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Statistical Experimental Design Course Paper

Introduction

A research paper published in 2006 titled "Process Analysis and Optimization for the Ionic Interactions of Quaternary Ammonium Salts with Nylon 66 Fibers Using Statistical Experimental Design" details a scientific study using statistical experimental design. The study sought to find the optimal pH, temperature, salt concentration, and finishing time "for developing durable antimicrobial nylon 66 fibers" (Ravikumar), with maximum percent exhaustion as a response variable. Maximum percent exhaustion refers to the quantity of quaternary ammonium salts (QASs) that remained after treatment and is calculated by taking the difference of the quantities of salt before and after treatment and dividing it by the quantity of salt before treatment. This study was applied for two different types of salt, "cetylpyridinium chloride (CPC) and benzyldimethylhexadecyl ammonium chloride (BDHAC)." Although the objective of the study may be in a subject field that is too advanced and complicated for the reader to understand, the study provides a good example of the use of statistical experimental design in a scientific experiment.

Experimental Design Used

The study utilizes a response surface central composite design with 31 sets of levels, among which are the 16 factorial design combinations, seven "center points", and eight "star points". The factorial design combinations are the different combinations of -1 and 1 for the four independent variables (pH, temperature, salt concentration, and finishing time), resulting in 2^4 = 16 different combinations. The center points are simply seven separate combinations with a level of 0 given for each variable (i.e., a 7 x 4 matrix with a 0 for every entry). The star points are two combinations with a level of 0 given for each variable except one, which instead has different combinations of $-\alpha$ and α. This process is repeated for all four independent variables, producing eight total combinations. (α is chosen by the researchers, but appears to not be explicitly defined in the article.) For example, in this study with independent variables (pH, temperature, salt concentration, and finishing time), the different combinations would be $(\alpha, 0, 0, 0)$, $(-\alpha, 0, 0, 0)$, $(0, \alpha, 0, 0)$, $(0, -\alpha, 0, 0)$, $(0, 0, \alpha, 0)$, $(0, 0, -\alpha, 0)$, $(0, 0, 0, \alpha)$, and $(0, 0, 0, -\alpha)$. These 31 sets of levels were compiled as a matrix and the resulting response variable, maximum percent exhaustion, was calculated in Minitab.

The design produced two main effects plots on the response variable, one for cetylpyridinium chloride (CPC) and another for benzyldimethylhexadecyl ammonium chloride (BDHAC), as shown in Figures 2 and 3. The plots for both are nearly identical, indicating that there may not be much significant difference between the two types of salts. Both show that the maximum percent exhaustion is obtained when pH is roughly 11, temperature is higher than 60°C, salt concentration is roughly 2.25%, and the experiment is performed for roughly 85 minutes.

Statistical Methods Employed

The study uses Solver function in Excel to develop a second-order polynomial regression equation, referred to as an empirical model, to separately predict maximum percent exhaustion. The empirical model is noted as $Y = \beta_0 + \Sigma\, \beta_i x_i + \Sigma\, \beta_{ij} x_i^2 + \Sigma\, \beta_{ij} x_i x_j$, with Y as maximum percent exhaustion, β as the regression coefficient, and x as the data from the independent variables.

Root mean square error (RMSE) is also calculated to test how accurate the model was at predicting the response variable.

The final empirical models for both salt types included the intercept term, each independent variable and its quadratic term (the variable squared), and each two-way interaction term. As in the case of the main effects plots, the models were very similar, although the interaction term between temperature and salt concentration (X_2X_3) had a negative coefficient for the CPC model and a positive coefficient for the BDHAC model. T-tests for significance were performed on all terms in both models, and the standard error for each term and results of the tests were listed in two separate tables (Tables 3 and 4). The tables showed that all terms except the quadratic term for finishing time (X_4X_4), the interaction term between pH and temperature (X_1X_2), and the interaction term between temperature and finishing time (X_2X_4) are highly statistically significant at $\alpha = .01$.

Additionally, ANOVA that were run on both models (Tables 6 and 7) indicated that the regression along with all three types of variables (linear, quadratic, and interaction terms) were highly statistically significant. The fact that nearly all of the terms in the two models in addition to the ANOVA are highly statistically significant indicates that the models are likely a very good fit for the data.

Critique of Statistical Methods

The experimental design and second-order regression equation were a good choice of statistical methods for this study. However, the method in which the equation was obtained may have led to some overfitting of the data. The study stated that the model perfectly predicts the "behavior of the system" when the RMSE is zero when in reality a RMSE of zero would simply indicate a perfect fit to the data. In accordance with its assertion, the study used Solver function in Excel repeatedly to fit the model until the lowest RMSE was obtained. This process could lead to overfitting the data used in the study and may not accurately predict the response variable of other unseen data. The study notes that the ANOVA had “a very high coefficient of determination (R^2 = 0.9996 for CPC and R^2 = 0.9989 for BDHAC).” These correlation values for R^2 are nearly impossible to obtain in practice and may be a result of overfitting in the model.

Additionally, neither the raw data nor the sample size used in the models are disclosed to the reader and the hypotheses for performing the t-tests and ANOVA are not explicitly checked in the study. This means that the reader is not certain that the data does not violate testing conditions, especially those of normality and homoscedasticity.

Appendix

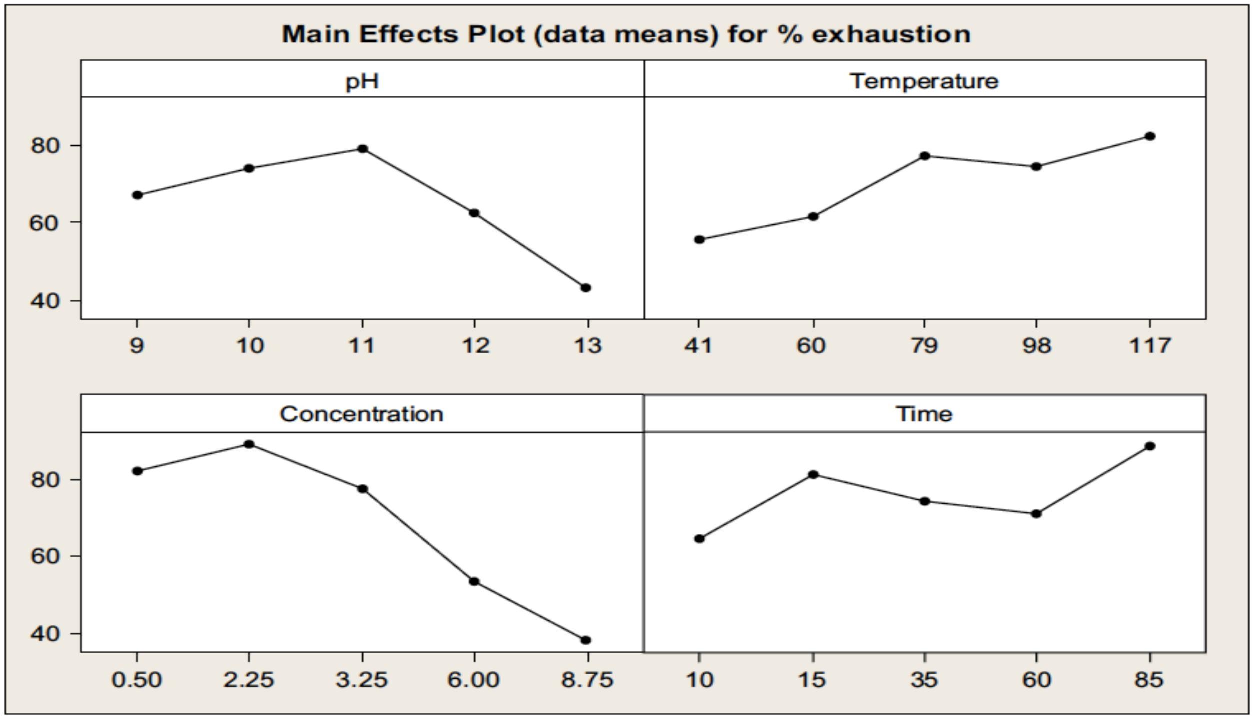

Fig. 2. Main effects plot of variables on % exhaustion of CPC onto nylon 66 fibers.

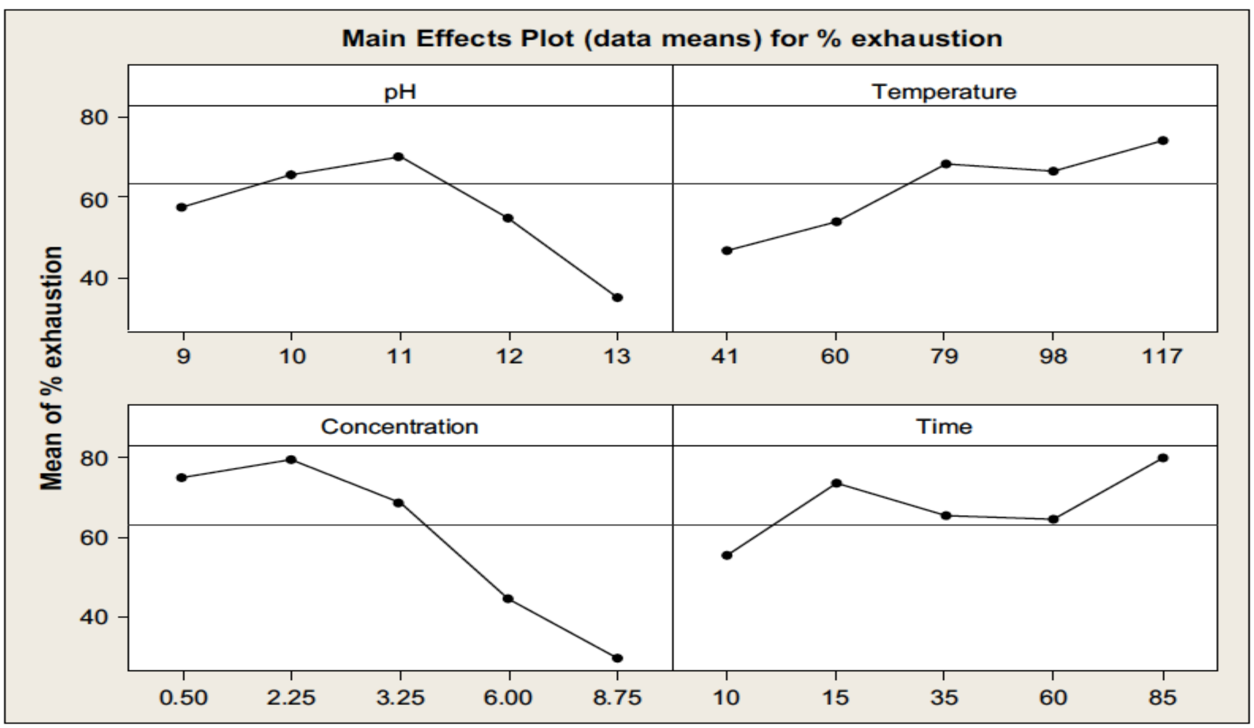

Fig. 3. Main effects plot of variables on % exhaustion of BDHAC onto nylon 66 fibers.

Table 3
Estimated regression coefficients and corresponding t- and P-values for CPC

Term	Coefficients	SE coefficients	t	P
Constant	−862.9203	26.9876	−31.946	0.000
X_1	159.6317	4.3735	36.594	0.000
X_2	1.5452	0.1729	8.460	0.000
X_3	6.5007	1.1213	7.128	0.000
X_4	1.2408	0.1259	9.185	0.000
X_1X_1	−7.3816	0.1913	−38.761	0.000
X_2X_2	−0.0110	0.0005	−20.372	0.000
X_3X_3	−0.5839	0.0253	−27.059	0.000
X_4X_4	−0.0012	0.0004	−2.053	0.057
X_1X_2	0.03134	0.0135	2.819	0.012
X_1X_3	−0.7357	0.0934	−8.796	0.000
X_1X_4	−0.0942	0.0103	−8.518	0.000
X_2X_3	0.0261	0.0049	6.003	0.000
X_2X_4	0.0026	0.0005	4.087	0.001
X_3X_4	−0.0566	0.0037	−14.447	0.000

Table 4
Estimated regression coefficients and corresponding t- and P-values for BDHAC

Term	Coefficients	SE coefficients	t	P
Constant	−855.07928	43.7518	−19.890	0.000
X_1	156.9943	7.0984	22.480	0.000
X_2	1.5100	0.2810	5.487	0.000
X_3	7.1706	1.8525	3.884	0.001
X_4	1.0530	0.2051	5.166	0.000
X_1X_1	−7.2419	0.3105	−23.611	0.000
X_2X_2	−0.0104	0.0009	−12.186	0.000
X_3X_3	−0.5092	0.0555	−9.169	0.000
X_4X_4	−0.0014	0.0007	−2.136	0.048
X_1X_2	0.0279	0.0220	1.178	0.256
X_1X_3	−0.9528	0.1520	−6.298	0.000
X_1X_4	−0.0045	0.0167	−3.902	0.001
X_2X_3	0.03923	0.0080	4.925	0.000
X_2X_4	0.0014	0.0090	1.618	0.113
X_3X_4	−0.0565	0.0061	−9.306	0.000

Table 6
ANOVA for % exhaustion of CPC onto nylon polymer

Source	Degrees of freedom (df)	Sum of squares (SS)	Mean square (MS)	$F_{statistics}$	P
Regression	14	9676.15	154	654.25	0.000
Linear	4	6832.27	1483.67	351.11	0.000
Square	4	6832.27	600.225	568.18	0.000
Interaction	6	442.98	73.830	69.89	0.000
Residual error	16	16.90	1.056		
Lack of fit	10	16.90	1.690		
Pure error	6	0.00	0.00		
Total	30	9693.06			

Table 7
ANOVA for % exhaustion of BDHAC onto nylon polymer

Source	Degrees of freedom (df)	Sum of squares (SS)	Mean square (MS)	$F_{statistics}$	P
Regression	14	9825.67	701.834	251.02	0.000
Linear	4	7143.39	367.754	131.53	0.000
Square	4	2207.25	551.812	197.37	0.000
Interaction	6	475.03	79.17	28.32	0.000
Residual error	16	44.73	2.796		
Lack of fit	10	44.73	4.473		
Pure error	6	0.00	0.00		
Total	30	9870.41			

Bibliography

Ravikumar, K., and Young-A. Son. “Process Analysis and Optimization for the Ionic Interactions of Quaternary Ammonium Salts with Nylon 66 Fibers Using Statistical Experimental Design.” Dyes And Pigments, vol. 75, no. 1, 2007, pp. 199–206.

Ravikumar, K., & Son, Y. (2007). Process analysis and optimization for the ionic interactions of quaternary ammonium salts with nylon 66 fibers using statistical experimental design. Dyes And Pigments, 75(1), 199-206.