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Treatment of Sea Food Industry Wastewater Using Zinc Oxide Nano Catalyst Based Photo Oxidation Process

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Abstract - **In this present study, Response surface methodology (RSM) coupled with three factor and three level BBD design was employed to optimize the process variables such as catalyst dose, pH, radiation on COD and BOD removal from sea food industry wastewater. A mathematical model and ANOVA was developed to correlate the influencing parameter on the pollutant removal and used to predict the treatment efficiency. Operating conditions was found to be as follows: Catalyst dose of 55 mg/100ml, radiation time of 60min and pHof 4. Under this conditions 91 % of BOD removal and 93% of COD removal was achieved.**

Keywords: **Sea food industry wastewater, Nano catalyst, Photo oxidation, COD removal , Optimization**

I. INTRODUCTION

Water is an important commodity in the world for drinking, sanitation, agriculture and industrial activities. Rapid globalization, industrialization and population growth generates huge amount of waste water that will create a negative impact on the ecological system [1]. A few decades before there is no stringent law and regulation for disposing of industrial and municipal effluent but nowadays many new regulations were framed to implement zero discharge concept [2]. Therefore effluent treatment is an important element in for different industries, of which sea food industry generates huge quantity of waste water originated from the unit operations scalding, washing, evisceration, cooking, thawing and freezing which is rich in organic pollutants because of presence of blood, dissolved protein and phosphorous so that it requires great concern to prevent the threatening of environment [3].

Numerous effluent treatment methods such as coagulation, filtration, sedimentation, membrane processing, ozonation, flocculation and biological method [4] are followed to treat the various industrial effluents. Among those methods photo catalytic oxidation method has received much attention for industrial wastewater treatment due to its eco friendliness and superior removal of organic pollutants without any sludge formation [5]. In photo catalytic oxidation process electron and hole pairs was produced, when the UV energy was incident on the catalyst surface that generates the hydroxyl radical which can oxidize the organic pollutants present in the waste water [6].
Recently nano catalyst synthesis has been focused by many researchers to develop the nano photo catalyst with better size and surface morphology [7] There are several physical and chemical methods such as solgel technique [8] inert gas condensation technique , plasma based synthesized method, spray pyrolysis method, precipitation method and hydro thermal synthesis have been reported for zinc oxide nano catalyst synthesis. However these methods use high energy and expensive chemical in addition to that it was very difficult to control the size of the nano catalyst. So there is a urgent need for developing new method of synthesis to overcome the draw backs in the physical and chemical methods. Currently plant mediated green synthesis of different nano particles from various plants such as Cassia alata [9], Camellia sinensis [10], Mangifera indica [11], Azadirachta indica[12], Syzygium cumini [13] and Ocimum basilicum [14] have been reported. Hence the present study uses the sesbania grandiflora leaf extract as a reducing agents to synthesis the zinc oxide nano catalyst because sesbania grandiflora leaf contains good source of phytochemicals such as phenolic acids, poly phenol and flavanoids [15] that capable to reduce the precursor effectively.

An extensive literature review shown that no research report is available for treating of sea food industry waste water by photo catalytic oxidation using zinc oxide nano catalyst. Hence, the present study deals about the utilization of the prepared zinc oxide nano catalyst synthesized by sesbania grandiflora leaf extract to treat the sea food industry waste water and optimize the photo oxidation process variables such as dosage of catalyst, pH and radiation time on the reduction of BOD and COD levels.

II. MATERIALS AND METHODS

A. Raw materials

Sesbania grandiflora was procured from local market near Perundurai, Tamil Nadu, India and it was utilized for the synthesis of nano catalyst. The wastewater was collected from an industry located at Thoothukudi, Tamil Nadu, India and stored at 4ºC for furtherexperimental analysis. All the chemicals used in this study were obtained from Sigma chemical, Chennai. The initial characteristics of effluent used in the present study are given in the Table 1.

TABLE 1 CHARACTERISTICS OF SEA FOOD INDUSTRY EFFLUENT

Characteristic	Value
COD	912ppm
BOD	625ppm
Total suspended solids	7892.22ppm
Turbidity	859 NTU
Total Dissolved Solids	2057 ppm
pH	6.56

B.Preparation of nano catalyst

Fresh leaves with uniform size and without any blemishes were manually separated from the stem of the plant and washed in running tap water in order to remove the impurities present on the surface. An known quantity of leaves were taken in a beaker, add 100 ml of distilled water and kept it in a hot plate at the temperature of 60ºC until the color of the water was turned to green. Then the extract was filtered using filter paper (What man No-1), 50 ml of the filtered leaf extracts were taken in a glass beaker, add 5 g of zinc nitrate precursor on the extract, the mixture was kept it on a hot plate at the temperature of 60 ºC and heating was carried out until the formation of yellow color paste. After cooling the yellow paste, the paste was collected in a ceramic crucible and placed in a muffle furnace at 500 ºC until the paste was turned in to powdered form [16]. Then the powder was scrapped carefully from the crucible and packed in a hermetically sealed container for further experimental analysis.

III. EXPERIMENTAL SETUP AND PROCEDURE

Photo catalytic reactor was designed and fabricated to treat the sea food industry waste water was shown in the Fig 1. The reactor consists of UV lamp (λ= 288) which act as a light source for photo catalytic reaction. The reactor contains sample inlet and out let to pour the effluent inside the rector. The UV light source was surrounded with the quartz tube in which cold water was circulated to maintain the temperature of the reactor. At the bottom of the reactor magnetic stirring system was located in order to prevent the settling of nano catalyst while processing and also at the top reactor the lamp was connected to the power supply.

A known quantity of effluent was taken in a beaker and pH was adjusted using 0.1N HCl and NaOH then nano catalyst was added. This mixture was poured in to the reactor via the sample inlet after a particular time the effluent was taken from the reactor through sample out let and filtered to separate the nano catalyst from the effluent. After that the treated effluent water was undergone the experimental work for as per the method described by the American Public Health Association (APHA) to determine the BOD and COD removal. Removal efficiency of BOD and COD was calculated by the following equation given by[15]

$$\mathrm{RE}(\%) = \frac{C_i - C_o}{C_i} * 100 \qquad (1)$$

where C_i, C_o were the initial and final concentration of COD and BOD, respectively.

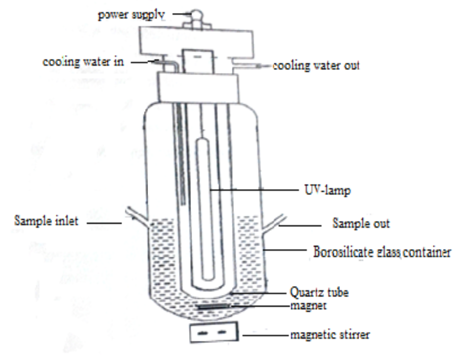

Fig.1 Schematic diagram of photo catalytic oxidation unit

A.Experimental design

Response Surface Methodology (RSM) was a statistical technique employed for multiple regression analysis. It was also be an effective tool to optimize and design under RSM was adopted in this present study for optimization of process variables such as radiation time, catalyst dosage and pH. Each independent variable was coded as -1, 0 and +1 which correspond to lower level, middle level and higher level respectively [16]. Coding of variables were done based on following equation,

$$x_i = \frac{X_i - X_o}{\Delta X_i} \qquad (2)$$

where x_i is the dimension less variable of an independent variable, X_i is the real value of an independent variable and X_o is the real value of an independent variable at center point. ΔXi is step change of the real value of the variable 'i' corresponding to a variation of a unit for the dimensionless value of the variable 'i'.

Second order polynomial equation was developed to evaluate the correlation between the responses and responses and the equation was given below,

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ij} X_i X_j + \sum \beta_{ii} X_i^2 \qquad (3)$$

where Y is the response, X_i, X_j are independent variables, β_o is a model intercept, β_i, β_{ij}, β_{ii} are the interaction co efficient of linear, quadratic and second order terms respectively. Ranges of independent variables and their levels are shown in the Table 2.

TABLE 2 RANGES OF INDEPENDENT VARIABLES AND THEIR LEVELS

Variables	Factors (X)	Levels		
		-1	0	1
Dosage of catalyst (mg/100ml)	A	10	55	100
Radiation time (min)	B	30	60	90
pH	C	2	4	6

B.Statistical analysis

Design Expert 8.0.7.1 (star ease Inc.,USA) software package used for statistical analysis. Analysis of variance (ANOVA) was performed to identify the significance of factors, responses and their interaction in addition to that probability value (p value) and lack of fit indicates the level of significance quantitatively. Moreover R^2, adjusted R^2 and predicted R^2 were used to check the adequacy of various models (linear, quadratic, cubic and 2FI).

C.Optimization and validation of model

Optimum conditions for removal of COD and BOD depends on dosage of catalyst, radiation time and pH and it was obtained from derringer's methodology. It could be carried out by setting goals and expected values along with level of importance [17]. Actual and predicted values were compared in order to find the effective model.BBD design matrix along with observed responses were shown in Table 3.

TABLE 3 BBD DESIGN MATRIX ALONG WITH OBSERVED RESPONSES

Run	Dosage of catalyst (mg/100ml)	Radiation time (min)	pH	BOD removal (%)	COD removal (%)
1	100	60	2	77.5	78.9
2	10	60	6	71.5	74.3
3	55	60	4	90.4	92.7
4	55	90	2	70.7	72.1
5	55	60	4	90.3	92.3
6	10	30	4	72.7	74.3
7	55	90	6	79.6	81.7
8	100	30	4	82.5	83
9	100	90	4	77	79
10	55	60	4	90.5	92.2
11	10	60	2	69.3	71.4
12	100	60	6	80.8	82.3
13	10	90	4	71.2	73.2
14	55	60	4	90.9	92.5
15	55	60	4	90.8	92.4
16	55	30	6	65.3	68.9
17	55	30	2	73.6	75.7

IV. RESULTS AND DISCUSSION

A.Effect of process variables on treatment efficiency

1.Effect of pH

pH was a significant factor that offer a greater influence on photo catalytic oxidation process. In this present study pH of the effluent was varied in the range of 2 to 6 in order to investigate its effects on photo catalytic degradation of pollutant present in the sea food industry waste water. From the results (Fig 2&3), it was found that the photo catalytic efficiency was increased when increasing pH 2-4. This is because of the formation of per hydroxyl radical and hydroxide ions under acidic conditions [18] which could effectively take part in the degradation of pollutant present in the sea food industry effluent. Also pH alters the surface properties of the molecules at pH 4which allows the strong adsorption of water and hydroxyl radical resulting in effective BOD and COD removal.

2.Effect of catalyst dosage

Optimum level of catalyst dosage is an important parameter to be examined in order to avoid the ineffective usage of ZnO nano catalyst. For this study, the catalyst dosage was varied from 10 to 100mg for 100ml of sea food industry waste water. when the amount of catalyst dosage increased the photo catalytic degradation of pollutant was increased slightly up to 55mg/100 ml. After that drastically decrease in removal efficiency was obtained. However this might be due to the particle agglomeration and turbidity formation, which causes inaccessible active site for adsorbing radiation resulting minimum level of free radical generation [19].

3.Effect of irradiation time

Irradiation time plays a key role on photo oxidation process for BOD and COD removal. This was studied at a range of 30-90 min and its influence was shown in the Fig2&3. From the results, it was observed that at initially the pollutant removal efficiency was low, because at the initial period was required to initiate the equilibrium adsorption of radiation on the catalyst surface [20]. When increasing the time up to 60 min, the removal efficiency was maximum. This is due to the fact that the hydroxyl radical level increased which had a capability to oxidize the organic matter present in the sea food industry waste water. Thereafter there was drastic decrease in the removal efficiencies that can be found by the fact at longer time produces more radical but these radicals were unstable in nature, which leads to decrease the photo catalytic degradation process.

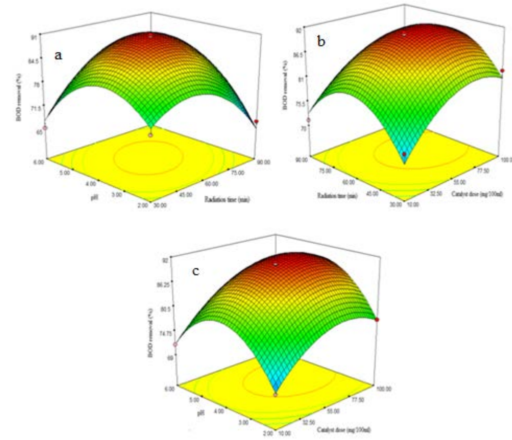

Fig.2 Effect of process variables on BOD removal

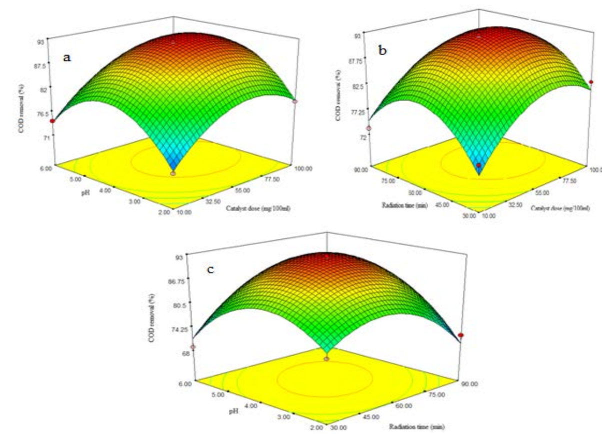

Fig.3 Effect of process variables on COD removal

B.Development of mathematical model

Fitting of data to the various models such as linear, quadratic, cubic and interactivewas performed to obtain the regression equation. The model summary was depicted in theTable 4. The outcome of the model summary indicated that quadratic model wassuggested and cubic model was aliased [21]. Cubic model was not suggested for the experiment due to insufficientpoints to correlate the coefficient of the mathematical model. F-value is the ratio ofregression mean square and the real error mean which indicates the influence of eachcontrolled factor on the tested model. ANOVA results in the Table 4 shows that Fvalue for BOD removal and COD removal was high in the quadratic modelwhich implies the model was highly significant and also the probability value of quadraticmodel was lower than cubic model. So that quadratic model had been recommended for theeffluent treatment process.

TABLE 4 MODEL SUMMARY STATISTICS FOR BOD AND COD REMOVAL

Source	SD	R^2	Adj- R^2	Pre-R^2	Press	p value	F value	Remark
Model summary statistics for BOD removal								
Linear	9.41	0.1143	-0.0901	-0.3466	1750.01	0.6512	0.56	-
$2F_1$	10.2	0.2001	-0.2779	-1.0007	2600.15	0.7851	0.36	-
Quadratic	2.03	0.9779	0.9495	0.6494	455.58	<0.0001	141.5	Suggested
Cubic	0.26	0.9998	0.9992			0.0012	82.14	Aliased
Model summary statistics for COD removal								
Linear	8.94	0.1074	-0.0986	-0.3272	1543.92	0.6750	0.52	-
$2F_1$	9.84	0.1671	-0.3327	-1.0294	2360.86	0.8674	0.24	-
Quadratic	1.98	0.9765	0.9462	0.6255	435.71	<0.0001	245.2	Suggested
Cubic	0.19	0.9999	0.9995			0.0420	80.28	Aliased

C.Adequacy of developed model

Adequacy of developed model was investigated using ANOVA. ANOVA fitted quadratic model of photo catalytic oxidation were shown in the Table 5. The higher F value and lower p value (0.0001) denoted that the model was significant and the model equation can effectively used to illustrate the photo catalytic treatment process under wide range of operating conditions. The p value lower than 0.05 for the model and coefficients indicates its significance [22].

TABLE 5 ANOVA FOR THE RESPONSES

Source	BOD removal		COD removal	
	F value	***P* value**	**F value**	***P* value**
Model	180.372	< 0.0001	110.854	< 0.0001
A	154.625	< 0.0001	89.8713	< 0.0001
B	0.81984	0.3953	1.20052	0.3095
C	57.5421	0.0001	34.8946	0.0006
AB	19.9587	0.0029	19.572	0.0031
AC	56.0073	<0.0001	36.7646	0.0005
BC	14.5393	0.0066	4.45613	0.0727
A^2	885.03	< 0.0001	554.365	< 0.0001
B^2	51.5798	0.0002	36.9707	0.0005
C^2	282.784	< 0.0001	157.62	< 0.0001

D.Optimization of photo catalytic oxidation process parameter

Optimization was performed on the basis of Derringer's desirability function to find out the optimal conditions for COD removal and BOD removal. The results shown that the optimum conditions were catalyst dosage of 55 mg/100ml, radiation time of 60min and pH of 4. Under this conditions 90.92 % of BOD removal and 92.75% of COD removal was taken place and it was checked experimentally.

V. CONCLUSION

Response surface methodology coupled with three factor and three level BBD design was employed to optimize the process variables such as catalyst dose, pH, radiation on COD and BOD removal. A mathematical model and ANOVA was developed to correlate the influencing parameter on the pollutant removal and used to predict the treatment efficiency. Operating conditions was found to be as follows: Catalyst dose of 55 mg/100ml, radiation time of 60minand pHof 4. Under this conditions 90.92 % of BOD removal and 92.75% of COD removal was taken place. It shows that effectiveness of photo catalytic oxidation method for sea food industry waste water treatment.

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