Application of Response Surface Methodology for Modeling the Color Strength of Natural Hair Colorant

Mohsen Hadizadeh*, Mohammad Khajeh Mehrizi, and Zahra Shahi

***Abstract*- Conventional methods of hair dyeing involve the use of chemical materials that result in unpleasant side effects, such as breakage of hair and cancer. A need was felt to formulate a dye containing plant products which is safe for use and does not have the problems of hypersensitive reactions. In this study, formulations containing natural hair colorants with madder dye and additives like herbal oils (almond, olive and coconut), ammonia and lemon juice were prepared. Response surface method was used to analyze color strength of hair colorant as dependent variable. Dye concentration, bath temperature and additives have been selected as independent variables. Color strength predictive model of natural hair colorants with madder dye is provided and this model has a high coefficient of determination. Also, it was indicated that, bath temperature has a great effect on enhancing the color strength of natural hair colorant. The optimization conditions of dyeing process parameters for polyhedral hair colorant production using response surface methodology were identified.**

***Keywords*: response surface methodology, natural colorant, madder, color strength, modeling**

I. INTRODUCTION

Hair dye is one of the oldest known preparations that have been used since the time of earliest man. The dyeing of hair was used by ancient cultures, such as ancient Egyptians, Persians and Chinese [1]. The premature graying of hair occurs due to reasons like stress, genetics and disease that the principal reason is hereditary. It is reported that by the age of fifty, half of the world's population will have gray hair. Hence there is a massive demand for hair dyes in the market [2]. Synthetic hair dyes that are available in the market contain combination of peroxide and ammonia and para-phenylenediamine (PPD), which causes allergic reactions, such as skin rashes, reddening of scalp, bladder cancer and non-Hodgkin's lymphoma in many people. The word "natural" on a bottle of hair color does not necessarily mean chemical-free. In other words, most of the marketed natural formulations intended for colouring hair contain PPD (harmful synthetic agent) at 20-25% concentrations [3,4]. The current preference for natural dyes is due to their excellent performance and healthfulness [5]. Natural dyes are derived from natural resources, such as plants (saffron); animals (some species of mollusks); insects (cochineal) and minerals (ferrous sulfate) [6]. Natural hair dyes solve the problem of irritation and scalp hair damaging and do not have the problems of skin staining and hyper sensitive reaction [7]. 100% Natural dyes (without mordants and synthetic agent), such as turmeric, henna, chamomile, etc. are biodegradable, eco-friendly and non-toxic to humans. However, natural dyes are not able to penetrate enough into the hair depth to protect dyed hair from fading or washing. The addition of some materials to hair dyes, such as developer and mordant, can improve hair dyeability. Lemon juice and ascorbic acid have been used as natural developers in hair products. The developer can open the hair cuticle and allows the dye molecules to penetrate deeper into the hair shaft [8]. From ancient days various materials from plants like henna, chamomile, madder, etc. are used to dye hair [9].

The major part of natural dyes, such as madder, anthocyanin and flavonoid dyes can be used to obtain red, yellow and brown shades [10]. Madder plant (Rubia tinctoria L.) and plants of the Rubiaceae family have been used since prehistoric times as source of natural red dye [11]. Madder produces a variety of anthraquinone pigments in its root. The main components are alizarin, purpurin and their derivatives, ruberythric acid and pseudopurpurin [12]. Anthraquinone structure in various regions is different. For example, the major pigments obtained from European madder and Indian madder are alizarin and purpurinanthraquinones, respectively [13]. This plant has also been used as natural food colourants and as natural hair dyes, too. In addition, this plant has anticancer, antimicrobial, antifungal, blood purifier and antirheumatic

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properties [14,15]. Madder is used to cleanse open wounds and remove skin blemishes. The madder extracts can be used for skin problems, especially tubercular conditions of the skin and mucous tissue. The decoction of madder can also be used as a bath additive [16].

Hair oils have been used for the prevention and treatment of baldness or other ailments of hair. They also promote the growth of hairs and are used as hair tonic [17]. For example, olive oil contains triolein, squalene and tocopherol¸ that gives softening and moisturizing properties to the hair [18]. It is used as skin and hair conditioner in cosmetics [19]. Coconut oil, which is containing polyunsaturated fatty acids, is useful in cosmetic formulations to protect and prevent drying of the skin [20]. Coconut oil which is used as a basic material for preparing hair oils enhances strength of hair and also prevents dryness of hair [21,22]. Almond oil has several important nutrients including fatty acids as well as vitamins E, D, B1, B2, B6, and A. The high vitamin E content in almond oil is helpful for conditioning the hair. Almond oil is used in some of hair care products because of the nourishing and smoothing benefits and the fact that it makes thick, strong and shinier hair grow [23].

Multivariate statistics techniques allow a significant reduction in the number of experiments, and the description of the impact of the independent variables in the process. Response surface methodology (RSM) is a fundamental tool in the field of engineering. Annadurai *et al.* used response surface method to model direct dye absorption by chitosan with experimental variables, temperature, pH and chitosan particle size [24]. Yingngam *et al.* analyzed and optimized the effect of independent variables (water to flower weight, distillation time) on the extraction yields of essential oil from Roxb flowers for cosmetic applications by using central composite design [25]. Sadeghi-Kijani *et al.* developed a response surface method to estimate the simple and combined effects of the operating variables in removing reactive colors with chitosan polypropylene amine (CS-PPI). Primary pH, color concentration, time contact and temperature were selected as independent variables in the color removal process [26]. Sinha *et al.* developed central composite design to predict the relationship between the experimental variables (pH, extraction time and amount of Annatto seeds used in extraction) on the total amount of natural dye extraction from seeds of bixaorellana (Annatto) as response variable. The study can be used as a guide for prediction of natural dye extraction under different experimental conditions in case of Annatto seeds [27]. Haji *et al.* analyzed and optimized the effect of plasma treatment time, concentrations of TiO_2 nanoparticles and citric acid on the self-cleaning properties of the polyester/wool fabric by using RSM [28].

The present study aims to formulate and evaluate polyhedral hair colorant of madder and additives, which is safe to use. Also, the study tried to evaluate the influence of the concentration, temperature and additive on color strength. Besides, using RSM, a model for natural hair colorants with madder dye was provided.

II. EXPERIMENTAL

A. Method

Response surface methodology is the procedure for determining the relationship between the input processes with the response and exploring the effect of these process parameters on the responses. The RSM also aims to reduce the cost and save time [29]. This approach has been widely used to optimize products and processes in manufacturing, chemical and other industries. The RSM results could be shown by contour plots or a function of the variables which was modeled by two types of approximating functions; first and second-order models, Eqs. (1) and (2):

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i \quad (1)$$

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_i^2 + \sum \sum_{i<j}^{n} \beta_{ij} X_i X_j + \in \quad (2)$$

In Eq. (1), Y is the responding variable, β_0 is the intercept of regression function, β_i is the regression coefficient and X_i is the independent variable. In Eq. (2), β_{ii} is the curvature term of independent variable and β_{ij} is the interaction coefficient between variables X_i and X_j [30]. There are many designs available for fitting a second-order model. The most popular one is the central composite design (CCD). This design was introduced by Box and Wilson. It consists of factorial points, central points, and axial points [31]. Fig. 1 shows central composite designs for two-and three-variable optimization, respectively [32].

CCD is appropriate for sequential experimentation and provides a reasonable amount of information for testing lack-of-fit while not involving an unusually large number of experimental runs [31]. Additionally, CCD provides high quality predictions of linear and quadratic interaction

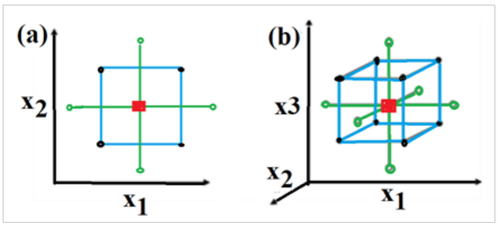

Fig. 1. Central composite designs for the optimization of: (a) two variables (α=±1.41) and (b) three variables (α=±1.68). (●) Points of factorial design, (○) axial points and (■) central point [32].

TABLE I
VARIABLES USED IN THE CENTRAL COMPOSITE DESIGN AND THEIR LEVELS

Numeric factors	Variable	Units	Levels		
			-1	0	+1
A	Temperature	°C	30	45	60
B	Concentration	%	2	3.5	5

effects of parameters affecting the process [33].

The plant powder of madder (Rubia cordifolia) and herbal oils (olive, coconut and almond oil) were purchased from the local herbal market in Yazd, Iran. Freshly squeezed lemon juice (Lemon fruits from a local market) was selected as natural developer. Also, ammonia used as alkaline (Ghatran Shimi Co., Ltd, Iran). Black human hair for dye testing was collected from barber shop and used for the study.

The hair samples were bleached with 5 mL of 12 %v/v hydrogen peroxide (a chemical developer) and mixed with 2 g of potassium persulfate (bleaching powder) for 40 min.

TABLE II
CATEGORICAL VARIABLE

Category factor	Variable	Units	Level 1	Level 2
C	Additives: olive oil coconut oil almond oil lemon juice ammonia	g	With additives	Without additives

The design expert software (version 7.0) was used for design of experiments and data analysis. The software examines all the variables and their interactions to be included in the proposed model. In this study, a face-centered central composite design (CCF design) was applied to analyse the three important variables with α=±1 for dyeing process. The codes and lower and higher values

TABLE III
DESIGN OF EXPERIMENTAL AND EXPERIMENTAL RESPONSES FOR BLACK HAIR AND BLEACHED HAIR

Run	Temperature (°C)	Concentration (%)	Additives (g)	Response (black hair)	Response (bleached hair)
1	45	3.5	Level 2	12.7	9.06
2	60	5	Level 2	14.78	12.41
3	45	3.5	Level 1	14.46	6.38
4	45	2	Level 2	9.77	9.3
5	45	2	Level 1	13.66	5.3
6	45	5	Level 2	12.72	11.17
7	45	3.5	Level 2	12.66	9.29
8	60	3.5	Level 2	13.36	10.75
9	60	5	Level 1	18.62	9.6
10	30	5	Level 2	7.64	10.04
11	30	2	Level 1	8.86	4
12	45	3.5	Level 1	14.8	6.66
13	60	3.5	Level 1	17.87	7.88
14	45	3.5	Level 1	14.79	5.79
15	30	3.5	Level 2	6.86	8.02
16	60	2	Level 1	16.89	6.62
17	45	3.5	Level 2	12.62	9.25
18	45	3.5	Level 1	14.31	6.15
19	30	5	Level 1	8.77	6.42
20	45	3.5	Level 2	12.6	9.3
21	45	3.5	Level 2	11.81	9.46
22	60	2	Level 2	11.55	9.72
23	45	3.5	Level 1	13.93	6
24	30	2	Level 2	6.61	7.46
25	45	5	Level 1	14.74	8.4
26	30	3.5	Level 1	8.88	4.83

TABLE IV
MODEL SUMMARY STATISTICS RESULTS OF THE FITTING THE EXPERIMENTAL DATA TO VARIOUS MODELS

Source model		STD. DEV.	R-squared	Adj. R-squared	Predicted R-squared	Press	
Black hair	Linear	1.16	0.885	0.869	0.83	43.75	
	2FI	1.03	0.921	0.896	0.818	46.73	
	Quadratic	0.5	0.984	0.976	0.961	10.10	Suggested
	Cubic	0.44	0.991	0.981	0.911	22.90	Aliased
Bleached hair	Linear	0.42	0.965	0.96	0.951	5.40	
	2FI	0.43	0.968	0.959	0.938	6.93	
	Quadratic	0.26	0.989	0.984	0.973	2.95	Suggested
	Cubic	0.29	0.991	0.981	0.903	10.82	Aliased

for each variable are listed in Tables I and II.

B. Dyeing Process

A smooth paste was made with distilled water (temperature: 30-60 °C), various concentration of madder (2-5 g) and additives (herbal oils, lemon juice, ammonia). The hair was kept in the paste for 2 h and then washed with water. The color strength of natural hair colorants with madder dye was considered as the target response. As can be seen, Table III shows 26 runs for dyeing black and bleached hair with conditions of the variables.

The results were examined using analysis of variance (ANOVA). The quality of the model was expressed by the coefficient of determination R^2 and its statistical significance was checked by the F-test.

C. Color Strength

The color strength (K/S value) was calculated from the diffuse reflectance of the samples using the Kubelka–Munk Eq. (3):

$$\frac{K}{S}=\frac{(1-R)^2}{2R} \tag{3}$$

Where, K is the absorption coefficient, S is the scattering coefficient and R is the reflection of the dyed hair [34]. Reflection behavior of samples in the visible area was evaluated under D65/10 illuminant/observer using an X-rite SP62 reflectance spectrophotometer (maximum absorbance wavelength was 400 nm).

III. RESULTS AND DISCUSSION

The RSM was applied to visualize the effect of three independent variables (concentration, temperature and additive) on the response (color strength) and models of the dyeing process were developed. The data were fitted to various models, and their subsequent model summary

TABLE V
RESULTS OF ANOVA OF BLACK HAIR FOR RESPONSE SURFACE QUADRATIC MODEL FOR COLOR STRENGTH

Source	Sum of squares	Degree of freedom	Mean square	F-value	P-value	
Model	252.65	8	31.58	127.69	<0.0001	Significant
A-temperature	172.14	1	172.14	696.00	<0.0001	
B-concentration	8.22	1	8.22	33.22	<0.0001	
C-additive	46.85	1	46.85	189.41	<0.0001	
AB	2.02	1	2.02	8.17	0.0109	
AC	5.73	1	5.73	23.16	0.0002	
BC	1.68	1	1.68	6.79	0.0184	
A^2	10.50	1	10.50	42.46	<0.0001	
B^2	0.88	1	0.88	3.55	0.0766	
Residual	4.20	17	0.25			
Lack of fit	3.11	9	0.35	2.54	0.1024	Not significant
Pure error	1.09	8	0.14			
Cor total	256.86	25				

statistics is shown in Table IV.

The quadratic models were suggested and the dyeing process was described with this model. Index statistics, standard deviation and R-squared coefficient for black hair, were determined 0.5, 0.98, and for bleached hair, were determined 0.26 and 0.99, respectively.

A high R-squared value implies that the model was statistically significant and only 2% of the total variations in dyeing black hair and 1% in dyeing bleached hair was not explained by the model. The "Adj R-Squared" was as close to the "Pred R-Squared" as one might normally expect. In our model, for black hair, the Pred R-Squared of 0.961 is in reasonable agreement with the Adj R-Squared of 0.976. Also, for bleached hair, the Pred R-Squared of 0.973 is in reasonable agreement with the Adj R-Squared of 0.984. Tables V and VI show the ANOVA results of the model for responses of dyeing black and bleached hair and the factors significant at 5% level were identified.

The analysis of variance is considered to be useful to test the statistical significance of the response surface quadratic model. This model F-value of 127.69 in dyeing black hair and F-value of 196.95 in dyeing bleached hair implies that this model is significant.

The significance of each term was determined by P-value (Prob>F), which is listed in Tables V and VI. In dyeing black hair, the "Lack of Fit F-value" of 2.54 compares the residual error to the pure error from replicated design points. There is 10.24% chance that this value of lack of fit will be occurred due to error. The non-significance lack-of-fit showed that the model was valid. The model equations in terms of coded factors for color strength of dyeing black and bleached hair are presented in Eqs. (4) and (5), respectively:

$$\frac{k}{s} = 13.37 + 3.79A + 0.83B - 1.34C + 0.5AB - 0.69AC + 0.37BC - 1.38A^2 - 0.4B^2 \quad (4)$$

$$\frac{k}{s} = 7.79 + 1.35A + 1.30B + 1.58C + 0.084AB - 0.12AC - 0.11BC - 0.055A^2 + 0.62B^2 \quad (5)$$

In these equations, A, B, and C are temperature, concentration and additives, respectively.

To evaluate the validity of the model that has satisfied the assumptions of the analysis of variance. In this study, a normality assumption for the response is satisfied. Fig. 2 shows the normal plots of residual. Residual is the difference between the observed and predicted value. A low value of this index is necessary for a good mathematical model fitted on observed data [31].

Residuals versus predicted plots in Fig. 3 indicate the residuals versus the ascending predicted response values. This plot tests the assumption of constant variance. The plot shows a random scatter.

The predicted responses and observed responses are shown in Fig. 4. It was indicated that the empirical models showed a good fit to the observed data and gave high value of determination coefficient (black hair: R^2=0.98, bleached hair: R^2=0.99). From the plots it can be concluded that the model has satisfied the assumptions of the analysis of variance.

In order to study the interaction among the different independent variables (temperature, and concentration)

TABLE VI
RESULTS OF ANOVA OF BLEACHED HAIR FOR RESPONSE SURFACE QUADRATIC MODEL FOR COLOR STRENGTH

Source	Sum of squares	Degree of freedom	Mean square	F-value	P-value	
Model	110.28	8	13.79	196.95	<0.0001	Significant
A-temperature	21.90	1	21.90	312.84	<0.0001	
B-concentration	20.38	1	20.38	291.23	<0.0001	
C-additive	65.29	1	65.29	932.75	<0.0001	
AB	0.056	1	0.056	0.80	0.3831	
AC	0.19	1	0.19	2.64	0.1224	
BC	0.15	1	0.15	2.20	0.1561	
A^2	0.016	1	0.016	0.24	0.6340	
B^2	2.11	1	2.11	30.13	<0.0001	
Residual	1.19	17	0.070			
Lack of fit	0.65	9	0.073	1.08	0.4607	Not significant
Pure error	0.54	8	0.067			
Cor total	111.47	25				

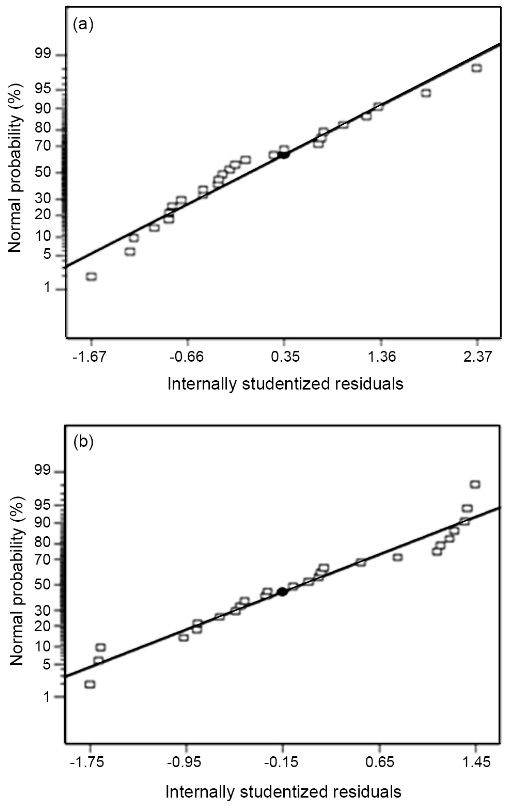

Fig. 2. Normal plots of residual: (a) bleached hair and (b) black hair.

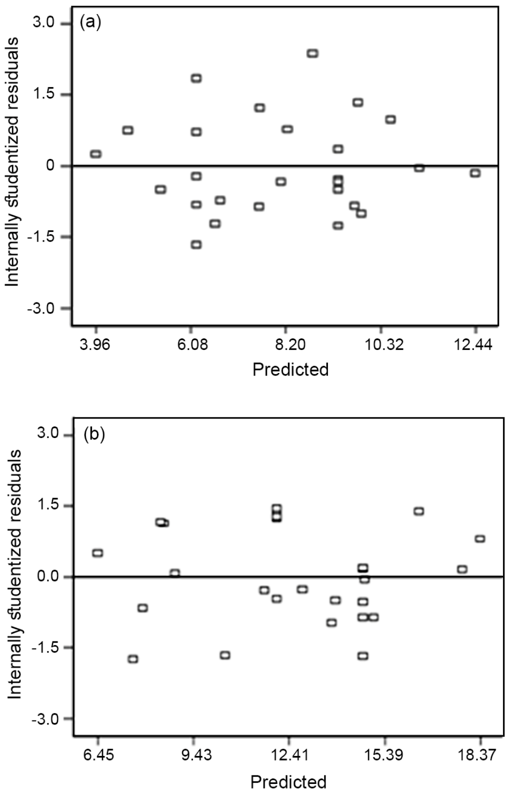

Fig. 3. Residual versus predicted plots: (a) bleached hair and (b) black hair.

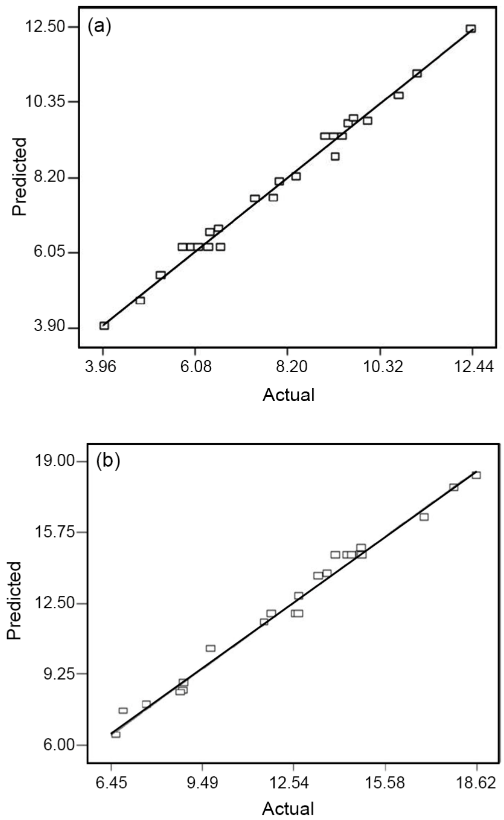

Fig. 4. Actual values versus predicted plots: (a) bleached hair and (b) black hair.

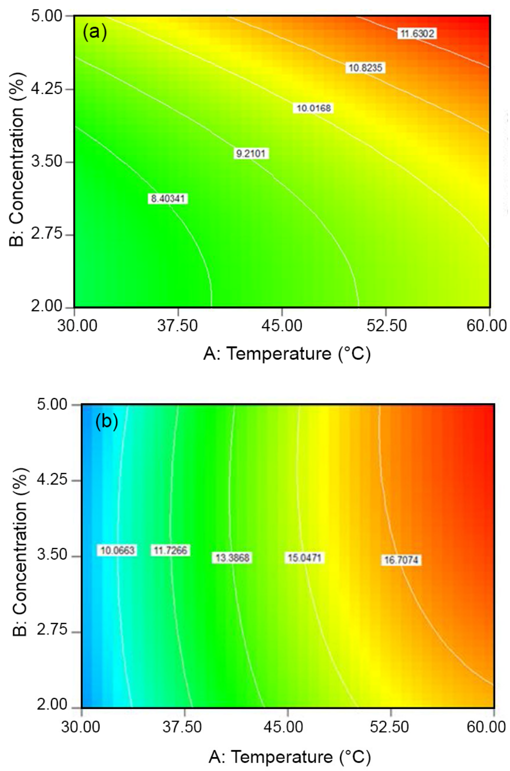

Fig. 5. Contour plots for the effect of temperature and concentration on color strength: (a) bleached hair and (b) black hair.

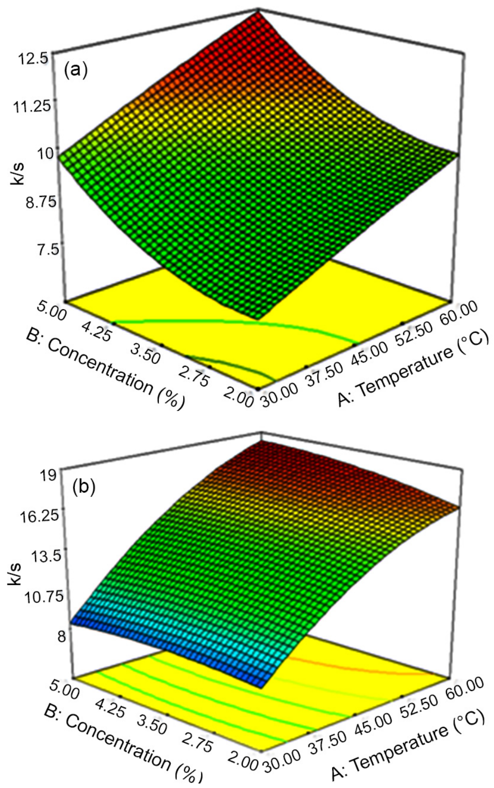

Fig. 6. 3-D plots for response surface for the effect of temperature and concentration on color strength: (a) bleached hair and (b) black hair.

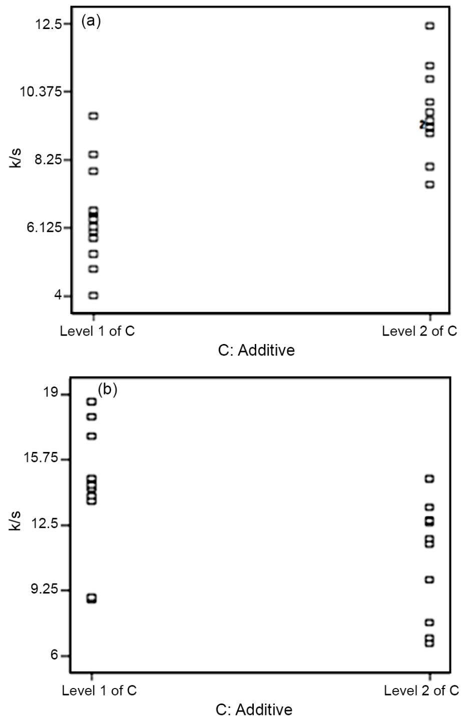

Fig. 7. Effect of additive types on the color strength: (a) bleached hair and (b) black hair.

and their corresponding effect on the response, contour plots and 3-D plots were drawn (Figs. 5 and 6).

A contour plot is a graphical representation of a three dimensional response surface as a function of two independent variables, maintaining all other variables at fixed level. These plots can be helpful in understanding both the main and interaction effects of the independent variables on the response [27]. Also, 3-D plots indicate that, bath temperature has a great effect on enhancing the color strength of natural hair colorant. As it can be seen, color strength increases in the direction of temperature axis.

Fig. 7 shows the effect of the additive on the response factor. Each additive is affecting the color strength in a different value. Therefore, the effect on the color strength was not the same. It can be seen that the additive presence (level 1) in dyeing black hair caused more color strength value and in dyeing bleached hair caused less color strength.

Microscopical observations of the effects of temperature and additive on black and bleached hair dyed with madder are shown in Fig. 8.

By using numerical optimization, a desirable value for each input factor and response can be selected. In this study, the numeric input variables were given specific ranged values and categorical variable were given at levels 1 and 2,

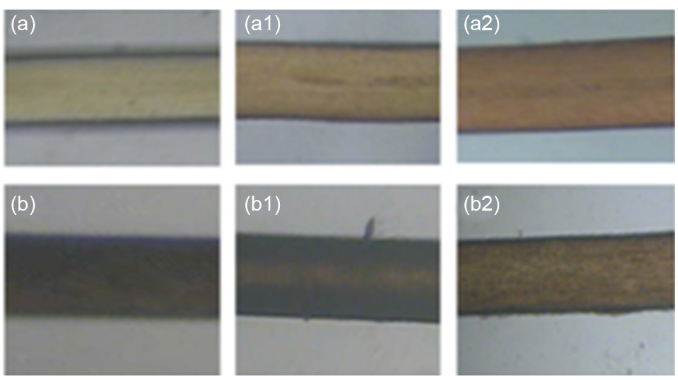

Fig. 8. Microscopic features (20X): (a) bleached hair, (b) black hair, (a1) colored bleached hair with additive presence and T=30 °C, (a2) colored bleached hair without additive presence and T=60 °C, (b1) colored black hair without additive presence and T=30 °C, and (b2) colored black hair with additive presence and T=60 °C.

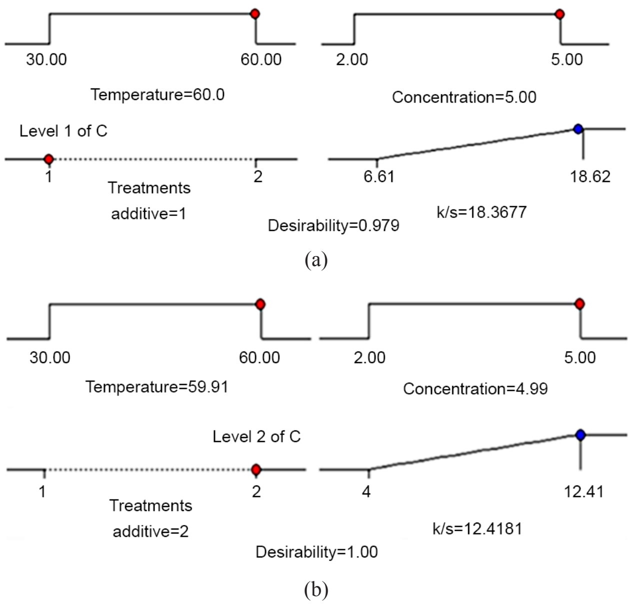

Fig. 9. Desirability ram: (a) black hair and (b) bleached hair.

whereas the response was designed to achieve a maximum. The maximum color strength for black hair (18.37) was achieved with the conditions having temperature 60 °C, concentration 5% and the additive presence (level 1) with the CCD experimental results as shown in Fig. 9a. Also, the maximum color strength for bleached hair (12.42) was achieved with the conditions having temperature 60 °C, concentration 5% and the additive presence (level 2) with the CCD experimental results as shown in Fig. 9b.

The effect of additives and change of the bath pH (acidic) can be attributed to the reaction between the dye structure and hair. Since the used dye is containing OH groups, it would interact with the protonated terminal amino groups of hair, that this ionic attraction would increase the dyeability of the black hair. By adding additives in bleached hair, the dyeability decreases due to destruction of chemical bonds in the hair and it causes decrease in the number of protonated terminal amino groups of hair and finally decline of the ionic interaction. In the other words, bleaching (oxidation of hair melanin) causes to break disulfide bonds of the hair keratin and breakdown of the cell membrane complex [8].

IV. CONCLUSION

In recent years, there has been a growing interest in the revival of natural dyes. This is mainly because natural dyes are environmental friendly and less allergenic compared with their synthetic dyes. In this study, color strength of natural hair colorant with madder dye was studied. Mathematical modelling can lead to a better understanding of the role of variables in hair dyeing process. The results of this research demonstrate that the color strength of hair dyed with madder dye can be modeled through response surface method. The effects of concentration, temperature and additives were investigated using RSM and CCD methods. R^2 and R^2_{adj} of the models indicate that the models enjoy a good fit. According to the results, the color strength significantly increased with increase in temperature as well as concentration. The bath temperature has a great effect on enhancing the color strength. Also, the additives presence in dyeing black hair caused higher and in dyeing bleached hair caused lower color strength. The optimization of experimental statistical design is a useful tool for prediction and understanding the interaction effects between experimental factors. Also, formulations of natural hair colorants containing madder dye and additives like herbal oils (almond, olive and coconut), ammonia and lemon are one of the achievements of the present research.

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