

A Novel Approach for Estimating the Relation between K/S Value and Dye Uptake in Reactive Dyeing of Cotton Fabrics

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Abstract: This paper focuses on the application of a novel mathematical limit approach derived for K/S values in reactive dyeing of cotton fabrics. The relation obtained from Kubelka-Munk equation is used because the Kubelka-Munk equation is the basic relationship among fabric reflectance, fabric dye content and dyestuff characteristics. The limit approach derived in a former paper is applied to the laboratory dyeings and the dyeing behavior of some reactive dyes on cotton knitted fabric has been obtained. The results of the laboratory experiments are discussed using the new mathematical approach. When the actual K/S values obtained from the dyeings and the calculated K/S values derived by the limit approach are considered independently, it is observed that the limit relation is valid for low dye concentration applications. When the K/S values are calculated taking the K/S value of the initial dyeing concentration (0.1 % owf) as the starting concentration by applying the result of the derived limit approach, the calculated K/S values fit with the ones obtained in actual dyeings. It is concluded that the novel approach presented in the paper can be used in calculating the K/S values when the initial dyeings at low dye concentrations are carefully carried out.

Keywords: Reactive dye, Cotton reactive dyeing, K/S value, Dye uptake, Reflectance

Introduction

The relationship between reflectance value and dyestuff concentration of a fabric has a complicated structure and this relationship must be known in order to solve the problems related to color measurement methods. This relationship is also very significant being a basis for calculation of dye formulation where one or more combination of several dyes is involved [1-6].

Reflectance of a Dyed Fabric

There is a systematic relationship between reflectance and dye concentration of a fabric. As the dye content of the fabric increases, reflectance (R) values decrease. At the maximum absorption wavelength (λ_{max}), R values theoretically and practically approach very close to zero. The reflectance (R) is measured as a function of wavelength and plotted against the related wavelengths in order to obtain a curve family of the dyed fabric [1,7-9].

A direct comparison of the reflectance curve of a dyeing enables us to determine the dye concentration of the fabric. However, knowledge of the entire reflectance curve is not necessary in this case. An evaluation at the absorption maximum (maximum absorption wavelength) is sufficient for color measurement purposes. The dye concentration on a fabric can be determined more simply and without using numerous standard dyeings.

Kubelka-Munk Equation

An opaque textile substrate not only absorbs but also scatters

incident light. A function based on this fact was developed by Kubelka and Munk who theorized in 1931 that the ratio of the coefficient of light absorption (K) to the coefficient of light scattering (S) is related to the fractional reflectance of the light (R) of the opaque substrate at a given wavelength like equation (1) [2,7-12].

$$R = 1 + (K/S) - [(K/S)^2 + 2(K/S)]^{1/2} \quad (1)$$

When it is solved for K/S , equation (2) is obtained.

$$K/S = (1 - R)^2 / 2R \quad (2)$$

In textile substrates, K is primarily determined by the dyestuff and S solely by the substrate.

The depth of color of a textile material is related to the dye content when all the other factors are equal. The functional relationship which is often used in textile industry today in order to display color and dye concentration changes is given in equation (3) [1,2,10]

$$(K/S) = A \cdot C \quad (3)$$

where 'A' is a constant referred to reflectance absorptivity coefficient of the dyestuff; 'C' is the uniformly distributed dye content of a substrate [2]. In equation (3), A is a constant which must be experimentally determined and is dependent on the dyestuff, dyeing conditions, textile substrate and the wavelength. However, A is independent -or nearly so- of the concentration C.

If we combine equation (2) and equation (3), we obtain equation (4) in which we can see the effects of different parameters at the same time.

$$(K/S) = (1 - R)^2 / 2R = A \cdot C \quad (4)$$

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Equation (4) gives us the ability to obtain relations between light absorptivity (K) and scattering (S) properties, reflectance (R), and dye content (C) of the substrate.

Limit Relation between Fabric Reflectance and Dye Content

From equation (4), one can obtain a basic relationship between reflectance (R), dye content (C) and K/S value. Let us consider an assumption: If we decrease the fabric reflectance n times; i.e., R to R/n , what would be the change in concentration (C) and K/S value in equation (4).

Starting from equation (4), we obtain;

$$C = [(1 - R)^2 / 2RA] = (K/S) / A \quad (5)$$

If we put R/n for R in equation (5), we obtain;

$$C = [(1 - (R/n))^2 / 2(R/n)A] = [(n - R)^2 / n^2] / 2A(R/n) = (n - R)^2 / 2RAn = (K/S) / A \quad (6)$$

In order to obtain the limit value for concentration change, we can define C in equation (6) as C_2 , and C in equation (5) as C_1 .

By dividing equation (6) by equation (5), we obtain (C_2/C_1);

$$C_2/C_1 = [(n - R)^2 / 2RAn] / [(1 - R)^2 / 2RA] = [(n - R)^2 / n] / [(1 - R)^2] = (n - R)^2 / n(1 - R)^2 \quad (7)$$

At the same time equation (7) is equal to;

$$C_2/C_1 = [(K/S)_2 \cdot A^{-1} / (K/S)_1 \cdot A^{-1}] = (n - R)^2 / n(1 - R)^2 \quad (8)$$

By taking the limit of equation (8), we obtain;

$$\lim_{R \rightarrow 0} \frac{C_2}{C_1} = \lim_{R \rightarrow 0} \frac{(K/S)_2}{(K/S)_1} = \lim_{R \rightarrow 0} \frac{(n - R)^2}{n(1 - R)^2} = \frac{n^2}{n} = n \quad (9)$$

$$\text{And finally, } C_2/C_1 = [(K/S)_2 \cdot A^{-1} / (K/S)_1 \cdot A^{-1}] = n \quad (10)$$

Equation (10) is valid for low dye concentrations mathematically [7]. From equation (10), we observe that when we want to decrease the reflectance by n times (R to R/n), we must increase the dye content of the fabric also n times. This 'limit' is obtained at the maximum absorption wavelength of the dyestuff [7].

Relation between K/S Value and Dye Content

The linearity of the Kubelka-Munk function is only applied at low dye concentrations. Deviations from linearity are very common at high dye concentrations and at low reflectance values. These stem from limited substantivity of some dyes for certain substrates, saturation effects in dyeing, and optical effects such as the limiting lowest reflectance of a substrate which is greater than zero even when dyed with the darkest black. Corrections can be introduced to compensate these deviations from linearity [10]. A straight line is to be achieved for low dye concentrations, when depth of shade (K/S) is plotted as a function of dye content of the textile material.

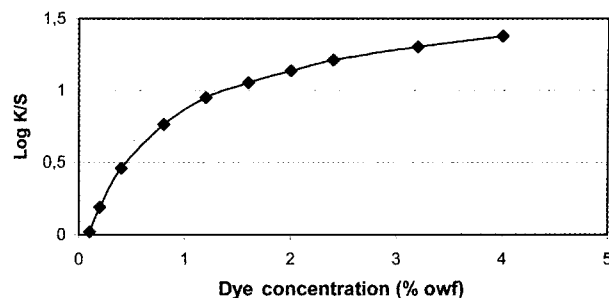


Figure 1. Log K/S values of Reactive Black (mix dye) for different % owf.

As the dye content of the textile substrate increases, the straight line becomes a curve which is parallel to the concentration axis at high dye contents. From the shape of the curve a saturation value for the fiber can also be estimated. An example for this kind of curve obtained for a black reactive dye (Dye IV in the experimental part) on cotton knitted fabric is given in Figure 1.

It is clear that at low dye content; i.e., the line is still a straight line, the slope of the line will give useful information about the dyeing system. This line also characterizes a relation between the dye content and the observed K/S value. The slope of the line will vary according to the substrate characteristics and the dyeing conditions. The effects which can be listed under substrate characteristics are "type of polymer and fiber, construction of the fabric, orientation of fibers and yarns and surface characteristics of the fabric, etc". Other physical properties can also be taken into account when a more detailed research is to be carried out. The effects that can be listed under dyeing conditions can be "type of the dyeing machines and their properties, concentration of dye in dye liquor, dyeing auxiliaries, dyeing methods, and etc". It is obvious that the line obtained for a dye under test will not keep its characteristics when dyeing conditions are changed and a specific line and slope will be obtained for each dyeing condition.

This paper reports a novel approach for estimating the linearity of the K/S values of the dyed fabric at low dye concentrations for cotton reactive dyeing. In order to make the approach and to establish the statement on a mathematical basis, the Kubelka-Munk equation is used.

Materials and Method

Materials

The reactive dyeings were performed on cotton plain knitted (single jersey) fabric (148.8 g/m^2) made from Ne 30/1 cotton yarns. The fabric was scoured under controlled mill conditions and prepared for dyeing in the laboratory.

Reactive dyes used in the experimental part are given in Table 1.

Dye concentrations (% owf) and the amounts of chemicals used in dyeings are presented in Table 2.

Table 1. Reactive dyes and properties

Dye	C.I. No.	Explanation	λ_{\max} (nm)
I	Reactive Red 180	Cold Reactive Dye	550 nm
II	Reactive Yellow 176	Cold Reactive Dye	430 nm
III	Reactive Blue 171	Hot Reactive Dye	620 nm
IV	Reactive Black (Mix Dye)	Cold Reactive Dye	600 nm

Table 2. Chemicals and amounts

Dye concentration (% owf)	Salt (g/l)		Soda (g/l)
	Hot (Dyes I, II, IV)	Cold (Dye III)	
0.1	20	20	10
0.2	20	20	10
0.4	30	20	10
0.8	45	30	15
1.2	60	40	15
1.6	60	40	15
2.0	60	40	15
2.4	80	60	20
3.2	80	60	20
4.0	80	60	20

Dyes of different hues were selected to see the results of the novel approach in different absorption areas of the spectrum. The black reactive dye was chosen because at high dye concentrations the reflectance of the black dyed substrates goes to a minimum value which is very close to zero as shown in equation (9).

Method

The dyeings were carried out in a laboratory-type dyeing machine (Roaches) under laboratory conditions. All the chemicals used were in commercial purity.

Dyeing with reactive dyes (Dyes I, II and IV) at warm temperatures began at 40 °C. After 10 minutes the temperature was raised to 60 °C by 1 °C/min. The dyeing continued for 90 minutes at this temperature and then the temperature was decreased to 45 °C and the fabric samples were taken out from the dyeing machine. Dyeing with reactive dye (Dye III) at hot temperatures began at 60 °C. After 15 minutes the temperature was raised to 95 °C by 2 °C/min. The dyeings continued at this temperature for 20 minutes. Later the temperature was decreased to 82 °C and soda was added to the dyebaths. Dyeings continued at 82 °C for 90 minutes and then the temperature was decreased to 45 °C. The dyed samples were taken out from the dyeing machine. All the dyeings were made under 15:1 liquor-to-goods ratio. The dyed samples weighed 10.000 (± 0.005) grams and dyeing liquor was 150 ml. All the dye baths contained 1 ml/l anionic wetting agent and 1 ml/l sequestering agent. All the chemical additions were made according to the instructions of the

dyestuff manufacturer.

The dyed samples were cold (tap water) and hot (60 °C) rinsed. After that, the samples were soaped at 95 °C for 30 minutes in the presence of an anionic soaping agent (2 g/l). After soaping, the samples were hot (60 °C) and cold (tap water) rinsed and left to dry under laboratory conditions.

Evaluation of the Results of the Dyeing Experiments

The results were obtained according to the color measurements of the samples with a Macbeth reflectance spectrophotometer (MS 2020+) coupled to a PC under D65/10° illuminant between 400-700 nm.

Results and Discussion

Measured and calculated K/S values for the dyeings carried out by using the different reactive dyes are presented in Figures 2-5. Measured K/S values are the actual K/S values obtained from the color measurement of the dyed samples. Calculated K/S values are obtained by the use of the measured actual K/S value of the 0.1 % owf dyeing; i.e., the calculated K/S value of Reactive Black (Mix Dye) at, say 2.0 % owf, is the multiplication of 0.93×20 which is equal to 18.6; 0.93 is the actual K/S value of the dyeing at 0.1 % owf. The 20 is obtained from $2.0/0.1$ which is the application of the limit approach in dyeing (equation (10)).

In Figures 2-5, the plot of the measured K/S values become almost parallel to the x-axis at high dye concentration and the plot of the calculated values form a straight line as expected. It is observed from the Figures that the limit relation gives close values to the actual values at low dye concentrations; i.e., 0.1-1 % owf. At higher dye concentrations the measured and calculated K/S values are far from each other pointing that the limit relation is no longer acceptable. The reason for that is the sorption behavior of reactive dyes at increasing dye concentrations. At lower dye concentrations the number of covalent bonding sites for reactive dye molecules is enough for almost all the dye molecules which make sorption from the dye bath into the fiber to make covalent bonds. At higher dye concentrations the number of dye molecules is in excess when compared with the covalent bonding sites in the fibers.

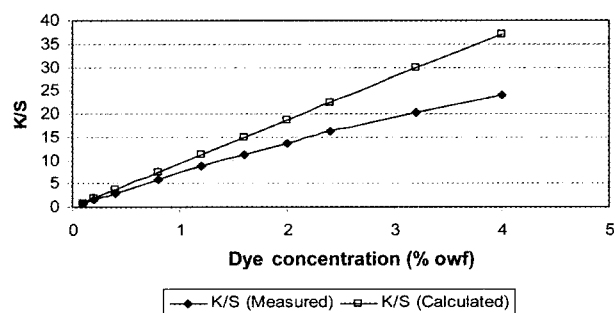


Figure 2. K/S (measured) and K/S (calculated) values against dye concentration for Black Reactive Dye.

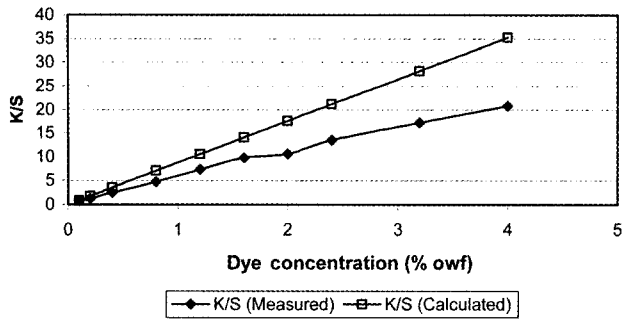


Figure 3. K/S (measured) and K/S (calculated) values against dye concentration for Reactive Red 180.

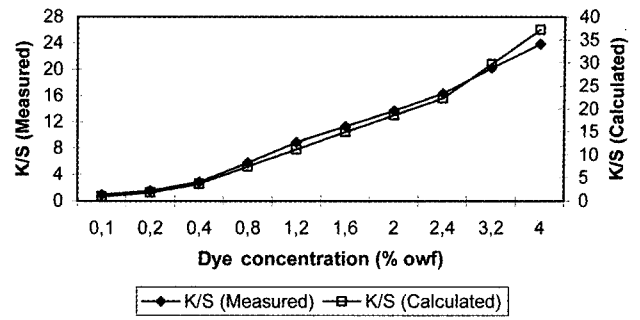


Figure 6. K/S (measured) and K/S (calculated) values against dye concentration for Black Reactive Dye.

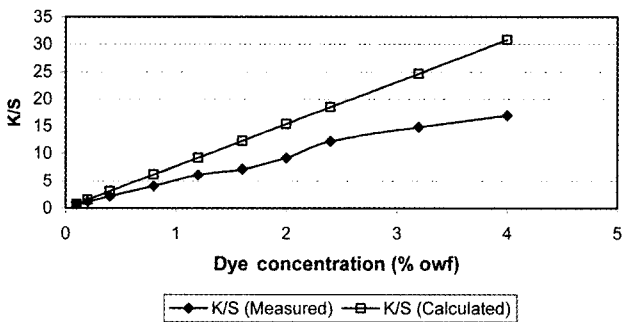


Figure 4. K/S (measured) and K/S (calculated) values against dye concentration for Reactive Yellow 176.

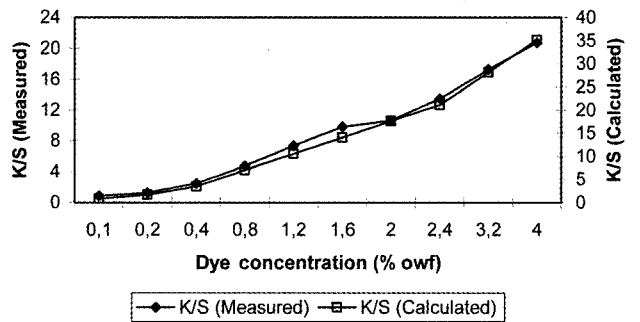


Figure 7. K/S (measured) and K/S (calculated) values against dye concentration for Reactive Red 180.

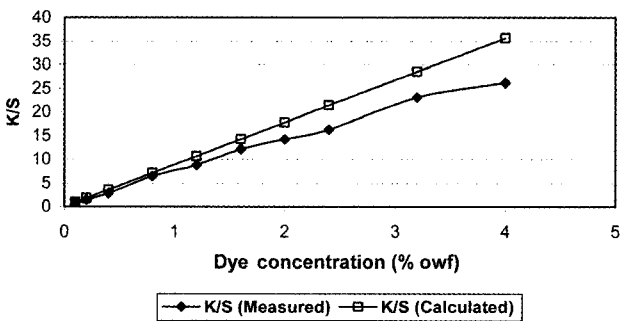


Figure 5. K/S (measured) and K/S (calculated) values against dye concentration for Reactive Blue 171.

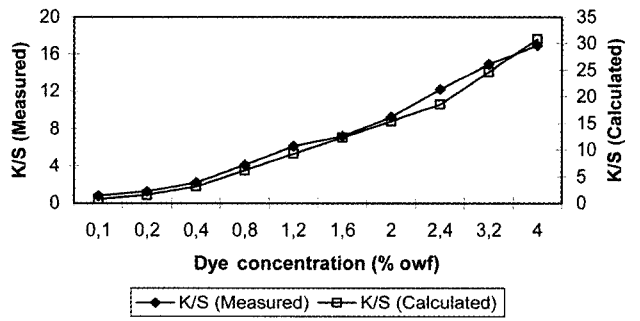


Figure 8. K/S (measured) and K/S (calculated) values against dye concentration for Reactive Yellow 176.

For that reason more dyes stay in the dyebath unfixed and K/S values do not continue to rise rapidly. The limit approach derived in this paper does not take the number of covalent bonding sites in the fiber into account.

The K/S values given in Figures 2-5 are presented again in Figures 6-9 in two y-axis scales. It is observed from Figures 6-9 that the measured and calculated K/S values fit with each other almost at all dye concentrations indicating the validity of the limit approach when the K/S values are plotted in the same figure according to their own scales. If the limit approach was useless, the measured and calculated K/S values would not be very close to each other.

The advantage of the two scale plot is that the measured

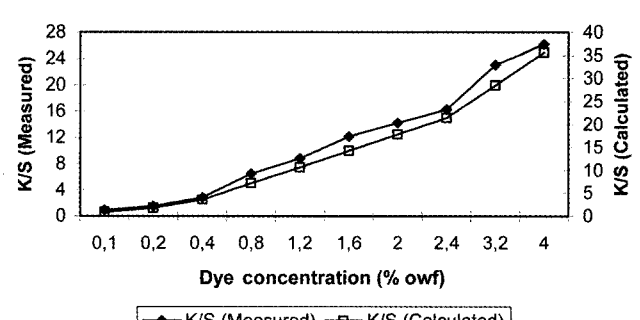


Figure 9. K/S (measured) and K/S (calculated) values against dye concentration for Reactive Blue 171.

and calculated K/S values are placed according to their own scales and the relation of the values are observed by taking the two scales into account. If the limit relation was not an acceptable one, then the plots would be much different than the ones observed in Figures 6-9. The measured and calculated K/S values almost fit with each other indicating the experimental application of the limit approach in reactive dyeing.

Conclusions

The experimental application of a novel approach regarding the use of K/S values is presented in the paper. The experimental presentation is carried by using reactive dyes on cotton knitted fabric. It is well-known from the dyeing theory that the dyeing of cotton fibers with ionic dyes follows the Freundlich isotherm which does not present a limit dye uptake concentration in practical concentration ranges. The initial slope of the Freundlich isotherm is almost a straight line which shows that there is a proportion between the dye in the dyebath (g/l) and the dye on the substrate (mol/kg). The limit relation given in the paper can be useful to calculate predicted K/S values at the initial part of the isotherm where the dye concentration is low. Also by using the K/S value of the initial dyeing which is carried out at very low concentration,

predicted K/S values can be calculated by using equation (10).

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