STUDY ON EFFECTI[illegible] EMOVAL THROUGH THE [illegible] NG EUCHEUMA COTTONII

CHERYN LIM SHIN CHING

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
B.Eng (Hons.) Civil Engineering

Faculty of Civil Engineering and Earth Resources
UNIVERSITI MALAYSIA PAHANG

JUNE 2014

ABSTRACT

The high concentration of heavy metals such as zinc, cadmium, iron and lead are found in industrial wastewater and will bring negative effect to human health like mental illness and blood disease. Therefore, treatment is very important to remove the high content of heavy metal in the water before using as drinking purpose. Absorption treatment is one of the wastewater treatments that remove the heavy metal by using biomass like seaweed. Therefore, a study is needed to investigate the relationship of seaweed and heavy metals in industrial wastewater. The objectives of this study are to determine the characteristics of the industrial wastewater and to investigate the effectiveness of seaweed in the removal of lead and cadmium. The tests that will be carried out are biochemical oxygen demand, chemical oxygen demand and removal of the heavy metals. The standard method used to determine for BOD is APHA 5210 B, HACH DR/2500 Spectrophotometer with Method 8000 is for COD and AAS for the concentration removal of heavy metals. The maximum removal of BOD were 17.95% for cadmium solution and 24.91% for lead solution while the maximum percentage removal of COD were 58.9% for cadmium solution and 58.73% for lead solution. The concentration of the heavy metals such as lead and cadmium was removed by the process of biosorption using *Eucheuma Cottonii*. From the result of AAS, the concentration of the heavy metals reduced compare to the concentration before biosorption process. 77.9% of lead was removed from the lead solution and 62.96% of the cadmium was adsorbed from the synthetic solution after 30 hours. As a conclusion, the amount of the *Eucheuma Cottonii* will affect the effectiveness of the BOD, COD and heavy metals removal therefore seaweed can be used to treat the wastewater that released by industries.

ABSTRAK

Kepekatan logam berat yang tinggi seperti zink, kadmium, besi dan plumbum yang terdapat dalam air sisa industri dan akan membawa kesan negatif kepada kesihatan manusia seperti penyakit mental dan penyakit darah. Oleh itu, rawatan adalah sangat penting untuk menghapuskan kandungan yang tinggi logam berat di dalam air sebelum menggunakan sebagai tujuan minum. Rawatan serapan ialah salah satu rawatan air sisa yang menyingkirkan logam berat dengan menggunakan biomass seperti rumpai laut. Oleh itu, kajian yang diperlukan untuk menyiasat hubungan rumpai laut dan logam berat dalam air sisa industri. Objektif kajian ini adalah untuk menentukan ciri-ciri air sisa industri dan untuk melihat keberkesanan rumpai laut dalam penyingkiran plumbum dan kadmium. Ujian yang akan dijalankan adalah keperluan oksigen biokimia, keperluan oksigen kimia dan penyingkiran logam berat. Kaedah yang digunakan untuk BOD adalah APHA 5210 B, HACH DR/2500 Spectrophotometer dengan Kaedah 8000 adalah untuk COD dan AAS untuk penyingkiran kepekatan logam berat. Penyingkiran BOD maksimum adalah 17.95% bagi kadmium larutan dan 24.91% bagi larutan plumbum manakala peratusan penyingkiran maksimum COD adalah 58.9% untuk kadmium larutan dan 58.73% bagi larutan plumbum. Kepekatan logam berat seperti plumbum dan kadmium boleh dikurangkan melalui proses biosorption menggunakan *Eucheuma cottonii.* Merujuk keputusan daripada eksperimen AAS, kepekatan logam berat telah dikurangkan berbanding dengan kepekatan sebelum biosorption proses dijalankan. Sebanyak 77.9% plumbum boleh dikeluarkan daripada larutan plumbum dan 62,96% daripada kadmium yang terserap daripada larutan sintetik selepas 30 jam. Kesimpulannya, jumlah rumpai laut akan memberi kesan kepada efficienciness BOD, COD dan logam berat penyingkiran oleh itu rumpai laut boleh digunakan untuk merawat air sisa yang dilepaskan oleh industri.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

μ	Micro
°C	Celsius
c_f	Final Concentration of Heavy Metal
c_i	Initial Concentration of Heavy Metal
COD_0	Chemical Oxygen Demand at Initial
COD_n	Chemical Oxygen Demand at nth Hour
D_0	Initial Dissolved Oxygen
D_5	5th Day Dissolved Oxygen
P	Dilution Factor
p	Percentage of BOD_5 removal
q	Removal Efficiency
x	Percentage of COD removal

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
APHA	American Public Health Association
BOD	Biochemical Oxygen Demand
$BOD5_o$	BOD_5 at Initial
$BOD5_n$	BOD_5 at n^{th} Hour
BOD_5	5-Day Biochemical Oxygen Demand
Cd	Cadmium
Co	Cobalt
COD	Chemical Oxygen Demand
Cr	Chromium
Cu	Copper
DO	Dissolved Oxygen
EDTA	Ethylenediaminetetraacetic acid
Fe	Iron
g	Gram
H_2CrO_4	Chromic Acid
H_2O	Water
Hg	Mercury
L	Liter
m	Meter
mg	Milligram
mL	Milliliter
Ni	Nickel

Pb	Lead
pH	Measurement for acidity and alkalis solution
ppm	Parts Per Million
US EPA	United States Environmental Protection Agency
Zn	Zinc

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Water is polluted due to the development of industrial purpose and become polluted industrial wastewater. This industrial wastewater highly contain of heavy metal such as cadmium, iron and lead that will affect to life on the earth. This is because water is an essential requirement for life to live. The industrial wastewater will affect ecosystem on the earth especially human beings. High contain of heavy metal in the water will bring negative effect to human health such as mental illness and blood disease. Therefore, wastewater treatment needed to remove the heavy metal content in water.

From previous researches show that seaweed does have potentially remove heavy metal like cadmium and lead. However, variants of seaweed such as red seaweed, brown seaweed and green seaweed show the different result of heavy metal removal. At the same time, different location source of seaweed also show different result as well. Therefore the study of heavy metal removal efficiency is made by use of our country's seaweed on wastewater treatment.

1.2 PROBLEM STATEMENT

Industrial wastewater are highly contain of heavy metals like cadmium, lead and iron that affect our daily lives. Moreover, the wastewater is very dangerous to human being if used to drinking purpose. This is the reason that wastewater treatment is important to remove the heavy metals in the industrial wastewater before it used as drinking water. Many of the small plants could not afford the wastewater treatment that using high cost of chemical products before discharged the waste water to the open water. The heavy metals in the wastewater had highly contaminated the surface water. The purpose of this study is to know the removal efficiency of heavy metal content in wastewater using seaweed in treatment process.

1.3 SIGNIFICANCE OF STUDY

Heavy metal is toxic element that will harm to living things. It will caused various of illness to the human being. From previous researches showed that seaweed does have the potential to remove heavy metal thus it is much more economic compare to other wastewater treatment method. However, different type of seaweed and varies of geographic source show the different result on heavy metal removal efficiency. Therefore, the heavy metal removal efficiency using seaweed is study. The type of seaweed chosen is *Eucheuma Cottonii* that naturally abundant based from Sabah, Malaysia.

1.4 OBJECTIVES

i. To determine the characteristics of wastewater.
ii. To investigate the effectiveness of seaweed in the removal of lead and cadmium.

1.5 SCOPE OF STUDY

This study will focus on heavy metal removal efficiency in wastewater treatment. Heavy metal is the substances that have metallic properties and it may pollute the environment. Heavy metal will bring negative effect to human health such as mental illness and blood disease. There are many treatment methods that can used to remove the heavy metal in the wastewater, however these methods is much more expensive than biosorption treatment. Seaweed is chosen to be used as a biomass in biosorption treatment because it is easily available and abundant. The small particle of the seaweed will bind with the heavy metals' ions to produce suspended solids so the heavy metals can be removed. The type of seaweed and method to prepare to seaweed sample is analysis and study.

Synthetic wastewater will be prepared using lead and cadmium. Each of the heavy metal solution is 10 mg/L. *Eucheuma Cottonii* collected then grinded and sieved into the desired sizes that is between 350 μm and 600 μm. At the same time, several factors will be tested such as heavy metals removal, BOD and COD of the synthetic wastewater .

1.6 EXPECTED OUTCOME

The heavy metals that contain in the waste water can be removed by using economical source like biomass. Efficienciness of the seaweed to remove the heavy metals can help to the industries on waste water treatment to remove large amount of the heavy metals in an easier and environmental friendly.

1.7 CONCLUSION

The heavy metal removal efficiency in wastewater treatment will be tested by using seaweed as biomass in the biosorption process. The result will be analysis and study under this research so that human beings can drink the safe and healthy water without any threat in the future of time.

CHAPTER 2

LITERATURE REVIEW

2.0 INTRODUCTION

The literature review related information of industrial wastewater treatment of heavy metal using seaweed discussed in this chapter. Besides that, it also discussed on the wastewater heavy metal characteristic, type of treatment, type of biomaterial, type of seaweed and bio-adsorption process.

2.1 HEAVY METAL

Rapid industrial development has lead the disposal of heavy metals into the environment. The tremendous increase in the use of the heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in the aquatic environment. The metals are special because of their persistency in the environment. At least 20 metals are classified as toxic, and half of these are emitted into the environment in quantities that pose risks to human health. (Amuda, Giwa and Bello, 2007)

One of the heavy metal is Chromium, Cr. Choromium is the top priority list of toxic pollutants defined by the US EPA present in the electroplating wastewater as Cr (VI) in the form of oxy anion such as chromates, dichromates and bichromates, depend on pH and Cr concentration. Due to its high solubility, Cr (VI) is very toxic to living organisms. If Cr is ingested beyond the maximum concentration (0.1 $mg|^{-1}$), it can cause health disorders such as vomiting and hemorrhage. (Babel and Kurniawan, 2004)

$$H_2CrO_4 \leftrightarrow H^+ + HCrO_4^- \quad k_1 = 0.18 \ (pK_1 = 6.51)$$

$$HCrO_4^- \leftrightarrow H^+ + CrO_4^{2-} \quad k_2 = 3.2 \times 10^{-7} \ (pK_2 = 5.65)$$

$$2HCrO_4^- \leftrightarrow Cr_2O_7^{2-} + H_2O \quad k_3 = 33.3 \ (pK_3 = 14.56)$$

Zinc (Zn), one of the important heavy metals widely used in electroplating industries, is the model solute used in the present study. Zinc is an essential element for enzyme activators in humans, but it is toxic at levels of 100–500mg/day and it is a known carcinogen. (Senthikumar et al., 2006)

Lead (Pb) is very toxic to mammals and aquatic life. Its presence in the environment as a result of extensive and wide applications in mining, chemical, electroplating, paper and pulp industries, poses serious health hazards to living organisms. (Senthikumar et al., 2007)

If allowed to enter the environment Cu (II) can cause serious potential health issues. Even at low concentrations Cu (II) may be harmful to humans. It has been found that absorption of excess copper results in ''Wilson's disease'' where Cu (II) is deposited in the brain, skin, liver, pancreas and myocardium. (Murphy et. al., 2007)

2.3 TYPE OF TREATMENT

There are several treatment introduced to remove heavy metal in water such as electro-chemical precipitation, ion exchange method, ultra filtration and reverse osmosis. However, these treatments cost a lot especially on the operational cost. (Babel and Kurniawan, 2004)

Most of the treatment methods such as ion exchange, electrochemical reduction, evaporation, solvent extraction, reverse osmosis, chemical precipitation and membrane filtration involve high capital cost and are not suitable for small-scale industries. (Demirbas et al., 2002)

Conventional treatment methods such as chemical precipitation and reverse osmosis become inefficient or expensive when the metals are present in trace quantities. (Chu and Hashim, 2007)

Cost effective alternative technologies or sorbents for treatment of metal contaminated waste streams are needed when compare to existing treatment process such as chemical precipitation, membrane filtration, ion exchange, carbon absorption, and co-precipitation/adsorption. (Bailey et. Al., 1998)

The simplest and cheapest method of removing most heavy metals from solution is to increase the pH of the effluent, thus converting the soluble metal into an insoluble form like hydroxide. Precipitation by adjusting the pH is, however not selective. Any iron like ferric iron present in the liquid effluent will be precipitated first, followed by other heavy metals. Consequently, precipitation by alkali addition usually lime produces large quantities of solid sludge for disposal. Nonetheless, precipitation process can be highly efficient as they rely mainly on the insolubility of the precipitate and secondarily on the effectiveness of solid-liquid separation. (Eccles Harry, 1999)

However, at the same time, the cost of this method include of the concentration of the metal in solution, the operational mode of the equipment, the need for secondary treatments such as regeneration of the granulated activated carbon or ion exchange resins, the selectivity of granulated activated carbon or ion exchange resins, coupled with their respective capacities for the target metals and disposal of secondary waste such as sludge. (Eccles Harry, 1999)

Ethylenediaminetetraacetic EDTA extraction and acid treatment, have been suggested for solubilization of heavy metals from sewage sludge. Addition of EDTA to sewage sludge showed high removal efficiencies of Cu, Pb and Cd, but low efficiencies for Fe, Ni and Cr. In acid treatment, mineral and organic acids have been commonly used to solubilize heavy metals at low pH. In spite of the good extraction achieved in the acid treatment method for most metals, Cu does not show a high solubilization. The high cost, operational difficulties and large consumption of chemical agents have made these chemical methods unattractive. (Xiang et al, 2000)

2.4 TYPE OF BIOMATERIAL

Because of high cost of conventional heavy metal removal treatment, bio-adsorption method has introduced with the great advantage which is cheap. This is because the material uses in this method are cheap and available in large quantities such as natural materials, agricultural waste and industrial by-product. At the same time, this method also helps industries reduce the cost of waste disposal.

2.5 TYPE OF SEAWEED

Seaweed is an abundant source of metal-sorbing biomass. Some seaweed has been identified for the ion exchange properties associated with their polysaccharide content. These properties are particularly pronounced in brown algae. Experiments by Volesky and Prasetyo (1994) used the brown marine algae, Ascophyllum nodosum, in sorption columns to remove Cd. The maximum adsorption capacity for the seaweed was shown to be approximately 67 mg Cd/g seaweed. In an experiment by Wilson and Edyvean (1994) the brown seaweeds, Fucus serratus and Laminaria digitata, outperformed other biological materials such as fungi, green seaweed and unicellular green alga for Cd and Hg removal. The green seaweed, Ulva lactuca, was just slightly less effective than the two brown seaweeds. (Bailey et. Al., 1999)

In terms of metal sorption capacity, brown seaweed is superior to other algal species such as red and green seaweeds. (Tsui et. al., 2006)

In general, brown seaweeds always performed well irrespective of metal ions employed. This is due to the presence of alginate, which is present in a gel form in their cell walls. On the other hand, green algae usually comprised of xylans and mannans; whereas red algae contains sulfate esters of xylans and galactans in their cell walls. (Senthilkumar et. al., 2005)

Seaweeds are found throughout the world's oceans and come in three basic colours that are brown (Phaeophyta), red (Rhodophyta), and green (Chlorophyta). Brown and red seaweeds are almost exclusively marine plants but the vast majority of green coloured seaweeds are freshwater and terrestrial. The brown colour of the Phaeophyta results from the dominance of the xanthophyll pigment fucoxanthin which masks the other pigments while the red colour of the Rhodophyta is due to the presence of the pigment phycoerythrin which reflects red light and absorbs blue light. The green colour of the Chlorophyta comes from chlorophyll a and b. Many of the studies to date on metal biosorption by seaweeds have largely been restricted to various species of brown seaweeds. (Hashim and Chu, 2003)

Seaweeds possess a high metal-binding capacity with the cell wall playing an important role in binding. This is due to the presence of various functional groups such as carboxyl, amino, sulphate and hydroxyl groups, which can act as binding sites for metals. The main mechanisms of binding include ionic interactions and complex formation between metal cations and ligands on the surface of the seaweeds (Murphy et. al, 2007)

Of the three basic seaweeds, brown seaweeds are extensively used for biosorption. Its polysaccharide content is believed to be responsible for its excellent metal binding capacity. Sargassum, Ascophyllum and Fucus are some of the important brown seaweeds; which are excellent in metal biosorption .On the other hand, green and red seaweeds have not been evaluated to any great extent. (Senthilkumar et. al., 2007)

Table 1
Biosorption of heavy metals by some reported seaweed species

Seaweed species	Metals	Reference
Pachymeniopsis sp. (red)	Cr(VI)	[2]
Sargassum hystrix (brown)	Pb	[3]
Sargassum natans (brown)		
Padina pavonia (brown)		
Ulva lactuca (green)		
Cladophora glomerata (green)		
Gracilaria corticata (red)		
Gracilaria canaliculata (red)		
Polysiphonia violacea (red)		
Sargassum baccularia (brown)	Cd, Cu	[4–6]
Sargassum sp. (brown)	Cd, Cu, Zn	[7]
Sargassum siliquosum (brown)	Cr(VI)	[8]
Laminaria japonica (brown)	Cd, Cu	[9]
Sargassum kjellmanianum (brown)		
Macrocystis pyrifera (brown)	Cd, Pb	[10,11]
Kjellmaniella crassifolia (brown)		
Undaria pinnatifida (brown)		
Eckonia maxima (brown)	Cd, Cu, Pb, Zn, Ni	[12,13]
Lessonia flavicans (brown)		
Durvillea potatorum (brown)		
Sargassum asperifolium (brown)	Cd, Cu, Ni,	[14]
Cystoseira trinode (brown)	Co(II), Cr(III)	
Turbinaria decurrens (brown)		
Laurencia obtusa (red)		
Ascophyllum nodosum (brown)	Cd, Cu, Ni	[15]
Lessonia flavicans (brown)		
Laminaria hyperborea (brown)		
Durvillea potatorum (brown)		
Sargassum vulgare (brown)	Cd, Cu	[16]
Sargassum fluitans (brown)		
Sargassum fillpendula (brown)		
Sargassum muticum (brown)		
Ascophyllum nodosum (brown)	Cd, Cu, Pb	[17–19]
Lessonia flavicans (brown)		
Lessonia nigresense (brown)		
Laminaria japonica (brown)		
Laminaria hyperbola (brown)		
Eckonia maxima (brown)		
Eckonia radiata (brown)		
Durvillaea potatorum (brown)		
Padina sp. (brown)		

Figure 2.1 : Species of seaweed used for biosorption of heavy metals

2.6 BIOSORPTION PROCESS

Microorganisms have the ability to accommodate a variety of pollutants, both organic and inorganic, it is important to appreciate from the outset that microorganisms cannot destroy metal. However, they can influence metals mobility in the environment by modifying their chemical and/or physical characteristic. (Eccles Harry, 1999)

Bio-adsorptive processes are essentially pseudo-ion-exchange processes in which the metal ion is exchanged for a counter ion attached to the biomass or resin. Bio-adsorption, in general, involves more than one functional group on the biomass, depending on the pH of the liquid and the chemical characteristics of the metal. (Eccles Harry, 1999)

2.7 HEAVY METAL REMOVAL

A research did on biosorption using biomass to cadmium mention on high metal binding capacities due to presence of polysaccharides, proteins or lipid on the cell wall surface containing functional groups such as amino, hydroxyl, carboxyl and sulphate in seaweed. Besides that, it also mentions that different types of biomass have been investigated for the biosorption characteristics of lead and cadmium ions from aqueous solution. (Ahmet Sari, 2007) There is same view of seaweed towards heavy metal in other researches in Raize et al, 2004, Kaewsarn and Yu, 2001, Holan and Volesky 1994, Holan et al, 1993, Chu and Hashim, 2004, Amini and Younesi 2009. (Sibel Yalcin, 2012)

On the other hand, Santos et al in 2014 mention lead is not an essential element for biological process, but it can be easily absorbed and accumulated in different parts of the organism. The same point of view agreed by another research that lead has no essential biological function and all lead compounds are potentially harmful or toxic. (Ronda et al, 2013)

2.8 CONCLUSION

As a conclusion, biomass has been proved that having the properties that can remove the heavy metals from the solution through the biosorption process. Different group of seaweed can removed different types of heavy metals. Some of the seaweed species can removed more than one type of heavy metals. Wastewater treatment can be done using seaweed that can be obtained easily.

CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

This chapter will discuss on the methodology of this research. The flow chart described the methodology for this research show in Figure 3.1. There are several parameters will be tested to reach the objectives of the research.

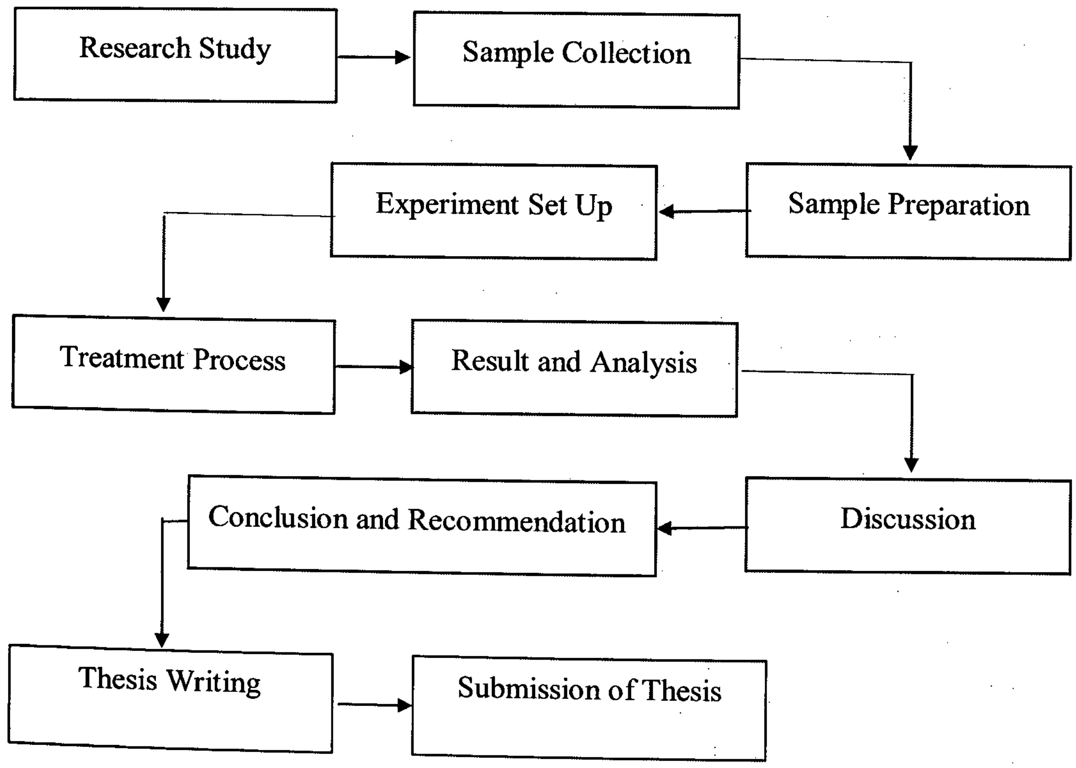

Figure 3.1: Methodology flow chart

that, the incubation bottle will be stored in the BOD incubator at the controlled temperature 20 °C. At the fifth day, the incubation bottle will be taken out to test for the dissolved oxygen. The BOD_5 was calculated using the equation (1).

$$BOD_5 = \frac{D_0 - D_5}{P} \quad (1)$$

where D_0 is the dissolved oxygen that contained in the mixture of dilution water and sample solution before stored in the BOD incubator (mg/L), D_5 is the dissolved oxygen that contained in the mixture of dilution water and sample solution after 5 days stored in the BOD incubator (mg/L) and P is the dilution factor.

BOD test had been done before and after the seaweed sample had put into to treat the heavy metals inside the synthetic wastewater sample as a comparison to the result. The BOD tested during the seaweed biosorption process with time controlled which are the 1st hour, 2nd hour, 4th hour, 8th hour, 24th hour and 30th hour. Each of the testing for different time controlled will have three duplicates to monitor the accuracy and precision of the data obtained.

3.4.2 Chemical Oxygen Demand (COD)

Chemical Oxygen Demand is a measure of the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals such as ammonia and nitrate. The equipment used to measure COD in wastewater sample is HACH DR/2500 Spectrophotometer with Method 8000.

The method used is open vial method. 2mL of each synthetic wastewater and deionized water added to the vial with 45 degree angled using Micro Pipette before inverted gently for several times to well mixed. The vials heated in the preheated COD Reactor for two hours at 150 °C. Inverted each vials again after two hours heated and placed at the rack to cool down to the room temperature. Colorimetric Determination Method 8000 will be tested on the sample of synthetic wastewater. The results will be recorded to further determination.