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Research article

Using Chitosan/CHPATC as coagulant to remove color and turbidity of industrial wastewater: Optimization through RSM design

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ABSTRACT

One of the most important solid-liquid separation processes is coagulation and flocculation that is extensively used in the primary treatment of industrial wastewater. The biopolymers, because of biodegradable properties and low cost have been used as coagulants. In this study, chitosan as a natural coagulant of choice, was modified by (3-chloro 2-hydroxypropyl)trimethylammonium chloride and was used to remove the color and turbidity of industrial wastewater. To evaluate the effect of pH, settling time, the initial turbidity of wastewater, the amount of coagulant, and the concentration of dye (Melanoidin) were chosen to study their effects on removal of wastewater color and turbidity. The experiments were done in a batch system by using a jar test. To achieve the optimum conditions for the removal of color and turbidity, the response surface methodology (RSM) experimental design method was used. The results obtained from experiments showed that the optimum conditions for the removal of color were as: pH = 3, concentration of dye = 1000 mg/L, settling time = 78.93 min, and dose of coagulant = 3 g/L. The maximum color removal in these conditions was predicted 82.78% by the RSM model. The optimal conditions for the removal of turbidity of the waste water were as: pH = 5.66, initial turbidity = 60 NTU, settling time = 105 min, and amount of coagulant = 3 g/L. The maximum turbidity removal in these circumstances was predicted 94.19% by the model. The experimental results obtained in optimum conditions for removal of color and turbidity were 76.20% and 90.14%, respectively, indicating the high accuracy of the prediction model.

1. Introduction

Color and turbidity are two major pollutants in industrial wastewaters. Color and turbidity are two major pollutants in an industrial wastewater (Verma et al., 2012). The industries such as pulp, paper, rubber, textile and polymer are the mainly sources of surface and underground water polluters (Ong et al., 2010). Discharged wastewater into surface waters such as rivers and lakes reduces the transmission of light in the water which reduces photosynthesis and the amount of dissolved oxygen in the water (Ali and Singh, 2009). Researchers have found that some kind of dyes can also decompose and produce carcinogenic aromatic amines. These poisoning compounds without the proper treatment, could stand quite stable in the environment for a very long time (Hao et al., 2000). The turbidity is created due to the presence of suspended solids such as clay, mud, minerals, organic and water-soluble particles. In addition to creating an unpleasant appearance for water, it is a safe haven for resistance of microorganisms against disinfection (Steel and McGhee, 1979; Wef, 1998).

Because of the complexity and variety of dyes used in various industries, finding an unique method which is able to remove dyes completely, is difficult (Mounir et al., 2007). Several methods are used for the treatment of the wastewater which include processes of coagulation and flocculation, membrane and biological methods (Mamba et al., 2014; Singh et al., 2014). A main problem for a membrane technology is fouling. High concentrations of dye cause severe fouling on the membrane (Zaroual et al., 2009). Biological treatment processes are not effective for complex dyes removal. Coagulation and flocculation is a simple and efficient method for

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removal of colloidal particles and dyes from water and wastewater due to its low capital cost (Golob et al., 2005; Zahrim et al., 2011). For wastewater treatment, this method includes the addition of chemicals to change the physical state of dissolved and suspended solids and to facilitate their removal by sedimentation. In general, coagulants are divided into three categories: mineral, synthetic polymers and natural coagulants. The use of mineral coagulants such as aluminum sulfate in wastewater treatment processes can produce non-organic sludge which is a secondary pollution (Anjaneyulu et al., 2005). The remaining metals of coagulants such as aluminum in the human body would cause some of the inefficiencies such as Alzheimer's disease (Ali et al., 2010). Because most synthetic polymers do not have the ability to biodegrade, they are considered as secondary pollution, too. Residual oligomers and monomers of some synthetic polymers such as polyacrylamide are toxic and some of them lead to cancer in humans (Yang et al., 2011). For this reasons, in some countries, strict laws have been considered for using these types of coagulants (Krentz et al., 2006). So, in order to resolve problems arising from the use of mineral and synthetic polymers coagulants, natural coagulants are suitable replacements. Chitosan is a kind of polysaccharide obtained by deacetylation of chitin, the second most abundant polysaccharide in nature after cellulose (Prado and Matulewicz, 2014). Although natural polymers such as chitosan or modified natural polymers have wide applications, how to improve their flocculation effectiveness is the main focus, because they are cost-effective and environmental friendly (Wang et al., 2007). Cationized chitosan has better properties than untreated chitosan. Cationic chitosan has several applications such as a dermal permeation enhancer of drugs, protein release controller, reduction of carbonyls to alcohols, removal of Mo(IV) and Cr(VI) and coagulant agent in papermaking because of its unique properties (Faizuloev et al., 2012; Spinelli et al., 2004; Xu et al., 2003).

The objective of this study is to use chitosan biopolymer as a coagulant for the removal of color and turbidity of discharged wastewater from Iran Mayeh plant, Tabriz, I.R.I and to determine the optimal conditions for the process to reuse it in the production process. The reason behind using this wastewater was that it consisted a very complex dye named Melanoidin which is resistant against many treatment processes and causes color and turbidity in wastewater (Crini, 2006; Wang et al., 2005). Melanoidin is the result of the reaction between amino acids and carbohydrates, which is called the Millard reaction (Naik et al., 2010). Melanoidin is a structurally complex macromolecule, muddy brown color, with odor like phenol. The brown color of Melanoidin is because of the presence of C = C and C = N bonds in the molecular structure of the material (Stavropoulos, 2012). The chemical structure of Melanoidin is shown in Fig. 1 (Jiranuntipon et al., 2009).

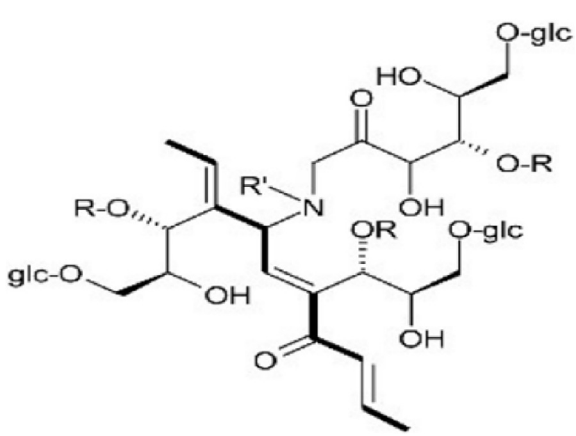

Fig. 1. Chemical structure of Melanoidin.

Releasing of this highly colored compound in surface waters reduces the influence of sunlight which prevents photosynthesis. Also, it reduces alkalinity level of soil and oxygen level of water and puts aquatic plant and animal life in danger (Naik et al., 2010).

The efficiency of the coagulation depended on appropriate selection of coagulant, optimization of process parameters such as pH, dosage of coagulant agent, mixing time, settling time and etc. An appropriate optimization of these factors could significantly increase the treatment efficiency. Response surface methodology (RSM) is an efficient way to achieve such an optimization by analyzing and modeling the effects of multiple variables and their responses and finally optimizing the process. The main objective of using RSM is to determine the optimum operational conditions for the system or to determine a domain that satisfies the operating specifications (Box and Wilson, 1951; Zaroual et al., 2009). The RSM reduces the number of experiments significantly and has an ability to study a large number of parameters and interaction between them. Response surface methods can describe the behaviors of complex systems in various experimental conditions. Optimization based on response surface methodology can be used in different processes to achieve the highest efficiency (Khataee et al., 2011).

In this study, the potential and effectiveness of a cationic chitosan was studied as an alternative and a low cost coagulant for the removal of Melanoidin. So, a modified natural polymer, prepared through the grafting of (3-chloro 2-hydroxypropyl)trimethylammonium chloride (CHPTAC) onto chitosan was used as flocculent. The grafting of this compound onto chitosan can increase the cationic content of the flocculent, and thus improve its flocculation efficiency. A yeast factory wastewater was selected as the target to be treated by the coagulation and flocculation process which was optimized by RSM. The turbidity and color of the treated water were chosen as the response variables. The optimal conditions for the two responses were also obtained and compared with experimental results.

2. Methods and materials

2.1. Wastewater

In this study, wastewater was provided from a yeast factory, which had high levels of turbidity and color at the same time. Melanoidin was the main source of its pollution. Some characteristics of the wastewater and their standard levels are shown in Table 1. It is clear that wastewater pollution is very high and it needs to be treated for reusing.

2.2. Coagulant

Dried chitosan (24 g) was mixed with 250 mL of distilled water. 10 mL of 10 mol/l NaOH was added to the mixture and then it was heated at 50 °C under controlled stirring for half of hour. 50 mL of the cationic monomer (CHPTAC) was added to the mixture as dripping. The reaction was then allowed to continue for next 24 h and was heated constantly at 50 °C under controlled stirring. Diluted hydrochloric acid was added to the mixture to decrease the reaction pH around 7 for stopping the reaction (Larsson and Wall, 1998). The precipitated modified chitosan was washed with ethanol and distilled water to remove the impurities. Then, it was dried under vacuum condition at 65 °C for 48 h. Chitosan can react with CHPTAC to form a crosslinked species at amine group and results in a cationic chitosan as shown in Fig. 2.

The physical and chemical properties of modified coagulant were studied. X-ray diffraction (XRD), elemental analysis (CHNOS)

Table 1
Characteristics of the studied wastewater and standard values.

Pollutant	Wastewater	The maximum limit for irrigation	The maximum limit for discharge
Color (TCU)	30,000	75	75
Turbidity (NTU)	300	50	50
COD (mg/L)	36,000	200	60
TSS (mg/L)	1020	100	40

and infrared spectroscopy (FTIR) were done to determine these properties.

Analysis to determine the crystal structure was carried out by a D8 Avance (Bruker, Germany) XRD system working at scan rate of 0.05 s^{-1}, in the range of 10–90° and using Cu-Kα radiation with a wavelength of 0.154 nm.

The analysis of samples was done by a CHNOS model 2400 Elemental Analysis system (Perkin Elmer) at ignition temperature of 950 °C.

The functional groups on the surface of modified coagulant were studied with a Tensor 27 FTIR spectrophotometer (Bruker, Germany) in the wave number range of 400–4000 cm^{-1}.

2.3. Experimental design

In this study, color and turbidity removal were considered as the responses in the design. Also, the concentration of dye, initial turbidity of wastewater, coagulant dose, settling time and pH were chosen as process parameters variables.

The response surface methodology combined with the CCD with a value of $a = \pm 2$ was used for the modeling and optimization of operating parameters of coagulation and flocculation processes. Using CCD matrix, the designed experiments included 31 trials. The experimental levels for each factor are provided in Table 2.

In all experiments the mixing time was constant and equal to 20 min and the wastewater volume was considered 200 mL for each test. In order to obtain optimal conditions for the removal of color and turbidity, same quantities of coagulants in different pH values were added to 200 mL of wastewater at the same time. The jar test device mixed the mixture for 20 min at constant mixing rate. Then, specific statement times were given to containers. Upon completion of the sedimentation, 10 mL samples were taken from each of the containers. Each sample was filtered twice and absorption of filtered samples was measured by a spectrophotometer at the length of 475 nm for remained color in solutions. Also, remained turbidity was measured by a Nephelometer. It should be noted that different turbidity and concentrations values were obtained by dilution of raw wastewater. Then, the experimental data was analyzed by RSM to obtain the optimal amount of each factors (pH, coagulant dose, settling time, initial turbidity and initial dye concentration of Melanoidin).

Table 2
Experimental ranges of the factors examined in the CCD design.

Factor	Levels	
	−2	+2
Turbidity removal		
pH	5	7
Settling time (min)	40	120
Dose (g/L)	2	3
Initial turbidity (NTU)	50	300
Color removal		
pH	3	7
Settling time (min)	40	120
Dose (g/L)	2	3
Initial dye concentration (mg/L)	1000	5000

3. Results and discussion

3.1. Modified coagulant characterization

The infrared spectrum of chitosan, modified chitosan and CHPTAC are shows in Fig. 3(a). As it can be seen in the infrared spectrum of chitosan, the absorption band occurring at 804 cm^{-1}, which is related to the primary amine group, does not exist in modified chitosan. Also, the absorption band occurring at 748 cm^{-1} in the spectrum of modified chitosan related to the existence of secondary amine does not appear in the chitosan and CHPTAC. So, it seems that during the synthesis, the primary amine groups of chitosan are converted to secondary amines. Therefore, it can be concluded CHPTAC was successfully attached to the chitosan. The peaks occurring at of 953 and 1491 cm^{-1} are attributed to the unreacted methylammonium groups of CHPTAC existed in the CHPTAC modified chitosan. These peaks were not observed in the unmodified chitosan. The peak appearing at 1237 cm^{-1} is related to ammonium group of CHPTAC, which was not observed in chitosan; the amine groups of the chitosan are primary amines. The peaks

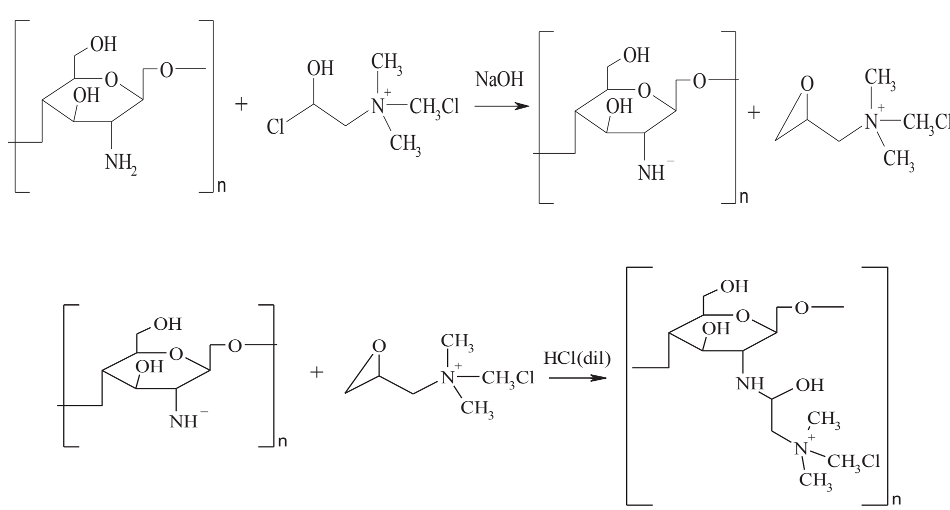

Fig. 2. Schematic representation of the crosslinking reaction of chitosan with CHPTAC.

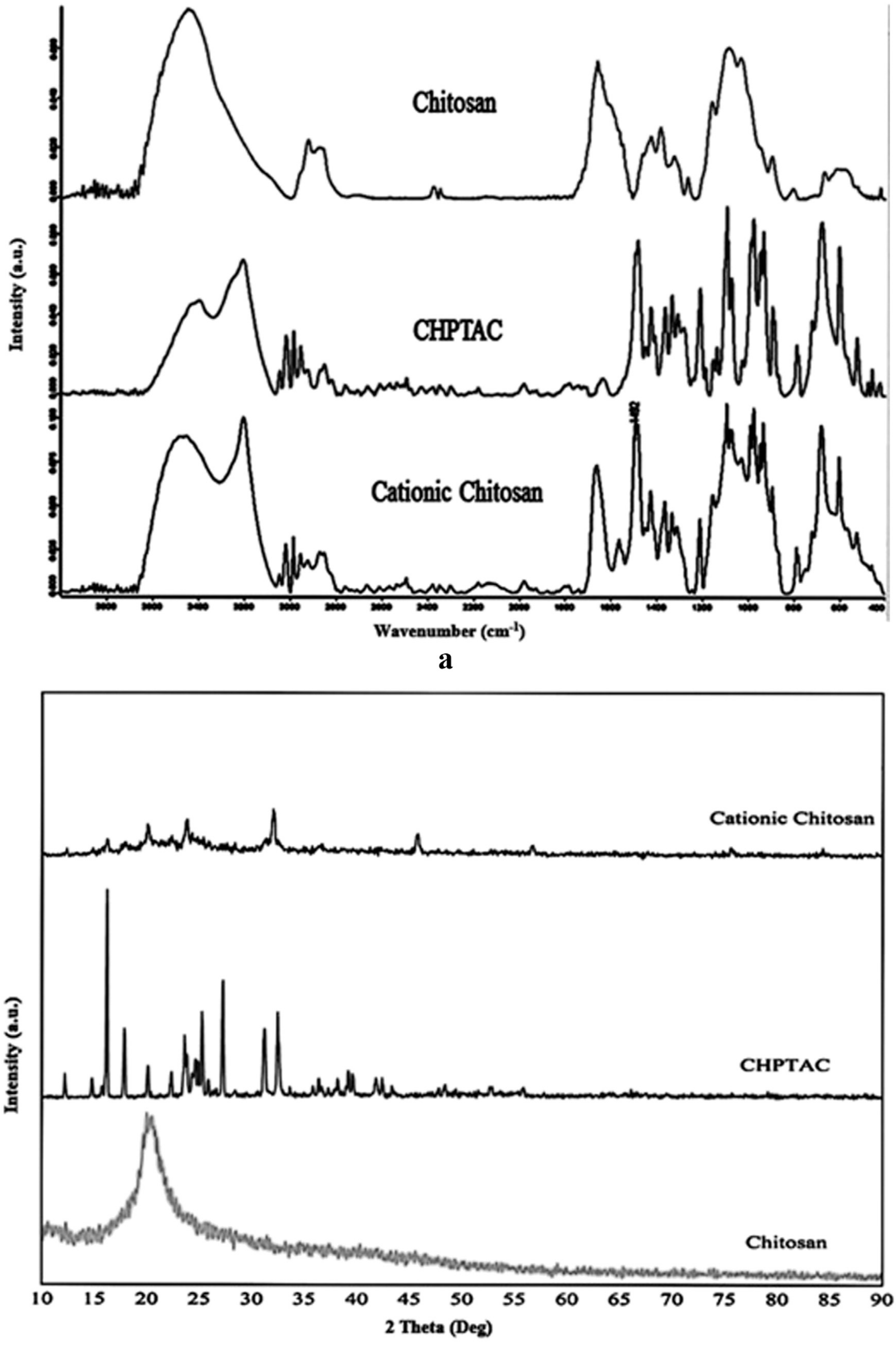

Fig. 3. (a) FT-IR spectra for chitosan, CHPTAC and modified chitosan. (b) XRD patterns for chitosan, CHPTAC and modified chitosan.

occurring at 3023 and 3212 cm^{-1} are related to the vibrations of symmetrical methyl groups and quaternary methylene ammonium in CHPTAC.

The XRD patterns of chitosan, CHPTAC, and cationic chitosan are shown in Fig. 3(b). The polar nature of CHPTAC and its larger size compared to hydrogen, modify the crystalline structure of chitosan. Incorporation of CHPTAC modifier to the chitosan creates new crystal faces, but the contribution of these new faces is less than crystallinity of chitosan, therefore the diffraction peaks of chitosan are stronger than those of the modified chitosan. Also, the area under the diffraction peak of chitosan is greater than the area under the diffraction peak of modified chitosan. CHPTAC has many sharp peaks in a small range, which is due to its ionic properties. As a result, apart from the size and polarity of the modifier, the crystalline structure of chitosan is obvious. By considering characteristic diffraction peaks of samples, maximum peak width at half height and using the Scherrer formula (Eq. (1)) the crystallite size can be calculated.

$$t = \frac{0.9\ \lambda}{B\ cos\theta_B} \tag{1}$$

where λ is X-ray wavelength (0.154 nm), B is maximum width at half height (rad), and θ_B is the angle of observed diffraction peak. The average crystal sizes for chitosan and modified chitosan were calculated 8.85 and 22.4 nm, respectively.

Elemental analysis data indicating the weight percent of carbon, hydrogen and nitrogen compounds is shown in Table 3. From Table 3 the nitrogen content has increased with adding CHPTAC to chitosan. It means that larger number of CHPTAC modifier was attached to the chitosan. So, the synthesis process was successfully.

3.2. Experimental results

The designed CCD matrix experiments included 31 trials. Modeling and analysis of experimental data were performed by using the Minitab v.16. Experimental results were fitted to a second-order polynomial model by using the least square method to optimize the variables in the coagulation-flocculation process. The quadratic equation model for predicting the optimal conditions can be expressed as Eq. (2):

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \beta_{ij} x_i x_j \tag{2}$$

where Y, β_0, β_i, β_{ii}, β_{ij} are the predicted response, the regression constant coefficient, the linear coefficients, the quadratic coefficients, and the interaction coefficients, respectively, and x_i and x_j are the coded values of the variables.

The coefficients of the response function (Eq. (2)) and P-values for turbidity removal were obtained using experimental data and are presented in Table 5. Eq. (3) shows a second-order polynomial equation for the relationship between factors and turbidity removal in coagulation and flocculation processes. In the following equation, x_1, x_2, x_3 and x_4 represent the process pH, turbidity of wastewater, sedimentation time and the amount of coagulants.

Table 3
Elemental percentage analysis data for chitosan, CHPTAC and modified chitosan.

Sample	C	H	N
Chitosan	40.1	6.62	7.56
CHPTAC	37.81	7.84	7.36
Cationic Chitosan	40.3	8.37	8.13

$$\begin{aligned} Y = 75.9286 &- 2.8541x_1 - 2.9625x_2 + 2.4791x_3 + 2.5625x_4 \\ &- 0.0312x_1x_2 + 0.0312x_1x_3 - 0.2812x_1x_4 - 0.5937x_2x_3 \\ &- 0.2812x_2x_4 + 0.1562x_3x_4 - 0.9915x_1^2 + 0.5959x_2^2 \\ &- 0.8040x_3^2 - 0.8665x_4^2 \end{aligned} \tag{3}$$

Positive sign in front of the terms indicates favorable effect, whereas negative sign indicates antagonistic effect of each factor. So, between individual factors, pH and settling time had negative effects and coagulant dose and initial turbidity had positive effects on turbidity removal.

Statistical analysis of variance (ANOVA) was used for analysis of the predicted model used. The obtained results of statistical analysis of variance model for turbidity removal efficiency are shown in Table 4. The high F value (66.83 for the regression model) and low p values (0.000) show that the model is statistically acceptable. The higher F values and lower P values than 0.05 show that how the factor affects the response. In general, according to the 95% confidence level for regression model prediction, if the value of a P for a factor is less than 0.05, its variation will be effective on the model. But if the P-value is greater than 0.05, its variation on the model will not be significant (Montgomery, 2008). Lack of fit value compares the residual error and the pure error (Mathews, 2005). Lack of fit value for a model should not be effective. In other words, its P value should be greater than 0.05. According to the results presented in Table 4, P value for the lack of fit is greater than 0.05, which confirms accuracy of predicted model. The correlation coefficient (R^2) indicates that how variability in response values can be explained by the independent variables and their interactions (Montgomery, 2008). Actually, R^2 value shows the varying responses that can be justified by the model. If the R^2 value approaches one, the ability of model to explain the variations in response would be greater. As shown in Table 4, R^2 value is 0.983 which indicates that 98.3% of the variation in the efficiency of turbidity removal by coagulation and flocculation is justified.

Based on the results (Table 5), independent factors including pH, settling time, coagulant dose and initial turbidity also interaction between the settling time and initial turbidity are significant effect on the turbidity removal efficiency.

Fig. 4(a) shows the effect of each variable and their interactions on response. As can be seen, all studied independent operational variables are effective on turbidity removal by coagulation and flocculation. Among them, initial turbidity, coagulant dose and settling time are the most important effective factors on turbidity removal efficiency.

3D surface plots show schematically the interaction of two variables on a response. Fig. 5(a) shows the interaction between initial turbidity and coagulant dose on turbidity removal. By increasing the initial turbidity of wastewater, turbidity removal

Table 4
Results of analysis of variance (ANOVA) (The turbidity removal).

Source of variations	Values			
	DF	Mean Square	F-value	P-value
Regression	14	56.883	66.83	.000
Linear	4	177.812	208.91	.000
Square	4	19.131	22.48	.000
Interaction	6	1.432	1.68	.189
Residuals Error	16	0.851	–	–
Lack-of-Fit	10	1.090	2.41	.147
Pure Error	6	0.452	.	–

R^2 = 0.9830.

Table 5
Regression coefficients and P-values for each factor (The turbidity removal).

Terms	P-value	Coefficient
β_0 (Constant)	.000	75.9286
β_1 (pH)	.000	−2.8541
β_2 (settling time)	.000	−2.9625
β_3 (Coagulant dose)	.000	2.4791
β_4 (Initial turbidity)	.000	2.5625
β_{12}	.894	−0.0312
β_{13}	.894	0.0312
β_{14}	.240	−0.2812
β_{23}	.020	−0.5937
β_{24}	.240	−0.2812
β_{34}	.508	−0.5937
β_{11}	.000	−0.9915
β_{22}	.003	0.5959
β_{33}	.000	−0.8040
β_{44}	.000	−0.8665

efficiency reduced. With the increase in initial turbidity, the number of colloidal particles in wastewater has increased and thus the number of active sites on the colloidal particles increases for a certain amount of coagulant. This phenomenon causes the negatively charged colloidal particles will be more dominant on positively charged coagulants and as a result, zeta potential be negative. So, formed clots will be more stable and have not settling capability. In this situation, greater amounts of coagulant will be need to be added to the wastewater treatment until bridging process between polymers be done well. At the all initial turbidity values, turbidity removal efficiency has increased by increasing the dose of coagulant. It is because of this issue that by adding the coagulant to the wastewater, more chitosan molecules attract solid particles on active sites and will absorb them. In addition, by adding a coagulant to the water, neutralizing of electrical load will increased until the zeta potential reaches to zero. The dose of coagulant that zeta

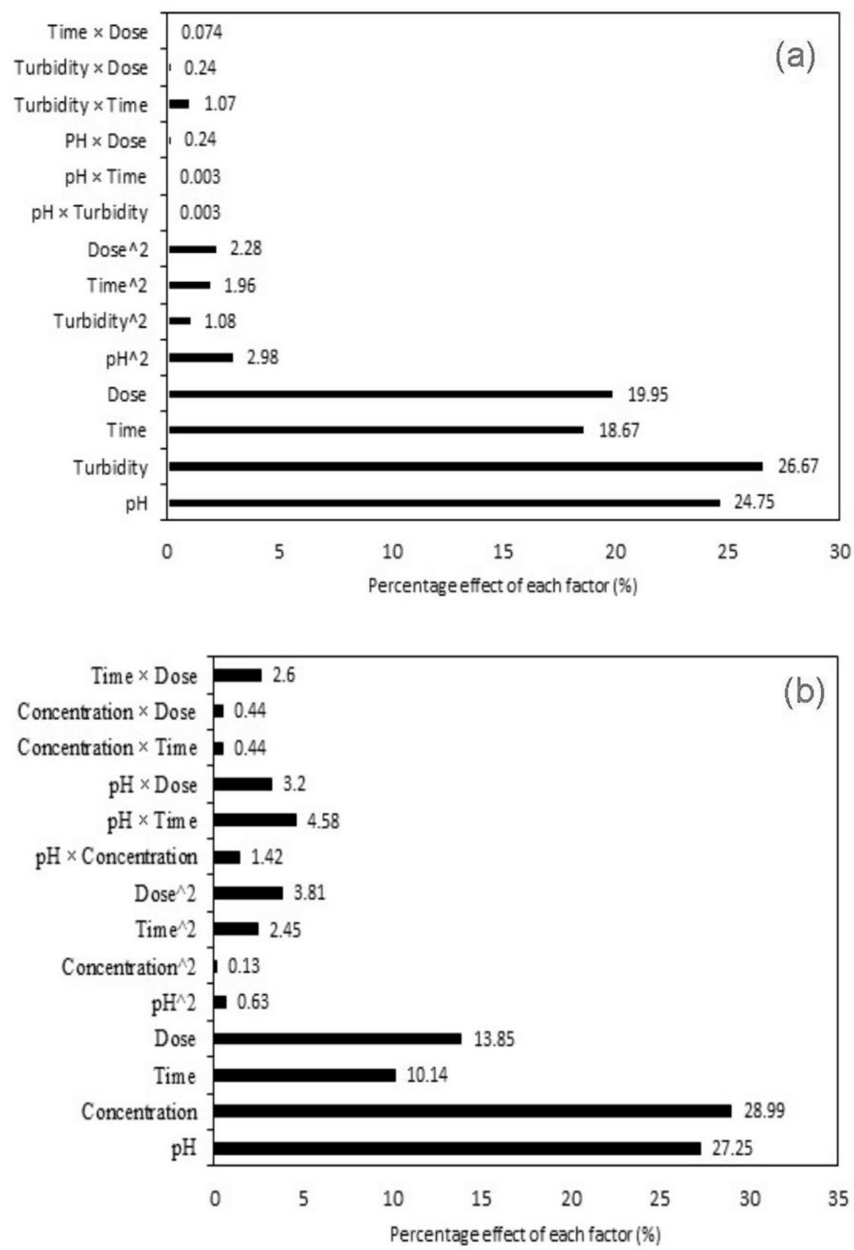

Fig. 4. Percent of each factor effect on response ((a) turbidity removal and (b) color removal).

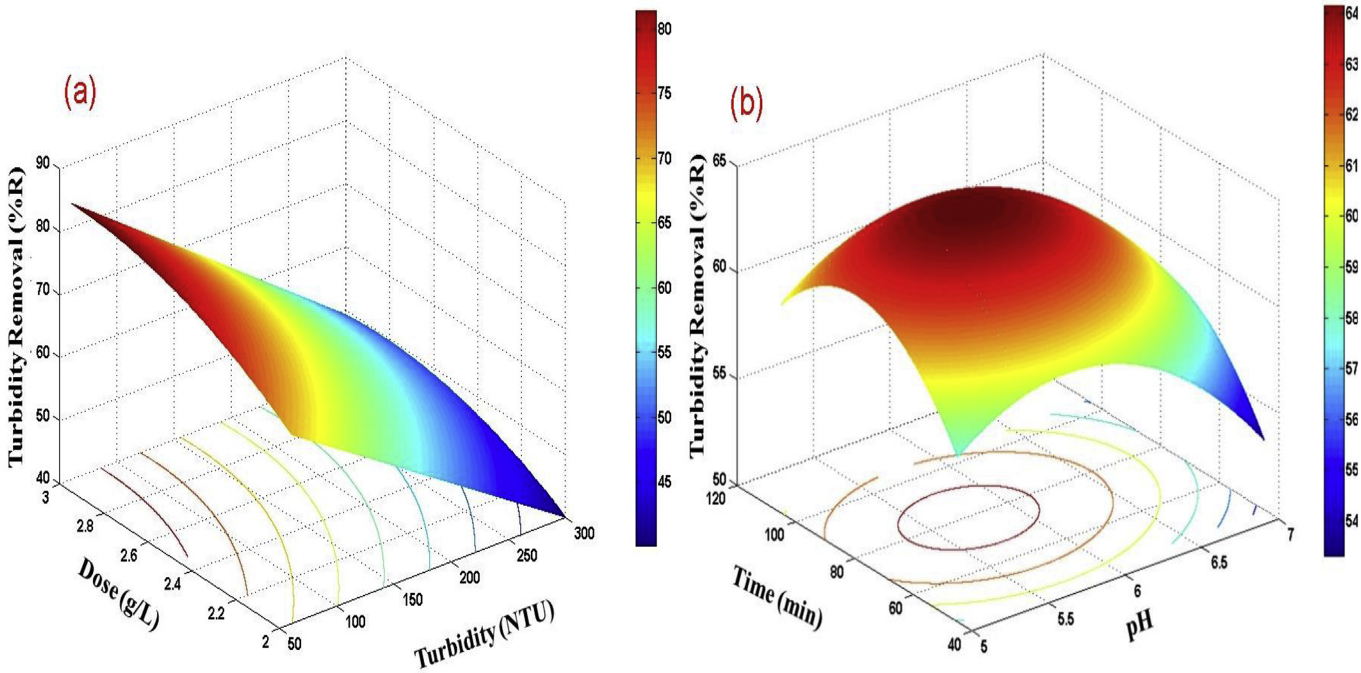

Fig. 5. 3D diagram for turbidity removal efficiency as a function of the (a) initial turbidity (NTU) and coagulant dose (g/L) (pH = 6.5, settling time = 75 min) and (b) pH and settling time (min) (initial turbidity = 180 NTU, coagulant dosage = 2.5 g/L).

potential reaches zero, is called the optimum dose. Also, it can be seen that the increase in coagulant dosage increased gradually turbidity removal and it is possible that with the addition of greater amounts of coagulant will has not noticeable effect on turbidity removal and it may reduce the percentage of turbidity removal. It can be said that adding more coagulant to wastewater, positively charged particles will increase and thus, electrostatic repulsion force between particles will be created. Also, at higher doses of polymer, active sites cover colloidal particles and reduce the effect of bridging between particles.

Turbidity removal efficiency as a function of pH and settling time is shown in Fig. 5(b). As can be seen in Fig. 5(b), turbidity removal efficiency was decreased with an increase in pH levels. With the increase in pH, the hydrodynamic radius R_H of coagulant will be reduced, because the polymer chains and the number of active sites on the coagulant surface have reduced. This reduces bridging effect between particles and ultimately and it increases the optimum dose for turbidity removal. At lower pH values, the morphology of the polymer chains extends widely and the hydrodynamic radius will increase. This is due to the electrostatic repulsion force reduction in the presence of cationic chitosan molecules, which can increase the effect of bridging between particles of chitosan and colloids. Also, it shows that turbidity removal efficiency increases with increasing in settling time. The reason for this phenomenon is clear, because with the increase in settling time, created small clots from mixing come together to form large clumps and bulkier because of the nature of bridging between the particles. These masses after reaching to right size will be settled with gravitational force and will be separated easily from the waste water.

Optimal operating parameters for turbidity removal were estimated by the model as following conditions: pH = 5.66, initial turbidity 60 NTU, settling time 105 min and amount of coagulant 3 g/L. The maximum turbidity removal in these circumstances was predicted 94.19% by the model. In order to evaluate the predicted results by the model, some experiments were done with predicted optimum conditions. The experimental results (90.14%) are very close to the predicted results by the model (94.49%) which indicates the acceptable validity of the model.

In this part, the effects of initial Melanoidin dye concentration, amount of coagulant, pH and settling time on color removal were studied. As well as Eq. (3), a second-order polynomial equation for the relationship between factors and removal efficiency of dye were obtained by using least square method. In the following equation (Eq. (4)), x_1 to x_4 represent the pH, initial concentration, settling time and the amount of coagulants, respectively.

$$\begin{aligned} Y = 39.5714 - 9.2916x_1 - 9.5833x_2 + 5.6666x_3 + 6.6250x_4 \\ - 2.125x_1x_2 + 3.8125x_1x_3 - 3.1875x_1x_4 + 1.1875x_2x_3 \\ - 1.1875x_2x_4 + 2.875x_3x_4 - 1.4136x_1^2 + 0.6488x_2^2 \\ - 2.7886x_3^2 - 3.47614x_4^2 \end{aligned} \tag{4}$$

Statistical analysis of variance results for the second response is shown in Table 6. The results show that because of higher F values (57.96) and low P value (P = .000), the model is statistically

Table 6
Results of analysis of variance (ANOVA) (The color removal).

Source of variations	Values			
	DF	Mean Square	F-value	P-value
Regression	14	523.60	57.96	.000
Linear	4	1525.06	168.81	.000
Square	4	146.36	16.2	.000
Interaction	6	107.46	11.89	.000
Residuals Error	16	9.03		
Lack-of-Fit	10	5.63	0.38	.913
Pure Error	6	14.7		

$R^2 = 0.9807$.

Table 7
Regression coefficients and P-values for each factor (The color removal).

Terms	P-value	Coefficient
β_0 (Constant)	.000	39.5714
β_1 (pH)	.000	−9.2917
β_2 (settling time)	.000	−9.5833
β_3 (Coagulant dose)	.000	5.6667
β_4 (Initial dye concentration)	.000	6.6250
β_{12}	.023	−1.4137
β_{13}	.265	0.6488
β_{14}	.000	−2.7887
β_{23}	.000	−3.4762
β_{24}	.012	−2.125
β_{34}	.000	3.8125
β_{11}	.001	−3.1875
β_{22}	.134	1.1875
β_{33}	.134	−1.1875
β_{44}	.001	−0.8665

acceptable. Also, The P value of lack of fit is greater than 0.05, which confirms the ineffectiveness of lack of fit parameter.

Fig. 4(b) shows the effect of each variable and their interactions on turbidity removal. Among them, initial color concentration (28.99%), pH (27.25%), coagulant dose (13.85%) and settling time (10.14%) are the most important factors on turbidity removal efficiency, respectively.

According to the results of Table 7, it can eliminate less important factors from regression model (Eq. (4)). The new and modified quadratic model is shown below.

$$\begin{aligned} Y = 39.5714 - 9.2917x_1 - 9.5733x_2 + 5.6667x_3 + 6.625x_4 \\ - 1.4137x_1x_2 + 0.6488x_1x_3 - 2.7887x_1x_4 + 3.8125x_3x_4 \\ - 3.1875x_1^2 - 1.1875x_3^2 + 2.875x_4^2 \end{aligned} \tag{5}$$

As it can be seen in Fig. 6(a), the increase in initial Melanoidin concentration from 1000 to 5000 mg/L reduced removal rate from 63% to 20.5% which can be related to generated electrostatic repulsion by the dye molecules accumulation on the coagulant surface. In other words, increasing in initial concentration of Melanoidin would create a competition for active sites on protonated amine groups of coagulant and each molecule of Melanoidin would prevent other molecules adsorption on the coagulant. As a result, Melanoidin molecules form tiny clots on coagulant and will stop the adsorption process. Also, it is observed that increasing in coagulant doses to a specific limit (2–3 g/L), increased color removal efficiency, but probably after adding more coagulant, the removal efficiency of color will not be changed noticeably.

It can be seen in Fig. 6(b); the color removal has reduced with increasing pH from 3 to 7. A decrease in pH levels increases cationic amine groups in the chitosan coagulant and causes electrostatic link between these positive particles and negative charged molecules of dye Melanoidin. The alkali pH values, in addition to less protonated amino groups, carboxylic acid groups on the molecules are ionized and charged negatively. As a result, the negative electric charge due to the presence of Melanoidin in wastewater would be increased and would be formed weaker electrostatic bond than the weak acid pH values. The color removal efficiency in the process increased with increasing in time and after a while there was no change. Because, with increase in the settling time, a limited amount of clots will be formed which is deposited by gravity. The reason was that the most of the color removal is happened because of the adsorption process. With the increase in settling time, Melanoidin dye molecules will cover over the surface of coagulant and after the while, adsorption locations in the polymer chain of chitosan will be saturated.

Optimal operating parameters for color removal were obtained at following conditions: pH = 3, initial concentration 1000 mg/L, settling time 78.93 min and amount of coagulant 3 g/L. The maximum color removal in these circumstances was predicted 82.87% by the model. In order to evaluate the predicted results by the model, some experiments were done with predicted optimum conditions. The experimental results (76.20%) are close to the predicted results by the model (82.87%) that indicates the acceptable validity of the model.

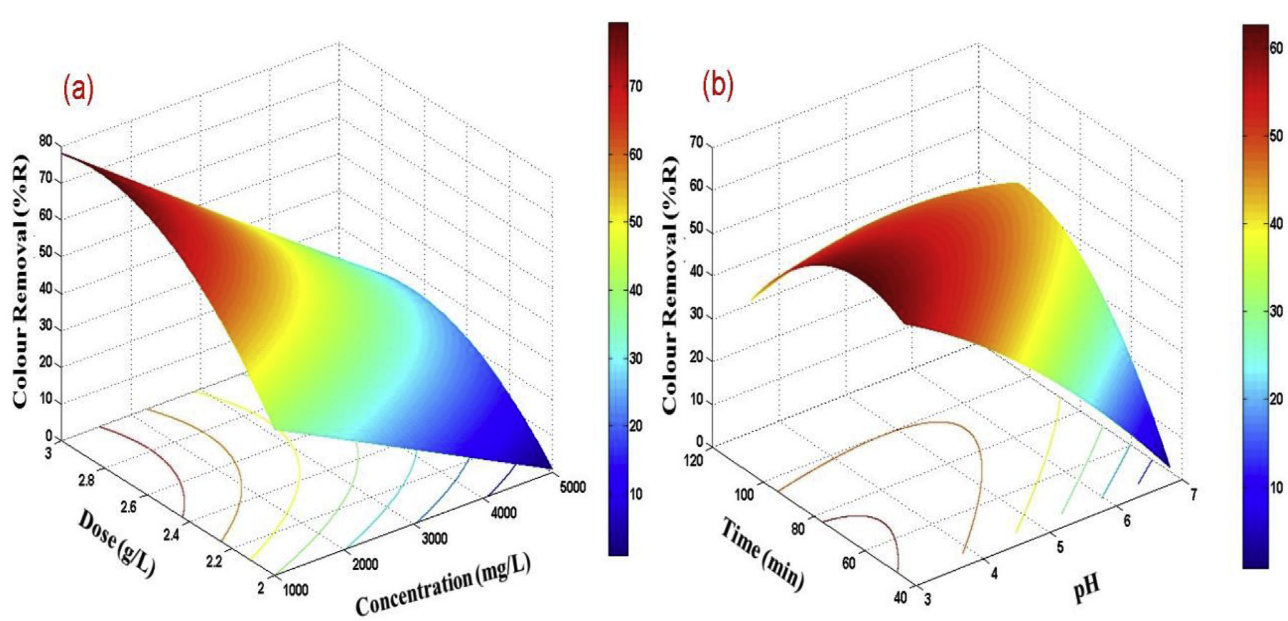

Fig. 6. 3D diagram for color removal efficiency as a function of (a) coagulant dose and initial concentration (mg/L) (pH = 4, settling time = 60 min) (b) pH and settling time (min) (initial concentration = 2000 mg/L, coagulant dosage = 2.25 g/L).

4. Conclusions

In this study, a coagulation-flocculation process was studied to remove Melanoidin dye from industrial waste water by using a modified cationic chitosan. A central composite design (RSM) was successfully employed to obtain the optimum process conditions while the interactions between process factors were demonstrated. The results showed that turbidity and color removal was influenced by investigated experimental factors. ANOVA showed a high R^2 value of regressions model equation ($R^2 = 0.9807$ for turbidity removal and 0.9830 for color removal), thus confirming a satisfactory adjustment of the second-order regression model with the experimental data. The investigation of taken characterization analysis from chitosan, CHPTAC and synthetic coagulant provided a strong proof of cationic monomer CHPTAC grafted onto the structure of chitosan. Results showed that the addition of the cationic chitosan to industrial wastewater was found to be an effective way of removing Melanoidin. The highest removal percentages for this process with synthetic coagulant were 76.20% for color removal and 90.14% for turbidity removal which were obtained in optimum conditions. Also, RSM was proved to be a powerful tool for optimizing the coagulation and flocculation process and the CHPTAC/chitosan can be considered as an appropriate coagulant for color and turbidity removal from industrial wastewater.

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