Application of Nonparametric Optimization Methods for Dyeing of Wool

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Abstract: In this study, the preparation and production of multilamellar liposome from Soya lecithin with 75% phosphatidylcholine were carried out and the behavior of liposome in dye-bath at different temperature, time, Sodium Sulphate, pH and concentration (five factors) were considered and compared by two different optimization approaches, namely, parametric and nonparametric using Box-Behnken standard design matrix of Response Surface Methodology (RSM) in both cases to produce representative data. The comparative results show that when parametric model is not a good fit for data, nonparametric approach can be considered as one of the proper alternatives.

Key words: Liposome • Wool dyeing • Color strength (K/S) • Central composite design • Robust parameter design

INTRODUCTION

Low temperature of wool dyeing has benefits such as lower energy conservation and wool fibers protection by either decreasing the temperature or shortening the processing time at high temperature during dyeing. The wool fabric dye at low temperature has both more natural feeling and improved durability, using some of the known synthetic auxiliaries in dye-bath during low-temperature dyeing [1]. Liposomes are spherical synthetic layers of phospholipids, which has been formed like closed vesicles with an aqueous core and ranging from 10 nm to 10 μm in diameter [2, 3]. Liposome composes of lipid vesicle bilayers enclosing a volume. These structures have hydrophobic and hydrophilic parts. The hydrophilic part is composed of phosphate and choline groups and the hydrophobic part is made up of hydrocarbon chains [4]. Phosphatidylcholine is the most widely used in biological lipid for producing liposome. Wool dyeing and wool blends with liposome have demonstrated to improve quality, energy conservation and lower environmental impacts. Recently, commercial liposome were incorporated into textile auxiliaries, mainly for wool dyeing [5-7]. This is a clean technology that has already been adapted by some textile industries. These are additional benefits for material-weight yield during subsequent spinning. These improved smoothness and mechanical properties of the dyed textiles and showed a clear reduction in the contamination load of the dye-baths [8]. Use of liposome as an auxiliary in wool dyeing can be related to the bilayer structure of lipids from the cell membrane complex (CMC) of wool that is similar to the liposome and the action of this morphological fraction of the fiber in wool processing. A wool fiber includes of cuticle and cortical cells held together by the CMC and forms the continuous phase in the keratin [9]. This phase contains a small amount of lipid material. Diffusion properties of wool fibers are influenced by the lipid structure of the intercellular spaces that could act as “solvents” for hydrophobic chemical. The dyes diffuse with ease into swollen regions such as the CMC (intercellular diffusion) rather than through the cuticle cells (transcellular diffusion) [10]. Last few years, several articles have related the potential application of liposome in wool dyeing. Meza et al. have investigated liposome as doer in wool dyeing with acid [11, 12], disperse [13, 14] and metal complex dyes [15]. Also they have worked on the effects of commercially available liposome as a simple additive [16]. Recently they used an optimized mixture of commercial liposome and cationic surfactant to improve leveling property [17]. In the previous article, the influence of temperature on stability of multilamellar liposome (MLV) in wool dyeing was studied and it was found that the presence of 1% o.w.f. (on weight of fabric) of liposome at 85°C could improve the dye exhaustion of Irgalan Blue FBL on wool fabric. It has also reported that
the wash fastness properties of dyed samples with liposome have also improved. There is no report on using liposome in wool dyeing with natural dyes. Therefore, we try to prepare and produce MLV from Soya lecithin with 75% phosphatidylcholine and study the influence of liposome in dye-bath at different temperature, time, Sodium Sulphate, pH and concentration during wool dyeing with madder as a most famous natural dye. The dyeing temperature and time were optimized with optimum concentration of liposome and the morphology of the liposome dyed samples has been investigated by scanning electron microscope (SEM).

The preparation and production of multilamellar liposome from Soya lecithin with 75% phosphatidylcholine were carried out and the behavior of liposome in dye-bath at different temperature, time, Sodium Sulphate, pH and concentration were considered [18] and compared by two different optimization approaches, namely, with and without Robust Parameter Design [19]. Since it is impractical and unnecessary to produce all data points of the different combinations of levels of four considered factors, a standard design matrix, namely, Central Composite Design (CCD) of Response Surface Methodology (RSM) was used in both cases to produce representative data. This design of experiment, not only produces effective data, but also provides us an opportunity of modeling the whole experimental space.

MATERIALS AND METHODS

The wool fabric with plain woven structure from 48/2 Nm yarns was supplied by Iran Merino. The fabric was scoured with 1% anionic detergent VEROLAN-NBO (supplied by Rodulf) at 70°C for 45 min and then washed with tap water and dried at room temperature. Industrial grade of aluminium sulphate was used for mordanting of wool samples. Soya lecithin (containing 75% phosphatidylcholine) with phase transition temperature (Tc) of 218°C was gifted by Lipoid (Germany). Madder (1) was prepared from Yazd providence of Iran. The reflectance spectra of the dyed samples were recorded on an ACS Spectra Sensor II integrated with an IBM-PC. The wash-fastness of the liposome treated madder-dyed fabric were measured according to ISO 150-C01. For light-fastness measurements, the samples were exposed to the daylight for 7 days according to the daylight ISO 105-B01 and changes in the color (fading) were assessed by the blue scale. Also the dry and wet rub fastness of the samples evaluated according to ISO 105-X12. The sample pictures were taken with Philips XL30 SEM with 34000. The drop absorbency of the fabric samples was also measured by dropping of water droplet from 1 cm on the fabric surface on the glass by a small syringe. The time of complete absorption of the water droplets on the fabric surface was recorded and the mean value of 20 replicates was reported. Dyeing The mordanted wool samples were steeped in the dye bath with liquor-to-goods ratio of 40: 1 that was prepared by 2% o.w.f. of extracted dye at pH 2-4 (acetic acid) with different concentrations of freshly prepared MLV liposome (0, 1, 2, 3% o.w.f.). Dyeing was started at room temperature and then raised 28°C/min to the final desired temperature including 75, 85 and 95°C. The dyeing was carried out with liposome and without liposome in various times of 30, 45 and 60 min. The samples were rinsed with tap water and dried at room temperature. The amount of reflectance was selected at the maximum wavelength and the K/S value which is of the type “the larger the better” was calculated according to the Kubelka-Munk equation:

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

Methods

Parametric Approach: Given the data from a crossed array, there are a number of potential approaches to directly modeling the mean and variance as a function of the control factors. A general approach is to assume that the underlying functional forms for the mean and variance models can be expressed parametrically. Assuming a \( d \) point design with \( n \) replicates at each location \( (i = 1, 2, \ldots, d) \), the point estimators of the process mean and variance, \( \bar{y}_i \) and \( \sigma_i^2 \), respectively, form the data for the dual response system. Since the purpose of this article is to demonstrate the utility of a hybrid approach (combining a parametric and nonparametric approach to modeling) for robust design, we will consider an “off the shelf” model for the mean. An “off the shelf” model for the process mean is linear in the model parameters and can be written as:

\[
\bar{y}_i = x_i' \beta + g^{1/2}(x_i' \gamma) \varepsilon_i
\]  

Where \( x_i \) and \( y_i \) are \( 1 \times k \) and \( 1 \times l \) vectors of means model and variance model regressors, respectively, expanded to model form, \( \beta \) and \( \gamma \) are \( k \times 1 \) and \( m \times 1 \) vectors of mean and variance model parameters, respectively, \( g \) is the underlying variance function and \( \varepsilon_i \) denotes the random error for the mean function. The \( \varepsilon_i \) are assumed to be uncorrelated with mean zero and variance of one. Note that the model terms for the \( i \)-th observation in the means model are denoted by \( X_i \) while the model terms for the variance model are denoted by \( Y_i \). This allows for the fact that the process mean and variance may not depend on the same set of regressors.
Similar to the modeling of the mean, various modeling strategies have been utilized for estimating the underlying variance function. Bartlett and Kendall [20] demonstrated that if the errors are normal about the mean model and if the design points are replicated, the variance can be modeled via a log-linear model with the $d$ sample variances utilized for the responses. A great deal of work has also been done using generalized linear models for estimating the variance function. Although not an exhaustive list, the reader is referred to Box and Meyer [21], Aitkin [22], Grego [23] and Myers et al. [24, 25]. As mentioned previously, since the purpose of this manuscript is to demonstrate the utility of a hybrid approach to modeling, we choose an “off the shelf” approach to variance modeling. The log-linear model proposed by Bartlett and Kendall [20] is a popular one [see Vining and Myers [26] and Myers and Montgomery [24] and is written explicitly as:

Variance model: $\ln(s_i^2) = g^*(X_i^*) + \eta_i = X_i^* \gamma + \eta_i$  \hspace{1cm} (2)

Where $\eta_i$ denotes the model error term whose expectation is assumed to be zero and whose variance is assumed constant across the $d$ design points.

Assuming the model forms for the mean and variance given in (1) and (2), the model parameters are estimated using the following estimated weighted least squares (EWLS) algorithm:

**Step 1:** Fit the variance model: $\ln(s_i^2) = X_i^* \gamma + \eta_i$, via ordinary least squares (OLS), obtaining $\hat{\gamma}_{OLS} = (X^* X^*)^{-1} X^* s^2$ where $y'$ is the $d \times 1$ vector of log transformed sample variances.

**Step 2:** Use $\hat{\sigma}_i^2 = \exp(X_i^* \hat{\gamma}_{OLS})$ as the estimated variances to compute the $d \times d$ estimated variance-covariance matrix for the means model, $\hat{\Sigma} = \text{diag}(\hat{\sigma}_1^2, \hat{\sigma}_2^2, ..., \hat{\sigma}_d^2)$.

**Step 3:** Use $\hat{\sigma}^{-1} = \tilde{y}^{-1}$ as the estimated weight matrix to fit the means model, yielding $\beta_{(EWLS)}^{(EWLS)} = (X' \hat{\Sigma}^{-1} X)^{-1} X' \hat{\Sigma}^{-1} \tilde{y}$ where $\tilde{y}$ denotes the $d \times 1$ vector of sample averages.

The algorithm above yields the following estimates of the process mean and variance functions:

Estimated process mean:

$E[y_j]^{(EWLS)} = x_j^* \hat{\beta}_{(EWLS)}^{(EWLS)}$ \hspace{1cm} (3)

Estimated process variance:

$\text{Var}[y_j]^{(OLS)} = \exp(x_j^* \hat{\gamma}^{(OLS)})$.  \hspace{1cm} (4)

Once estimates of the mean and variance have been calculated, the goal becomes finding the operating conditions for the control factors such that the mean is as close as possible to the target while maintaining minimum process variance.

Any control factor which influences the expression in (4) is known as a dispersion factor. Any control factor that does not influence the expression in (4) but does influence the expression in (3) is known as an adjustment factor. When both dispersion and adjustment factors are present, the robust design problem can be approached in a two-step fashion. Specifically, levels of the dispersion factors are chosen so as to minimize the estimated process variance in (4) and then the levels of the adjustment factors are chosen so as to bring the estimated process mean in (3) to a desired level. If only dispersion factors are present and these factors also influence the process mean, the researcher is left with finding the levels of the control factors that yield a desirable trade-off between low variance and a deviation from the targeted mean. This is often accomplished via minimization of an objective function such as the squared error loss (SEL):

$SEL = E[y(x) - T]^2 = \{E[y(x)] - T\}^2 + \text{Var}[y(x)]$, \hspace{1cm} (5)

Where T denotes the target value for the process mean. Minimization can be accomplished via non-linear programming using a method such as the generalized reduce gradient or the Nelder-Mead simplex algorithm. The SEL approach is also useful when adjustment factors are present but are not strong enough to bring the mean to the targeted value. Note that the determined set of optimal operating conditions is highly dependent on quality estimation of both the mean and variance functions. Misspecification of the forms of either the mean or variance models can have serious implications in process optimization [20, 21].

**Nonparametric Approach:** Situations may arise in which the user cannot explicitly state parametric forms for the dual model. In these situations, parametric specifications may result in serious bias of the estimated mean and/or variance. To prevent the bias induced by parametric model misspecification, VB and Anderson-Cook and Prewitt (2005) (henceforth referred to as AP) suggest the use of nonparametric regression for estimating the process mean and variance. Expressing the dual model where the mean and variance functions ($h$ and $g^*$, respectively) are assumed to have unknown but smooth forms we have:
Means model \[ \tilde{y}_i = h(x'_i) + g'(x'_i)e_i \]

Variance model \[ \ln(s_i^2) = g(x'_i) + \eta_i \]

Similar to parametric regression, estimators are linear combinations of the response values \( \tilde{y}_i \) and \( \ln(s_i^2) \); however, the weighting schemes in some nonparametric regression methods assign more weight to observations closest to the point of prediction, \( x_i \). The nonparametric fits are more flexible than the parametric fits as they are not confined to the user’s specified form. This enables the nonparametric approach to more adequately fit processes whose underlying models have more complicated forms than those expressed by the linear models in (1) and (2).

Several fitting techniques have been proposed in the nonparametric regression literature such as kernel regression [see for example Nadaraya (1964)[27], Watson (1964)[28], Priestley and Chao (1972)[29], Gasser and Müller (1984)[30], local polynomial models [see for example Fan and Gijbels (1996)[31]], spline-based smoothers and series-based smoothers [see for example Ruppert et al. (2003)[32]]. VB first applied nonparametric smoothing in the RPD setting by using the Gasser-Müller estimator for the dual response problem. AP continued with this idea by using the Nadaraya-Watson estimator and local polynomial regression (LPR), the method used in this research. LPR is a popular class of nonparametric smoothing methods and is particularly appealing in response surface applications due to its robustness to biased estimates at the boundary of the design space. LPR is essentially a weighted least squares (WLS) problem where the weights are given by a kernel function. The polynomial form of the local polynomial fit can be of order one or greater and we focus on degree \( p = 1 \) (local linear regression (LLR)) in this article.

For the multiple regressor case, at point \( x_0 = (x_{01},x_{02},...,x_{0k}) \) where prediction is desired, we define the kernel function as:

\[
K(\tilde{x}_0,\tilde{x}_i) = \frac{1}{b^k} \prod_{j=1}^{k} K\left( \frac{\tilde{x}_{0j} - \tilde{x}_{ij}}{b} \right),
\]

where \( \tilde{x}_i = (x_{i1},x_{i2},...,x_{ik}) \). \( K_{\tilde{x}_0,\tilde{x}_i} \) is a univariate kernel function and \( b \) is the bandwidth. Note that when estimating both the mean and variance nonparametrically, a different kernel function may be used for the mean than for the variance since the regressors effecting the mean do not necessarily effect the variance. The choice of kernel function is not crucial to the performance of the estimator (Simonoff, 1996[33]). Thus, for convenience, we will use the simplified Gaussian kernel, \( K(u) = e^{-u^2} \).

The smoothness of the estimated function is controlled by the bandwidth, \( b \). Since the coding of variables in response surface designs typically involves centering and scaling, the units are comparable in all directions. Thus, it is reasonable to use the same bandwidth, \( b \), in all dimensions as expressed in (6). The choice of bandwidth is critical and the literature is rich with bandwidth selection methods [see for example Härdle (1990)[34], Härdle et al. (2004)[35]]. Typically the bandwidth is chosen to minimize some optimality criteria such as MSE. Mays et al. (2001)[36] [henceforth referred to as MBS] introduce a penalized cross-validation technique, \( RESSS^* \), for choosing an appropriate bandwidth. The approach chooses the bandwidth as the value \( b \) that minimizes \( RESSS^* \), defined as:

\[
PRESS^* = \frac{PRESS}{d - \text{trace}(H^{(LLR)}) + (d - (k + 1)) \frac{\text{SSE}_{\max} - \text{SSE}_b}{\text{SSE}_{\max}}}
\]

Where \( \text{SSE}_{\max} \) is the largest error sum of squares over all possible bandwidth values, \( \text{SSE}_b \) is the error sum of squares associated with a particular bandwidth value \( b \), \( k \) is the number of regressors and the prediction error sum of squares, \( PRESS \), is given by:

\[
PRESS = \sum_{i=1}^{d} (y_i - \hat{y}_{i,-i})^2,
\]

Where \( \hat{y}_{i,-i} \) denotes the estimated response obtained by leaving out the \( i \)th observation when estimating at location \( x_i \). The LLR smoother matrix, \( H^{(LLR)} \) is defined as:

\[
H^{(LLR)} = \begin{bmatrix}
h_1^{(LLR)} \\
h_2^{(LLR)} \\
\vdots \\
h_d^{(LLR)}
\end{bmatrix}
\]

Where \( h'_i \) defined below. MBS show that \( PRESS^* \) performs well by guarding against very small and very large bandwidths.
The nonparametric estimate of the dual model is found by first estimating the underlying variance function and then, using the estimated variances as weights, an estimated weighted local linear regression (EWLLR) fit is found for the mean. For more information regarding weighted LLR, the reader is referred to Lin and Carroll (2000)[37]. Expressions for the fits are provided below:

Estimated process mean: \( \hat{E}(y_0)_{(EWLLR)} = X_0' \hat{\beta}^{(EWLLR)} \)

\[ = X_0'(X'W_0X)^{-1}X'W_0y = h_0^{(EWLLR)}y, \]  

(7)  

Estimated process variance: \( \hat{\text{Var}}(y_0)_{(LLR)} = \exp\left(\hat{\gamma}_{(LLR)}\right) \)

\[ = \exp[X_0'(X^*W_0^*X^*)^{-1}X^*W_0^*y^*] = \exp(h_0^{(LLR)}y^*). \]  

(8)  

Regarding notation for the means fit, \( h_{0i}^{(KER)} = x_0'(X'W_0X)^{-1}x'w_0, \) \( W_0 = \sqrt{\text{diag}(h_{0i}^{(KER)})} \) where \( \sqrt{\text{diag}(h_{0i}^{(KER)})} \) is the diagonal matrix containing the square roots of the kernel weights associated with \( x_0 \), \( \text{diag}(h_{0i}^{(KER)}) = \text{diag}(\sqrt{h_{01}^{(KER)}}, \sqrt{h_{02}^{(KER)}}, ..., \sqrt{h_{0d}^{(KER)}}) \) with \( h_{0i}^{(KER)} = \sum_{i=1}^{d} K(x_0, \tilde{x}_i) \) and \( \tilde{\gamma} \) is the estimated variance-covariance matrix, \( \tilde{\gamma} = \text{diag}(\hat{\sigma}_1^2, \hat{\sigma}_2^2, ..., \hat{\sigma}_d^2) \). Regarding notation for the variance fit, \( \gamma_{0i}^{(LLR)} = x_0'(X'W_0X)^{-1}x'w_0^* \) and \( W_0^* \) is the diagonal matrix containing the kernel weights associated with \( x_0 \). Under the assumption of normality of \( \tilde{\gamma} \) and \( y^* \), the estimates of \( \hat{E}[y_0] \) and \( \text{Var}[y_0] \) given by (7) and (8) are the local maximum likelihood estimates of Fan et al. (1995)[38].

Similar to the parametric approach to robust design, once estimates of the mean and variance functions have been calculated, a SEL approach will be used for process optimization. Unfortunately, most of the analytic optimization methods suggested for the parametric approach are based on gradient techniques which require continuous functions with derivatives for the estimated mean and variance functions. Since the mean and variance estimates from nonparametric methods do not result in closed form expressions, these optimization routines are no longer applicable. VB utilize a simplex search based on the AMOEBA algorithm (Vetterling et al., 1992[39]) which does not require the calculation of derivatives; however, simplex methods tend to be time consuming and often find local, as opposed to global optima [for details, see Haupt and Haupt (2004)[40]]. Therefore, we advocate the use of genetic algorithms (GAs) for optimization.

The GA, originally developed by Holland (1975)[41], has become a popular optimization technique. It is especially useful for optimizing functions that do not have known parametric forms, as it does not require derivatives to find the optimal solutions. Instead, the GA is based on the principles of genetics and uses evolutionary concepts such as selection, crossover and mutation to find the optimal solutions. Furthermore, GA uses an intelligent, sequential search strategy which enables the user to find global, not local, solutions more efficiently (Goldberg, 1989[42]). Thus, we will use the GA for process optimization.

**Parametric Vs. Nonparametric:** Parametric and nonparametric approaches to modeling each possess positive and negative attributes. The parametric method is superior if the true, underlying functions can be adequately expressed parametrically and if the user correctly specifies the parametric forms. However, if either of the models is misspecified, the estimates may be highly biased and optimal control factor settings may be miscalculated. On the other hand, if the user has no idea about the true form of the underlying functions, nonparametric methods offer a nice alternative. Nonparametric methods can provide superior fits by capturing structure in the data that a misspecified parametric model cannot. However, nonparametric methods were originally developed for situations with large sample sizes whereas a main underpinning of RSM is the use of cost-efficient experimental designs (i.e., small sample sizes). In small sample settings, nonparametric fitting techniques may fit irregularities in the data too closely thereby creating estimated mean and variance functions that are highly variable. Consequently, optimization may be based on non-reproducible idiosyncrasies in the data. MBS introduce methods which are essentially hybrids of the parametric and nonparametric methods. These semi-parametric approaches produce estimated functions which are characterized by lower bias than parametric approaches and lower variance than nonparametric approaches. The details of this hybrid approach appear in the next section.
### Table 1: Statistical summary of variables and Observed Data

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### Experimental Design:
The Box-Behnken Design used for experimental plan with five variables (liposome amount, temperature, time, Sodium Sulphate and pH) along with their ranges and K/S amount measured (two repeated measures and their average) for each test of design matrix are shown in Table 1 and 2, respectively.

The ANOVA table (Table 4) calculated from the obtained data shows that none of the considered factors and fitted model are significant.

Also the influence of the variable on the results Y [color strength (K/S)] is adjusted using the following second order polynomial function:

### Table 2: Design Matrix of the Experiment

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### Table 3: Design Matrix of the Experiment (continued Table 2)

### Table 4: Analysis of Variance of Data

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<th>Source</th>
<th>SS</th>
<th>df</th>
<th>MS</th>
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<td>0.07</td>
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<td>D-Sodium Sulphate</td>
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CONCLUSION

The analysis results of using parametric model approach in which it uses functional mean along with a variance model show that the model is insignificant with adjusted R-squared of 0.03 and therefore it is regarded as improper. Therefore, one of the alternative proper approaches may be nonparametric.

REFERENCES


