

### Pretreatment of Food Industry Wastewater by Coagulation: Process Modeling and Optimization

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#### Abstract

In this study, coagulation processes using FeCl<sub>3</sub>6H<sub>2</sub>O and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O as coagulants were employed and designed for chemical oxygen demand (COD) and total suspended solids (TSS) removal from food industry wastewater via response surface methodology (RSM). RSM was used for the optimization of coagulation processes and evaluation of the effects and interactions between process variables (pH, coagulant dosage and reaction time). ANOVA was used to analyze the experimental data obtained in the study and secondary regression models were developed by using Statgraphics Centurion XVI.I software. The optimum conditions were pH 9, dosage 1500 mg/L and time 25 min for maximum COD removal efficiency for FeCl<sub>3</sub>6H<sub>2</sub>O and pH 9, dosage 1493 mg/L and time 25 min for Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O. Under optimum conditions, COD and TSS removal efficiencies were 46.4% and 96.7% for FeCl<sub>3</sub>6H<sub>2</sub>O and 31.2% and 96.2% for Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O, respectively. ANOVA results showed that the responses of model have high coefficient values ( $R^2 > 0.80$ ), and hence the second order regression model can be explained with these experimental data. The proposed model fits very well with the experimental data with  $R^2$  of 0.9677 for COD and 0.9543 for TSS removal for FeCl<sub>3</sub>6H<sub>2</sub>O and 0.9456 for COD and 0.9260 for TSS removal for Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O, respectively. Model results showed that the RSM for coagulation processes using both coagulants is a powerful tool for optimizing the experimental conditions. Moreover, it can be concluded that both coagulation processes may be an effective alternative pre-treatment process for food industry wastewater.

Keywords: Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O, Coagulation, FeCl<sub>3</sub>6H<sub>2</sub>O, Optimization, RSM.

#### 1. Introduction

Wastewater treatment is important for protection of natural resources. Besides conventional physical and biological treatment applications coagulation/flocculation is an essential process in domestic and/or industrial wastewater treatment. Coagulation/flocculation process stands out as a pretreatment method that can be applied before biological treatment in order to increase the efficiency [1]. This process, in which coagulants such as iron (II) sulfate, iron (III) chloride, iron chlorosulfate (FeClSO<sub>4</sub>), and aluminum sulfate (alum) are widely used [2], is applied in water/wastewater treatment to convert colloidal materials into easily settable aggregates [3]. Coagulation/flocculation process is very effective in the removal of organic matter and suspended solids [4]. Although alternatives have been tried to be developed since the process causes residual metal ions in treated water, low efficiency of synthetic polymers in addition to low cost, ease of operation and energy efficiency of coagulation/flocculation process [1], an easily feasible

treatment alternative method to metal ions could not have been developed [5].

Coagulation process efficiency depends on many variables such as coagulant type, coagulant dosage, pH, property of wastewater, and addition of flocculants [6]. Many studies have been conducted to optimize process parameters in treatment of landfill leachate, industrial wastewater, domestic wastewater, and wastewater from animal farms [1,3]. FeCl<sub>3</sub>.6H<sub>2</sub>O and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O are commonly used coagulants in the treatment of industrial wastewaters and it has been applied to wastewaters from different industries such as potato chips production, soap/detergent production, and cork production [3].

Food industry wastewaters mainly contain leavenings, carbohydrate, organic and inorganic salts, oil and grease, cleaning products and proteins which are difficult to treat by conventional physicochemical pretreatment applications [7]. Conventional biological processes applied for the treatment of these wastewaters are insufficient to meet discharge standards in many

countries and new treatment methods are needed [8]. Thus, researchers have recommended addition of chemical coagulants for treatment of these wastewaters [9,10]. Moreover, coagulation process was used as a pretreatment application in the treatment of various food industry wastewaters. Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> was used as coagulant to treat wastewaters from instant coffee and coffee products [11] and table olive processing [12] while FeCl<sub>3</sub> was applied in the pretreatment of vegetable processing [13] and table olive processing [12] wastewaters.

In order to achieve high treatment performances, optimization of process parameters is needed. Traditionally, optimization of process is conducted by determining the effect of one factor while the others are held constant [14]. However, this application is disadvantageous both in terms of time and evaluating the effect of different factors together [15,16]. Therefore, statistical methods are practical for minimizing the time required for experiments, reducing cost and evaluating the effects of many factors together. For this purpose, response surface methodology (RSM) is commonly used for modeling of various variables and optimization of operation parameters [14,16]. The most widely used method in RSM is central composite design (CCD) which is an effective method that demonstrates the effect of binary interaction and curvilinear variables [16].

In this study, application of coagulation with  $FeCl_36H_2O$  and  $Al_2(SO_4)_318H_2O$  as coagulants for removal of total suspended solids (TSS) and chemical oxygen demand (COD) from food industry wastewater was investigated. The operational parameters such as coagulant type and dosage, pH, and operation time were optimized using CCD as a statistical experimental design.

# Materials and Methods Food Industry Wastewater

The characteristics of real wastewater used in this study are given in Table 1. Food industry wastewater was obtained and analyzed according to the Standard Methods [17]. COD was measured by closed reflux titrimetric method and TSS was determined by 2540 D method of APHA [17]. The pH and electrical conductivity were measured using WTW Multi 9620 IDS device.

#### 2.2. Experimental and Analytical Procedure

FeCl<sub>3</sub>6H<sub>2</sub>O and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O coagulant solutions were prepared as 10 g/L. The pH of wastewater (400 mL) was adjusted to the desired level using few drops of 1 N H<sub>2</sub>SO<sub>4</sub> and 1 N NaOH solutions before each sets. And then, initial electrical conductivity of wastewater was measured and recorded. The coagulant dosage (500, 1000 and 1500 mg/L) determined by CCD was added to the wastewater sample placed in the jar-test apparatus. After mixing rapidly during 1 min at 200 rpm and slowly for desired time at 30 rpm, the liquid was settled for one hour, then; the supernatant was collected to measure COD and TSS.

Table 1.	Characteristics	of real	wastewater	used in	this
study.					

Parameter	Value	
pH	6.09	
COD, mg/L	17,600	
Conductivity, mS/cm	4.08	
TSS, mg/L	940	

#### **2.3. Design of the Experiments**

Statistical methods of experimental design can consider the interactions of the factors, while the required number of experimental set is limited. Therefore, many researchers have recently interested in the methods for optimization of wastewater treatment. RSM, which is one of the experimental design statistical tools, can optimize the operational factors and also develop a mathematical descriptive model for the process [18]. In this study, CCD model for coagulation processes using FeCl<sub>3</sub>6H<sub>2</sub>O and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O coagulants was used for producing the effects of experimental parameters on COD and TSS removal from food industry wastewater.

15 experimental sets representing the interactions between independent variables and optimizing the parameters were conducted with 3 different levels of CCD (-1, 0, +1) and with 3 independent variables. The ranges of three most important variables (X1: pH, X2: coagulant dosage and X<sub>3</sub>: reaction time) are given in Table 2. According to the preliminary study results, the coded values of the independent variables were specified. Also, the ranges of the independent variables were determined and given in Table 2. The experimental design and statistical analysis of data were performed using the Statgraphics Centurion XVI.I software. The suitability of the secondary model was verified using the  $R^2$  correlation coefficient, the student t-test assessed its statistical significance, and the conditions of the model were checked using probability (p) values at a confidence interval of 95 percent. The significance level of the model and each factor can be interpreted from obtained results from variance analysis of the model. R<sup>2</sup> expressed the fit quality of the polynomial model and Fisher's F-test verified its statistical significance. The model terms were evaluated by their p-value and F-value.

The relationship between the independent variables and responses is shown by Eq. (2.1).

$$Y = b_0 + \sum_{j=1}^{n} b_j x_j + \sum_{j=1}^{n} b_{jj} x_j^2 + \sum_{i=1}^{n} b_{ij} x_i x_j + e_i$$
(2.1)

Coagulant type	Symbol	Factor	Coded variables		bles
			-1	0	1
	$\mathbf{X}_1$	pН	5	7	9
FeCl <sub>3</sub> 6H <sub>2</sub> O	$X_2$	Dosage, mg/L	500	1000	1500
	$X_3$	Reaction Time, min.	5	15	25
Coagulant type	Symbol	Factor	Coded variables		bles
			-1	0	1
	$\mathbf{X}_1$	pН	5	7	9
$Al_2(SO_4)_318H_2O$	$X_2$	Dosage, mg/L	500	1000	1500
	$X_3$	Reaction Time, min.	5	15	25

Table 2. The coded values of variables of the experimental design matrix.

where Y is the assumed response (COD and TSS removal);  $b_0$  is the constant coefficient;  $b_i$ ,  $b_{ii}$  and  $b_{ij}$  are the coefficients for the linear, quadratic and interaction effects respectively;  $X_i$  and  $X_j$  are the independent variables; n is the number of independent variables, and e is the error of prediction.

## Results and Discussion Statistical Analysis by CCD

To fit the experimental findings acquired by CCD, quadratic polynomial surface reaction model was implemented. The regression equations obtained in coagulation process for COD and TSS removal are presented as shown in Eq. (3.1-3.4).

In Eq. (3.1-3.4)  $X_1$ ,  $X_2$ , and  $X_3$  show the effects of the linear main factor, while  $X_1^*X_2$ ,  $X_1^*X_3$  and  $X_2^*X_3$  and  $X_1^2$ ,  $X_2^2$  and  $X_3^2$  show the interaction between the two factors and the quadratic effects, respectively. The positive sign of coefficients indicates a synergistic effect, whereas the negative sign of coefficients

indicates an antagonistic effect. According to Eq. (3.1-3.2) it can be seen that COD and TSS removal efficiencies increase with rising pH but decrease with rising dosage. Also, COD removal efficiency decreases with increase in reaction time, whereas TSS removal efficiency increases with increase in reaction time in Eq (3.1-3.2). In Eq. (3.3-3.4), COD and TSS removal efficiencies increase with increase in pH and reaction time but decrease with increase in dosage.

Three independent variables were analyzed as responses COD and TSS removals, in order to obtain optimum initial pH, coagulant dosage and reaction time and to achieve highest removal of COD and TSS for the treatment of food industry wastewater using FeCl<sub>3</sub>6H<sub>2</sub>O and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O coagulants. The experimental design and actual values of responses by FeCl<sub>3</sub>6H<sub>2</sub>O and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O coagulants are given in Table 3 and Table 4, respectively. ANOVA results from obtained process using FeCl<sub>3</sub>6H<sub>2</sub>O and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O coagulants were given in Table 5 and Table 6. The findings indicate a high level of reliability in COD

FeCl<sub>3</sub>6H<sub>2</sub>O coagulant;

$$\begin{array}{l} \textit{COD removal, \%} \\ &= 22.0125 + 4.70625 * X_1 - 0.01805 * X_2 - 1.57875 * X_3 - 0.44375 * X_1^2 \\ &+ 0.001675 * X_1 * X_2 + 0.06 * X_1 * X_3 + 0.0000058 * X_2^2 + 0.000565 * X_2 * X_3 \\ &+ 0.02275 * X_3^2 \end{array} \tag{3.1} \\ \textit{TSS removal, \%} = 37.9875 + 12.8875 * X_1 - 0.11125 * X_2 + 4.605 * X_3 - 0.6875 * X_1^2 + 0.001 \\ &+ X_1 * X_2 - 0.16 * X_1 * X_3 + 0.0000576 * X_2^2 - 0.00028 * X_2 * X_3 - 0.0855 \\ &+ X_3^2 \end{aligned}$$

Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O coagulant;

$$COD \ removal, \% = 5.6875 + 3.375 * X_1 - 0.0003 * X_2 + 0.075 * X_3 - 0.1875 * X_1^2 + 0.00025$$
(3.3)  

$$* X_1 * X_2 + 0.0 * X_1 * X_3 + 0.0000022 * X_2^2 + 0.00005 * X_2 * X_3 - 0.002 * X_3^2$$

$$TSS \ removal, \% = 55.65 + 3.81458 * X_1 - 0.00681667 * X_2 + 0.22625 * X_3 - 0.151042 * X_1^2$$

$$+ 0.00015 * X_1 * X_2 + 0.00375 * X_1 * X_3 + 0.0000112833 * X_2^2 - 0.00043 * X_2$$
(3.4)  

$$* X_3 + 0.0174583 * X_3^2$$

estimation of COD and TSS removal efficiencies of  $R^2$  values of 96.77 and 95.43 for FeCl<sub>3</sub>6H<sub>2</sub>O coagulant, 94.56 and 92.59 for Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O coagulant, respectively. High  $R^2$  values ensure satisfactory adjustment of the quadratic model to the experimental results. It can be inferred that only 3.23 (COD removal) and 4.57 (TSS removal) of the variability in the

responses were not explained for FeCl<sub>3</sub>6H<sub>2</sub>O coagulant. In addition, only 5.44 (COD removal) and 7.41 (TSS removal) of the variability in the responses were not explained for  $Al_2(SO_4)_318H_2O$  coagulant. The model F-values implies that the models are significant for COD and TSS removal efficiencies (Table 5 and Table 6).

Table 3. The e	experimental	design	matrix and	l actual	values	of respo	nses by	FeCl <sub>3</sub> 6H <sub>2</sub>	) coagulant
		0					~		0

Run	Independ	lent variables	Responses		
	рН	Dosage, mg/L	Reaction time, min	COD (%)	TSS (%)
1	5	500	15	21.9	85.9
2	9	500	15	22.9	87.2
3	5	1500	15	30.9	87.5
4	9	1500	15	38.6	92.8
5	5	1000	5	26.4	49.7
6	9	1000	5	28.2	67.7
7	5	1000	25	28.2	69.5
8	9	1000	25	34.8	74.7
9	7	500	5	28.2	70.1
10	7	1500	5	37.7	82.8
11	7	500	25	21.9	85.1
12	7	1500	25	42.7	92.2
13	7	1000	15	28.2	72.7
14	7	1000	15	28.7	80.1
15	7	1000	15	29.8	77.3

Table 4. The experimental design matrix and actual values of responses by Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O coagulant.

Run		Independent variables		Respo	nses
	рН	Dosage, mg/L	Reaction time, min	COD (%)	TSS (%)
1	5	500	15	19.7	77.0
2	9	500	15	22.4	82.8
3	5	1500	15	27.1	84.8
4	9	1500	15	30.8	91.2
5	5	1000	5	20.8	76.5
6	9	1000	5	25.6	85.5
7	5	1000	25	22.9	80.1
8	9	1000	25	27.7	89.4
9	7	500	5	22.9	72.8
10	7	1500	5	27.7	89.7
11	7	500	25	22.9	87.2
12	7	1500	25	28.7	95.5
13	7	1000	15	25.0	80.4
14	7	1000	15	24.5	81.6
15	7	1000	15	26.1	83.2



The associated p value was used to estimate whether statistical significance is large enough [19]. The lower values of Prob>F (<0.05) imply that the model terms are significant, whereas higher values than 0.1 show that the model terms are insignificant at 95% probability level [20]. As it can be seen from Table 5, response surface quadratic models for independent variables were significant at 5% confidence level since p values were less than 0.05. F value and p value were determined to be 16.62 and 0.003226 for COD removal, 11.60 and 0.007403 for TSS removal, showing that the models are significant. It can be seen from Table 5, pH and dosage of linear coefficients and dosage\*time of interactive coefficients has significant effect, whereas all the rest

have insignificant effect on COD removal. pH and reaction time of linear coefficients, dosage\*dosage and reaction time\*reaction time of quadratic coefficients have significant effect on TSS removal.

As it can be seen from Table 6, F value and p value were determined to be 9.61 and 0.011313 for COD removal, 6.94 and 0.022995 for TSS removal, showing that the models are significant. It can be seen from Table 6, pH and dosage of linear coefficients have significant effect, whereas all the rest have insignificant effect on COD removal. pH, dosage and reaction time of linear coefficients, have significant effect on TSS removal.

COD removal	Sum of Squares	Df	Mean Square	f	р
Model	511.7746	9	56.86384	16.62	0.003226
X1	36.5513	1	36.5513	10.73	0.0221
$X_2$	378.125	1	378.125	111.00	0.0001
X <sub>3</sub>	6.30125	1	6.30125	1.85	0.2319
$X_1 X_1$	11.6331	1	11.6331	3.41	0.1239
$X_1 X_2$	11.2225	1	11.2225	3.29	0.1292
$X_1 X_3$	5.76	1	5.76	1.69	0.2502
$X_2 X_2$	7.76308	1	7.76308	2.28	0.1915
$X_2 X_3$	31.9225	1	31.9225	9.37	0.0281
$X_3 X_3$	19.11	1	19.11	5.61	0.0641
Total error	17.0325	5	3.4065		
Total (corr.)	527.616	14			
$R^2 = 96.77\%$					
TSS removal	Sum of Squares	Df	Mean Square	f	р
Model	1732.147	9	192.4608	11.60	0.007403
X1	111.005	1	111.005	6.69	0.0490
$X_2$	91.125	1	91.125	5.49	0.0661
X <sub>3</sub>	327.68	1	327.68	19.76	0.0067
$X_1 X_1$	27.9231	1	27.9231	1.68	0.2511
$X_1 X_2$	4.0	1	4.0	0.24	0.6442
$X_1 X_3$	40.96	1	40.96	2.47	0.1769
$X_2 X_2$	765.637	1	765.637	46.16	0.0011
$X_2 X_3$	7.84	1	7.84	0.47	0.5223
X <sub>3</sub> X <sub>3</sub>	269.917	1	269.917	16.27	0.0100
Total error	82.02	5	16 586		
	82.93	5	10.500		
Total (corr.)	82.95 1815.08	5 14	10.500		

Table 5. ANOVA results for responses by FeCl<sub>3</sub>6H<sub>2</sub>O coagulant.

COD removal	Sum of Squares	Df	Mean Square	f	р
Model	126.2241	9	14.0249	9.61	0.011313
$\mathbf{X}_1$	32.0	1	32.0	21.98	0.0054
$X_2$	87.12	1	87.12	59.84	0.0006
$X_3$	3.38	1	3.38	2.32	0.1881
$X_1 X_1$	2.07692	1	2.07692	1.43	0.2859
$X_1 X_2$	0.25	1	0.25	0.17	0.6958
$X_1 X_3$	0.0	1	0.0	0.00	1.0000
$X_2 X_2$	1.11692	1	1.11692	0.77	0.4212
$X_2 X_3$	0.25	1	0.25	0.17	0.6958
$X_3 X_3$	0.147692	1	0.147692	0.10	0.7630
Total error	7.28	5	1.456		
Total (corr.)	133.857	14			
$R^2 = 94.56\%$					
TSS removal	Sum of Squares	Df	Mean Square	f	р
TSS removal Model	<b>Sum of Squares</b> 486.3332	<b>Df</b> 9	<b>Mean Square</b> 54.03702	<b>f</b> 6.94	<b>p</b> 0.022995
TSS removal Model X <sub>1</sub>	Sum of Squares           486.3332           116.281	<b>Df</b> 9	Mean Square           54.03702           116.281	<b>f</b> 6.94 14.95	<b>p</b> 0.022995 0.0118
TSS removal Model X <sub>1</sub> X <sub>2</sub>	Sum of Squares           486.3332           116.281           214.245	<b>Df</b> 9 1 1	Mean Square           54.03702           116.281           214.245	<b>f</b> 6.94 14.95 27.55	p           0.022995           0.0118           0.0033
TSS removal       Model       X1       X2       X3	Sum of Squares           486.3332           116.281           214.245           95.9113	<b>Df</b> 9 1 1 1	Mean Square           54.03702           116.281           214.245           95.9113	<b>f</b> 6.94 14.95 27.55 12.33	p           0.022995           0.0118           0.0033           0.0171
TSS removal       Model       X1       X2       X3       X1 X1	Sum of Squares           486.3332           116.281           214.245           95.9113           1.34776	<b>Df</b> 9 1 1 1 1	Mean Square           54.03702           116.281           214.245           95.9113           1.34776	<b>f</b> 6.94 14.95 27.55 12.33 0.17	p           0.022995           0.0118           0.0033           0.0171           0.6945
TSS removal           Model           X1           X2           X3           X1 X1           X1 X2	Sum of Squares 486.3332 116.281 214.245 95.9113 1.34776 0.09	<b>Df</b> 9 1 1 1 1 1	Mean Square           54.03702           116.281           214.245           95.9113           1.34776           0.09	<b>f</b> 6.94 14.95 27.55 12.33 0.17 0.01	p           0.022995           0.0118           0.0033           0.0171           0.6945           0.9185
TSS removal           Model           X1           X2           X3           X1 X1           X1 X2           X1 X3	Sum of Squares 486.3332 116.281 214.245 95.9113 1.34776 0.09 0.0225	<b>Df</b> 9 1 1 1 1 1 1 1	Mean Square         54.03702         116.281         214.245         95.9113         1.34776         0.09         0.0225	<b>f</b> 6.94 14.95 27.55 12.33 0.17 0.01 0.00	p           0.022995           0.0118           0.0033           0.0171           0.6945           0.9185           0.9592
TSS removal           Model           X1           X2           X3           X1 X1           X1 X2           X1 X2           X1 X2           X1 X2           X2 X2	Sum of Squares 486.3332 116.281 214.245 95.9113 1.34776 0.09 0.0225 29.3801	<b>Df</b> 9 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	Mean Square         54.03702         116.281         214.245         95.9113         1.34776         0.09         0.0225         29.3801	f         6.94         14.95         27.55         12.33         0.17         0.01         0.00         3.78	P           0.0229955           0.0118           0.0033           0.0171           0.6945           0.9185           0.9592           0.1096
TSS removal           Model           X1           X2           X3           X1 X1           X1 X2           X1 X3           X2 X2           X3	Sum of Squares 486.3332 116.281 214.245 95.9113 1.34776 0.09 0.0225 29.3801 18.49	<b>Df</b> 9 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	Mean Square54.03702116.281214.24595.91131.347760.090.022529.380118.49	f         6.94         14.95         27.55         12.33         0.17         0.01         0.00         3.78         2.38	p           0.022995           0.0118           0.0033           0.0171           0.6945           0.9185           0.9592           0.1096           0.1837
TSS removal           Model           X1           X2           X3           X1 X1           X1 X2           X1 X3           X2 X2           X3           X1 X3           X2 X2           X3 X3	Sum of Squares 486.3332 116.281 214.245 95.9113 1.34776 0.09 0.0225 29.3801 18.49 11.2539	Df 9 1 1 1 1 1 1 1 1 1 1 1 1 1	Mean Square54.03702116.281214.24595.91131.347760.090.022529.380118.4911.2539	f         6.94         14.95         27.55         12.33         0.17         0.01         0.00         3.78         2.38         1.45	p         0.022995         0.0118         0.0033         0.0171         0.6945         0.9185         0.9592         0.1096         0.1837         0.2828
TSS removal           Model           X1           X2           X3           X1 X1           X1 X2           X3           X1 X1           X1 X2           X1 X3           X2 X2           X2 X3           X3 X3           Total error	Sum of Squares 486.3332 116.281 214.245 95.9113 1.34776 0.09 0.0225 29.3801 18.49 11.2539 38.8842	<b>Df</b> 9 1 1 1 1 1 1 1 1 1 5	Mean Square         54.03702         116.281         214.245         95.9113         1.34776         0.09         0.0225         29.3801         18.49         11.2539         7.77683	f         6.94         14.95         27.55         12.33         0.17         0.01         0.00         3.78         2.38         1.45	P         0.022995         0.0118         0.0033         0.0171         0.6945         0.9185         0.9592         0.1096         0.1837         0.2828
TSS removal           Model           X1           X2           X3           X1 X1           X1 X2           X1 X3           X2 X2           X3           X1 X3           X2 X2           X3 X3           Total error           Total (corr.)	Sum of Squares486.3332116.281214.24595.91131.347760.090.022529.380118.4911.253938.8842525.217	Df 9 1 1 1 1 1 1 1 1 5 14	Mean Square         54.03702         116.281         214.245         95.9113         1.34776         0.09         0.0225         29.3801         18.49         11.2539         7.77683	<b>f</b> 6.94 14.95 27.55 12.33 0.17 0.01 0.00 3.78 2.38 1.45	p         0.022995         0.0118         0.0033         0.0171         0.6945         0.9185         0.9592         0.1096         0.1837         0.2828

Table 6. ANOVA results for responses by Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O coagulant.

The three-dimensional plots of the regression models are given in Figures 1 and 2 for the graphical explanation of the interactions. The software-based response surface plots provide a three-dimensional interpretation of COD and TSS removal efficiencies surface with varying combinations of independent variables. All response surface plots have clear peaks, meaning that the optimum conditions for maximum values of the responses are attributed to all variables in the design space. 3D surface plots indicate that at optimum operating conditions COD and TSS removal efficiencies were found to be maximum but moving away from these points indicates reduction in removal efficiencies, which means an increase or decrease in any of the tested variables is desired. As can be seen in Figure 1 and 2, COD and TSS removal efficiencies were determined to be much higher by process using FeCl<sub>3</sub>6H<sub>2</sub>O than Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O coagulant.

Table 7 shows the experimental results and the optimum conditions for both processes. Based on response surface models, optimum conditions for maximum COD and TSS removal from food industry wastewater were determined. Optimized conditions for COD removal were obtained at pH 9, dosage 1500 mg/L and reaction time 25 min and pH 9, dosage 1493 mg/L and reaction time 25 min for process using FeCl<sub>3</sub>6H<sub>2</sub>O and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O coagulants, respectively. Under these

Time, min=15,0

Time. min=15.0

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Figure 1. Response surface graphs for the process using FeCl<sub>3</sub>6H<sub>2</sub>O coagulant .

conditions, 46.4% and 31.2% of COD removals for FeCl<sub>3</sub>6H<sub>2</sub>O and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O coagulants were obtained, respectively. The COD removal efficiencies for both coagulants in this study are comparatively higher than that of Ozbey-Unal et al. [12] who achieved to remove 13.6% and 10.5% of COD with FeCl<sub>3</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> coagulants, respectively. Also COD removal with FeCl<sub>3</sub>6H<sub>2</sub>O in this study is higher than Weng et al. [13] who provided 14% removal. On the other hand, Can et al. [11] managed to remove 51% of COD by using Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in coffee and coffee products wastewater.

Optimized conditions for TSS removal were obtained at pH 8.5, dosage 1500 mg/L and reaction time 16.5 min and pH 9, dosage 1498 mg/L and reaction time 25 min for process using FeCl<sub>3</sub>6H<sub>2</sub>O and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O coagulants, respectively. Under these conditions, 96.7% and 96.2% of TSS removals for FeCl<sub>3</sub>6H<sub>2</sub>O and

Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O coagulants obtained, were respectively. For both coagulants TSS removal is considerable higher than Ozbey-Unal et al. [12] who removed 6% and 3.2% of TSS by FeCl<sub>3</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> coagulants, respectively. In order to confirm the accuracy of the predicted model and the reliability of the optimum conditions, additional verification experiments were performed under optimum conditions. It was found that the experimental values were complied well with the predicted values. The verification experiment results were 43 and 30.3% for COD removal and 87.8 and 86.2% for TSS removal with FeCl<sub>3</sub>6H<sub>2</sub>O and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O coagulants, respectively.

Predicted and actual responses are presented in Figure 3. For a specific run, actual values are experimentally measured reaction information and the expected values are assessed from the model and produced using the equation of classification.



Figure 2. Response surface graphs for the process using Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O coagulant.

Table 7. Optimum operating conditions of maximum removal of responses.

	Coagulant type					
Independent variables	FeCl	36H2O	Al <sub>2</sub> (SO <sub>4</sub> )	318H2O		
	COD	TSS	COD	TSS		
pH	9	8.5	9	9		
Dosage, mg/L	1500	1500	1493	1498		
Time, min	25	16.5	25	25		
Removal (%)	46.4	96.7	31.2	96.2		





Figure 3. Comparison of predicted and experimental values for the processes using  $FeCl_36H_2O$  (a-b) and  $Al_2(SO_4)_318H_2O$  (c-d) coagulants.

#### 4. Conclusions

- RSM and CCD were applied to model and optimize the performance of coagulation processes using FeCl<sub>3</sub>6H<sub>2</sub>O and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O and to determine the optimal experimental conditions for COD and TSS removal from food industry wastewater.
- Coagulation processes using FeCl<sub>3</sub>6H<sub>2</sub>O and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O were conducted for the treatment of food industry wastewater to achieve maximum COD and TSS removal. pH of wastewater, coagulant dosage and reaction time were investigated and found to be important parameters for effective treatment of food industry wastewater.
- The results of the quadratic model and analysis of variance developed in this study showed a good agreement between experimental and predicted values and high corelaiton coefficient values. R<sup>2</sup> coefficients of the quadratic model were found to be 96.77 % (COD removal) and 95.43% (TSS removal) for FeCl<sub>3</sub>6H<sub>2</sub>O coagulant and 94.56% (COD

removal) and 92.59% (TSS removal) for  $Al_2(SO_4)_318H_2O$  coagulant.

At optimum conditions 46.4% of COD and 96.7% of  $\geq$ TSS removal were achieved by FeCl<sub>3</sub>6H<sub>2</sub>O coagulant whereas 31.2% of COD and 96.2% of TSS removals were achieved by Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O process coagulant. The coagulation using FeCl<sub>3</sub>6H<sub>2</sub>O coagulant offered higher removal efficiency for COD but no significant difference for TSS removal efficiency among processes. Hence, coagulation process using FeCl<sub>3</sub>6H<sub>2</sub>O coagulant can be recommended as a powerful pre-treatment technique for food industry wastewater.

#### **Author's Contributions**

**Senem Yazici Guvenc:** Performed the model, design of the experiments, statistical analyses, and the experiments, wrote the manuscript.

**Emine Can Guven:** Performed the experiments, wrote the manuscript.



#### Ethics

There are no ethical issues after the publication of this manuscript.

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