

Optimization of Tobacco Leaf Thinnings Wastewater Flocculation Pretreatment Process Based on Response Surface Methodology

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Abstract. Using cationic polyacrylamide (CPAM) as a coagulant aid and polymeric ferric sulfate (PFS) as a flocculant, a PFS-CPAM composite coagulant was prepared to investigate the influence of single factors such as wastewater temperature, pH value, types and dosages of flocculants and coagulant aids on the flocculation process of wastewater. Based on the Box-Behnken experimental design principle, the Design-Expert 10.0 software was employed to establish a quadratic response surface numerical model for COD removal rate. Analysis of the model revealed that the highest COD_{Cr} removal rate, at 64.13%, was achieved when the pH was 6.8, with a PFS dosage of 485.5 mg/L and a CPAM dosage of 4.8 mg/L. Verification test results showed that the deviation was 0.23%, indicating a good agreement between the predicted values obtained by the response surface methodology and the actual values. This method is an effective approach for optimizing the flocculation pretreatment of wafer wastewater.

Keywords: Wastewater from paper-making reconstituted tobacco sheet; the flocculation-flotation method; COD; response surface methodology.

1. Introduction

Reconstituted tobacco leaf, as a by-product of the tobacco industry, is produced from tobacco dust, stems, and other raw materials through a papermaking process, serving as an important filler in cigarettes^[1]. However, its production generates 60-80 tons of wastewater per ton of product^[1-2], which is complex in composition and challenging to treat. The wastewater contains high concentrations of suspended solids, BOD, COD, as well as organic compounds that are difficult to biodegrade, with a dark color and susceptibility to decomposition. Therefore, the efficient treatment of this type of wastewater has become a pressing issue for the reconstituted tobacco leaf industry. Flocculation-air flotation, a commonly used wastewater pretreatment technology, aggregates and removes suspended solids by introducing dissolved air and flocculants. However, the treatment effectiveness is influenced by various factors, including the type and dosage of flocculant, inlet water temperature, and pH value.

To optimize these factors, this study employed the Response Surface Methodology (RSM) in conjunction with the Box-Behnken design principle to establish a quadratic polynomial mathematical model. Through experimentation, we identified the optimal flocculation system and process parameters, including the type and dosage of flocculant and coagulant, as well as the initial water pH value, temperature, and influent flow rate. This research not only provides technical support for the pretreatment of wastewater from reconstituted tobacco leaf production but also demonstrates the potential application of RSM in the field of wastewater treatment. By optimizing the treatment process, we can more effectively reduce the concentration of pollutants in the wastewater, contributing to the sustainable development of the reconstituted tobacco leaf industry.

2. Materials and Methods

2.1. Materials and instruments

(1) Raw Material: The wastewater samples were collected from the initial sedimentation pool of a tobacco sheet manufacturing enterprise located in Hubei Province. This facility generates approximately 1600-1800 cubic meters of wastewater daily. The primary and secondary treatment processes for this wastewater are illustrated in Figure 1, while the quality indicators of the wastewater are presented in Table 1.

Flocculant

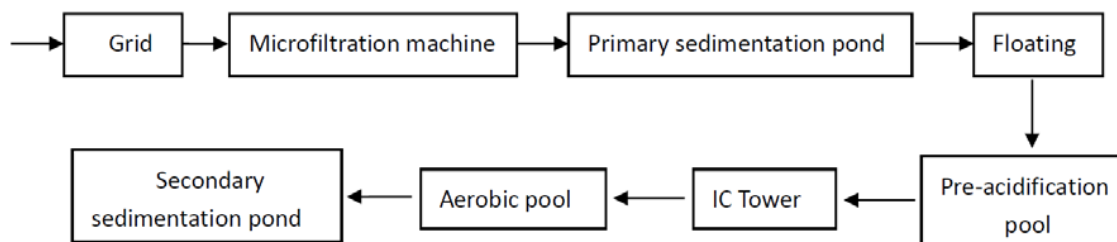


Figure 1. Flowchart of reprocessing tobacco leaf wastewater

Table 1. List of Water Quality Indicators for Wastewater

Section	PH	Temperature (°C)	COD _{Cr} (mg/L)	BOD ₅ (mg/L)	SS (mg/L)	TN (mg/L)	TP (mg/L)	Ammonia Nitrogen (mg/L)	Colority
Into water	6.8	30-35	11000-12000	5000-6000	4000-5000	142.8	92.5	94.15	2560
Primary water	6.8	30-35	8000-9000	3500-4000	2000-2500	138.5	89.6	91.5	2320

(2) Reagent. PFS is an industrial product, light yellow solid powder, total iron content $\geq 20\%$; PAM is an industrial product, white solid particles, and the three PAM properties selected are shown in Table 2. Potassium dichromate, silver sulphate, mercury sulphate, sulphuric acid, and sodium oxide are all analytically pure.

Table 2. Properties of Different Cationic Polyacrylamides (CPAM)

Species	Types	Molecular weight	Ionization degree/%
CPAM1		450	15
CPAM2	cation	800	30
CPAM3		1100	40

(3) Instrument. pH meter; Analytical balance; Electro thermal thermostatic blast drying oven; 722G visible light spectrophotometer; SHP-250 biochemical incubator; Plug colorimetric tube; ZR4-6 type six coagulator; SS-1Z suspension measurement; SS-1Z suspension analyser; 752 UV spectrophotometer.

2.2. Method

Response Surface Methodology (RSM) optimization experiment: The optimization experiment of the flocculation treatment process for tobacco sheet wastewater using Response Surface Methodology (RSM) adopts a Central Composite Design (CCD). With the COD removal rate as the target value Y, three variable conditions that have a relatively significant impact on the COD removal rate (PAF dosage X1, CPAM dosage X2, and pH X3) were selected for the Box-Behnken experiment. The COD removal rates under different combinations were measured, and the optimal combination of conditions was selected. The factors and levels of the Box-Behnken experimental design are shown in Table 3.

Table 3. Factors and Levels of Box-Behnken Experimental Design

Level	Dosage of PFS / mg/L	Dosage of CPAM / mg/L	PH
-1	300	4	6
0	400	5	6.5
1	500	6	7

3. Results and Discussion

3.1. Response Surface Experimental Design and Results

Based on the experimental design outlined in Table 3, a model was established with COD as the response value. The independent variables include PAF dosage, CPAM dosage, and pH, while the response value is the COD removal rate. The model is formulated as follows:

$$Y = \beta_0 + \sum_{i=1}^f a_i X_i + \sum_{i=1}^f a_{ii} X_i^2 + \sum_{i=1}^f \sum_{j=1}^f a_{ij} X_i X_j + e$$

In the formula, Y represents the predicted value of the COD removal rate; β_0 is the constant term; a_i represents the linear coefficient; a_{ii} represents the quadratic coefficient; and a_{ij} represents the interaction coefficient. X_i and X_j are the independent variables, e represents the random error, and f represents the number of variables. A model was established with the COD removal rate during the flocculation pretreatment of tobacco sheet production wastewater as the response value. The results of the model are shown in Table 4.

Using Design-Expert 10.0 software, a multiple regression analysis was performed on the experimental results in Table 3 to obtain the regression equation for COD removal rate. The analysis of variance (ANOVA) for this regression equation is presented in Table 5.

$$Y = 65.94 + 47.86X_1 + 12.41X_2 + 0.23X_3 - 0.82X_1X_2 + 1.8X_1X_3 + 0.075X_2X_3 - 0.006X_1^2 + 2.05X_2^2 - 0.026X_3^2$$

An analysis of variance (ANOVA) was conducted on the regression equation, and the results are presented in Table 4.

Table 4. Box-Behnken Experimental Design and Results

Experiment Serial Number	Level			COD Removal Rate (Y) /%	
	X1	X2	X3	Measured Value	Predicted Value
1	300	4	6	57.28	57.88
2	300	4.5	6.5	58.12	57.69
3	300	4	7	58.16	58.14
4	500	5	6	61.32	63.53
5	400	4.5	6	58.46	60.62
6	500	4.5	6.5	62.34	63.99
7	300	5	7	56.56	60.05
8	400	4.5	6	60.13	61.06
9	400	4.5	6.5	59.43	60.84
10	400	4.5	7	59.43	60.84
11	500	5	6	64.13	63.79
12	400	4.5	6.5	62.56	60.84
13	400	4.5	7	62.14	60.84
14	500	4	7	63.12	61.89
15	400	5	6.5	63.21	60.84
16	300	5	6	61.25	59.79
17	500	4	6	63.15	61.63

According to the ANOVA results in Table 5, the model has a high significance, with the order of significant influence being CPAM, pH, and PFS (assuming PFS was a typo for PAF, as mentioned previously). Figure 2 shows the scatter plot of the actual COD removal rates obtained from the experiments on tobacco sheet wastewater, indicating the degree of deviation between the measured values and the model's predicted values. The lack of fit term for this model is not significant, and the coefficient of determination $R^2 = 0.9815$, indicating a good correlation between the predicted and measured values.

Table 5. Variance Analysis of the Regression Equation

Source	Degrees of Freedom	Sum of Squares	Mean Square	F-value
Model	1	567.3221	63.03579	161.3425
X1	1	59.3791	59.3791	151.9831
X2	1	0.002572	0.002572	0.006582
X3	1	67.69291	67.69291	173.2626
X1X2	1	26.802	26.802	68.60075
X1X3	1	17.78217	17.78217	45.51415
X2X3	1	45.72535	45.72535	117.0358
X12	1	29.6058	29.6058	75.77719
X22	1	179.4056	179.4056	459.1957
X32	1	136.648	136.648	349.7558
Residual Error	7	2.734868	0.390695	
Lack of Fit Term	3	2.014193	0.671398	3.726493
Pure Error	4	0.720675	0.180169	
Total Deviation	16	570.057		

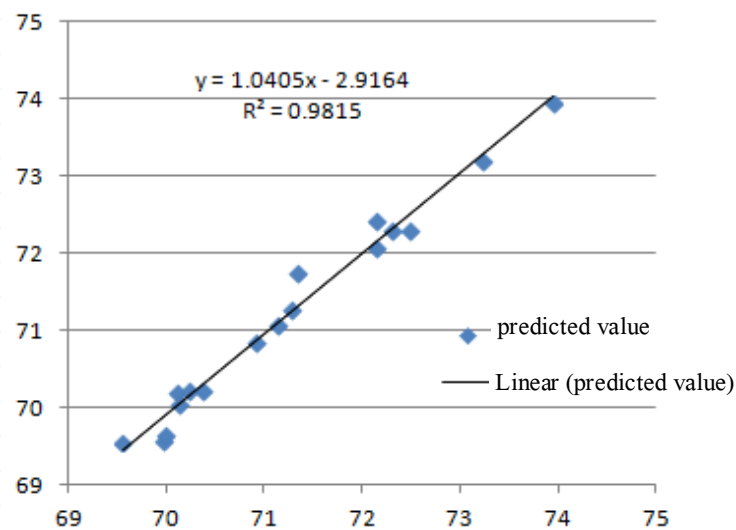


Figure 2. Fitting curve of predicted versus measured COD removal rate

3.2. Response Surface Model Analysis

To investigate the effects of various factors and their interactions on the COD removal rate, Design Expert 10.0 software was utilized to generate graphs. By fixing the conditions of other factors,

response surface plots and contour plots were obtained to illustrate the impact of any two factors and their interactions on the COD removal rate. The results are shown in Figures 3 to 5.

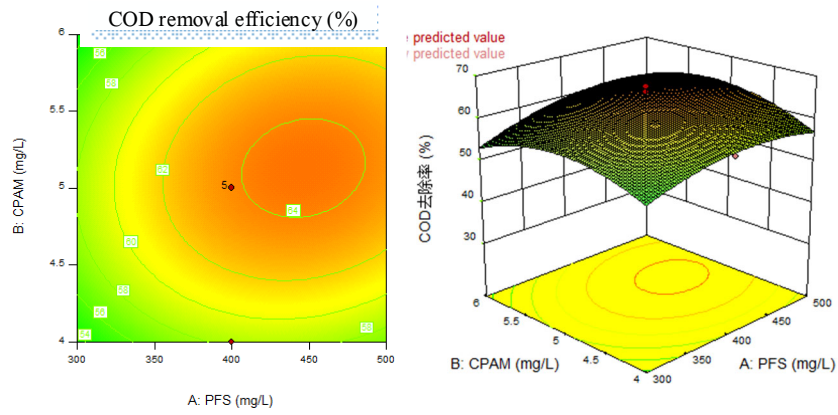


Figure 3. Response Surface Plot and Contour Plot Showing the Interactive Effect of CPAM and PFS on COD Removal Rate

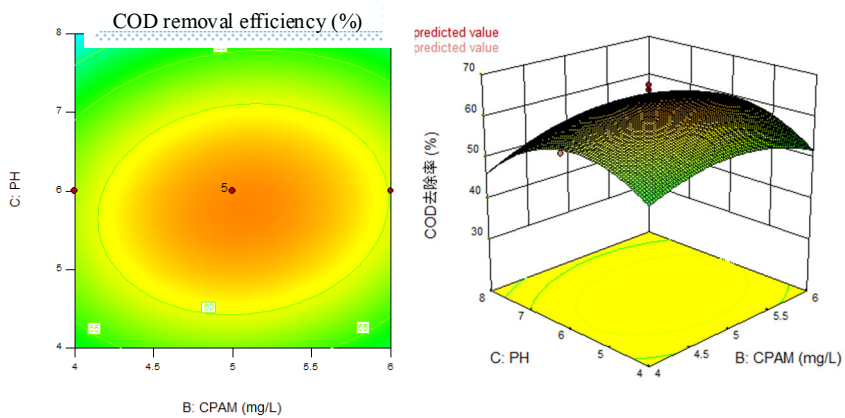


Figure 4. Response Surface Plot and Contour Plot Showing the Interactive Effect of CPAM and pH on COD Removal Rate

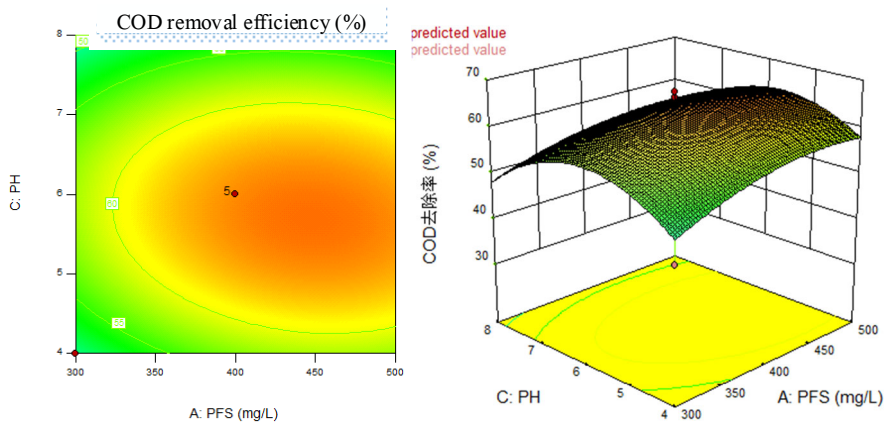


Figure 5. Response Surface Plot and Contour Plot Showing the Interactive Effect of PFS and pH on COD Removal Rate

Each response surface and contour line in Figure 6 reflects the level changes of two factors among the three factors (PFS dosage, CPAM dosage, and pH value). As shown in Figure 6-1, with the increase in PAC (assuming it's a typo for PAF or a different flocculant used in your context, but for consistency, let's stick with the original term for now) and CPAM dosages, the COD removal rate significantly rises, and the response surface plot appears steep. When a certain value is reached and further increased, the COD removal rate decreases instead. This is because when the dosage exceeds the isoelectric point for colloidal destabilization, although the number of complex ions increases, the surface active sites required for adsorption bridging decrease, making bridging difficult; even causing re-turbidity and reducing the coagulation effect [3].

Similarly, under the same PFS and CPAM dosages, as the pH increases, the COD removal rate first rises and then decreases, with a steep response surface plot. This phenomenon occurs because when the pH is ≤ 4 , the high-valent multinuclear complex ions of iron transform into free iron ions, losing their coagulation effect [4]. As the pH becomes alkaline, the charge of the hydrolysis products of aluminum ions decreases and converts to anions such as $[\text{Al}(\text{OH})_4]^-$, and the charge repulsion reduces their adsorption effect on suspended matter, and the system destabilization worsens [5].

3.3. Model Validation

Through software analysis, the optimal conditions for the flocculation pretreatment of tobacco sheet wastewater were obtained as follows: PFS = 485.5 mg/L, CPAM = 4.8 mg/L, pH = 6.8, with a predicted COD removal rate of 64.13%. Experiments were conducted using the above optimal conditions, with three parallel control experiments for validation. The actual COD removal rate obtained was 63.98%, with a test deviation of 0.23%. The actual value closely matches the predicted value, indicating that the model is accurate and reliable for analyzing the flocculation pretreatment of tobacco sheet wastewater. The use of the response surface methodology can optimize process parameters, providing experimental evidence for the flocculation pretreatment mechanism of tobacco sheet wastewater.

4. Conclusion

Based on the Box-Behnken experimental design principle, a quadratic response surface numerical model for COD removal rate was established using Design-Expert 10.0 software. Analysis of the model revealed that the highest COD_{Cr} removal rate, at 64.13%, was achieved when the pH was 6.8, the PFS dosage was 485.5 mg/L, and the CPAM dosage was 4.8 mg/L. Validation test results showed a deviation of 0.23%, indicating that the predicted values from the response surface methodology closely matched the actual values. Therefore, the response surface methodology is an effective method for optimizing the flocculation pretreatment of tobacco sheet wastewater.

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