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	PROGRESS PERIOD : 25	June 2015 – 24 March :	2018	121	3.
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ভণ্না	WARY OF RESEAROR IFINDINGS (Ringkesen Penemuen Projek Penyelidiken)	
G	The wastewater from petrochemical industry are consists of many heavy metal that extremely dangerous and demanding environmental management (Munter, 2013). One of the chemical substances exist in the wastewater is cyanide. Cyanide treatment usually discuss in wide range industry either to treat it biologically or other chemically and physical treatment (Dash et al., 2009). Extremely hazardous chemical, cyanide can kill a person only by 2% solution of teaspoon poisoning through inhalation, ingestion and skin or eye contact (Naveen et al., 2009). In this study, cyanide were treated biologically by using activated sludge composed by protozoa and microorganism. The method for this study is consists of five steps starts from the collection of wastewater and the sludge. First, wastewaters sample and activated sludge were collected from the bottom of retention pond. Second, selected parameters were determined. They were temperature, agitation, types of system, ratio WW/AS and RT. Several parameters were conducted to analyze the wastewater such as Chemical Oxygen Demand (COD). Total Suspended Solid (TSS) and cyanide test. All responses from the study were analyzed by using Design Expert software. The software was utilized to obtain the best condition for treat the cyanide content in the petrochemical wastewater. Thus, second objective were achieved. The cyanide removal (%) was ranged from 8 to 95.45%. The COD removal (%) was ranged from 2.4 to 60.16%. For cyanide removal (%) was ranged from 8 to 95.45%. The COD removal (%) was ranged from 2.4 to 60.16%. For cyanide removal, it showed that temperature and RT (AB) then followed by and interaction of temperature and ratio WW/AS (BE), the interaction of RT and agitation (AC) and interaction of agitation and ratio VW/AS (CE). For COD removal, its showed that agitation factor (C) gave the highest contribution for COD removal and followed by RT factor (A) and ratio WW/AS factor (E). For interaction effects, it showed that three interaction effects showed most contributed in C	
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# 1. Introduction

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Petrochemical industry produces wastewater during the production of targeted products such as oils. The wastewater contains organic compounds and heavy metal pollutants including cyanide [1].

Cyanide is toxic to human and aquatic life. More than 14 million kg cyanide is released into the environment every year [2]. Cyanide enters human body via eyes, skin, mucous membranes, ingestion and inhalations and this exposure cause neurological disorder, thyroid dysfunction, hypoxia and nerve damage [2]. Cyanide in waste streams is present in the form of simple cyanide such as HCN, CN<sup>-</sup>, NaCN, cyanates, nitriles, and metal cyanide complexes [3]. Cyanide is a triple bonded molecule with a single negative, and it is usually discussed and examined by researchers and others due to its potential toxicity and environmental impact [4].

Cyanide is removed from the wastewater by chemical, physical or biological methods before it is released to the environment such that it reaches nature harmless [5]. Alkaline chlorination at one time was the most widely applied of the cyanide treatment processes, but it has gradually been replaced by other processes and is now only used occasionally. Alkaline chlorination is effective at treating cyanide to low levels, but the process can be relatively expensive to operate due to high reagent usages [6]. Recently zinc peroxide was used as a nanomaterial to remove cyanide from wastewater yet the method is expensive to broad applications [7]. This work focus on cyanide removal using a biological method, activated sludge.

Use of anaerobic digestion to a mixture of primary and secondary (waste activated) sludge stabilize sludge and reduce sludge quantity to 40-50% because of biogas production. Waste activated sludge is more difficult to digest compared to the primary sludge [8]. In anaerobic digestion, process steps include hydrolysis, methanogenesis, and acidogenesis [9]. Among these step, hydrolysis is the rate-limiting steps due to less solubility of complex substances and to improve this sludge are pretreated with the biological, chemical, thermal and mechanical process. With the use of this pretreatment, the complex compounds degrade and cell wall rupture and release intracellular substances that increase the rate of hydrolysis [10]. A laboratory scale experiment was conducted on thermal pretreatment and characteristics of waste activated sludge degradation with anaerobic digestion at 35±1 °C [9]. The temperature applied was in the ranges of 62 to 175°C and times applied were 15, 30, 60, 90 and 120 minutes. Thermal treatment either solubilized organic molecules of carbohydrates, proteins, and lipids or changed them into low molecular weight complexes including volatile fatty acids. Anaerobic digestion increased the gas production and degraded waste activated sludge and duration of the digestion reduced to 5 days. The optimum temperature found was 170°C and the optimum time for anaerobic digestion was 1 h. The method solubilized and anaerobically degraded mostly carbohydrates followed by proteins and lipids [9].

In this study, the experiments were performed with an open system and closed system that is an aerobic and anaerobic process, respectively. Aerobic cyanide removal by bacteria from cassava factory wastewater was found successful [11]. Both aerobic and anaerobic condition has potential to remove the cyanide but in a different period of time [11]. According to research conducted by Abdel-Raouf *et al* [12], they used a working volume of 2 L on reducing hydrogen cyanide in activated sludge process. The study was carried out in activated sludge bioreactors. They inoculated 1.5 L of the wastewater with 0.5 L of activated sludge or 3:1. The study showed that hydrogen cyanide reduced 72% to 62.5 % at a certain retention time (RT). By considering the ratio WW/AS from their study, the selected range for wastewater to activated sludge ratio of 1:1 and 3:1 were employed for this study. For agitation factors, a research of wastewater treatment by

aerobic activated sludge at high-speed agitation was conducted by Kandasamy *et al* [11]. By using 140 rpm of agitation, the highest cyanide removal achieved was 80%. Therefore agitation of 0 and 100 rpm was chosen for this research.

The aim of this study was cyanide removal from petrochemical industry wastewater using activated sludge and to analyze the factors that affect the cyanide removal process. The activated sludge and wastewater were collected at the bottom of retention pond from the petrochemical industry. The wastewater samples were analyzed to check the content for cyanide and TSS. The activated sludge was acclimatized for certain period of time. The data were collected and analyzed. Then five factors were selected for the study together with their ranges. Afterward, two level factorial analysis was utilized to construct experimental design in the Design Expert software.

## 2. Materials and Methods

### 2.1. Samples Collection

Wastewater (10 L) and activated sludge (5 L) were collected from the retention pond in the petrochemical industry which is located in Gebeng, Pahang, Malaysia. The wastewater and activated sludge were analyzed within less than 24 h to ensure the quality of the samples is same as in the petrochemical industry.

### 2.2. Total Suspended Solid test (TSS)

A blank filter paper was dried for 1 h in the oven and weighed in a weighing balance. Then 50 ml of the samples were filtered using the dried filter paper. The filter paper with suspended solid was dried in the oven for 1 h and weight recorded. Then suspended solid concentration was calculated as the difference of mass between blank filter paper and filter paper with suspended solid. The

solid concentration (mg/L) was calculated as solid weight (mg) multiplied by 1000 ml/L and divided by the total weight of the samples (mL).

For the acclimatization process, the suspended solid data was determined daily to monitor the performance of the sludge.

### 2.3. Cyanide Test

Cyanide treatment was analyzed using HACH Spectrophotometer followed by Pyridine Pyrazolone method. The procedure of the process followed powder pillow procedure. The sample cell was filled with 10 mL of sample. CyaniVer 3 Cyanide Reagent Powder Pillow was added to the sample. Then the stopper was placed and the sample cells were shaken for 30 seconds. Afterward, the samples were left for another 30 seconds, and then CyaniVer 4 Cyanide Reagent Powder Pillow was added and the sample cell was sealed and shaken for 10 sec. Then, immediately CyaniVer 5 Cyanide Reagent Powder Pillow was added and shaken the sample vigorously. If cyanide is in the sample, pink color shows. The samples were then analyzed in the spectrophotometer (DR2400).

#### 2.4. Synthetic Wastewater Preparation

Synthetic wastewater was prepared if the cyanide concentration for the initial wastewater is low (< 1.0 mg/L) by adding Potassium cyanide to maintain the concentration of cyanide to 1.0 mg/L. The synthetic wastewater pH was maintained throughout.

### 2.5.Acclimatized Activated Sludge

Acclimatization process was conducted to adapt the microorganism in sludge with the cyanide concentration. For this study, the acclimatization was carried out in the 10 L acclimatization reactors.

Activated sludge (1 L) is placed in the reactors and pH was recorded. Synthetic wastewater (528 mL) was also poured into the reactors and mixed by shaking the reactors. Then sample (100 mL) was taken from the mix for TSS analysis. After 24 h, sampling was repeated for TSS analysis. Then 528 mL synthetic water was again added into the reactors and initial and final sampling were conducted to analyze TSS as before. This process was carried out for more than 20 days to maintain a high-quality sludge activity and avoid negative impact from toxic substrates.

### 2.6. Preliminary Study

Once the activated sludge was acclimatized and achieved the design basis preliminary test was carried out. The main purpose of the preliminary tests was to validate ranges proposed on this research. Besides, this study helped to check whether there was cyanide removal based on the ranges proposed. The working volume used for this study was 200 mL and duration of every study was 24 h [13]. The study was done in 500 mL of conical flask and tests were done in duplicate for each range of all the factors; Ratio WW/AS 1:1 and 3:1; types of system, open and closed; temperature, 30°C (ambient) and 37°C; agitation, 0 and 100 rpm and RT, 0, 2, 4, 6, 8 and 24 h. The experimental design was then conducted once the study confirmed the cyanide removal based on the proposed factors (preliminary data results not shown).

# 2.7. Experimental design and statistical analysis

Empirical and statistical methods are used to optimize a process because the one-factor-at-a-time (OFAT) is not able to analyze the interaction effects of the factors [14]. Response surface methodology (RSM) is a statistical method that can optimize, improve and develop effects between the factors and their interactive variables [15, 16]. Optimization of variables and their interactions are achieved using regression analysis that can predict the dependent variables based on the input

variable values [17, 18]. This study used RSM to optimize and investigate variables that affect cyanide removal. Central Composite Design (CCD) and RSM was used to design the experiment and optimize the factors to remove cyanide from the wastewater. The second order model as shown in equation 1 was used to fit the model for the removal of cyanide from the wastewater.

$$Y = b_0 + \sum_{n=1}^n b_n x_n + \sum_{n=1}^n b_{nn} x_n^2 + \sum_{n \neq m=1}^n b_{nm} x_n x_m$$
(1)

Where

Y = predicted response variable of the Yield (%) for cyanide removal

 $b_0$  = average response obtained at the replicated center point of the CCD

 $b_n$ ,  $b_{nn}$  and  $b_{nm}$  = the linear, quadratic and interaction regression coefficients, respectively

The experimental values were analyzed using analysis of variance (ANOVA) and F and p values were determined at 95% significant level. The generated models were tested for accuracy using coefficients of determination ( $R^2$ ), adjusted coefficient of determination ( $R^2$ -adj) and predicted coefficient of determination ( $R^2$ -pred). A measure of the failure of the model was tested by calculating the lack of a fit test for the models where model fail to represent data of the experiment that were excluded from the regression at p> 0.05 [18].

#### 2.8. Screening Study

All the factors proposed influence in the rate of cyanide removal and were analyzed using 2-level of factorial design using Design Expert software. All the five factors were temperature, ratio

WW/AS and activated sludge, agitation, types of system and the RT expected to affect the cyanide removal rate.

Wastewater samples were examined to determine the initial condition. Wastewater (WW) and acclimatized activated sludge (AS) were mixed in the ratio of WW/AS; 1:1 and 1:3, in 500 mL conical flask. The samples were agitated between 0 to 100 rpm at 30 and 37°C. The open and closed system was used and the retention time (RT) of the process was in between 17 to 32 h.

In the screening study, the best condition for cyanide removal was determined. It also provided the best factors that contribute the most in the removal. There were total 16 randomized experimental runs and the parameters of each experiment were based on the design (Table 1).



	стр	Dun	Easter 1, DT	Factor 2:	Factor 3:	Factor 4: Types of	Factor 5: Ratio
	310	Kuli		Temperature	Agitation	system	WW/AS
•	1	1	17	30	0	Open	3:1
	2	6	32	30	0	Open	1:1
	3	9	17	37	0	Open	1:1
	4	2	32	37	0	Open	3:1
	5	10	17	30	100	Open	1:1
	6	11	32	30	100	Open	3:1
	7	8	17	37	100	Open	3:1
	8	16	32	37	100	Open	1:1
	9	14	17	30	-0	Closed	1:1
	10	3	32	30	0	Closed	3:1
	11	13	17	37	0	Closed	3:1
	12	12	32	37	0	Closed	1:1

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Table 1. Experimental design table by Design Expert

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#### 3. Results and discussion

#### 3.1. Wastewater Analysis

The wastewater collected from the retention pond contained TSS, COD and cyanide content as 28 mg/L, 104 mg/L, and 0.002 mg/L, respectively. The pH of wastewater sample was 11. Thus, synthetic wastewater was produced to maintain 1.0 mg/L cyanide to proceed into acclimatization and factorial analysis study.

### **3.2.** Acclimatization of Activated Sludge Reactor (ARC)

For the acclimatization process, total suspended solid (TSS) was analyzed. The acclimatization was done in a sequencing batch reactor. The synthetic wastewater was introduced to replicate the wastewater effluent.

The result for acclimatization of activated sludge showed that pH and TSS level decreased. During 25 days of acclimatization, pH dropped from 11 to 8 remained at pH 8 for the rest of 25 days. TSS level was initially 151.45 mg/L and on the 25<sup>th</sup> day, it was 51.23 mg/L.

#### **3.3.**Factorial analysis

#### 3.3.1. Experimental Design

In the present study, five factors; ratio WW/AS, type of system, temperature, agitation and retention time (RT), were taken into account to investigate their effects on cyanide removal (%). A  $2^4$  fractional factorial design was employed to study these factors. Table 2 shows the design factors and levels coded as -1 (low level) and +1 (high level) where low level indicates the lowest range of the factors and high level indicates the highest range of the factors.





Total 16 experiments were run for this study (Table 3). RSM was used to optimize the factors that affect cyanide removal. The results were analyzed using Design Expert Software and a significant difference was tested using ANOVA at p-value with 95% of confidence level.

Table 3. 2<sup>4</sup> fractional factor design

## 3.3.2. Screening of Factors Affecting on the Cyanide Removal (%)

The identification of the factors that were likely to be effective on the cyanide removal was carried out with 16 experimental runs obtained from the 2-factor factorial design. This is to determine the degree of the effect of the factors on the response. Independent factors; ratio WW/AS, type of

· <u> </u>		Factor 1:	Factor 2:	Factor 3.	Factor 4:	Factor 5:	Response 1:
Std	Run	DT	Tanta anti-		Types of	f Ratio	Cyanide
		KI	Temperature	Agitation	system	WW/AS	removal (%)
1		-1	-1	-1	+1	+1	58 33
•	1 (			1		<u> </u>	01.67
2	6	+1	-1	-1	+1	-1	91.67
3	9	-1	+1	-1	+1	-1	72.72
4	2	+1	+1	-1	+1	+1	40
5	10	-1	-1	+1	+1	-1	90.91
6	11	+1	-1	+1	+1	+1	95.45
7	8	-1	+1	+1	+1	+1	83.33
8	16	+1	+1	+1	+1	-1	82.54
9	14	-1	-1	-1	-1	-1	41.67
10	3	+1	-1	-1	-1	+1	86.36
11	13	-1	+1	-1	-1	+1	41.67
12	12	+1	+1	-1	-1	-1	25.8
13	5	-1	-1	+1	-1	+1	75
14	4	+1	-1	+1	-1	-1	91.67
15	15	-1	+1	+1	-1	-1	90.91
16	7	+1	+1	+1	-1	+1	8

system, temperature, agitation, and RT have been taken into account to investigate their effect on

cyanide removal (%). The cyanide removal (%) varied between the ranges of 8% to 95.45% in the 16 experimental runs. Thus the highest removal of cyanide was 95.45% at optimum variable conditions of retention time (32 h), temperature (30°C), agitation (100 rpm), type of system (open)-

aerobic, and ratio 3:1 (wastewater/activated sludge). Cyanide removal was also optimized from wastewater by RSM method where the optimum removal was 95.07% [19]. Also, cyanide was removed by 93% using simultaneous absorption and biotreatment process from cyanide-containing aqueous solutions [20].

# 3.3.3. Analysis of Variance (ANOVA) For Cyanide Removal

Table 4 shows the ANOVA analysis of cyanide removal (%) using activated sludge. The regression model was highly significant as the p-value was 0.001. The p-value of main effects; temperature (B), types of system (D) and ratio WW/AS (E) were smaller than 0.05 implies the significance of the independent factors but the p value was greater than 0.05 for the retention time and agitation stating that they are not significant in cyanide removal.



Source	Sum	df	Mean	F Value	p-value
	of Squares		Square		Prob > F
Model	11210.58	10	1121.06	27.49	0.001
A-RT	68.27	1	68.27	1.67	0.2523
В-					
Temperature	2164.34	1	2164.34	2164.34	0.0008
C-Agitation	1591.81	1	1591.81	1	1
D-Types of	f				
System	1479.75	1	1479.75	36.28	0.0018
E-Ratio					
WW/AS	621.88	1	621.88	621.88	0.0114
AB	3350.38	1.	3350.38	3350.38	0.0003
AC	528.2	L	528.2	12.95	0.0156
BD	311.08	1	311.08	7.63	0.0398
BE	602.58	1	602.58	14.77	0.0121
CE	492.29	1	492.29	12.07	0.0178
Residual	203.92	5	40.78		

Table 4. ANOVA Analysis of cyanide removal

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Cor Total	11414.5	15
R <sup>2</sup>	0.9821	
Adjusted R <sup>2</sup>	0.9464	

It is necessary to examine any interactions that are important in the experimental design analysis; the 2-way interactions of all the factors experimented are significant at 95% confidence level (p<0.05). The coefficients of variance;  $R^2$  and adjusted  $R^2$ , are 0.9821 and 0.9464, respectively showing the goodness of fit of the model is highly accurate.

# 3.3.4. Main Effect and Interaction Effect between Factors on Cyanide Removal

Table 5 and Pareto Chart in Figure 1 shows percentages contribution for both effects and the main effects and interaction effects of the factors for the cyanide removal.

Term	% Contribution
В	18.96
С	13.95
D	12.96
AB	29.35
BE	5.28
AC	4.63
CE	4.31
<u> </u>	

Table 5. Contribution percentages for selected single and interaction effect for cyanide removal

For the main effect, it showed that temperature factor (B) gave the highest contribution for cyanide removal followed by agitation factor (C) and types of system (D).



Figure 1. Chart of contribution of independent and interaction effect to cyanide removal

For interaction effects, it showed that there were four negative interaction effects that contributed to the removal of cyanide (Figure 1). Negative effects referred to increase of cyanide removal as the value of factors decreased. There highest interaction effects were the interaction of temperature and RT (AB) followed by interaction of temperature and ratio WW/AS (BE), the interaction of RT and agitation (AC) and interaction of agitation and ratio WW/AS (CE) (Table 5).

# 3.3.5. Effect of Independent Processing Parameters on Cyanide Removal

Cyanide removal increased with increasing of agitation rate. The cyanide removal achieved 90.2% at 100 rpm and 80.2% at 0 rpm. It also showed there was a small significant difference of cyanide removal between 0 rpm and 100 rpm of agitation.

At temperature 30°C, cyanide removal achieved 79.3% but at temperature, 37°C achieved 60.2%. It showed that higher cyanide removal was achieved at ambient temperature, 30°C. It also showed that there was a highly significant difference of cyanide removal at both temperatures.

In the open system 79.1% of cyanide was removed while in the closed system, cyanide removal achieved was 70.3%. There were the small significant difference between an open system and closed system for cyanide removal.

3.3.6. Interaction Effects between Factors on Cyanide Removal

Figure 3a shows the interaction effect between temperature and different RT on cyanide removal at certain conditions. Other conditions were kept constant; WW/AS ratio at 3:1, no agitation, and use of the open system. Figure 3a illustrates that at 30°C high cyanide removal was achieved and lower cyanide removal observed at 30°C and higher RT (32 h). At lower RT (17 h), cyanide removal at 30°C and 37°C were approximately equal.

Figure 3b shows the interaction effect between temperatures and WW/AS ratio on cyanide removal. The best condition for other factors were set by Design expert; agitation at 100 rpm, RT at 24 h and used the open system. The figure 3b showed that the cyanide removal with ratio WW/AS 1:1 was nil and cyanide removal decreased at ratio 3:1 and at 37°C.

Figure 3c, shows the interaction effect between RT and agitation on cyanide removal. It showed that cyanide removal increased as the RT increased with both agitation condition applied.

Figure 3d showed the interaction effect between agitation and different ratio WW/AS on cyanide removal. It showed the significant difference on cyanide removal at different ratio WW/AS within the agitation. From the Figure 3d, cyanide removal increased with the ratio WW/AS of 1:1 while cyanide removal remained the same at ratio WW/AS of 3:1. This is due to the low volume of wastewater to the volume of activated sludge at 1:1 ratio.



Figure 3a. Interaction effect between temperatures and ratio WW/AS temperature and different RT





Figure 3d. Interaction effect between agitation and different ratio WW/AS

Figure 3c. Interaction effect between RT and agitation

Figure 3 a, b, c, d. Interaction effect between factors; temperature vs RT (a), temperature vs ratio (WW/AS) (b), RT vs agitation (c), and agitation vs ratio (WW/AS) (d).

### 4. Conclusion

A 2<sup>4</sup> fractional factorial design was conducted and 16 experimental runs based on it was conducted using five factors; ratio WW/AS, type of system, temperature, agitation, and RT to investigate their effects on cyanide removal (%). The cyanide removal (%) within these 16 experiments ranged from 8 to 95.45%. Temperature (B) gave the highest contribution for cyanide. The highest interaction effects found were the interaction of temperature and RT (AB) followed by interaction of temperature and ratio WW/AS (BE), the interaction of RT and agitation (AC) and interaction of agitation and ratio WW/AS (CE). Therefore, With the use of activated sludge optimum cyanide removal from wastewater of petrochemical industry was 95.45% at optimum variable conditions of retention time (32 h), temperature (30°C), agitation (100 rpm), type of system (open)- aerobic, and ratio 3:1 (wastewater/activated sludge).

## **Acknowledgements**

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24