Drill Cuttings Treatment by Bioremediation

by

Siti Halizah Binti Abu Bakar

15578

Dissertation submitted in partial fulfilment of

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Universiti Teknologi PETRONAS

32610, Bandar Seri Iskandar

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

_____

(AP DR Suzana Binti Yusuf)

UNIVERSITI TEKNOLOGI PETRONAS

BANDAR SERI ISKANDAR, PERAK

September 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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SITI HALIZAH BINTI ABU BAKAR

ABSTRACT

This research study focuses on the removal treatment of oil residue on the drill cuttings before disposal. For this project, the method that we are interested is bioremediation process and it occurs when we mix together the sand and drilling cuts with the surfactant solutions (GraphSolve12 or GraphBioSolve). GraphSolve12 and GraphBioSolve solutions will be provided by Platinum Sdn. Bhd. as this is a joint venture project between Platinum Sdn. Bhd. and Universiti Teknologi PETRONAS. The surfactant solutions are the new solution synthesize by Platinum and the author will study the potential of GraphSolve12 and GraphBioSolve to remove oil from the drilling mud. The Total Petroleum Hydrocarbon (TPH) of the final drilling mud are compared while maintaining other parameters such as sand weight, drill cuttings weight and total amount of water and surfactant mixture. All 4 test has constant amount of water and surfactant mixture which is at 3,000 mL but different dosing percentage based on the surfactant amount such as 1ml, 10ml and 20ml for GraphSolve12 and 10mL GraphBioSolve. The Gas Chromatography-Mass Spectrometry (GC-MS) analysis show that for GraphSolve12, the best dosing is at 20% of surfactant where the result of TPH percentage shows preeminent decreasing curve of TPH percentage in the sand samples over time. It also means that the process of bioremediation is better during the 80% dosing of water for GraphSolve12. However, when we compare GraphSolve12 and GraphBioSOlve, GC-MS analysis proved that the GraphBioSolve is a better option for the bioremediation process rather than the other option because the TPH percentage achieved is lower. The TPH percentage for GraphBioSolve is 30.11% while GraphSolve12 shows 31.48% of TPH at week 10.

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I also would like express my deepest thank to Mr Taufiq from Platinum Sdn. Bhd. who had help in supplying the materials for my final year project. During that period, he had been very helpful in working together and helping me to understand the research topic. I hereby would like to give my many thanks to him for all the contributions and time spend on me.

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ABBREVIATION AND NOMENCLATURE

EPA	Environmental Protection Agency
GC-MS	Gas Chromatography – Mass Spectrometry
MSDS	Material Safety Data Sheets
OBM	Oil based mud
PPM	Part per Million
PTFE	Polytetrafluoroethylene
RPM	Rotation per minute
SEM	Scanning electron microscope
SEM-EDS	Scanning Electron Microscopy with X-ray microanalysis
TPH	Total petroleum hydrocarbon
UCM	Unresolved complex mixture
UTP	Universiti Teknologi PETRONAS
WBC	Water based cuttings
wt%	weight percentage

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Drill cuttings are created when a well was drilled through rock to reach an oil or gas reservoir and they can vary in size and characteristics. It happens depending on the types of drill that is used to bust the seabed during the exploration and extraction. Usually drilling mud (sand and water) will be pumped down the well to bring back the drill cuttings to the surface to keep it clean and helps to lubricate the drill bit for the oil extraction and maintain the well pressure. The disposal of the mixture (drill cuttings and drilling mud) must be properly executed to protect the aquatic habitat and reduce additional perils during pipeline maintenance. Drill cuttings can either be disposed into the sea or be taken back offshore for land disposal. However, both acts will only be allowed under the country legislation of the rig's location.

One of the most efficient drilling muds or also known as drilling fluids is oil based mud (OBM). The sticky OBM will coat the cuttings and make it hard to disperse. Even most of the OBM is removed during the process through the rig, some oil residue is still accessible on the cuttings. Upon accumulations, it will cluster below the installations and can permit lots of disturbances in future.

1.2 Problem Statement

The oil and gas exploration and exploitation have become one of the main causers for the pollution in Malaysia. Even though the legislation does exist for petroleum exploration which comprise of exploration, development, production, transportation, treatment and storage, on each year, the level of pollutions keeps increasing. Currently Malaysia has six refining facilities and an average of 150 ships/day comprising of 90 cargo ships, 40 tankers and other vessels go through the Straits of Malacca (YEONG, 1990). This busy petroleum operation to meet the demands has exposed the coastal and marine habitat to contamination.

The bigger the number of oil and gas exploration, the greater the number of the drilling cuts that are available to be disposed into the sea. Over a lifetime, an oil rig can produce beyond 90,000 metric tons of drilling fluid and metal cuttings. Imagine this huge amount of waste just been thrown away into the sea and endanger our life. A recent article by Markets and Markets.com report stated that "*Recently, high growth has been noticed in drilling waste management due to increasing environmental concerns and regulatory norms imposed by the government. Major services include solids control, containment & handling, and treatment & disposal activities for safe discharge of drilling waste generated*". It shows us that in near future, by throwing drilling waste without processing it can cause you serious issues regarding environmental law obligation. Figure 1.1 shows that the drilling waste management market had increased over the years from 2012 to 2014 and the expected demand on 2019 that the world might need.

Figure 1.1 Drilling Waste Management Market Size by Region from 2012 – 2014 and the market demand on 2019

(Source: Markets and Markets.com, 2015)

As for today, water based cuttings (WBC) are directly discharged into seabed because the materials are environmentally inert and the long term effect are considered to be significant. But for OBM, the hydrocarbon disposal into the sea is a dangerous threat to the aquatic animals and human food resources. Each disposal is estimated to hold around 25,000 pounds of toxic metals and potent carcinogens such as lead, chromium, mercury, toluene, benzene, and xylene into the sea.

Due to this matters, most of the drilling cuts are being taken back to shore for land disposal. Nevertheless, this drilling cuts still contain heavy metal, hydrocarbon and other chemicals. That is why we cannot just simply throw the drilling cuts. There is numerous preferred methodology for the drilling cuts disposal alternatives. There is reduction method, recycle method and the most promising method is the waste treatment method through bioremediation before the drill cuts is being dispose.

In this project, the drilling cuts will undergo bioremediation treatment and the final product will be tested for the Total Hydrocarbon Petroleum (TPH) values before disposal. This is a crucial methodology to ensure that the final product is legally disposed.

1.3 Objectives and Scope of Study

The main objectives of this project are:

i. Test the performance of the GraphSolve12 and GraphBioSolve towards the bioremediation process.

ii. Test the performance of the GraphSolve12 and GraphBioSolve towards the bioremediation process at different dosing.

iii. Observe the difference of surface structure of sand before and after the bioremediation process.

This project will focus on the final TPH value of the drilling mud and the studied relationship between parameters. In order to achieve that, this project will focus on the outcome such as:

i. The relation between oil contents and usage of the GraphSolve12.
ii. The relation between oil contents and usage of the GraphBioSolve.
iii. The relation between oil contents and time for bioremediation.
iv. The relation between oil contents and fresh water quantity.

CHAPTER 2

LITERATURE REVIEW

According to Environmental Protection Agency (EPA), bioremediation is a treatment that uses naturally occurring organisms to break down hazardous substances into non-toxic substances. The treatment of the Alaskan shoreline of Prince Williams Sound after the oil spill of Exxon Valdez in 1989 is one common example in which bioremediation methods got public attention (Boopathy, 2000). Bioremediation technologies can be classified as *in situ* and *ex situ*. For *in situ*, it involves treating the contaminated material at the site, while *ex situ* involves the removal of the contaminated material to be treated elsewhere.

(Boopathy, 2000) said that bioremediation has numerous applications, including clean-up of groundwater, soils, lagoons, sludge and process waste streams. It has been used on a very largescale application, for instance the shoreline clean-up efforts in Prince William Sound, Alaska, after the Exxon Oil spill. However, this method does have the advantages and disadvantage depending on the microbe selection and environmental factors. The microbe is a single cell organism that are known as the oldest form of life on earth which are fungi or bacteria. The advantages and disadvantage of bioremediation are:

Advantages:

- Can be done on site
- Less expensive than other treatment methods
- Eliminates waste permanently

Disadvantages:

- Has limitation because some chemicals are not amenable to biodegradation such as heavy metals, radionuclides and some chlorinated compound
- Sometimes, microbial metabolism of the contaminants may produce toxic metabolites.

Although bioremediation field trials were often carried out, there is insufficient information on the indigenous microbial communities that catalyse oil degradation under in situ conditions (Joel E. Kostka, 2011; Jorge Alonso-Gutierrez, 2009). The scientific factors that are affecting bioremediation are the energy sources, bioavailability, bioactivity and biochemistry. These factors have long been recognized as the parameters that influence the rate of bioremediation. Sometimes the parameter is comparably unimportant while others are crucial for a specific reaction. It shows us that certain sites may be favourably for *in situ* or *ex situ* approach.

(Atlas, 1995) has studied regarding the bioremediation to remove petroleum pollutants by seeding. He had used fertilizer in both laboratory demonstration and field demonstration and he believed that by adding a large biomass of hydrocarbon degraders, the rates of hydrocarbon biodegradation can be increased if the added cultures are able to survive and express their hydrocarbon-degradation activities in the environments to which they are added. His study has received a favourable result when both polynuclear aromatic and aliphatic hydrocarbons were biodegraded more rapidly in the fertilized than in the control shoreline sediments (Figure2.1). It is an

important finding since there was concern that biodegradation might remove only some of the components of the spilled oil.

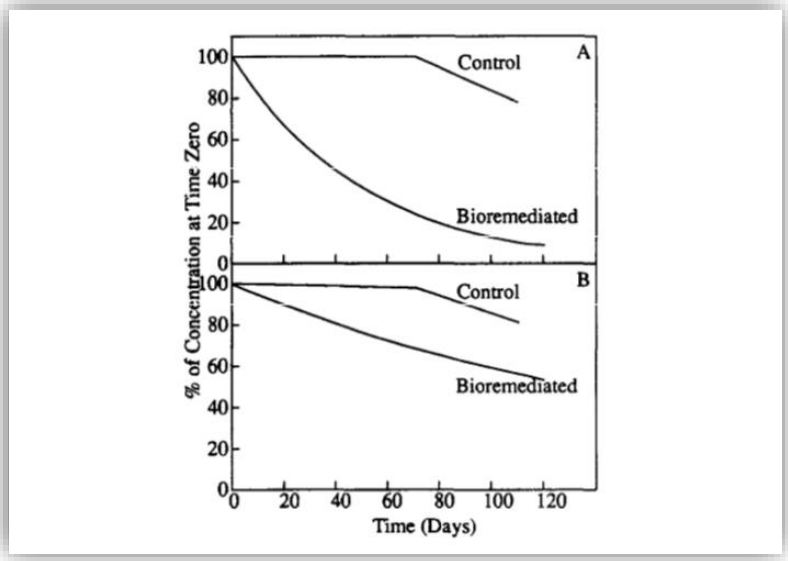


Figure 2.1 The changes in total resolvable hydrocarbon (A) and polynuclear aromatic hydrocarbon (B) concentration through the bioremediation period.

More recently (Chaillan, Chaîneau, Point, Saliot, & Oudot, 2006) research study has taken oily drill cuttings and a soil contaminated with weathered crude oils and they are evaluated by enhanced biodegradation treatment under tropical conditions in industrial scaled experiments. After 12 months of bioremediation process, the removal of hydrocarbons reached by biodegradation an extent of 60%. They also find that the residual hydrocarbons in the field treated materials were 15% - 20% further degraded when metabolic by-products resulting from biodegradation were diluted or removed under the laboratory conditions.

The result shows that the linear alkanes were not completely removed but the saturated hydrocarbons including linear, branched and cycloalkanes were degraded up to 80% (Figure 2.2). The aromatic fractions were less degraded, 38 wt% in WS and 22 wt% in WM. The aromatic unresolved complex mixture (UCM) was less assimilated than the resolved peaks confirming its resistance to microbial degradation (Chaillan et al., 2006). However, all biodegradable compounds were not

removed after 12 months as indicated by the persistence of some n-alkanes, pristane and phytane, drill fluid UCM, and bicyclic aromatics.

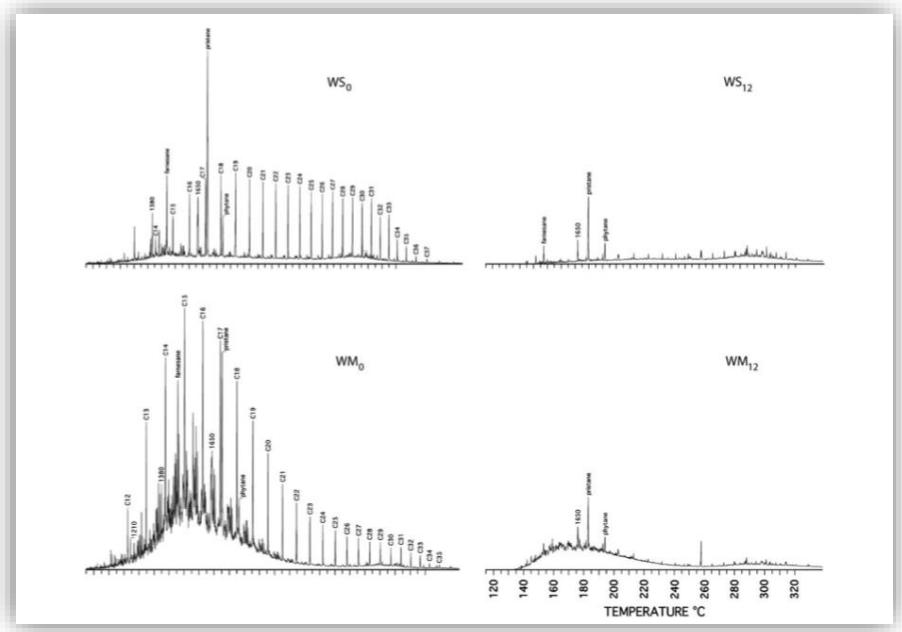


Figure 2.2 TPH chromatogram of the residual oil before treatment (WS_0, WM_0) and after 12 months of bioremediation (WS_{12}, WM_{12}).

For this project, the author will use *ex situ* bioremediation method as it will be done in a laboratory scale. The surfactants that will be used are GraphSolve12 and GraphBioSolve for their drilling cuts treatment. The procedures will be defined more clearly on the methodology section. The TPH percentage of the contaminated soil will be tested before and after the bioremediation treatment and samples will be taken for every two consecutive weeks and tested by using GC-MS analysis.

At the same time, the author is interested to study on the surface structure of sand used for bioremediation process. These objective can be done by using scanning electron microscope (SEM) that is used particularly for observing a fine structure of a specimen surface at high magnification. Based on (Corporation, 2009), the features of SEM are that it is applicable for all solid surfaces and can be observed in a range from low to high magnifications. SEM can allow the user to have greater focal depth than an optical microscope, allowing us to acquire a

stereoscopic image and a combination with an x-ray analyser during sample testing permits compositional analysis of a microscopic area.

The principle of how SEM works is by irradiating the sample with an electron beam in a vacuum, secondary electrons, backscattered electrons, characteristics x-rays and other signals. The illustrated signals on how SEM function are given in Appendix A. In order to form an image, SEM mainly utilizes the secondary electron or backscattered electron signal. Secondary electron is produced near the sample surface, and the secondary electron image is obtained when the electrons of the fine topographical structure of sample are detected. For the backscattered electrons, it is reflected upon striking with the atom composing the sample and the electrons is dependent on the composition of atomic number, crystal orientation and others in the sample.

Before the sample is ready to be tested, it should undergo metal coating procedure. The purpose of the coating is to make the sample surface become conductive so that any charge up can be prevented. Other than that, the coating can help to increase the production rate of secondary electrons hence increasing the image formation. This metal coating will also help to prevent any damage to the sample. Generally, SEM will use gold or gold-palladium as the metal for coating by using general magnetron sputtering device. The best metal for coating is gold as it can enhance the particle to be observed at a magnification of x50, 000, x60, 000 or even higher.

CHAPTER 3

METHODOLOGY/PROJECT WORK

3.1 Project Flow Chart

Below is the project flow chart for this project that is recommended in order to achieve the objective.

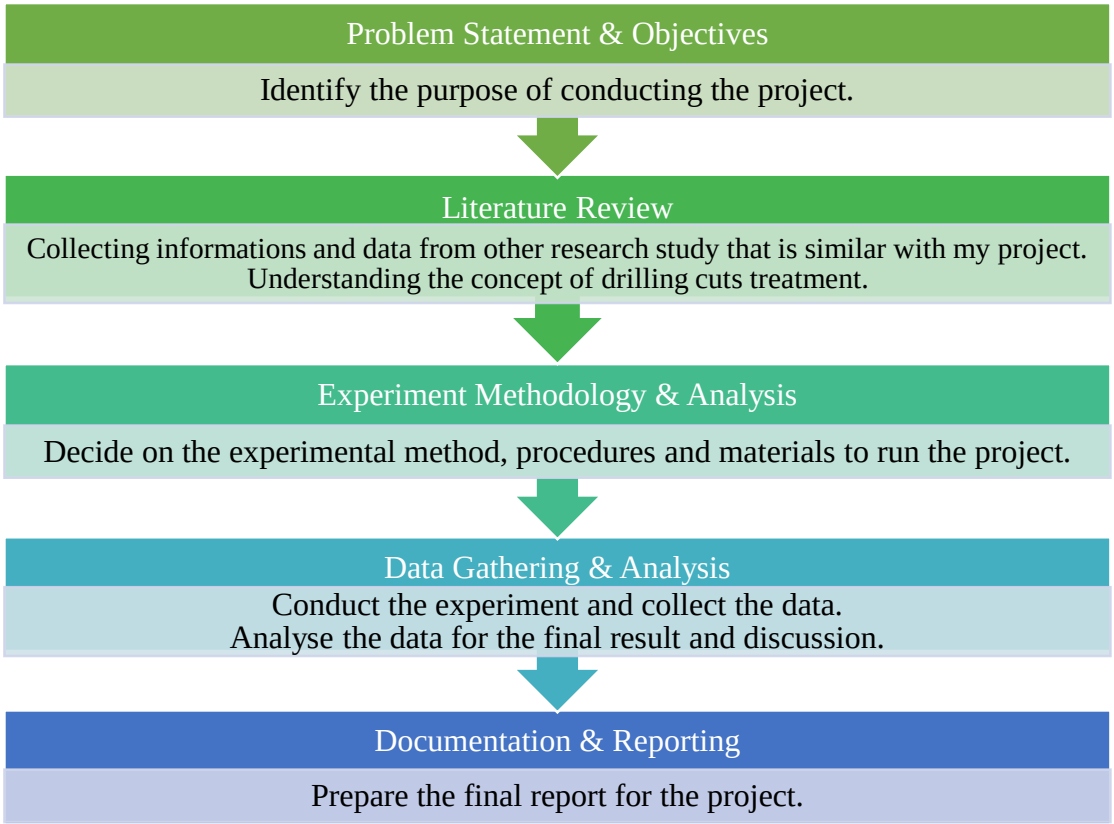


Figure 3.1 Project Flow Chart of Research Activities

3.2 Gantt Chart and Key Milestones

Table 3.1 Final Year Project I Gantt chart and Key Milestone

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of Project Topic														
2	Preliminary Research Work														
3	Submission of Extended Proposal														
4	Proposal Defence														
5	Project Work Continues														
6	Submission of Interim Draft Report														
7	Submission of Interim Report														

Process | Key Milestone

Table 3.2 Final Year Project II Gantt chart and Key Milestones

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Project Work Continues															
2	Submission of Progress Report															
3	Project Work Continues															
4	Pre-SEDEX															
5	Submission of Draft Final Report															
6	Submission of Dissertation (soft bound)															
7	Submission of Technical Paper															
8	Viva															
9	Submission of Project Dissertation (hard bound)															

Process | Key Milestone

3.3 Preparation of Sample

For this experiment, the author need to use the contaminated drilling cuts that come from an oil rig. With the help from Platinum, the drilling cuts is obtained from one of Thailand oil rig that has been posted to the Senawang, Platinum plant. In order to study the disposal effect of the drill mud to the land, some amount of sand is being mixed with the drilling cuts to act as a contaminated sand for the bioremediation process. When the contaminated sand is ready, then the surfactant is mixed together and the sample is observed. The illustration of this method is given as in Appendix B.

Procedure:

1) 1kg of cutting and 4kg of soil is blended with water.
2) 3 litre of surfactant solution is mixed together with the sample.
3) The soil is submerged by approximately 1 inch under the water.
4) The mixture is stirred for 24 hours at 200RPM.
5) Pour in the flat basin and leave it for some time. The soil sample is taken periodically every 2 weeks.

For this project, GraphSolve12 will have three difference concentrations and GraphBioSolve will have only one concentration to be tested. For every test, a different ratio of water with solvent are used as stated in Table 3.3 and Table 3.4. The author has the chance to work on the sample preparation for the first sample Test 1 preparation by using 1% of GraphSolve12 as the surfactant. All the samples preparation is done by the help from Platinum Senawang plant.

Table 3.3 GraphSolve12 Sample Preparation Data

Test	Cutting Cuts (kg)	Sand (kg)	Water (ml)	GraphSolve12 (ml)	GraphSolve12 Amount (%)
1	1	4	2970	30	1
2	1	4	2700	300	10
3	1	4	2400	600	20

Table 3.4 GraphBioSolve Sample Preparation Data

Test	Cutting Cuts (kg)	Sand (kg)	Water (ml)	GraphBioSolve (ml)	GraphBioSolve Amount (%)
4	1	4	2970	30	10

The sample taken is transferred into a 4-ounce jar (with a Teflon^{TM}-lined lid) and it is sent to UTP by using a standard courier services. According to (Saitas, 2001), upon received in laboratory, samples can be held at 4°C or lower if the laboratory can analyse the samples within 2 days or the samples should be placed in a maintain freezer until extracted and analysed. Because of the time constraint and the unavailability of chemicals for sample preparation for the gas chromatograph test, the samples are properly placed in the freezer once the author receive the samples. This method is based on the Total Petroleum Hydrocarbons (TNRCC) Method 1005, Revision 03, 2001 (Saitas, 2001).

3.4 Scanning Electron Microscope (SEM) Analysis

During this project, the author is interested to study on the difference of the sand surface structure before and after the bioremediation treatment. The experiment is conducted under the guidance of Miss Revie, student of Dr Yoshimitsu Uemura. The experiment is done by using scanning electron microscope (SEM) model TM3030-Tabletop Microscope, HITACHI. For this test, the author has chosen uncontaminated sand and 3 samples from the bioremediation process to be tested. The metal coating process is done by using a magnetron sputtering device.

Procedure (Sample Preparation):

1) The conductive both-side tape is applied on top of a specimen stub.
2) A small amount of powder is spread thinly on top of the conductive both-side tape.
3) Any excess powder is blow off by using a blower.
4) After all 4 samples are prepared, the specimen stub is place in a magnetron sputtering device for a metal coating process.
5) The sample is ready for SEM analysis.

Procedure (SEM Analysis):

1) The instrument power is turn ON.
2) The PC is log in and start up the SEM software.
3) The specimen stub is set on exclusive holder and the height is adjusted with "height gauge".
4) The AIR button on front panel of column is pressed ON to introduce air into the specimen chamber.
5) Gently pull out the specimen stage and set the specimen stage on the centre.
6) The EVAC button on the front panel of column is pressed to evacuate the specimen chamber.
7) The sample is ready to be observe when the evacuation of the specimen chamber is finished.
8) The accelerating voltage "ON" icon is clicked.
9) The brightness and focus is automatically being set at low magnification.
10) A field of interest is search and the magnification is set.
11) A capture box image is selected and the image is captured.
12) Input a file name and save the image captured.

This method is based on the Hi-Tech Instrument booklet about SEM (Corporation, 2009).

3.5 Gas Chromatograph–Mass Spectrometry (GC-MS) Analysis

Before we do the extraction, the sample are being dried by using a Vacuum Dryer to make sure that zero water content are available in the sample. This is because the GC-MS analysis will not give the accurate result if water still exists in the sample. For this experimental analysis, the materials and tools needed are gasoline, diesel 2-D, 99% n-pentane, 99% methanol, trifluoromethyl benzene, 1-chlorooctane, weight balance, glass jar (40mL), 10mL – 50mL volumetric flask, VOA vials with PTFE-caps, syringes, vortex shaker (optional) and Pasteur pipet.

3.5.1 Extraction of Sample for Gas-Chromatography Mass-Spectrometry (GC-MS) Analysis (Based On TPH, TNRCC Method 1005, Revision 03)

Procedure:

1) The sample vial is removed from refrigeration.
2) Allow it to reach room temperature.
3) The outside of the vial is wiped with tissue.
4) Each vial and its contents is weighted on a loading balance and the weight is recorded to the nearest 0.01g.
5) The tare weight of the VOA vial is subtracted.
6) The resulting sample weight is recorded.
7) 250 ml of the Petroleum Calibration Standard is transferred into the sample using a gas-tight glass syringe. Vortex or hand shaking the sample to mix the solution for about 1 minute.
8) 250 ml of the Surrogate Stock Solution is transferred into the sample using a gas-tight glass syringe. Vortex or hand shaking the sample to mix the solution for about 1 minute.
9) 10 ml of n-pentane is added to all samples through the septa of the vials using a 10 ml gas-tight glass syringe and vortex or hand shaking the mixture for about 1 minute. The particulate materials is let to settle within a minimum of 1 hour but can take as long as overnight.

10) 1-2 mL of extract sample is transferred into an auto-sampler vial using a Pasteur pipet. The auto-sampler vial is cap with a PTFE-lined cap.
11) Samples are ready for the GC-MS analysis by using Method 8270D.

All of the experimental work is done with the proper PPE and the MS-DS of the chemicals used are attached as the appendices.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 TPH Percentage (GC-MS Analysis).

The chemical compound of sample product was analysed by using Gas Chromatography – Mass Spectroscopy (GC-MS). The TPH percentage produced at different time and dosing of surfactant is analysed for its chemical composition. Total petroleum hydrocarbon (TPH) is the measurable amount of petroleum-based hydrocarbons in an environmental matrix (Sadler R., Connell, D. 2002). Based on this study, a range of hydrocarbon from C6 – C36 are expected to be detected. According to (Sadler, R. and Connell, D. 2003) this huge range of hydrocarbon can be classified into paraffin alkenes, aliphatic and aromatics.

The lists of properties of a range of simple paraffin alkanes, which could be found in the samples are listed in Table 4.1. Then, Table 4.2 shows some corresponding physical properties for aromatic molecules that has the potency to occur in the samples. Table 4.3 and 4.4 provide some representative of physical parameters for the TPH analytical fractions based on correlations with the boiling point indices for aliphatic and aromatics.

Table 4.1 Simple Paraffin Alkanes

Molecular Formula	Name	Boiling Point (°C)	Melting Point (°C)	Density at 20°C
C_6H_{14}	n-Hexane	69	-94	0.658
C_8H_{18}	n-Octane	126	-98	0.702
$C_{10}H_{22}$	n-Decane	174	-32	0.747
$C_{12}H_{26}$	n-Dodecane	215	-12	0.768
$C_{16}H_{34}$	n-Hexadecane	287.5	18	0.775 (at mp)
$C_{20}H_{42}$	n-Eicosane	205	36.7	0.778 (at mp)
$C_{30}H_{62}$	n-Triacontane	449.7	66	0.775
$C_{35}H_{72}$	n-Pentatriacotane	490	74.6	0.781

Table 4.2 Aromatic Compounds

Molecular Formula	Name	Boiling Point (°C)	Melting Point (°C)
C_6H_6	Benzene	80	5.5
$C_{10}H_8$	Naphthalene	218	80.3
$C_{14}H_{12}$	Phenanthrene	338	100.5
$C_{18}H_{12}$	Chrysene	448	253
$C_{20}H_{12}$	Benzo(a)pyrene	310-312	179
$C_{22}H_{12}$	Benzo(g,h,l)perylene	542	278

Table 4.3 Physical Parameters for TPH Aliphatic Fractions

Carbon Equivalent Fraction	Log S_w (mg L^{-1})	Vapor Pressure (atm)	Henry's Law Constant (cm^3 cm^{-3})	Log K_{oc}
C_5 - C_6	1.56	3.5×10^{-1}	47	2.9
$C_{>6}$ - C_8	0.73	6.3×10^{-2}	50	3.6
$C_{>8}$ - C_{10}	-0.36	6.3×10^{-3}	55	4.5
$C_{>10}$ - C_{12}	-1.46	6.3×10^{-4}	60	5.4
$C_{>12}$ - C_{16}	-3.12	7.6×10^{-5}	69	6.7
$C_{>16}$ - C_{35}	-5.6	1.1×10^{-6}	85	8.8

Table 4.4 Physical Parameters for TPH Aromatic Fractions

Carbon Equivalent Fraction	Log S_w (mg L^{-1})	Vapor Pressure (atm)	Henry's Law Constant (cm^3 cm^{-3})	Log K_{oc}
C_5 - C_7	2.34	1.1×10^{-1}	1.5	3.0
$C_{>7}$ - C_8	2.11	3.5×10^{-2}	8.6×10^{-1}	3.1
$C_{>8}$ - C_{10}	1.81	6.3×10^{-3}	3.9×10^{-1}	3.2
$C_{>10}$ - C_{12}	1.4	6.3×10^{-4}	1.3×10^{-1}	3.4
$C_{>12}$ - C_{16}	0.76	4.8×10^{-5}	2.8×10^{-2}	3.7
$C_{>16}$ - C_{21}	-0.19	1.1×10^{-6}	2.5×10^{-3}	4.2
$C_{>21}$ - C_{35}	-2.18	4.4×10^{-10}	1.7×10^{-5}	5.1

The hydrocarbons will be connected with sorbed organic matter in the soil and later the rate of the hydrocarbon sorption will differ based on the nature of the hydrocarbon (as indexed by the Koc values) and the organic matter content of the soil. Based on Table 4.3 and 4.4, the Organic Carbon-Normalized Partition Coefficient (log K_{oc}) is depended on the water solubility [log S_w (mg L^{-1})].

(Sadler, R. and Connell, D., 2003) stated that the typical results that can be obtained from sand is a mixture of various hydrocarbons. Figure 4.1 below shown the GC-MS analysis range of type of hydrocarbon that is in the soil.

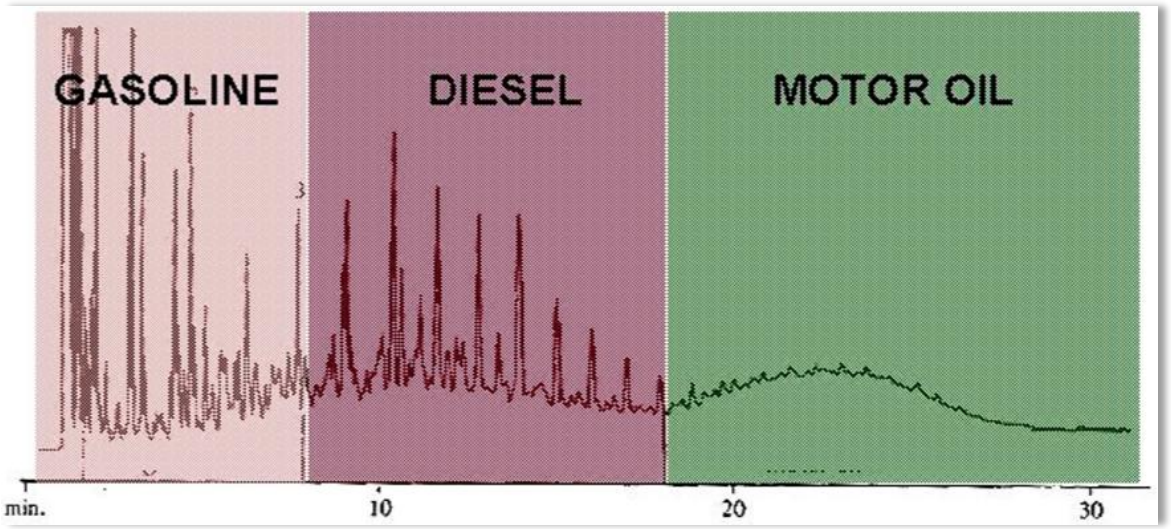


Figure 4.1 Hydrocarbon ranges as determined by Gas Chromatography

By referring to Figure 4.1, the GC-MS analysis reading can also provide the range hydrocarbon that the sample has. Figure 4.2 shows one of the sample GC-MS analysis result from this study and from the graph, we know that the sample contain gasoline, diesel and about 5% motor oil types of hydrocarbon ranges. From the analysis, most of the graph start after 4 minutes and end around 20 minutes later. The author can conclude that the hydrocarbon that still in the sand are mostly come from the gasoline and diesel range of hydrocarbons.

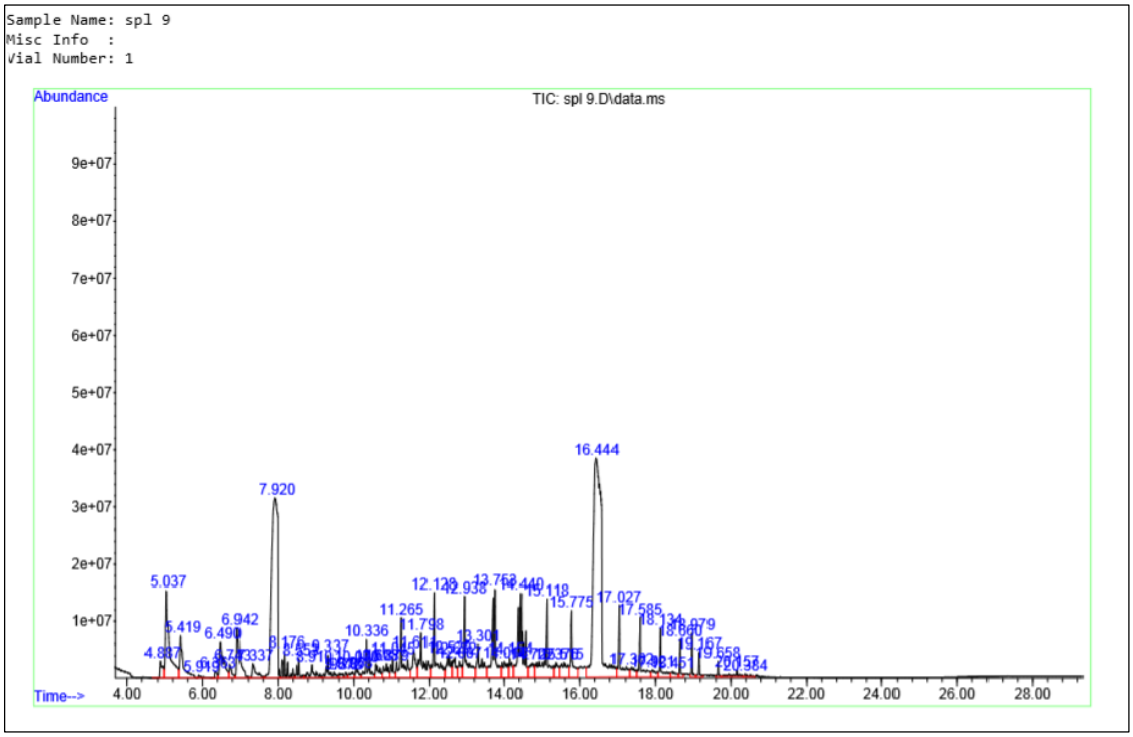


Figure 4.2 The GC-MS analysis result from Sample week10 of Test 4

4.1.1 Test 1 (GraphSolve12 at 1% dosing)

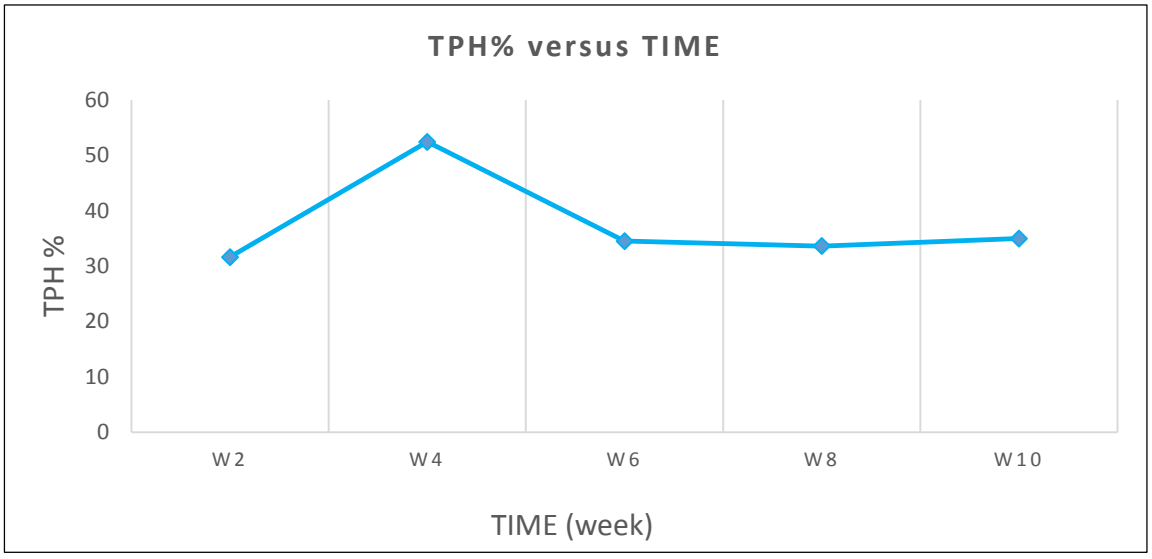


Figure 4.3 TPH% of GraphSolve12 at 1% dosing versus Time

From the result for Test 1 samples, the TPH line over time is irregular as it shows that the hydrocarbon is increasing and decreasing over the weeks. The TPH percentage shows good result from week 4 to week 10 as the TPH percentage decreases from 53% to 35% respectively. However, the TPH value for week 2 was so diverge and low compared to the other samples where it contains only 32% TPH value. Hence, the author can conclude that the sample at week 2 might have been continuing the bioremediation process even though the samples are properly kept inside the fridge as stated in the literature review section.

4.1.2 Test 2 (GraphSolve12 at 10% dosing)

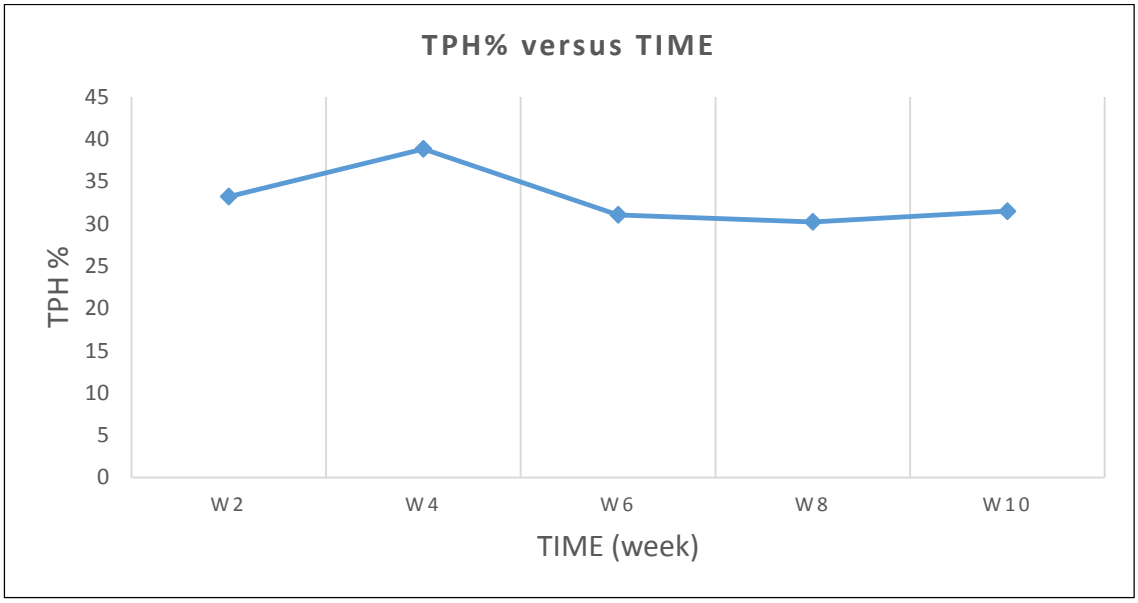


Figure 4.4 TPH% of GraphSolve12 at 10% dosing versus Time

Figure 4.4 shows the result for Test 2 samples, the TPH line over time is irregular as does not give a linear decreasing line. The values are almost similar to Test 1 result where the TPH values are increasing and decreasing over the weeks. The TPH percentage shows more decent result from week 4 to week 10 as the TPH percentage decreases from 38% to 31% respectively. However, the TPH value (33%) for week 2 differ from the expectation where the TPH percentage is supposed

to be higher than week 4. However, the value are still higher than the TPH percentage at week 10. This shows that the error might happen during week 2 or week 4. The author can conclude that the sample at week 2 might have continued the bioremediation process even though the samples are properly kept inside the fridge or the sample at week 4 is the error. It can happen as the author is using GC-MS for this study and as we know, GC-MS is very sensitive and it has the capability to detect the hydrocarbon within the standard solution given and also other hydrocarbon outside from the standard range.

4.1.3 Test 3 (GraphSolve12 at 20% dosing)

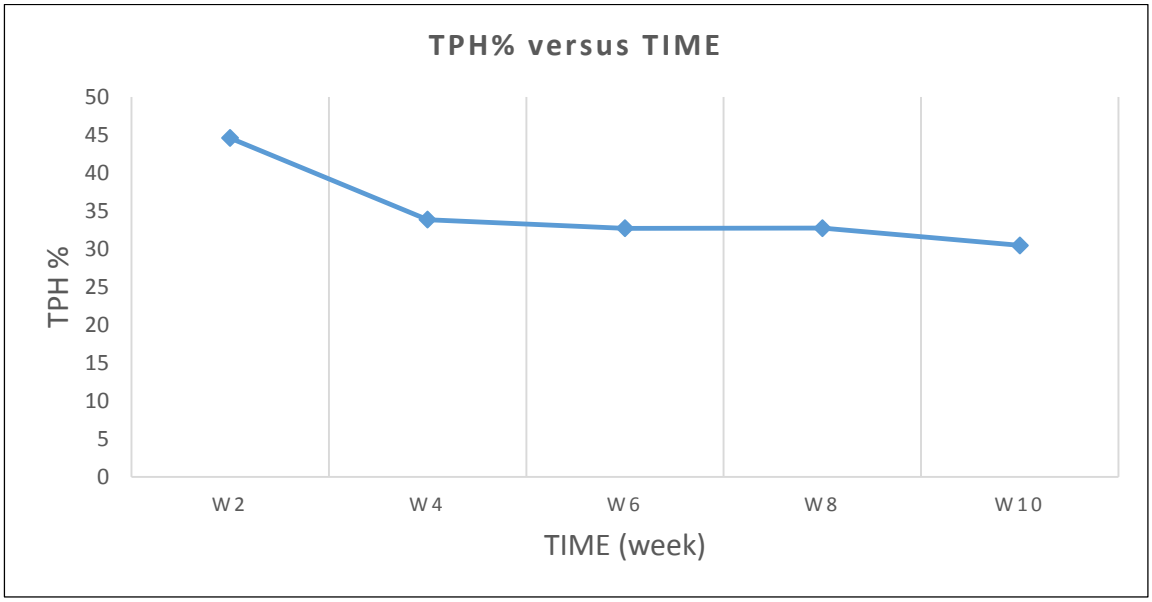
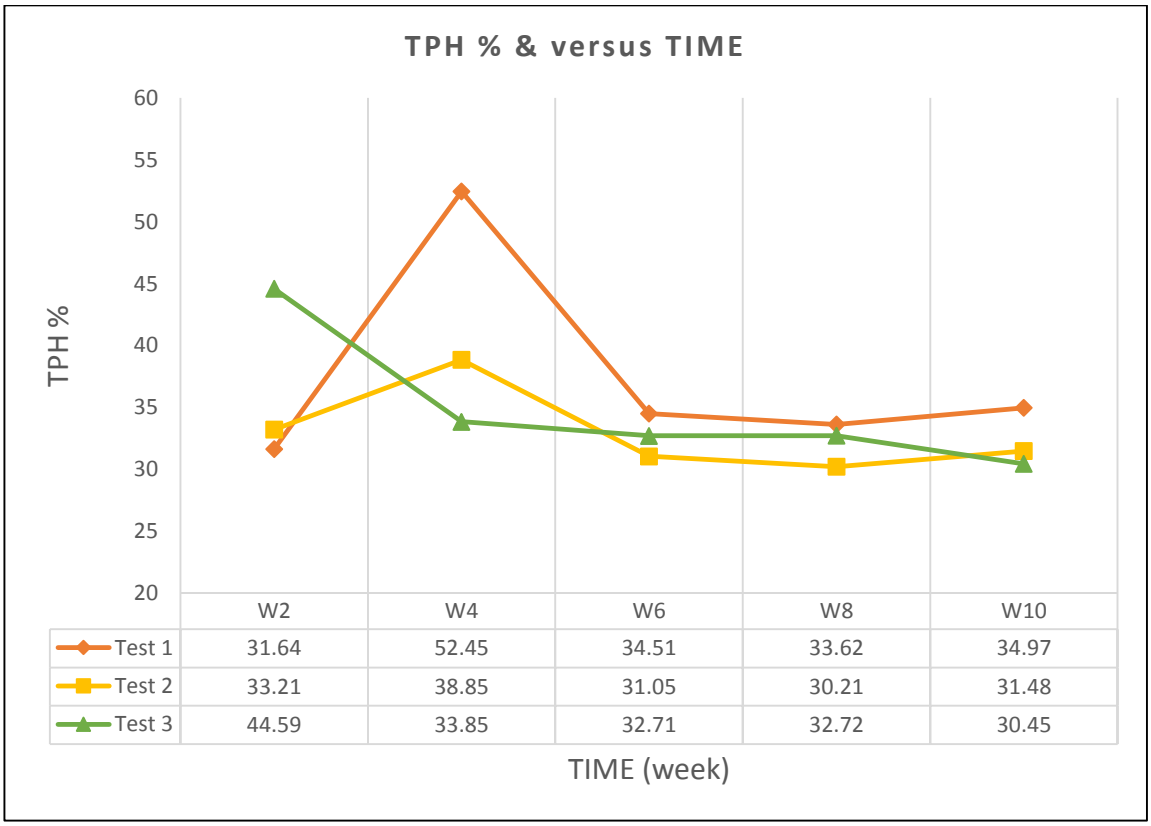


Figure 4.5 TPH% of GraphSolve12 at 20% dosing versus Time

For Test 3 samples, the TPH value is as shown in Figure 4.5 where the line is decreasing from week 2 to week 10 which is from 45% to 30% of TPH. The decreasing line match with the author knowledge at first where the bioremediation process should be decreasing over the time. The graph shows a more stable TPH values of samples over the time and hence the author can conclude that the surfactant (GraphSolve12) give more reliable and stable results. From all the three

tests for GraphSolve12, the 20% dosing of surfactants is more reliable and effective towards the bioremediation process. The experiment should be continued so that the study can expand the scope larger to find the best surfactant amount to enhance the bioremediation process. Other than that that, the result of TPH percentage also prove to be the lowest at week 10 for Test 3.



	W2	W4	W6	W8	W10
Test 1	31.64	52.45	34.51	33.62	34.97
Test 2	33.21	38.85	31.05	30.21	31.48
Test 3	44.59	33.85	32.71	32.72	30.45

Figure 4.6 Comparison of GraphSolve12 at different dosing versus Time

Figure 4.6 shows TPH percentage of Test 1, Test 2 and Test 3 which use GraphSolve12 as their surfactant for the bioremediation process. From the graph, the author can conclude that the best dosing of surfactant so far is during Test 3 which is 20% dosing of surfactant. The result gives the lowest TPH percentage at week 10 which is 31% and not only that, the graph shows a smooth decreasing order of the TPH percentage with respect to time. The author believes that, the amount of the surfactant also does effect the bioremediation process that happen on the microbe level.

4.1.4 Test 4 (GraphBioSolve at 10% dosing)

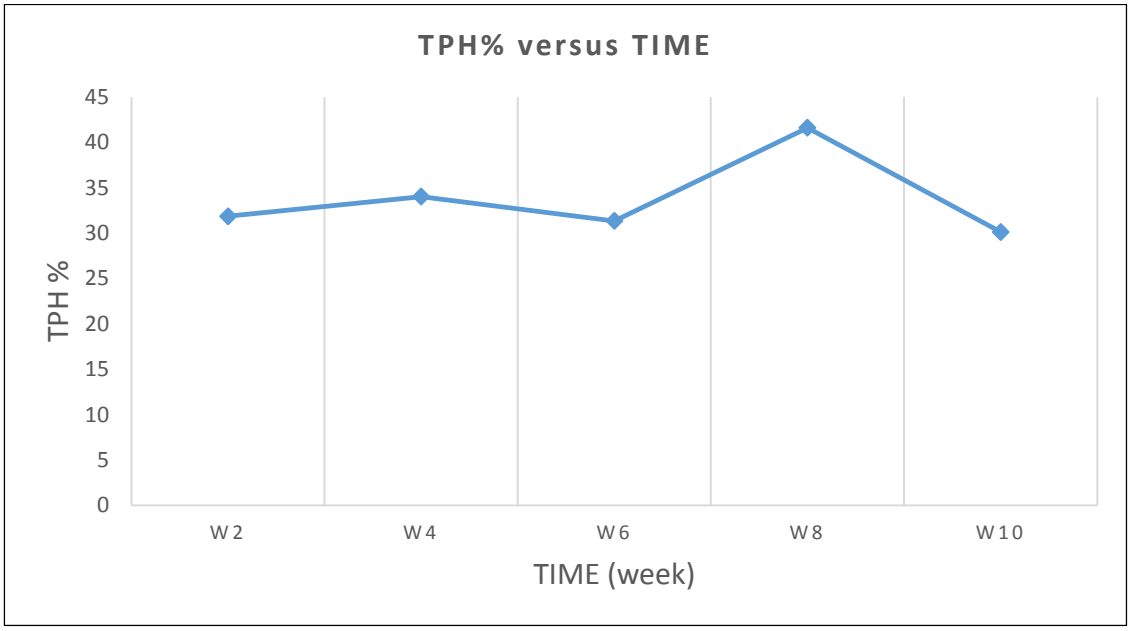


Figure 4.7 TPH% of GraphBioSolve at 10% dosing versus Time

As shown in Figure 4.7, the TPH % of Test 4 are decreasing from 31.85% at week 2 to 30.11% at week 10. However, the sample at week 8 suddenly increases and this can happen due to the condition the sample is being kept. As stated in (Method 8270D and Saitas. 2001), the sand sample taken periodically should be kept in a lined lid Teflon jar and the head gap between sample and lid should be minimize as much as possible to reduce the air gap that can affect the sand. Other

than that, the sample was not being kept immediately into the freezer after the sample was taken due to the project limitation. As the samples are being transferred from Platinum, Senawang to UTP, the journey has taken at least two days before the author received the samples and kept them into the freezer. Due to this condition, the TPH% of the samples are affected and it happen to all the samples, not particularly for test 4 samples only.

At the final week which is week 12, the TPH% show that around 30% of hydrocarbon still exist inside the sand. In order to achieve a lower TPH%, these experiment should be continued in order to obtain the time that is required to obtain low TPH% that is around 10%.

All the samples from Test 1 until Test 4 shows that the TPH value at week 10 is around 30%. According to (Chaillan, Chaîneau et al. 2006), the 12 months bioremediation process from their study ahs able to remove hydrocarbon to the extend of 60% which means that the TPH percentage is around 40% remain. Compared to this research study, we are able to achieve 10% lower of TPH value and also almost 9 months faster than the research study. Hence, the author can conclude that the surfactants that is used in this experiment which is GraphSolve12 and GraphBioSolve is better and will have a significant contributaion to the environment. Based on the situation, the author believe that if the new surfactant solution is used and the bioremediation process is studied until the 12^{th} months, the result of the TPH value will decrease more to only around 1% of TPH value.

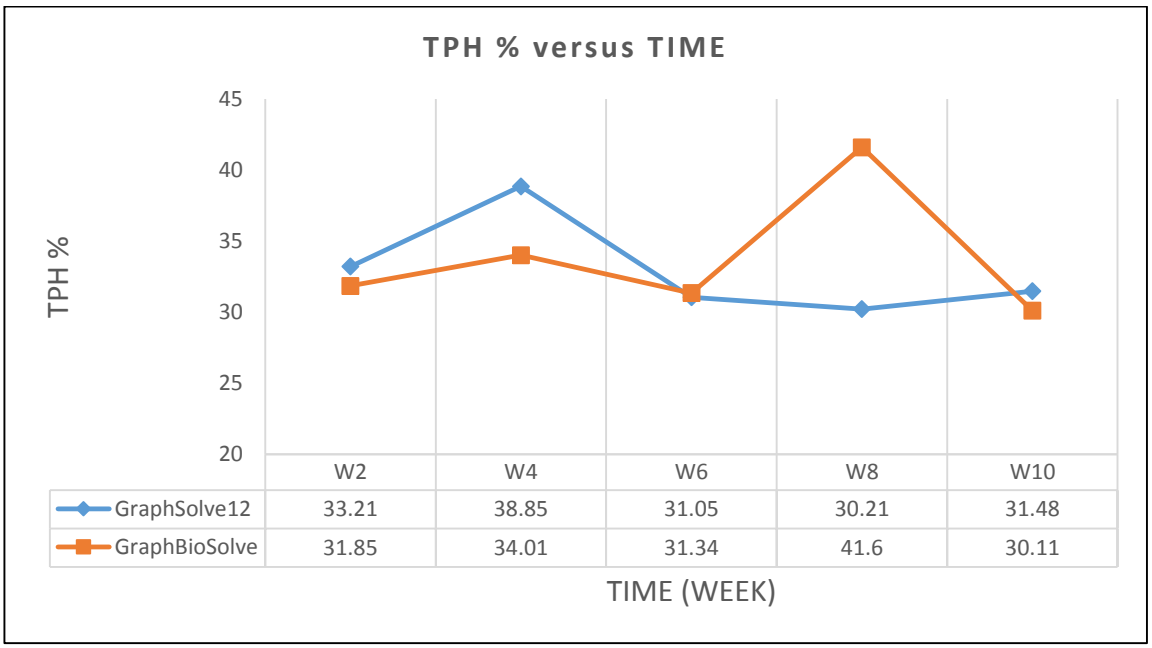


Figure 4.8 Comparison of TPH % of GraphSolve12 and GraphBioSolve at 10% dosing versus Time

Based on Figure 4.8, the comparison between the two surfactants TPH % are not significant. But if we compare based on the TPH percentage at week 10, GraphBioSolve gives a lower TPH which is 30.11%. From this findings, the author concludes that the best performance for the bioremediation process at 10% dosing is GraphBioSolve because it gives a lower TPH value compared to GraphSolve12. However, the TPH values between these two surfactant are only 1.37% difference, the experiment should be continued in order to study more on the TPH values trend that the sample can give beyond week 10. By continuing the experiment, the author believes that the final result to choose the surfactant between GraphSolve12 and GraphBioSolve will be more reliable.

4.2 Surface Structure of Sand Before and After Treatment.

The four samples for this study is denoted by native soil sample, S1_T1 (Sample 1 for Test 1), S2_T1 (Sample 2 for Test 1) and S3_T1 (Sample 3 for Test 1). Scanning electron microscope (SEM) identifies the surface structure as illustrated in Figure 4.9, 4.10, 4.11 and 4.12.

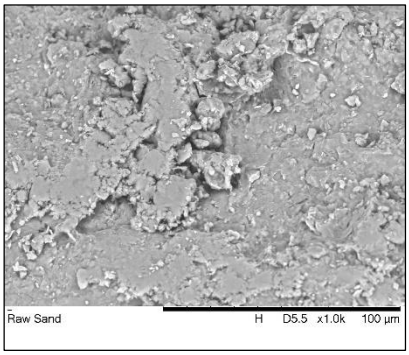


Figure 4.9 Surface structure of S1 native soil sand at x1.0k magnification

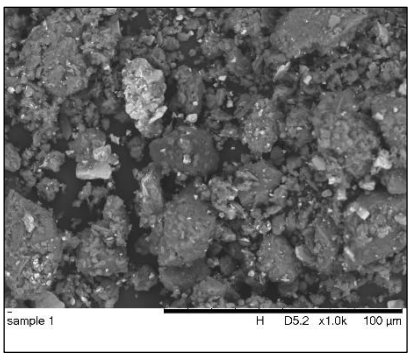


Figure 4.10 Surface structure of S2_T1 at x1.0k magnification

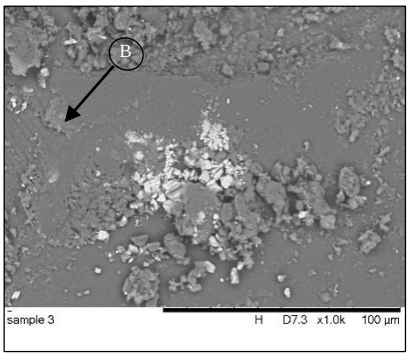


Figure 4.11 Surface structure of S3_T1 at x1.0k magnification

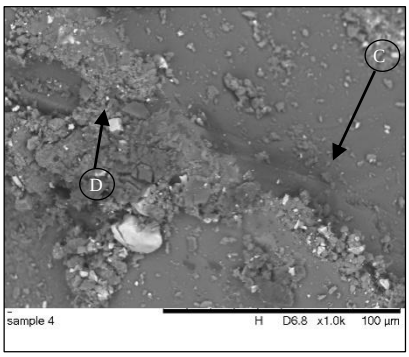


Figure 4.12 Surface structure of S4_T1 at x1.0k magnification

Figure 4.9 shows the sand surface seems to have straight and irregular steps under higher magnification (Figure4.13), the surface shows an irregular breakage blocks that looks like rough rocks. On the other hand, S2_T1 structure is rough with angular outline like an accumulation of lots of rough rocks. The colour is noticeable that it is darker than the native soil and it proves that chemical reaction is started to affect the sand structure. From Figure 4.14, the S2_T1 surface has a slightly weathered area (A) which mean the sand has undergone chemical weathering.

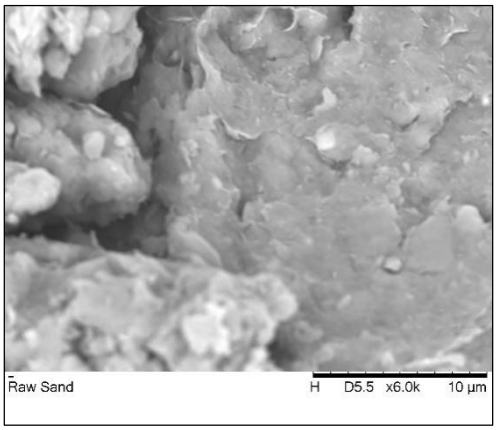


Figure 4.13 Native sand surface structure at x6.0k magnification

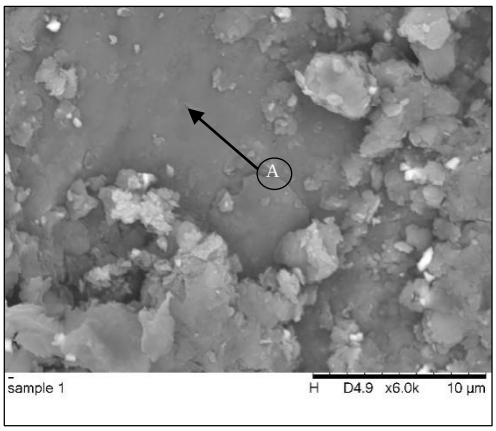


Figure 4.14 S2_T1 surface structure at x6.0k magnification

S3_T1 surface structure in Figure 4.11 show a conchoidal fracture with a straight and arcuate steps (B). The image also shows a little clearer surface as the rough rocks formation is getting lesser. Under higher magnification, the diameter of the sand crystal can be seen varies around 10 – 40 µm (Figure 4.15). The sand particle after the bioremediation treatment is reducing its diameter and as a consequence, the quality of sand are becoming finer and better. Figure 4.12 is the surface structure of S4_T1 shows that precipitation has occur on the sand and this happen when the area undergone intense chemical weathering (C, D). When the observation is done under higher magnification, the image in Figure 4.16 shows that the surface has a few inclined slope that is the result from the intense chemical weathering. The size of the sand particles is getting smaller and the diameter are around 5 – 20 µm.

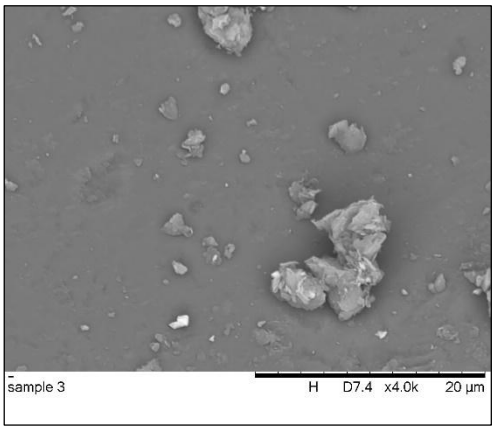


Figure 4.15 S3_T1 surface structure at x4.0k magnification

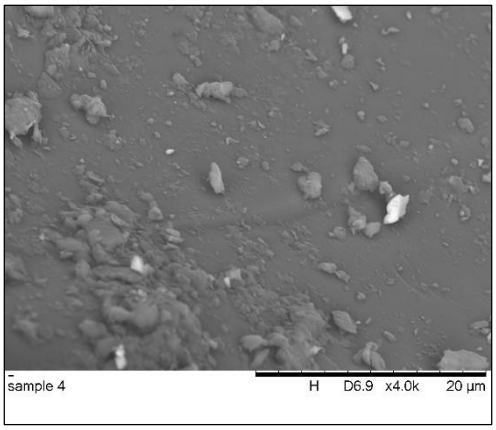


Figure 4.16 S4_T1 surface structure at x4.0k magnification

Most of the surface from Figure 4.10 – 4.12 and Figure 4.14 – 4.16, there are white colour particles that keep increasing and larger in size. (Tian et al., 2012) stated that from their finding the SEM-EDS spectrum did show the presence of metallic impurities such as Fe, Al and Ni over the figure that has lots of white particles as shown in Figure 4.17. At the same time, (Corporation, 2009) stated that in one of the example, the fibre sample observed at x4,000 magnification shows numbers of white particle that is refer to as an inorganic matter. From this study result, the white particles can be said as some inorganic materials that contain in the samples. However, the amount and types of the materials cannot be determined as more study need to be done to prove the existence. The surface structure that is

shown here can likely be a factor for the bioremediation as the transport of surfactant is affected by the porous media of the sand.

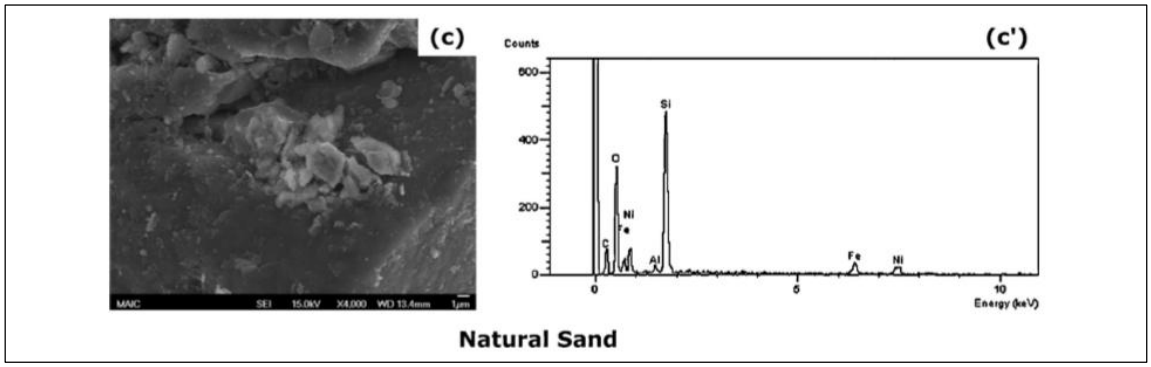


Figure 4.17 SEM image and corresponding EDS spectra of natural sand at 4000x from (Tian, Gao et al. 2012)

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

As a conclusion, this project research has successfully discovered that the best dosing for the surfactant is at 20% when mix with water. The result is based on the performance of surfactant GraphSolve12 only, but the author believe that the same result will also occur for GraphBioSolve. The experiment for GraphBioSolve is done only for one test due to the limited amount of drill cuttings. The comparison between these two surfactants also shows that GraphBioSolve is better than GraphSolve12 because it gives lower TPH percentage than GraphSolve12 at the same condition.

Overall, the bioremediation process proves to be faster and more efficient than other research findings and the author believe this surfactant will bring a big impact in the bioremediation process industry. These surfactants can help Platinum to expand their company forward and also in term of finance where they can sell the surfactant to other countries that often has major oil spills and help the environment towards a sustainable ecosystem.

5.2 Recommendations

As the research regarding bioremediation process is indefinitely wide, lots of future works can be done to further study and continue the research in other aspect of characterization of sand before, during and after the treatment. In order to commercialize the surfactants that is used in this research study, the bioremediation process should be upgraded to a bigger scale of study. The experimental works in the lab scale is only the best way to explore the process utilization of bioremediation. In future, some of the scope of study than can be explore and expanded is:

i. Use other alternatives to obtain the TPH values from the sample other than GC-MS analysis.
ii. Detailed study on the chemicals (surfactant) that is used in the bioremediation in advance so that the final result and the overall process is more detailed.
iii. Run a lot more test on different dosing for both surfactants before the final decision is made for the best surfactant for bioremediation process.

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APPENDICES

APPENDIX A

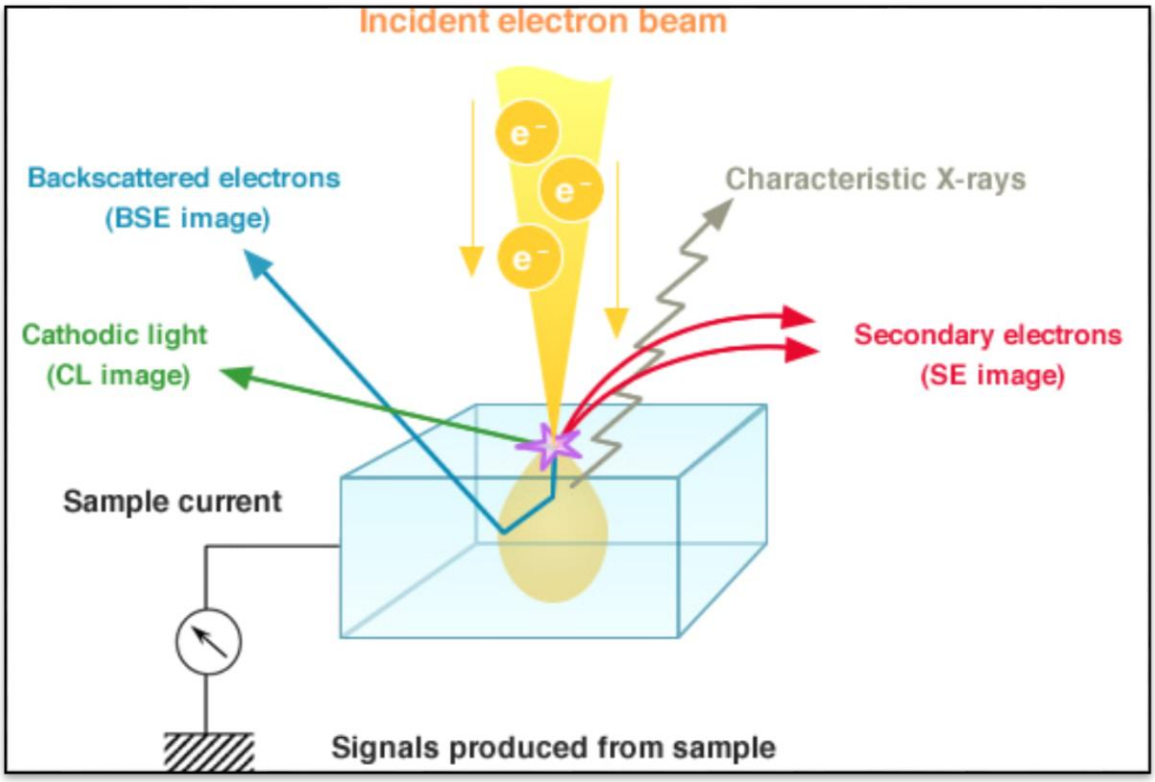

Figure A Details illustration on how the SEM signals are projected to obtain the image

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APPENDIX B

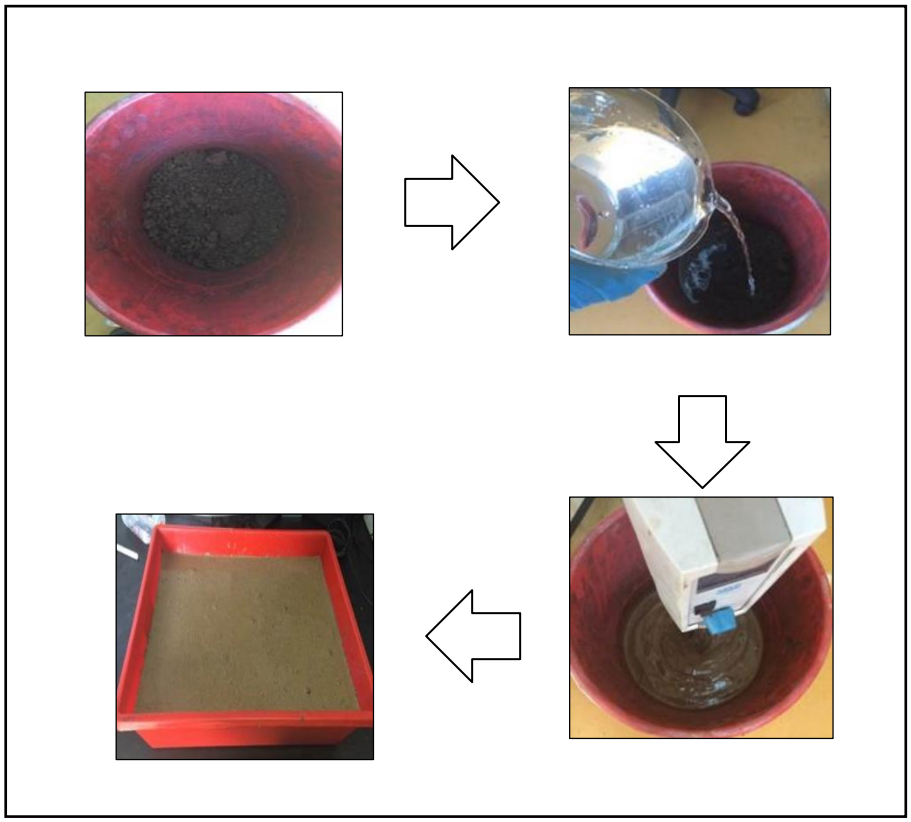


Figure B Step by step illustration of the sample preparation of contaminated sand with surfactant

APPENDIX C

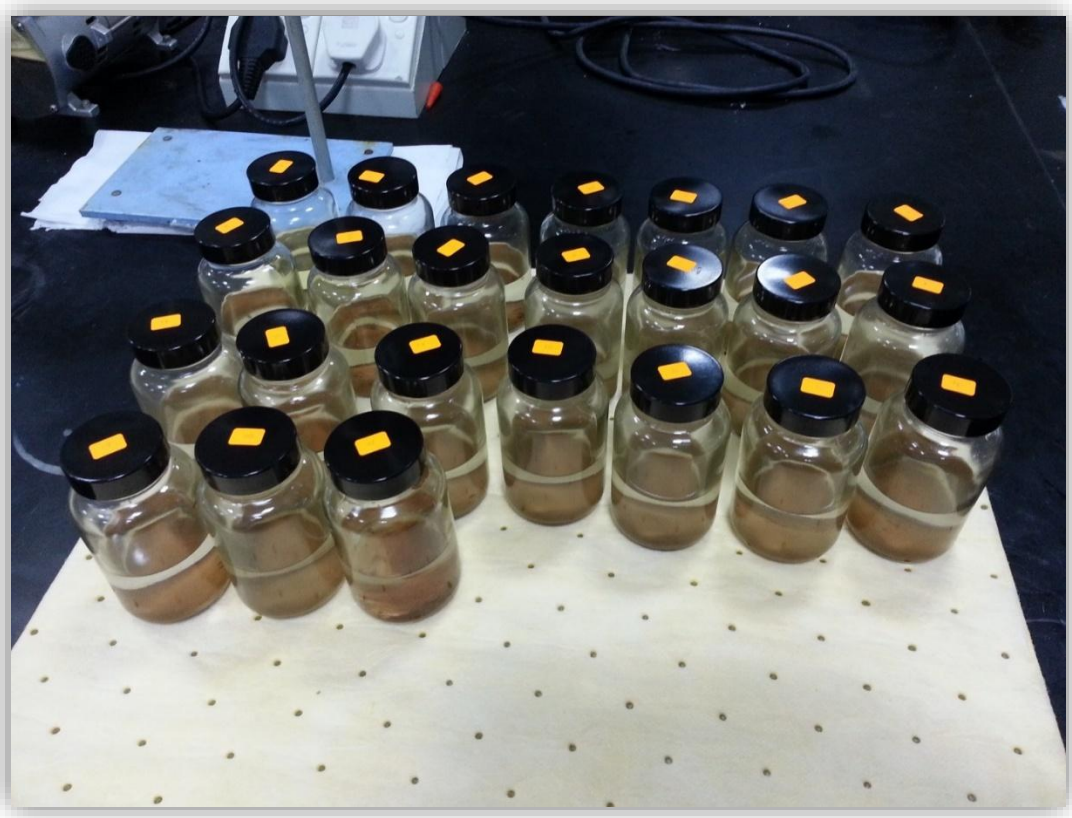


Figure C Samples preparation for GC-MS Analysis

APPENDIX D

Example of GC-MS reading (standard at 2ppm)

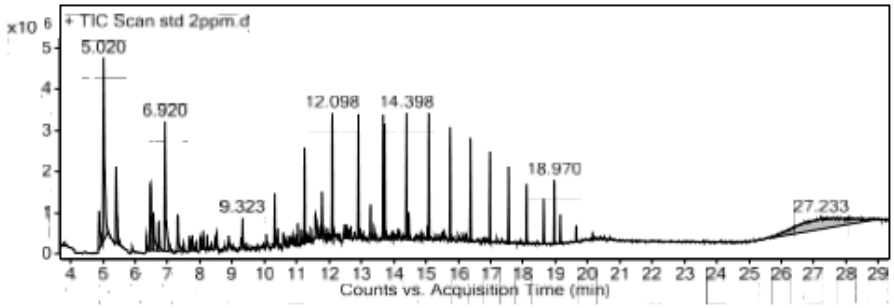
Qualitative Analysis Report

Data Filename	std 2ppm.D	**Sample Name**	std 2ppm
Sample Type		**Position**	1
Instrument Name	GCMS	**User Name**	
Acq Method	hydrocarbon.M	**Acquired Time**	12/10/2015 12:51:39 PM
IRM Calibration Status	Not Applicable	**DA Method**	default.m
Comment			

Expected Barcode		**Sample Amount**	
Dual Inj Vol	1	**TuneName**	ATUNE.U
TunePath	D:\MassHunter\GCMS\1\5977\	**MSFirmwareVersion**	6.00.21
Acquisition Time #2	2015-12-10 20:51:39Z	**OperatorName**	
RunCompletedFlag	True	**Acquisition SW Version**	MassHunter GC/MS Acquisition B.07.02.1938 08-Sep-2014 Copyright © 1989-2014 Agilent Technologies, Inc.

User Chromatograms

Fragmentor Voltage **Collision Energy** 0 **Ionization Mode** Unspecified



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	4.987	5.02	5.163	4440238.36	13141472.25	46.97
2	6.889	6.92	7.046	3141010.93	7795614.16	27.87
3	12.07	12.098	12.129	3034251.94	3642515.55	13.02
4	12.874	12.905	12.928	3021003.75	3427930.58	12.25
5	13.632	13.672	13.695	3018205.8	3771412.7	13.48
6	13.695	13.723	13.746	2797846.11	3512382.22	12.56
7	14.364	14.398	14.438	3071520.82	3436431.04	12.28
8	15.062	15.091	15.12	3078392.05	3333109.37	11.91
9	15.714	15.749	15.783	2767211.02	3182169.81	11.37
10	16.339	16.378	16.418	2523504.51	2934733.99	10.49

Fragmentor Voltage **Collision Energy** 0 **Ionization Mode** Unspecified

APPENDIX E

Example of GC-MS reading (Test 2, Week 2)

Area Percent Report

Data Path : C:\Users\Admin\Desktop\student\halizah\
Data File : spl16.D
Acq On : 11 Dec 2015 21:52
Operator :
Sample : spl16
Misc :
ALS Vial : 8 Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method : D:\MassHunter\GCMS\1\methods\hydrocarbon.M
Title :

Signal : TIC: spl16.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	4.895	173	211	226	BV	2187216	152136432	2.67%	0.637%
2	5.045	226	237	295	VV	13795119	1028422618	18.04%	4.305%
3	5.426	295	304	381	VV	5538991	433148411	7.60%	1.813%
4	5.925	381	391	458	VV	375059	35217822	0.62%	0.147%
5	6.368	458	468	480	PV	1052809	48938120	0.86%	0.205%
6	6.496	480	491	528	VV	6101218	442858005	7.77%	1.854%
7	6.749	528	535	560	VV	2069561	109073602	1.91%	0.457%
8	6.947	560	570	625	VV	8014577	436996349	7.67%	1.829%
9	7.342	625	639	691	VV 3	2280731	174726858	3.07%	0.731%
10	7.916	691	739	766	VV 6	30548873	3518768251	61.73%	14.729%
11	8.183	766	786	809	VV 2	4183208	163432366	2.87%	0.684%
12	8.407	809	825	834	VV 3	1560236	46598590	0.82%	0.195%
13	8.558	834	851	861	VV	3297056	86691747	1.52%	0.363%
14	8.914	861	914	960	VV 6	2181865	191223270	3.35%	0.800%
15	9.339	960	988	1031	VV 3	3807278	195674055	3.43%	0.819%
16	9.683	1031	1048	1058	VV 10	528926	48599757	0.85%	0.203%
17	9.789	1058	1066	1074	VV 6	905599	32792301	0.58%	0.137%
18	10.072	1074	1116	1137	VV 4	2038289	173352571	3.04%	0.726%
19	10.339	1137	1162	1201	VV 3	6395518	284776175	5.00%	1.192%
20	10.610	1201	1210	1236	VV 3	1295437	149886741	2.63%	0.627%
21	10.881	1236	1257	1271	VV 9	2427640	172952610	3.03%	0.724%
22	11.046	1271	1286	1298	VV 3	3159143	138058347	2.42%	0.578%
23	11.154	1298	1305	1313	VV 3	2580840	80452243	1.41%	0.337%
24	11.268	1313	1325	1349	VV	10095865	379477771	6.66%	1.588%
25	11.451	1349	1357	1367	VV	2851284	108005372	1.89%	0.452%
26	11.611	1367	1385	1401	VV 5	4495463	308426187	5.41%	1.291%
27	11.799	1401	1418	1458	VV 6	7133915	513449695	9.01%	2.149%
28	12.129	1458	1475	1525	VV 2	15795390	703910496	12.35%	2.947%
29	12.528	1525	1545	1585	VV 2	3685184	510101011	8.95%	2.135%
30	12.808	1585	1594	1608	VV 7	2766412	163123935	2.86%	0.683%
31	12.939	1608	1617	1668	VV	16109259	664980588	11.67%	2.784%
32	13.300	1668	1680	1722	VV 2	5694335	463582272	8.13%	1.941%
33	13.750	1722	1759	1799	VV 2	14197843	983213722	17.25%	4.116%
34	14.016	1799	1805	1824	VV 8	2720629	198416099	3.48%	0.831%
35	14.152	1824	1829	1855	VV 8	3211703	245133938	4.30%	1.026%
36	14.429	1855	1877	1906	VV	13058241	658179769	11.55%	2.755%
37	14.720	1906	1928	1947	VV	2389775	298966430	5.25%	1.251%
38	14.842	1947	1950	1957	VV 3	2503566	74893853	1.31%	0.314%
39	15.116	1957	1997	2032	VV	12454308	716895178	12.58%	3.001%
40	15.375	2032	2043	2057	VV 7	2493360	177815622	3.12%	0.744%
41	15.513	2057	2067	2104	VV 7	2420973	324886813	5.70%	1.360%

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 42  15.773  2104 2112 2141 VV   10424731 388182987   6.81%   1.625%
 43  16.444  2169 2230 2286 VV 6 36573740 5699822705 100.00%  23.859%
 44  16.812  2286 2294 2322 VV 8 2254097 217604301   3.82%   0.911%
 45  17.029  2322 2332 2380 VV   12515656 432397004   7.59%   1.810%

 46  17.362  2380 2390 2414 VV 4 1803285 148922862   2.61%   0.623%
 47  17.584  2414 2429 2479 VV   9007072 383141104   6.72%   1.604%
 48  17.920  2479 2487 2512 VV 4 1252530 105536931   1.85%   0.442%
 49  18.131  2512 2524 2551 VV   7375342 203689349   3.57%   0.853%
 50  18.450  2551 2580 2609 VV 6  935145 136209884   2.39%   0.570%

 51  18.656  2609 2616 2631 VV   5533185 115828246   2.03%   0.485%
 52  18.977  2662 2672 2689 VV   8280025 143337742   2.51%   0.600%
 53  19.164  2689 2705 2722 VV   4083316  85467651   1.50%   0.358%
 54  19.654  2780 2790 2805 VV   2503897  46056137   0.81%   0.193%
 55  19.950  2805 2842 2852 VV 2  537139  41217216   0.72%   0.173%

 56  20.153  2852 2878 2909 VV 2 1022614  65794967   1.15%   0.275%
 57  20.379  2909 2917 2962 VV 2  527430  37822539   0.66%   0.158%


                       Sum of corrected areas: 23889267617

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APPENDIX F

MSDS of Drill Cuttings

MATERIAL SAFETY DATA SHEET

1. PRODUCT IDENTIFICATION

Product Name	Drilling Cutting, Oil Based (Fine and Coarse)
Product Description	Not Available

2. MANUFACTURER'S DETAILS

Manufacturer	Platinum Green Chemical Sdn. Bhd.
Address	Lot 15-19, PT 1409 Senawang Industrial Estate Batu 4, Jalan Tampin 70450 Seremban Negeri Sembilan
Phone	+606-6778080
Fax	+606-6770309

3. COMPOSITION/INFORMATION ON INGREDIENTS

Materials	Composition	CASRN	GHS Classification
C13-17 alkanes	>60%	90622-45-0	**H303**: Acute Toxicity (oral) Category 5, **H333**: Acute Toxicity (Inhalation) Category 5, **H320**: Eye Irritation Category 2B, **H335**: STOT – SE (Resp. Irr) Category 3, **H336**: STOT-SE (Narcosis) Category 3, **H304**: Aspiration Hazard Category 1,
Barium Sulfate	5 to <10%	7727-43-7	**H335**: STOT – SE (resp. Irr) Category 3
Calcium chloride	5 to <10%	10043-52-4	**H302**: Acute Toxicity (Oral) Category 4, **H319**: Eye Irritation Category 2A

4. HAZARDS IDENTIFICATION

Hazard Statement (s):	H303: May be harmful if swallowed H333: May be harmful if inhaled H320: Causes eye irritation H335: May cause respiratory irritation H336: May cause drowsiness or dizziness H304: May be fatal if swallowed and enters airways

1

Pictogram	Labelling (GHS)  
Signal Word	Not available
Environmental Hazards	None Identified
Precautionary statement(s):	
Prevention	P271: Use only outdoors or in a well-ventillated area P261: Avoid breathing dust/fume/mist/vapours/spray P264: Wash all exposed external body areas thoroughly after handling
Response	P301 + P310: IF SWALLOWED: Immediately call a POISON CENTER/doctor/physician/first aider P331: Do NOT induced vomiting. P304 + P312 IF INHALED: Call a POISON CENTER/doctor/physician/first aider if you feel unwell P305 + P361 + P338 : If In EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing P337 + P313: If eye irritation persists, get medical advice/attention
Storage	P405: Store locked up P403 + P233: Store in a well-ventillated place. Keep container tightly closed.
Disposal	P501: Dispose of content/container to authorized chemical landfill or if organic to high temperature incineration

5. FIRST AID MEASURES

Eyes	Immediately flush eyes with plenty of flowing water for 10 to 15 minutes holding eyelids apart. Subsequently consult an ophthalmologist. Removal of contact lenses after an eye injury should only be undertaken by skilled personnel
Skin	Remove residues with soap and water. Change contaminated clothing. In case of skin reactions, consult a physician.
Inhalation	Provide fresh air. Seek medical treatment in case of troubles.
Ingestion	Rinse mouth and drink large quantities of water. Never give anything by mouth to an unconscious person.

	Avoid giving milk or oils Avoid giving alcohol Seek medical attention.
Indication of immediate medical attention and special treatment needed	Any material aspirated during vomiting may produce lung injury; hence emesis should not be induced mechanically or pharmacologically. If spontaneous vomiting has occur after ingestion, the patient should be monitored for difficult breathing, as adverse effect of aspiration into the lungs may be delayed up to 48 hours.

6. FIRE FIGHTING MEASURES

Extinguishing Media	Water spray or fog (large fire only), foam, dry extinguishing powder, carbon dioxide.
Special Hazard	Avoid contamination with oxidizing agents i.e. nitrates, oxidizing acids, chlorine bleaches, as ignition may result. In case of fire may be liberated: carbon monoxide, carbon dioxide, and acrid smoke. Mist containing combustible materials may be explosive.
Special Fire Fighting Procedure	Wear self-contained breathing apparatus. Wear suitable protective clothing.
Additional Information:	Hazchem-Code: Collect contaminated fire extinguishing water separately. Do not allow entering drains or surface water. Equipment should be thoroughly decontaminated after use.

7. ACCIDENTAL RELEASE MEASURES

Personal Precautions	Avoid contact with the substance. Provide adequate ventilation. Wear personal protection equipment.
Environmental Precautions	Should not be released into the environment. Do not allow to enter into ground-water, surface water or drains. Prevent further leakage or spillage if safe to do so.
Clean-up methods-small spillage	Absorb with liquid-binding material (e.g. sand, diatomaceous earth, acid- or universal binding agents). Collect in closed containers for disposal and place in clean, dry, sealed container. Use non-sparking tools.
Additional information	Special danger of slipping by leaking/spilling product

Refer to Section 9 for additional personal protection information

Refer to Section 14 for disposal considerations.

8. HANDLING AND STORAGE

Handling	Avoid contact with the incompatible substance. Provide adequate ventilation, and local exhaust as need. Keep container sealed when not used. Wear protective clothing when risk of exposure occurs. Do NOT cut, drill, grind, weld or perform similar operation on or near container. Always wash hand with soap and water after handling. Use good occupational work practice. DO NOT allow material to contact exposed food or food utensil. Work cloth should be laundered separately.
Storage	Keep container tightly closed in a dry and well-ventilated place. Store away from sources of heat or ignition. Store away from foodstuffs.
Storage Class	Not available
Specific end use(s)	Not available

Refer to Section 7 for cleanup spillage

Refer to Section 14 for disposal considerations

9. EXPOSURE CONTROLS/PERSONAL PROTECTION

General Precautions

Avoid contact with skin and eyes.
Change contaminated clothing.
When using, do NOT eat, drink or smoke.
Wash hands before breaks and after work.
Have eye wash bottle or eye rinse ready at work place.

Occupational Exposure Standards:

US ACGIH Treshold Limit Values (TLV)

material	TWA	STEL	Peak
Barium sulfate	5 mg/m^3	Not available	Not available

Emergency Limits

Material	STEEL-1	STTEL-2	STEEL-3
Barium sulfate	30 mg/m^3	330 mg/m^3	2000 mg/m^3
Calcium chloride	3 mg/m^3	33 mg/m^3	200 mg/m^3

Respiratory Protection

Respiratory protection in case of aerosol or vapour formation
Use filter type A (= against vapours of organic substances)

	according to EN 14387.
Hand/feet Protection	Neoprene gloves. Chemical protective gloves e.g. PVC Wear safety footwear or safety gumboots e.g. rubber
Eye Protection	Tightly sealed goggles according to EN 166
Body Protection	Overalls, PVC apron, eye wash unit
Additional information	Not available

10. PHYSICAL AND CHEMICAL

Physical State	Non slump paste
Appearance	Liquid, does not mix with water
Odour:	Mild characteristic odour
Odour threshold	Not available
Flash Point	>105 °C
Flammability	Not available
Explosive properties	Not explosive (method EC A14)
Vapor Pressure	0.087 kpa
Solubility in Water	Insoluble
pH	Not available
Explosive properties	None
Auto Ignition Temperature	204 °C
Oxidizing characteristics	Non oxidising

11. STABILITY AND REACTIVITY DATA

Reactivity	No dangerous reaction known under condition of normal use.
Chemical stability	Product is consider stable and hazardous polymerization will not occur
Possibility of hazardous reactions	Refer section 6
Hazardous Decomposition Products	Refer section 6
Thermal decomposition	Not available

12. TOXICOLOGICAL INFORMATION

Animal toxicity data	Not available
Acute toxicity:	Not available
Eye Irritation	Petroleum hydrocarbon may produce pain after direct contact with the eyes.

	Alight, but transient disturbances of the corneal epithelium may also result.
Inhalation	Inhalation of aerosols (mist, fumes), generated by the material during the course of normal handling may be damaging to the health of the individual.
Skin Irritation	Repeated exposure may cause skin cracking, flaking or drying following normal handling and use. Open cuts, abraded or irritated skin should not be exposed to this material.
Ingestion	May cause abdominal pain,headache,nausea and diarrhea. Large doses affect liver and kidneys. May have narcotic effect
Sensitisation	Not available
Specific target organ toxicity (single exposure)	Not available
Specific target organ toxicity (repeated exposure)	Not available
Aspiration hazard	Not available

13. ECOLOGICAL INFORMATION

Aquatic toxicity:	Not available
Water Hazard Class:	Not available
Toxicity to other organisms	Not available
Biodegradation	Not available
Bioaccumulative potential	Not available
Mobility in soil	Not available

14. DISPOSAL CONSIDERATION

Dispose of waste and residues in accordance with local authority requirenments.

15. TRANSPORT INFORMATION

Not classified as dangerous under UN, IMO, ADR/RID, and IATA/ICAO codes

16. REGULATORY INFORMATION

Safety, health and environmental regulations/legislation specific for the substance or mixture	Not available

APPENDIX G

MSDS of GraphSolve

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MATERIAL SAFETY DATA SHEET

1. PRODUCT IDENTIFICATION

Product Name	Graph Solve
Product Description	Non-ionic water based liquid blend for industrial cleaner and remediation agent.

2. MANUFACTURER'S DETAILS

Manufacturer	Platinum Nanochem Sdn Bhd (Company No. 707356-X)
Address	Lot 15-19 & PT 1409, Senawang Industrial Estate, Batu 4, Jalan Tampin, 70450 Seremban, Negeri Sembilan.
Phone	+606 6778080
Fax	+606 6770309

3. COMPOSITION/INFORMATION ON INGREDIENTS

Materials	Composition	CASRN	GHS Classification
Proprietary blend of Ethoxylated Alkylphenolic surfactants	>60%	Not available	Acute toxicity-Oral (Category 4); Skin Corrosion/irritation (Category 3); Eye Damage/Irritation (Category 2B); Target Organ Specific Toxicity: Single (Category 3); Target Organ Specific Toxicity: Repeated (Category 2)

4. HAZARDS IDENTIFICATION

Hazard Statement (s):	Harmful if swallowed Causes mild skin irritation Causes eye irritation May causes respiratory irritation Causes serious eye irritation

Pictogram	Labelling (GHS) 
Signal Word	WARNING!
Environmental Hazards	None Identified
Precautionary statement(s):	
Prevention	Use personal protective equipment as required. Do not handle until all safety precautions have been read and understood Obtained special instructions before use. Use only outdoors or in a well ventilated area Avoid breathing dust/fume/gas/mist/vapors/spray. Wash all exposed skin thoroughly after handling.
Response	IF swallowed: immediately call doctor/physician. Rinse mouth. In case of fire: use dry sand, dry chemical or alcohol resistant foam for extinction.
Storage	Store locked up Store in a well-ventilated place. Keep container tightly closed.
Disposal	Dispose of content/container in accordance with local/regional/national/international regulations.

5. FIRST AID MEASURES

Eyes	Immediately flush eyes with plenty of flowing water for 10 to 15 minutes holding eyelids apart. Subsequently consult an ophthalmologist. Removal of contact lenses after an eye injury should only be undertaken by skilled personnel
Skin	Remove residues with soap and water Change contaminated clothing. Wash clothing before reuse. In case of skin reactions, consult a physician
Inhalation	Remove victim to fresh air and keep at rest in a position comfortable for breathing. If breathing is difficult, give oxygen. Seek medical treatment in case of troubles.
Ingestion	Do NOT induce vomiting. If vomiting occurs, lean patient forward or place on the left-side (head-down position, if possible) to maintain open

	airway and prevent aspiration. Never give anything especially liquid by mouth to an unconscious person or to a person showing signs of being sleepy or with reduced awareness. Avoid giving alcohol Seek medical attention.
Indication of immediate medical attention and special treatment needed	Any material aspirated during vomiting may produce lung injury; hence emesis should not be induced mechanically or pharmacologically.

6. FIRE FIGHTING MEASURES

Hazardous Combustion Products	Carbon monoxide and carbon dioxide
Extinguishing Media	Small fire: Any extinguisher suitable for Class B fires, dry chemical, CO_2, water spray, fire-fighting foam. Large fires: Water spray, fog or fire-fighting foam. Water may be ineffective for fighting the fire, but may be used to cool fire-exposed containers.
Special Fire Fighting Procedure	Wear self-contained breathing apparatus. Wear suitable protective clothing.
Additional Information:	Use water spray to cool unopened containers. Do not allow entering drains or surface water. Equipment should be thoroughly decontaminated after use.

7. ACCIDENTAL RELEASE MEASURES

Personal Precautions	Avoid contact with the substance. Provide adequate ventilation. Wear personal protection equipment.
Environmental Precautions	Should not be released into the environment. Do not allow to enter into ground-water, surface water or drains. Prevent further leakage or spillage if safe to do so.
Clean-up methods-small spillage	Absorb with liquid-binding material (e.g. sand, diatomaceous earth, or universal binding agents). Collect in closed containers for disposal and place in clean, dry, sealed container. Wash spill area thoroughly. Dispose of collected material according to local regulation.
Additional information	Special danger of slipping by leaking/spilling product

Refer to Section 9 for additional personal protection information

Refer to Section 14 for disposal considerations.

8. HANDLING AND STORAGE

Handling	Provide adequate ventilation, and local exhaust as need. Keep container sealed when not used. Wear protective clothing when risk of exposure occurs. Do NOT breath dust/vapor/gas. Always wash hand with soap and water after handling. Use good occupational work practice. No smoking. DO NOT allow material to contact exposed food or food utensil. Work cloth should be laundered separately.
Storage	Store in cool place. Keep container tightly closed in a dry and well-ventilated place. Store away from sources of heat or ignition. Store away from foodstuffs. Protect container against physical damage and check regularly for leaks.
Storage Class	Not available
Specific end use(s)	Not available

Refer to Section 7 for cleanup spillage
Refer to Section 14 for disposal considerations

9. EXPOSURE CONTROLS/PERSONAL PROTECTION

General Precautions	Avoid contact with skin and eyes. Change contaminated clothing. When using, do NOT eat, drink or smoke. Wash hands before breaks and after work. Have eye wash bottle or eye rinse ready at work place.
Occupational Exposure Standards:	Not available
Respiratory Protection	Respiratory protection in case of aerosol or vapour formation Use filter type A (= against vapours of organic substances) according to EN 14387.
Hand/feet Protection	Neoprene gloves. Chemical protective gloves e.g. PVC Wear safety footwear or safety gumboots e.g. rubber
Eye Protection	Tightly sealed goggles according to EN 166
Body Protection	Overalls, PVC apron, eye wash unit

Additional information	N/A

10. PHYSICAL AND CHEMICAL

Physical State	Liquid
Appearance	Red
Odour:	Wintergreen
Flash Point	Above 93 °C
Boiling Range	Not available
Explosive properties	Not available
Explosive limits	Not available
Vapor Pressure	Not available
Vapor Density	Not available
Specific Gravity	1.03 ± 0.05
Solubility in Water	Miscible
Kinematic Viscosity	Not available
pH	8.5 ± 0.5
Explosive properties	Not available
Auto Ignition Temperature	Not available
Oxidizing characteristics	Not available

11. STABILITY AND REACTIVITY DATA

Reactivity	Keep away from strong oxidizers and strong acids
Chemical stability	Product is consider stable and hazardous polymerization will not occur
Possibility of hazardous reactions	Not known
Hazardous Decomposition Products	Not known
Thermal decomposition	Not available

12. TOXICOLOGICAL INFORMATION

Animal toxicity data	Not available
Acute toxicity:	Not available
Eye Irritation	Contact with eyes may cause moderate to severe irritation.
Inhalation	Excessive exposure may cause irritation to nose, throat, lungs, and respiratory tract.
Skin Irritation	May cause skin irritation with prolonged or repeated contact. Liquid may be absorbed through the skin in toxic amounts if

	large areas of skin are exposed repeatedly.
Ingestion	There may be irritation of the throat. May be fatal in case of large quantity ingestion.
Sensitisation	Not available
Specific target organ toxicity (single exposure)	Not available
Specific target organ toxicity (repeated exposure)	Not available
Aspiration hazard	Not available

13. ECOLOGICAL INFORMATION

Aquatic toxicity:	Not available
Toxicity to other organisms	Not available
Biodegradation	Not available
Bioaccumulative potential	Not available
Mobility in soil	Not available

14. DISPOSAL CONSIDERATION

Dispose of waste and residues in accordance with local authority requirenments.

15. TRANSPORT INFORMATION

Not classified as dangerous under UN, IMO, ADR/RID, and IATA/ICAO codes

16. REGULATORY INFORMATION

Not available

Disclaimer:
The information provided is in good faith as a guide for handling of the product and should be treated only under the condition lay out. The data may be revised from time to time. We cannot anticipate all conditions under which the information or our product may be used. We assume no liability or responsibility for loss or damage resulting from improper use or handling of our product, from incompatible product contamination or from the failure to follow instructions, warnings and advisories in the product's Material Safety Data Sheet