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Optimizing the Coagulation Process in a Textile ETP Plant and Validation by Multiple Responses Optimization using RSM Jar Test

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Abstract

Textile mill wastewater, collected from Gazipur, Bangladesh having higher than allowable Turbidity and TSS, was treated using the coagulation-flocculation process with a view to optimizing the dosage of coagulant and coagulant aid. Three different coagulants, Alum, $FeCl_3$ and Polyaluminium chloride, along with coagulant aid, Anionic Polymer, were used for traditional jar test to find out the best one, which was $FeCl_3$ and Anionic Polymer, for further simulation. A combination of two statistic tools, namely Response Surface Methodology (RSM) and Central Composite Design were used where two main influential factors, coagulant dosage and coagulant aid dosage were chosen to investigate the complete scenario by understanding the interaction among factors. The optimum conditions were achieved by compromising the two desirable responses, Turbidity and TSS. Finally, a coagulant dosage of 569.63 ppm and a coagulant aid dosage of 59.69 ppm were chosen from the list of solutions, Turbidity and TSS predicted by the models were 9.92 NTU and 6.15 ppm respectively, the confirmation experiments were in close agreement showing the values of Turbidity and TSS 8.67 NTU and 6.67 ppm respectively, which validates the models predicted and approves the use of RSM in wastewater treatment.

Keywords: Coagulation-flocculation, jar test, response surface methodology, optimization, textile wastewater

1. Introduction

Bangladesh became a developing country from an underdeveloped one during the last two decades with a vision to become a developed country by 2041 and textile industry holds a key contribution for this success. It also played an influential role in empowerment of women in our country. Right now, Bangladesh is number two garment exporter worldwide and is aiming to reach into the top. Though textile industries have a major impact on Bangladesh's economy, it poses a serious threat to environment as it is one of the largest water consuming industries and produces an enormous amount of wastewater. Freshwater, being limited, needs to be used carefully, which can only be ensured through water recycling as demand of freshwater is increasing day by day, but the supply is decreasing due to mismanagement. Textile industries use many chemicals and dyes of which most end up in wastewater. It uses 250-350 kg water to produce 1 kg of cotton fabric [1]. This huge amount of wastewater ends up in nearby rivers, channels, ponds etc. without any treatment that causes environmental pollution. It also percolates into groundwater. Buriganga and Shitholokkha rivers are already moribund. No fish can survive the pollution. If this continues, whole country will face serious environmental issues, let alone health issues and others. So, considering the present needs in this sector, this research was undertaken.

The chemicals and dyes used in textile industries increase pH, color, TSS, Turbidity and COD of water. Coagulation, Flocculation and Physiochemical treatment are more conventional process due to their color and pollutant removal efficiency. The most common coagulants are Aluminium Sulphate ($Al_2(SO_4)_3$), Ferric Sulphate ($Fe_2(SO_4)_3$) and Ferric Chloride ($FeCl_3$) [2]. Studies on the performance of polymerized inorganics such as Polyaluminium Chloride (PAC) [3] and Polyferric Chloride (PFC) [4] has also been done. In the coagulation-flocculation process, the efficiency is governed by various factors, such as the type and dosage of coagulant/flocculant, pH, mixing speed and time, temperature and retention time [5]. A proper dosage of these factors can increase the treatment efficiency as well as reduce cost and waste.

Conventional One Factor at a Time (OFAT) optimization experiment by varying one factor and fixing others is time consuming and can scarcely reach the real optimum condition, because of ignoring the interaction among the factors. A statistical method, response surface methodology (RSM), has been proposed as a solution to consider both the influences of individual factors and their interactive influences. RSM is an empirical statistical modeling technique for designing experiments, building models, evaluating the effects of several factors and searching optimum conditions for desirable response, with limited number of planned experiments [9]. Response surface methodology (RSM) has been widely used for the optimization of various processes in food chemistry, material science, chemical engineering and biotechnology [6]. Despite the application of the RSM in many experimental studies, its use in optimizing coagulation conditions with jar testing in water treatment is apparently lacking [5].

Hence, the objectives of this study were to treat textile effluent by coagulation-flocculation method in a cost-effective way, to determine different parameters before and after treatment and compare it with allowable limit and to optimize the result with Stat-Ease Design-Expert version 12 to find a better solution.

2. Materials and Methods

A Sampling and conservation

Textile wastewater samples used in this study were collected from a textile mill located in Gazipur, Bangladesh. The water was a homogeneous mixture of knitting, dyeing, printing, embroidery and washing water, the major processes used in the mill. The collected wastewater was then stored below 7°C without addition of any chemicals at Environmental Engineering Laboratory, BUET.

B Characterization of sample

The sample wastewater was characterized according to APHA Standard Methods [8], which demonstrated higher than allowable Chemical Oxygen Demand, Total Dissolved Solids, Total Suspended Solids, Turbidity, Color and pH. pH was measured using HANNA pH meter, TDS was measured using HANNA TDS meter, TSS and Color were measured using HACH spectrophotometer DR 6000, Turbidity was measured using HACH spectrophotometer DR 2000. COD of the samples were measured after digestion of samples by using potassium dichromate oxidant in acidic environment at 150°C in HACH COD Reactor and by using HACH spectrophotometer DR 6000. **Table 1** summarizes the sample quality compared to the Environment Conservation Rules (1997).

Table 1: Characteristics of raw textile wastewater and comparison with ECR '97

Parameters	Color (Pt - Co)	TSS (mg/L)	Turbidity (NTU)	pH	TDS (mg/L)	COD (mg/L)
Results	2044	188	231	8.05	2140	609
DoE guidelines	-	150	10	6-9	2100	400

C Chemicals and operation

Alum, Polyaluminium Chloride (PAC) and $FeCl_3$, three different coagulants of Laboratory grade were purchased from Hatkhola Road to find out the suitable ones for textile wastewater treatment with optimum removal efficiency. Besides coagulants, anionic polymer was used as coagulant aid for better removal result by flocculation. During coagulation process 200, 400, 600, 800 ppm solutions of alum, $FeCl_3$, PAC were prepared by adding 40, 80, 120, 160 mg of solute respectively in raw wastewater so that the solution was of 200 mL. All the experiments were carried out at room temperature using jar test method to determine the optimum coagulant. Four beakers were placed on magnetic stirrers and were stirred rapidly at 200 rpm for 90 seconds for coagulation. Then in 200 mL solution, 12 mg (60 ppm) of Anionic Polymer was added which acted as coagulant aid and stirred slowly at 10 rpm for 15 minutes for flocculation. The solution was allowed to settle for half an hour and then samples were taken for analysis.

Two different parameters, Turbidity and Total Suspended Solids (TSS) were characterized for all of the coagulants. From the experiments performed, the optimum coagulant, the one which showed better removal with minimum requirement and was in accordance with the limits of ECR '97, was chosen for further simulation.

D Simulation study

RSM jar test is substituted for the traditional jar test to get a complete view of the analysis and to find out the optimum region for which Turbidity and TSS removal were in accordance with the ECR '97. A two-factor CCD (Central Composite Design) with five center points and eight non-center points was employed in designing the RSM jar test. The two independent factors were $FeCl_3$ and Anionic Polymer, two levels for each factor were chosen to investigate the influence and interaction of the factors. **Table 2** exhibits the experimental range and levels of the design.

Table 2: Experimental range and levels of central composite design

Variables	Range and levels	
	Low	High
A. $FeCl_3$ (ppm)	0	800
B. Anionic Polymer (ppm)	0	60

Turbidity and Total Suspended Solids (TSS) were chosen as dependent output variables in order to represent the overall treatment efficiency. The response variable was fitted by a sufficient model, which is able to describe the relationship between the dependent output variable and the independent variables using the regression method.

$$Y = b_0 + \sum_{i=1}^{j} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i}^{i<j} \sum_{j} b_{ij} X_i X_j \quad (1)$$

where Y is the response variable to be modeled; X_i and X_j are the independent variables which influence Y; b_0, b_i, b_{ii} and b_{ij} are the offset terms, the i-th linear coefficient, the quadratic coefficient and the ij-th interaction coefficient, respectively [6]. The parameters of the response equations and corresponding analysis on variations were evaluated using Stat-Ease Design-Expert version 12. The interactive effects of the independent variables on the dependent ones were illustrated by three dimensional contour plots and two dimensional overlay plots. Finally, three additional experiments were conducted to verify the validity of the statistical experimental strategies.

3. Results and Discussions

A Traditional jar test

Figure 1 shows the results of the traditional jar test for the experiments performed. It can be clearly observed that among the three coagulants $FeCl_3$ showed better results in both cases of Turbidity and TSS removal. Also, almost all runs gave acceptable results in case of TSS removal as it was within acceptable conditions of 150 ppm, whereas only a few cases showed acceptable results in case of turbidity. With the increase in coagulant dose $FeCl_3$ shows better result than others and reach a saturated value at 600 ppm with 97.84% removal. Thus, $FeCl_3$ was chosen for RSM jar test i.e. simulation study to find out the optimal region of operation.

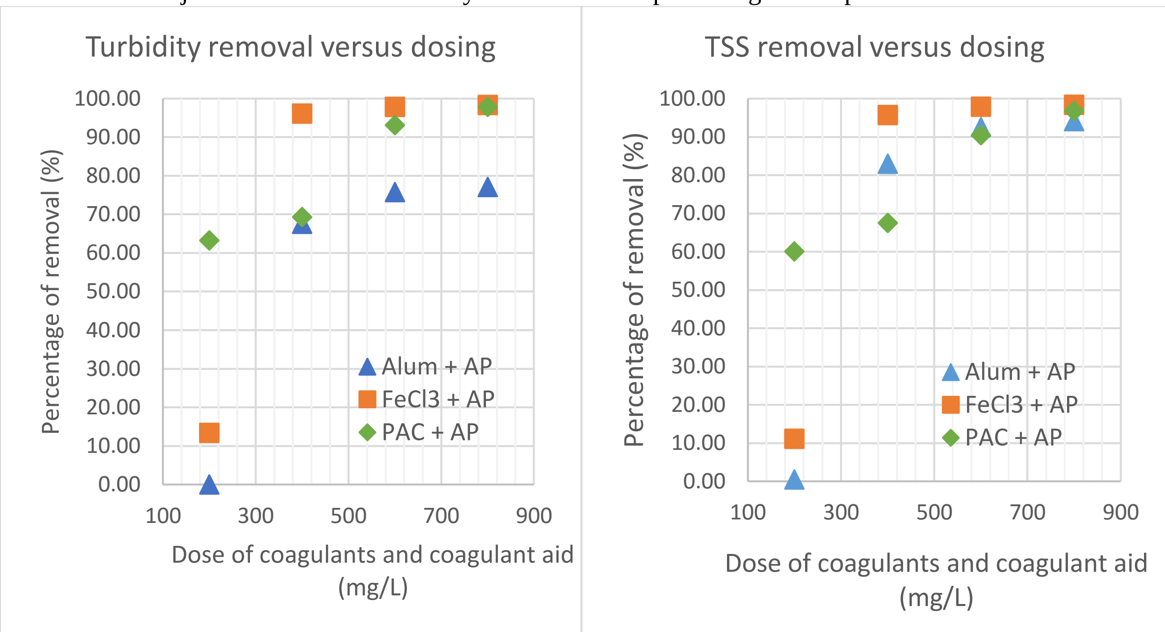


Figure 1. Percentage removal of Turbidity and TSS for different doses of coagulants with coagulant aid

B RSM jar test

In total, 13 runs were required in order to complete the experiment. This approach was to fit a surface which leads to optimization of the coagulant and coagulant aid doses. **Table 3** delineates the experimental results.

Table 3: CCD and response results for the study of two experimental variables

Run	Factor 1	Factor 2	Response 1	Response 2
	$FeCl_3$ (ppm)	Anionic Polymer (ppm)	Turbidity (NTU)	TSS (ppm)
1	0	0	231	188
2	0	30	135	110
3	0	60	130	107
4	400	0	137	50
5	400	30	31	23
6	400	30	32	24
7	400	30	31	23
8	400	30	30	23
9	400	30	30	23
10	400	60	13	12
11	800	0	7	8
12	800	30	14	7
13	800	60	4	3

In order to obtain the optimum coagulation conditions through the optimization procedure in the Design-Expert guide, the regression models formulated by the software relating responses and factors in terms of coded factors need to be examined. Whenever necessary, statistically insignificant terms were eliminated through backward method and/or response transformation were carried out to form significant models [4].

For Turbidity and TSS, a linear and a quadratic model respectively were suggested by Design-Expert software. The generated multiple regression equations in terms of actual factors are as follows,

$$Log_{10}Turbidity \ = \ +2.45199 - 0.001673 * FeCl_3 - 0.008419 * Anionic\ Polymer \qquad (2)$$

$$\sqrt{TSS} = 13.59955 - \ 0.021890 * FeCl_3 - 0.098210 * Anionic\ Polymer + 0.000047 * FeCl_3 * Anionic\ Polymer + 0.000011 * FeCl_3^2 + 0.000574 * (Anionic\ Polymer)^2 \qquad (3)$$

Equation (2) and **(3)** suggest that, in this particular water sample, turbidity depends on the first degree effect of the values of $FeCl_3$ and Anionic Polymer, whereas TSS depends both on the first and second degree effects of the values of $FeCl_3$ and Anionic Polymer. Hydrolysis of $FeCl_3$ produces ferric hydroxide with hydrogen chloride and reduces the pH of the solution that favors the coagulation process. Produced Iron (III) Hydroxide particles, have an affinity towards many unwanted particles found in water such as Arsenic, sulfide and excess phosphates. So, they adsorb very strongly onto the surface of colloids. Such adsorption causes a reduction of surface potential and a resulting destabilization of the colloidal particle [12]. Anionic Polymer facilitates the process by creating flocs. The analysis of variance (ANOVA) for the above regression models is tabulated in **Table 4**.

Table 4: ANOVA results for response parameters in RSM jar test

Response	**Model p-value**	**LOF p-value**	**R^2**	**Adjusted R^2**	**C.V. (%)**	**AP**	**SD**	**PRESS**
Turbidity	<0.0001	<0.0001	0.8962	0.8755	12.32	20.3583	0.1885	0.7373
TSS	<0.0001	<0.0001	0.9878	0.9791	8.78	33.6898	0.5157	18.84

LOF: Lack of Fit; C.V.: Coefficient of Variance; AP: Adequate Precision; SD: Standard Deviation; PRESS: Prediction Error Sum of Squares.

C Significance of predicted models

A model is significant at the 95% confidence level if the Fisher F-test has a probability value (p-value) below 0.05. The lack of fit (LOF) F-test describes the deviation of actual points from the fitted surface, relative to pure error [10]. A high R^2 value is desirable and a reasonable agreement with adjusted R^2 is crucial [11]. Adequate precision (AP) is defined as a measure of the experimental signal to noise ratio [10]; an AP that exceeds 4 usually indicates that the model will give reasonable performance in prediction. The standard deviation (SD) and the coefficient of variation (CV) are shown in Table 4. PRESS, the prediction error sum of squares, is a measure on how well the model for the experiment is likely to predict the responses in a new experiment. The SD, CV and PRESS values are preferred to be small [7].

The generated regression models (2) and (3) both are significant models as their p-value is less than 0.0001, which are smaller than 0.05. Also, the adequate precision of the model (2) and (3) are 20.3583 and 33.6898 respectively, which is greater than 4, hence indicates an adequate signal. The R^2 value is high and agrees reasonably with adjusted R^2. The AP value exceeds 4 and SD, CV and PRESS values are preferably small. In order to judge whether the models are satisfactory, diagnostic plots such as the predicted vs actual values as well as 3D surface graphs can help us, which are generated by the Design-Expert software. Two such plots are shown in **Figure 2** and **3**. In case of **Figure 2**, in the horizontal axis, the experimental values were plotted, whereas in the vertical axis, the values predicted by the model were plotted. The graph shows that the values are in close agreement to each other. **Figure 3** delineates the predicted 3D surface plots by Design-Expert.

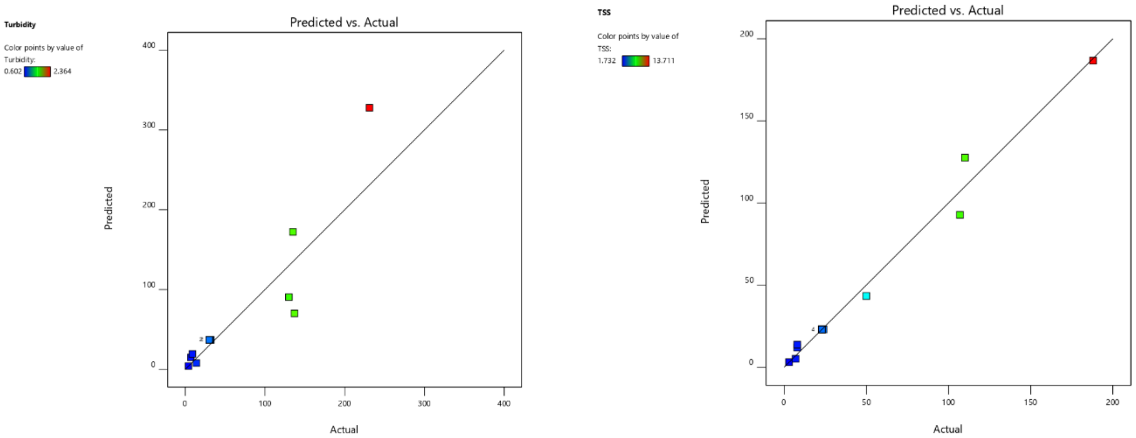


Figure 2: Design-Expert plot; predicted versus actual values plot for turbidity and TSS

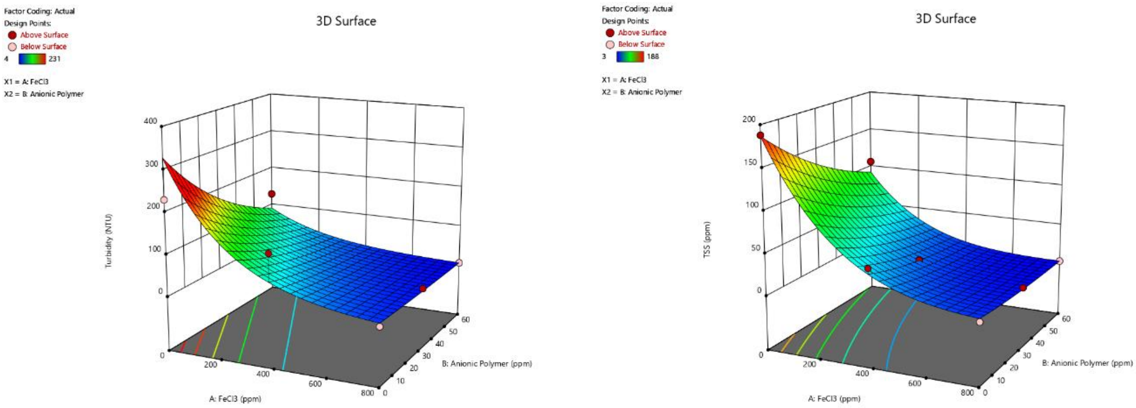
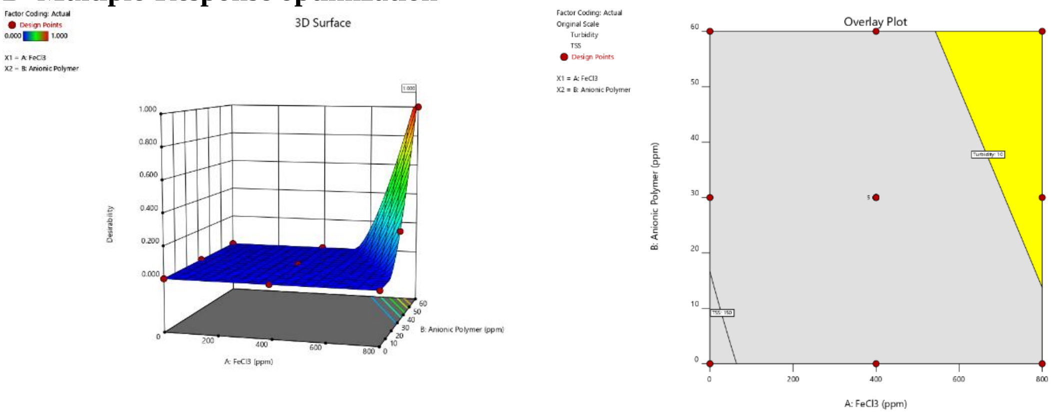


Figure 3: Design-Expert plot; 3D surface plots for turbidity and TSS

D Multiple-Response optimization



(A) **(B)**

Figure 4. (A) 3D surface plot according to desirability; (B) Overlay Plot for optimal region

For optimization, desirable criteria were set up, which was to minimize Turbidity and TSS. A turbidity value less than 10 and a TSS value less than 150 is desirable according to the Environment Conservation Rules (ECR '97). For multiple responses, the optimum condition is one at which all parameters simultaneously meet the said desirable criteria [5]. This result could be visualized graphically by superimposing the contours of the response surfaces of the regression models (2) and (3) in an overlay plot. Graphical optimization displays the area of feasible response values in the factor space and the regions that do fit the optimization criteria would be yellow in color. The yellow area in **Figure 4(B)** shows the RSM optimum jar test condition for the desirable criteria mentioned earlier. Any point belonging to this area would produce a value of Turbidity less than 10 as well as a value of TSS less than 150.

A lot of solutions are thus possible to meet the design criteria. Numerical Optimization is the technique in such a case to generate the desirable solutions. The solutions are usually listed in Design-Expert as from best to worst according to desirability of the solution. One of the solutions was thus chosen to check out the accuracy of the predicted models.

E Confirmation of experimental results

Experiments were conducted to determine the Turbidity and TSS values. The experiments were carried out in triplicate and the responses expressed in **Table 5** were the mean of the three experimental results.

Table 5: Experimental and predicted values of the responses at the optimal levels predicted by RSM

Optimal Conditions	Response	Predicted	Measured
$FeCl_3$ (569.63 ppm)	Turbidity (NTU)	9.92	$\frac{9+8+9}{3} = 8.67$
Anionic Polymer (59.69 ppm)	TSS (ppm)	6.15	$\frac{7+6+7}{3} = 6.67$

The predicted values by the produced linear and quadratic models were **9.92** NTU and **6.15** ppm respectively, whereas the experimental values obtained by us were **8.67** NTU and **6.67** ppm respectively, which show TSS was in closer agreement than Turbidity. Initially, for the values of coagulant dose, the Turbidity removal were not totally accurate. But, addition of further coagulants increases the TSS removal drastically. So, the response surface predicted by the Design-Expert guide might be a whit deviated from the actual surface. Hence, it can be said that, these models can be used to optimize the doses of $FeCl_3$ and Anionic Polymer if the conditions are as such the textile wastewater used in the laboratory.

F Recommendations

Obtaining the characteristics of feed water to the facility, the history of pollution could have been understood which would have helped to improve the treatment process. It would be better if the chemicals used in the process were known, which could help us determining the best treatment agents. Also, pH in this experiment was not controlled, pH of the sample was well in the working range of the coagulants used, which demands a different research. Turbidity and TSS values calculated in HACH spectrophotometer DR 2000 was not totally accurate as it gave only integer values which could be improved by using advanced machine. In case of simulation, a better result can be obtained by confirming the same experiment again and again, also better number of runs could have predicted a better model.

4. Conclusion

Turbidity is not considered in textile effluent discharge regulations. As a result, there is no guideline to monitor it for textile industries though they discharge the effluent into nearby channels, rivers that affect the aquatic life critically. According to ECR'97, Turbidity and TSS of public water need to be below 10 NTU and 150 ppm respectively. RSM jar test and Analysis of Variance (ANOVA) were done to optimize the process for coagulant dosage and coagulant aid dosage. A successful study was performed where optimum dosage for coagulant ($FeCl_3$) was 569.63 ppm and for coagulant aid (Anionic Polymer) was 59.69 ppm, which were comparatively lower than analytical values that indicates cost effectiveness and were also following standards for both Turbidity and TSS. Further confirmation experiment demonstrated the result found in the study was effective for textile wastewater treatment that can be discharged into the river without destroying aquatic life.

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