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Determination of optimum treatment conditions for paint industry wastewater with the coagulation/flocculation method

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ABSTRACT

In this study, optimum treatment conditions for paint industry wastewater were determined by response surface methodology (RSM). Wastewater treatment experiments were performed in jar test using the coagulation/flocculation method. $FeCl_3·6H_2O$, $Al_2(SO_4)_3·18H_2O$, and $FeSO_4·7H_2O$ coagulants were used in the treatment experiments. pH, coagulant dose, and mixing speed were selected as the most important parameters for wastewater treatment and chemical oxygen demand (COD), total suspended solids (TSS), turbidity, and color analyses were examined for each coagulant. After determining the coagulant ($FeCl_3·6H_2O$) which provided the best treatment efficiency, a central composite design (CCD) was applied for optimization of treatment conditions by using RSM. Design Expert 7.0.0. the program was used for the design of treatment experiments and analysis of results. COD, TSS, color, and turbidity values were processed by the program after experiments. 3D graphs and statistical results created by the program were interpreted. The equations obtained using the coefficients in the model created by the program were solved and the optimum values of the independent variables were calculated. Using these values, the lowest pollution values were determined as (mg/L) COD 68.636, color 2.42, turbidity 1.79 NTU, and TSS 10.135. Optimization results from the program were examined and the optimum values of treatment parameters were suggested as pH 7.54, coagulant amount 1,080.49 mg/L, and mixing speed 146.16 rpm. The lowest pollution values under optimum conditions were (mg/L) COD 71.07, color 1.00, turbidity 2.74 NTU, and TSS 7.50. Under optimized conditions COD, TSS, color, and turbidity removal were 94.1%, 95.3%, 97.1%, and 99.5%, respectively.

Keywords: Wastewater treatment; Paint industry; Coagulation/flocculation; Central composite design; Response surface methodology

1. Introduction

Discharge of industrial wastewater into the environment without treatment causes soil, water, and air pollution, low levels of dissolved oxygen in receiving water resources, and negative impacts on ecology [1,2]. Discharge of paint industry wastewater into receiving environments not only has negative esthetic effects, but also can cause carcinogenic, mutagenic, and harmful effects on health [3]. Paints are generally a mixture of pigment, binders, solvents, and additives, and the properties of the paint changes with the type and proportion of the components that they contain. The composition of paint industry wastewater varies according to the specific production mode of each industrial unit [4]. Paint industry wastewater is formed by washing tanks and equipment used in the production of paint during mixing and packaging [5]. This intensely colored, high turbidity, and malodorous wastewater contains

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high amounts of organic and toxic chemicals such as surfactants, bactericides, oils, solvents, and preservatives. In addition, changes in the chemicals used depending on the type of products and the transport of pigments and solvents changes the characteristics of these wastewaters [6,7]. Therefore, paint industry wastewater must be treated before discharging into the environment because this wastewater poses a serious threat to the ecosystem and human health [8]. Treatment methods such as microfiltration [9], oxidation [10], coagulation/flocculation [11], membrane separation, or combinations of these methods are used in order to meet the required water quality standards for the discharge of industrial wastewater into the environment [12,13].

Coagulation/flocculation is one of the widely used and efficient physicochemical methods for the treatment of industrial wastewater. Colloidal particles, soluble compounds, and very small solid suspensions in wastewater are removed from wastewater using the coagulation/flocculation method by destabilization and flock formation [14]. Also, the most important advantage of the coagulation/flocculation method is that harmful dye molecules and toxic aromatic compounds are removed from wastewater without decomposition [15]. Parameters such as wastewater characteristics, coagulant/flocculant type and dosage, pH, mixing speed, and time can affect the efficiency of this method [16,17]. The importance of the coagulation/flocculation treatment mechanism depends on single, binary, and/or multiple effects of these parameters [18,19]. Coagulants such as $Al_2(SO_4)_3$, $FeSO_4$, and $FeCl_3$ are widely used and are effective for chemical oxygen demand (COD), suspended solids (SS), and color removal in the treatment of industrial wastewater. The selection of coagulants significantly affects the treatment efficiency and sludge formation [20].

Most of the optimization studies have been carried out by changing only one variable with the trial and error method [21]. Optimization studies performed in this way are time-consuming and expensive in terms of energy and costs. In addition, since multiple interactions between variables cannot be determined, it is insufficient in creating the optimal combination of variables. However, given that wastewater treatment processes are multivariate and analysis of all interactions of these variables will take a very long time [22], response surface methodology (RSM) is an optimization method using less energy and cost in a shorter time by evaluating the effects and interactions of variables together. Today, RSM is widely and effectively implemented for the optimization of water and wastewater treatment processes in order to obtain the maximum benefit from the process [23]. RSM analyzes the effect of simultaneous modification of the variables, ensuring most data are obtained from a small number of experiments [24,25]. RSM uses mathematical and statistical techniques to create models from process data, evaluates the effects of various factors, and determines the optimal conditions for the desired responses [26]. It uses an important and effective experimental design, such as central composite design (CCD), to determine response data in RSM using the least squares technique (LST). Control tests with ANOVA determine the reliability and adequacy of the proposed model [27]. In addition, 3D surface figures help examine the relationship between variables and responses [28]. RSM was applied in different studies for the optimization of process variables for wastewater treatment [29–33].

In this study, the treatment of paint industry wastewater by the coagulation/flocculation method was investigated. The aim of this study is to determine the optimum treatment conditions using RSM which investigates the interactions of the variables selected for the treatment of paint industry wastewater. Within the scope of this study, CCD was applied to optimize process parameters and to create a mathematical model. By selecting pH, coagulant dose, and mixing speed as independent variables, the effects on COD, TSS, color, and turbidity removal measurements were evaluated as responses.

2. Materials and method

The paint wastewater was obtained from a paint manufacturing plant which produces water-based paint in Van, Turkey. Process wastewater was consists of water from washing tanks and mixing equipment in production units. Wastewater was collected by grab sampling technique using plastic bottles in wastewater reservoir. Characterization of the wastewater was performed and pollution values were determined [34]. pH and electrical conductivity measurements were measured on-site using a multiparameter device (WTW 3320). The color of the samples was monitored by UV-VIS spectrophotometer (HACH/DR6000) at 455 nm wavelength and turbidity of samples was measured by a turbidimeter (HACH/2100Q), respectively. The COD and color were measured according to ISO 6060 method [ISO 6060, 1986] and ISO 7887 method [ISO 7887, 1987], respectively. Other analyses of samples were carried out following the Standard Methods for Examination of Water and Wastewater (APHA Standart Methods, 1998) [35].

2.1. Coagulation/flocculation experiments

The coagulation/flocculation method has high COD and TSS removal capacity for paint wastewater and $FeCl_3{\cdot}6H_2O$, $Al_2(SO_4)_3{\cdot}18H_2O$, $FeSO_4{\cdot}7H_2O$ coagulants were used in this study. Coagulation/flocculation experiments were carried out with the six paddle stirrer jar-test set up (Velp Scientifica) which is shown in Fig. 1. Equal volume beakers are used to examine the different dosages of coagulant/flocculant in each run. Each beaker was filled with a volume of 500 mL of paint wastewater. COD, TSS, color, and turbidity were selected as responses, and removal efficiencies of these parameters were evaluated based on parameters such as pH, coagulant dose, and mixing speed. In the treatment experiments, initial rapid mixing was conducted at 100 rpm for 5 min, followed by slow mixing at 20 rpm for 30 min and the settling time was 30 min. Coagulant was added during rapid mixing and pH adjustment was made immediately after. After settling, analyses of samples were completed in the wastewater taken from the supernatant. All experiments were conducted in duplicate.

2.2. Determination optimum treatment conditions

CCD was used to study the individual and synergetic effects of the three factors on the defined responses. This method can reduce the number of experimental trials

Fig. 1. Jar test set-up used in wastewater treatment.

required to evaluate the main effect of each parameter and their interactions. It is characterized by three operations namely: 2^n factorial runs, $2n$ axial runs, and six center runs [36]. The most important parameters affecting the treatment efficiency of pH, coagulant dose, and mixing speed were selected as independent parameters and COD, TSS, color, and turbidity values were selected as responses in coagulation experiments. The upper and the lower limits of the independent variables were loaded to the Design Expert program and two axial points were determined by the program to expand the boundaries of these points and reduce the margin of error. Also, center point experiments were created under the same conditions in order to estimate the error that may occur during the experiments. In this case, a total of 20 experiments were proposed by the program, placed at eight factorial points, six axial points, and six center points. After experiments, each response value was determined by analysis of supernatant samples. The determined response values were inserted in the proposed experiments in the CCD section which is a part of the Design Expert program. ANOVA tables and 3D graphics were obtained by running the program. Selected factorial, axial, and center points of the variables for CCD are given in Table 1.

2.3. Required optimization criteria for treatment conditions

The optimum treatment conditions for pH (X_1), coagulant dose (X_2), and mixing speed (X_3) selected as the most effective parameters were determined for the paint industry wastewater. Statistical analysis of the obtained data was carried out with the Design Expert program to determine the most suitable function. Standard deviation, R^2, adjusted R^2, and predicted R^2 values were calculated for each function and the most suitable model was determined by the value of R^2 closest to 1.0 [37]. In the next stage, the model that best represents the studied system was determined with ANOVA. While the model represents the selected system, it requested the following conditions:

- Model; "significant."
- Lack of fit; "insignificant."
- All model terms; "95% confidence interval."
- Calculated R^2; ~1,
- Adjusted R^2; ~1,
- Predicted R^2; ~1,
- Coefficient of variation (C.V.%); minimum (lowest).

After determining the model that best represents the system, 3D figures were created by the Design Expert program, which is an experimental design program that can perform three different optimizations; "numerical optimization," "graphical optimization," and "point prediction." The numerical optimization results recommended by the program for different conditions were used in this study. Selected optimization criteria:

- pH value: "in range."
- Coagulant dose: "in range."
- Mixing speed: "in range."
- Maximum treatment percentage: "maximize."
- The optimum treatment conditions that provide the highest treatment percentage and desirability value closest to 1 were chosen as the solution.

Data were processed using Design Expert program including ANOVA to obtain the interaction between the process variables and the responses. The quality of the fit of polynomial model was expressed by the coefficient of

Table 1
Selected parameters for treatment and experimental levels

Independent variables	$-\alpha$	–1	0	+1	$+\alpha$
pH (X_1)	1.95	4.00	7.00	10.00	12.05
Mixing speed (X_2) (rpm)	65.91	100.00	150.00	200.00	234.09
Coagulant dose (X_3) (mg/L)	159.10	500.00	1,000.00	1,500.00	1,840.90

determination (R^2), and its static significance was checked by the *F*-test in the same program. The polynomial model determined for the optimal points. Mathematical solution can be obtained by Eq. (1) for the location of the stationary points. Writing the polynomial model in matrix notation:

$$y = \beta_0 + x^I b + x^I B x_S \quad (1)$$

$$x_S(\text{stationary points}) = \begin{bmatrix} X_1 \\ X_2 \\ X_k \end{bmatrix}, \; b = \begin{bmatrix} \beta_1 \\ \beta_2 \\ \beta_k \end{bmatrix}$$

$$\text{and} \quad B = \begin{bmatrix} \beta_{11} & \beta_{12}/2 & \beta_{1k}/2 \\ & \beta_{22} & \beta_{2k}/2 \\ \text{Sym} & & \beta_{kk} \end{bmatrix}$$

That is, b is a (kx_1) vector of the first order regression coefficient and B is a (kx_k) symmetric matrix. The stationary points (x_S) were determined with the solution of Eq. (2).

$$x_S = -\frac{1}{2}B^{-1}b \quad (2)$$

where x_S, b, and B matrixes in Eq. (2) were arranged as derived by Design Expert program and the optimum treatment conditions for paint industry wastewater were determined by solving the matrices in Eq. (2). This optimization procedure was explained in [38,39].

3. Results and discussion

COD, TSS, color, and turbidity values which constitute significant pollution were determined by characterization of the paint industry wastewater. According to the experimental results, the best and the lowest removal efficiency in the coagulation/flocculation process was achieved by $FeCl_3$ and $FeSO_4$ coagulants, respectively. The removal efficiencies of $Al_2(SO4)_3$ and $FeSO_4$ coagulants were found to be close to each other. Optimization experiments were carried out with $FeCl_3$ coagulant, which provides the best removal efficiency. pH, coagulant dose, and mixing speed were selected as independent variables and COD, TSS, color, and turbidity were selected as dependent variables in the optimization experiments for wastewater treatment.

3.1. Discussion of experimental results for optimization

The optimum values of pH, mixing speed, and coagulant dose were determined in jar test experiments for wastewater treatment conditions. A total of 20 experiments were performed in order of two factorial, two axial, and one central point, where the values of pH, mixing speed, and coagulant dose was changed. Six of these experiments were at the center point, which was completed under the same condition. Design of experiments were proposed by the Design Expert program and the responses (COD, TSS, color, and turbidity) obtained in these experiments are shown in Table 2. According to the results, the results of the experiments at the center point were close to each other and the margin of error was negligible. ANOVA tables

Table 2
Experimental design and obtained results

Run number	X_1 (pH)	X_2 (Coagulant dose)	X_3 (Mixing speed)	Y_1 (COD)	Y_2 (Color)	Y_3 (Turbidity)	Y_4 (Suspended solid)
1	7	1,000	234.08	81.13	2	11.70	21.66
2	10	1,500	100	110.55	6	7.25	20.00
3	10	1,500	200	114.47	5	8.78	31.66
4	7	1,000	150	72.52	1	2.74	12.00
5	10	500	200	123.78	15	11.60	45.00
6	7	1,000	150	72.03	2	3.76	17.50
7	4	500	100	193.15	15	8.82	23.00
8	7	1,000	150	72.37	2	3.36	12.50
9	7	1,840.90	150	97.86	11	17.50	14.90
10	7	1,000	150	71.62	1	3.32	10.00
11	7	1,000	150	71.07	1	3.21	7.50
12	4	1,500	200	125.25	5	15.50	31.65
13	7	1,000	65.91	121.64	17	7.90	13.33
14	10	500	100	145.00	12	9.03	20.00
15	4	500	200	117.30	13	17.30	25.00
16	7	159.10	150	128.72	22	6.98	16.66
17	4	1,500	100	95.85	9	19.50	26.66
18	1.95	1,000	150	140.00	10	22.60	23.33
19	12.05	1,000	150	142.45	13	4.12	26.66
20	7	1,000	150	72.03	2	3.00	10.00

were created and 3D figures were created by the Design Expert program for the response values of CCD.

3.2. Statistical analysis and 3D graphs

After the obtained data were processed in the Design Expert program, the model equations recommended by the program for COD, TSS, color, and turbidity are shown in Eqs. (3)–(6), respectively. The sum of squares of the variables in the model proposed for COD, SS, color, and turbidity by the program are shown in Tables 3–6, respectively. According to these tables, the quadratic model selected for optimization has higher F-values and smaller p-values than the other models. ANOVA results given by the program for COD, TSS, color, and turbidity responses are given in Tables 7–10, respectively. The p-values of the quadratic model selected for optimization were found to be very significant considering that the p-values were very small for COD, color, and turbidity results based on these tables. The coagulant dose was found to be a more effective parameter than pH and mixing speed according to the ANOVA results given in Tables 7 and 8. However, it was observed that pH is more effective than the coagulant dose and mixing speed with the ANOVA results in Table 9. R^2 values that were determined by the program for COD, TSS, color, and turbidity responses are given in Tables 11–14, respectively. According to Tables 11 and 13, it was determined that the calculated R^2 values for COD and turbidity are greater than 0.90, so it is more compatible with the experimental results and the calculated data from the model. But, based on Tables 12 and 14, it was determined that R^2 values calculated for color and TSS were 0.87 and 0.79, respectively. Also, 3D figures for COD (Figs. 2–4), color (Figs. 5–7), turbidity (Figs. 8–10), and TSS (Figs. 11–13) were created by the program.

$$\text{COD} = 71.72 - 2.46[X_1] - 13.55[X_2] - 9.66[X_3] + 5.70[X_1][X_2] + 3.64[X_1][X_3] + 16.30[X_2][X_3] + 25.91[X_1]^2 + 16.0[X_2]^2 + 11.82[X_3] \quad (3)$$

$$\text{Color} = 1.60 + 0.077[X_1] - 3.55[X_2] - 2.14[X_3] - 0.25[X_1][X_2] + 1.00[X_1][X_3] - 0.75[X_2][X_3] + 2.87[X_1]^2 + 4.63[X_2]^2 + 2.16[X_3]^2 \quad (4)$$

Table 3
Sum of squares of suggested model for COD removal

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value	
Mean vs. total	2.35E+05	1	2.352E+05			
Linear vs. mean	3,862.67	3	1,287.56	1.21	0.33	
2FI vs. linear	2,491.22	3	830.41	0.74	0.54	
Quadratic vs. 2FI	**13,260.10**	**3**	**4,420.03**	**34.40**	**<0.001**	**Suggested**
Cubic vs. quadratic	1,140.16	4	285.04	11.80		
Total	2.561E+05	20	12,804.08			

Table 4
Sum of squares of suggested model for color removal

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value	
Mean vs. total	1,344.80	1	1,344.80			
Linear vs. mean	234.87	3	78.29	2.35	0.11	
2FI vs. linear	13.00	3	4.33	0.11	0.95	
Quadratic vs. 2FI	**426.16**	**3**	**142.05**	**15.25**	**0.0005**	**Suggested**
Cubic vs. quadratic	59.63	4	2,850,414.91	2.67	0.1362	
Total	2,112.00	20	105.60			

Table 5
Sum of squares of the suggested model for turbidity removal

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value	
Mean vs. total	1,766.64	1	1,766.64			
Linear vs. mean	277.63	3	92.54	3.33	0.04	
2FI vs. linear	45.58	3	15.19	0.50	0.69	
Quadratic vs. 2FI	**339.81**	**3**	**113.27**	**19.22**	**0.0002**	**Suggested**
Cubic vs. quadratic	58.32	4	14.58	138.96	0.0052	
Total	2,488.60	20	124.43			

Table 6
Sum of squares of the suggested model for TSS removal

Source	Sum of squares	Degree of freedom	Mean square	*F*-value	*p*-value	
Mean vs. total	8,364.46	1	8,364.46	–	–	
Linear vs. mean	264.69	3	88.23	1.06	0.39	
2FI vs. linear	193.34	3	64.45	0.74	0.54	
Quadratic vs. 2FI	**811.71**	**3**	**270.57**	**8.36**	**0.0045**	**Suggested**
Cubic vs. quadratic	63.13	4	15.78	0.36	0.8269	
Total	9,958.04	20	497.90	–	–	

Table 7
ANOVA results of suggested model for COD removal

Source	Sum of squares	Degree of freedom	Mean square	*F*-value	*p*-value
Model (Quadratic)	19,613.34	9	2,179.33	16.96	<0.0001
X_1 (pH)	82.81	1	82.81	0.64	0.4408
X_2 (Coagulant dose)	2,506.34	1	2,506.34	19.50	0.0013
X_3 (Mixing speed)	1,273.51	1	1,273.51	9.91	0.0104
X_1X_2	259.81	1	259.81	2.02	0.1855
X_1X_3	106.22	1	106.22	0.83	0.3847
X_2X_3	2,125.19	1	2,125.19	16.54	0.0023
X_1^2	9,675.03	1	9,675.03	75.29	<0.0001
X_2^2	3,429.30	1	3,704.95	28.83	0.0003
X_3^2	2,015.10	1	2,015.10	15.68	0.0027

Table 8
ANOVA results of suggested model for color removal

Source	Sum of squares	Degree of freedom	Mean square	*F*-value	*p*-value
Model (quadratic)	674.03	9	74.89	8.04	0.0016
X_1 (pH)	0.080	1	0.080	8.58E-03	0.9280
X_2 (coagulant dose)	172.24	1	172.24	18.49	0.0016
X_3 (mixing speed)	62.55	1	62.55	6.71	0.0269
X_1X_2	0.50	1	0.50	0.054	0.8215
X_1X_3	8.00	1	8.00	0.86	0.3759
X_2X_3	4.50	1	4.50	0.48	0.5029
X_1^2	118.47	1	118.47	12.72	0.0051
X_2^2	309.59	1	309.59	33.23	0.0002
X_3^2	67.24	1	67.24	7.22	0.0228

$$\text{Turbidity} = 3.23 - 4.07[X_1] + 1.61[X_2] + 1.10[X_3] - 1.68[X_1][X_2] - 0.047[X_1][X_3] - 1.69[X_2][X_3] + 3.56[X_1]^2 + 3.16[X_2]^2 + 2.30[X_3]^2 \quad (5)$$

$$\text{TSS} = 11.33 + 1.17[X_1] - 0.44[X_2] + 4.22[X_3] - 2.96[X_1][X_2] + 3.71[X_1][X_3] - 1.29[X_2][X_3] + 6.42[X_1]^2 + 3.17[X_2]^2 + 3.77[X_3]^2 \quad (6)$$

The COD removal is at the highest level at the point where pH 7 and the coagulant dose is about 1,100 mg/L (Fig. 2). Considering the effect of mixing speed and pH value on COD removal in Fig. 3, COD removal is highest while mixing speed is approximately 150 rpm and pH value is 7. Fig. 4 shows that COD removal becomes fixed when mixing speed is above 150 rpm and coagulant dose is above 1,100 mg/L. Also, according to these figures, the low COD removal was obtained at the lowest mixing speed, and the lowest coagulant dose values. This is because the very low coagulant dose is not sufficient to balance the ions of the impurities in the wastewater and low mixing speed is not sufficient for flock formation. In the paint industry wastewater treatment, 39% and 87% COD removal were obtained using activated sludge at 1.2 and 2.4 retention times, respectively [40]. At pH 3.5 70% COD removal and at alkaline pH only 35% COD removal were obtained by coagulation/flocculation of wastewater samples taken from

Table 9
ANOVA results of suggested model for turbidity removal

Source	Sum of squares	Degree of freedom	Mean square	*F*-value	*p*-value
Model (quadratic)	663.02	9	73.67	12.50	0.0002
X_1 (pH)	225.87	1	225.87	38.32	0.0001
X_2 (coagulant dose)	35.35	1	35.35	6.00	0.0343
X_3 (mixing speed)	16.41	1	16.41	2.78	0.1262
X_1X_2	22.71	1	22.71	3.85	0.0781
X_1X_3	0.018	1	0.018	3.062E-03	0.9570
X_2X_3	22.85	1	22.85	3.88	0.0773
X_1^2	182.68	1	182.68	30.99	0.0002
X_2^2	144.31	1	144.31	24.48	0.0006
X_3^2	76.35	1	76.35	12.95	0.0049

Table 10
ANOVA results of suggested model for TSS removal

Source	Sum of squares	Degree of freedom	Mean square	*F*-value	*p*-value
Model (quadratic)	1,269.75	9	141.08	4.36	0.1560
X_1 (pH)	18.63	1	18.63	0.58	0.4657
X_2 (coagulant dose)	2.63	1	2.63	0.081	0.7816
X_3 (mixing speed)	243.44	1	243.44	7.52	0.0208
X_1X_2	69.92	1	69.92	2.16	0.1725
X_1X_3	110.04	1	110.04	3.40	0.0951
X_2X_3	13.39	1	13.39	0.41	0.5347
X_1^2	594.74	1	594.74	18.37	0.0016
X_2^2	144.46	1	144.46	4.46	0.0608
X_3^2	205.09	1	205.09	6.33	0.0306

Table 11
Statistical values of suggested model for COD removal

Standard deviation	11.34	R^2	0.9385
Mean	108.44	Adjusted R^2	0.8832
C.V. %	10.45	Predicted R^2	0.4733

Table 12
Statistical values of suggested model for color removal

Standard deviation	3.05	R^2	0.8786
Mean	8.20	Adjusted R^2	0.7693
C.V. %	37.22	Predicted R^2	0.0905

Table 13
Statistical values of suggested model for turbidity removal

Standard deviation	2.43	R^2	0.9184
Mean	9.40	Adjusted R^2	0.8449
C.V. %	25.83	Predicted R^2	0.3492

Table 14
Statistical values of suggested model for TSS removal

Standard deviation	5.69	R^2	0.7968
Mean	20.45	Adjusted R^2	0.6139
C.V. %	27.83	Predicted R^2	0.3473

a paint production factory [41]. In another study, the optimum pH was determined as 9.7 with 2 g/L $FeSO_4$ dose, and 30%–80% COD removal efficiency was achieved without the need for pH adjustment at 2.5 g/L of $Al_2(SO_4)_3$ dose using the coagulation/flocculation method [42].

The effects of the binary interactions of independent parameters on color removal were analyzed in Figs 5–7. In Fig. 5, the effect of pH and coagulant dose on color removal is seen with the best removal at pH 7. The interactions of pH and mixing speed are shown in Fig. 6; the measured color values were the same in the pH 6–8 range. Mixing speed of approximately 150 rpm and pH 7 provided the best color removal. In Fig. 7, color removal is at the highest level when the coagulant dose is about 1,000 mg/L and the mixing speed is 150 rpm. In addition, having a coagulant dose above 1,100 mg/L at 150 rpm mixing speed negatively affects color removal. These results will cause excessive use of chemical coagulants and increase the cost of wastewater treatment.

Table 15
Optimum treatment conditions determined by matrix method

	pH	Coagulant dose (mg/L)	Mixing speed (rpm)	Optimum value
COD (mg/L)	6.99	1,165.50	159.02	68.64
Color	7.05	956.62	140.62	2.42
Turbidity (NTU)	8.57	901.76	134.76	1.79
Suspended solid (mg/L)	7.24	991.60	119.94	10.14

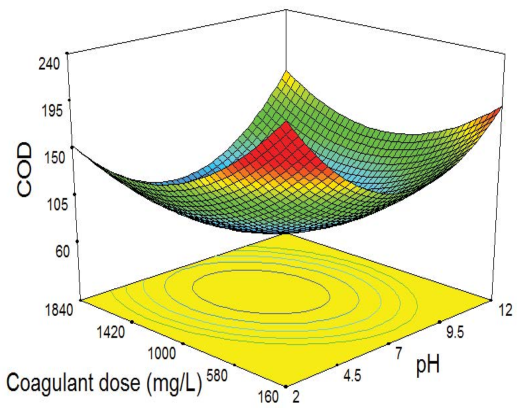

Fig. 2. Effect of coagulant dose and pH on COD removal.

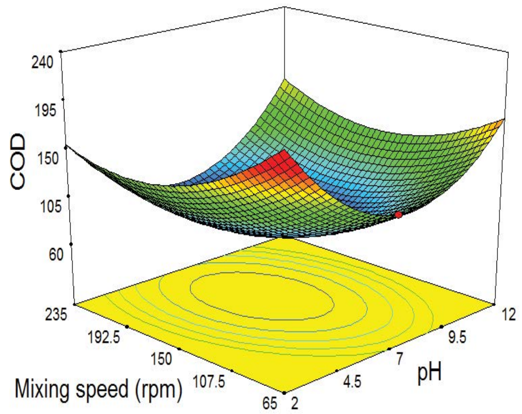

Fig. 3. Effect of mixing speed and pH on COD removal.

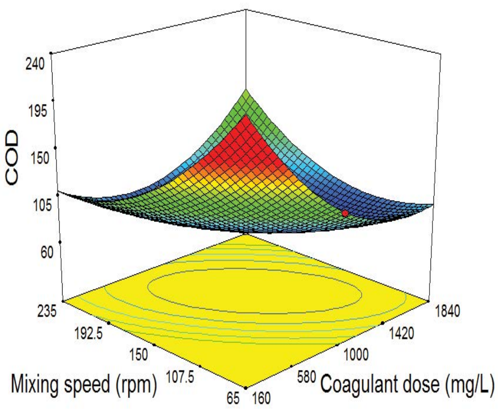

Fig. 4. Effect of mixing speed and coagulant dose on COD removal.

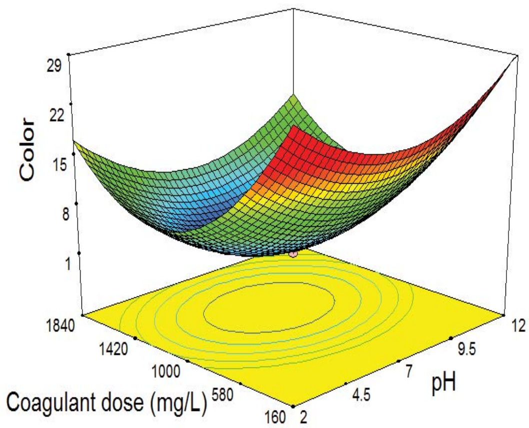

Fig. 5. Effect of coagulant dose and pH on color removal.

The effects of the binary interactions of independent parameters on turbidity removal were analyzed in Figs 8–10. It was observed that with increasing coagulant dose in Figs. 8 and 10, the turbidity increases, and similarly, in Figs. 9 and 10 the turbidity increases as the mixing speed increases. It was observed that the pH value of about 7.50 has highest turbidity removal in Figs. 8 and 9. The effect of coagulant dose and mixing speed on turbidity removal is observed with turbidity removal increasing when the coagulant dose is increased from 160 mg/L to approximately 1,000 mg/L in Fig. 10. The optimum treatment conditions of pH 7.50, coagulant dose 1,000 mg/L, and mixing speed 150 rpm were determined for turbidity removal from these figures. In a similar study conducted in the literature, with the addition of $FeSO_4$, $Al_2(SO_4)_3$, and polyaluminum chloride (PAC), 70%, 90%, and 98% turbidity removal efficiency were reported, respectively [41].

The effects of the binary interactions of independent parameters on suspended solid removal were analyzed in Figs. 11–13. In Fig. 11, the highest level of TSS removal was seen at pH 7 and a coagulant dose of 1,000 mg/L. It was observed that the values of TSS increased above pH 7 and with a coagulant dose above 1,000 mg/L. Increasing the mixing speed did not significantly affect the TSS removal according to Figs. 12 and 13. The optimum conditions for TSS removal were determined as pH 7, coagulant dose 1,000 mg/L, and mixing speed 150 rpm.

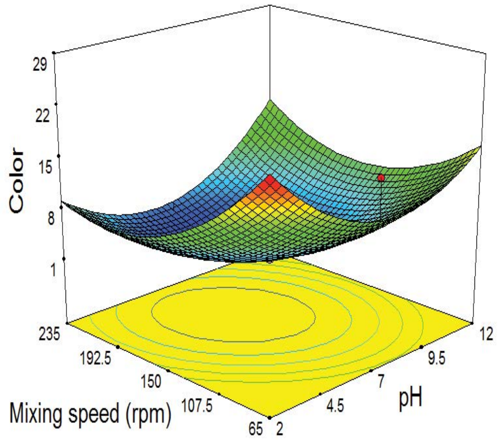

Fig. 6. Effect of mixing speed and pH on color removal.

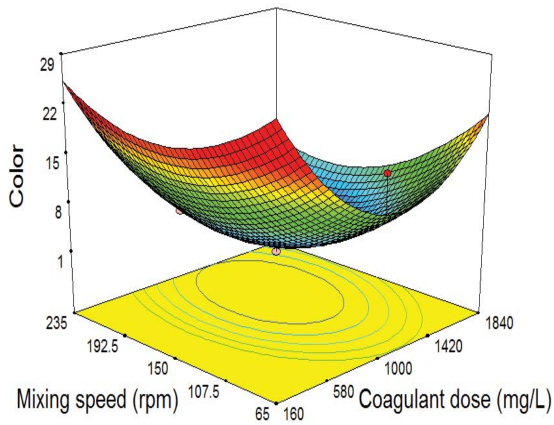

Fig. 7. Effect of mixing speed and coagulant dose on color removal.

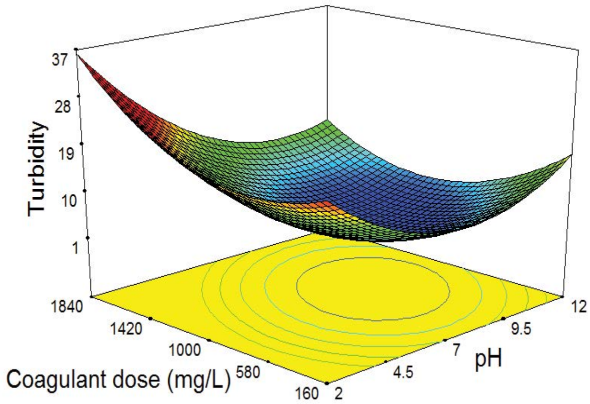

Fig. 8. Effect of coagulant dose and pH on turbidity removal.

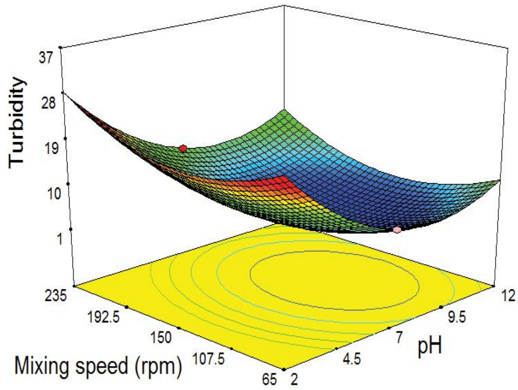

Fig. 9. Effect of mixing speed and pH on turbidity removal.

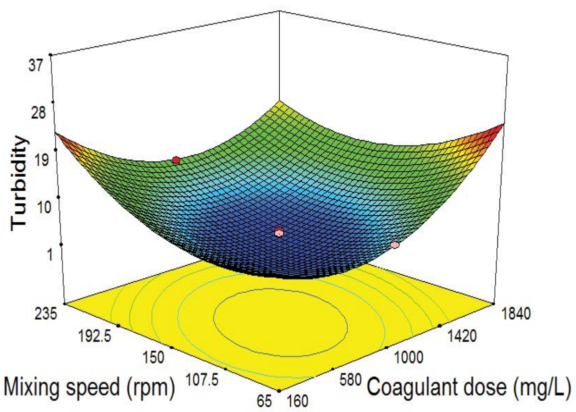

Fig. 10. Effect of coagulant dose and mixing speed on turbidity removal.

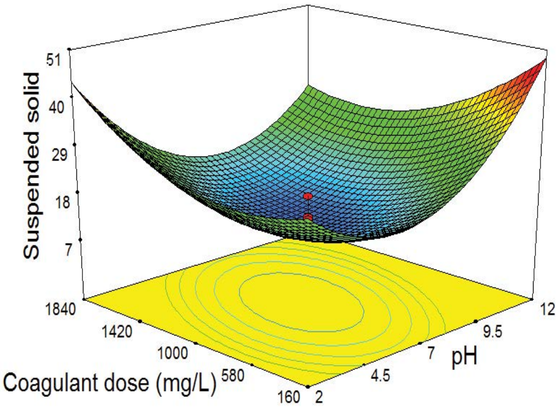

Fig. 11. Effect of coagulant dose and pH on TSS removal.

3.3. Optimization results for wastewater treatment conditions

Treatment efficiency is very important for the wastewater optimization procedure and therefore optimum conditions in which the removal efficiency is high should be determined. In order to obtain the desired level and quality, it is necessary to determine the optimum values of the process parameters (pH, coagulant dose, mixing speed). Therefore, the range of the experiments selected in the optimization procedure must be economical in terms of time and cost. It is very important to correctly interpret the obtained figures for the optimization of the parameters.

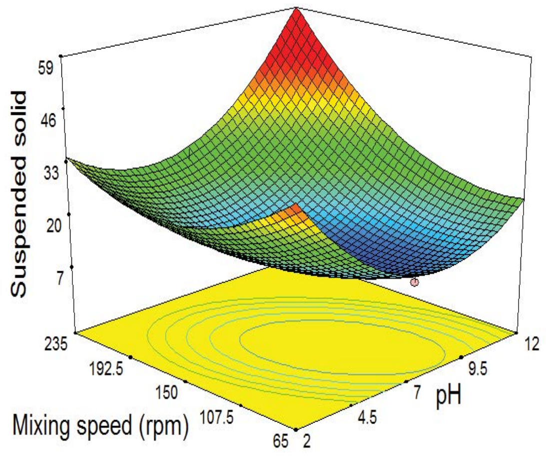

Fig. 12. Effect of mixing speed and pH on TSS removal.

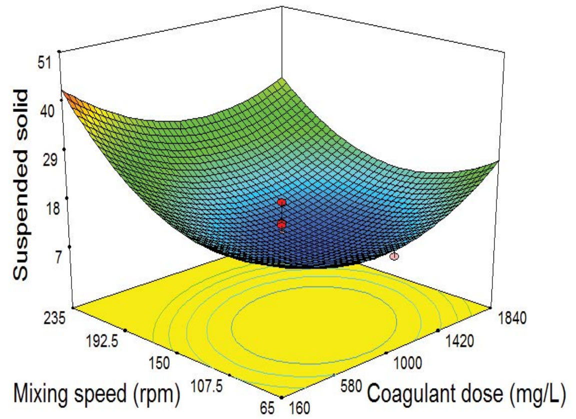

Fig. 13. Effect of coagulant dose and mixing speed on TSS removal.

The model equation based on the actual values proposed by the program can be solved with the matrix method to determine the optimum treatment conditions for the paint industry wastewater. The optimum treatment conditions which were obtained with the solution of the created matrices are given in Table 15. Numerical optimization was used to determine the optimum treatment conditions in the coagulation/flocculation experiments performed in the jar test set-up. The optimization criteria from the Design Expert program for coagulation treatment conditions are given in Table 16 and the numerical optimization solutions proposed by the program are given in Table 17. The optimum values of the parameters in the treatment experiments were determined as pH 7.54, coagulant dose 1,080.49 mg/L, and mixing speed 146.16 rpm in order to obtain the lowest values of COD, TSS, color, and turbidity. Under optimized conditions COD, TSS, color, and turbidity removals were completed at 94.1%, 95.3%, 97.1%, and 99.5%, respectively.

3.4. Economic analysis of wastewater treatment conditions

Economic studies based on the estimated cost of dosage, cost of day, and the treated wastewater quality results obtained is presented in Table 18. Based on the unit price ordering the estimated dosage cost, from the lowest to the highest was $FeCl_3 \cdot 6H_2O$ < $Al_2(SO_4)_3 \cdot 18H_2O$ < $FeSO_4 \cdot 7H_2O$ for optimum dosage, respectively. Economically $FeSO_4 \cdot 7H_2O$ is the most expensive and it is insufficient coagulant for the treatment of paint industry wastewater. The obtained results were showed that $FeSO_4 \cdot 7H_2O$ coagulant did not supply the discharge limit to the environment. Pollutant removal may be the major criteria for the selection of appropriate coagulant and performance of $FeCl_3 \cdot 6H_2O$ is better than other two coagulants due to its cost-effective and the best removal values. Cost is not the only important in wastewater treatment: additional factors such as the effects of acidification on wastewater quality need to be evaluated for safe use of the recovered coagulant. Ferric compounds are also used to prevent corrosion and manage odors in pipelines of wastewater plants [43]. $Al_2(SO_4)_3 \cdot 18H_2O$ coagulant is expensive for treatment and it is insufficient for TSS and color removal. Although Al-based coagulants, particularly $Al_2(SO_4)_3 \cdot 18H_2O$ effective for removing turbidity and organic materials, may result in elevated concentrations of residual Al in treated water [44].

Iron and aluminum-based coagulants such as $FeCl_3$, $Al_2(SO_4)_3$, and $FeSO_4$ are the most widely applied inorganic and commercial coagulants, which remove pollutants from wastewater by charge neutralization, adsorption, entrapment, and complexation mechanism. The addition of these coagulants to wastewater undergoes a series of reactions with the hydroxyl ions producing monomeric and polynuclear species. Decomposition of these metal salts to affranchise their trivalent ions, which are $Al(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{3+}$ for aluminum and iron, respectively. The replacement of the water molecules by hydroxyl ions to form

Table 16
Optimization criteria for the studied range

Parameters	Goal	Lower limit	Upper limit
pH	is in range	4.00	10.00
Coagulant dose (mg/L)	is in range	500.00	1,500.00
Mixing speed (rpm)	is in range	100.00	200.00
COD (mg/L)	minimize	71.07	193.15
Color	minimize	1.00	22.00
Turbidity (NTU)	minimize	2.74	22.60
Suspended solid (mg/L)	minimize	7.50	45.00

Table 17
Optimum treatment conditions recommended by the program

		Optimum treatment values			
		COD (mg/L)	Color	Turbidity (NTU)	Suspended solid (mg/L)
pH	7.54				
Coagulant dose (mg/L)	1,080.49	71.07	1.00	2.74	7.50
Mixing speed (rpm)	146.16				

Table 18
Economic analysis and removal performance of coagulants

Coagulant	$FeCl_3·6H_2O$	$Al_2(SO_4)_3·18H_2O$	$FeSO_4·7H_2O$
Molecular weight (g/mol)	270.30	666.43	278.01
*Cost ($/kg)	85.83	103.96	153.43
Cost per day ($/d)	0.481	0.593	0.872
Cost per dose ($/m^3)	0.185	0.228	0.335
Removal performance (%)			
COD (mg/L)	94.1	75.2	59.3
TSS (mg/L)	95.3	14.5	17.8
Color (mg/L)	97.1	61.9	15.5
Turbidity (NTU)	99.5	93.2	45.2

*Cost of coagulants were derived from https://us.vwr.com/store/product

soluble $Al(OH)^{2+}$ and $Fe(OH)_2$ which increases the coagulation performance by the trivalent ions being strongly adsorbed onto the negatively charged of the colloids.

4. Conclusions

In this study, paint wastewater was obtained from a paint factory in Van, Turkey. The treatment of the paint wastewater was carried out with the jar test set up using $FeCl_3$, $Al_2(SO_4)_3$, and $FeSO_4$ chemical coagulants. The best treatment efficiency was achieved by $FeCl_3$ coagulant in the coagulation/flocculation experiments which were performed under the same conditions for each coagulant. Treatment conditions were optimized using RSM and the Design Expert program was used to design the experiments and analyze the obtained results. pH, coagulant dose, and mixing speed were selected as independent parameters, and COD, TSS, color, and turbidity values were selected as responses in the optimization experiments. The equations obtained using the coefficients in the model created by the program were solved and the optimum values of the independent variables were calculated. Using these values, the lowest pollution loads were determined as (mg/L) COD 68.64, color 2.42, TSS 10.14, and turbidity 1.79 NTU. Optimization results from the program were examined, the optimum values of treatment parameters were suggested as pH 7.54, coagulant amount 1,080.49 mg/L, and mixing speed 146.16 rpm. The lowest pollution values under optimum conditions were (mg/L) COD 71.07, color 1.00, TSS 7.50, and turbidity 2.74 NTU. Under optimized conditions COD, TSS, color, and turbidity removals were 94.1%, 95.3%, 97.1%, and 99.5%, respectively.

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