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Application of Hessian Matrix to Optimize Coagulation Treatment of Tannery Industry Wastewater Using Salt Solution Extracted *Moringa oleifera* Seeds Protein Coagulant

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The coagulation process using NaCl and KCl salt solution extracted protein from *Moringa oleifera* seeds is reported for tannery wastewater treatment in the present study. The important process parameters coagulant dosage and pH were optimized using Hessian matrix approach. Central composite design employing coagulant dose and pH as input variables was considered for developing response surface models for colour (%) and turbidity (%) removal. The dosage 45 mL and pH 7 was found to be optimum conditions for maximum 84 % colour removal by NaCl extracted coagulant, whereas for KCl extracted coagulant optimal point was 46.1 mL dosage and pH 6.9. For turbidity (%) removal using NaCl extracted coagulant the optimum condition was 40.2 mL dosage and pH 7.5. The removal efficiency of NaCl extracted coagulant was more than KCl extracted coagulant suggesting that NaCl salt solution is more effective in extracting the active agent from *Moringa oleifera* seeds.

Keywords: Tannery industry wastewater, *Moringa oleifera* seeds coagulant, Central composite design, Hessian matrix.

INTRODUCTION

The tannery industry utilize enormous volume of water for leather processing and generates equally large amounts of wastewater [1]. In order to meet the increasing water demand, many environmental regulations and legislations have been enacted to define the quality of water, set emission standards for wastewater and to control the emission of dangerous pollutants. Tannery wastewater is characterized by high organic loading, dissolved solids, suspended solids and toxic metals like chromium [2]. A large number of chemicals such as dyes, acids, tanning agents and salts are used in the tannery industry to convert raw animal skin into useful leather products [3]. Tannery wastewater is considered as one of the most hazardous wastes for the environment [4]. Various physico-chemical techniques such as coagulation, ozonation, reverse osmosis and activated carbon adsorption have been used for tannery waste treatment [5]. The turbidity in wastewater indicates the quality of water with respect to colloidal and residual suspended matter. Turbidity is a measure of the total suspended solids in water. The size of the colloidal particles in wastewater is typically in the range of 0.01 to 1.0 μm. The colour in tannery wastewater is due to the presence of various dissolved salts, colouring agents, dyeing material, dissolved metals and organic matter. The presence of residual impurities such as colour, turbidity, organic material *etc.* in tannery industry effluent is aesthetically undesirable and causes problems for the aquatic biosphere due to the reduction of sunlight penetration and depletion of the dissolved oxygen. Typical characteristics of tannery wastewater are shown in Table-1.

TABLE-1
PHYSICO-CHEMICAL CHARACTERISTICS OF RAW TANNERY WASTEWATER SAMPLE

Parameter	Magnitude
pH	8.4 ± 0.3
COD (mg/L)	3600 ± 300
Chromium (mg/L)	21 ± 2.5
Turbidity (NTU)	52 ± 2
TDS (mg/L)	19300 ± 300
Colour	Dark green

Coagulation has been used for many years either as a main or pretreatment of wastewater due to its low capital cost. Coagulation is a widely used process to treat turbid wastewater [6]. Traditional coagulants such as alum, ferric chloride, aluminium chloride and ferric sulfate are most widely used in water treatment [7]. Chemical coagulants show better performance in activity compared to plant based natural coagulants. Still the water treatment plants are looking for suitable alternate to chemical based coagulants. Some of the reasons cited are:

(i) wastewater treated using alum salts contain residual aluminium which is responsible for causing Alzheimer's disease [8] and neurological disorder namely 'per-senile dementia' [9]; (ii) There is a significant reduction in pH of treated water when alum reacts with natural alkalinity already present in water [10]; (iii) Many wastewater treating units across the world can hardly afford the rising prices of chemicals for water treatment [11]. The treated water produced by biological treatment system cannot be reused by the plant [12].

Natural coagulants of vegetable origin like *Moringa oleifera*, *Cactus latifaria*, *nirmali seeds* and *Prosopis juliflora* were used for the water treatment before the development of chemical salts. In remote areas of some developing countries, *Moringa oleifera* seeds were used for removing turbidity from drinking water [13]. About 4000 years ago, the seeds of nirmali tree were used to remove turbidity from surface water [14]. Plant based coagulants are cost effective, highly bio degradable and would not produce treated water with undesirable properties. Natural coagulants are generally either polysaccharides or proteins [15].

Moringa oleifera, a native tree of India, is grown most widely in tropical regions. *Moringa* seeds contain water soluble coagulant [16] and can be effective in the treatment of tannery wastewater because they contain cationic electrolytes [17]. Muller and Jahn studied the use of *Moringa oleifera* as a natural coagulant for surface water treatment [18]. It was suggested that *Moringa* seed coagulant is a cationic protein with a molecular mass less than 6.5 Kilo Dalton and iso electric point greater than 9.6 [19]. It has been proved that the active component from an aqueous salt extraction is an organic polyelectrolyte with a molecular weight of approximately 3 Kilo Dalton [20]. It is not suitable for the *Moringa* seed coagulant to form inter particle bridging, as it has a low molecular weight of 13 Kilo Dalton [21]. The *Moringa* coagulant rarely alters the pH and conductivity of treated water. Hence it is suggested that the *Moringa* seed coagulant is a suitable material for tannery wastewater treatment, as it is more efficient in treatment and eco friendly.

Response surface methodology (RSM) is a quadratic modeling technique that gives the relationship between the factors and the responses of an experiment. Response surface methodology includes the influences of the individual factors as well their interaction [22]. The present paper studies the treatment of tannery wastewater using the coagulation process and is an attempt for determining the optimum conditions for the removal of colour and turbidity from tannery wastewater using Hessian matrix.

EXPERIMENTAL

Preparation of coagulant: Dry *Moringa oleifera* seeds were collected from rural areas in Tamil Nadu, India. The husk covering the seeds was removed manually, good quality seeds were selected and the seed kernel was ground to a fine powder using an electric blender. Sodium chloride solution (0.25 M) and potassium chloride solution (0.25 M) were used to extract the active component from the seeds. 5 g of seed powder in 100 mL salt solution (5 % concentration) was used for the coagulant preparation. A magnetic stirrer was used to stir the contents for 15 min at room temperature. The resulting suspension was filtered and the filtrate solution was used as a coagulant for further studies. Fig. 1 reveals the protein characteristics of the *M. oleifera* seeds as shown by SDS-PAGE. Dialysis was performed to remove the salt content before identifying the nature of coagulating protein. Sodium chloride extracted coagulant show excellent coagulating ability as high intensity bands are observed at two molecular weight regimes (5 KDa and 35 KDa).

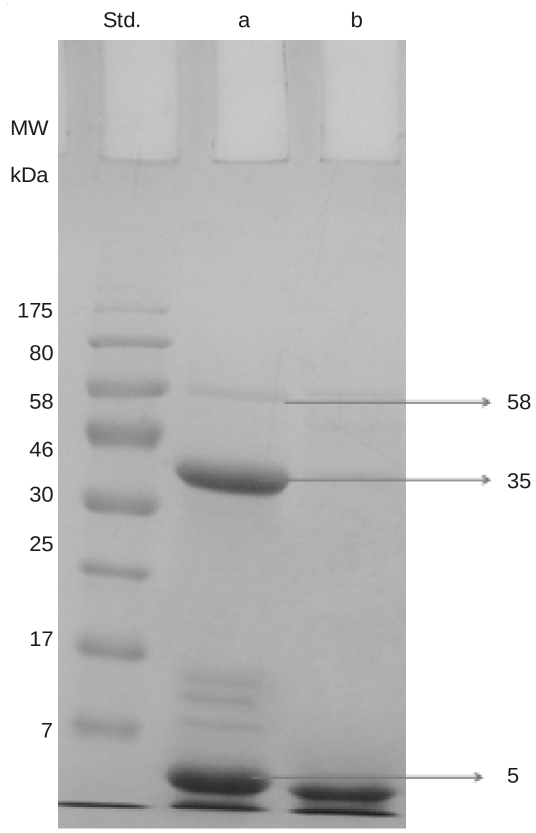

Fig. 1. SDS-PAGE separation on *Moringa* proteins. (a) NaCl salt solution extracted coagulant (b) KCl salt solution extracted coagulant. Std: molecular weight standards

Coagulation experimental procedure: Tannery effluent was collected from a common effluent treatment plant (CETP) in chromepet area near Chennai city of Tamil Nadu. Samples were diluted to 10 % of their initial concentration and the diluted samples were used for analysis. The pH of the sample was adjusted, before the addition of the coagulant, using 0.5 N H_2SO_4 or 0.5 N NaOH solution as required.

Coagulation experiment was conducted using the conventional jar test experiment. It consists of six 1 L beakers, which were agitated simultaneously, using a stirrer. The beakers were filled with 500 mL of diluted wastewater and the coagulant was added to each beaker in varying quantities from 10 to 50 mL. Rapid mixing for 3 min was carried out at 150 rpm. It was subsequently followed by slow mixing for 30 min at 30 rpm. After coagulation, sedimentation was allowed for 30 min [23]. Slow mixing permits the formation of the aggregate solids and flocs, which could be removed by plain sedimentation and the ultra filtration process. The supernatant was filtered using the Whatman filter paper and the filtrate was analyzed for residual colour and residual turbidity. The filtrate was analyzed for absorbance, using the UV spectrophotometer (Hitachi-U3210, Japan) at a maximum wavelength of 391 nm. Colour removal efficiency was measured as a decrease in the optical density at 391 nm. Turbidity analyses were conducted using the digital Lovibond turbidity meter.

Experimental design using central composite design and data analysis: The range of critical parameters that were obtained from the preliminary studies was used in central composite design as input to design 13 experiments for two factors. The most popular class of second-order design called central composite design was used in the experimental design. Central composite design is well suited for fitting a quadratic surface and works well for the process optimization. In this study, the rotatable experimental plan was implemented as a central composite design. The effect of two variables namely coagulant dosage and pH was studied. In the coagulation process the colour removal and turbidity removal efficiency was investigated. A total of 13 experiments according to a 2^2 full factorial central composite design, consisting of four cube points (-1,+1), (+1,+1), (-1,-1), (+1,-1), four axial points (0,+α), (0,-α), (-α,0), (+α,0) and five replicate points at the centre (0,0) were conducted. The value of α depends on the number of points in the factorial portion of design which is given as, $\alpha = (N_F)^{1/4}$ where N_F is the number of points in the cube portion of the design and is calculated by $N_F = 2^n$, n is the number of factors. In this study, n = 2 factors and thus $\alpha = (2^2)^{1/4} = 1.414$. A value of α = 1.414 is the axial distance from the center point and makes the design rotatable. Such a design provides equally good predictions at points equidistant from the center, a very desirable property for optimization. The level of two main parameters which was generated by central composite design based on input values for experimental design procedure is presented in Table-2. For regression analysis, the relation between actual variable (with dimension) and coded variable (dimensionless) in this study is given by:

$$\text{Actual dose} = (20 \times \text{coded dose}) + 30 \tag{1}$$

$$\text{Actual pH} = (2.5024 \times \text{coded pH}) + 6.5 \tag{2}$$

Eqns. 1 and 2 are useful in converting coded variables to actual variables. Hessian matrix is used to solve model equations in order to find the optimum dose and pH values.

The experiments were performed based on the design matrix provided by central composite design, as shown in Table-3 and the responses were found for both the NaCl and KCl extracted coagulant. The data were analyzed using Design Expert software (version 8.0.7.1) and MiniTab (Version 15) and the effect of process variables on the responses was studied using the 3D surface graph, contour plot, diagnostic plot, main effect and interaction effect plots. The significance of the regression coefficients for models is explained based on statistics. The quality of the fitted model was also suggested by various statistical parameters, such as the coefficient of determination R^2, adjusted R^2, coefficient of variation, model F-value *etc*.

Response surface methodology and Hessian matrix: The relationship between the process responses (% colour removal and % turbidity removal) and independent variables (coagulant dose and pH) is well represented by second order quadratic model. central composite design is a very useful design tool for fitting the second-order models [24,25]. The collected data's were analyzed statistically using the regression technique. The quadratic equation model for predicting the optimal conditions can be expressed as

$$z = b_o + b_1x_1 + b_2x_2 + b_{12}x_1x_2 + b_{11}x_1^2 + b_{22}x_2^2 \tag{3}$$

where 'z' is the predicted response (colour removal or turbidity removal efficiency), b_o the constant coefficient, b_1 and b_2 are

TABLE-2
CENTRAL COMPOSITE DESIGN EXPERIMENTAL FACTORS AND THEIR LEVELS

Factors	Coded factor level (x_i)				
	Lowest {-1.414(-α)}	Low {-1}	Center {0}	High {+1}	Highest {+1.414 (+α)}
A, coagulant dose (mL)	1.72	10	30	50	58.28
B, pH	2.96	4	6.5	9	10.04

TABLE-3
CENTRAL COMPOSITE DESIGN IN CODED UNIT AND RESULTS FOR NaCl AND KCl EXTRACTED COAGULANT

Run	Central composite design data's		NaCl extracted coagulant		KCl extracted coagulant	
	Dose (A)	pH (B)	Colour removal (%)	Turbidity removal (%)	Colour removal (%)	Turbidity removal (%)
1	0	0	74.99	66.23	67.25	58.88
2	0	-1.414	39.93	45.44	34.23	38.22
3	0	0	75.13	64.13	66.98	57.17
4	0	0	74.01	66.97	68.12	59.23
5	1	1	72.13	64.67	67.01	63.67
6	0	1.414	47.12	56.12	42.67	49.73
7	0	0	75.67	67.11	66.12	58.22
8	1.414	0	79.22	62.14	71.25	61.93
9	1	-1	60.32	56.33	55.22	54.11
10	0	0	73.99	65.12	67.23	56.32
11	-1	1	23.14	49.93	19.14	40.93
12	-1	-1	21.37	39.20	19.42	27.32
13	-1.414	0	04.33	03.84	03.92	06.82

the linear coefficients, b_{12} the interaction coefficient, b_{11} and b_{22} are the quadratic coefficients and x_1, x_2 are the coded values of the variables dosage and pH respectively. Design expert software was used for generating response surface plot, contour plots respectively. The complete model equations for all the responses were developed based on statistical significance of the regression coefficients. Such coefficients were computed by means of multiple linear regression method in order to minimize the sum of squares of the residuals. The quality of the proposed models revealed by using the diagnostic checking tests provided by analysis of variance (ANOVA). The statistical analyses are done by Fisher's F test and P-value (based on probability). All the model terms were evaluated by the P-value with 95 % confidence level. Finally, the optimal values of the critical parameters were obtained by analyzing the response surface and contour plots and also by solving the regression equation using Hessian matrix method.

Hessian matrix is the square matrix of second order partial derivatives of a multi variable function. It describes the local curvature of a function of many variables [26]. Hessian matrix is helpful in solving a multi variable function for calculating independent variables value. The calculated Eigen value from Hessian matrix is used to predict the nature of the optimum points.

For a multi variable function $z = f(x_1,x_2)$, optimal point is calculated through

$$X = -(H^{-1} \times b) \quad (4)$$

where

$$H = \begin{pmatrix} \frac{\partial^2 z}{\partial x_1^2} & \frac{\partial^2 z}{\partial x_1 \partial x_2} \\ \frac{\partial^2 z}{\partial x_2 \partial x_1} & \frac{\partial^2 z}{\partial x_2^2} \end{pmatrix} = \text{Hessian matrix}$$

$$H^{-1} = \text{Hessian matrix inverse} = \frac{\text{Adjoint of matrix H}}{\text{Determinat of matrix H}} = \frac{\text{adj(H)}}{|H|}$$

$$b = \text{Column matrix of linear term coefficients} = \begin{pmatrix} b_1 \\ b_2 \end{pmatrix}$$

X = Column matrix of independent variables =

$$\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \begin{pmatrix} \text{coded dosage} \\ \text{coded pH} \end{pmatrix}$$

The adjoint and determinant of a given 2 × 2 square matrix $A = \begin{pmatrix} a_1 & a_2 \\ a_3 & a_4 \end{pmatrix}$ is calculated using,

$$\text{adj (A)} = \begin{pmatrix} a_4 & -a_2 \\ -a_3 & a_1 \end{pmatrix} \text{ and } |A| = (a_1 \times a_4) - (a_2 \times a_3)$$

Enq. 4 is derived based on the principle that the slope of tangent plane becomes zero at the peak response value, thus making the partial derivatives of multi variable function with respect to x_1 and x_2 equal to zero. If the model equations were developed in terms of dimensionless coded factor, then solution through eqn. 4 would give result in coded factors. These coded factor were converted to actual factor using eqns. 1 and 2. The nature of the stationary points (maximum, minimum or saddle point) is checked by predicting the Eigen values of Hessian matrix. Eigen values were calculated by the equation:

$$|H - (e \times I)| = 0 \quad (5)$$

where the parallel lines mean determinant, 'e' is the column matrix of Eigen value and 'I' represents 2 × 2 unit matrix. The expansion of the determinant in eqn. 5 yields a quadratic equation which on solving calculates the two Eigen values. The nature of Eigen value is used to characterize the nature of optimum point (maximum, minimum or saddle point).

RESULTS AND DISCUSSION

Effect of coagulant dosage on colour removal and turbidity removal efficiency: It was observed from the preliminary study that optimum range for the process is 10-50 mL dosage and pH 4-9. The experiments were carried out by varying a single factor while keeping all other factors constant. These experiments were conducted to determine a narrower range of pH and coagulant dosage prior to designing the experimental runs. The experimental results showed that coagulant dosage presented high performance at neutral pH value. By increasing dosage beyond a specific value, the colour removal efficiency was attenuated and finally the curve approached a flat profile. The turbidity removal was decreased beyond certain dosage limit. It may be due to increase in stability of suspended impurities.

Response surface model equations: By using multiple regression analysis, the responses (% colour removal and % turbidity removal) were correlated with the two variables using the second order polynomial represented by eqn. 4. In terms of coded factor, the quadratic regression model equation developed for all the responses is,

$$\text{Colour removal (\%)} = +74.76 + 24.23\,A + 2.97\,B + 2.51\,AB - 16.09\,A^2 - 15.22\,B^2 \quad (6)$$

(NaCl coagulant)

$$\text{Turbidity removal (\%)} = +65.91 + 14.29\,A + 4.27\,B - 0.6\,AB - 13.8\,A^2 - 4.9\,B^2 \quad (7)$$

(NaCl coagulant)

$$\text{Colour removal (\%)} = +67.14 + 22.36\,A + 2.93\,B + 3.02\,AB - 14.23\,A^2 - 13.80\,B^2 \quad (8)$$

(KCl coagulant)

$$\text{Turbidity removal (\%)} = +57.97 + 15.93\,A + 4.93\,B - 1.01\,AB - 9.96\,A^2 - 5.16\,B^2 \quad (9)$$

(KCl coagulant)

where A and B are the independent variables representing coded values of the process variables namely coagulant dosage and pH respectively. The objective function for all models is represented generally as,

Maximize:

Colour (%) or turbidity removal (%) =
f (A, B) = f (coded dosage, coded pH)

Subject to non-negative constraints: $10 \leq A \leq 50$
$4 \leq B \leq 9$
$A > 0; B > 0$

The statistical analysis gives comparative measure for the model selection. Model having high R^2 statistics is the best one.

Process analysis and effect of process variables: The process analysis was done based on the data correlation pattern which shows that the removal mechanism for colour and turbidity is almost similar. The values of R^2 for % colour removal and % turbidity removal by the NaCl extracted coagulant were 0.9938 and 0.8512 respectively. This is evident from Figs. 2 and 3, which show a straight line pass through the origin and slope approximately equal to unity. The line equation is of the form y = mx (*i.e.*) predicted value = (slope) x (actual value) with slope equal to one. The linear trend shows that the equation is (predicted value) ≈ (actual value). The graph shows that the angle between the line passing through the origin and the positive direction X-axis is almost, equal to 45°, which indicates that the slope of line is unity. The responses for KCl coagulant also have higher R^2 values of 0.9957 and 0.9322 respectively. This clearly shows that the models are better predictors of the response. The result well matches for colour removal between experimental and model predicted values. For turbidity removal, there is a slight deviation between experimental and predicted values at initial dose level.

The graphical representations of the model eqns. 6-9 explain the effect of experimental factors on the responses. The 3D surface graphs and contour plots between the factors were obtained using the analysis software and were presented in Figs. 4 and 5. The response surface graph shown in Fig. 4(a) implies that the % colour removal increases with the coagulant dosage and reaches an optimum at 45 mL and pH 7. Increase in % colour removal is attributed to the greater availability of the active coagulating agent. The surface curvature shows that interactions between the factors are not significant. The optimum dosage and pH lie well within the design boundary. It can be concluded that the % colour removal decreases slowly after the optimum point, indicating surface slope is changing at a slower rate. At an optimal point, the necessary condition is that the response surface slope becomes equal to zero. The tangent plane at the optimal point would be parallel to the dosage-pH plane. An increase in dosage and pH beyond the optimum point shows a decrease in the colour removal efficiency. This may be attributed to the increase in surface zeta potential of individual impurity particles which promote the Brownian motion of particles. Thus there is a significant reduction in interaction between the impurities and coagulant cations.

Fig. 4(b) shows the variation of % turbidity removal with respect to the coagulant dosage and pH. Surface graph reveals less curvature which implies less interaction between the process factors. At low coagulant dosage range (10-25 mL) pH had a constant effect on the % turbidity removal. The

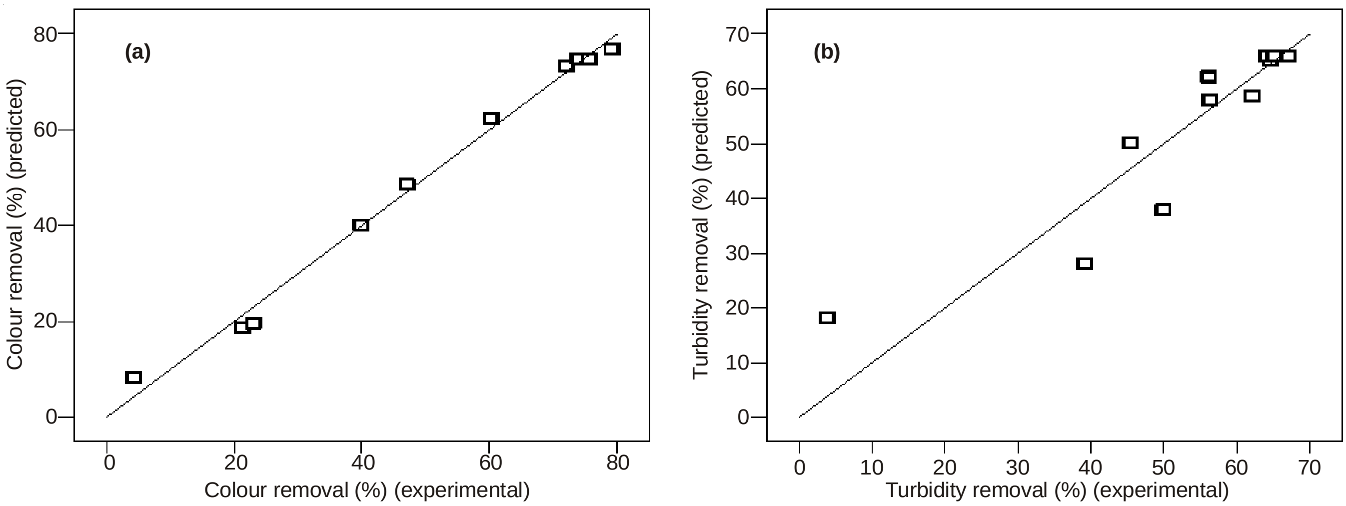

Fig. 2. Predicted *vs*. experimental data for NaCl extracted coagulant for (a) colour removal (%) (b) turbidity removal (%)

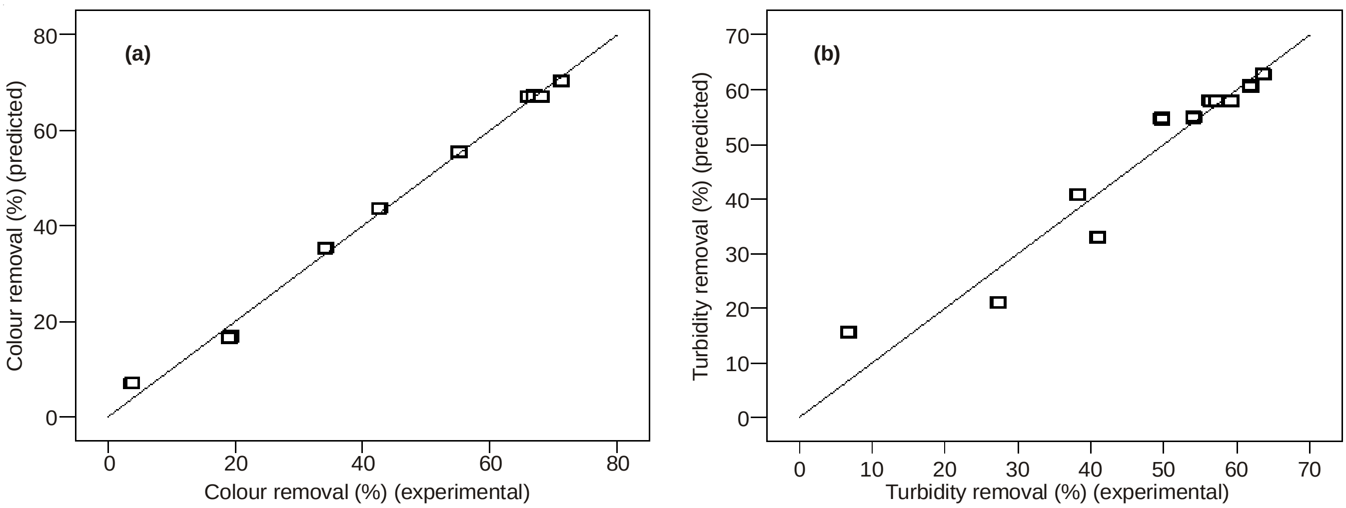

Fig. 3. Predicted *vs*. experimental data for KCl extracted coagulant (a) colour removal (%) (b) turbidity removal (%)

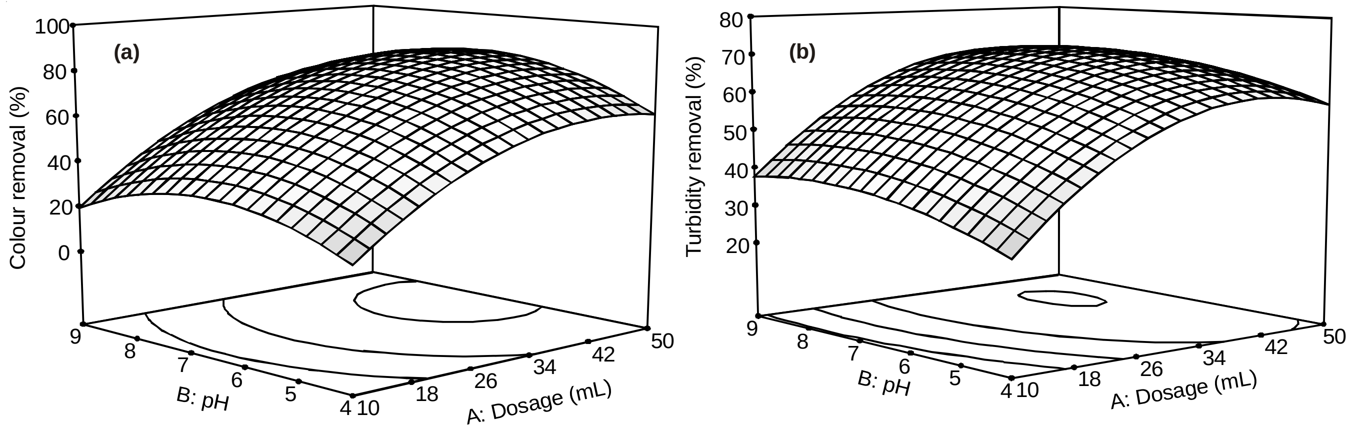

Fig. 4. Effect of coagulant dosage (NaCl extracted) and pH on (a) colour removal (%) (b) turbidity removal (%); 3D surface graph and contour plot

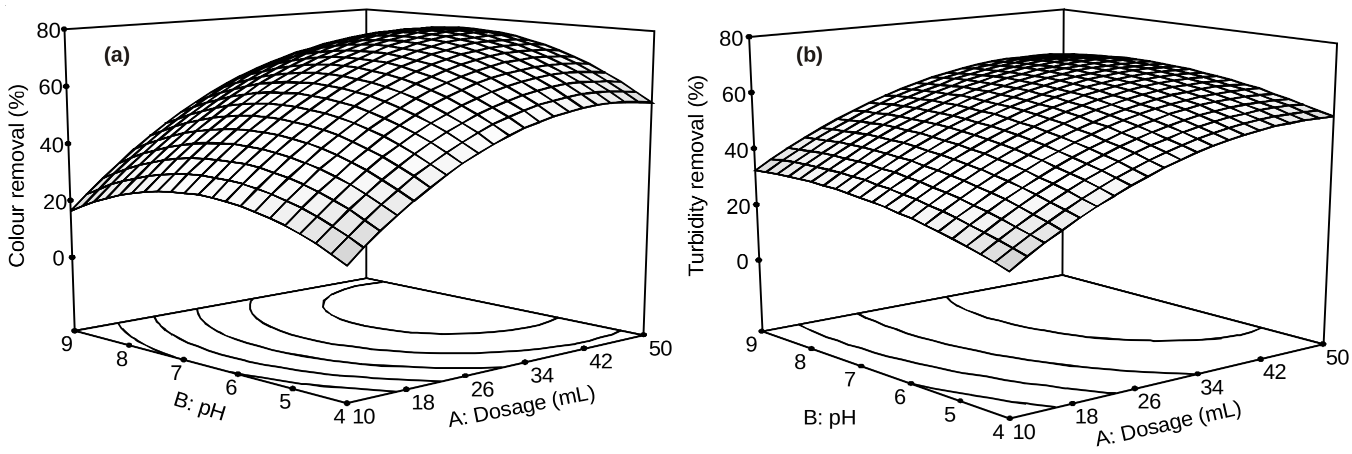

Fig. 5. Effect of coagulant dosage (KCl extracted) and pH on (a) colour removal (%) (b) turbidity removal (%); 3D surface graph and contour plot

response was affected mainly by dosage. The maximum % turbidity removal was obtained at 40 mL dosage and 7.5 pH. The response surface graph for % colour removal and % turbidity removal for the KCl coagulant is shown in Fig. 5(a) and 5(b). In Fig. 5(a) the response shows the peak value at 45 mL coagulant dosage and pH 7. The non elliptical contour lines in the dosage-pH plane indicate the poor interaction effect of factors. The optimal point is situated at the extreme right end of the design boundary. The response surface slope increases initially at a faster rate, reaches the maximum and then decreases at a slower rate. In Fig. 5(b) the response surface shows that the maximum turbidity removal efficiency is obtained at 45 mL dosage and 7.5 pH. The response surface has a small slope initially, which increases at a slow rate and reaches a maximum. This indicates that the % turbidity removal efficiency is more or less constant for each dosage-pH combination. The response surface shows less curvature and almost resembles a plane which is parallel to the reference plane (dosage-pH plane). The contour lines on this plane show that at lower dosage range, pH has little effect on the % turbidity removal whereas the coagulant dosage is the major dominating factor. The centre point of elliptical contour curve is the optimum points ($dosage_{opt}$, pH_{opt}), which gives the maximum response value.

Main effect plots and interaction plots for colour removal and turbidity removal: The main effect and interaction effect of factors are shown for both responses in Figs. 6-9. It is inferred from Fig. 6(a) that as the dosage increases, the % colour removal increases indicating the greater availability of the active coagulation component. In an acidic pH region, the colour removal efficiency decreases due to the restabilization of suspended colloidal particles. Fig. 6(b) shows that the mean % turbidity removal is approximately 55 %. It was observed that the pH had less effect on turbidity removal efficiency, when compared to dosage. Hence, it can be concluded that dosage is the influencing factor for turbidity removal. The interaction plot for all variables is shown in Figs. 8 and 9. It was observed for colour removal that both dosage and pH had a significant effect. The variation in turbidity removal efficiency was found to be less with respect to the change in pH. This decrease in the turbidity removal with increasing dosage may be due to restabilization of the suspended particles at higher pH values. It could be due to the better availability of H^+ ions in the acidic medium, there by enhancing the charge repulsive force between the coagulant cation and H^+ ions. The strong repulsive force prevents the cation from adsorbing onto the impurity particle, thus making the coagulation process passive.

Statistical analysis: The statistical parameters obtained from ANOVA for the proposed models are given in Table-4. The model F-value for all the responses shows that the model is significant. F-test was used to determine the significance of

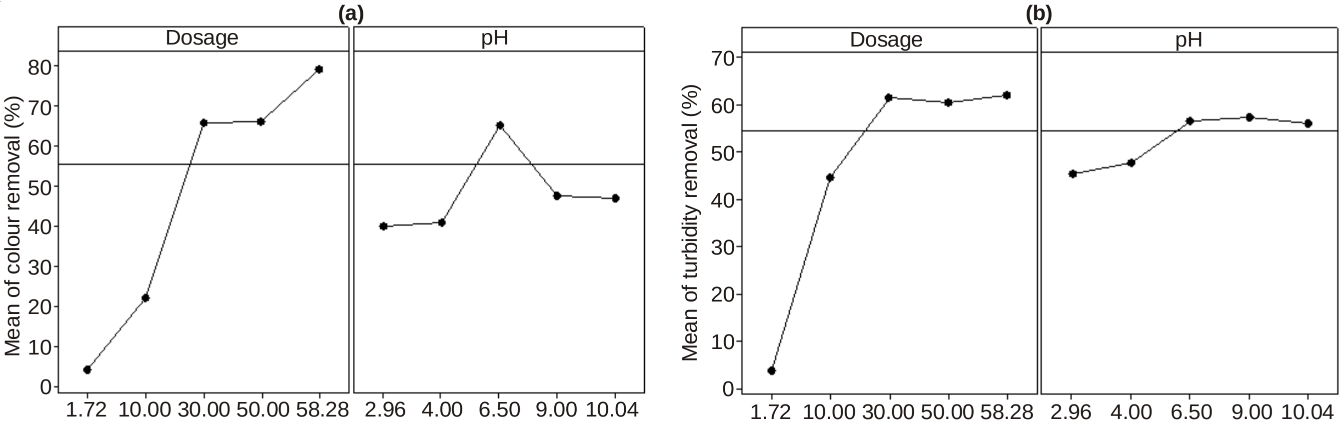

Fig. 6. Main effects plot using NaCl coagulant for (a) colour removal (%) (b) turbidity removal (%)

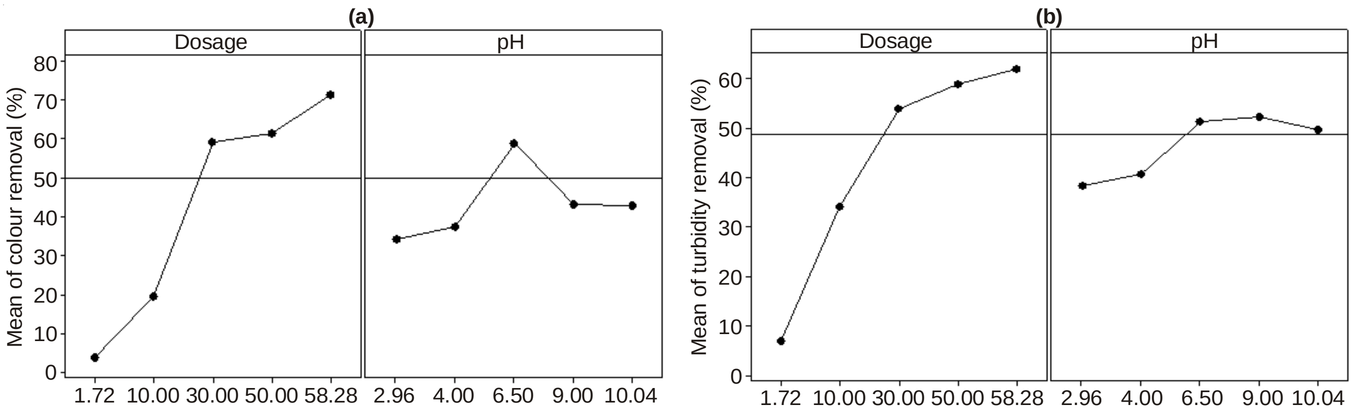

Fig. 7. Main effects plot using KCl coagulant for (a) colour removal (%) (b) turbidity removal (%)

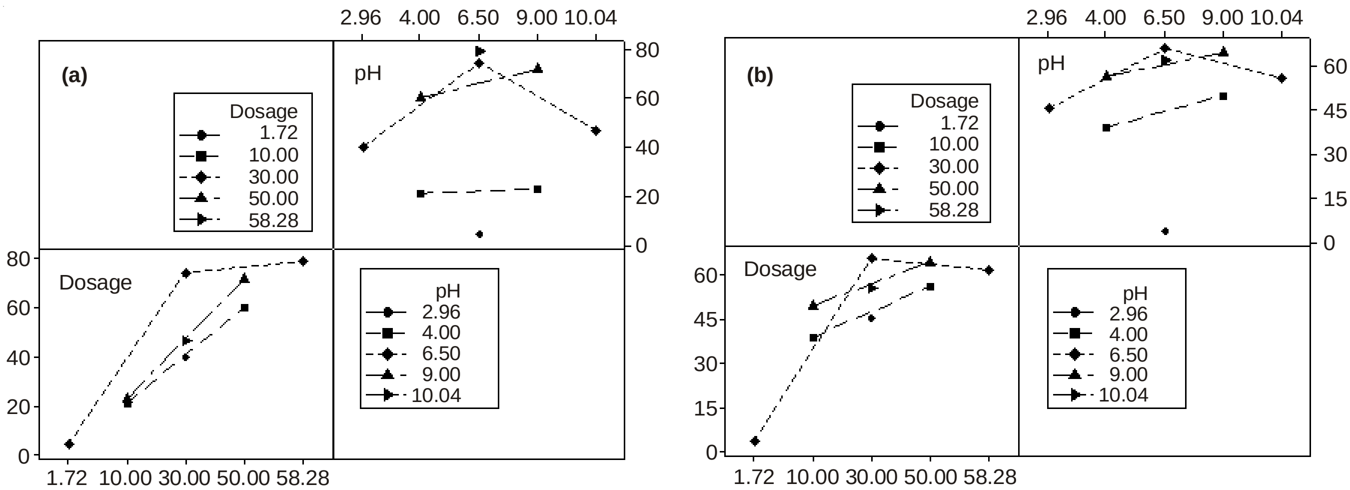

Fig. 8. Interaction plot using NaCl coagulant for (a) colour removal (%) (b) turbidity removal (%)

the regression coefficients of the parameters. The larger the magnitude of F value and smaller the "p > F", the more significant is the corresponding model. The values of R^2 for % colour removal and % turbidity removal by the NaCl and KCl extracted coagulant were 0.9938, 0.8512, 0.9957 and 0.9322 respectively. This indicates that only 0.62, 14.88, 0.43 and 6.78 % of the total variation is not explained by the model. The values of the adjusted R^2 are also high indicating the significance of the model. The coefficient of variation is a measure of the reproducibility of the model. A model can be considered reproducible if its coefficient of variation % is not greater than 10 % [27]. The ANOVA table has shown that the models which fall short in terms of reproducibility are the models for % turbidity removal.

The model F-value of 222.87 for % colour removal (NaCl coagulant) implies that the model is significant. There is only a 0.01 % chance that a model F-value this large could occur due to noise. For the rest of the models, the chances that a model F-value this large could occur due to noise were 0.82 %, 0.01 % and 0.06 % respectively. Adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable. It is observed from the model statistics that all the models

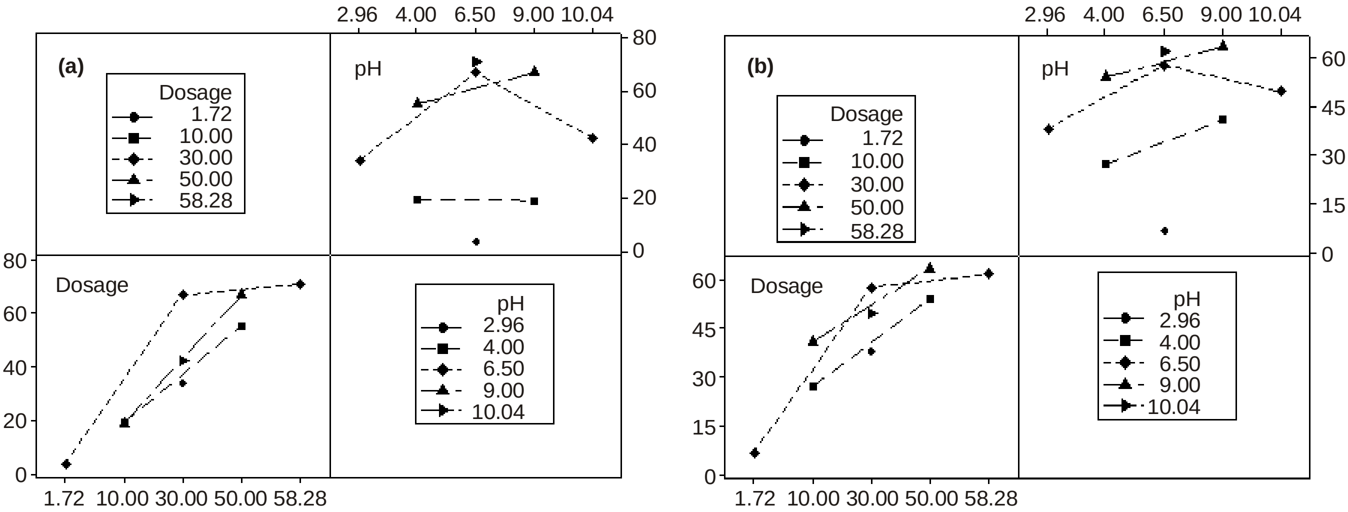

Fig. 9. Interaction plot using KCl coagulant for (a) colour removal (%) (b) turbidity removal (%)

TABLE-4
STATISTICAL PARAMETERS OBTAINED FROM ANOVA FOR THE MODELS

Variable	NaCl coagulant		KCl coagulant	
	colour removal (%)	Turbidity removal (%)	Colour (%) removal	Turbidity removal (%)
Model F-value	222.87	8.01	323.12	19.24
R^2	0.9938	0.8512	0.9957	0.9322
R^2 adjusted	0.9893	0.7449	0.9926	0.8837
Prob > F for model	< 0.0001	0.0082	< 0.0001	0.0006
Standard deviation	2.65	8.90	2.01	5.61
Coefficient of variation (%)	4.77	16.37	4.03	11.53
PRESS	337.09	3910.33	189.67	1533.16
Lack of fit 'F' value	29.09	113.36	17.12	49
Adequate precision	38.10	7.903	46.329	12.383

adequate precision is greater than 4 and indicates an adequate signal. Hence based on the adequate precision ratio, it is concluded that the models can be used to navigate the design space.

The coefficient terms are considered to be significant if the value of "Prob > F" is less than 0.05. The result for colour removal by the NaCl coagulant shows that except the interaction term and linear term (pH), the other terms are statistically significant at 95 % confidence level. The reduced form of the model, leaving out these terms, would be a better predictor of the process response.

Process optimization: For a process, containing multiple responses, the optimum condition could also be visualized graphically, by superimposing the contours (iso response curves) of response surface in an overlay plot. Graphical optimization displays the area of feasible response values in the factor space and the regions that fit the optimization criteria. Fig. 10(a) shows that the optimum removal was obtained with

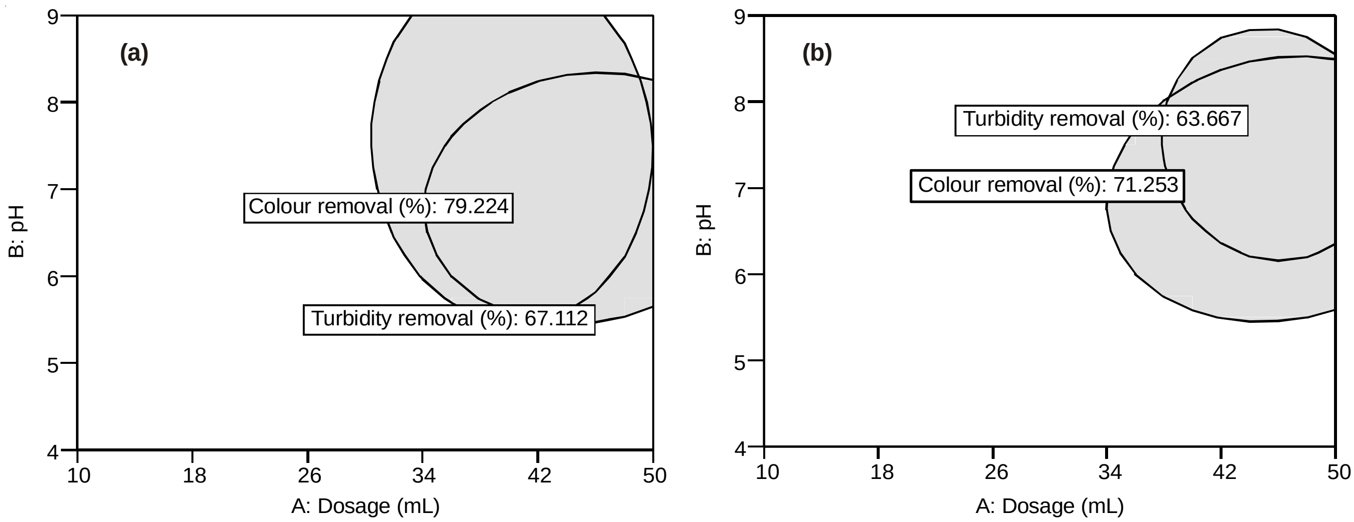

Fig. 10. Overlay plot for optimal point using (a) NaCl extracted coagulant; (b) KCl extracted coagulant

43 mL dosage and at pH 7 for the NaCl extracted coagulant. Similarly for KCl coagulant, the optimum operating conditions were 45 mL dosage and pH 7.3, respectively. The optimum condition from the overlay plot was obtained, based on the intersection area between the two response plots as shown in overlay plot. The plot shows that the optimum for NaCl extracted coagulant lies well with in the design range whereas for KCl extracted coagulant the optimum was found near the right end of the design range.

Hessian matrix was used to solve the response surface model equations to calculate the exact values for the optimum parameter values. Table-5 shows the Hessian matrix obtained from the response surface model equations. The solution of individual response model equations was calculated using eqn. 4. Eigen values for each Hessian matrix were calculated through eqn. 5 and the nature of optimum was reported based on the Eigen values. It was found that both the Eigen values are negative for all models and hence it could be concluded that the function attains the maximum at optimal point. The value of process factors in coded unit given in Table-6 was calculated by solving response surface model equations using Hessian matrix. Coded factors were converted to actual values of factor using linear regression technique. The maximum response values were calculated by substituting the optimum operating conditions in the respective model equations. Table-7 shows the results of confirmation experiment carried out at optimum conditions. This experimental result matches very well with that of response surface model equation results. It is observed that for all the response values, error % is less than 2 which shows the adequacy of model equation to predict the response values.

Conclusions

The present study clearly shows the scope of using *Moringa oleifera* seed protein as an effective natural coagulant in tannery wastewater treatment. This investigation has demonstrated that coagulation with *Moringa oleifera* seeds protein is an effective method to clarify tannery wastewater by reducing the colour and turbidity content of the wastewater. *Moringa* seed coagulant provides a better alternative for the conventional chemical coagulants because *Moringa oleifera* hardly affects the pH and conductivity of treated water.

In this study, NaCl salt solution extracted coagulant produced better treatment efficiency compared to KCl salt solution coagulant. This result shows that salting-out mechanism is predominant in KCl salt solution coagulant when compared to NaCl salt solution coagulant. This is the reason for better treatment efficiency of NaCl salt solution coagulant. Response surface methodology involving an experimental design was used to evaluate the effects of pH and coagulant dosage on the

TABLE-5
HESSIAN MATRIX, INVERSE OF HESSIAN MATRIX AND EIGEN VALUES FOR EACH RESPONSE MODEL

Response surface model	Hessian matrix (H)	Hessian matrix inverse (H^{-1})	Eigen values of Hessian matrix		Nature of optimum
			e_1	e_2	
Eqn. 6	$\begin{pmatrix} -32.18 & 2.51 \\ 2.51 & -30.44 \end{pmatrix}$	$\begin{pmatrix} -0.03127 & -0.002578 \\ -0.002578 & -0.03306 \end{pmatrix}$	-28.65	-33.96	Maximum
Eqn. 7	$\begin{pmatrix} -27.6 & -0.6 \\ -0.6 & -9.8 \end{pmatrix}$	$\begin{pmatrix} -0.03628 & 0.002221 \\ 0.002221 & -0.10218 \end{pmatrix}$	-9.77	-27.62	Maximum
Eqn. 8	$\begin{pmatrix} -28.46 & 3.02 \\ 3.02 & -27.6 \end{pmatrix}$	$\begin{pmatrix} -0.03555 & -0.00389 \\ -0.00389 & -0.03666 \end{pmatrix}$	-24.97	-31.08	Maximum
Eqn. 9	$\begin{pmatrix} -19.92 & -1.01 \\ -1.01 & -10.32 \end{pmatrix}$	$\begin{pmatrix} -0.05045 & 0.004938 \\ 0.004938 & -0.09738 \end{pmatrix}$	-10.21	-20.02	Maximum

TABLE-6
SOLUTIONS (PROCESS FACTOR VALUE IN CODED UNIT) OBTAINED FROM RESPONSE SURFACE MODEL EQUATIONS USING HESSIAN MATRIX

S. No.	Response surface model equation	Process factor value				Maximum response value for coded factor (%)
		Optimum dosage		Optimum pH		
		Coded	Actual (mL)	Coded	Actual	
1	Eqn. 6	0.7655	45.3	0.1607	6.90	84.27
2	Eqn. 7	0.5089	40.2	0.4045	7.50	70.41
3	Eqn. 8	0.8063	46.1	0.1944	6.98	76.43
4	Eqn. 9	0.7793	45.6	0.4014	7.50	65.16

TABLE-7
CONFIRMATION EXPERIMENTS AT OPTIMUM CONDITIONS

		Experiment conditions		Response values		Error (%)
		Dose (mL)	pH	Experimental	Predicted	
NaCl extracted coagulant	Colour removal (%)	45.3	6.90	83.76	84.27	0.61
	Turbidity removal (%)	40.2	7.50	70.06	70.41	0.49
KCl extracted coagulant	Colour removal (%)	46.1	6.98	75.12	76.43	1.71
	Turbidity removal (%)	45.6	7.50	64.98	65.16	0.28

colour removal and turbidity removal from wastewater. Central composite design approach for two factors reduces the number of experiments to be carried out and conserve process time. The process variable such as the coagulant dosage and pH were found to have great effect on colour removal and turbidity removal efficiency. Hessian matrix provides the idea for the numerical optimization using the model equations. The experimental results of confirmation report show that they match well with the values predicted by the model equations. This study shows that the treatment of tannery wastewater by *Moringa* seed coagulant is efficient, environment friendly and more economical compared to chemical coagulants.

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