〈연구논문(학술)〉

Empirical modeling and statistical analysis of the adsorption of reactive dye on nylon fibers

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나일론섬유에 대한 반응성 염료 흡착의 실험적 모델링 및 통계적 분석

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Abstract— 나일론섬유에 대한 프탈로시아닌 반응성 염료의 염착거동을 관찰하기 위하여 온도 및 pH를 변화하여 이에 관한 흡착율(%) 및 고착율(%)의 변화를 관찰하였다. 또한, 염착실험과정과 관련하여 새로운 적용 방법으로 실험적 모델링 방법을 도입하여 흡착율(%) 및 고착율(%)을 예측하고, 이의 결과를 여러 온도 및 pH 조건에서의 실제실험과의 상호작용 및 효과를 확인하였다. 수학적 모델링의 타당성은 Excel 회귀분석단위를 이용하여 확인하였다. 예측 모델에 있어서 얻어진 높은 계수간의 상관관계(흡착율(%) R^2=0.9895, 고착율(%) R^2=0.9932)는 실제로 진행되지 않은 실험조건에 대한 결과에 있어서도 우수한 예측 정보를 제공할 수 있다. 그리고 실험적 결과로부터 확립된 예측가능한 다항식이 ANOVA 통계적 개념에 의해 자세하게 분석되었다. (A phthalocyanine reactive dye was applied to nylon fibers to study the effects of the temperature and pH on % exhaustion and fixation. In addition, appropriate predictable empirical models, relatively new approaches in dyeing process, were developed incorporating interactions effects of temperature and pH for predicting the both % exhaustion and fixation. The significance of the mathematical model developed was ascertained using Excel regression (solver) analysis module. A very high correlation coefficient was obtained (R^2=0.9895 for % exhaustion, R^2=0.9932 for fixation) for the model which shows prominent prediction capacity of the model for the unknown conditions. The predictable polynomial equations developed from the Experimental results were thoroughly analyzed by ANOVA (Analysis of Variance) statistical concepts.)

Keywords: Phthalocyanine reactive dye, Polyamide substrate, Exhaustion (%), Fixation (%), Empirical modeling, Statistical analysis

1. Introduction

Phthalocyanines(Pc) 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[1]. Phthalocyanines in particular are possess a wide range of chemical and physical properties that make them interesting building blocks for a number of applications and materials. It is well known that the presence of amino end groups(AEG) in nylon imparts substantivity towards various classes of anionic dye and it is widely held that the substantivity of such anionic dyes under acidic conditions is based mainly

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on electrostatic forces of interaction operating between anionic(typically sulphonate) groups in the dye and the protonated amino end groups in the fiber. Thus the adsorption of anionic dyes on nylon substrates is considered to be site-specific[2]. In the present work, phthalocyanines dye based on the C.I. Reactive Blue 21[3] was applied on to the nylon substrates and the effects of temperature and pH[4] were explored in detail. Dyeing was performed at various pH values which were adjusted using McIlvaine buffer system[5-7].

Though literatures could be found for the investigation of the effects of various process variables on the dye exhaustion and fixation with the substrate, developing the empirical polynomial model equations relating the process variables with dye exhaustion and fixation to predict the dynamic behaviour of the process is relatively new approach in the dyeing process. In this context, this article is aimed to develop an empirical model to relate the process variables with the phthalocyanine reactive dye exhaustion and fixation. In addition to this, statistical analysis of the data and model equation, a relatively new study in the dyeing process, was carried out for the experimental data to assess the quality of the model.

2. Experimental and model development

2.1 Reagents and Materials

All chemicals used were of analytical grade and doubly distilled water was always used. Nylon substrates were purchased from Korea Apparel Testing and Research Institute(KATRI). The phthalocyanine reactive dye(Fig.1.), used to study the effect of pH and temperatures on the dye exhaustion, was
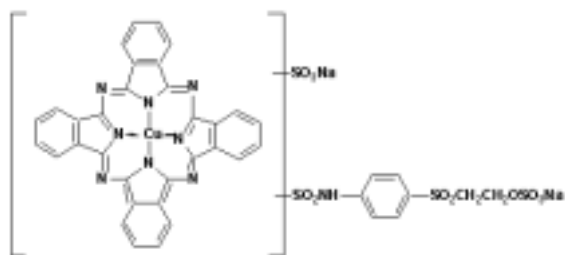

Fig. 1. Structure of reactive copper phthalocyanine dye.

supplied from *Clariant Co.* All other chemicals used were of laboratory grade reagents.

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.

2.3 Dyeing of the polyamide substrates

Nylon substrate(4g) was dyed with 2% o.w.f phthalocyanine reactive dye in a sealed stainless steel dyepots of $120cm^3$ capacity in a laboratory-scale dyeing machine(ACE-6000T). Samples were placed in a 40^0C dye bath of liquor ratio 25:1. After 10min, the temperature was raised until reaching 100^0C at $2^oC/min$ and then continued for 60min. The dyed samples were washed off using water and dried at room temperature. The pH was adjusted using 0.1N Na_2CO_3 and 0.1N CH_3COOH. At the end of dyeing process, the nylon substrates were removed, rinsed thoroughly in tap water and dried in open air. The exhaustion rate(%E) was then calculated using the formula,

$$\%E = \frac{[D_o - D_t]}{D_o} \times 100 \qquad (1)$$

The extent fixation (%F) was calculated by the formula,

$$\%F = \frac{[D_o - D_t - D_e]}{[D_o - D_t]} \times 100 \qquad (2)$$

where , D_0 and D_t is the quantity of dye in the initial and final bath respectively. Those values were calibrated through absorbance measurement of original and exhausted bath by using UV-Vis Spectrophotometer.

2.4 Empirical modeling

Empirical model i.e., second order polynomial regression equations were developed using Excel Solver function to predict the % exhaustion, relating the process variables i.e., pH, temperature, concentration and time. 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]:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ij} x_i^2 + \sum \beta_{ij} x_i x_j \qquad (3)$$

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],

$$RMSE = \sqrt{\frac{\sum_{0}^{N}(Exp. - Pred.)^2}{N}} \qquad (4)$$

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

2.5 Data analysis

Statistical analysis of the experimental data was performed. 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 discussions

The experiments were performed at various pHs and temperatures. It was found that low pH and high temperature favored high exhaustion and low

fixation. At low pH conditions, high extent of protonation of the amino groups within nylon substrates leads to high exhaustion(%E) and low fixation(%F), because the 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 the sulphatoethlysulphone form and, therefore, few dye molecules were present in the reactive vinyl sulphone form. In contrast, at higher pH conditions, initial dye exhaustion(%E) was low due to the low extent of amino group protonation, although dye exhaustion did undergo covalent reaction to give the high fixation(%F) levels seen.

The increase in efficiency at higher temperature 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 substrate swelling would have contributed to the increased dye exhaustion.

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 and process variables were developed and are given in equations (5) and (6) respectively, Polynomial regression equation for % exhaustion of Phthalocyanine into Polyamide substrates

$$Y = -49.52 - 150.63(X_1) + 7.75(X_2) + 2.20(X_1X_1)$$
$$- 0.052(X_2X_2) + 1.079(X_1X_2) \quad R^2 = 0.9895 \qquad (5)$$

Polynomial regression equation for fixation of Phtahlocyanine into Polyamide substrates

$$Y = 53.54(X_1) + 18.49 - 1.765(X_2) - 0.0207(X_2X_2)$$
$$+ 1.1733(X_1X_1) - 0.574(X_1X_2) \quad R^2 = 0.9932 \qquad (6)$$

Where,

X_1=pH

X_2=temperature

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 explaina 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 experimental and the predicted values from the model equations of % exhaustion and fixation are plotted and shown in Fig 2 and 3 for temperature and pH respectably. The fitted model shows very high coefficient of determination(R^2 = 0.9895 for % exhaustion and R^2 = 0.9932 for Fixation). The model was found to be exactly predicting the dye uptake theoretically and thus could be effectively used to predict the dye
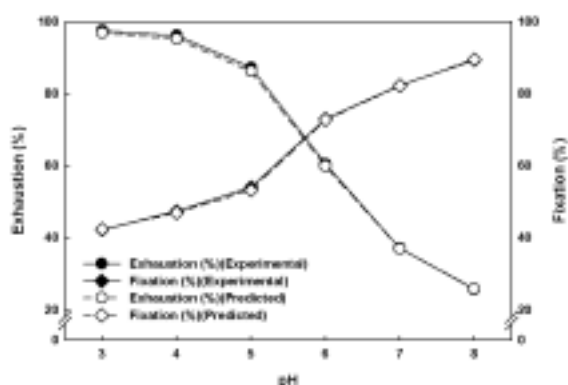
uptake even without performing any experiments within the experimental ranges[9]. This implies that 98.95% and 99.32% of the sample variation for % exhaustion and fixation are explained by the independent variables and this also means that the model did not explain only about 0.001% and 0.006% of sample variation for exhaustion and fixation respectively.

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 1 and Table 2.

It was observed that the coefficients for the linear effect of pH and temperature was highly significant for both % exhaustion(P=0.000, P=0.002) and fixation

Fig. 2. Experimental and predicted exhaustion (%) and fixation (%) values at various pHs.
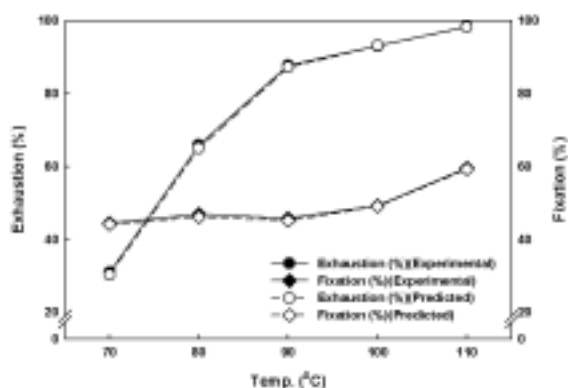
Fig. 3. Experimental and predicted exhaustion (%) and fixation (%) values at various temperatures.

Table 1. Estimated regression coefficients and corresponding t and p values for % exhaustion

Term	Coefficients	SE coefficients	t	P
Constant	-49.52	83.5851	-7.973	0.000
X_1	-150.63	13.5611	8.943	0.000
X_2	7.75	0.5369	1.195	0.002
$X_1 X_1$	2.20	3.5391	0.983	0.340
$X_2 X_2$	-0.052	0.3917	1.782	0.194
$X_1 X_2$	1.079	0.5932	-9.171	0.004

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

Term	Coefficients	SE coefficients	t	P
Constant	53.54	143.418	3.210	0.001
X_1	18.49	20.171	-3.018	0.003
X_2	-1.765	3.434	-1.874	0.001
$X_1 X_1$	-0.0207	3.320	-0.284	0.782
$X_2 X_2$	1.1733	0.240	-0.438	0.671
$X_1 X_2$	-0.574	143.418	3.210	0.009

(P=0.003, P=0.001). The squared effect of pH and temperature(P=0) were considered to least significant with higher P value for both % exhaustion (P=0.340, P=0.194) and fixation(P=0.782, P=0.671). The interaction effect has found to be moderately significant for pH and temperature for both % exhaustion(P=0.004) and fixation(P=0.009).

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 3 and Table 4 for % exhaustion and fixation respectively, the $F_{Statistics}$ 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. 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. 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 30.96 and 29.94 for both % exhaustion and fixation are greater than tabulated $F_{14,16}$ 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 5 and 6) was highly significant and adequate to represent the actual relationship between the response(% exhaustion) and the variables.

4. Conclusions

Nylon substrates were successfully treated with phthalocyanine reactive dye and the effects of temperature and pH were studied on % exhaustion and fixation. The pH 3 and 110^{0}C were found to be suitable experimental conditions for maximum % exhaustion and lower fixation. An appropriate

Table 3. ANOVA for % exhaustion

Source	Degree of freedom (d.f.)	Sum of squares (SS)	Mean square (MS)	$F_{statistics}$	P
Regression	5	2420.07	115.720	30.94	0.000
Linear	2	1563.35	201.554	20.73	0.000
Square	2	852.19	263.048	45.38	0.001
Interaction	1	4.53	0.755	0.07	0.998
Residual Error	7	163.27	10.204		
Lack of fit	3	163.27	16.327		
Pure error	4	0.00	0.00		
Total	12	2583.34			

Table 4. ANOVA for % fixation

Source	Degree of freedom (d.f.)	Sum of squares (SS)	Mean square (MS)	$F_{statistics}$	P
Regression	5	478.597	53.1774	29.94	0.013
Linear	2	227.825	40.297	13.51	0.057
Square	2	246.843	82.280	12.17	0.007
Interaction	1	3.929	1.3096	4.26	0.950
Residual Error	7	114.760	11.4760		
Lack of fit	3	114.760	22.9520		
Pure error	4	0.00	0.00		
Total	12	593.357			

empirical model was developed using excel solver functions and very high correlation coefficient was obtained. The statistical significance of the model equations were thoroughly analyzed and discussed.

Acknowledgement

References

1. Neal R. Armstrong, *J. Porphyrins and Phthalo-cyanines, ***4**, 414-417(2000).

2. S. M. Burkinshaw, Young-A Son, The after-treatment of acid dyes on nylon 6,6 fibers Part 1. 1:2 pre-metallised acid dyes, *Dyes and Pigments,* **48**, 57-69(2001).

3. Li-yan Fu, Xiang-hua Wen, Li-jie Xu, Yi Qian, Removal of a copper-phthalocyanine dye from wastewater by acclimated sludge under anaerobic or aerobic conditions, *Process Biochemistry* **37,** 1151-1156(2002).

4. D. M. Lewis, Y. C. Ho, Improved fixation of dyes on polyamide fibres-IV. The use of a nucleo-philic aminoethylsulphonyl cationic dye for dyeing nylon followed by a fixation aftertreat-ment with 2-chloro-4,6-di(aminobenzene-4´-sulpha-toethylsulphone)-s-triazine [XLC], *Dyes and Pigments,* **31**, 111-129(1996).

5. S. M. Burkinshaw, A. E. Wills, *Dyes and pigments,* **34**, 243-253(1997).

6. S. M. Burkinshaw, S. N. Chevil, D. J. Marfell, Printing of nylon 6,6 with reactive dyes part I: preliminary studies, *Dyes and pigments,* **45,** 235-242(2000).

7. S. M. Burkinshaw, K. Gandhi, The dyeing of conventional and microfibre nylon 6,6 with reactive dyes. Part 2. α-bromoacrylamido dyes, *Dyes and Pigments,* **33,** 259-280(1997).

8. E. Mordecai, "*Methods of correlation analysis,* 3rd ed.", John Wiley & Sons Inc, New York, pp.21-30, 1951.

9. H. R. Mickly, T. K. Sherwood, C. E. Reed, "*Applied Mathematics in Chemical Engineering,* 2nd ed.", TataMcGraw-Hill, New Delhi, 1975.

10. D. C. Montgomery, "*Design and Analysis of Experiments,* 3rd ed.", Wiley, New York, 1991.