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〈Research Paper〉

Central Composite Design Matrix (CCDM) for Phthalocyanine Reactive Dyeing of Nylon Fiber: Process Analysis and Optimization

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Abstract— The objective of this study was to apply the statistical technique known as design of experiments to optimize the % exhaustion variables for phthalocyanine dyeing of nylon fiber. In this study, a three-factor Central Composite Rotatable Design (CCRD) was used to establish the optimum conditions for the phthalocyanine reactive dyeing of nylon fiber. Temperature, pH and liquor ratio were considered as the variable of interest. Acidic solution with higher temperature and lower liquor ratio were found to be suitable conditions for higher % exhaustion. These three variables were used as independent variables, whose effects on % exhaustion were evaluated. Significant polynomial regression models describing the changes on % exhaustion and % fixation with respect to independent variables were established with coefficient of determination, R2, greater than 0.90. Close agreement between experimental and predicted yields was obtained. Optimum conditions were obtained using surface plots and Monte Carlo simulation techniques where maximum dyeing efficiency is achieved. The significant level of both the main effects and interaction was observed by analysis of variance (ANOVA) approach. Based on the statistical analysis, the results have provided much valuable information on the relationship between response variables and independent variables. This study demonstrates that the CCRD could be efficiently applied for the empirical modeling of % exhaustion and % fixation in dyeing. It also shows that it is an economical way of obtaining the maximum amount of information in a short period of time with least number of experiments.

Keywords: *factorial design, optimization, statistical analysis, phthalocyanine reactive dye, nylon fiber*

1. Introduction

As nylon has a compact structure and high crystallinity, the choices of dyes and dyeing methods for nylon have long attracted research interest. Copper phthalocyanine (CuPc), well-known colorants for almost a century, is an appealing compound for a variety of applications. Besides its intense colour and efficient energy absorption, more remarkable properties have been discovered due to their 18p-electron conjugated system[1]. Due to their wide range of chemical and physical properties, it is extensively being applied in light-emitting diodes (OLEDs), organic thin film transistors (OTFTs), photoconductive layers of photocopying machines, solar cells and some of the biomedical applications include semiconductors, catalysts, chemical sensors, liquid crystals, nonlinear optics and electrochromic displays[2]. Depending on the choice of the metal ion, these complexes maybe used for applications ranging from conventional dyestuffs to catalysis, from coatings for read/write CD-ROMs to an anti-cancer agent. Nowadays their use as dyestuffs is increasing, because of colour fastness on the fabric[3]. Thus, phthalocyanine reactive dye is investigated in this study for its dyeing characteristics with nylon fiber. Phthalocyanine dyes[4] based on C.I. Reactive Blue 21 (Fig. 1) used in this study having reactive group react chemically with amino groups within the nylon substrates to form covalent bonds. By virtue of the covalent nature of the dye - fiber

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bond, these reactive dyes commonly display excellent fastness to washing and light exposure without recourse to an aftertreatment. Though investigating the dyeing characteristics is not a new approach in dyeing industry, use of statistical experimental design to design skillful experiments is relatively a new approach. The optimization of dyeing variables through factorial experimental design might play an important role in improving their exhaustion efficiency. Exhaustion studies may reveal the amount of dye uptake in the fiber, and when it is higher, the fiber can exhibits strong coloring properties. In this part of study, the optimization for % exhaustion was mainly carried out.

Different strategies can be used for the optimization of variables. Conventional 'one variable at a time' approach has been traditionally used for investigating any system in any industry.

However, it is time consuming and often leads to confusion in understanding the process parameters. On the other hand, use of statistical methods, enables easy selection of important parameters from a large number of factors and also interactions between important variables can be understood. A number of statistical experimental designs have been used for optimizing the process variables. Central composite rotatable design is a well established and widely used statistical technique for screening and selection of variables. Factorial experimental design provides important information regarding the optimum level of each variable, its interactions with other variables and their effects on product yield. Factorial experimental design has been reported to be an effective tool for optimising a process, when the independent variables have a combined effect on the desired response. Such experiments were generally performed using different combination of experimental variables or factors according to a predetermined design such as central composite rotatable design (CCRD).

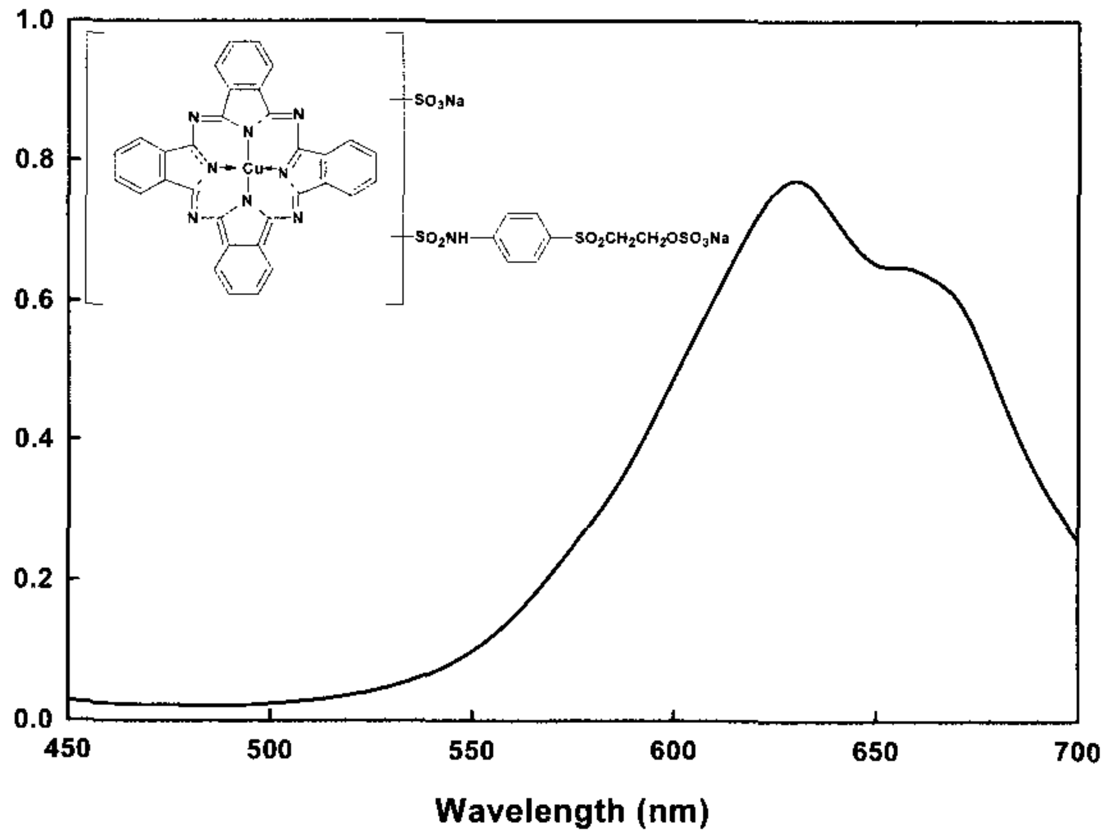

Fig. 1. Molecular structure and UV spectrum of the phthalocyanine reactive dye.

2. Factorial experimental design and data analysis

The experimental design chosen for this study was that central composite rotatable design, a fractional factorial design for three variables5).

This design was preferred as only a few experimental combinations of the variables are adequate to estimate the complex response functions. Three levels, such as low, medium and high, denoted as -1, 0 and +1, respectively in coded level of variables, were employed to fit a full quadratic response surface model and later approximated to obtain the optimal response.

Independent variables, experimental ranges and levels for phthalocyanine treatment are given in Table 1. The design variables selected in this study with actual levels along with response variables are shown in Table 2. Seven duplicates are included at the centre of the design. The total number of test runs needed for this design was 20. The experimental conditions were selected for each variable based on prior studies.

Experiments were carried out according to the design points with independent variables such as pH (X_1), temperature (X_2), and liquor ratio (X_3).

Factorial statistical analysis was applied to analyse the effect of independent variables on response parameters (%E and %F) by matching the responses studied (Y) with the code factors using the polynomial model associated with experimental design.

Table 1. Experimental ranges and levels of variables for % exhaustion and % fixation of phthalocyanine reactive dye with nylon

Independent variables	Range and level				
	-α	-1	0	1	+α
pH (X_1)	1	1	2.5	4	5
Temperature (X_2)	73	80	90	100	106
Liquor ratio (X_3)	16	20	25	30	33

Table 2. Central Composite Rotatable Design (CCRD) for dyeing of phthalocyanine reactive dye with nylon

No	pH	Temperature	Liquor ratio	% Exhaustion		% Fixation	
				(Exp.)	(Pred.)	(Exp.)	(Pred.)
1	1	80	20	60.56	67.89	38.53	40.07
2	4	80	20	6.00	9.22	48.39	52.19
3	1	100	20	93.94	104.29	55.01	54.63
4	4	100	20	17.34	14.24	59.39	61.59
5	1	80	30	56.39	63.72	39.01	38.04
6	4	80	30	1.99	1.874	43.94	45.52
7	1	100	30	89.89	100.143	50.74	48.15
8	4	100	30	10.92	6.92	54.42	54.12
9	1	90	25	81.12	78.88	27.37	31.55
10	5	90	25	15.52	17.34	53.13	49.85
11	2.5	73	25	26.04	16.93	59.57	56.92
12	2.5	106	25	46.12	49.30	69.06	70.58
13	2.5	90	16	27.37	22.43	44.98	42.07
14	2.5	90	30	15.61	15.28	26.09	30.31
15	2.5	90	25	16.17	18.56	32.42	31.43
16	2.5	90	25	16.17	18.56	32.42	31.43
17	2.5	90	25	16.17	18.56	32.42	31.43
18	2.5	90	25	16.17	18.56	32.42	31.43
19	2.5	90	25	16.17	18.56	32.42	31.43
20	2.5	90	25	16.17	18.56	32.42	31.43

RMSE (Root Mean Square Error) is an important tool to validate the model equations for its prediction capacity6). The RMSE is the distance, on average, of a data point from the fitted line, measured along a vertical line. If the value of RMSE is zero, then the model is perfectly predicting the behaviour of the system i.e., ideal model. The predicting capacity of the model thus decreases with respect to the corresponding value of RMSE from zero. Thus, a series of equations by varying the combinations of the variables likelinear, 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 value of the model depends on clarity and un-ambiguity of the relationships between the independent variables.

The behaviour of the system was explained by the following empirical model[6]:

$$Y = \beta_o + \sum \beta_i x_i + \sum \beta_{ij} x_i^2 + \sum \beta_{ij} x_i x_j \quad (1)$$

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[6],

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

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

Statistical package Minitab (StatSoft, USA) was used for design, regression and ANOVA analysis. Response surface graphs were obtained from the regression equation in actual levels of variables, keeping the response function on the Z axis with X and Y axes representing the independent variables while keeping the other variable constant at the center (corresponding to 0, 0 coded level) points. The results were validated and confirmed by carrying out the experiments with values, which were not the design points.

2.1 Nature of optimum and simultaneous optimization

Monte Carlo analysis[7] was performed on the predicted quadratic polynomial model to examine the overall shape of responses and characterize the nature of the stationary point. Optimization of the response function consists of its transition from the origin to the stationary points. The response function was expressed in terms of the new variables, the axis of which corresponds to the principal axis of the contour system. The roots of the auxiliary equation were calculated initially to know the nature of optimum. The response would be maximum if all the roots show negative values and minimum if all the roots show positive values. If they show a combination of positive and negative values, it represents a saddle point or minimax. Simultaneous optimization was done according to the method suggested by Monte Carlo. All the individual desirability functions were combined into an overall desirability function, which is defined as geometric mean of individual desirability functions. Higher the desirability value more desirable is the system.

3. Experimental methods

3.1 Reagents and materials

All chemicals used were of analytical grade and doubly distilled water was always used. Nylon 6.6 was purchased from Korea Apparel Testing and Research Institute (KATRI). Phthalocyanine reactive dye was kindly supplied by Clariant Co.

3.2 Apparatus

A Hewlett Packard UV-Vis spectrophotometer, Model HP8452 was used for measuring the absorbance and recording the normal and derivative spectra. A Corning model 220 pH meter was used for pH measurements.

3.3 Nylon treatment

Nylon 6.6 fiber (warp 70f24, weft 140f48, 2g) were treated with phthalocyanine in a sealed stainless steel dye pots of 120 cm^3 capacities. These were analysed in a laboratory-scale infra red dyeing machine (ACE-6000T). Experiments were performed according to response surface central composite rotatable design given in Table 2. Buffer solution[8] was used to maintain the pH. At the end of the experiments, nylon sample was removed, rinsed thoroughly in tap water and dried in open air. The exhaustion rate (%E) was then calculated using the formula,

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

where D_o and D_t is the quantity of phthalocyanine in the initial and final bath, respectively.

4. Results and discussions

Factors like pH, temperature and liquor ratio have always been of great interest to researchers in dyeing industry. These factors have also been determined to play a significant role in the determination of the efficiency of the dyeing processes. Therefore, it is of great significance to optimize the conditions for cost-efficient dyeing operations. In this context, phthalocyanine reactive dye is treated with nylon fiber and significance of the above mentioned factors is studied and collectively optimized using factorial experimental design concept. Experiments were designed using the statistical software Minitab ranging the independent variables as given in Table 1. Then, experiments were performed using the set of conditions given in the design matrix in Table 2.

4.1 Main effects of factors on dyeing efficiency

Nylon fiber was treated with phthalocyanine reactive dye and its feasible reaction mechanism is given in Fig. 2. The experimental results obtained were analyzed and the effects of each variable on % exhaustion were evaluated from the main effects plot shown in Fig. 3. It is observed from the Fig. 3 that acidic solution with higher temperature and lower liquor ratio were found to be suitable condition for higher % exhaustion.

In the case of lower pH, higher extent of protonation of the amino groups within nylon substrates leads to high exhaustion (%E), because the ensuing low concentrations of neucleophilic 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 sulphatoethlysulphone form and, therefore, few dye molecules were present in the reactive vinyl sulphone form[9]. But, at the same time, strong acidic pH of the dyeing solution leads to the degradation of the nylon polymer substrates. It is proposed that the degradation occurs in the amide bond of the nylon polymer chains which cause to the more number of amino groups in the nylon segmented chains. Thus, it is believed that the maximum % exhaustion occurs at the cost of basic functional groups of the nylon polymer chains in the strong acidic pH conditions. Based on the above scientific facts, strong pH ($3 < pH$) is not recommended in the commercial dyeing unit though the % exhaustion is very high. In this context, pH above 3 is normally preferred to avoid the damage to the basic functional groups of the nylon substrates. In contrast, at higher pH conditions, dye exhaustion (%E) was low due to low extent of amino group protonation.

Dye coloration underwent covalent reaction to give high fixation (%F) levels. High temperature (~ 100 °C) was found to yield higher exhaustion.

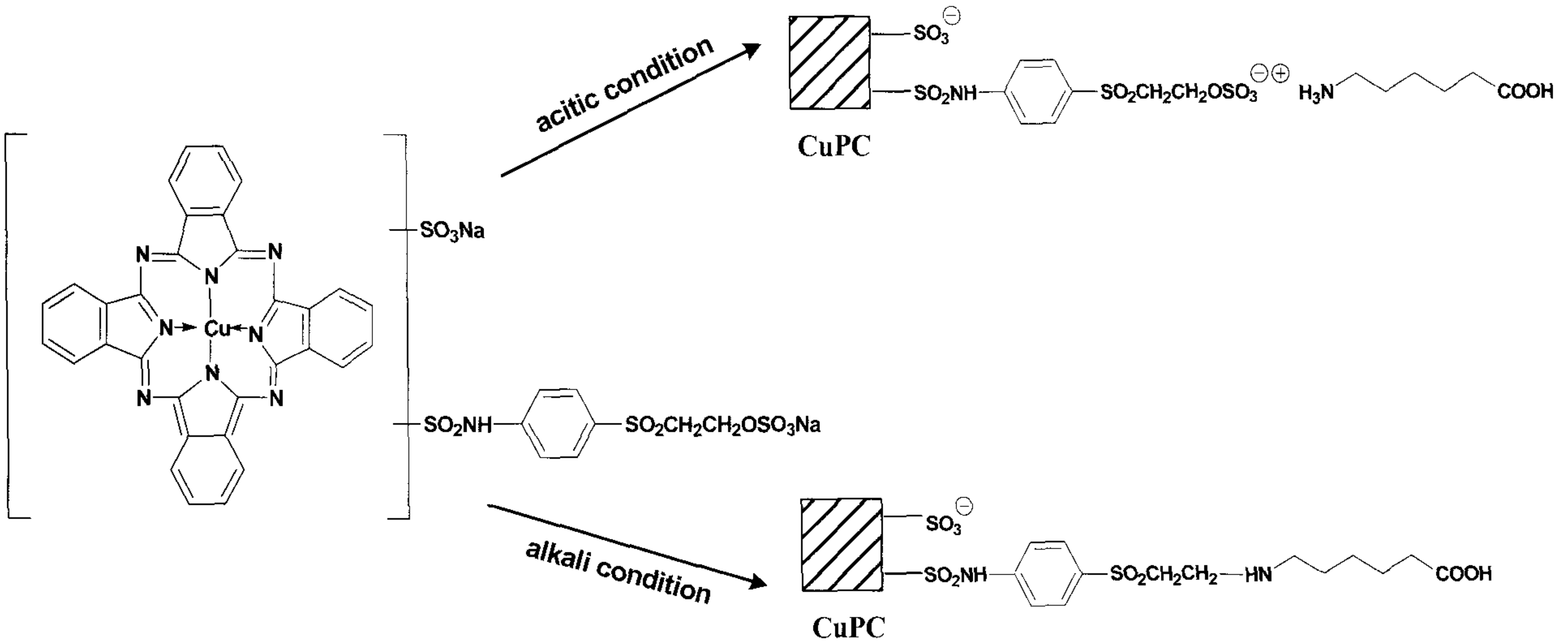

Fig. 2. Reaction mechanism of the nylon treatment with phthalocyanine reactive dye.

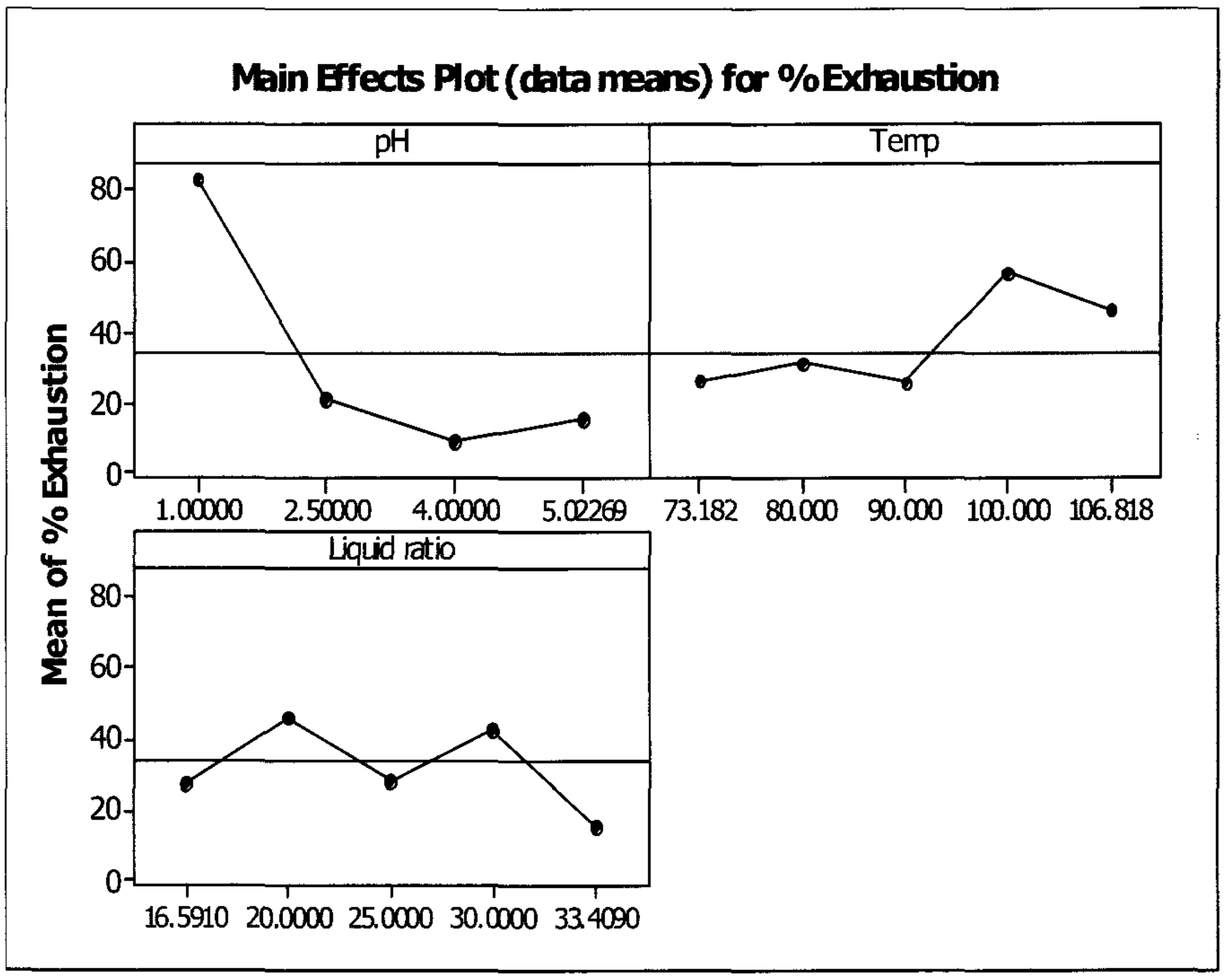

Fig. 3. Main effects plot of variables on % exhaustion of phthalocyanine reactive dye with nylon.

This may be due to the fact that swelling effect of fiber leads to the reaction of more functional groups with reactive groups of dye and also the higher kinetic energy at higher temperature leads to higher % exhaustion. Lower liquor ratio leads to the concentrated solution so that maximum probable collision between the reaction mixtures leads to higher % exhaustion. These results clearly indicate that the chosen factors had a major influence on the treatment performance.

4.2 Fitting of data and optimization strategy

In order to optimize the dyeing variables by a statistically based experimental design, initial pH, temperature and liquid ratio were chosen as important process variables based on earlier findings. The experimental results of the CCRD were fitted to second order polynomial equations. The values of regression coefficients were calculated and the fitted equations are shown in below,

The analytical procedure was optimized using design of experimental concept. A central composite experimental design for three variables was applied to the system with the objective of localizing experimental conditions that provide highest responses. Results obtained after running 20 trials according to statistical design are shown in Table 2. The validity of the model was determined by comparing experimental and predicted values (Fig. 4). The regression coefficients (R^2) for the empirical model were more than 0.90 (R^2 = 0.962 for % exhaustion and R^2 = 0.954 for % fixation), this shows good predicting ability of the model. This high R^2 values shows that the model explains the response variations, which are as high as 96.2% for % exhaustion and 95.4% for % fixation. The model did not explain, only about 0.038% for % exhaustion and 0.046% for % fixation in predicting the variations of the response to the prevailing conditions.

$$Y_1 = 379.15 - 25.079X_1 - 7.251X_2 - 0.812X_3 - 0.522(X_1X_2) - 0.103(X_1X_3) - 0.004(X_2X_3) + 9.875(X_1X_1) + 0.053(X_2X_2) + 0.004(X_3X_3) \qquad R^2 = 0.962 \qquad (4)$$

$$Y_2 = 931.67 + 14.42X_1 - 19.526X_2 - 1.638X_3 - 0.2075(X_1X_2) - 0.6409(X_1X_3) - 0.0283(X2X3) + 1.862(X_1X_1) + 0.119(X_2X_2) + 0.0686(X_3X_3) \qquad R^2 = 0.954 \qquad (5)$$

Where, X_1 = pH, X_2 = temperature, X_3 = liquor ratio, Y_1 = % exhaustion and Y_2 = %fixation

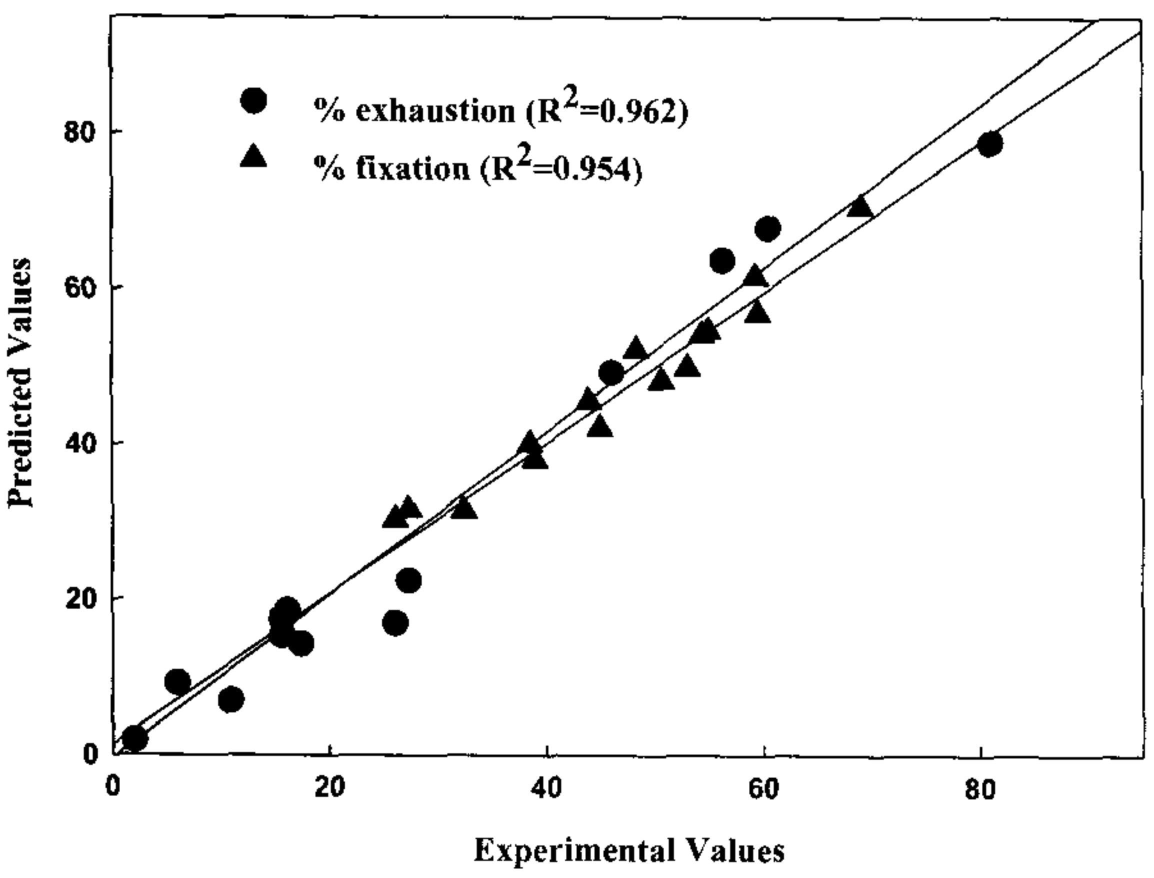

Fig. 4. Experimental and predicted values of % exhaustion and % fixation of phthalocyanine reactive dye with nylon.

The surface plots are useful in representing the effect of variables on the response and selecting the range of parameters to get the maximum or minimum value of the response. In the present study, maximum % exhaustion was desirable to have good dyeing characteristics. The surface plots for % exhaustion were developed between two variables keeping other variable at constant point. Typical surface plots for % exhaustion are shown in Fig. 5.

These surface plots can be used to see the effect of change in variable levels on the response and choose the range of variable level. The surface plot models are dependent and useful for establishing desirable response values along with operating conditions. A surface plot displays a three-dimensional view that may provide a clear picture of the response surface. The coordinates of the central point within the highest surface levels in each of these figures will correspond to the optimum values of respective constituents. The Fig. 5 shows the relative effects of any two variables when the remaining one variable is kept constant for all combinations and optimum conditions were obtained graphically.

The optimum values drawn from these figures are in close agreement with those obtained by optimizing the regression model equations (4) and (5) using Monte-Carlo Simulation techniques. The optimum values shown in Table 3 were also obtained by running the optimization program with MINITAB - 13 within the experimental range investigated. This confirms that the design of experiments could be effectively used to optimize

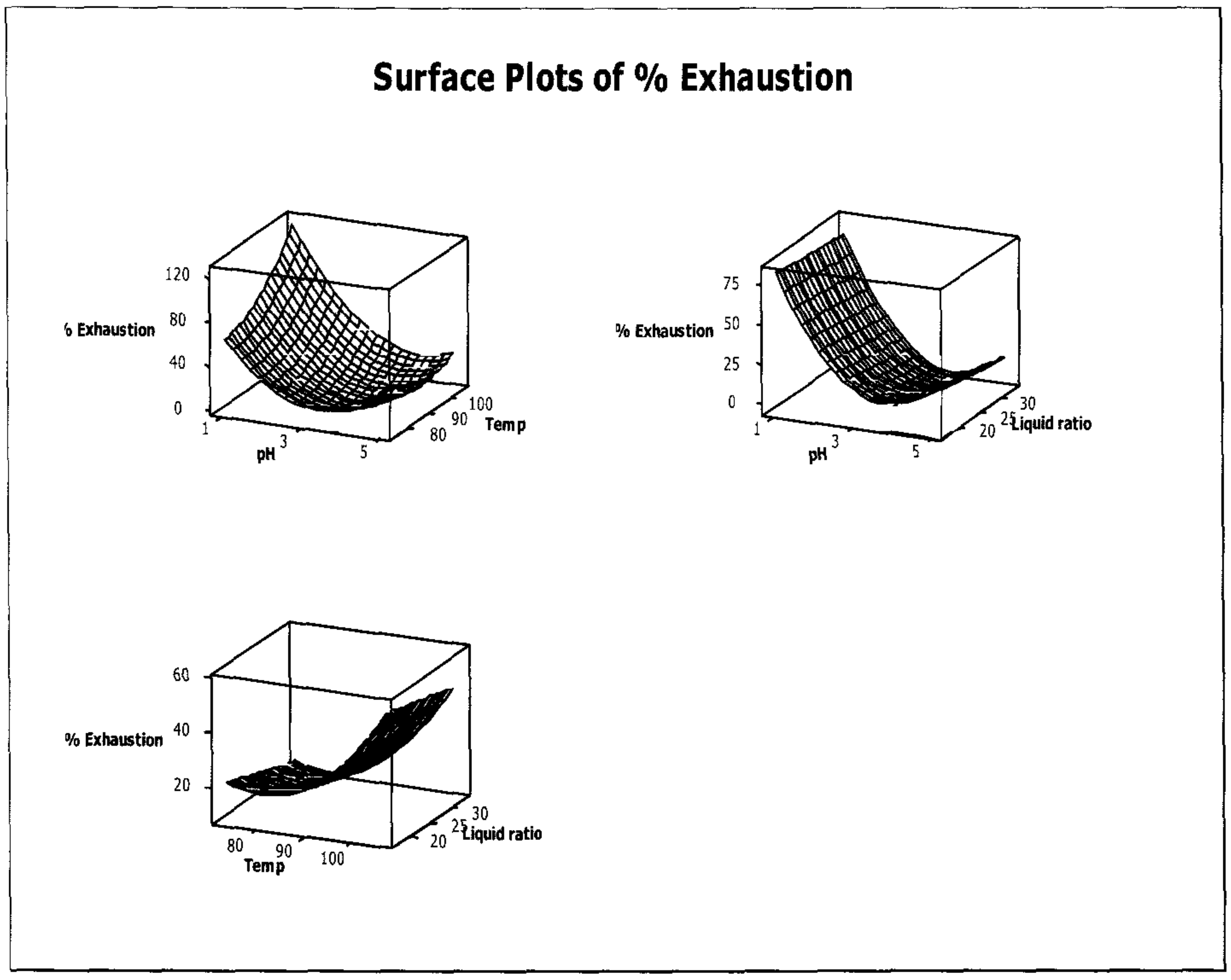

Fig. 5. Response surface plot of % exhaustion of phthalocyanine reactive dye with nylon.

the process variables using statistical design of experiments concept. The optimum conditions obtained by the theoretical analysis were experimentally investigated and the highly feasible results were obtained. At an optimum point, % exhaustion of 98% was obtained. Furthermore, the predicted operating conditions for maximum % exhaustion were experimentally verified in an additional study. Experiments were performed in triplicate using the optimized conditions to verify the model. The mathematical investigation of the numerical experimental data shows the strong acidic pH conditions as optimum values. But, the commercial dyeing unit in the industry commonly maintains the pH above 3 in order to avoid the damage in the basic functional groups of the nylon fiber.

4.3 ANOVA analysis and interpretation

The factorial experimental design methods are widely used for controlling the effects of parameters in many processes because its usage decreases the number of experiments, time and material resources. Furthermore, the analysis performed on the results is easily realized and experimental errors are minimized. The method used to compare the magnitude of estimated effects of factors with the magnitude of experimental error is called analysis of variance (ANOVA). If the magnitude of a factor effect is large when compared to experimental errors, it is decided that the changes in the selected response cannot occur by chance and those changes in the response can be considered to be effects of the factors. The factors causing a variation in the response are called significant.

The results of analysis of variance (ANOVA) for the second order response surface model fitting and the effect of independent process variables on % exhaustion are presented in Table 4. The ANOVA model for % exhaustion showed that linear and quadratic effects were more significant (P = 0.000) than the interaction effect (P = 0.806). The model fit was highly significant (P = 0.000) with reasonably high correlation coefficients i.e., 0.962 for % exhaustion and 0.954 for % fixation. Statistical significance of all main effects, linear, quadratic, and interaction of effects calculated for each response can also be shown in Table 4. The ANOVA also showed that lack of fit was not significant for all response surface models at 95% confidence level.

Table 3. Optimum values of the variables for maximum % exhaustion phthalocyanine reactive dye with nylon

Process variables	Optimum conditions
pH	1.2
Temperature	102
Liquor ratio	21

Table 4. ANOVA for % exhaustion of dyeing of phthalocyanine reactive dye with nylon

Term	Coefficients	SE coefficients	t	P
Constant	379.157	246.710	1.537	0.015
X_1	-25.079	22.268	-1.126	0.002
X_2	-7.251	4.416	-1.642	0.012
X_3	-0.812	7.252	-0.112	0.098
X_1X_2	-0.522	0.205	-2.548	0.029
X_1X_3	-0.103	0.409	-0.252	0.806
X_2X_3	0.004	0.061	0.069	0.946
X_1X_1	9.875	1.283	7.680	0.000
X_2X_2	0.053	0.023	2.304	0.044
X_3X_3	0.004	0.040	0.969	0.069

From the statistical parameter estimates, it can be determined which variable contributes most to the prediction model. Thus allowing the researcher to focus on the variables that are most important to the process acceptance. Apart from linear effect of variables for the exhaustion, the design of experiments gives an insight into quadratic and interaction effects of the variables. These 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 variables. The P-values were used as a tool to check the significance of variables, which in turn may indicate patterns of the interactions among the variables. In general,

Table 5. Estimated regression coefficients and corresponding t and P values % exhaustion

Source	Degree of freedom (DF)	Sum of squares (SS)	Mean square (MS)	$F_{statistics}$	P
Regression	9	18843.5	2093.72	27.75	0.000
Linear	3	13482	97.48	1.29	0.330
Square	3	4866.5	1622.18	21.50	0.000
Interaction	3	495	165	2.19	0.153
Residual Error	10	754.5	75.45		
Lack of fit	5	754.5	150.90		
Pure error	5	0.00	0.00		
Total	19	19598			

larger the magnitude of *t* and smaller the value of *P*, the more significant is the corresponding coefficient[5]. The regression coefficient, *t* and *P*-values for all linear, quadratic and interaction effects of the variables are given in Table 5 for % exhaustion. The analysis shows that linear effect of pH (P = 0.002) and temperature (P = 0.012) is more significant. Liquor ratio (P = 0.098) plays a less significant factor when compared to other two variables. The squared effect of pH (P = 0.000) and temperature (P = 0.044) were observed as significant factors. None of the combinations in the interaction effect is significant, as *P*-value is much higher.

5. Conclusions

The optimal exhaustion conditions for phthalocynine reactive dye with nylon fiber were investigated in this study. For this purpose, the experimental variables namely, reaction temperature, pH and liquor ratio have been explored by using statistically designed experiments. The 2^3 central composite design was applied to establish second order polynomial model relating % exhaustion and fixation with the independent variables. The standard error between experimental values and model values was sufficiently low to confirm the high predictive power of the model. Optimum conditions were graphically drawn from the surface plots, which are similar to theoretical value by solving the model equations. At the optimum conditions, maximum % exhaustion was obtained. But, as mentioned above in the result and discussions, this condition results the feasible damage to the functional groups of the nylon fiber. In conclusion it is evident that the application of 2^3 central composite design of experimental techniques can be a practical useful tool for optimization of reaction parameters for the enhanced % exhaustion during the dyeing processes.

Acknowledgement

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