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COD Removal Efficiency of Pararubber Wastewater by Ozonation using the Central Composite Design Model

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Abstract

Pararubber is one of the major plants contributing to both Thai and Asian's economy. Pararubber wastewater having a high strength can cause several environmental problems to community nearby the industry. The research aimed to study the characteristics of pararubber wastewater and investigate the optimal conditions for treatment of pararubber wastewater using the ozonation process. The results revealed that the pararubber wastewater has a black color with a pungent odor like sludge from a septic tank. Wastewater characteristics obtained from the preliminary analysis are as follows; pH of 4.99, Chemical Oxygen Demand (COD) of 55,448.52 mg/L, Total Dissolved Solid (TDS) of 10,240 mg/L, and SS of 1,516.67 mg/L. Factors affecting the ozonation process studied are dosage rate of ozone and contact time. The Central Composite Design (CCD) model or box-wilson design, which is an experimental design at 3 levels (popularly represented by symbols -1, 0, +1) and useful in response surface methodology (RSM) for generating a second order (quadratic) model for the response variables, was applied to investigate the optimal condition for the treatment process. From the results, it was found that both of factors significantly affected the COD removal efficiency and can be expressed in the form of equations or a mathematical model for predicting COD removal efficiency, in which %COD R.E. = 13.3408 + 0.0613A + 0.5587B + 0.000619A*B - 0.000063A^2 - 0.004270B^2. The coefficient of determination was 92.14%. The mathematic model was applied to develop the graph displaying the relationship between these two factors and COD removal efficiency using the Responsive Surface Methodology. It was found that the removal efficiency of COD was increased with increasing contact time and dosage rate of ozone, which has a maximum value of 89.67% at ozone dosage rate of 900 mg/hr and contact time of 120 minutes.

Keywords : Wastewater treatment; Pararubber wastewater; Ozonation; Response surface methodology; Central Composite design model

Introduction

The pararubber processing industry is one of the industries that is important to Thai economy in terms of both income and employment. Thailand is one of the leaders in pararubber producer with the product of 4.5 Mton/yr accounting for 35.7% of the world's production [1]. The pararubber processing industry, however, produces high strength of wastewater from the production process. Pararubber wastewater have a very high concentration of organic matter and acid odor which leads to pollution problems affecting community nearby. There are several methods for treating pararubber wastewater such as anaerobic filter, UASB, and biological method incorporated with sulphate reduction system, which are the conventional systems [2, 3]. In addition, there are advanced or alternative processes including electro chemical method, solar distillation systems, flocculation and flotation method, Fenton process, and so on [4-7]. Previous studies revealed that the advanced oxidation process is one of the treatment processes that have been found to be effective in reducing pollutants in wastewater or change them into more easily degradable compounds using hydroxyl radical which is a strong oxidizing agent that can oxidize various toxic organic matter [8]. This research uses ozonation process for treatment of pararubber wastewater. Ozone is a strong oxidant and can react with many substances by both direct and indirect reaction especially the indirect oxidation mechanism has a better ability to oxidize when ozone reacts with wastewater to break down into hydroxyl radical ($OH^{\bullet}$), which are highly susceptible to oxidizing organic compounds as well. Ozone degrades chemical bonds of complex organic compounds into simple structures [7]. In addition, ozone is readily converted to oxygen, which is beneficial for water. Thus this technology does not create further problems such as odor, taste, and chemical residual in water. Therefore, ozone can be applied to treat wastewater including wastewater from the pararubber processing industry [7].

The response surface methodology (RSM) is a method of experimental design and statistical analysis. RSM is widely used to analyze the relationship of variables where the responds of interest depends on several variables [9]. The purpose of the RSM is to determine the best value of the response or of the experiment. The analyzed experimental results will come out in the form of a set of correlation equations. Currently, there are complete programs such as Design-Expert that have been developed to help in the complexity of processing data quickly and accurately including displaying the data and presenting the conclusions of the experimental results in both variables and graphs. Treatment efficiency of ozonation process can be affected by several factors including dosage rate of ozone and contact time. The objective of this research was to study the characteristics of pararubber wastewater and investigate the suitable conditions for treatment of pararubber wastewater using ozonation process. The Central Composite Design (CCD) model is the most commonly used fractional factorial design in the response surface model. In this model, the center points are augmented with a group of axial points called star points. With this design, quickly first-order and second-order terms can be generated for the response variables without requirement of using a complete three-level factorial experiment [10]. Thus, the CCD with Design-Expert (Trial Version 13), which is a widely used tool for experimental design and statistical analysis [11], was exploited to obtain the optimal conditions and statistical analysis.

Methodology

Analysis of pararubber wastewater characteristics

Pararubber wastewater from a pararubber factory in Ubonratchathani province was sampled and analyzed prior to the ozonation treatment. The characteristics of water sample is shown in Table 1 [12].

Table 1 Analysis of Wastewater parameters and methods

Parameters	Method	characteristics of pararubber wastewater
1. pH	pH Meter	4.99 ±0.01
2. COD (mg/L)	Close Reflux, Colorimetric Method	55,448.52 ±192.39
3. Suspended solid; SS (mg/L)	Gravimetric Method	1,516.67 ±16.07
4. Total dissolved sold; TDS (mg/L)	Gravimetric Method	10,240 ±9.54

Ozone dosage rate measurement

Ozone dosage rate obtained from the ozone generator' were performed followed the standard method [12]. The first step is passing the ozone gas through two serial KI trap (Traps A and B) for about 10 min. For best results, gas flow rate should be kept below approximately 1 L/min. Each trap is a gas washing bottle containing a known volume (at least 200 mL) of 2% KI. Contents of each trap was quantitatively transferred into a beaker. Next, 10 mL of 2N H_2SO_4 was added and titrated with standardizer (0.005N $Na_2S_2O_3$) until the yellow iodine color almost disappeared. Then, adding 1 to 2 mL starch indicator solution and continue titrating until the blue color disappeared. A known volume (at least 200 mL) of sample was added into a separate gas washing bottle (label gas washing bottles to avoid contaminating the reaction vessel with iodide). Finally, ozone gas was directed through this reaction vessel [12]. The equation for calculating dosage rate of ozone is shown in Equation 1 [12].

$$\text{Dosage rate of ozone (mg/min)} = \frac{(A+B)\times N\times 24}{T} \quad (1)$$

In which A = mL titrant for trap A
B = mL titrant for trap B
N = Normality of $Na_2S_2O_3$
T = Ozonation time, min

Experimental design

Treatment of pararubber wastewater using ozonation were conducted to study the impact of ozone dosage rate and contact time on COD removal efficiency. These two factors were varied as shown in Table 2. The CCD model was applied for experimental design. Totally, there were 13 sets of experiments as shown in Table 3, triplet of each set were repeated. Wastewater from a pararubber processing industry was collected and diluted with the ratio of 1:10 so that the COD value of water sample would be in the range of 5,000-6,000 mg/L, which is about 5 times of the COD value from our previous work [7]. Ozone was blown into 2 L of diluted wastewater in a 5 L Erlenmeyer flask closed system as displayed in Fig. 1.

Mathematical model derivation, statistical analysis, and model validation

The mathematical model derivation and statistical analysis were carried out by the Design-Expert (Trial Version 13). The first part involved the model derivation and the second part included the analysis of variable variance (ANOVA). In this step, the mathematical model or empirical regression model and graphical data (ANOVA, variance analysis) were obtained from analysis of the optimal response of the operation factors via the RSM model. Analysis of variance examines the sources of variance for a model based on the P-values of the terms in the tables of the analyzed variance compared to the given statistical significance. Equation 2, a second-degree polynomial regression model, was obtained from the experimental data of 13 runs that were analyzed through the CCD matrix [13].

$$y=\beta_0+\sum_{i=1}^{k}\beta_i X_i+\sum_{i=1}^{k}\beta_{ii}X_i^2+\sum\sum_{i<j}\beta_{ij}X_iX_J+\varepsilon \quad (2)$$

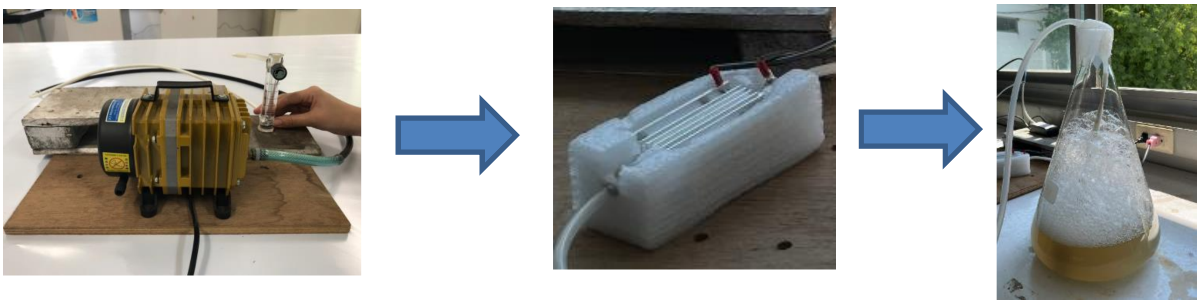

Figure 1 Experimental set up of wastewater treatment by ozonation process

Table 2 Degree of factors

Factors	level		
	low	**middle**	**high**
1. Dosage rate of ozone (mg/hr)	500	700	900
2. Contact time (min)	60	90	120

Table 3 Sets of experiment received from the CCD model

Experiments	**Dosage rate of ozone (mg/hr)**	**Contact time (min)**
1	500	60
2	900	60
3	500	120
4	900	120
5	500	90
6	900	90
7	700	60
8	700	120
9	700	90
10	700	90
11	700	90
12	700	90
13	700	90

in which y is the predicted response, X_i, X_j are experimental factors, k is number of factor, β_0 is a constant, $\beta_i, \beta_{ii}, \beta_{ij}$ are regression coefficients, $\sum_{i=1}^{k} \beta_i X_i$ is a linear effect term, $\sum_{i=1}^{k} \beta_{ii} X_i^2$ is a quadratic effect term, and $\sum\sum_{i<j} \beta_{ij} X_i X_J + \varepsilon$ is a cross-product effect term.

The quadratic model received from the RSM was validated by conducting a set of experiment under the following conditions; the ozone dosage of 600 mg/hr and contact time of 100 min. COD removal efficiencies obtained from the experiment and model prediction were compared to ensure the model validation.

Investigation of the optimal conditions

Determination of the optimal factor for optimal treatment efficacy was performed by using the response optimizer function in a statistical program. The response optimizer function was exploited to explore the level of the optimal conditions with the measured Composite Desirability: D, which has a value between 0-1. If D value is equal to 1, the response is completely satisfied [14].

Results and Discussions

Analysis of pararubber wastewater

From the characteristics analysis of pararubber wastewater using the methods in Table 1, it was found that the values of COD, TDS, SS, and pH were 55,448.52±192.39 mg/L, 10,240±9.54 mg/L, 1,516.67±16.07 mg/L, and 4.99±0.01, respectively. Pararubber wastewater also has strong acid odor and dark brown color.

Treatment of pararubber wastewater using ozonation

1. COD removal efficiency

COD removal efficiencies obtained in this study were in the range of 60-90%, which are comparable with the results from previous study [7]. The effluent properties pass the standards [15] and can be released into natural water sources. COD removal efficiencies received from the experiments and model prediction are listed in Table 4. As seen from the table, the predicted values are in a good agreement with the experimental values. Thus, it can be concluded that this mathematical model is accurate. Then the data of COD removal efficiency were input into the Design Expert model to check for the data accuracy.

2. Statistical analysis

2.1 Mathematical model and variance analysis

In this part, mathematical model for predicting COD removal efficiency of pararubber wastewater treatment by ozonation process was derived from the RSM model. The final empirical model suggested by the RSM model was the quadratic model as written in Equation 3. The P-value of the quadratic equation (Equation 3) is 0.0275 indicating that the quadratic model is significant. The P-value of Lack-of-Fit is higher than 0.05 and the R^2 of 0.9235 is in reasonable agreement with the adjusted R^2 of 0.8689 (the difference is less than 0.2) as shown in Table 5. Thus it could be concluded that the accuracy of the quadratic model is satisfied [16-17].

$$\text{COD R.E.} = 13.3408 + 0.0613A + 0.5587B + 0.000619A*B - 0.000063A^2 - 0.004270B^2 \quad (3)$$

In which
COD R.E. = COD removal efficiency (%)
A = dosage rate of ozone (mg/hr)
B = contact time (min)

The results show that most of the terms in Equation 3 except for the second last and the last term have significant effect on COD removal using ozonation. Table 6 demonstrates the variance analysis for response surface quadratic model. The statistical significance for the regression coefficient of the model terms were confirmed by the p-value (less than 0.0500). The model F-value of 16.90 implies the model is significant. From the results, it is could be concluded that the quadratic model can be successfully applied to predict the optimum conditions for the response of the maximum COD removal efficiency via ozonation.

Figure 2 demonstrates the normal percent probability versus externally studentized plot of the residuals. As seen from the figure, it is confirmed that any apparent problems with the normal probability plot could not be observed. A good relationship between input and output variables could be derived from the quadratic model that was established by forming a normal probability plot of the residuals. The normality assumptions were assured as the residual plot approximated along a straight line indicating that the quadratic model is accurate for decision.

Table 4 Comparison of COD removal efficiencies from experiments and model prediction

Experiments	Dosage rate of ozone (mg/hr)	Contact time (min)	COD removal efficiency (%)	
			Experimental values	Predicted values
1	500	60	63.24±0.52	65.02
2	900	60	68.86±0.45	69.22
3	500	120	69.18±0.48	71.00
4	900	120	89.16±0.48	90.06
5	500	90	75.45±0.92	71.85
6	900	90	84.25±1.52	83.49
7	700	60	71.78±0.49	69.64
8	700	120	85.26±0.05	83.04
9	700	90	81.64±0.48	80.18
10	700	90	76.25±0.49	80.18
11	700	90	79.16±0.52	80.18
12	700	90	80.87±0.75	80.18
13	700	90	78.63±0.48	80.18

Table 5 Model summary statistics for COD removal

Source	R^2	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	
Linear	0.7043	0.0023	0.0423	0.6451	0.2834	
2FI	0.7865	0.0954	0.0588	0.7154	-0.2002	
Quadratic	**0.9235**	**0.0275**	**0.1956**	**0.8689**	**0.5898**	**Suggested**
Cubic	0.9325	0.7319	0.0670	0.8380	-3.8161	**Aliased**

Table 6 Variance analysis (ANOVA) for response surface quadratic model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	619.73	5	123.95	16.90	0.0009	**Significant**
A	203.00	1	203.00	27.69	0.0012	
B	269.61	1	269.61	36.77	0.0005	
A*B	55.20	1	55.20	7.53	0.0288	
A^2	17.45	1	17.45	2.38	0.1668	
B^2	40.80	1	40.80	5.56	0.0504	
Residual	51.33	7	7.33			
Lack of Fit	33.61	3	11.20	2.53	0.1956	**not significant**
Pure Error	17.71	4	4.43			
Cor Total	671.06	12				

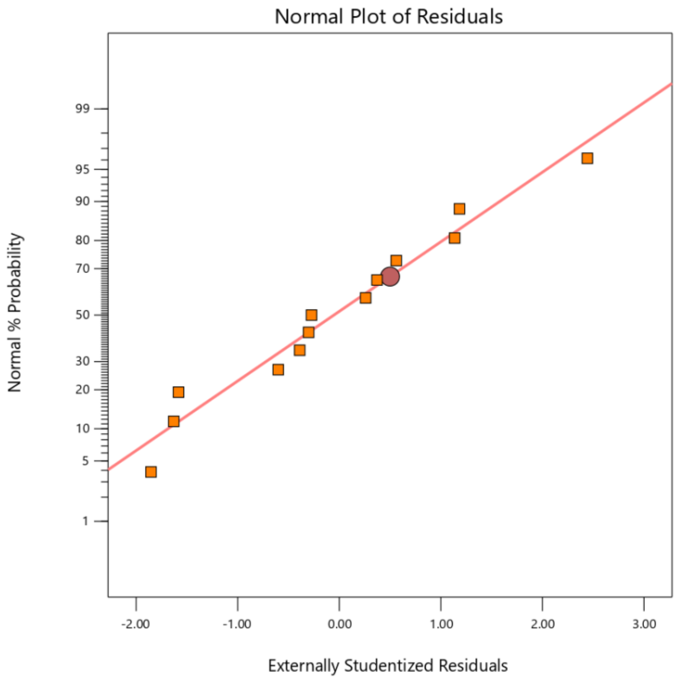

Figure 2 Normal percent probability of residuals versus externally studentized residuals plots for COD removal using ozonation

2.2 Model validation

The quadratic model or correlation equation between the response, which is the COD removal efficiency, and the affecting factors (ozone dosage rate and contact time) as obtained in Equation 2 was validated for the model accuracy for prediction. A set of experiment was conducted under the following conditions; the ozone dosage rate of 600 mg/hr and contact time of 100 min, to evaluate the model validation. The COD removal efficiencies obtained from the experiment and the model prediction were 75.94±0.58 and 77.67, respectively. The values are in good agreement confirming that the quadratic model received from the RSM can be successfully used to predict COD removal efficiency via ozonation.

2.3 Optimal conditions

Investigation of the optimum conditions for the removal efficiency of pararubber wastewater treatment by ozonation process was accomplished using the response optimizer function in a statistical package. A function is used to find the optimal value of a factor and measure the composite desirability (D), which has a value between 0-1. If D is equal to 1, then the result is completely satisfied. From the response optimizer results, five conditions were derived from the model, however, the optimal conditions suggested by the model were at the ozone dosage rate of 900 mg/L and the contact time of 120 min. Since these conditions yield the highest COD removal efficiency of 90.0605 and the D value of 1.000 as shown in Figure 3.

Upon receiving the optimal conditions from the model, a set of experiment (triplet runs) was conducted to confirm the optimal conditions. The average value of COD removal efficiency obtained from the experiment was 89.66±0.48, which agrees well with that from the model. This result confirms great appropriateness of the quadratic model for optimization of COD removal via ozonation.

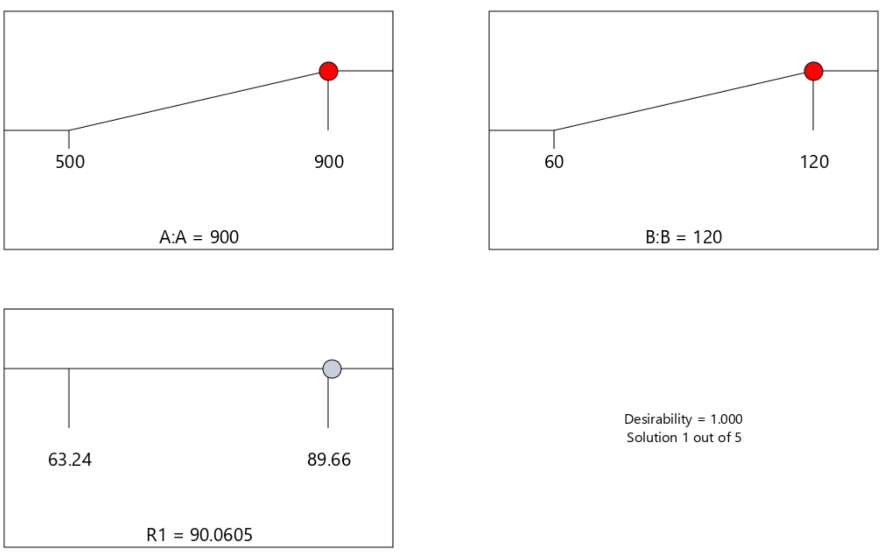

Figure 3 Desirability ramps for COD removal via ozonation at the optimal conditions

Conclusion

COD removal efficiency obtained in this study were in the range of 60-90%. The effluent properties pass the standards [15] and can be released into natural water sources. The most suitable mathematical model for prediction of COD removal efficiency was found to be a quadratic model. The optimal conditions suggested by the RSM model were at the ozone dosage rate of 900 mg/hr and the contact time of 120 min. The results from this study could be applied for the treatment of wastewater from pararubbing industry. However, the effect of pH on the COD removal efficiency should be further investigated.

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