

# Optimization of process parameters for COD removal by Coagulation Treatment using Box–Behnken design

V Sangeetha<sup>1</sup>, V Sivakumar<sup>2</sup>, A Sudha<sup>3</sup>, KS Priyenka Devi<sup>4</sup>

Department of Food Technology, Kongu Engineering College, Perundurai,  
Tamil Nadu, India

<sup>1</sup>sanpranati@gmail.com

<sup>2</sup>drvsivakumar@yahoo.com

<sup>3</sup>sudhaseshu@gmail.com

<sup>4</sup>priyenka1989@gmail.com

**Abstract** –Coagulation treatment of sago wastewater was studied and laboratory studies were carried out using alum as coagulant. Coagulation treatment conditions were optimised through response surface methodology (RSM). Operational parameters namely dosage of alum ( $\text{Al}_2(\text{SO}_4)_3$ ) (mg/l), pH and wastewater concentration (g/l) were varied between 50-150mg/l, 3–5 and 10-30g/l respectively. The results were analysed using Pareto analysis of variance (ANOVA). Optimum condition at 100mg/l of alum dosage, 4.5 pH and 23.5 g/l concentration, COD removal efficiency was found to be 67.86%. These results reveal the applicability of coagulation treatment to the sago wastewater as an alternative approach.

**Keyword**-Coagulation, Alum, Sago wastewater, COD removal

## I. INTRODUCTION

Modernisation and increasing industrial activities have accelerated water pollution in the environment as well as making water a limited resource. Sago processing requires large amount of water and wastewater treatment is problem to the industry. In Southern part of India, in Tamilnadu more than 800 small scale units of sago industries discharging about 40,000 to 50,000 L of effluent [1,2]. Sago industries require water for washing and peeling of cassava in a rotary drum with low chemical oxygen demand (COD) and the extraction process which own a high contaminating load of COD and biochemical oxygen demand (BOD). Sago wastewater does not have any toxic substances, but high organic matter which cause increase in COD level. Owing to the industrial growth, purification and recycling of industrial waste waters have become imperative.

The most common physico-chemical treatment method includes coagulation [3]. Coagulation has been defined as the addition of a positively charged ion of metal salt or catalytic polyelectrolyte which results in particle destabilization and charge neutralization. The colloid particles exhibit Brownian movement through the water [4]; it is cost effective to remove colloidal and slowly settleable small particles [5]. Most widely used coagulant in wastewater treatment is aluminium sulphate ( $\text{Al}_2(\text{SO}_4)_3$ ) or alum and Ferrous sulphate ( $(\text{FeSO}_4)_3$ ). Treatment of wastewater concerned with production of potato chips and other food processing industry and dairy industry uses the alum and ferrous sulphate as coagulant [6-8]. The conventional coagulation process with alum as the single coagulant is capable of achieving significant organic removal. The pH of the water during coagulation has intense influences on effectiveness of coagulation for organic removal and it is much better in slightly acidic condition. The optimum pH for alum dosage is subjected by the concentration of organic matter in the wastewater [4]. Both advantages and disadvantages are concerned with coagulation process used in wastewater treatment: alum reacts to form precipitation of sulphur compounds, easier sludge dewatering, increased efficiency in elimination of pollutants and the addition of treatment chemicals may increase the total volume of sludge [8].

The objective of the present study is to optimise the removal efficiency of COD for coagulation process with minimum cost and time. RSM is statistical tool used to evaluate, analyse and optimise the process parameters. RSM has important application in the improvement of existing design. It defines the effect of the independent variables alone or in combination and also it generates a mathematical model which describes the processes interaction [9, 10]. Hence this study focussed on optimisation of three factors at three levels using Box Behnken design approach.

## II. MATERIALS AND METHODS

### A. Wastewater preparation.

The synthetic sago wastewater was prepared by mixing a finely ground sago powder ( $-500 + 400 \mu\text{m}$  DIN Standard sieve size) with tap water along trace elements including sulphide were added to represent the typical composition of industrial sago wastewater having initial COD ranges from 950mg/l to 1700mg/l [11,12].

### B. Experimental Procedure.

The wastewater samples were prepared for 10, 20, 30 g/l concentration as per above mentioned procedure. 50, 100, 150 mg/l of alum ( $\text{Al}_2\text{SO}_4$ ) $_3$ .18H $_2$ O was added to the wastewater samples as per the design matrix calculation. The coagulant was added to 1L beakers containing wastewater sample, pH was adjusted using 0.1N H $_2$ SO $_4$  or 0.1N NaOH. The solution was mixed rapidly using magnetic stirrers at 200rpm for 2 min and stirring period was adjusted to 60rpm for 30min, the liquid was clarified for 1 h, then the supernatant was collected and analysed for COD using standard methods [13]. After collecting the supernatant, wet sludge volume of cake settled was also calculated.

### C. Box-Behnken Design (BBD).

First, single factor experiment has been employed as a traditional method by changing one variable at a time. By this method it is difficult to study the optimised and interaction effect among the variables [14]. Therefore, the Box-Behnken statistical design combined with RSM was used to optimise the study. RSM is a group of empirical techniques relating a controlled experimental factors and measured responses agreeing to one or more selected criteria [15, 16]. The advantages of Box-Behnken designs comprise the fact that they are all spherical designs and require factors to be run at only three levels. The designs are also rotatable and provide orthogonal blocking. In these designs the block effects are orthogonal to the other factor effects [17]. Instead of complete factorial design, this design provides minimum effort and accurate result. Mostly, this optimization process involves three major steps 1) performing the statistically designed experiments: ANOVA is a statistical technique that subdivides the total variation in a set of data into component parts related with specific sources of variation for the purpose of testing hypotheses on the parameters of the model 2) estimating the coefficients in a mathematical model 3) predicting the response and checking the adequacy of the model [18, 19].

Three factors at 3 levels were varied in the present study to study the optimisation of coagulation parameters such as alum dosage ( $X_1$ ), pH ( $X_2$ ) and wastewater concentration ( $X_3$ ) respectively. Independent variables were coded as -1(low), 0(centre point) and +1(high) in the ranges determined by preliminary work. Table 1 gives the experimental range and levels of independent variables considered in this study. A total number of 17 experiments were carried out in a randomized order with five centre points and the corresponding response % COD removal (Y) are presented in Table 2. The experimental design consists of a set of points lying at the midpoint of each edge and the replicated centre point of the multidimensional cube. It defines the region of interest used to evaluate the main effects, interaction effects, and quadratic effects and to optimize the process. The regression model was used to fit the second-order polynomial equation, to identify the relevant model terms. The performance of the system is explained by the following quadratic equation (1)

$$Y = \beta_o + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^k \sum_{j=1}^k \beta_{ij} x_i x_j + \varepsilon$$

where Y is the process response or output (dependent variable), k is the number of the patterns, i and j are the index numbers for pattern,  $\beta_o$  is the free or offset term called intercept term,  $x_1, x_2, \dots, x_k$  are the coded independent variables,  $\beta_i$  is the first-order (linear) main effect,  $\beta_{ii}$  is the quadratic (squared) effect,  $\beta_{ij}$  is the interaction effect, and  $\varepsilon$  is the random error between predicted and measured values [17].

Table 1 Coagulation parameter and their levels

Variables	Factors	Level		
		-1	0	1
Alum Dosage (mg/l) Cd	$X_1$	50	100	150
pH	$X_2$	3	4	5
Concentration (g/l) C	$X_3$	10	20	30

Each experiment was repeated three times to observe the reproducibility and the result were subjected to three step process. The statistical significance of the ratio of mean square variation due to regression and mean square residual error was tested using ANOVA. The adequacy of model was performed by three different tests, viz., Sequential model Sum of Squares, Lack of Fit Tests and Model Summary Statistics were carried out in the present study. The response plots such as 3D and contour plot was used to found an optimum condition. The quality of the fit of polynomial model was expressed by coefficient of determination  $R^2$ , adjusted  $R^2$  and adequate precision. Fischer's F-Test was used to evaluate the statistical significance and optimise the desired goals fixed for maximum COD removal.

Table 2 Experimental and predicted values of Y for %COD removal

Run	Cd	pH	C	%COD removal		
	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	Y <sub>exp</sub>	Y <sub>pre</sub>	Error
1	150	3	20	18.21	18.12	-0.48
2	100	3	30	28.64	27.92	-2.57
3	100	5	10	37.9	38.62	1.86
4	50	4	10	31.57	30.77	-2.61
5	100	4	20	65.24	66.53	1.94
6	100	4	20	66.58	66.53	-0.07
7	100	4	20	68.14	66.53	-2.41
8	100	5	30	73.81	71.31	-3.51
9	50	5	20	38.62	38.71	0.22
10	150	5	20	50.27	51.97	3.26
11	50	3	20	20.41	18.71	-9.06
12	150	4	10	17.59	17.18	-1.05
13	50	4	30	24.65	27.06	8.92
14	100	4	20	67.43	66.53	-1.35
15	100	3	10	25.67	28.17	8.87
16	100	4	20	65.28	66.53	1.88
17	150	4	30	52.52	53.32	1.51

### III.RESULTS AND DISCUSSION

#### A. BBD Statistical analysis.

The ANOVA results for % COD removal was shown in Table 3, the F values for all regressions were higher. The large value of F indicates that most of the variation in the response can be explained by the regression equation. The associated p value is used to estimate whether F is large enough to indicate statistical significance. The values of  $p > F$ , less than 0.05 indicates that the model is considered to be statistically significant [20]. The p values for all the regressions were lower than 0.01. This means that at least one of the terms in the regression equation has a significant correlation with the response variable. The ANOVA table also shows a term for residual error, which measures the amount of variation in the response data left unexplained by the model. The form of the model chosen to explain the relationship between the factors and the response is correct [21, 22]. The ANOVA result for the % removal of COD for coagulation process, shows that the model F-value is 129.83, implying that the model is significant. There is < 0.01% probability that a model F-value this could be large occurs due to noise.

Table 3 ANOVA for % COD removal

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	6489.15	9	721.017	129.83	< 0.0001
X <sub>1</sub>	80.26	1	80.264	14.45	0.0067
X <sub>2</sub>	1449.10	1	1449.104	260.93	< 0.0001
X <sub>3</sub>	526.34	1	526.339	94.78	< 0.0001
X <sub>1</sub> X <sub>2</sub>	47.96	1	47.956	8.64	0.0218
X <sub>1</sub> X <sub>3</sub>	397.01	1	397.006	71.49	< 0.0001
X <sub>2</sub> X <sub>3</sub>	271.26	1	271.261	48.84	0.0002
X <sub>1</sub> <sup>2</sup>	2045.22	1	2045.219	368.28	< 0.0001
X <sub>2</sub> <sup>2</sup>	670.27	1	670.268	120.69	< 0.0001
X <sub>3</sub> <sup>2</sup>	648.66	1	648.664	116.80	< 0.0001
Residual	38.87	7	5.554		
Lack of Fit	32.24	3	10.748	6.48	0.0513
Pure Error	6.63	4	1.658		
Cor Total	6528.03	16			

R<sup>2</sup>=0.9940, Adj R<sup>2</sup>=0.9864, Pred R<sup>2</sup>=0.9194, Adeq Precision=29.951

#### B. Fitting of Second order polynomial equation.

The ANOVA analysis indicates a linear relationship between the main effects, quadratic effect and interaction effect of X<sub>1</sub>, X<sub>2</sub>, and X<sub>3</sub> respectively. The final mathematical equation in terms of actual factors (confidence level above 95%) as determined by Design-expert software is given below

$$\% \text{ COD Removal (Y1)} = -216.107 + 1.15 X_1 - 90.99 X_2 + 0.48943 X_3 + 0.06925 X_1 X_2 + 0.0199 X_1 X_3 + 0.8235 X_2 X_3 - 0.0088 X_1^2 - 12.61 X_2^2 - 0.124 X_3^2 \quad (2)$$

In the present study X<sub>2</sub>, X<sub>3</sub>, X<sub>1</sub>X<sub>3</sub>, X<sub>1</sub><sup>2</sup>, X<sub>2</sub><sup>2</sup> and X<sub>3</sub><sup>2</sup> are highly significant parameters, while X<sub>1</sub>, X<sub>1</sub>X<sub>2</sub> and X<sub>2</sub>X<sub>3</sub> are significant parameters. A lack-of-fit value of 6.48 also supports the fitness of the model. There is a 5.13% possibility of this deviation being mostly due to noise. Quadratic model was chosen for further analysis because predicted value of (R<sup>2</sup> = 0.9194) and the adjusted value of (R<sup>2</sup> = 0.9864) were found to be maximum respectively. The high value of adequate precision at 29.951, which measures a signal-to-noise ratio greater than 4, is desirable in support of the fitness of the model [23].

#### C. Effect of independent variable on COD removal.

After studying the effect of the independent variables on the response, the levels of the variables that give the optimum response were determined. 3D and contour plots of the relationship between concentrations, pH and their effect on the percentage removal of COD at 50,100,150mg/l dosages is shown in Fig. 1, 2 and 3 respectively. At pH of 4.5 COD removal was increased to 67.86% with a desirability of 0.92 respectively. Alum was found to be very effective in reducing solids and organics [8]. The figures clearly indicate that the percentage removal of COD increases with increasing alum concentration of 50 to 100mg/l, whereas 150mg/l of alum dosage cause the COD removal in slightly diminishing fashion [24]. The point prediction is used for the optimization of the process parameters.

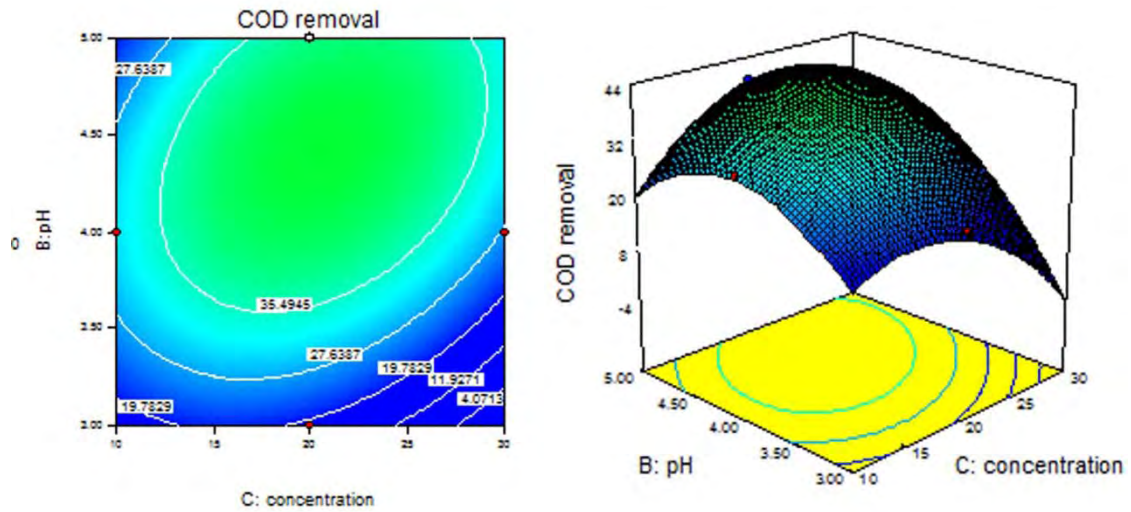


Fig.1 Effect of pH and concentration on % COD removal at 50mg/l

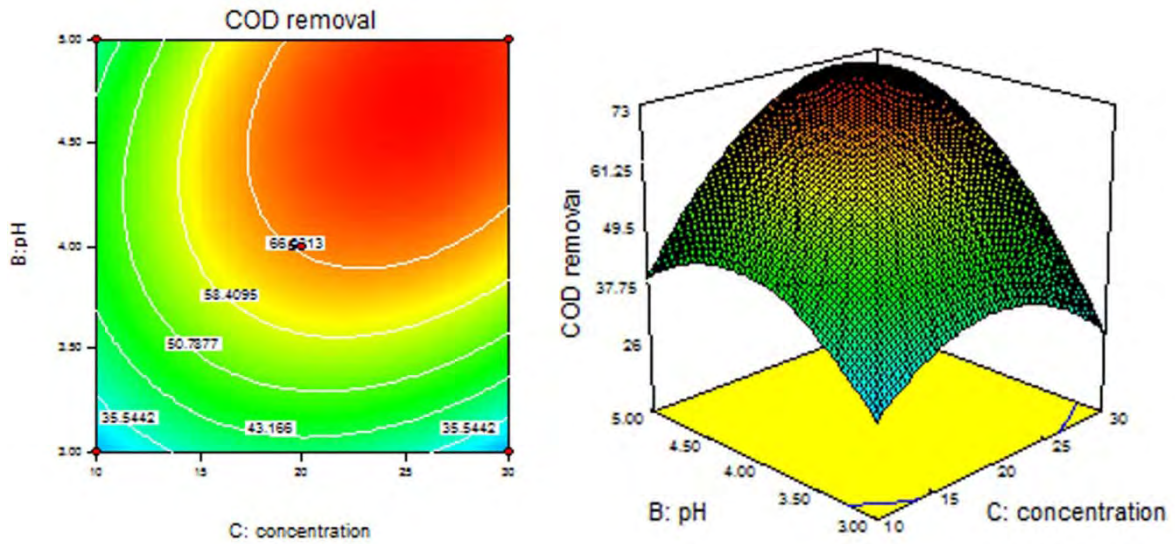


Fig.2 Effect of pH and concentration on % COD removal at 100mg/l

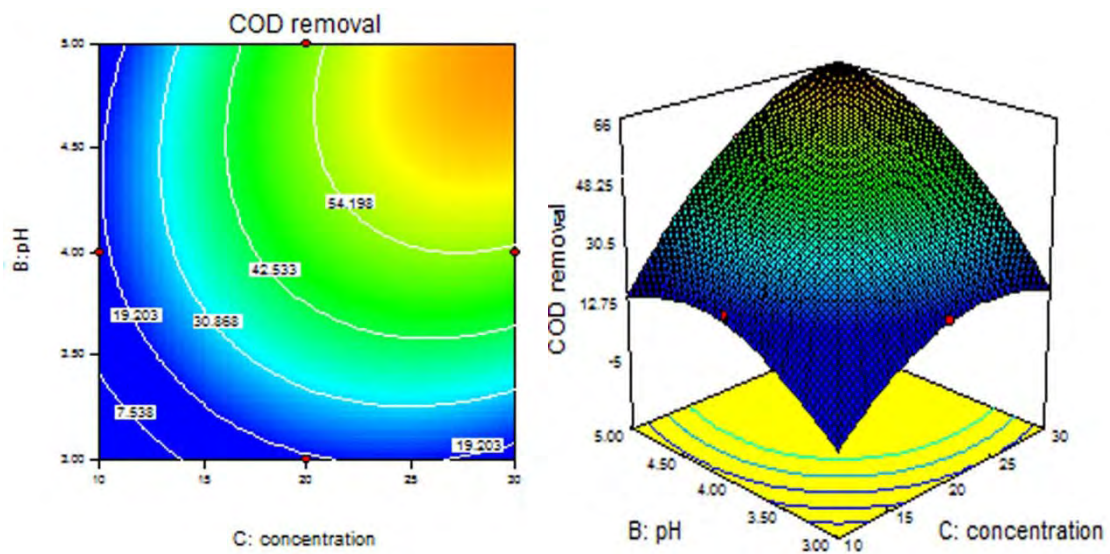


Fig.3 Effect of pH and concentration on % COD removal at 150mg/l

#### IV. CONCLUSION

The results of RSM showed good correspondence between experimental and predicted values. This shows that the sago behaves as negatively charge polymer, which enhances the coagulation process. The optimum condition at which organic matter reduction is obtained for sago wastewater was at pH 4.5, alum dosage of 100mg/l for concentration of 23.5g/l. The analysis of variance showed high coefficient of determination ( $R^2$ ) of 0.9194 and desirability of 0.92 for % removal of COD and thus ensuring the satisfactory fit for the regression model.

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