

DIESEL REMOVAL EFFICIENCY IN SOIL WASHING PROCESS BY MIXED SOLUTION OF  
NONIONIC SURFACTANT AND BIOSURFACTANT



A Thesis Submitted in Partial Fulfillment of the Requirements  
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ประสิทธิภาพในการบำบัดเชื้อในดินด้วยกระบวนการล้างโดยใช้สารละลายผสมที่ประกอบด้วยสาร  
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ปาจารย์ บุญยงไทย : ประสิทธิภาพในการบำบัดดินด้วยกระบวนการล้างโดยใช้สารละลายผสมที่ประกอบด้วยสารลดแรงตึงผิวชนิดไม่มีประจุและสารลดแรงตึงผิวชีวภาพ. ( DIESEL REMOVAL EFFICIENCY IN SOIL WASHING PROCESS BY MIXED SOLUTION OF NONIONIC SURFACTANT AND BIOSURFACTANT) อ.ที่ปรึกษาหลัก : ผศ. ดร.จันทรา ทองคำเกา, อ.ที่ปรึกษาร่วม : ดร.ณัฐพงศ์ ดันตวิวัฒน์พันธ์

ในการศึกษาครั้งนี้ได้ทำการผสมสารละลายลดแรงตึงผิวชนิดไม่มีประจุ Tween 80 และสารละลายลดแรงตึงผิวชีวภาพ 3 ชนิด ได้แก่ แรมโนลิปิด (ชนิดประจุลบ), ซาฟอนิน และ ลิโปเปปไทด์ เพื่อพัฒนาสูตรสารละลายลดแรงตึงผิวชนิดผสมที่มีความเหมาะสมกับการใช้งาน สารละลายลดแรงตึงผิวชนิดผสมเตรียมที่ความเข้มข้นรวมเท่ากับ 5% w/v ของปริมาณเนื้อสาร โดยมีสัดส่วนของ Tween 80 ต่อสารละลายลดแรงตึงผิวชีวภาพ ในอัตราส่วน 9:1, 8:2 และ 7:3 ของความเข้มข้นรวมและมีการวัดค่าจุดวิกฤตของการเกิดไมลเซลล์ (critical micelle concentration, CMC) ของสารลดแรงตึงผิวผสมที่สัดส่วนต่างๆ รวมทั้งวัดค่าแรงตึงผิวสัมผัสระหว่างสารลดแรงตึงผิวและดีเซล (Interfacial tension, IFT) และนำมาเปรียบเทียบกับค่าทั้งสองนี้ในระบบสารลดแรงตึงผิวเดี่ยว ผลการศึกษาที่ได้พบว่า สารลดแรงตึงผิวชนิดผสม Tween 80 และ ลิโปเปปไทด์ ในอัตราส่วน 9:1 มีค่าแรงตึงผิวระหว่างสารลดแรงตึงผิวและดีเซลต่ำที่สุด ซึ่งต่ำกว่าถึง 10 เท่าเมื่อเปรียบเทียบกับการใช้สารลดแรงตึงผิวแบบเดี่ยว สำหรับค่าจุดวิกฤตของการเกิดไมลเซลล์ สารลดแรงตึงผิวแบบผสมทุกสัดส่วนแสดงค่าวิกฤตของการเกิดไมลเซลล์ที่ต่ำกว่าสารลดแรงตึงผิวชีวภาพแบบเดี่ยว แต่ยังมีค่าสูงกว่าสารลดแรงตึงผิว Tween 80 แบบไม่ผสม ในการศึกษาต่อมาสารลดแรงตึงผิวผสมระหว่าง Tween 80 และ ลิโปเปปไทด์ถูกเลือกมาศึกษาผลของการผสมสารลดแรงตึงผิวชีวภาพลิโปเปปไทด์ต่อการดูดซับของ Tween 80 บนดินและประสิทธิภาพในการล้างน้ำดีเซลในดินแต่ละชนิด จากการศึกษาพบว่า สารลดแรงตึงผิวชนิดผสมสามารถลดการดูดซับของ Tween 80 ลงบนดินได้ดีกว่าเมื่อเปรียบเทียบกับการใช้สารลดแรงตึงผิวแบบเดี่ยว Tween 80 ซึ่งเป็นผลมาจากแรงผลักระหว่างประจุลบที่ผิวของไมลเซลล์และผิวดิน แต่สารละลายลดแรงตึงผิวชนิดผสมกับมีความสามารถในการล้างดีเซลได้น้อยกว่าสารลดแรงตึงผิว Tween 80 แบบเดี่ยวเล็กน้อยเนื่องจากความเข้มข้นที่สูงเกินไปของสารลดแรงตึงผิวชนิดผสมลดผลกระทบของการดูดซับของสารลดแรงตึงผิวที่ส่งผลต่อประสิทธิภาพในการล้างดีเซล นอกเหนือจากนี้ผลการศึกษายังแสดงให้เห็นว่า ความเข้มข้นของสารลดแรงตึงผิวชนิดผสมสามารถลดลงมาให้เหลือเพียง 3% w/v ของความเข้มข้นรวม (Tween 80 2.7% w/v และลิโปเปปไทด์ 0.3% w/v) โดยไม่ทำให้ประสิทธิภาพในการล้างดีเซลลดลง นอกจากความเข้มข้นของสารละลายลดแรงตึงผิวชนิดผสมแล้ว ได้ศึกษาผลของอัตราส่วนระหว่างสารลดแรงตึงผิว (มิลลิลิตร) ต่อ มวลของดิน (กรัม) และความเร็วในการปั่นเหวี่ยงต่อประสิทธิภาพในการล้างดีเซลโดยใช้โปรแกรม central composite rotatable design (CCRD) ผลการศึกษาพบว่าความเข้มข้นของสารลดแรงตึงผิวและอัตราส่วนระหว่างสารลดแรงตึงผิวต่อมวลของดินมีอิทธิพลต่อประสิทธิภาพในการล้างดีเซลอย่างมีนัยสำคัญ ประสิทธิภาพสูงสุดในการล้างดีเซลโดยใช้สารลดแรงตึงผิวชนิดผสมเท่ากับ 79.90% ค่าความเข้มข้นของสารลดแรงตึงผิวชนิดผสมที่คำนวณได้จาก CCRD เท่ากับ 3% w/v โปรแกรม CCRD ได้แนะนำให้เพิ่มอัตราส่วนระหว่างสารลดแรงตึงผิวต่อมวลของดินและความเร็วในการปั่นเหวี่ยงเพื่อเพิ่มประสิทธิภาพในการล้างดีเซลที่ปนเปื้อนในดิน

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KEYWORD: Mixed surfactant, Surfactant sorption, Interfacial tension, Critical micelle concentration,  
Tween 80, Rhamnolipid, Saponin, Lipopeptide, Diesel soil washing

Pajaree Boonyathai : DIESEL REMOVAL EFFICIENCY IN SOIL WASHING PROCESS BY MIXED SOLUTION  
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In this study, Tween 80 and three biosurfactant (Rhamnolipid, Saponin and Lipopeptide) were mixed to formulate the appropriate surfactant solution for diesel removal from contaminated soil by washing process. The mixed surfactant system was fixed at 5% w/v of active surfactants concentration in total with different mass ratio of Tween 80 to biosurfactant at 9:1, 8:2 and 7:3 of total concentration. The critical micelle concentration (CMC) of various ratio surfactant mixtures and their interfacial tension (IFT) with diesel were determined and compared with their individual surfactant. The results illustrate that mixed Tween and Lipopeptide at 9:1 mass ratio had the lowest IFT with 10 times lower than its individual surfactants. All mixed surfactant formulations showed the lower CMC than the individual biosurfactant, but still higher than that of Tween 80. The selected mixture of Tween 80 and Lipopeptide was investigated the influence of surfactant on TW sorption and diesel removal efficiency on various of soil texture. The mixed surfactant decreased the sorption of Tween 80 on soil compared to the system of individual TW because of the effect of charge repulsive between negative charge on mixed micelle and soil surface. The diesel removal by mixed Tween 80 and Lipopeptide was slightly lower than that of the individual TW. This might be due to the DI rinsing step, which increased the total diesel removal efficiency of single Tween 80. Moreover, the results displayed that the concentration of mixed Tween 80 and Lipopeptide could be decreased to 3% w/v (2.7% w/v of Tween 80 and 0.3% of Lipopeptide) with negligible loss of diesel removal efficiency. Besides the concentration of mixed surfactant, liquid-solid ratio (L-S ratio) and centrifuge speed were evaluated the optimal level in diesel removal efficiency by central composite rotatable design (CCRD). The results showed that surfactant concentration and L-S ratio significantly influenced on diesel removal efficiency. The highest diesel removal efficiency was 79.90 %. The predicted optimal level of surfactant concentration was approximately 3% w/v. For L-S ratio and centrifuge speed, the model suggests that these two factors could be increased for improving the diesel removal efficiency in the further study.

Field of Study: Hazardous Substance and  
Environmental Management

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## LIST OF ABBREVIATIONS

IFT	=	Interfacial tension (mN/m)
L-S ratio	=	Liquid-Solid ratio
CCRD	=	Central composite rotatable design
CMC	=	Critical micelle concentration (mg/L)
HOCs	=	Hydrophobic organic compounds
PAHs	=	Polycyclic aromatic hydrocarbons
SOVs	=	Semi-volatile organic compounds
POPs	=	Persistent organic pollutants
EO	=	Oxyethylene, Polyethylene
OM	=	Organic matter
SOM	=	Soil organic matter

## CHAPTER 1

### INTRODUCTION

#### 1.1 Theoretical Backgrounds

During the past decade of the twentieth century, global liquid fuel consumption is increasing up to 95.6 million barrels per day. Most of the growth in liquid fuels consumption is in the transportation and industrial sectors. Diesel is one form of liquid fuel, which is widely used in the world (EIA, 2018). The major consumption of diesel fuel are on-road transportation, off-road used (e.g., mining construction and logging), farming, rail transportation, marine shipping, electricity power generation and military transportation. However, diesel has been recognized as a major contaminant in soil from accidental transportation, leakage of pipeline and underground storage tank, as well as illegal disposal (Yu *et al.*, 2007). The soil contaminated with diesel can cause negative impact to environment because it harms to microorganism, earthworm, and plant growth (Bona *et al.*, 2011; Tang *et al.*, 2011). For human health, it irritants to eyes, respiratory system, and skin; moreover diesel fume can cause cancer due to the substance (i.e. polycyclic aromatic hydrocarbons (PAHs)) in its structure. Therefore, solving this problem is still an issue to be concerned.

In general, there are three types of soil remediation technologies: 1) biological method (i.e. bioventing and phytoremediation), 2) physiochemical method (i.e. solidification/stabilization and soil vapor extraction), and 3) thermal method (i.e., incineration). These technologies may unsustainable due to their limitations. For example, biological method is mostly used due to low cost and environmental friendly; however, it takes long time and is cannot degrade chlorinated compounds. Solidification/stabilization is much recommended for metals, but it does not treat the contaminant only immobilization. Thermal method is very high efficiency and



rapid process, but it uses high cost and generates secondary pollutant to the atmosphere (i.e. dioxin) (Gimello, 1998; Namkoong *et al.*, 2002; Dadrasnia *et al.*, 2013). Thus, soil washing is the common treatment technology for the remediation of diesel contaminated soil because it can apply in site that can reduce time and transportation cost. Moreover, this method can treat both organic and inorganic contaminants, especially heavy metal that mostly found in diesel contaminated soil (Namkoong *et al.*, 2002; Khan *et al.*, 2004; Hernández-Espriú *et al.*, 2012).

Normally, soil washing is an ex-situ treatment process that use liquids and mechanical process to scrub the contaminants soil. However, in a case of diesel that has low solubility and strongly adsorb on soil, makes a difficulty to be removed from soil by mere water (Khan *et al.*, 2004). Consequently, surfactants are the appropriate liquid to apply in soil washing process for enhancing solubility of diesel fuel and soil washing efficiency due to their unique structure, which can dissolve both polar and non-polar compounds. Generally, this technology use single surfactant to remove pollutants, particularly nonionic surfactants because of their properties such as lower critical micelle concentration (CMC), cost effective and easily biodegradable (Ahn *et al.*, 2008). In addition, they show the high petroleum removal efficiency in soil washing process. Several researches applied nonionic surfactants in their studies to remediated hydrophobic organic compounds (HOCs) (i.e. petroleum and PAHs) from the contaminated soil such as Tergitol series (HeoandLee, 2015; Li *et al.*, 2016), Tween series (Torres *et al.*, 2003; Iturbe *et al.*, 2004; Zhou *et al.*, 2013; HeoandLee, 2015; Li *et al.*, 2016) and Brij series (Ahn *et al.*, 2008). Tween 80, especially, has earned interest due to low cost, low polarity, low toxicity, high hydrophile-lipophile balance (HLB) and high solubilization capacity (M. Cheng *et al.*, 2017). However, some researchers indicated that the efficiency of nonionic surfactant enhanced soil washing is significantly decreased by the sorption of nonionic surfactant on soil, particularly

for the contaminated soil which usually have high soil organic matter content (Lee *et al.*, 2000; S. KangandJeong, 2015; Li *et al.*, 2016). The sorption of surfactant on soil can decrease the concentration of surfactant in solution, thus the removal efficiency in soil washing process decreases (PariaandKhilar, 2004; Zhou *et al.*, 2013).

To solve the high sorption of nonionic surfactant on soil, mixed surfactants are currently interested for remediation application due to their synergistic advantages compared with single surfactant (ZhangandZhu, 2010; M. Cheng *et al.*, 2017). Researchers have observed that sorption of nonionic surfactant (Tween80) in soil can be reduced by adding anionic surfactant (SDBS). Adding of SDBS can increase the negative charge of SDBS-Tween 80 mixed micelles, then the electrostatic attraction between Tween 80 and soil surface is decreased (Yang *et al.*, 2006; ZhangandZhu, 2010). Adding anionic surfactant not only decreases the sorption of nonionic surfactant, but also decreases CMC of mixed surfactant (Zhao *et al.*, 2005). Nevertheless, using synthetic surfactants in soil and groundwater have the potential of toxicity risk, and hazard to the ecological function (Mulligan, 2005; Zhou *et al.*, 2013; Liu *et al.*, 2016). For example, using an anionic (SDS) and nonionic (TritonX-100) surfactants in soil have toxic to plant growth and nutrient uptake (MohammadandMoheman, 2012).

Therefore, biosurfactants are a good alternative to use for enhancing soil washing efficiency because several studies have shown that biosurfactants exhibit the better environmental compatibility, lower toxicity, and higher biodegradability than synthetic surfactant (Zhou *et al.*, 2013). For example, Lai *et al.* (2009) investigated the efficiency of biosurfactant to enhance removal of total petroleum hydrocarbons (TPH) from contaminated soil compared with synthetic surfactant. The result showed that biosurfactants (especially, rhamnolipid) exhibited much higher TPH removal efficiency than that of the synthetics (Tween 80 and Triton X-100). Singh and

Cameotra (2013) reported that lipopeptide biosurfactant obtained from *Bacillus subtilis* A21 removed a significant amount of petroleum hydrocarbon (64.5%) and metals from soils from industrial dumping site in a soil washing. Moreover, mixing biosurfactant (Saponin) with TX100 and Brij35 can decrease CMC of surfactant solution and enhance solubility of PAH compounds, anthracene and phenanthrene (Wu *et al.*, 2013).

Most of previous studies have focused on enhanced soil washing of HOCs by mixing solution of two synthetic surfactants such as TX100-SDBS and Tween 80-SDBS. Moreover, there were a few works regarding to the adsorption of mixed surfactants on soil which is important factor of soil washing efficiency. Although, some researchers studied the mixed synthetic surfactant and biosurfactant, but they did not apply mixed surfactant solution in the soil washing application. For example, Jian *et al.* (2011) mixed tea saponin biosurfactant (TS) with three synthetic surfactants (cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), and polyoxyethylene lauryl ether (Brij35)), for studying the molecular interactions between biosurfactant and different types of synthetic surfactants at CMC. They mentioned that CTAB-TS, SDS-TS mixtures showed the significant synergism in surface tension reduction, mixed micelle formation, and foaming efficiency, whereas that was not shown in Brij35-TS mixtures. Nguyen *et al.* (2008) also mixed rhamnolipid biosurfactant and synthetic surfactant for improving the interfacial activity of the surfactant system against several light non-aqueous-phase liquids (LNAPLs). Their result reported that the rhamnolipid had excellent phase behavior at low concentrations and can be used in surfactant mixtures to achieve the low IFT values needed for environmental remediation. Hence, the main objective of this study was to investigate the potential of using mixed synthetic surfactant and biosurfactant on diesel contaminated soil washing process.

## 1.2 Objectives

1. To study the sorption of synthetic surfactants, biosurfactant and mixture of them on soil.
2. To formulate the suitable surfactant solution for diesel contaminated soil washing process.
3. To optimize the process conditions of diesel contaminated soil washing using aqueous surfactant.

## 1.3 Hypotheses

1. Mixing synthetic surfactant with biosurfactant could decrease the sorption of surfactant on soil due to steric hindrance.
2. The surfactant system with higher soil sorption might have lower diesel removal efficiency.
3. The mixed synthetic - biosurfactant could provide better diesel removal efficiency compared to that of single surfactant due to decreasing of critical micelle concentration (CMC) and interfacial tension (IFT).

## CHAPTER 2

### LITERATURE REVIEWS

#### 2.1 Petroleum

##### 2.1.1 General information

Petroleum, also known as crude oil, is a complex mixture of naturally hydrocarbons, which is derived from decaying plants and animals living in the earth surface over millions years ago. The major components of petroleum are hydrocarbons and some small amount of other elements shown in Table 2.1. Hydrocarbons can display their molecule structure in great variation as follows: paraffins (chain-shaped), naphthenes and aromatics (ring-shaped). The amount of element and types of hydrocarbon in petroleum are depended on pressure and temperature conditions during the accumulation process (Speight, 2007).

**Table 2.1** Overall Elemental Composition of Petroleum<sup>a</sup> (Viswanathan, 2017)

Element	Percentage Composition
Carbon	83-87
Hydrogen	10-14
Nitrogen	0.1-2
Sulfur	0.05-6
Oxygen	0.05-1.5

<sup>a</sup> Petroleum also contains trace levels of nickel and vanadium (≥1000 parts per million).

However, petroleum is not generally useful in industrial applications. It needs to be cracked down into parts and refined before use. To separate petroleum, fractional distillation is generally used. This process is a fundamental refinery process, which separated petroleum into fractions by different boiling-point. Crude oil is heated and sent up along the fractionating column that has decreasing temperatures with height and several platforms at different levels to collect the condensate. High

molecular weight hydrocarbon (the heavier fraction) have higher boiling points and condense at lower part of the column; while lighter fraction with lower boiling point rise to top of tower to condense. The approximate boiling-point range and carbon range of main petroleum products are shown in Figure 2.1

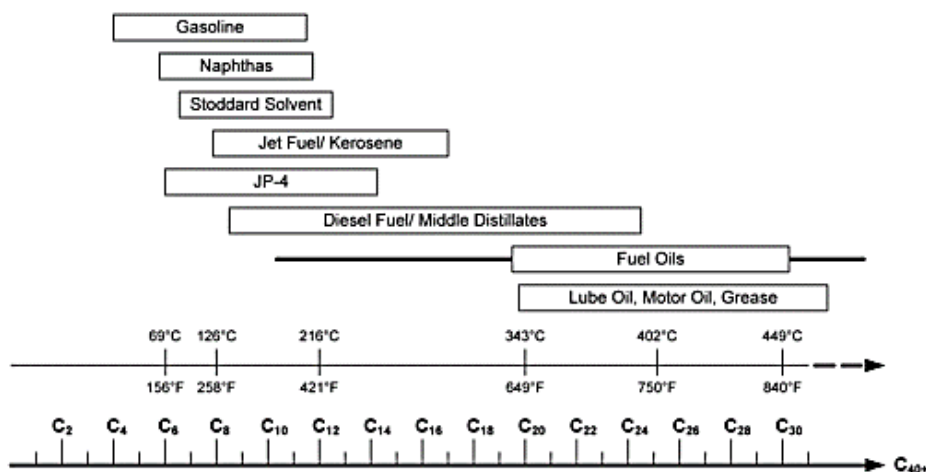


Figure 2.1 Carbon range and boiling-point of petroleum products

(<http://www.orionenv.com/projects/contaminants/>)

### 2.1.2 Diesel fuel

Diesel fuel, also called diesel oil, is one of the product from petroleum distillation, which is widely used in the world. The major consumption of diesel fuel are on-road transportation, off-road used (e.g., mining construction and logging), farming, rail transportation, marine shipping, electricity power generation and military transportation. From the distillation process, the diesel fuel contains more than thousands of compounds, most with carbon numbers between 10 and 22. The majority of these compounds are 75% saturated hydrocarbons (primarily paraffins including n, iso-, and cycloparaffins), and 25% aromatic hydrocarbons (including naphthalenes and alkylbenzenes) (Viswanathan, 2017).

Khalladi *et al.* (2009) characterized a composition of diesel fuel in their study. They found that 30% of the diesel fuel that was shown in GC chromatogram is

19 hydrocarbons ranging from  $C_8$  to  $C_{26}$ . Moreover, they also investigated the diesel composition in effluent after soil washing using ionic surfactant sodium dodecyl sulfate (SDS). They found that the diesel effluent could be divided into three different fraction including  $C_{12}$  to  $C_{14}$  (6.5-11.5% of n-alkanes),  $C_{15}$  to  $C_{20}$  (4.1-14.9% of n-alkanes) and  $C_{21}$  to  $C_{26}$  as the small amount in all fractions.

## 2.2. Soil composition

Soil is composed of four components: 45% inorganic particle, 5% organic matter and 50% pore space filled with 25% liquid and 25% gases (Figure 2.2) (Bohn *et al.*, 2002). Soil composition plays an important role on soil remediation efficiency, for example high proportion of clay and organic matter have effect on surfactant loss that also influence on efficiency of soil washing using surfactant (Liang *et al.*, 2016).

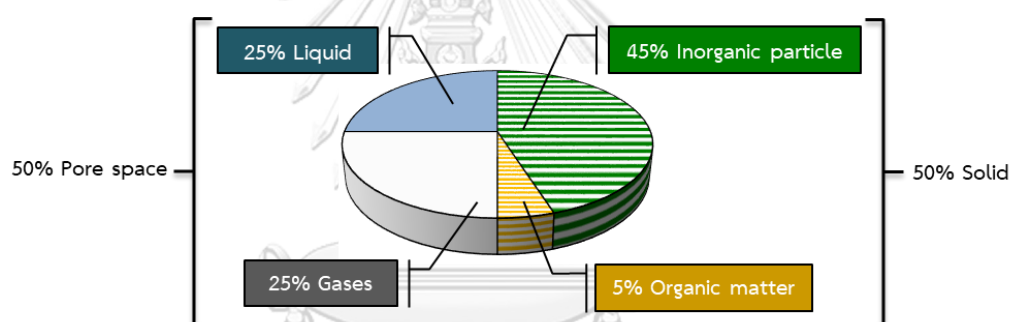


Figure 2.2 Soil components.

### 2.2.1 Inorganic particles

Inorganic particle, often called mineral particles, includes both primary and secondary minerals. The primary minerals are formed by the break-up of the bigger rocks. These minerals are mainly found in sand and silt particles, whereas the secondary minerals result from the weathering of the primary minerals are normally presented in the clay fraction. Some of the important minerals in soil are shown in Table 2.2. Soil mineral particle range in size over 3 orders from 2.0 mm to smaller than 0.002 mm in diameter (Figure 2.3). The proportions of particles in these various size ranges are called soil texture. The texture classes of soil are shown on the USDA

textural triangle (Figure 2.4). Soil texture influence on soil aggregation, water holding capacity, water infiltration and nutrient storage (Tan, 1998; Bohn *et al.*, 2002).

**Table 2.2** Some important minerals in soil (MillerandGardiner, 2001).

Name	Properties
<i>Primary minerals</i>	
Quartz	SiO <sub>2</sub> ; hard; weathers(decomposes) very slowly; major component of sand
Feldspar (orthoclase and plagioclase)	Hard; weathers slowly or moderately to form clay; provides plant nutrients; minor component of sand
Mica (muscovite and biotite)	Appearance of glitter in rock and sand; provides potassium; weathers to form clay
Dark minerals (e.g., augite and hornblende)	Easily weathers to form clay
<i>Secondary minerals</i>	
Carbonates (calcite and dolomite)	CaCO <sub>3</sub> and (Ca·Mg)CO <sub>3</sub> ; slowly soluble sources of plant nutrients; common in soil of arid regions
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O; soft; soluble material common in soil of arid regions
Oxide clays (e.g., goethite and gibbsite)	Hydrated (containing structural water) microscopic particles formed iron and aluminum; common in tropical soil
Silicate clays (montmorillonite, illite, vermiculite, and kaolinite)	Microscopic particles formed mostly from silica and aluminum; common in soils of temperate climates



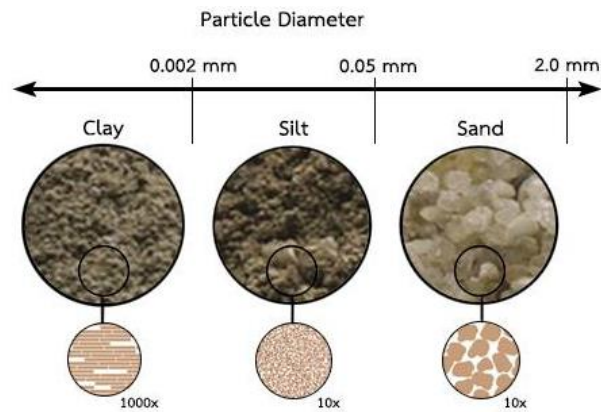


Figure 2.3 Type of inorganic particle.

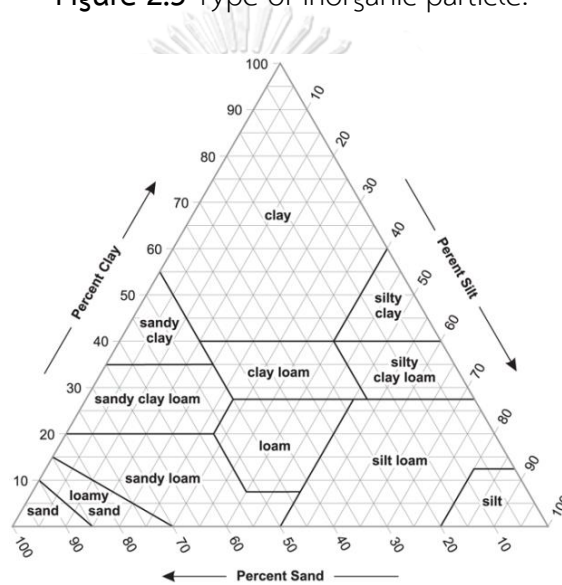


Figure 2.4 Soil texture triangle (Yolcubal *et al.*, 2004).

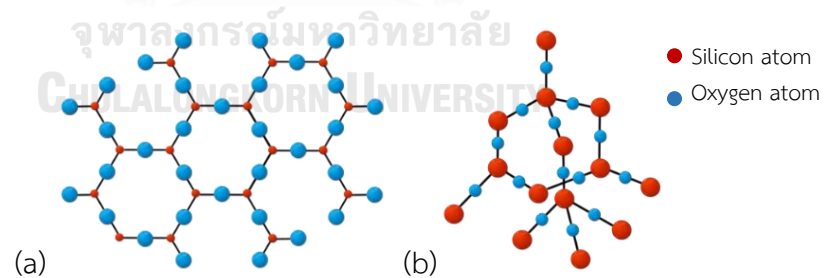
In spite of the composition variability, the silicates and oxides are the predominant of inorganic fractions. Soil silicate can be classified into six types depend on the arrangement of the  $\text{SiO}_4$  tetrahedral in their structure as shown in Table 2.3. Sand and the major part of silt fraction are the cyclo-, ino-, neso-, soro-, or tectosilicates, whereas clay is mostly phyllosilicates (Tan, 1998).

**Table 2.3** Structure classification of silicates (Tan, 1998).

Classification	Structural arrangement	Mineral Example
Nesolicates	Single tetrahedral	Olivene, garnet
Sorosilicates	Two or more linked tetrahedral ( $\text{Si}_2\text{O}_7$ , $\text{Si}_2\text{O}_5$ )	Hemimorphite
Cyclosilicates	Closed rings or double rings of tetrahedral ( $\text{SiO}_3$ , $\text{Si}_2\text{O}_5$ )	Beryl
Inosilicates	Single or double chains of tetrahedral ( $\text{SiO}_3$ , $\text{Si}_4\text{O}_{11}$ )	Pyroxene (augite), Amphiboles (hornblende)
Phyllosilicates	Sheets of tetrahedral ( $\text{Si}_2\text{O}_5$ )	Illite, kaolintine, montmorillnite
Tectosilicates	Framework of tetrahedral ( $\text{SiO}_2$ )	Quartz, feldspars, zeolite

### 2.2.1.1 Sand

Sand is the coarse fraction and make up the skeleton of the soil body. The most component of sand is silica (silicon dioxide, or  $\text{SiO}_2$ ), normally in term of quartz (Figure 2.5). Due to the size of particle, sand has low specific surface area and does not show colloidal properties.

**Figure 2.5**  $\text{SiO}_2$  structure (a) 2D, (b) 3D.

### 2.2.1.2 Silt

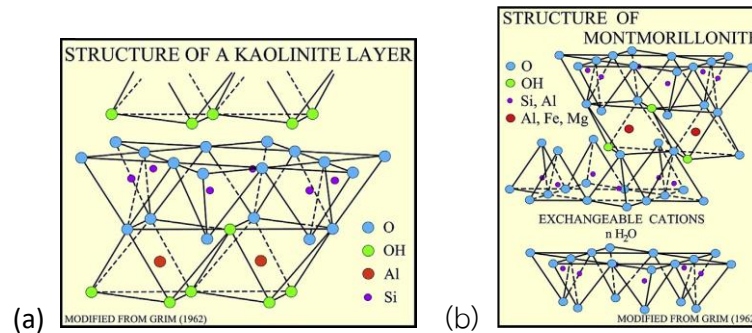
Silt is an intermediate soil fraction that has particle size and chemical and physical properties between clay and sand. Mineral composition of silt is similar to that of sand; however, silt has more surface area and more hydrophobicity due to the smaller particle size (Chiu *et al.*, 2009).

### 2.2.1.3 Clay

Clay is the fine fraction. Due to its fine size, the clay fraction is colloidal, very reactive, has large surface area and high charge density. The clay minerals include the phyllosilicates or sheet silicate, which composed of sheets of silica ( $\text{SiO}_4$ ) tetrahedral attached with octahedral sheets (containing aluminum (Al), magnesium (Mg), iron  $(\text{Fe})(\text{O},\text{OH})_6$ ). Clay minerals are classified into three types based on the number and arrangement of tetrahedral and octahedral sheets in their structure. The classification and the structure of clay mineral are shown in Table 2.4 and Figure 2.6, respectively. This study selected Kaolinite, which has uncomplicated structure (1:1 layer, Figure 2.5a) to study the sorption of surfactant on soil.

**Table 2.4** Clay mineral classification (Tan, 1998).

Layer type	Group name	Common minerals
1:1	Kaolinite-serpentine	Kaolinite, halloysite, chrysotile, lizardite, antigorite
2:1	Pyrophyllite-talc	Pyrophyllite and talc
	Smectite or montmorillonite	Montmorillonite (smectite), beidellite, nontronite, saponite, hectorite, saucanite
	Mica	Muscovite, paragonia, biotite, phlogoite
	Brittle mica	Margarite, clintoite
	Illite	Illite
	Vermiculite	Vermiculite
2:1:1	Chlorite	Chlorite



**Figure 2.6** Structure of clay (Bibi *et al.*, 2016)

(a) The tetrahedral-octahedral layer of kaolinite

(b) The smectite mineral, montmorillonite.

### 2.2.2 Organic matter

Soil organic matter (SOM) is <5% living bacteria, plant root, and >95% dead animals and plant. This fraction contains humic substances and non-humic substances (e.g. proteins, carbohydrate). The SOM content is an important parameter in the adsorption and desorption of HOCs. The HOCs in the contaminated soil can strongly sorbed to the SOM, resulting in low mobility and removal rates (M. Cheng *et al.*, 2017). On the other hand, the presence of SOM inform of dissolve organic matter (DOM) can enhanced PAHs desorption from soil by increasing PAH dissolve rate (Liang *et al.*, 2016).

### 2.3 Soil remediation technologies

Soil are often contaminated with diesel fuel by various routes such as leaking of fuels from general using and engine maintenance of vehicles, boats or aircraft, underground and above ground storage tanks, accidental spills during transportation, and leaching landfills (John Bacha *et al.*, 2007; Hernández-Espriú *et al.*, 2012; Koshlaf *et al.*, 2016; Lahel *et al.*, 2016). These contaminated soil cause damage to environment and human health in many ways. The remediation technologies for oil contaminated soil can be classified into biological, physicochemical and thermal methods. The description, advantage and disadvantage of each method is exhibited

in Table 2.5. After comparing pros and cons of each remediation technology, soil washing is selected in this study to remediate diesel contaminated in soil because it can treat both organic and inorganic compounds, especially heavy metal that found in diesel contaminated soil (Khan *et al.*, 2004).



**Table 2.5** Description, advantage and disadvantage of soil remediation.

Methods		Advantage	Disadvantage
Biological remediation technologies			
Bioventing (In-situ)	Aerating soils to stimulate in-situ biological activity and promote bioremediation	<ul style="list-style-type: none"> <li>Minimal Soil preparation</li> <li>Successfully uses with soils contaminated with organic compounds</li> </ul>	<ul style="list-style-type: none"> <li>May not improve degradation of chlorinated compounds</li> <li>May be limited with low permeability soil</li> </ul>
Phytoremedia tion (In-situ)	Using plants to extract, degrade, or immobilize contaminants in soil	<ul style="list-style-type: none"> <li>Low cost</li> <li>Prevent and minimize surface erosion by forming a self-sufficient ecosystem</li> <li>Environment-friendly</li> </ul>	<ul style="list-style-type: none"> <li>Slower than the other methods</li> <li>Soil properties, toxicity level and climate should be suitable for plant growth</li> <li>Contaminants can be incorporated into the food chain through plants</li> </ul>
Landfarming (Ex-situ)	Excavating the contaminated soil and turn over the soils to aerate the waste to promote bioremediation	<ul style="list-style-type: none"> <li>Simple design and implementation</li> <li>Large soil volumes can be treated</li> </ul>	<ul style="list-style-type: none"> <li>Large treatment area is required</li> <li>Limit to removal of biodegradable pollutants</li> <li>Risk to human pollutant exposure</li> </ul>
Solidification/ Stabilization (In-situ)	Mixing additives or reagents with contaminants to reduce the solubility or mobility of contaminants by physical or chemical processes	<ul style="list-style-type: none"> <li>Simple design</li> <li>Cost-effective</li> <li>Large soil volume can be treated</li> <li>Very recommended for metals</li> </ul>	<ul style="list-style-type: none"> <li>Does not promote the treatment of the contaminant only immobilization</li> <li>Short-lived</li> <li>Dependent on the soil characteristics and homogeneity of the mixture</li> </ul>

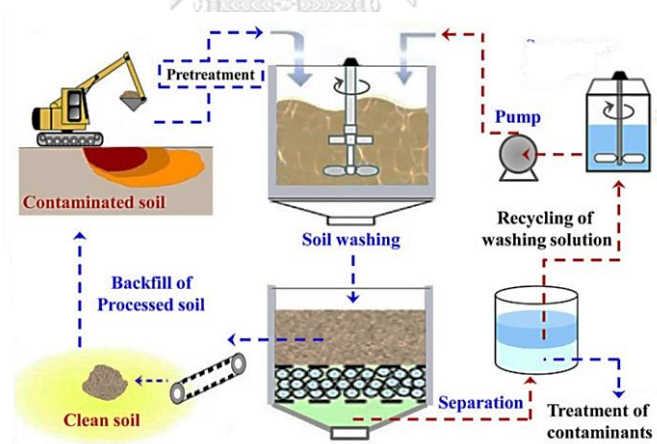
Sources: (Gimello, 1998; Dadrasnia *et al.*, 2013; Lim *et al.*, 2016)

**Table 2.5** Description, advantage and disadvantage of soil remediation (cont.)

Methods	Advantage	Disadvantage
<b>Biological remediation technologies</b>		
Soil vapor extraction (In-situ)	<ul style="list-style-type: none"> <li>Applying a vacuum to extract contaminated vapor that is adsorbed to soils and to collect the vapor for further treatment</li> <li>No excavation required</li> <li>Highly effective in volatile organic compound (VOC) removal</li> </ul>	<ul style="list-style-type: none"> <li>Long time treatment for heterogeneous soils</li> <li>Not effective in the saturated zone</li> <li>Cannot remove heavy oils, metals, PCBs, or dioxins</li> </ul>
Soil washing (Ex-situ)	<ul style="list-style-type: none"> <li>Using liquids and a chemical process to wash or scrub the contaminated soils</li> <li>Cost-effective because it reduces both organic and inorganic contaminant</li> <li>Treated soil can be redeposited on site</li> <li>Generally removal of pollutant efficiency is between 60-90%</li> </ul>	<ul style="list-style-type: none"> <li>Unsuitable for soil contained with proportion of high silt and clay</li> <li>Require additional treatment for contaminated effluent/water</li> </ul>
Soil flushing (In-situ)	<ul style="list-style-type: none"> <li>Similar to soil washing but apply in situ</li> <li>Generally removal of pollutant efficiency is between 60-90%</li> <li>Remove both organic and inorganic contaminant</li> </ul>	<ul style="list-style-type: none"> <li>High investment cost and post-reclamation monitoring and management</li> </ul>
<b>Thermal remediation technologies</b>		
Incineration (Ex-situ)	<ul style="list-style-type: none"> <li>Using high temperatures to volatilize and combust halogenated and other refractory organics in soil</li> <li>High efficiency</li> <li>Rapid process</li> <li>Compounds mineralization</li> </ul>	<ul style="list-style-type: none"> <li>High cost</li> <li>Release of secondary compounds to the atmosphere (i.e. dioxin)</li> </ul>

### 2.3.1 Soil washing

Soil washing is an ex-situ treatment process that uses liquids (usually water, occasionally combined with solvents) and mechanical process to remove the contaminants include semi-volatile organic compounds (SVOCs), petroleum and fuel residual, heavy metals, PAHs and pesticides in soil to liquid by solubilization. This treatment can be physical and/or chemical process, which results in the separation, volume reduction of hazardous materials and/or the chemical transformation of contaminant to nonhazardous and can be used as a backfill (SemerandReddy, 1996; Khan *et al.*, 2004). The general procedure of washing process is schematically illustrated in Figure 2.7. Briefly, the excavated contaminated soil is pretreated (e.g., remove the rocks) and mixed with the washing solution. After the washing process, the soil particles can be separated out and the washing solution can be treated and recycled into the process (Mao *et al.*, 2015).



**Figure 2.7** General procedure of an ex-situ washing for soil remediation,

modified from Cheng *et al.* (2017)

In this study, the main target pollutant is the diesel fuel, which has low solubility and high hydrophobicity leading to strongly adsorb on soil and low available to microorganisms for degradation (Franzetti *et al.*, 2008). Consequently,

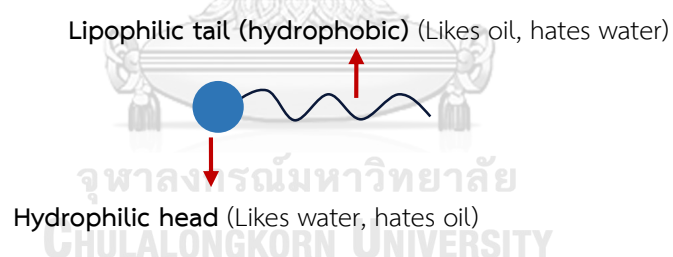


the diesel fuel is difficult to remove from contaminated soil by mere water. For enhancing solubility and bioavailability of this contaminant and efficiency of diesel soil washing, surfactants that contain both hydrophilic and hydrophobic parts are the suitable reagent solution to apply in the process (Mao *et al.*, 2015).

## 2.4 Surfactants

### 2.4.1 Synthetic surfactant

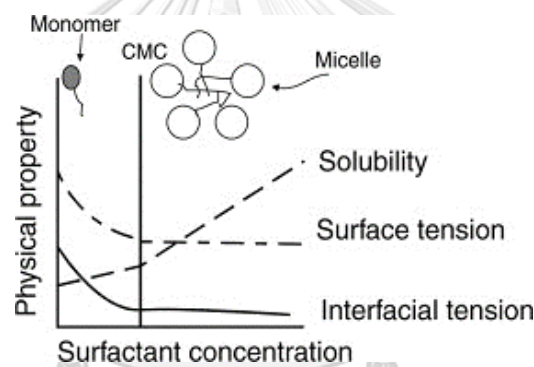
Surfactants (surface-active-agent) are the amphiphilic molecule which are consisted of two different parts: hydrophobic part (tail part) and hydrophilic part (head part) (Figure 2.8). Due to having both hydrophobic and hydrophilic part, surfactants dissolve both polar and non-polar compound, resulting in increased the aqueous solubility of hydrophobic organic pollutants (HOCs) (UrumanPekdemir, 2004; Mao *et al.*, 2015). Because of the unique structure of surfactants, they can reduce surface tension and IFT of interface.



**Figure 2.8** Schematic of surfactant structure.

By definition, IFT is a force per unit length existing at the interface between two immiscible liquid phases. In a case of air and liquid interface, it is named surface tension. When surfactants are added into a system of water and oil, they are adsorbed at the interface and replace water and/or oil molecule. Now the interaction over the interface change to be between hydrophilic groups of surfactants and water molecules on a side of interface; and between hydrophobic groups of surfactants and oil molecules on another side of the interface. These interactions are

stronger than the original interaction (water and oil); therefore, the IFT over the interface of water and oil is decreased by the presence of surfactants. Because air composes of mostly non-polar molecules; therefore surface tension that is a force pulls the molecules of interface together is also reduced by surfactants at the air-aqueous solution interface. The surface tension and IFT decrease with increasing of surfactant concentration. After surfactants reach the certain concentration level, the surface tension and IFT are negligible decreased. On the other hand, the solubilization of oil into micelles is increased (Figure 2.9). This certain surfactant concentration is named the critical micelle concentration (CMC), which the first micelle structure is formed (Schramm *et al.*, 2003; Rosen, 2004).

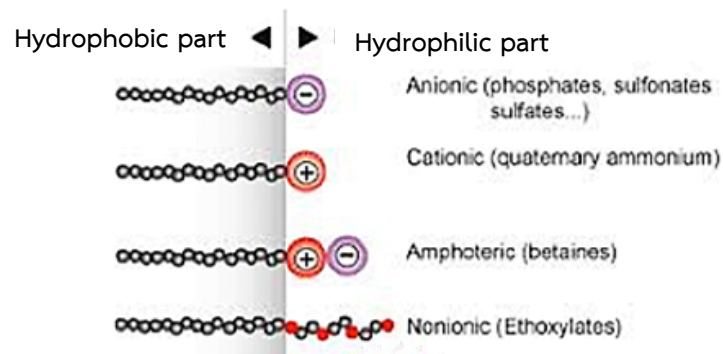


**Figure 2.9** Relationship of CMC, surface tension, IFT and solubility

(Mulligan *et al.*, 2001)

Surfactants are classified into 4 types based on head polar of surfactant: non-ionic, anionic, cationic and zwitterionic or amphoteric surfactant (Salager, 2002; UrumandPekdemir, 2004). Type of surfactants were displayed in Figure 2.10. However, several studies have shown that anionic surfactants can be precipitated with the multivalent electrolyte such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in soil, while cationic surfactant can be adsorbed strongly onto soil particles via electrostatic interaction (Guo *et al.*, 2009; ZhangandZhu, 2010; M. Cheng *et al.*, 2017). In addition, amphoteric or zwitterionic surfactants are often sensitive to pH (Cornwell, 2018). Therefore,

nonionic surfactants are the appropriate surfactant solution to use for soil washing process in this study.

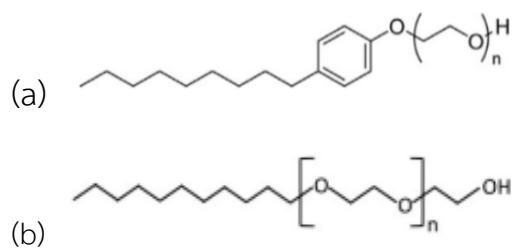


**Figure 2.10** Type of surfactant base on head polar of surfactant

(<http://www.uniqchem.com/dispersing-technology/>)

Nonionic surfactants are one of the surfactant types. They have no charge in head part and do not ionize in aqueous solution because their hydrophilic group is a non-dissociable type such as phenol, alcohol, ester, ether, or amide. The hydrophilic part of nonionic surfactants are usually created from oxygen-containing groups such as hydroxyl and polyoxyethylene (Figure 2.11) (Salager, 2002). When nonionic surfactants are added into a system, they are dissolved in aqueous phase by the formation of hydrogen bonds between the hydrophilic groups and water molecules. The micelle formation of nonionic surfactants is formed easier than those of ionic surfactant type. This is due to the aggregation mostly occurs from the hydrophobic attraction among non-polar chains, whereas hydrophilic chains are easily separated in an aqueous phase. Therefore, nonionic surfactants usually provide low CMC, which is useful for the remediation works, particularly in soil washing applications (Mao *et al.*, 2015). Furthermore, these surfactants have low toxicity and more environmental friendly than those of surfactant type (Mao *et al.*, 2015; Liu *et al.*, 2016; M. Cheng *et al.*, 2017). In Table 2.6, examples of the nonionic

surfactants used in the remediation of crude oil, diesel, PAHs and persistent organic pollutants (POPs) contaminated soil are summarized.



**Figure 2.11** Nonionic surfactant structure (Mao *et al.*, 2015)

(a) Tergitol NP-10

(b) Dehydol structure



**Table 2.6** Application cases of nonionic surfactants for the remediation of crude oil, diesel, PAHs and persistent organic pollutants (POPs) contaminated soil

Surfactant concentration	Soil texture	Liquid-Solid ratio	Major contaminant	Results	References
0.5% Canarcel TW80 at pH 7.8	38% porosity	-	TPH Initial concentration was 4600 mg/kg	TPH removal was 87.1%	Iturbe et al. (2004)
Tergitol NP-10 at concentration $10^{-4}$ to $10^{-8}$ mol/L	sandy loam soil	20 : 1 ratio w/v	Diesel initial concentration was 10,000 mg/kg	Diesel oil was removed 50% at surfactant concentration higher than CMC.	Vreysen and Maes (2005)
2 g/L of Tween 40, Tween 80, Brij 30 and Brij 35	sandy loam	1 : 10	PHE concentration was 200 mg/kg	PHE removal efficiency followed order: Brij 30 (84%) > Tween 80 (72%) > Brij 35 (71%) > Tween 40 (55%)	Ahn et al. (2008)
5–1,000 mg/L of Tween 80, TX-100, Brij 35 and SDBS (anionic surfactant)	sandy loam soil	5 : 1 ratio w/v	DDT at a concentration of 2.5 mg/kg	Tween80 showed the highest solubilization capacity and soil washing ability for DDT contaminated soil	Guo et al. (2014)
Tergitol 15-S-7 and Tergitol 15-S-9 at concentration 2% w/w *Only soil washing part	sand	1 : 3 ratio w/v	TPH concentration of the soil was 223,754 mg/kg	More than 97% of the crude oil in the soil was removed. (Five times repeat)	Heo and Lee (2015)

## 2.4.2 Biosurfactant

Natural surfactants or biosurfactant are produced by bacteria, fungi and yeasts and are able to be extracted from plant. All of biosurfactants are consisted of hydrophobic part and hydrophilic part, which called amphiphilic molecule. According to the amphiphilic property, they can increase the solubility of HOCs, which simplifies their mobility and biodegradability. Biosurfactants have several advantages compared with chemical surfactants such as easily biodegradation, lower CMC, lower toxicity, and less sensitive under wide range of environmental conditions (i.e., extreme temperatures, pH and salinity) (UrumandPekdemir, 2004; Lamichhane *et al.*, 2017).

Biosurfactants that are produced from microorganisms can divided into 2 groups based on molecular weight including (1) low-molecular-mass, which are efficiently reduce surface tension (liquid-air) and IFT (liquid-liquid) between two phases; and (2) high-molecular-mass, which are more potentially stabilize oil-in-water emulsion (Pacwa-Plociniczak *et al.*, 2011; Karlapudi *et al.*, 2018). Another group of biosurfactant is phytogetic surfactant, such as lecithins and saponins (Bustamante *et al.*, 2012).

Due to several benefits of biosurfactants, they were applied in many soil remediation technologies, especially in soil washing. For example, Urum and Pekdemir (2004) compared the efficiency of crude oil contaminated soil washing using biosurfactants with SDS. The selection of biosurfactants was based on their different origins as follow: 1) aescin or saponin was produced from the seeds of the horse chestnut tree: *Aesculus hippocastanum* L. (Hippocatanacea), 2) lecithin was derived from soybean, and 3) rhamnolipid (microbial) is a blend of  $C_{26}H_{48}O_9$  and  $C_{32}H_{58}O_{13}$ . The concentration of surfactants were varied from 0.0001-0.5% w/v, which cover CMC of all surfactants. The results indicated that biosurfactants, especially

rhamnolipid show crude oil removal efficiency more than 80% similar to SDS. On the other hand, the oil removal efficiency were decreased when the concentrations of aescin, lecithin, saponin above CMC. This might be due to the bulk structure biosurfactants may lead to micelle instability and reduction of detergency.

Urum *et al.* (2006) investigated the efficiency of different surfactant solution in removing crude oil from contaminated soil using soil washing process. They found that the order of crude oil removal efficiency was SDS > rhamnolipid > saponin. However, the surfactants illustrated different preference typed of crude oil removal. Rhamnolipid and SDS would like to remove the aliphatic compounds, whereas saponin can remove aliphatic and aromatic components.

Lai *et al.* (2009) studied the effect of two surfactants: rhamnolipids and surfactin, and two synthetic surfactants: Triton X-100 and Tween 80 on the removal of total petroleum hydrocarbon (TPH) from the low TPH-contaminated (LTC) and high TPH-contaminated (HTC) soils (3,000 and 9,000 mg/kg dry soil of TPH, respectively) by soil washing technology. They found that adding 0.2% w/w of rhamnolipids, surfactin, TX-100 and Tween 80 to LTC soil resulted in a TPH removal of 23%, 14%, 6%, and 4%, respectively. Meanwhile TPH removal efficiency of HTC soil significantly higher by 63%, 62%, 40% and 35%, respectively.

S. W. Kang *et al.* (2010) also evaluated the effectiveness of sophorolipid in washing and biodegradation of crude oil and hydrocarbon in soil on their laboratory scale. The results illustrated that the addition of this biosurfactant in soil improved the washing and the biodegradation efficiency of the tested hydrocarbons.

Singh and Cameotra (2013) evaluated feasibility of using anionic lipopeptides biosurfactants produced by *Bacillus subtilis strain A21* in petroleum hydrocarbon soil washing process. This biosurfactant, consisting of surfactin and fengycin could be used as washing solution. In the experiment, the lipopeptides

biosurfactant was prepared at 0, 0.5\*CMC, CMC, 10\*CMC, 50\*CMC. The result showed that the concentration of surfactant at 50CMC removed significant amount of petroleum hydrocarbon (64.5 %) and metals namely copper (26.2 %), cadmium (44.2 %), cobalt (35.4 %), lead (40.3 %), and zinc (32.0 %) from the contaminated soil.

## 2.5 Surfactant sorption on soil

### 2.5.1 Mechanism of surfactant sorption on soil

The sorption of surfactants at solid-liquid surface is strongly affected by several factors: (1) the nature of structure groups on the solid surface (i.e. the amount of charge, nonpolar grouping on the surface and the nature of atom); (2) surfactant structure (i.e. ionic or nonionic, type of hydrophobic group such as aliphatic or aromatic, straight chain or branched); (3) the environment of liquid phase (i.e. the presence of additives such as alcohol, its pH, its electrolyte, its temperature) (Rosen, 2004). There are many mechanisms that surfactants can sorb on soil from aqueous solution.

#### (1) *Ion Exchange*

Substitution of counterions adsorbed on the substrate from solution by similarly charged surfactant ions (Figure 2.12a).

#### (2) *Ion Pairing*

Sorption of surfactant ions from solution on differently charged sites unoccupied by counterions (Figure 2.12b).

#### (3) *Acid-Base Interaction*

Sorption mechanism occurs by either hydrogen bond between substrate and adsorbate (Figure 2.12c) or Lewis acid-Lewis base reaction (Figure 2.6d).

#### (4) *Sorption by Polarization of $\pi$ Electrons*

Sorption mechanism occurs when the adsorbate composes of electron-donating group with ring and the solid sorbent has greatly positive sites. Attraction between electron-donating group of the adsorbate and positive sites on the substrate causes adsorption.

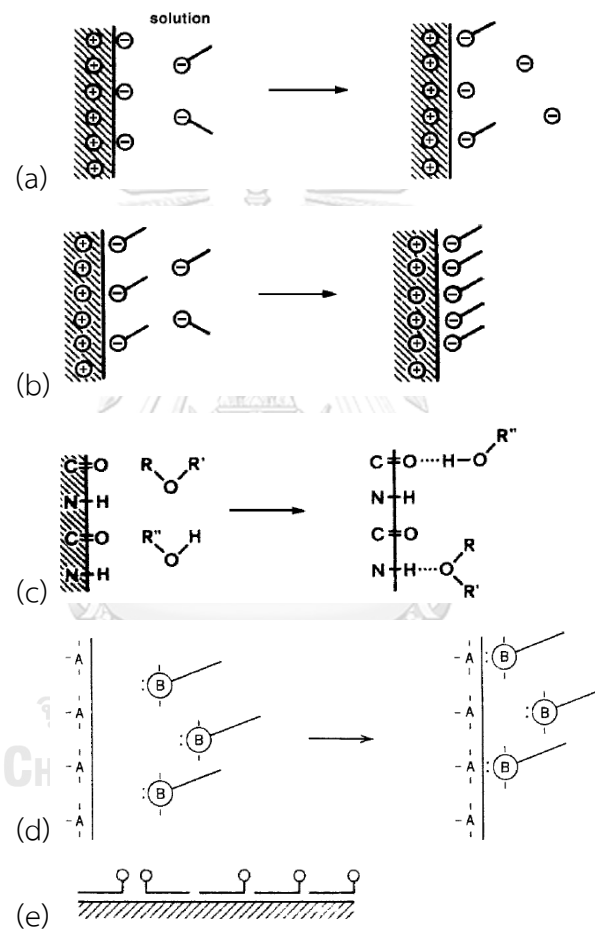


(5) Sorption by Dispersion Forces

Sorption mechanism occurs via London–van der Waals forces between adsorbent and adsorbate molecules (Figure 2.12e).

(6) Hydrophobic Bonding

Sorption mechanism occurs when the hydrophobic groups of surfactant combine with their tendency to escape from an aqueous environment to adsorb on the solid adsorbent.



**Figure 2.12** Surfactant sorption mechanisms; (a) ion exchange, (b) ion pairing, (c) hydrogen bonding, (d) sorption via Lewis acid–Lewis base interaction, and (e) sorption by dispersion forces (Rosen, 2004).

### 2.5.2 Surfactant sorption on silica (Sand and silt)

Nonionic surfactants sorb on silica via hydrogen bonding between the oxygens of the oxyethylene (EO) group and SiOH group on the surface. When EO chain length increases the sorption of surfactants decrease due to the large size of hydrophilic group. Moreover, the length of EO groups relative to the characteristic of surfactant sorption. If the hydrophilic head contains short EO chains, bilayers are formed on the surface. When the EO chains are long, the layer of sorption composes of small admicelle (IshiguroandKoopal, 2016). For anionic surfactants, the sorption of anionic surfactant on silica is very limited due to the negative charge in hydrophilic head of these surfactants.

### 2.5.3 Surfactant sorption on clay

The sorption of nonionic surfactant on clay is similar to silica. The surfactant also sorbs on the kaolinite by hydrogen bonding between the EO group and the hydroxyl groups on the surface (IshiguroandKoopal, 2016). Brownawell *et al.* (1997) reported that the sorption of nonionic surfactant on soil was controlled primary by the swelling of clay. The EO chain length of nonionic surfactant also effect on sorption capacity of clay that similar to the silica. For anionic surfactant, the loss of anionic surfactant in the solution is a result of the surfactant abstraction. The abstraction are combining of adsorption and precipitation mechanism. Anionic surfactant adsorb on kaolinite by ion exchange and hydrophobic attraction. Meanwhile, the anionic surfactant also precipitate with  $Al^{3+}$  ions that release from clay lay at acidic condition (IshiguroandKoopal, 2016).

## 2.6 Enhanced the efficiency of surfactant

In soil washing process, surfactant is an important key point to clean up the contaminated soil. Good surfactants should have high solubilization and low IFT. There are many factor to reduce surface tension and IFT for example, temperature, electrolytes, co-surfactant and mixed surfactant (Rosen, 2004; Acosta *et al.*, 2007). Therefore, the efficiency of surfactant can enhance by following approaches:

### 2.6.1 Addition of electrolyte

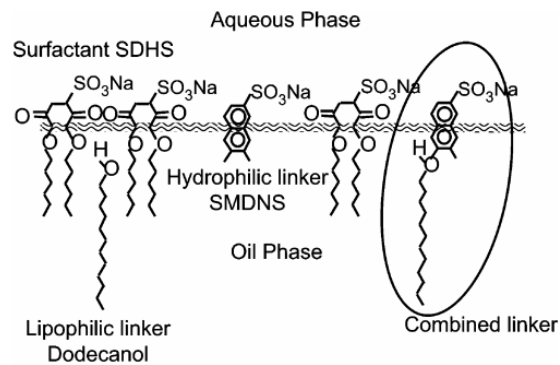
For ionic surfactants, adding electrolyte (i.e., NaCl) can minimize the electrostatic repulsions between the similarly charge of ionic head groups. This interaction decreases the CMC and increases the aggregation of micelles, resulting in increased the internal volume and the solubilization of hydrophobic contaminant in micelle (Rosen, 2004).

### 2.6.2 Temperature increasing

Most nonionic surfactants interact with water through hydrogen bounding. Increasing the temperature decreases the hydrogen bounding interactions, resulting in the surfactants more hydrophobic. This interaction caused nonionic surfactants are more hydrophobic at high temperature. When the temperature increase leading to a closely packed palisade region and an expansion of micelle inner core. Therefore, an area of hydrophobic contaminant solubilization are raised (Rosen, 2004).

### 2.6.3 Addition of Linker

Linker or co-surfactant is a small amphiphilic molecule, which has smaller head and tail parts as compared with a surfactant molecule. Linker is divided into 2 types: lipophilic linker (i.e., Dodecanol) and hydrophilic linker (i.e., sodium mono- and dimethyl-naphthalene sulfonates, SMDNS). Lipophilic linker is consist of polar organic molecule and long alkyl chain, thus it uses links between oil molecules and the surfactant tail (Figure 2.13). In case of hydrophilic linker, it comprises of mainly hydrophilic, hence it used as a linker between water molecules and the surfactant head. Adding both of linkers in the surfactant system can reduce IFT and improve the interaction of oil-water interface, resulting in higher solubility of oil (Acosta *et al.*, 2007).

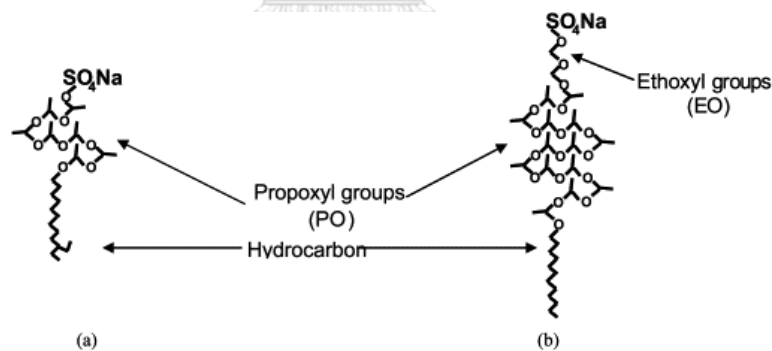


**Figure 2.13** Schematic of the lipophilic, hydrophilic and combined linker effects

(Acosta *et al.*, 2007)

#### 2.6.4 Addition of extended surfactant

Extended surfactant is a surfactant that contains intermediate polarity molecules, i.e., polyethylene (EOs) and/or polypropylene oxide groups (POs), which are filled the gap between hydrophilic head and hydrophobic tail (Figure 2.14). Due to their unique structures, extended surfactant can reduced IFT; moreover, their solubilization capacities higher than other surfactants.



**Figure 2.14** Structure of extended surfactants, (a)  $R-(PO)_x-SO_4Na$ , (b)  $R-(PO)_y-(EO)_2-$

$SO_4Na$  (Witthayapanyanon *et al.*, 2008)

### 2.7 Surfactant enhanced soil washing

#### 2.7.1 Mechanism of surfactant enhanced soil washing

Surfactants' applications in environmental remediation have been growing interested, especially, in soil washing process. Many researches have studied the

removal of oil through soil washing using aqueous surfactant solutions. They conclude that using surfactant for removal pollutants from soil occurring at concentrations below and above the surfactant CMC. Thus, two mechanisms have been proposed which are mobilization occurred below CMC and solubilization occurred above CMC. In the mobilization mechanism, surfactant monomers accumulate at soil/oil and soil/water interfaces, then they reduced IFT. After that, contact angle of soil/oil system is increased, hence the oil and the soil particles are separate (Figure 2.15). The second mechanism for enhanced soil washing is solubilization. When the concentration of surfactant monomers above the CMC, the hydrophobic part of surfactants is combined together inside the micelle structure with the hydrophilic part is exposed to the aqueous phase at the external micelle structure. For this reason, the interior of micelle is a compatible environment for hydrophobic molecule, then the oil can be solubilized into the micelle as shown in Figure 2.16 (Deshpandea *et al.*, 1999; Urum *et al.*, 2003; UrumandPekdemir, 2004).

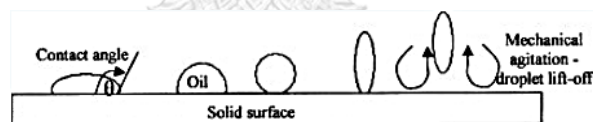


Figure 2.15 Mobilization mechanism (Childs *et al.*, 2004)

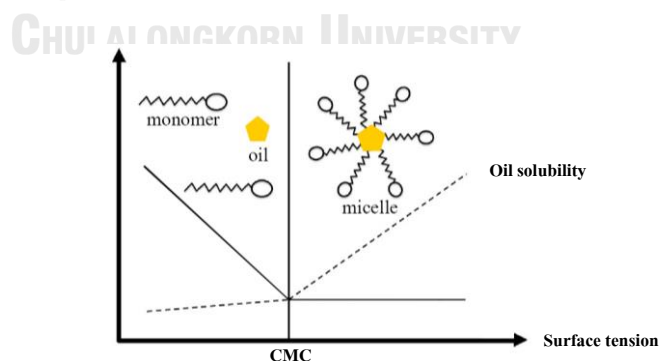
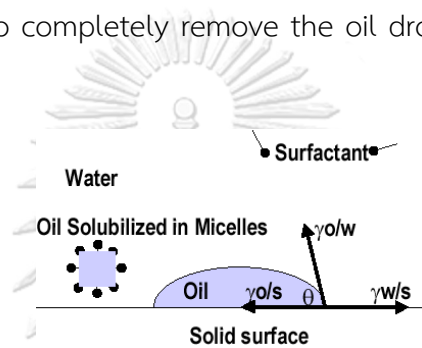


Figure 2.16 Solubilization mechanism, modified from Mao *et al.* (2015)

Sabatini *et al.*, (2001) also investigated the mechanism to remove oil droplet from drill cuttings exhibit in Figure 2.17. They proposed that there are three

main mechanisms: solubilization, snap-off and roll-up to remove oil droplet. When the oil is dissolved in the hydrophobic part of micelles, the solubilization is occurred (Figure 2.16). The snap-off mechanism is appeared when the mechanical agitation is stronger than the work of cohesion ( $WC=2\gamma_{O/W}$ ) of the droplet. This mechanism lead to a breakdown of droplet but some oil film is still attached to the solid surface (Figure 2.18). For the roll-up mechanism, the work of adhesion of the droplet ( $WA=\gamma_{O/W}(\cos\theta+1)$ ) to the surface is zero or negative ( $\theta>90^\circ$ ) that makes it easier for the mechanical forces to completely remove the oil droplet from the solid surface (Figure 2.15).



**Figure 2.17** Schematic of an oil droplet on a solid surface, showing the interfacial tensions between the oil droplet (O), the aqueous phase (W) and the solid surface (S), and the contact angle ( $\theta$ )

([https://cfpub.epa.gov/ncer\\_abstracts/index.cfm/fuseaction/display.highlight/abstract/6017/report/F](https://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.highlight/abstract/6017/report/F))



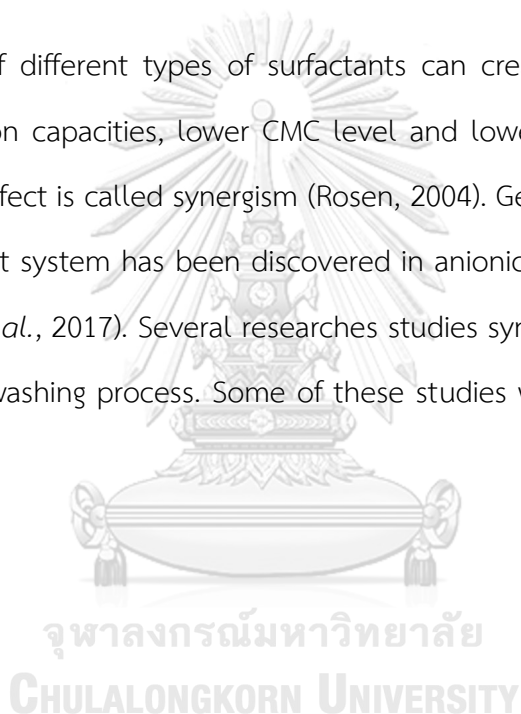
**Figure 0.1** Snap-off mechanism (Childs *et al.*, 2004)

In general, soil washing technology normally uses single surfactant to enhance the efficiency. However, the solubilization capacities of surfactants are minimized from the adsorption of individual surfactant on soil by decreasing the availability of surfactants for micelles solubilization. The sorption of nonionic surfactant on soil increased with the amount of oxyethylene and alkyl chain length

(Rao and He, 2006) and soil organic matter (M. Cheng *et al.*, 2017). In addition, several studies report that hydrogen bonding and van der Waals attraction forces between nonionic surfactant and mineral oxides in soil cause the adsorption of nonionic surfactant on soil (Shen, 2000; S. Kang and Jeong, 2015). To solve these problems, mixed surfactant is a good alternative in scientific and industrial applications because of the synergistic advantages compared with single surfactant.

### 2.7.2 Synergism of mixed surfactants

Mixing of different types of surfactants can create better properties (i.e., higher solubilization capacities, lower CMC level and lower IFT) than the individual surfactants. This effect is called synergism (Rosen, 2004). Generally, synergist behavior of mixed surfactant system has been discovered in anionic and nonionic (Mao *et al.*, 2015; M. Cheng *et al.*, 2017). Several researches study synergist interaction in mixed surfactant in soil washing process. Some of these studies were summarized in Table 2.7.



**Table 2.7** Summary of mixed surfactant enhancing soil washing

Surfactant	Soil properties	Liquid/Solid ratio	Application	References
SDBS - Tween80 (anionic-nonionic)	- Organic matter (OM) 1.02% - Clay content (d < 0.2 mm) 37.6%	20 mL of surfactant : 2 g of soil	Enhanced p-nitrochlorobenzene (pNCB) removal	Guo <i>et al.</i> (2009)
SDBS - TX100 (anionic-nonionic)	- Organic carbon 1.43% - Clay contents 47.8%	20 mL of surfactant : 2 g of soil	Enhanced Phenanthrene removal	Yang <i>et al.</i> (2006)
SDBS - Tween80 (anionic-nonionic)	- Organic carbon 0.97%	15 mL of surfactant : 3 g of soil	Enhanced PAHs removal	Zhang and Zhu (2010)
SDS - TX100 and SDBS - TX100 (anionic-nonionic)	- Total organic matter (TOC) 0.65%	10 mL of surfactant : 1 g of soil	Enhanced remediation of PAH-contaminated soil	Shi <i>et al.</i> (2015)

Guo *et al.* (2009) evaluated the sorption of Tween 80 by the soil in the mixed surfactant system with different SDBS/Tween80 ratio. Results exhibited that the amount of adsorbed Tween 80 was significantly dropped when increasing SDBS/Tween80 ratio from 0 to 1:1. It is due to the adding of the SDBS can increase the negative surface charge of mixed micelles; therefore the electrostatic attraction between Tween 80 and soil particles decreased. Similar results were obtained by Zhang and Zhu (2010) and Yuan *et al.* (2007) who evaluated the performance of mixed SDBS–Tween 80 in soil washing system.

Yang *et al.* (2006) studied sorption of the mixtures of a nonionic surfactant (TX100) and an anionic surfactant (SDBS) by a phenanthrene-contaminated soil and evaluated the performance of anionic-nonionic mixed surfactants in phenanthrene desorption. They found that the lowest adsorption (15 mg/g) of surfactants was obtained when TX100 and SDBS were mixed at a mass ratio of 1:9 (total



concentration was 7 g/L). On the other hand, the adsorption loss of individual TX-100 and SDBS approximately 70 and 50 mg/g, respectively. This is due to a mixing of surfactants could inhibit the adsorption of individual surfactant onto soil in a mixed system. Moreover, Phenanthrene desorption by mixed solutions was better than that of individual surfactants because of the low sorption loss of mixed surfactants to soil.

Zhang and Zhu (2010) examined sorption of SDBS–Tween 80 on soil; and the effect of mixed surfactants on the distribution of PAHs in soil–water system. The results showed that SDBS-Tween 80 mixed surfactant minimized their sorption on soil mutually, hence the effective concentration of surfactants in solution and the desorption efficiency of PAHs were better. The highest desorption efficiency was achieved with the lowest proportion of SDBS (SDBS/Tween 80=1:9), which indicated that adding the suitable amount of anionic surfactant could significantly promote the efficiency of PAHs desorption.

Even though using mixed synthetic surfactants in soil washing provide many good advantages such as high capability and low cost, they also have disadvantages, for example, applying synthetic surfactants in environmental remediation are often toxic and harmful to the ecological function (Liu *et al.*, 2016). In addition, Mohammad and Moheman (2012) investigated the effect of an anionic (SDS) and nonionic (TritonX-100) surfactants on growth and nutrients uptake by wheat plants. They found that anionic surfactant (SDS) in soil have more toxic to plant growth and nutrient uptake of more than nonionic (TritonX-100). Therefore, microbial derived emulsifiers designed as biosurfactants can be the best alternative to use in soil washing process.

Nowadays, most studies have focused on combination of two types of synthetic surfactant for enhancing soil washing performance such as TX100-SDBS and Tween 80-SDBS. There were a few studies of using synthetic and biosurfactant in soil washing application. Therefore, this could be a highlight of our work.

### 2.7.3 Physical conditions for enhanced soil washing

Influence of physical factors on oil removal efficiency will be studied to determine the optimum condition for achievable the highest soil washing performance. Several researchers found that surfactant concentration, pH, temperature, shaking speed and liquid/soil ratio significantly affected on oil soil washing process.

Urum *et al.* (2003) examined the optimum conditions for washing Ekofisk crude oil contaminated soil with biosurfactant solution using the Taguchi experimental design method. A synthetic surfactant, sodium dodecyl sulphate (SDS) and the biosurfactants namely aescin, lecithin, rhamnolipid, saponin, tannin were tested. They reported that the optimum condition for temperature and time for all the surfactant solution were 50 °C and 10 min. Meanwhile, other parameters showed optimum values at different points. SDS, rhamnolipid and saponin showed an oil removal higher than 79%.

Yan *et al.* (2011) evaluated the optimum conditions which achieved the best organics and TPH removal from oil-based drill cuttings (ODC) contaminated soil using rhamnolipid biosurfactant. They studied five factors including biosurfactant concentration, liquid-solid ratio (L-S, v/m), washing time, stirring speed, and temperature. The results showed that the optimum conditions were rhamnolipid concentration, 360 mg/L; liquid/solid ratio, 3:1; washing time, 20 min; stirring speed, 200 rpm; temperature, 60 °C gave approximately 83% and 85% of organics and TPH removal, respectively.

## CHAPTER 3

### METHODOLOGY

#### 3.1 Experimental design for research

The research was divided into three phases, including Phase I formulation of mixed surfactant, Phase II effect of mixed surfactant on surfactant sorption on soil and diesel soil washing efficiency, and Phase III optimizing soil washing condition. The main objective of Phase I was formulation the appropriate mixed Tween 80 and biosurfactant solution, which showed the lowest IFT with diesel and lowest CMC for applying in Phase II and Phase III. Phase I was composed of two parts: Part I-A: measuring IFT of surfactant with diesel and Part I-B: measuring CMC of surfactants. A synthetic surfactant, Tween 80 and mixture of Tween 80 with three biosurfactant (rhamnolipid, saponin and lipopeptide) were studied in Part I-A and Part I-B. The main objectives of Phase II were to determine the sorption of surfactants on soil and the effect of the surfactant sorption on diesel soil washing. Phase II consisted of two parts as: Part II-A: sorption of surfactant on artificial soil (sand, silt, and clay) and Part II-B: diesel soil washing test. In part II-B, two types of soil, artificial soil and natural soil samples were used to compare the efficiency of diesel soil washing. The phase III aimed to evaluate the optimizing process conditions of diesel contaminated soil washing mixed surfactant solution to examine effect of physical factors on the diesel removal. Flowchart of the research was illustrated in Figure 3.1.

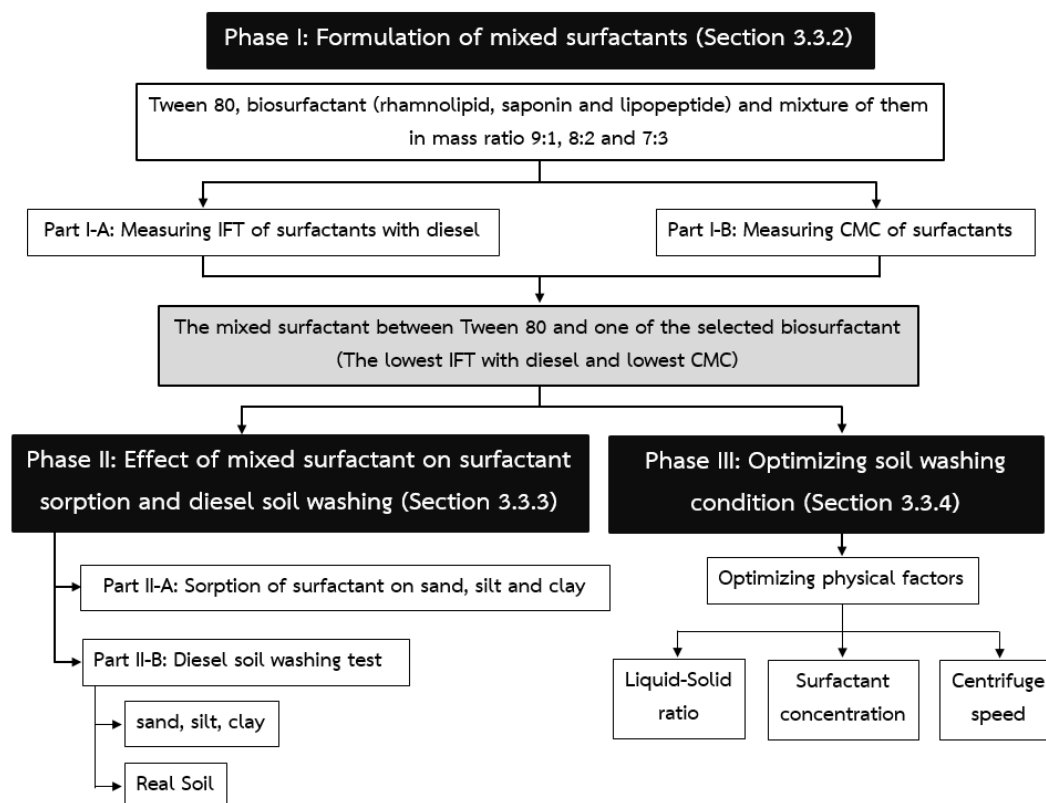


Figure 3.1 Experimental design for research.

## 3.2 Materials

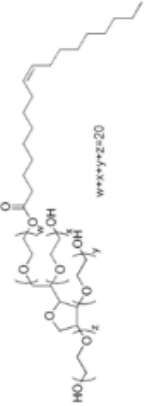
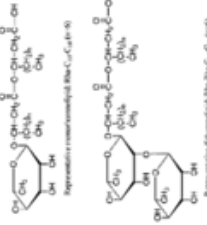
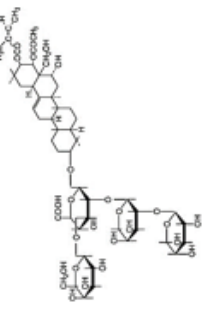
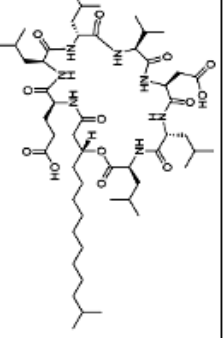
### 3.2.1 Surfactants

The experiment was conducted using one type of synthetic surfactant named Tween 80 and three types of biosurfactant, which were rhamnolipid, saponin and lipopeptide. Tween 80 was purchased from Ajax Finechem. Rhamnolipid was purchased from Zhonglan Industry Co., Ltd (China) whose product is a mixture of mono- and di- RL in the ratio of 55:45. Saponin was purchased from Xian Lukee Bio-Tech Co., Ltd (China). Saponin used in this study was produced from tea saponin with the purity more than 60%. Lipopeptides power was received from Department of Microbiology, Faculty of Science, Chulalongkorn University. The lipopeptide active 50% (w/w) was produced from *Bacillus sp.* GY19 and recovered from cell-freebroth

by foam fractionation. The properties and molecular structure of surfactants were exhibited in Table 3.1.



Table 3.1 Surfactant properties and structures

Surfactant	Type	Producing strain	CMC (mg/L)	MW (g/mol)	Molecular structure
Tween80	Nonionic	Chemical synthesis	15.7	1310.0 <sup>a</sup>	
Rhamnolipid	Anionic	<i>Pseudomonas aeruginosa</i>	479.0	486.0	
Saponin	Nonionic	Tea saponin (Plant)	1,395.0	1190.0	
Lipopeptide (Surfactin)	Anionic	<i>Bacillus sp. GY19</i>	500.0 <sup>b</sup>	1049.0 <sup>b</sup>	

<sup>a</sup>MW of TW from M. Cheng *et al.* (2017)

<sup>b</sup>CMC and MW from Rongsayamanont *et al.* (2017)

### 3.2.2 Diesel fuel

The diesel fuel used in this experiment was purchased from Esso gas station located in Bangkok, Thailand.

### 3.2.3 Soil

Sand and clay (kaolin) were purchased from Fisher scientific. For silt, this soil was prepared by grinding the sand using a stone crushing machine and sieved through mesh number 324 (0.045 mm).

Soil sample was collected from a non-contaminated area in Suphanburi Province, Thailand. The sample was sieved at 2 mm to remove large debris and ensure homogeneous mixing. The soil properties were analyzed by the research and Development Division of agricultural production, Department of Agriculture, Bangkok, Thailand. This soil was classified as a clay loam with medium organic matter content. Proportions of sand, silt, and clay content were 24.0%, 40.5%, and 35.2%, respectively. The values of OM and CEC were 2.04% and 17.90 cmol/kg, respectively.

### 3.2.4 Chemicals

Hexane 95% (AR Grade) and acetonitrile (HPLC Grade) were purchased from RCI LABSCAN CO., LTD.

## 3.3 Methods

### 3.3.1 Diesel contaminated soil preparation

Artificially contaminated soil was prepared by thoroughly mixing the soil with dissolved diesel in hexane to achieve the initial concentration at 50,000 mg/kg to cover the highest concentration of diesel in soil that widely found at hot spots (Lin *et al.*, 2011). The soil sample was placed in the hood for 3 days. The diesel content in the contaminated soils after 3 days stabilization were approximately

35,000-40,000 mg/kg dry soil. Every batch experiment, initial diesel concentration in soil were determined followed section 3.3.5.

### 3.3.2 Formulation of mixed surfactants (Phase I)

#### 3.3.2.1 Measuring IFT of surfactants with diesel fuel (Part I-A)

Tween 80, three biosurfactant (rhamnolipid, saponin, and lipopeptide) and mixed surfactants were prepared at 5% w/v of active surfactants. For mixed solution, the ratio of mixed Tween 80 (synthetic surfactant) and biosurfactants were varied at mass ratio of 9:1, 8:2, and 7:3 of total concentration. The IFT between the aqueous surfactant solution and the diesel was measured using a Spinning Drop Tensiometer (Dataphysics, model SVT20). A small amount of diesel (light phase) was injected into the tube filled with the surfactant solution (heavy phase). The spinning speed was set at 6000 rpm. All the measurements were done in triplicate at  $25\pm 1^\circ\text{C}$ .

#### 3.3.2.2 Measuring CMC of surfactants (Part I-B)

Mixed surfactants (synthetic surfactant, Tween 80 and biosurfactants named rhamnolipid, saponin, and lipopeptide) were prepared at concentration 4000 mg/L. The ratio of mixed solution was varied at mass ratio of 9:1, 8:2, and 7:3 of total concentration (Tween 80 to biosurfactants). Mixed surfactant solutions were diluted into different concentration. Then, the surface tension was measured for each concentration by Tensiometer (Dataphysics - DCAT 11, Germany) at  $25^\circ\text{C}$  using the plate method. The CMC value was obtained from the cross section of the plot between surface tension and serial dilution of surfactant solution.



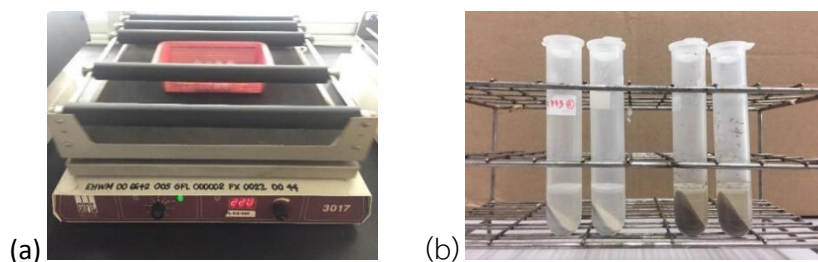
### 3.3.3 Effect of mixed surfactant on surfactant sorption on soil and diesel soil washing (Phase II)

#### 3.3.3.1 Sorption of surfactants on soil (Part II-A)

Mixed surfactant between Tween 80 and one of the selected biosurfactant that provided the lowest IFT (section 3.3.2.1, part I-A) and CMC (section 3.3.2.2, part I-B) was applied in this section. One-gram of soil was mixed with 3 ml of surfactant solution in a centrifuge tube. The soil mixture was shaken at 220 rpm for 30 min, and then centrifuged at 3000 rpm for 20 min. After that, supernatant was collected and analyzed for the residual surfactant by HPLC-ELSD. Soil compositions (proportion of sand, silt and clay in the experiment) were prepared followed the mixture design. The results of the mixed surfactant sorption were compared with those of single surfactant under the similar process conditions.

#### 3.3.3.2 Diesel soil washing test (Part II-B)

Mixed surfactant between Tween 80 and one of the selected biosurfactant that provided the lowest IFT (section 3.3.2.1, part I-A) and CMC (section 3.3.2.2, part I-B) was applied in this section. The diesel contaminated soil at 1 g and 3 ml of surfactant solution were added into a centrifuge tube. A control test was performed by mixing 1 g of contaminated soil and 3 mL of distilled water. The centrifuge tube was placed on a shaker. Then, these following factors were set: shaking speed 220 rpm, and shaking time 30 min (Figure 3.2a). After washing, the suspended particles of the tube was settled by centrifugation at 3000 rpm over 20 min (Figure 3.2b). The washing solution was separated from the tube. The washed soil was rinsed with distilled water 3 ml to remove the residual diesel and surfactant solution before extracting with solvent. The residual diesel concentration in soil was analyzed by GC-FID (section 3.5.2).



**Figure 3.2** Soil washing experiment

(a) Washing method in laboratory scale

(b) Settlement of soil after washing and centrifugation

### 3.3.4 Optimizing soil washing condition (Phase II)

The appropriate formulation of mixed two surfactants from Phase I was applied in this phase. Surfactant concentration (1, 2 and 3 % w/v of active surfactant concentration), Liquid-solid ratio (L-S ratio, 1:2, 1:3, and 1:4) and centrifuge speed (1500, 2000, and 2500 rpm) were varied to optimize the conditions using central composite rotatable design (CCRD). The results of the optimal conditions were compared with those of single surfactant under the similar process conditions.

### 3.3.5 Analytical method

#### 3.3.5.1 Surfactants measurement

The concentration of residual surfactants in the supernatant was analyzed using a Shimadzu-HPLC with auto injection (model Shimadzu-10Avp, Japan) and a Sedere-ELSD (model Sedex 75, France) as a detector. The Inertsil ODS-3 C18 column (4.6×150 mm, 5 μm, Japan) was used with a mobile phase consisting of water and acetonitrile. The mobile phase flow rate was fixed at 1.0 mL/min with 10 μL of injection volume. During the first 5 min of the run, the water was maintained at 100%. The water was decreased to reach 40% at 6 min and 20% at 10 min. After maintaining 20% water from 10 to 15 min, the mobile phase was changed back to

100% water at 15.1 min, and the column was equilibrated until 25 min. The detection temperature and pressure of ELSD were 45°C and 2.8 bar, respectively.

### 3.3.5.2 Diesel extraction and diesel measurement

After removing surfactant solution and rinsing with 3 ml of distilled water, the residual diesel in washed soil was extracted by hexane. The washed soil 1 g in a tube was mixed and shook with 3 ml of hexane using vortex for 1 min. Then, this tube was centrifuge at 3000 rpm for 15 min and the supernatant was collected. The extraction process was repeated six times. The supernatant was pooled together and adjusted volume to 20 ml by hexane. Before analyzing, the supernatant was filtered through 0.45  $\mu\text{m}$  PTFE filter and kept in GC glass vial. The diesel concentration in the supernatant was determined by a GC (Agilent 6890N, Germany) equipped with a flame ionization detector (FID), and a column HP-5 (30 m x 0.32mm x 0.25  $\mu\text{m}$ ). The temperature of the oven remained at 40°C for 5 min, and then was raised at a rate of 15°C/min to a temperature of 300°C, which was held for 5 min. The injector and detector were 300 and 330°C, respectively. The carrier gas was nitrogen at a flow rate of 2 mL/min.

### 3.3.6 Statistical analysis

The data was analyzed using ANOVA by STATISTICA 10 program (StatSoft Tulsa, OK, USA). Fisher's LSD (Least Significant Difference) of post hoc test was applied to explore the multiple mean comparison when a significant difference of the treatment is showed (p-value <0.05).

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Formulation of mixed surfactant

Tween 80 is a nonionic surfactant that has been widely used in soil remediation due to its high removal efficiency, low cost and low toxicity. However, the information about mixed Tween 80 with other biosurfactant to create the better efficiency has not been reported. In this study, Tween 80 was mixed with three types of biosurfactant (Rhamnolipid, Saponin and Lipopeptide) in different mass ratio to formulate the appropriate mixed Tween 80 and biosurfactant solution. The performance of mixed surfactant can be evaluated by measuring physical parameters such as IFT and CMC.

##### 4.1.1 IFTs of single and mixed surfactants with diesel fuel

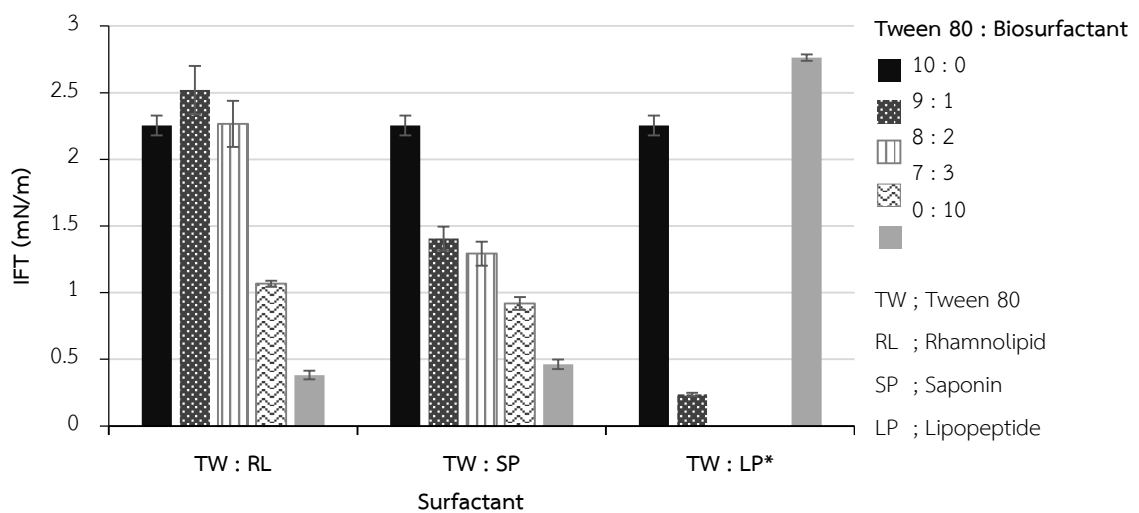
IFT is a force per unit length existing at the interface between two immiscible phases. Lowering of IFT can enhanced the oil movement from soil to extraction media (UrumanPekdemir, 2004). In this study, IFTs of surfactant with diesel were measured using a Spinning Drop Tensiometer. The results showed that the mixture of Tween 80 and Lipopeptide at 9:1 ratio of total concentration provided the lowest IFT with diesel, compare to other ratios with other biosurfactants 9 (Figure 4.1).

The IFTs from a Spinning Drop Tensiometer were calculated using Eq. (1) suggested by Bernard Vonnegut (Viades-TrejoandGracia-Fadrique, 2007). The schematic illustration of the spinning drop method between mixed surfactant solution (Tween 80 and Lipopeptide) and single Tween 80 with diesel is displayed in Figure 4.2. When compared the shape of a diesel drop and the radius of the cylinder ( $r$ ) in the tube, it can be seen that the diesel drop in the mixture of Tween 80 and Lipopeptide was more cylindrical than the single Tween 80 surfactant solution. Meanwhile,  $r$  in the mixed Tween 80 and Lipopeptide also lower than the single

Tween 80 surfactant solution. The correlation between IFT and  $r$  could be described by Eq. (1) that IFT decreased with the decreasing of  $r$ . The lowest IFT of mixed Tween 80 and Lipopeptide with diesel is a result of the structure of hydrophobic tail of Lipopeptide that contains longer straight carbon chain compared to other biosurfactants. Moreover, adding Lipopeptide might increase the solubility of diesel due to the amides in its hydrophobic group.

$$IFT \text{ (mN/m)} = \frac{\Delta\rho\omega^2r^3}{4} \quad (1)$$

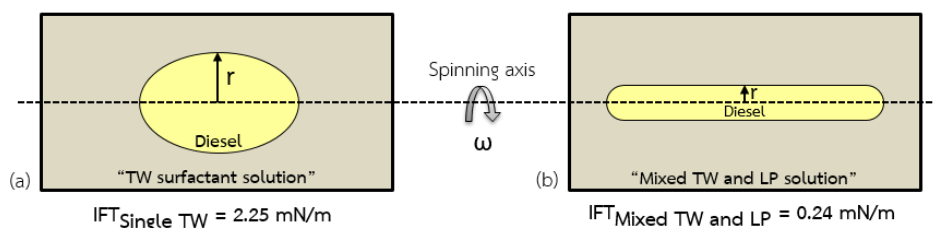
Where  $\Delta\rho$  is the density difference between phases,  $\omega$  is the rotational velocities and  $r$  is the radius of the cylinder.



**Figure 4.1** IFT values of single Tween 80, biosurfactants, and mixed Tween 80 and biosurfactant solution with diesel.

\*Single Lipopetide was prepared at concentration 0.5% w/v.

\*Mixed Tween 80 and Lipopeptide was prepared at mass ratio 9:1.



**Figure 4.2** Schematic illustration of the spinning drop method of surfactant solution and diesel; (a) single Tween 80 surfactant solution as a dense phase and (b) mixed Tween 80 and Lipopeptide solution as a light phase

#### 4.1.2 CMC values of single and mixed surfactants

CMC is the lowest concentration that the first micelle can be formed. CMCs of individual and mixed surfactant from experimental are present in Table 4.1. The result showed that mixing Tween 80 and biosurfactant especially Tween 80 and Lipopeptide at mass ratio of 9:1 dramatically reduced the CMC value compared to that of the single biosurfactants. However, the CMCs of mixed surfactants were still higher than the CMC of single Tween 80 solution.

**Table 4.1** CMCs of single Tween 80, biosurfactants, and mixed Tween 80 with biosurfactant solutions from experimental.

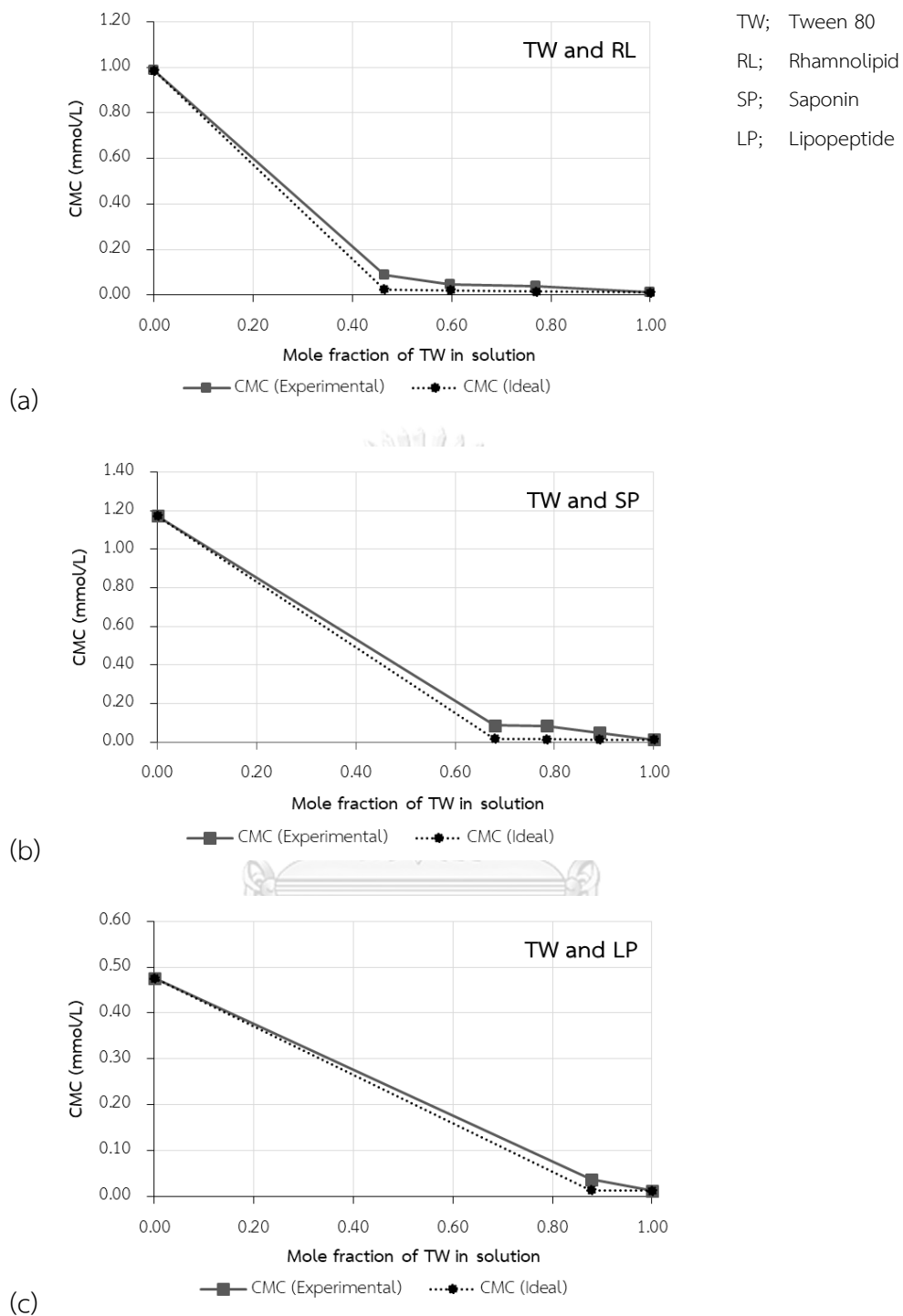
Single surfactant	CMC of single surfactant		Mass ratio of Tween 80 and biosurfactant	CMC of mixed surfactant	
	mg/L	mM		mg/L	mM
Tween 80	15.7	0.01	-	-	-
Rhamnolipid	479.1	0.99	9 : 1	49.7	0.04
			8 : 2	54.3	0.05
			7 : 3	78.0	0.09
Saponin	1395.0	1.17	9 : 1	63.4	0.05
			8 : 2	107.0	0.08
			7 : 3	111.0	0.09
Lipopeptide	500.0	0.48	9 : 1	47.2	0.04

To investigate the interaction between Tween 80 and three biosurfactants in mixed surfactant solution, ideal and non-ideal solution theory as mentioned by Zhou and Zhu (2005) was used in this study. In ideal mixed surfactant solution, the CMCs can be calculated by Eq. (2).

$$\frac{1}{CMC_{Mixed}} = \frac{X_{TW}}{CMC_{TW}} + \frac{X_{Bio}}{CMC_{Bio}} \quad (2)$$

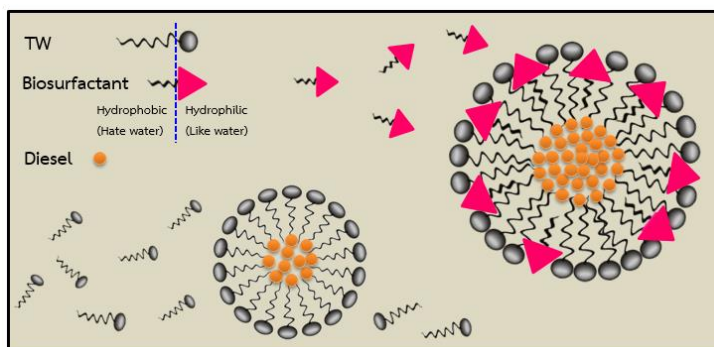
Where  $CMC_{mixed}$ ,  $CMC_{TW}$  and  $CMC_{Bio}$  are the critical micelle concentration of mixed surfactant and individual pure surfactants Tween 80 and biosurfactants, respectively.  $X_{TW}$  and  $X_{Bio}$  are the mole fraction of Tween 80 and biosurfactants in the mixed surfactant solution, respectively.

The experimental and ideal CMCs of mixed Tween 80 and biosurfactant were illustrated in Figure 4.3. It could be found that the experimental CMCs decrease with increasing mole fraction of Tween 80. However, the experimental CMCs of mixed Tween 80 and Lipopeptide were slightly higher than those predicted by Eq. (2), indicating that the mixed micelle formation between Tween 80 and three biosurfactants showed negatives synergistic effect on CMC value. This due to the bulky structure of biosurfactant. When biosurfactants aggregate with Tween 80 micelle, the size of micelle was increased. The bigger of micelle required more surfactant monomer to form the micelle; therefore, the CMC of micelle was increased (Figure 4.4).



**Figure 4.3** Experimental and ideal CMCs of mixed Tween 80 and biosurfactant solution.





**Figure 4.4** Effect of adding biosurfactants on mixed surfactant micelle

## 4.2 Effect of mixed surfactant on surfactant sorption and diesel soil washing

According to the results from section 4.1, mixture of Tween 80 and Lipopeptide at mass ratio 9:1, which showed the lowest IFT with diesel and CMC, was selected to study the effect of mixed surfactant solution on surfactant sorption (Tween 80 and Lipopeptide) and diesel removal efficiency on the difference soil type. To determine the relationship between the response variables (sorption of surfactant and diesel removal efficiency) and the soil texture, the mixture design was applied using a Statistica program 9 (version 10).

### 4.2.1 Sorption of surfactants on soil

The results of surfactant sorption on soil are shown in Table 4.2. The details of experimental data are in the Appendix (Table A4 – A7.). The sorption of Tween 80 from single Tween 80 solution on the soil with single texture shows the trend as expected that the sorption result was found on sand < silt < clay according to their particles size. Surprisingly that the sorption of Lipopeptide which is classified as anionic surfactant shows insignificantly affected by the texture of soil (% sorption in the range of 22.36 to 26.53) (see Table 4.2). On the other hand Tween 80 shows significantly interaction with soil texture. This can be seen from % sorption of Tween 80 in different type of soil. Soil sample with higher clay ratio tended to have higher % sorption of Tween 80 in both single Tween 80 and mixed Tween 80 and Lipopeptide solution. Once proportion of clay in the soil texture reduced, i.e., from 100% clay (no.3) to 16.7% clay soil (no. 8), the sorption of clay was reduced dramatically reduced to 69.66% and 22.08% for the systems of single Tween 80 and

mixed Tween 80 and Lipopeptide solutions, respectively. This confirms that Tween 80 has stronger interaction with clay than those of Lipopeptide.

**Table 4.2** Sorption of surfactants from the single and mixed surfactant solutions on the different soil texture

No.	Soil	Sorption (%)			
		Tween 80 from single Tween 80 solution AVG $\pm$ SD	Tween 80 from mixed solution AVG $\pm$ SD	Lipopeptide from single Lipopeptide solution AVG $\pm$ SD	Lipopeptide from mixed solution AVG $\pm$ SD
1	Sand 1 g	4.47 $\pm$ 3.8	19.67 $\pm$ 1.1	23.43 $\pm$ 0.3	4.63 $\pm$ 3.5
2	Silt 1 g	58.32 $\pm$ 3.8	22.74 $\pm$ 0.4	25.81 $\pm$ 7.1	2.80 $\pm$ 0.8
3	Clay 1 g	86.94 $\pm$ 3.0	85.12 $\pm$ 0.2	22.73 $\pm$ 0.3	10.85 $\pm$ 7.8
4	0.5 g (Sand and Silt)	58.88 $\pm$ 8.8	22.52 $\pm$ 0.4	26.51 $\pm$ 0.7	34.09 $\pm$ 7.8
5	0.5 g (Sand and Clay)	89.51 $\pm$ 0.7	37.93 $\pm$ 4.7	23.92 $\pm$ 0.2	10.50 $\pm$ 0.3
6	0.5 g (Silt and clay)	87.82 $\pm$ 0.9	29.42 $\pm$ 1.5	23.15 $\pm$ 0.8	10.15 $\pm$ 0.3
7	0.667 g (Sand) + 0.167 g (Silt and Clay)	71.87 $\pm$ 1.1	7.99 $\pm$ 1.8	26.53 $\pm$ 0.4	12.20 $\pm$ 0.0
8	0.667 g (Silt) + 0.167 g (Sand and Clay)	69.66 $\pm$ 1.3	22.08 $\pm$ 1.8	25.16 $\pm$ 0.1	10.60 $\pm$ 2.5
9	0.667 g (Clay) + 0.167 g (Sand and Silt)	81.36 $\pm$ 0.1	41.94 $\pm$ 1.5	22.36 $\pm$ 0.7	7.82 $\pm$ 0.1
10	0.333 g (Sand, Silt and Clay)	68.60 $\pm$ 1.7	22.32 $\pm$ 6.4	23.48 $\pm$ 1.0	11.49 $\pm$ 0.3

In order to evaluate the complicate correlation of adsorbate (surfactant and adsorbent (soils with different texture), the sorption experimental data were analyzed and generated the predicted equation based on regression analysis for sorption of Tween 80 in single (equation 3), mixed surfactant (equation 4) as well as sorption of Lipopeptide in mixed surfactant (equation 5) system. For sorption of Lipopeptide in single surfactant solution, the result of model prediction is not presented here because the sorption behavior of Lipopeptide could not be fitted with any model in the mixture design ( $R^2$  0.43). Table 4.3 listed the ANOVA and statistical analysis for the response variables. Finally, the predicted equations were

used to generate the contoured graphs for each surfactant system as shown in Figure 4.5.

*Sorption Tween 80 in single (%)*

$$= 4.95X_1 + 58.80X_2 + 87.42X_3 + 111.85X_1X_2 + 177.14X_1X_3 + 62.68X_2X_3 - 446.88X_1X_2X_3 + 69.26X_1X_2(X_1 - X_2) + 214.17X_1X_3(X_1 - X_3) \quad (3)$$

*Sorption Tween 80 in mixed (%)*

$$= 19.29X_1 + 22.37X_2 + 84.75X_3 + 3.76X_1X_2 - 59.36X_1X_3 - 99.52X_2X_3 - 160.21X_1X_2X_3 - 131.79X_1X_2(X_1 - X_2) - 22.54X_1X_3(X_1 - X_3) \quad (4)$$

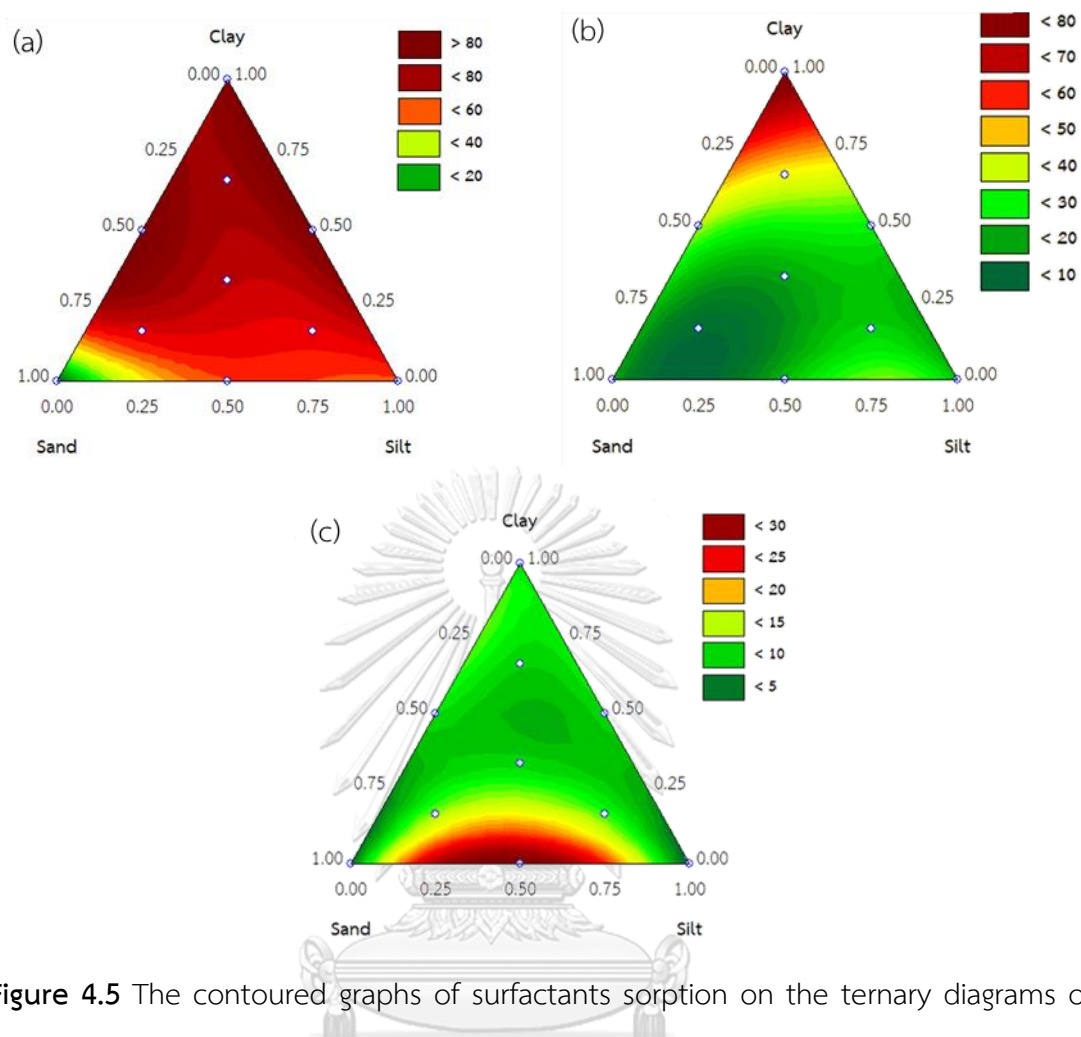
*Sorption Lipopeptide in mixed (%)*

$$= 4.39X_1 + 2.56X_2 + 10.62X_3 + 120.57X_1X_2 + 10.12X_1X_3 + 12.39X_2X_3 - 333.73X_1X_2X_3 + 19.59X_1X_2(X_1 - X_2) - 23.54X_1X_3(X_1 - X_3) \quad (5)$$

Where  $X_1$ ,  $X_2$ ,  $X_3$  were mass of sand, silt, clay, respectively.

**Table 4.3** ANOVA and statistical analysis of the studied model (Surfactant sorption)

Surfactant solution	Model	Fitting model	P value	R <sup>2</sup>	R <sup>2</sup> adjusted
Tween 80 5% w/v (Single solution)	Equation 3	Full cubic	0.000000	0.981	0.967
Tween 80 4.5% w/v (Mixed solution)	Equation 4	Full cubic	0.000001	0.984	0.972
Lipopeptide 0.5% w/v (Mixed solution)	Equation 5	Full cubic	0.000022	0.884	0.830



**Figure 4.5** The contoured graphs of surfactants sorption on the ternary diagrams of difference soil type composition; (a) the Tween 80 sorption on the soil from the 4.5% single surfactant solution, (b) the Tween 80 sorption on the soil from the 4.5% mixed surfactants solution, and (c) the Lipopeptide sorption on the soil from the 4.5% mixed surfactants solution.

The results showed that presence of Lipopeptide in mixed surfactant rapidly decreased the sorption of Tween 80 on soil compared to that of the single Tween 80 solution (Figure 4.5a and 4.5b). In general, the sorption of Tween 80 is attributed to hydrogen bonding (Yang *et al.*, 2006) and double bond (Al-Koofee, 2013) in its structure. When anionic surfactants were added, the negative surface charge of mixed micelle could generate the repulsive power to the soil which naturally has a same negative charge on its surface (Yang *et al.* 2006, Zhang and Zhu 2010, Cheng *et al.* 2017). Moreover, this result agreed well with the previous studies

by Yang et al. (2006) and Zhang and Zhu (2010). They mentioned that adding SDBS (anionic surfactant) minimizes the sorption of Tween 80 on soil due to charge repulsive effect between Tween 80 and SDBS.

To confirm the effect of mixed Tween 80 and Lipopeptide, the sorption of Lipopeptide on soil also determined. It can be seen from Figure 4.5c that the sorbed Lipopeptide on soil is lower than the sorbed Tween 80 (Figure 4.5a and 4.5b) because of the electrostatic repulsion between the negative charge on soil surface and the hydrophobic head of Lipopeptide anionic surfactant (Yang et al. 2006). Therefore, LP did not adsorb on soil instead of Tween 80. In addition, Tween 80 also reduce the loss of Lipopeptide from 22-26% (in single solution) to 5-30% (in mixed solution, Figure 4.5c) because the adding Tween 80 (nonionic surfactant) decreases the precipitation between Lipopeptide (anionic surfactant) and multivalent electrolyte in soil (e.g.  $Al^{3+}$  and  $Ca^{2+}$ ) (Yang et al. 2006, Zhang and Zhu 2010, Cheng et al. 2017). The sorption of Lipopeptide in the single Lipopeptide solution is not presented here.

For influence of soil texture on Tween 80 and Lipopeptide sorption, p-value from Table 4.3 can be implied that soil texture significantly affected Tween 80 (in the single and mixed solutions) sorption (p-value < 0.05). When compared the amount of sorbed Tween 80 in single and mixed solution, the contour plot (Figure 4.5a and 4.5b) illustrated that the sorption of Tween 80 (in the mixed solution) was still high in the soil consisting of high clay proportion (approximately 80%). It could be explained by the effect of high surface area of clay minerals. In case of Lipopeptide (in the mixed solution), soil texture showed slightly effect to Lipopeptide sorption. On the other hand, the statistical analysis confirmed that soil texture was insignificantly effect to Lipopeptide (in mixed solution) sorption (p-value < 0.05).

#### **4.2.2 Diesel soil washing test**

The artificially contaminated soil was prepared by mixing dissolved diesel in hexane with artificial soil to achieve the initial concentration 50,000 mg/kg. After 3 days stabilization, they remained in soil 35,000-40,000 mg/kg. The results of diesel

removal from various soil compositions with the single and mixed surfactant solutions are shown in Table 4.4. The details of experimental data are in the Appendix (Table A8 - A10). The results show that for the same pure soil texture, i.e. 100% of sand, silt and clay, mixed surfactant of Tween 80 and Lipopeptide yields slightly higher efficiency than the single system of both Tween 80 and Lipopeptide. However, it should be noted here that single Lipopeptide solution used for soil washing was only 0.5% w/v due to the limitation of the purity of Lipopeptide. This may be an important factor resulted to the lower removal efficiency. Besides that, for soil washing with the system of single surfactant both Tween 80 and Lipopeptide, it seems to have a better performance with the pure clay and the soil mixture with clay. Similar result was found with the mixed surfactant solution.

**Table 4.4** Diesel removal Efficiency of soil washing by the single and mixed surfactant solutions

No.	Soil	Diesel Removal Efficiency (%)		
		5.0% (w/v) Tween 80 solution	0.50% (w/v) Lipopeptide solution	5.0% (w/v) mixed solution of Tween 80 and Lipopeptide (9:1 ratio)
		AVG	AVG	AVG
1	Sand 1 g	75.75±1.9	53.82±0.8	77.33±0.6
2	Silt 1 g	73.67±1.9	43.02±1.5	74.06±1.2
3	Clay 1 g	77.59±0.7	61.35±8.4	78.47±0.0
4	0.5 g (Sand and Silt)	77.61±0.8	48.78±6.2	70.38±0.2
5	0.5 g (Sand and Clay)	82.99±0.4	63.05±2.6	77.10±0.1
6	0.5 g (Silt and clay)	84.76±0.2	60.68±0.2	78.12±0.4
7	0.667 g (Sand) + 0.167 g (Silt and Clay)	81.59±1.8	58.08±1.0	76.08±0.4
8	0.667 g (Silt) + 0.167 g (Sand and Clay)	77.00±0.5	53.66±1.9	74.52±0.2
9	0.667 g (Clay) + 0.167 g (Sand and Silt)	80.19±1.6	60.81±1.3	78.51±0.6
10	0.333 g (Sand, Silt and Clay)	78.36±1.0	55.85±0.8	73.04±1.9

In order to evaluate the effect of soil composition on diesel removal efficiency of different surfactant solution, the results were analyzed and generated

the predicted equation based on regression analysis for single Tween 80 (Eq.(5)), single Lipopeptide (Eq. (6)) and mixed surfactant solution (Eq.(7)). Table 4.5 listed the ANOVA and statistical analysis for the response variables. Finally, the predicted equations were used to generate the contoured graphs for each surfactant system as shown in Figure 4.6.

*Diesel removal efficiency Single Tween 80 (%)*

$$= 75.80X_1 + 73.72X_2 + 77.64X_3 + 11.79X_1X_2 + 25.46X_1X_3 + 36.68X_2X_3 - 139.01X_1X_2X_3 + 27.38X_1X_2(X_1 - X_2) + 25.88X_1X_3(X_1 - X_3) \quad (5)$$

*Diesel removal efficiency Single Lipopeptide (%)*

$$= 53.96X_1 + 43.16X_2 + 61.50X_3 + 2.01X_1X_2 + 22.45X_1X_3 + 34.56X_2X_3 - 61.65X_1X_2X_3 - 22.15X_1X_2(X_1 - X_2) + 44.79X_1X_3(X_1 - X_3) \quad (6)$$

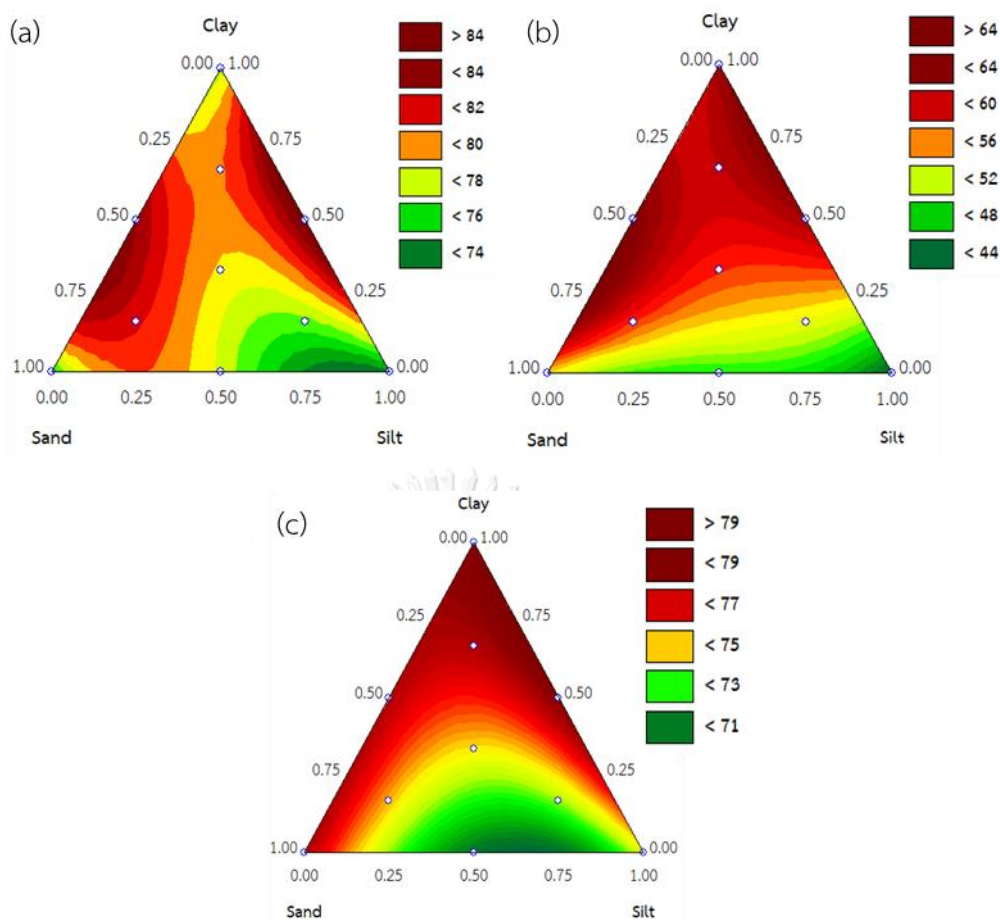
*Diesel removal efficiency Mixed solution (%)*

$$= 77.51X_1 + 74.24X_2 + 78.65X_3 - 20.56X_1X_2 - 2.49X_1X_3 + 8.13X_2X_3 - 13.52X_1X_2X_3 + 6.57X_1X_2(X_1 - X_2) + 1.50X_1X_3(X_1 - X_3) \quad (7)$$

Where  $X_1$ ,  $X_2$ ,  $X_3$  were mass of sand, silt, clay, respectively.

**Table 4.5** ANOVA and statistical analysis of the studied model (Diesel removal efficiency)

Surfactant solution	Model	Fitting model	P value	R <sup>2</sup>	R <sup>2</sup> adjusted
Tween 80 (5% w/v)	Equation 5	Full cubic	0.000036	0.9255	0.8713
Lipopeptide (0.5% w/v)	Equation 6	Full cubic	0.001821	0.8409	0.7253
Mixed Tween 80 and Lipopeptide (5% w/v)	Equation 7	Full cubic	0.000893	0.8618	0.7612



**Figure 4.6** The contoured graphs of diesel removal efficiency on the ternary diagrams of difference soil type composition from the washing by; (a) 5% w/v of the single Tween 80 solution, (b) 0.5% w/v of the single Lipopeptide surfactants solution, and (c) 5.0% w/v of the mixed surfactants solution.

On the other hand, the diesel removal efficiency of the single Tween 80 was found higher than those of the mixed Tween 80 and Lipopeptide surfactant solution for all cases of mixed texture soils. Although mixed surfactant dramatically reduced the sorption of Tween 80 and Lipopeptide on soil, the mixed surfactant was found not able to enhance diesel removal efficiency. This result was disagreed with the previous studies. For example, Yang *et al.* (2006) reported that phenanthrene removal from soil by mixed solution of TX100 (nonionic surfactant) and SDBS (anionic surfactant) was higher than individual surfactants due to the low sorption loss of surfactants on soil. Zhang and Zhu (2010) also investigated the sorption of mixed



Tween 80 and SDBS on soil and the effect of mixed surfactants on the PAHs removal. They found that the mixture of nonionic and anionic surfactants minimized the sorption loss of surfactant on soil. Because of the low sorption of surfactants, the nonionic-anionic mixed surfactant showed better performance on PAHs removal. However, for the soil containing clay as a composition shows slightly lower performance of the mixed surfactant compared to other type of soil.

Form this present study, the mixed Tween 80 and Lipopeptide showed the lower diesel removal efficiency compared to the single Tween 80 solution on the same weight concentration basis (5%) for the soil containing mixed texture. This might be due to the DI rinsing step. As mentioned earlier that the highly clay soil had high percent sorption of Tween 80. Therefore, some part of Tween 80 in single Tween 80 system still adsorb on soil and facilitate some mobilized diesel on the surface film, once DI was added for rinsing, Tween 80 and solubilized diesel that remains in soil surface were detached. The total washing efficiency (washing and rinsing steps) was found higher than those of mixed surfactants. It is assumed that in the washing step, the mobilization of diesel from soil porous occur, however, some diesel completely mobilize into bulk solution but some was remained on the thin film of the surfactant cover on the soil surface.

To confirm the validity of the predicted equation by regression analysis of the diesel removal efficiency using mixed Tween 80 and LP (Eq. (7)), the proportion of sand, silt and clay were substituted in term of  $X_1$ ,  $X_2$  and  $X_3$ , respectively in equation 6. Moreover, artificially contaminated soil and real contaminated were prepared to verify the equation. Figure 4.7 showed that the diesel removal efficiency from the predicted equation and the artificially contaminated soil is slightly different (approximately 3.3%). In case of the real contaminated soil, this soil showed higher washing efficiency than the prediction and artificial soils as mentioned previously due to the presence of organic matter in soil. K. Y. Cheng *et al.* (2008) reported that PAHs removal efficiency of Tween 80 can be simplified by co-existence of dissolved organic matter (DOM). Owing to the formation of Tween 80 - DOM complex, the combination of Tween 80 and DOM exhibited greater removal efficiency than the individual Tween 80 solution. Liang *et al.* (2016) also mentioned that combing

between TX-100 with DOM might lead to the higher removal efficiency of phenanthrene from soil.

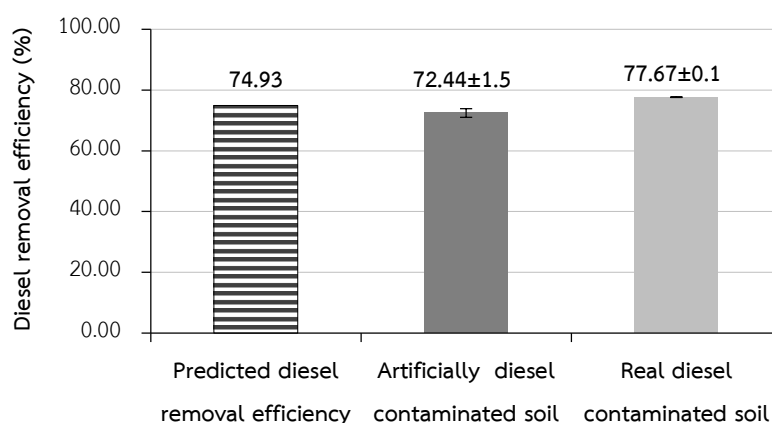
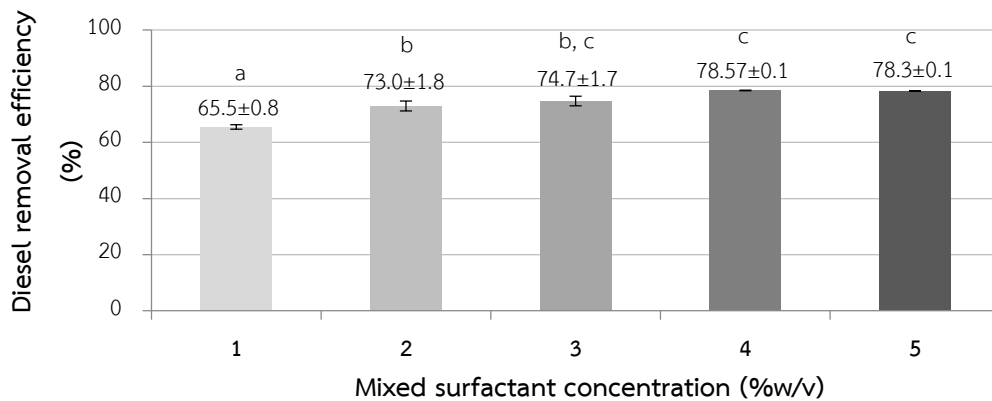


Figure 4.7 Diesel removal efficiency of different soil.

### 4.3 Optimizing soil washing condition

#### 4.3.1 Screening the appropriate mixed surfactant concentration

According to the results from section 4.2.2, the result indicated that the exceed concentration of surfactant may minimize the influence of surfactant sorption and hence resulted to diesel removal efficiency. It might be possible that the concentration of mixed Tween 80 and Lipopeptide at mass ratio 9:1 could decrease to be lower than 5% w/v. Thus, total concentration of mixed Tween 80 and Lipopeptide was prepared at 1, 2, 3, 4 and 5% w/v and the diesel removal efficiency was evaluated with the real diesel contaminated soil. The diesel removal efficiency of each concentration was analyzed by post hoc test after the analysis of variance (ANOVA) to screen the proper concentration of mixed Tween 80 and Lipopeptide. The results from the post hoc tests showed that total concentration of mixed Tween 80 and Lipopeptide were classified into three groups based on the diesel removal efficiency (Figure 4.8). The diesel removal efficiency was not significant different once the concentration of mixed Tween 80 and Lipopeptide was exceed 3% w/v. Thus, the mixed Tween 80 and Lipopeptide at total concentration 1, 2 and 3% w/v were selected to represent low, center and high concentration in the optimization part.



**Figure 4.8** Diesel removal efficiency from soil washing process using mixed surfactant at various concentration. (The latter a, b, and c indicate a significant difference in each treatment [ $p \leq 0.05$ ])

#### 4.3.2 Optimization of soil washing process

In this part, three factors were selected to optimize the soil washing condition including mixed surfactant concentration, L-S ratio and centrifuge speed. The CCRD was applied to design the experiment and Statistica program (version 10) was used to analyze the ANOVA result and regression coefficient.

Base on CCRD, 16 treatments were required for this optimization. The design of the experiment and the results of the diesel removal efficiency of each treatment were presented in Table 4.6.

The ANOVA results showed that surfactant concentration and L-S ratio significantly affected to diesel removal efficiency (Table A11). The predicted equation (equation 8) was used to generate the contour plot of diesel removal efficiency as shown in Figure 4.8. The optimum conditions and its diesel removal efficiency were exhibited in Table 4.7.

$$\text{Diesel removal efficiency (\%)} = 25.02 + 27.11X_1 - 2.50X_1^2 + 5.38X_2 + 0.12X_2^2 - 0.0005X_3 - 2.28X_1X_2 \quad (8)$$

Where  $X_1$  was surfactant concentration (% w/v),  $X_2$  was L-S ratio and  $X_3$  was centrifuge speed.

**Table 4.6** Design of experiment for optimizing diesel soil washing and diesel washing efficiency.

Treatment	Mixed surfactant concentration (%w/v)	L-S ratio	Centrifuge speed (rpm)	Diesel washing efficiency (%)
1	1.00	4.00	2000.00	65.66±4.7
2	1.00	4.00	4000.00	69.81±3.0
3	1.00	6.00	2000.00	76.46±0.4
4	1.00	6.00	4000.00	77.93±0.2
5	3.00	4.00	2000.00	78.20±0.2
6	3.00	4.00	4000.00	78.16±0.1
7	3.00	6.00	2000.00	77.20±0.0
8	3.00	6.00	4000.00	79.86±0.1
9	0.32	5.00	3000.00	56.55±7.4
10	3.68	5.00	3000.00	79.89±3.1
11	2.00	3.32	3000.00	73.10±0.4
12	2.00	6.68	3000.00	78.17±0.2
13	2.00	5.00	1318.21	73.83±0.2
14	2.00	5.00	4681.79	79.05±0.5
15	2.00	5.00	3000.00	76.62±0.1
16	2.00	5.00	3000.00	76.83±0.0

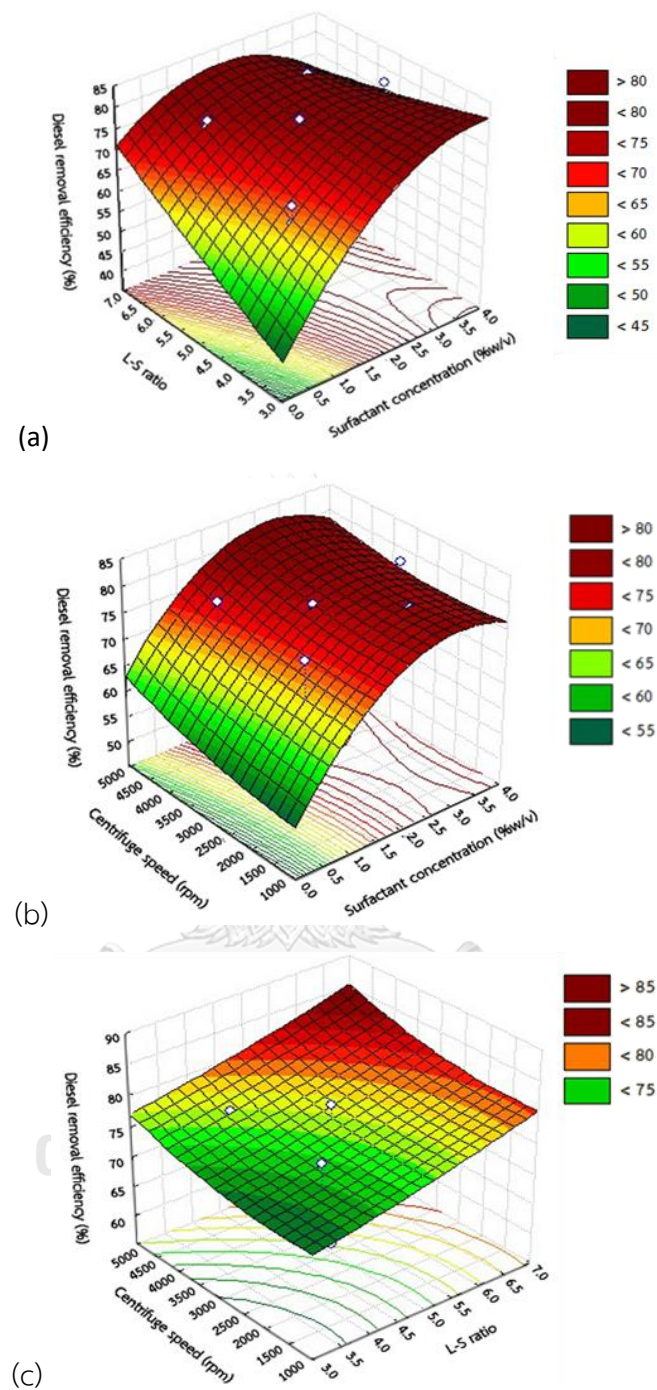
**Table 4.7** Optimum condition of diesel soil washing process and its diesel removal efficiency.

Parameter	Optimum condition
Surfactant concentration (% w/v)	2.924
L-S ratio	5.176
Centrifuge speed	1896.796
Predicted diesel removal efficiency (%)	78.12
Observed diesel removal efficiency (%)	79.60±2.4

According to the results, the diesel removal efficiency increase sharply with increasing surfactant concentration up to 3% w/v. After that point, further

increase of concentration did not improve the diesel removal (Figure 4.8a and 4.8b). This result agrees with Urum and Pekdemir (2004) and Peng *et al.* (2011). They mentioned that surfactant solution may enhance oil removal from soil at concentration higher than its CMC up to a certain level. At low surfactant concentration, the increase in liquid-solid ratio and centrifuge speed showed a corresponding increase in the washing efficiency. It should be noted that further improving diesel removal efficiency could be achieved by increasing liquid-solid ratio and centrifuge speed as shown in Figure 4.9a, 4.9b, 4.9c and Table A11.





**Figure 4.9** Contour plot of diesel removal efficiency from soil washing process of different conditions; (a) surfactant concentration and liquid-solid ratio at centrifuge speed 3000 rpm, (b) surfactant concentration and centrifuge speed at liquid-solid ratio 5/1, and (c) liquid-solid ratio at centrifuge speed at surfactant concentration 2%

## CHAPTER 5

### CONCLUSIONS AND SUGGESTIONS

#### 5.1 Conclusions

In the formulation of mixed Tween 80 and biosurfactants, Lipopeptide at 9:1 ratio of 5%w/v total concentration is the most appropriate biosurfactant to mix with Tween 80 when compared to Rhamnolipid and Saponin. It performed the highest efficiency on lowering the IFT between diesel and surfactant solution due to the hydrophobic moiety of Lipopeptide structure. In part of CMC, all mixed surfactant solutions presented the slightly negative synergistic effect because of the bulky structure of biosurfactant. When bulky structure of biosurfactant aggregates with Tween 80 to form a micelle, it tends to generate a larger micelle which contain high number of monomers resulted to the higher CMC of mixed surfactant than that of the single Tween 80 surfactant.

The suitable formulation, mixed Tween 80 and Lipopeptide at 9:1 ratio, was evaluated the effect of mixed biosurfactant on surfactant sorption and diesel removal efficiency on various of soil texture. Mixture of Tween 80 and Lipopeptide significantly reduced Tween 80 sorption on soil compared to the system with only Tween 80. This can be explained by charge repulsive effect between negative charge on mixed micelle and soil. In part of diesel soil washing, the diesel removal efficiency of mixed surfactant was slightly lower than that of single Tween 80 surfactant solution. This might be due to the DI rinsing step, which increased the total washing efficiency of single Tween 80 solution. The total washing efficiency of single Tween 80 came from washing and rinsing steps. Moreover, the results exhibited that the concentration of mixed Tween 80 and Lipopeptide could be minimized to 3% w/v

(Tween 80 2.7% w/v and Lipopeptide 0.3% w/v). This concentration was applied the process optimization.

Besides the surfactant concentration, L-S ratio and centrifuge speed were evaluated for their optimal level in diesel removal efficiency by CCRD. The results showed that surfactant concentration and L-S ratio significantly affected to diesel removal efficiency. The highest diesel removal efficiency was 79.9% when the initial diesel concentration 37,360 mg/kg. The optimal condition of surfactant concentration was approximately 3% w/v. However, for L-S ratio and centrifuge speed, the model suggested that the optimal level was beyond the range set up in the experiment. As a consequence, in the range of L-S ratio and centrifuge speed should be expanded to reach the optimum condition for diesel removal.

## 5.2 Suggestion for future study

The finding from this study shows that the interaction of soil texture as adsorbent and surfactants as adsorbate are complicated and influence to diesel removal efficiency. In addition, several factors, i.e., organic matter (OM) content in soil, physical conditions, surfactant concentration etc. can affect the removal efficiency. Therefore, future studies should be further investigated as in the following aspects:

- Effect of OM on surfactant sorption and soil removal efficiency
- Effect of surfactant structure on the sorption and soil removal efficiency
- Physical conditions for examples wider range of L-S ratios, shaking speed, and temperature in washing process should be evaluated.
- Effect of initial diesel concentration in soil on surfactant sorption and soil removal efficiency
- Surfactant reusing for the washing process

The remaining diesel in soil may be further cleaned up by natural attenuation or bioremediation, and the washing solutions may be reused by pumping back into the process.



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## APPENDIX A

**Table A1** IFT of single Tween 80 and biosurfactants, and mixed Tween 80 and biosurfactant solution with diesel.

Single surfactant solution						
Name	IFT (mN/n)					AVG
	1	2	3	4	5	
Tween 80	2.320	2.349	2.214	2.214	2.177	2.255±0.1
Rhamnolipid	0.363	0.351	0.379	0.379	0.436	0.382±0.0
Saponin	0.412	0.447	0.485	0.466	0.504	0.463±0.0
Lipopeptide	2.78	2.781	2.766	2.724	2.765	2.763±0.0

**Table A2** IFT of mixed Tween 80 and biosurfactant solution with diesel.

Mixed surfactant solution							
Name	Mass ratio of Tween 80 and biosurfactant	IFT (mN/n)					AVG
		1	2	3	4	5	
Tween 80 and Rhamnolipid	9 : 1	2.542	2.405	2.277	2.659	2.718	2.520±0.2
	8 : 2	2.053	2.219	2.259	2.535	2.269	2.267±0.2
	7 : 3	1.044	1.069	1.059	1.057	1.105	1.067±0.0
Tween 80 and Saponin	9 : 1	1.294	1.291	1.586	1.663	1.197	1.406±0.2
	8 : 2	1.285	1.171	1.249	1.372	1.389	1.293±0.1
	7 : 3	0.859	0.923	0.99	0.898	0.921	0.918±0.0
Tween 80 and Lipopeptide	9 : 1	0.226	0.250	0.227	0.251	0.227	0.236±0.0

**Table A3** CMCs experimental and ideal of single Tween 80, biosurfactants, and mixed Tween 80 with biosurfactant solutions.

Surfactant	Mass ratio	MW (g/mol)	Mole Fraction of Tween 80	Mole Fraction of RL	CMC (Experimental)		CMC (Ideal)	
					mg/L	mmol/L	mg/L	mmol/L
Tween 80 and Rhamnolipid	10::0	1,310.0	1.00	0.00	15.720	0.012	15.720	0.012
	9::1	1,227.6	0.77	0.23	49.711	0.040	19.074	0.016
	8::2	1,145.2	0.60	0.40	54.343	0.047	22.816	0.020
	7::3	866.8	0.46	0.54	77.946	0.090	22.107	0.026
	0::10	486.0	0.00	1.00	479.090	0.986	479.090	0.986
Tween 80 and Saponin	10::0	1,310.0	1.00	0.00	15.720	0.012	15.720	0.012
	9::1	1,298.0	0.89	0.11	63.436	0.049	17.459	0.013
	8::2	1,286.0	0.78	0.22	107.003	0.083	19.624	0.015
	7::3	1,274.0	0.68	0.32	111.050	0.087	22.393	0.018
	0::10	1,190.00	0.00	1.00	1,395.04	1.172	1,395.040	1.172
Tween 80 and Lipopeptide	10::0	1,310.0	1.00	0.00	15.720	0.012	15.720	0.012
	9::1	1,283.9	0.88	0.12	47.166	0.037	17.494	0.014
	0::10	1,049.0	0.00	1.00	600.000	0.572	600.000	0.572

**Table A4** Sorption of Tween 80 (%) (In single surfactant solution)

Replication	Soil (g)			Initial concentration of Tween 80 (%w/v)	Final concentration of Tween 80 (%w/v)	% Tween 80 sorption	
	Sand	Silt	Clay			AVG	
1	1	0	0	5.13	4.76	7.15	4.47±3.8
2					5.03	1.80	
1	0	1	0	5.13	2.00	61.03	58.32±3.8
2					2.27	55.60	
1	0	0	1	5.13	0.56	89.04	86.94±3.0
2					0.78	84.85	
1	0.5	0.5	0	5.13	1.79	65.10	58.88±8.8
2					2.43	52.66	
1	0	0.5	0.5	5.13	0.51	90.00	89.51±0.7
2					0.56	89.03	
1	0.5	0	0.5	5.13	0.59	88.49	87.82±0.9
2					0.66	87.15	
1	0.67	0.67	0.67	5.13	1.40	72.64	71.87±1.1
2					1.48	71.10	
1	0.17	0.67	0.17	5.13	1.51	70.60	69.66±1.3
2					1.60	68.72	
1	0.17	0.17	0.67	5.13	0.95	81.46	81.36±0.1
2					0.96	81.27	
1	0.33	0.33	0.33	5.13	1.55	69.78	68.60±1.7
2					1.67	67.42	

**Table A5** Sorption of Tween 80 (%) (In mixed surfactant solution)

Replication	Soil (g)			Initial concentration of Tween 80 (%w/v)	Final concentration of Tween 80 (%w/v)	% Tween 80 sorption	
	Sand	Silt	Clay				AVG
1	1	0	0	4.28	3.47	18.88	19.67±1.1
2				4.28	3.40	20.46	
1	0	1	0	4.28	3.29	23.02	22.74±0.4
2				4.28	3.32	22.46	
1	0	0	1	4.28	0.64	87.47	85.12±0.2
2				4.28	0.63	87.68	
1	0.5	0.5	0	4.28	3.31	22.77	22.52±0.4
2				4.28	3.33	22.26	
1	0	0.5	0.5	4.28	2.51	50.96	37.93±4.7
2				4.28	2.80	45.39	
1	0.5	0	0.5	4.28	2.98	41.93	29.42±1.5
2				4.28	3.06	40.21	
1	0.67	0.17	0.17	4.28	3.88	24.22	7.99±1.8
2				4.28	3.99	22.15	
1	0.17	0.67	0.17	4.28	4.39	14.27	22.08±1.8
2				4.28	4.28	16.43	
1	0.17	0.17	0.67	4.28	3.44	32.86	18.58±1.5
2				4.28	3.53	31.18	
1	0.33	0.33	0.33	4.28	3.13	19.50	22.32±6.4
2				4.28	3.52	31.35	

**Table A6** Sorption of Lipopeptide (%) (In single surfactant solution)

Replication	Soil (g)			Initial concentration of Lipopeptide (%w/v)	Final concentration of Lipopeptide (%w/v)	% Lipopeptide sorption	
	Sand	Silt	Clay			AVG	
1	1	0	0	0.52	0.40	23.67	23.43±0.3
2					0.40	23.19	
1	0	1	0	0.52	0.36	30.85	25.81±7.1
2					0.41	20.77	
1	0	0	1	0.52	0.40	22.52	22.73±0.3
2					0.40	22.93	
1	0.5	0.5	0	0.52	0.39	26.00	26.51±0.7
2					0.38	27.01	
1	0	0.5	0.5	0.52	0.40	23.77	23.92±0.2
2					0.40	24.07	
1	0.5	0	0.5	0.52	0.40	22.59	23.15±0.8
2					0.40	23.70	
1	0.67	0.67	0.67	0.52	0.38	26.25	26.53±0.4
2					0.38	26.82	
1	0.17	0.67	0.17	0.52	0.39	25.24	25.16±0.1
2					0.39	25.08	
1	0.17	0.17	0.67	0.52	0.40	22.88	22.36±0.7
2					0.41	21.84	
1	0.33	0.33	0.33	0.52	0.40	22.81	23.48±1.0
2					0.40	24.16	

**Table A7** Sorption of LP (%) (In mixed surfactant solution)

Replication	Soil (g)			Initial concentration of Lipopeptide (%w/v)	Final concentration of Lipopeptide (%w/v)	% Lipopeptide sorption	
	Sand	Silt	Clay			AVG	
1	1	0	0	0.52	0.51	2.17	4.63±3.5
2					0.48	7.09	
1	0	1	0	0.52	0.51	2.23	2.80±0.8
2					0.50	3.36	
1	0	0	1	0.52	0.44	16.38	10.85±7.8
2					0.49	5.32	
1	0.5	0.5	0	0.52	0.37	28.58	34.09±7.8
2					0.31	39.59	
1	0	0.5	0.5	0.52	0.47	10.71	10.50±0.3
2					0.47	10.29	
1	0.5	0	0.5	0.52	0.47	9.97	10.15±0.3
2					0.47	10.34	
1	0.67	0.67	0.67	0.52	0.46	12.23	12.20±0.0
2					0.46	12.17	
1	0.17	0.67	0.17	0.52	0.46	12.36	10.60±2.5
2					0.48	8.84	
1	0.17	0.17	0.67	0.52	0.48	7.92	7.82±0.1
2					0.48	7.72	
1	0.33	0.33	0.33	0.52	0.46	11.29	11.49±0.3
2					0.46	11.69	

**Table A8** Diesel removal efficiency of single Tween 80 (%)

Replication	Soil			Diesel concentration (mg/kg)		Tween 80 - Diesel Removal efficiency (%)	
	Sand	Silt	Clay	Initial	Final		AVG
1	1.00	0.00	0.00	39,998.44	9164.13	77.09	75.75±1.9
2					1,0233.21	74.42	
1	0.00	1.00	0.00	38,989.95	1,0786.64	72.33	73.67±1.9
2					9,743.52	75.01	
1	0.00	0.00	1.00	42,701.41	9,774.97	77.11	77.59±0.7
2					9,361.79	78.08	
1	0.50	0.50	0.00	39,427.49	9,064.17	77.01	77.61±0.9
2					8,589.67	78.21	
1	0.50	0.00	0.50	41,897.21	7,254.31	82.69	82.99±0.4
2					6,999.72	83.29	
1	0.00	0.50	0.50	41,010.03	6,188.59	84.91	84.76±0.2
2					6,315.18	84.60	
1	0.67	0.17	0.17	38,980.06	6,679.30	82.86	81.59±1.8
2					7,674.27	80.31	
1	0.17	0.67	0.17	39,034.16	8,827.91	77.38	77.00±0.5
2					9,124.66	76.62	
1	0.17	0.17	0.67	37,119.01	7,787.64	79.02	80.19±1.6
2					6,921.54	81.35	
1	0.33	0.33	0.33	39,022.63	8,175.92	79.05	78.36±1.0
2					8,715.94	77.66	

**Table A9** Diesel removal efficiency of single Lipopeptide (%)

Replication	Soil			Diesel concentration (mg/kg)		Lipopeptide - Diesel Removal efficiency (%)	
	Sand	Silt	Clay	Initial	Final	AVG	
1	1.00	0.00	0.00	39,252.87	17,918.16	54.35	53.82±0.8
2					18,336.36	53.29	
1	0.00	1.00	0.00	36,134.50	20,202.71	44.09	43.02±1.5
2					20,975.92	41.95	
1	0.00	0.00	1.00	38,880.93	12,712.43	67.30	61.35±8.4
2					17,341.21	55.40	
1	0.50	0.50	0.00	37,140.95	20,648.34	44.41	48.78±6.2
2					17,400.23	53.15	
1	0.50	0.00	0.50	41,382.89	16,050.19	61.22	63.05±2.6
2					14,528.69	64.89	
1	0.00	0.50	0.50	35,878.26	14,150.15	60.56	60.68±0.2
2					14,062.84	60.80	
1	0.67	0.17	0.17	37,969.02	15,658.42	58.76	58.08±1.0
2					16,174.21	57.40	
1	0.17	0.67	0.17	36,794.79	17,543.02	52.32	53.66±1.9
2					16,555.58	55.01	
1	0.17	0.17	0.67	37,426.02	14,999.14	59.92	60.81±1.3
2					14,332.36	61.70	
1	0.33	0.33	0.33	38,069.83	16,589.88	56.42	55.85±0.8
2					17,026.37	55.28	



**Table A10** Diesel removal efficiency of mixed Tween 80 and Lipopeptide (%)

Replication	Soil			Diesel concentration (mg/kg)		Mixed - Diesel Removal efficiency (%)	
	Sand	Silt	Clay	Initial	Final		AVG
1	1.00	0.00	0.00	39,998.44	8,902.08	77.74	77.33±0.6
2					9,232.33	76.92	
1	0.00	1.00	0.00	38,989.95	10,447.17	73.21	74.06±1.2
2					9,779.11	74.92	
1	0.00	0.00	1.00	41,632.45	8,958.63	78.48	78.47±0.0
2					8,971.24	78.45	
1	0.50	0.50	0.00	37,140.95	10,942.02	70.54	70.38±0.2
2					11,061.34	70.22	
1	0.50	0.00	0.50	41,382.89	9,437.08	77.20	77.10±0.1
2					9,516.22	77.00	
1	0.00	0.50	0.50	39,561.24	8,780.83	77.80	78.12±0.4
2					8,531.48	78.43	
1	0.67	0.17	0.17	37,085.01	8,984.57	75.77	76.08±0.4
2					8,758.28	76.38	
1	0.17	0.67	0.17	38,460.11	9,736.73	74.68	74.51±0.2
2					9,866.50	74.35	
1	0.17	0.17	0.67	39,360.54	8,631.99	78.07	78.51±0.6
2					8,288.82	78.94	
1	0.33	0.33	0.33	39,160.87	10,039.70	74.36	73.04±1.9
2					11,072.48	71.73	

**Table A11** ANOVA results of diesel removal efficiency from optimizing soil washing condition

Factor	ANOVA: Diesel removal efficiency (%); R-sqr=.86884; Adj.:.67209 3 factors, 1 Blocks, 16 Runs; MS Pure Error=.0219319				
	SS	df	MS	F	p
Surfactant concentration ( $X_1$ )	288.8882	1	288.8882	13172.04	0.005547
Surfactant concentration ( $X_1^2$ )	57.8246	1	57.8246	2636.55	0.012397
L/S ratio ( $X_2$ )	58.0731	1	58.0731	2647.88	0.012370
L/S ratio ( $X_2^2$ )	0.1401	1	0.1401	6.39	0.239868
Centrifuge speed ( $X_3$ )	21.2407	1	21.2407	968.48	0.020450
Centrifuge speed ( $X_3^2$ )	1.5390	1	1.5390	70.17	0.075639
$X_1$ by $X_2$	41.4672	1	41.4672	1890.72	0.014638
$X_1$ by $X_3$	1.1372	1	1.1372	51.85	0.087846
$X_2$ by $X_3$	0.0000	1	0.0000	0.00	0.971794
Lack of Fit	75.3723	5	15.0745	687.33	0.028950

## APPENDIX B

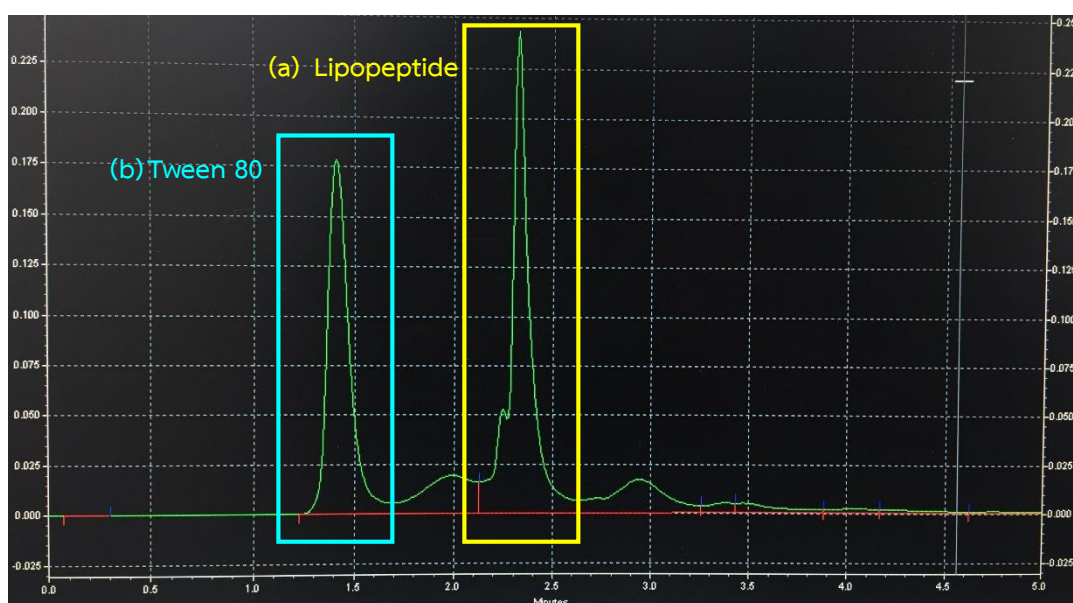
The HPLC/ELSD CHROMATOGAM OF MIXED TWEEN 80 AND  
LIPOPEPTIDE BIOSURFACTANT

Figure B1 Chromatogram of mixed Tween 80 and Lipopeptide biosurfactant

- (a) Tween 80
- (b) Lipopeptide



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