously.[2]

Chitin from a crabshell source was used (supplied by Sigma Co. Ltd.), and the four dyestuffs used were C.I. Acid Blue 25 (Telon Blue ANL supplied by Bayer), C.I. Acid Blue 158 (premetallized Neolan Blue 2G supplied by Ciba-Geigy), C.I. Mordant Yellow 5 (Eriochrome Flavine supplied by Ciba-Geigy) and C.I. Direct Red 84 (Solophenyl Brown 3RL supplied by Ciba-Geigy). Dye solution concentrations were made by absorption spectrophotometry at the wavelength corresponding to maximum absorbance.

The chitin particle size ranges used were 150–250, 250–355, 355–500, 500–710, 710–850, 850–1000, and 1000–1180 μm.

The batch adsorber vessel was a baffled 2-L beaker, and the volume of dye used in each run was 1.7 L. Constant and uniform agitation was achieved using a Heidolph motor and a six-bladed (flat) stainless steel impellor.

THEORY

The transport rate for dyes between the bulk of the liquid phase and the outer surface of the chitin particles is governed by the molecular or ionic diffusivity and also, in turbulent flow, by the eddy diffusivity which controls the effective thickness of the boundary layer.

The rate of mass transfer for dye involves the driving potential between the bulk fluid and particle surface:

$$\frac{dq}{dt} = k_f a_p (C_t - C_{e,t}) \tag{1}$$

In a well-agitated batch adsorber, mixing in the liquid phase is rapid and the concentrations of dye and chitin particles in the liquid will be uniform throughout the vessel. Consequently, the change in C with respect to time is given by

$$\frac{dC_t}{dt} = -k_f a_p (C_t - C_s) \tag{2}$$

$$C_t = C_0 \qquad \text{at } t = 0 \tag{3}$$

If effective diffusion coefficients are neglected, then, since C_s approaches zero and C_t approaches C_0, as $t \to 0$, eq. (2) becomes

$$\left[\frac{d\left(\frac{C_t}{C_0}\right)}{dt} \right]_{t=0} = -k_f a_p \tag{4}$$

The external surface area a_p has been evaluated by various investigators using eqs. (5)[3,4] and (6)[5,6]:

$$a_p = \frac{6m}{d_p \rho_t (1 - \epsilon)} \tag{5}$$

$$a_p = \frac{4\pi R^2}{V_p} \tag{6}$$

Consequently, k_f can be obtained from slopes of C_t/C_0 vs. t although the uncertainty in evaluating the slope at $t = 0$ is somewhat erroneous.

By assuming the surface concentration is negligible and by using a first-order rate equation, eq. (7), it is possible to obtain mass transfer coefficients:

$$\frac{dC_t}{dt} = -k_f \frac{6m}{d_p \rho_t (1 - \epsilon)} C_t \tag{7}$$

Integrating from $(0, C_0)$ to (t, C_t), an equation for k_f is obtained:

$$k_f = \frac{d_p \rho_t (1 - \epsilon)}{6m} \frac{\ln\left(\frac{C_0}{C_t}\right)}{t} \tag{8}$$

Equations (4), (7), and (8) can be used for obtaining k_f but strictly valid for time $t = 0$. The equations do not take into account effective diffusion and isotherm shape.

The differential mass balance of dye within the chitin is, assuming a constant total, the effective intraparticle diffusivity D, given by eq. (9):

$$D\left(\frac{\partial C_r^2}{\partial r^2} + \frac{2}{r} \frac{\partial C_r}{\partial r}\right) - \rho_t \frac{\partial q_r}{\partial t} = \epsilon \frac{\partial C_r}{\partial t} \tag{9}$$

Boundary and initial conditions corresponding to the experimental conditions are given by eqs. (3), (10), (11), and (12):

$$D\left(\frac{\partial C_r}{\partial r}\right)_{r=R} = k_f(C_t - C_s) \tag{10}$$

$$\frac{\partial C_r}{\partial r} = 0 \qquad \text{at } r = 0 \tag{11}$$

$$C_r = 0 \qquad \text{at } t = 0 \text{ for } 0 < r < R \tag{12}$$

Since equilibrium is assumed for adsorption at an interior site, n_r and C_r are related by the instantaneous equilibrium expression

$$\frac{\partial q_r}{\partial t} = \frac{\partial}{\partial C_r}\left(\frac{KC_r}{1 + aC_r}\right) \frac{\partial C_r}{\partial t} \tag{13}$$

When intraparticle diffusion is negligible and when the isotherm is linear, an analytical solution for C_t vs. t is possible given by eq. (14):

$$\frac{C_t}{C_0} = \frac{1}{1 + mK} + \frac{mK}{1 + mK} \exp\left(-\frac{1 + mK}{mK} k_f a_p t\right) \tag{14}$$

The mathematical solution for eq. (14) was derived previously.[7] As $t \to \infty$, external mass transfer will predominate and the assumption discussed will be valid. Consequently, a plot of

$$\ln\left(\frac{C_t}{C_0} - \frac{1}{1 + mK}\right)$$

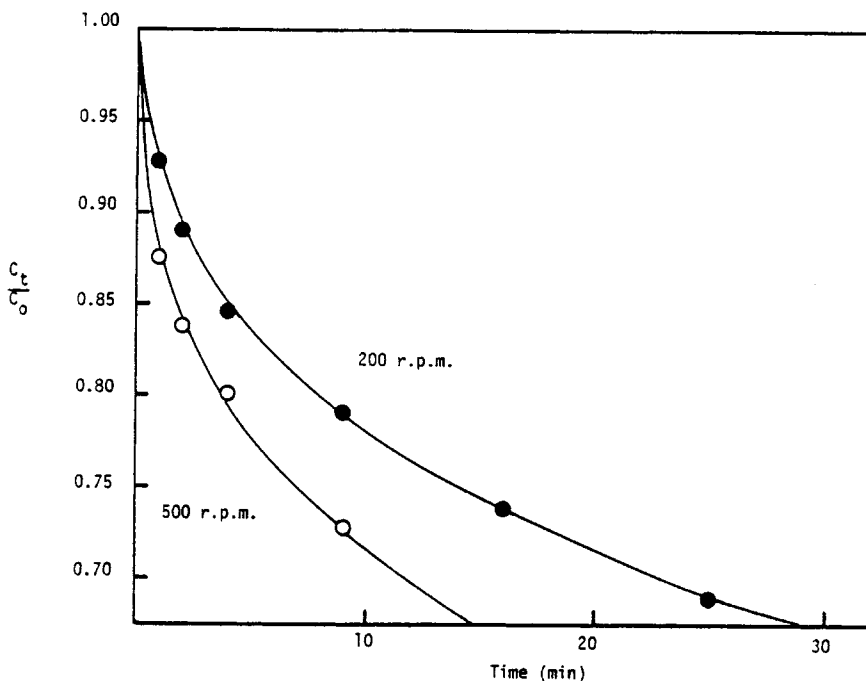Fig. 1. Effect of agitation on the adsorption of Mordant Yellow 5 on chitin.

vs. t will yield a straight line as $t \to 0$ of intercept $\ln [mK/(1 + mK)]$ and slope $[(1 + mK)/mK] \times k_f a_p$ at $t = 0$, from which the external mass transfer coefficient k_f can be obtained.

DISCUSSION

General

The film mass transfer coefficient can be determined from eqs. (4), (7), and (14), and all methods were tested and the results generally agreed within a factor of 2. Equations (4) and (7), however, are dependent on drawing slopes at $t = 0$ on the concentration-vs.-time decay curves. Since the initial slopes of many of these curves are very steep, there is considerable error in estimating these gradients.

Similar values for k_f using the various techniques are expected since rearrangement of eq. (8) indicates C_t/C_0 is dependent on $\exp(-k_f a_p t)$, and eq. (14) shows that C_t/C_0 depends on $\exp(-1 + mK/mK \, k_f a_p t)$. In the case of all four dyestuffs, the value $(1 + mK/mK \approx 1$.

Since the initial slopes of the plots using eq. (14) are less steep than the gradients based on plots of eqs. (4) and (7), the results reported in the discussion are based on eq. (14); and, to be consistent, gradients were fitted to the points at $t = 0$ and $t = 30$ s.

The major controlling factor in external mass transfer is the thickness of the boundary layer. All experiments were undertaken at high agitation rates to achieve completely mixed systems (usually 400 rpm), i.e., 200–500 rpm. Con-
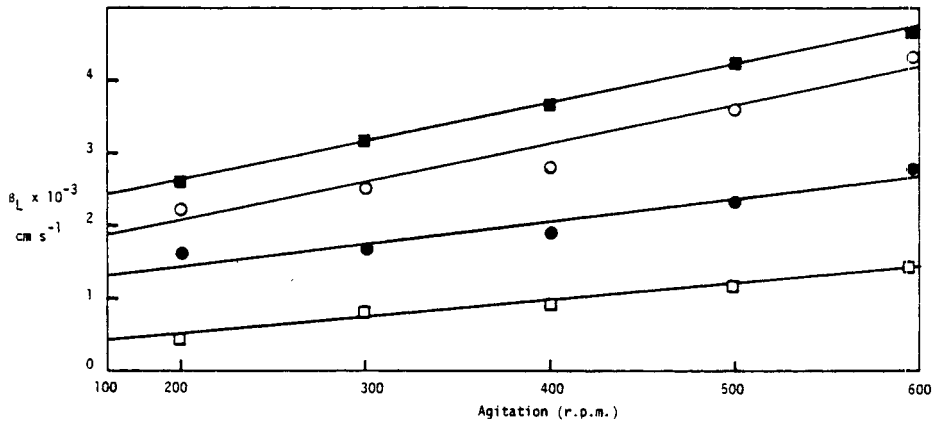
Fig. 2. Effect of agitation on the film mass transfer coefficient: ($\bullet$) Acid Blue 25; ($\circ$) Acid Blue 158; ($\blacksquare$) Mordant Yellow 5; ($\square$) Direct Red 84.

sequently, there is a considerable shear force on the boundary layer making this initial resistance to mass transfer fairly low, and therefore the intrinsic absorption rate is very rapid until there is an external surface coverage of dye on the chitin particle.

Effect of Agitation

The influence of agitation is shown in Figure 1 for the adsorption of Mordant Yellow 5 onto chitin at two agitation speeds, namely, 200 and 500 rpm. The results are plotted according to eq. (14); and from the initial gradients, i.e., $t \rightarrow 0$, the film mass transfer coefficients k_f are determined.
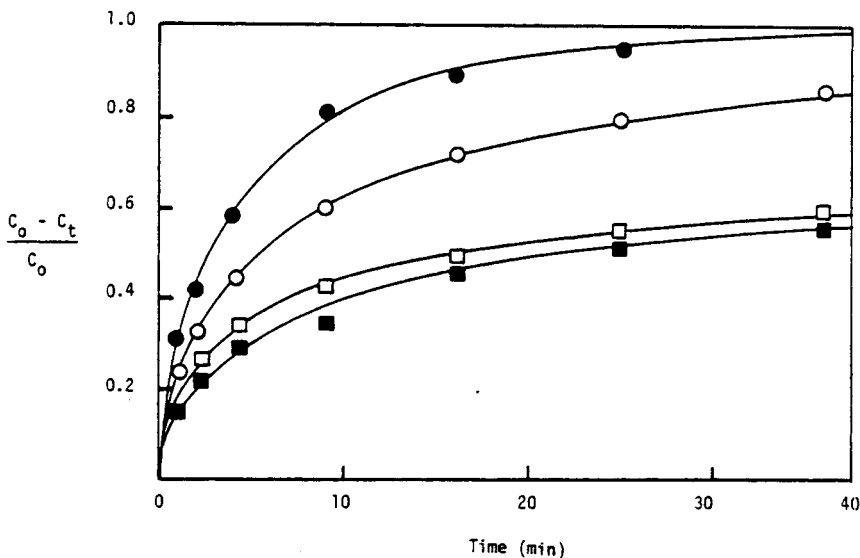
Fig. 3. Plot of $(C_0 - C_t)/C_0$ vs. time for the adsorption of Mordant Yellow 5 on chitin: ($\bullet$) C_0 = 100 mg/dm^3; ($\circ$) C_0 = 150 mg/dm^3; ($\square$) C_0 = 200 mg/dm^3; ($\blacksquare$) C_0 = 250 mg/dm^3. d_p = 605 μm; 400 rpm; 20°C; M = 2.94 g/dm^3; V = 1.7 dm^3.
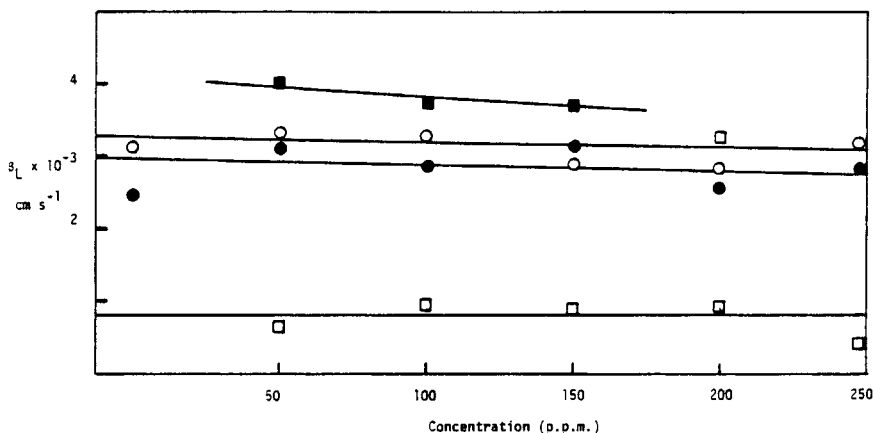
Fig. 4. Effect of initial dye concentration on the film mass transfer coefficient. Symbols as in Fig. 2.

The mass transfer coefficients were obtained for several agitation speeds and using four dyestuffs. Figure 2 shows a plot of k_f against agitation speed; and although the variation is only small, there is a gradual increase in k_f with agitation. Consequently, the effect of agitation is to lower the boundary layer thickness or resistance surrounding the chitin particle. The variation in k_f with agitation might have been more significant if very low agitation speeds had been used, for instance, rpm < 50, when the chitin particles were not completely mixed within the system. However, complete mixing was achieved in all studies due to the low chitin density of 475 kg/m^3 and all agitation rates being 150 rpm and greater.

Effect of Initial Dye Concentration

Several experiments were undertaken to study the effect of varying the initial dye concentration on the rate dye removal from solution. Figure 3 shows the

TABLE I
Chitin Specific Surfaces a_p

Size Range, μ	Mean diameter d_p, cm	Chitin mass, g/1.7 dm^3	Specific surface a_p, eq. (5), cm^{-1}
500–710	0.0605	0.4	0.0866
500–710	0.0605	0.7	0.152
500–710	0.0605	1.0	0.216
500–710	0.0605	1.2	0.259
500–710	0.0605	1.5	0.325
500–710	0.0605	2.5	0.541
500–710	0.0605	5.0	1.08
500–710	0.0605	7.5	1.62
250–355	0.0302	1.0	0.433
355–500	0.0427	1.0	0.306
710–850	0.0780	1.0	0.168
850–1000	0.0925	1.0	0.141

experimental results for the adsorption of Mordant Yellow 5 onto chitin using initial dye concentrations from 100 to 250 mg/dm^3. The difficulty in analyzing such data between 0 and 30 s is highlighted in the figure where no apparent difference in the initial gradients and hence film mass transfer coefficients can be observed.

The results for all four dyestuffs are shown in Figure 4, and k_f appears to be independent of initial dye concentration. The conclusion is not unexpected, since all parameters in the system that affect mixing power number and energy dissipation[3] rate in the system are constant. The mean film mass coefficients for Acid Blue 25, Acid Blue 158, Mordant Yellow 5, and Direct Red 84 are 2.9×10^{-3}, 3.2×10^{-3}, 3.8×10^{-3}, and 0.8×10^{-3} cm, respectively.

Effect of Adsorbent Mass

The influence of chitin mass on the adsorption rate was studied using the masses listed in Table I. Constant conditions were used throughout, namely, the agitation speed was 400 rpm; the initial dye concentration and chitin particle size were maintained constant for each particular dyestuff. The specific surfaces for various chitin masses are given in Table I. The plots of eq. (14) are shown in Figure 5 for the adsorption of Acid Blue 158 on chitin. Due to the different masses, the intercepts vary according to the value of $\ln [mK/(1 + mK)]$.

The film mass transfer coefficients were determined and plotted against chitin mass in Figure 6 for the four dyestuffs. The k_f values are virtually independent of mass and are constant for each dyestuff. In the mathematical analysis, it was assumed that the chitin particles were spherical; consequently, varying mass, and hence a_p, tested this assumption; and the fact that the k_f values are constant indicates that this approximation is reasonable. The film mass transfer coefficients for Acid Blue 25, Acid Blue 158, Mordant Yellow 5, and Direct Red 84 are 2.8×10^{-3}, 2.4×10^{-3}, 3.7×10^{-3}, and 0.9×10^{-3} cm/s, respectively.
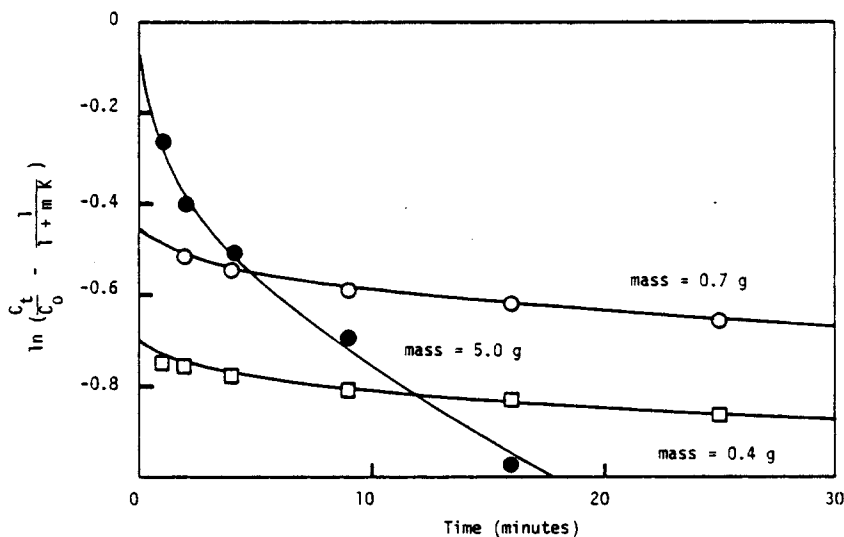

Fig. 5. Plot of $\ln (C_t/C_0 - 1/1 + mK)$ vs. time for the absorption of Acid Blue 158 on chitin: d_p = 605 μm; T = 20°C; V = 1.7 dm^3; C_0 = 200 mg/dm^3; 400 rpm.
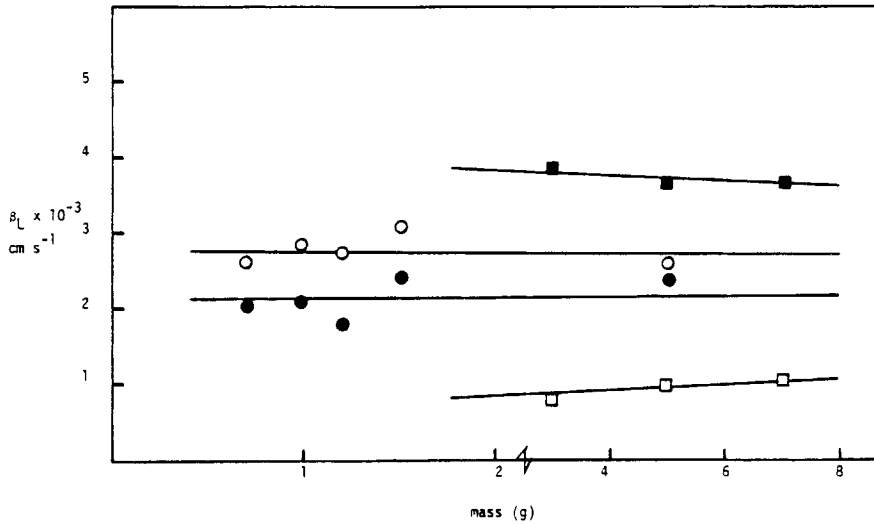
Fig. 6. Effect of chitin mass on the film mass transfer coefficient. Symbols as in Fig. 2.

Effect of Particle Size

The influence of particle size on chitin was studied using the particle size ranges listed in Table I with the appropriate specific surfaces. Since the Langmuir constants K, reported previously,[1] sometimes showed a variation with d_p, the relevant equilibrium constant was used. Figure 7 shows the plot of eq. (14) for the adsorption of Acid Blue 25 onto chitin.

The film mass transfer coefficients were determined as before and are shown in Figure 8 as a function of d_p for all four dyestuffs. In the case of Mordant
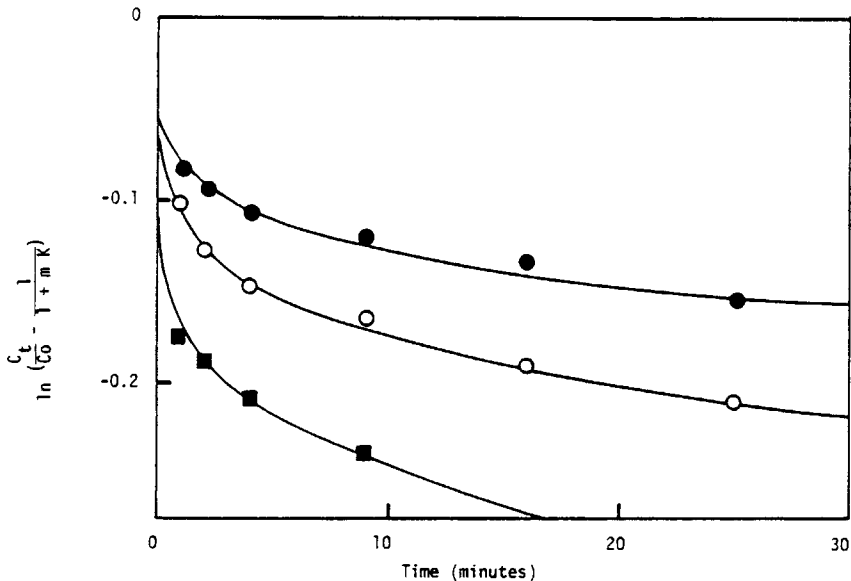

Fig. 7. Plot of $\ln (C_t/C_0 - 1/1 + mK)$ vs. time for the adsorption of Acid Blue 25 on chitin: $M = 0.59$ g/dm^3; $T = 20°$C; $V = 1.7$ dm^3; $C_0 = 200$ mg/dm^3; 400 rpm. ($\bullet$) $d_p = 302$ μm; (O) $d_p = 427$ μm; ($\blacksquare$) $d_p = 605$ μm.
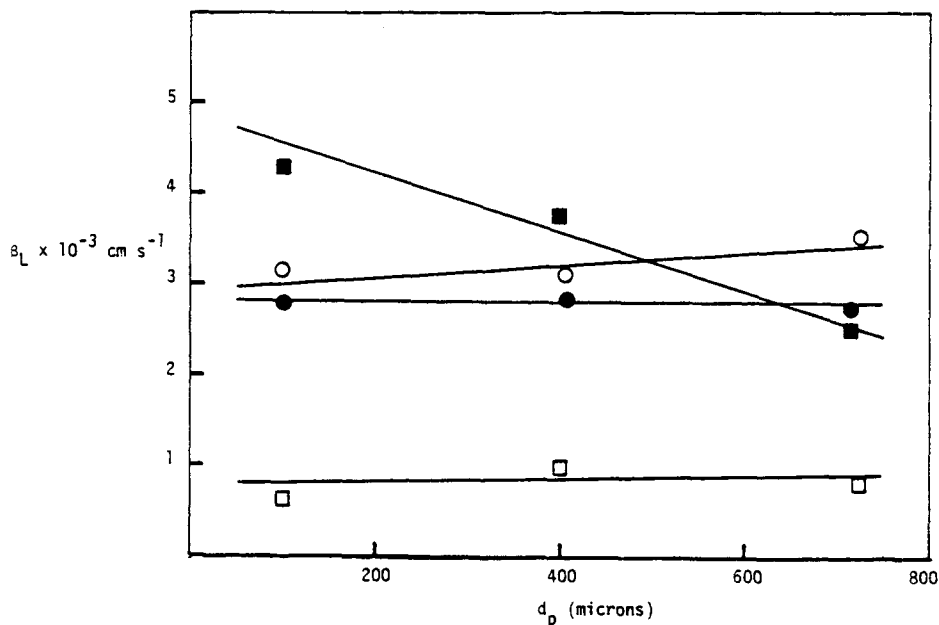
Fig. 8. Effect of chitin particle size on the film mass transfer coefficient. Symbols as in Fig. 2.

Yellow 5, there appears to be a decrease in k_f as d_p increases. However, no such trend is observed for the other three dyestuffs, and the k_f values are relatively constant. It seems likely, therefore, that the k_f values for Mordant Yellow do not vary with d_p. The range of k_f values is 2.6×10^{-3} to 4.3×10^{-3} cm/s, and since a factor of 2 is involved in drawing the initial slopes accurately, it seems reasonable to assume that k_f in all cases is independent of k_p. The mean film mass transfer coefficients for Acid Blue 25, Acid Blue 158, Mordant Yellow 5, and Direct Red 84 are 2.8×10^{-3}, 3.2×10^{-3}, 3.7×10^{-3}, and 0.9×10^{-3} cm/s, respectively.
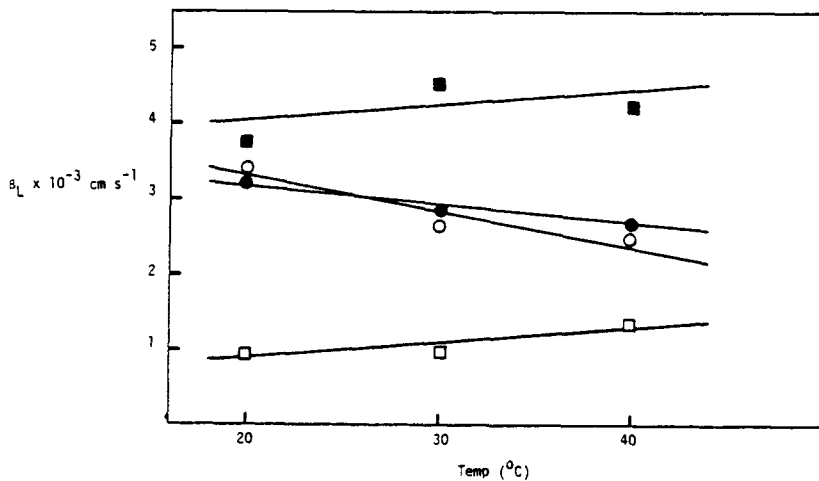

Fig. 9. Effect of temperature on the film mass transfer coefficient. Symbols as in Fig. 2.

By comparing Figures 1, 3, 5, and 7, it can be seen that the plots of eq. (14) are nonlinear. This effect can be due to a number of reasons: (1) the influence of intraparticle diffusion; (2) the assumption of a linear isotherm is invalid; (3) the assumption of particle sphericity is invalid. The latter two reasons are thought to be improbable since the effects of chitin mass and chitin particle size resulted in constant k_f values; and, furthermore, at the low concentrations, studied in the section dealing with initial dye concentration, the isotherm is approximately linear. Therefore, the nonlinearity of the figures after such short time intervals is due to the rapid onset of intraparticle diffusion, thus producing a two-resistance model. Consequently, the slope of the plots were measured as time tends to zero, when external mass transfer is the predominant mechanism.

Effect of Temperature

The contact times at different temperatures were undertaken using the four dyestuffs and the results analyzed as before. The film mass transfer coefficients were determined and are plotted in Figure 9. There is no obvious trend with temperature; if an Arrhenius dependence had been involved, much greater increases in k_f values would be expected. The differences in k_f values with temperature fall within the error limits of the analytical method. The mean values of k_f for Acid Blue 25, Acid Blue 158, Mordant Yellow 5, and Direct Red 84 are 2.9×10^{-3}, 2.8×10^{-3}, 4.2×10^{-3}, and 1.1×10^{-3} cm/s, respectively. Since the film mass transfer coefficient is independent of temperature indicated that the external adsorption step is not an activated process.

CONCLUSIONS

The external mass transport processes which govern the initial uptake of dyestuffs onto chitin were studied. A model has been considered which enables the film mass transfer coefficients to be determined. Several important design variables were studied, and only agitation had a small effect on the coefficient. The mean film mass transfer coefficients for all runs at 400 rpm are 2.8×10^{-3}, 2.9×10^{-3}, 3.9×10^{-3}, and 0.9×10^{-3} cm/s for Acid Blue 25, Acid Blue 158, Mordant Yellow 5, and Direct Red 84, respectively.

NOMENCLATURE

a_p	specific surface of chitin (cm^{-1})
C_e	concentration in bulk liquid at equilibrium (mg/dm^3)
C_0	concentration in bulk liquid
C_r	concentration in liquid-filled pore at radius r
C_s	concentration in liquid at outer surface of particle
C_t	concentration in liquid at time t
d_p	particle diameter (cm, μm)
K	adsorption equilibrium constant (dm^3/g)
k_f	film mass transfer coefficient (cm/s)
m	mass of chitin particles per dm^3 (g/dm^3)
q	solid-phase dye concentration (mg/g)
r	radial coordinate in chitin particle
R	particle radius (cm)

t time (min, s)
V_p volume of chitin particle (cm^3)
Greek
ϵ porosity of chitin particles
ρ_t density of chitin particles (kg/m^3, g/cm^3)

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