Adsorption of Direct Dyes on Cotton: Kinetics of Dyeing from Finite Baths Based on New Information

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ABSTRACT

Adsorption time curves were determined for cotton fabric dyed with direct dyes under different conditions. A new simple method is described for kinetic analysis of adsorption time curves. Adsorption equilibria, specific rate constants, diffusion coefficients, diffusion resistance, steady-state equilibrium constants, adsorbent capacities, finite bath exhaustions, activation energies, and reaction enthalpies were determined from the time curves. Specific rate constants and the diffusion coefficients correlated with the chemical structures of direct dyes (number of aromatic rings and ionizable sulfo groups).

Dyeing kinetics is directly related to diffusion. Diffusion rates in simple geometric shapes can be obtained for a variety of initial and boundary conditions from Fick's differential equation in the form of trigonometric, error, or Bessel series [5–9]. It is difficult to describe the diffusion rates in more complex, irregular, or porous structures, because the shape and size cannot be defined with confidence. Additionally, even in simple geometric shapes, calculating the diffusion rates from these infinite series is laborious because the individual members of the series often converge to zero slowly.

We have found from experiments with different dyes and dyed materials, especially by dyeing from finite baths, that dyeing rates can be accurately expressed by exponential converging binomial series. We applied similar equations for diffusion-limited enzyme reactions, adsorption on proteins, and other diffusion-limited systems [1–4]. For diffusion-limited adsorption on textile materials, the equation can be written in the form

$$a = a_e[1 - \exp(-kA_o t)]^n \quad , \qquad (1)$$

where a is the adsorption in time t, a_e is the equilibrium adsorption (at $t \to \infty$), A_o is the concentration of an adsorbent, k is the specific rate constant, and n is the heterogeneous structural diffusion resistance constant $(0 < n < 1)$.

In this study, we have tried to describe the time kinetics of dyeing cotton fabrics with typical direct dyes from finite baths under different conditions. For this purpose, we determined the constants of Equation 1 for selected dyes and compared them with experimental results.

Experimental

All chemicals and dyes were analytical grade or the highest purity grade available from Aldrich Chem. Co., Milwaukee, WI. The fabric was a desized, scoured and bleached all-cotton mercerized printcloth, weighing approximately 3.5 oz/yd^2, obtained from Testfabrics, Inc., Middlesex, NJ.

The untreated cotton print cloth was cut into pieces approximately 0.5 cm^2 and dyed in a beaker with 50 ml dye solution containing 10 g/l NaCl at pH 8. Solutions of the dyes were prepared from commercial dyes, which were corrected for the dye content shown by the manufacturer. The temperature was kept constant with a water bath. The dye solutions and cotton were mixed slowly by a magnetic stirrer. After selected time intervals, 0.2 ml of the supernatant was pipetted in 2.8 ml distilled water in the test tubes. Absorbance was measured on a Shimadzu 260 double beam spectrophotometer. Direct yellow 29 was read at 402 nm, Direct yellow 50 at 390 nm, Direct violet 51 at 549 nm, Direct orange 31 at 428 nm, Direct red 81 at 508 nm, Direct red 75 at 522 nm, Direct red 23 at 507 nm, and Direct blue 71 at 594 nm.

Results and Discussion

Constant n in Equation 1 characterizes the overall heterogeneous diffusion structure of the adsorbent. When diffusion resistance is small, $n = 1$ and the reaction is of the first order. In systems strongly limited by diffusion resistance, n is small. Changes in adsorbent structure resulted in changes in n (not shown here). Constant n was independent of the dye concentration

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d_o, adsorbent concentration A_o, adsorption equilibrium a_e, and temperature T.

The specific rate constants k depended on diffusion coefficients and adsorption capacity of the adsorbent, but were independent of adsorbent concentration A_o. With low initial concentrations of the dyes, k depended on d_o by the initial velocity kinetics [3] ($k = [V_{\max} d_o / a_e(d_o + Km)]^{-1/n}/A_o$), but with higher initial concentrations of the dyes, it remained practically independent of d_o. In the mixtures, k depended on both competitive and noncompetitive interactions [3].

The equilibrium adsorption a_e depended on interactions between the diffusing dye, diffusion medium (solvent), and adsorbent. Additionally, a_e depended on d_o and A_o. From the mass action law in a finite bath we can write

$$k_1(d_o - a_e)(\beta A_o - a_e) \rightleftarrows k_2 a_e \quad , \tag{2}$$

where β is the maximum adsorption capacity of the adsorbent, and $k_2/k_1 = K_a$. From Equation 2 we get

$$a_e = [(K_a + \beta A_o + d_o) - \sqrt{(K_a + \beta A_o + d_o)^2 - 4\beta A_o d_o}]/2 \quad . \tag{3}$$

Both k and a_e depended on temperature using the Arrhenius equation:

$$k = \exp(-\Delta E^*/RT + e) \tag{4}$$

and

$$a_e = \exp(-\Delta H/RT + h) \quad , \tag{5}$$

where T is the absolute temperature, R is the gas constant, ΔE^* is the activation energy, and ΔH is the reaction heat.

Both constants k and n in Equation 1 were determined by regression analysis of the time curves [2]. It was also easy to determine the constants graphically from the log-log plots [3] (Figure 1).

The cotton fabric dyeing capacities β (maximum dye adsorption) and the adsorption steady-state equilibrium constants K_a were calculated from two or more time curves with two or more d_o and A_o concentrations using regression equations:

$$\beta = \frac{\sum a_e(d_o - a_e) \sum a_e A_o(d_o - a_e) - \sum a_e \sum a_e A_o(d_o - a_e)}{\sum A_o(d_o - a_e) \sum a_e A_o(d_o - a_e) - \sum a_e \sum A_o^2(d_o - a_e)^2} \tag{6}$$

and

$$K_a = \frac{\beta \sum A_o(d_o - a_e) - \sum a_e(d_o - a_e)}{\sum a_e} \quad . \tag{7}$$

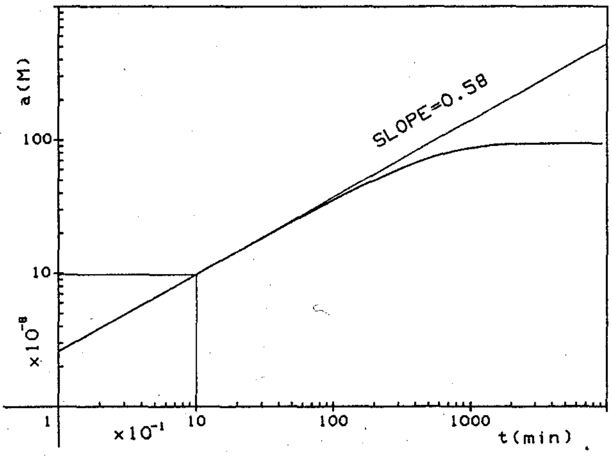

FIGURE 1. Example of the graphical determination of constants in Equation 1 from the time curve. The equilibrium a_e is 9.4×10^{-7} M, the diffusion resistance constant n (slope) is 0.58, and the rate constant from the intercept at $t = 1$ is $k' = kA_o = -\ln(1 - (a/a_e)^{1/n}) \approx (a/a_e)^{1/n} = 2.05 \times 10^{-2}\ \mathrm{min}^{-1}$.

From the changes in n and β, we could deduce structural diffusion interactions between the dye and the cotton fabric. By means of β, K_a, and Equation 3, we could also predict exhaustion α (in %) = 100 a_e/d_o of a finite bath with different initial concentrations of the dye or the adsorbent (cotton).

For short reaction times, Fick's equation for a cylinder can be approximated [5, 6, 8, 9] by

$$D = \frac{\pi r^2}{16t}\left(\frac{a}{a_e}\right)^2 \quad , \tag{8}$$

where r is the radius of the cylinder. From Equation 1 at short reaction times, we may approximate

$$\left(\frac{a}{a_e}\right)^{1/n} = kA_o t \quad , \tag{9}$$

and by comparison with Equation 8 where $t = 1$ second, we get

$$D = (kA_o)^{2n}\pi r^2/16 \quad , \tag{10}$$

where $kA_o = k'$ is in second^{-1}.

From the experiments, it was apparent that the diffusion resistance constant n did not depend significantly on the chemical structure of the dyes (Tables I and II). With all direct dyes used in our experiments, n remained within the limits 0.41–0.45; thus the diffusion resistance of cotton fiber was not influenced by the dyes. We expected this because n depends mainly on structural changes of the adsorbent and not on other factors.

TABLE I. Kinetic constants of dyeing cotton with direct dyes in a finite bath with constant cotton concentration A_o.[a]

Direct dye	d_o (M) × 10^{-5}	a_e (M) × 10^{-5}	n	k' (min^{-1}) × 10^{-2}	D ($\text{cm}^2\ \text{s}^{-1}$) × 10^{-10}	β (Mlg^{-1}) × 10^{-5}	K_a (M) × 10^{-5}
Yellow 29	6.25	6.11	0.417	3.39	3.84	1.82	1.89
	12.5	12.21	0.417	3.37	3.82		
	25.0	24.31	0.416	3.36	3.87		
Yellow 50	6.25	6.12	0.417	3.48	3.92	1.94	1.88
	12.5	12.23	0.414	3.48	4.10		
	25.0	24.37	0.416	3.46	3.96		
Orange 31	6.25	6.09	0.455	5.66	3.47	2.13	2.61
	12.5	12.16	0.458	5.66	3.33		
	25.0	24.23	0.460	5.60	3.20		
Red 81	6.25	6.09	0.410	5.60	6.43	1.97	2.49
	12.5	12.15	0.412	5.55	6.21		
	25.0	24.19	0.411	5.55	6.30		
Red 75	6.25	6.14	0.414	2.83	3.46	2.23	1.85
	12.5	12.27	0.417	2.82	3.29		
	25.0	24.48	0.410	2.80	3.64		
Red 23	6.25	6.12	0.405	6.04	7.33	2.48	2.54
	12.5	12.22	0.424	6.04	5.64		
	25.0	24.38	0.412	6.05	6.67		
Violet 51	6.25	6.12	0.416	4.59	5.01	2.26	2.29
	12.5	12.22	0.414	4.56	5.13		
	25.0	24.37	0.410	4.57	5.45		
Blue 71	6.25	6.14	0.416	3.54	4.04	1.98	1.62
	12.5	12.27	0.421	3.54	3.75		
	25.0	24.47	0.420	3.50	3.77		

[a] Averages from duplicates. The constants were calculated from the time curves by computer mathematical regression of Equations 1, 6, 7, and 10. The computer program for mathematical regression of Equation 1 is described in Computers & Chemistry [2]. Correlation coefficients of these calculations were between 0.98 and 1. Cotton concentration $A_o = 50$ g/l, temperature 50°C, $k = k'/A_o$.

TABLE II. Kinetic constants of dyeing cotton with direct dyes in a finite bath with constant dye concentration d_o.[a]

Direct dye	A_o (g/l)	a_e (M) × 10^{-5}	n	k' (min^{-1}) × 10^{-2}	D ($\text{cm}^2\ \text{s}^{-1}$) × 10^{-10}	β (Mlg^{-1}) × 10^{-5}	K_a (M) × 10^{-5}
Yellow 29	10	10.23	0.419	0.675	0.96	1.84	1.96
	20	11.51	0.420	1.34	1.86		
	50	12.21	0.417	3.37	3.82		
Yellow 50	10	10.45	0.410	0.498	0.88	1.97	1.97
	20	11.59	0.416	1.40	1.87		
	50	12.23	0.414	3.48	4.10		
Orange 31	10	10.03	0.460	1.15	0.75	1.86	2.09
	20	11.63	0.452	2.23	1.56		
	50	12.16	0.458	5.66	3.33		
Red 81	10	9.86	0.410	1.10	1.69	1.76	2.06
	20	11.57	0.413	2.24	2.89		
	50	12.15	0.412	5.55	6.21		
Red 75	10	10.87	0.410	0.568	0.99	2.19	1.87
	20	11.73	0.412	1.13	1.67		
	50	12.27	0.417	2.28	3.29		
Red 23	10	10.70	0.424	1.21	1.44	2.32	2.40
	20	11.61	0.426	2.42	2.52		
	50	12.22	0.424	6.04	5.64		
Violet 51	10	10.40	0.408	0.910	1.50	1.89	1.72
	20	11.80	0.416	1.84	2.34		
	50	12.22	0.414	4.56	5.13		
Blue 71	10	10.72	0.416	0.706	1.06	2.02	1.72
	20	11.71	0.420	1.42	1.77		
	50	12.27	0.421	3.54	3.75		

[a] Averages from duplicates. The constants were calculated from the time curves by computer mathematical regression of Equations 1, 6, 7, and 10. The computer program for mathematical regression of Equation 1 is described in Computers & Chemistry [2]. Correlation coefficients of these calculations were between 0.98 and 1. Dye concentration $d_o = 1.25 \times 10^{-4}$ M, temperature 50°C, $k = k'/A_o$.

The specific rate constants k were different with each dye, and so were the diffusion coefficients calculated by Equation 10 with the average radius of cotton fibers $r = 0.0010$ cm.

The dyeing capacity constants β of the untreated cotton fabric (for A_o in gl^{-1} and d_o in moles) with all dyes studied were in the range $1.8\text{–}2.5 \times 10^{-5}\ \text{Mlg}^{-1}$. The equilibria a_e were in the range $0.6\text{–}2.5 \times 10^{-4}$ M.

The activation energies of the dyes calculated from Equation 2 were between 4–5 kcal/mole, but the reaction heats calculated from Equation 3 differed considerably from 200 to 1500 cal/mole (Table III).

TABLE III. Activation energies and reaction heats of direct dyes on cotton.[a]

Direct dye	ΔE^* (cal/mol)	ΔH (cal/mol)
Yellow 29	5158	−1471
Yellow 50	5693	−1067
Orange 31	3888	−570
Red 81	4494	−628
Red 75	4491	−796
Red 23	5090	−248
Violet 51	5292	−1060
Blue 71	4253	−225

[a] Activation energies and enthalpies were calculated from dyeing at 50, 70, and 90°C by Equations 4 and 5. Average from duplicates. Correlation coefficients were between 0.99 and 1. Cotton concentration $A_o = 50$ g/l; dye concentration $d_o = 1.25 \times 10^{-4}$ M. Dyeing is a more complex process and dyed materials usually have complex structures. Thus the enthalpies calculated from kinetic data are only apparent relative values (see Vickerstaff [9]).

When the same cotton fabric was dyed with selected direct dyes in a finite bath, the most apparent kinetic differences were in the rate constants, diffusion coefficients, and reaction heats. Much smaller differences occurred in the dyeing capacities and the activation energies.

The specific rate constants and the diffusion coefficients seemed to be related to the chemical structures of the dyes, for example, to the number of aromatic rings and sulfo groups. Both the rate constants and diffusion coefficients decreased with an increasing number of aromatic rings and sulfo groups (Table IV).

TABLE IV. Relationship between dye structures and rate constants.[a]

Direct dye	X = no. of aromatic rings	Y = no. of Na^+	$X + Y$	k'
Yellow 29	10	2	12	0.03
Blue 71	8	4	12	0.03
Yellow 50	6	4	10	0.03
Red 75	6	4	10	0.03
Red 23	6	2	8	0.06
Violet 51	5	2	7	0.05
Red 81	5	2	7	0.06
Orange 31	5	2	7	0.06

[a] See Table I.

The highest rate constants and diffusion coefficients occurred with Direct reds 23 and 81. The rate constants of other dyes were lower. The lowest enthalpies occurred with Direct red 23 and Direct blue 71. The relationship between the dye structures and the activation energies or enthalpies seemed to be more complex.

The most significant differences in the kinetic properties of direct dyes in finite baths with cotton fabric were in the rate constants and diffusion coefficients, and not so much in dyeing capacities. The cotton fabric structure is complex and can only be idealized as a set of long cylinders. Thus the diffusion coefficients calculated using Equations 8–10 are only apparent diffusion coefficients.

Equations 1–10 agreed well with experimental results. Once we determined the constants of these equations from one (or more) selected time curves, we could predict not only the reaction equilibria, diffusion coefficients, maximum dyeing capacities, exhaustions of finite baths, and reaction rates, but also the structural changes in dyed materials (constants n) in a wide range of dyeing conditions.

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