WASTE TO WEALTH PROJECT WITH MERCU RESOLUTION

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ABSTRACT

Waste generation involves serious environmental pollution and degradation which consequently increased the environmental costs for its collection, treatment and disposal. Thus, the call for environmentally and economically sustainable growth is set out loud and simple. The present and future generations must therefore ensure that all resources are conserved, fully utilized and well managed. Various waste has been explored in this research such as municipal solid waste, fish waste and food waste. These wastes were utilized to become valuable resources and at the same time to reduce waste production. A total of seven studies have been done including biological degradation of municipal solid waste using mixed culture, production of biofertilizer using landfill leachate, oil extraction for a production of fatty acid from fish waste, fish feed production from fish waste, process simulation of anaerobic digestion process for biogas production from food waste, adsorbent from landfill sludge and finally, microwave irradiation and wet rendering to improve torrefaction of food waste. In conclusion, this research has successfully turned waste into wealth which later can be used for better future.

Keywords: Municipal solid waste(MSW), fish waste, leachate, anaerobic digestion, simulation, microwave irridiation

ABSTRAK

Penjanaan sampah melibatkan pencemaran alam sekitar yang serius dan seterusnya meningkatkan kos persekitaran untuk pengumpulan, rawatan dan pembuangannya. Oleh itu, permintaan untuk pertumbuhan yang mampan dari segi persekitaran dan ekonomi dinyatakan dengan tegas. Generasi masa kini dan masa depan mesti memastikan bahawa semua sumber terpelihara, digunakan sepenuhnya dan diurus dengan baik. Pelbagai sampah telah diterokai dalam penyelidikan ini seperti sisa pepejal bandar, sisa ikan dan sisa makanan. Bahan buangan ini digunakan untuk menjadi sumber yang berharga dan pada masa yang sama untuk mengurangkan pengeluaran sampah. Sebanyak tujuh kajian telah dilakukan termasuk degradasi biologi sisa pepejal perbandaran menggunakan mikrob campuran, penghasilan baja organik menggunakan cecair pelupusan sampah, pengekstrakan minyak untuk pengeluaran asid lemak dari sisa ikan, pengeluaran makanan ikan dari sisa ikan, proses simulasi proses pencernaan anaerobik untuk pengeluaran biogas dari sisa makanan, pencerap dari lumpur pelupusan sampah dan penyinaran gelombang mikro dan rendering basah untuk meningkatkan tindak balas sisa makanan . Sebagai kesimpulan, penyelidikan ini berjaya mengubah sampah menjadi kekayaan yang kemudian dapat digunakan untuk masa depan yang lebih baik.

Kata kunci: Sisa pepejal, Sisa ikan, Sisa cairan pelumpusan sampah, Pencernaan anaerob, simulasi, sinar gelombang mikro

TABLE OF CONTENT

LIST OF SYMBOLS

%	percentage
°C	Celcius
mm	millimetre
g	gram
mL	millilitre
L	litre
M	moles of solute per litre of solution
mL/min	millilitre per minute
µL	microlitre
nm	nanometre
mg/L	Milligram per litre
g/100g	gram per 100 gram
mg/g	milligram per gram
h	hour
M	molarity
W	watt

LIST OF ABBREVIATION

MSW	Municipal solid waste
PET	Polyethelene trephthelate
HRT	Hydraulic rentention time
COD	Chemical oxygen demand
TS	Total solid
K	Potassium
P	Phosphorus
N	Nitrate
FAME	Fatty acid methyl esters
SEM	Scanning electron microscopy
EDX	Energy dispersive X-ray spectrometer
TGA	Thermogravimetric analysis
FTIR	Fourier transform infrared spectroscopy
TGA	Thermogravimetric analysis
AD	Anaerobic digestion
NRTL	Non-random two liquid
VFA	Volatile fatty acid
LCFA	Long chain fatty acid
CSTR	Continuous stir tank reactor
RSM	Response Surface Methodology

CHAPTER 1

INTRODUCTION

1.1 Background

The 'Waste to Wealth' project lead by Dr Azilah Ajit with Mercu Re Solution Sdn Bhd is focusing to develop the renewable energy from waste materials. Mercu RE Solution Sdn. Bhd. (Mercu RE Solution) is a fully-owned Bumiputera company and incorporated on 8th May 2015 with a paid-up capital of RM 400,000.00. Mercu signed a Memorandum of Understanding (MoU) with Faculty of Chemical & Natural Resources Engineering (FKKSA), Universiti Malaysia Pahang (UMP) to expand cooperation to produce renewable energy from waste materials. This project has had received RM 15,000 for the seed grant money to carry out the research related renewable energy from rubbish and the project has parked and coordinated under Bioprocess and Biosystems Engineering Cluster FKKSA, UMP.

The list project that involved in this research are:

1. Biological degradation of municipal solid waste using mixed culture

2. Production of biofertilizer using landfill leachate

3. Oil extraction for a production of fatty acid from fish waste

4. Fish feed production from fish waste

5. Process simulation of anaerobic digestion process for biogas production from food waste.

6. Adsorbent from activated landfill sludge

7. Microwave irradiation and wet rendering improve torrefaction of food waste

The list of members involved in this project are listed as below:

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17. Dr. Noor Ida Amalina Binti Ahamad Nordin
18. Dr. Nur Hidayah Binti Mat Yasin
19. Dr. Noor Asma Fazli Bin Abdul Samad
20. Dr. Farhan Binti Mohd Said

1.2 Problem Statement

Resources are depleting from years to years and more worse, waste generation are also increasing with a continued population growth in the years to come. Waste generation has become one of the most alarming issues that the world is facing at the moment where 2 billion tonnes of waste generation per year has been reported. In Malaysia, an average of 1.64 kg of solid waste generated per day which is higher than the average generation of 1.2 kg per person worldwide (Jaafar et al., 2018). Thus, in the near future, more solutions are definitely needed in order to tackle this issue effectively. By finding solutions that can turn waste to wealth, not only will save the environment but also benefit financially as businesses and economies are able to grow with minimal used of natural resources. This research is developed to explore the possibilities of turning waste into valuable resources (wealth) in Malaysia.

1.3 Objective

The objective of this research is:

1. To develop the renewable energy from various waste materials

1.4 Scopes of study

The scope of this study is focusing on how to utilize various waste materials and convert it to valuable resources. Six studies were conducted to fulfil the objective requirement.

CHAPTER 2:

BIOLOGICAL DEGRADATION OF MUNICIPAL SOLID WASTE USING MIXED CULTURE

PROJECT LEADER: ASSOC. PROF. IR. DR. NORAZWINA BINTI ZAINOL

2.1 Abstract

This report provides a factorial analysis study, optimization and kinetic study of the COD production from Municipal Solid Waste (MSW). Methods of analysis include sample collection, substrates preparation, acclimatization process, preliminary study of 5 factors which are pH, temperature, ratio of AMC and substrates, specimen size and Hydraulic Retention Time (HRT) and lastly is the experimental study by using factorial analysis, optimization and kinetic study. Result of data analyzed show that the result of COD production which in term of COD increment (Final COD / Initial COD). This report finds the major factor that give highest contribution in COD production by using Design Expert Software. From the result in factorial analysis, we can see that single factor of temperature gives the highest contribution in COD production of MSW. Lastly, validation run has been done for the confirmation of the factor and range for the COD production from MSW. Besides that, the analysis factors in optimization have been performed to identify the optimum condition of design factor that has large effects for the concentration of COD. There were two factors involved in this study. The factors were hydraulic retention time (HRT) and temperature. These factors were analyzed and optimized by using Design Expert software to determine the optimum condition to get high concentration of COD. As for the kinetic study the equation for the calculation are found in a journal and the constant of the equation are determined. In this experiment, the COD and Total solid (TS) data are taken to know the growth rate of the AMC. TS are the weight of the AMC after each hour the experiment are done.

2.2 Introduction

The purpose of this project is to determine the ability of the mixed culture to degrade the organic waste and plastics (PET) of MSW. Along with the increasing of population in Malaysia, the MSW generate will also increase. Thus, there needs to processing the MSW that have been generate to become valuable resources. In this study, the mixed culture needed to be acclimatize into a new habitat, then the experimental study can be proceeded.

2.2.1 Objectives

1) To utilize mixed culture from landfill area for production on high COD bio-liquid from municipal solid waste.
2) To optimize the production on high COD of bio-liquid from municipal solid waste by using mixed culture.

2.2.2 Scopes of study

In this research study, the scopes were functioning as a guideline to achieve the objectives. As mixed culture naturally acclimatize with municipal solid waste in landfill area. The optimum condition for reaction must be determined to get high concentration of COD from the conducted experiment. The experiment has been conducted to extract the data collect in the experiment by using equation found. In preliminary study, the experiments are done by five factors. The factors are pH, temperature, ratio, specimen size and HRT. The scopes of the research are:

1. Sample collection of soil, organic waste and PET plastic from landfill Kg. Sg. Ikan, Kuala Terengganu
2. Substrate preparation by using 1:3 of organic waste and water and addition 1 cm x 1 cm of PET plastics.
3. Acclimatization process of soil mixed culture from landfill and MSW.
4. Preliminary study of 5 factors that affect the biodegradation.
    - Factors: pH, Temperature, Ratio of AMC and substrate, Specimen size, and Hydraulic Retention Time (HRT)
5. Experimental study on factorial analysis, optimization and kinetic study

2.3 Methodology

2.3.1 Preparation of organic substrate for acclimatization of soil mixed culture

The mixture of 9L of water and 3L of organic waste was known as substrates. The new substrates prepared at second week of acclimatization process which is at day 8th of the acclimatization process. Plastic and cellulosic wastes was added in the reactor for the preparation of substrates.

2.3.2 Preparation of organic substrate for preliminary study and optimization

The mixture of 9L of water and 3L of organic waste was known as substrates. The new substrates were prepared a day before the experiments were conducted. Plastic and cellulosic wastes were added in the reactor for the preparation of substrates.

2.3.3 Acclimatization of soil mixed culture

The organic waste was mixed with water with the volume ratio of 1:3 and also known as substrates. Substrate was the mixture of organic waste, water and plastic. The substrates were mixed with the SMC and the COD level was determined. This process was performed daily for two weeks. After acclimatization process, the SMC will be changed to acclimatized mixed culture (AMC). The acclimatization process was undergoing in working volume of 8L acclimatization reactors. Firstly, 1L of SMC was poured into the reactor. Then, 500mL of substrates poured into the reactor to be mixed with the SMC. The reactor was shaken to make sure the SMC well mixed with substrates. After 24 hours, 50mL was extracted to calculate the COD data from acclimatization process. Then, 2mL of samples was diluted with deionized water. The calculation of dilution factor is shown in Equation 1.

$$\frac{Final\ Volume}{Sample\ Volume} = Dilution\ Factor \qquad \text{(Equation 1)}$$

After that, another 500mL of substrates was added in the reactor. The steps was repeated daily for 14 days. The acclimatization process can be shown as in schematic diagram Figure 1 and the procedures as in Figure 2.

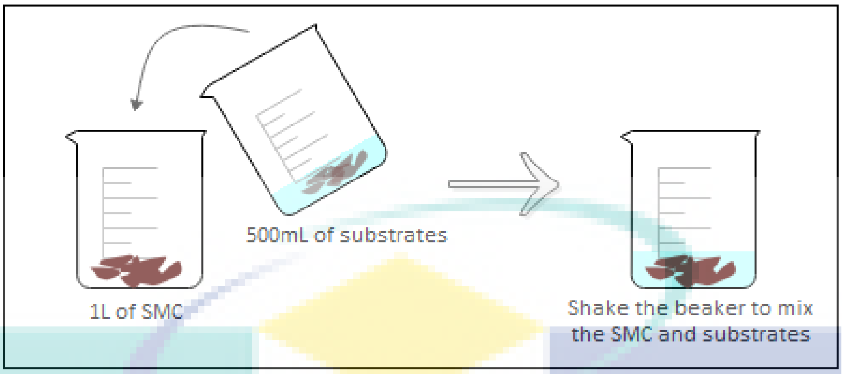
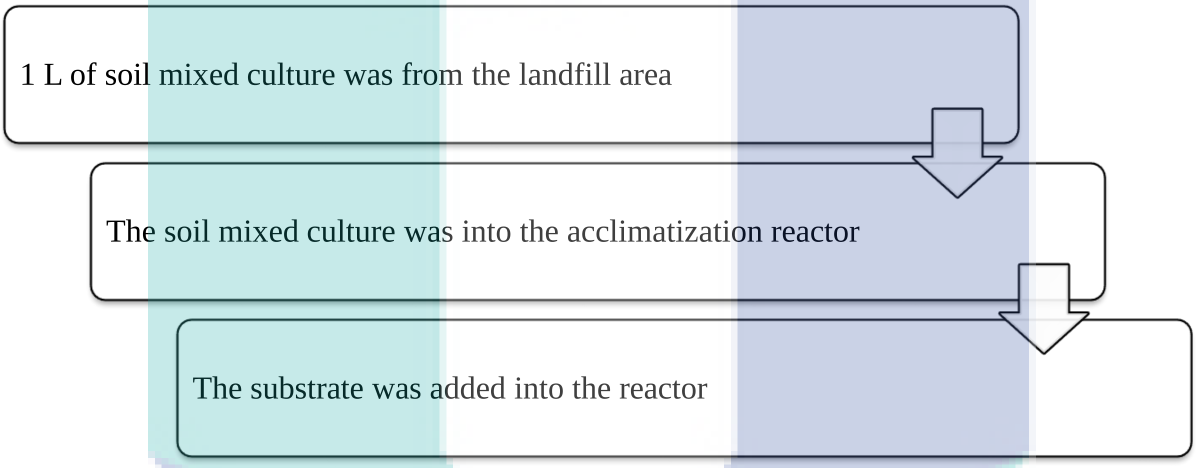


Figure 1: Acclimatization process


1 L of soil mixed culture was from the landfill area

The soil mixed culture was into the acclimatization reactor

The substrate was added into the reactor

Figure 2: Acclimatization of soil mixed culture procedure

2.3.4 Preliminary study

2.3.4.1 Preliminary study 1: Temperature

There were two different of temperature tested which were ambient temperature as shown on Figure 3 and 35°C (Optimization) or 37°C (Factorial analysis and Kinetic study) as shown in Figure 4. Figure 5 showed the experimental setup for preliminary study 1. Based on Figure 4, the sample was set at 35°C or 37°C in the incubator and the other sample was set at the ambient temperature. Fixed condition for preliminary study 1 were ratio of 1:5 of AMC and substrates, pH of 5, and 24 hours reaction time. After that, the initial and final readings for both temperatures of COD were taken to determine the COD production.

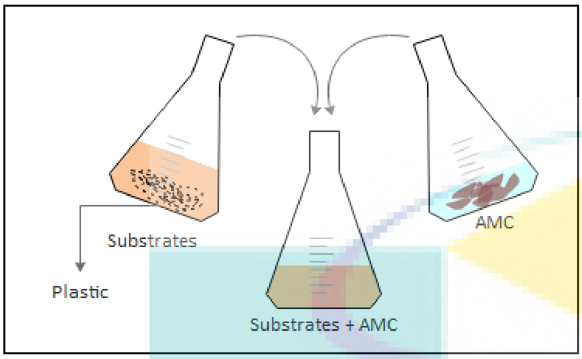


Figure 3: Temperature of ambient

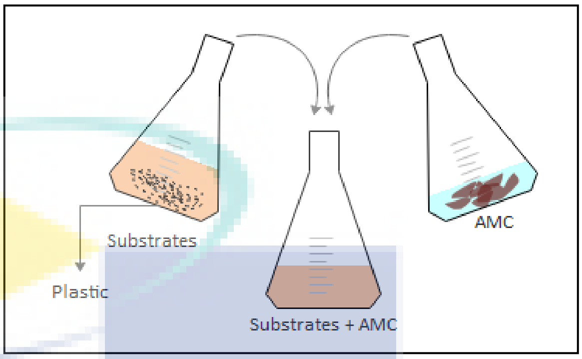
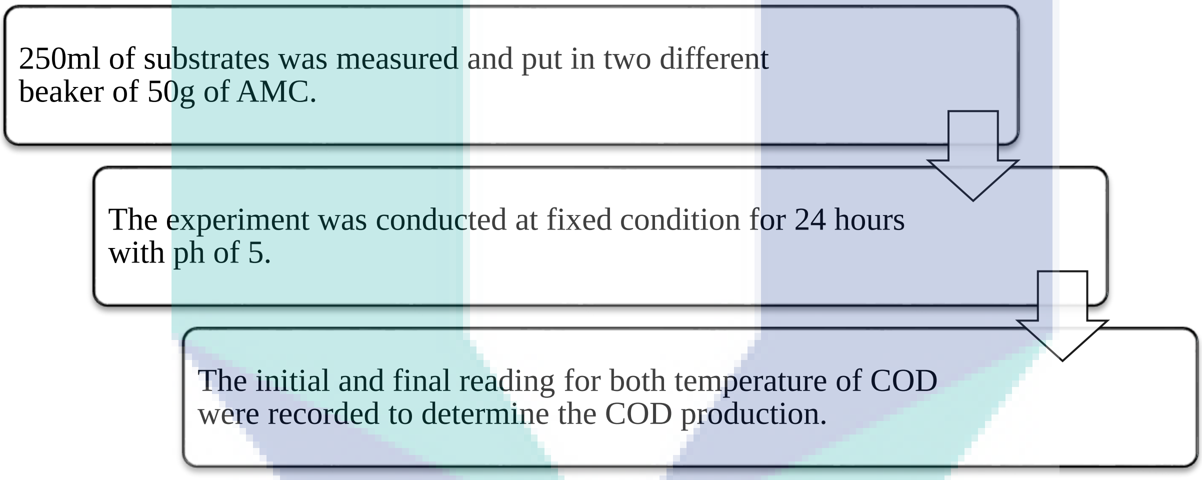


Figure 4: Temperature of 35^{o}C / 37^{o}C



250ml of substrates was measured and put in two different beaker of 50g of AMC.

The experiment was conducted at fixed condition for 24 hours with ph of 5.

The initial and final reading for both temperature of COD were recorded to determine the COD production.

Figure 5: Temperature flowchart

2.3.4.2 Preliminary study 2: Ratio of AMC and substrates

There were two different ratio of AMC and substrates were tested which are ratio of 1:2 and 1:5. Figure 25 showed the experimental setup for preliminary study 2. For ratio 1:2, 100g of AMC and 200ml of substrates were used in Figure 6. For ratio 1:5, 50g of SMC and 250 substrates were used. Fixed condition for preliminary study 1 was pH of 5, 1cm x 1cm of specimen size, room temperature and 24 hours reaction time. After that, the initial and final readings for both ratios of COD were taken to determine the COD increment.

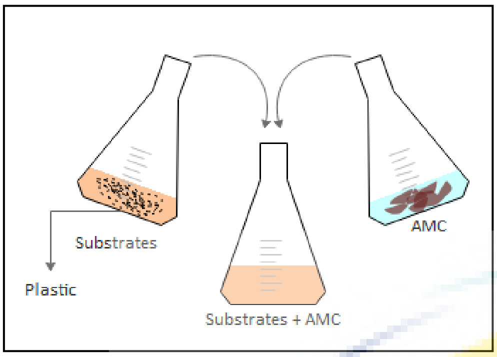


Figure 6: Ratio of 1:2

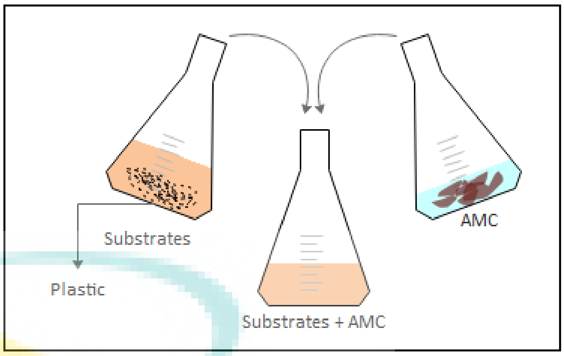
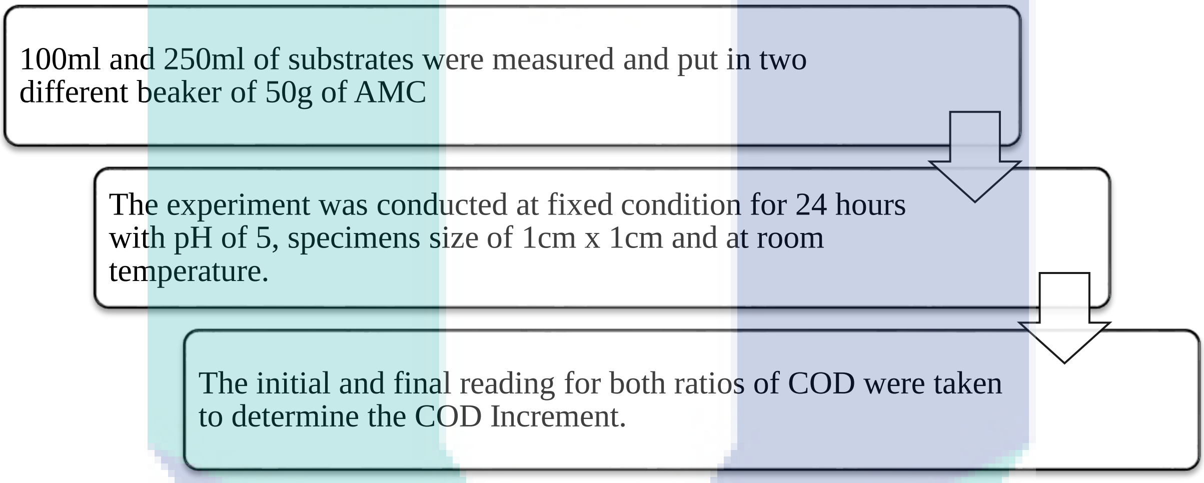


Figure 7: Ratio of 1:5



100ml and 250ml of substrates were measured and put in two different beaker of 50g of AMC

The experiment was conducted at fixed condition for 24 hours with pH of 5, specimens size of 1cm x 1cm and at room temperature.

The initial and final reading for both ratios of COD were taken to determine the COD Increment.

Figure 8: Ratio flowchart

2.3.4.3 Preliminary study 3: pH

There were two different pH tested which were pH of 5 as shown in Figure 9 and pH of 9 as shown in Figure 10. Figured 11 showed the experimental setup for preliminary study 3. Fixed condition for preliminary study 3 were ratio of 1:5 of AMC and substrates, temperature of 25°C, 1cm^2 of specimen size and 24 hours reaction time. After that, the initial and final readings for both pH of COD were taken by using pH paper to determine the COD increment.

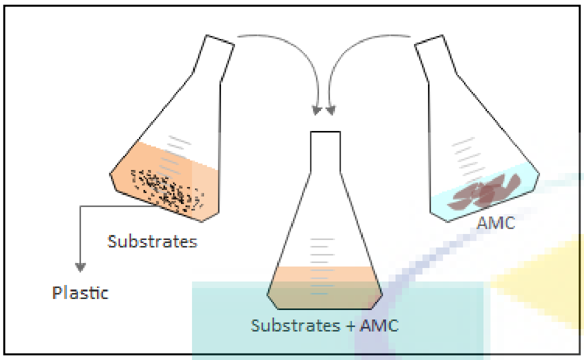


Figure 9: pH of 5

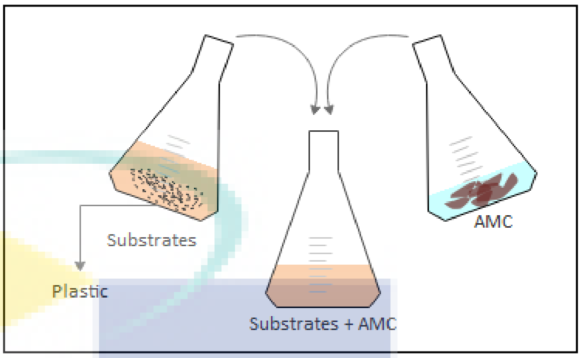
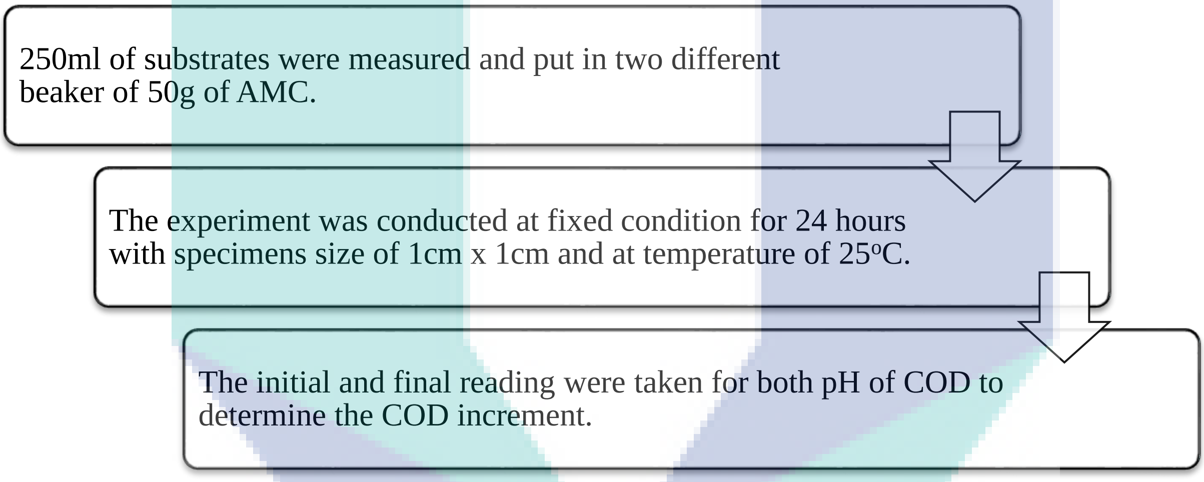


Figure 10: pH of 9



250ml of substrates were measured and put in two different beaker of 50g of AMC.

The experiment was conducted at fixed condition for 24 hours with specimens size of 1cm x 1cm and at temperature of 25°C.

The initial and final reading were taken for both pH of COD to determine the COD increment.

Figure 110: pH flowchart

2.3.4.4 Preliminary study 4: Specimen size

There were two different of specimen size of plastic were tested which are 1cm^2 and 4cm^2. Figure 12 and Figure 13 showed the experimental setup for preliminary study 4. Fixed condition for preliminary study 4 were ratio of 1:5 of AMC and substrates, pH of 5, temperature of 25°C and 24 hours reaction time. After that, the initial and final readings for both specimen sizes of COD were taken to determine the COD increment.

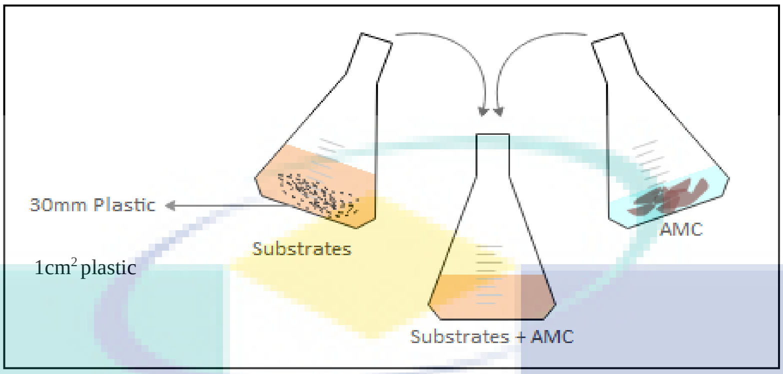


Figure 12: $1cm^2$ of specimen size

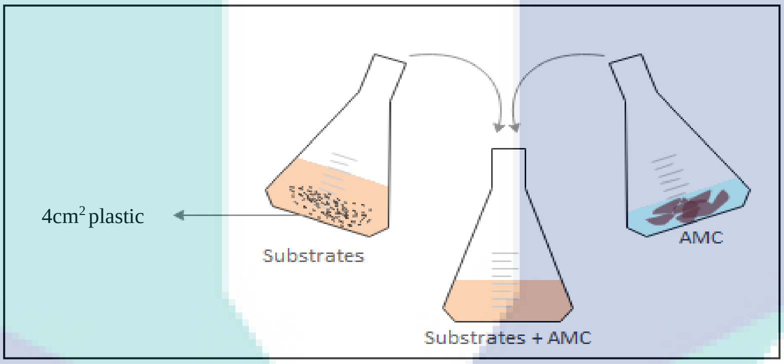
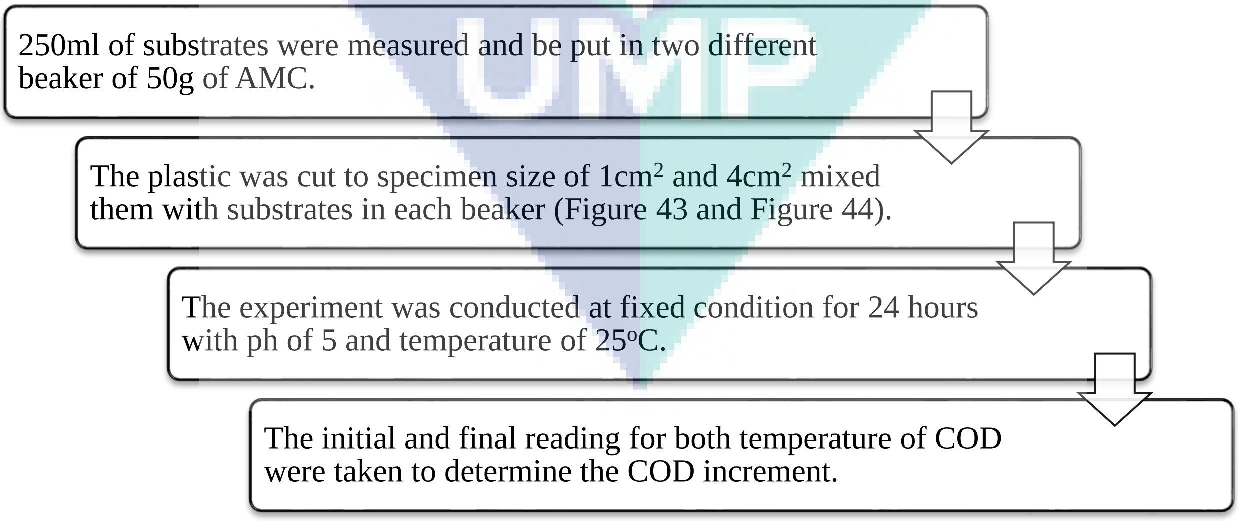


Figure 13: $4cm^2$ of specimen size



250ml of substrates were measured and be put in two different beaker of 50g of AMC.

The plastic was cut to specimen size of $1cm^2$ and $4cm^2$ mixed them with substrates in each beaker (Figure 43 and Figure 44).

The experiment was conducted at fixed condition for 24 hours with ph of 5 and temperature of 25°C.

The initial and final reading for both temperature of COD were taken to determine the COD increment.

Figure 14: Specimen Size flowchart

2.3.4.5 Preliminary study 5: Hydraulic Retention Time (HRT)

Figure 15 show the set-up for preliminary study 5. The factor tested was Hydraulic Retention Time (HRT) as shown in Figure 16. There were 6 retention times that were tested to find best time for COD production. Production of COD was obtained at 0 hour, 2 hour, 4 hour, 6 hour, 8 hour, 10 hour and 24 hour. In this preliminary study 2, fixed condition were ratios of 1:5 of AMC and substrates, pH of 5, and ambient temperature.

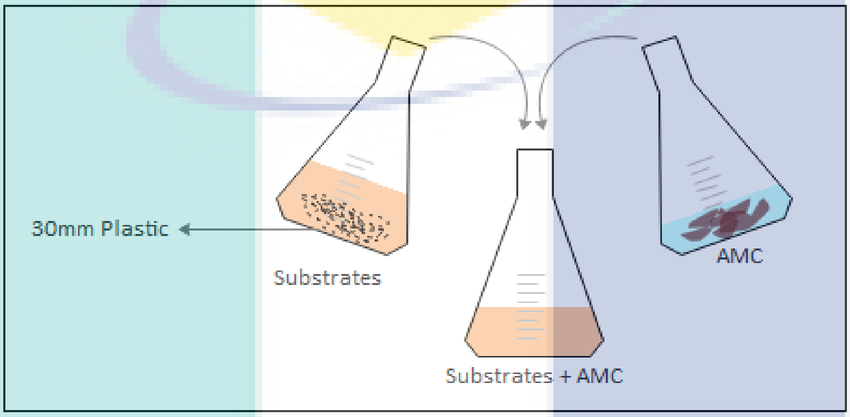
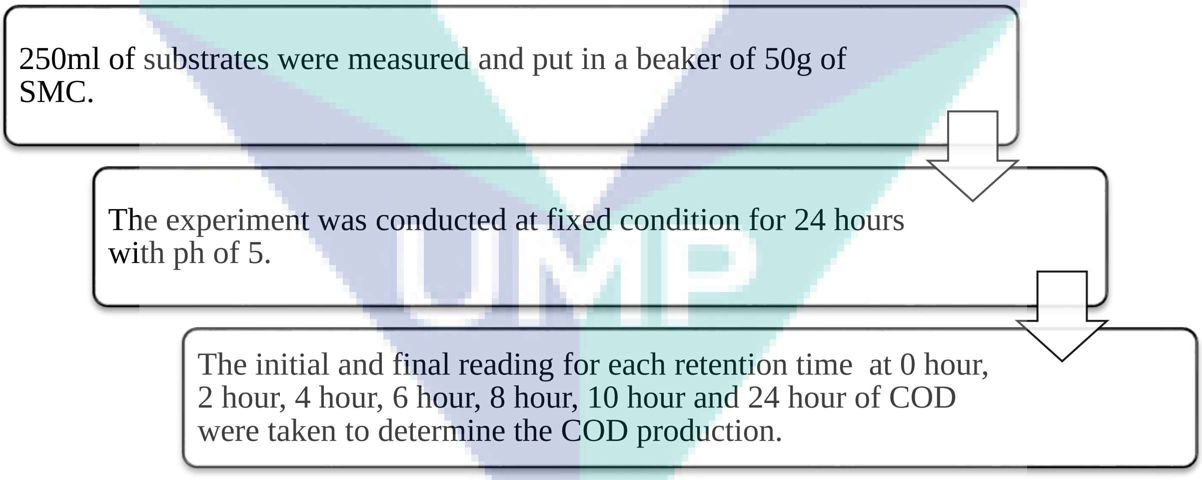


Figure 15: HRT experimental set-up



250ml of substrates were measured and put in a beaker of 50g of SMC.

The experiment was conducted at fixed condition for 24 hours with ph of 5.

The initial and final reading for each retention time at 0 hour, 2 hour, 4 hour, 6 hour, 8 hour, 10 hour and 24 hour of COD were taken to determine the COD production.

Figure 16: HRT flowchart

2.3.5 Experimental study

2.3.5.1 Factorial analysis

There are five factors involve in this study as shown in Table 1. The factors are ratio of SMC and organic waste, pH, temperature, specimen size and Hydraulic Retention Time (HRT). The design of experiment was performed by Design Expert software where all factors will be randomized. Shake flask method was applied to study the reaction between substrates and AMC. The mixture of AMC and substrates were reacted at certain retention time as shown in Figure 17. Besides that, analysis factors were performed in this study to identify the design factors that have large effects for the experiment. Experiment was conducted according to set-up in Design Expert software. Later, experimental data was analyzed and optimized using Design Expert software to determine the most contributing factor and interaction between factors.

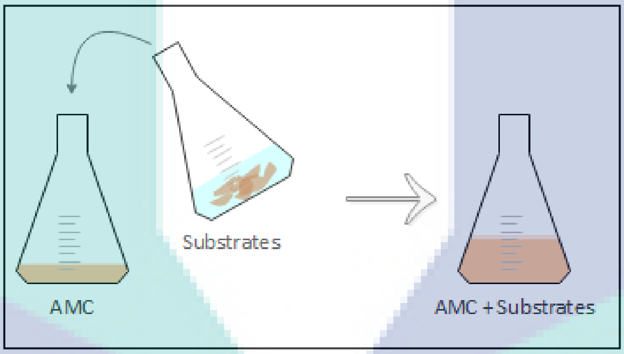


Figure 17: Mixture of AMC and substrates

Table 1: Ranges for screening

Factors	Ranges
Ratio of AMC and Substrates	1:2 and 1:5
pH	Initial and Adjusted (7)
Temperature	Room Temperature and 37^{o}C
Specimen Size	1cm^2 and 4cm^2
HRT	3 hours and 9 hours

2.3.5.2 Optimization

Soil mixed culture used in the optimization experiment was obtained from Kampung Sg. Ikan, Kuala Terengganu, Malaysia. The soil mixed culture was acclimatized for two weeks with the substrate that contain organic waste, water and pieces of PET plastics. 1L of soil mixed culture was put into the reactor and 500mL of substrate were poured into the reactor. The reactor was leave at ambient temperature at UMP laboratory. The mixture of ratio 1:3 of organic waste was known as substrates. The new substrates were prepared a day before the experimental of optimization. Plastic and cellulosic wastes were added in the reactor for the preparation of substrates. The reactor was shaken to make sure the SMC well mixed with substrates. After 24 hours, 50mL was extracted from the acclimatization reactor and mixed with 250mL of substrate to calculate the COD data as shown in Figure 19. Then, 2mL of samples were diluted with deionized water. After that, another 500mL of substrates will be added in the reactor. The schematic diagram of acclimatization process is shown in Figure 18.

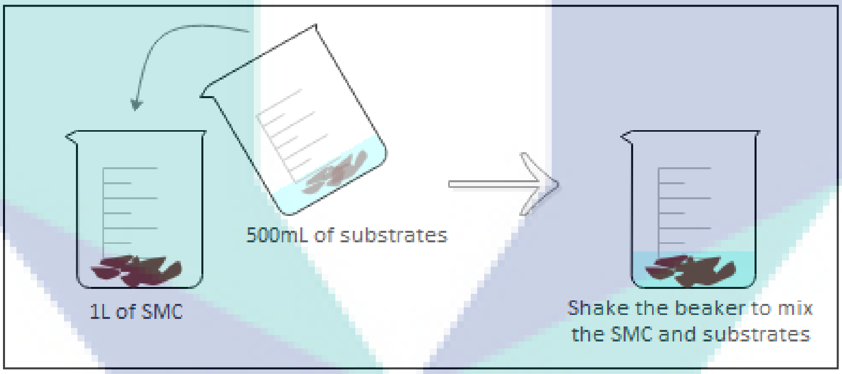


Figure 18: Schematic diagram for acclimatization process

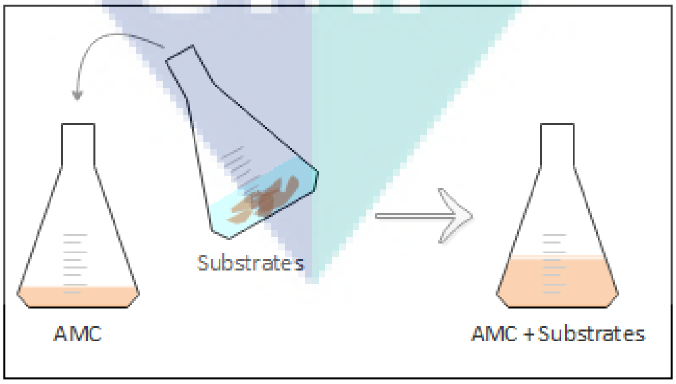


Figure 19: Schematic diagram for optimization experiment

The factors and range of the optimization experimental set-up was shown the Table 2 based on the result of preliminary study. The factors are ratio of SMC and organic waste, pH, temperature, specimen size and Hydraulic Retention Time (HRT). The design of experiment will be performed by Design Expert software where all factors will be randomized.

Table 2: Range of factors for optimization

Factors	**Ranges**
Temperature	25°C and 35°C
HRT	2 hours and 9 hours

2.3.5.3 Kinetic study

In this section, Kinetic Experiment was done to study the COD and the total solid (TS) of the AMC. There are five selected factors in this study. The factors were ratio, specimen size of plastic, pH, HRT and temperature. The preliminary data was taken to determine the parameter that will be used in this experiment as shown in Table 3.

Table 3: Selected parameter of the factors

Factors	Parameter
Temperature	37°C
pH	7
Ratio	1:5 AMC:Substrate
Specimen Size	1x1 cm
HRT	9 hours

Figure 20 showed the whole process to determine the TS of the sample collected. For the first step, filter paper was dried for 1 hour. The dried filter paper was weighed and 50 ml of sample was measured and filtered. Then, the suspended solid was dried in the oven for one hour. After one hour, the dried suspended solid was weighed.

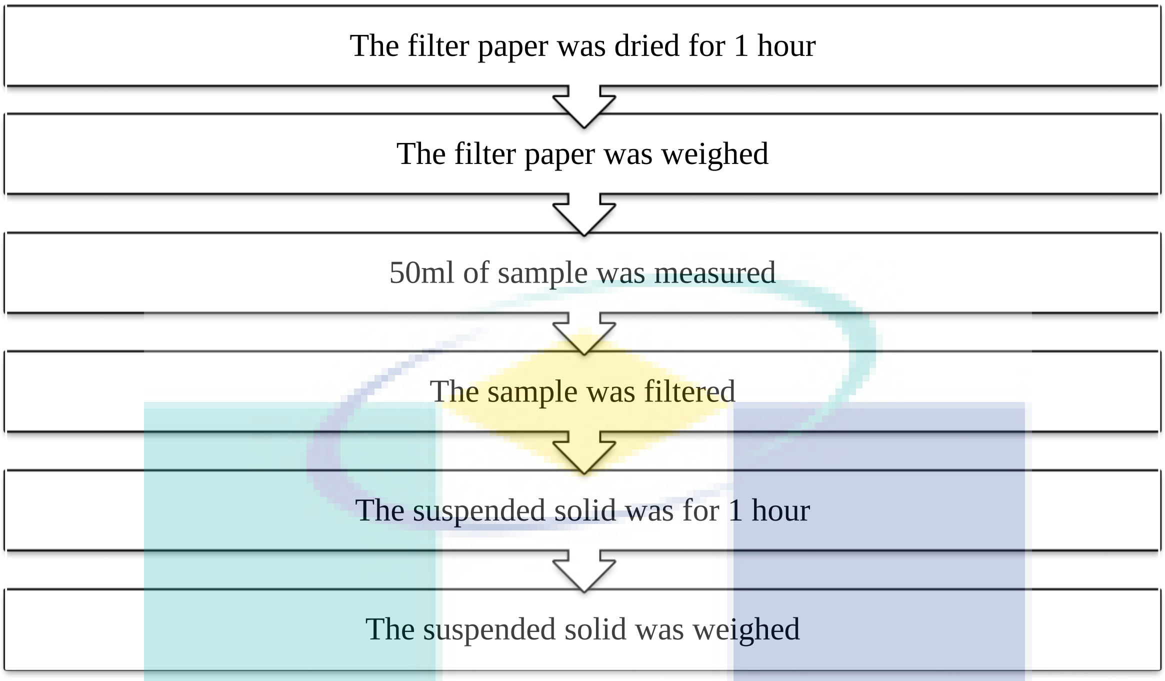


Figure 20: TS flowchart

2.4 Findings

2.4.1 Acclimatization process

From the result in 14 days, the COD concentration showed start increasing drastically from day 3 to day 7 as shown in Figure 21. This may occur because of the substrates added to the AMC was low strength organic waste. During weekend which was 5th and 6th day, the COD data was not taken because of laboratory in UMP was closed during weekend. At the 8th day, it start decreasing because of the substrates of high strength of organic waste was used and PET plastic was added in the sample. A few days after added of the high strength of organic waste and PET plastic, the COD data start increase steadily until day 10 and start decreasing back because of weekend.

Table 4: COD data from acclimatization process

Day	Reactor 1 (mg/L)	Reactor 2 (mg/L)	Reactor 3 (mg/L)
1- Tuesday			
2-Wednesday			
3- Thursday	45750	60275	31700
4- Friday	88100	64137	106287
5- Saturday			
6- Sunday			
7- Monday	26613	95920	182800
8- Tuesday	57493	46186	81173
9-Wednesday	38693	40960	40533
10- Thursday	49253	46000	51573
11- Friday	109146	119093	174693
12- Saturday			
13- Sunday			
14- Monday	32800	35520	69840

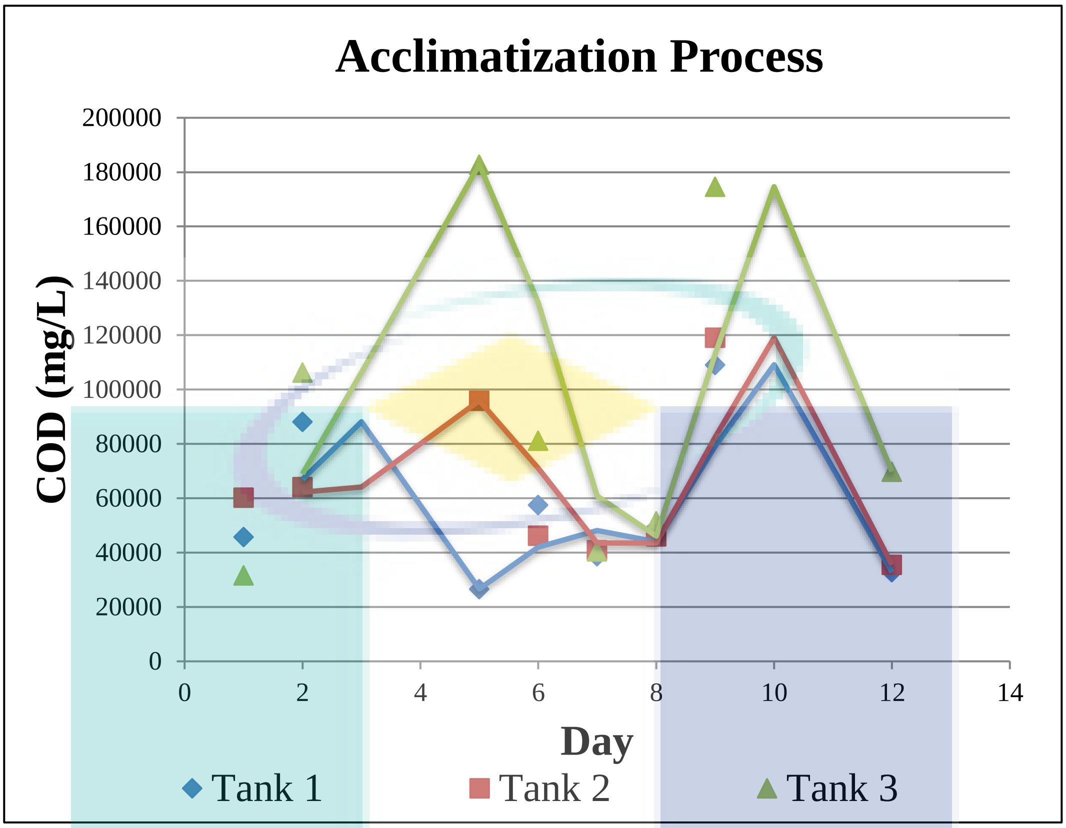


Figure 21: Acclimatization Process

Based on Table 4 the COD reading was firstly taken on day 3 of acclimatization process. The low strength of substrate was used to feed into the reactor for one week. Another week, the high strength of substrate was used to feed the mixed culture. The high strength of substrate is substrate with pieces of PET plastics inside it. The concentration of COD increased until day 7, yet it showed rapidly declined after the high strength of substrate was used from day 8 to day 10. At day 11, the COD concentration increased and dramatically declined until day 14. Due to the graph illustrated at Figure 21, the overall trend of acclimatization process showed a fluctuation trend due to the adaption of microorganisms to the organic substrate and plastics.

2.4.2 Preliminary study

2.4.2.1 Temperature (Factorial analysis and Kinetic study)

Table 5 showed the result of COD increment for preliminary study 1. There were significant differences of COD increment between both temperatures as shown in Figure 22. Based on this result, room temperature was used for the next preliminary study.

Table 5: COD data of preliminary study of temperature (Factorial analysis and Kinetic study)

Initial	**Tank 1**	**Tank 2**
Ambient	4.41	3.782
37°C	2.22	5.992

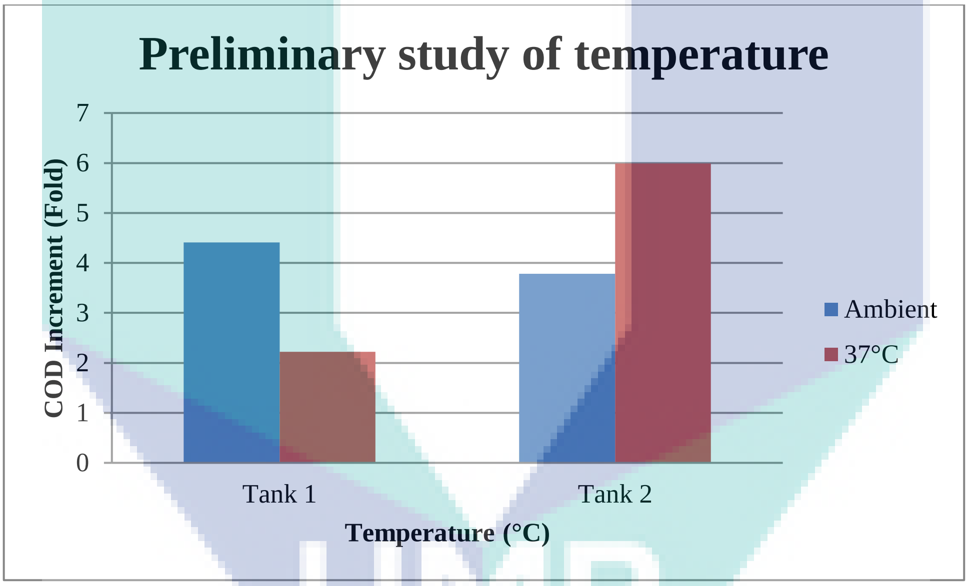


Figure 22: Graph of fold vs temperature

Figure 22 showed the graph of temperature between room temperature and at 37^{o}C. At Tank 1, it showed that COD increment at room temperature was 4.41 higher than at 37^{o}C which was 2.22. At room temperature of Tank 2, the AMC showed a lower metabolism rate at room temperature than temperature of 37^{o}C. The data collected showed a rather significant increase at temperature 37^{o}C with fold of 5.992, while at room temperature, the fold is 3.782. It had a same initial data because it starts at a same temperature. The difference of data between the final and initial at room temperature is 67600 mg/L, while at 37ºC is 121300 mg/L, that is double the amount at room temperature. The data showed that the AMC prefer more stable temperature or an optimum temperature for the AMC to be more active rather that at room temperature that can be unstable.

2.4.2.2 Temperature (Optimization)

Table 6 showed the COD data of preliminary study of temperature for optimization process (Tank 3).

Table 6: COD data of preliminary study of temperature (Optimization)

Temperature	**Initial**	**25°C**	**35°C**
COD (mg/L)	18000	216000	69900
Fold	-	12	3.8833

Figure 23 illustrated the COD increments (fold) between two different temperatures.

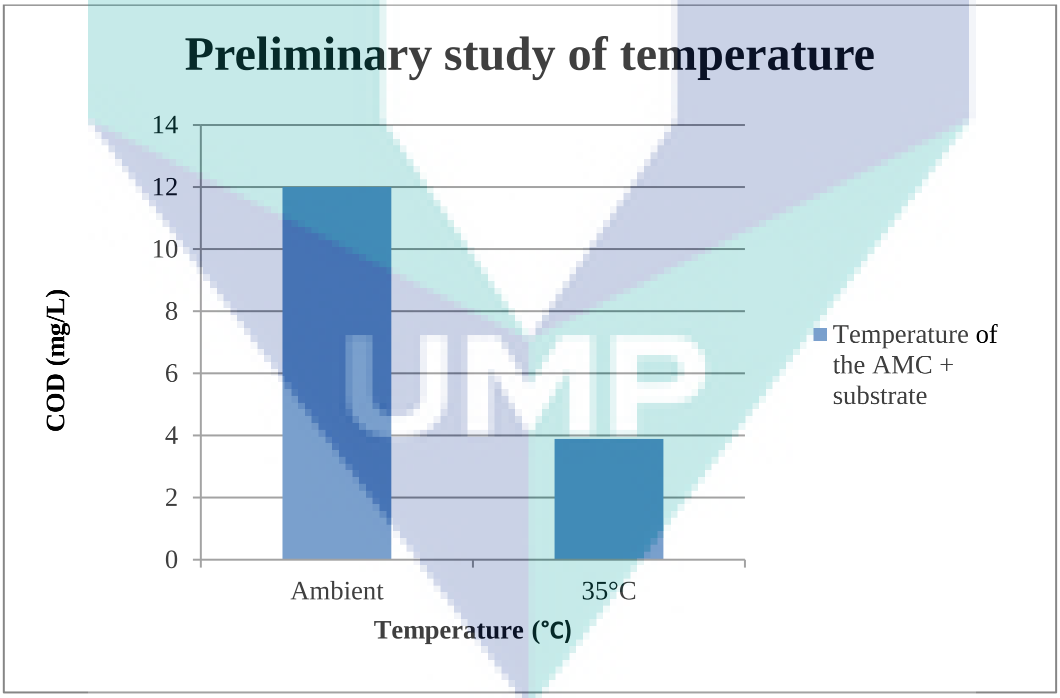


Figure 23: Graph of preliminary study on temperature

Based on Figure 23, both temperatures showed the improvement of COD reading. The increment of COD at ambient temperature is higher than temperature at 35°C. At ambient temperature, the increment of COD increase by 12, while the increment of COD at temperature of 35°C increase by 3.8833. This preliminary study illustrated that the reaction of mixed culture and substrate is higher at ambient temperature instead of temperature of 35°C. Due to high increment of COD reading at ambient temperature, the ambient temperature was chosen to perform next preliminary study.

2.4.2.3 Ratio of AMC and substrate

Table 7 showed the result of COD increment for preliminary study 1. Based on Figure 24, the increment of COD of ratio 1:5 was 1.91 higher than 1:2 ratios which were 1.86 at Tank 1. The chosen factor was ratio of 1:5 because of the difference in COD increment to perform next preliminary study.

Table 7: COD data of preliminary study of ratio of AMC and substrate

Ratio	Tank 1	Tank 2
1:02	1.86	0.735
1:05	1.91	1.741

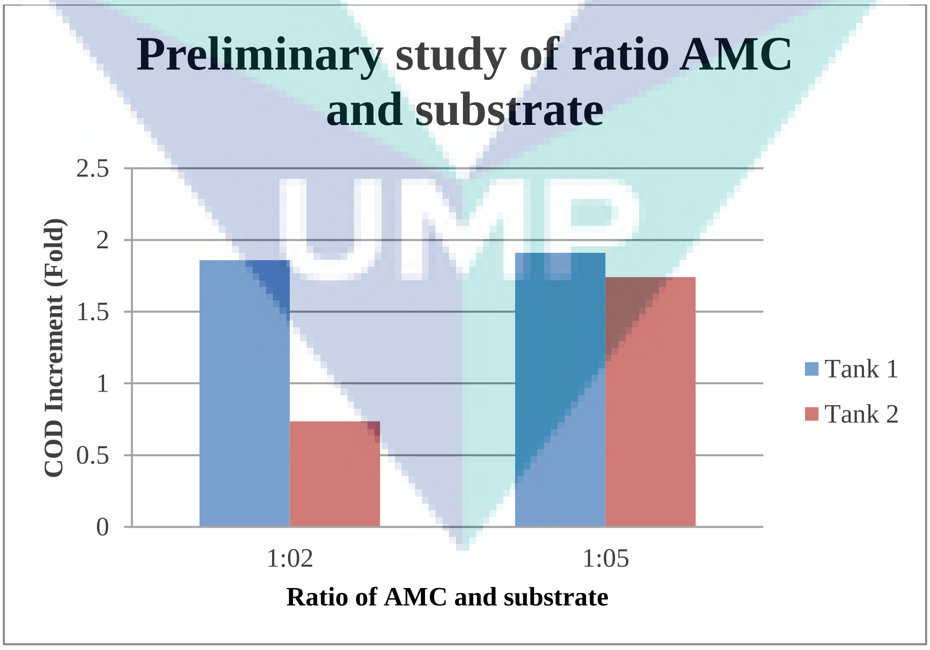


Figure 24: Graph of fold vs ratio of AMC and substrate

From the graph, it can be shown that on the ratio of 1:5 has a higher COD removal rather than at ratio 1:2. A higher COD level at ratio 1:5 can be explained by a higher amount of food, which is the substrate given to the AMC, while at ratio 1:2, the substrate given was lower causing lower COD level. The COD data at ratio 1:5 is about double the amount of COD at ratio 1:2 with a difference of 1.006. Given at the initial with ratio of 1:5, the COD measure was at an average of 50900 mg/L then increase to an average of 88600 mg/L with difference of 37700 mg/L. On the other hand, at ratio 1:2, the data collected showed a decreased in the COD reading with negative data of 39500 mg/L. As conclusion, the best ratio for the AMC is at ratio 1:5.

2.4.2.4 pH

Table 8 showed the result of COD increment for preliminary study 2. Based on Figure 25, it showed that COD increment at pH 9 was 4.28 higher from ph 5 which was 1.44 at Tank 1. While at Tank 2, it showed that COD increment at pH 9 was 2.698 higher from ph 5 which was 1.362. Due to the big difference in COD increment was 4.28 and 2.698 for Tank 1 and Tank 2 respectively, pH 5 was chosen for next preliminary study.

Table 8: COD data of preliminary study of pH

pH	Tank 1	Tank 2
5	1.44	1.362
9	4.28	2.698

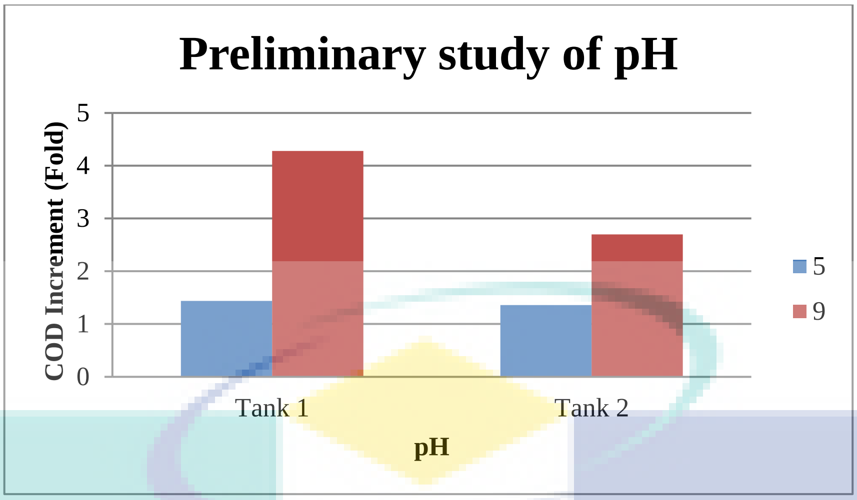


Figure 25: Graph of fold vs pH

From the graph, at pH 9 at Tank 2, the COD removal was greater than at pH 5. The difference of fold is about 1.336 that is double the amount of COD reading at pH 5 with reading of 1.362. While the difference of final and initial between the two pH are 29600 mg/L for pH 5 and 39900 mg/L for pH 9. Both of the data have showed an increasing trend with a higher increment at pH 9. As the data shown, it can be said that the AMC has more preferable at pH 9 or an alkaline solution to be living.

2.4.2.5 Specimen size

Table 9 showed the result of COD increment for preliminary study 4. Based on Figure 26, size of 1 cm^2 were 9.94 higher that size 2 cm^2 which was 4.70. Due to the difference in removal was 9.94, specimen size of 1 cm^2 was used for the next preliminary study.

Table 9: COD data of preliminary study of specimen size

Specimen Size	**Tank 1**	**Tank 2**
1 cm x 1 cm	9.94	1.478
1 cm x 2 cm	4.7	1.325

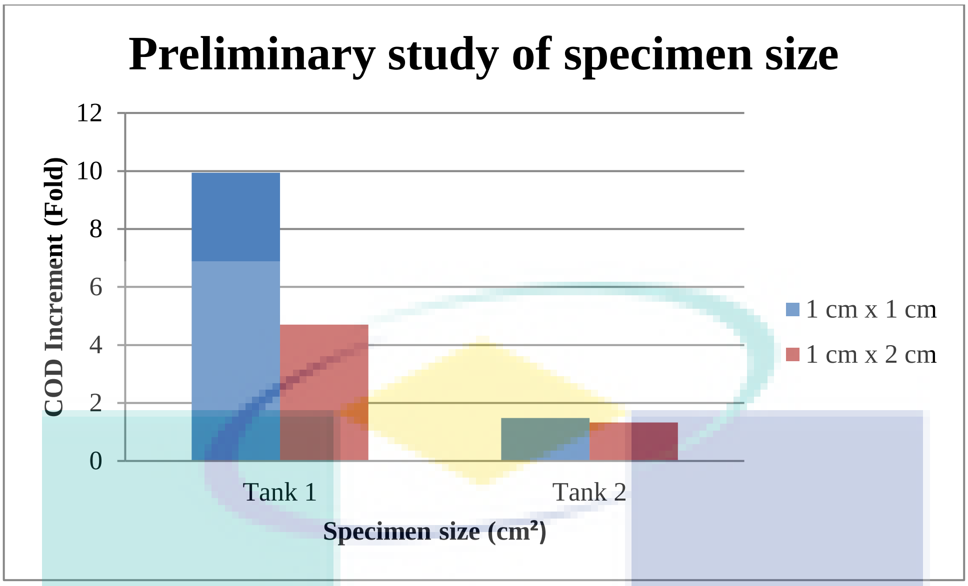


Figure 26: Graph of fold vs specimen size

The specimen size used in this study was 1x1cm and 1x2cm of PET plastic. The data showed between the two specimen sizes given a difference fold of 0.153 at Tank 2, which does not show a much of difference between the two specimen sizes. Although the fold did not have a significant difference, the data of specimen size of 1 cm x 2 cm has an increase of 26300 mg/L from the initial and an increase of 39600 mg/L from initial of 1 cm x 1 cm specimen size. The data can be explained that the AMC has preferred more on 1 cm x 1 cm of specimen size because it has a smaller surface.

2.4.2.6 Hydraulic retention time (HRT)

Table 10 showed the COD data of preliminary on hydraulic retention time (HRT) for Tank 1, Tank 2, and Tank 3. Figure 27 illustrated the graph of preliminary study 5 on hydraulic retention time (HRT).

Table 10: COD data of preliminary study of specimen size

Time	Tank 1	Tank 2	Tank 3
0	48700	63100	63500
2	63000	138000	70600
4	52900	69000	58000
6	47100	59000	72400
8	40700	124900	42600
10	40200	58500	52600
24	36900	114200	56300

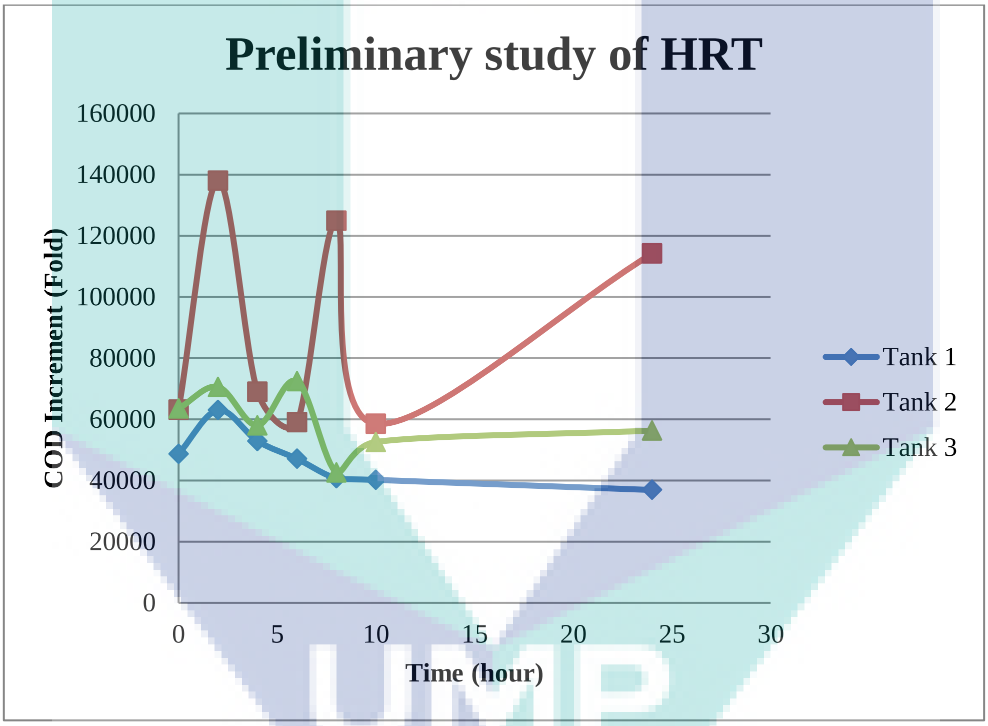


Figure 27: Graph of fold vs HRT

The graph showed the removal of COD against the time of reaction that has two peak times for Tank 2 and Tank 3, but only one peak for Tank 1. Based on Figure 27, the highest COD value was at 2 hours with COD of 63000 mg/L. Thus, the range to perform factorial analysis study was from 3 hours to 9 hours. The highest COD level was at 2 hours for Tank 2, with data of 138000 mg/L and the second was at 8 hours, with data of 124900mg/L. The data collected showed a fluctuation along the 24 hours of experiment. The final data at 24 hours was

114200mg/L. The data can be explained by the activity or reaction of the AMC that increase and decrease with time that influence by the other factor such as temperature and pH. The experiment was done at room temperature that can give an unstable data because of increasing or decreasing of temperature in the room. Thus, the time taken for the kinetic experiment to be done is about 9 hours. Based on Figure 27, the COD reading showed highest reading at 6 hours at Tank 3. The graph showed the removal of COD against the time of reaction, that has two peak times. The highest COD level was at 2 hours, with data of 70600 mg/L and the second was at 6 hours, with data of 72400 mg/L. The data collected showed a fluctuation along the 24 hours of experiment. The final data at 24 hours was 56300 mg/L. The data can be explained by the activity or reaction of the AMC that increase and decrease with time that influence by the other factor such as temperature. The experiment was done at room temperature that can give an unstable data because of increasing or decreasing of temperature in the room. Thus, the range to perform optimization was from 2 to 9 hours.

2.4.3 Experimental study

2.4.3.1 Factorial analysis

Table 11 showed that factor of temperature gave the highest contribution to COD increment. Meanwhile, specimen size factor gave the lowest contribution to COD increment.

Table 11: Contribution Factor of COD Increment

	Term	**% Contribution**
Model	A-Ratio	3.28
Model	B-pH	0.66
Model	C-Temperature	37.75
Model	D-Specimen Size	0.034
Model	E-HRT	6.66

Table 12 showed the contribution of factors interaction. The interaction of temperature and HRT, (CE) showed the highest contribution of COD increment. It can be concluded that temperature and HRT had a strong relationship in order to increase COD of the sample.

Table 12: Contribution of factors interaction for COD increment

	Term	**% Contribution**
Model	AB	0.15
Model	AE	2.07
Model	BD	9.05
Model	BE	5.94
Model	CD	3.81
Model	CE	27.07
Model	DE	3.38

Table 13 showed the ANOVA table for response 1, COD increment (fold). It showed that the model was significant. This model showed R-Squared was above 0.8, so this model was accepted (Table 14). It can be concluded that this model can be used for optimization. Based on Figure 52, it showed that the data was well distributed.

Table 13: ANOVA table for COD increment

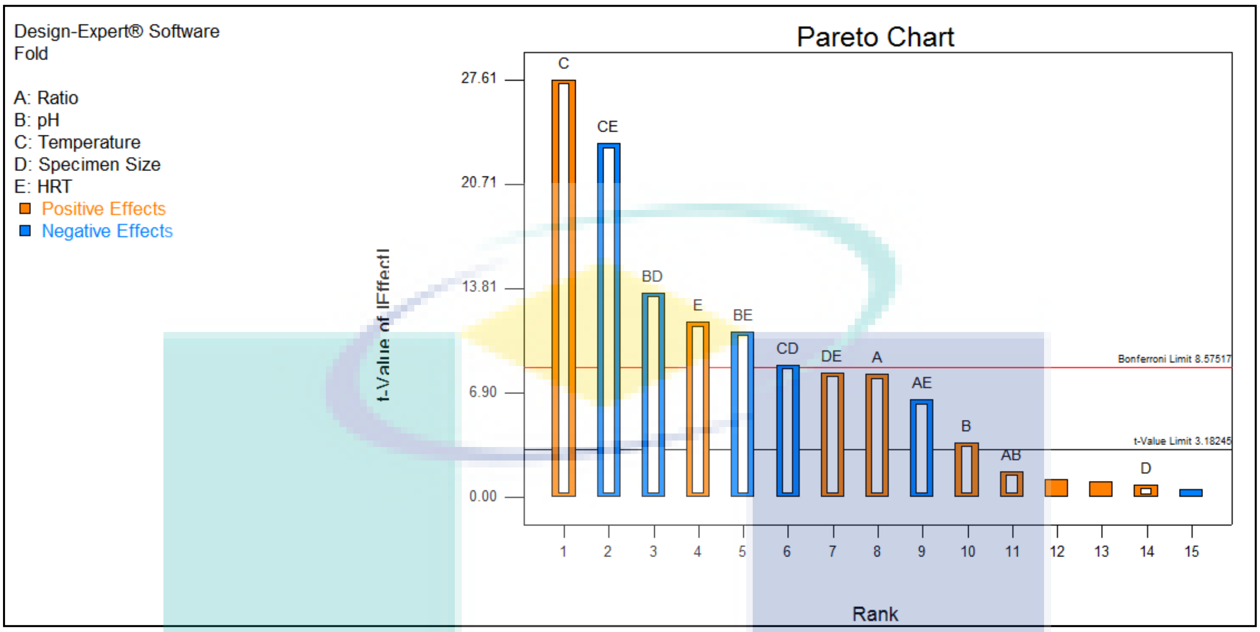
ANOVA for selected factorial model						
Source	Sum of Square	Df	Mean Square	F value	P-value Prob > F	
Model	**3.07**	**12**	**0.26**	**168.06**	**0.0007**	**Significant**
A-Ratio	0.10	1	0.10	66.19	0.0039	
B-pH	0.02	1	0.02	13.33	0.0355	
C-Temperature	1.16	1	1.16	762.36	0.0001	
D-Specimen Size	1.056E-03	1	1.056E-03	0.69	0.4661	
E-HRT	0.20	1	0.20	134.45	0.0014	
AB	4.556E-03	1	4.556E-03	2.99	0.1821	
AE	0.064	1	0.064	41.86	0.0075	
BD	0.28	1	0.28	182.71	0.0009	
BE	0.18	1	0.18	120.00	0.0016	
CD	0.12	1	0.12	77.03	0.0031	

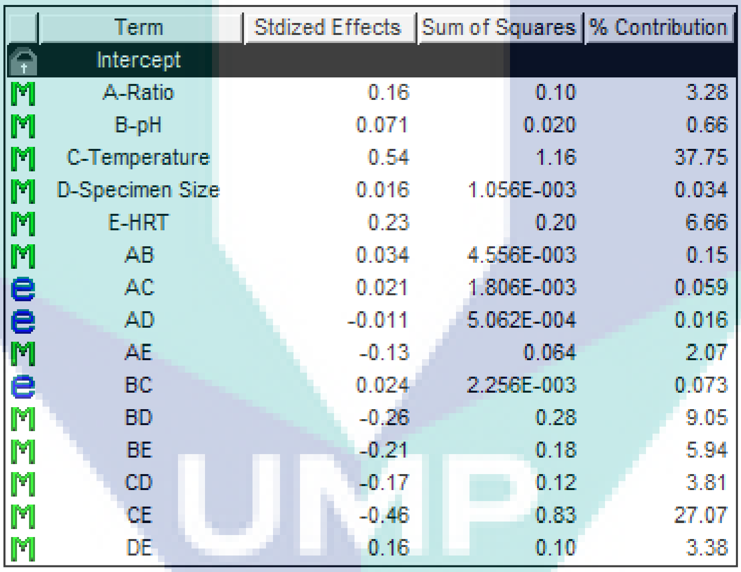
CE	0.83	1	0.83	546.75	0.0002	
DE	0.10	1	0.10	68.29	0.0037	

Table 13: R-Squared table

Based on Figure 28, the COD increment Pareto Chart from Design Expert software, it can be observed that the Factor C (Temperature) has highest positive effect since it is above the Bonferroni Limit. The factor C gives the most contribution with 37.75% which almost significant as shown in Figure 29. Thus, from the Pareto Chart indicate that the temperature has the most significant factor on COD increment reading in MSW with positive effect. For the next positive effect contribution is Factor E (HRT). Factor E gives the second highest positive effect contribution with 6.66% (Figure 29). From the Pareto Chart indicate that the Factor E is the second highest positive effect factor on COD increment reading in MSW. Meanwhile the last one factor effect is Factor A (Ratio) which is the third highest as one factor positive effect. Factor A is below the Benforroni Limit but above the t-Value Limit. The Factor A gives contribution with 3.28% (Figure 29). From the Pareto Chart indicate that the Factor A is the third highest positive on COD increment. This shows that the Factor A also play the vital role in COD increment.

Followed by interaction between Factor C (Temperature) and Factor E (HRT) but gives the negative effect with 27.07%. Since the interaction between CE is the highest with negative effects, the higher the temperature and the longer the HRT, the availability of COD increment will be disrupted. Same goes to interaction factor of BD, BE and CD that give negative effects to the COD increment in MSW. Lastly, interaction factor between Factor D (Specimen Size) and Factor E (HRT) give the positive effect that below the Benforroni Limit but above t-Value Limit. This interaction factor gives effect of 3.38% to the COD increment.





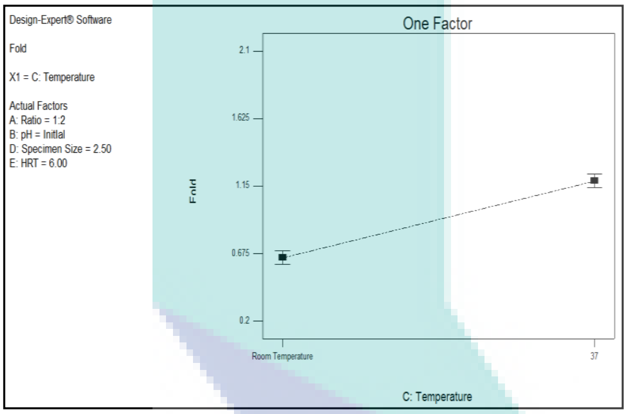
	Term	Stdized Effects	Sum of Squares	% Contribution
	Intercept			
M	A-Ratio	0.16	0.10	3.28
M	B-pH	0.071	0.020	0.66
M	C-Temperature	0.54	1.16	37.75
M	D-Specimen Size	0.016	1.056E-003	0.034
M	E-HRT	0.23	0.20	6.66
M	AB	0.034	4.556E-003	0.15
e	AC	0.021	1.806E-003	0.059
e	AD	-0.011	5.062E-004	0.016
M	AE	-0.13	0.064	2.07
e	BC	0.024	2.256E-003	0.073
M	BD	-0.26	0.28	9.05
M	BE	-0.21	0.18	5.94
M	CD	-0.17	0.12	3.81
M	CE	-0.46	0.83	27.07
M	DE	0.16	0.10	3.38

Figure 29: Effect list of COD increment

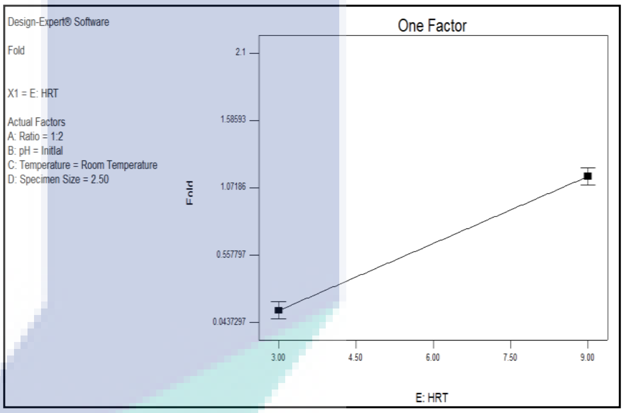
Based on the Figure 29, the factor like Temperature, HRT and ratio has positive effect. The temperature has the highest contribution with 37.75%, followed by HRT with 6.66% and ratio with 3.28% (Figure 30). According to some study, the ambient temperature will give the highest COD increment because of it suitable with surrounding temperature. Besides, the COD increment highly depends on the temperature. It is proved as the Figure 30(a) shows the slope which indicate the COD increment value in MSW increase as the temperature increase. The best condition for obtaining highest amount of COD increment is at temperature 37°C. Thus, it can be concluded that the temperature highly affects the COD increment in MSW

Besides, the HRT also give positive effect where that the longer the HRT, the higher the COD increment. Figure 30(b) shows that HRT also play the vital role in the availability of COD increment in MSW.

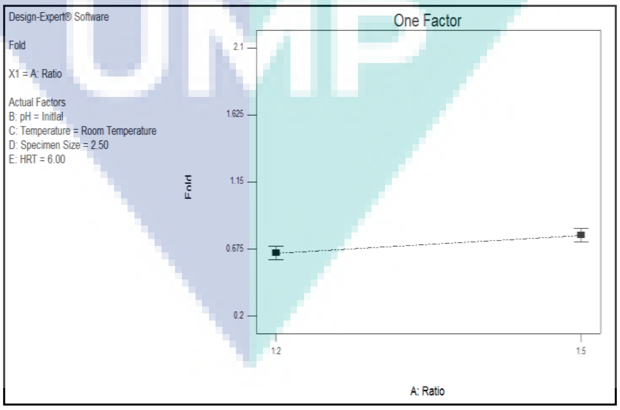
The last single factor that gives positive effect to COD increment is ratio. Figure 30(c) showed that the slope is slightly increase when the ratio increases from 1:2 to 1:5. Thus it can conclude from Figure 30(c) where there is no significant difference on ratio to the COD increment.



(a)



(b)



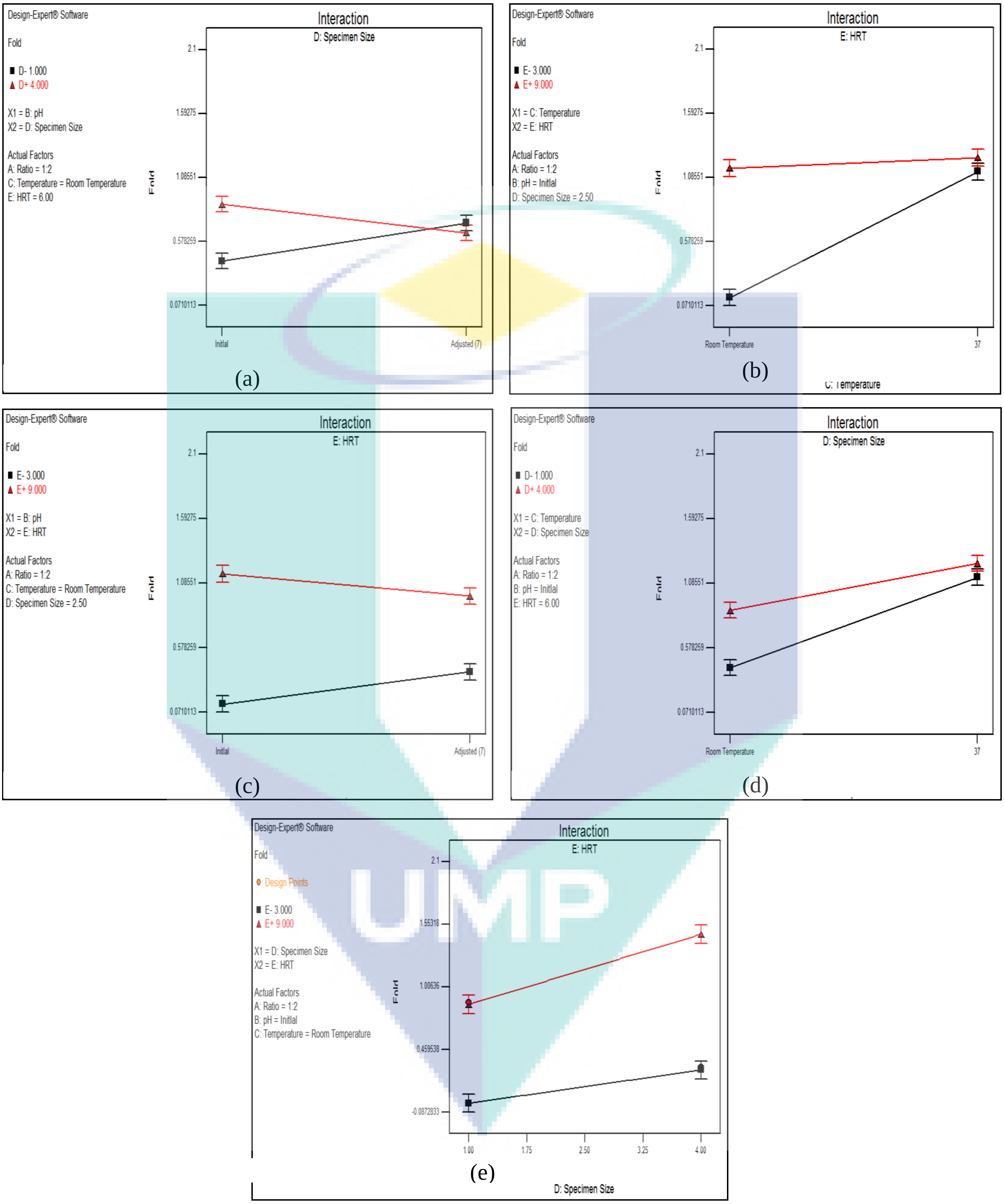
(c)

Figure 30: Analysis of main factor of COD increment

According to the Design Expert Software analyzed data, the interaction give positive effect with highest contribution is interaction between Factor D (Specimen Size) and Factor E (HRT) with a percentage of 3.38%. Basically, from Figure 31(e), it can be observed increment of COD increases as the factor D in high level (4cm^2) for both HRT. But, as referred to Figure 31(d) the slope increases drastically when specimen size is 4cm^2 and HRT is 9.00 hours.

Interaction between BD, CE, BE and CD give negative effect to the COD increment. From Figure 31(a), interaction between factors BD, it can observe the interaction has 2 behaviors; where when the specimen size is 4cm^2 and ph adjusted (7), it will decrease the COD increment. But when specimen size is 1cm^2 and ph adjusted the increment of COD increase slightly.

Same goes to interaction factor of CE, CD and BE which contains two types of behaviors. Interaction of factor CE (Figure 31(b)), when the when the temperature is 37^{o}C and HRT is 3 hours, the COD increment increase drastically but when the HRT is 9 hours, it slightly changed.



(a) (b) (c) (d) (e)

Figure 31: Interaction curve between factors

In this section, optimization was done to validate the suggested best condition. Table 14 showed the goal for every factors and responses. All factors were set in range and the Fold was set to get the maximize value. The purpose of set goal was to fulfill the requirement of increasing the COD.

Table 14: Optimization Table

Name	Goal	Lower Limit	Upper Limit
Ratio	Is in range	1:2	1:5
pH	Is in range	Initial	Adjusted (7)
Temperature	Is in range	Room Temperature	37^{o}C
Specimen Size	Is in range	1cm^2	4cm^2
HRT	Is in range	3 hours	9 hours
Fold	Maximize	0.25	2.02

After all the goal was set to the factors and response, Design Expert gave the suggested best condition for the factors and predicted values for response (Table 15).

Table 15: Suggested Condition

Ratio	1:5
pH	Adjusted (7)
Temperature	37^{o}C
Specimen Size	1cm^2
HRT	3 hours
Fold	1.99187

By using these suggested conditions, 3 run experiments were done to validate the COD increment.

2.4.3.2 Optimization

Table 16 showed the actual and coded levels of the independent variables in the experimental design. Temperature was set to be in range between 25°C and 35°C. Then, the HRT was set in range between 2 and 9 hours. For response, fold was chosen instead of initial and final COD. The fold was set to get maximize value. The purpose of setting the goal was to fulfill the objective to get high concentration of COD production.

Table 16: Actual and coded levels of the independent variables in the experimental design

Independent variable	**Actual**		**Coded**	
	Low	**High**	**Low**	**High**
Temperature (A)	27.5°C	32.7°C	-1.000	1.000
HRT (B)	3.75	7.25	-1.000	1.000

A two-factor-one-level face centered central composite design (CCRD) was applied where the values of the independent variables were in range of -1 and +1 level shown in Table 5. The mathematical transformation of any actual level of applied temperature and HRT into the coded level can be obtained respectively.

An analysis of variance table (ANOVA) and R^2 (coefficient of determination) statistic were used to check adequacy of the developed model. Using an F-test, it was possible to test the variation of the data around the fitted model (lack of fit). The significance level was stated at 18.55%, with p-value 0.0007. Confirmatory experiments were carried out to validate the equations using the combinations of independent variables. These were not part of the original experimental design, but within the experimental region. The optimal conditions for the mixed culture to produce high COD were obtained using the software's numerical optimization function.

The optimization table was given by the Design Expert software after setting all the limits as shown in Table 17 below.

Table 17: Optimization experimental result

Std	**Run**	**Factor 1 (Temperature, ^oC)**	**Factor 2 (HRT, hr)**	**Response 1 (Initial COD, mg/L)**	**Response 2 (Final COD, mg/L)**	**Response 3 (Fold)**
1	10	27.50	3.75	49400	54000	1.0931
2	6	32.50	3.75	36800	45800	1.2446
3	3	27.50	7.25	49400	53100	1.0749
4	8	32.50	7.25	36800	68700	1.8668
5	4	25.00	5.50	19100	23400	1.2251
6	1	35.00	5.50	14700	49400	3.3605
7	12	30.00	2.00	62800	71900	1.1449
8	5	30.00	9.00	62800	67800	1.0796
9	2	30.00	5.50	62800	70100	1.1162
10	9	30.00	5.50	62800	70700	1.1258
11	7	30.00	5.50	62800	68800	1.0955
12	13	30.00	5.50	62800	72100	1.1481
13	11	30.00	5.50	62800	72800	1.1592

In order to determine the optimum process parameters, i.e. temperature and HRT for high COD concentration production, the experiments were designed according to a face centered composite design in three variables following the Response Surface Methodology (RSM). The experimental set up and corresponding experimental responses are shown in Table 6. The concentration of COD production from the samples exhibited an increase with increasing the temperature. The lowest value of 1.0749 was obtained at temperature 27.5^oC and HRT 7.25 hours; the highest value of 3.3605 was obtained at temperature 35^oC and HRT 5.50 hours.

Fitting of the data to various models (linear, two factorial, quadratic and cubic) and their subsequent analysis of variance showed that the production of COD concentration from mixed culture is most properly described with quadratic polynomial model. The Adjusted R^2 of the quadratic model (0.8797) was higher than that of linear (0.3667) and two factorial (0.3246) models. The cubic model was found to be aliased. The second-order polynomial model used to express the fold of COD (Y) as a function of independent variables as shown in Equation 2 and Equation 3 in term of coded and actual levels.

$$Fold\ (coded) = 1.10 + 0.43A + 0.039B + 0.16AB + 0.29A^2 - [5.831x10^{-3}(B^2)]$$

(Equation 2)

$$Fold\ (actual) = 43.40495 - 2.80481A - 1.05434B + 0.036594AB + 0.046289A^2 - [1.90394x10^{-3}(B^2)]$$

(Equation 3)

The analysis of variance table extracted from Design Expert software has been shown in Table 18.

Table 18: Analysis of variance table

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	4.50	5	0.90	18.55	0.0007[a]
A-Temperature	2.27	1	2.27	46.73	0.0002
B-HRT	0.019	1	0.019	0.39	0.5545
AB	0.10	1	0.10	2.11	0.1892
A^2	1.92	1	1.92	39.55	0.0004
B^2	$7.790x10^{-4}$	1	$7.790x10^{-4}$	0.016	0.9027
Residual	0.34	7	0.048		
Lack of Fit	0.34	3	0.11	174.54	0.0001[a]
Pure Error	$2.573x10^{-3}$	4	$6.433x10^{-4}$		
Correction Total	4.84	12			
R^2	0.9298				
Adj. R^2	0.8797				

[a] Significant

Table 18 summarizes the ANOVA (F-test) and p-value that are used to estimate the coefficient of the model, to check the significance of each parameter, and to indicate the interaction strength of each parameter. It was observed from the ANOVA analysis that the confidence level was greater than 95% while the p-value of the model was less than 0.0001. The model with the p-value below 0.05 was statistically significant, which implied that the model was suitable for this experiment. The "Lack of Fit F-value" of 174.54 implies the Lack of Fit is significant. There is only a 0.01% chance that a "Lack of Fit F-value" this large could occur due to noise. Significant lack of fit was bad; we want the model to fit. The "Pred R^2" of 0.3079 is not as close to the "Adj R^2" of 0.8797 as one might normally expect. This may indicate a large block effect or a possible problem with the model and/or data. Things to consider are model reduction, response transformation, outliers, etc. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 15.361 indicates an adequate signal. This model can be used to navigate the design space.

The coefficient of determination (R^2) and adjusted coefficient of determination (R^2_{adj}) were 0.9298 and 0.8797, respectively which indicates that the estimated model fits the experimental data satisfactorily. Lee et al. (2010) suggested that for a good fit of a model, R^2 should be at least 0.80. The R^2 for these response variables was higher than 0.80, indicating that the regression models explained the mechanism well. Figure 32 showed the result of actual versus predicted data while Figure 33 showed the normal plot of residuals.

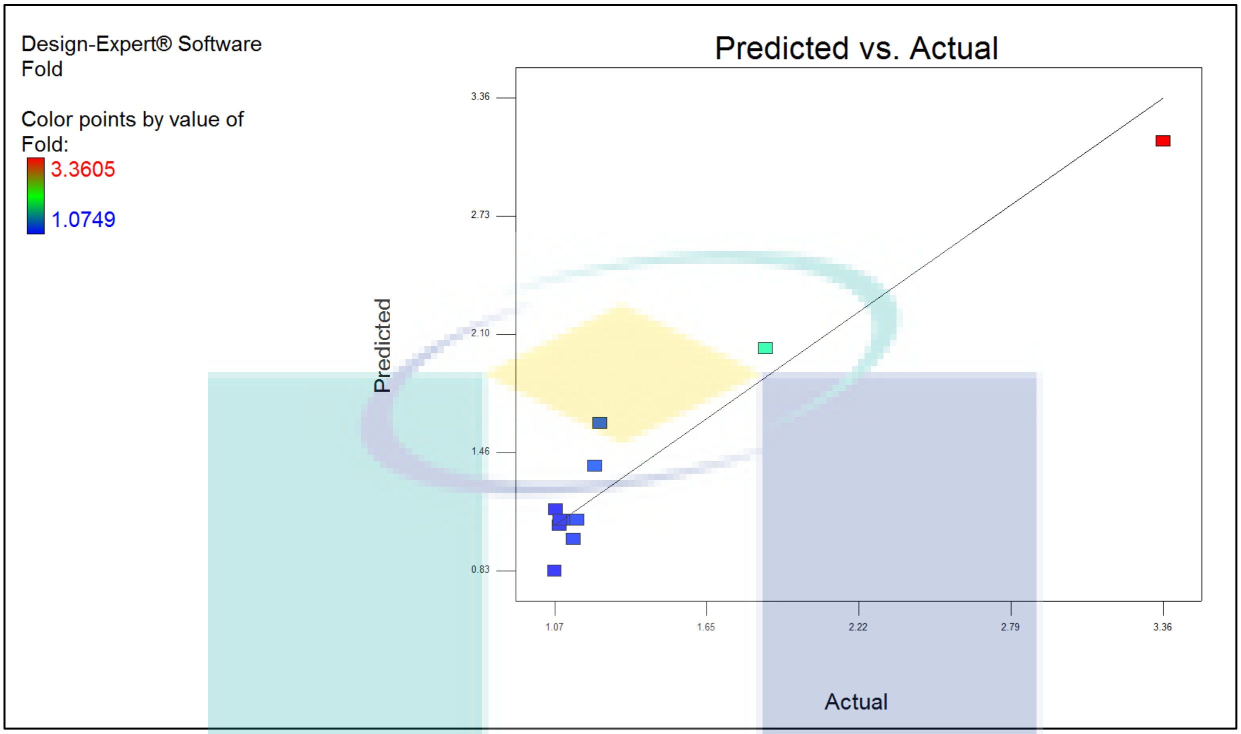


Figure 32: Graph of predicted vs actual data

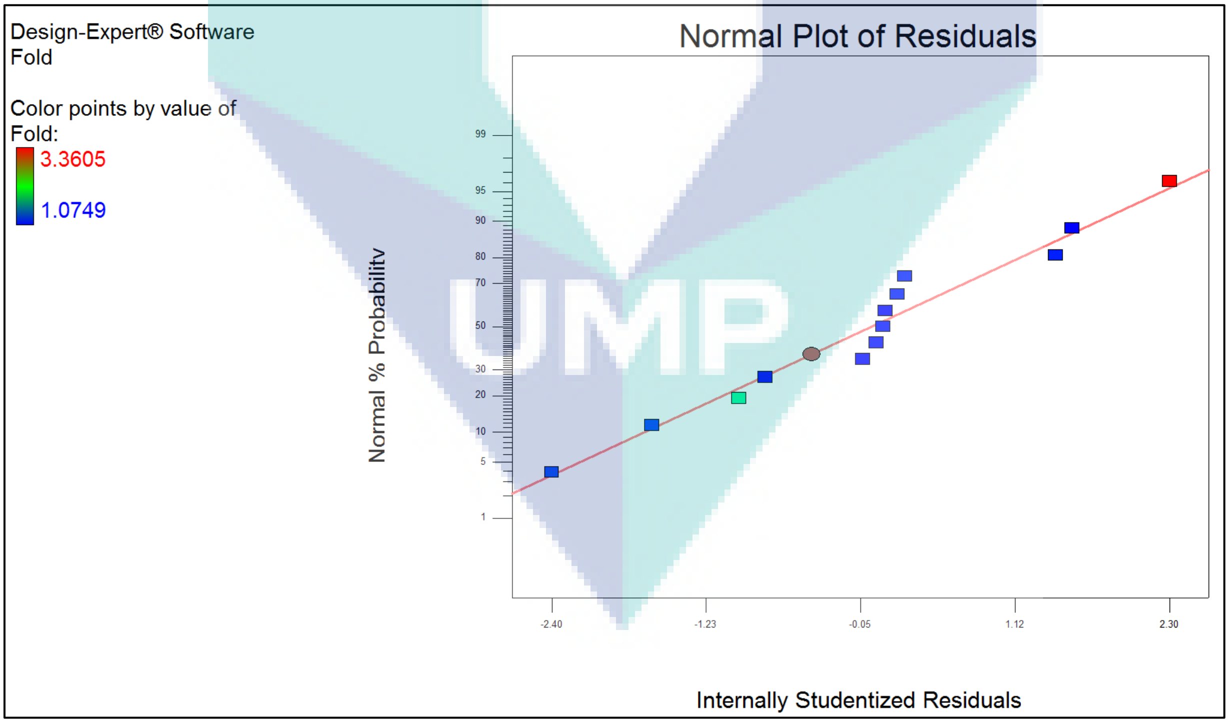


Figure 33: Graph of normal plot of residuals

A linear distribution is observed which is indicative of a well-fitting model. The values predicted were close to the observed values of COD increments (fold). The plot indicates that the difference between actual and predicted values follow a normal distribution and form an approximately straight line. From Table 6, the p-value of factor A (temperature) is smaller than factor B (HRT) which is 0.0002 and 0.5545 respectively. These values proved that temperature was the main factor that effects the reaction of the mixed culture. The effect of temperature to fold of COD was shown as in Figure 34.

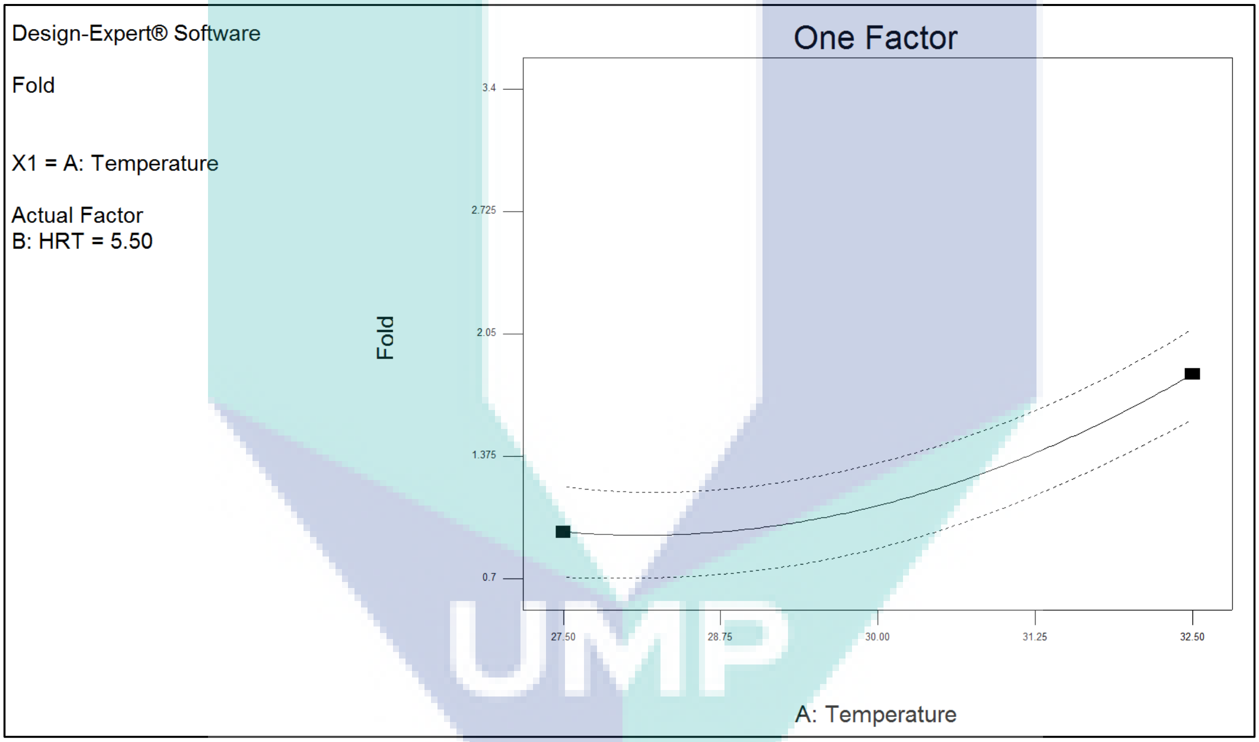


Figure 34: Graph of fold vs temperature

Due to high p-value of B (HRT), the reaction is not much effected by the HRT. The increment of COD by the HRT can be illustrated as shown in Figure 35.

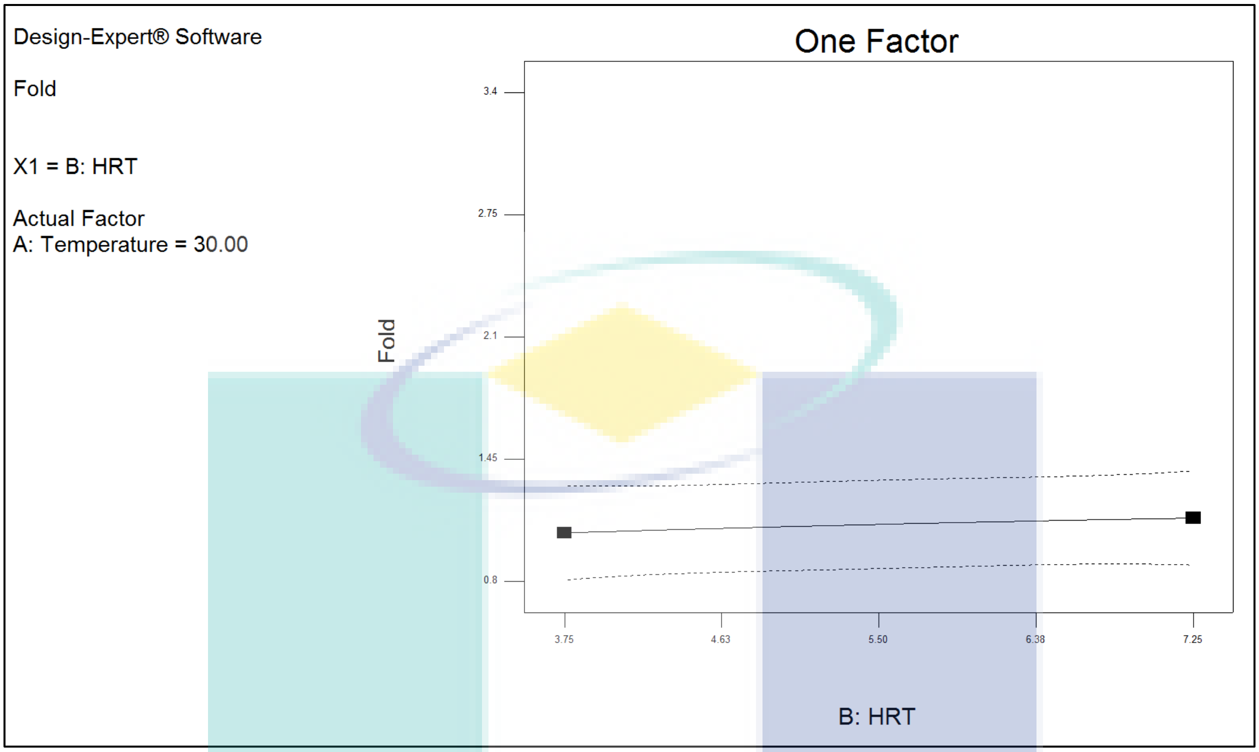


Figure 35: Graph of fold vs HRT

The contour plot and 3D surface plot of the data were showed in the Figure 36 and Figure 37.

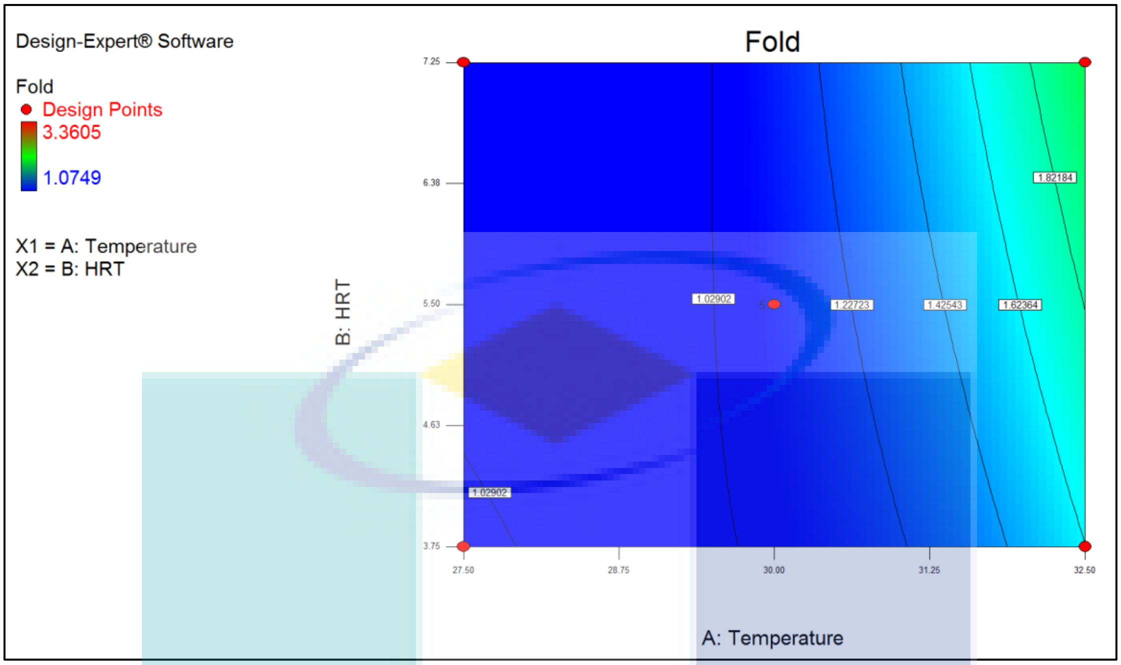


Figure 36: Contour plot of the data

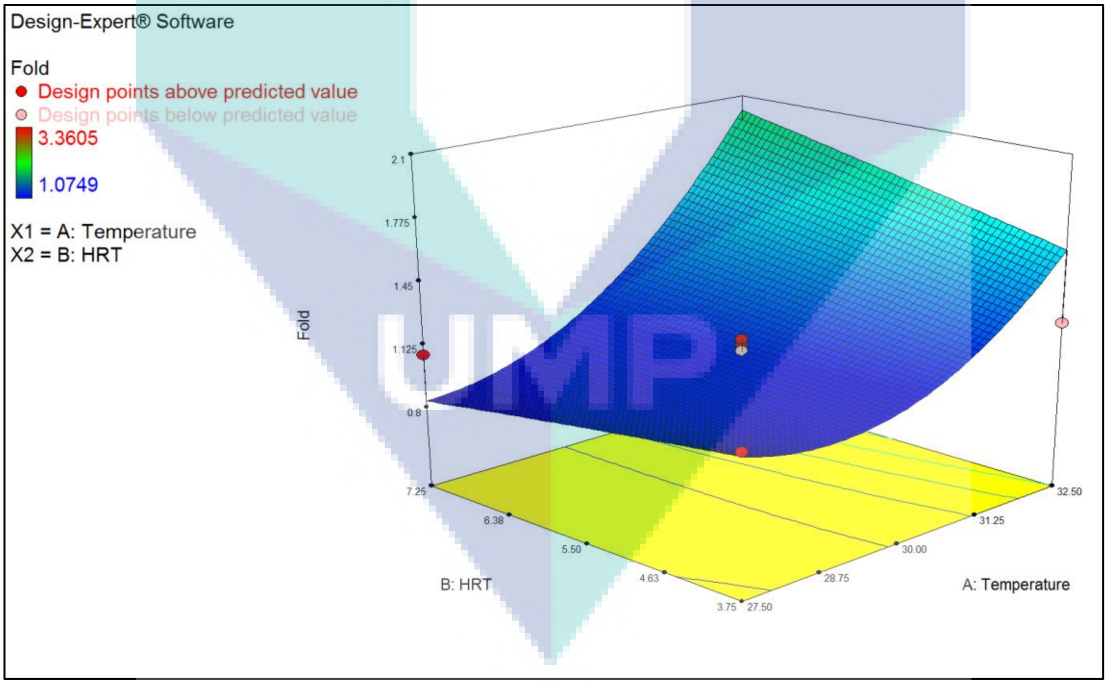


Figure 37: 3D surface plot of the data

The effects of interaction between factors, i.e. temperature, HRT and fold are shown in Figure 36 and Figure 37. The plotted data depicts the effect of temperature and HRT on the concentration of COD production with fold 3.3605. The effect of fold is more significant at high temperature. The effect may be attributed to the interaction of temperature and reaction time. Which at optimum conditions the reaction in the reactor is higher and tend to produce high concentration of COD. A comparative study of the results showed that the COD production at any temperature was affected by the HRT. The effect of temperature and HRT is shown in Figure 36 and Figure 37.

2.4.3.3 Kinetic study

Table 19 showed the kinetic data of the experiments.

Table 19: Kinetic Experimental Data

Time (hour)	**COD (mg/L)**					**TS (mg/ml)**			
	R1	**R2**	**R3**	**AV**	**DF=100**	**Initial**	**Final**	**Δ**	**per 50 ml**
0	178	151	147	159	15900	0.9980	2.3417	1.3437	0.0269
1	179	246	191	205	20500				
2	302	299	296	299	29900				
3	234	247	210	230	23000				
4	303	295	315	304	30400				
5						1.0377	2.7346	1.6969	0.0339
6									
7	420	486	474	460	46000	1.0221	2.7666	1.7445	0.0349
8	558	595	592	582	58200	1.0376	2.9305	1.8929	0.0379
9	986	953	970	970	97000	1.0375	3.1567	2.1192	0.0424

Figure 38 showed the graph of COD from the experimental data and Figure 39 showed the graph of TS from the experimental data.

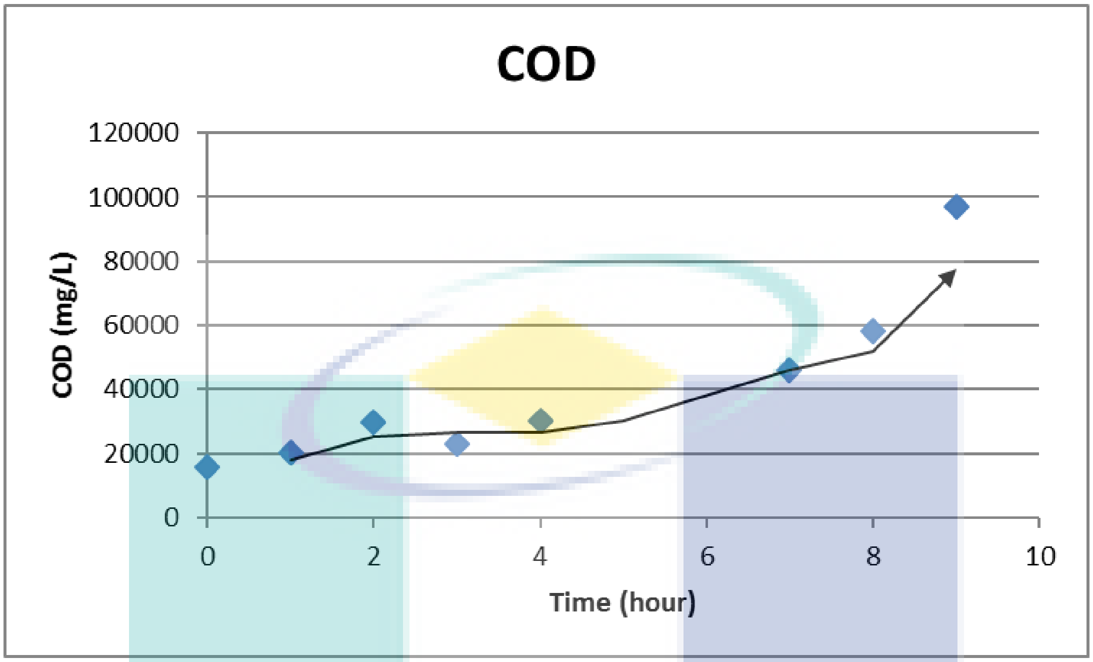


Figure 38: Graph of COD

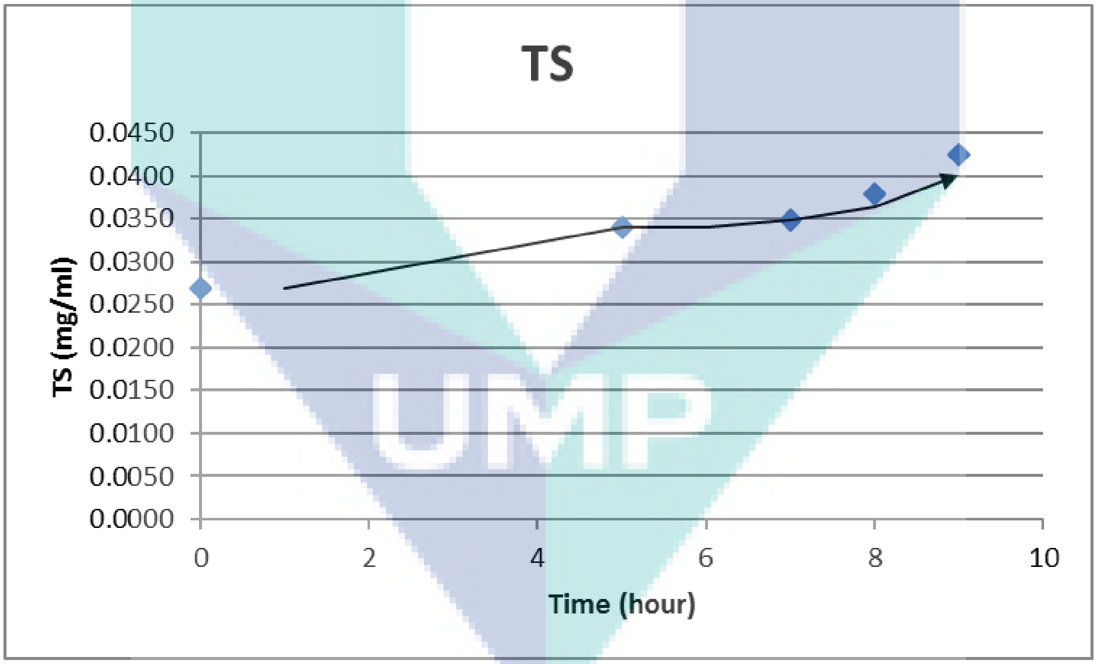


Figure 39: Graph of TS

Based on the data collected, the result showed that the COD level has an increment within the retention time with the highest level at 9 hours. Therefore, the data that was collected was valid for kinetic study. The second highest data collected for COD was at 6 hours. The data showed an increasing of 81100mg/L of COD from the initial at 0 hour. The suspended solid showed fluctuation within the first until third hour but it began to rise steadily within the retention time. Firstly, for TS data, it showed a steady decreasing of TS collected until 4 hours of retention time. The data for TS can be related with the COD data collected because at the first phase, the AMC are just beginning to adapting to the new surroundings. It can be also said that at 6 hours the COD data are second highest and TS data are the highest at 6 hours. Both of the graphs also display a trend of increasing starting at the hour of 4 until 9. In this section, the data collected in the experiment are being extracted by using the equation founded. The kinetic model for the microbe was found in a journal of Kinetics of the aerobic biological degradation of shredded municipal solid waste in liquid phase by Ewa et al. The mass balance for the batch reactor is presented in the form of the system of ordinary differential equations. Taking into account the rate expressions for the reactions and division into the phases of the process two systems of ordinary differential equations for were obtained (Moser equation):

For the first phase ($t<t_B$) (hydrolysis and intensive aerobic biodegradation in the high-loaded systems),

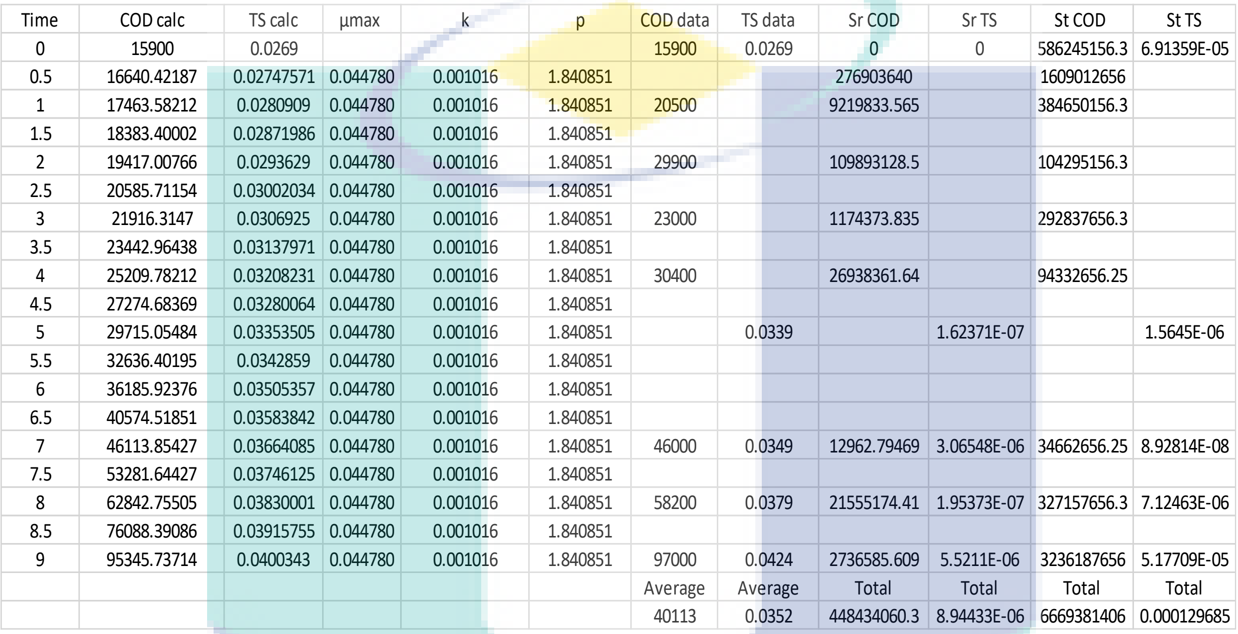
$$\frac{d([COD])}{dt} = k([COD])^P X, \qquad \text{(Equation 4)}$$

$$\frac{dX}{dt} = \mu_{max} X. \qquad \text{(Equation 5)}$$

The data are calculated in the excel software and represent in the Table 20.

Table 20: Kinetic Calculation using Excel

µmax	0.044780
k	0.001016318
p	1.840851296



Time	COD calc	TS calc	µmax	k	p	COD data	TS data	Sr COD	Sr TS	St COD	St TS
0	15900	0.0269				15900	0.0269	0	0	586245156.3	6.91359E-05
0.5	16640.42187	0.02747571	0.044780	0.001016	1.840851			276903640		1609012656	
1	17463.58212	0.0280909	0.044780	0.001016	1.840851	20500		9219833.565		384650156.3	
1.5	18383.40002	0.02871986	0.044780	0.001016	1.840851						
2	19417.00766	0.0293629	0.044780	0.001016	1.840851	29900		109893128.5		104295156.3	
2.5	20585.71154	0.03002034	0.044780	0.001016	1.840851						
3	21916.3147	0.0306925	0.044780	0.001016	1.840851	23000		1174373.835		292837656.3	
3.5	23442.96438	0.03137971	0.044780	0.001016	1.840851						
4	25209.78212	0.03208231	0.044780	0.001016	1.840851	30400		26938361.64		94332656.25	
4.5	27274.68369	0.03280064	0.044780	0.001016	1.840851						
5	29715.05484	0.03353505	0.044780	0.001016	1.840851		0.0339		1.62371E-07		1.5645E-06
5.5	32636.40195	0.0342859	0.044780	0.001016	1.840851						
6	36185.92376	0.03505357	0.044780	0.001016	1.840851						
6.5	40574.51851	0.03583842	0.044780	0.001016	1.840851						
7	46113.85427	0.03664085	0.044780	0.001016	1.840851	46000	0.0349	12962.79469	3.06548E-06	34662656.25	8.92814E-08
7.5	53281.64427	0.03746125	0.044780	0.001016	1.840851						
8	62842.75505	0.03830001	0.044780	0.001016	1.840851	58200	0.0379	21555174.41	1.95373E-07	327157656.3	7.12463E-06
8.5	76088.39086	0.03915755	0.044780	0.001016	1.840851						
9	95345.73714	0.0400343	0.044780	0.001016	1.840851	97000	0.0424	2736585.609	5.5211E-06	3236187656	5.17709E-05
						Average	Average	Total	Total	Total	Total
						40113	0.0352	448434060.3	8.94433E-06	6669381406	0.000129685

Total error	448434060.3
R2 for COD	0.932762271
R2 for TS	0.931030463

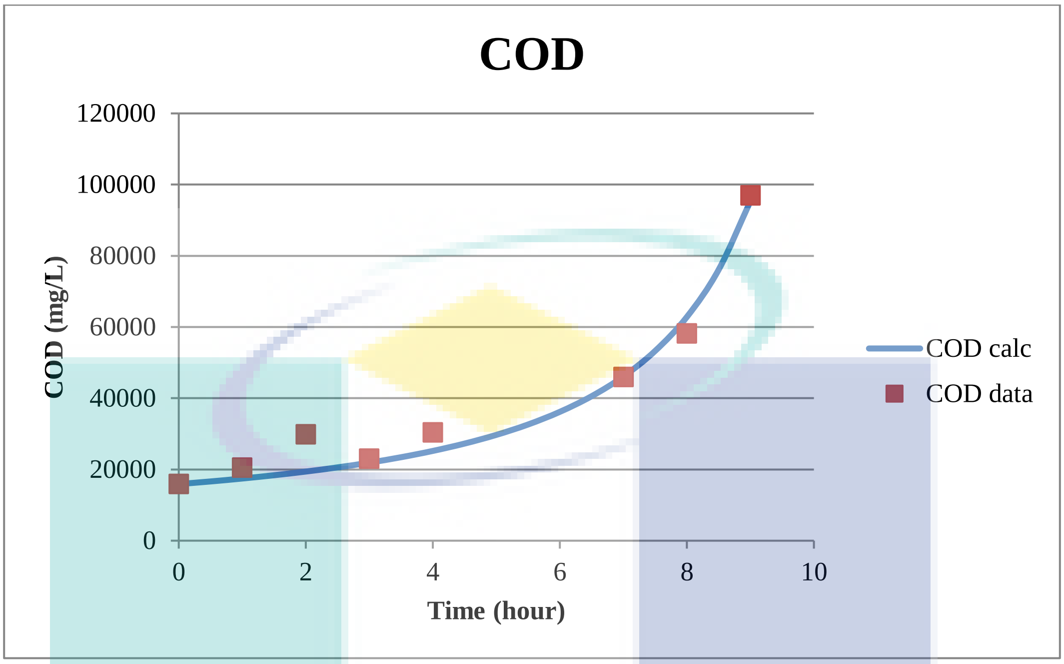


Figure 40: Graph of data and calculated COD

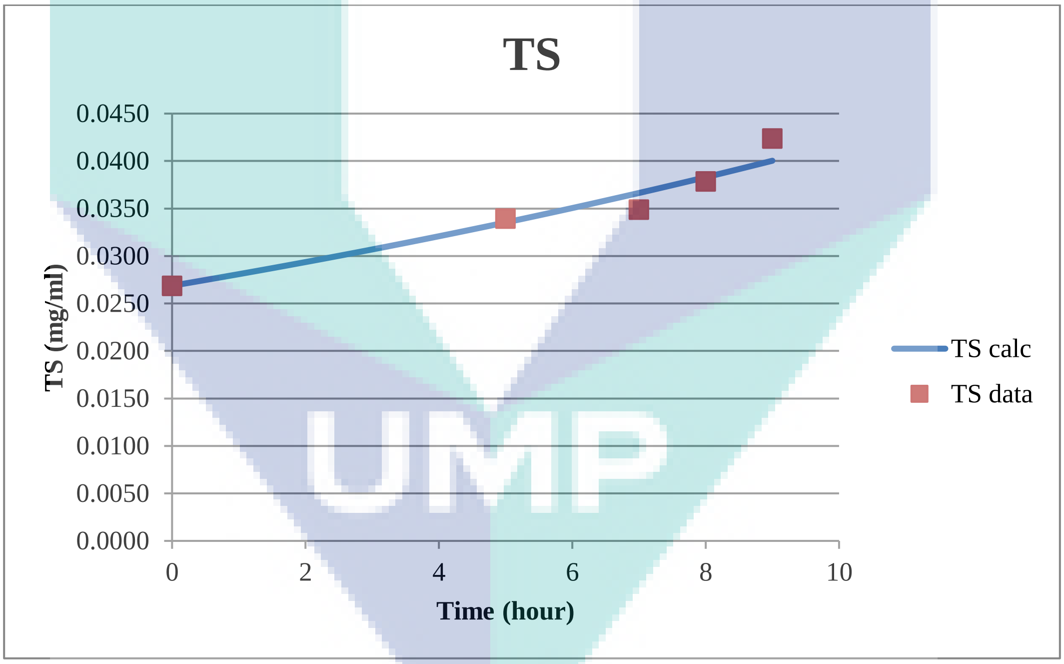


Figure 41: Graph of data and calculated TS

From the data calculated in the excel, for COD in Figure 40, it displays in the graph that the data calculated and the data from the experiment has approximately same data with R square of 0.8, that is acceptable for a biological reaction. While for TS in Figure 41, the data calculated has significantly difference with the data collected from the experiment. Thus, the R square for TS is about 0.38, which may not be acceptable for the reaction. The large difference of calculated data and experiment data may cause the value of small R square, with the fluctuation in the experimental data. The constant value was calculated with data of 0.052399, 913.444997 and 0.52365304 of μmax, k and p respectively as shown in Table 20.

2.4.4 Economic potential

The experimental set up started from 11th July 2016 until 17th August 2016 (38 days). Total water consumption of the experiment is approximately 60.0 L (0.0606 m^3). The samples of food waste or organic waste do not have any charges due to the availability of the sample at the landfill. Calculation of the water needed for scale up process was shown as below. The total amount of water consumption was shown in Table 21.

Lab scale water consumption and sample,

Acclimatization process : 18.0 L (0.018 m^3)
Experimental (1 flask) : 0.30 L (0.0003 m^3)
Total : 18.3 L (0.0183 m^3)

Sample : 3 kg

High COD production : 72800 mg/L

Scale up value based on Mercu REsolution Sdn Bhd data for three weeks (total 11 compacters),

Food waste : 12154.8 kg

$$\frac{Water\ lab\ scale}{Food\ waste\ lab\ scale} = \frac{Water\ scale\ up}{Food\ waste\ from\ MERCU\ data}$$

$$\frac{0.0183\ m^3}{3\ kg} = \frac{Water\ scale\ up}{12154.8\ kg}$$

$$\boldsymbol{Water\ scale\ up = 74.14\ m^3}$$

Table 21: Water consumption for scale up process (Commercial)

Billing period	11/07/2016 – 21/08/2016
	38 days ÷ 31 days = 1.2258
Consumption	74.14 m^3
Calculation	35 m^3 x 1.2258 = 42.90 m^3 x RM 2.07 = RM 88.81 31.24 m^3 x RM 2.28 = RM 71.28
Total bill	**RM 160.09**

$$\frac{COD\ production\ lab\ scale}{Food\ waste\ lab\ scale} x\ working\ volume = \frac{COD\ production\ scale\ up}{Food\ waste\ from\ MERCU\ data}$$

$$\frac{72800\ mg/L}{3\ kg} x\ 0.3\ L = \frac{COD\ production\ scale\ up}{12154.8\ kg}$$

$$\boldsymbol{COD\ production\ scale\ up = 88.49\ kg\ COD}$$

The theoretical value of concentration of COD production from food waste samples of 11 vehicles is 88.49 kg COD. This value is based on the optimization’s highest value of final COD production for 3 kg of food waste samples.

2.5 Conclusion

As the summary to all of the experiment that have been done in this project, from the preliminary data showed all of the three tanks showed a same pattern at the end of the process that can be the indicator that the AMC have been acclimatized to the surrounding. Then, move on to the preliminary study by the five selected factors, each of the tanks showed a different condition on each of the preliminary done. Next, the experiments of factorial analysis, optimization and kinetic study. From the factorial analysis result it can be concluded that COD increment in MSW was able to increase by using AMC and substrates from sites. The targeted final increment of COD, 1.99187 was achieved based on optimization and validation of experiment. From the selected actual data, it shows that final increment of COD was 2.19. Since the error was below than 10%, it is acceptable. Thus, the objectives of this research were successfully achieved. Optimization experiment is run to determine the optimum parameter in this study. From this research, it can be concluded that the higher concentration of COD can be achieved in a short time of reaction based on the experiment Run 1 with an error 8.6735% which is below 10%. The high concentration of COD bio-liquid was able to produce by using soil mixed culture from landfill area. The higher final concentration of COD was achieved based on optimization analysis and validation of experiment. From the experimental data, it illustrated that the final concentration of COD was increased to 100200 mg/L after 7.25 hours from 45300 mg/L at the beginning. The increment of COD (fold) from the validation experiment was increased by 2.2119. While from the selected actual data based on the optimization analysis by using Design Expert, the increment of COD (fold) increased by 2.02005. For kinetic study, from the data that have been collected and calculated in this experiment, the data for COD and TS can be accepted as the R square are above 0.8 with the highest experimental data of 97000 mg/L, 0.0424 mg/ml and the calculated data of 86056 mg/L, 0.04003 mg/ml for COD and TS respectively. The R square for the COD and TS are 0.9327 and 0.9310 respectively. The constant of the experiment are determine as 0.04478 h^{-1}, 0.00102 $l^{p}\ g_{\text{biomass}}^{-1}\ h^{-1}\ g\ O_2^{1-p}$ and 1.84085 for $\mu_{\max}$,maximum specific growth rate of biomass, k(t), hydrolysis constant and p, hydrolysis exponent respectively. The theoretical value of concentration of COD production from food waste samples of 11 vehicles is 88.49 kg COD. This value is based on the optimization’s highest value of final COD production for 3 kg of food waste samples. Thus, the objective of this research project was successfully achieved.

CHAPTER 3

PRODUCTION OF BIOFERTILIZER USING LANDFILL LEACHATE

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PROJECT TEAMS:

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3.1 Abstract

Nowadays, the accumulation of waste in landfill site is largely due to increasing of urbanization and industrialization in Malaysia. The non-proper management of wastes have worsened the condition whereby the amount of leachate produced from the waste

led to critical environment issue. Thus, the objective of the study was to determine the effects of vermicomposting of landfill leachate using earthworms on biofertilizer production in 31 days. Liquid leachate that majorly consist of organic matter can yield highly nutritive biofertilizer through vermicomposting process. The process used earthworms to convert organic matter in leachate into plant-nutrients that enhance the growth of the plants and plants productivity. The amount of nitrate (N), phosphorus (P) and potassium (K) in vermicompost was found to increase while pH and number of earthworms declined at the end of the vermicomposting period. The vermibin containing 90 earthworms (approximately 52g) in a mixture of 150 ml of leachate and 800 g of soil obtained the highest concentration of NPK in vermicompost compared to those containing 39 earthworms and 15 earthworms. This indicates that the concentration of NPK increased with the high number of earthworms. The number of earthworms decreased with decrease in pH in all vermibins after 31 days of vermicomposting period. V1 experienced increase 53–fold in N, 194-fold in P and 210–fold in K with 6.13 in pH after vermicomposting period due to earthworm activity during the process, thus improving the number of leaves (32 leaves). The data shows that vermicomposting is a suitable technology for the decomposition of landfill leachate into nutritive biofertilizer.

3.2 Introduction

3.2.1 Objectives

1) To study the effects of vermicomposting of leachate using earthworms on biofertilizer production.
2) To determine the growth of tomato plants as affected by the application of vermicompost as a biofertilizer

3.2.2 Scopes of study

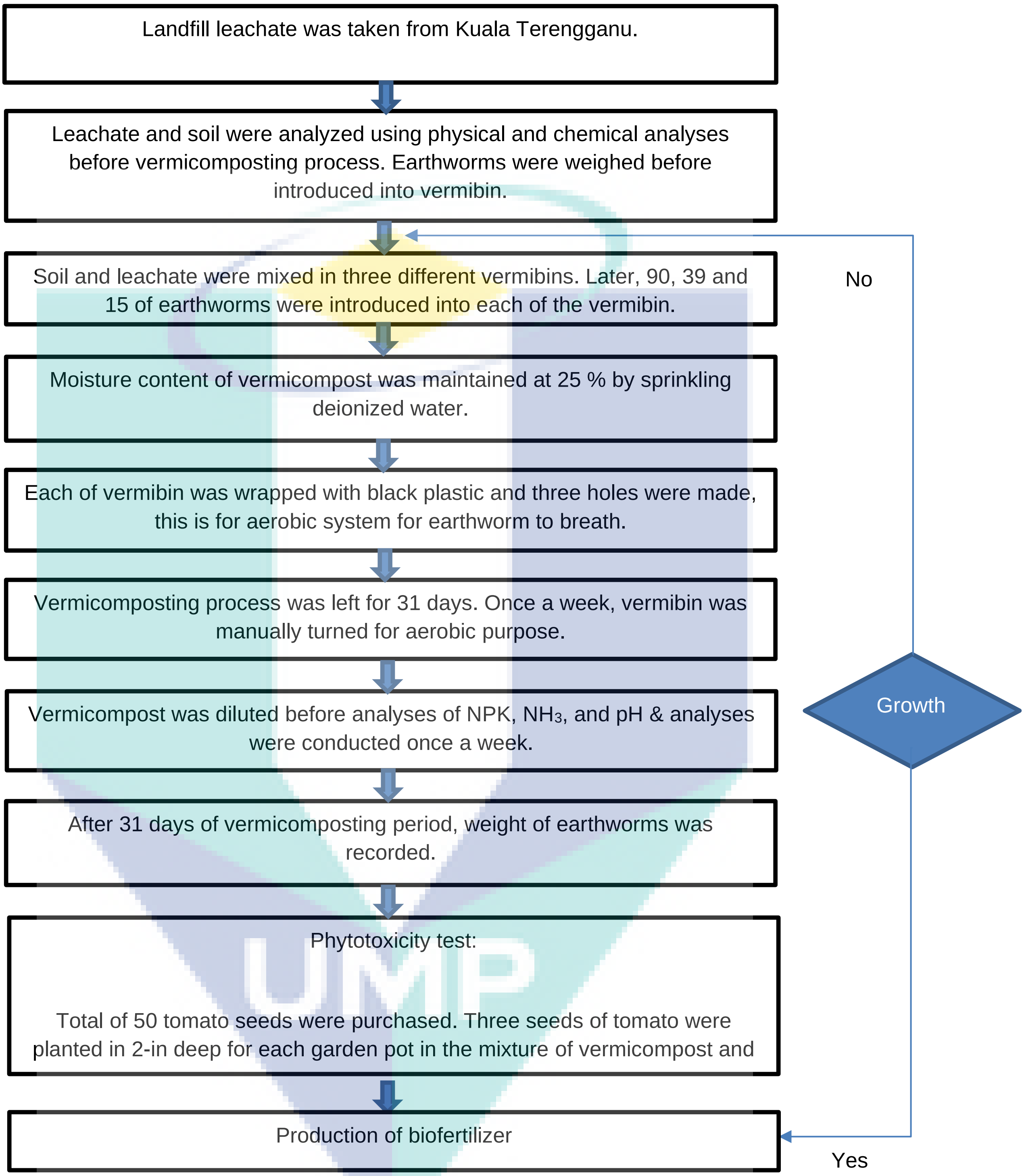
1) Characterization of biofertilizer from vermicomposting of leachate in terms of pH, Nitrate(N), Phosphate(P), and Potassium(K).

2) Study on the effect of different ratios of landfill leachate, soil and earthworms (L: S: E) (% wt./wt./vol.) on the NPK production (15: 79.8: 5.2; 15: 82.0: 3.0; 15: 84.2: 0.8).
3) Phytotoxicity test on tomato plants such as plant height, and number of leaves

3.3 Methodology

3.3.1 Overview

This research was performed to investigate the effect of varied amounts of earthworms used on soil mixed with landfill leachate and their effects on the growth and productivity of tomato plants. This observation was to study on how the amount of earthworms facilitate the degradation of organic matter in leachate. The soil content was analyzed using several parameters such as the concentration of nitrates (N), phosphate (P), potassium (K), ammonia-nitrogen (NH_3) and pH. These parameters are important elements for plant growth where they are micronutrients that are absorbed by the plant. Process flow for the overall research design is shown in Figure 1. The NPK and ammonia reading for each vermibin were compared with control. In order to determine the efficiency of the vermicompost, number of leaf and length of shoot were measured to determine the best vermicomposting conditions.


Landfill leachate was taken from Kuala Terengganu.

Leachate and soil were analyzed using physical and chemical analyses before vermicomposting process. Earthworms were weighed before introduced into vermibin.

Soil and leachate were mixed in three different vermibins. Later, 90, 39 and 15 of earthworms were introduced into each of the vermibin.

Moisture content of vermicompost was maintained at 25 % by sprinkling deionized water.

Each of vermibin was wrapped with black plastic and three holes were made, this is for aerobic system for earthworm to breath.

Vermicomposting process was left for 31 days. Once a week, vermibin was manually turned for aerobic purpose.

Vermicompost was diluted before analyses of NPK, NH_3, and pH & analyses were conducted once a week.

After 31 days of vermicomposting period, weight of earthworms was recorded.

Phytotoxicity test:

Total of 50 tomato seeds were purchased. Three seeds of tomato were planted in 2-in deep for each garden pot in the mixture of vermicompost and

Production of biofertilizer

Figure 1 Overall research design.

3.3.2 Collection of Earthworms

Local worms were selected as vermicomposter for this study. Over 200 earthworms (approximately 243g) were purchased from a local seller in Gambang, Pahang, Malaysia. Three vermibins containing 90, 39, and 15 worms (approximately 52g, 30g. 8.g) respectively were used in this study (Domínguez et al., 2000; Kim et al., 2012; Rostami, 2011).

3.3.3 Preparation of Landfill Leachate

Landfill leachate was obtained from leachate pond at Sg. Ikan Landfill site Terengganu, Malaysia. Ten liters of leachate were tightly closed in a plastic bottle and kept in a refrigerator at 4°C temperature condition. The volume of leachate given for each vermibin was 150ml for 10cm depth of soil. Leachate was initially characterized for Nitrate-Phosphorus-Potassium (N-P-K), ammonium contents, and its pH before being introduced in vermibin.

3.3.4 Experimental Design

The experiments were conducted in plastic vermibin of size (m x m and m deep), each of capacity 150 ml of leachate, with holes at the bottom. The composting mixture consisted of different number of earthworms mixed with leachate and soil in the ratio; V1= 15:79.8:5.2 (% wt/wt/vol); V2= 15:82:3 (% wt/wt/vol) and V3=15:84.2:0.8 (% wt/wt/vol) (refer Table 3.1). Earthworms were introduced after soil and leachate were mixed in the vermibin (refer Figure 3.2). The duration of the experiment was 31 days. The moisture content in each vermibin was maintained to 25-50% for three days by sprinkling adequate quantity of water on vermibin. Each vermibin was covered with a black plastic to avoid vermicompost from the sun and left at room temperature. Vermicompost was manually turned over every week to aerate the waste and maintain good porosity in the vermibin. All three vermibins were replicated two times and soil-leachate without earthworms was used as control.

Table 1: Composition of different soil and earthworms in Vermibeds

Vermibeds	Total volume of leachate,%	Total amount of soil, %	Amount of earthworms added, %
V1	15	79.8	5.2
V2	15	82.0	3.0
V3	15	84.2	0.8
V4	15	79.8	5.2
V5	15	82.0	3.0
V6	15	84.2	0.8
Control	15	85.0	0

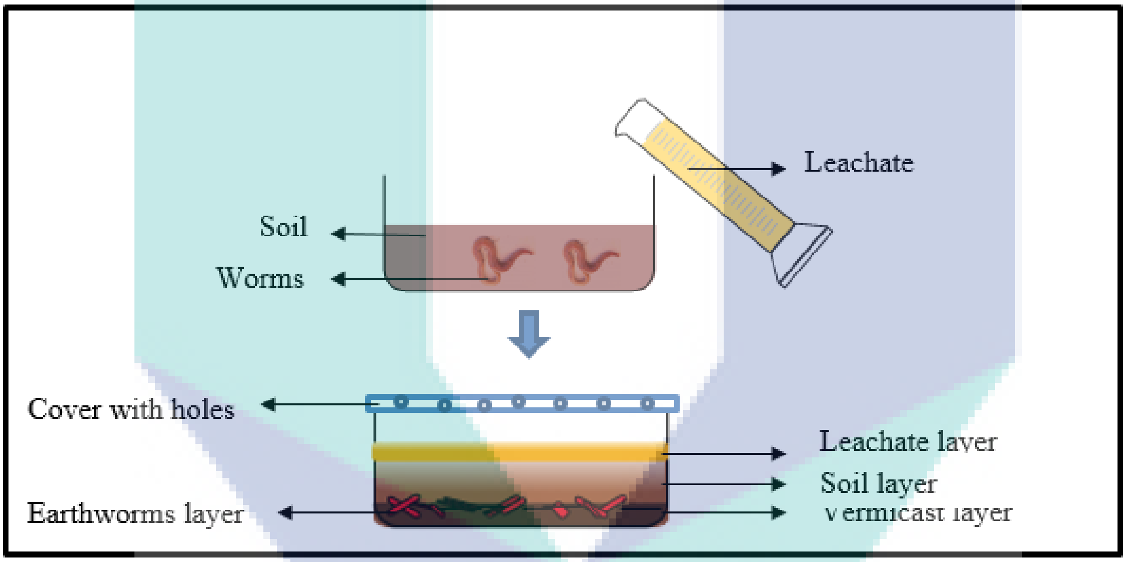


Figure 2 Schematic design of vermibin and experimental setup.
Source: (Zularisam, et al., 2010)

3.3.5 Physical Analysis

In this section, analysis using equipment such as Atomic Absorption Spectrometry and Total Solid Suspended were conducted for soil and leachate. Zainol, et al., (2012) reported in Characterization of Leachate from Kuala Sepetang and Kulim Landfill, leachate mainly consists of a large amount of organic matter including ammonical-nitrogen, phosphate, heavy metals and other toxicant. Thus, AAS was able to analyze the concentration of heavy metals and micro and macro nutrient present in soil and leachate.

3.3.5.1 Atomic Absorption Spectrophotometry (AAS) for heavy metals identification

50 ml of leachate was measured using measuring cylinder and diluted with 100 distilled water. The mixture was filtered using a vacuum pump and ready for AAS analyses. The selected heavy metals such as Ni, Cr, Fe, Cu, and Zn were measured using AAS.

3.3.5.2 Total Suspended Solid (TSS)

Solids suspended in leachate consist of inorganic and organic particles or of immiscible liquids. Howard et. al., (1985) in “Environmental Engineering” book, claimed that leachate contains inorganic solids (silt, clay, soil, etc.) and organic matters such as biological solids (bacteria, pathogens, etc.) and plant fiber are familiar constituents in surface water. These suspended are exist due to the flow of water leachate from the accumulation of waste in the landfill. Therefore, analyze of leachate was conducted using TSS to determine the concentration of solids suspended in leachate.

Filter disk was dried in the oven at 105°C for 1 hour, cooled in a desiccator and weighed. Along the time of drying, filtering apparatus was assembled, filtered and the suctioned was begin. The filter was wet with a small volume of distilled water. After that, 50mL of leachate was pipetted onto the center of filter disk in Buchner flask under vacuum condition. The filter was washed with 10mL of distilled water three times and suction continue for 3minutes. The wet filter was dried in the oven for 1 hour at 105°C and cooled in a desiccator and ready for weighed.

3.3.6 Chemical Analysis

Vermicompost contains plant nutrients such as N-P-K. In this research, chemical analyses were done on vermicompost to determine the concentration of N-P-K and ammonium.

Moreover, N-P-K are the major nutrients uptake by the plant for better performance in growth and productivity. The vermicompost were analyzed before and after vermicomposting as well determine the suitable ratio for the tomato plants. Thus, chemical analyses for each vermicompost were done on soil once per week during vermicomposting. This is to study the degradation of organic matter in a mixture of soil and leachate by earthworms on the concentration of N-P-K. The concentration of N-P-K was determined by Hach spectrometry method DR/2400.

3.3.7 Measurement of soil pH

pH is greatly tied with the availabilities of plant nutrients intake for plant growth (Lucas, & Davis, 1961). Thus, in this research, observation on pH changes during the vermicomposting process and the effect of end-product, vermicompost on the plant are conducted. Ideal pH for vermicompost is 5.0 to 9.0 as for better performance in plant growth (Narkhede, et al., 2011; Zularisam, et al., 2010). Referring to Figure 3.3, 1 g of soil was introduced into the 1000 ml beaker, distilled water 5 ml was added to soil sample (1:5 diluted) (Marangon, et al., 2014). pH meter was used for measurement and data was recorded. The above steps were repeated for V2, V3, V4, V5, and V6 (Table 3.1).

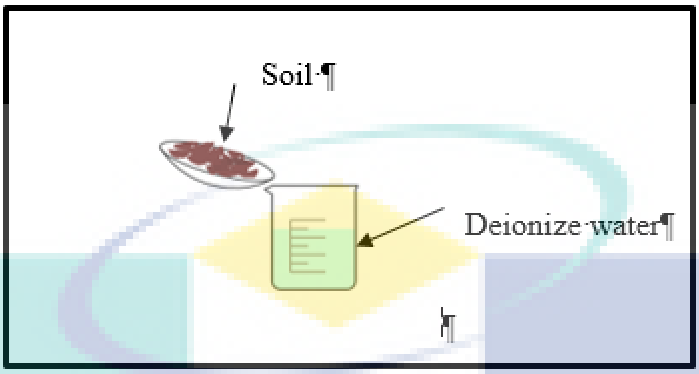


Figure 3 Soil pH analysis setup

3.3.8 Determination of Biochemical Oxygen Demands (BOD)

By referencing to Howard et. al., (1985) in "Environmental Engineering" book, dilution water was prepared by adding 1ml each of phosphate buffer, magnesium sulfate, calcium chloride and ferric chloride solution. Distilled water was added until 1L in a volumetric flask. The leachate was measured up to 10ml and dilution prepared were added until 300ml in incubation bottle. pH leachate mixture was adjusted between 6.5 to 7.5 by adding acid/alkali. 300ml of dilution water was poured into another incubation bottle as a control. Measurement of dissolved oxygen concentration (DO_1) was performed using Dissolved Oxygen meter and the data was recorded. Before incubate both bottles labeled as 'Blank' and 'Sample' in BOD Incubator for five days at a temperature of 20°C. Reading DO_2 was taken after five days of incubation.

3.3.9 Determination of Chemical Oxygen Demands (COD)

COD analysis was tested on leachate before vermicomposting started and soil after the process. High levels of COD in leachate often correlate with threats to human health including seafood contamination and toxic algae blooms bacteria from organic wastes when released it to water stream (StormwateRx LLC, 2016). Therefore, vermicomposting was an alternative to decrease the levels of COD in leachate aside of leachate treatment. The measurement was performed using Hach method (DR/2400, method8000)(Anon 2004). The analysis was done before and after vermicomposting and the data was recorded.

3.3.10 Determination of Nitrogen, Phosphorus, Potassium and Ammonia

Nitrogen, potassium, and phosphorus are important nutrients for fertilizers as it enhances the plant's growth. However, vermicomposting is involved with earthworms that will be the emission of odor during the process. Therefore, soil and vermicompost were performed using Hach Spectrometry DR/2400; nitrate (N) (method8039), available phosphorus (P) (method8190), exchangeable potassium (K) (method8049) and ammonia nitrogen (NH_3) (method8155).(Anon 2004).

3.3.11 Phytotoxicity test on tomato plants

Phytotoxicity test is to evaluate the potential of vermicompost as a biofertilizer. These experiments were held for 60 days (November to December). Each treatment was conducted in duplicate. Eighteen tomato seeds were planted in garden pots filled with 2-inch depth of vermicompost mixed with soil. Plants were grown in the pot with one control without vermicompost. All plants were irrigated with tap water ranging from 300 to 500 ml per day depending on crop maturity and soil water content till the tomato plants were grown fully. After that, the tomato plant’s height was measured every week for a month, and 2 weeks for the next months.

3.4 Findings

In this present study, the results show the mixture of soil and leachate enriching in micronutrients (NPK) after vermicomposting. This is because their nutrients in plant-available forms are released slowly during vermicomposting period. Thus, vermicomposting of leachate appears to be high value biofertilizer beside vermicomposted from sewage sludge, kitchen waste and animal manure which not only increases the plant growth in term of plant height but also pollution free and cost effective. The use of vermicompost promotes soil aggregation where it is improves the air-water relationship of soil, thus encourages extensive development of root system of plants and increasing the water retention capacity (Khan, & Ishaq, 2011).

3.4.1 Characterization of leachate

Table 2 shows the characterization of leachate at Sg. Ikan, Terengganu. Data were presented for the chosen parameters. Values of discharge limit EQA 1947 were listed as a comparison. As a rule of thumb, leachate presented by high values of pH, COD, ammonia nitrogen and heavy metals, as well as strong color and bad odor. However, the composition of waste, climate, rainfall, seasonal variations, solid waste management practices and biodegradable matter present in the leachate over the time influence the characteristics of the leachate (Meeroff, et al., 2015).

The pH values for leachate at Sg. Ikan was recorded at 8.41. This indicate that this leachate was in the methane fermentation phase (Mohd Zin, et al., 2012). Fortunately, the result analysis in Table 2 showed that the elements of heavy metal such as Cr, Ni, Fe, Cu and Zn recorded low value in the leachate and passed the permissible for leachate discharge. At this phase, the solubility of heavy metal to soil solution decreased as the pH of leachate was at alkalinity.

Table 2: Chemical-physical characteristic of leachate used in the experiment (the value in ppm)

Parameter	Unit	Value	Standard
pH	-	8.41	6.0 – 9.0
BOD_5	° C	155.11	20
COD	mg/L	5,443.5	400
SS	mg/L	20.88	50
Fe	mg/L	34.65	5.0
Cu	mg/L	0.03	0.20
Zn	mg/L	0.23	2.0
Ammonia Nitrogen	mg/L	155	5
Cr	mg/L	Undetected	0.20
Ni	mg/L	Undetected	0.20

The pond has been in operation since five year ago. The leachate was characterized by high BOD, and low dissolved solids as well as heavy metals. BOD was chosen as a measure of the amount of oxygen uptake by microorganism during biological degradation of organic compound (Mohd Zin, et al., 2012). It was used as indicator in measuring the strength of organic matter. Table 2 recorded about 87 % of BOD leachate exceeded the permissible from EQA 1974 for discharge. This shows that leachate has high organic matter and able to be used as feeding stock for earthworms during vermicomposting process.

The landfill leachate of Sg. Ikan contained COD of 5,443.5 mg/l, N 75 mg/l and P 33.5 mg/l. Sg. Ikan was found of being rich in COD which presents great toxicity risks on natural water bodies; however, the toxicity can be remove once the pH rise. This is due to the conversion of volatile acids to methane (CH_4) and carbon dioxide (CO_2) throughout the leachate recirculation phase (Tittlebaum, 2010). The COD: N: P ratio is 162:2.2:1. The nutrient content is low for aerobic treatment processes but vermicomposting treatment processes has been used widely to transform waste in to value added product. Vermicomposting technology is efficient to enhance the nutrient content by decompose the organic matter using microorganisms. Prior to this characterization of leachate, the vermicomposting technology may be possible to decompose the organic matter in leachate into valuable fertilizer for agriculture purpose.

3.4.2 Earthworm biomass

The number of earthworm before and after vermicomposting is shown in Table 3. The number of earthworms decrease in all vermibin. Decreasing the number of earthworms from 90 to 78 per kg of vermicompost in V1 by 13 % is greater than V2(5 %) and V3 (7 %). The decrease in the number of earthworms from each vermibin is may due to short-period of vermicomposting; young earthworms takes many months to grow into mature adults and they are easily affected by the toxicity of the waste (Frederickson, & WRC, 2002).

Table 3: The number of earthworm before and after vermicomposting

Vermibin	**Initial** **Number of worms**	**Final** **Number of worms**
V1	90	78 ± 2.82
V2	39	37 ± 1.41
V3	15	14 ± 0.70

The number of earthworms showed the same trend of reduction in the final weight of earthworms. However, the final average weight of individual earthworms was found to be merely equivalent with the initial weight even though, the final total weight of earthworm was found to be lower by the end of vermicomposting period. As recorded in Table 4, earthworms have lost their weight by 34 % (V1), 52 % (V2) and 41 % (V3) from their initial number reading. The possible cause is the earthworms might lack of nutrient. According to Mississippi

Department of Environmental Quality, the earthworms need to eat about over half their weight in food each day. In this study, the earthworms were only fed150 ml of leachate at the initial of the experiment setup and followed by deionizer water for the next 30 days (MDEQ, 2007).

Table 4: Growth rate of earthworms in vermibin

Vermibin	Period (days)	Initial weight of worms (g)	Final weight of worms (g)
V1	31 days	52.1 ± 1.697	34.62 ± 1.754
V2		32.4 ± 0.495	15.46 ± 3.917
V3		7.7 ± 0.424	4.52 ± 1.895

The main factors influencing the growth and activity of earthworm is the physio-chemical characteristics of soil; like soil texture and presence of organic matter. Decreased supply of food as the organic matter content gradually decreases with repeated cultivations, growth (mature, formative, immature) and mechanical damage during vermicomposting (Clive, & P.J, 1996). Department of Primary Industries reported that worms can lose 20% of their body weight each day in mucus and castings, so the soil must be kept moist at the optimum moisture content. However, the moisture content in this study was about 46% which did not achieved the optimum standard moisture at 60 % -80% (Singh, et al., 2016). This is because the bedding depth in this research did not achieved the standard height, which in the range of 4 – 6 inches ("Worm Care and Feeding", 2017). Thus, this resulted flood in the vermibin due to less amount of soil to absorb the water. Not only that, this effected in the weight loss of earthworms. Therefore, the moisture content plays an important role in the distribution of earthworm species.

3.4.3 pH

From the results in Figure 4, the effect decreased after 3-weeks of vermicomposting did not differ for V2 and V3 except for V1. pH of vermicompost in V1 recorded the highest pH from the range of 6.42 to 6.13, compared to control (6.7 to 6.1). V3 showed the highest reduction by 14 % while control reduce by 8 % after 31-days of experiment. The application of earthworms may produce acidic compound by-product, which resulted in lowering of pH. Moreover, pH has a significant role in concentration of nitrate, where high pH cause nitrogen lost as volatile ammonia, while neutral pH stabilizes the content of nitrates (Sharma, et al., 2011).

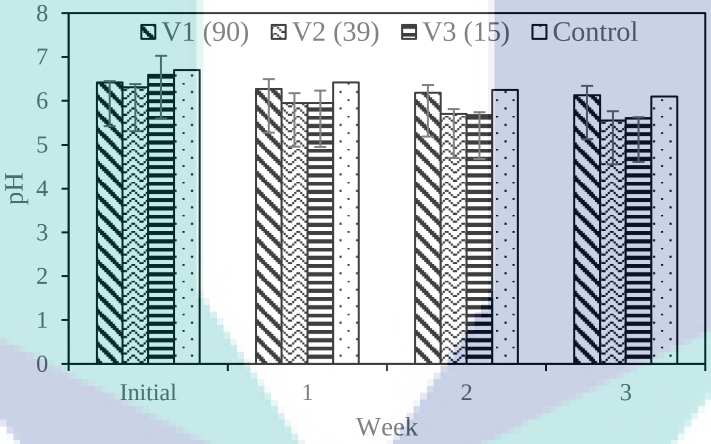


Figure 4 Changes of pH during vermicomposting

The reduction in pH (Figure 4) might be due to the anaerobic process and acidification phase occurred during vermicomposting (Rostami, 2011). In fact, the reduction in pH may due to production of CO_2, NH_3, NO_3^- , and organic acids by microbial decomposition during vermicomposting (Sharma, et al., 2011) (refer Figure 4.1). Arancon, et al., (2004) also reported that vermicompost tended to have pH values near neutrality due to organic acids produced during microbial metabolism and production of CO_2.

3.4.4 Nitrates (N)

The concentration of ammonium in leachate utilized in the experiments showed comparatively low value (155 mg/l) which indicate low nitrogen intensification process (Bityutskii, et al., 2007; Domínguez, et al., 2000). However, the results in Figure 5 showed that the highest concentrations of $NO_3^- - N$ corresponded to the vermicompost and the lowest to the control, where $NO_3^- - N$ in all vermibins increase at the end of day 31. The increase of nitrate concentration in vermicompost may due to the additional of earthworms in the process of degradation. As shown in Figure 5, the application of 90 earthworms to 150 ml leachate was found to increase 54-fold of nitrate concentration; while control has the lowest nitrate concentration with increase 2-fold from initial reading. The number of earthworms in V1 reduce from 90 to 78 (Table 3) indicating that microbial communities used the available energy more efficiently. As a consequence, the large increase V1 in the rate of decomposition of organic matter and in the rates of nitrogen mineralization (Dominguez, 2011).

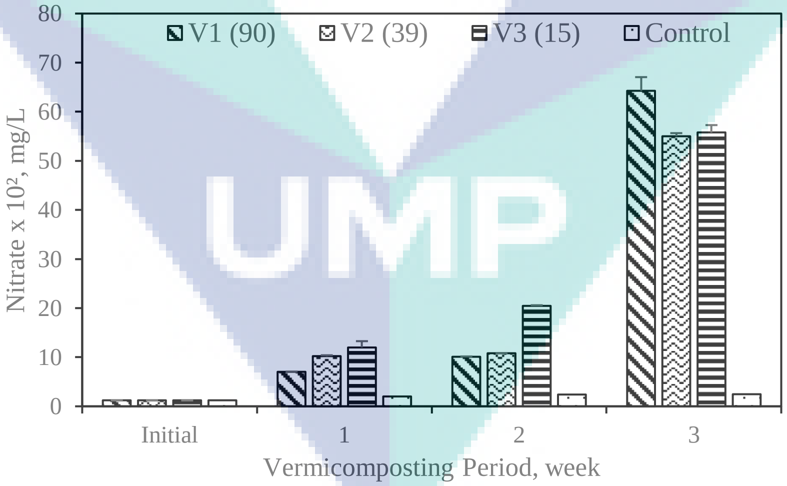


Figure 5 Concentration of Nitrates of vermicompost

The increase in concentration of nitrates values in vermicompost might be due to an increased surface to volume ratio which favoured microbial activity, and consequent N mineralization (Tognetti, et al., 2007). Other research claimed that the increased in $NO_3^- - N$ in vermicomposted indicates that these was no loss of $NO_3^- - N$ during the process of vermicomposting (Francou, et al., 2005; Sharma, et al., 2011). Therefore, retention time of N might be facilitated in the phytotoxicity process. Nitrate content (plant-available form of nitrogen) was high when vermicompost from sewage sludge (35,700 mg/L) compared to cow manure (600 mg/L) after one month vermicomposting. This confirms that the different wastes as a substrate for feeding the earthworms affects the amount of nitrogen from the compound and mineralization of nitrogenous organic compound. Furthermore, nitrogen was released by earthworms during vermicomposting possibly from the formation of various metabolic products such as growth stimulating hormones and dead tissues get attached to the available nitrogen (Shamini, & Fauziah, 2014).

3.4.5 Phosphorus content (P)

As shown in Figure 6, Phosphorus content in vermicompost was enhanced within 31-day vermicomposting, whereas control decrease after 2-week of vermicomposting. Among the vermicomposts, V1 (291.62 mg/L) containing 90 earthworms recorded the highest phosphorus content followed by V2 (218.25 mg/L) and V3 (165.225). Phosphorus in V1 increase 194-fold from 1.5 to 291.62 mg/L at the end of vermicomposting. This result showed that the vermibin containing earthworms enhance the phosphorus content in the vermicompost by degradable the organic matter in the leachate compared to control.

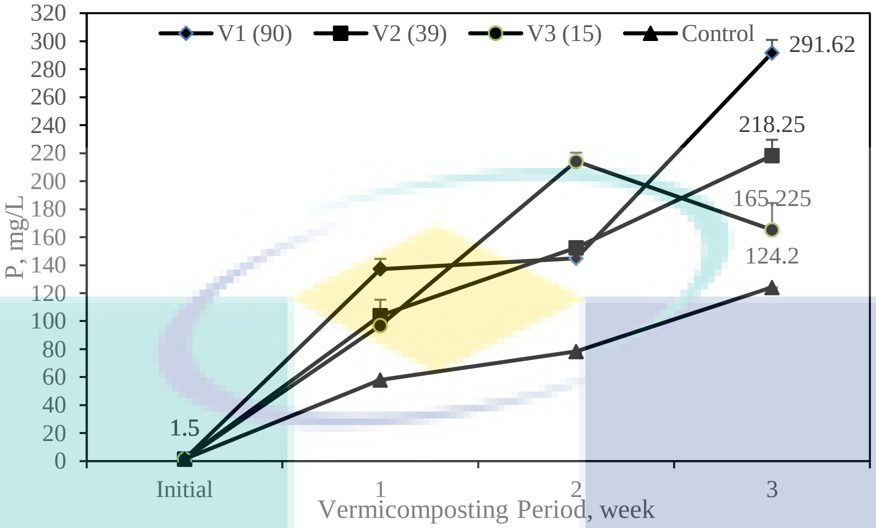


Figure 5 Concentration of Phosphate of vermicompost

Moreover, the earthworms degrade the phosphorus contents in organic matter to the available form for plant uptake. Adhikary, et al., (2012) reported that earthworms consumed large amount of soil with organics, grind them in their gizzard and digest them in their intestine with aid of enzymes. Phosphorus solubilizing microorganisms living the earthworms gut produce enzyme, which will react on the substrate and then releasing phosphorus via secretion (Zularisam, et al., 2010). About 5-10 percent of the chemically digested and indigested material is absorbed into worms' body and the rest is excreted as vermicast; a fine mucus coated granular which are rich in NPK and beneficial soil microbes.

3.4.6 Potassium content (K)

Figure 6 recorded that the highest values were after 31-days of vermicomposting than initial feed mixtures (Figure 4.4). In week 1, vermicompost showed almost the same value for K. However the concentration of K increased significantly in V1 from 327 to 1263 mg/L compared to control which slightly decrease from 100 to 84 after 2-weeks of vermicomposting. Higher amount of earthworm in V1 (90 earthworms) resulted in higher amount of K. This finding were supported by Zularisam, et al., (2010), who reported an increased in K in sewage sludge; Das, et al., (2014), who also reported an increased in K when vermicomposting with different substrates (cattle manure, paddy straw, municipal solid waste and fly ash).

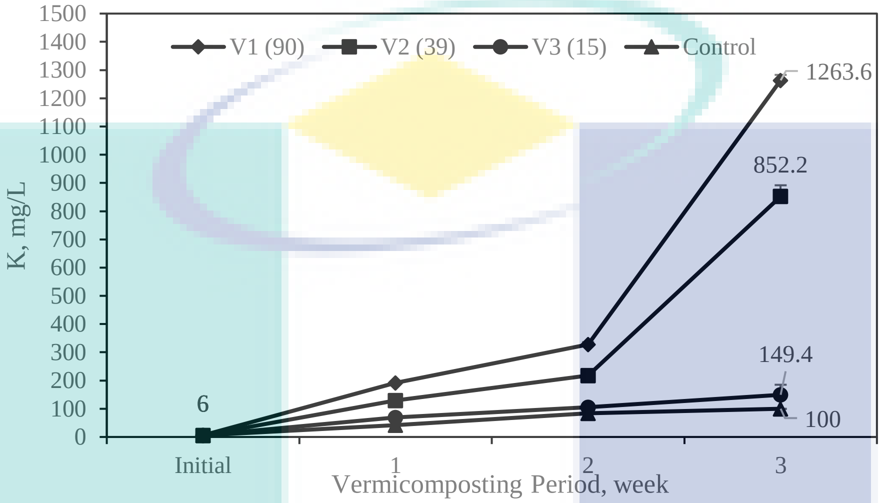


Figure 6 Concentration of Potassium of vermicompost

Earthworm secreted mucus and water to increase the degradation of ingested organic matter and released the exchangeable potassium, thus enhancing K content in vermicompost (Suthar, 2007). In addition, organic acids produced by these microorganisms in earthworms influences the status of K (Das, et al., 2014; Sharma, et al., 2011). According to Fulton, et al., (2010), potassium undergoes exchange reactions with other cations in the soil such as sodium, calcium, magnesium, and hydrogen. The present of heavy metals in leachate might as well react, thus resulted in the enhancing of K content in vermicompost compared control which recorded lowest K (100 mg/L).The colour and texture of the vermicompost started changing to the dark-brown color of soil which indicated of the stabilization process that started in week 2. Similarly, Sinha, et al., (2010) claimed if the vermicompost changed to the color of soil, then the stabilization process occurred.

3.4.7 Phytotoxicity test

According to Figure 7, the plant height was significantly higher in the tomato plants that were added with vermicompost as compared to control after 4-weeks of planting. This probably due to increase in soil fertility, as vermicompost is rich in nitrate content. The leaf number of tomato plants did not show any sign of disease. V1 consists of 90 earthworms has high NPK compared to V2 and V3. Thus, the highest plant height in V1 (14.4 cm) while the lowest value (4 cm) was recorded for the control. In addition, V1 was measured to have 32-number of leaves. This indicate that N-P-K (6,247- 291 -1263 mg/L) of V1 is suitable for tomato plant.

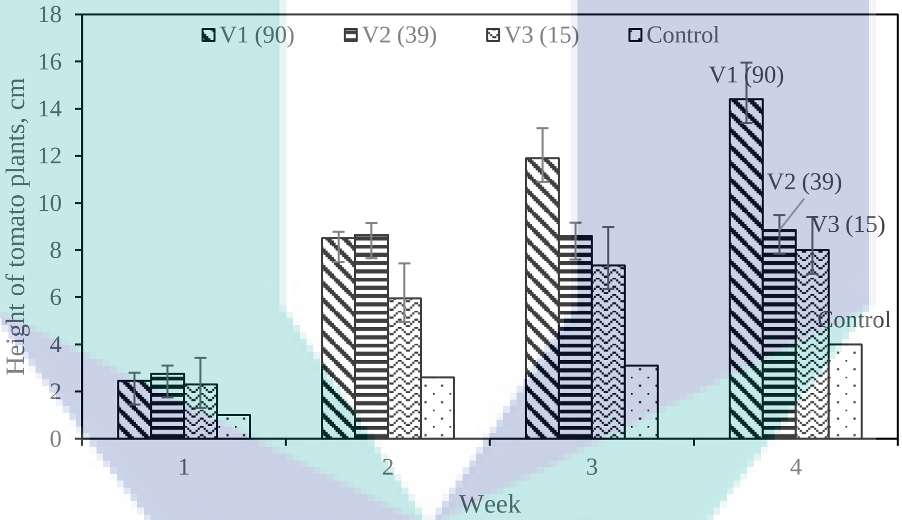


Figure 7. Height of tomatoes stem (means±SE). Standard deviations are given at the top of the column.

The tomato plants resulted from the vermicompost was significantly higher than control. These results were agreed with the finding of Mengistu, et al., (2017) who reported the significant impact in height of tomato after the application of vermicompost.

3.5 Conclusion

Leachate production may contaminate the soil and underground water as well as the release of unpleasant smell. A way of handling this leachate is by converting into vermicompost or biofertilizer, which is rich in important nutrients required for plants. In this research, biofertilizer production by vermicomposting of leachate showed significant result in enhancing NPK and the texture of the soil. Vermicompost in V1 showed the best biofertilizer, which contain high N-P-K with pH of 6.13. In our present study, V1 containing 90 earthworms enhanced the nutrient content of N-P-K (6,247-291-1263 mg/L). This indicate that the number of earthworms influenced the enhancement of NPK during vermicomposting period. The phytotoxicity test showed remarkable height of tomato plant of 14.4 cm with 32-number of leaves after 4-weeks from the application of vermicompost.

3.6 Recommendations / Way Forward

For the further research, the moisture content need to reach at least 60 % – 80 % and maintain during vermicomposting process (Mehta, & Karnwal, 2013). This is to help earthworms in retaining moisture and enhance their activity to produce vermicompost that exceptionally valuable fertilizer. Considering the moisture content, height of soil should be 8 to 12 inches to avoid the soil become muddy and to increase the mobilization of earthworms in soil (Hashemi, et al., 2004). Optimum condition will help production of earthworm besides enriching the element such as nitrate, phosphorus and potassium.

CHAPTER 4

OIL EXTRACTION FOR A PRODUCTION OF FATTY ACID FROM FISH WASTE

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4.1 Abstract

The waste produced from fish processing industries had been proposed as raw materials for fish oil production. These fish wastes were discarded into the environment without any recovery and it will cause environmental pollution. Preliminary experiment was conducted to determine the effect of temperature and mixing time on the production of fatty acid. The evaluation of temperature and mixing time were done by conducting experimental works that were constructed by using Design Expert Software. The experiments were started with collecting the fish waste and processes it till becomes a fine powder. Solvent Extraction method were used to elucidated the best operating conditions with various temperatures (50 to 70 °C) and mixing time (3 to 5 hours) under constant mixing rate. The result showed that the highest oil yield (10.56%) and oleic acid (26.85 mg/g) were obtained at 80 °C and 4 hours of extraction. After that, the validation experiment was performed in triplicates under the optimized condition (70 °C and 3.28 hours) that obtained from CCD to validate the predicted value. The maximum response for oil yield and oleic acid obtained from the experiment were 18.19% and 23.12 mg/g respectively, whereas the predicted value using were 10.48% and 18.19mg/g. Based on the result, it showed that to study the effects of each factor using RSM through CCD in

optimization of oil yield and oleic acid were accepted to be used for biodiesel production from fish waste.

4.2 Introduction

4.2.1 Objectives

The objective of this research is to study the effects of temperature and mixing time on the production of fatty acid from fish waste.

4.2.2 Scopes of study

1) Extraction of fish oil from fish waste using solvent extraction method.
2) Optimization of operating conditions such as temperature (50-70 °C) and mixing time (3-5 hours) using Response Surface Methodology (RSM).
3) Analyzing the fatty acids profile from fish oil extraction using Gas Chromatograph Mass Spectrometry (GC-MS).
4) Performing a test to determine the validation of the result from Central Composite Design (CCD).

4.3 Methodology

The raw material use for the oil extraction is fish wastes which obtain from the market in Jaya Gading Kuantan, Pahang. In this research, only the outside parts of fish wastes are selected to be used in experiment

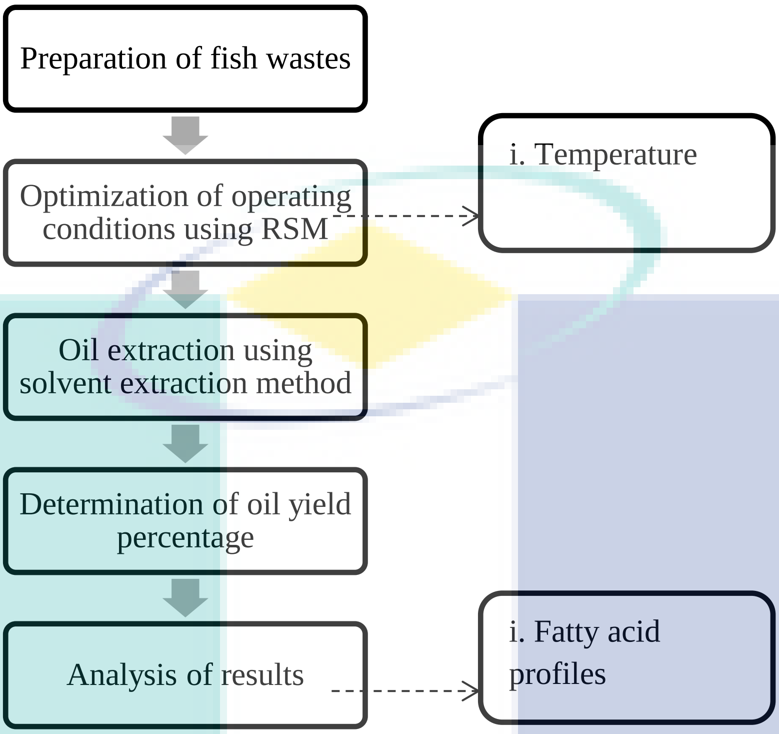


Figure 1 Process flow chart of the experiment.

4.3.1 Sample Preparation

Fish wastes were obtained from nearest market in Jaya Gading, Kuantan Pahang. The wastes then were separate by heads, fins, scales and tails manually from all the wastes obtained. Selected wastes then were clean by using water and dried in oven for 24 hours at 50 ℃. Then the dried fish wastes were grind into fine powder using electrical grinder.

Figure 2: The procedures for sample preparation.

4.3.2 Solvent Extraction Method

For the extraction of fish oil, 0.72 g of fish wastes powder was weighed and mix together with 12 mL of ethanol. The test tube was added with magnetic stirrer. Then, the sample was sonicated for 10 minutes. After that, the test tube was clamp and put into 1 L beaker. The experiments were conducted with various temperatures and mixing time. Approximately the range of temperature and mixing time are 60 to 80°C and 3 to 5 hour, respectively. After the extraction process, the sample was transferred into the centrifuge tube and centrifuge with speed of 3000 rpm for 5 minutes. After 5 minutes of centrifugation, there are two layers formed in centrifuge tube where the upper layer is oil and the bottom layer is biomass. The oil that we needed was transferred into the vial using micropipette and the biomass was discharged into the bin. The vial was heated for 24 hours until the oil content fully evaporated. After that, the weight of the oil was determined to calculate the percentage of oil yield. All the experiments were conducted in triplicate to obtain a better result for the fish oil extraction.

4.3.3 Optimization using Design expert

The effect of each factor involved in Fatty Acid and Oil Yield production was studied through RSM by determining the optimum condition. RSM was performed through central composited design (CCD) using Design Expert Software, version 7.0.0 (State-Ease, Inc). Optimization was performed using two independent variables which were identified as having significant effect on Fatty Acid and Oil Yield production. The independent variables considered were Temperature (50 to 70°C) and mixing time (3 to 5 hour).

4.3.4 Validation Experiment

Maximum oil yield and oleic acid were predicted using the optimum conditions where the temperature and mixing time were set at 70 °C and 3.28 hours, respectively. A validation experiment was performed in triplicates under the optimized condition and the results were compared with predicted value to confirm the validity of the model.

4.3.5 Fatty Acid Methyl Esther Analysis

The fatty acid profiles from the extracted fish oil were analyzed using Gas Chromatography Mass Spectrometry (GCMS) after each extraction by using Agilent Technologies (G3171A, China) (Ghazali et al., 2016) as shown in Fig 3.8. The samples were injected into capillary column HP-5 (30 m length, 0.25 mm ID). Helium was used as the carrier gas with a flow rate of 1 mL/min. The inlet temperature and the detector temperature were kept constant at 250 °C and 280 °C, respectively with temperature programming of 100 °C for 3 minutes with increase by 10°C per minutes up to injector temperature of 250 °C (Gaikwad et al., 2011). The fatty acid compounds consisted of C16:0, C16:1, C18:0, C18:1, C18:2 and C18:3 were identified by comparing the peak areas and retention time with standard chemicals. All the analysis was replicated three times.

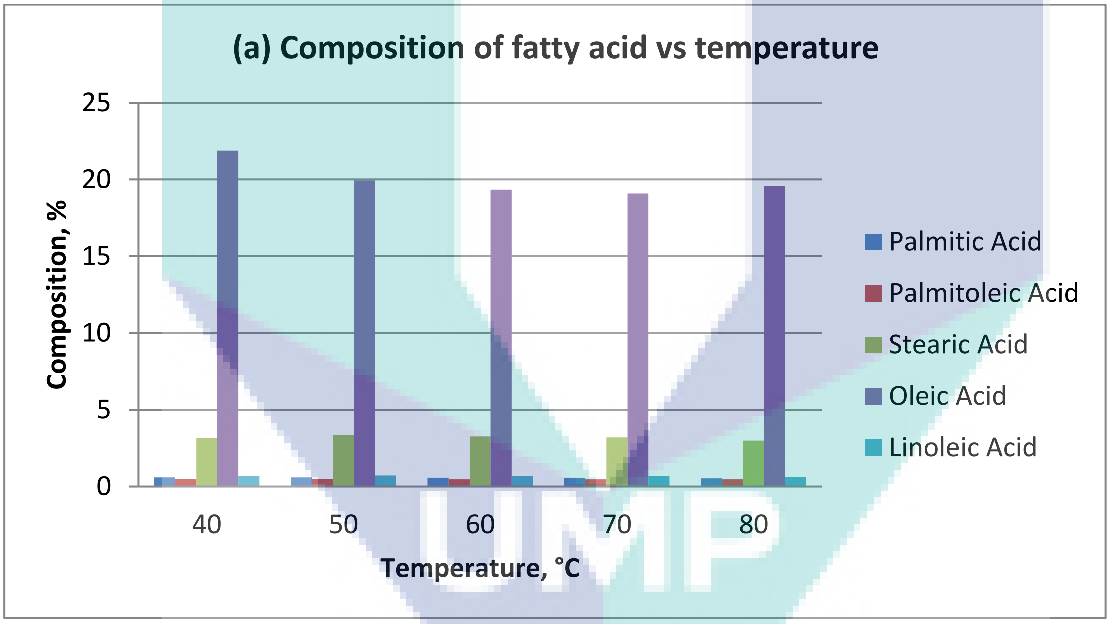
4.4 Findings

4.4.1 Fatty acid methyl esters (FAME) profile of fish oil

This current study, fish oil was extracted from fish wastes by the solvent extraction method. The amount of FAME (%) was identified from the chemical analysis of GCMS. The FAME obtained from fish waste was analyzed at different temperature (50 to 70 °C) and mixing times (3 to 5 hour).

Fig 3 shows the composition of FAME (%) which affected by temperature and mixing time. There are five FAME compounds detected in the fish oil which are oleic acid, palmitic acid, palmitoleic acid, stearic acid and linoleic acid. Based on the figure, oleic acid shows the highest percentage of FAME compositions among other FAME after extraction of fish oil from fish waste. However, there are only small amount of palmitic acid, palmitoleic acid and linoleic acid identified in fish oil at all range of temperature and mixing time. Based on Fig 3(a), among of five temperatures used, the highest composition of oleic acid obtained at the temperature of 40 °C which is 21.89%. It is also shows that the percentage of oleic acid decreased as the temperature increase until 70 °C and keep maintain the trend even the temperature increase. Meanwhile, Fig 3(b) shows the different pattern for the composition of oleic acid where the highest percentage obtained at 3 hours of mixing time.

The major constitutes of FAME was consistently of oleic acid. The presence of oleic acids was in agreement with Khoddami et al. (2009) who disclosed that oleic acid (C18:1) act as major components in fish oil. The ratio of oleic to linoleic acid (O/L) was considered an important criterion to evaluate the oil quality (Kodad et al., 2008). Increasing O/L ratio by increasing oleic acid and decreasing linoleic acid contents confers better stability and longer shelf life. In addition, Enascuta et al. (2018) evaluated SO_4^{2-}/SnO_2 in the esterification reaction of Free Fatty Acid (FFA). As mention in their report, the esterification reaction of oleic acid with ethanol (molar ratio 10:1) at 80°C and 3 wt.% catalysts give 50% of conversion after 4 hours of reaction time.



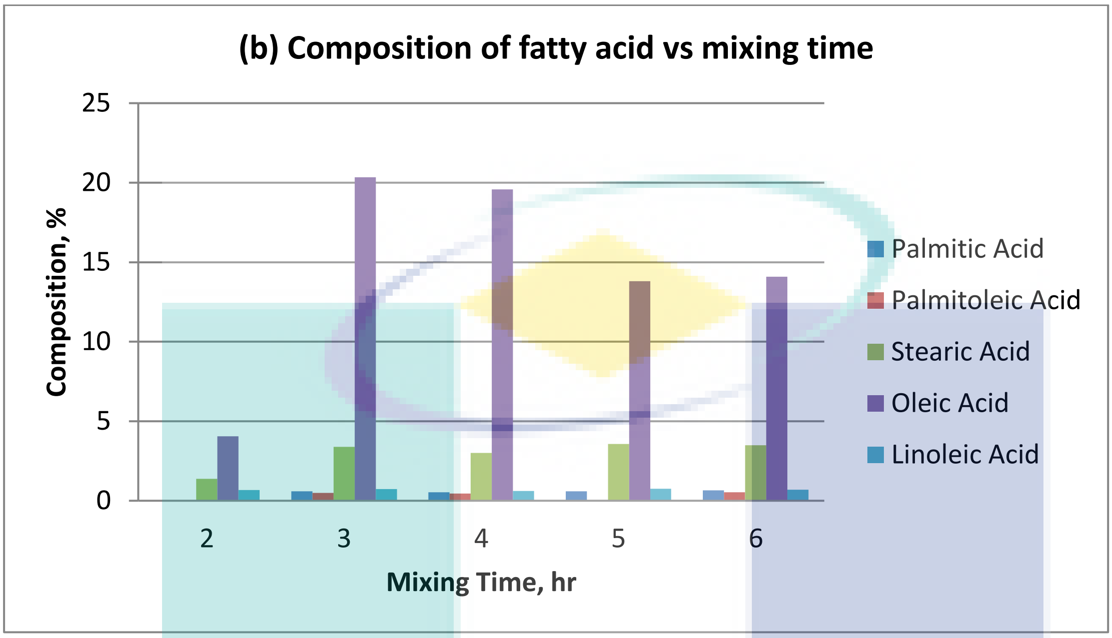


Figure 3: The effect of (a) temperature and (b) mixing time on the composition of FAME.

Fatty acid profiles of the oil extracted from the fish waste for two different samples are shown in Table 1. Sample 1 and 2 represents the effect of temperature at 40 °C and mixing time at 3 hours respectively. GCMS analysis illustrate that the sample were containing of the common fatty acid methyl ester which were consisted of oleic acids (C18:1), stearic acids (C18:0), palmitic acids (C16:0), palmitoleic acids (C16:1) and linoleic acids (C18:2).

Table 1: Fatty acid profile of fish wastes lipid

FAME	**Amount of FAME (mg/g)**	
	Sample 1	**Sample 2**
C16:0	0.60	0.60
C16:1	0.50	0.49
C18:0	3.17	3.39
C18:1	21.89	20.34
C18:2	0.69	0.73
SFA (%)	3.77	3.99
UFA (%)	23.08	21.56
Total FAME	26.85	25.55

With reference to Table 1, the fatty acids of the fish oil were generally composed of saturated fatty acid (Palmitic Acid and Stearic Acid) and unsaturated fatty acid (Palmitoleic Acid, Oleic Acid and Linoleic Acid). The extracted fish oil for both samples contained greater percentage of UFA which is 23.08% and 21.56% respectively. While the amount of SFA obtained were much lower than SFA which are 3.77% and 3.99% for sample 1 and sample 2. The SFA in both sample were palmitic acid and stearic acid with the highest level of C16:0 (0.60%) and C18:0 (3.39%) were determined in sample 2. The UFA identified was predominantly compose of oleic acids (C18:1) followed by palmitoleic acids (C16:1) and linoleic acids (C18:2). The highest oleic acids were obtained in sample 1 (21.89%), compared to the sample 2 (20.34%). In comparison between sample 1 and 2, the amount of each FAME is not much different for both samples.

The composition of FAME was similarly showed by other fish oil, such as salmon and rainbow trout (Khoddami et al., 2009). Comparatively the results which expressed the different proportion of monounsaturated (MUFA) and polyunsaturated (PUFA) with other fish lipids may be due to the environmental effect of tropical fish species. According to Gladyshev et al. (2006), the distinctive difference of the SFA and UFA content in fish oil may be attributed to the seasonal changes and the changes in plankton species in their diet and also in the post-spawning period.

FAMEs of fish oils were found suitable for use as biodiesel in diesel engine. The most important biodiesel properties are carbon number, oxidative stability and energy content. Unsaturated fat are oils in which one or more of the carbon to carbon bonds in the fatty acid chain which is a double bond. The more highly unsaturated a fat is, the lower the gel point typically is. Typically, biodiesel made from highly unsaturated fats will require an oxidative stabilizer to be used safely as fuel. The heating value of a fuel also increases with increasing carbon number in fuel molecules. Therefore, unsaturated fats are excellent for cold weather biodiesel production and use. In this case, UFA which is oleic acid (C18:1) was chosen as the highest percentage composition and the longest carbon among others, so oleic acid was chosen as response for next study which is CCD.

4.4.2 Analysis of Variance (ANOVA)

For more detailed explanation in mathematics, ANOVA was applied to generate the sum of squares, mean squares, F values, and p values by fitting the experimental data in Table 4.2 and 4.3 to the second-order polynomial equation. According to the results, P value for both result was 0.0098 and 0.0301, respectively. If "*p*-value" less than 0.05, it showed that the model terms were significant (Samad et al., 2017). In this study, both of the models show A^2 and B^2 are significant model terms. Meanwhile, the "lack of fit" was not significant with *p*-value of 0.5339 and 0.1557 for both of the models, signified that the model adequately explained the data in the region of experimentation. The lack of fit test was used to check the adequacy of the model (Wu et al., 2017). By referring to the results in Table 2 and 3, the coefficient of determination, R^2 values obtained were 0.8431 and 0.7781 in which it demonstrated that the model was well fitted for the predicted and experimental data. According to Shamsuddin et al. (2015), a good model was verified through the R^2 value which should be above 80%.

Table 2: ANOVA analysis for oil yield

Source	**Sum of Squares**	**Mean Square**	**F Value**	**p-value Prob> F**	
Model	1.17	0.23	7.52	0.0098	Significant
A-Temperature	0.28	0.28	8.85	0.0207	
B-Mixing Time	0.46	0.46	14.88	0.0062	
AB	0.24	0.24	7.70	0.0275	
A^2	0.018	0.018	0.57	0.4768	
B^2	0.13	0.13	4.24	0.0784	
Residual	0.22	0.031			
Lack of Fit	0.085	0.028	0.85	0.5339	not significant
Pure Error	0.13	0.033			
Cor Total	1.39				
R-Squared	0.841				
Adj R-Squared	0.7310				

Table 3: ANOVA analysis for oleic acids

Source	**Sum of Squares**	**Mean Square**	**F Value**	**p-value Prob> F**	
Model	235.79	47.16	4.91	0.0301	Significant

A-Temperature	12.06	12.06	1.26	0.2994	
B-Mixing Time	17.30	17.30	1.80	0.2214	
AB	5.98	5.98	0.62	0.4560	
A^2	0.29	0.29	0.031	0.8660	
B^2	179.86	179.86	18.73	0.0034	
Residual	67.23	9.0			
Lack of Fit	46.71	15.57	3.04	0.1557	not significant
Pure Error	20.52	5.13			
Cor Total	303.02				
R-Squared	0.7781				
Adj R-Squared	0.6197				

4.4.3 Validations of the model

The predicted value to select the highest oil yield and oleic acid is given in Table 4. Validation experiment was run in order to validate the predicted value. The experimental response values of the optimized condition were slightly further to the predicted values, proving the validity of the predicted model. The maximum response for oil yield and oleic acid obtained from the experiment were 18.19% and 23.12 mg/g respectively, whereas the predicted value using Eq. (3 and 4) is 10.48% and 18.19 mg/g, respectively. The error for oil yield and oleic acid is very high which is 76.24% and 36.89%, respectively. This might be happened because of the sample stored for too long, so the sample exposed to the surrounding and the damage were affected the result. As for the response model is satisfactory to express the expected optimization and the model (Eq. 2 and 3) is accurate and acceptable.

Table 4: Validation result of optimum conditions from CCD

Run	Oil Yield (%)	Oleic Acid (mg/g)

	Predicted Value	Experimental Value	Error Percentage (%)	Predicted Value	Experimental Value	Error Percentage (%)
1	10.48	18.19	73.57	18.19	11.48	36.89
2	10.48	18.33	74.90	18.19	11.52	36.67
3	10.48	18.47	76.24	18.19	11.66	35.90

4.5 Conclusion

A correlation analysis between classical one factor at a time (OFAT) approach and statistical experimental design using a Response Surface Methodology (RSM) model with Central Composite Design (CCD) have provided well-founded results for oil yield and oleic acid production. The effect of temperature and mixing time were well described by RSM. The low p-values of 0.0207 and 0.0062 for temperature and mixing time, respectively, show that both factors are significant and very important in order to produce high oil yield from fish waste by solvent extraction. The optimum condition at 70 °C of temperature and 3.28 hours of mixing time had successfully increased the oil yield (10.48%) and oleic acids (18.19 mg/g). A high correlation second order polynomial equation between observed and predicted responses was developed by RSM for the oleic acid production. It presents the relationship between each factor and the oleic acid production efficiently. Therefore, it is useful to study the effects of each factor using RSM through CCD in optimization of oil yield and oleic acid for biodiesel production from fish waste.

4.6 Recommendations / Way Forward

For the recommendation, the research can be improved by study on the different temperature such as 70 °C, 80 °C and 90 °C. This temperature might increase the oil extraction yield of fish waste. However, it cannot be too higher to avoid damage of cell structure that causing decrease oil extraction yield. Besides that, in this study the analysis result only was analysed up to two design parameter level. It was suggested for future study to analyse more different parameter such as mixing rate, mixing time and temperature. This different parameter will affect more result that can be used in RSM. The result of optimization analysis will be clearer and less error when do the validation comparison between predicted and experimental value. Compared to using “one to one factor” method, RSM is far better since in RSM the several process variables simultaneously interact with each other.

CHAPTER 5

FISH FEED PRODUCTION FROM FISH WASTE

PROJECT LEADER:

DR. ZATUL IFFAH BTE MOHD ARSHAD

5.1 Abstract

This study presents about the formulation of fish feed from fish waste, soybean (*Glycine max*), and groundnut (*Arachis hypogea*) as alternative substitutes to the conventional fish meal in the formulation of fish feed. The formulation composition was designed through the two-level factorial analysis using the Design Expert software. There were four responses observed in this research which were moisture content, nitrate content, pH value, and leaching rate. After analysis, there are two important attributes of fish feed formulation which were the nitrate content and the leaching rate. The obtained R^2 for nitrate content was 0.9950 and 0.9825 and for the leaching rate was 0.9254, respectively. Meanwhile, the obtained adjusted R^2 for the nitrate content was 0.9825 and for the leaching rate was 0.8258, respectively. An optimization was done which resulted the nitrate content of 8.1 mg/L and the leaching rate of 9.63755%. Run 3 was selected as the best-formulated fish feed with the desirability of 0.548 which based on the low nitrate content and leaching rate. The validation run was conducted to verify the predicted result. The percentage error obtained for the nitrate content and leaching rate were 2.1% and 7.71%, respectively which were acceptable as the tolerable maximum percentage

error of below 10%. Therefore, fish waste, soybean meal and groundnut meal were proven to be the alternative substitutes to the conventional fish feed formulation

5.2 Introduction

5.2.1 Objective

To formulate fish feed from fish waste

5.2.2 Scopes of study

1. Collection of fish waste from fish market at Gambang, Pahang.
2. Fish feed formulation consist of fish waste (20% to 30%), soybean meal (50% to 60%) and groundnut meal (15% to 20%).
3. Screening the best formulation of fish feed using the two-level factorial analysis by measuring the responses:
    I. Moisture content percentage
    II. Concentration of nitrate ions
    III. pH value
    IV. Leaching rate percentage

5.3 Methodology

5.3.1 Overview

The illustration of the methodology for the whole research is shown in Figure 1. Firstly, the fish waste was collected from the fish market at Gambang, Pahang. After that, the fish waste was undergone the heat treatment process. Next, the formulation of different ratio of fish feeds was done. Then, the designed experiment by the Design Expert software on the factorial analysis was conducted. Finally, the experimental data were analysed to determine the best-formulated fish feed that have the best attributes according to its responses.

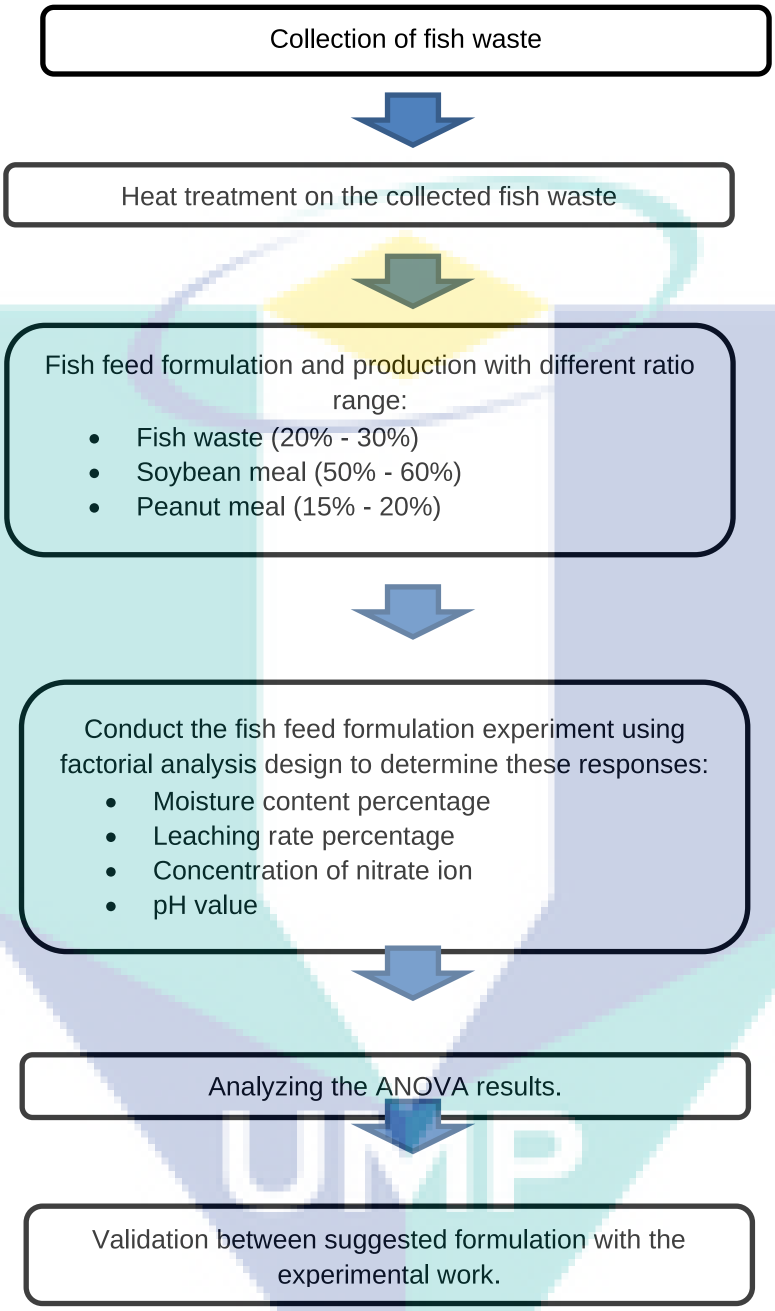


Figure 1: Process flowchart of experiment

5.3.2 Fish Waste Collection

Fish was collected from the fish market at Gambang for twice a week to ensure the continuation of the fish waste source in this research. The fish waste was stored in the refrigerator at the temperature below 5°C. The storage of fish waste needs to be at a low temperature to lower the microorganism activity and inhibit anaerobic digestion before introduced into fish feed formulation.

5.3.3 Heat Treatment of Fish Waste

The fish waste was undergoing heat treatment process to reduce the moisture content below 10% to prevent the condition that favours the microbial growth and activity. The fish waste is enough to be heated at minimum temperature condition at 65°C for 20 minutes using the oven. Therefore, the formulated fish feed will have longer shelf life.

5.3.4 Preparation of Formulated Fish Feed Production

The collected fish waste was utilized in the formulation of fish feed by adding soybean meal and groundnut meal. Eight different formulations of fish feed with different proportion of fish waste to soybean meal and groundnut meal were used to produce the fish feed. By using the Design Expert software, the experimental design was outlined through the two-level factorial analysis tool. Table 1 shows the experimental design of eight types of fish feed formulation with its composition per 100g.

Table 1: Factors of 2-Level Factorial Design

	Name	**Units**	**Type**	**Low**	**High**	**Reference**
A.	Fish Waste	%	Numeric	20	30	(Wong et al., 2016)
B.	Soybean Meal	%	Numeric	50	60	(Silva-Carrillo et al., 2012)
C.	Peanut Meal	%	Numeric	15	20	(Puspasari et al., 2015)

This formulation experiment was conducted to determine which factors that give the best quality for the production of fish feed. The low and high of each factor were determined through the references stated. Each range was selected based on its positive results in the previous study. Table 2 shows the layout of the formulation experiment of fish feed in this study. The responses involve were moisture content, nitrate content, pH value and leaching rate.

Table 2: Experimental Layout for Factorial Analysis

Std.	Run	Factor 1 A: Fish Waste %	Factor 2 B: Soybean Meal %	Factor 3 C: Peanut Meal %
8	1	30.00	60.00	20.00
7	2	20.00	60.00	20.00
5	3	20.00	50.00	20.00
6	4	30.00	50.00	20.00
2	5	30.00	50.00	15.00
4	6	30.00	60.00	15.00
3	7	20.00	60.00	15.00
1	8	20.00	50.00	15.00

5.3.5 Production of Formulated Fish Feed

The method of producing the fish feed was referred from Ighwela et al. (2013). The following steps in the formulation of fish feed are shown below:

1. All the ingredients were weighed according to its weight composition designed through the factorial analysis tool of Design Expert software. The total weight of the composition of the fish feed was per 100g of production.

Figure 2: The raw ingredients for the fish feed formulation

2. Water was added to mix all the raw ingredients.

Figure 3: Addition of water to mix the ingredient

3. The ingredients were mixed until it forms a dough-like texture.

Figure 4: Mix the ingredients to form a dough

Figure 5: The form of dough

4. The dough was inserted into the hand operated noodles maker with aperture approximately 2.5 mm to form long strands that later were cut into smaller pieces.

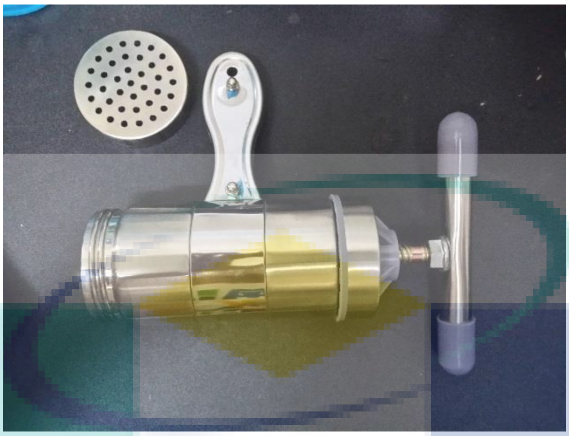


Figure 6: Hand operated noodles maker

5. The produced fish feed in the form of long strand was let to dry at room temperature overnight.

Figure 7: The fish feed was dried at room temperature overnight

6. After dried for overnight at room temperature, the dried fish feed was ready to be packaged.

Figure 8: The dried fish feed

7. The final products of fish feed produced with a different formulation.

Figure 9: The final product of the formulated fish feed

The colour was different for each formulated fish feed. The high the percentage of fish waste resulted in the darker colour of the pellet. Meanwhile, the low the percentage of fish waste in the formulation resulted in the lighter of the colour of the fish feed pellet.

5.3.6 Determination of Nitrate Ions Content in Water

Fish feed sample analysis was conducted to test the nitrate ions content using spectrophotometer of Hach method DR/400. A nitrate reagent powder pillow was added to the 10mL sample. The concentration of nitrate ions in the fish feed was analysed by using the spectrophotometer. The suitable nitrogen content in the water must be kept at low level to make an ideal condition for fish to live.

5.3.7 Determination of Water pH Level

Water sample analysis to test the pH level was conducted using the portable digital pH meter. The sensor of the portable digital pH meter was immersed in the water to obtain the pH level value of the water on the digital screen. The pH level of water should be within the range of 6.5 to 9 as an optimal pH level to promote fish reproduction and growth.

5.3.8 Determination of Leaching Rate

Each of the formulated fish feed was weighed up to a minimum 3 grams as the initial weight for the leaching rate experiment. The initial weight was recorded before it was immersed into a beaker containing 250 mL of distilled water for one hour. The remaining solids after the immersion were dried in the oven and were further dried until a constant weight was recorded.

The lower the leaching rate confirms the good quality of the formulated fish feed as it is also affected by its water stability. The leaching rate of the formulated fish feed was computed using the equation (Eq.1) (Ighwela et al., 2013) below:

$$\text{Leaching Rate} = \frac{A \times (1-r) - R}{A \times (1-r)} \times 100\% \qquad \textbf{(Eq. 1)}$$

where,
A = Weight of fish feed before immersion
r = Moisture content of fish feed
R = Dry weight of the remaining solid

The remaining solids of the formulated fish feed were filtered through filter paper and dried in the oven for 105°C for 30 minutes. The residual was kept heated at 65°C until constant weight was obtained.

Figure 10: The fish feeds were weighed at maximum 3 grams for the experiment

Figure 11: The fish feeds were immersed into distilled water for one hour

5.4 Findings

5.4.1 Leaching Rate

Table 3 shows the results on the leaching rate of the formulated fish feed. From the results, formulation G (fish waste 20%, soybean meal 60% and groundnut meal 15%) had the lowest percentage of leaching rate which was 3.3118% compared to other formulation. The leaching rate can be used to determine the water stability of the fish feed pellets. As the leaching rate decreases, the water stability of the fish pellets was also increased (Ighwela et al., 2013).

The fish feed should have high water stability to ensure that there are fewer proteins are leached to enhance the growth of fish. However, this experiment was conducted at one hour and based on the similar experiment done by Ighwela et al. (2013) with some modifications, prove that the formulate that contained the highest maltose composition had 30% of leaching rate. In this research, the highest leaching rate obtained was from formulate A (fish waste 30%, soybean meal 60% and groundnut meal 20%) which was 19.4517%. This showed that the formulated fish feeds in this study is a potential formulation for future production of fish feed.

Table 3: The moisture content and leaching rate of formulated fish feed

Formulate	Initial Weight, g	Remaining dry weight, g	Moisture content, %	Leaching rate, %
A	3.0021	2.2842	5.529	19.4517
B	3.0019	2.3219	5.005	18.5771
C	3.0027	2.5198	6.977	9.78812
D	3.0007	2.5718	9.673	5.11513
E	3.0012	2.6178	9.071	4.07339
F	3.0013	2.5970	10.507	3.3118
G	3.0025	2.4327	10.082	9.89292
H	3.0021	2.4221	9.163	11.1814

5.4.2 Factorial Analysis Study

Table 4 shows the results on the fish feed formulation that was designed through the two-level factorial analysis using Design Expert Software. The attributes were determined by their results on the four different responses in this study which were moisture content, nitrate content, pH value and the leaching rate. Each response of the experimental design was analysed by using ANOVA based on the *p*-value with a 95% confidence level.

Table 4 : Factorial analysis results

Std.	Run	Factor 1 A: Fish Waste %	Factor 2 B: Soybean Meal %	Factor 3 C: Groundnut Meal %	Response 1 Moisture Content %	Response 2 Nitrate Content mg/L	Response 3 pH	Response 4 Leaching Rate %
8	1	30.00	60.00	20.00	5.529	8.9	6.14	19.4517
7	2	20.00	60.00	20.00	5.005	8.5	6.22	18.5771
5	3	20.00	50.00	20.00	6.977	8.1	6.15	9.78811
6	4	30.00	50.00	20.00	9.673	8.7	6.52	5.11512
2	5	30.00	50.00	15.00	9.072	8.3	6.05	4.07339
4	6	30.00	60.00	15.00	10.507	8.4	5.76	3.3118

3	7	20.00	60.00	15.00	10.082	8.6	5.82	9.89292
1	8	20.00	50.00	15.00	9.163	8.2	5.88	11.1814

Moisture content plays an important role in the fish feed attributes as it may improve the feed intake and growth of fish which related to the disintegration of feed pellets (Oehme et al., 2014). Furthermore, the feed moisture content can be used as a mean to adjust the pellet quality (Oehme et al., 2014). Based on the result obtained in Table 4, the moisture content percentage recorded was ranged from 5.005% – 10.507%. This was supported by a study done by Sorensen (2003), where the moisture content of fish pellet was usually reduced to below 8% after the extrusion to increase the shelf life during storage. There is no specific literature mentioned about the ideal range of moisture content in the fish feed pellet. However, the moisture content is needed to be kept at a low percentage as it would affect the lifetime of fish feed during the storage. After all, the final quality of the pellets is affected by many production conditions during grinding, conditioning, extruding and drying as well as physiochemical properties of ingredients (Oehme et al., 2014).

Besides, the concentration of nitrate content in formulated fish feed recorded in the Table 4.2 was ranged from 8.1 – 8.9 mg/L. The nitrate content of the fish feed should be kept at a low level to prevent the poisoning to the fish. The nitrates in the fish feed will increase the toxicity concentration in the water and exposed the fish to diseases due to the nitrate poisoning (Richard, Anderson, and Kononoff, 2014). However, the level of nitrate still can be controlled by reducing the feeding rate (Durborow et al., 1997).

Meanwhile, the result tabulated in Table 4.2 for the pH value was in range from 5.76 – 6.52. The pH value of fish feed should be maintained at the range of 6.5 – 9 which is the suitable range for fish growth (Yokogawa, 2016). From the Table 4.2, only run 4 was in the desirable range with 6.52 pH value while the other runs were less than the favourable range. As for the leaching rate, the preferable leaching rate according to the Ighwela et. al., (2013) was below 30% in one-hour experiment. Each of the run have the desired leaching rate less than 30%. Therefore, each of the formulated fish feed have a low leaching rate.

5.4.3 Analysis of Variance (ANOVA)

The interactions between independent factors were determined with ANOVA (Özbay et. al., 2013). Table 5 shows the ANOVA for each of the responses; moisture content, nitrate content, pH value and leaching rate. The *p*-value with more than 95% of confident level (Özbay et al., 2013) for each response showed that the model was significant. The *p*-value for Table 4.3 (a), (b), (c) and (d) were 0.0467, 0.0125, 0.0091 and 0.0487, respectively were less than 0.05 (Zakaria et al., 2012) and, thus, make each of the responses to be statistically significant and accepted. The R^2 measured the proportion of total variability explained by the model (Kukreja et. al., 2011). As the R^2 approaches unity, the better the empirical model fits the actual data. The smaller the values of R^2 represent less relevance of the dependent variables in the model in explaining the variation behaviour (Motri et al., 2015). The R^2 obtained for each response shown in Table 4.3 (a), (b), (c), and (d) were 0.9274, 0.9950, 0.9761, and 0.9254, respectively. Meanwhile, the adjusted R^2 obtained were 0.8307, 0.9825, 0.9443, and 0.8258, respectively. Each of the R^2 and the adjusted R^2 obtained was higher than 0.8 for biological process, therefore this model was accepted.

Table 5: ANOVA of responses

a) Moisture content

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	29.25	4	7.31	9.59	0.0467	Significant
R^2	0.9274					
Adj R^2	0.8307					

b) Nitrate content

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	0.50	5	0.099	79.40	0.0125	Significant
R^2	0.9950					
Adj R^2	0.9825					

c) pH value

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	0.42	4	0.11	30.66	0.0091	Significant
R^2	0.9761					
Adj R^2	0.9443					

d) Leaching rate

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	247.84	4	61.96	9.30	0.0487	significant
R^2	0.9254					
Adj R^2	0.8258					

5.4.4 Analysis on the Main Effect and Interaction Effect

The contribution of the main effect and the interaction effect of each factor is shown in Table 6. The terms A, B, C, and D in the Table 6 are referred as fish waste, soybean meal, and groundnut meal.

Table 6: Contribution of main factors and interaction factors

a) Moisture content

Term	**Contribution (%)**
A	5.00
B	5.61
C	53.69
AB	1.09
AC	3.30
BC	28.44
ABC	2.87

b) Nitrate content

Term	**Contribution (%)**
A	20.30
B	30.33
C	12.28
AB	6.27
AC	30.33
BC	0.25
ABC	0.25

C) pH value

Term	**Contribution (%)**
A	4.64
B	12.62
C	66.95
AB	13.40
AC	0.94
BC	0.046

ABC	1.40

D) Leaching rate

Term	**Contribution (%)**
A	14.27
B	20.73
C	27.95
AB	1.72
AC	4.57
BC	29.58
ABC	1.18

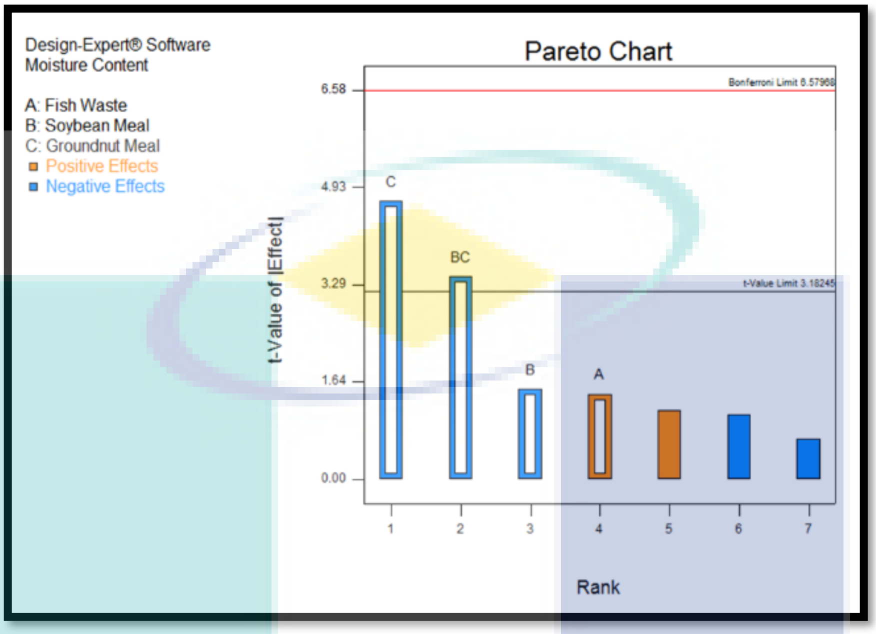
Table 6 (a) shows that the groundnut meal gave the highest contribution to the moisture content. It means that, the higher the composition of groundnut meal in the formulated fish feed will result to the high percentage of moisture content of the fish feed. Meanwhile, the fish waste gave the lowest contribution of moisture content. The soybean meal and groundnut meal interaction (BC) gave the highest contribution to maximize the moisture content value compared to other interaction. From the contribution results, it can be concluded that soybean meal and groundnut meal had a strong relationship to maximize the moisture content of the formulated fish feed. The soybean and groundnut have relatively high moisture content of 25% (Darvishi, Khoshtaghaza, and Minaei, 2015) and 35% – 40% (Singh and Ojha, 1974), respectively. Therefore, it is favourable to formulate fish feed with a composition of soybean meal and groundnut meal to reduce the percentage of moisture content in the fish feed.

Table 6(b) shows that the soybean meal gave the highest contribution to the concentration of nitrate followed by fish waste and groundnut meal. Meaning that, the higher the composition of soybean meal in the formulated fish feed, the higher the possibility of nitrate content in the fish feed. Meanwhile, the groundnut meal gave the lowest contribution to the concentration of nitrate. The fish waste contributed 20.30% to the concentration of nitrate in the fish feed formulation. The interaction between the fish waste and groundnut meal (AC) gave the highest contribution to maximize the nitrate content value compared to other interactions. Therefore, from the contribution results, it can be concluded that the interaction of fish waste and groundnut meal had a strong relationship to maximize the nitrate content of the formulated fish feed. Usually, the high content of nitrate concentration in the fish waste is due to the action of bacteria that convert fish waste into nitrate (Sallenave, 2016). Hence, it is favourable to formulate fish feed with a low composition of the fish waste and groundnut meal to reduce the percentage of nitrate content in the fish feed.

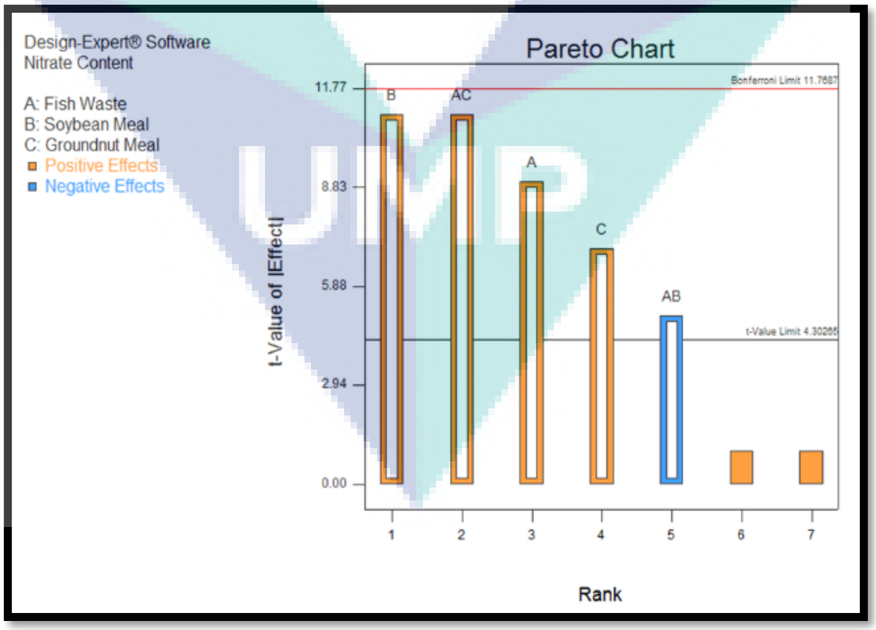
Table 6(c) shows that the groundnut meal gave the highest contribution to pH value. Hence, the higher the composition of groundnut meal in the formulated fish feed, the higher the pH value of the fish feed. Meanwhile, the fish waste gave the lowest contribution to pH value. Therefore, to formulate fish feed with suitable pH, the composition of the groundnut meal needs to be lowered as it contributes strong relationship to maximize the pH value. The interaction between fish waste and soybean meal (AB) gave the highest contribution among the other interaction factors.

Table 6(d) shows that the groundnut meal gave the highest contribution to leaching rate. Therefore, the higher the composition of groundnut meal in the formulated fish feed, the higher the leaching rate of the fish feed. However, the fish waste gave the lowest contribution to leaching rate. The soybean meal and groundnut meal interaction (BC) gave the highest contribution to maximize the leaching rate value compared to other interactions. Hence, it can be concluded that soybean meal and groundnut meal had a strong relationship to maximize the leaching rate of the formulated fish feed. However, it is favourable to formulate fish feed with low composition of soybean meal and groundnut meal to reduce the percentage of leaching rate of the fish feed.

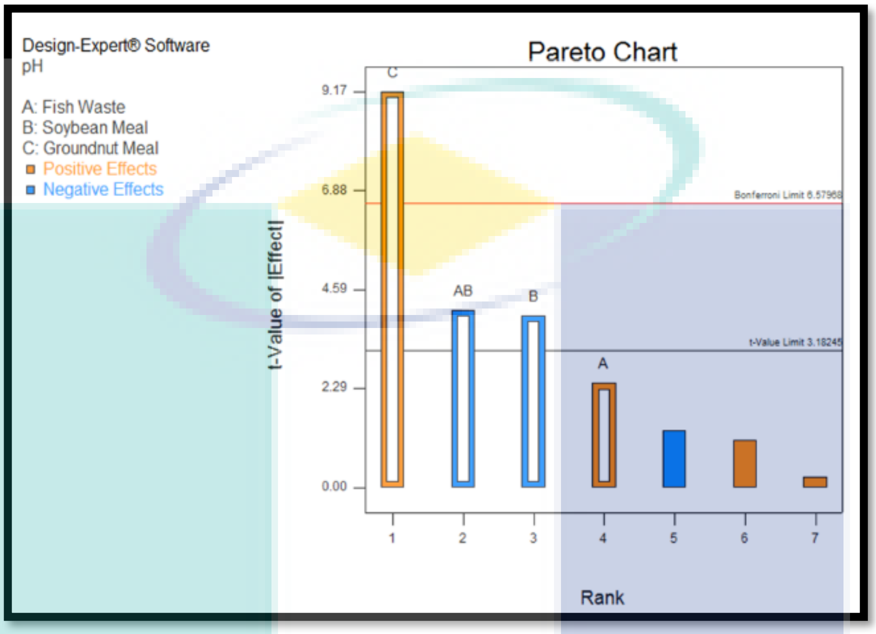
The Pareto Chart in Figure 12 is one of the useful tool available in the Design Expert software to determine others relative effects and defining the target (Ahmed & Ahmad, 2011). It shows the most frequent occurring factors and help to make the best use of limited resources by pointing at the most important problems to tackle (Ahmed & Ahmad, 2011). It contains two important lines between the bar chart which were Bonferroni limit coloured in red and t-Value limit coloured in black. These lines are used to determine the effects that are statistically significant toward the response observed. The chart displays the absolute value of the effects and draws a reference line at the t-value limit for each of the response studied which were the moisture content, the nitrate content, pH value, and the leaching rate. Any effect that extends within this reference line is statistically insignificant (Kukreja et. al., 2011). There were three factors used in this analysis which were A, B, and C that referred as fish waste, soybean meal and groundnut meal, respectively.



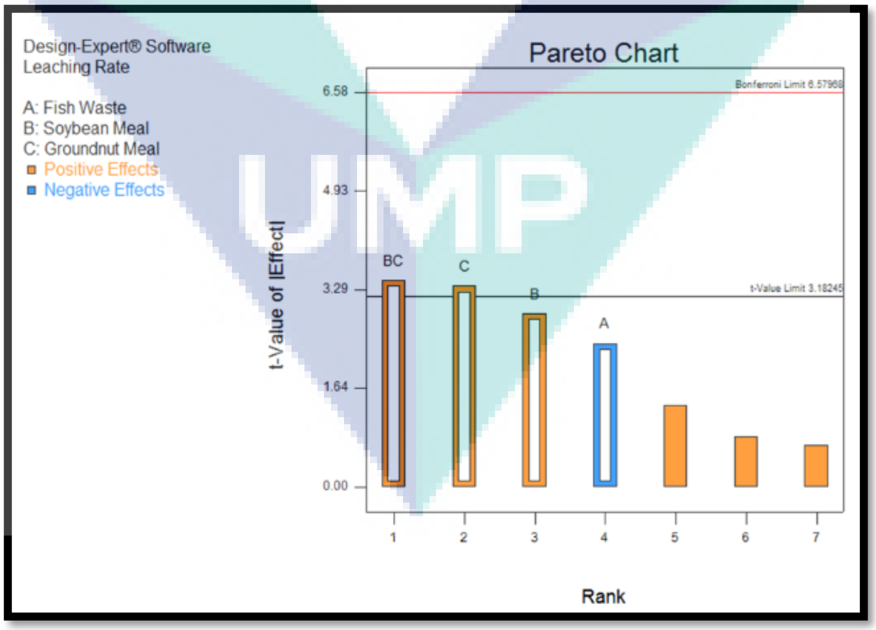
(a) Moisture content



(b) Nitrate content



(c) pH value



(d) Leaching rate

Figure 12: The Pareto Chart

From Figure 12(a), the chart indicates that both of the main effects A and B were statistically insignificant. The effect of C had the highest standardized effect on the moisture content followed by BC. Both of these main and interaction effects were negative effect. The negative effect means that the factor value is not proportional to the response value. Therefore, the moisture content increase as the composition of the significant factors decreases. In this study, the range of groundnut meal composition used was between 15% - 20% and from the chart Figure 12(a) proved that formulation with 15% of groundnut meal is more favourable to be selected as it could decrease the moisture content in the fish feed produced. Hence, the term A and B should not be considered for the empirical relation.

From Figure 12(b), the effect of A, B, C, AB, and AC were all statistically significant. All of these main effects were the positive effect except for the AB interaction. The positive effect means that the factor value is proportional to the response value. Therefore, the nitrate content increase as the composition of the significant factors increases. Meanwhile, for the interaction effect, AB showed the negative effect which means the factor value is not proportional to the response value. Hence, as the nitrate content decrease, the composition of the significant factors increases. However, the effect of B and AC had the highest standardized effect on the nitrate content. Therefore, all the significant effects should be considered for the empirical relation.

From Figure 12(c), it was obvious that both of main effect A and B were statistically insignificant. The effect of B and AB were both shared as the highest standardized effect on the pH value. Both of these main effect and interaction effect were the positive effect. Therefore, the pH value increase as the composition of the significant factors increase. For that reason, A and B were excluded from the empirical relation.

From Figure 12(d), main effects of A and B were proven to be statistically insignificant. Meanwhile, the effects of BC and C were both the highest standardized effect on the leaching rate. Both of these main effect and interaction effect were the positive effect. Therefore, the leaching rate increase as the composition of the significant factors increase. In this study, the range of groundnut meal composition used was between 15% - 20% (Puspasari et al., 2015) and from the Figure 4.1(d) proved that the formulation with 15% of groundnut meal was more favourable to decrease the leaching rate percentage in the fish feed produced. Consequently, the effects of A and B should not be considered into the empirical relation.

It is necessary to examine any interaction that is important in the experimental design analysis.The two-way interactions show their significance at 95% confidence level. A higher order of regression model such as the quadratic model was required to fit the responses. The regression equations (Eq.2), (Eq.3), (Eq.4) and (Eq.5) represent the best description after the elimination of non-significant parameters for each response. These equations can be used to find out the values of the three factors to be set in order to achieve the desired fish feed formulation (Kukreja et al., 2011). Therefore, final empirical models in terms of actual parameters were determined as follows:

$$\text{Moisture Content} = -60.14762 + 0.088824*\mathbf{A} + 1.38840*\mathbf{B} + 4.07710*\mathbf{C} - 0.084710*\mathbf{B}*\mathbf{C}$$

(Eq.2)

$$\text{Nitrate Content} = +7.15 - 0.0325*\mathbf{A} + 0.09*\mathbf{B} - 0.24*\mathbf{C} - 2.5\text{E-}003*\mathbf{A}*\mathbf{B} + 0.011*\mathbf{A}*\mathbf{C}$$

(Eq.3)

$$\text{pH Value} = +0.72 + 0.197\mathbf{*A} + 0.0685\mathbf{*B} + 0.076\mathbf{*C} - 3.4\text{E-}003\mathbf{*A*B}$$

(Eq.4)

$$\text{Leaching Rate} = +213.02631 - 0.43719\mathbf{*A} - 3.87884\mathbf{*B} - 12.62295\mathbf{*C} + 0.25176\mathbf{*B*C}$$

(Eq.5)

5.4.5 Best Condition and Validation Run

Acknowledging that the nitrate content (Richard et al., 2014) and the leaching rate (Ighwela et al., 2013) were the important attributes for the fish feed formulation by depending on the value of R-squared and adjusted R-squared obtained, hence validation of best condition was conducted. The determination of best condition was based on the purpose of reducing the nitrate content and the leaching rate of the fish feed formulation. The solution suggested by the software was Run 3 (fish waste 20%, soybean meal 50% and groundnut meal 20%) with the desirability of 0.548. The desirability of the predicted results asses its closeness to the target value on a scale of 0 to 1 (Kukreja et al., 2011). Table 7 shows the optimization prediction on the result of nitrate content and the leaching rate.

Table 7: Predicted best condition from the Design Expert Software

Fish Waste %	Soybean Meal %	Groundnut Meal %	Nitrate Content mg/L	Leaching Rate %	Desirability
20.00	50.00	20.00	8.1	9.63755	0.548

A validation experiment was conducted to verify this study according to the desired condition; minimize nitrate content and leaching rate. Triplicate samples were tested for each significant response on the desired formulation of Run 3. Table 7 shows the comparison result of the predicted and actual data for both concerned responses. The percentage error was calculated using the equation (Eq.6) (Chowdary, Shankar, and Kumar, 2014).

$$\text{Percentage error} = \frac{\text{Predicted result -Observed results}}{\text{Predicted results}} \times 100\%$$

(Eq.6)

Table 8: Comparison of prediction and actual data

Percentage Error	**Nitrate Content mg/L**		**Leaching Rate %**	
	Prediction	Actual	Prediction	Actual
	8.1	8.27 ± 0.153	9.63755	8.8946 ± 0.450
Ɛ (%)	2.10		7.71	

The percentage error obtained for the nitrate content and leaching rate were 2.10% and 7.71, respectively. The error was in an acceptable range which is below 10% (Chowdary et al., 2014). Therefore, Run 3 was selected as the best condition that can be applied in the formulation of fish feed to produce a nutritional and quality fish feed that have low nitrate content and leaching rate.

5.5 Conclusion

In this study, fish waste, soybean meal and groundnut meal were studied to formulate the fish feed. There were 8 formulations with different composition designed by the Design Expert software in the two-level factorial analysis. Each formulation was observed with four responses which were moisture content, nitrate content, pH value and leaching rate.

Nitrate content and leaching rate were the two main important attributes of fish feed formulation, hence an optimization was done converging on these two responses. From the result, Run 3 (fish waste 20%, soybean meal 50% and groundnut meal 20%) with desirability of 0.548 was selected to be the best-formulated fish feed in this study. Run 3 was expected to have nitrate content and leaching rate of 8.1 mg/L of and 9.63755%, respectively. A validation run was done to verify the prediction results. It showed that Run 3 resulted with 2.1% error for nitrate content and 7.71% error for the leaching rate.

Fish waste, soybean meal and groundnut meal have a high potential for future alternative formulation of fish feed. It can produce fish feed with good attributes; low nitrate content and low leaching rate.

5.6 Recommendations / Way Forward

Based on the results of the experiments, a few recommendations could be outlined for further study.

1. The formulated fish feed should be studied on the determination of fish feed quality based on fish growth in terms of weight gain, specific growth rate, protein efficiency ratio and feed conversion ratio.
2. Further analysis on the nutrient leaching of the fish feed is recommended. Thus, the details of nutrient composition of the fish feed could be identified and improved according to the result and will increase the quality of the fish feed.
3. The type binding agent in the fish feed such as starch and maltose should be investigated. The binding agent are the substances that can affect the leaching rate of the fish feed. A good type of binding agent like maltose is important in ensuring the nutrient leaching in the fish feed is low and can increase the growth rate of fish.

CHAPTER 6

PROCESS SIMULATION OF ANAEROBIC DIGESTION PROCESS FOR BIOGAS PRODUCTION FROM FOOD WASTE

PROJECT LEADER

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PROJECT TEAMS

PM IR DR NORAZWINA ZAINOL, DR WAN HANISAH BINTI W. IBRAHIM

6.1 Abstract

Anaerobic digestion is a process that breaks down organic materials into biogas without the presence of oxygen. Anaerobic digestion process is among available method to treat municipal solid waste. Plastics, metals, papers and food waste are the examples of municipal solid waste. This study aims to simulate anaerobic digestion process to produce biogas from food waste. Biogas consists mostly of methane and carbon dioxide. It is one of the excellent sources of energy. The simulation of anaerobic digestion is performed using Aspen Plus software. Anaerobic Digestion Model No. 1 kinetic model

is applied in this study. The component list, thermodynamic property package, reaction list, reactor, process condition and the input of the process is specified in the Aspen Plus. The results are validated using pilot plant data published in open literature. Sensitivity analysis is performed after the validation step to analyse the effect of residence time and food waste composition on the biogas production. It was observed that the increase in residence time decreased the methane composition in biogas. Methane composition increased as the carbohydrate composition in feed stream is increased. Besides, increased in fat composition will also increase the production of biogas. However, addition of protein will affect the production of biogas where it will produce ammonia and slow down the anaerobic digestion process. Hence, the composition of methane is decreased. The simulation result was fitted with the composition of biogas. Thus, it can be concluded that the simulation can be accepted to represent the anaerobic digestion process.

6.2 Introduction

6.2.1 Objective

The objective of this research is to develop an anaerobic digestion (AD) process model in treating food waste to produce biogas.

6.2.2 Scopes of study

Aspen Plus software was applied to develop the AD process model.

Food waste composition was approximated with weight composition of carbohydrates, proteins, and fat specified at 55%, 26%, and 19%, respectively.

Two stages of AD process is considered at thermophilic condition with temperature setting at 50^{o}C and pressure at 1 atm.

Performing sensitivity analysis to study the effect of different process conditions i.e waste composition and quantity, temperature, residence time to the production of biogas.

6.3 Methodology

6.3.1 Simulation steps using Aspen Plus software

Process simulation model for anaerobic digestion process is developed using Aspen Plus software. This tool has rigorous method that can be used to estimate the properties of the components and detail thermodynamic calculation. A flow chart of the simulation process is shown in Figure 1.

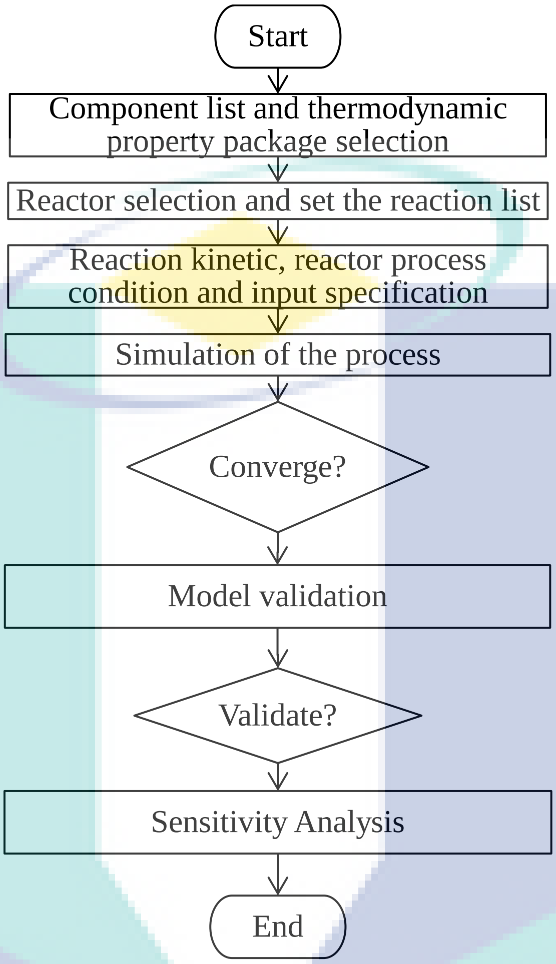

Figure 1: Process flow chart of simulation

6.3.2 Component List and Thermodynamic Property Package Selection

The thermodynamic property package that will be used in this simulation is Non-Random Two-Liquid (NRTL) method because the activity coefficients are taken into account (Nguyen, 2014). Some of the compound in this process do not have enough data in the Aspen Plus data bank. Hence, the data with similar components will be copied to the compound needed (Serrano, 2010). The compounds list for this process are:

- Volatile fatty acid (VFA) represented by acetic acid, propionic acid, butyric acid, linoleic acid, palmitic acid, & valeric acid.
- Long chain fatty acid (LCFA) represented by oleic acid.
- Carbohydrates represented by starch, cellulose, hemicellulose and xylose
- Fats represented by trolein, tripalmate, palmito-olein and palmito-linolein.
- Soluble and insoluble protein. The insoluble protein represented by keratin.
- Glucose represented by dextrose.
- Main amino acids: asparagine, glutamine, arginine, histidine, lysine, tyrosine, tryptophan, phenylalanine, cysteine, methionine, threonine, serine, leucine, isoleucine, valine, glutamic acid, aspartic acid, glycine, alanine, & proline.
- Water, ammonia, ethanol, glycerol.
- Biomass represented by ethyl cyanoacetate.
- Acid based ions: H^+, OH^-, NH_4^+, CH_3COO^-, HCO_3^-, CO_3^{2-}, & HS^-.
- Final products: carbon dioxide, hydrogen, methane, indole, formamide, hydrogen sulfide, methanethiol, benzene, phenol, & carbonic acid.

6.3.3 Reactor Selection and Set the Reaction List

A stoichiometric reactor will be used for hydrolysis step due to incomplete data for hydrolysis reaction (Al-Rubaye et al., 2017). There are only few inputs needed for stoichiometric reactor, however it need the extent of reaction. The next steps of anaerobic digestion will be conducted in continuous stirred tank reactor (CSTR). There are two sets of reactions in this process. The first one is the hydrolysis reactions that based on the extent of reaction. The second one is the other reactions that depend on the reaction kinetic. The reaction kinetics are obtained from Rajendran et al. (2014).

6.3.4 Reactor process condition and input specification

Table 1 shows the range for optimum condition of the reactors in this process (Al-Rubaye, et al., 2017).

Table 1: The optimum parameter values for anaerobic digestion

Parameter	**Hydrolysis / Acidogenesis**	**Methanogenesis**
Temperature (ºC)	25 - 35	Mesophilic: 30 – 40 Thermophilic: 50 - 60
pH value	5.0 – 6.0	6.5 – 7.5
C:N ratio	10 - 45	20 - 30
Redox potential	400 to -300 mV	Less than -250mV
C:N:P:S ratio	500:15:5:3	600:15:5:3
Trace elements	No special requirements	Essential: Ni, Co, Mo, Se

The characteristics of food waste based on the previous case studies are shown in Table 2 (Zhang, et al., 2014).

Table 2: Food waste characteristics

Parameters	**(Zhang, et al., 2011)**	**(Zhang, et al., 2013)**	**(Zhang, et al., 2007)**	**(Li, et al., 2010)**
TS (% w.b.)	18.1	23.1	30.90	24
VS (% w.b)	17.1	21.0	26.35	232
VS/TS (%)	0.94	90.9	85.30	94.1
pH	6.5	4.2	-	-
Carbohydrate (% d.b)	6.19	-	-	55.2

Protein (% d.b)	-	-	-	15
Fat (% d.b)	23.3	-	-	23.9
Oil (% d.b)	-	4.6	-	-

The characteristics of food waste from Li et al., (2010) were used as an input data to the process simulation. However, the composition of carbohydrate, protein and fat were adjusted to match the characteristic of Malaysian food. Mohd Shariff, et al., (2015) stated that fast food and restaurant meals are relatively high in total fats. The percentage of energy from total fat and saturated fats exceeded 30% and 10% respectively among older children. The composition of food waste that was used for the simulation is 55% carbohydrate, 40% fats and 2% protein.

There are quite a number of fermented food in Malaysia such as tapai, tempeh, and tempoyak. Any product of fermentation contain a small amount of alcohol such as ethanol. Furthermore, ethanol can be produced through production of bread. Yeast will consume sugars in the dough to produce ethanol and carbon dioxide. Thus, ethanol is also added as a feed. The percentage of ethanol in the feed is around 1.95%.

6.3.5 Simulation of the Process

Figure 2 shows the Aspen Plus model for anaerobic digestion.

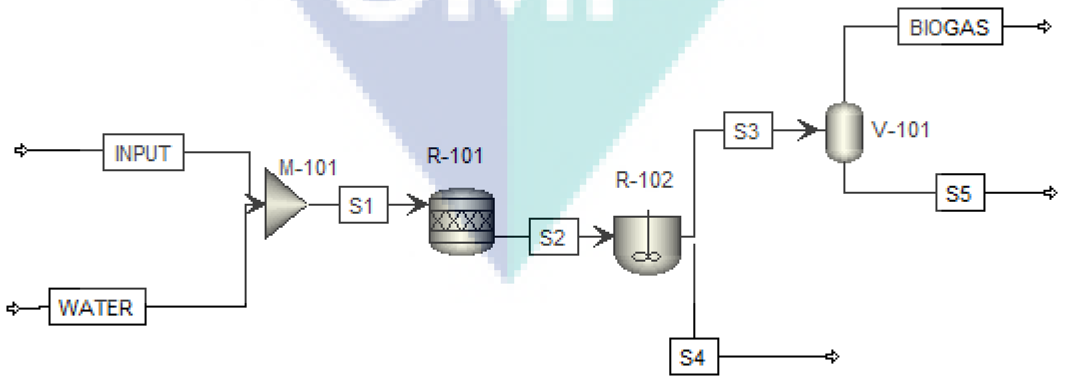

Figure 2: Aspen Plus model for anaerobic digestion process

The input stream is the food waste input that contains carbohydrate, protein and fats. It is then mixed with water with a ratio of 1:10. Then, the mixture of food waste and water enter the jacketed reactors that maintain the temperature at 55°C. Hydrolysis process occurred in the stoichiometric reactor while the other three reactions occurred in the CSTR. The product from CSTR, which is the biogas at stream S3 entered the flash column to remove water by decreasing the temperature to 5°C.

6.3.6 Model Validation

The model was validated with experimental results based on the percentage of methane produced. The expected result of biogas production (European Biogas Association, 2013) is shown in Table 3.

Table 3: Composition of biogas

Compound	Molecular Formula	Percentage
Methane	CH_4	50 – 75
Carbon dioxide	CO_2	25 – 50
Nitrogen	N_2	0 – 10
Hydrogen	H_2	0 – 1
Hydrogen sulfide	H_2S	0 – 3
Oxygen	O_2	0 – 0

6.3.7 Sensitivity Analysis

A sensitivity analysis of the model was performed in Aspen Plus. The residence time and the composition of the food waste are predicted to affect the simulation model. Residence time is one of the most important design parameter affecting the economics of digester. A small digester will result in a shorter residence time. Thus, the capital cost will be lower. However, the time might not be long enough to obtain an optimum result for biogas production. Shi, et al. (2017) stated that residence time could influence biogas production, methane content, pH value and VFA component. Higher residence time will have more stability compared to lower residence time. Food waste mainly consists of carbohydrates, proteins, lipids and traces of inorganic compounds. The composition is different according to the type of food waste. Food waste that consists of rice is abundant in carbohydrates while food waste that consists of meat and eggs has higher quantity of proteins and lipids (Paritosh, et al., 2017). It is quite hard to know the exact percentage of components in the food waste. Hence, a sensitivity analysis was performed in order to study the effect of food composition in biogas production.

6.4 Findings

6.4.1 Input data

The input data for the simulation is shown in Table 4.

Table 4: Simulation input data

Component	**Vol%**
Carbohydrate	55
Protein	40
Fat	2
Ethanol	1.95

Ethanol is included in food waste because Malaysian food contain quite a number of fermented food such as tapai, tempeh and tempoyak. In addition, ethanol can be produced through production of bread. Yeast will consume sugars in the dough to produce ethanol and carbon dioxide. Therefore, a small amount of ethanol is included. The input stream has a total of 200kg/day of food waste and the water stream has a total of 2000kg/day of water. The temperature of anaerobic digestion process is maintained at 55°C.

6.4.2 Simulation result

The simulation results obtained from Aspen Plus are recorded and compared with the typical biogas composition obtained from Al-Rubaye et al. (2017). The comparison is done based on the percentage of the product produced. The main component produced in this simulation is methane. The result for stream S3 and BIOGAS are shown in Table 5.

Table 5. Simulation result

Component	Vol%	
	Aspen Plus (S3)	Aspen Plus (BIOGAS)
Water	12.19	0.58
Carbon dioxide	39.39	42.52
Methane	44.36	52.91
Hydrogen sulfide	0.30	0.36
Acetic acid	0.42	0.04
Ammonia	0.04	0.03
Hydrogen	0.06	0.07
Benzene	0.03	0.04
Ethanol	0.32	0.16

Table 5 shows the detail results from Aspen Plus simulation. The result shows that the major component of the product is carbon dioxide and methane and also small traces of hydrogen sulphide, acetic acid, ammonia, hydrogen, benzene and ethanol. Based on the Biogas Stream, it shows that the composition of methane and carbon dioxide is within the range of the composition of typical biogas. The percentage of carbon dioxide is 42.52% while for methane is 52.91%. This composition is within the range of typical biogas composition which the composition of carbon dioxide is between 25% to 50% and for methane is between 50% to 75%.

6.4.3 Effect of residence time on methane production

There are two sensitivity analyses that have been done in the simulation. The first sensitivity analysis is to study the effect of residence time. The residence time of CSTR has been changed from 15 days to 30 days. Figure 3 shows the changes of methane composition according to the changes in residence time with different composition of carbohydrate.

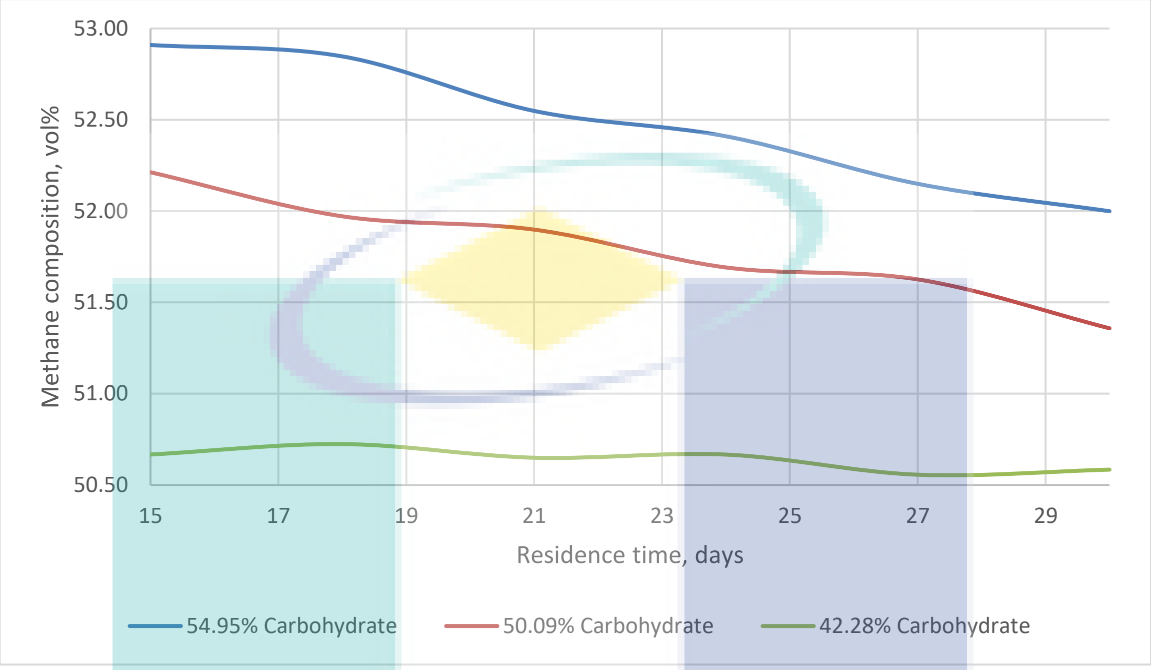

Figure 3: Methane composition versus residence time.

Based on Figure 3, the methane composition is decreasing as the residence time increase. According to Getahun et al. (2014), the quality of methane is increase as the residence time increase. However, it was found that the biogas and methane production is depends on the type of input. There are certain cases where the methane composition is increase as the residence time increase. Biogas production could become low with a long residence time required to produce sufficient amount of biogas from cow dung and corn husk (Mel, et al., 2015). Ezekoye et al. (2011) stated that the reaction rate will decrease with increasing residence time. A shorter residence time will produce a higher rate of production but with a lower degradation.

6.4.4 Effect of carbohydrate composition on methane production

The next sensitivity analysis is to change the food waste composition. The first component of food waste that has been changed is carbohydrate. The composition of carbohydrate varies from 50% until 55%. Figure 4 shows the changes of methane composition according to the changes in carbohydrate composition with different residence time.

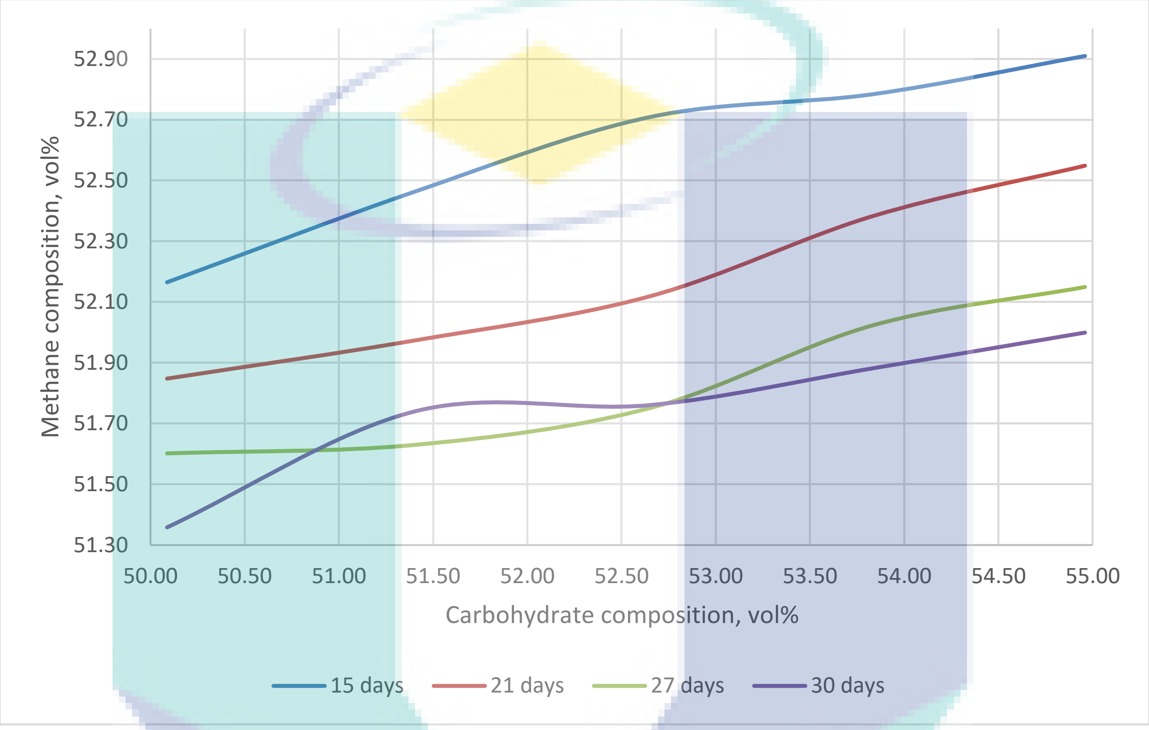

Figure 4: Methane composition versus carbohydrate composition

It shows that for all residence time, the methane composition in increase as the carbohydrate composition increased. Lima et al. (2016) stated that addition of carbohydrate could increase the methane production. Carbohydrate will provide extra energy for microorganisms, which will increase the biogas production. Besides that, addition of carbohydrate can also decrease the inhibition of ammonia.

6.4.5 Effect of fat composition on methane production

The next component of food waste that has been changed is fat. The composition of fat varies from 40% until 50%. Figure 5 shows the changes of methane composition according to the changes in fat composition with different residence time.

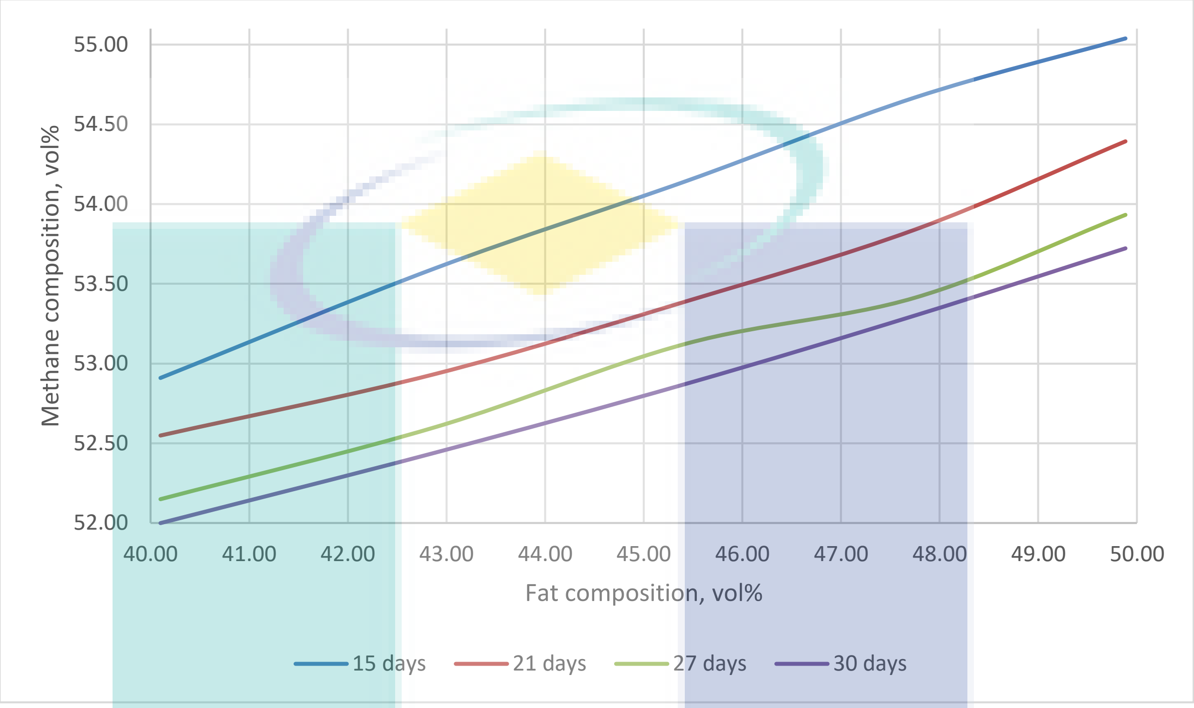

Figure 5: Methane composition versus fat composition

Lipid rich materials are known to have high biogas potential (Martinez, et al., 2016). However, the accumulation of lipid during the digestion process may slow down the process due to inhibition. There are several studies that suggested that inhibition cause by long chain fatty acid (LCFA) could be reversible. The VFA and LCFA that has been produced from lipids were oxidised and produce acetic acid, hydrogen and carbon dioxide. The acetic acid and hydrogen will then be converted into methane and carbone dioxide during methanogenesis.

6.4.6 Effect of protein composition on methane production

The last component of food waste that has been changed is protein. The composition of protein varies from 2% until 5%. Figure 6 shows the changes of methane composition according to the changes in protein composition with different residence time.

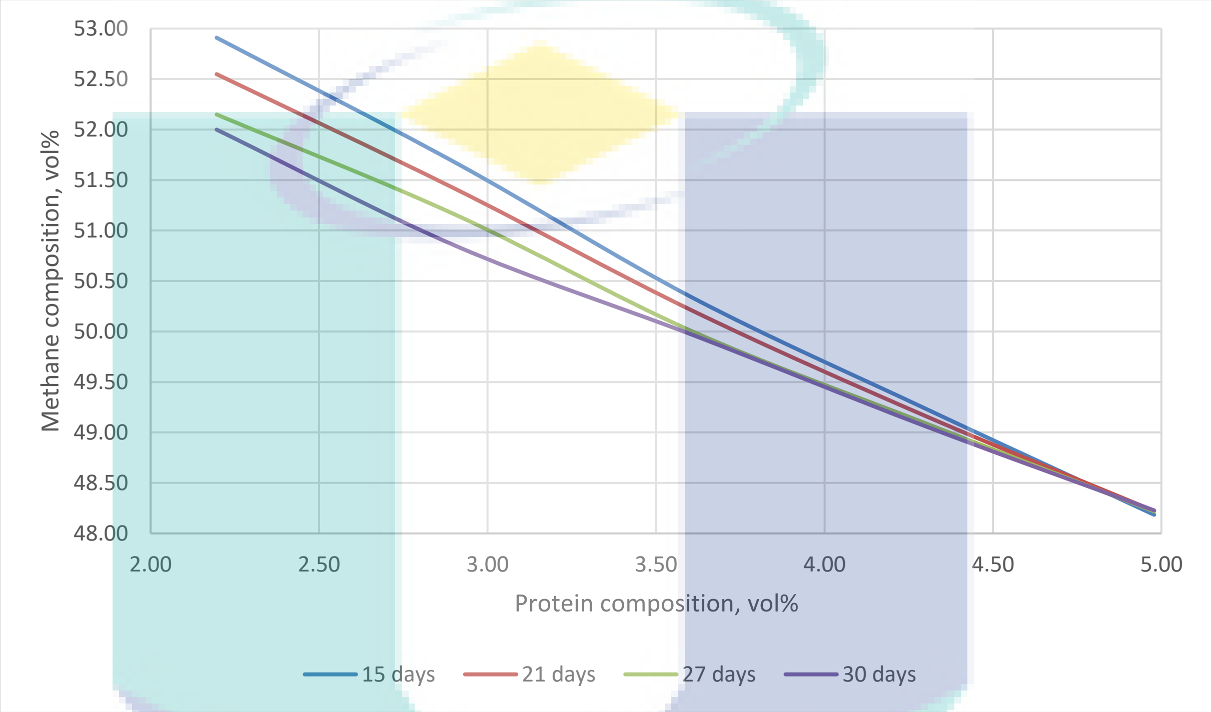

Figure 6: Methane composition versus protein composition.

Addition of protein will increase the ammonia concentration in the reactor. Insoluble protein will degrade into amino acids. These amino acids will the break down into ammonia. Thus, the anaerobic digestion process might slow down due to inhibition of ammonia. The methanogenic activity decreased as the concentration of ammonia increased (Eliyan et al., 2007). Ammonia is an essential nutrients for bacterial growth. However, it can inhibit methanogenic process if the concentration is high (Yenigun & Demirel, 2013). When the ammnonia become as inhibitors, it will slow down or even stop the anaerobic digestion process.

6.5 Conclusion

There is various way to treat municipal solid waste such as incineration, composting, landfilling and anaerobic digestion. Anaerobic digestion was chosen for this work because other method need high temperature and pressure. In this study, a simulation of anaerobic digestion to produce biogas from municipal solid waste by using Aspen Plus was conducted. Industries and researchers usually used process simulation to simulate their processes because if can predict the real situation accurately. Furthermore, it is cheaper to perform a simulation. A stoichiometric and continuous stirred-tank reactor were used in this simulation. Hydrolysis, acetogenesis, acidogenesis and methanogenesis reactions were considered.

The temperature used is thermophilic temperature at 55°C and the pressure is 1 atm. The simulation is focused on food waste with composition of 55% carbohydrate, 40% fats and 2% protein. The result obtained from simulation shows that the percentage of methane and carbon dioxide is 52.91% and 42.52% respectively. The composition is within the range where the percentage of carbon dioxide is 25% - 50% and methane is 50% - 75%.

There are a lot of issues with convergence that have been found. This is due to a lot of reactions and components needed in the simulation. Some flowsheets configuration could be applied in order to decrease the convergence issues. The error tolerance is set to 0.0001 instead of 0.00001. Other than that, the number of iterations can be increase but it will make the simulation slower to get the result. The decrease in residence time will decrease the convergence issues. Despite that, if a recycle is included, the convergence issues will increase.

Based on the parameters, it was observed that the increase in residence time will decrease the methane composition in biogas. It was also determined that the methane composition increase as the carbohydrate composition in feed stream increase. Besides, increase in fat composition will also increase the production of biogas. However, addition of protein will affect the production of biogas where it will produce ammonia and slow down the anaerobic digestion process. Hence, the composition of methane is decrease. The simulation result were fitted with the composition of biogas. Thus, it can be concluded that the simulation can be accepted to represent the anaerobic digestion process.

6.6 Recommendations / Way Forward

Based on the simulation results, it was obvious that the model is capable of predicting the result of anaerobic digestion process. A few recommendation could be outlined for further study.

- Calculation block could be added into the simulation to consider inhibition and pH effect. When the concentration of inhibition is too high or too low, it can slow down or even stop the anaerobic digestion process. Also the same with pH value. The optimal pH value for the growth of methanogenic bacteria is in the range of 6.7 – 7.5.
- The accuracy of simulation result can be enhanced by carrying out laboratory experiments on local food waste.

CHAPTER 7

ADSORBENT FROM LANDFILL SLUDGE

PROJECT LEADER

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7.1 Abstract

Activated carbon was found as a friendly solver adsorbent in the removal of many organic and inorganic pollutants in wastewater. One of the materials that can be used to produce activated carbon is sludge. Leachate from municipal solid waste (MSW) disposal in the landfills is a major problem due to pollution threat to surface water and groundwater. Applying treatment process to the leachate, such as dissolved air flotation (DAF), can reduce leachate contamination. Large amount of sludge is usually generated

as waste from leachate treatment process, creating sludge disposal problem. The quality of water resources is impacted by the continuous addition of undesirable chemicals in water. The presence of heavy metals in the water as a result of industrial activities is a matter of concern. For these reasons, the waste sludge was used as alternative material to produce activated carbon for heavy metal degradation. The sludge was treated by physical and chemical method thus the activated carbon P800 and C800 was tested onto copper solution by manipulating the effect of contact time. As a result, 10 kg of raw sludge will produce at least 660.3 g of activated carbon. Moreover, by testing the adsorbent onto copper solution, the highest percentage removal was 73.04% and then can be increase again by increasing the mass of adsorbent. Furthermore, based on the calculation of 1 MT of raw sludge, the profit of adsorbent can be gained and has potential to be used in the Sg. Ikan landfill as well.

7.2 Introduction

7.2.1 Objective

The objective of this research is to convert landfill sludge to adsorbent for heavy metal removal.

7.2.2 Scopes of study

To produce adsorbent from leachate treatment process sludge for copper removal.

To characterize the synthesized adsorbent.

To prepare thin-film composite (TFC) membranes of polyvinylidene fluoride (PVDF) and adsorbent from landfill sludge

To investigate the potentials of TFC in removing copper from aqueous solution.

7.3 Methodology

7.3.1 Adsorbent Preparation and Treatment

To prepare the adsorbent, there are two different of methods, namely physical method and chemical method. The physical method was performed by carbonisation process and the sludge was activated by using acids as chemical methods. The raw material, sludge was collected from leachate process in Gebeng landfill, Kuantan. The raw sludge was dried in oven at 105 °C for 12 h in order to remove the water and moisture content. Then, the sludge was ground by using grinder and sieved to obtain particle sizes smaller than 600 µm (Zaki, 2014).

7.3.2 Preparation of Adsorbent

7.3.2.1 Physical Method

The sludge went through a carbonisation process where the sample was placed in the crucible dish and heated in a furnace at three different temperatures, which were 400, 600, and 800 °C. The sample was heated at 10 °C/min until it reached the required temperature and continued for 1 h. After carbonisation, the sample was ground and sieved again to obtain the range 45–125 µm of adsorbent.

7.3.2.2 Chemical Method

According to Zaki (2014), 100 g of 600 µm of dry sludge was activated by using 1 M zinc chloride, $ZnCl_2$. Then, the mixture was stirred for 24 h at room temperature using magnetic stirrer. After that, the sample was filtered and dried in an oven at 105 °C for 24 h. The sample then underwent through a pyrolysis process by heating to 800 °C for 1 h then drained at room temperature. Next, the sample was soaked using 0.5 M HCl for 30 min and washed again by using deionized water until the deionized water obtained pH 6. Lastly, the sample was dried in an oven at 105 °C for 24 h.

7.3.3 Characterization of Adsorbent

The adsorbent characteristics were analyzed by using five different analysis. The surface morphology was determined by using surface electron microscopy (SEM). Then, the elements in the adsorbent were analyzed by using energy dispersive X-ray spectrometer (EDX). Furthermore, proximate analysis was determined by using thermogravimetric analysis (TGA). Fourier transform infra-red (FTIR) was used to examine the functional groups of adsorbent surface. Lastly, N_2 adsorption-desorption analysis was used to analyze the adsorbent surface and pore size respectively.

7.3.3.1 Surface Morphology Analysis

The adsorbent surface morphology were observed by using surface electron microscopy (SEM) (Zaini et al., 2014). The surface morphology of adsorbent P400, P600, P800, and C800 were analyzed in details. The adsorbent with pore surface shows that it is the characteristic of the adsorbent.

7.3.3.2 Element Analysis

Energy dispersive X-ray spectrometer (EDX) was used to determine the element content in the adsorbent (Yu & Zhong, 2006). The element content for adsorbent P400, P600, P800, and C800 were analyzed. The details weight percent for each element were determined by using EDX.

7.3.3.3 Functional group

Fourier Transform Infra-Red (FTIR) was used to examine the functional groups of adsorbent surface before and after the adsorption process. The range used is 400–4000 cm^{-1} region (Yang et al., 2016). The adsorbent C800 was analyzed to detect the functional group.

7.3.3.4 Proximate Analysis

Proximate analysis was used to measure the total and rate of change in weight of a substance based on temperature or time in a controlled environment. Moisture, ash, volatile matter and fixed carbon contents (Wen et al., 2011) for P400, P600, P800, C800 were determined by using thermogravimetric analysis (TGA). The analysis was carried out up to 950 °C under N_2 atmosphere (De Filippis et al., 2013)

7.3.3.5 N_2 adsorption–desorption analysis

Surface area, pore total volume and pore average diameter of adsorbents produce were determined by using N_2 adsorption–desorption analysis. For this analysis, all the adsorbent produced which were A105, P400, P600, P800 and C800 were analyzed. The type of N_2 adsorption–desorption isotherms was also determined.

7.3.4 Adsorption study

For adsorption testing, the experiment of copper adsorption was tested using 1000 ppm (mg/L) copper standard solution. The solution was diluted to 50 ppm (mg/L). The sludge adsorbent (0.5 g) was equilibrated with 100 mL of 50 ppm of copper solution at room temperature by using orbital shaker at 200 rpm for known period (30–180 min). During the adsorption process, 10 mL of sample was collected from conical flask at time interval of 30, 60, 120, and 180 min. The suspension of the adsorbent was separated from solution by filtration (Dwivedi & Rajput, 2014).

7.3.5 Copper analysis

After filtration, the concentration of copper solutions was determined using atomic absorption spectrophotometer (AAS). The amount of adsorption, q_e (mg/g) and the percentage of copper removal are calculated using Equations 1 and 2, respectively (Wang et al., 2011).

$$q_e = \frac{(C_i - C_f)V}{W} \tag{1}$$

$$Percent\ removal\ (\%) = \frac{C_i - C_f}{C_i} \times 100\% \tag{2}$$

where q_e is adsorption capacity (mg/g) at equilibrium, C_i and C_f are initial and final copper concentration (mg/L), respectively, V is the volume (litres) of copper solution used, and W is the mass (gram) of dry adsorbent.

7.3.6 Preparation of thin-film composite membrane

TFC membranes were prepared by preparing the dope solutions and then proceeded with the interfacial polymerization process. Firstly, the dope solutions were prepared at different ratios of N-methyl-2-pyrrolidone (NMP):PVDF:adsobernt which were 90:9:1, 90:7:3 and 90:5:5. The total weight of the dope solution was 100 g. For instances, in order to prepared TFC (90:9:1) membrane, needed to weight the 90 g of NMP, 9 g of PVDF pellet and 1 g of sludge and put them into 250 ml beakers respectively. Then, heated the NMP by using a hotplate constantly at 170°C and stirred at 200rpm. Next, added in the PVDF and sludge slowly into the NMP and heated until they were fully dissolved and that mixture was known as dope solution. Table 1 shows the ratios of NMP:PVDF:adsorbent in dope solutions.

Table 1: Ratios of NMP: PVDF: sludge in dope solutions**.**

NMP (wt%)	PVDF (wt%)	Sludge (wt%)
90	10	0
90	9	1
90	7	3
90	5	5

TFC membranes were prepared by the interfacial polymerization process. The process was extremely simple and it did not need high amount of cost and time. Therefore, it was very ideal method to produce TFC membranes. Firstly, an unmodified PVDF membrane was put in a petri dish. Then, the dope solution was added drop by drop onto the unmodified PVDF membrane surface by using 10 mL of syringe. Then, needed to make sure that the entire surface of the unmodified PVDF membrane was covered evenly with the thin layer of dope solution. Then, the membrane was dried at room temperature for more than 24 h. The combination of dope solution and the unmodified PVDF membrane was known as the TFC.

7.3.7 Ultrafiltration using thin-film composite membrane

Ultrafiltration (UF) adsorption study was performed using a stirred cell unit (Sterlitech) which was pressurized using nitrogen gas. The concentrations of copper were varied at 10, 20, 30, 40, and 50 mg/L.

Filtrate flux of the copper solution with different concentration of copper was calculated using Equation 3:

$$J_v = V/At \qquad (3)$$

where J_v is the volumetric filtrate flux with the filtrate flux ($L/m^2 \cdot h$), V is the volume of copper solution being filtered (L), A is the area of the TFC membranes which acted as UF membranes (m^2), and t is the time taken of the ultrafiltration process (h).

The permeability of membranes in an ultrafiltration process was calculated using Equation 4:

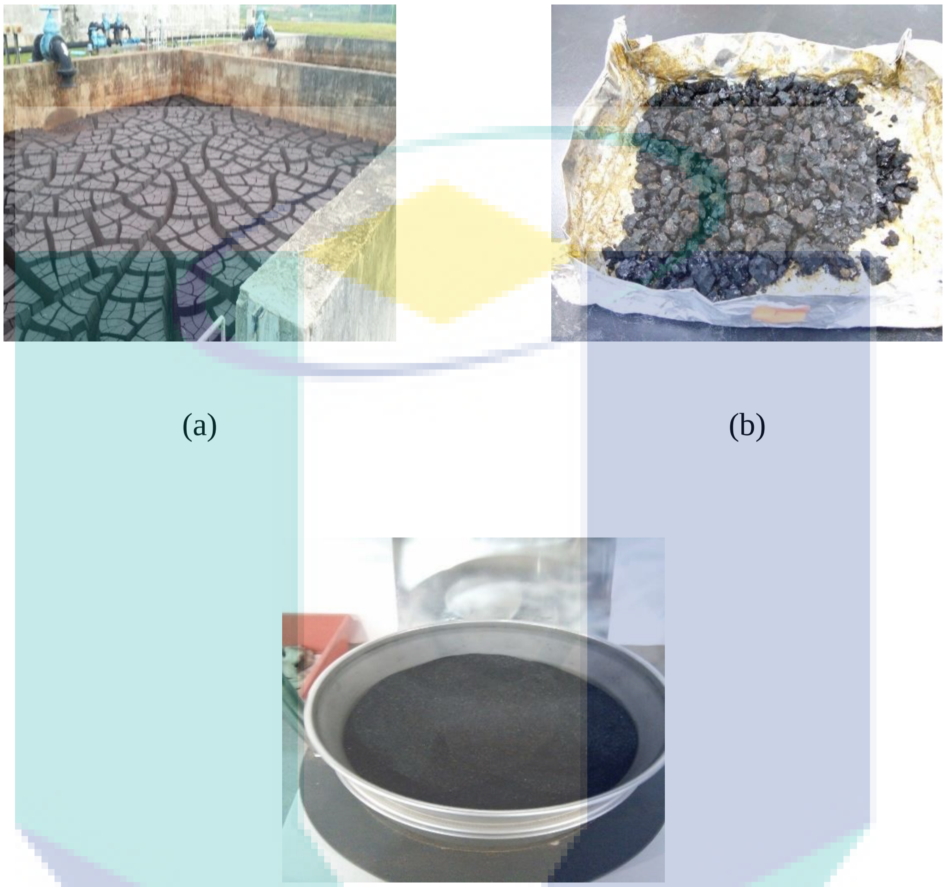
$$P = J_v \Delta P \tag{4}$$

where P is the membrane permeability ($L/m^2 \cdot h \cdot bar$), J_v is the volumetric filtrate flux ($L/m^2 \cdot h$), and ΔP is the TMP in bar.

7.4 Findings

7.4.1 Adsorbent production

The adsorbent was produced by using physical method adsorbent and chemical method adsorbent. The preparation of adsorbent sample (A105) was produced. Then, the physical method adsorbent produced was heated at 400 °C (P400), 600 °C (P600), and 800 °C (P800). The chemical method adsorbent that undergone carbonation process was heated at 800°C (C800). Figure 1 shows the changes of sludge from leachate treatment process to adsorbent that needed in this research. Figure 1(a) shows the sludge from leachate treatment process that taken from drying bed at Gebeng Landfill. The sludge produced is moist and in solid form. Figure 1(b) shows dried sludge after put in oven for 12 h at 102 °C. Figure 1(c) shows the adsorbent produced after undergo carbonisation produced. The adsorbent is black in colour and in powder form.



(a)

(b)

(c)

Figure 1: (a) Raw sludge, (b) dried sludge after put in oven, and (c) adsorbent produced from leachate treatment process sludge.

7.4.2 Characterization of adsorbent

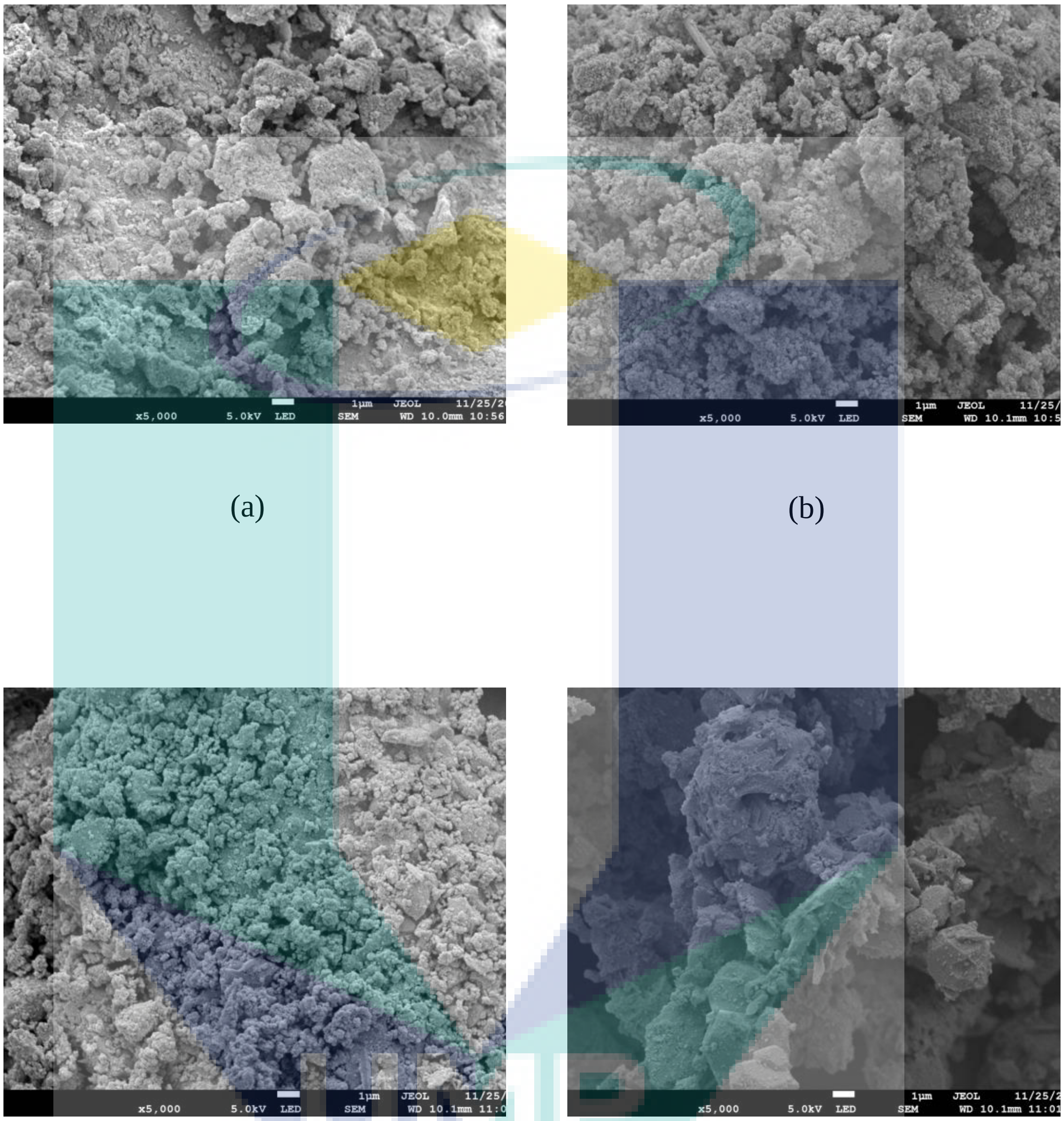
The physical and chemical properties of adsorbent that had been characterized included scanning electron microscopy (SEM), energy dispersive X-ray spectrometer (EDX), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and N_2 adsorption-desorption analysis.

7.4.2.1 Scanning Electron Microscopy (SEM)

The surface morphology of adsorbent surface was analysed by scanning electron microscopy (SEM) at scale of 5000× magnification. Figure 4.2 shows the surface morphology of adsorbent produced by physical method at 400, 600, and 800 °C. The texture of adsorbent (C800) that produced from chemical method also shown.

Based on Figure 2 adsorbent P400, P600, and P800 presented a dense structure with no obvious pores. The fibrous structure with rough surface can be observed clearly at all three activated carbon. The activated carbon that produced from sludge from activation term at temperature 200-800°C also showed the fibre structure and the rough surface (Singh et al., 2008). The pore for adsorbent C800 can be seen. The adsorbent C800 showed a loose structure and pores distributed unevenly on the surface. According to Liu et al. (2016) the pore structure was due to the decomposition of organic matter during the carbonization process.

This showed the sludge that undergo the physical and chemical method adsorbent at high temperature were affected the formation of surface and the structure of pore produced. The pore formed at adsorbent surface was the place where the copper heavy metal was absorbed.



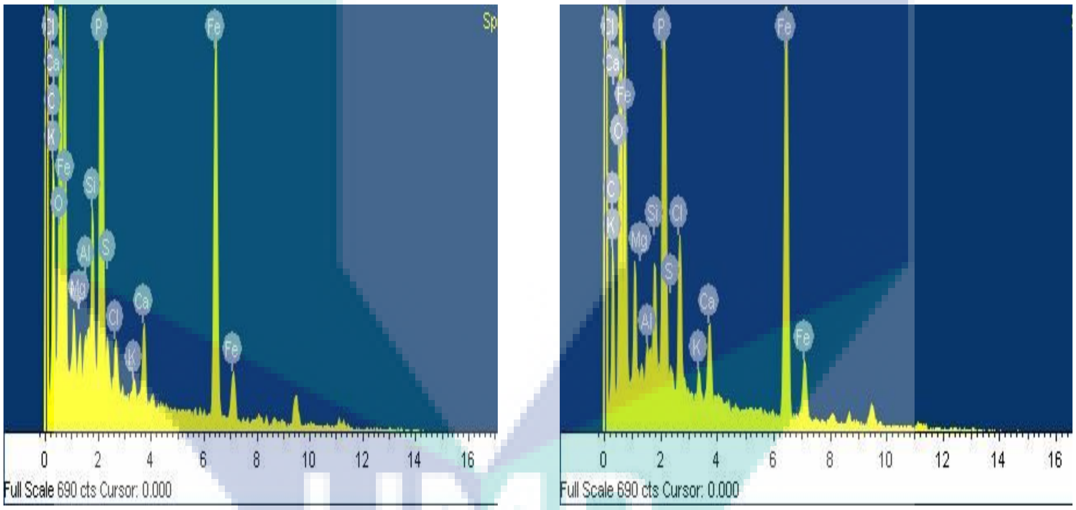
(a) (b)

(c) (d)

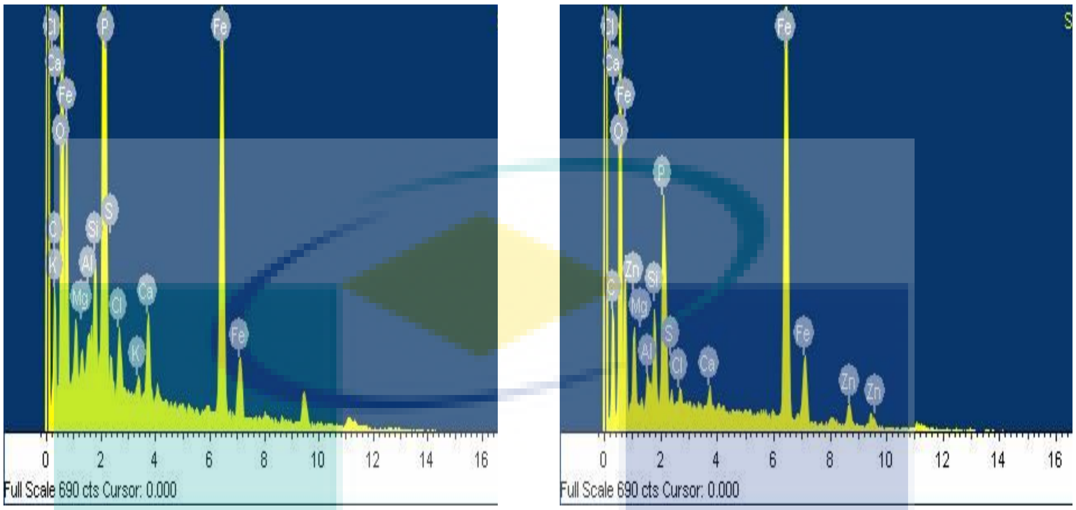
Figure 2: Surface images of (a) P400, (b) P600, (c) P800, and (d) C800 at 5000× magnification.

7.4.2.2 Energy Dispersive X-ray Spectrometer (EDX)

Element analysis was carried out to identify element composition that contain in adsorbent. Figure 3 shows the elements that contain in the surface of adsorbent P400, P600, P800 and C800. The elements contains in the surface of adsorbent P400, P600, P800 were carbon (C), oxygen (O), magnesium (Mg), aluminium (Al), silicon (Si), phosphorus (P), sulphur (S), chlorine (Cl), potassium (K), calcium (Ca), and iron (Fe). For adsorbent C800 contain all the element that contain in adsorbent P400, P600 and P800 except potassium (K) but contained zinc (Zn). Zinc chloride used as an activation agent was the reason the adsorbent C800 contain zinc element.



(a) (b)



(c)

(d)

Figure 3: Element analysis micrographs for (a) P400, (b) P600, (c) P800, and (d) C800.

Based on the data shown in Table 2, the percentage of carbon and oxygen were highest compare to other elements. This showed that carbon and oxygen are the main element for the adsorbent produced. At lower temperature of carbonation process, the contain of carbon element is higher because the substance contain carbon less expose to heat. Silicon and aluminium elements also present in high percentage after carbon and oxygen.

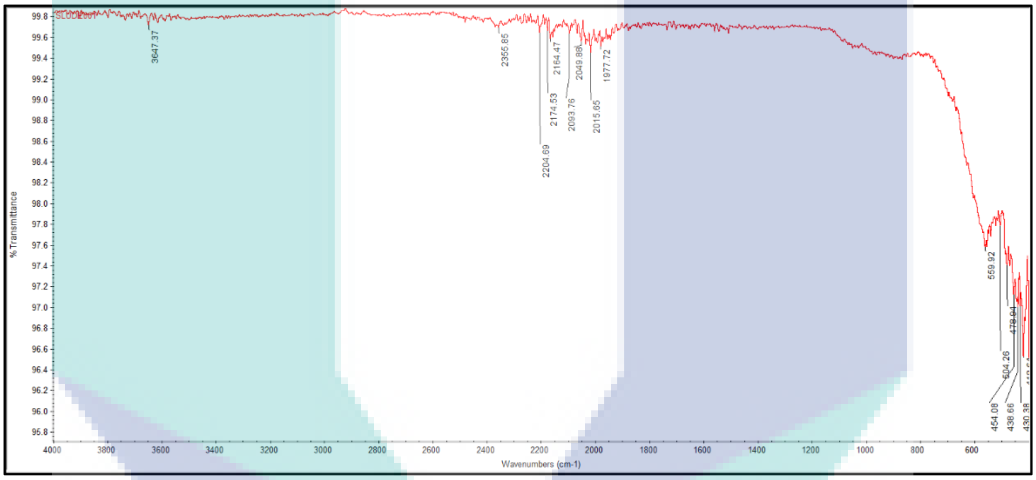
Table 2: Element analysis by using EDX Spectrometer

Element	Adsorbent, Weight (wt %)			
	P400	P600	P800	C800
C	17.89	12.51	11.36	11.93
O	39.40	34.04	30.39	20.62
Mg	0.68	0.23	0.61	0.24
Al	0.17	0.36	0.23	0.45
Si	2.14	1.61	1.97	1.85
P	1.06	1.19	1.36	0.94
S	0.97	0.62	0.73	0.41
Cl	0.83	3.12	1.19	0.34
K	0.32	0.58	0.55	-
Ca	2.04	2.03	2.37	0.50
Fe	34.49	43.73	49.23	57.04
Zn	-	-	-	5.68
Total	100	100	100	100

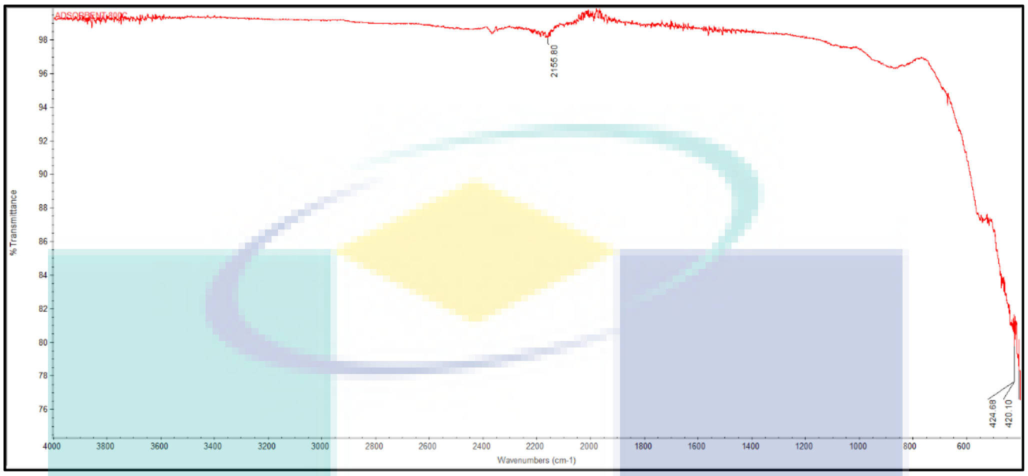
The element contains such as magnesium, phosphorus, sulphur, chlorine, potassium, calcium, and iron were low. The same element such oxygen, magnesium, aluminium, silicon, phosphorus, sulphur, chlorine, potassium, calcium, and iron also were found in native rice husk adsorbent (Zhang et al., 2014). The carbon content was also found in high percentage in pine needle and lantana shoots adsorbent (Malik et al., 2015).

7.4.2.3 Fourier-Transform Infrared Spectrophotometer (FTIR)

Functional groups were analyzed using FTIR techniques. Figure 4 shows the FTIR spectrum for C800 based on the transmittance before and after the adsorption of copper heavy metal. The C800 before the adsorption of copper heavy metal contained more bands than C800 after the adsorption of copper heavy metal. As shown in Figure 4.4, the band at 3647.37 cm^{-1} for C800 before adsorption is assigned to the hydrogen bonded –OH group of alcohol (O–H stretch) and phenols (H-bonded) (Al-Qodah & Shawabkah, 2009). The band at 2355.85 cm^{-1} for C800 before adsorption is attributed to the –OH strongly hydrogen-bonded and NH stretching mode (Zheng et al., 2016). The main band which was at 2164.47 cm^{-1} for C800 before adsorption and 2155.80 cm^{-1} for C800 after adsorption with copper heavy metal were corresponded to the functional group alkynes which is C≡C (Hesas et al., 2013). The bands at 1977.72 cm^{-1} for C800 before adsorption is representing carbonyl C=O stretch (Montes-atenas & Schroeder, 2016). The band at 559.92, 438.66, and 424.68 cm^{-1}for C800 are associated with the inplane and out-of-plane aromatic ring deformation C–H bending mode (K et al., 2015).



(a)



(b)

Figure 4: FTIR spectra for C800 (a) before adsorption and (b) after adsorption

7.4.2.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was used to measure the total and rate of change in weight of a substance based on temperature or time in a controlled environment. The main purpose of TGA analysis is to determine the composition and terms of stability of the material. The changes or loss of weight of a substance is due to decomposition, oxidation, and dehydration. The properties of the materials specified is moisture content, volatile content, fixed carbon, and ash content. At first stage, the minor weight loss was due to desorption of moisture as bound water on the surface and pores of the sample. Then, the increase in the weight loss after 200 °C was due to the release of volatiles (Gottipati, & Mishra, 2010). In the temperature range between 750 and 900 °C, it is referred to as fixed carbon and at 900 °C the ash content in the adsorbent involved. The total carbon content is a combination of volatile and fixed carbon content. Figure 5 shows different weight of P400, P600, P800 and C800. For C800 adsorbent, volatile contents, fixed carbon, and ash content were totally decomposed at 600 °C. The ash content cannot be detecting. Maybe higher temperature needed to get the value of ash weight percent.

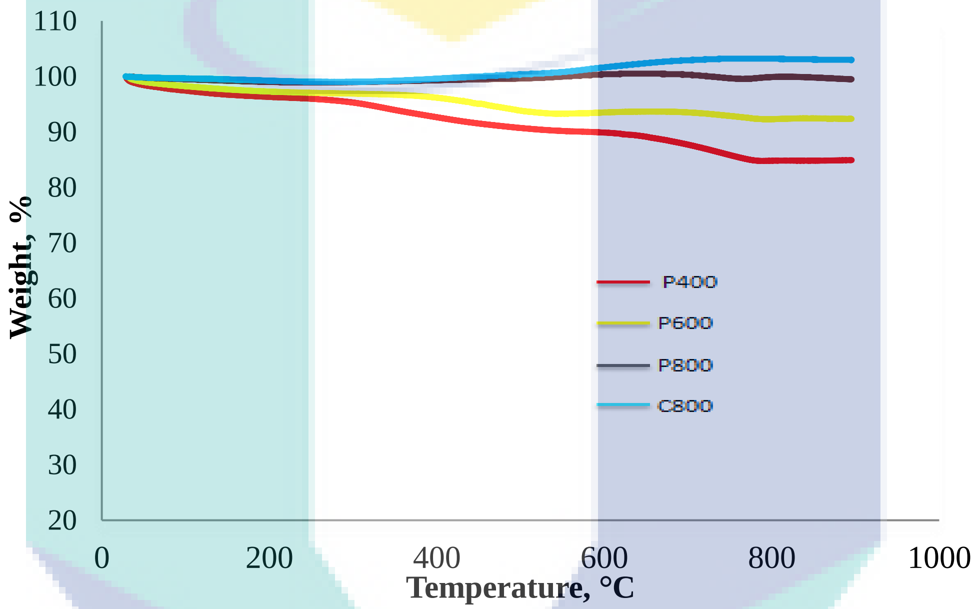
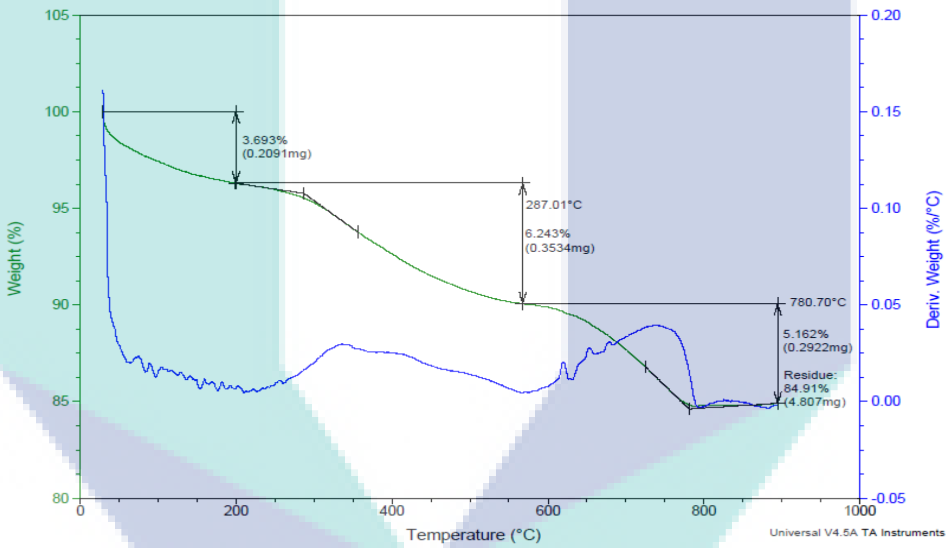


Figure 5: Thermogravimetric analysis curves for P400, P600, P800 and C800

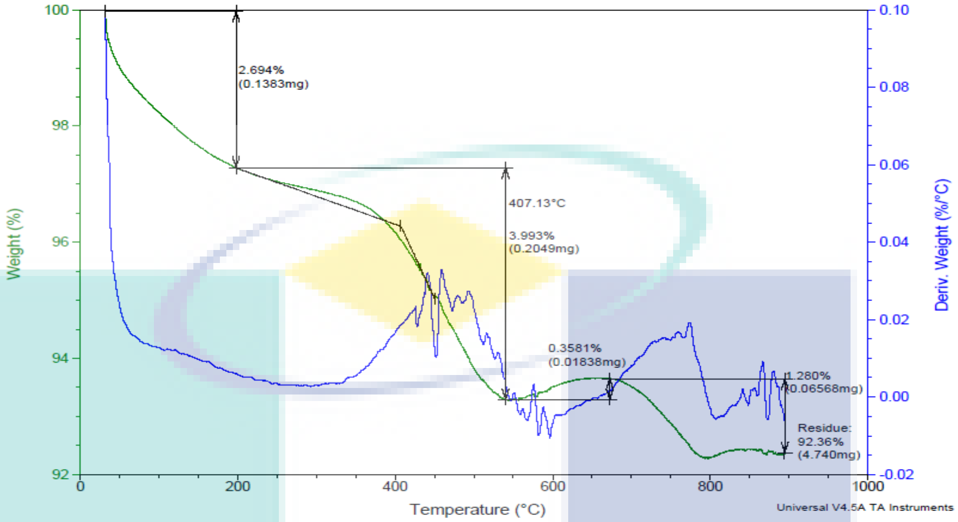
Table 3 shows the proximate analysis data for each sample. The percentage of weight moisture, volatile content, and fixed carbon are shown. For adsorbent P800 and C800, the value of weight percent is not available due the carbonization process. The adsorbent P400 had the higher percentage of moisture, volatile, and fixed carbon compare to adsorbent P600. The remaining weight became residue is shown in Figure 6.

Table 3: The proximate analysis at different adsorbent.

Weight %	P400	P600
Moisture	3.693	2.694
Volatile	6.243	3.993
Fixed carbon	5.162	1.638
Residue	84.91	92.36



(a)

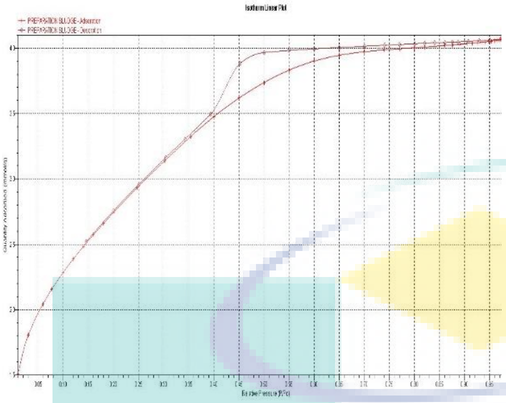


(b)

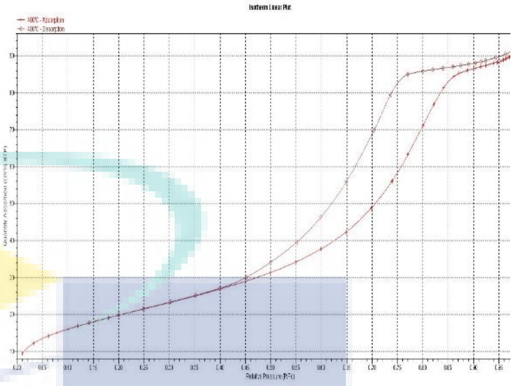
Figure 6: TGA analysis for (a) P800 and (b) C800.

7.4.2.5 N_2 adsorption–desorption analysis

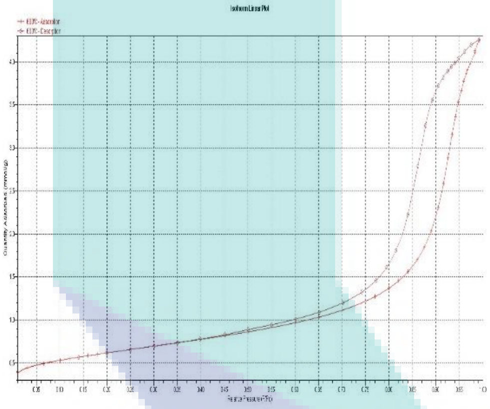
The N_2 adsorption–desorption isotherms and the pore size distributions of A105, P400, P600, P800 and C800 are shown in Figure 7. Based on Figure 7, the N_2 adsorption–desorption isotherms of adsorbent A105 and C800 were type IV. A small H_4 hysteresis loop is observed at high relative pressures so it is the presence of mesoporous (Liu et al., 2016). For adsorbent P400, P600 and P800 based on Figure 4.7 shows the N_2 adsorption-desorption isotherms type V.


Isotherm Linear Plot
PREPARATION SLUDGE - Adsorption
PREPARATION SLUDGE - Desorption
Quantity Adsorbed (mmol/g)
Relative Pressure (P/Po)

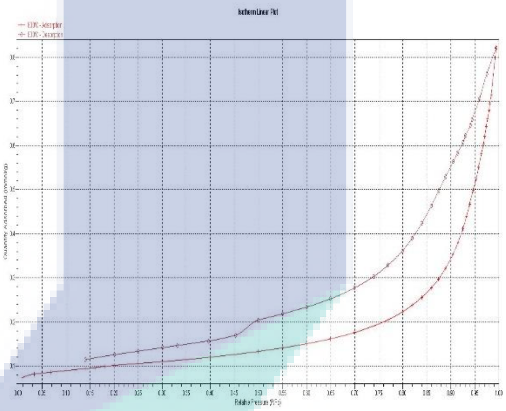
(a)


Isotherm Linear Plot
Adsorption
Desorption
Quantity Adsorbed (mmol/g)
Relative Pressure (P/Po)

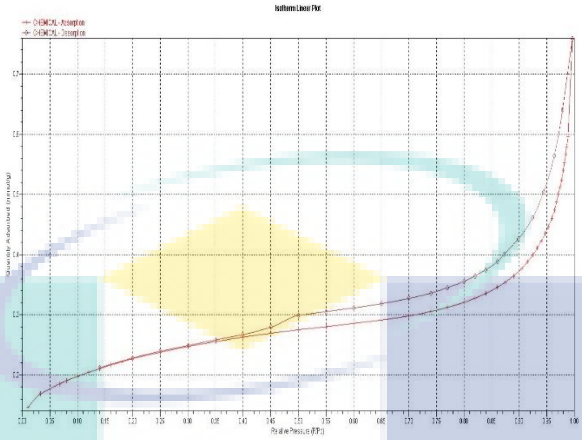
(b)


Isotherm Linear Plot
Adsorption
Desorption
Quantity Adsorbed (mmol/g)
Relative Pressure (P/Po)

(c)


Isotherm Linear Plot
Adsorption
Desorption
Quantity Adsorbed (mmol/g)
Relative Pressure (P/Po)

(d)



(e)

Figure 4.7: The N_2 adsorption-desorption isotherms and pore size distributions for (a) A105, (b) P400, (c) P600 (d) P800 and (e) C800.

Table 4 summarizes the textural properties of adsorbent based on BET surface area, external surface area, total pore volume and average pore diameter. The adsorbent A015 had the higher value of BET surface area (221.0904 m^2/g) and external surface area (225.73 m^2/g) compare to adsorbent P400, P600, P800 and C800. The adsorbent P800 had the lowest value of BET surface area (7.5696 m^2/g) and external surface area (5.5188 m^2/g). The total pore volume of adsorbent A105, P400, and P600 are almost the same which is at the range between 0.1406 m^3/g and 0.1432 m^3/g. The total pore volume for adsorbent P800 and C800 are 0.024803 m^3/g and 0.019653 m^3/g respectively. For the average pore diameter, adsorbent P800 had the higher value followed by adsorbent P600. The adsorbent A105 had the lower value of average pore diameter.

Table 4: The textural properties of adsorbent

Adsorbent	BET surface area (m^2/g)	External surface area (m^2/g)	Total pore volume (m^3/g)	Average pore diameter (Å)
A105	221.0904	225.73	0.141303	28.917
P400	73.9833	83.4311	0.140589	64.630
P600	48.3891	43.0023	0.143235	127.361
P800	7.5696	5.5188	0.024803	173.426
C800	17.1457	14.1433	0.019653	92.619

7.4.3 Adsorption study

Effect of contact time on percentage adsorption of copper onto activated carbon was studied over a shaking speed of 200 rpm for 180 min. By using 0.5 g of adsorbent with 50 mg/L of copper solution concentration, the data was measured at time intervals of 30 min. The highest percentage removal of copper was at the first 30 min of adsorption for P800 and 90 min for C800. Adsorbent P800 and C800 were tested to remove copper from aqueous solution and the percentage removal achieved was 73.04%.

7.4.4 Surface Morphology of TFC

The SEM analysis confirmed the presence of sludge on the unmodified PVDF membranes as shown in Figure 8. For the TFC, the upper layer was the customized thin-film layer made up of NMP:PVDF:adsorbent at different ratios of 90:9:1, 90:7:3, and 90:5:5. The pores allowed the copper solutions to pass through and the meantime some of the coppers were being adsorbed by the sludge. Therefore, it performed the filtration property (Widjojo, Chung, Weber, Maletzko, & Warzelhan, 2011).

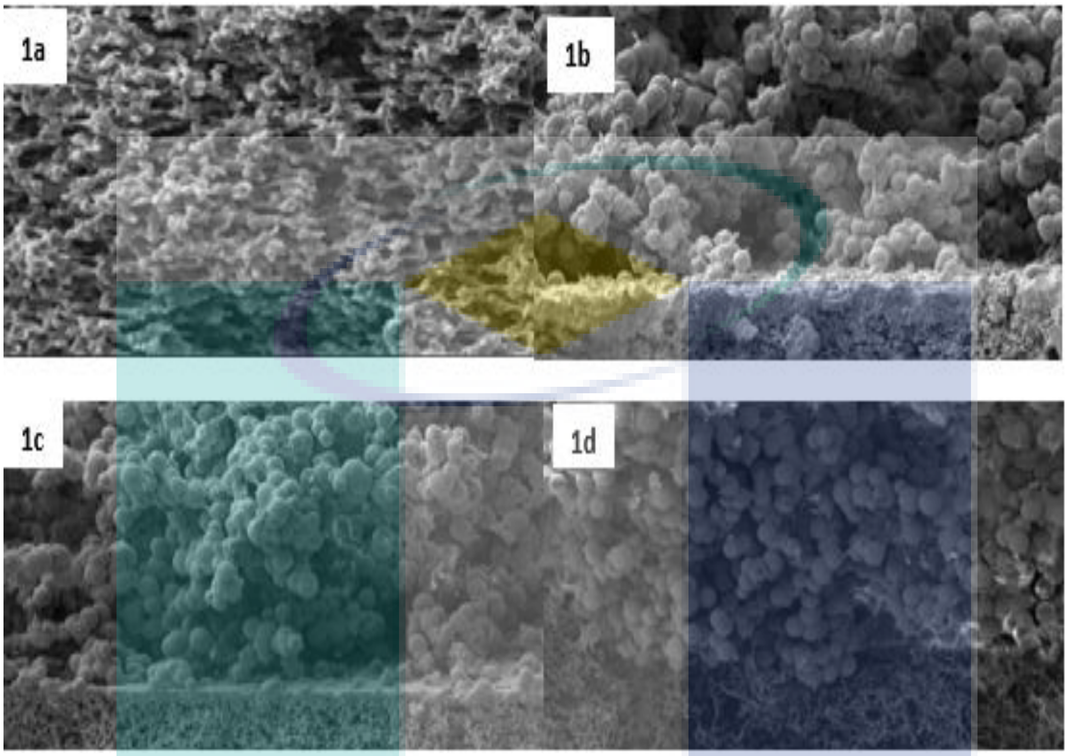


Figure 8: SEM images of (a) unmodified PVDF, TFC with (b) 1.0 wt % (c) 3.0 wt %, and (d) 5.0 wt % adsorbent from landfill sludge

Table 5 lists the permeability values for raw PVDF and all the prepared TFC membranes. Permeability is directly proportional to filtrate flux. Therefore, when the filtrate flux is high, the permeability of membrane is also high, and vice versa. When a membrane has high permeability, it means that it allows the particles to pass through it faster. The TFC membrane prepared at the ratio of 90:5:5 was the best because of the highest amount of sludge adsorbent. Yet, the copper solution had to pass through the thin-film layer before passing through the lower PVDF layer. In addition, the larger copper particles were adsorbed on the surface of the sludge. When the amount of sludge was higher, the surface area was also higher. In short, TFC membrane (90:5:5) was the most efficient TFC membranes among all of the membranes because it removed the highest amount of copper content from the copper solution.

Table 5: Permeability of each type of TFC membranes

Membranes	Permeability (L/m^2·h·bar)				
	Copper solutions				
	10 mg/L	20 mg/L	30 mg/L	40 mg/L	50 mg/L
Raw PVDF	309.44	300.82	292.716	300.824	285.009
TFC (90:9:1)	277.70	277.70	270.758	270.758	277.707
TFC (90:7:3)	251.87	246.14	257.868	251.868	257.865
TFC (90:5:5)	216.61	208.28	212.359	216.607	204.346

7.5 Conclusion

The production of adsorbent from leachate treatment process sludge for copper removal was a success as the adsorbent P800 and C800 successfully removed copper from aqueous solution and the percentage removal achieved was 73.04%. The characterization of prepared sludge adsorbent was done using scanning electron microscopy (SEM), energy dispersive X-ray spectrometer (EDX), fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and N$_2$ adsorption–desorption analysis. The surface morphology of the adsorbent P400, P600, and P800 presented a dense structure with no obvious pores.

For adsorbent C800, the pore can be seen. The adsorbent C800 showed a loose structure and pores distributed unevenly on the surface. The elements contained in the surface of adsorbent P400, P600, P800 were carbon (C), oxygen (O), magnesium (Mg), aluminium (Al), silicon (Si), phosphorus (P), sulphur (S), chlorine (Cl), potassium (K), calcium (Ca), and iron (Fe). For adsorbent C800 contain all the element that contain in adsorbent P400, P600 and P800 except potassium (K) but contained zinc (Zn). The main functional group of adsorbent C800 before and after test with copper heavy metal were determined at 2164.47 cm^{-1} for C800 before adsorption and 2155.80 cm^{-1} for C800 after adsorption with copper heavy metal were corresponded to the functional group alkynes. The properties of the materials specified such as moisture content, volatile content, fixed carbon, and ash content of each adsorbent P400, P600, P800 and C800 were determined. For N_2 adsorption–desorption analysis, the adsorbent A105 and C800 were shows as type IV. The adsorbent P400, P600 and P800 were shows the N_2 adsorption–desorption isotherms type V.

Adsorbent from landfill sludge was successfully incorporated onto the PVDF membrane to produce thin-film composite membrane. The surface area of 14.2675 m^2/g made the TFC membrane to be potential to be used in the removal of copper ion. Also, the TGA analysis shows that the TFC membrane had a good thermal stability. Via ultrafiltration, the TFC membranes were capable of removing copper ion.

7.6 Recommendations/Way Forward

The research can be continued by testing the adsorbent for the removal of other heavy metals. Also, the adsorbent can be incorporated into the membrane in the mode of mixed-matrix membrane where the efficiency may be further enhanced.

CHAPTER 8

MICROWAVE IRRADIATION AND WET RENDERING TO IMPROVE TORREFACTION OF FOOD WASTE

PROJECT LEADER: DR. RUWAIDA BINTI ABDUL RASID

PROJECT TEAMS:

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8.1 Abstract

Municipal solid waste (MSW) is one type of waste that can use as renewable energy sources. The MSW disposal becomes one of the main issues affecting environmental and sustainable development. Food waste is the highest constituent in the MSW which is contributing to the problem and need to be fully utilized. However, the food waste is characterized by its high moisture content and low high heating value (HHV) which lower the energy efficiency. The objective of this work is to investigate the feasibility of microwave irradiation and wet rendering in enhance the quality of torrefied food waste. The sample for torrefaction is prepared by treating the food waste with microwave irradiation and wet rendering prior to torrefaction. In the pre-treatment process, the food waste was boiled in the water with 1:1 ratio of food waste in the 1L beaker is used in the microwave irradiation and wet rendering. The food waste was dried

at 105 ˚C for 24 hour until the weight is constant. For the sample preparation without wet rendering, the food waste was dried at 105 ˚C for 24 hour. The parameter for microwave irradiation are power and time which is vary at 240, 400, 560 and 720 Watt for 10-20 minutes, while for wet rendering parameter is vary at temperature 60, 70, 80 and 90 ˚C for 30, 40, 50 and 60 minute. For torrefaction process, the temperature and time is varies at 260, 280, 300 and 320 °C for 30 and 60 minutes with the presence of inert condition of 10 mL of nitrogen gas. The moisture content, proximate analysis, elementary analysis, high heating value (HHV) and mass and energy yield of the torrefied products were characterized accordingly. It was found that the appearance of the food waste that undergo pre-treatment light brown in colour while the food waste that has not undergo pre-treatment has dark brown in colour. After the torrefaction, the torrefied sample has turned black for both direct torrefaction and pre-treatment sample. In addition, mass yield and moisture content show declined trend with increasing torrefaction temperature at constant torrefaction time.

8.2 Introduction

8.2.1 Objectives

The objective of this work is to investigate the feasibility of wet rendering and microwave irradiation in enhancing the quality of torrefied food waste.

8.2.2 Scopes of study

The scopes of this study are as follows:

1) To study the effect of microwave irradiation on the properties of torrefied food waste at 5, 10, 15 and 20 minutes, and power of 240 W, 400 W, 560 W and 720 W.
2) To study the effect of wet rendering on the properties of torrefied food waste at 60, 70, 80 and 90 ˚C and residence time of 30, 40, 50 and 60 minutes.

3) The torrefaction process will be carried out at 260, 280, 300 and 320°C for 30 to 60 minutes.

8.3 Methodology

8.3.1 Materials

In this study, the food waste (FW) samples were collected from a cafeteria near Block V, University Malaysia Pahang (UMP). The food waste consists of rice, egg shell, fruit peels, chicken bone, fish bone and vegetables. Distilled water was used for pre-treatment food waste and silica gel was used for storage of dried food waste sample to make sure that no moisture content in the air inside the plastic seal bag.

A flow chart of the whole process is shown in Figure 1. For the first step, food waste will be collected. After that, the sample will undergo microwave irradiation process and followed by drying at 105°C for 24 hour. Analysis of sample will be conducted. The dried sample will be torrefied. Finally, the torrefied food waste will be analyzed,

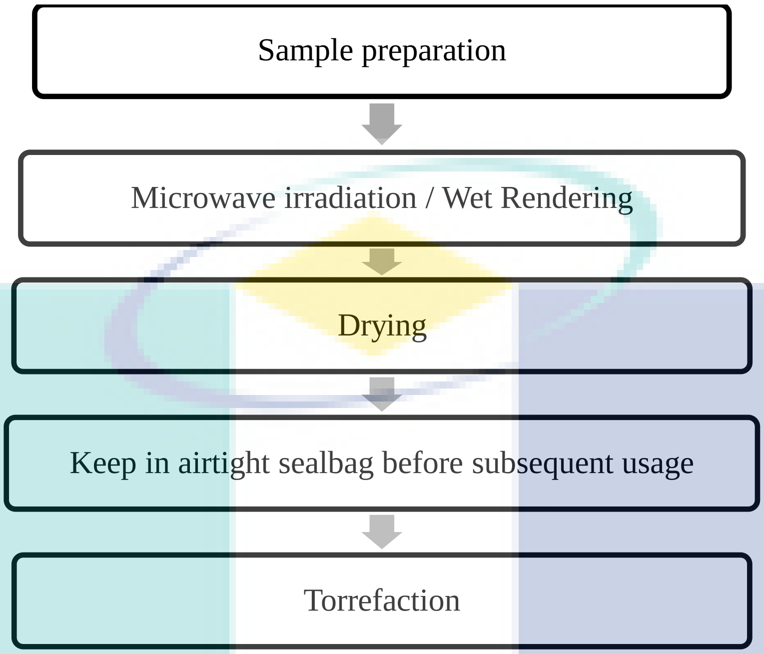


Figure 1 The flowchart for the overall process

8.3.2 Sample Preparation

The food waste sample which consists of mixed composition of rice, egg shell, fruit peels, chicken bone, fish bone and vegetables were collected from the cafeteria in University of Malaysia Pahang (UMP). The sample is crushed first into smaller pieces before proceed with microwave irradiation and wet rendering.

8.3.3 Microwave Irradiation

In this study, domestic microwave oven (SHARP, model: R207EK) is used with maximum power up to 800 W. The sample (300 g) was added into 1000 mL beaker with 300 mL of distilled water (solid/distilled water ratio = 1/1 (w/v)). The beaker was placed in the microwave. The experiment was carried out using a microwave power of 560 W for 10 minutes. Next, the sample is take out from the microwave and filtered by using the plastic kitchen sieve to separate the solid and liquid. The solid is placed in the aluminum foil for drying. The experiment was repeated at different power (240 W, 400 W, 560 W, and 720 W) and time (5, 10, 15 and 20 minutes) as summarized in Table 3.1.

8.3.4 Wet Rendering Process

A hotplate model was used to heat the sample. The food waste sample was immersed with distilled water with the ratio of 1:1 (weight/volume) (Suseno, Nurjanah, Yoshiara, & Saraswati, 2015). For the first run, the temperature and time was set at 80 ˚C and 50 minute for heating process and the conical flask was placed on the hot plate. Once the temperature has reached 80 ˚C, the timer was started for 50 minute (El-rahman, Mahmoud, & Youns, 2018). After 50 minute, the sample was filtered to separate the solid and liquid fraction by using stainless steel sieve. The wet rendering process is repeated with different temperature and time which shown in Table 1. The condition is maintained like the first run.

Table 1: Tabulation of data for microwave irradiation at different power (W) and time (min), and wet rendering at different temperature (˚C) and time (min).

Microwave Irradiation			Wet Rendering		
Set of sample	Power (Watt)	Time (min)	Set of sample	Temperature, ˚C	Time, minute
1	240	5	1	60 ˚C	30
		10			40
		15			50
		20			60
2	400	5	2	70 ˚C	30
		10			40
		15			50
		20			60
3	560	5	3	80 ˚C	30
		10			40
		15			50
		20			60
4	720	5	4	90 ˚C	30
		10			40
		15			50
		20			60

8.3.5 Drying Process

The solid sample was dried at 105 ˚C for 24 hour and then weighed the sample for 3 times until the weight is constant (Poudel, Ohm, Lee, & Oh, 2015). Then, the dried sample was crushed by mortar into pieces to please the grinding process. The sample was sieved by sieve tray shaker (2 mm, 1 mm and 250 mm), and then collected the sample which pass through a 250 mm only and the sample was stored in a plastic sealed bag. In order to achieve an effective and uniform heat transfer during torrefaction, this size range was selected and hence removes the effect of particle size (Pahla, Ntuli, & Muzenda, 2018). The desiccator was used to store the dried food waste sample with silica gel to keep the sample free from moisture content until the torrrefaction process and characterization was carried out.

8.3.6 Torrefaction Process

Fixed bed reactor is used in this process. This reactor has inner diameter 3.7 cm and length of 10 cm as shown in Figure 2.

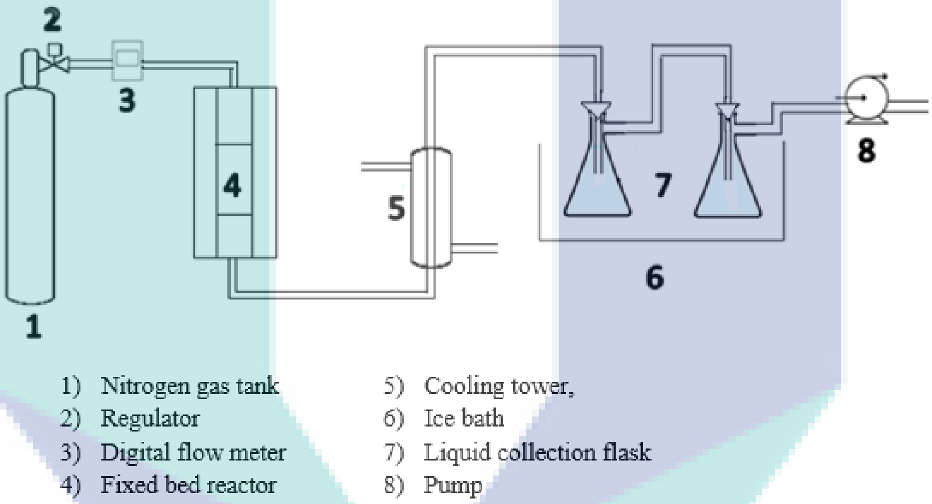


Figure 2: Schematic diagram of torrefaction process

8 g of the sample is weigh and placed into the reactor with temperature at 260°C for 30 and 60 minutes. The reactor that contained the dried sample was purged by nitrogen gas with continuous flow of 10 L/min to create an inert environment. The released gas from this process was trapped in condenser. After 30 min, the power of the reactor was switched off. The solid product was collected when the reactor was cooled down. Analysis of the product was made. Each of the experiments was repeated thrice under the same conditions to ensure reproducibility of the results (Rago et al., 2017). The procedure

is repeated using different temperature at 280, 300 and 320°C for 60 min torrefaction residence time.

Table 2 Tabulation data of torrefaction process at different temperature (°C) and time (min)

Set of samples	Temperature (°C)	Time (min)
1	260	30
		60
2	280	30
		60
3	300	30
		60
4	320	30
		60

8.3.7 Characterization

8.3.7.1 Moisture Content

The moisture content of raw food waste and torrefied biomass was determined by Moisture Analyser model that is available in Biotechnology Lab, FKKSA. Firstly, the temperature was set up at 105 ˚C. 1 g of the raw food waste was weighed and placed it on the plate. The button ‘START’ was pressed and waited for the reading. Once the ‘BEEP’ sound ringing, the reading of moisture content was recorded. The steps were repeated by using the torrefied sample. They were repeated at least three times to ensure consistency.

8.4 Findings

8.4.1 Mass Yield

8.4.1.1 Torrefaction undergo microwave irradiation with different in temperature and time

Figure 3 and Figure 4 show the mass yield for the torrefaction of food waste. The Figure 3 shows the data for direct torrefaction at different temperature while the torrefaction time is constant for 30 minutes. However, Figure 4 it shows the mass yield for the torrefaction of food waste that has been undergo microwave irradiation at 560 W for 10 minutes.

Based on Figure 3 and Figure 4, the mass yield for torrefaction of food waste are decreased linearly as the torrefaction temperature is increasing at constant torrefaction time (30 minutes). The mass yield for direct torrefaction is decreased from 90.83% to 85.19% at temperature of 260°C and 280°C respectively. The mass yield continuously drop to 79.56% and 75.38% as the temperature is increased to 300°C and 320°C respectively. Furthermore, the mass yield for the torrefaction of food waste that has been undergo microwave irradiation pre-treatment are 92.79%, 84.60%, 73.75% and 70.38% at torrefaction temperature at 260, 280, 300 and 320°C.

The decreasing trend of mass yield is caused by the loss of moisture content as the torrefaction temperature is increasing (Abdul Samad, Jamin, & Saleh, 2017). In this context, when the torrefaction temperature is increased, the nutrient such as proteins and carbohydrates will restructure their molecule by releasing the gaseous product such as carbon monoxide (CO), carbon dioxide (CO_2) and water (H_2O) (G, F, & E, 2017).

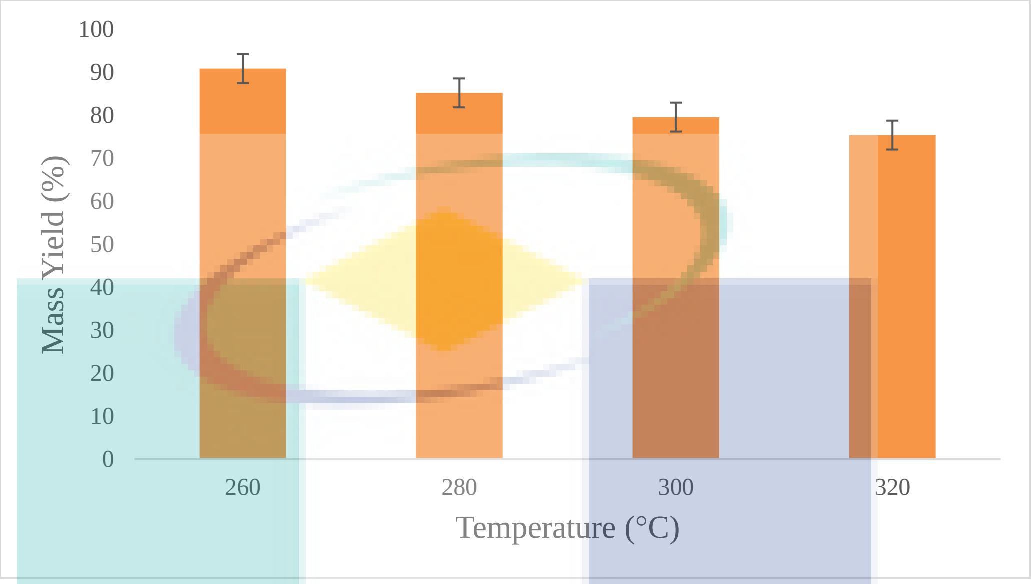


Figure 3: Mass yield for direct torrefaction of food waste

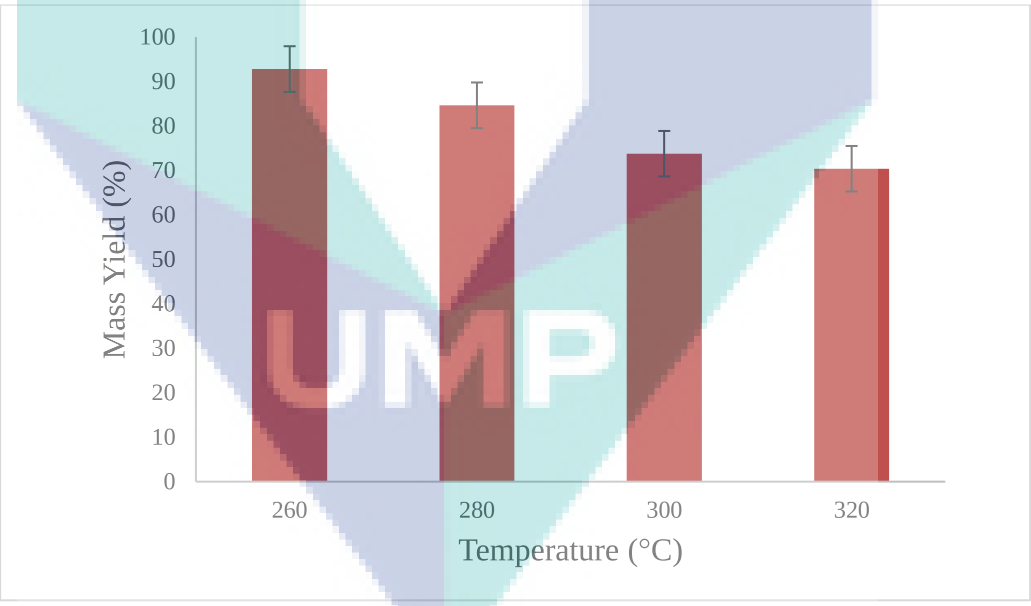


Figure 4: Mass yield for torrefaction of food waste undergo microwave irradiation at 560 W and 10 min

8.4.1.2 Torrefaction undergo microwave irradiation with constant in temperature and time

Figure 5 show the mass yield for the torrefaction of food waste for direct torrefaction and torrefied biomass with various power of microwave irradiation. Based on Figure 4.3 the mass yield for torrefaction of food waste is decreased linearly as the torrefaction temperature is increasing at constant torrefaction time (30 minutes). The mass yield for torrefied biomass is decreased from 82.69% to 76.69% at power of 240 W and 400 W respectively. The mass yield continuously drops to 70.38% at power 560 W and slightly drops to 69.75%.at power of 720 W.

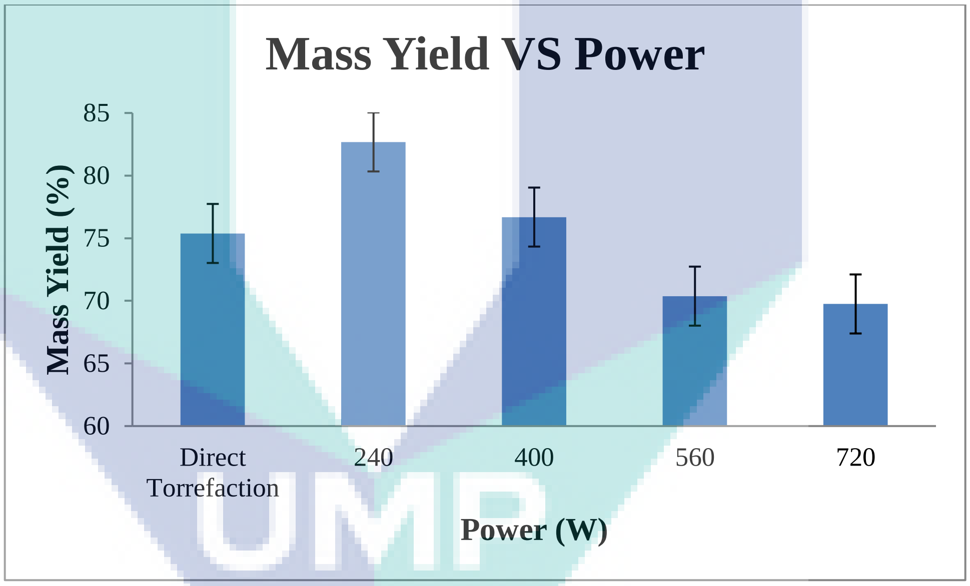


Figure 5: Mass yield of torrefied food waste with different power of microwave irradiation

8.4.1.3 Torrefaction of food waste undergo wet rendering (80 ˚C, 50 minute)

The experiments with respect to torrefaction temperature were performed at mild temperature of 260 ˚C, 280 ˚C, 300 ˚C and 320 ˚C with residence time of 30 minute by using food waste sample with and without wet rendering. According to (Pahla et al., 2018), factor that influence to a high yield of volatile and a low mass yield is when the temperature of torrefaction increase, the valorisation also increases. The mass yield of torrified biomass with wet rendering at temperature 80 ˚C and time 50 minute and direct torrefaction were calculated by using Eq. (1) and the result is showed in Fig. 6.

The mass yield of food waste sample with wet rendering and direct torrefaction that shows in Fig 6 is decreased linearly with an increase torrefaction temperature from 260 ˚C to 320 ˚C. The highest mass yield for wet rendering and direct torrefaction of 92.88% and 90.83% were recorded at 260 ˚C then drastically decreased approximately 73.5% and 75.38% at 320 ˚C. This trend shows that the highest the temperature, the lower the mass yield obtained due to loss of moisture content as the temperature is increased. Furthermore, at highest torrefaction temperature of 320 ˚C, there are more volatile gaseous are released such as carbon dioxide (CO_2), carbon monoxide (CO), acetic acid and other organics which contribute more mass loss compared to a lower temperature (Asma et al., 2017).

The mass yield of direct torrefaction shows lower than with wet rendering in Fig 6. This is because of the devolatilization of oily compound that left in the food waste which had not go through pre-treatment. According to (El-rahman et al., 2018), the optimum condition of wet rendering is at temperature 80 ˚C and time 50 minute that will produced 20% of oil yield. Food waste which undergo wet rendering has lower oil content compared to food waste which not undergo wet rendering. During torrefaction, food waste that contain oil compound without undergo wet rendering has high mass loss and will be volatized in biochar compare to food waste that undergo wet rendering. Therefore, the devolatilization of oil content in the food waste without undergo wet rendering has high mass loss compared to the food waste with undergoing wet rendering.

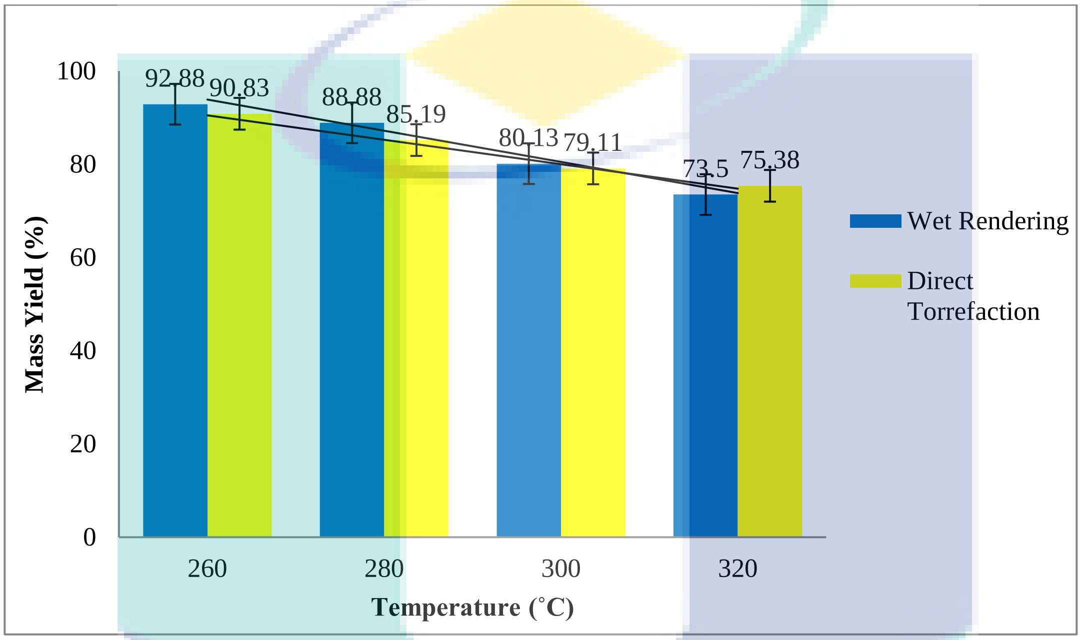


Figure 6: Mass yield for torrefaction with and without wet rendering.

8.4.1.4 Torrefaction of biomass that undergo wet rendering (60 ˚C, at 30, 40, 50 and 60 minutes)

The torrefaction process is done at fixed temperature and residence time which is at 320 ˚C and 30 minutes by using food waste sample with and without wet rendering. The mass yield of torrified biomass with wet rendering at temperature 60 ˚C and time at 30, 40, 50, and 60 minutes and direct torrefaction were calculated by using Eq. (1) and the result is showed in Fig. 7.

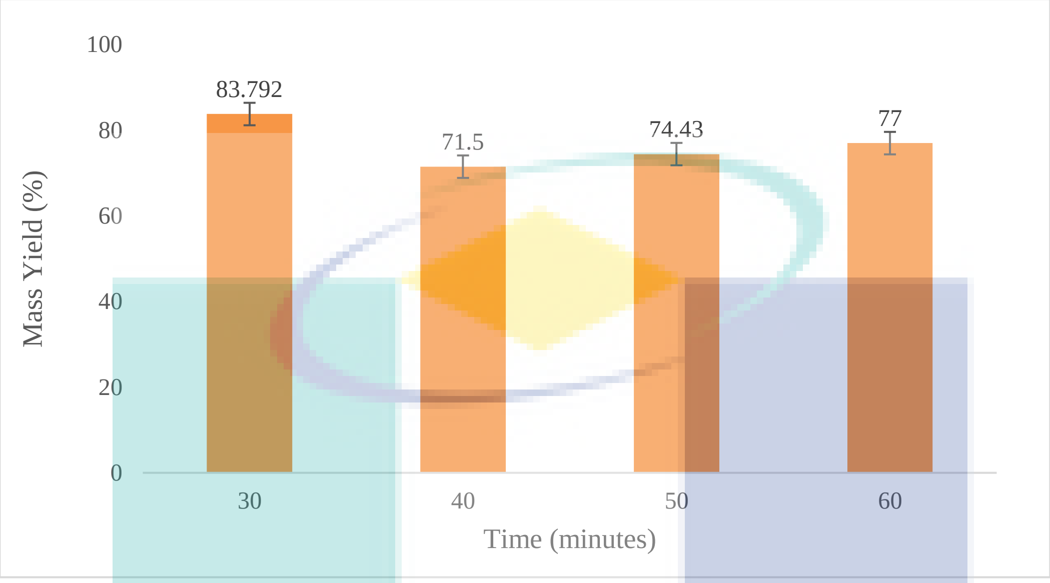


Figure 7: The mass yield of torrefied biomass with wet rendering at temperature 60 ˚C and time at 30, 40, 50, and 60 minutes

The mass yield of food waste sample with wet rendering and direct torrefaction that shows in Fig 4.5 and Fig 4.6 shows no trend. In Fig 7, at wet rendering 30 minutes the mass yield is 83.792 % which is the highest. After that at wet rendering 40 minutes, the mass yield is decrease into 71.5 % which is the lowest and the mass yield starts to increase at wet rendering at 50 and 60 minutes which are 74.43 % and 77 % respectively.

In Fig 8, it shows mass yield of torrefied raw sample and torrefied rendered sample at temperature 60 ˚C and time at 30, 40, 50, and 60 minutes. The mass yield of direct torrefaction which is 75.38 % is lower than mass yield of wet rendering sample at time 30 and 60 minutes which is 83.792% and 77% respectively and slightly higher than mass yield of wet rendering sample at time 40 and 50 minutes which is 71.5% and 74.43% respectively.

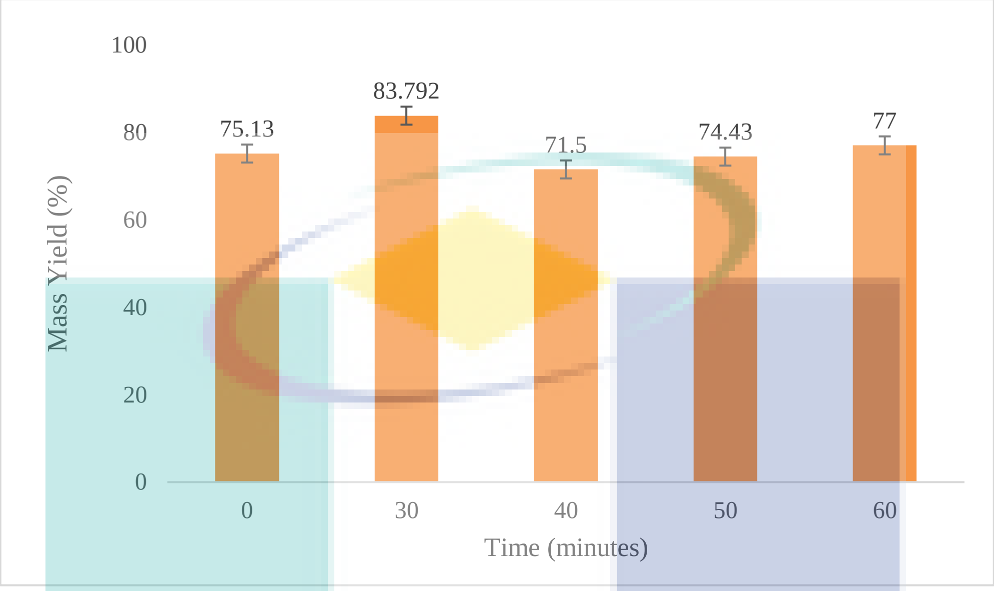


Figure 7: The mass yield of torrified biomass with wet rendering at temperature 60 ˚C and time at 30, 40, 50, and 60 minutes and raw sample

In a nutshell, there is no trend at Fig 6 and Fig 7 because the experiment is only done at 60 ˚C so there is no conclusion that can be made. Thus, the experiment must be done at different temperature to ensure that experiment is done correctly and to get a clear view about the trend, which is 75.38 % is lower than mass yield of wet rendering sample at time 30 and 60 minutes which is 83.792% and 77% respectively and slightly higher than mass yield of wet rendering sample at time 40 and 50 minutes which is 71.5% and 74.43% respectively.

8.4.2 Moisture Content

8.4.2.1 Torrefaction undergo microwave irradiation with different in temperature and time

Food waste has high value of moisture content which lowering the energy efficiency (Abdul Samad, Jamin, & Saleh, 2017). The raw food waste has moisture content about 68.1%. Figure 8 shows the moisture content of the torrefied sample after 30 minutes of torrefaction by varying it torrefaction temperature. Based on Figure 8, the moisture content of direct torrefaction and the torrefaction of food waste that undergo microwave irradiation pre-treatment (560 W, 10 min) is decreased as the torrefaction temperature is increased.

After torrefaction process, the improvement of the moisture in the food waste has increased. For direct torrefaction, the moisture content is 1.50% at 260°C which is decreased slightly from the initial moisture content before torrefied the sample which is 1.56%. Then, the moisture content dropped to 1.43%, 1.28% and 0.89% at torrefaction temperature at 280°C, 300°C and 320°C. Besides, the moisture content of the torrefied food waste that undergo microwave irradiation pre-treatment is decreased as the torrefaction temperature is increased. At temperature of 260°C, the moisture content is 1.53%. Then, the moisture content is decreased to 1.51%, 1.45% and 1.39% for torrefaction temperature at 280°C, 300°C and 320°C respectively. Meanwhile, the moisture of the sample before torrefaction is 2.64%.

Other than that, the moisture content of the direct torrefaction is lower compared to the torrefaction of food waste undergo pre-treatment. High in moisture content for the pre-treatment food waste can be caused by the microwave irradiation pre-treatment since the water is used as the solvent to extract the oil from the food waste. The less in moisture content, the better the sample. However, the quality of the samples cannot based on the moisture content only since high heating value of the torrefied samples need to be analysed too.

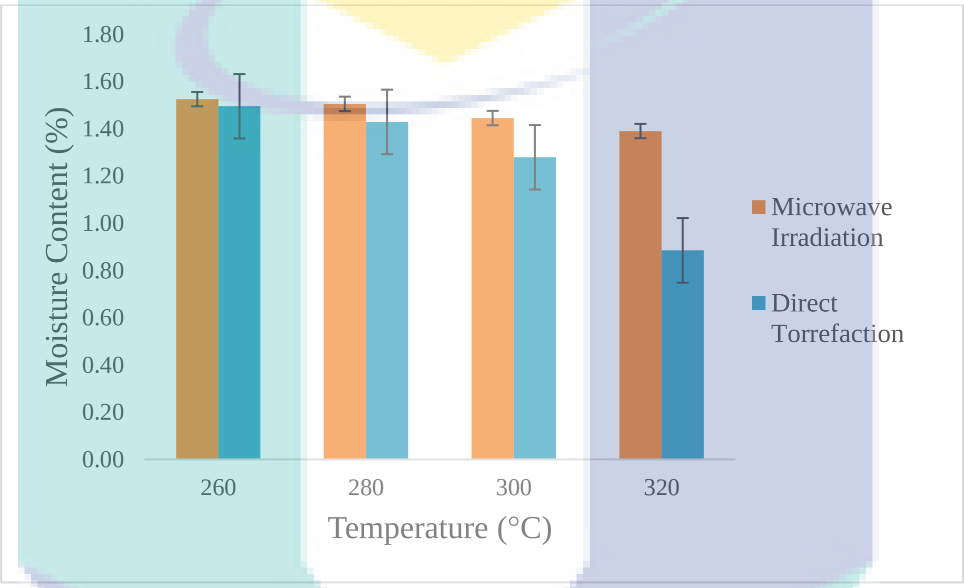


Figure 8: The moisture content of torrefied sample

8.4.2.2 Torrefaction undergo microwave irradiation with constant in temperature and time

The moisture content of the torrefied sample for direct torrefaction and the torrefaction of food waste undergo microwave irradiation at different power level (240, 400, 560 and 720 W) for 10 minutes can be seen in the Figure 9. The moisture content for the direct torrefaction is 0.89% while for the other power level is 1.27%, 1.06%, 1.39% and 1.02% at 240, 400, 560 and 720 W respectively.

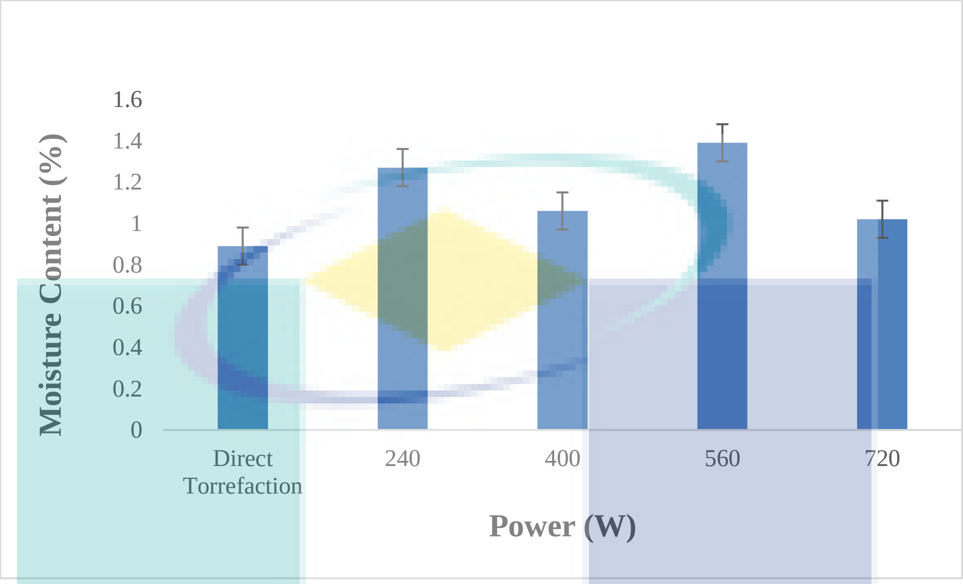


Figure 9: The moisture content of torrefied food waste with different power of microwave irradiation

8.4.2.3 Moisture content of food waste undergo wet rendering (80 ˚C, 50 minute)

The moisture content of raw food waste from cafeteria Block V is 65. 67%. The moisture content of raw food waste that has been studied by (Pahla et al., 2018) and (Kim, 2014) are 62.15% and 77.1% respectively. The vary moisture content of experimental data and other previous study could be explained by the variability of the sample probably due to different country food. From Fig 6 shows that the moisture content of food waste that undergo wet rendering is decreased linearly with increase in torrefaction temperature same as moisture content of food waste that not undergo wet rendering from 260 ˚C to 320 ˚C in Fig 10. The highest moisture content for wet rendering and without wet rendering of 1.35% and 1.50% were recorded at 260 ˚C then slightly decreased approximately 1.11% and % at 320 ˚C. This trend shows that the highest the temperature, the lower the moisture content obtained due to loss majority of moisture content during pre-drying process.

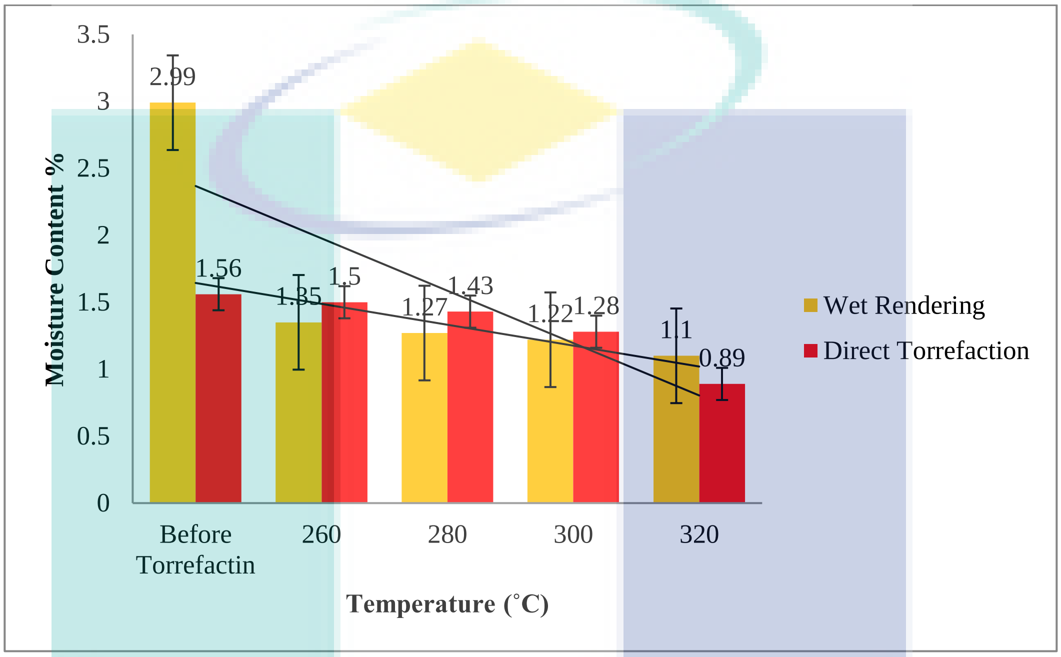


Figure 10: Moisture content for torrefaction with and without wet rendering.

8.4.2.4 Torrefaction of biomass that undergo wet rendering (60 ˚C, at 30, 40, 50 and 60 minutes)

In Fig 4.11, it shows moisture content versus time of wet rendering at 60 ˚C. From the graph, at wet rendering at 30 minute, the moisture content is 1.02%. At 40 minutes of wet rendering at 60 ˚C, the moisture content is highest which is 1.26% and the value of moisture content is decrease at 50 and 60 minutes of wet rendering which is 1.15% and 1.14% respectively. In Fig 4.12, it shows moisture content of wet rendering and raw sample versus time of wet rendering. From the graph, the raw sample moisture content is 0.89% which is lowest compare to wet rendering sample at temperature 60 ˚C and time at 30, 40, 50, and 60 minutes.

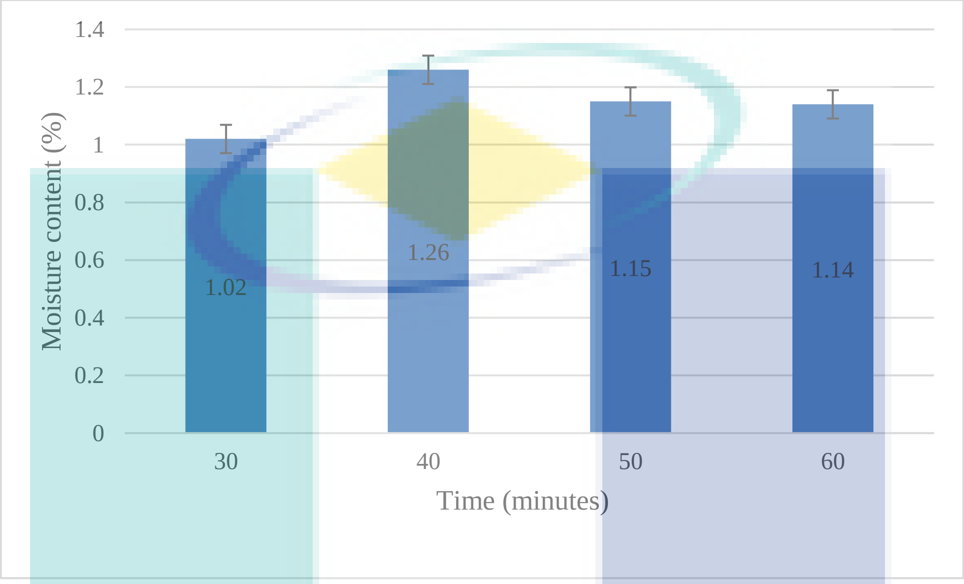


Figure 4.11: Moisture content versus time for wet rendering at 60 ^{O}C

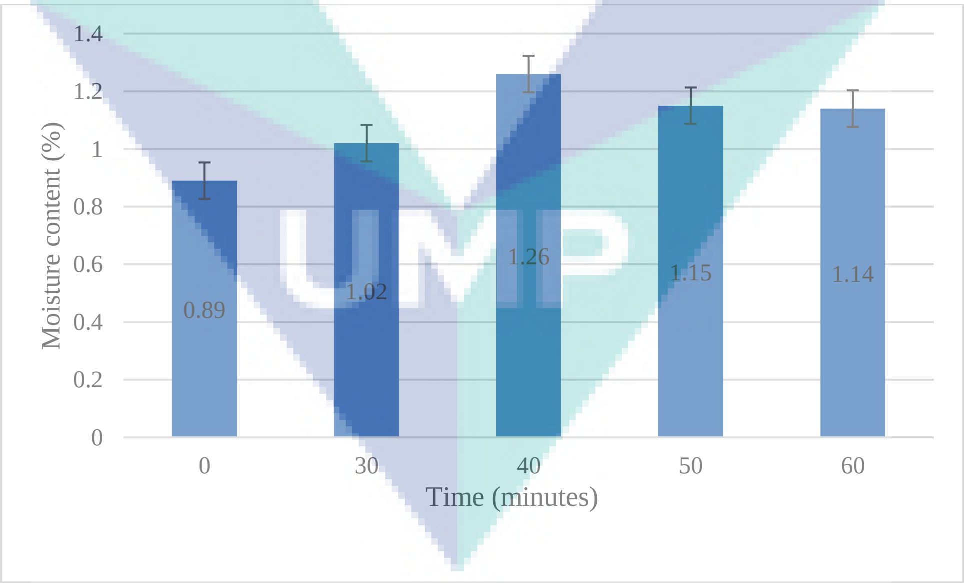


Figure 4.12: Moisture content of wet rendering and raw sample versus time of wet rendering

8.4.3 Appearance of Torrefied Sample

Figure 4.13 shows the appearance of the sample before torrefaction process. Based on the Figure 4.13, the food waste that undergoes microwave irradiation and wet rendering is light brown in color compare to the food waste without undergoing pre-treatment which is dark brown.

The appearance for the torrefied sample can be seen in Figure 4.13 and Figure 4.14. The color for all torrefied samples is quite similar both direct torrefaction and the microwave irradiation sample which is black. This colour change is may be attributed to high carbonization since the temperature used for torrefaction is more than 260°C. The sample then will be set for scanning electron microscopic (SEM).


Microwave and Wet Rendering Direct Torrefaction

Figure 4.13: Appearance of sample before torrefaction process.

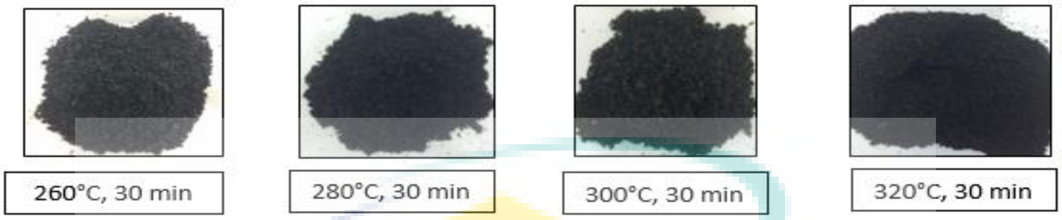
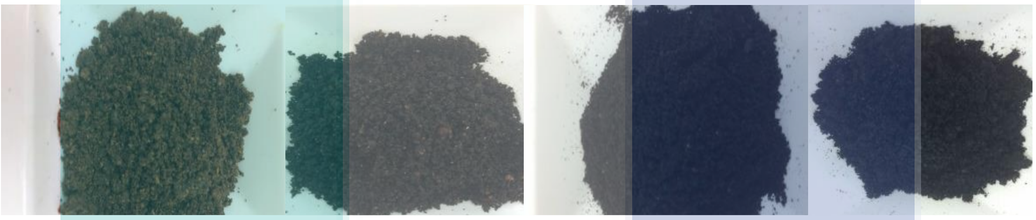


Figure 4.14: Appearance of biochar after torrefaction for food waste undergo microwave irradiation



260 ˚C, 30 min 280 ˚C, 30 min 300 ˚C, 30 min 320 ˚C, 30 min

Figure 4.15: Appearance of biochar after torrefaction for food waste undergo wet rendering.

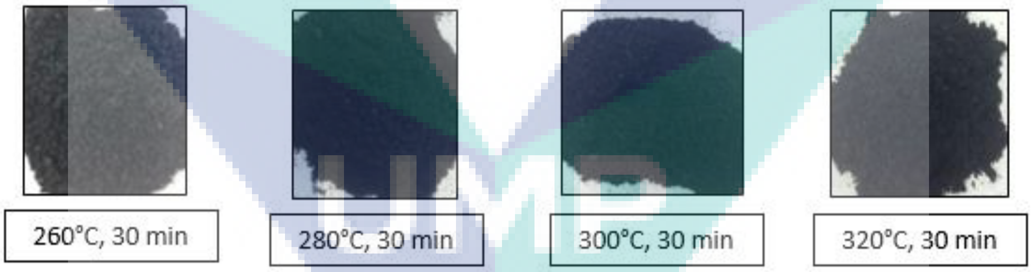


Figure 4.16: Appearance of biochar after torrefaction for direct torrefaction sample

8.5 Conclusion and recommendation

In this study, the torrefaction process help in reducing the moisture content of the food waste. The moisture content of the torrefied product is decreasing as the torrefaction temperature is increased. It is important to have low moisture content for biochar production. The mass yield for both microwave irradiation and wet rendering for the torrefied product also decreasing as the torrefaction temperature and power of microwave is increasing. Thus, the temperature effect has more significant impact to the characterization of torrefaction product compared to residence time and the characteristics of the torrefied food waste with and without wet rendering had similar trend that induced the food waste as potential energy source. Microwave irradiation can help in enhancing the torrefaction of food waste by lowering the moisture content and the percentage of mass yield of the torrefied product. The better quality of the torrefied samples cannot be based on the mass yield and moisture content only since other analysis has been done yet.

CONCLUSION AND RECOMMENDATION

In conclusion, this research has successfully achieved the objective requirement which is to develop the renewable energy from various waste materials. Municipal solid waste, food waste, leachate and fish waste were from various location were obtained for this study. In summary, the first study reported the factorial analysis study, optimization and kinetic study of the COD production from Municipal Solid Waste (MSW) where the mixed culture mixed culture successfully degraded the organic waste and plastics (PET) of MSW. For second study, the effects of vermicomposting of landfill leachate using earthworms on biofertilizer production in 31 days were investigated. Based on the data, vermicomposting is a suitable technology for the decomposition of landfill leachate into nutritive biofertilizer. Thirdly, the effects of temperature and mixing time on the production of fatty acid from fish waste were studied and as a result, oil yield and oleic acid were accepted to be used for biodiesel production from fish waste.

Next, moisture content percentage, concentration of nitrate ions, pH value and leaching rate percentage were measured to formulate fish feed and at the end, the fish waste, soybean meal and groundnut meal were proven to be the alternative substitutes to the conventional fish feed formulation. Fifth study involved in developing an anaerobic digestion (AD) process model in treating food waste to produce biogas. Aspen Plus software was applied and the result showed that the simulation can be accepted to represent the anaerobic digestion process. Additionally, in order to produce adsorbent from the waste sludge, the sludge was treated by physical and chemical method. As a result, 10 kg of raw sludge can produce at least 660.3 g of activated carbon.

Finally, the last study showed the quality of torrefied food waste can be enhanced by treating the food waste with microwave irradiation and wet rendering. All of these studies proved that waste not only can be utilized to produce new products or energy but also significantly helped to reduce waste and most importantly to save the earth and make wealth from it. However, some studies were not able to be completed due to time constraint and budget. In future, more research on waste utilization should be done in order to produce more valuable resources. For starter, it is recommended for the researcher to utilize waste around UMP campus before going for a larger scale.

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APPENDICES

1. Human capital

List student involved 2017

1. Nur Jazmina Binti Md Azmi
2. Siti Zulaikha Binti Mohd Subri
3.Muhammad Najib Bin Hamzah
4. Ezree Farhan Bin Abu Hanipah
5. Aiman Basir Bin Musthafa
6. Nor Hidayah Binti Nordin
7. Irma Binti Ibnoer
8. Siti Nor Amira Rosli
9. Muhammad Yusreen Bin Ismail
10. Siti Aisyah Azhar
11. Mohd Muntaqim Bin Rusdi
12. Nurhidayatul Akma Binti Razali
13. Wan Farhana Bt W Idris
14. Wan Amirah Bt Wan Abdullah
15. Siti Hajarul Asma Binti Ahmad
16. Nor Akmalina Bt Mustazar
17. Rahsya Nur Udzaifa Binti Abdul Rahman
18. Siti Nur Shakina Binti Abu Samah
19. Norazlin Binti Supandi
20. Nurul Nurshaqira Binti Mohd Razman
21. Muhammad Hafizuddin Bin Mat Yusoff
22. Nur Fathin Shamirah Binti Daud
23. Muhamad Faez Bin Lukman
24. Nur Afifah Binti Ahmad Sabri
25. Siti Amirah Binti Abdul Ghani

List student involved 2018

1. Raja Ibrahim Bin Raja Mohamad Ali
2. Abdul Muiz Bin Moktar
3. Nurazmin Syafiq Bin Md. Sidek
4. Muhammad Zaid Bin Ahmad Shafi
5. Muhammad Amir Asyraf Bin Ahmad Kamal
6. Nurul Izzma Binti Alias

7. Nur'atikah Bt Md Salleh
8. Nur Suhaila Binti Anang Japar
9. Nur Idayu Bt Ab Wahab
10. Muhamad Yazid Bin Ahmad Shafiei
11. Nur Asmaa' Asilah Binti Azman
12. Noor Zalina Binti Hj Hashim
13. Mohamed Zainul Ariff Bin Zaharuddin
14. Thye Mei Chin A/P Thye Ah Chai
15. Raj Krishna Roshan A/L Kanasan
16. Nor Amira Rosli

List student involved 2019

1.Wan Nadja Julika Wan Hamizan

2. Achievement and awards

i. UMP (CITReX 2019) - Silver (Preparation of thin-film composite membrane (TFC) of PDVF/sludge adsorbent for copper removal)
ii. UMP (CITReX 2017) - Bronze (From waste to wealth: Sludge to adsorbent)
iii. UMP (CITReX2017)- Silver (Production of Biofertilizer from Landfill Leachate)

3. List of publications

i. Harun N., Ibrahim W.H.W., Zainol N. (2018). Process simulation of anaerobic digestion for bioliquid production from food waste. In: Ramli, A., Mat Piah, R., and Abu Samah, R. Engineering, ethics professionalism and its application. UMP Publisher, Malaysia (Book Chapter- Published)

ii. Harun N., Ibrahim W.H.W., Lukman M.F., Yusoff M.H.M., Daud N.F.S., Zainol N. (2018). Process Simulation of Anaerobic Digestion Process for Municipal Solid Waste Treatment. In: Horan N., Yaser A., Wid N. (eds) Anaerobic Digestion Processes. Green Energy and Technology. Springer, Singapore. DOI: 10.1007/978-981-10-8129-3_5 (Book Chapter-Published)

iii. N. Harun, N. A. Othman, N. A. Zaki, N. A. Mat Rasul, R. A. Samah, H. Hashim. Simulation of Anaerobic Digestion for Biogas Production from Food Waste Using SuperPro Designer. (Materials Today proceeding – Submitted)

iv. Harun, N., Hassan, Z., Zainol, N., Ibrahim W.H.W, Hashim, H.. Anaerobic Digestion Process of Food Waste for Biogas Production: A Simulation Approach. (CET Journal Submitted)

v. Vermicomposting of Landfill Leachate using Earthworms for Biofertilizer Production, Shalyda Md Shaarani , Noor Zalina Hashim, Zatul Iffah Mohd Arshad, Rohaida Che Man, Aainaa Izyan Nafsun, Siti Kholijah Abdul Mudalip and Siti Zubaidah Sulaiman, AIP Proceeding (Accepted)

vi. Co-composting landfill leachate with sugarcane bagasse for biofertilizer production, Shalyda Md Shaarani , Nor Jannah Mokhtar, Zatul Iffah Mohd Arshad, Rohaida Che Man, Siti Kholijah Abdul Mudalip and Siti Zubaidah Sulaiman, AIP Proceeding (Accepted)

vii. Isolation and characterization of bacteria from earthworms' intestines, Shalyda Md Shaarani, Yap Shu Jia, Zatul Iffah Mohd Arshad, Rohaida Che Man, Siti Kholijah Abdul Mudalip and Siti Zubaidah Sulaiman, International Journal of Engineering & Technology (Published)