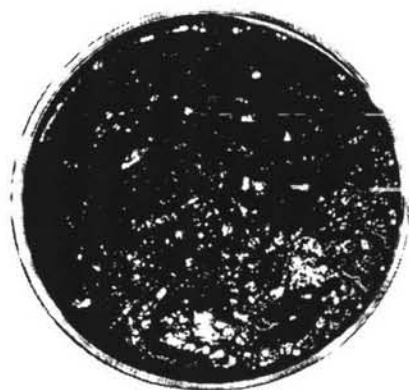


## CHAPTER IV

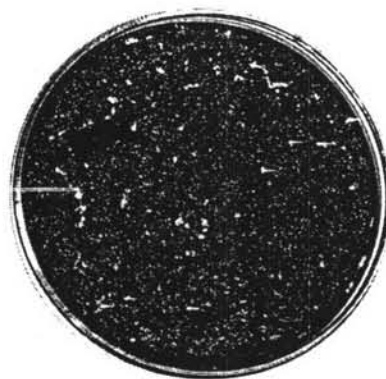
### RESULTS AND DISCUSSION

#### 4.1 Determination of the Oil Sludge Component

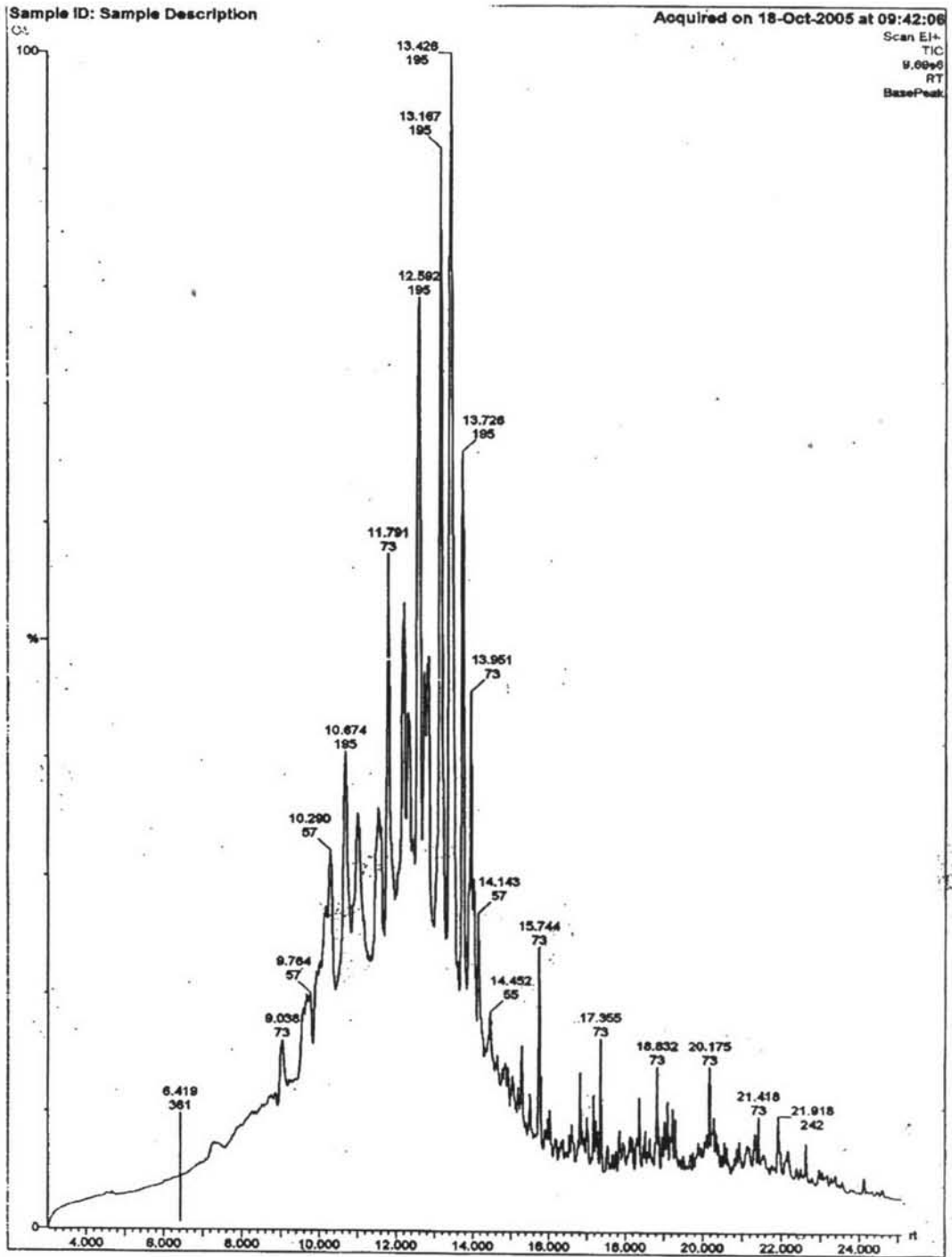
Firstly, the component of oil sludge obtained from Dr. Thawach Chatchuphong at the PTT PLC in the AFI separator unit was determined. The original oil sludge was a black slurry and slightly viscous. Sludge was sampled after being mixed to be homogenous. Then, the slurry was decanted for 15 minutes to let the solid particle settled down. The upper part of slurry was transferred to the glass plates and air-dried for 5 days under atmospheric conditions. The hydrocarbons in the air-dried oil sludge were extracted by using n-hexane as a solvent. The mixed solution was filtered by passing through the filter paper (Whatman No.4) to remove any solid particles. The air-dried oil sludge solution was then diluted and injected into GC/MS to analyze for the hydrocarbon contents. The conditions of GC/MS were as follow: column OV-1 0.25 micron, column size 30 m x 0.32 m, and carrier gas flow (He) at 12 Psig. Figure 4.1 shows the oil sludge sample obtained from PTT PLC and Figure 4.2 shows the oil sludge after air-dried for 5 days. Figure 4.3 shows the peak identification of hydrocarbon components in the oil sludge analyzed by GC/MS and Table 4.1 shows the main components in the air-dried oil sludge.



**Figure 4.1** Oil sludge obtained from PTT PLC.


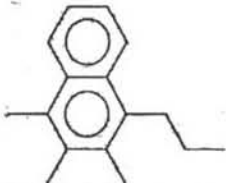
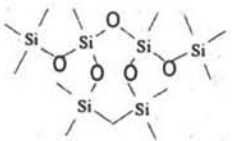

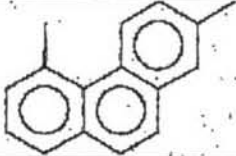
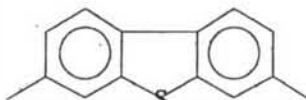
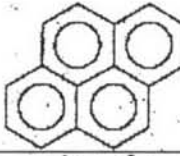
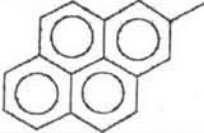


**Figure 4.2** Air-dried oil sludge.

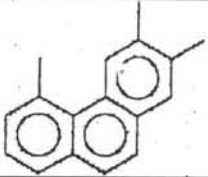

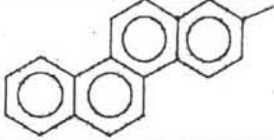
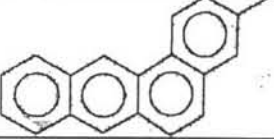
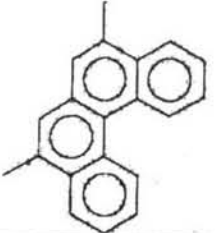
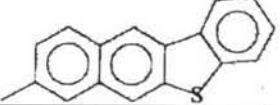
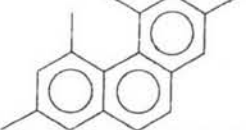


**Figure 4.3** The identification peaks of the hydrocarbon in the oil sludge analyzed by GC/MS.

**Table 4.1** The hydrocarbon contents in the extracted oil from oil sludge

Type of hydrocarbons in the extracted oil from oil sludge	Pictures of hydrocarbons in extracted oil from oil sludge	Molecular weight	% Fraction
Tritetracontane		604	40.3612
1, 2, 3-Trimethyl-4-Propenyl Naphthalene		210	41.5195
Trimethylsiloxy Tetrasiloxane		458	12.8315
Cyclic Octaatomic Sulfur		256	0.4997
2,5-Dimethyl Phenanthrene		206	0.4429
2,8-Dimethyl Dibenzothiophene		212	0.2381
Pyrene		202	0.2211
2-methyl Pyrene		216	0.5995

**Table 4.1** The hydrocarbon contents in the extracted oil from oil sludge (cont.)

Type of hydrocarbons in the extracted oil from oil sludge	Pictures of hydrocarbons in extracted oil from oil sludge	Molecular weight	% Fraction
2,3,5-Trimethyl Phenanthrene		220	0.2655
1,3-Dimethyl pyrene		230	1.2021
2-Methyl Chrysene		242	0.5861
3-Methylbenz(a)anthracene		242	0.5555
5,8-Dimethyl-Phenanthrene		256	0.1670
8-Methyl Benzo Naphthano 2,3-D Thiophene		248	0.4095
2,4,5,7-Tetramethylphenanthrene		234	0.0999

## 4.2 Enhanced Solubilization of Hydrocarbons in Oil Sludge by Nonionic Surfactant

### 4.2.1 Determination of Contact Time Required for Solubilization of Oil Sludge by Nonionic Surfactant System

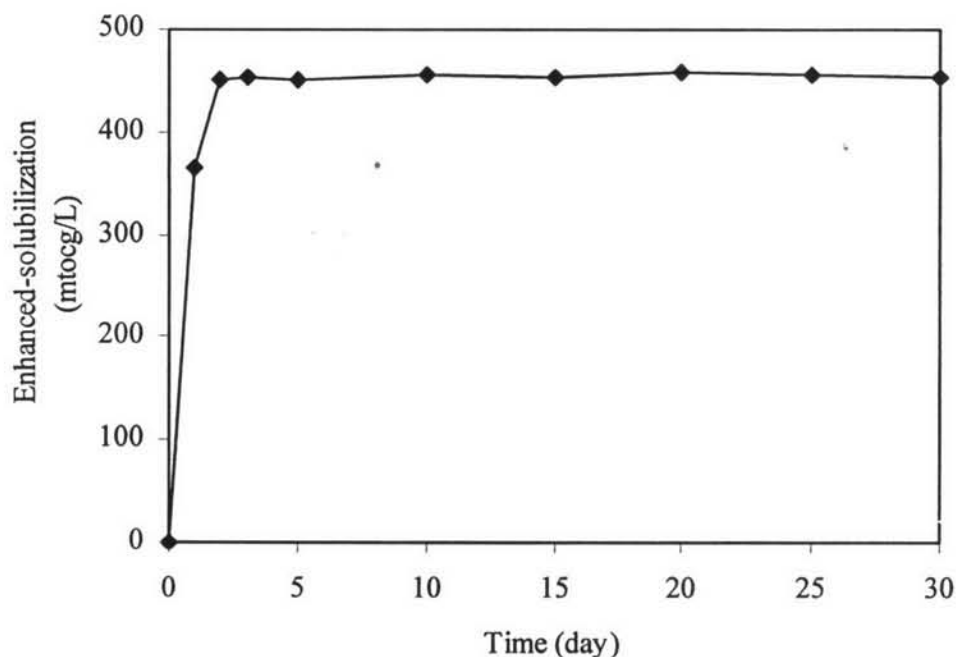
In order to study the effect of nonionic surfactant on the solubilization of petroleum hydrocarbons in the extracted oil from crude oil sludge, it is imperative to first determine the amount of time required for the solubilization process in the presence of nonionic surfactant (Tween 80) to reach equilibrium. The surfactant was added into the sets of 4 dam vial containing oil sludge with the MSM. The samples were taken and analyzed for solubilization of hydrocarbons at specific time intervals. The increased solubilization from the control experiment as a result of added surfactant was reported in term of "Enhanced Solubilization" as calculated below:

$$\text{Enhanced Solubilization} = (\text{Solubilization}_{\text{oil+surf.}} - \text{Solubilization}_{\text{surf.}}) - \text{Solubilization}_{\text{control}}$$

where  $\text{solubilization}_{\text{oil+surf}}$  = TOC (Total Organic Carbon) of oil sludge and surfactants,  $\text{solubilization}_{\text{surf}}$  = TOC of surfactants alone and  $\text{solubilization}_{\text{control}}$  = TOC of oil sludge alone.

In this study, the concentration of surfactant used was 0.1% w/v and the concentration of oil was 1% w/v in vial containing 20 ml MSM. The vials were shaken on the orbital shaker at 150 rpm at room temperature and they were left to stay still for 1 month. Aqueous phase was filtered and injected into the TOC analyzer in the: 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup>, 5<sup>th</sup>, 10<sup>th</sup>, 15<sup>th</sup>, 20<sup>th</sup>, 25<sup>th</sup>, and 30<sup>th</sup> day. The results showed that the solubilized hydrocarbon in the aqueous phase required 2 to 3 days to reach the maximum solubilization which was about 450 mg/L on the average. Figure 4.4 shows the number of carbon staying in the aqueous phase and it should have the possibility to be degraded by the microorganisms in the biodegradation study. Therefore, it can be concluded that equilibration time of 2 days is adequate for the solubilization of extracted oil from oil sludge in the presence of Tween 80 to complete. Consequently, in all experiments in the next parts of the study, the

complete. Consequently, in all experiments in the next parts of the study, the samples were taken into the reactor after 48 hours or 2 days. This condition was further used for the biodegradation study.

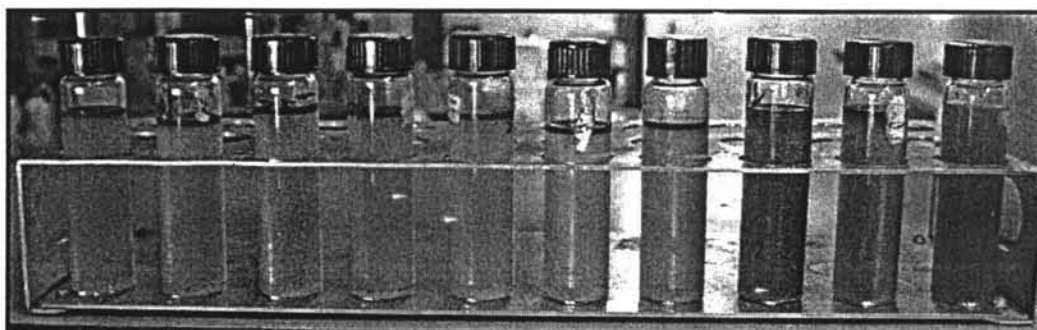


**Figure 4.4** Equilibrium Time Required for Solubilization of Oil Sludge by Nonionic Surfactant System.

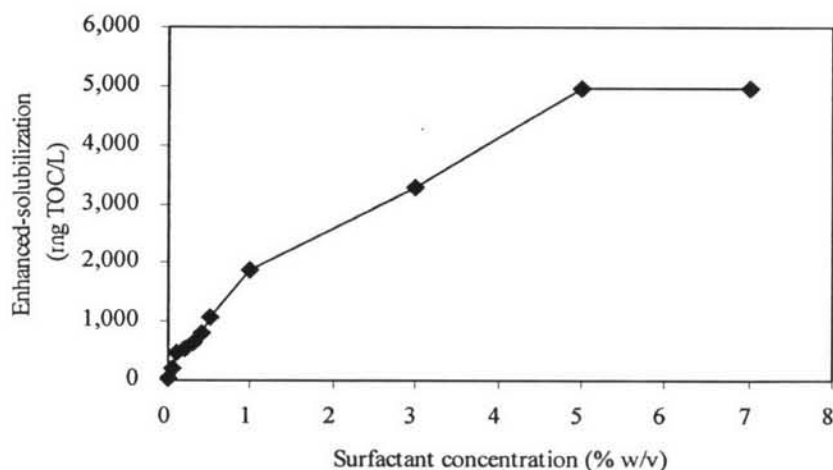
#### 4.2.2 Effect of Nonionic Surfactants on Solubilization of Hydrocarbons in Oil Sludge

In this study, the amount of extracted oil from oil sludge used was 1% w/v and the surfactant concentration was varied from 0.05 to 7% w/v in 20 ml of MSM in 4-dam vials. The results obviously showed that different emulsion phases occurred at different concentrations of surfactant. After 30 days, it was found that 0.1% w/v of Tween 80 provided the most stable emulsion phase than others concentration. However, all vials had 2 phases which were oil and aqueous phase as shown in Figure 4.5. At Tween 80 concentration of 0.05 to 3% w/v, all the oil did not solubilize completely as we can see the trace amount of oil remained in the upper phase. However, beyond the concentration of 5% w/v of Tween 80, all the oil could solubilize into the aqueous. From the results, it showed that the solubilized carbon increased with increasing surfactant concentration. Higher 5 % w/v of surfactant, all

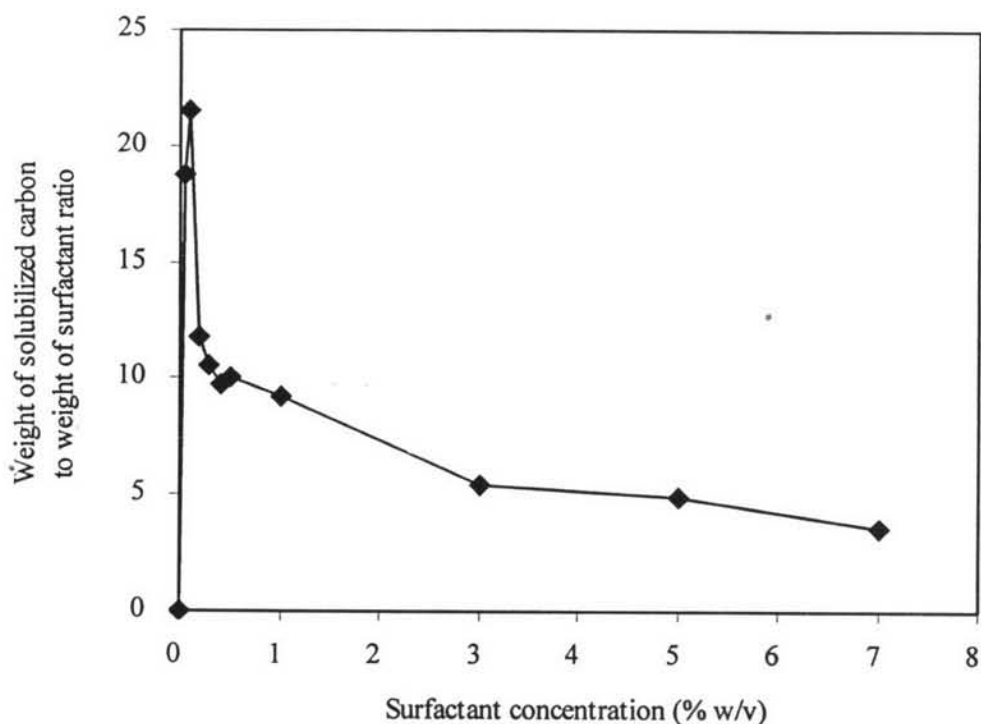
the oil at the concentration of 1% w/v could solubilize into aqueous phase and the enhanced total organic carbon in the aqueous phase was stable at 5,000 mg/l as shown in Figure 4.6. However, Figure 4.7 shows that the surfactant concentration of 0.1% w/v provided the highest ratio between the weight of solubilized carbon and the weight of surfactant compared with the other surfactant concentration. It means that this surfactant concentration was the most suitable to apply in the biodegradation study. Figure 4.6 and Figure 4.7 shows the enhanced-solubilization of hydrocarbons at the various concentrations and the weight of solubilized carbon to weight of surfactant ratio respectively.



**Figure 4.5** Phase study of 1% w/v of extracted oil from oil sludge with the varying concentration of nonionic surfactant from 0.05 to 7% w/v.



**Figure 4.6** The enhanced-solubilization of hydrocarbons at the various concentrations.



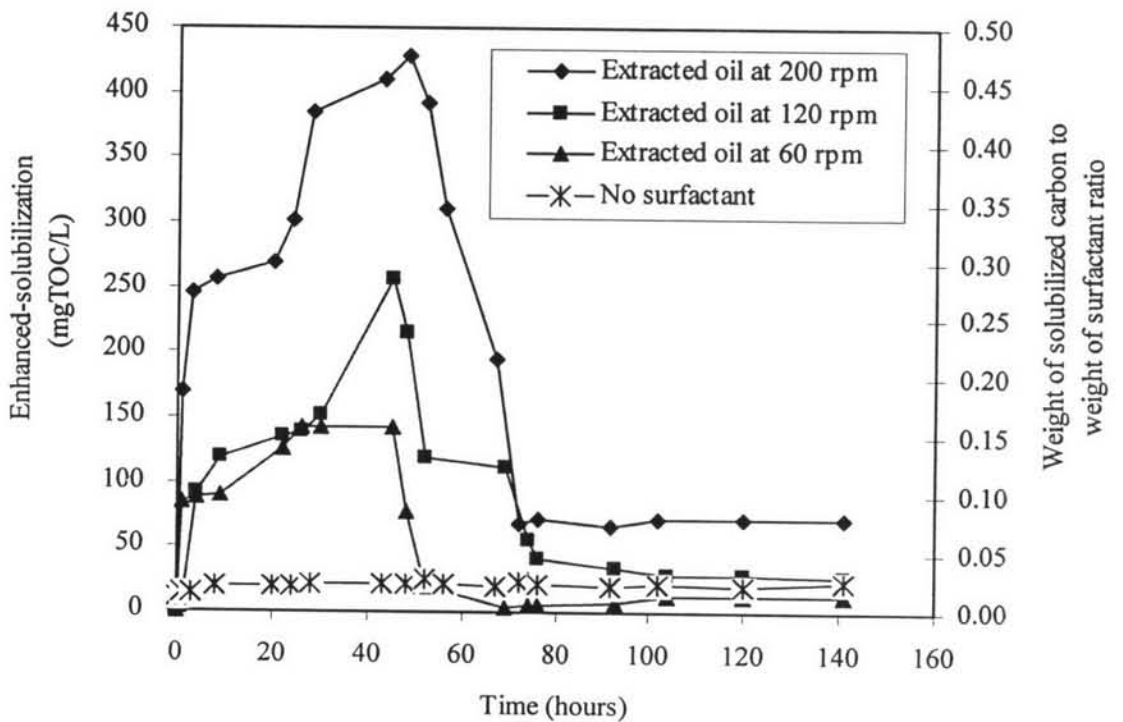
**Figure 4.7** The weight of solubilized carbon to weight of surfactant ratio.

#### 4.2.3 Determination of Suitable mixing Speed Required for Solubilization of Oil Sludge by Nonionic Surfactant System

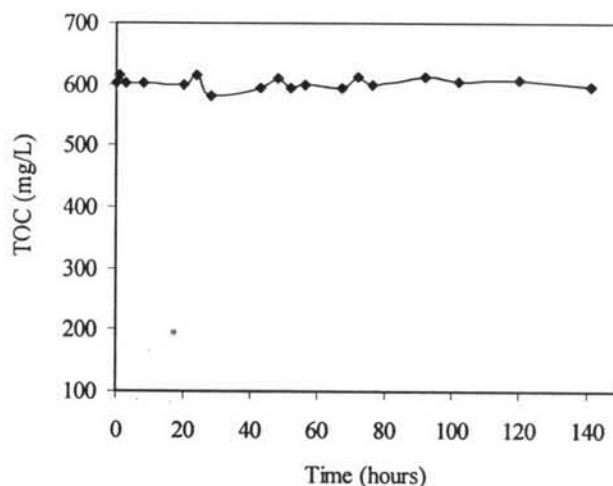
After the equilibration time of the enhanced-solubilization was studied, the effect of mixed was also need to be studied. Three mixing speeds, 60, 120, and 200 rpm, were chosen in this study. The procedure was the same as the enhanced-solubilization study using mixed surfactant. Figure 4.8 shows that the agitation speeds of 200 rpm provided the highest solubilization of hydrocarbon in the extracted oil from oil sludge. However, 48 hours the solubilization decreased in all systems studied. It might be due to the fact that the hydrocarbons did not solubilize entirely into the micelles but dispersed as the macroemulsion in the aqueous phase. At first, nonionic surfactant might adsorb on the oil droplets and each droplet could disperse the in the aqueous phase but the mixing energy was not intense enough to keep the system stable or equilibrium. Thus, oil droplets came back to stay in the oil phase. This phenomenon caused the oil phase and aqueous phase separate out from each other, leading to the decreased in the solubilization of hydrocarbons in the



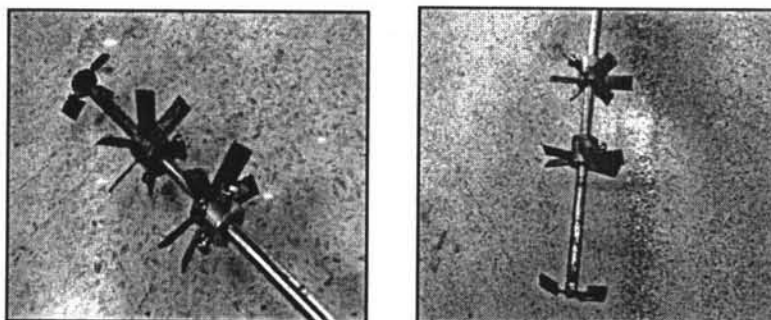
aqueous phase. It might be the type of stirrer was not design properly leading to the poor mixing into the system. For this reason when the time increased, each droplet might coalesce together and finally it would separate out of the aqueous phase and became the oil phase as the beginning. It could be noticed that the amount of solubilized carbon ratio increased with the high agitation speed or the effect of mixing in the system. Nonionic surfactant was not biodegraded by any microorganisms because Figure 4.9 shows that the amount of carbon in Tween 80 did not decrease with time. Thus, the coalescing of extracted oil did not occurred from the biodegradation of nonionic surfactant. Figure 4.10 shows the Characteristics of propeller that used in the enhanced-solubilization of extracted oil from oil sludge by nonionic surfactant.



**Figure 4.8** Contact time profile of the enhanced-solubilization at various agitation speeds. 1% w/v of extracted oil and 0.1% w/v of nonionic surfactant in 1,000 ml of MSM.



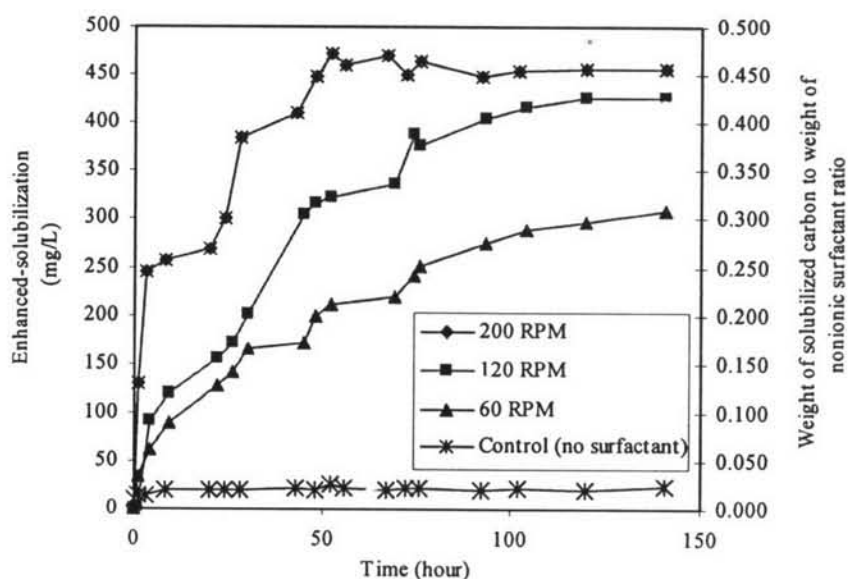
**Figure 4.9** Contact time profiles of the nonionic surfactant (Tween 80) with the mixing speed 200 rpm using TOC analyzer.



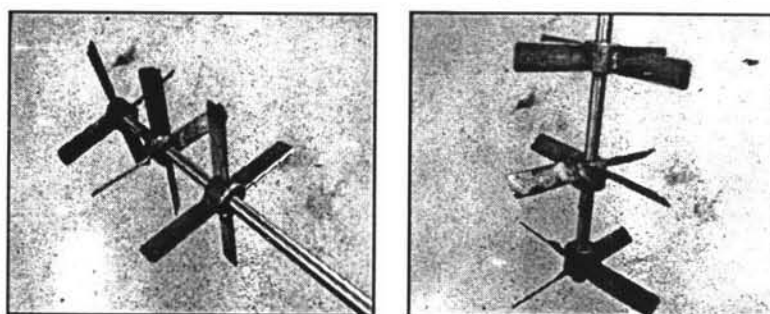
**Figure 4.10** Characteristics of the propeller using in the enhanced-solubilization of extracted oil from oil sludge by nonionic surfactant.

According to the assumption in mixing effect, stirrer had been changed to have more contact area in the mixing as shown in Figure 4.12. The new propeller provided the better mixing and also the higher energy of mixing. It forced oil droplets efficiently solubilized into the aqueous phase and finally reached the equilibrium. The 200 rpm agitation still was the best condition as same as the previous propeller. It provided 2 days to reach the maximum solubilization of hydrocarbons in the aqueous phase at about 450 mg/L. The other types of agitation speed were not the suitable conditions because they required time more than 2 days to reach the maximum solubilization and they also had the solubilized hydrocarbons in the aqueous phase less than the 450 mg/L. The weight of solubilized carbon to

weight of nonionic surfactant ratio was achieved at 0.45. It showed that pure nonionic system provided the better solubilization efficiency than the mixed surfactant system between nonionic and anionic surfactant, which achieved the ratio at only 0.275 (the result presents in the Appendix A). For this reason, the highest mixing speed was the best condition to use in the solubilization study. Because of the ability of microorganisms, the more hydrocarbons solubilized into the aqueous phase, the more carbon source for the microorganisms have. Figure 4.11 shows the amount of hydrocarbon solubilized into the aqueous phase using TOC analyzer.

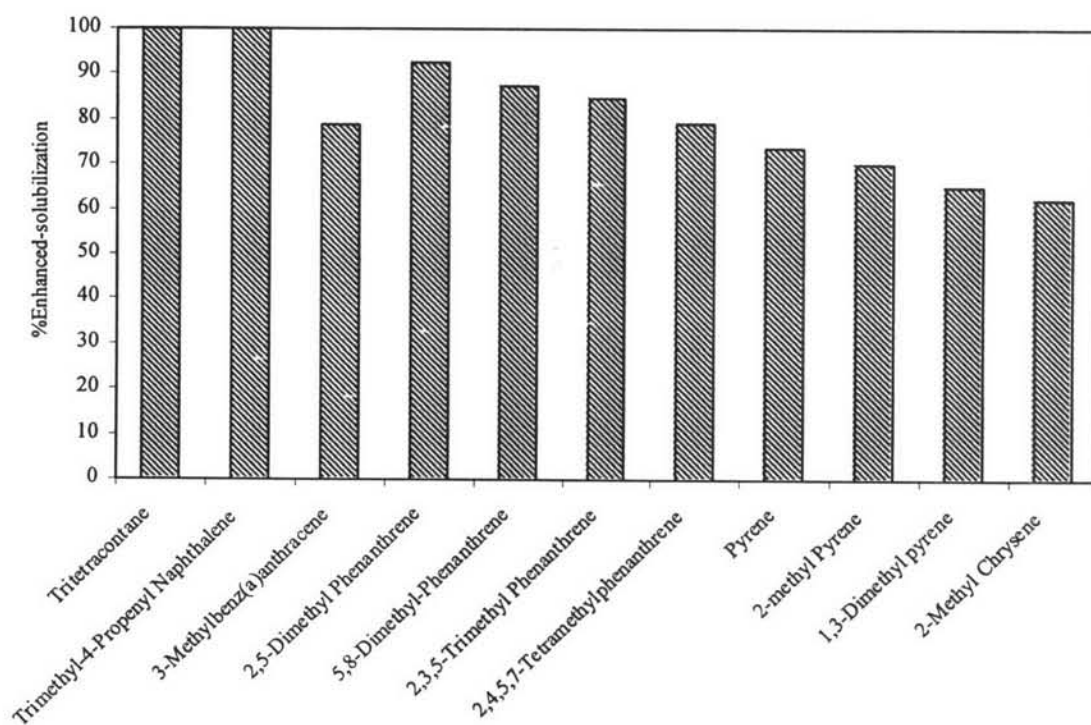


**Figure 4.11** Contact time profile of the enhanced solubilization of 1% w/v of extracted oil from oil sludge by 0.1% w/v nonionic surfactant system in 1,000 ml of MSM at the varied agitation speed using TOC analyzer and New propeller.



**Figure 4.12** Characteristics of the propeller using in the enhanced-solubilization of extracted oil from oil sludge by nonionic surfactant.

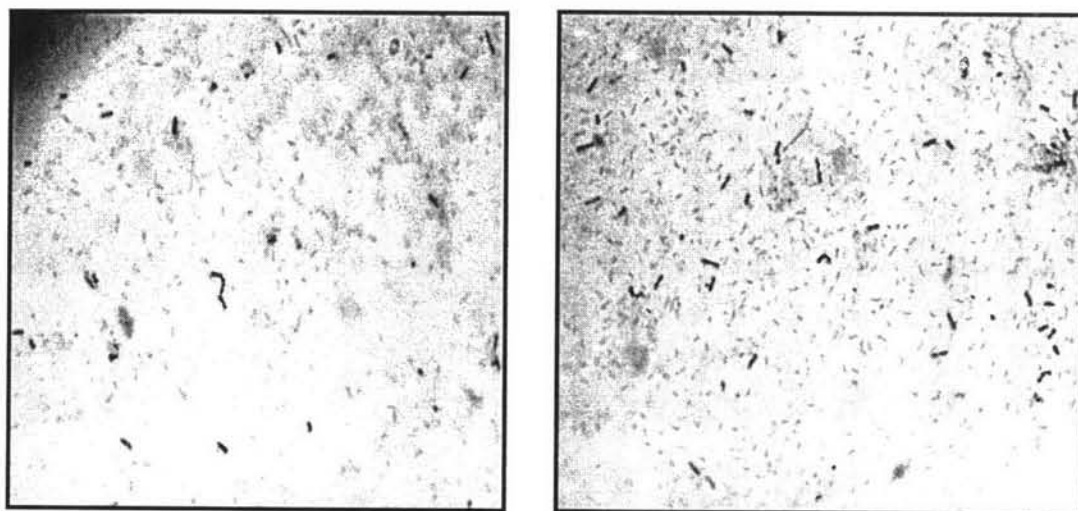
Figure 4.13 shows the extent of hydrocarbons that solubilized in the aqueous phase as analyzed by GC/MS. In the presence of Tween 80, the solubilization of Tirtetracontane and Naphthalene was 100% enhanced whereas Phenanthrene was enhanced close to 90% when compared to the control. PAHs with more than 3 rings were solublized into the aqueous phase just only 60-70% when compared to the control. The percent enhanced-solubilization decreased with the increasing number of rings in the structure. These components could further be degraded or utilized by the oil sludge degrader that was cultivated in the bioreactors.



**Figure 4.13** GC/MS results showing the percent enhanced-solubilization of various hydrocarbon present in oil sludge using Tween 80.

### 4.3 Cultivated Microorganisms

The mixed culture of oil sludge degrader was taken to analyze the type of microorganisms by using the Gram Stain method, which can be seen under (1,000x) magnified microscope. In general, two kinds of the gram negative and gram positive bacteria were observed. Figure 4.14 shows the 2 different types of microorganisms present in the oil sludge which are gram negative and gram positive bacteria. Red color expresses the gram negative bacteria, which is the main microorganisms in the bioreactors. They were the rod and round shape with different sizes depend on their growth. This study was not intended to specify species of the microorganisms, but rather to show the postures of the oil sludge degraders. As this work focused on the biodegradation of oil sludge, the identification may be done in the future study.



**Figure 4.14** 1,000 times recorded microscopy pictures of the oil sludge degrader in bioreactors using gram-stain method.

## 4.4 Biodegradation Study

### 4.4.1 Total Petroleum Hydrocarbon Extraction (TPH)

In the biodegradation study, the effect of oil loading was first examined by varying amount of oil loading from 1 to 10 kg/m<sup>3</sup>d. The results were quantified by 4 methods, which are: Total Petroleum Hydrocarbons Extraction (TPH); Chemical Oxygen Demand (COD); Total Organic Carbons (TOC), and Dry Weight Cells methods. For the TPH extraction, it was shown that the biodegradation efficiencies decreased with increasing oil loading. The lowest of oil loading (1 kg/m<sup>3</sup>d) in the presence of Tween 80 in MSM showed more than 95% TPH removal efficiency compared to the control (no surfactant) as shown in Figure 4.15 and 4.16. The hydrocarbons were utilized by the microorganisms cultivated inside the reactors as a carbon source for their growth. However, it still had the trace amount of oil remain undegraded, which likely were polycyclic aromatics hydrocarbons (PAHs) with more than 2 rings e.g., phenanthrene, pyrene, and chrysene. These components are very stable in the nature and require a long time to be degraded by the degrading microorganisms. It can be seen that the percent TPH removal decreased with increasing oil loading in the system. The higher the oil loading, the more oil remained in the system. When increasing oil loading to 10.0 kg/m<sup>3</sup>d, it showed that the ability to utilize carbon source of mixed cultures was only about 320-330 mg/L per day. The percent TPH removal decreased from 95 to 53% when increased the oil loading from 1.0 to 10.0 kg/m<sup>3</sup>d respectively. Figure 4.17 shows the average of percent TPH removal of oil loading 1.0 to 10.0 kg/m<sup>3</sup>d.

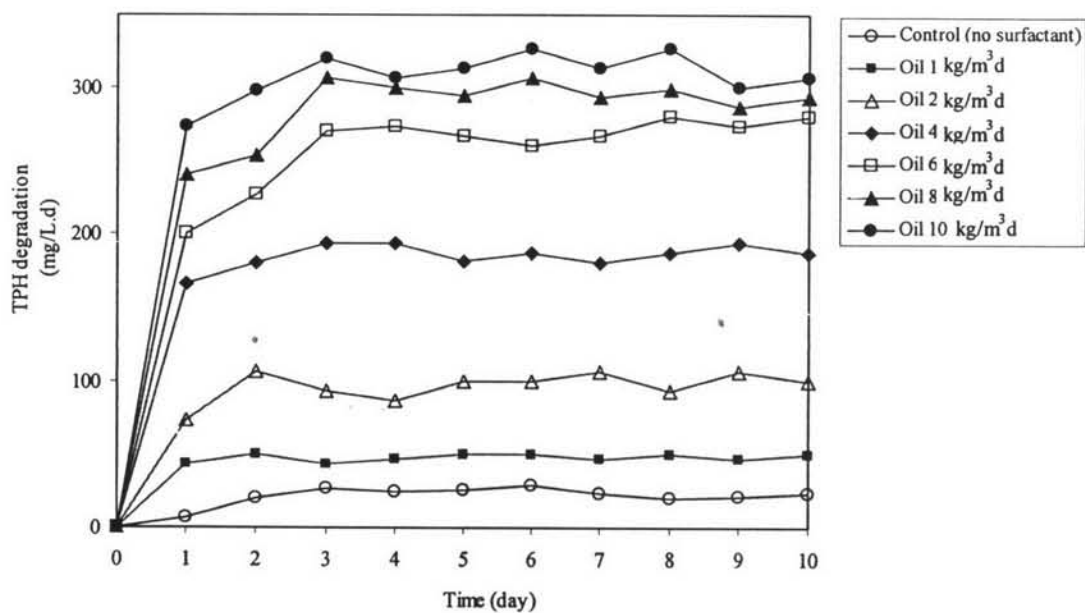


Figure 4.15 The TPH degradation of oil loading from 1.0 to 10.0 kg/m<sup>3</sup>d.

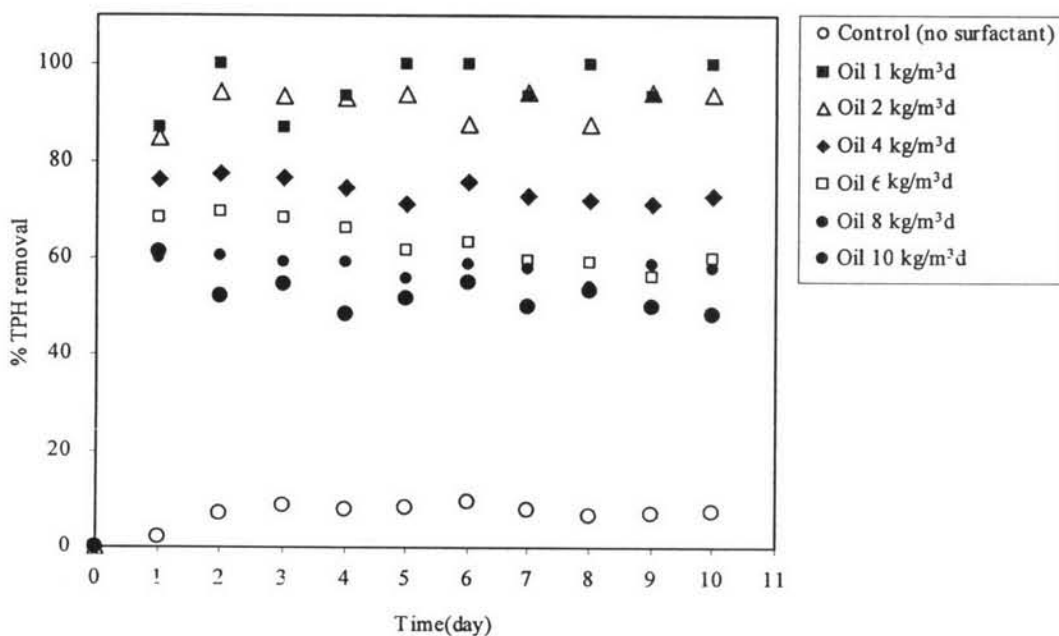
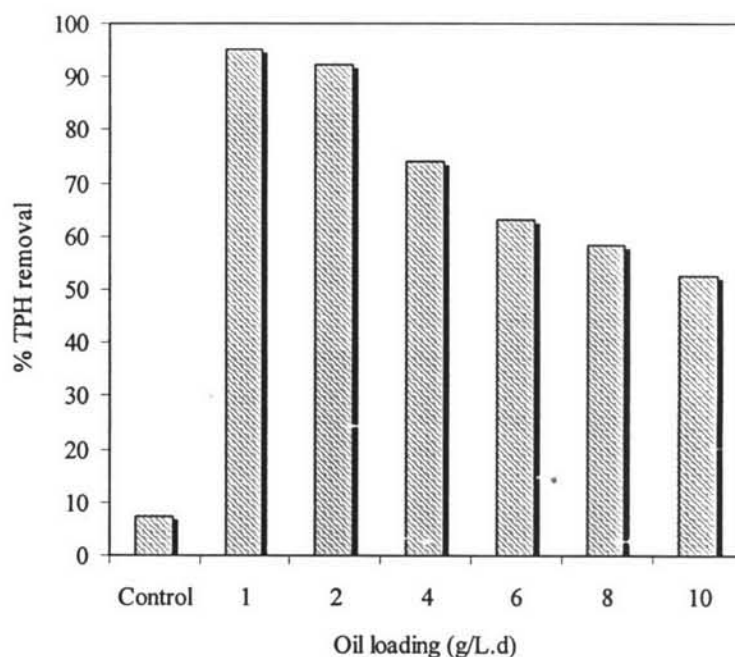


Figure 4.16 The percent TPH removal of oil loading 1.0 to 10.0 kg/m<sup>3</sup>d.

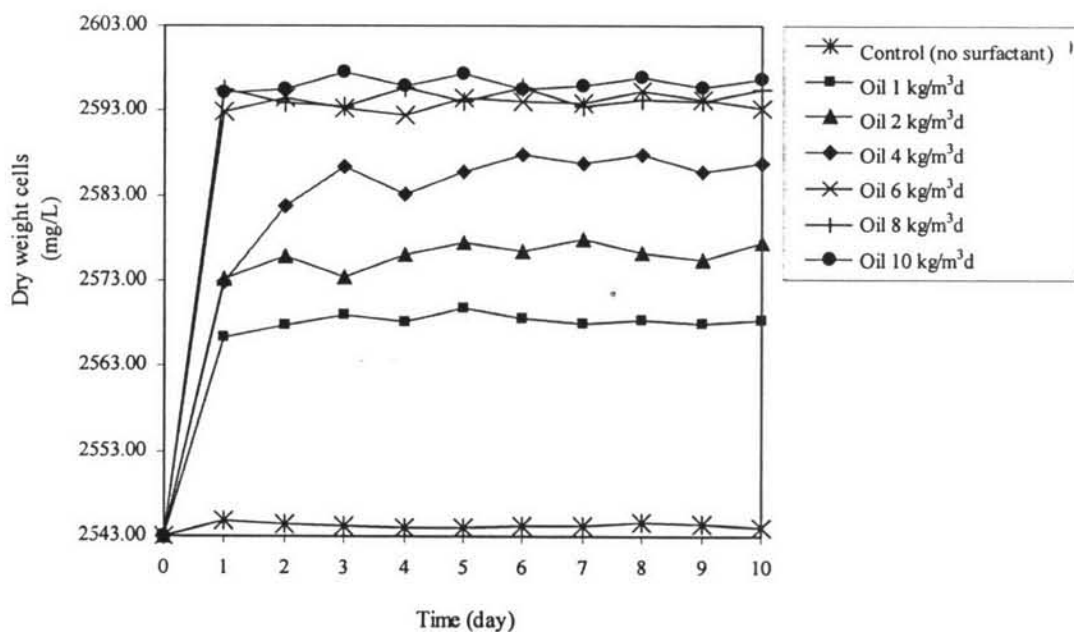


**Figure 4.17** The average percent TPH removal for oil loading of 1.0 to 10.0 kg/m<sup>3</sup>d.

#### 4.4.2 Dry Weight Cell Analysis

The dry weight cell method was performed in order to quantify the growth of the microorganisms inside the reactors. The initial cell mass before the biodegradation was about 2,000 mg/L. After the oil was loaded into the bioreactor the growth of the microorganisms came from the utilization of the hydrocarbons in the extracted oil from oil sludge. Figure 4.18 shows the increased dry weight cell of the microorganisms inside the reactors as the oil loading increased. The results show that the growth was quite proportional to the oil loading. Nevertheless, too high oil loading was not accommodated by the microbes cultivated in the in a short time period as the increase in dry weight cell was relatively small when compared to those at lowing oil loading. The increase in the dry weight of the microorganisms was in the range of 2,655 to 2,600 mg/L for 1.0 to 10.0 kg/m<sup>3</sup>d of oil loading respectively.

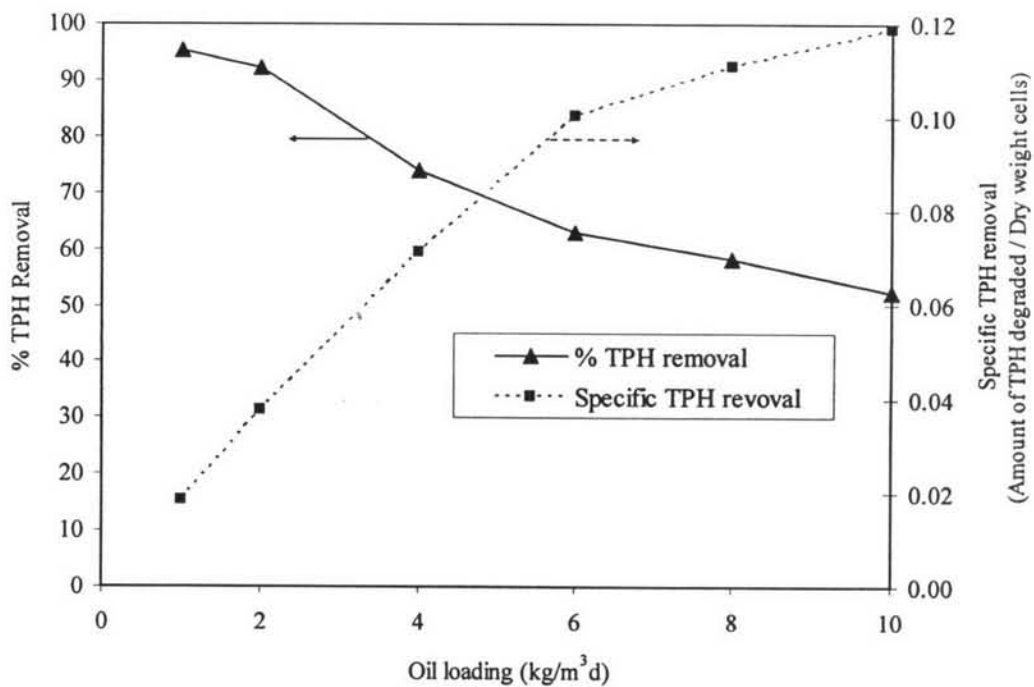




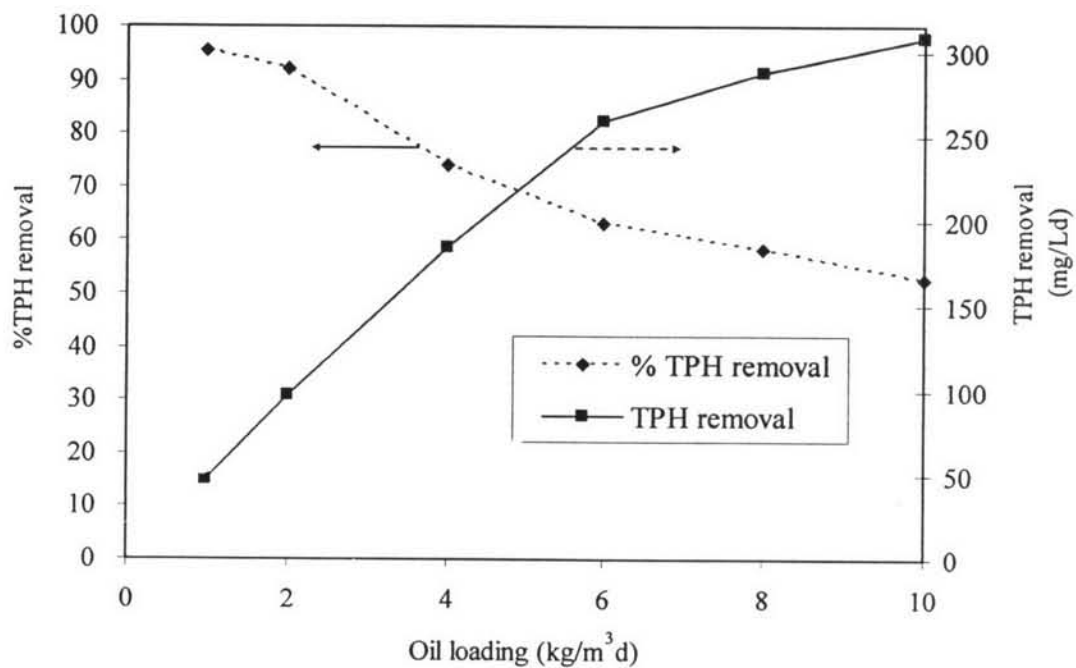
**Figure 4.18** Growth of the indigenous microorganisms at various oil loadings from oil 1.0 to 10.0 kg/m<sup>3</sup>d.

#### 4.4.3 The relation between %TPH removal and specific TPH removal

From the TPH degradation and the growth of the microorganisms, the specific TPH removal could be calculated, which was defined as the degradation capabilities per a unit cell mass. Figure 4.20 shows the plots of percent TPH removal with the specific TPH removal and percent oil removal with the amount of TPH removal, the specific TPH removal was increased with increasing of oil loading and then it became quite constant at high oil loading. The %TPH removal was decreased with increasing of oil loading. If the operation required high %removal efficiency, low oil loading should be selected. Thus, the maximum quantity of oil feed should not exceed 4.0 kg/m<sup>3</sup>d in the 50 ml fill and draw operation. The oil loading in the range of 1.0 to 4.0 kg/m<sup>3</sup>d should be performed in this SBR process because at high oil loading the specific TPH removal was decreased. It's not necessary to operate at the high oil loading because the microorganisms had the limitation to treat polycyclic aromatic hydrocarbons. Figure 4.21 shows the relation between %TPH removal and specific TPH removal and the capability of removing extracted oil from oil sludge at the various organic loading respectively.



**Figure 4.19** The relation between %TPH removal and specific TPH removal.



**Figure 4.20** The capability of removing extracted oil from oil sludge at various organic loadings.

#### 4.4.4 COD Method

The COD method was conducted to determine the degradation capability of the microbe in utilizing organic substances as their nutrients, which is usually used to measure the wastewater treatment efficiency. Each organic loading has different chemical oxygen demand (COD) and COD is always higher than TOC because it also represents other nutrients in the system. COD include TOC and other nutrients in the system and show in the demanding of oxygen within each organic concentration. Table 4.3 shows the amount of chemical oxygen demand in each organic loading.

**Table 4.2** The chemical oxygen demand in the organic loading from 1 to 10 kg/m<sup>3</sup>d

Oil loading (g/L.d)	COD (mg/L)
Control	1,784
1	2,225
2	2,621
4	3,050
6	3,450
8	4,053
10	4,623

The maximum ability of microorganisms to treat the organic substances was about 3,200 mg/L. The biodegradation in the low organic loading provided the high COD removal to as high as 90% whereas the removal efficiency in high oil loading decreased to 70%. Initially, the capability of degrading organic in the range of 1.0 to 6.0 kg/m<sup>3</sup>d increased as shown in Figure 4.21. When the experiment applied high oil loading above 6 g/L.d, the microorganisms could utilize the organic substances at quite the same values as in the low organic loading and Figure 4.22 represents to the average COD influent and effluent in the various organic loading. This phenomenon might because the microorganisms had the biodegradation limit for treating organic substances at 3,200 mgCOD/L. It might require time more than a day to degrade organic substances at the high oil loading. Low oil loading: 1.0 to 6.0 kg/m<sup>3</sup>d provided the higher COD removal than beyond the 6 kg/m<sup>3</sup>d oil loading as shown in Figure 4.23. The maximum utilization

capability of the microorganisms was at about 3,200 mgCOD/L.d, so the organic loading above 3,200 mg COD/L was too much for the microbes. The oil loading in of 1.0 to 5.0 kg/m<sup>3</sup>d was the most appropriate organics loading, so it might be a supported reason that made the COD removal similar to the TPH removal.

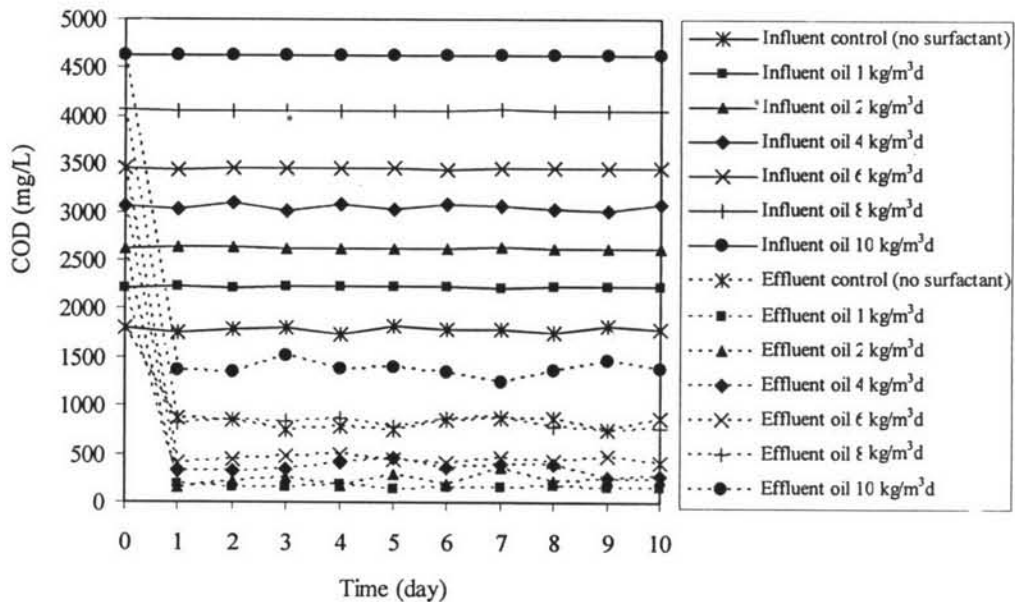


Figure 4.21 COD influent and effluent in the various organic loading.

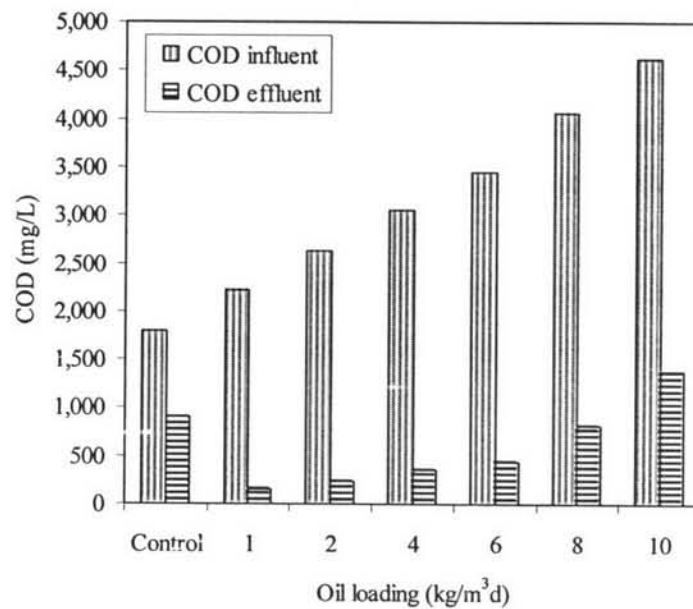
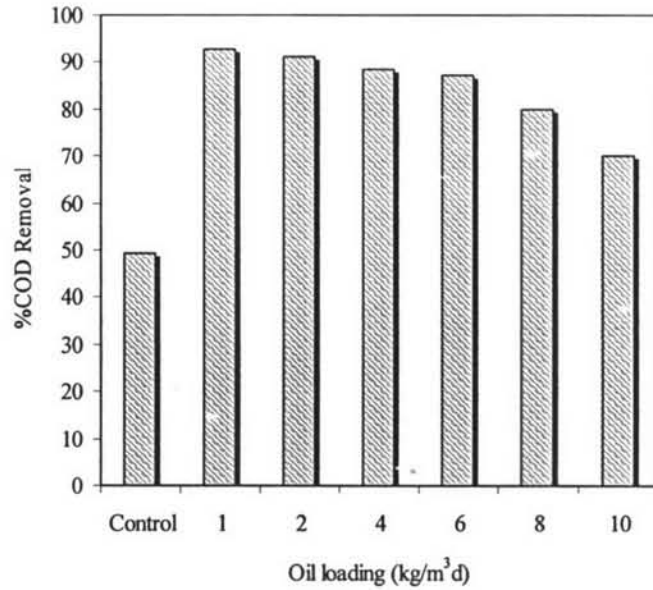


Figure 4.22 The average COD influent and effluent in the various organic loading.



**Figure 4.23** The percent COD removal in the various organic loading.

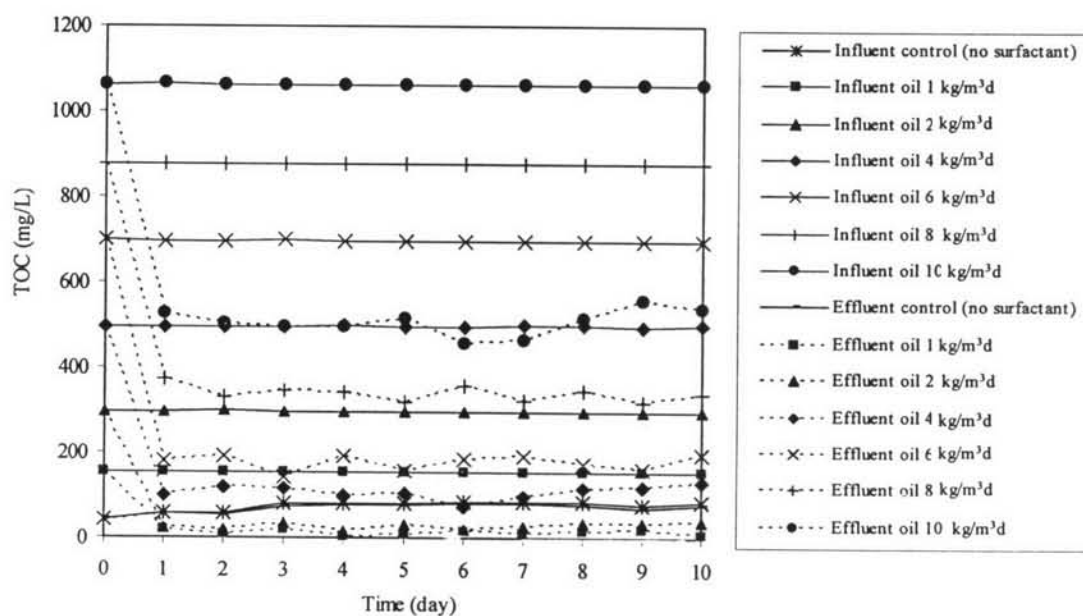
#### 4.4.5 TOC Method

TOC method indicated the amount of carbon that it was utilized in the study and the trend of results was close to the COD method. The number of carbons in the varied oil loading came from the sampling in aqueous solution. They were injected into the TOC analyzer before fed into the bioreactor. The mass balance was needed to calculate the added and disappeared carbons and Table 4.4 shows the average organic carbon on the varied organic loading.

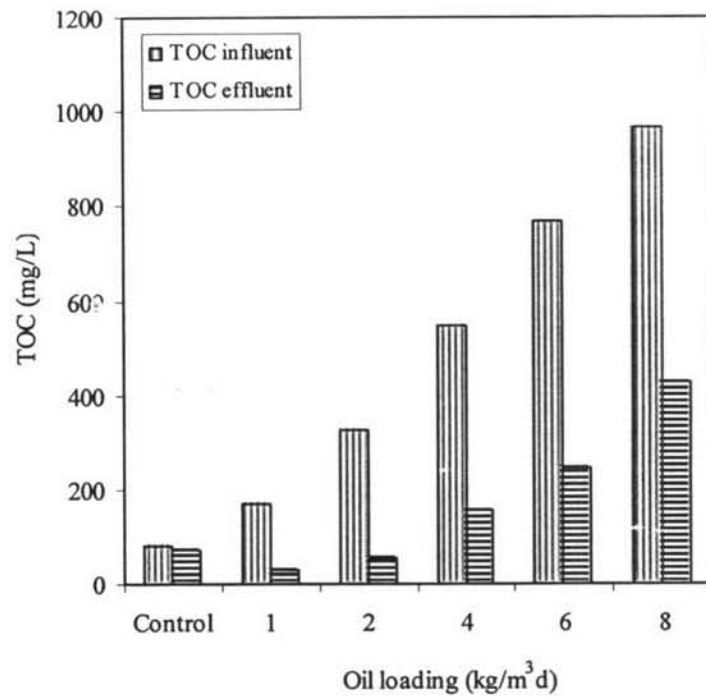
**Table 4.3** The amount of enhanced-solubilized carbons in the aqueous phase at the varied condition before added into the bioreactors

Oil loading (g/L.d)	TOC (mg/L)
Control	81
1	155
2	298
4	498
6	678
8	878
10	1060

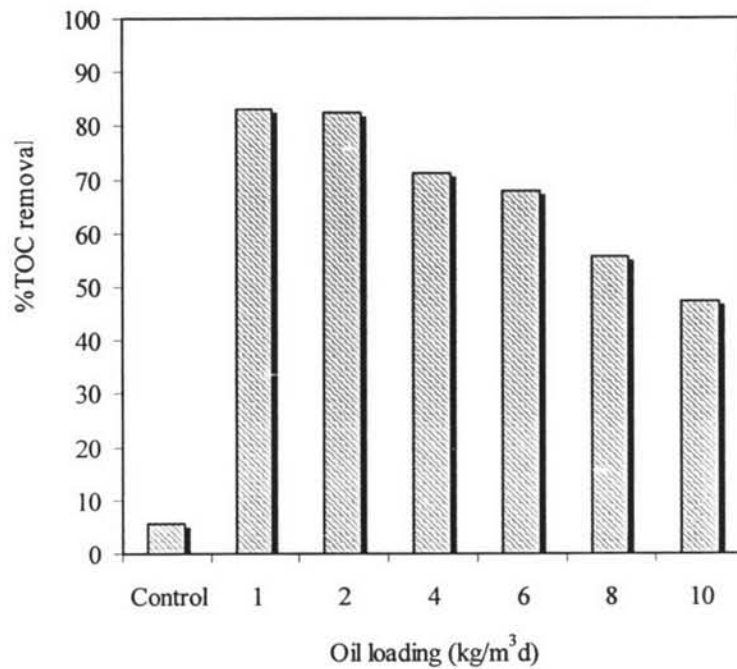
After the biodegradation, the microorganisms had the maximum capability to degrade carbon atoms about 550 mg/L.d in the range of organic loading from 1.0 to 10.0 kg/m<sup>3</sup>.d. Figure 4.24 shows TOC influent and effluent of the various organic loading and Figure 4.25 shows the average TOC influent and effluent of the various organic loading. It showed that too high oil loading had the effect to the system because the rest of carbon source remained a lot in the bioreactors. The microbes could only utilize the carbon sources at maximum about 550 mg per day, thus above the oil loading that had TOC values above 550 mg/L was not suitable in this process. Most of the hydrocarbons were long chain alkane and the polycyclic aromatic hydrocarbons more than 2 rings. They were not only very stable in the environments but they were also carcinogenic compounds i.e. phenanthrene, pyrene or chrysene. Not surprisingly that why the microorganisms could utilize organic carbon at maximum about 550 mg/L per day, stability of the PAHs forced the microorganisms to require a long time in the biodegradation process. The percent TOC removal was shown in Figure 4.26.



**Figure 4.24** TOC influent and effluent of the various oil loading.

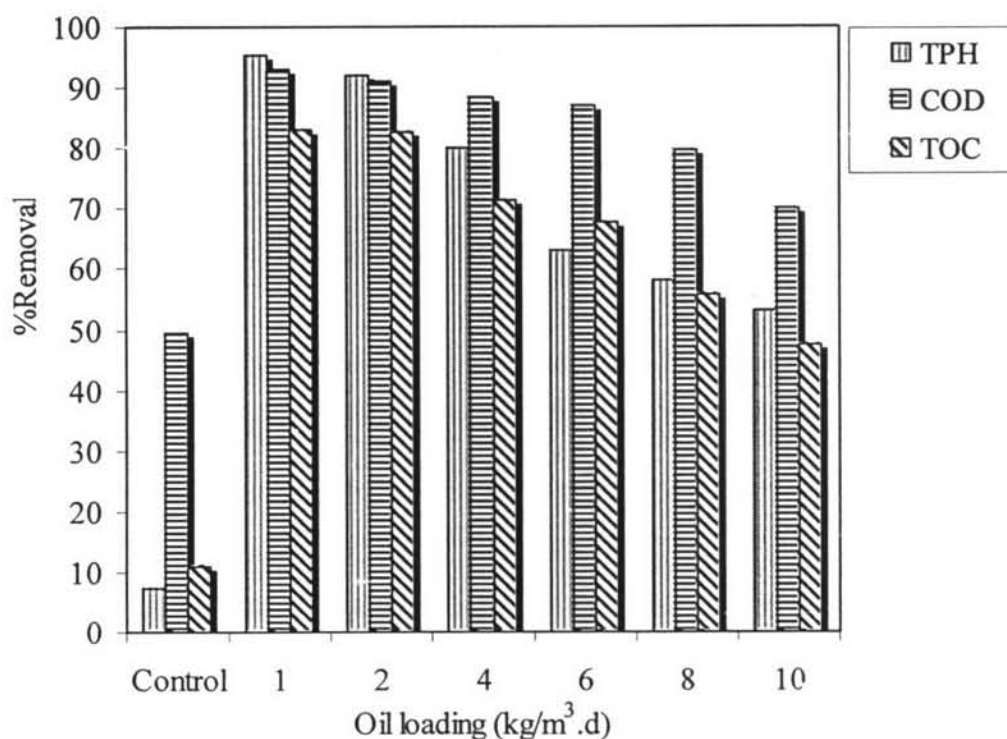


**Figure 4.25** The average TOC influent and effluent in the various organic loading.



**Figure 4.26** The percent TOC removal in the various organic loading.

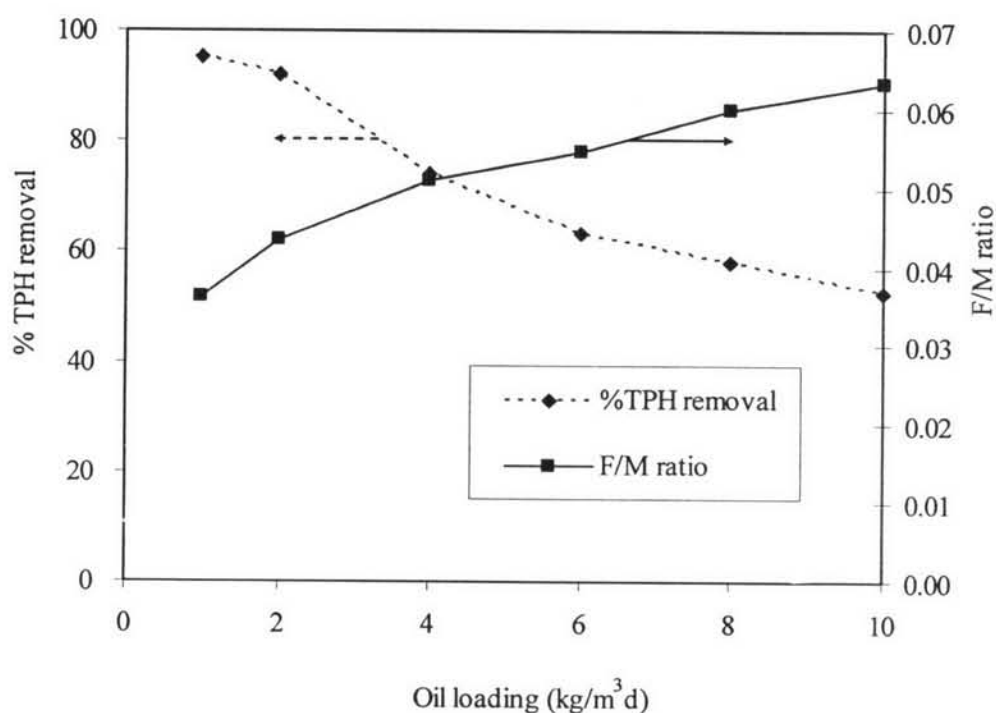
All of the results showed the corresponding between TOC, COD and TPH extraction as shown in Figure 4.27 and they gave the same trend that the system was optimized at the range of organic loading from 1.0 to not higher than 4.0 kg/m<sup>3</sup>.d. This range provided the most appropriate quantity of nutrients or the amount of carbon and other minerals in the aqueous phase to the microorganisms. Too high chemicals influent might disturb and obstruct the utilization of microorganisms as they had a limitation on the biodegradation capability. COD showed the highest percent removal compared to TPH and TOC. It because COD included the mineral salts in the organic loading and the microorganisms could utilize this mineral for their living. The results showed that oil loading at 1.0 to 2.0 kg/m<sup>3</sup>.d represents the 80% removal in all measurement and gradually decreased when oil loading increased beyond the 2.0 kg/m<sup>3</sup>.d.



**Figure 4.27** The percent removal of TPH, COD and TOC at the various organic loading.



Finally, the all of organic loading were food for the microorganisms inside the bioreactors, hence the amount of food per the number of microorganisms was necessary to calculate. The amount of food per the number of microorganisms was called the F/M ratio. This ratio showed the amount of food to the microbes whether it proper or not. If the ratio was close to 0.1, it expressed the suitable organic loading to the microorganisms. Figure 4.28 shows the F/M ratio and % oil removal in each condition of organic loading and it showed that the F/M ratio increased with the increasing amount of oil loading. Although the F/M ratio did not reach the 0.1 but the system could not accept the oil loading higher than 10 g/L.d. Because all of the oil was not degraded in one day and it resulted in the accumulation of oil inside the bioreactors. For this reason, the high quantity of oil was not appropriate to the system, although it made the F/M ratio higher than the others. However, the way to solve the problems might be increasing the other mineral salts instead of oil. The oil loading should be in the range of 1.0 kg/m<sup>3</sup>d to maximum at 4.0 kg/m<sup>3</sup>d and increased the other nutrients instead of oil into the system.



**Figure 4.28** The F/M ratio of the ail organic loading per day.

#### 4.5 Surfactant Degradation

The surfactant solution was fed to study the biodegradation of surfactant in various concentration the same as in the hydrocarbon biodegradation conditions. Surfactant was used as a carbon source of microorganisms about 1 month before feeding these concentrations of surfactant into the bioreactors to study its biodegradation. To do this because the nutrients inside bioreactors must be changed to have only the carbon source from surfactant itself not from glucose or others. Table 4.5 shows the various concentrations of surfactant solution that was fed into the bioreactors.

**Table 4.4** Conditions in surfactant degradation study

Tween 80 (g)	Total volume with MSM (L)	TOC (mg/L)	Surfactant loading (kg/m <sup>3</sup> d)
0.1	1.0	63	0.1
0.2	1.0	133	0.2
0.4	1.0	253	0.4
0.6	1.0	375	0.6
0.8	1.0	493	0.8
1.0	1.0	610	1.0

\* Fill 50 ml, Draw 50 ml, Reaction time = 23 hours

Figure 4.29 shows that the biodegradation of nonionic surfactant (Tween 80) was in the range of 50 to 70 mg/Ld. Low concentration of surfactant had a possibility to degrade much more than surfactant at higher concentration. Because of long molecular structure of polyoxyethylene sorbitan monoleate (Tween 80), it probably resulted in small degradation by microorganisms when increasing its concentration. Thus, the percent degradation as shown in Figure 4.30 decreased steadily when increasing the surfactant concentration. The lowest concentration was degraded about 40% from its total carbon whereas the others was degraded only 10 to 20% depending on its concentration. The higher the concentration, the lower the percent degradation was. However, when compared the terminated carbons from

hydrocarbons with terminated carbon from surfactant, the amount of carbon from hydrocarbons was much more degraded than the carbon from surfactant. This phenomenon might be due to the fact that polyoxyethylene sorbitan monooleate (Tween 80) have high molecular weight (1,310 g/g.mole) but the hydrocarbons from oil sludge just high as maximum at 604 g/g.mole. It could be cleared that microorganisms preferred to utilize carbon from oil sludge more than carbon from surfactant.

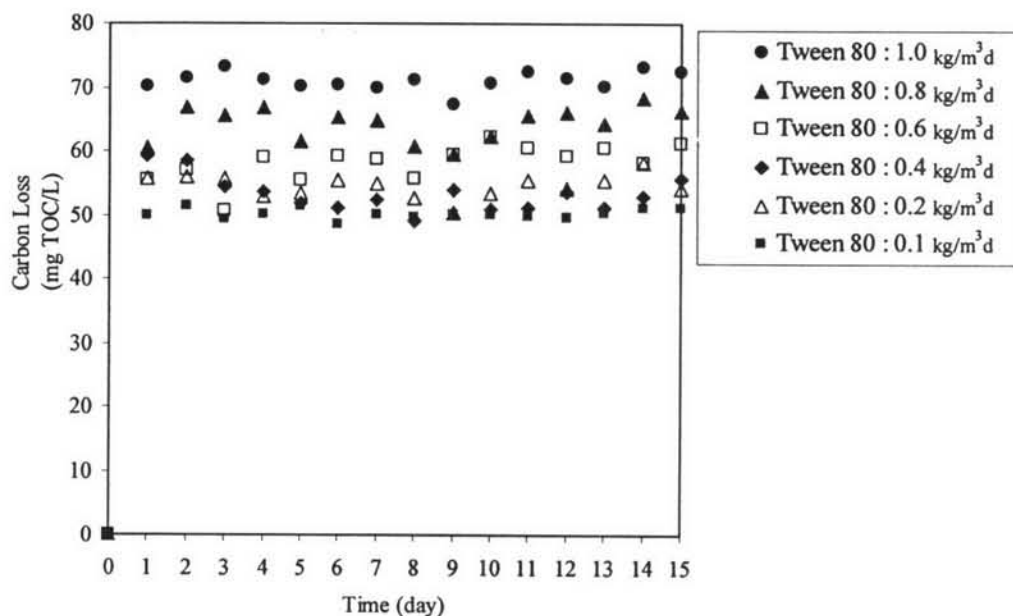


Figure 4.29 Surfactant degradation profiles.

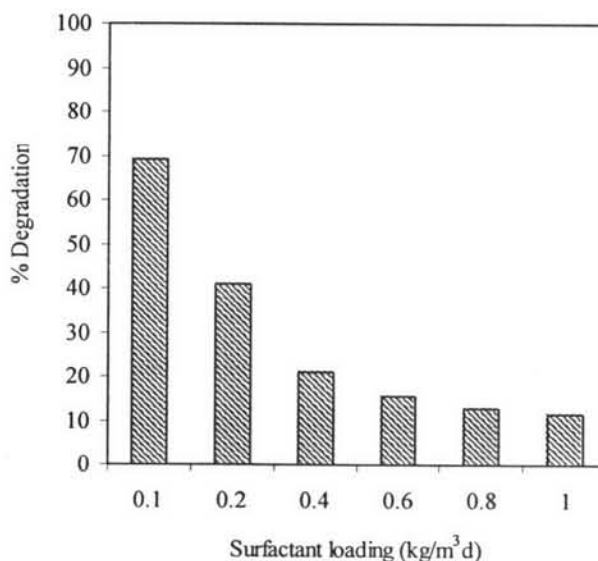
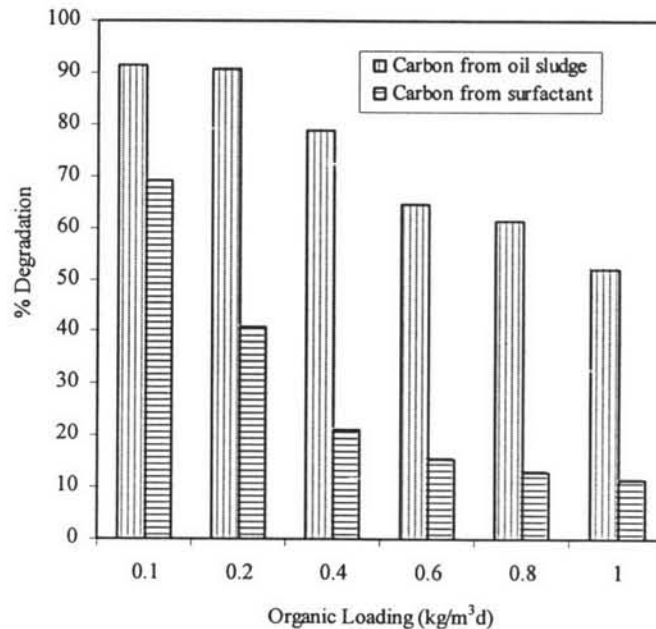


Figure 4.30 The average percent surfactant degradation.

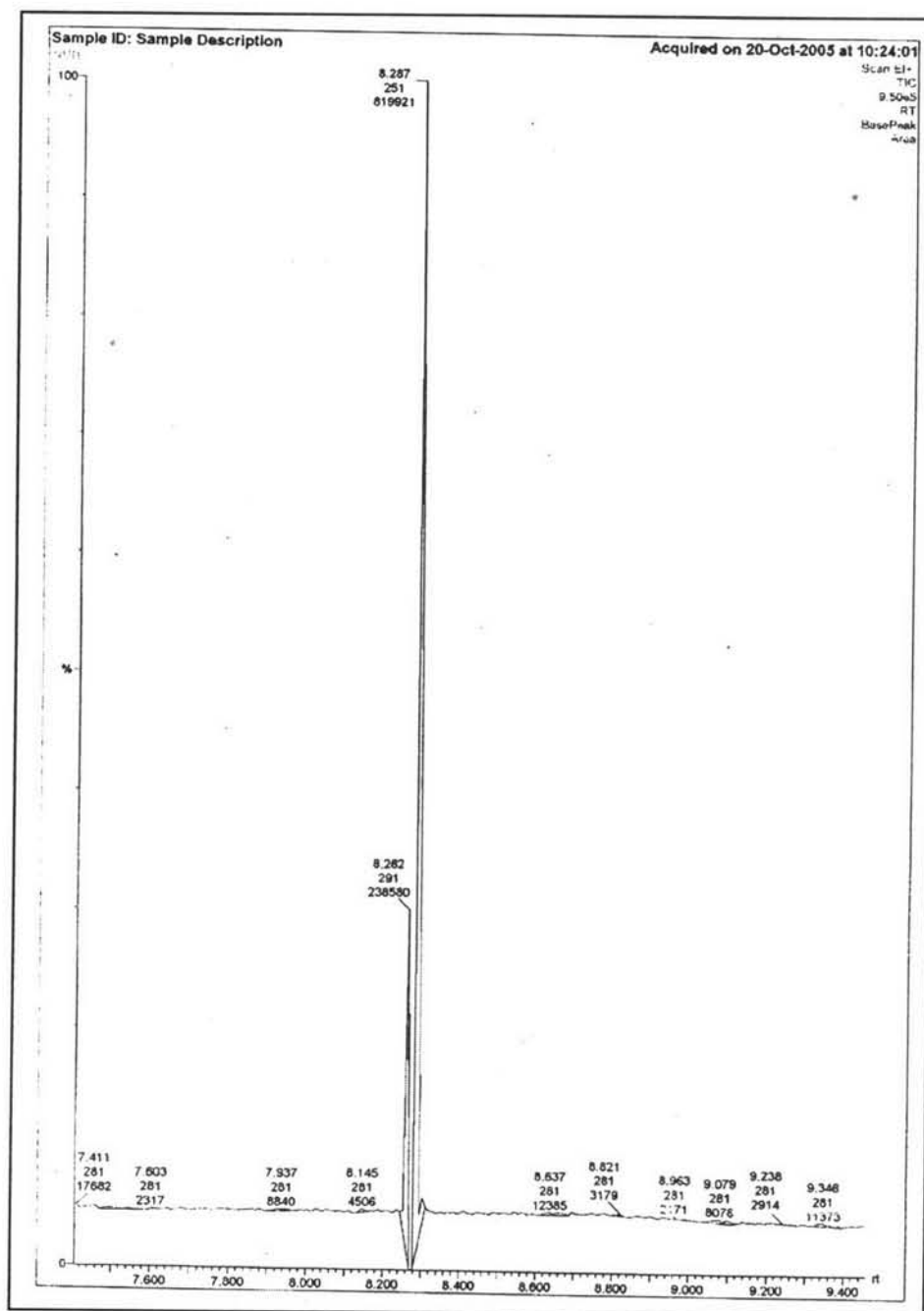
When did a comparison between hydrocarbon degradation and surfactant degradation, the TOC results show the microorganisms preferred to degrade carbon from oil sludge much more than carbon from surfactant as shown in Figure 4.31. This result was an advantage to the surfactant-enhanced biodegradation of oil sludge because microorganisms focused on the biodegradation of oil sludge not from surfactant. If the surfactant was degraded more than hydrocarbons, the hydrocarbons would not be solubilized into the aqueous phase but it would separate as an oil phase on the top of solution. This effect might occur in some kind of surfactant but not for Tween 80. Tween 80 was very suitable surfactant to aid the biodegradation of oil sludge.



**Figure 4.31** The percent degradation of carbon from oil sludge and carbon from surfactant in various organic loading.

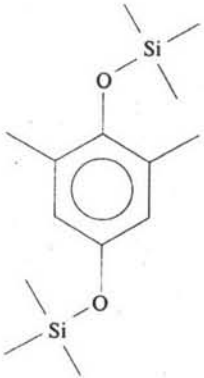
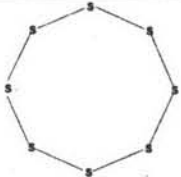
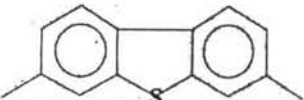
The hydrocarbon in the oil sludge was utilized by microorganisms and the rest of hydrocarbon that hard to degrade were the hydrocarbon bond with silicon oxide, Cyclic Octatomic Sulfur, and 2,8-Dimethyl Dibenzothiophene. These components presented in the treated organic solution, which passed the degradation process for 2 weeks. The treated organic solution was analyzed by GC/MS to see

what component still presented. Figure 4.32 shows the result from GC/MS expresses the rest of treated organic solution after degradation process for 2 weeks.



**Figure 4.32** Result from GC/MS expresses the rest of treated organic solution after degradation process for 2 weeks.

**Table 4.5** The remained components of hydrocarbon from oil sludge

Type of hydrocarbons after biodegradation	Pictures of hydrocarbons after biodegradation	Molecular weight	% Remaining after treatment
2,6-Dimethyl-1,4-Siloxy Benzene		281	8.19
Cyclic Octaatomic Sulfur		242	0.13
2,8-Dimethyl Dibenzothiophene		212	0.15