Dyeing Process in a Finite Dyebath

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Synopsis

The processes of adsorptive and reactive dyeings of polymer film in a finite bath were formulated on the basis of pore model concept. The influence of the bath ratio on the fractional uptake or fixation was numerically analyzed. The time of half-dyeing is proportional to the bath ratio to the power of about 0.9 within the present computational conditions. This fact is in contrast to the finding that, in an infinite bath with the same dye concentration as the initial value in a finite bath, the time of half-dyeing is inversely proportional to the dye concentration. The relation of the total uptake or fixation to the dimensionless dyeing time θ multiplied by $\gamma^{0.9}$ is independent of the bath ratio within an error of 5% or 8%.

INTRODUCTION

The dyeing of textiles is considered a combined process comprised of intrafiber diffusion of dye molecule or ion and chemical reaction with or adsorption upon the fiber substrate. From this standpoint, chemical engineering approaches to transport phenomena in multiphase systems may be applied to the analysis and synthesis of the dyeing process.

In the previous paper,[1] the process of dyeing of hydrophilic textile fiber was formulated on the basis of diffusion of dyestuff in pores within fiber accompanied by chemical reaction or adsorption, viz., the pore model, and the validity of the proposed model was confirmed by comparison with existing experimental data on dyeings of reactive dyes in cellulose and acid dyes in nylon. The dyebath, however, had been assumed to be infinite in order to make such comparison possible. The practical dyeing processes are usually operated batchwise, and the concentration of dye liquor in a bath is apt to decrease as the dyeing proceeds.

In this respect, the dyeing process should be distinguished from adsorption and solid-catalyzed reaction in multiphase transport phenomena. That is, the latter systems are usually operated continuously.

It was proved in the previous work[1] that the transfer of dye species in a hydrophilic textile fiber can be formulated by the pore model stated above. In the present paper, thus, the previous treatment on reactive and adsorptive dyeings was extended to that for a finite dyebath and the influence of the bath ratio, i.e., volume of dye liquor per unit volume of polymer phase to be dyed, on the dyeing rate or time variation of fractional uptake or fixation was mainly discussed.

SIMULATION MODEL OF DYE-IMMOBILIZATION PROCESS

Adsorptive Dyeing

Consider the case where a dyestuff A diffuses into pores of polymer phase, simultaneously adsorbing upon the substrate sites which are distributing uni-

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formly on the wall of pores. The rate of adsorption of the dye species can be expressed by $k_a C_A (q_A^0 - q_A)$, while the rate of desorption of the adsorbed dye species can be expressed by $k_d q_A$. The diffusion of dye is controlled by the one-dimensional Fick's equation. Thus, the conservation equations in the pores and adsorbed phase can be written as

$$\epsilon \frac{\partial C_A}{\partial t} + (1 - \epsilon) \frac{\partial q_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} \tag{1}$$

$$\frac{\partial q_A}{\partial t} = k_a C_A (q_A^0 - q_A) - k_d q_A \tag{2}$$

The dyebath is operated in a finite volume of dye liquor, and the polymer phase is regarded as being a slab with thickness $2L$ but not a cylindrical fiber. The initial and boundary conditions to be imposed are

$$t = 0, \quad x > 0, \quad C_A = q_A = 0 \tag{3}$$

$$t = x = 0, \quad C_A = C_{A0} \tag{4}$$

$$t > 0, \quad x = 0, \quad C_A = C_{Ai} \quad \text{(variable)}$$

$$(C_{A0} - C_{Ai})v = \int_0^t \left(-D_A \frac{\partial C_A}{\partial x} \Big|_{x=0} \right) dt' = \int_0^L [\epsilon C_A + (1 - \epsilon)q_A] dx \tag{5}$$

$$t > 0, \quad x = L, \quad \frac{\partial C_A}{\partial x} = 0 \tag{6}$$

Here v represents the volume of dye liquor per unit surface area of the polymer phase. Equation (5) implies that the reduced amount of dyestuff in the bath is equal to the total amount of diffusion into the polymer phase. As the dyeing proceeds, only the concentration of dyestuff in the bath decreases according to eq. (5), but the other conditions such as temperature, pH of dyeing liquor, and salt concentration are assumed to remain unchanged. Equation (6) reflects symmetry of the polymer phase. The analysis based on the above formulation, which considers only one half of the slab, might give by analogy the dyeing behavior in a cylindrical fiber.

After introducing such dimensionless variables as $Y_A = C_A/C_{A0}$, $\omega_A = q_A/q_A^0$, $\xi = x/L$, and $\theta = D_A t/L^2$, the basic mass balance equations (1) and (2) are rewritten in the dimensionless form as

$$\frac{\partial^2 Y_A}{\partial \xi^2} - \epsilon \frac{\partial Y_A}{\partial \theta} = M_a \left[Y_A (1 - \omega_A) - \frac{\omega_A}{K_A C_{A0}} \right] \tag{7}$$

$$\frac{\partial \omega_A}{\partial \theta} = \frac{M_a}{1 - \epsilon} \left[Y_A (1 - \omega_A) - \frac{\omega_A}{K_A C_{A0}} \right] \tag{8}$$

with the initial and boundary conditions

$$\theta = 0, \quad \xi > 0, \quad Y_A = \omega_A = 0 \tag{9}$$

$$\theta = \xi = 0, \quad Y_A = 1 \tag{10}$$

$$\theta > 0, \quad \xi = 0, \quad Y_A = Y_{Ai} = 1 + \frac{L}{v} \int_0^\theta \left(\frac{\partial Y_A}{\partial \xi} \right)_{\xi=0} d\theta'$$

$$= 1 - \frac{L}{v} \int_0^1 \left[\epsilon Y_A + \frac{(1 - \epsilon)\omega_A}{\gamma} \right] d\xi \tag{11}$$

$$\theta > 0, \quad \xi = 1, \quad \frac{\partial Y_A}{\partial \xi} = 0 \tag{12}$$

Here the parameter M_a is defined by $k_a q_A^0 L^2 / D_A$ and is equivalent to the square of the adsorption–diffusion modulus. γ is the initial dimensionless concentration of dye in the bath, which is defined by C_{A0}/q_A^0, and v/L is equivalent to the bath ratio for a plane slab.

When the adsorption equilibrium is instantaneously attained, ω_A is related to Y_A by

$$\omega_A = \frac{K_A C_{A0} Y_A}{1 + K_A C_{A0} Y_A} \tag{13}$$

and, accordingly, the mass balance equation in the polymer phase is put into

$$\frac{\partial^2 Y_A}{\partial \xi^2} - \left[\epsilon + \frac{(1 - \epsilon) K_A C_{A0}}{(1 + K_A C_{A0} Y_A)^2} \right] \frac{\partial Y_A}{\partial \theta} = 0 \tag{14}$$

A convenient way to express computational results is in terms of fractional uptake. The local fractional uptake is given by ω_A, whereas the total fractional uptake is defined by

$$\omega_{\text{tot}} = \int_0^1 \omega_A d\omega \tag{15}$$

Reactive Dyeing

The reactive dyeing can be regarded as a process in which a dyestuff A diffuses into a polymer phase, reacting with the substrate S dispersing uniformly within the phase. The reaction between the dyestuff and the substrate is assumed to be of second-order relative to both species and the diffusion of dye is in one-dimensional media. Then, conservation equation of the dyestuff in the polymer phase is described as

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} - k C_A C_S \tag{16}$$

If the stoichiometric factor for the reaction is v, viz., $A + vS \rightarrow P$, the rate of consumption of the substrate can be written as

$$\frac{\partial C_S}{\partial t} = -vk C_A C_S \tag{17}$$

Also, the dyebath is considered to be finite and the polymer phase is regarded as a slab with thickness $2L$ but not a cylindrical fiber. The initial and boundary conditions are

$$t = 0, \quad x > 0, \quad C_A = 0, \quad C_S = C_{S0} \tag{18}$$

$$t = x = 0, \quad C_A = C_{A0} \tag{19}$$

$$t > 0, \quad x = 0, \quad C_A = C_{Ai} \quad \text{(variable)}$$

$$(C_{A0} - C_{Ai})v = \int_0^L \left(C_A + \frac{C_{S0} - C_S}{v} \right) dx \tag{20}$$

$$t > 0, \quad x = L, \quad \frac{\partial C_A}{\partial x} = 0 \tag{21}$$

Only the concentration of dyestuff in the bath changes according to eq (20), whereas it is assumed that the other conditions such as temperature, pH of dyeing liquor, and salt concentration are also kept constant. The conservation equation in the dimensionless form can be written as

$$\frac{\partial Y_A}{\partial \theta} = \frac{\partial^2 Y_A}{\partial \xi^2} - M Y_A Y_S \tag{22}$$

$$\frac{\partial Y_S}{\partial \theta} = -M\gamma Y_A Y_S \tag{23}$$

subject to

$$\theta = 0, \quad \xi > 0, \quad Y_A = 0, \quad Y_S = 1 \tag{24}$$

$$\theta = \xi = 0, \quad Y_A = 1 \tag{25}$$

$$\theta > 0, \quad \xi = 0, \quad Y_A = Y_{Ai} = 1 - \frac{L}{\upsilon} \int_0^1 \left(Y_A + \frac{1 - Y_S}{\gamma} \right) d\xi \tag{26}$$

$$\theta > 0, \quad \xi = 1, \quad \frac{\partial Y_A}{\partial \xi} = 0 \tag{27}$$

Here the parameter M is defined by $k C_{S0} L^2 / D_A$ and is equivalent to the square of the Thiele modulus, and the parameter γ is the initial dimensionless concentration of dye in the bath which is here given by $\upsilon C_{A0}/C_{S0}$.

The local and total fractional fixation are defined as

$$f = 1 - Y_S \tag{28}$$

and

$$f_{\text{tot}} = 1 - \int_0^1 Y_S d\xi \tag{29}$$

respectively.

COMPUTATIONAL RESULTS AND DISCUSSION

The solution of the basic mass balance equations (1) and (2) or (16) and (17) poses a nonlinear boundary value problem. Accordingly, the simultaneous differential equations with the relevant initial and boundary conditions were numerically solved by using the quasilinearization technique proposed by Lee.[2]

If the total amount of dyestuff fed batchwise to the bath is constant, the concentration of dye liquor should be inversely proportional to the volume of dyebath per unit volume of polymer phase to be dyed, viz., the bath ratio will have a significant influence on the dye-immobilization process. Figure 1 shows a typical example of the influence of the bath ratio upon the spatial distribution of immobilized dye in the polymer phase for adsorptive dyeing, where the Langmuir adsorption equilibrium is instantaneously established. It is obvious that the fractional uptake increases with decreasing the bath ratio, and the concentration
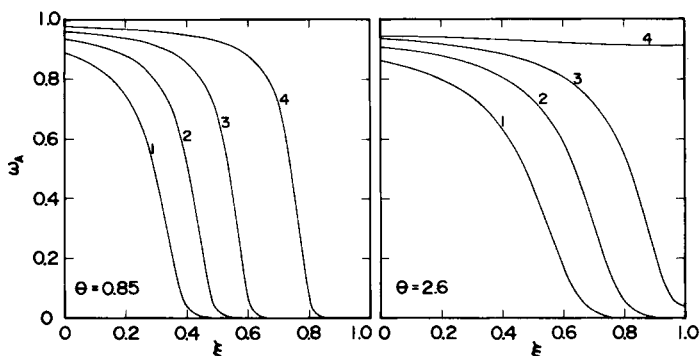
Fig. 1. Effect of bath ratio on spatial distribution of adsorbed dye for adsorptive dyeing:

Curve	v/L	γ	$K_A C_{A0}$
1	20	0.05	10
2	10	0.1	20
3	5	0.2	40
4	2	0.5	100

of dye on the surface of polymer phase gradually decreases as the dyeing process proceeds. The variation of the total amount of adsorbed dye and the concentration of dye in the bath with the dyeing time were shown for various bath ratios in Figure 2. The fractional exhaustion commonly used is equal to $1 - Y_{Ai}$. At the limit when $\theta \to \infty$, eq. (11) reduces to

$$Y_{Ai} = 1 - (v/L) \left[\epsilon Y_{Ai} + (1 - \epsilon)\omega_{tot}/\gamma \right] \tag{30}$$

where ω_{tot} is given by the adsorption equilibrium relationship (Langmuir adsorption isotherm):

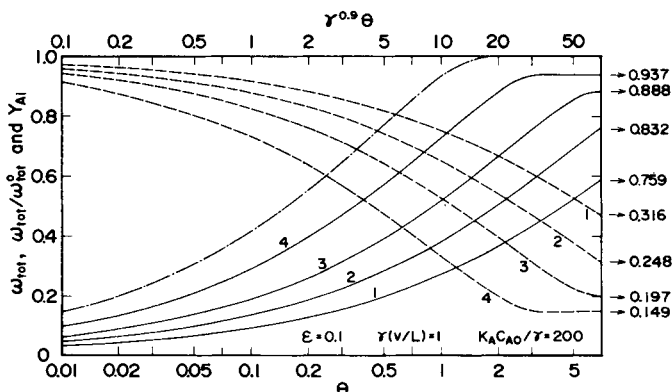$$\omega_{tot} = \frac{K_A C_{A0} Y_{Ai}}{1 + K_A C_{A0} Y_{Ai}}$$

Fig. 2. Total uptake and dimensionless dye concentration in the dyebath as a function of dimensionless dyeing time in adsorptive dyeing. v/L: (1) 20; (2) 10; (3) 5; (4) 2.
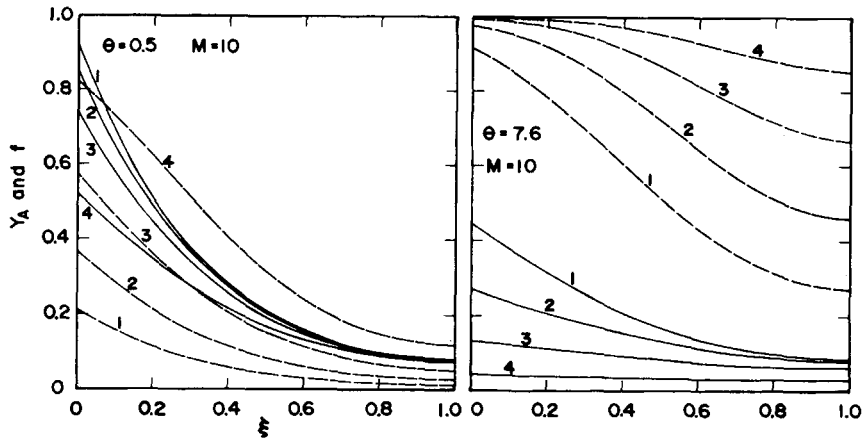
Fig. 3. Spatial distribution of mobil and immobilized dye species for reactive dyeing: (——) mobil; (- - -) immobilized.

Curve	v/L	γ
1	20	0.05
2	10	0.1
3	5	0.2
4	2	0.5

So Y_{Ai} can be explicitly determined.

The numerical values on the right side of Figure 2 represent the values of ω_{tot} and Y_{Ai} for various dyebaths calculated by eqs. (30) and (31). As the bath ratio decreases, the total amount of adsorbed dye is increased, and the concentration and amount of remaining dye are decreased. If the ratio of ω_{tot} at any θ to ω_{tot} at $\theta \to \infty$, viz., ω_{tot}^{0}, is plotted against $\gamma^{0.9}\theta$ instead of θ, then the relationship between the two factors becomes independent of the bath ratio within an error of 5% as shown by a dot–dash line. The reason why an exponent on γ is selected 0.9 will be mentioned later.
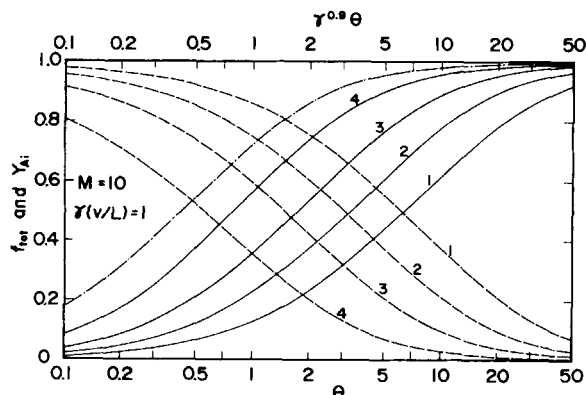

Fig. 4. Total fixation and dimensionless dye concentration in the dyebath as a function of dimensionless dyeing time for reactive dyeing. v/L: (1) 20; (2) 10; (3) 5; (4) 2.
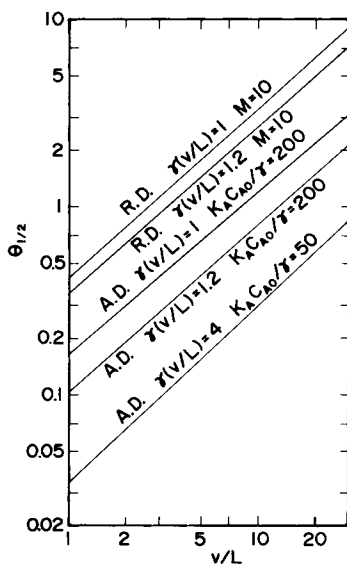
Fig. 5. Relationship between dimensionless time of half-dyeing and dyebath ratio for adsorptive and reactive dyeings. A.D. and R.D. stand for adsorptive and reactive dyeings, respectively.

Typical examples of computational results on reactive dyeing are indicated as solid and broken curves in Figure 3, where the concentrations of mobile and immobilized dye species are plotted against the dimensionless position in the polymer phase.   Figure 4 shows the time variation of the total fixation and the dye liquor concentration in the bath for various bath ratios.   It is obvious that the dyeing time can be reduced by lowering the bath ratio.   When the fractional fixation is plotted against $\gamma^{0.9}\theta$ instead of θ alone as in the case of adsorptive dyeing, the relationship between these two factors, which is shown by the dot–dash line, reduces to a single curve within an error of 8% irrespective of the bath ratio.

It is concluded from above numerical analyses that the lower the bath ratio is, the higher the uptake or fixation at a given dyeing time.   To make it clearer, the relationship between the time of half-dyeing and the bath ratio for adsorptive and reactive dyeings are shown in Figure 5.   Here the time of half-dyeing is defined by the time required to reach a fixation of 50% of its final or equilibrium value.   The dyestuff is fed stoichiometrically or 20% excess of its stoichiometrical value in advance.   It is proved that the time of half-dyeing is proportional to the bath ratio to the power of about 0.9 within the present computational conditions. This fact is in contrast to the finding in the previous paper[1] that in an infinite dyebath with the same dye concentration as the initial concentration in the finite bath, where the dye concentration is kept constant at the initial value, the time of half-dyeing is inversely proportional to the concentration of dye.

CONCLUSION

The kinetic models for adsorptive and reactive dyeings in a finite bath were proposed on the basis of diffusion of dyestuff in pores within the polymer phase accompanied by adsorption and chemical reaction, respectively.   The influence

KUMAZAWA AND SADA

of the dyebath ratio on the uptake or fixation was numerically analyzed. The time of half-dyeing is proportional to the dyebath ratio to the power of about 0.9 within the present computational conditions. The relation of $\omega_{tot}/\omega_{tot}^0$ in the adsorptive dyeing or f_{tot} in the reactive dyeing to dimensionless dyeing time θ multiplied by $\gamma^{0.9}$ is independent of the bath ratio within an error of 5% or 8%.

NOMENCLATURE

C_A	concentration of dye in pore or polymer phase (mol/m^3)
C_S	concentration of reactive site in polymer phase (mol/m^3)
D_A	diffusion coefficient of dye in pore or polymer phase (m^2/s)
f	local fractional fixation in polymer phase
f_{tot}	total fractional fixation in polymer phase
k	rate constant of second-order reaction (m^3/mol·s)
k_a	adsorption rate constant (m^3/mol·s)
k_d	desorption rate constant (1/s)
K_A	adsorption equilibrium constant = k_a/k_d (m^3/mol)
L	half-width of polymer phase (slab) (m)
M	$kC_{S0}L^2/D_A$
M_a	$k_a q_A^0 L^2/D_A$
q_A	concentration of adsorbed dye (mol/m^3)
q_A^0	saturation concentration of adsorbed dye (mol/m^3)
t	dyeing time (s)
$t_{1/2}$	time of half-dyeing (s)
v	dye liquor volume per unit surface area of polymer phase (m^3/m^2)
x	distance from surface of polymer phase (m)
Y_A	dimensionless concentration of dye in pore or polymer phase = C_A/C_{A0}
Y_S	dimensionless concentration of reactive site in polymer phase = C_S/C_{S0}
Greek	
γ	C_{A0}/q_A^0 in adsorptive dyeing and vC_{A0}/C_{S0} in reactive dyeing
ϵ	voidage of polymer phase
θ	dimensionless dyeing time = $D_A t/L^2$
$\theta_{1/2}$	dimensionless time of half-dyeing = $D_A t_{1/2} L^2$
ν	stoichiometric factor appearing in reaction $A + \nu S \rightarrow P$
ξ	dimensionless distance from surface of polymer phase = x/L
ω_A	dimensionless concentration of adsorbed dye = q_A/q_A^0
ω_{tot}	degree of saturation of adsorbed dye in polymer phase = $\int_0^L q_A dx/Lq_A^0 = \int_0^1 \omega_A d\xi$
Subscripts	
A	dye
S	substrate or reactive site
0	initial value

References

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