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〈Research Paper〉

Coloration behaviors of phthalocyanine reactive dye on nylon substrates: experiments, empirical modeling and statistical analysis

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Abstract— This research article explores the use of phthalocyanine reactive dye on nylon substrate. The effect of factors such as pH, temperature, liquor ratio and alkali addition on level of dye exhaustion, fixation and total fixation efficiency. Low pH, high temperature and low liquor ratio were found to be suitable conditions for maximum % exhaustion values. The effect of sulphatoethylsulphone (SES) and vinylsulphone (VS) form of the dyes on level of dye fixation was also discussed. The optimized exhaustion (%E), fixation (%F) and total fixation efficiency were determined. Modification of the dyeing process with alkali addition displayed that dye fixation (%) increased by alkali addition. Vinylsulphone (VS) moiety of the dye was found to be superior for maximum fixation (%F). Appropriate predictable empirical models, relatively a new approach in dyeing processes, were developed incorporating interactions effects of temperature, pH and liquor ratio for predicting % exhaustion, fixation and total fixation efficiency. The significance of the mathematical model developed was ascertained using microsoft excel regression (solver) analysis module. High correlation coefficient was obtained (R2=0.9895 for % exhaustion, R2=0.9932 for fixation, R2=0.9965 for total fixation efficiency) for the model which shows prominent prediction capacity of the model for any conditions. The predictable polynomial equations developed from the experimental results were thoroughly analyzed by ANOVA (Analysis of Variance) statistical concepts.

Keywords: *nylon substrate, phthalocyanine reactive dye, empirical modeling, statistical analysis*

1. Introduction

Phthalocyanines are well documented group of synthetic dyes that can be used as industrial dyes, optical sensors, in electrocatalytic oxidation etc. Phthalocyanines and porphyrins appear most attractive candidates as photo sensitizer dyes since they absorb throughout the visible region and into near IR. In particular, phthalocyanines having sulphonte anions are readily soluble peripherally substituted derivatives; possess a wide range of chemical and physical properties[1]. This makes them interesting building blocks for a number of applications and materials.

Generally, it is well known that considerable substantivity is imparted to anionic dyes, specifically acid dyes and direct dyes and reactive dyes due to the presence of terminal amino groups in nylon substrates. The 1:2 pre-metallised acid dyes are generally being used on nylon substrates when reasonable levels of wet fastness are required[2,3]. However, colorations or dyeings on nylon materials using these dyes suffer color loss during laundering with the result that the vagrant dye is able to stain adjacent materials.

Therefore, to secure highest levels of wet treatment durability, recourse is often required to an aftertreatment with commercial fixing systems[4].

From this point of view, application of reactive dyes has attracted interests to solve these problems[5]. Phthalocyanine dyes based on C.I. Reactive Blue 21[6] used in this study having

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reactive group react chemically with amino groups within the nylon substrates to form covalent bonds. Theoretically, by virtue of the covalent nature of the dye-nylon fiber bond, reactive dyeings on nylon substrates can display excellent wet treatment fastness without any recourse to an aftertreatment. However, in terms of the dyeing of nylon substrates with the above mentioned phthalocyanines dye; the nature investigation of the interaction between dye and fiber has been interested. Thus, the aim of this work is to examine the use of phthalocyanine dyes on nylon fibers and to explore the effect of factors such as pH, temperature and liquor ratio on level of dye exhaustion. In addition, the effect of factors such as alkali addition and SES/VS conversion on level of dye fixation was determined.

Literatures could be found for the investigation of the effects of various process variables on the dye exhaustion, fixation and total fixation efficiency with the substrate. But, developing the empirical polynomial model[7] equations relating the process variables with dye exhaustion, fixation to predict the dynamic behaviour of the process is relatively new approach in the dyeing processes. Thus, this article is also aimed at developing an empirical model to relate the process variables with the phthalocyanine dye exhaustion and fixation. In addition to this, statistical analysis of the data and model equation, a relatively new study in the dyeing processes, was carried out for the experimental data to assess the quality of the model.

2. Experimental

2.1 Reagents and materials

All chemicals used were analytical grade and doubly distilled water was always used. Nylon fibers were obtained from Korea Apparel Testing and Research Institute (*KATRI*). Phthalocyanine reactive dye was kindly supplied from Clariant Co. The chemical structure of copper complex phthalocyanine reactive dye is shown in Fig. 1. All other chemicals used were laboratory grade reagents.

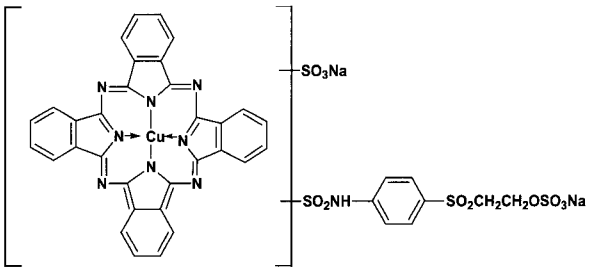

Fig. 1. Structure of the reactive copper phthalocyanine(CuPc) reactive dye.

2.2 Apparatus

A TU-1800 PC UV/Vis spectrophotometer was used for measuring the absorbance and recording the normal and derivative spectra. A Corning model 220 pH meter was used for pH measurements. Colorimetric data of the dyeings were determined using a Datacolor SF 600 plus spectrophotometer interfaced to a PC.

2.3 Dyeing

Nylon fiber (4g) was dyed with 2% o.w.f. phthalocyanine dye in a sealed, stainless steel dye pots of 120cm^3 capacity in a laboratory-scale dyeing machine (ACE-6000T). Samples were placed in a 40°C dye bath of four different liquor ratios. After 10min, the temperature was raised until it reaches 70°C-110°C at 2°C/min and then continued for 60min.

The dyed samples were washed off using water and dried at room temperature. Fig. 2 shows the reaction scheme of the dyeing of phthalocyanine reactive dye with nylon fiber.

2.4 Color strength (K/S) of nylon fiber

Reflectance measurements on the dry dyed fibers were carried out using a Datacolor SF 600 plus spectrophotometer interfaced to a PC.

Measurements were taken with the specular component of the light excluded and the UV component included, using illuminant D_{65} and 10° standard observer. The average of three reflectance measurements, taken at different

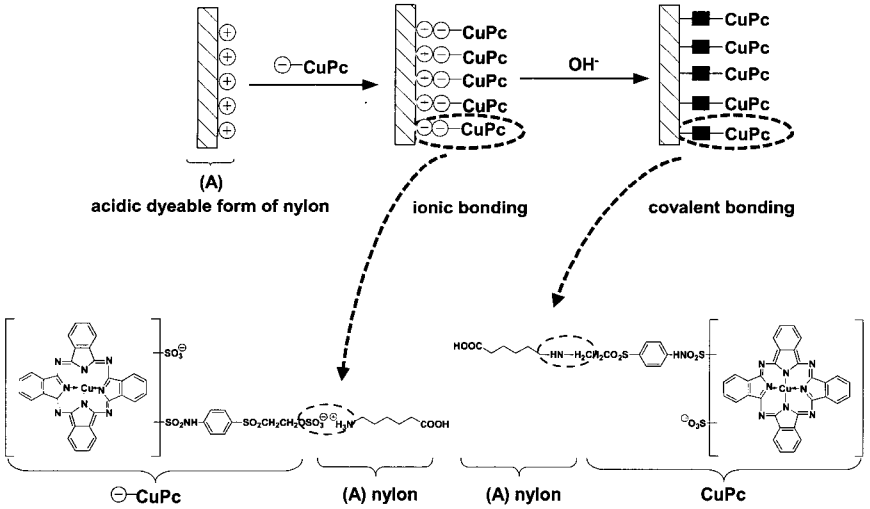

Fig. 2. Reaction mechanism of nylon fiber with copper complex phthalocyanine(CuPc) reactive dye.

positions on the dyed fibers, was used. Color strength (K/S) was calculated by the Kubelka-Munk formula:

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

where K, S and R are the coefficient of absorption, scattering of the dye and the reflected light at wavelength respectively at λ_{max}.

2.5 Determination of exhaustion(%E), fixation (%F) and fixation efficiency(%FE)

Using a previously established absorbance /concentration relationship at the λ_{max} of the phthalocyanine reactive dye, the quantity of dye in solution was calculated and then extent of exhaustion(%E) was determined using the formula:

$$\%E = \frac{[D_o - D_t]}{D_o} \times 100 \quad (2)$$

Unfixed phthalocyanine dye from the substrates was extracted using 25% aqueous pyridine solution and then measured with spectrophotometer. The extent of fixation(%F) and fixation efficiency(%FE) were calculated by the formula:

$$\%F = \frac{[D_o - D_t - D_e]}{[D_o - D_t]} \times 100 \quad (3)$$

$$\%FE = \frac{[E \times F]}{100} \quad (4)$$

where D_0 and D_t are the quantity of dye in initial and residual dye in final bath respectively. D_e is the amount of extracted dye. Those values were calibrated through absorbance measurement of original and exhausted bath by UV-Vis spectrophotometer.

2.6 Empirical modeling

Empirical model i.e., second order polynomial regression equations were developed using excel solver function to predict the % exhaustion, % fixation and total fixation efficiency relating the process variables i.e., pH, temperature and liquor ratio. RMSE (Root Mean Square Error) is the important tool to validate the model equation for its prediction capacity[8]. The RMSE is the distance, on average, of a data point from the fitted line, measured along a vertical line. If the value of the RMSE is zero, then the model is perfectly predicting the behaviour of the system i.e., ideal model. The prediction capacity of the model thus decreases with respect to the corresponding value of the RMSE from zero. Thus, series of the equations varying the combinations of the variables like interactions effects and squared effects were run using solver function so as to get the least value of the RMSE. The goodness of fit is a

measure of how well the model fits the data. Model is only developed with a sample, and the value of the model depends on the clarity and un-ambiguity of the relationships between the independent variables.

The behaviour of the system was explained by the following empirical model[8]:

$$Y = \beta_0 + \Sigma \beta_i x_i + \Sigma \beta_{ij} x_i^2 + \Sigma \beta_{ij} x_i x_j \quad (5)$$

where, Y is the dependent variable, β are the regression coefficients, x are independent data. Root Mean Square Error (RMSE) was calculated using the following formula[8],

$$RMSE = \sqrt{\frac{\sum_{0}^{N} (Exp. - Pred.)^2}{N}} \quad (6)$$

where, Exp. is the experimental value, Pred. is the predicted value from model equations and N is the total number of experiments.

2.7 Data analysis

Statistical analysis of the experimental data was performed in detail. The quality of the fit of the polynomial model equation was expressed by the coefficient of determination R^2 and its statistical significance was analyzed by Fisher's *F*-test and Student's *t*-test[Analysis of Variance (ANOVA)]. The level of significance was given as values of *P* less than 0.0001.

3. Results and Discussion

3.1 Effect of pH, dyeing temperature and liquor ratio

An initial study was made on the effect of pH on dyeing. At first, dyeing was conducted under acidic (pH 3), neutral (pH 7) and alkaline (pH 12) condition. The pH was adjusted using 2g/ℓ Na_2CO_3 for alkaline condition and 2g/ℓ CH_3COOH for acidic condition. The results in Table 1 show that acidic condition shows high color strength. The color strengths obtained under neutral and alkaline conditions were very low compared with acidic conditions. Fig. 3 shows that exhaustion(%E) of the dye on nylon increases with decrease in pH and fixation(%F) of the dye on nylon increases with increasing pH. Fig. 4 shows that higher total fixation efficiency was obtained at pH 3. From the results, pH 3 was chosen as optimum value to achieve maximum exhaustion and fixation efficiency.

Table 1. Effect of pH on color strength (K/S, 629nm)

	Color strength of dyeings (K/S, 629nm)		
	Acidic (pH 3)	Neutral (pH 7)	Alkaline (pH 12)
Phthalocyanine dye	3.66	1.74	0.69

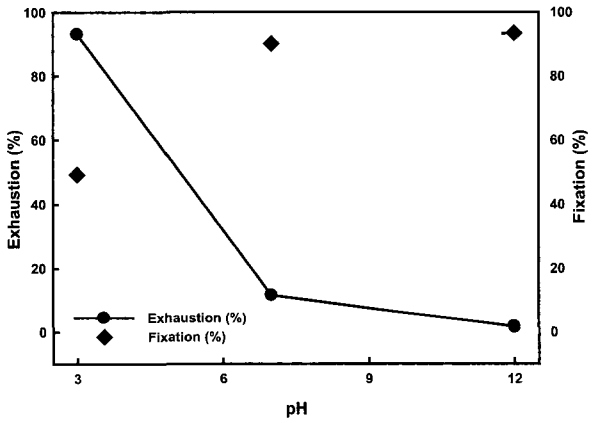

Fig. 3. Effect of pH on exhaustion(%E) and fixation(%F).

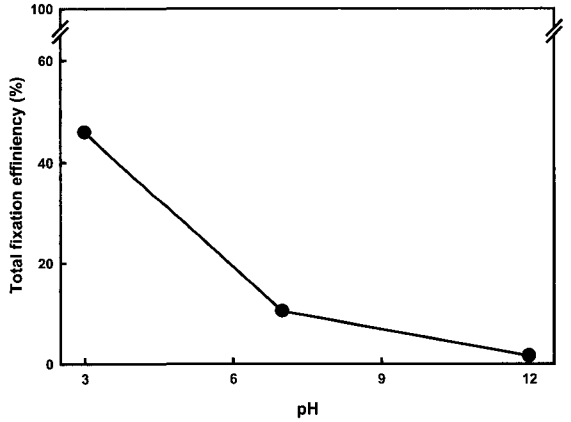

Fig. 4. Effect of pH on fixation efficiency(%FE).

In the case of lower pH, higher extent of protonation of the amino groups within nylon substrates leads to high exhaustion(%E) and low fixation(%F), because the ensuing low concen-

trations of nucleophilic amino groups in the substrates are unable to react with the dye. In addition, under these conditions, it can be assumed that the dye was largely in sulphato-ethylsulphone form and, therefore, few dye molecules were present in the reactive vinyl sulphone form. In contrast, at higher pH conditions, dye exhaustion(%E) was low due to the low extent of amino group protonation, although dye coloration did undergo covalent reaction to give the high fixation(%F) levels seen.

Having ascertained that dyeing was optimally achieved at acidic condition (pH 3), effect of dyeing temperature was studied at this pH value.

The results in Fig. 5 and Fig. 6 show that maximum exhaustion(%E), fixation(%F) and total fixation efficiency(%FE) were obtained at higher-temperature of 100-110°C. This efficiency can be attributed to the higher kinetic energy of the dye molecules and their consequent greater migration power within the substrates.

In addition, a higher extent of fiber swelling would have contributed to the increased dye exhaustion.

Another important variable to be considered in the processes is liquor/fiber ratio. Selection of appropriate liquor ratio contributes to producing desired results. The experiments were carried out at four different liquor ratios 15:1, 20:1, 25:1 and 30:1. The results in Fig. 7 and Fig. 8 show that lower liquor ratio resulted in higher %exhaustion and increase in liquor ratio resulted in decrease in % exhaustion. This may be attributed to the fact that lowering the liquor ratio results in concentrated solution with maximum probable molecular collisions between nylon and phthalo

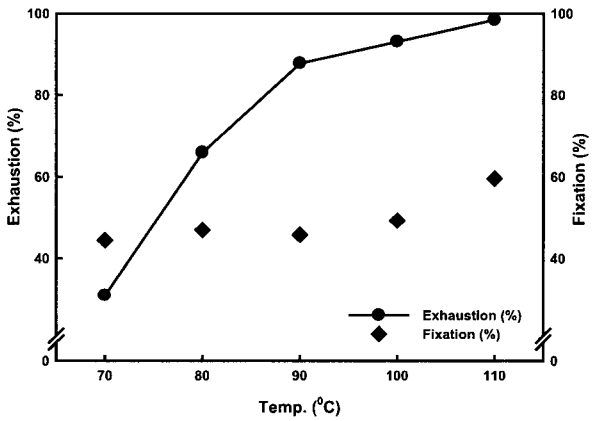

Fig. 5. Effect of temperatures on exhaustion (%E) and fixation(%F).

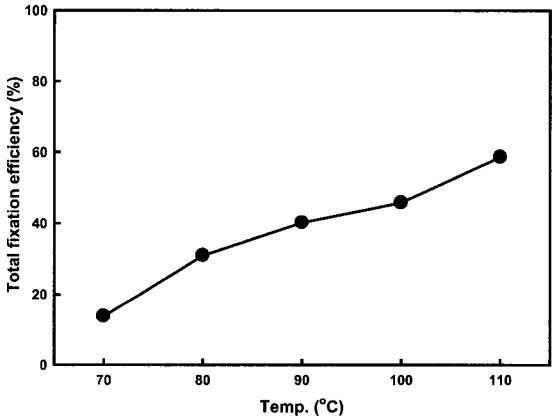

Fig. 6. Effect of temperatures on fixation efficiency (%FE).

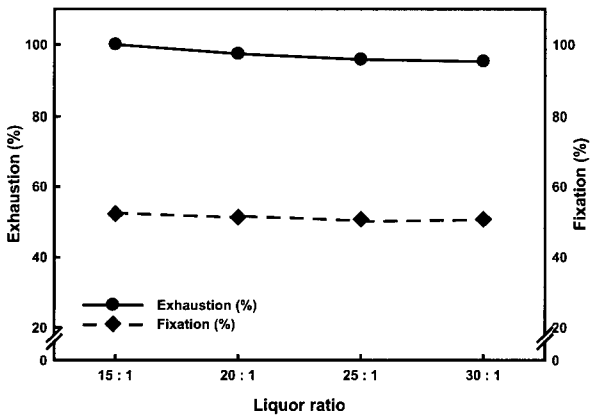

Fig. 7. Effect of liquor ratio on exhaustion(%E) and fixation(%F).

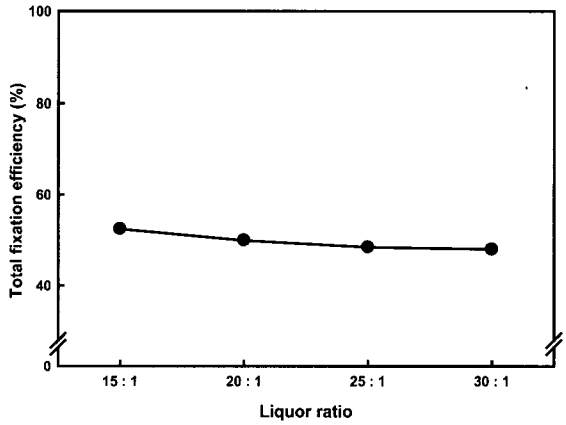

Fig. 8. Effect of liquor ratio on fixation efficiency (%FE).

cyanine. Thus, making more number of phthalocyanine molecules to interact with fiber. Hence the % exhaustion was increased. On the other hand, higher liquor ratio leads to more diluted state and less probable collision of the molecules and thus making less number of phthalocyanine molecules available for the reaction.

3.2 Effect of alkali addition for increasing fixation(%F)

To achieve higher dye fixation, alkali addition to the dyebath was carried out with the modification that 2g/l Na_2CO_3 was added after 15, 30 and 50 min at 100°C. The results of dyeing carried out with alkali additions are given in Fig. 9 and Fig. 10. It is shown that dye fixation(%) increased by alkali additions. However, at the initial alkali addition, exhaustion(%E) was decreased by interfered exhaustion effects due to low amino group protonation. In addition, this inefficiency could occur, presumably, as a consequence of the loss of dye as dye desorbed from the fiber under the increased pH conditions.

3.3 Effect of SES/VS form for increasing fixation(%F)

The study of increasing fixation(%F) under the conditions employed led to an examination of the dye structure in which the vinylsulphone (VS) moiety was present during fixation process. In other words, it should be possible to convert the sulphatoethylsulphone (SES) moiety of the dye to the reactive vinylsulphone (VS) form in a separate step, before dyeing is carried out. It is proposed that this modified dye might then be applied at a pH more appropriate to exhaustion and still undergo an efficient reaction with fiber substrates. An aqueous solution of the dye was prepared at 70°C and pH 8 was continued for 30min using Na_2CO_3. The pH value is most important in this stage. An outline process for converting the dye from the sulphatoethylsulphone form to the vinylsulphone form[9] is given in Fig. 11.

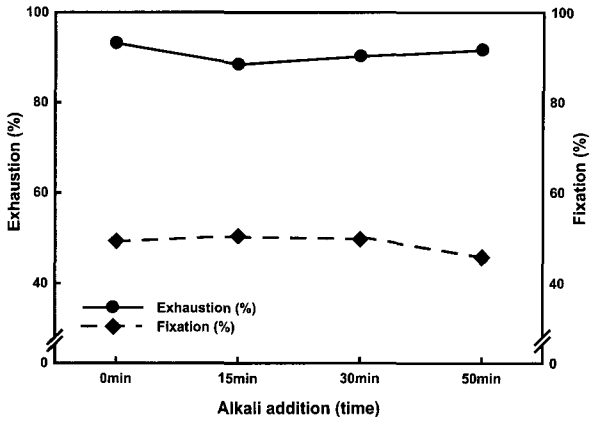

Fig. 9. Effect of process modification on exhaustion (%E) and fixation(%F).

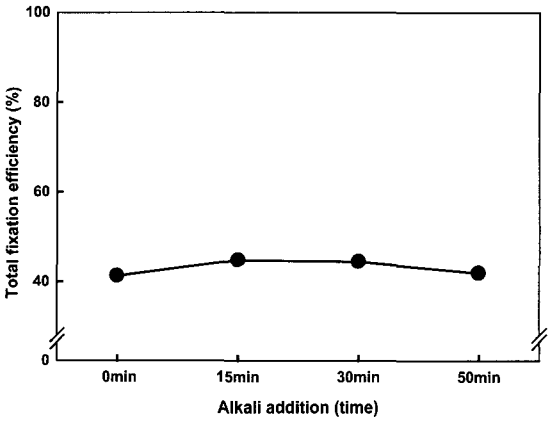

Fig. 10. Effect of process modification on fixation efficiency(%FE).

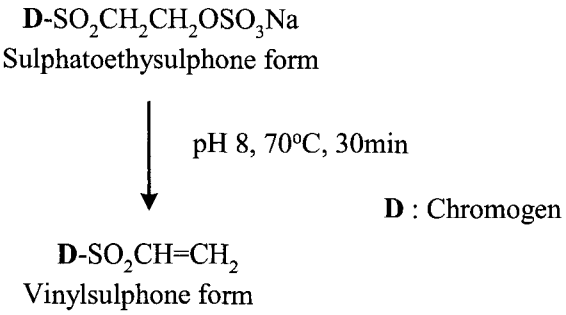

Fig. 11. Conversion of sulphatoethylsulphone form to vinylsulphone form.

Dyeing was then carried out under acidic condition (pH 3) at 100°C using both the original dye (SES form) and the converted dye (VS form). The extent of exhaustion and fixation of these two forms of the dye on nylon fiber are shown in Fig. 12. As expected the applied pH was resulted with good exhaustion for both forms of the dye. However, the vinylsulphone

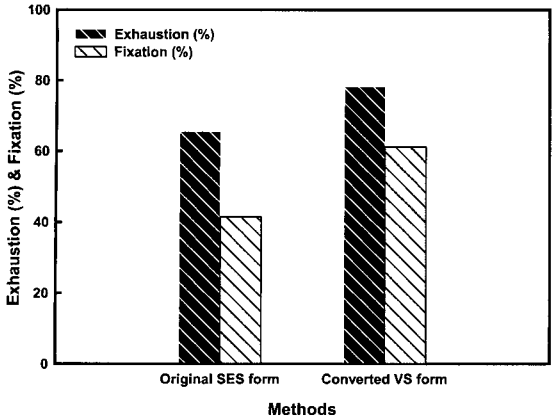

Fig. 12. Dyeing comparisons on exhaustion(%E) and fixation(%F) between original(SES) and converted(VS) forms.

form of the dye reacts more readily under this pH condition and gives much better fixation than the sulphatoethylsulphone form. In order to achieve the good fixation, the correct form the dye needs to be used. A separate pre-conversion step is very unlikely to be followed; hence efforts are needed to modify the dyeing process to accomplish the conversion as part of the dyeing itself.

3.4 Model fitting

An empirical model is a simplified mathematical representation of a system or a phenomenon by polynomial regression equations that is based on experimentation. An empirical model is necessarily developed to predict the dynamic behaviour of the processes at various conditions. In this context, to predict the behaviour of phthalocyanine dye exhaustion and fixation at various experimental conditions, a polynomial regression equation was successfully developed using Excel solver function.

Using the experimental results, the regression model equations (second order polynomial) relating the % exhaustion, fixation, total fixation efficiency and process variables were developed and are given in equations (7),(8) and (9) respectively.

Polynomial regression equation for % exhaustion of phthalocyanine on nylon substrates;

$$Y= - 354.05 - 42.1880(X_1) + 10.9546(X_2) - 1.2348(X_3) + 2.1146(X_1X_1) - 0.0519(X_2X_2) + 0.02044(X_3X_3) \quad R^2=0.9895 \qquad (7)$$

Polynomial regression equation for % fixation of phthalocyanine on nylon substrates;

$$Y=69.23(X_1) + 20.1235 -1.8493(X_2) - 0.52293(X_3) - 1.02571(X_1X_1) - 0.0122(X_2X_2) + 0.00931(X_3X_3) \quad R^2=0.9932 \qquad (8)$$

Polynomial regression equation for total fixation efficiency of phthalocyanine on nylon substrates;

$$Y= -55.59(X_1) - 17.99 + 2.4867(X_2) - 1.2293(X_3) + 0.8526(X_1X_1) - 0.0081(X_2X_2) + 0.0206 (X_3X_3) \quad R^2=0.9965 \qquad (9)$$

where, X_1=pH, X_2= temperature, X_3= liquor ratio.

The empirical model consists of a function that fits the data. The graph of the function goes through the data points approximately. Thus, although we cannot use an empirical model to explain a system, we can use such a model to predict behavior where data do not exist. Data are crucial for an empirical model.

An empirical model is based only on data and is used to both predict and explain a system. An empirical model consists of a function that captures the trend of the data. The fitted model shows very high coefficient of determination (R^2 = 0.9895 for % exhaustion, R^2 = 0.9932 for fixation and R^2 = 0.9965 for total fixation efficiency).

The model was found to be exactly predicting the dye uptake theoretically and thus could be effectively used to predict the dye uptake even without performing any experiments within the experimental ranges[7]. This implies that 98.95%, 99.32% and 99.65% of the sample variation for % exhaustion, fixation and total fixation efficiency are explained by the independent variables and this also means that the model did not explain only about 0.0105%, 0.0068% and 0.0035% of sample variation for exhaustion and fixation respectively. The predicted values from the model equations were plotted against experimental values and are shown in Fig. 13.

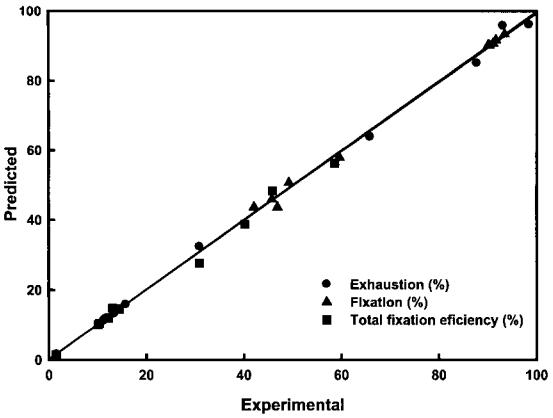

Fig. 13. Experimental and Predicted values of % exhaustion, fixation and total fixation efficiency.

3.5 Statistical study

The statistical analyses were done by means of Fisher's *F*-test and Student's *t*-test. The student's *t*-test was used to determine the significance of the regression coefficients of the variables. The *P*-values were used as a tool to check the significance of the variables, which in turn may indicate the patterns of the interactions among the variables. In general, larger the magnitude of *t* and smaller the value of *P*, the more significant is the corresponding coefficient[10]. The regression coefficient, *t* and *P* values for all linear, quadratic and interaction effects of the variables are given in Table 2-4 for % exhaustion, fixation and total fixation efficiency respectively.

It was observed that the coefficients for the linear effect of pH and temperature was highly significant for % exhaustion (*P*=0.000, *P*=0.002), fixation (*P*=0.000, *P*=0.002) and total fixation efficiency (*P*=0.000, *P*=0.097). The linear effect of liquor ratio was considered to be least significant for all three responses. The squared effect of pH and temperature for % exhaustion (*P*=0.000, *P*=0.001), fixation (*P*=0.000, *P*=0.068) were considered to be significant. Only pH was considered to be significant for total fixation efficiency (*P*=0.000).

The squared effect of liquor ratio for all three responses was considered to be least significant with higher *P* value.

The statistical significance of the ratio of mean square variation due to regression and mean square residual error was tested using Analysis of Variance (ANOVA). ANOVA is a statistical technique that subdivides the total variation in a set of data into component parts associated with specific sources of variation for the purpose of testing hypotheses on the parameters of the model[10]. According to the ANOVA, which is shown in Table 5-7 for % exhaustion, fixation and total fixation efficiency respectively, $F_{Statistics}$ values for all regressions were higher. The large value of $F_{Statistics}$ indicates that most of the variation in the response can be explained by the regression model equation.

Table 2. Estimated regression coefficients and corresponding t and p values for % exhaustion

Term	Coefficients	SE coefficients	*t*	P
Constant	-354.05	2.035	-2.071	0.093
X_1	-42.1880	1.454	-32.410	0.000
X_2	10.9546	1.570	20.315	0.000
X_3	-1.2348	1.702	-1.386	0.224
X_1X_1	2.1146	2.082	20.577	0.000
X_2X_2	-0.0519	2.684	-7.775	0.001
X_3X_3	0.02044	2.657	0.449	0.672

Table 3. Estimated regression coefficients and corresponding t and p values for % fixation

Term	Coefficients	SE coefficients	*t*	P
Constant	67.67	1.604	55.026	0.000
X_1	20.12	1.146	18.601	0.000
X_2	-1.814	1.238	5.773	0.002
X_3	-0.5232	1.342	-0.581	0.587
X_1X_1	-1.0258	1.642	-12.654	0.000
X_2X_2	0.01201	2.116	2.317	0.068
X_3X_3	0.00934	2.095	0.250	0.812

Table 4. Estimated regression coefficients and corresponding t and p values for total fixation efficiency

Term	Coefficients	SE coefficients	*t*	P
Constant	-55.5966	59.1094	-0.941	0.390
X_1	-17.9998	1.4871	-12.104	0.000
X_2	2.4867	1.2203	2.038	0.097
X_3	-1.2279	2.1459	-0.572	0.592
X_1X_1	0.8526	0.1041	8.190	0.000
X_2X_2	-0.0081	0.0068	-1.186	0.289
X_3X_3	0.0206	0.0478	0.431	0.684

The associated *P*-value is used to estimate whether $F_{Statistics}$ is large enough to indicate statistical significance. A *P*-value lower than 0.0001 (i.e., α = 0.0001, or 99.99% confidence) indicates that the model is considered to be statistically significant[10]. The ANOVA table also shows a term for residual error, which measures the amount of variation in the response data left unexplained by the model. The form of the model chosen to explain the relationship between the factors and the response is correct.

The $F_{Statistics}$ values of 426.61, 222.72 and 94.12 for % exhaustion, fixation and total fixation efficiency are greater than tabulated $F_{6,7}$ values indicate that the fitted model exhibits no lack of fit (0.001) at the confidence level. ANOVA indicated that the second-order polynomial model (Equation 7,8 and 9) was highly significant and adequate to represent the actual relationship between the response and the variables.

Table 5. ANOVA for % exhaustion

Source	Degree of freedom (DF)	Sum of squares (SS)	Mean square (MS)	$F_{statistics}$	P
Regression	6	17023.6	2837.26	426.61	0.000
Linear	3	13468.1	2751.69	413.74	0.000
Square	3	3555.5	1185.15	178.20	0.000
Residual Error	5	33.3	6.65		
Lack of fit	3	33.3	11.08		
Pure error	2	0.00	0.00		
Total	11	17056.8			

Table 6. ANOVA for % fixation

Source	Degree of freedom (DF)	Sum of squares (SS)	Mean square (MS)	$F_{statistics}$	P
Regression	6	5523.31	920.552	222.72	0.000
Linear	3	4686.37	613.636	148.46	0.000
Square	3	836.94	278.980	67.50	0.000
Residual Error	5	20.67	4.133		
Lack of fit	3	20.67	6.889		
Pure error	2	0.00	0.000		
Total	11	5543.98			

Table 7. ANOVA for total fixation efficiency

Source	Degree of freedom (DF)	Sum of squares (SS)	Mean square (MS)	$F_{statistics}$	P
Regression	6	3849.86	641.643	94.12	0.000
Linear	3	3306.35	419.402	61.52	0.000
Square	3	543.51	181.170	26.58	0.002
Residual Error	5	34.09	6.817		
Lack of fit	3	34.09	11.362		
Pure error	2	0.00	0.000		
Total	11	3883.94			

4. Conclusions

Phthalocyanine reactive dyes provide the opportunity for efficient dye-fiber reaction it shows that exhaustion(%E) of the dye on nylon substrates increased with increasing temperature, decreasing pH and liquor ratio values.

However, fixation(%F) of the dye on nylon fiber increased with increasing pH. When the dye was pre-converted to its VS form, much higher fixation(%F) was obtained. VS form of the dye was favorable to covalent bonding reaction on fiber substrates. An appropriate empirical model was developed to predict the behaviour of the process using excel solver functions and very high correlation coefficient was obtained. The statistical significance of the model equations were thoroughly analyzed and discussed.

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