EFFECTS OF SOIL COMPOSITION, SURFACTANT STRUCTURE AND WASHING CONDITIONS ON DIESEL CONTAMINATED SOIL REMOVAL EFFICIENCY USING MICELLAR SOLUTION

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A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in Hazardous Substance and Environmental Management
Inter-Department of Environmental Management
GRADUATE SCHOOL
Chulalongkorn University
Academic Year 2020

ผลขององค์ประกอบของดิน, โครงสร้างของสารลดแรงตึงผิว และสภาวะการล้างต่อประสิทธิภาพในการชะล้างดินที่ปนเปื้อนด้วยน้ำมันดีเซลโดยสารละลายไมเซลล์

น.ส.อังคณา จันทนะประสาทพร

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
สาขาวิชาการจัดการสารอันตรายและสิ่งแวดล้อม สหสาขาวิชาการจัดการสิ่งแวดล้อม
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ปีการศึกษา 2563

Thesis Title	EFFECTS OF SOIL COMPOSITION, SURFACTANT STRUCTURE AND WASHING CONDITIONS ON DIESEL CONTAMINATED SOIL REMOVAL EFFICIENCY USING MICELLAR SOLUTION
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สารลดแรงตึงผิวมักถูกใช้ในการบำบัดดินที่ปนเปื้อนด้วยปิโตรเลียมเนื่องจากสามารถชะล้างปิโตรเลียมออกได้ดี อีกทั้งยังช่วยให้ลดเวลาและค่าใช้จ่ายได้อีกด้วย อย่างไรก็ตาม การใช้สารลดแรงตึงผิวมากเกินไปอาจทำให้เกิดการตกค้างในดิน ซึ่งอาจเป็นพิษกับจุลินทรีย์ในดินและพืช ดังนั้นการใช้สารลดแรงตึงผิวในความเข้มข้นที่เหมาะสมจึงมีความสำคัญมากในกระบวนการล้างดิน จึงเป็นที่มาของวัตถุประสงค์ของการศึกษานี้ เพื่อศึกษาผลขององค์ประกอบของดิน (ทราย ทรายแป้ง ดินเหนียว และอินทรียวัตถุ) และ โครงสร้างของสารลดแรงตึงผิว (Tween 20, 40, 60 และ 80, และ Tergitol 15-S-7, 9 และ 15) และเพื่อเพิ่มประสิทธิภาพของกระบวนการล้างดินด้วยสารละลายลดแรงตึงผิว ได้มีการคัดเลือกสารลดแรงตึงผิวจาก แต่ละกลุ่ม มาทำการศึกษา สภาวะการล้างที่เหมาะสม (อัตราส่วนระหว่างสารละลายและดิน ความเร็วในการเขย่า และเวลาที่ใช้ในการล้าง) ต่อประสิทธิภาพในการชะล้างดินที่ปนเปื้อนด้วยน้ำมันดีเซลโดยกระบวนการล้างดิน

จากผลการทดลองที่ได้ ในการชะล้างน้ำมันดีเซลที่ปนเปื้อนในดินนั้น Tween ที่มีความยาวของสายคาร์บอนที่สั้นกว่าจะมีความเข้มข้นวิกฤตของการเกิดไมเซลล์สูงกว่าในทราย แต่ในทางกลับกัน Tween ที่มีความยาวของสายคาร์บอนที่ยาวกว่าจะมีความเข้มข้นวิกฤตของการเกิดไมเซลล์สูงกว่าในดินเหนียว สำหรับ Tergitol นั้น สารลดแรงตึงผิวที่โครงสร้างที่มีจำนวนกลุ่มอีทอกซิเลตในส่วนหัวที่น้อยกว่าจะใช้ความเข้มข้นวิกฤตของการเกิดไมเซลล์สูงกว่าในดินทุกชนิด ส่วนในกรณีที่มีอินทรียวัตถุอยู่นั้น อินทรียวัตถุส่งผลให้เกิดการลดความเข้มข้นวิกฤตของการเกิดไมเซลล์ในทรายและทรายแป้ง

ในกระบวนการชะล้างดินที่ปนเปื้อนที่ใช้สารละลายที่มีค่าความเข้มข้นของสารลดแรงตึงผิวสูงกว่าความเข้มข้นวิกฤตของการเกิดไมเซลล์นั้น ดินเหนียวเป็นดินที่แสดงให้เห็นถึงประสิทธิภาพสูงสุดในการชะล้าง ซึ่งจากผลของ FTIR แสดงให้เห็นว่าสารลดแรงตึงผิวที่ถูกดูดซับบนดินเหนียวลดภาวะที่มีความชอบน้ำต่ำของดิน ทำให้ดินเหนียวไม่สามารถที่จะกลับมาดูดซับน้ำมันดีเซลอีกครั้งได้ ด้วยเหตุนี้ เนื่องจากดินเหนียวนั้นสามารถพบได้ในพื้นที่ส่วนมากของประเทศไทย ทำให้ Tween 80 และ Tergitol 15-S-15 ที่มีประสิทธิภาพในการชะล้างน้ำมันดีเซลในดินเหนียวสูงถูกเลือกมาเพื่อใช้ในการทดลองถัดไป

ในการทดลองเพื่อหาสภาวะการล้างที่เหมาะสมสำหรับการชะล้างดินที่ปนเปื้อนด้วยน้ำมันดีเซลนั้น จะเริ่มจากการทดสอบผลของอัตราส่วนระหว่างสารละลายและดิน และความเร็วในการเขย่าก่อน โดยผลที่ได้นั้นแสดงให้เห็นว่า ความเร็วในการเขย่าส่งผลต่อประสิทธิภาพการชะล้างมากกว่าอัตราส่วนระหว่างสารละลายและดิน ซึ่งอัตราส่วนระหว่างสารละลายและดินและความเร็วในการเขย่าที่เหมาะสมคืออัตราส่วนระหว่างสารละลาย 3 ส่วนต่อดิน 1 ส่วน โดยใช้ความเร็วในการเขย่าที่ 100 รอบต่อนาที ด้วยสภาวะนี้ เวลาที่ใช้ไม่มีใด ๆ ผลต่อประสิทธิภาพในการชะล้าง

สาขาวิชา การจัดการสารอันตรายและสิ่งแวดล้อม ลายมือชื่อนิสิต ....
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5887812820 : MAJOR HAZARDOUS SUBSTANCE AND ENVIRONMENTAL MANAGEMENT
KEYWORD: Micellar solution, Soil washing, Diesel, Soil composition, Surfactant structure, Washing conditions

Angkana Jantanaprasartporn : EFFECTS OF SOIL COMPOSITION, SURFACTANT STRUCTURE AND WASHING CONDITIONS ON DIESEL CONTAMINATED SOIL REMOVAL EFFICIENCY USING MICELLAR SOLUTION. Advisor: Asst. Prof. Chantra Tongcumpou, Ph.D. Co-advisor: Dr. Nattapong Tuntiwiwattanapun, Ph.D.

Surfactant solutions are commonly used for the remediation of petroleum-contaminated soil due to their good petroleum removal performance, time-saving capability, and cost effectiveness. However, applying surfactants in excess concentrations could make oil recovery difficult. Moreover, residual surfactants in soil are toxic to microorganisms and plants. Thus, it is crucial to identify a suitable surfactant concentration for soil washing applications.

The main objective of this study was to evaluate the effect of soil composition (sand, silt, clay and organic matter), surfactant structure (Tween 20, 40, 60 and 80, and Tergitol 15-S-7, 9 and 15). Subsequently, two surfactants from each series (Tween and Tergitol) were selected for diesel removal from diesel-contaminated soil by surfactant-assisted soil washing. Then the optimizing condition was examined based on physical factors, i.e., shaking speed, Liquid: Solid (L/S) ratio and time.

The results showed that Tween surfactants with shorter carbon chain lengths required higher CMC for diesel removal from sand, while those with longer carbon chains needed higher CMC for clay cleanup. Tergitol surfactants with less ethoxylate group on the hydrophilic head have higher CMC in all soil texture. At a certain OM concentration, OM exhibited antagonistic effects with sand and silt, resulting in CMC reduction. In soil washing application, the mixture design shows that maximum diesel removal could be achieved from sand. Interestingly, there are high diesel removal efficiency from soil with highly clay, which surfactants exhibited the highest CMC. Based on FTIR results, the adsorbed surfactant could reduce the hydrophobicity of the clay surface, thus preventing the re-deposition of detached diesel. The soil with highly clay content was found in most area of Thailand. Therefore, Tween 80 and Tergitol 15-S-15, which have high diesel removal efficiency in clay, were selected.

In optimizing physical condition test, effect of shaking speed and L/S ratio were tested. The result showed that shaking speed was more significant and the optimal physical condition was 3:1 L/S ratio with shaking speed at 100 rpm. At these conditions, time has no significant effect.

Field of Study:	Hazardous Substance and Environmental Management	Student's Signature ....
Academic Year:	2020	Advisor's Signature ....
		Co-advisor's Signature ....

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my advisor, Asst. Prof. Chantra Tongcumpou and my co-advisor, Dr. Nattapong Tuntiwiwattanapun for their consistent support, and guidance throughout this study. I also would like to thank the International Postgraduate Program in Hazardous Substance and Environmental Management (IP-HSM), Mr. Watcharin Kaewmaneewan, and Department of mining and petroleum engineering for allowing us to use their laboratory facilities. Moreover, this study was financially supported by The 100th Anniversary of Chulalongkorn University Fund for Doctoral Scholarship, The 90th Anniversary of Chulalongkorn University Fund (Ratchadaphiseksomphot Endowment Fund), and the Research Program on Remediation Technologies for Petroleum Contamination, Center of Excellence on Hazardous Substance Management (HSM), Thailand for financially supported

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CMC = Critical micelle concentration (mg/L)

OM = Organic matter

DOM = Dissolved organic matter

PHCs = Petroleum hydrocarbons

PAHs = Polycyclic aromatic hydrocarbons

IFT = Interfacial tension

TW20 = Tween 20

TW40 = Tween 40

TW60 = Tween 60

TW80 = Tween 80

TS7 = Tergitol 15-S-7

TS9 = Tergitol 15-S-9

TS15 = Tergitol 15-S-15

HLB = Hydrophilic-lipophilic balance

EO = Oxyethlene group

CEC = Cation exchange capacity

CMC_m = Measured CMC

CMC_a = Appearance CMC

X_{CMC} = The difference (times) between CMC_m and CMC_a in the presence of each soil component

RE = Diesel removal efficiency

L/S ratio = Liquid: Solid ratio

CHAPTER 1

INTRODUCTION

1.1 Statement of Problems

Nowadays, the world diesel demand is very high up to 25 million barrels per day, which is about 28% of the world oil demand (IEA, 2017). Soil contamination by petroleum hydrocarbons (PHCs) has become a global issue as accidentals spills during transportation and due to improper storage which lead to the widespread distribution of these pollutants (Gallego *et al.*, 2001; Hasan *et al.*, 2010; Roy *et al.*, 2014; Koshlaf *et al.*, 2016; Lahel *et al.*, 2016). Among PHCs, diesel is widely used and contaminated in environment.

Diesel contaminated soil has negative impacts to the ecosystem and agricultural products because of its toxicity to plant (Sverdrup *et al.*, 2003; Bona *et al.*, 2011; Tang *et al.*, 2011), earthworm (Dorn *et al.*, 1998; Dorn & Salanitro, 2000; Tang *et al.*, 2011; Hentati *et al.*, 2013) and microorganisms in the soil (Wyszkowska & Kucharski, 2001; Tang *et al.*, 2011). In addition, an exposure to diesel can harm human health as it is recognized as a mutagenic carcinogenic substance (Rundle *et al.*, 2000; Wang *et al.*, 2007; Devi *et al.*, 2016). Consequently, diesel contaminated sites are environmental concern and need remediation process.

Soil washing is generally used for remediation of PHC-contaminated soil. It can simultaneously treat both organic and inorganic pollutants (Khan *et al.*, 2004;

Chu, 2014), such as heavy metals typically present in diesel and petroleum oil (Pulles *et al.*, 2012). Moreover, soil washing is relatively time saving, cost effective, and simpler than the other contaminated soil remediation methods (Sharma & Reddy, 2004). A soil washing facilities can potentially be established near a contaminated site and could therefore dramatically reduce the cost of transporting contaminated and clean soil.

Surfactants have been used for several decades to increase the pollutant removal efficiency of soil washing, especially for diesel-contaminated soils, since surfactants reduce interfacial tension (IFT) and enhance diesel solubility. Mobilization and solubilization are the two primary mechanisms for diesel removal from diesel-contaminated soil using surfactants. To maximize the efficiencies of these mechanisms, surfactants must be in the form of capsule-like structures called micelles. Diesel, a hydrophobic substance, can be dissolved in the hydrophobic core of a micelle and dispersed in a washing solution.

Critical micelle concentration (CMC) is the concentration of surfactant at which micelles can be firstly formed. To ensure good oil removal efficiency, the concentration of surfactant in the system must be above the CMC, which can be influenced by the adsorption of surfactants on contaminated soil (Pugh & Tjus, 1990; Somasundaran *et al.*, 1991; Behl & Moudgil, 1992; Shen, 2000). Thus, additional surfactants must be added to compensate for the surfactants adsorbed on soil, thereby potentially increasing the cost of remediation and generating secondary pollutant is the adsorbed surfactant in soil. Besides an additional cost, the residual surfactant in soil can cause toxicity to microorganism and plant due to the excess surfactant (Laha & Luthy, 1992; Makkar & Rockne, 2003; Rebello *et al.*, 2014). In summary, the suitable surfactant should have low soil adsorption whereas provided the high diesel removal efficiency. Nevertheless, there is lack of information regarding to interaction between soil, surfactant and pollutants toward the performance of surfactant-assisted soil washing process.

Therefore, it is very crucial to study the effect of different soil minerals (quartz and kaolin), organic matter contents, and surfactant structures on CMC value and diesel removal efficiency. The results of this study can potentially serve as a guideline for the selection of suitable surfactants and their optimum concentration for the remediation of diesel-contaminated soil based on the properties of the contaminated soil

1.2 Objectives

1) To evaluate surfactant adsorption capacity on various soil compositions (sand, silt, clay and organic matter content) and their effect on diesel removal efficiency from contaminated soil by surfactants solution washing.
2) To determine the effect of surfactant structure on soil sorption and washing efficiency.

3) To optimize the surfactant concentration and washing conditions for removing diesel from soil in different soil compositions.

1.3 Hypotheses

1) Sorbitan nonionic surfactant series (Tween series) would be more adsorbed than secondary alcohol ethoxylate nonionic surfactant series (Tergitol 15-s series) due to their sorbitan head group.

2) Present of double bond in surfactant structure would enhance sorption of surfactant in soil.

3) Higher molecular weight of surfactant would decrease the adsorption in soil due to steric hindrance.

4) There would be a synergism effect between soil and organic matter on surfactant sorption on soil

1.4 Methodology framework

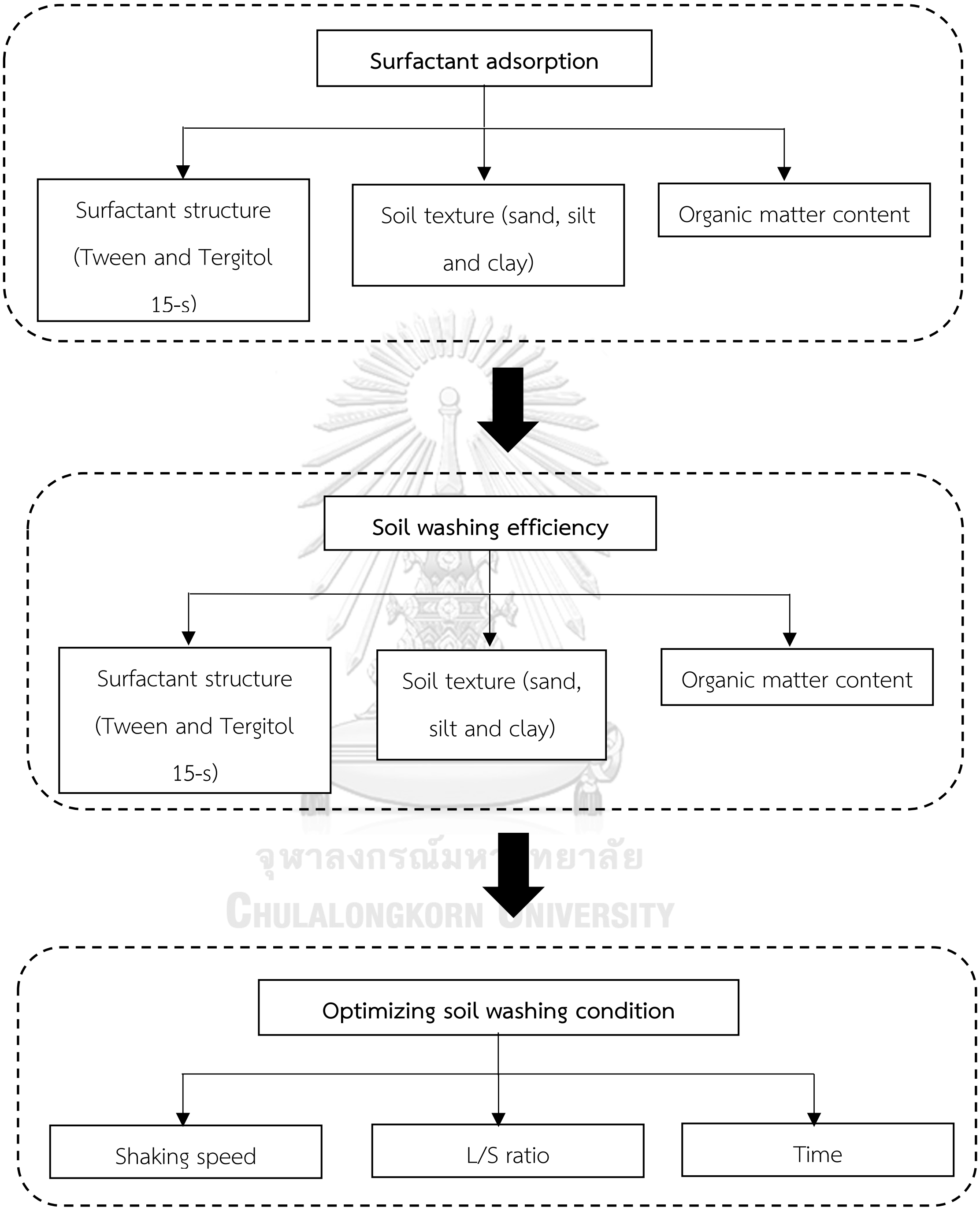


Figure 1.1 Methodology framework

1.5 Structure of thesis book

This thesis is divided into 6 chapters. Chapter 1 “Introduction” describes the state of the problem related contaminated diesel in soil and how this study would fill the research gap. The objective, hypothesis and framework are also presented in this chapter. Chapter 2 “Literature review” presents the current knowledge and previous researches that related to this thesis, such as, soil composition, soil remediation process, PHCs and surfactant. Chapter 3 “Methodology” explains the material and method that were used in this experiment. The result and discussion are divided into 2 chapters, Chapter 4 “Effect of soil texture, organic matter and surfactant structure on CMC” and Chapter 5 “Soil washing efficiency affected by various factors”. Chapter 4 shows the results and the findings of the effect of soil composition, surfactant structure and organic matter content on surfactant adsorption through CMC measurement. Chapter 5 focus on the effect of surfactant structure and soil texture on washing efficiency, and optimal condition like time, shaking speed and Liquid: Solid (L/S) ratio. Chapter 6 “Conclusion” summarized all results from this study, for example, the suitable surfactant types and concentration, and the optimal physical condition for diesel contaminated soil by soil washing using surfactant. The scope of this study was to select the most suitable surfactant and create the equation for calculate the suitable concentration for different soil composition at the lowest and the most effective concentration to reduce time and cost for cleanup diesel contaminated soil.

CHAPTER 2

LITERATURE REVIEW

2.1 Petroleum oil spill

Petroleum or crude oil is a mixture of a wide range of hydrocarbon (**Figure 2.1**). It comes from the remaining of plant and animals that accumulated under the earth surface by pressure and temperature over million years, so called “fossil fuel”. The compositions of petroleum are mainly hydrocarbon and some small amount of other elements shown in **Table 2.1**. Hydrocarbon in petroleum can be divided into 4 groups: 1) paraffins (alkanes) 2) naphthenes (cycloalkanes) 3) aromatics and 4) asphaltics. The proportion of each hydrocarbon is shown in **Table 2.2**. The amount of element and types of hydrocarbon in petroleum are depended on pressure and temperature conditions during the accumulation process.

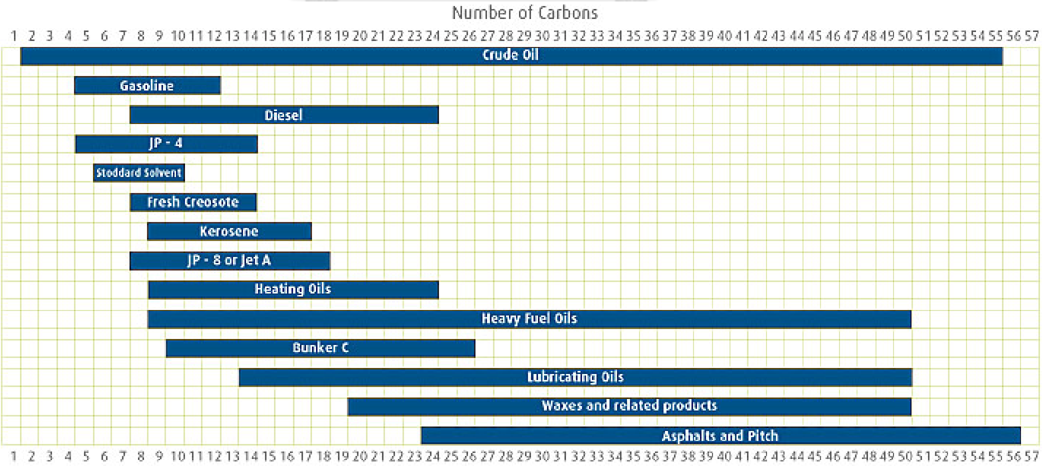


Figure 2.1 Carbon range of petroleum

(http://www.caslab.com/Petroleum-Hydrocarbon-Ranges/)

Table 2.1 The composition of element in petroleum (Hyne, 2001)

Element	Proportion (%)
Carbon	83-87
Hydrogen	10-14
Nitrogen	0.1-2
Oxygen	0.05-1.5
Sulfur	0.05-6
Metals	<0.1

Table 2.2 Hydrocarbon type in petroleum (Mullins & Sheu, 1999)

Hydrocarbon	Proportion (%)
Paraffins	15-60
Naphthenes	30-60
Aromatics	3-30
Asphaltics	remainder

To separate each hydrocarbon type from petroleum, fractional distillation is used due to the different boiling point of each hydrocarbon. Petroleum will be heat in boiler at very high temperature that can change petroleum into steam and sent them to the fractionating tower. The hydrocarbon with lighter fraction is condensed at the top of tower which has the lowest temperature, and then followed by the heavier fraction. The smaller molecules have low boiling point, light color easy to ignite and not viscous, while the larger molecules have high boiling point, dark color, hard to ignite and viscous.

Diesel fuel is one of the hydrocarbons that can be separated from petroleum. It has been used widespread around the world in the most types of transportation. The amount of carbon in diesel is between 8 and 24 carbon atoms. For using as car fuel, several properties are assigned the standards to ensure the good quality of diesel for car engine, such as cetane number, flashpoint and sulfur concentration as shown in **Table 2.3**.

Table 2.3 Diesel properties (https://www.energyinst.org)

Properties	Value
Density (kg/L)	0.84-0.86
Energy content (MJ/L)	35.7-36.7
Cloud point (℃)	0-(-55)
Flashpoint(℃)	68-94
Distillation final boiling point(℃)	307-352
Viscosity (cSt @ 40 ℃)	2.04-3.23
Sulfur (ppm)	1-10
Cetane number	41-48
Stability	Good
Oxygen content (%)	0
Lubricity	Good*

*have to add additive to meet spec

2.2 Soil composition

Soil is composed of 45-49% mineral, 1-5% organic matter and 50% pore, which are 20-30% air and 20-30% water (**Figure 2.2**) (Brady & Weil, 2002). The main minerals in soil are sand, silt and clay. Sand has the biggest particle size (0.05 – 2 mm), followed by silt (0.002 – 0.05 mm) and clay (lower than 0.002 mm), which shown in **Figure 2.3**.

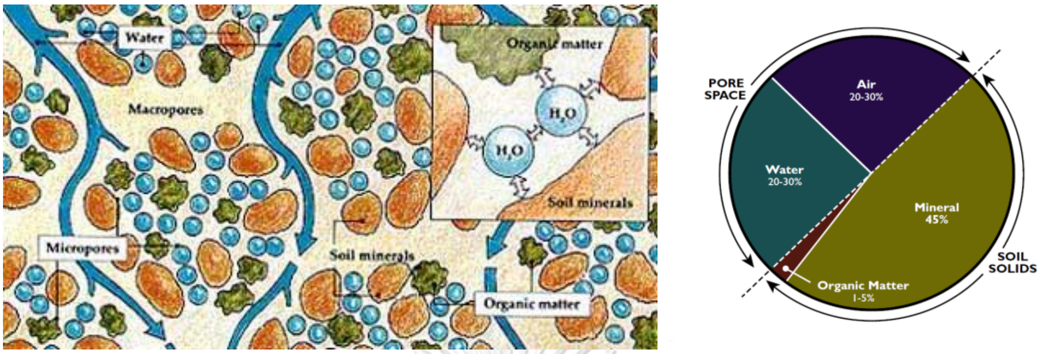


Figure 2.2 Soil composition (McCauley *et al.*, 2005; DeGomez *et al.*, 2015)

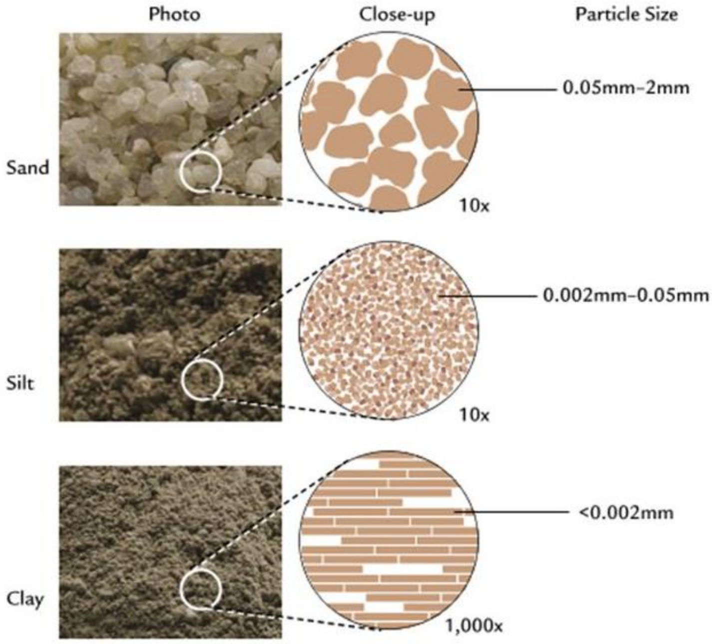


Figure 2.3 Mineral identification in soil (https://support.rainmachine.com/hc/en-us/articles/228001248-Soil-Types?mobile_site=true)

Soil can be divided into 6 types depended on the SiO_4 tetrahedra arrangement in the structure as shown in **Table 2.4**. Sand and the main part of silt are cyclo-, ino-, neso-, soro, or tectosilicates, while clay is phyllosilicates. The proportion of soil minerals is called 'soil texture' (**Figure 2.4**). Soil texture affects to many factors such as, water capacity, soil fertility and permeability rate.

Table 2.4 Soil silicates types (K. H. Tan, 1998)

Soil silicate	**Mineral species**	**SiO_4 tetrahedra arrangement**
Cyclosilicates	Tourmaline, Bentonite	Closed rings or double rings of tetrahedra (SiO_3, Si_2O_5)
Inosilicates	Amphibole, Pyroxene, Hornblende	Single or double chains of tetrahedral (SiO_3, Si_4O_{11})
Nesolicicates	Garnet, Olivine, Zircon, Topaz	Separate SiO_4tetrahedra
Phyllosilicates	Chlorite, Vermiculite, Illite, Kaolinite, Smectite	Sheets of tetrahedral (Si_2O_5)
Sorosilicates	Epidote	Two or more linked tetrahedral (Si_2O_7, Si_5O_{16})
Tectosilicates	Feldspars, Quartz, Zeolite	Framework of tetrahedral (SiO_2)

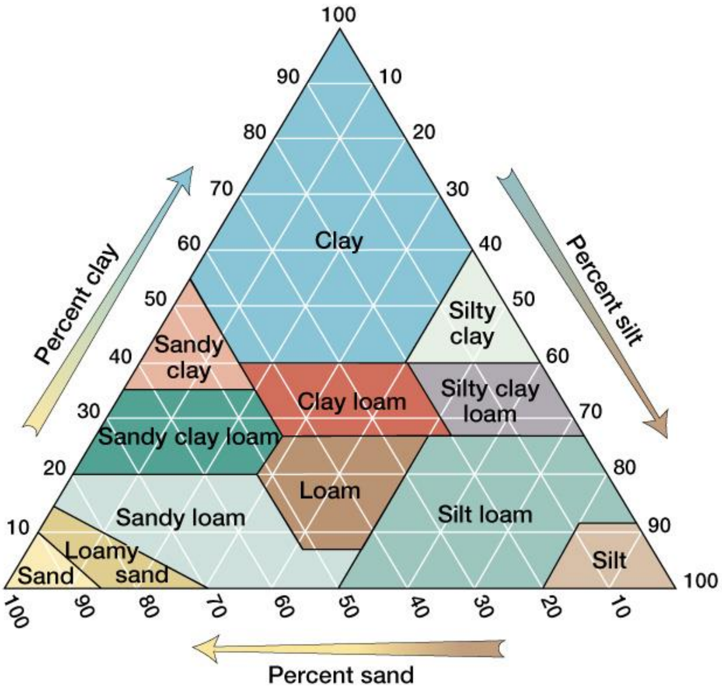


Figure 2.4 Soil textural triangle

(http://www.ncwcom.com/~jones/Geology/weather2.htm)

2.2.1 Clay

Clay has the smallest particle size and the highest surface area, which lead to the sticky property when it wet. Although it has high water capacity, this property makes clay has very low water and air permeability. Therefore, in the soil with high clay content, plant cannot penetrate its root and adsorb water for its growth due to the very low water and air permeability (Sheard, 1991; K. H. Tan, 1998; Sparks, 1999; Mukherjee, 2013).

The structure of clay is mainly composed of silica plane and alumina plane. These planes are holding by oxygen atoms (O) (ionic bond) in crystal forms with a repeat atoms arrangement. Clay has negative charged due to its structure (K. H. Tan, 1998; Sparks, 1999; Mukherjee, 2013). Thus, the nutrients for plant growth, such as Ca, Mg, K, P and trace elements, are mostly adsorbed by clay. The classification of clay is divided by the number silica sheet per alumina sheet, which are 1:1 and 2:1 (Hillier, 2003). The clay classification and the structure example of each clay type are shown in **Table 2.5** and **Figure 2.5** respectively. In this study, Kaolin, which is the simplest clay with 1:1 layer clay without interlayer site, will be selected.

Table 2.5 Clay mineral classification (Hillier, 2003)

Layer type		**Group**	**Subgroup**	**Species (e.g.)**
1:1	**Layer charge (q)**			
	$q\approx0$	Kaolin-Serpentine	Kaolin	Kaolin
			Serpentine	Berthierine
2:1	$q\approx0$	Pyrophyllite-talc ($q\approx0$)	Pyrophyllite	Pyrophyllite
			Talc	Talc
	Increasing layer charge ↓	Smectite ($q\approx0.2$-0.6)	Di.smectite	Montmorillonite
			Tri.smectite	Saponite
		Vermiculite ($q\approx0.6$-0.9)	Di. vermiculite	Di. vermiculite
			Tri.vermiculite	Tri.vermiculite
		Mica ($q\approx1.0$)	Di.mica	Illite, Muscovite
	$q\approx1$		Tri.mica	Biotite
		Chlorite	Di.chlorite	Sudoite
			Tri.chlorite	Chamosite
		Sepiolite-Palygorskite	Sepiolite	Sepiolite
			Palygorskite	Palygorskite
Variable	q Variable	Mixed-layer	Di.mica-di.smectite	Rectorite
			Tri.chlorite-tri.smectite	Corrensite

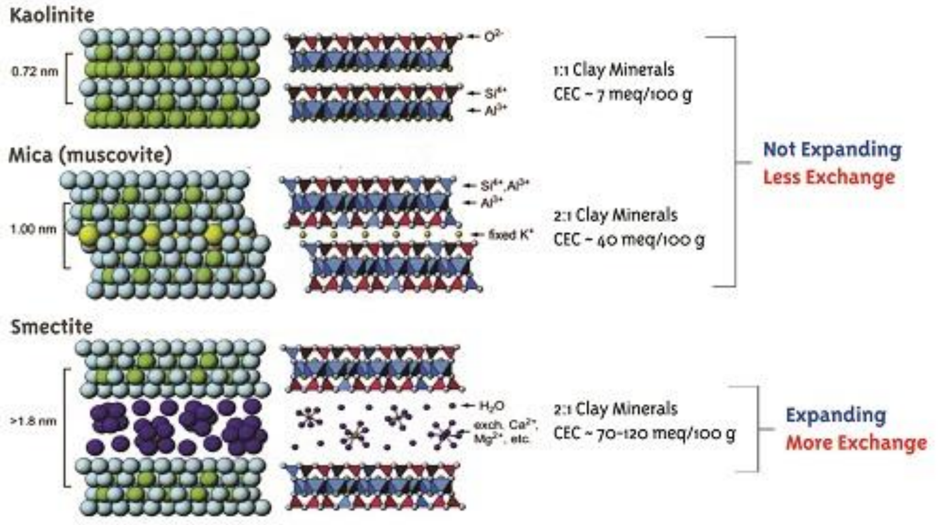


Figure 2.5 The example of clay structure

(http://www.soils4teachers.org/mineralogy)

Kaolin is white soft powder. The shape of kaolin is hexagonal (**Figure 2.6**). The chemical structure of kaolin is hydrated aluminium silicate ($H_2Al_2Si_2O_8$-H_2O). Oneunit structure is composed of one silica tetrahedral sheet and one alumina octahedral sheet (**Figure 2.7**). Two sheets form layer by sharing O atoms between Si and Al atoms and become a unit. Each unit is bonding by hydrogen bond from H atoms in OH ions on one plane to O atoms on another plane. Because of the strong hydrogen bond between each layer, kaolin has low swelling and shrinkage properties (no interlayer sites). Therefore, CEC of kaolin is very low (1-10 mEq/100 g) (K. H. Tan, 1998).

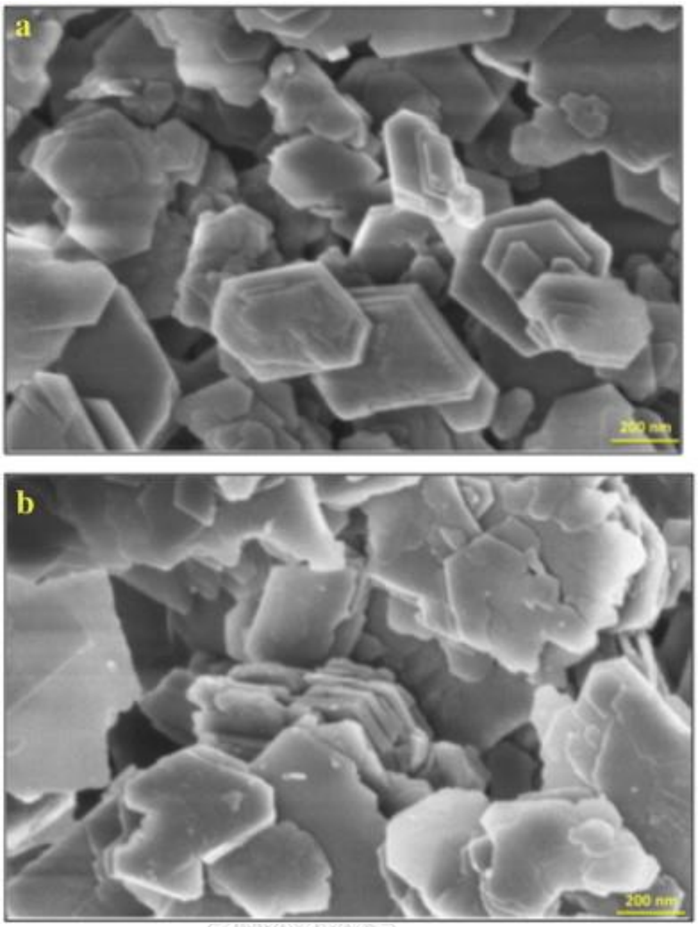


Figure 2.6 The kaolin shape (Zegeye *et al.*, 2013)

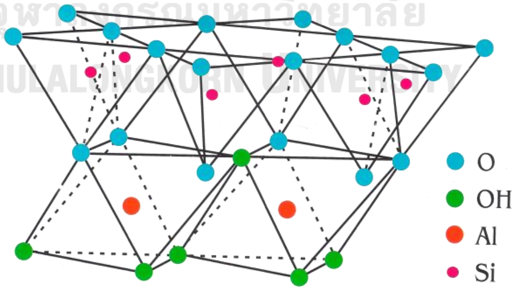


Figure 2.7 Kaolin chemical structure

(http://shreeramminerals.com/minerals/about-kaolin/)

pH and electrolyte concentration can affect to the plastic viscosity of kaolin (Michaels & Bolger, 1964; D. J. A. Williams & Williams, 1982; Diz & Rand, 1989; Diz *et* *al.*, 1990; S. H. Chang *et al.*, 1993; Hocking *et al.*, 1999; Johnson *et al.*, 2000). The plastic viscosity of kaolin increases with the decrease of pH. Under the acidic condition (low pH), a lot of H^+ in solution bond with the O atoms at the edges of kaolin (**Figure 2.8**). Thus, the edge-to-face formation between the positively charged at edges and the negatively charged at faces occurred. This formation is called "house of cards" (**Figure 2.9**). In contrast, under the alkaline condition (high pH), the charged at edges becomes negative. With the same charged at edge and face, the repulsive occurred and lead to the decreasing of viscosity.

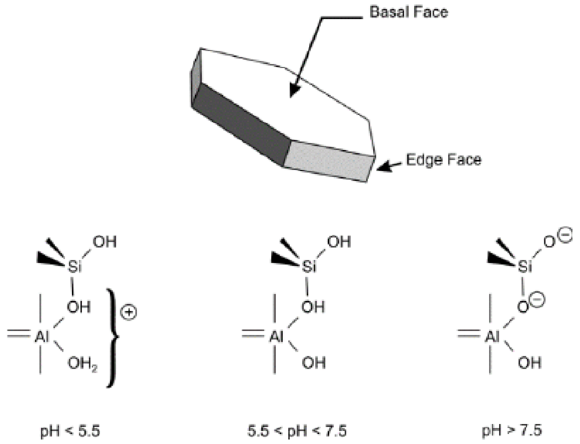


Figure 2.8 Kaolin platelet and effect of pH on surface chemistry at the edge face

(Hocking *et al.*, 1999)

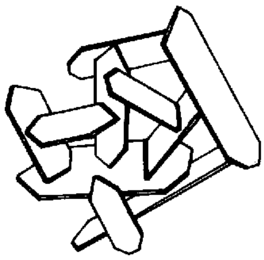


Figure 2.9 House of cards formation

(http://community.dur.ac.uk/sharon.cooper/lectures/colloids/interfacesweb3.html)

However, increasing electrolyte (such as NaCl) at low pH can decrease viscosity because the counter ion from the electrolyte form double layer on both edges and faces, which reduce the electrostatic attraction. On the other hands, the viscosity of kaolin increases at high pH with high electrolyte concentration because the electrolyte created double layers and form face-to-face formation (**Figure 2.10**), which increases the attractive forces from the van der Waals force (Diz & Rand, 1989; Diz *et al.*, 1990).

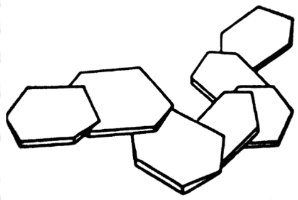


Figure 2.10 Face-to-Face formation (Chaiwong & Nuntiya, 2008)

Moreover, kaolin is not only used in ceramic industry for porcelain crafting, but it is also widely used in many applications, for example, in paper industry where kaolin is used to coat and fill paper to change the paper texture and color (Prasad *et al.*, 1991; Murray, 2006). In medications, people in the past ate kaolin to absorbed bacteria and viruses (Wilson, 2003; Carretero *et al.*, 2006; Gomes & Silva, 2007; L. B. Williams & Haydel, 2011). In skincare product, it is commonly used in powdered forms, masks and creams to adsorb oil out of the skin (Carretero *et al.*, 2006; Gomes & Silva, 2007; L. B. Williams & Haydel, 2011).

2.2.2 Silt

Silt is a spherical particle that has size, physical and chemical properties between sand and clay. The main mineral of silt is quartz and feldspar, which create from both physical and chemical rock weathering process. Silt has moderate capability to keep and release nutrients and water to plant. Compare with clay, silt has lower nutrients and water capability, but has higher water permeability. In contrast, silt has higher water capability, but has lower permeability when compare with sand. Silt has a slippery feeling when it wet, but has a floury feel when it dries due to its moderate surface area (Sheard, 1991; Darrah, 1993; Assallay *et al.*, 1998).

2.2.3 Sand

Sand chemical structure is Silicon dioxide (SiO_2) (**Figure 2.11**). It comes from weathered of rock. The major role of sand in soil is to make soil loose to increase air and water permeability in soil (Sheard, 1991; Darrah, 1993). Sand has no or little ability to support nutrient to plant because the net charge of sand is non-polar. However, sand has high adhesive force because Oxygen atom (O) has high electronegativity (EN). So, due to the high EN of O, each O atom has partial negative charge. But in each Si atom connects with four O atoms. Therefore, the negative charge of each O is canceling out and makes SiO_2 total charge become zero.

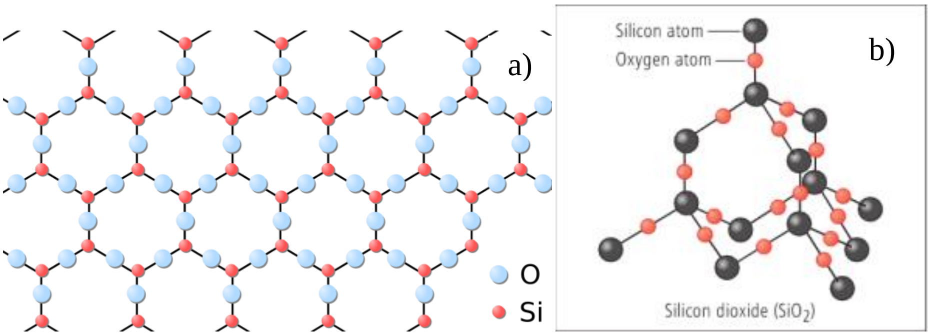


Figure 2.11 SiO_2 structure in a) 2D and b) 3D

(http://www.cram.com/flashcards/c7-covalent-bonding-6666159)

2.2.4 Organic matter

Soil organic matter (SOM) is the natural fertility in soil. It composed of living organisms, and plant and animal residues (**Figure 2.12**), mostly from plant accumulation. SOM provides Nitrogen (N), Phosphorus (P) and Sulfur (S) for plant growth and also provides Carbon (C) as energy sources for microorganism in soil. However, the composition of SOM is depended on the ecosystem (like plant species, microbial diversity, animal and climate) in that area. SOM is consisted of many compounds, for example, carbohydrates, lipids, lignins, and humic substances. (Kohnke & Franzmeier, 1995; K. H. Tan, 1998; Sparks, 1999; Schmidt & Noack, 2000; Bohn *et al.*, 2001; Gleixner *et al.*, 2001; Cecillon *et al.*, 2012).

The SOM content in soil affected the hydrophobic organic compounds (HOCs) adsorption in soil because HOCs, which has high octanol/water partition coefficient (K_{ow}), are likely to adsorb on SOM (Cheng *et al.*, 2017). However, Grasso *et al.* (2001) found that there are some organic matter which dissolved into aqueous phase increase the PAHs desorption from soil by increasing PAH diffusion rate.

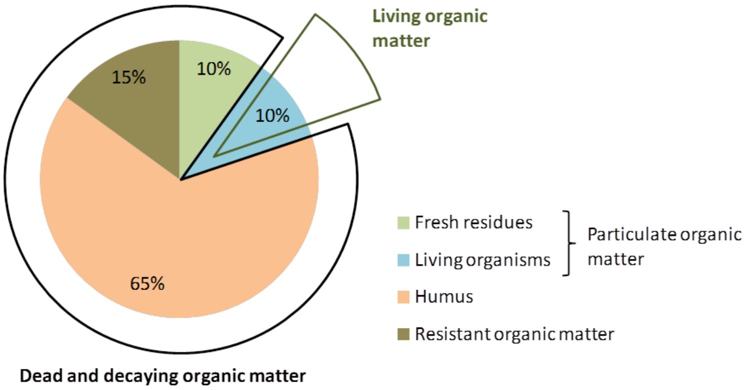


Figure 2.12 The composition of SOM (Griffin, 2017)

2.2.4.1 Carbohydrates

Carbohydrates are account in soil between 5 and 20% of total SOM (Mehta *et al.*, 1962; Lowe, 1978; Stevenson, 1994; Schnitzer, 1999; Sparks, 1999). The origins of carbohydrates in soil are come from many sources, such as live plants, microorganisms, animal and residue, but mostly from plant residue. Carbohydrates in soil are important to microorganisms as carbon sources.

Carbohydrates can be divided into 3 groups; 1) Monosaccharides2) Oligosaccharides and 3) Polysaccharides. Monosaccharides are simple carbohydrates that cannot be hydrolyzed anymore. The examples of monosaccharides in soil are glucose, galactose, xylose and fructose (**Figure 2.13**) (Forsyth, 1948; Alvsaker & Michelson, 1957). Oligosaccharides are complex carbohydrates that composed of two to six simple carbohydrates (K. H. Tan, 1998). Finally, polysaccharides are also complex carbohydrates like oligosaccharides, but have the bigger molecular size due to the higher simple carbohydrates.

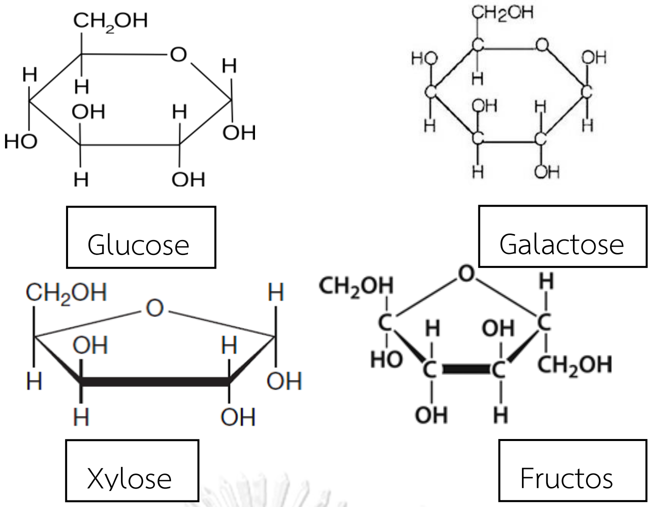

Glucose
Galactose
Xylose
Fructos

Figure 2.13 The example of monosaccharides

2.2.4.2 Lipids

Lipids are heterogeneous compounds of organic substances that can soluble in organic solvents, which called “lipid solvents”, like ether, chloroform, acetone, methanol or benzene. Lipids have various compounds, which can be divided into 3 groups: 1) simple lipids 2) compound lipids and 3) derived lipids (**Figure 2.14**). Simple lipids are the ester of fatty acids such as neutral lipids, fat, oils and waxes. Compound lipids are the lipids with alcohol and other groups like nitrogen, phosphorus or sulfur. The examples of these lipids are phosphatides, sulfolipids and glycolipids. Lastly, derived lipids come from hydrolysis of simple and compound lipids. Derived lipids can be fatty acids, alcohols and sterols, for example, unsaturated fatty acids (oleic acids) and saturated fatty acids (palmitic acids in palm oil or coconut oil), and cholesterol. (Morrison, 1969; K. H. Tan, 1998; Sparks, 1999).

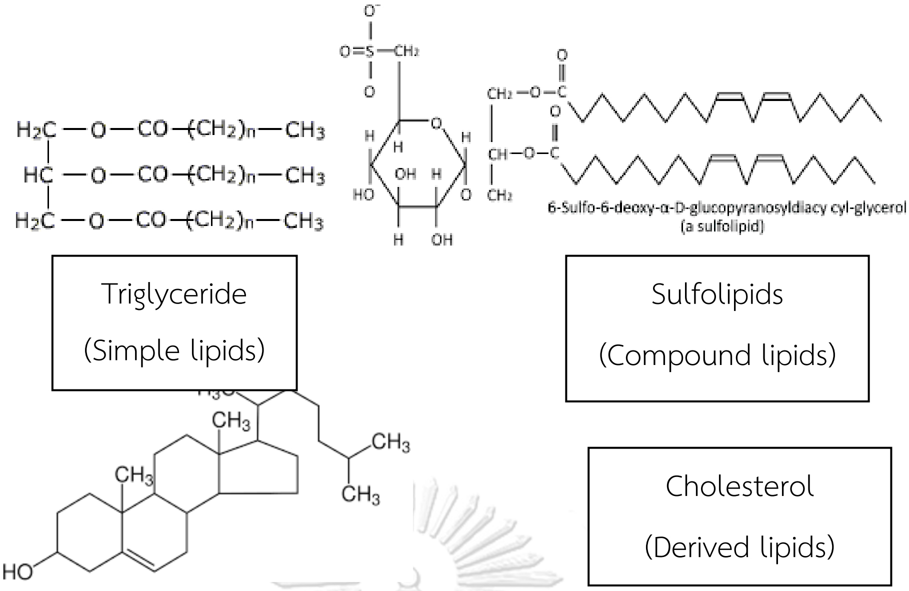


Figure 2.14 The example of lipids

2.2.4.3 Lignins

Lignin is an important component to form plant cell wall. About 20-35% of dry plant cell wall weight is lignin (Galbe & Zacchi, 2007; Christopher *et al.*, 2014). Lignin consists of phenylpropane units, which called monolignols or lignin monomer. There are three types of precursors which are 1) Coniferyl alcohol (from soft wood) 2) Sinapyl alcohol (from hardwood) and 3) p-coumaryl alcohol (from grasses) (Tan, 1998; Sparks, 1999). **Table 2.6** shows the amount of lignin precursors in grasses, softwood and hardwood. These monomers bond together by covalent bonds (C-C and C-O) and become complex molecules (**Figure 2.15**) (Adler, 1977; Karhunen *et al.*, 1995). Due to the complex structure, it leads to the hardly degradation of lignin (Ruiz-Dueñas & Martínez, 2009).

Table 2.6 The percentage of lignin precursors in each wood type

(https://www.e-education.psu.edu/egee439/node/665)

Lignin Sources	Grasses	Softwood	Hardwood
p-coumaryl alcohol	10-25%	0.5-3.5%	Trace
Coniferyl alcohol	25-50%	90-95%	25-50%
Sinapyl alcohol	25-50%	0-1%	50-75%

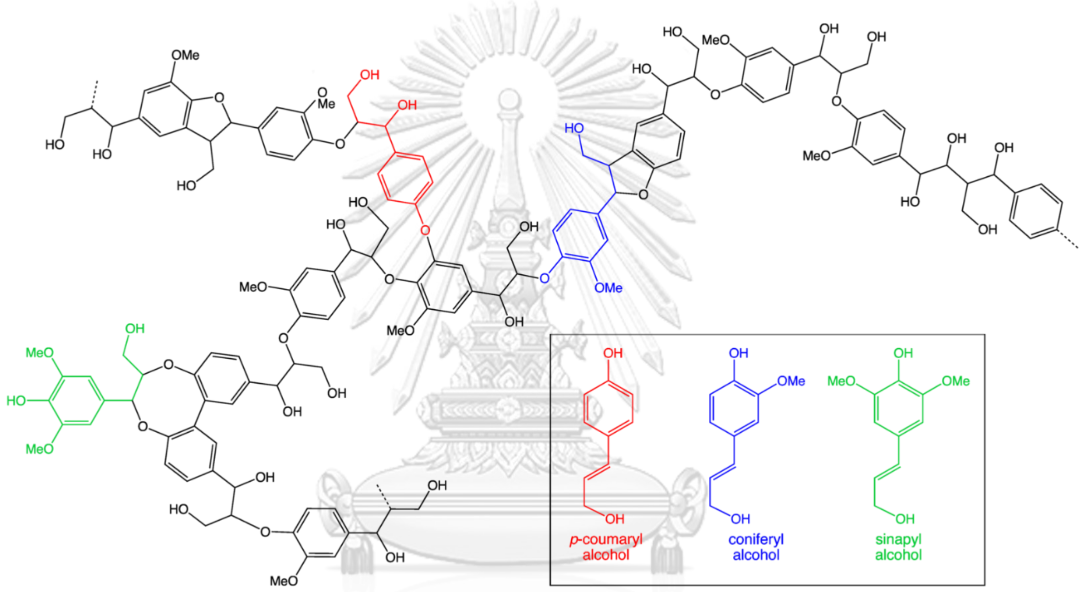


Figure 2.15 The example of lignin structure and basic monomer

(https://www.e-education.psu.edu/egee439/node/665)

2.2.4.4 Humic substances

Humic substances are the largest component of SOM and are the important sources of nutrient for plant and energy sources for microorganisms in soil. The color of humic substances is yellow to brown-black. They occur during the plant and animal decomposition process. The structure of humic substances is very complex and heterogeneous. Humic substances can be divided in to 3 fractions based on their solubility characteristics: 1) humic acids (**Figure 2.16**), which are dissolved in water only under alkaline condition; 2) fulvic acids (**Figure 2.17**), which are dissolved in water under all conditions; and 3) humin (**Figure 2.18**), which are not soluble in water (Jones & Bryan, 1998; K. H. Tan, 1998; Sparks, 1999). Humic substances are not easily degradable because they were too complex for microorganisms to degrade. Humic substances contain a lot of specific functional groups, which mostly carry a charge that is variable with pH (Ishiguro & Koopal, 2016).

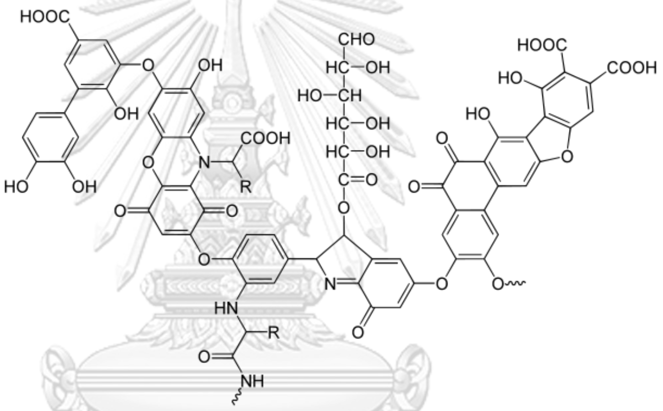


Figure 2.16 Model structure of humic acid (Stevenson, 1994)

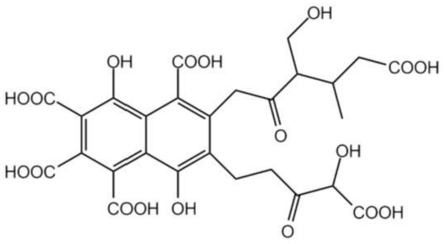


Figure 2.17 Model structure of fulvic acid (Antonious, 2015)

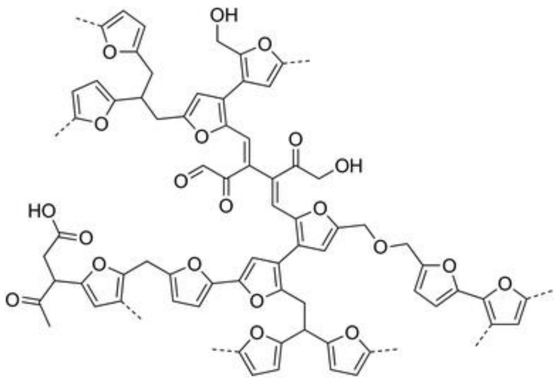


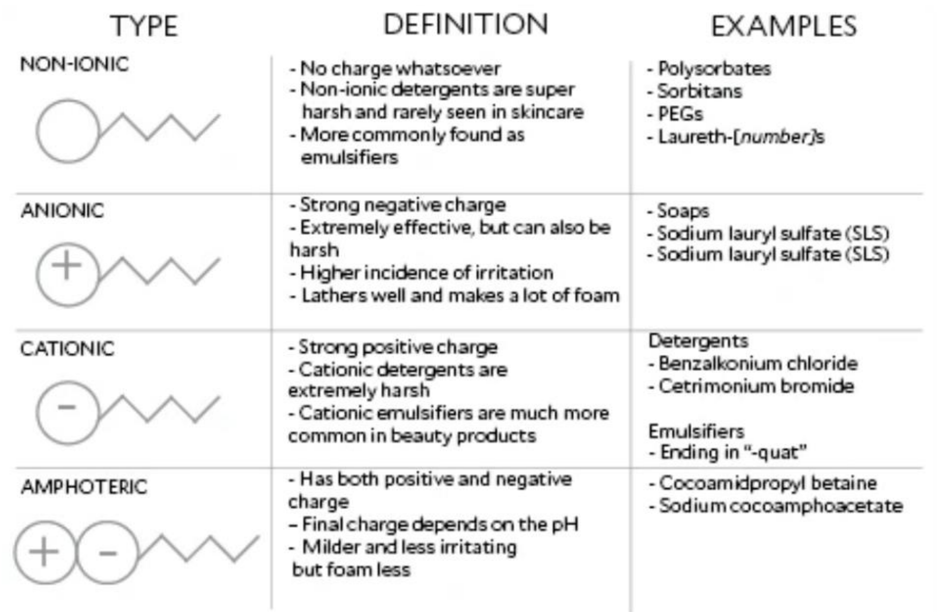
Figure 2.18 Model structure of humin (Zandvoort *et al.*, 2015)

2.4.1 Surfactant

Surface active agent (surfactants) are chemical which reduce the IFT or surface tension between two separated phases. Each surfactant molecule contains hydrophilic head and hydrophobic tail (or lipophilic tail), which is called amphiphilic molecule.

2.4.2 Surfactant types

Surfactant can be divided into 4 types based on their hydrophilic head group properties, which are 1) anionic surfactant, 2) cationic surfactant, 3) nonionic surfactant and 4) zwitterionic or amphoteric surfactant (Paria, 2008; Rosen & Kunjappu, 2012; Befkadu & Chen, 2018). **Figure 2.19** illustrated four types of surfactants.



TYPE	DEFINITION	EXAMPLES
NON-IONIC	- No charge whatsoever - Non-ionic detergents are super harsh and rarely seen in skincare - More commonly found as emulsifiers	- Polysorbates - Sorbitans - PEGs - Laureth-[*number*]s
ANIONIC	- Strong negative charge - Extremely effective, but can also be harsh - Higher incidence of irritation - Lathers well and makes a lot of foam	- Soaps - Sodium lauryl sulfate (SLS) - Sodium lauryl sulfate (SLS)
CATIONIC	- Strong positive charge - Cationic detergents are extremely harsh - Cationic emulsifiers are much more common in beauty products	Detergents - Benzalkonium chloride - Cetrimonium bromide Emulsifiers - Ending in "-quat"
AMPHOTERIC	- Has both positive and negative charge - Final charge depends on the pH - Milder and less irritating but foam less	- Cocoamidpropyl betaine - Sodium cocoamphoacetate

Figure 2.19 Surfactant types

(https://www.stratiaskin.com/blogs/lab-notes/ingredient-spotlight-surfactants)

1) Anionic surfactant

Anionic surfactants carry negative-charged hydrophilic head and hydrophobic tail. Generally, cations that found with anionic surfactants are sodium, potassium, ammonium, calcium, and various protonated alkyl amines (Q. X. Zhou *et al.*, 2005). Anionic surfactants are the most commonly used in many applications such as detergents and personal care products like soap and shampoo. However, the precaution of anionic surfactants is that they can precipitate with cation in surround environment (Fabbri *et al.*, 2008; Muherei, 2008). The examples of anionic surfactants are Sodium/Ammonium Lauryl Ether Sulphate, Sodium/Ammonium Lauryl Sulphate and Linear Alkyl Benzene Sulphonate (LAS).

2) Cationic surfactant

Cationic surfactants are composed of positive-charged hydrophilic head connected with hydrophobic chain. Cationic surfactants mostly bond with halogen group like bromide and chloride then dissociated into an amphiphilic cation and a halogen anion in water. Due to the positively charged head group, cationic surfactant tent to adsorb on negatively charged surface like soil (M. Zhang & Zhu, 2010; Ishiguro & Koopal, 2016). Thus, cationic surfactants are not suitable for soil washing. Normally, cationic surfactants were used as antistatic products like fabric softeners and hair conditioners. The examples of cationic surfactants are Alkyl dimethyl benzyl ammonium chloride (ADBAC), Cetyltrimethyl ammonium bromide (CTAB), Alkyldimethylbenzylammonium chloride (ADBAC or Zephiran), Polyquaternium and Alkyltrimethyl ammonium chloride

3) Nonionic surfactant

Nonionic surfactants are comprised of non-charged hydrophilic head and hydrophobic tail. The main functional groups of hydrophilic head of nonionic surfactants are alcohols, phenol, esters and amide. Due to the non-charged hydrophilic head, nonionic surfactants have less sensitivity to electrolytes (ElSayed *et al.*, 2013; Rosas *et al.*, 2013). So, they can be used in soil with wider range of salinity compared to the ionic surfactants. The examples of nonionic surfactants are ethoxylated and alkoxylated fatty acids, *ethoxylated amines, ethoxylated alcohol,* *alkyl and nonyl-phenol ethoxylates, ethoxylated sorbitan esters,* and *castor oil ethoxylate.*

4) Zwitterionic or amphoteric surfactant

Amphoteric surfactants are the surfactant that have both positive and negative charge at hydrophilic head group. Therefore, the net charge of this surfactant is zero. They are very sensitive to pH. Their final charge depends on pH of surrounding environment (Tadros, 2013). The surfactants become positive-charged in acidic environment, while become negative-charged in alkaline environment. The examples of amphoteric surfactants are betaines and real amphoteric surfactants.

2.4.3 Mechanism involved in surfactant-assisted soil washing process

Once surfactant dissolves in water, the hydrophilic head of surfactant will align along with water whereas the hydrophobic tail will align together in order to reduce the energy of the system. This surfactant formation is named micelle as shown in **Figure 2.20**. To form micelle, concentration of surfactant is important. If the surfactant concentration is too low, it cannot form micelle because most of surfactants are align at the water surface and the rest is not enough to form micelle. The concentration that surfactants start to form micelle called critical micelle concentration (CMC) as shown in **Figure 2.21** (Vishnyakov *et al.*, 2013). Surfactants increase the solubility of diesel by surrounding around diesel and forming micelle, which make diesel can be detached from soil easier and increase the washing efficiency.

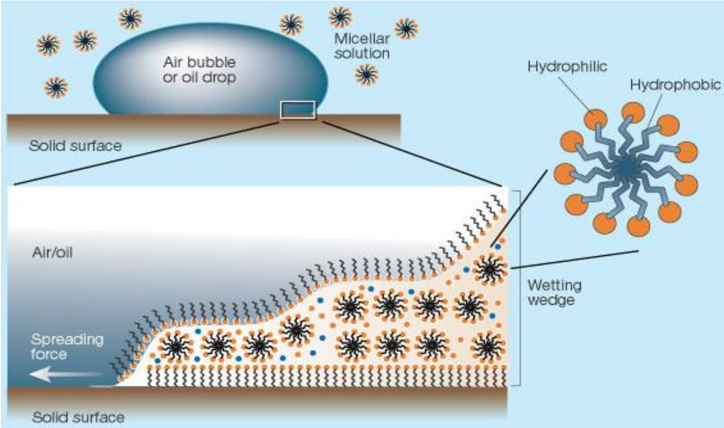


Figure 2.20 The mechanism of surfactant in soil washing process (Wasan & Nikolov, 2003)

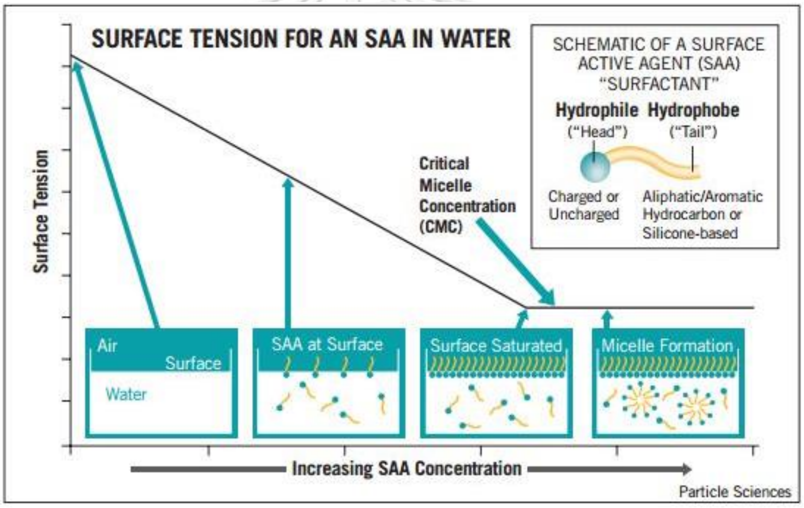


Figure 2.21 Behavior of surfactants at different concentration (Ernest, 2015)

2.4.3.1 Contaminant removal mechanism

The mechanism of surfactant in soil washing process can be divided in to 3 steps based on the surfactant concentration, which are.

1) At low concentration (lower than CMC value), the surfactant in solution stays as monomers. The contaminant still retained in soil due to its high affinity. Surfactant monomers adsorb onto soil to reduce IFT by the

electrostatic interaction and can der Waals interactions (Kamal *et al.*, 2017). There are no effective of soil removal efficiency in this step.

2) As the surfactant concentration increase (at CMC value), the free contaminant in washing solution was reduced. The contaminant in soil was detached and trapped into hydrophobic cores of surfactant micelles (Chu & Chan, 2003). The removal efficiency increased.
3) At higher surfactant concentration, all free contaminant was trapped in surfactant micelle. The removal efficiency rapidly increase because the contaminant in soil was the only source of contaminant in the system (Chu & Chan, 2003).

2.4.3.2 Surfactant adsorption mechanism

The interaction between surfactant and soil can be affected by surfactant structure, soil properties (i.e. soil surface charge, interlayer swelling) and primary charge characteristics (i.e. nutrient in soil, pH) (Ishiguro & Koopal, 2016). The surfactant adsorption mechanism on soil can be divided in to 6 mechanisms (Heinz *et al.*, 2017), which are;

1) Ion exchange

The replacement between acidic or basic groups on soil surface and surfactant that has similar charge. It is a substitution process with no change in zeta potential.

2) Ion pairing

The sorption of surfactant that has the opposite charge with soil. This process reduces zeta potential by neutralizing the charge of soil surface

3) Hydrogen bonding

The attractive force between hydrogen atom (H) with the atom that has high electronegativity (EN) such as, oxygen atom (O). The contribution of hydrogen bonds to adsorption increases towards the point of zero charge (lower pH).

4) Dispersion interactions (dipole attraction)

The attractive force between two electrons that occupy positions that make atoms form temporary dipoles.

5) Polarization of π electrons effects

The attractive force between the electron-rich group on surfactant structure and the positive sites of soil surface.

6) Hydrophobic interactions

The hydrophobic part of surfactant was trying to remove itself from aqueous phase, resulting in physical adsorption with soil.

2.4.3.3. Surfactant usage in soil washing remediation

In soil washing process, cation surfactants cannot be used because they are easily to sorb on soil which commonly has negative charge. Amphoteric surfactants are very sensitive to pH, so they are not suitable for soil washing. Anionic surfactants have low adsorption in soil, but they have higher toxicity compare to nonionic surfactants and might be precipitated with the nutrients in soil (K^+, Ca^{2+}, and Mg^{2+}). Therefore, nonionic surfactants are selected for soil washing in this study.

However, the problem of using surfactant in soil washing process is the adsorption of surfactant on soil. Hydrogen bonding and Van Der Waals force between nonionic and mineral oxides lead to the adsorption of nonionic surfactant on soil (Pugh & Tjus, 1990; Somasundaran *et al.*, 1991; Behl & Moudgil, 1992; Shen, 2000). There are several studies those found the adsorption of surfactant on soil. Moreover, the structure of surfactant also affects to the surfactant adsorption on soil (Zacarias–Salinas *et al.*, 2013). Therefore, this study will be focus on the effect of soil composition and surfactant structure on surfactant adsorption on soil and investigate the relationship between each factor.

2.4.4. Surfactant adsorption on silica (sand and silt)

The surfactant adsorption on soil minerals are important because soil minerals are the main part of soil solid (90% of total soil solid). There are many researchers that studied about the adsorption of both ionic and nonionic surfactant on soil minerals. Thus, the adsorption on silica or silicon dioxide (SiO_2), which was the main minerals in sand and silt, was one of the topics that received the attention.

1) Ionic surfactants adsorption on SiO_2

Cationic surfactants has high adsorption on SiO_2 because SiO_2 has high adhesive force from partial negative charge at O atom, while anionic surfactant has low adsorption on SiO_2 (Chen *et al.*, 2013). Therefore, there are no attention on anionic surfactant adsorption on SiO_2.

In presence of high salt concentration, the mutual hydrophilic group repulsion and the attraction between hydrophobic tail of cationic surfactants and soil surface was decreased because there are many counter ions near the soil surface which lead to the high surface charge and decrease the soil surface hydrophobicity. In contrast, in presence of low salt concentration, the surfactant ion that adsorbed head-on (the head group of surfactants directed on soil surface) was desorbed. At all salt concentration, the surfactant ions that appeared with counterion may adsorb on the surfactant, that adsorbed on soil surface in head-on position, in head-out position (the head group of surfactants directed on solution) and become small admicelles (B. Y. Zhu & Gu, 1989). At low surfactant adsorption, the hydrophobicity of soil surface was increase because hydrophobic tail of adsorbed surfactant was directed on solution. In contrast, the hydrophobicity of soil surface was decrease when the adsorption of surfactant was high because admicelles, which the hydrophilic head of surfactant was directed on solution, was occurred (Koopal *et al.*, 1999; Koopal, 2012).

2) Nonionic surfactants adsorption on SiO_2

Nonionic surfactants can adsorb on SiO_2, which has hydrophilic surface. The oxyethylene (EO) group in hydrophilic head of surfactants bound with the silinol groups of SiO_2 surface by hydrogen bonding. However, compare to the ionic surfactant, the adsorption of nonionic surfactant was relatively low because of the low affinity between EO group and SiO_2 surface (Levitz, 2002). There are 2 steps mechanism for nonionic surfactant adsorption on SiO_2 which divided by surfactant concentration. At low surfactant concentration, the hydrophobicity of SiO_2 surface was increased. At higher concentration, the SiO_2 surface hydrophobicity was decrease. However, both surfactant concentrations were still lower than CMC value (Denoyel & Rouquerol, 1991).

2.4.5. Surfactant adsorption on clay

As told in previous section that surfactant adsorption on soil minerals, which was 90% of soils solid, was caution. Clay, which is one of soil minerals, was consider due to its high adsorption capacity. Clay has many types divided by the number silica sheet per alumina sheet. There are 2 types of clay surfaces which are basal plates and edges. Each clay type has different surfactant adsorption capacity due to its structure characteristic. Therefore, there are many studies that investigated about the adsorption of each surfactant type on each clay types.

1) Cationic surfactants adsorption on Kaolin

The cationic surfactants (Hexadecyl Trimetyl Ammonium Bromide - C16TAB and Dodecyl-phosphocholine - C12PC) are likely to adsorb on plate surfaces of kaolin than on the edge of kaolin. They adsorbed on kaolin surfaces with head-on position as the first layer. Then, the surfactant adsorbed on the head-on adsorbed surfactant with head-out position as the second layer and became admicelles. The cationic surfactant adsorption on kaolin was independent by the electrolyte in both head-on and head-out surfactant adsorption, while the head-out cationic surfactant adsorption was affected by temperature. The increasing of hydrophobic chain length of surfactant has no effect on head-on surfactant adsorption (first layer), but it was effect with head-out adsorption (second layer) (de Keizer *et al.*, 1990).

2) Cationic surfactants adsorption on montmorillonite

The adsorption on montmorillonite was different from kaolin because montmorillonite has an interlayer swelling, which increased the surfactant adsorption capacity. Cationic surfactant adsorbed on plate surfaces of montmorillonite, which was the same as the cationic surfactant adsorption on kaolin. The increasing of cationic surfactant adsorption at the montmorillonite surface decreased the electrostatic repulsion between montmorillonite particles (reduce dispersion) because the net negative charge of montmorillonite was decreased and also increased the hydrophobicity of particles by the head-on surfactant (the hydrophobic tail of surfactant directed to solution). Then, the admicelles occurred from the head-out surfactant adsorption on the adsorbed surfactant which decreased the hydrophobicity of montmorillonite and increased the dispersion of montmorillonite. However, the main adsorption part in montmorillonite was in the interlayers of montmorillonite. The amount of surfactant adsorption in the interlayer of montmorillonite depended on the distance between the interlayer and the structure of adsorbed surfactant (Ishiguro & Koopal, 2016). The interlayer space was increased in the presence of water by hydrophobic attraction from the aggregation of hydrophobic tail of surfactant in the interlayer (J. Zhu *et al.*, 2008; Q. Zhou *et al.*, 2014).

3) Anionic surfactants adsorption on kaolin

In contrast with cationic surfactants, anionic surfactants are likely to adsorb on the edge of kaolin than on the plate of kaolin. The proton charge of the edge of kaolin was affected by pH. At low pH, the net proton charge of the kaolin edge was positive, while it became negative charge at high pH (Tertre *et al.*, 2006). Anionic surfactant (Sodium dodecylbenzene sulfonate - SDBS) precipitated with cationic of dissolved aluminum species at acidic condition (pH < 3.7), which shown the highest adsorption of surfactant with kaolin. The anionic surfactants adsorption was decreased with the increasing pH due to the reducing of dissolve aluminum species (pH ≈ 4.4 – at point of zero net proton charge of sample) (Ishiguro & Koopal, 2016). Anionic surfactants adsorbed on kaolin using hydrophobic tail of surfactant (del Hoyo *et al.*, 2008). Therefore, the main factors that affect the sulfonate surfactant on kaolin were electrostatic and hydrophobicity interactions (Torn *et al.*, 2003).

4) Anionic surfactants adsorption on montmorillonite

Anionic surfactants were mainly adsorbed on the edges of montmorillonite. Anionic surfactants also precipitated with the dissolve mineral species as the anionic surfactant adsorption on kaolin. For example, in presence of Ca^{2+}, anionic surfactant (sodium dodecylbenzene sulfonate - SDBS) was adsorbed significantly by montmorillonite saturated with Ca^{2+} (Yang *et al.*, 2007).

5) Nonionic surfactants adsorption on kaolin

The adsorption of nonionic surfactants on kaolin was occurred by hydrogen bonding between EO group of surfactants and the hydroxyl group of kaolin surface (Deng *et al.*, 2006). Thus, the number of EO group in hydrophilic head of surfactant affected the adsorption of nonionic surfactant on kaolin. The Increasing of EO number in hydrophilic head decreased the adsorption on kaolin because of steric hindrance.

6) Nonionic surfactants adsorption on montmorillonite

Nonionic surfactants were adsorbed on the plate of montmorillonite surface like cation surfactant adsorption on montmorillonite. The interlayer swelling was also the main adsorption part as in cationic surfactant adsorption. In the interlayer of montmorillonite, EO groups at hydrophilic head of surfactant were placed with disorder arrangement in the presence of water in the system and made the space of interlayer expanded (Deng *et al.*, 2006).

2.4.6 Surfactant adsorption on humic substances

Humic substances was one of factor that effect the adsorption capacity in soil because they have high adsorption ability and can bind with both organic and inorganic chemicals due to their complexation (Klučáková & Pavlíková, 2017; Meng *et al.*, 2019). However, due to the the surfactants characteristic, surfactants can both attractive or repulsive with the functional group of humic substances depend on the charge of surfactants and humic substances. Mostly, the negative charge of humic substances was the main part that interact between humic substances and other chemicals (W. F. Tan *et al.*, 2011). The studies about the adsorption of surfactant on humic substances were shown in **Table 2.7**. Ishiguro and Koopal (2016) realized that there are 2 hydrophobic interactions between surfactant and humic substances that should be focus, which are 1) the hydrophobic effect of adsorption of hydrophobic tail of surfactant onto hydrophobic parts of humic substances and 2) the lateral hydrophobic attraction between bound surfactants. However, these 2 hydrophobic interactions were contradicted. If the hydrophobic effect of adsorption of hydrophobic tail of surfactant onto hydrophobic parts of humic substances is large, the lateral hydrophobic attraction between bound surfactants will be small.

Table 2.7 The studies on the surfactant adsorption on humic substances

Condition	Result	Method	Reference
In the presence of various humic substances	- Increase anionic surfactant (sodium dodecyl sulfate - SDS) aggregation prior to micellization - Form ionic pair with cationic surfactant (cetyltrimethylammonium bromide - CTAB)	Pulsed-field gradient nuclear magnetic resonance (PFG-NMR) diffusion measurements	(Otto *et al.*, 2003)
In the presence of humic acid - at pH 9.18 at 0.03 M electrolyte concentration - at pH 3.98 at 0.10 M electrolyte concentration	- No binding between anionic surfactant (SDS) and humic acid - Has electrostatic repulsion between humic acid and anionic surfactant (SDS)	Potentiometric titration and dynamic light scattering (DLS) methods	(Yee *et al.*, 2009)

Table 2.7 The studies on the surfactant adsorption on humic substances (cont.)

Condition	Result	Method	Reference
In the presence of humic acid at pH 5, 7 and 10 at 0.025 M electrolyte concentration	- No binding between humic acid and anionic surfactant (SDS) - Increasing of binding between humic acid and cationic surfactant (dodecyl- and cetylpyridinium chloride - DPC and CPC) with increasing pH	Potentiometric method with a surfactant electrode	(Koopal *et al.*, 2004)
In the presence of humic acid at pH 8 with 0.5 mM divalent metal salts	- The binding constant of cationic surfactant (decyl- and dodecyl trimethylammonium - C10TAB and C12TAB) and humic acid decreased	Surfactant ion-selective electrode	(Matsuda *et al.*, 2009)

Table 2.7 The studies on the surfactant adsorption on humic substances (cont.)

Condition	Result	Method	Reference
In the presence of humic acid at pH 5 and 0.1 M NaCl	- The cationic surfactant (cetyl- or hexadecyl-pyridinium chloride - C12PC and C16PC) binding to humic substances by electrostatic and hydrophobic attraction	Mutek Particle Charge Detector (PCD)	(Ishiguro *et al.*, 2007)

2.4.7 Effect of physical condition in soil washing process

To increase the petroleum removal efficiency in soil washing process, there are several researchers studied to determine the optimum condition. The physical condition factors that affected on petroleum removal efficiency were mixing speed, time, L/S ratio and temperature.

1) *Mixing speed*

Increasing mixing speed increased the petroleum removal efficiency (Urum *et al.*, 2004; Lai *et al.*, 2009; Peng *et al.*, 2011; Baziar *et al.*, 2013; Wei *et al.*, 2015; Alquzweeni, 2016). These might be because when the mixing speed increased, there are more change for contaminated soil to contact with surfactant solution and make the solution can remove contaminant from soil. Moreover, the shearing force from mixing speed pull out the adsorbed contaminant in soil and crusted the contaminated soil, then release the contaminant (L. Zhang *et al.*, 2001; Urum *et al.*, 2004).

2) *Time*

The sufficient contact time, which was the time for surfactant to interact with contaminant in soil, was important parameter for the effective removal efficiency. In the first period, the longer time rapidly increase the removal efficiency until its meet the optimum time. After that, the removal efficiency was almost stable level (Urum *et al.*, 2004; Peng *et al.*, 2011; Baziar *et al.*, 2013; Alquzweeni, 2016).

3) L/S ratio

The increasing of L/S ratio can increase the petroleum removal efficiency (Urum *et al.*, 2004; Peng *et al.*, 2011; Alquzweeni, 2016). The increasing of L/S ratio lead to the increasing of micelles amount to remove petroleum from soil and enhance the interaction between the solution and contaminant. However, increasing L/S ratio mean that the higher water used and the higher wastewater generation. Therefore, (Peng *et al.*, 2011) suggested the optimum L/S ratio of 10:1 (mL/g).

4) Temperature

The increasing of temperature increased the petroleum removal efficiency (Dong *et al.*, 2004; Urum *et al.*, 2004; Tremblay *et al.*, 2005; Viamajala *et al.*, 2007; Wei *et al.*, 2015). These might be because increasing temperature increased the solubility of petroleum and decreased the fraction of petroleum sorbed to the soil (Dong *et al.*, 2004; Tremblay *et al.*, 2005; Viamajala *et al.*, 2007). The petroleum viscosity was reduced, and the mobility and interaction with surfactant solution was increased with the increasing temperature (Urum *et al.*, 2004). However, in Peng *et al.* (2011) studied, there are no effect of temperature on PAHs removal efficiency, which might be because the dissolution and desorption of PAHs were the minor influence, while the incrustation and soil-trapped PAHs are play more important role.

2.5 Case study

Petroleum contaminated soil is become a global problem because these soils affect agricultural products and human health. Therefore, there are many studies that interested in treating petroleum contaminated soil. **Table 2.8** showed the example of studies that used surfactant to clean up petroleum contaminated soil by soil washing process.

Table 2.8 The example of studies that used surfactant in petroleum contaminated soil clean up by soil washing

Surfactant types	**Surfactant name**	**Contaminant**	**Soil texture**	**Initial contaminant concentration**	**Removal efficiency**	**References**
Anionic	Sodium dodecyl sulfate (SDS)	Fuel oil	Silt	-	97%	Khalladi *et al.*, 2009
		Crude oil	Silty clay Clay Sand	92,200 mg/kg 89,100 mg/kg 87,500 mg/kg 37,600 mg/kg	85% 90% 80% 90%	Urum *et al.*, 2004
			Sand	108,980 mg/kg	20%	Torres *et al.*, 2005
		Diesel	Sand	10,000 ppm 20,000 ppm	35% 45%	Salehian *et al.*, 2012
		Wasted oils	Clay	14,705 mg/kg	60%	Zacarias–Salinas *et al.*, 2013
	Sodium dodecyl benzene Sulphonate (SDBS)	Wasted oils	Clay	14,705 mg/kg	57%	Zacarias–Salinas *et al.*, 2013
		Polycyclic aromatic hydrocarbons (PAHs)	Loam Loamy sand	208 mg/kg 3,495 mg/kg	46% 37%	Zhong-Yi *et al.*, 2014
Nonionic	Tween 20	Crude oil	Sand	108,980 mg/kg	13%	Torres *et al.*, 2005
		Wasted oils	Clay	14,705 mg/kg	54%	Zacarias–Salinas *et al.*, 2013

Table 2.8 The example of surfactant used in petroleum contaminated soil clean up by soil washing (cont.)

Surfactant types	**Surfactant name**	**Contaminant**	**Soil texture**	**Initial contaminant concentration**	**Removal efficiency**	**References**
Nonionic	Tween 40	Phenanthrene	Sandy loam	200 mg/kg	56%	Ahn *et al.*, 2008
	Tween 80	Crude oil	Sand	108,980 mg/kg	15%	Torres *et al.*, 2005
		Wasted oils	Clay	14,705 mg/kg	38%	Zacarias–Salinas *et al.*, 2013
		Phenanthrene	Sandy loam	200 mg/kg	54%	Ahn *et al.*, 2008
		Diesel	Sandy loam	18,000 mg/kg	71%	Baziar *et al.*, 2013
		Polycyclic aromatic hydrocarbons (PAHs)	Loamy sand	12.6 mg/kg	79%	Peng *et al.*, 2011
			Sandy loam	997 mg/kg	31%	Gong *et al.*, 2010
	Triton X-100	Polycyclic aromatic hydrocarbons (PAHs)	Loam Loamy sand	208 mg/kg 3,495 mg/kg	48% 42%	Zhong-Yi *et al.*, 2014
			Loamy sand	12.6 mg/kg	83%	Peng *et al.*, 2011
			Sandy loam	997 mg/kg	22%	Gong *et al.*, 2010

Table 2.8 The example of surfactant used in petroleum contaminated soil clean up by soil washing (cont.)

Surfactant types	**Surfactant name**	**Contaminant**	**Soil texture**	**Initial contaminant concentration**	**Removal efficiency**	**References**
Nonionic	Tergitol 15-S-7	Crude oil	Sand	223,754 mg/kg	64%	Heo & Lee, 2015
	Tergitol 15-S-9	Crude oil	Sand	223,754 mg/kg	65%	Heo & Lee, 2015
	Brij 30	Phenanthrene	Sandy loam	200 mg/kg	34%	Ahn *et al.*, 2008
	Brij 35	Crude oil	Sand	108,980 mg/kg	17%	Torres *et al.*, 2005
		Wasted oils	Clay	14,705 mg/kg	58%	Zacarias–Salinas *et al.*, 2013
		Phenanthrene	Sandy loam	200 mg/kg	55%	Ahn *et al.*, 2008
		Diesel	Sandy loam	18,000 mg/kg	54%	Baziar *et al.*, 2013
	Brij 58	Crude oil	Sand	108,980 mg/kg	0%	Torres *et al.*, 2005

CHAPTER 3

METHODOLOGY

3.1 Materials and Chemicals

3.1.1 Chemicals

Diesel was purchased from Esso, local petroleum gas station, in Bangkok, Thailand. The surfactants used in this study are Tween series and Tergitol series because both of them are widely used and biodegradable (Yeh *et al.*, 1998; Dow, 2020). Tween 20 (TW20), Tween 40 (TW40), Tween 60 (TW60) and Tween 80 (TW80) were selected for Tween series. Tergitol 15-S-7 (TS7), Tergitol 15-S-9 (TS9) and Tergitol 15-S-15 (TS15) were chosen for Tergitol series. Tween series surfactants are polyethoxylated sorbitan ester surfactants, while Tergitol series surfactants are secondary alcohol ethoxylate surfactants. All Tween series surfactants, except TW80 were purchased from Merck; TW80 was purchased from Ajax Finechem. All Tergitol series surfactants were purchased from Dow Chemical Company. All surfactants are Lab grade. The hydrophobic parts or tail groups of these surfactants are different and affect their hydrophilic-lipophilic balance (HLB) values as shown in **Table 3.1**.

Table 3.1 Properties of surfactants used in this study (Dow, 2020; Sigmaaldrich, 2020)

Surfactant	CMC (mg/L)	Density (g/mL)	Moles EO	Alkane length	HLB	MW (g/mole)
Tween 20	60.0	1.095	20	11	16.7	1228
Tween 40	34.5	1.083	20	15	15.0	1284
Tween 60	27.0	1.044	20	17	14.9	1309
Tween 80	15.7	1.060	20	17*	15.0	1310
Tergitol 15-S-7	38.0	0.991	7	13	12.1	508
Tergitol 15-S-9	52.0	1.006	9	13	12.6	596
Tergitol 15-S-15	162.0	1.007	15	13	15.4	860

*Have 1 double bond

3.1.2 Soil composition preparation

The artificial soil was prepared by mixing of sand (**Figure 3.1a**), silt (**Figure 3.1b**), clay (**Figure 3.1c**) and organic matter (**Figure 3.1d**). Quartz and kaolin, were used as sand and clay, respectively, in this study. Both minerals were purchased from Fisher scientific. Montmorillonite was purchased from Sigma Aldrich. Silt was prepared from sand (quartz) by grinding with Cup Mill. The ground sand which penetrated through a mesh number 325 (0.045 mm) was treated as a silt. **Table 3.2** shows the soil types classification. BET (Brunauer, Emmett and Teller) method was used to measure the surface area of each soil types.

Table 3.2 The soil types classification

Soil types	Size Range (μm)	Surface area (m^2/g)
Sand	150.0 - 425.0	< 1*
Silt	< 44.0	2.24
Clay	1.0 - 1.8	12.99
Organic matter	< 500	-

* Instrument detection limit

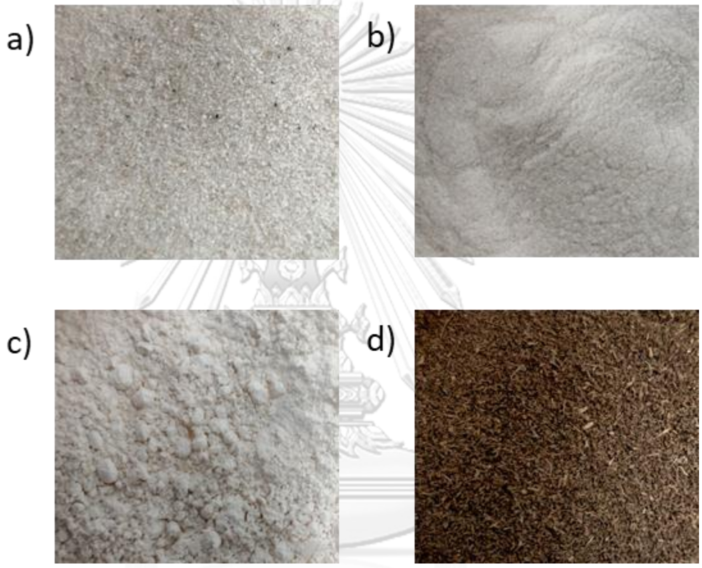


Figure 3.1 The artificial soil that were used in this study; a) sand, b) silt, c) clay and d) organic matter

To representative organic matter (OM), another component of the substrate, as in real soil composition, OM was prepared by composting Manila grass (*Zoysia matrella* Merrill) because grass was normally used as fertilizer in real situation (Sheremata *et al.*, 1997; Sheremata *et al.*, 2000). Actually, humic acid was widely used as organic matter in water source (Siddiqui *et al.*, 1997; Guan *et al.*, 2006;

Zularisam *et al.*, 2011). However, there are many substances in organic matter in real soil. Using only humic acid, which was one of humic substances that are dissolved in alkaline condition, might not know some effect from OM such as the effect from humic substances that can dissolved in water or dissolved organic matter (DOM). Therefore, to represent OM in real soil, composted grass was used as OM in this study. Manila grass was composted under aerobic condition for 45 days, and then dried overnight at 105°C (Sawang, 2017). The dried composted grass was ground and fractionated using a metal sieve of mesh number 35 (0.5 mm). Subsequently, the sieved composted grass was sterilized using an autoclave at 121°C for 30 min and then left at 30°C for 8 h. This sterilization process was repeated thrice.

To investigate the effect of dissolved organic matter (DOM) on surfactant adsorption, sand with 1%OM content using TW20 was tested. 0.1 g OM in 10 g soil with 30 mL TW20 solution was used. Therefore, to get the same DOM as in the sand with 1%OM content, 1%w/v of DOM solution was prepared using water and OM at a ratio of 300:1 (mL:g). The solution was filtrated through 0.45 μm PTFE membranes. The supernatant was then used to prepare the surfactant solution to investigate the behavior of DOM in surfactant adsorption on soil minerals.

To validate the diesel removal efficiency from the predicted model, real soil was collected from a non-contaminated area (in this study, soil from agriculture area from Suphanburi Province was collected due to it is closed to Bangkok, Thailand and the area has never been contaminated with diesel. The real soil composition was measured by Hydrometer Method. The composition was shown in **Table 3.3**.

Table 3.3 The composition of real soil

Soil Composition	%
Sand	24.0
Silt	40.8
Clay	35.2
OM	2.0

3.2 Diesel contaminated soil preparation

The initial diesel concentration of 50,000 mg diesel/kg soil was used because it was the concentration that found in hot spot area (Lin *et al.*, 2011). 2.5 g of diesel in 50 mL hexane was added to 50 g of soil mineral and mixed homogeneously. The spiked soil was incubated at room temperature for 3 days, and evaluated the diesel content by Gas Chromatography – Flame Ionization Detector (GC-FID) before used.

3.3 Measurement and Analysis Method

3.3.1 Critical Micelle Concentration (CMC) measurement

The CMC value is the surfactant concentration level which the first micelle structure is formed and it provides the lowest surface tension value. Tensiometer (Dataphysics - DCAT 11, Germany) was used to measure the surface tension of aqueous surfactant solution in different surfactant concentration at 25 °C.

Surface tensions were measured for at least eight different surfactant concentrations. Surface tension measurements were plotted against the surfactant concentrations in order to determine the CMC values of the surfactants. The CMC value was an intersection between line A (reducing surface tension) and line B (stable surface tension) shown in **Figure 3.3.** The CMC of surfactant without soil substrate is referred to as “measured CMC” (CMC$_m$), while that of surfactant with solid substrate is referred to as “appearance CMC” (CMC$_a$). In most cases, the CMC$_m$ is lower than the CMC$_a$. The Statistica program was used to create the mixture diagram to predict the CMC$_a$ in different soil texture with 2%OM.

For evaluating the CMC$_a$, the surfactant solution and soil, at a ratio of L/S ratio 3:1 (mL:g), was shaken at 200 rpm for 30 min, and then centrifuged at 4000 rpm for 10 min. Subsequently, the supernatant was collected and placed at room temperature for 15 min. The surface tension of the supernatant was measured for calculating CMC$_a$ of each surfactant in different soil system. The difference (times) between CMC$_m$ and CMC$_a$ in the presence of each soil component (X$_{CMC}$) was calculated using **equation 1**. Higher X$_{CMC}$ values imply that higher surfactant concentrations are required to form micelle structures in the presence of soil substrates (Liu *et al.*, 1992; Amirianshoja *et al.*, 2013). This means that more surfactants were adsorbed on the soil surface.

$$X_{CMC} = \frac{\text{Appearance CMC with soil mineral}}{\text{Measured CMC}} \qquad \textbf{Eq. 1}$$

To confirm surfactant adsorption on soil, Fourier-transform infrared spectroscopy (FTIR) (Perkin Elmer - Spectrum One, USA, range 4,000-400 cm^{-1}) was used to identify soil functional groups before and after surfactant adsorption.

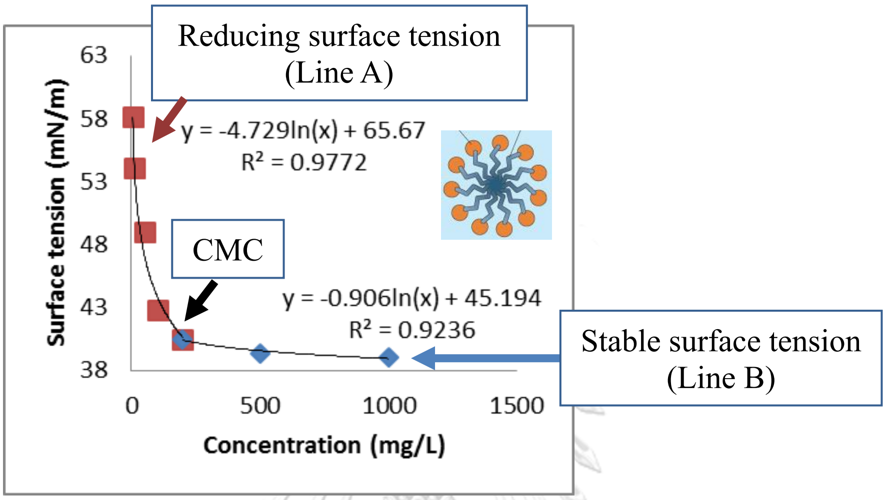


Figure 3.2 The example of CMC value measurement

3.3.2 Soil hydrophobicity measurement

Contact angle was measured using a Tensiometer (Dataphysics - DCAT 11, Germany), and the column wicking method was used to measure the differencebetween the hydrophobicity of the soil minerals (Alghunaim *et al.*, 2016). Briefly, dried soil mineral was packed into the column. Hexane and deionized water were used to measure the capillary constant and contact angle of each soil mineral. Higher contact angles indicate higher hydrophobicity.

3.3.3 Quantitative measurement of diesel by GC-FID

After removing the supernatant, residual diesel in the washed soil was extracted using a 3 mL mixture of hexane and acetone (1:1 volumetric ratio) (Haleyur *et al.*, 2016). The slurry was vortexed for 1 min, and then the extracted solvent was collected. This extraction process was repeated seven times (eight extraction cycles in total). All extracted solvents were pooled together, and the total volume was adjusted to 25 mL. The extracted solvent (1 mL) was filtered through a 0.25 µm PTFE membrane and the residual diesel concentration was analyzed by GC-FID (Agilent-8890). The in-house method for analyzing diesel by GC-FID used in this study was modified from Heo and Lee (2015) and Rongsayamanont *et al.* (2020) and the analytical conditions of this method are described in **Table 3.4**. The diesel chromatograph from GC-FID was shown in **Figure 3.4**. The diesel removal efficiency was calculated using **equation 2**.

Table 3.4 GC-FID analytical condition

Parameter	**Condition**
Column	VF-5ht (15 m x 320 µm x 0.210 µm)
Injection	2 µL (splitless)
Carrier gas	N_2 (2 mL/min)
Injection temperature	300 °C
Oven temperature gradient	50 °C (7 min hold) → 20 °C/min → 310 °C (5 min hold)
Detector temperature	330 °C
Run time	27 min

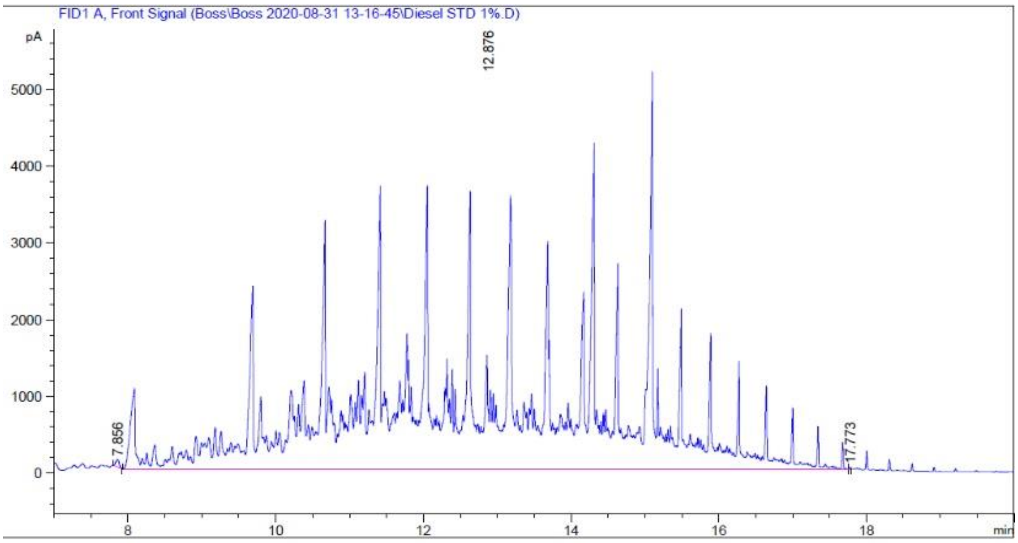


Figure 3.3 GC-FID chromatograph of diesel

$$\% \text{ Diesel removal efficiency} = \frac{\text{Residual diesel concentration (mg/kg)}}{50{,}000 \text{ mg/kg}} \times 100 \quad \textbf{Eq. 2}$$

3.4 Surfactant-assisted diesel contaminated soil washing process

Contaminated soil (1 g) was washed with 3 mL of the surfactant solution. The soil mixture was shaken at 200 rpm for 30 min, and then centrifuged at 4000 rpm for 10 min. Subsequently, residual diesel concentration in the washed soil was analyzed using gas chromatography with a flame ionization detector (GC-FID) as described in Section 3.3.3.

3.5 Design of experiment

3.5.1. Effect of soil properties on CMC_a of Tween and Tergitol

Pure sand, silt and clay with different OM content content (0%, 1%, 3% and 5%wt) were used to investigate the effect of soil properties on CMC value. The concentrations of Tween and Tergitol surfactant solution were varied to find the CMC value (as illustrated in **Figure 3.5**). The CMC value was measured by Tensiometer as described in Section 3.3.1.

The adsorptive capacity of each soil component was evaluated based on changing in CMC of surfactant using a surface tension technique (Liu *et al.*, 1992; Amirianshoja *et al.*, 2013).

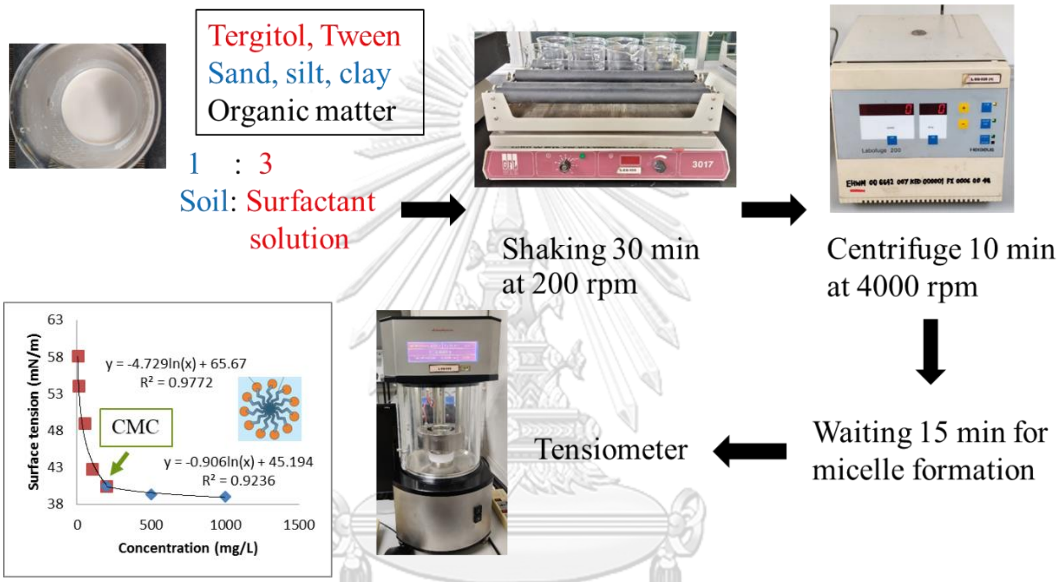


Figure 3.4 Effect of soil properties on CMC_a of Tween and Tergitol experimental procedure

3.5.2. Effect of soil properties on diesel removal efficiency by surfactant-assisted soil washing

Organic matter content (0%, 1%, 3%, and 5%wt), surfactant structure (Tween and Tergitol series), surfactant concentration (CMC_m, CMC_a, and 10X of CMC_a), and type of soil compositions (sand, silt and clay) were varied to determine the factors that significantly affect diesel removal efficiency washing efficiency.

To compare with the real soil, soil texture (sand, silt and clay) with 2% OM using TW80 and TS15 was varied in this section. **Table 3.5** shown the soil composition that were used in this study. The washing conditions from adsorption test were applied in this section. The surfactant concentration (i.e., measured CMC, 1X, 10X of appearance CMC) were varied to find the optimum concentration for each surfactant in soil washing process. The residual diesel concentration in soil was analyzed by GC-FID (Section 3.3.2). The mixture design was selected to generate the experimental framework for predicting the diesel removal efficiency in different soil texture with 2%OM.

Table 3.5 Soil composition ratio with 2% OM content that were used in this study

Test No.	Soil composition		
	%Sand	%Silt	%Clay
1	100.0	0.0	0.0
2	0.0	100.0	0.0
3	0.0	0.0	100.0
4	50.0	50.0	0.0
5	50.0	0.0.	50.0
6	0	50.0	50.0
7	66.7	16.7	16.7
8	16.7	66.7	16.7
9	16.7	16.7	66.7
10	33.3	33.3	33.3

3.5.3. Effect of soil hydrophobicity on diesel removal efficiency

Three alkanes with different hydrophobicity (decane (C10), tetradecane (C14) and octadecane (C18)) were used to investigate the effect of soil hydrophobicity on oil removal efficiency of silt and clay. Tween 80 was used in this study.

3.5.4. Optimizing surfactant-assisted soil washing process conditions

3.5.4.1 Surfactant selection based on soil composition

The surfactant with the highest cost-effective in each pure soil (i.e. sand, silt and clay) was selected from Phase I and II. Soil composition (texture and organic matter) were varied based on pseudo ternary phase diagram using mixture design. Finally, the guild-line to select surfactant based on soil composition was generated.

3.5.4.2 Optimizing physical conditions of soil washing

To prove the guideline generated from Phase III-A, a real soil was used in this study. The surfactants from previous part which has the highest diesel removal efficiency in soil with the same composition as real soil were selected. Adding rinsing condition (3 min using L/S ratio 3:1 mg/L at 200 rpm) was tested to improve the removal efficiency. Shaking speed (50, 100 and 200 rpm) and L/S ratio (3:1, 4:1 and 5:1) were varied to optimize the conditions using central composite rotatable design (CCRD). Then, the suitable shaking speed and L:S ration were used to optimize time (3, 5, 10, 15, 20, 30, 45 and 60 min). Finally, the effect of initial diesel content of contaminated soil was investigated using the optimal soil washing conditions.

3.6 Statistical Analysis

ANOVA test, multiple mean comparisons and design the experiment based on mixture design and CCRD will be used by STATISTICA 10 program (StatSoft Tulsa, OK, USA) to analyze the significant factors that effect to washing efficiency, guideline for selecting surfactant and the optimum physical condition.

CHAPTER 4

EFFECT OF SOIL TEXTURE, ORGANIC MATTER AND SURFACTANT STRUCTURE ON CMC

Surfactant solutions are commonly used for the remediation of petroleum-contaminated soil due to their good petroleum removal performance, time-saving capability, and cost effectiveness. However, applying surfactants in excess concentrations could make oil recovery difficult. Moreover, residual surfactants in soil are toxic to microorganisms and plants. Thus, it is crucial to identify a suitable surfactant concentration for soil washing applications. Nevertheless, there is lack of information regarding to interaction between structures of contaminated soil and surfactant on soil remediation performance. Such information could be used to guide the selection of suitable surfactants based on the soil texture of contaminated areas, thereby saving clean-up costs with minimum toxicity of surfactants to microorganisms and plants.

This chapter was divided into three main parts which were 1) Effect of soil texture and organic matter content on surfactant adsorption 2) Effect of surfactant structure on surfactant adsorption, and 3) Surfactant adsorption on soil containing mixed texture and OM. The objective of this part was to find the effect soil composition (soil texture and OM content) and surfactant structure (EO group and alkyl chain length) on surfactant adsorption on soil. Two series of nonionic surfactants were evaluated the effect of EO group (i.e. Tergitol series) and alkyl chain length (i.e. Tween series). The adsorptive capacity of each soil component was evaluated indirectly through CMC value using a surface tension technique (Liu *et al.*, 1992; Amirianshoja *et al.*, 2013). Statistica program was used to create the diagram and equation to find the relationship between factors.

4.1 Effect of soil texture and organic matter content on surfactant adsorption

4.1.1 Effect of soil texture on surfactant adsorption

As expected, clay showed the highest surfactant adsorption (i.e., highest X_{CMC}), followed by silt and sand (**Figure 4.1**). This is because clay has the smallest particle size and highest surface area and porosity, and therefore the largest adsorption area (Curry *et al.*, 2004; Osagie & Owabor, 2015).

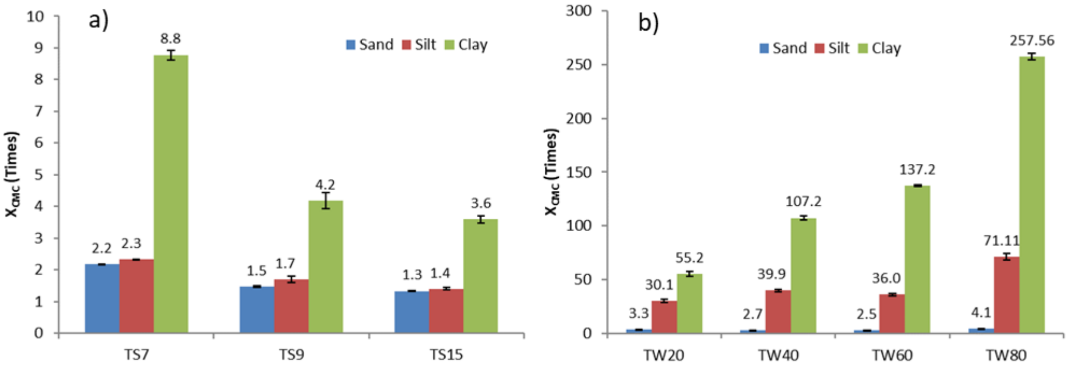


Figure 4.1 Effect of soil minerals on X_{CMC} of (a) Tergitol series surfactants and (b) Tween series surfactants

The results indicate that differences in the carbon chain length (TW20, TW40 and TW60 of Tween series) and double bond (TW60 and TW80) of Tween series surfactants and the EO number (TS7, TS9 and TS15 of Tergitol series) might affect their adsorption on soil minerals. For Tergitol series surfactants (**Figure 4.1a**), TS7, which has the lowest EO number, showed the highest adsorption in all soil texture. The reason for these phenomena was explained in Section 4.2.1.

Among the Tween series surfactants used in this study (without double bond), TW60 has the longest carbon chain and showed the highest adsorption on clay. TW40 and TW20, with shorter carbon chains, showed lower adsorption on clay than TW60. However, adsorption on sand and silt had a different trend as shown in **Figure 4.1b**. This was due to the difference in the hydrophobicity of the soil minerals and surfactants. The FTIR spectra of Tween series surfactants and soil minerals were used to explain these phenomena (**Figure 4.2**). The peaks at 2923 and 2859 cm^{-1}, which correspond to C-H stretching vibrations of alkane, in the FTIR spectra of the Tween surfactants indicate differences in their tail length (**Figure 4.2a**). The C=O stretching peak at 1735 cm^{-1} was detected in the FTIR spectra of all surfactants in the Tween series. Further, a signal for double bond was detected for TW80 at 2997 cm^{-1}, which is related to C-H stretching of alkene.

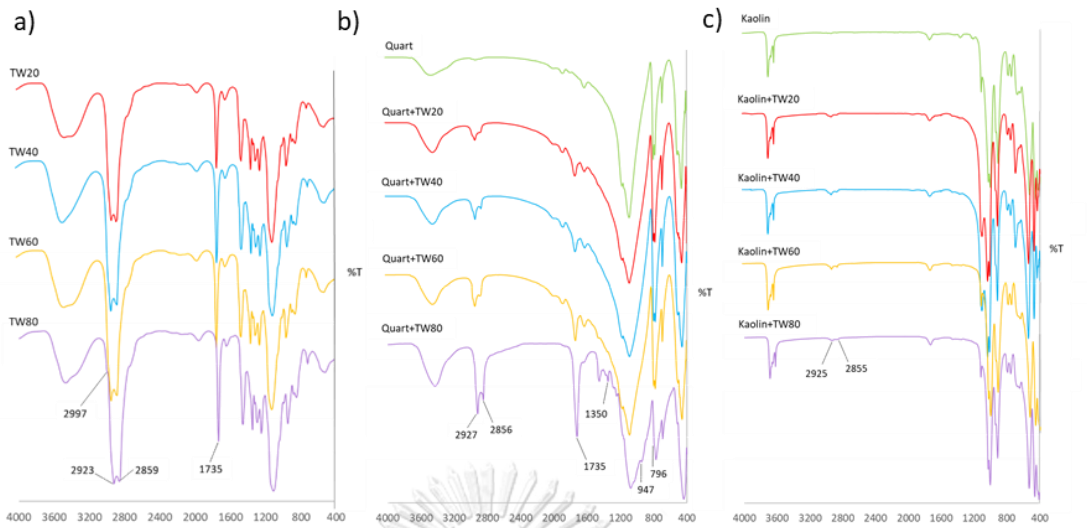


Figure 4.2 FTIR spectra of (a) Tween series surfactants, (b) quartz with the Tween surfactants, and (c) kaolin with the Tween surfactants

The FTIR spectra of quartz with Tween series surfactants are illustrated in **Figure 4.2b**. Peaks at 2927 and 2856 cm^{-1}, which correspond to C-H stretching vibrations of alkanes in the tail of the Tween surfactants, are observed in the FTIR spectra of the quartz surface. Moreover, quartz with adsorbed Tween series surfactants showed a peak at 1735 cm^{-1}, which can be attributed to C=O stretching. Therefore, it can be concluded that Tween surfactants were adsorbed on quartz through hydrophilic interactions. Furthermore, quartz with adsorbed TW80 gave rise to peaks at 1350, 947, and 796 cm^{-1}, which correspond to C-H stretching of alkene. It means that the double bond in TW80 affects its adsorption on quartz.

After adsorption of surfactant on kaolin (**Figure 4.2c**), peaks were observed at 2925 and 2855 cm^{-1}, which correspond to C-H stretching vibrations of alkanes in the tail of Tween surfactants. However, unlike quartz, kaolin did not exhibit peaks for

C=O stretching. Thus, it might be supposed that kaolin adsorbed surfactant through hydrophobic interaction.

Contact angle was measured to determine the hydrophobicity of each soil mineral (**Table 4.1**). Sand has the lowest contact angle followed by silt and clay, indicating that sand was the least hydrophobic, while clay was the most hydrophobic. Although sand and silt have the same chemical structure, their hydrophobicities differed due to differences in particle size. Several studies have reported that coarse soils have lower hydrophobicity than fine soil (Doerr *et al.*, 2000; Dekker *et al.*, 2005; Doerr *et al.*, 2006; Olorunfemi *et al.*, 2014). Chiu *et al.* (2009) found that with increase in particle size, the free energy of hydration changed from positive to negative. Thus, as particle size becomes smaller, the particles become more hydrophobic, while larger particles become increasingly hydrophilic. Further details about the relationship between surfactant structure and soil minerals are discussed in section *4.2.1.*

Table 4.1 Contact angle of each soil composition

Soil texture	Contact angle	Relative Hydrophobicity
Sand	67.7±0.9	Low
Silt	73.0±0.3	Moderate
Clay	81.9±1.6	High
Organic Matter	89.7±0.2	Highest

4.1.2 Effect of organic matter content on surfactant adsorption

OM in soil significantly affects the CMC_a of both surfactant series in different ways and at different extents depending on the OM content. For Tergitol surfactants, within the range of OM from 0 to 5% shows the same trend for all soil texture that the higher the OM content, the higher the X_{CMC} (**Figure 4.3**). Moreover, for Tergitol series, the X_{CMC} of T15 which is the highest hydrophilic (HLB 15.4) was found to be affected from OM less than those of TS7 and TS9 (HLB = 12.1 and 12.6, respectively), especially for sand and silt (from the slop of bar graphs in Figure 4.3a and Figure 4.3b) increase only the X_{CMC} of clay in Tween surfactant (**Figure 4.4**) as OM enhances the hydrophobicity of soil mineral. This is because OM facilitates hydrophobic sorption of nonionic surfactants (Barati-Haroon *et al.*, 2016; Befkadu & Chen, 2018)..

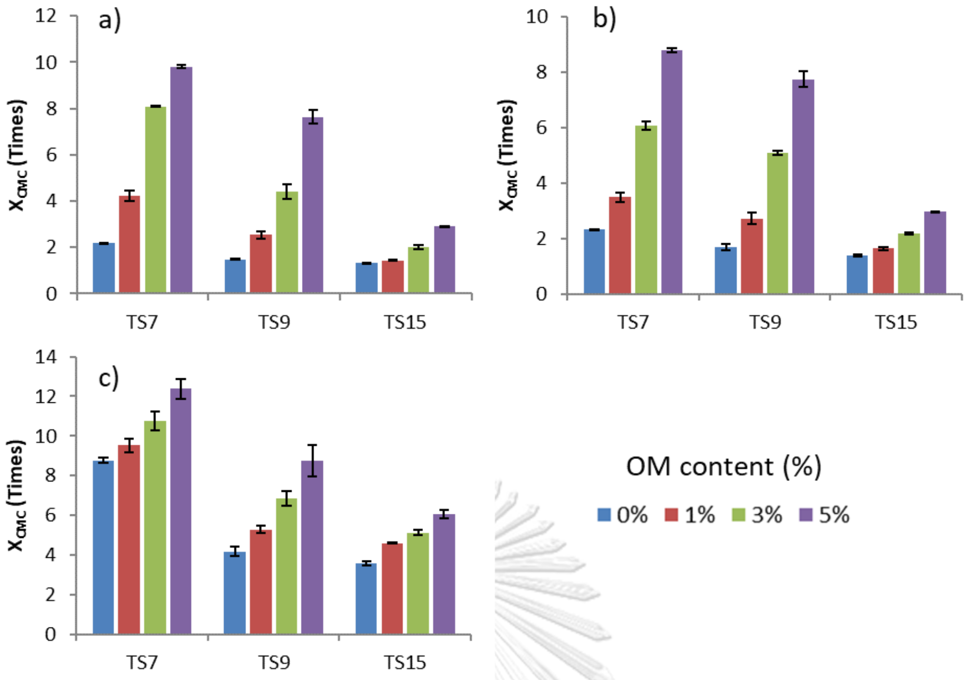


Figure 4.3 Effect of OM contents in (a) sand, (b) silt, and (c) clay on X_{CMC} of Tergitol surfactant

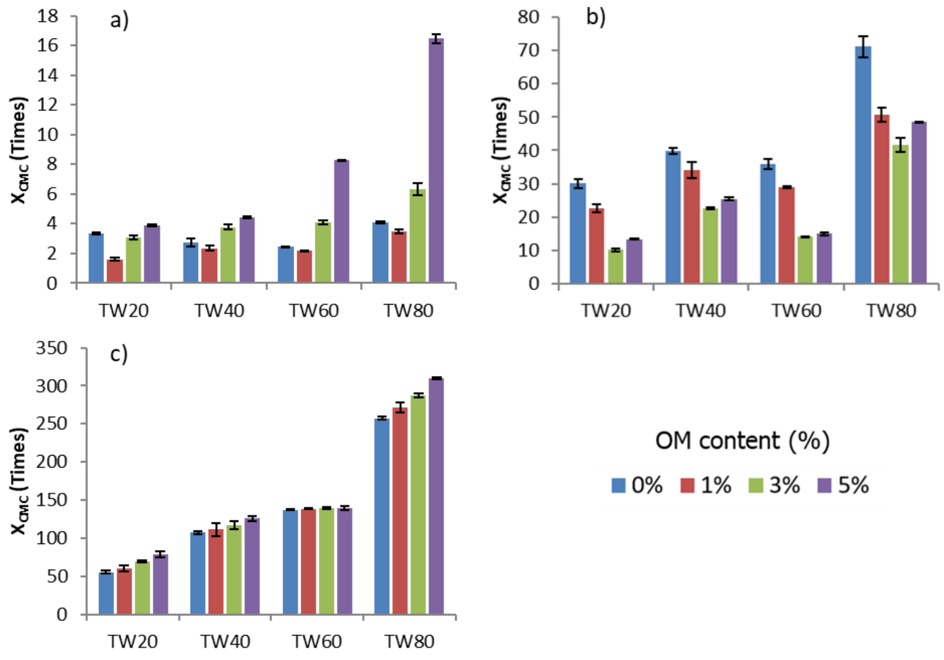


Figure 4.4 Effect of OM contents in (a) sand, (b) silt, and (c) clay on X_{CMC} of Tween surfactant

For the Tween series, the results were different for sand and silt, an increasing of OM content does not influence X_{CMC} value in the same trend as found in case of Tergitol. Sand and silt surface are generally hydrophilic, once OM is added, it can be expected that X_{CMC} value should be increased. However, the result from this experiment showed that the CMC_a values of Tween series surfactants in the presence of sand with 1% OM and silt with 1% and 3% OM were lower than in systems without OM (Figure 4.4a and Figure 4.4b). Dissolved organic matter (DOM) was hypothesized to play a role on these phenomena to get better understanding on these results. Thus, another experiment was conducted; solutions from 1%DOM, sand mixed with 1%DOM, 1%OM and sand mixed with 1%OM were measured for CMC as the result shown in Figure 4.5. However, DOM did not have a significant effect on clay, which might be because DOM was adsorbed only at the edge of clay, which is a very small area compared to that of the surface of clay (Schulthess & Huang, 1991; Kubicki *et al.*, 1997; Kaiser & Guggenberger, 2000).

To investigate the behavior of DOM, the system containing 1% OM, TW20, and sand was selected because the X_{CMC} of TW20 in sand, which was the preliminary laboratory, showed the highest change in X_{CMC} compare to other surfactants in Tween series. DOM was prepared by adding DI water to 1% OM. The liquid fraction was DOM (1%OM) and was used to prepare TW20 solution. As shown in Figure 4.5, the values of CMC of TW20, CMC_a values of TW20 in the presence of DOM (1%OM) and Sand+DOM (1%OM) were found not significantly different (55, 63, and 61 mg/L).

Thus, it can be assumed that DOM does not play a role as co-surfactant or additive in reducing the CMC. Similar result was found for CMCa values of 1%OM and sand+1%OM (90 and 87 mg/L, respectively).

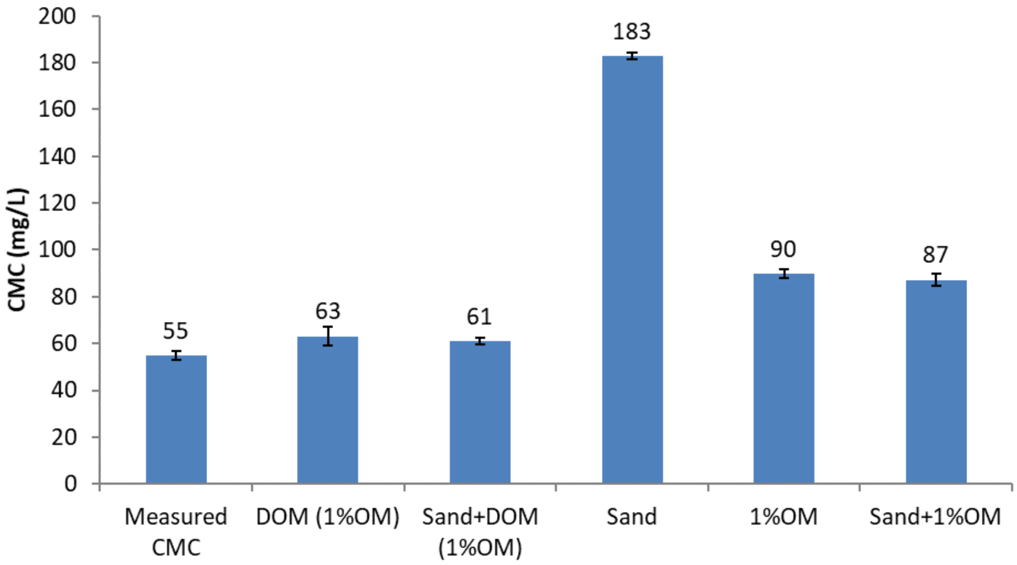


Figure 4.5 Effect of OM and DOM on CMC of TW20 in the sand system

On the other hand, DOM can be adsorbed on the active sites of quartz, thereby reducing available active sites for TW20 sorption. The presence of DOM in sand reduced the CMC_a of TW20 dramatically from 183 to 61 mg/L (**Figure 4.5**). These results agree with those of previous studies that reported that DOM competed with surfactants for sorption on soil minerals (Kaiser & Guggenberger, 2000; Guo & Chorover, 2003; Ahangar, 2012). This may be the reason to explain why the X_{cmc} of sand with 1%OM in TW20 solution is less than CMC of only TW20. These results conclusively prove that OM can act both as adsorbent and adsorbate (i.e., DOM). Thus, in the same soil composition with the same surfactant concentration, the presence of DOM can increase the diesel removal efficiency by competing between DOM and surfactant on soil adsorption, which finally, increased micelle concentration in solution.

4.2 Effect of surfactant structure on surfactant adsorption

4.2.1 Effect of EO group number of surfactant head group on surfactant adsorption

The EO group number were varied between 7-15 for Tergitol series (**Table 3.1**). The effect of EO number on the adsorption differed for each type of soil texture (**Figure 4.6**). TS7, which has the lowest EO number, showed the highest adsorption in all soil types. It might be because of the size structure of surfactant. The larger size structure of surfactant, the lower sorption was observed. This was due to the steric affect that limit facility for adsorption.

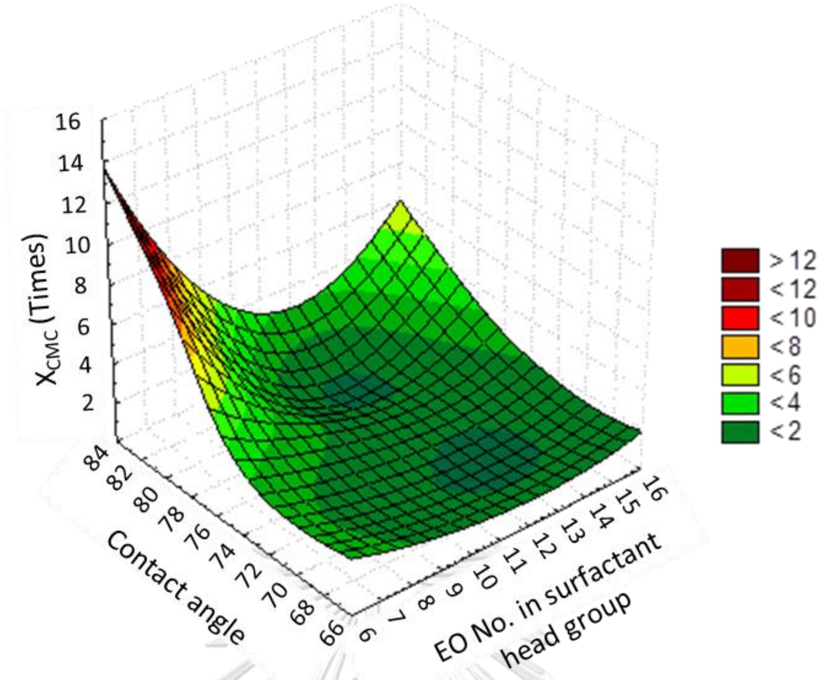


Figure 4.6 Effect of EO group number of Tergitol surfactant and contact angle of soil mineral on X_{CMC}

4.2.2 Effect of alkyl chain length of surfactant tail group on surfactant adsorption

For the Tween series surfactants used in this study, the carbon chain length of the hydrophobic tail varied from 11 to 17 (**Table 3.1**). The effect of carbon chain length on TW adsorption differed for each type of soil texture (**Figure 4.7**). The carbon chain length of TW surfactants is in the order: TW20 < TW40 < TW60. This is the same trend as that of the reduction in adsorption on sand with increase in carbon chain length of surfactant (**Figure 4.1**). In contrast, the X_{CMC} of TW60 was the highest in the presence of clay (higher than that of TW40 and TW20). However, TW40, with a relatively moderate carbon chain length compared to other TW surfactants, shows the highest adsorption on silt. Thus, it is assumed that the hydrophobicity of the silt surface is more compatible with TW40. In summary, the longer the carbon chain length, the higher is the adsorption on soil mineral, due to increase in hydrophobicity, which is indicated by higher contact angles (**Figure 4.7**).

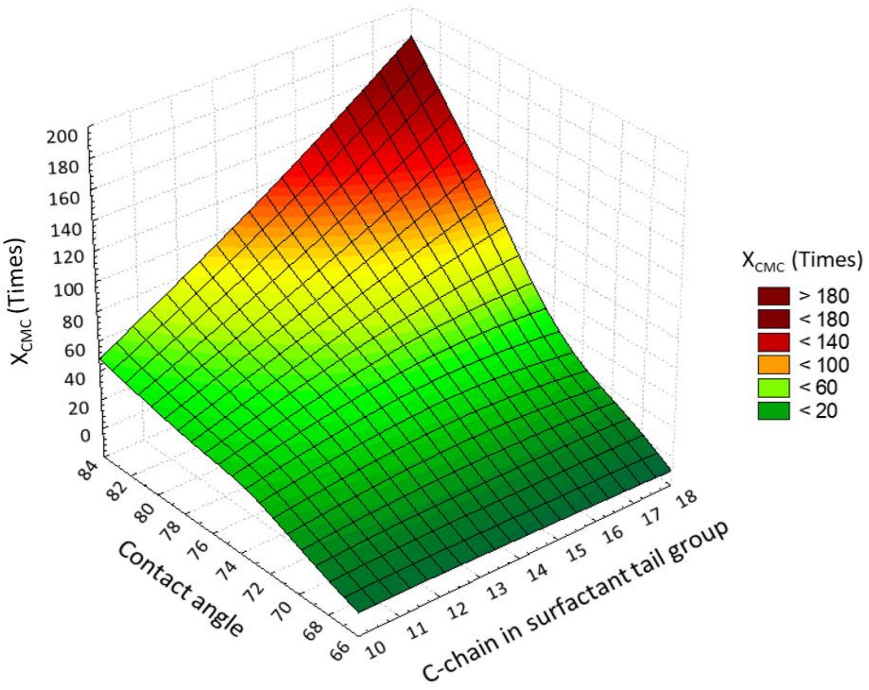


Figure 4.7 Effect of carbon chain length of Tween surfactant and contact angle of soil mineral on X_{CMC}

4.2.3 Effect of presence of double bond on surfactant adsorption

To evaluate the effect of double bonds in the tail group, the X_{CMC} values of TW60 and TW80 were compared as shown in **Figure 4.8**. TW80 had higher adsorption on all soil minerals because the double bond in its tail group increases the active area of its molecule. The double bond consists of one sigma bond, which is the strongest type of covalent bond, and one pi bond, which is a weaker bond due to the overlapping of electron orbital paths. The electrons in these weaker bonds are unstable and therefore an electron rich area develops. Thus, these active sites increase the adsorption of TW80 beyond that of TW60 on all soil minerals (Yokoyama & Nakagaki, 1993; Zhao *et al.*, 2010).

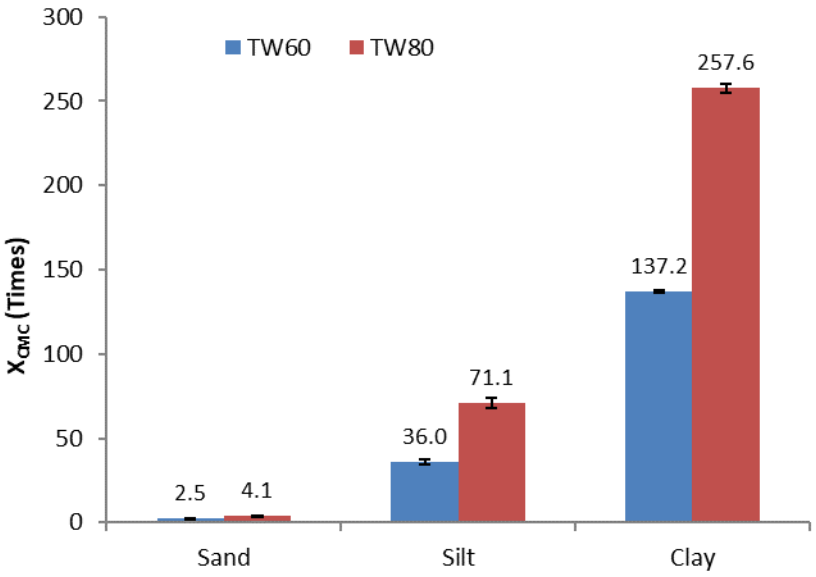


Figure 4.8 Effect of double bond in surfactant (TW60 and TW80) on X_{CMC} in the sand, silt, and clay systems

4.3 Surfactant adsorption on soil containing mixed texture and OM

In general, soil composition contains different textures (i.e., sand, silt clay) and OM. The higher OM content in soil lead to the higher adsorb of surfactant (Lee *et al.*, 2000; Li *et al.*, 2016). For a better understanding on effect of soil composition as well as OM content was conducted. This experiment investigated the various composition of soil using mixture design. Ten set of mix soil texture with 2% OM was prepared and measure for CMC of the two surfactants; TW80 and TS15. TW80 and TS15 were selected for this study since they showed a higher performance compared to other surfactant in their series (the result can be seen in Chapter 5) while 2% OM content in the soil samples was used in this study since it stimulated a real soil that was studied in the next section (result shown in Chapter 5).

The CMC_a of TW80 and TS15 in different soil texture with 2% OM were illustrated using mixture diagram (**Figure 4.9**). The equations for CMC_a of TW80 and TS 15 calculation in different soil texture with 2%OM from mixture diagram were shown below in Equations 3 to 4. The adsorption of TW80 was mainly depend on kaolin (clay) content (**Figure 4.9a**). The higher clay content lead to the higher TW80 sorption. DOM can adsorb on quartz (sand and silt) instead of TW80, therefore, clay became the main factor for TW80 adsorption. However, TS15 was depended on the fraction between kaolin (clay) and quartz (sand and silt) (**Figure 4.9b**). Pure kaolin had the lower TS15 adsorption than the mixture between kaolin and quartz. At the same amount of quartz, the particle size (silt and sand) affect to the adsorption. Silt (grinded quartz) has more impact on TS15 adsorption than sand. Pure sand (quartz) has the lowest adsorption in both TW80 and TS15. It might be because sand has the lowest surface area (Curry *et al.*, 2004; Osagie & Owabor, 2015).

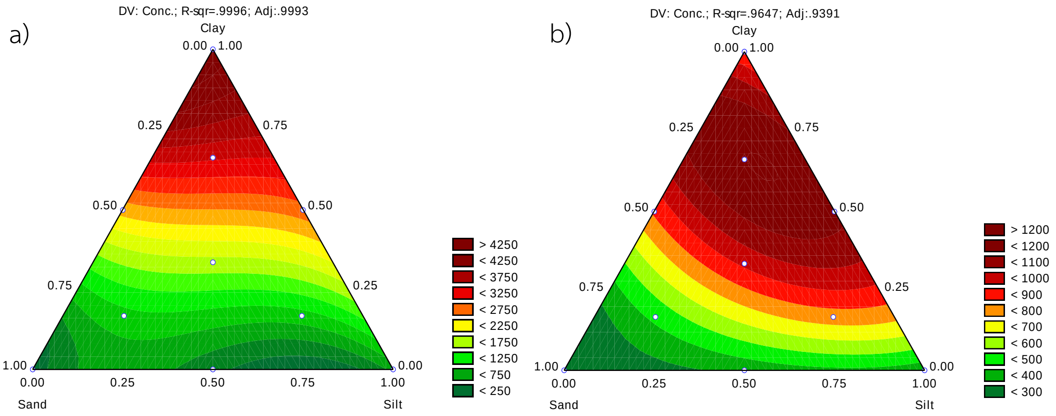


Figure 4.9 Effect of soil texture on CMC_a of (a) TW80 and (b) TS15

$$CMC_{a(TW80)} = 69.51x + 586.10y + 4421.70z + 0.30xy + 502.57xz + 603.09yz - 4209.37xyz + 4423.80xy(x-y) - 3778.70xz(x-z) \quad \textbf{Eq. 3}$$

$$CMC_{a(TS15)} = 279.08x + 334.48y + 794.12z + 91.44xy + 1132.15xz + 2253.93yz + 1668.97xyz - 438.12xy(x-y) - 2846.27xz(x-z) \quad \textbf{Eq. 4}$$

Whereas

x = Sand content (%)

y = Silt content (%)

z = Clay content (%)

To validate the mixture diagram, the chisquare test for goodness of fit was applied (**Table 4.2**). The P-value of Eq. 5 and Eq. 6 were higher than the significant level (0.05), which means that these two equations can use to predict the CMC_a of both surfactants.

Table 4.2 P-value of CMC_a calculation equation

Equation	P-value
Eq. 3	0.9172
Eq. 4	0.7077

These predicted models were applied to predict the CMC_a of artificial soil which have the same soil composition (i.e. sand, silt, clay and OM) as real soil (**Table 4.3**). These result shown that the equations might be used to calculate the accurated CMC_a value of TW80 and TS15 in different artificial soil composition.

Table 4.3 The calculated and measured value of CMC_a in artificial soil with the same soil composition as real soil using different surfactant concentration

Soil composition			TW80		TS15	
%Sand	%Silt	%Clay	Calculated value	Measured value	Calculated value	Measured value
100.0	0.0	0.0	70	73	279	267
0.0	100.0	0.0	586	589	334	322
0.0	0.0	100.0	4422	4425	794	782
50.0	50.0	0.0	328	334	310	305
50.0	0.0.	50.0	2655	2661	1128	1103
0	50.0	50.0	2371	2378	820	795
66.7	16.7	16.7	928	899	529	557
16.7	66.7	16.7	906	883	794	828
16.7	16.7	66.7	3334	3277	1259	1276
33.3	33.3	33.3	1645	1689	823	801

CHAPTER 5

SOIL WASHING EFFICIENCY AFFECTED BY VARIOUS FACTORS

In previous chapter, effect of soil texture on CMC of Tween and Tergitol series surfactant was observed. The influence of each soil mineral and their mixture on diesel removal performance by surfactant solution was investigated; and the interaction between soil mineral, surfactant and diesel was proposed.

To enhance the diesel removal efficiency, the physical factors such as L/S ratio, shaking speed and time were evaluated their impacts on diesel removal efficiency. Finally, the results of diesel removal efficiency of artificial soil were compared with the real soil, which has the similar soil texture and OM content.

5.1 Effect of surfactant structure on soil washing efficiency

5.1.1 Effect of number of EO group in Tergitol series

EO (Ethylene oxide) group is the hydrophilic part in most of nonionic surfactants. The increasing of EO group number decreases the hydrophobicity of surfactants. In this study, Tergitol surfactant series that vary EO group number in the structure with the same hydrophobic tail length, were used to determine the effect of EO group on soil washing efficiency. Overall result shows that the highest removal efficiency in sand, silt and clay were found in the systems of TS7, TS9, and TS15, respectively at all concentrations (**Figure 5.1**). However, once compared for the same concentrations of the surfactants, the effect of EO group number shows the opposite trend for sand and clay but deviate without trend in the case of silt. For hydrophilic substrate such as sand, TS7 was found best performance for all concentrations i.e. at CMC_m, CMC_a and $10xCMC_a$ while the most hydrophobic substrate clay, T15 shows the best performance. The lower number of EO resulted to the higher performance in case of sand, the reason to explain this result is expected from the structure of the surfactant and properties of sand. Even though the hydrophilicity of TS7 is less than those of TS9 and TS15, the less in number of EO group allow them (TS7) to sorb on sand surface more than others two surfactants (TS9 & TS15) due to less steric hindrance. This can be confirmed by the X_{CMC} of these surfactant (2.17, 1.47 and 1.33 for TS7, TS9 and TS15, respective; Figure 4.1a, Chapter 4). Consequently, the sorbed surfactants help to reduce interfacial tension between oil and sand and let the oil detaches from the sand surface. For the case of clay which shows the opposite direction on washing efficiency, however, these results of the X_{CMC} values of clay are still conformed with those found with sand (8.77, 4.19 and 3.59 for TS7, TS9 and TS15, respective; Figure 4.1b, Chapter 4). These results indicate that not only structure of the surfactant influence detachment of diesel from soil, but the interaction between clay and surfactants also plays a role on this performance. TS7 is the most hydrophobic among these 3 surfactants, thus it is expected to provide most preferable affinity than TS9 and TS16. Consequently, the more preferable affinity leads to the stronger interaction between clay and TS7 than those of TS7 and TS15 on the clay surface, hence in the washing process diesel detach from clay surface is less than from the other two surfactants. This is why the washing efficiency of diesel from silt which is a substrate that having properties of hydrophobicity and surface area in the middle of TS7 & TS15, shows the result in between the results from TS7 and TS.

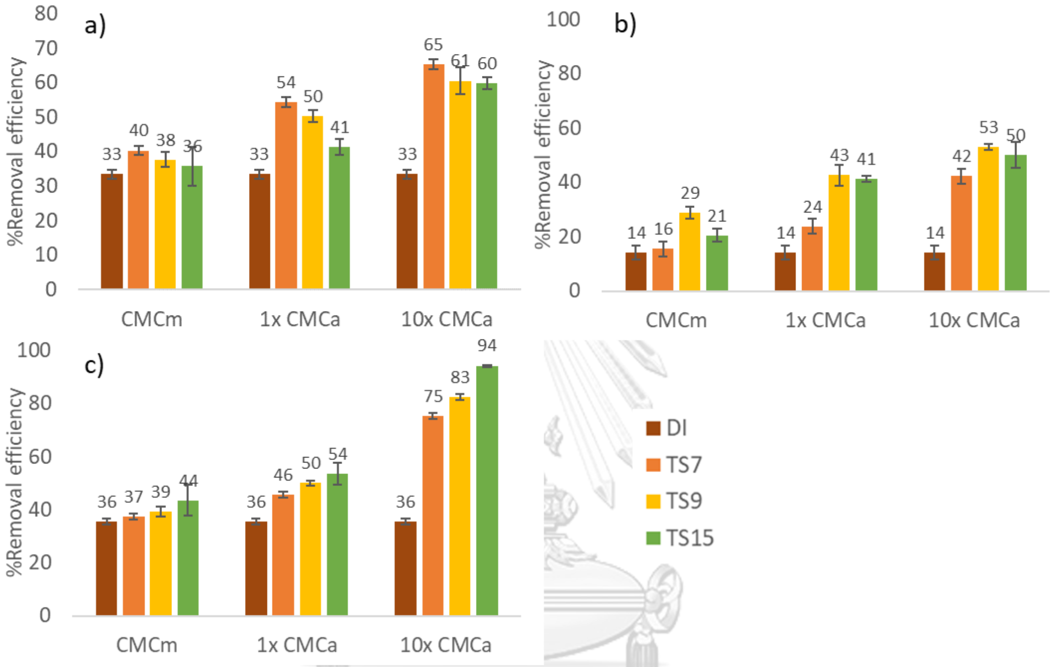


Figure 5.1 Diesel removal efficiency through washing of contaminated (a) sand, (b) silt and (c) clay using different types and concentrations of Tergitol series surfactants

To select the most suitable surfactant for soil washing process, soil profile was very important. In Thailand, soil with highly clay content can be found in most area. Therefore, TS15 was selected due to its high diesel removal efficiency in clay.

5.1.2 Effect of carbon chain length in Tween series

Tween surfactants are amphiphilic molecule that have hydrocarbon as hydrophobic part with the same hydrophilic head number (20 EO group). The longer carbon chain length of hydrocarbon increases the hydrophobicity of surfactants. For Tween series surfactants, TW60 and TW80 performed the best in terms of diesel removal from silt, while TW20 was the most suitable for diesel removal from sand. This might be due to the hydrophobic affinity between surfactant and soil minerals. Sand is likely to adsorb TW20, both of which are less hydrophobic than the other minerals and surfactants. Therefore, the diesel removal efficiency of TW20 from sand is the highest. However, at surfactant concentrations higher than CMC_a, the length of the hydrophobic tail did not have a significant effect on the efficiency of diesel removal from clay.

Surprisingly, diesel removal efficiency from clay, which has the highest surface area and surfactant adsorption capacity, was the highest **(Figure 5.2c)**. Moreover, silt, which has a larger surface area than sand, showed lower diesel removal efficiency than sand. According to these results, particle size is not the only factor that governs the diesel removal efficiency of the soil washing process. Surfactant adsorption and interaction between surfactant, soil, and diesel also affected diesel removal efficiency.

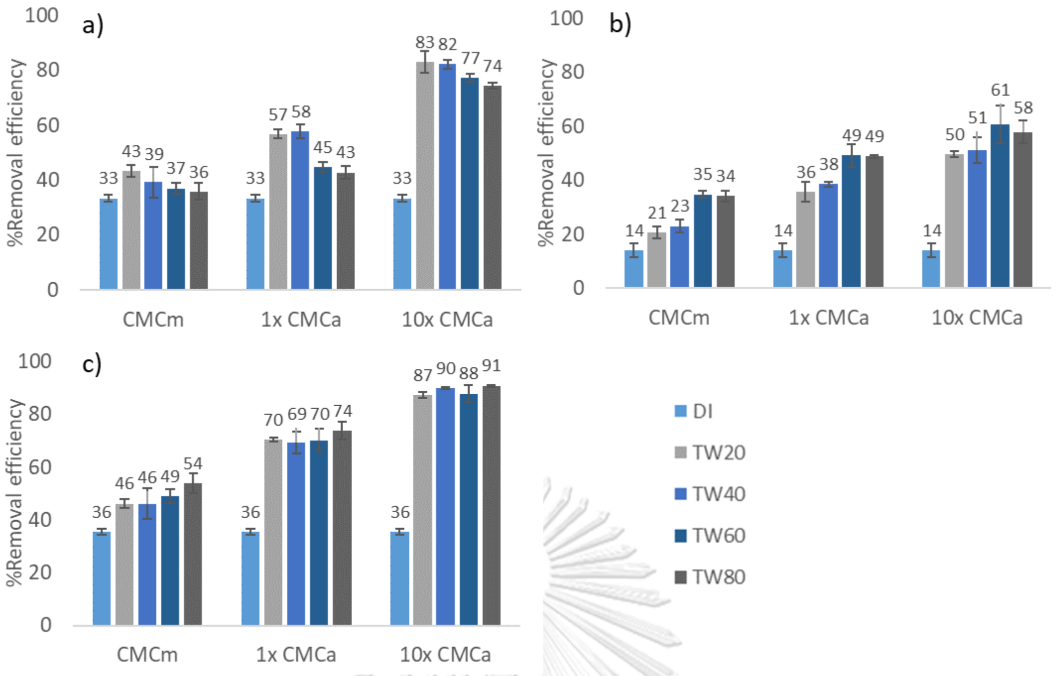


Figure 5.2 Diesel removal efficiency through washing of contaminated (a) sand, (b) silt and (c) clay using different types and concentrations of Tween series surfactants

Due to the fact that clay can be found in most area of Thailand. Thus, the washing efficiency in clay was become the most important. However, the washing efficiency in clay of all surfactant in Tween series was almost the same (**Figure 5.2c**). Therefore, silt, which can remove contaminated harder than sand, was the next priority for surfactant selecting. TW60 and TW80 were chose because they had almost similarly diesel removal efficiency (**Figure 5.2b**). To selected the surfactant, price and water solubility of both surfactants was concerned to reduce the treatment cost. In conclusion, TW80, which has lower price and higher water solubility, was selected.

5.1.3 Proposing interaction between soil mineral, surfactant and diesel in soil washing process

The diesel removal efficiencies achieved through washing of diesel-contaminated sand, silt, and clay with Tergitol series surfactants and Tween series surfactants are illustrated in **Figure 5.1** and **5.2** respectively. The results show that for all systems diesel removal efficiency improved with increase in surfactant concentration. This can be explained by increase in micelles in the systems. Peng et al. (2011) reported that enhancement of micelle formation facilitates diesel detachment from soil to water.

Sand and silt have the same chemical composition and structure but silt has a larger surface area. The higher surface area of silt enhanced the re-deposition of surfactant micelle, resulting in lower diesel removal efficiency. The surfaces of sand and silt are more hydrophilic than that of clay as shown in **Table 4.1**. The FTIR results confirmed that Tween surfactants were adsorbed on sand through hydrophilic interactions. This implied that the dissolved diesel within the core of surfactant micelles can be re-deposited on the hydrophilic surface of sand and silt. To prevent re-deposition of contaminant, re-deposition of micelles containing dissolved contaminants within their core structure should be worth investigating in future studies.

During washing of diesel-contaminated soil using surfactants, diesel detaches from the soil and dissolves in the hydrophobic core of surfactant micelles. The hydrophilic surface of surfactant micelles prevents the re-deposition of diesel on cleaned soil (**Figure 5.3**). This theory can be applicable to clay, which has a more hydrophobic surface than sand and silt (**Table 4.1**). The FTIR results also indicated that adsorption of Tween surfactants on clay was through hydrophobic sorption as mention above. Therefore, the diesel removal efficiency in all the clay systems was higher than that in the sand and silt systems.

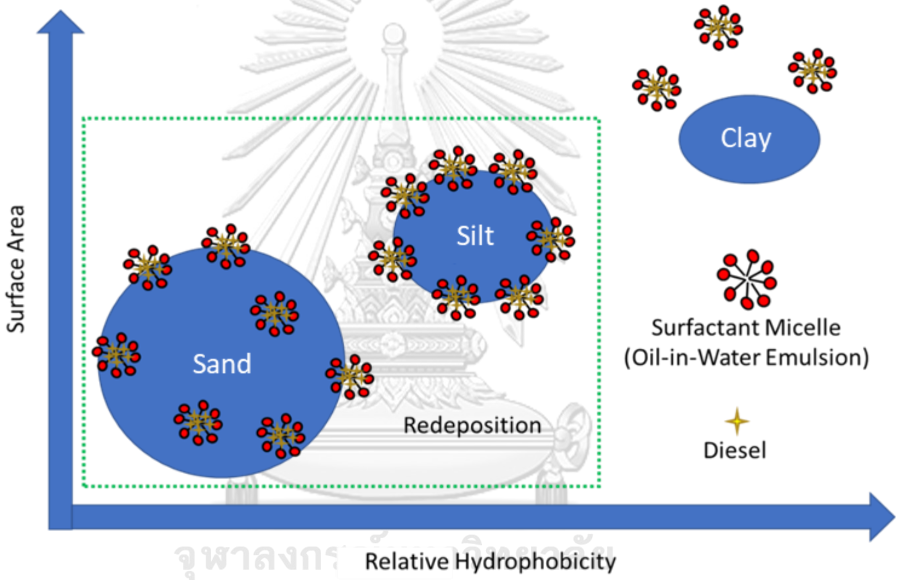


Figure 5.3 Proposed mechanism of micelle adsorption on minerals with different hydrophobicities and surface areas

In order to test this hypothesis, three alkanes with different hydrophobicity (decane (C10), tetradecane (C14) and octadecane (C18)) were used to investigate the effect of soil hydrophobicity on oil removal efficiency of silt and clay. The results showed that there was no significant result between silt and clay when using DI as washing solution (**Figure 5.4)**.

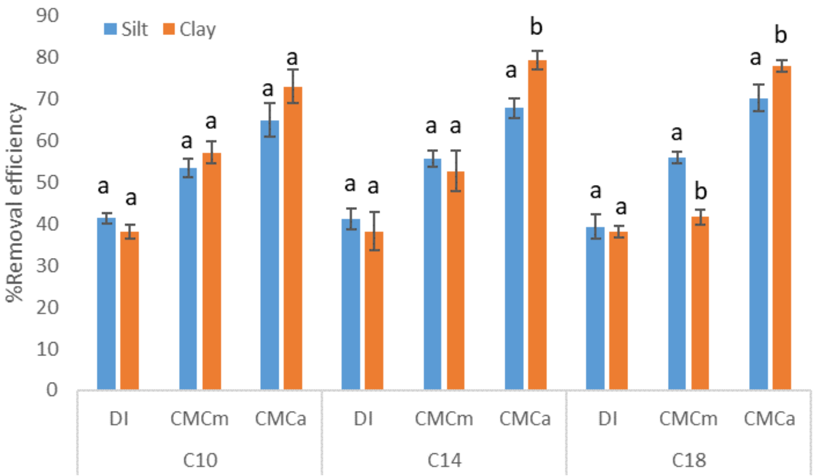


Figure 5.4 Effect of soil hydrophobicity on diesel washing efficiency using TW80 at L/S ratio 3:1 (mL/g) with 200 rpm

At CMC_m (surfactant monomer without micelle formation due to soil adsorption), the washing performance of each oil on silt and clay was similar, excepted that of C18. These might be because of the high affinity between C18, which has high density, and clay, which has more surface area and higher hydrophobicity. C18 was likely to adsorb in hydrophobic surface of clay, compared to the hydrophilic surface of silt.

At CMC_a (first surfactant micelle was formed), the washing performances on clay were higher than those of silt, especially on high hydrophobicity C14 and C18. This might be because the removed oil was dissolved in hydrophobic core of micelle; and the hydrophilic surface of micelle was repelled from the hydrophobic surface of clay as previously described in **Figure 5.3**

5.2 Effect of soil texture on soil washing efficiency

The soil washing efficiency for different mixture was evaluated using mixture design. Ten types of different compositions of sand, silt and clay with 2% organic (OM) matter was investigated (see **Table 3.5**). The mixture diagram of diesel removal efficiency is shown in **Figure 5.5**. The equations for diesel removal efficiency calculation in different soil texture with 2%OM from mixture diagram were shown below in Equations 5 to 11.

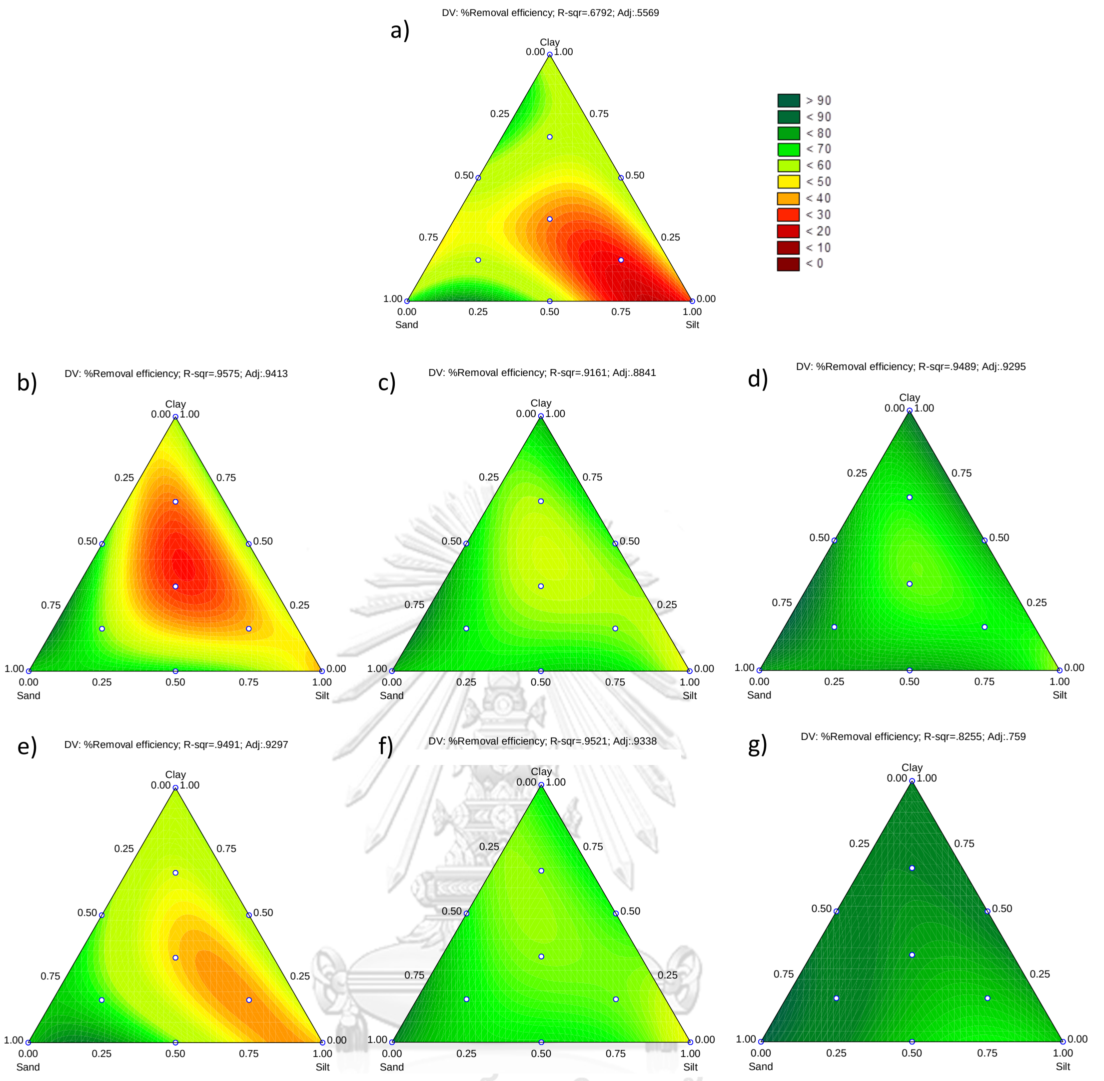


Figure 5.5 Effect of soil texture with 2% OM on diesel washing efficiency using (a) DI, (b) TW80 at CMC_m, (c) CMC_a and (d) x10 CMC_a and TS15 at (e) CMC_m, (f) CMC_a and (g) x10 CMC_a

$$\%RE_{DI} = 67.86x + 32.74y + 51.86z + 28.76xy - 6.54xz + 62.93yz - 639.32xyz + 232.15xy(x-y) - 204.84xz(x-z) \quad \text{Eq. 5}$$

$$\%RE_{TW80(CMC_m)} = 73.66x + 36.68y + 56.96z + 52.51xy + 3.69xz + 45.71yz - 1129.18xyz - 38.94xy(x-y) + 184.98xz(x-z) \quad \text{Eq. 6}$$

$$\%RE_{TW80(CMC_a)} = 78.74x + 44.27y + 79.14z + 41.42xy - 23.32xz + 8.18yz - 471.61xyz - 108.49xy(x-y) + 149.05xz(x-z) \quad \text{Eq. 7}$$

$$\%RE_{TW80(CMC_{10x\,CMC_a})} = 82.92\mathrm{x} + 57.78\mathrm{y} + 90.10\mathrm{z} + 42.91\mathrm{xy} - 7.94\mathrm{xz} + 29.71\mathrm{yz} - 581.56\mathrm{xyz} - 54.73\mathrm{xy}(\mathrm{x}-\mathrm{y}) + 145.34\mathrm{xz}(\mathrm{x}-\mathrm{z}) \quad \textbf{Eq. 8}$$

$$\%RE_{TS15(CMC_{CMC_m})} = 74.96\mathrm{x} + 39.60\mathrm{y} + 59.47\mathrm{z} + 21.31\mathrm{xy} - 16.59\mathrm{xz} + 31.70\mathrm{yz} - 630.17\mathrm{xyz} + 142.27\mathrm{xy}(\mathrm{x}-\mathrm{y}) + 45.32\mathrm{xz}(\mathrm{x}-\mathrm{z}) \quad \textbf{Eq. 9}$$

$$\%RE_{TS15(CMC_{CMC_a})} = 84.99\mathrm{x} + 47.83\mathrm{y} + 69.23\mathrm{z} + 7.89\mathrm{xy} - 42.60\mathrm{xz} + 27.13\mathrm{yz} - 187.68\mathrm{xyz} - 76.34\mathrm{xy}(\mathrm{x}-\mathrm{y}) + 64.84\mathrm{xz}(\mathrm{x}-\mathrm{z}) \quad \textbf{Eq. 10}$$

$$\%RE_{TS15(CMC_{10x\,CMC_a})} = 93.65\mathrm{x} + 73.50\mathrm{y} + 86.81\mathrm{z} - 45.67\mathrm{xy} - 23.97\mathrm{xz} + 9.41\mathrm{yz} - 21.25\mathrm{xyz} + 18.80\mathrm{xy}(\mathrm{x}-\mathrm{y}) + 38.92\mathrm{xz}(\mathrm{x}-\mathrm{z}) \quad \textbf{Eq. 11}$$

Whereas

RE = diesel removal efficiency

x = Sand content (%)

y = Silt content (%)

z = Clay content (%)

Surprisingly, pure silt shown the lowest removal efficiency for all cases while the higher clay content lead to the higher washing efficiency. The coefficient value of silt was also the lowest in all equations compare with the coefficient value of other pure soil texture. While the coefficient value of sand also shown the highest value in almost equation (except Eq.5 & Eq.6). The coefficient value of each factor can be implied the significant effect of soil on diesel removal efficiency. The lower coefficient value means the lower significant effect of soil on diesel removal efficiency. The results were corresponded to the coefficient value of pure soil in the equation that pure sand has the highest efficiency in most type of washing solution and soil which contain silt has lower efficiency in all type of washing solution. Gautam et al., (2020) reported that the soil with different particle size has higher removal efficiency than only fine particle size because the smaller particle size can compact densely, while the soil with different particle size can move easier due to the higher void in the soil. In the same soil mineral (sand and silt), the effect of particle size agreed with Gautam et al.'s result. Pure silt had lower washing efficiency than pure sand. However, pure clay, which has the finest particle size in this study, had higher washing efficiency than pure silt and the soil which has various particle (a mixture of sand, silt and clay) in all type of washing solution. It might be because micelle cannot re-adsorption back to clay surface.

To validate the mixture diagram, the chisquare test for goodness of fit was applied (**Table 5.1**). The P-value of Eq. 5 and Eq. 6 were less than the significant level (0.05), which means that these two equation cannot use to predict the removal efficiency.

Table 5.1 P-value of diesel removal efficiency equation based on goodness of fit test

Equation	P-value	Goodness of fit
Eq. 5	0.0358	Invalid
Eq. 6	0.0027	Invalid
Eq. 7	0.9970	Valid
Eq. 8	1.0000	Valid
Eq. 9	0.9967	Valid
Eq. 10	1.000	Valid
Eq. 11	0.9997	Valid

These predicted models were applied to predicted the diesel removal efficiency of artificial soil which have the same soil composition (i.e. sand, silt, clay and OM) as real soil (**Table 5.2**). All measured values were higher than calculated values, expecially, in CMC_m of TW80. TW80 has very different value between measured value and calculated value because the equation was not appropiate (P value = 0.027). These result shown that the equations might not be used to predict the accurated diesel removal efficiency in real application. However, we can used these equations to select the lowest surfactant concentration for clean up in different soil composition.

Table 5.2 The calculated and measured value of diesel removal efficiency in artificial soil with the same soil composition as real soil using different surfactant concentration

Washing solution	Concentration	Calculated value	Measured value
DI	-	36	41±3
TW80	CMC_m	25	44±2
	CMC_a	53	60±4
TS15	CMC_m	36	47±3
	CMC_a	60	65±3

Comparing between using TW80 and TS15 as washing solution, TS15 might be more suitable for cleanup diesel contaminated soil because TS15 has better efficiency in mixed soil texture. It might be because TS15 has lower IFT between diesel than TW80, which increased the oil removal due to mobilization, (**Table 5.3**). (Urum & Pakdemir, 2004; Tongcumpou et al., 2005; Rakowska, 2020)

Table 5.3 IFT between surfactant and diesel

Surfactant	IFT (mN/m)
TW20	1.27±0.03
TW40	3.14±0.11
TW60	3.59±0.13
TW80	2.55±0.06
TS7	1.17±0.10
TS9	1.08±0.04
TS15	0.99±0.04

Predicted CMC concentration in artificial soil with the same soil composition with real soil from section 3.1 was used with real soil. The result shown that the diesel washing efficiency of artifical soil was higher than real soil almost 2 times in both surfactants (**Table 5.4**). Moreover, these might be because the adsorption of TW80 and TS15 on the real soil were higher than the artificial soil. The predicted CMC from artificial soil might not be sufficient in a case of the real soil.

Table 5.4 Diesel removal efficiency in artificial soil and real soil

Washing solution	Concentration	%Removal efficiency in artificial soil	%Removal efficiency in real soil
DI	-	40.5±2.6	25.8±2.1
TW80	CMC_m	44.4±1.5	28.6±1.1
	CMC_a	60.4±3.3	32.7±2.9
	CMC_{rs}	-	37.0±1.6
TS15	CMC_m	46.7±2.9	27.2±1.1
	CMC_a	65.2±2.9	37.8±1.3
	CMC_{rs}	-	47.7±0.5

Kaolin was used as the representative clay in the predicted equation. Naturally, there are other clay minerals which have higher adsorption ability like montmorillonite (Alghunaim *et al.*, 2013). To prove this hypothesis, montmorillonite was used instead of kaolin in the same soil composition with real soil. The result shows that CMC_a value of both TW80 and TS15 in soil using montmorillonite as clay increased **(Figure 5.6)**. In contrast with kaolin, TS15 require much more surfactant concentration to achieve CMC_a compared to TW80. This might be the because the molecular size of TS15 was smaller than TW80, which lead to the higher amount of TS15 to infiltrate into interlayer of montmorillonite (P. H. Chang *et al.*, 2018).

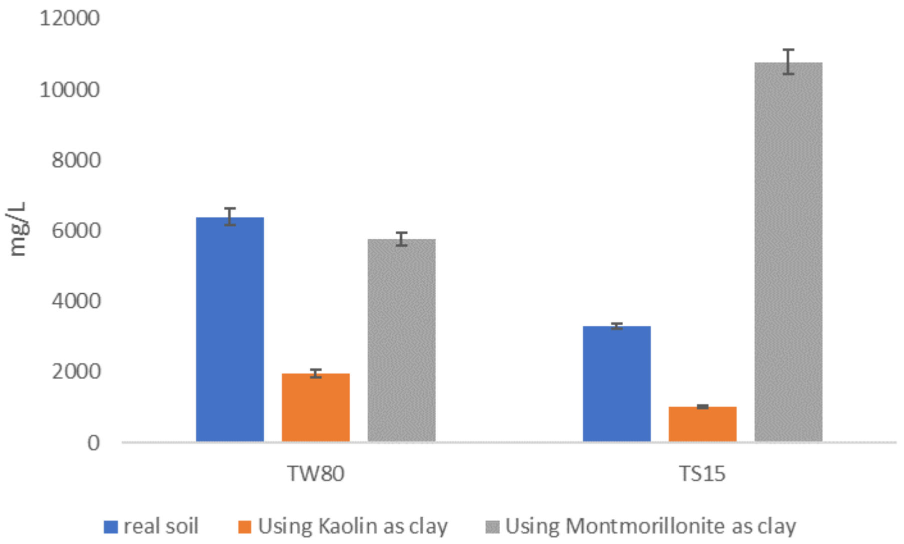


Figure 5.6 Effect of clay minerals on CMC_a of TW80 and TS15

Moreover, the mineral in silt is also not only quartz, but still has feldspars, mica, zircon, hematite and limonite (Hillel, 2008). Therefore, the CMC of both TW80 and TS15 in real soil were higher than the predicted CMC which used quartz as sand and silt, and kaolin as clay represent the real soil.

Moreover, comparing the diesel removal efficiency in real soil using different surfactant concentration; CMC_m, CMC_a and CMC_{rs} (the CMC value in real soil), CMC_{rs} shown the highest diesel removal efficiency in both surfactants, followed by CMC_a and CMC_m respectively.

5.3 Determination for the Optimizing physical condition

5.3.1 Effect of rinsing on diesel removal efficiency

Higher surfactant concentration can increase removal efficiency. However, it also increased the remediation cost and might not cost-effective. Adding rinsing condition can also increase the efficiency about 10% (**Figure 5.7**), except at 10x CMC_a

of TS15. Rinsing water can be dissolved adsorbed surfactant on soil and act as surfactant solution to remove diesel from soil. With rinsing condition, the remediation cost will be lower than increase surfactant concentration with almost the same efficiency.

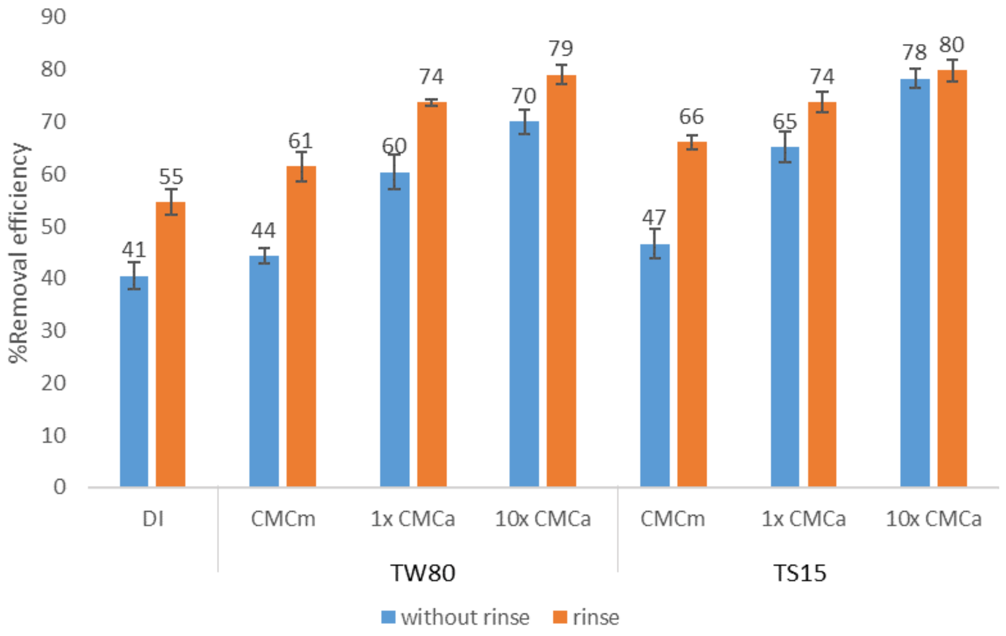


Figure 5.7 Efficiency comparing between rinsing and without rinsing condition in artificial soil at L/S ratio 3:1 (mL/g) with 200 rpm at 30 min

5.3.2 Effect of L/S ratio on diesel removal efficiency

Different surfactant showed the different optimal conditions. The optimal condition for TW80 was L/S ratio at 3:1 (mL/g) with shaking speed at 200 rpm, while TS15 was suitable with L/S ratio at 3:1 (mL/g) with 100 rpm shaking speed (**Figure 5.8**). Based on mixer instruction, the shaking speed is controlled by adjusting electrical resistance. Thus, reducing shaking speed does not reduce the electricity usage in the process. Nevertheless, mixing could reduce the usage of the surfactant solution, which was considered as the main cost of site remediation. Under shaking speed at 100 rpm, there was no significant effect of L/S ratio on diesel removal both TW80 and TS15. This is due to the shear force that help in proper mixing and increase the chance for surfactant solution to contact with the pollutant on soil surface. These make the weakly bound contaminants easier detach into surfactant solution (Peng *et al.*, 2011; Ayele *et al.*, 2020).

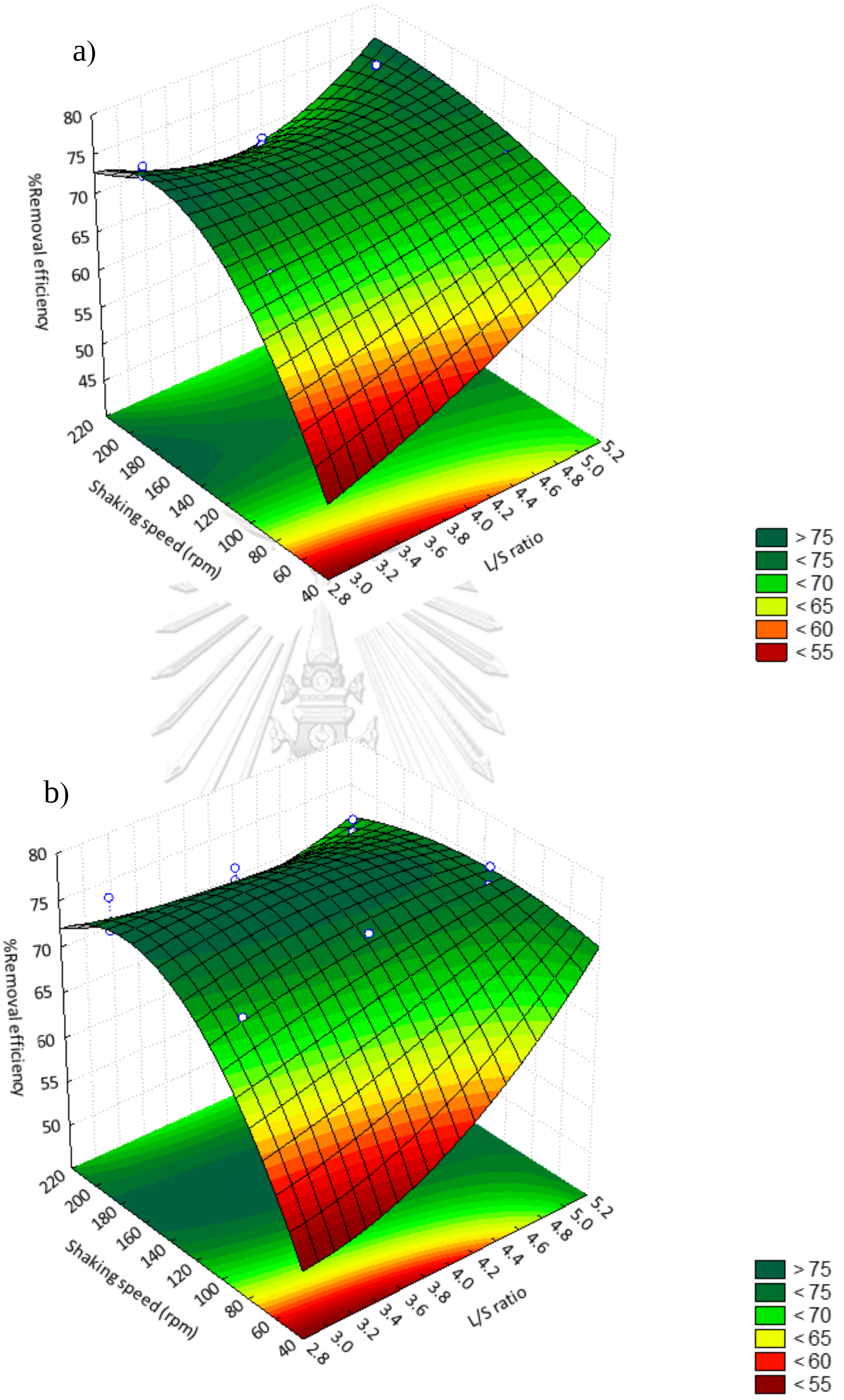


Figure 5.8 Effect of L/S ratio and shaking speed (rpm) on diesel removal efficiency of

(a) TW80 and (b) TS15 at CMC_a

5.3.3 Effect of washing time on diesel removal efficiency

From the previous result, the washing condition using L/S ratio at 3:1 mL/g with shaking speed 100 rpm was selected and used to observe the effect of time on diesel washing efficiency (**Figure 5.9**). The result showed that time did not has significant effect on washing efficiency (p-value >0.05) These might be because soil with different particle size has higher removal efficiency than only fine particle size because the smaller particle size can compact densely, while the soil with different particle size can move easier and has more collision (Gautam *et al.*, 2020). Based on these results, there will be a possibility to develop the high throughput diesel contaminated soil washing process such as hydrocyclone technology (Mouri & Ozaki, 2017).

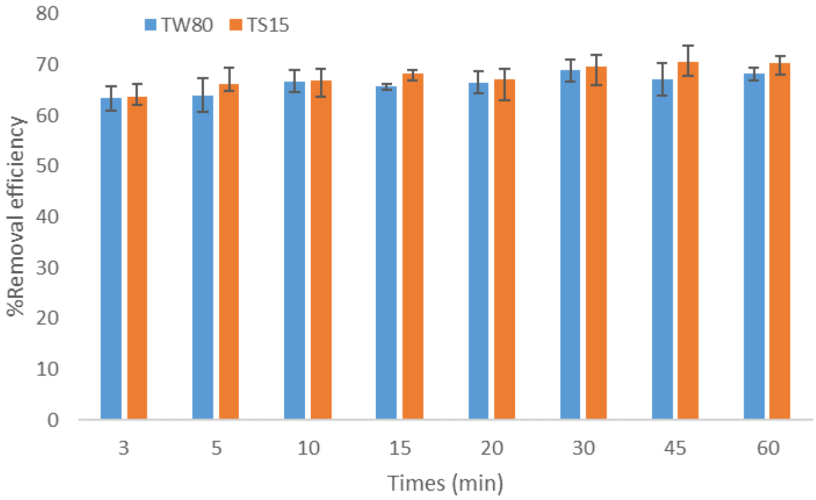


Figure 5.9 Effect of time on diesel washing efficiency at CMC_a of TW80 and TS15 at L/S ratio 3:1 (mL/g) with 100 rpm

CHAPTER 6

CONCLUSIONS AND SUGGESTIONS

6.1 Conclusions

To summarize overall picture of this study, **Table 6.1** explains briefly objective, hypothesis, experimental set up and important finding for surfactant selecting in soil washing process to reduce the cost and time for diesel contaminated soil clean up.

Table 6.1 Overall conclusion of the study

Objectives	Hypothesis	Experiments	Important Finding
1. To evaluate surfactant adsorption capacity on various soil compositions and their effect on diesel removal efficiency from contaminated soil by surfactants solution washing.	All four hypothesis below	- Effect of soil texture and organic matter content on surfactant adsorption (Section 4.1) - Surfactant adsorption on soil containing mixed texture and OM (Section 4.3) - Effect of soil texture on soil washing efficiency (Section 5.2)	- Adsorption capacity: Clay > silt > sand - DOM decreased adsorption on quartz (sand and silt) - High clay content lead to high removal efficiency - High silt content lead to low removal efficiency
2. To determine the effect of surfactant structure on soil sorption and washing efficiency	- Tween series surfactant (TW) would be more adsorbed than Tergitol 15-s series surfactant (TS) due to their sorbitan head group - Present of double bond in surfactant structure would enhance sorption of surfactant soil. - Higher molecular weight of surfactant would decrease the adsorption in soil due to steric hindrance.	- Effect of surfactant structure on surfactant adsorption (Section 4.2) - Effect of surfactant structure on soil washing efficiency (Section 5.1)	Tween surfactants - The shorter carbon chain likely to adsorb on sand, while the longer carbon chain likely to adsorb on clay - Double bond increased surfactant adsorption on soil - Sand was suitable with TW20 - Silt was suitable with TW60, TW80 - Clay did not have significant effect Tergitol surfactants - The smaller of head group, the higher adsorption - Sand was suitable with TS7 - Silt was suitable with TS9 - Clay was suitable with TS15

Table 6.1 Overall conclusion of the study (Cont.)

Objectives	Hypothesis	Experiments	Important Finding
3. To optimize the surfactant concentration and washing conditions for removing diesel from soil in different soil compositions.	- There would be a synergism effect between soil and organic matter on surfactant sorption on soil	- Determination for the Optimizing physical condition (Section 5.3)	- Rinsing process can increase removal efficiency - Shaking speed are more significant than L/S ratio - Washing time has no effect on removal efficiency

The results of this study reveal that the type of soil composition and surfactant structure affect the CMC_a of surfactants significantly as these parameters influence the adsorption of surfactants on soil minerals. Clay has the highest adsorption capacity as it has the highest surface area and porosity, followed by silt and sand. Beside soil mineral, OM also play an important role in surfactant adsorption. Surprisingly, increase in OM content decreased surfactant adsorption on sand and silt. This might be due to competition between surfactants and DOM for adsorption sites on the hydrophilic surfaces of sand and silt.

For the surfactant structure, increase in hydrophobic tail length hindered their adsorption on the hydrophilic surface of sand. In contrast, increase in tail length enhanced surfactant adsorption on the hydrophobic surface of clay. In a case of number of EO group in hydrophilic part, the more EO group could prevent surfactant adsorption on soil surface. This might be due to the steric hindrance of the bigger hydrophilic part in surfactant structure. Moreover, the presence of double bonds in the surfactant structure increased surfactant adsorption on soil by almost two times.

Although clay has the highest surfactant adsorption capacity, efficiency of diesel removal from it was very high, while silt has the lowest adsorption. This could be attributable to the re-deposition of micelles on sand and silt. Moreover, the surfactant structure differently affects the diesel removal efficiency of different soil mineral.

In Tween surfactants, TW20 has the highest diesel removal efficiency for sand, while TW60 and TW80 were more suitable for silt. However, surfactant tail length and the presence of double bonds did not affect the clay washing efficiency significantly. This indicates that the hydrophobic affinity between surfactant and soil mineral should be considered along with the interaction between surfactant and contaminant or pollutant. For Tergitol surfactants, TS7, TS9 and TS15 have the highest diesel removal efficiency from sand, silt and clay, respectively. Therefore, TW80 and TS15 were the suitable surfactant because clay can be found in most area of Thailand.

In optimizing physical condition test, the suitable conditions were shaking speed at 100 rpm with L/S ratio 3:1 (mL/g). At these conditions, time was no significant effect on diesel removal in both TW80 and TS15. The result shows that shaking speed has more significant than L/S ratio. Mixing could reduce the usage of the surfactant solution, which was considered as the main cost of site remediation.

6.2 Limitation of this study

It should be noted here that the limitation of this study was the artificial soil of mixing composition used in the soil washing experiment. Since in the real soil, there are many minerals not only quart and kaolin as sand, silt and clay, but also have other minerals, such as montmorillonite, illite and felspar, which affected to the adsorption capacity but these minerals are not exist in the artificial soil. Moreover, the nutrients like nitrogen (N). phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg) and sulfur (S) are also affected to the surfactant adsorption on soil. Therefore, the equations obtained from this study can only explain an effect of soil composition on washing efficiency. To get more accurate information for apply in real soil, further study should be conducted.

In addition, the result from this study can be a guideline for a selection of the suitable surfactant of other surfactant series for each soil composition. For example, in soil with high sand content, the surfactant that has shorter hydrophobic tail is more suitable than a longer one, while the surfactant that has higher hydrophobic tail is more suitable for soil with high clay content.

6.3 Suggestion for future study

Future studied should be further investigated as following aspects:

- Using other soil minerals, such as montmorillonite, on surfactant adsorption and diesel washing efficiency should be investigated for more accurately estimate prediction.
- Reducing surfactant adsorption is one topic that should be investigated because it can reduce the cost and the secondary pollutant effect from adsorbed surfactant on soil. However, surfactant adsorption on soil can reduce IFT and make the oil in soil soluble into water. Thus, further studied should be investigated on reducing surfactant adsorption on soil with the optimum concentration that did not reduce washing efficiency, for example, using mixed surfactant.

- The effect of oil type on removal efficiency should be investigated.
- Washing solution from soil washing should be further study for surfactant and oil recycle in order to prevent subsequent pollutants.
- The diesel removal efficiency and problem in scale-up washing process should be clarified.
- The results from this study should be implemented in soil flushing application as an on-site remediation process for oil contaminated area or oil recovery technology.

REFERENCES

Adler, E. (1977). Lignin chemistry – past, present and future. *Wood Science and Technology, 11*, 169-218.

Ahangar, A. G. (2012). The effect of minerals on non-ionic compound sorption by changing the sorption capacity of soil organic matter. *Journal of Soil Science and Plant Nutrition, 12*(4), 825-833.

Alghunaim, A., Kirdponpattara, S., & Newby, B. Z. (2013). A comparative study of surfactant adsorption by clay minerals. *Journal pf Petroleum Science and Engineering, 101*, 21-27.

Alghunaim, A., Kirdponpattara, S., & Newby, B. Z. (2016). Techniques for determining contact angle and wettability of powders. *Power Technology, 287*, 201-215.

Alquzweeni, S. S. (2016). Experimental Investigation of Phenantherne Pollutant Removal Efficiency for Contaminated Sandy Soil by Enhanced Soil Washing. *Journal of Babylon University, 24*(4).

Alvsaker, E., & Michelson, K. (1957). Carbohydrates in a cold-water extract of a pine forest soil. *Acta Chemica Scandinavica, 11*, 1794-1795.

Amirianshoja, T., Junin, R., Idris, A. K., & Rahmani, O. (2013). A comparative study of surfactant adsorption by clay minerals. *Journal pf Petroleum Science and Engineering, 101*, 21-27.

Antonious, G. F. (2015). Chapter 1: Reducing Herbicide Residues from Agricultural Runoff and Seepage Water. In A. Price (Ed.), *Herbicides, Physiology of Action and Safety*: InTech.

Assallay, A. M., Rogers, C. D. F., Smalley, I. J., & Jefferson, I. F. (1998). Silt: 2-62 μm, 9-4 ϕ. *Earth-Science Reviews, 45*, 61-88.

Ayele, B. A., Lu, J., & Chen, Q. (2020). Optimization of aeration enhanced surfactant soil washing for remediation of diesel-contaminated soils using response surface methodology. *PeerJ, 8*.

Barati-Haroon, A., Najafi-Marghmaleki, A., Tatar, A., & Mohammadi, A. H. (2016). Experimental and modeling studies on adsorption of a nonionic surfactant on sandstone minerals in enhanced oil recovery process with surfactant flooding. *Journal of Molecular Liquids, 220*, 1022-1032.

Baziar, M., Mehrasebi, M. R., Assadi, A., Fazli, M. M., Maroosi, M., & Rahimi, F. (2013). Efficiency of non-ionic surfactants – EDTA for treating TPH and heavy metals from contaminated soil. *Journal of Environmental Health Science & Engineering, 11*(41), 1-6.

Befkadu, A. A., & Chen, Q. Y. (2018). Surfactant-Enhanced Soil Washing for Removal of Petroleum Hydrocarbons from Contaminated Soils: A Review. *Pedosphere, 28*(3), 383-410.

Behl, S., & Moudgil, B. M. (1992). Mechanisms of polyethyleneoxide interactions with dolomite and apatite. *Journal of Colloid and Interface Science, 161*, 443-449.

Bohn, H. L., McNeal, B. L., & O'Connor, G. A. (2001). Chapter 6 Soil Organic Matter. In *Soil Chemistry* (pp. 155-171). USA: John Wiley & Sons, Inc.

Bona, C., Mendonca de Rezende, I., Santos, G. O., & Antonio de Souza, L. (2011). Effect of soil contaminated by diesel oil on the germination of seeds and the growth of Schinus terebinthifolius Raddi (Anacardiaceae) seedlings. *Brazilian Archives of Biology and Technology, 56*(6), 1379-1387.

Brady, N., & Weil, R. (2002). *The Nature and Properties of Soils*. New Jersey, USA: Prentice-Hall Inc.

Carretero, M. I., Gomes, C. S. F., & Tateo, F. (2006). Clays and human health. In F. F. Bergaya, B. Theng, K,G,, & G. Lagaly (Eds.), *Handbook of Clay Science* (pp. 717-741): Elsevier.

Cecillon, L., Certini, G., Lange, H., Forte, C., & Strand, L. T. (2012). Spectral fingerprinting of soil organic matter composition. *Organic Geochemistry, 46*, 127-139.

Chaiwong, N., & Nuntiya, A. (2008). Influence of pH, Electrolytes and Polymers on Flocculation of Kaolin Particle. *Chiang Mai Journal of Science, 35*(1), 11-16.

Chang, P. H., Jianga, W. T., & Li, Z. (2018). Mechanism of tyramine adsorption on Ca-montmorillonite. *Science of the Total Environment, 642*, 198-207.

Chang, S. H., Ryan, M. E., & Gupta, R. K. (1993). The Effect of pH, Ionic Strength, and Temperature on the Rheology and Stability of Aqueous Clay Suspensions. *Rheological Acta, 32*, 263-269.

Chen, Y., Hermens, J. L. M., & Droge, S. T. J. (2013). Influence of organic matter type and medium composition on the sorption affinity of C12-benzalkonium cation. *Environmental Pollution, 179*, 153-159.

Cheng, M., Zeng, G., Huang, D., Yang, C., Lai, C., Zhang, C., & Liu, Y. (2017). Advantages and challenges of Tween 80 surfactant-enhanced technologies for the remediation of soils contaminated with hydrophobic organic compounds. *Chemical Engineering Journal, 314*, 98-113.

Chiu, C. C., Moore, P. B., Shinoda, W., & Nielsen, S. O. (2009). Size-dependent hydrophobic to hydrophilic transition for nanoparticles: A molecular dynamics study. *The journal of Chemical Physics, 131*(244706), 1-8.

Christopher, L. P., Yao, B., & Ji, Y. (2014). Lignin biodegradation with laccase-mediator systems. *Frontiers in Energy Research, 2*, 1-13.

Chu, W. (2014). Remediation of contaminated soils by surfactant-aided soil washing. *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management, 7*, 19-24.

Chu, W., & Chan, K. H. (2003). The mechanism of the surfactant-aided soil washing system for hydrophobic and partial hydrophobic organics. *The Science of the Total Environment, 307*, 83-92.

Curry, C. W., Bennett, R. H., Hulbert, M. H., Curry, K. J., & Faas, R. W. (2004). Comparative Study of Sand Porosity and a Technique for Determining Porosity of Undisturbed Marine Sediment. *Marine Georesources and Geotechnology, 22*, 231-252.

Darrah, C. H. (1993). Sand, silt and clay: the soil minerals. *Landscape Management,* 24-26.

de Keizer, A., Böhmer, M. R., Mehrian, T., & Koopal, L. K. (1990). Adsorption of organic ions at the solid—electrolyte interface. Interpretation of common intersection points. *colloids and Surfaces, 51*, 339-357.

DeGomez, T., Kolb, P., & S., K. (2015). Basic Soil Components. Retrieved from http://articles.extension.org/pages/54401/basic-soil-components

Dekker, L. W., Oostindiee, K., & Ritsema, C. J. (2005). Exponentail increase of publications related to soil water repellency. *Australian Journal of Soil Ressearch, 43*, 403-441.

del Hoyo, C., Dorado, C., Rodriguez-Cruz, M. S., & Sanchez-Martin, M. J. (2008). Physico-chemical study of selected surfactant-clay mineral systems. *Journal of Thermal Analysis and Calorimetry, 94*, 227-234.

Deng, Y., Dixon, J. B., & White, G. N. (2006). Bonding mechanisms and conformation of poly(ethylene oxide)-based surfactants in interlayer of smectite. *colloids and Polymer Science, 284*, 347-356.

Denoyel, R., & Rouquerol, J. (1991). Thermodynamic (including microcalorimetry) study of the adsorption of nonionic and anionic surfactants onto silica, kaolin, and alumina. *Journal of Colloid and Interface Science, 143*(2), 555-572.

Devi, N. L., Yadav, I. C., Shihua, Q., Dan, Y., Zhang, G., & Raha, P. (2016). Environmental carcinogenic polycyclic aromatic hydrocarbons in soil from Himalayas, India: Implications for spatial distribution, sources apportionment and risk assessment. *Chemosphere, 144*, 493-502.

Diz, H. M. M., & Rand, B. (1989). The Variable Nature of the Isoelectric Point of the Edge Surface of Kaolinite. *British Ceramic Transaction Journal, 88*, 162-166.

Diz, H. M. M., Rand, B., & Inwang, I. B. (1990). The Effect of Organic Matter and Electrolyte on the Rheological Behaviour of Ball Clays. *British Ceramic Transaction Journal, 89*, 124-129.

Doerr, S. H., Shakesby, R. A., Dekker, L. W., & Ritsema, C. J. (2006). Occurrence, prediction and hydrological effects of water repellency amongst major soil and land-use types in a humid temperate climate. *European Journal of Soil Science, 57*, 741-754.

Doerr, S. H., Shakesby, R. S., & Walsh, R. P. D. (2000). Soil water repellency: its characteristics, causes and hydro-geomophological consequences. *Earth Science Reviews, 51*, 33-65.

Dong, J. F., Chowdhry, B. Z., & Leharne, S. A. (2004). Solubilisation of polyaromatic hydrocarbons in aqueous solutions of poloxamine T803. *Colloids and Surfaces A, 246*, 91-98.

Dorn, P. B., & Salanitro, J. P. (2000). Temporal ecological assessment of oil contaminated soils before and after bioremediation. *Chemosphere, 40*, 419-426.

Dorn, P. B., Vipond, T. E., Salanitro, J. P., & Wisniewski, H. L. (1998). Assessment of the acute toxicity of crude oils in soil using earthworms, Microtox, and plants. *Chemosphere, 37*, 845-860.

Dow. (2020). Tergitol 15-S Surfactant. Retrieved from https://www.dow.com/en-us/document-viewer.html?ramdomVar=1863113903363849967&docPath=/content/dam/dcc/documents/en-us/mark-prod-info/119/119-02578-0619-01-tergitol-15s-surfactants-for-coatings.pdf

ElSayed, E. M., Prasher, S. O., & Patel, R. M. (2013). Effect of nonionic surfactant Brij 35 on the fate and transport of oxytetracycline antibiotic in soil. *Journal of Environmental Management, 116*, 125-134.

Ernest, Z. (2015). How and why does the chain length of surfactants affect CMC? Retrieved from https://socratic.org/questions/can-anyone-explain-this-how-and-why-does-the-chain-length-of-surfactants-affect-

Fabbri, D., Prevot, A. B., Zelano, V., Ginepro, M., & Pramauro, E. (2008). Removal and degradation of aromatic compounds from a highly polluted site by coupling soil washing with photocatalysis. *Chemosphere, 71*, 59-65.

Forsyth, W. G. C. (1948). Colour reagents for the paper chromatography of sugars. *Nature, 161*, 239-240.

Galbe, M., & Zacchi, G. (2007). Pretreatment of lignocellulosic materials for efficient bioethanol production. *Advances in Biochemical Engineering/Biotechnology, 108*, 41-65.

Gallego, J. L., Loredo, J., Llamas, J. F., Vázquez, F., & Sánchez, J. (2001). Bioremediationof diesel-contaminated soils: evaluation of potential in situ techniques by study of bacterial degradation. *Biodegradation, 12*, 325-335.

Gautam, P., Bajagain, R., & Jeong, A. W. (2020). Combined effects of soil particle size with washing time and soil-to-water ratio on removal of total petroleum hydrocarbon from fuel contaminated soil. *Chemosphere, 250*, 126206.

Gleixner, G., Czimczik, C. J., Kramer, C., Lühker, B., & Schmidt, M. W. I. (2001). Plant compounds and their turnover and stabilization as soil organic matter. In *Global iogeochemical Cycles in the Climate System* (pp. 201-215). San Diego: Academic Presss.

Gomes, C. S. F., & Silva, J. B. P. (2007). Minerals and clay minerals in medical geology. *Applied Clay Science, 36*, 4-21.

Grasso, D., Subramaniam, K., Pignatello, J. J., Yang, Y., & Ratté, D. (2001). Micellar desorption of polynuclear aromatic hydrocarbons from contaminated soil. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 194*, 65-74.

Griffin, E. (2017). What is soil organic carbon? Retrieved from https://www.agric.wa.gov.au/soil-carbon/what-soil-organic-carbon

Guan, X. H., Shang, C., & Chen, G. H. (2006). Competitive adsorption of organic matter with phosphate onaluminum hydroxide. *Journal of Colloid and Interface Science, 296*, 51-58.

Guo, M., & Chorover, J. (2003). Transport and fractionation of dissolved organic matter in soil columns. *Soil Science, 168*(2), 108-118.

Haleyur, N., Shahsavari, E., Mansur, A. A., Koshlaf, E., Morrison, P. D., Osborn, A. M., & Ball, A. S. (2016). Comparison of rapid solvent extraction systems for the GC-MS/MS characterization of polycyclic aromatic hydrocarbons in aged, contaminated soil. *MethodX, 3*, 364-370.

Hasan, S. W., Ghannam, M. T., & Esmail, N. (2010). Heavy crude oil viscosity reduction and rheology for pipeline transportation. *Fuel, 89*, 1095-1100.

Heinz, H., Pramanik, C., Heinz, O., Ding, Y., Mishra, R. K., Marchon, D., . . . Ziolo, R. F. (2017). Nanoparticle decoration with surfactants: Molecular interactions, assembly, and applications. *Surface Science Reports, 72*, 1-58.

Hentati, O., Lachhab, R., Ayadi, M., & Ksibi, M. (2013). Toxicity assessment for petroleum-contaminated soil using terrestrial invertebrates and plant bioassays. *Environmental Monitoring and Assessment, 185*, 2989-2998.

Heo, H., & Lee, M. (2015). Surfactant-enhanced Soil Washing using Tween and Tergitol Series Surfactants for Kuwait Soil Heavily Contaminated with Crude Oil. *Journal of Soil and Groundwater Environment, 20*(5), 26-33.

Hillel, D. (2008). *Soil in the Environment*. New York: Elsevier Inc.

Hillier, S. (2003). Clay Mineralogy. In G. V. Middleton, M. J. Church, M. Coniglio, L. A. Hardie, & L. F.J. (Eds.), *Encyclopaedia of sediments and sedimentary rocks* (pp. 139-142). Dordrecht: Kluwer Academic Publishers.

Hocking, M. B., Klimchuk, K. A., & Lowen, S. (1999). Polymeric Flocculants and Flocculation. *Journal of Macromolecular Science Part C Polymer Reviews, 39*, 177-203.

Hyne, N. J. (2001). *Nontechnical Guide to Petroleum Geology, Exploration, Drilling, and Production* (2nd ed.). USA: PennWell Corporation.

IEA. (2017). *Oil Market Report: 10 February 2017*. Retrieved from Paris, France:

Ishiguro, M., & Koopal, L. K. (2016). Surfactant adsorption to soil components and soils. *Advances in Colloid and Interface Science, 231*, 59-102.

Ishiguro, M., Tan, W., & Koopal, L. K. (2007). Binding of cationic surfactants to humic substances. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 306*, 29-39.

Johnson, S. B., Franks, G. V., Scales, P. J., Boger, D. V., & Healy, T. W. (2000). Surface chemistry–rheology relationships in concentrated mineral suspensions. *International Journal of Mineral Processing, 58*, 267-304.

Jones, M. N., & Bryan, N. D. (1998). Colloidal properties of humic substances. *Advances in Colloid and Interface Science, 78*, 1-48.

Kaiser, K., & Guggenberger, G. (2000). The role of DOM sorption to mineral surfaces in the preservation of organic matter in soils. *Organic Geochemistry, 31*(711-725).

Kamal, M. S., Hussein, I. A., & Sultan, A. S. (2017). Review on surfactant fooding: phase behavior, retention, ift, and feld applications. *Energy Fuels, 31*(8), 7701-7720.

Karhunen, P., Rummakko, P., Sipilä, J., Brunow, G., & Kilpeläinen, I. (1995). The formation of dibenzodioxocin structures by oxidative coupling. A model reaction for lignin biosynthesis. *Tetrahedron Letters, 36*(25), 4501-4504.

Khan, F. I., Husain, T., & Hejazi, R. (2004). An overview and analysis of site remediation technologies. *Journal of Environmental Management, 7*, 95-122.

Klučáková, M., & Pavlíková, M. (2017). Lignitic Humic Acids as Environmentally-Friendly Adsorbent for Heavy Metals. *Journal of Chemistry*. doi:https://doi.org/10.1155/2017/7169019

Kohnke, H., & Franzmeier, D. P. (1995). Organic matter and Microbes of the soil. In *Soil Science simplified* (pp. 53-60). Illinois, USA: Waveland Press, Inc.

Koopal, L. K. (2012). Wetting of Solid Surfaces: Fundamentals and Charge effects.

Advances in Colloid and Interface Science, 179-182, 29-42.

Koopal, L. K., Goloub, T., Keizer, A., & Sidorova, M. P. (1999). The effect of cationic surfactants on wetting, colloid stability and flotation of silica. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 151*(1-2), 15-25.

Koopal, L. K., Goloub, T. P., & Davis, T. A. (2004). Binding of ionic surfactants to purified humic acid. *Journal of Colloid and Interface Science, 275*(2), 360-367.

Koshlaf, E., Shahsavari, E., Aburto-Medina, A., Taha, M., Haleyur, N., Makadia, T. H., . . . Ball, A. S. (2016). Bioremediation potential of diesel-contaminated Libyan soil. *Ecotoxicology and Environmental Safety, 133*, 297-305.

Kubicki, J. D., Itoh, M. J., Schroeter, L. M., & Apitz, S. E. (1997). Bonding mechanisms of salicylic acid adsorbed onto illite clay. An ART-FTIR and molecular orbital study. *Environmental Science and Technology, 31*, 1151-1156.

Laha, S., & Luthy, R. G. (1992). Effects of Nonionic Surfacrtants on the Solubilization and Mineralization of Phenanthrene in Soil-Water Systems. *Biotechnology and Bioengineering, 40*, 1367-1380.

Lahel, A., Fanta, A. B., Sergienko, N., Shakya, M., Lopea, M. E., Behera, S. K., . . . Park, H. S. (2016). Effect of process parameters on the bioremediation of diesel contaminated soil by mixed microbial consortia. *International Biodeteriotaion and Biodegradation, 113*, 375-385.

Lai, C. C., Huang, Y. C., Wei, Y. H., & Chang, J. S. (2009). Biosurfactant-enhanced removal of total petroleum hydrocarbons from contaminated soil. *Journal of Hazardous Materials, 167*, 609-614.

Lee, J. F., Liao, P. M., Kuo, C. C., Yang, H. T., & Chiou, C. T. (2000). Influence of a Nonionic Surfactant (Triton X-100) on Contaminant Distribution between Water and Several Soil Solids. *Journal of Colloid and Interface Science, 229*(2), 445-452.

Levitz, P. E. (2002). Adsorption of non ionic surfactants at the solid/water interface. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 205*(1-2), 31-38.

Li, G., Guo, S., & Hu, J. (2016). The influence of clay minerals and surfactants on hydrocarbon removal during the washing of petroleum-contaminated soil.

Chemical Engineering Journal, 286, 191-197.

Lin, C., Lin, T. C., Mao, W. M., Huang, C. L., Sheu, D. S., & Kao, J. C. M. (2011). *Application of Food Waste Composting Process for the Treatment of Diesel Contaminated Soil*. Paper presented at the 2011 2nd International Conference on Environmental Science and Technology, Singapore.

Liu, Z., Edwards, D. A., & Luthy, R. G. (1992). Sorption of non-ionic surfactants onto soil. *Water Research, 26*(10), 1337-1345.

Lowe, L. E. (1978). Chapter 2 Carbohydrates in Soil. *Developments in Soil Science, 8*, 65-93.

Makkar, R. S., & Rockne, K. J. (2003). Comparison of synthetic surfactants and biosurfactants in enhancing biodegradation pf polycyclic aromatic hydrocarbons. *Environmental Toxicity and Chemistry, 22*(10), 2280-2292.

Matsuda, M., Kaminaga, A., Hayakawa, K., Takisawa, N., & Miyajima, T. (2009). Surfactant binding by humic acids in the presence of divalent metal salts. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 347*, 45-49.

McCauley, A., Jones, C., & Jacobsen, J. (2005). Basic Soil Properties.Soil & Water Management Module I. *Montana State University Extension Service,* 1-12.

Mehta, N. C., Dubach, P., & Deuel, H. (1962). Carbohydrates in the Soil. *Advances in Carbohydrate Chemistry, 16*, 335-355.

Meng, Q., Sun, L., Chen, D., & Wu, G. (2019). Adsorption of Asphaltenes at Oil–Water and Oil–Clay Interfaces in the Presence of Humic Acids. *Langmuir, 35*(51), 16718-16725.

Michaels, A., & Bolger, J. (1964). Particle Interactions in Aqueous Kaolinite Suspensions. *Industrial Engineering Chemical Fundamentals, 3*, 14-20.

Morrison, R. I. (1969). Soil lipids. Organic Geochemistry. In G. Eglinton & M. T. J. Murphy (Eds.), *Organic Geochemistry*. Berlin, Heidelberg: Springer.

Mouri, M., & Ozaki, S. (2017). Combined Use of Soil Washing and Incineration for Remediation of Dioxin Contaminated Soils in Southern Vietnam. *Organohalogen Compounds, 79*, 411-414.

Muherei, M. A. (2008). Mixing effect of anionic and nonionic surfactants on micellization, adsorption and partitioning of nonionic surfactant. *Modern Applied Science, 2*, 3-12.

Mukherjee, S. (2013). *The Science of Clays*. India: Capital Publishing Company.

Mullins, O., & Sheu, E. (1999). *Structure& Dynamics of Asphaltenes* (1st ed.): Springer.

Murray, H. H. (2006). Kaolin Application. *Developments in Clay Science, 2*, 85-109.

Olorunfemi, I. E., Ogunrinde, T. A., & Fasinmirin, J. T. (2014). Soil Hydrophobicity: An Overview. *Journal of Scientific Research and Reports, 3*(8), 1003-1037.

Osagie, E. I., & Owabor, C. N. (2015). Adsorption of Naphthalene on Clay and Sandy Soil from Aqueous Solution. *Advances in Chemical Engineering and Science, 5*, 345-351.

Otto, W. H., Britten, D. J., & Larive, C. K. (2003). NMR diffusion analysis of surfactant–humic substance interactions. *Journal of Colloid and Interface Science, 261*(2), 508-513.

Paria, S. (2008). Surfactant-enhanced remediation of organic contaminated soil and water. *Advances in Colloid and Interface Science, 138*, 24-58.

Peng, S., Wu, W., & Chen, J. (2011). Removal of PAHs with surfactant-enhanced soil washing: influencing factors and removal effectiveness. *Chemosphere, 82*, 1173-1177.

Prasad, M. S., Reid, K. J., & Murray, H. H. (1991). Kaolin: processing, properties and applications. *Applied Clay Science, 6*(87-119).

Pugh, R. J., & Tjus, K. (1990). Flotation depressant action ofpoly(oxyethylene)alkyl ethers on talc. *colloids and Surfaces, 47*, 179-194.

Pulles, T., Van der Gon, H. D., Appelman, W., & Verheul, M. (2012). Emission factors for heavy metals from diesel and petrol used in European vehicles. *Atmospheric Environment, 61*, 641-651.

Rakowska, J. (2020). Remediation of diesel-contaminated soil enhanced with firefighting foam application. *Scientific Reports, 10*.

Rebello, S., Asok, A. K., & Mundayoor, S. (2014). Surfactants: toxicity, remediation and green surfactants. *Environmental Chemistry Letters, 12*, 275-287.

Rongsayamanont, W., Tongcumpou, C., & Phasukarratchai, N. (2020). Diesel-Contaminated Soil Washing by Mixed Nonionic Surfactant Emulsion and Seed Germination Test. *Water, Air, & Soil Pollution, 231*(267), 1-10.

Rosas, J. M., Vicente, F., Santos, A., & Romero, A. (2013). Soil remediation using soil washing followed by Fenton oxidation. *Chemical Engineering Journal, 220*, 125-132.

Rosen, M. J., & Kunjappu, J. T. (2012). *Surfactants and Interfacial Phenomena* (4th Edition ed.). Hoboken: Wiley.

Roy, A. S., Baruah, R., Borah, M., Singh, A. K., DekaBoruah, H. P., Saikia, N., . . . Chandra, B. T. (2014). Bioremediation potential of native hydrocarbondegrading bacterial strains in crude oil contaminated soil under microcosmstudy. *International Biodeteriotaion and Biodegradation, 94*, 79-89.

Ruiz-Dueñas, F. J., & Martínez, Á. T. (2009). Microbial degradation of lignin: how a bulkyrecalcitrant polymer is efficiently recycled in nature and how we can take advantage of this. *Microbial Biotechnology, 2*, 164-177.

Rundle, A., Tang, D., Hibshoosh, H., Estabrook, A., Schnabel, F., Cao, W., . . . Perera, F. P. (2000). The relationship between genetic damage from polycyclic aromatic hydrocarbons in breast tissue and breast cancer. *Carcinogenesis, 21*, 1281-1289.

Sawang, T. (2017). ทำปุ๋ยหมักในกะละมัง และในตะกร้า สไตล์ห้องเรียนปุ๋ยหมักแม่โจ้. Retrieved from http://www.thaicityfarm.com/2019/06/05/%E0%B8%97%E0%B8%B3%E0%B8%9B%E0%B8%B8%E0%B9%8B%E0%B8%A2%E0%B8%AB%E0%B8%A1%E0%B8%B1%E0%B8%81%E0%B9%83%E0%B8%99%E0%B8%81%E0%B8%B0%E0%B8%A5%E0%B8%B0%E0%B8%A1%E0%B8%B1%E0%B8%87-%E0%B9%81%E0%B8%A5%E0%B8%B0/

Schmidt, M. W. I., & Noack, A. G. (2000). Black carbon in soils and sediments: analysis, distribution, implications and current challenges. *Global Biogeochemical Cycles, 14*, 777-793.

Schnitzer, M. (1999). Soil organic matter. The Next 75 Years. *Soil Science, 151*, 41.

Schulthess, C. P., & Huang, P. M. (1991). Humic and fulvic acid adsorption by silicon and aluminum oxide surfaces on clay minerals. *Soil Science Society of America Journal 55*, 34-42.

Sharma, H. D., & Reddy, K. R. (2004). Soil Remediation Technologies. In *Geoenvironmental Engineering: Site Remediation, Waste Containment, and*

Emerging Waste Management Technologies (pp. 413-421). New Jersey: Wiley.

Sheard, R. W. (1991). Sand, Silt and Clay. *Sports Turf Newsletter*.

Shen, Y. H. (2000). Sorption of non-ionic surfactants to soil: the role of soil mineral composition. *Chemosphere, 41*, 711-716.

Sheremata, T. W., Yong, R. N., Ghoshal, S., & Guiot, S. R. (2000). Anaerobic Biodegradation of Trichloroethylene Sorbedby a Surrogate Soil Organic Matte. *Journal of Environmental Quality, 29*, 1033-1040.

Sheremata, T. W., Yong, R. N., & Guiot, S. R. (1997). Simulation and sterilization of a surrogatesoil organic matter for the study of the fate oftrichloroethylene in soil. *Communications in Soil Science and Plant Analysis, 28*(13-14), 1177-1190.

Siddiqui, M. S., Amy, G. L., & Murphy, B. D. (1997). Ozone enhanced removal of natural organic matter from drinking water sources. *Water Research, 31*(12), 3098-3106.

Sigmaaldrich. (2020). Tween. Retrieved from https://www.sigmaaldrich.com/catalog/search?term=tween&interface=All&N=0&mode=match%20partialmax&lang=en&region=TH&focus=product

Somasundaran, P., Snell, E. D., & Xu, Q. (1991). Adsorption behavior of Alkylarylethoxylated alcohols on silica. *Journal of Colloid and Interface Science, 144*, 165-173.

Sparks, D. L. (1999). The Chemistry of Soil Organic matter. In *Soil physical chemistry* (2nd ed., pp. 239-370). USA: CRC Press.

Stevenson, F. J. (1994). Humus Chemistry. In *Genesis, Composition, Reactions* (2nd ed.). New York: John Wiley & Sons.

Sverdrup, L. E., Krogh, P. H., Nielsen, T., Kjaer, C., & Stenersen, J. (2003). Toxicity of eight polycyclic aromatic compounds to red clover (Trifolium pratense), ryegrass (Lolium perenne), and mustard (Sinapsis alba). *Chemosphere, 53*, 993-1003.

Tadros, T. (2013). *Encyclopedia of Colloid and Interface Science*. Berlin, Heidelberg: Springer.

Tan, K. H. (1998). Chapter 5 Colloidal chemistry of inorganic soil constituents. In *Principles of soil chemistry* (3rd ed., pp. 177-259). New York: Marcel Dekker Inc.

Tan, W. F., Norde, W., & Koopal, L. K. (2011). Humic substance charge determination by titration with a flexible cationic polyelectrolyte. *Geochimica et Cosmochimica*

Acta, 75(19), 5749-5761.

Tang, J., Wang, M., Wang, F., Sun, Q., & Zhou, Q. (2011). Eco-toxicity of petroleum hydrocarbon contaminated soil. *Journal of Environmental Sciences, 23*, 845-851.

Tertre, E., Castet, S., Berger, G., Loubet, M., & Giffaut, E. (2006). Surface chemistry of kaolinite and Na-montmorillonite in aqueous electrolyte solutions at 25 and 60 °C: Experimental and modeling study. *Geochimica et Cosmochimica Acta, 70*(18), 4579-4599.

Tongcumpou, C., Acosta, E., Quencer, L. B., & Sabatini, D. A. (2005). Microemulsion formation and detergency with oily soils: III. Performance and mechanisms. *Journal of Surfactants and Detergents, 8*, 147-156.

Torn, L. H., de Keizer, A., Koopal, L. K., & Lyklema, J. (2003). Mixed adsorption of poly(vinylpyrrolidone) and sodium dodecylbenzenesulfonate on kaolinite. *Journal of Colloid and Interface Science, 260*(1), 1-8.

Tremblay, L., Kohl, S. D., Rice, J. A., & Gagné, J. P. (2005). Effects of temperature, salinity, and dissolved humic substances on the sorption of polycyclic aromatic hydrocarbons to estuarine particles. *Marine Chemistry, 96*, 21-34.

Urum, K., & Pakdemir, T. (2004). Evaluation of Biosurfactant for Crude Oil Contaminated Soil Washing. *Chemosphere, 57*(9), 1139-1150.

Urum, K., Pakdemir, T., & Copur, M. (2004). Surfactants treatment of crude oil contaminated soils. *Journal of Colloid and Interface Science, 276*, 456-464.

Viamajala, S., Peyton, B. M., Richards, L. A., & Petersen, J. N. (2007). Solubilization, solution equilibria, and biodegradation of PAH's under thermophilic conditions. *Chemosphere, 66*, 1094-1106.

Vishnyakov, A., Lee, M. T., & Neimark, A. V. (2013). Prediction of the critical micelle concentration of nonionic surfactants by dissipative particle dynamics simulations. *Journal of Physical Chemistry Letters, 4*, 797-802.

Wang, Z., Chen, J. W., Qiao, X. L., Yang, P., Tian, F. L., & Huang, L. P. (2007). Distribution and sources of polycyclic aromatic hydrocarbons from urban to rural soils: a case study in Dalian, China. *Chemosphere, 68*, 965-971.

Wasan, D. T., & Nikolov, A. D. (2003). Spreading of nanofluids on solids. *Nature, 423*, 131-132.

Wei, Y., Liang, X., Lin, W., Guo, C., & Dang, Z. (2015). Clay mineral dependent desorption of pyrene from soils by single and mixed anionic-nonionic surfactants. *Chemical Engineering Journal, 264*, 807-814.

Williams, D. J. A., & Williams, K. P. (1982). Colloid Stability and Rheology of Kaolinite Suspensions. *British Ceramic Transaction Journal, 81*, 78-83.

Williams, L. B., & Haydel, S. E. (2011). Evaluation of the medicinal use of clay minerals as anitibacterial agents. *International Geology Review, 52*, 745-770.

Wilson, M. J. (2003). Clay mineralogical and related characteristics of geophagic materials. *Journal of Chemical Ecology, 29*, 1525-1547.

Wyszkowska, J., & Kucharski, J. (2001). Correlation between number of microbes and degree of soil contamination with petrol. *Polish Journal of Environment Studies, 10*, 175-181.

Yang, K., Zhu, L., & Xing, B. (2007). Sorption of sodium dodecylbenzene sulfonate by montmorillonite. *Environment Pollution, 145*(2), 571-576.

Yee, M. M., Miyajima, T., & Takisawa, N. (2009). Study of ionic surfactants binding to humic acid and fulvic acid bypotentiometric titration and dynamic light scattering. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 347*, 128-132.

Yeh, D. H., Pennell, K. D., & Pavlostathis, S. G. (1998). Toxicity and biodegradability screening of nonionic surfactants using sediment-derived methanogenic consortia. *Water Science and Technology, 38*(7), 55-62.

Yokoyama, S., & Nakagaki, M. (1993). Effect of souble bond on the surface properties of aqueous solutions of eicosapolyenoic acids. *Colloid and Polymer Science, 271*, 512-518.

Zacarias–Salinas, M., Vaca, M., Flores, M. A., Bandala, E. R., & Torres, L. G. (2013). Surfactant-Enhanced Washing of Soils Contaminated with Wasted-Automotive Oils and the Quality of the Produced Wastewater. *Journal of Environmental Protection, 4*, 1495-1501.

Zandvoort, I. V., Koers, E. J., Weingarth, M., P.C.A., B., Baldus, M., & B.M., W. (2015). Structural characterization of 13C-enriched humins and alkali-treated 13C humins by 2D solid-state NMR. *Green Chemistry, 17*, 4383-4392.

Zegeye, A., Yahaya, S., Fialips, C. I., White, M. L., Gray, N. D., & Manning, D. A. C. (2013). Refinement of industrial kaolin by microbial removal of iron-bearing impurities. *Applied Clay Science, 86*(47-53).

Zhang, L., Somasundaran, P., Ososkov, V., & Chou, C. C. (2001). Flotation of Hydrophobic contaminats from soil. *colloids and Surfaces, 177*, 235-246.

Zhang, M., & Zhu, L. Z. (2010). Effect of SDBS-Tween 80 mixed surfactants on the distribution of polycyclic aromatic hydrocarbons in soil-water system. *The Journal of Soils and Sediments, 10*, 1123-1130.

Zhao, Y., Wang, Z., Zhang, W., & Jiang, X. (2010). Adsorbed Tween 80 is unique in its ability to improve the stability of gold nanoparticles in solutions of biomolecules. *Nanoscale, 2*, 2114-2119.

Zhou, Q., Shen, W., Zhu, J., Zhu, R., He, H., Zhou, J., & Yuan, P. (2014). Structure and dynamic properties of water saturated CTMA-montmorillonite: molecular dynamics simulations. *Applied Clay Science, 97-98*, 62-71.

Zhou, Q. X., Sun, F. H., & Liu, R. (2005). Joint chemical flushing of soils contaminated with petroleum hydrocarbons. *Environment International, 31*, 835-839.

Zhu, B. Y., & Gu, T. (1989). General isotherm equation for adsorption of surfactants at solid liquid interfaces. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases, 85*, 3813-3817.

Zhu, J., Zhu, L., Zhu, R., & Chen, B. (2008). Microstructure of organo-bentonites in water and the effect of steric hindrance on the uptake of organic compounds. *Clays and Clay Minerals, 56*, 144-154.

Zularisam, A. W., Ahmad, A., Sakinah, M., Ismail, A. F., & Matsuura, T. (2011). Role of natural organic matter (NOM), colloidal particles, and solution chemistryon ultrafiltration performance. *Separation and Purification Technology, 78*, 189-200.

APPENDIX

Table A1 CMC (mg/L) of Tween surfactants in water and in soil with different OM content

Soil composition	**TW20**			**TW40**			**TW60**			**TW80**		
	mg/L	**Avg.**	**SD**	**mg/L**	**Avg.**	**SD**	**mg/L**	**Avg.**	**SD**	**mg/L**	**Avg.**	**SD**
Solution	53.8	54.9	1.7	35.5	34.5	1.5	30.9	30.8	0.2	16.0	15.7	0.3
	56.1			33.4			30.6			15.5		
Sand	182.0	182.8	1.2	91.0	94.4	4.8	76.1	76.1	0.1	64.5	64.5	0.0
	183.7			97.7			76.2			64.5		
Silt	1667.8	1652.5	21.6	1391.2	1372.8	25.9	1081.8	1107.3	36.0	1099.0	1119.4	28.8
	1637.3			1354.5			1132.7			1139.8		
Clay	3042.4	3029.9	17.8	3764.6	3693.7	100.3	4230.1	4225.2	6.9	4143.6	4054.5	126.0
	3017.3			3622.7			4220.2			3965.4		
Sand+1%OM	89.0	87.1	2.7	79.7	80.9	1.8	65.9	66.7	1.2	53.8	54.6	1.1
	85.2			82.2			67.6			55.3		
Silt+1%OM	1262.9	1244.6	25.9	1148.3	1171.2	32.3	906.4	894.0	17.5	787.2	799.5	17.5
	1226.3			1194.0			881.6			811.9		
Clay+1%OM	3398.9	3326.5	102.3	3755.2	3842.6	123.6	4278.3	4265.5	18.2	4260.5	4272.3	16.7
	3254.2			3930.0			4252.6			4284.2		

Table A1 CMC (mg/L) of Tween surfactants in water and in soil with different OM content (cont.)

Soil composition	TW20			TW40			TW60			TW80		
	mg/L	Avg.	SD	mg/L	Avg.	SD	mg/L	Avg.	SD	mg/L	Avg.	SD
Sand+3%OM	168.5	167.0	2.1	129.5	130.3	1.2	123.8	126.0	3.0	96.2	99.3	4.4
	165.5			131.1			128.1			102.5		
Silt+3%OM	563.4	559.2	5.9	793.9	777.1	23.7	437.7	434.2	4.9	642.5	656.5	19.8
	555.1			760.4			430.7			670.5		
Clay+3%OM	3776.7	3821.0	62.7	4024.5	4024.1	0.5	4268.4	4276.3	11.2	4560.7	4529.7	43.8
	3865.4			4023.8			4284.2			4498.7		
Sand+5%OM	211.9	213.3	2.0	155.9	153.0	4.1	256.1	255.1	1.5	259.5	259.2	0.4
	214.7			150.1			254.0			258.9		
Silt+5%OM	720.8	730.1	13.2	894.2	876.9	24.4	472.4	461.6	15.3	775.0	763.9	15.7
	739.4			859.7			450.7			752.8		
Clay+5%OM	4364.6	4312.1	74.2	4396.6	4333.5	89.3	4365.4	4297.3	96.3	4958.9	4873.5	120.8

Table A2 CMC (mg/L) of Tergitol surfactants in water and in soil with different OM content

Soil composition	TS7			TS9			TS15		
	mg/L	Avg.	SD	mg/L	Avg.	SD	mg/L	Avg.	SD
Solution	37.0	36.5	0.7	57.5	59.1	2.3	164.8	162.3	3.5
	36.0			60.7			159.8		
Sand	80.0	79.2	1.2	85.3	86.8	2.1	213.1	215.3	3.1
	78.4			88.3			217.6		
Silt	85.8	84.9	1.2	102.3	100.4	2.8	228.3	227.6	0.9
	84.1			98.4			227.0		
Clay	328.2	319.9	11.6	250.7	247.1	5.0	586.9	582.6	6.1
	311.7			243.6			578.3		
Sand+1%OM	150.4	154.2	5.4	152.1	149.3	4.0	230.8	232.5	2.5
	158.0			146.5			234.3		
Silt+1%OM	123.9	127.0	4.3	164.5	160.7	5.4	269.7	266.5	4.5
	130.0			156.9			263.3		
Clay+1%OM	342.6	347.0	6.2	311.1	312.3	1.7	737.3	746.8	13.5
	351.4			313.5			756.4		
Sand+3%OM	298.8	294.3	6.4	266.3	260.3	8.5	331.3	327.4	5.6
	289.7			254.3			323.4		
Silt+3%OM	220.4	221.2	1.1	296.1	301.0	6.9	355.1	356.1	1.4
	222.0			305.9			357.1		

Table A2 CMC (mg/L) of Tergitol surfactants in water and in soil with different OM content (Cont.)

Soil composition	**TS7**			**TS9**			**TS15**		
	mg/L	**Avg.**	**SD**	**mg/L**	**Avg.**	**SD**	**mg/L**	**Avg.**	**SD**
Clay+3%OM	385.5	392.4	9.8	408.9	404.7	5.9	834.1	832.9	1.7
	399.3			400.5			831.7		
Sand+5%OM	360.6	357.6	4.2	451.6	451.1	0.7	462.5	470.9	11.8
	354.7			450.7			479.2		
Silt+5%OM	326.3	319.8	9.1	455.9	456.8	1.3	475.1	481.0	8.3
	313.4			457.7			486.9		
Clay+5%OM	444.6	451.6	9.8	535.5	516.2	27.3	995.4	983.7	16.5
	458.5			496.8			972.0		

Table A3 X_{CMC} (Times) of Tween surfactants in soil with different OM content

Soil composition	TW20			TW40			TW60			TW80		
	Times	Avg.	SD	Times	Avg.	SD	Times	Avg.	SD	Times	Avg.	SD
Sand	3.27	3.33	0.08	2.93	2.74	0.26	2.49	2.47	0.02	4.04	4.10	0.08
	3.39			2.56			2.46			4.15		
Silt	31.03	30.10	1.31	39.17	39.87	1.00	36.97	35.96	1.42	68.86	71.14	3.23
	29.18			40.58			34.96			73.42		
Clay	53.78	55.19	2.00	108.53	107.26	1.80	137.74	137.22	0.73	255.44	257.53	2.95
	56.60			105.99			136.70			259.62		
Sand+1%OM	1.52	1.59	0.10	2.46	2.35	0.15	2.13	2.17	0.05	3.57	3.47	0.14
	1.66			2.24			2.21			3.37		
Silt+1%OM	23.49	22.67	1.16	35.77	34.05	2.43	28.77	29.03	0.37	52.30	50.81	2.11
	21.86			32.33			29.29			49.32		
Clay+1%OM	63.23	60.62	3.70	117.73	111.73	8.49	138.79	138.53	0.38	275.97	271.46	6.38
	58.00			105.72			138.26			266.95		
Sand+3%OM	3.13	3.04	0.13	3.64	3.79	0.20	4.00	4.09	0.13	6.60	6.31	0.41
	2.95			3.93			4.18			6.03		
Silt+3%OM	9.89	10.19	0.42	22.35	22.56	0.30	14.06	14.10	0.06	43.19	41.72	2.08
	10.48			22.78			14.14			40.25		
Clay+3%OM	68.89	69.58	0.97	120.54	116.92	5.12	139.83	138.88	1.33	285.75	287.78	2.86
	70.26			113.30			137.94			289.80		

Table A3 X_{CMC} (Times) of Tween surfactants in soil with different OM content (cont.)

Soil composition	TW20			TW40			TW60			TW80		
	Times	Avg.	SD	Times	Avg.	SD	Times	Avg.	SD	Times	Avg.	SD
Sand+5%OM	3.83	3.88	0.08	4.50	4.44	0.08	8.28	8.28	0.01	16.68	16.47	0.30
	3.94			4.39			8.29			16.26		
Silt+5%OM	13.18	13.29	0.16	25.75	25.46	0.41	15.27	14.99	0.39	48.49	48.53	0.05
	13.41			25.17			14.71			48.56		
Clay+5%OM	81.20	78.56	3.73	127.93	125.85	2.93	138.03	139.55	2.15	308.44	309.57	1.60
	75.92			123.78			141.07			310.71		

Table A4 X_{CMC} (Times) of Tergitol surfactants in soil with different OM content

Soil composition	TS7			TS9			TS15		
	Times	Avg.	SD	Times	Avg.	SD	Times	Avg.	SD
Sand	2.17	2.17	0.01	1.49	1.47	0.02	1.32	1.33	0.01
	2.18			1.45			1.33		
Silt	2.34	2.33	0.01	1.62	1.70	0.11	1.38	1.40	0.04
	2.32			1.78			1.43		
Clay	8.88	8.77	0.15	4.01	4.19	0.25	3.51	3.59	0.12
	8.67			4.36			3.67		
Sand+1%OM	4.39	4.23	0.23	2.41	2.53	0.17	1.42	1.43	0.02
	4.07			2.65			1.44		
Silt+1%OM	3.61	3.48	0.18	2.86	2.72	0.20	1.60	1.64	0.06
	3.35			2.58			1.69		
Clay+1%OM	9.77	9.52	0.35	5.41	5.29	0.18	4.59	4.60	0.02
	9.27			5.16			4.61		
Sand+3%OM	8.06	8.07	0.02	4.19	4.41	0.31	1.96	2.02	0.08
	8.08			4.63			2.07		
Silt+3%OM	6.17	6.07	0.15	5.04	5.10	0.08	2.22	2.19	0.04
	5.96			5.15			2.17		
Clay+3%OM	10.43	10.77	0.47	7.12	6.86	0.37	5.22	5.13	0.12
	11.10			6.60			5.05		

Table A4 X_{CMC} (Times) of Tergitol surfactants in soil with different OM content (cont.)

Soil composition	TS7			TS9			TS15		
	Times	Avg.	SD	Times	Avg.	SD	Times	Avg.	SD
Sand+5%OM	9.86	9.81	0.07	7.44	7.64	0.29	2.91	2.90	0.01
	9.76			7.84			2.89		
Silt+5%OM	8.71	8.77	0.08	7.54	7.74	0.28	2.95	2.96	0.01
	8.83			7.93			2.97		
Clay+5%OM	12.75	12.39	0.51	8.18	8.75	0.80	5.90	6.06	0.23
	12.03			9.32			6.23		

Table A5 Effect of OM and DOM on CMC of TW20 in the sand system

Condition	mg/L	Avg.	SD
Measured CMC	53.8	54.9	1.7
	56.1		
DOM (1%OM)	60.2	63.1	4.1
	66.0		
Sand+DOM (1%OM)	61.9	60.9	1.3
	60.0		
Sand	182.0	182.8	1.2
	183.7		
1%OM	91.1	89.8	1.8
	88.5		
Sand+1%OM	89.0	87.1	2.7
	85.2		

Table A6 CMC$_a$ of TW80 in different soil composition with 2%OM

Soil composition			TW80				TS15			
%Sand	%Silt	%Clay	mg/L		Avg.	SD	mg/L		Avg.	SD
100.0	0.0	0.0	73	72	73	1	273	260	267	9
0.0	100.0	0.0	593	586	589	29	326	318	322	5
0.0	0.0	100.0	4453	4397	4425	40	793	770	782	16
50.0	50.0	0.0	344	325	334	13	301	308	305	5
0.0	50.0	50.0	2710	2612	2661	70	1074	1131	1103	40
50.0	0.0	50.0	2387	2368	2378	14	784	805	795	14
66.7	16.7	16.7	913	886	899	19	555	558	557	2
16.7	66.7	16.7	902	865	883	26	838	818	828	14
16.7	16.7	66.7	3263	3292	3277	20	1257	1295	1276	27
33.3	33.3	33.3	1721	1657	1689	46	805	798	801	5

Table A7 Diesel removal efficiency of Tween surfactants in different soil texture

Soil type	Surfactant Concentration	TW20					TW40					TW60					TW80				
		%Removal			Avg.	SD	%Removal			Avg.	SD	%Removal			Avg.	SD	%Removal			Avg.	SD
Sand	DI	34.6	31.9	33.8	33.4	1.4															
	CMC_m	41.0	44.1	44.9	43.3	2.1	44.9	34.3	38.7	39.3	5.3	37.5	35.0	38.5	37.0	1.8	33.9	34.4	39.3	35.9	3.0
	1x CMC_a	55.5	56.3	58.5	56.8	1.6	58.5	55.2	59.7	57.8	2.3	45.8	45.6	42.7	44.7	1.8	45.0	40.4	42.9	42.8	2.3
	10x CMC_a	83.7	86.4	78.9	83.0	3.8	81.3	84.1	81.4	82.3	1.5	75.9	78.5	77.6	77.3	1.3	73.2	75.1	74.8	74.4	1.0
Silt	DI	13.5	14.5	13.9	14.2	0.5															
	CMC_m	18.8	23.3	20.1	20.7	2.3	21.1	25.7	22.4	23.0	2.4	36.0	33.2	35.1	34.8	1.4	34.9	35.5	31.8	34.1	2.0
	1x CMC_a	37.3	38.4	31.4	35.7	3.8	39.5	37.6	38.4	38.5	0.9	53.1	49.3	45.0	49.1	4.1	48.4	49.5	48.6	48.8	0.6
	10x CMC_a	50.8	49.6	48.5	49.6	1.1	56.0	46.3	51.1	51.2	4.9	55.9	68.7	57.2	60.6	7.0	60.9	59.5	53.2	57.9	4.1
Clay	DI	36.7	35.2	34.6	35.5	1.1															
	CMC_m	47.1	47.1	44.4	46.2	1.6	47.0	40.7	50.9	46.2	5.2	51.4	49.0	46.8	49.1	2.3	54.4	57.1	50.2	53.9	3.5
	1x CMC_a	70.9	70.8	69.6	70.4	0.7	65.5	72.5	70.1	69.4	3.5	73.1	65.8	71.5	70.1	3.9	71.0	73.8	76.9	73.9	3.0
	10x CMC_a	86.2	88.3	87.2	87.2	1.0	90.0	89.6	90.2	90.0	0.3	84.9	88.3	90.6	87.9	2.9	91.2	90.6	90.8	90.9	0.3

Table A8 Diesel removal efficiency of Tergitol surfactants in different soil texture

Soil type	Surfactant Concentration	TS7					TS9					TS15				
		%Removal			Avg.	SD	%Removal			Avg.	SD	%Removal			Avg.	SD
Sand	DI	34.6	31.9	33.8	33.4	1.4										
	CMC_m	40.6	42.8	37.5	40.3	2.7	34.6	35.9	42.5	37.7	4.2	34.3	36.7	36.2	35.7	1.3
	1x CMC_a	53.1	58.8	51.2	54.4	4.0	49.6	51.4	50.0	50.3	1.0	39.5	43.0	41.5	41.3	1.8
	10x CMC_a	63.7	69.6	62.7	65.3	3.7	60.4	62.3	59.0	60.6	1.7	62.1	62.4	55.0	59.8	4.2
Silt	DI	13.5	14.5	13.9	14.2	0.5										
	CMC_m	19.7	13.1	13.8	15.6	3.6	27.9	28.4	30.2	28.9	1.2	16.9	19.0	25.7	20.5	4.6
	1x CMC_a	22.6	23.0	25.8	23.8	1.7	42.5	41.0	44.7	42.7	1.9	43.3	40.2	40.6	41.3	1.7
	10x CMC_a	43.7	40.9	42.4	42.3	1.4	52.7	50.8	55.8	53.1	2.6	52.7	48.2	49.7	50.2	2.3
Clay	DI	36.7	35.2	34.6	35.5	1.1										
	CMC_m	41.0	36.7	34.6	37.5	3.2	37.9	37.3	42.7	39.3	3.0	42.1	45.5	43.0	43.5	1.8
	1x CMC_a	44.3	47.1	45.8	45.7	1.4	47.5	53.6	49.0	50.0	3.2	51.3	52.6	57.0	53.6	3.0
	10x CMC_a	73.5	75.6	77.1	75.4	1.8	83.5	82.8	81.4	82.6	1.1	96.1	94.5	92.2	94.3	2.0

Table A9 Hydrocarbon (C10-C18) removal efficiency using TW80 at L/S ratio 3:1 (mL/g) with 200 rpm on silt and clay

Contaminant/washing concentration		Silt			Clay		
		%Removal	Avg.	SD	%Removal	Avg.	SD
C10	DI	42.8	41.4	1.3	37.4	38.1	1.7
		40.2			40.0		
		41.3			36.8		
	CMC_m	53.1	53.4	2.1	54.4	57.2	2.5
		55.7			57.7		
		51.4			59.4		
	CMC_a	64.4	64.9	4.1	69.0	73.0	4.0
		69.2			73.0		
		61.1			77.0		
C14	DI	41.6	41.1	2.4	35.8	38.2	4.6
		38.5			43.5		
		43.2			35.4		
	CMC_m	53.8	55.7	1.9	50.4	52.7	4.9
		55.8			58.3		
		57.5			49.3		
	CMC_a	69.1	67.9	2.3	79.8	79.2	2.2
		65.2			76.8		
		69.3			81.1		

Table A9 Hydrocarbon (C10-C18) removal efficiency using TW80 at L/S ratio 3:1 (mL/g) with 200 rpm on silt and clay (cont.)

Contaminant/washing concentration		Silt			Clay		
		%Removal	Avg.	SD	%Removal	Avg.	SD
C18	DI	35.9	39.3	3.0	36.7	38.2	1.4
		41.7			38.5		
		40.3			39.4		
	CMC_m	55.9	55.9	1.3	43.6	41.7	1.8
		54.7			40.1		
		57.2			41.3		
	CMC_a	71.5	70.2	3.2	78.6	77.9	1.3
		72.6			76.4		
		66.6			78.6		

Table A10 Diesel removal efficiency of TW80 in different soil composition with 2%OM

Soil composition			DI			CMC_m			1x CMC_a			10x CMC_a		
%Sand	%Silt	%Clay	%Removal	Avg.	SD	%Removal	Avg.	SD	%Removal	Avg.	SD	%Removal	Avg.	SD
100.0	0.0	0.0	70.3	69.7	0.6	74.0	74.3	0.9	81.0	79.4	1.6	84.6	83.2	1.7
			69.7			75.3			77.9			83.7		
			69.1			73.5			79.2			81.3		
0.0	100.0	0.0	33.7	34.6	1.3	41.2	37.3	3.4	43.9	44.9	3.7	63.1	58.0	4.5
			36.0			35.6			49.0			56.3		
			34.1			35.1			41.8			54.7		
0.0	0.0	100.0	55.3	53.7	3.5	57.8	57.6	0.6	78.8	79.8	3.2	88.5	90.4	2.2
			56.1			56.9			77.2			89.8		
			49.7			58.0			83.3			92.8		
50.0	50.0	0.0	62.2	61.2	2.3	67.8	69.5	1.7	72.6	73.1	0.8	82.7	81.6	1.3
			62.8			71.1			74.0			81.9		
			58.6			69.7			72.6			80.2		
0.0	50.0	50.0	59.5	61.8	1.9	62.7	59.5	2.8	67.1	65.0	2.0	84.5	81.9	3.5
			62.7			58.3			64.8			83.3		
			63.0			57.5			63.0			77.9		

Table A10 Diesel removal efficiency of TW80 in different soil composition with 2%OM (cont.)

Soil composition			DI			CMC_m			1x CMC_a			10x CMC_a		
%Sand	%Silt	%Clay	%Removal	Avg.	SD	%Removal	Avg.	SD	%Removal	Avg.	SD	%Removal	Avg.	SD
50.0	0.0	50.0	62.3	61.9	2.0	66.9	67.5	3.2	74.3	74.3	1.6	86.3	85.0	2.0
			63.8			64.6			76.0			86.1		
			59.8			70.9			72.7			82.7		
66.7	16.7	16.7	44.6	42.0	2.3	58.6	55.7	2.8	63.2	65.1	1.9	77.2	77.3	2.6
			41.4			55.3			67.1			80.0		
			40.1			53.1			65.1			74.7		
16.7	66.7	16.7	15.7	15.9	2.2	36.5	34.8	1.5	51.8	54.3	3.0	67.1	65.9	2.5
			18.1			33.4			53.4			67.6		
			13.8			34.5			57.6			63.0		
16.7	16.7	66.7	43.9	46.8	3.8	27.9	28.4	2.0	52.5	52.0	2.3	66.0	66.7	0.6
			45.4			26.8			49.5			67.0		
			51.0			30.6			54.1			67.2		
33.3	33.3	33.3	49.4	53.4	3.5	32.9	30.8	3.0	59.2	58.4	1.1	66.5	64.9	1.6
			56.0			27.4			58.8			65.0		
			54.8			32.1			57.1			63.3		

Table A11 Diesel removal efficiency of TS15 in different soil composition with 2%OM

Soil composition			DI			CMC_m			1x CMC_a			10x CMC_a		
Sand	Silt	Clay	%Removal	Avg.	SD	%Removal	Avg.	SD	%Removal	Avg.	SD	%Removal	Avg.	SD
100.0	0.0	0.0	70.3	69.7	0.6	75.0	75.5	1.3	85.1	85.1	3.0	93.4	94.1	2.5
			69.7			74.6			88.1			96.9		
			69.1			77.0			82.1			92.1		
0.0	100.0	0.0	33.7	34.6	1.3	40.5	40.2	2.3	47.9	47.9	3.4	73.6	74.0	3.8
			36.0			37.8			51.3			77.9		
			34.1			42.3			44.6			70.4		
0.0	0.0	100.0	55.3	53.7	3.5	62.1	60.0	2.7	68.9	69.3	2.1	88.5	87.3	3.0
			56.1			61.0			71.6			89.5		
			49.7			57.0			67.5			83.9		
50.0	50.0	0.0	62.2	61.2	2.3	64.7	63.7	0.9	69.6	68.6	1.6	73.3	73.1	0.5
			62.8			63.7			66.7			72.6		
			58.6			62.8			69.4			73.5		
0.0	50.0	50.0	59.5	61.8	1.9	59.3	58.6	2.1	62.8	65.5	2.5	83.1	83.5	2.7
			62.7			56.2			65.8			81.0		
			63.0			60.3			67.8			86.3		

Table A11 Diesel removal efficiency of TS15 in different soil composition with 2%OM (cont.)

Soil composition			DI			CMC_m			1x CMC_a			10x CMC_a		
%Sand	%Silt	%Clay	%Removal	Avg.	SD	%Removal	Avg.	SD	%Removal	Avg.	SD	%Removal	Avg.	SD
50.0	0.0	50.0	62.3	61.9	2.0	63.9	64.2	0.3	66.4	66.6	1.7	83.4	85.2	3.6
			63.8			64.4			65.1			82.8		
			59.8			64.3			68.5			89.3		
66.7	16.7	16.7	44.6	42.0	2.3	63.8	63.2	1.2	69.7	68.4	1.4	77.9	81.6	3.3
			41.4			63.9			68.4			82.5		
			40.1			61.9			67.0			84.3		
16.7	66.7	16.7	15.7	15.9	2.2	29.9	31.3	2.6	57.6	60.5	2.6	68.9	70.0	1.1
			18.1			29.7			62.3			70.0		
			13.8			34.2			61.6			71.2		
16.7	16.7	66.7	43.9	46.8	3.8	40.8	43.4	2.4	60.8	59.1	2.1	76.5	77.4	0.8
			45.4			43.9			56.8			77.3		
			51.0			45.5			59.8			78.2		
33.3	33.3	33.3	49.4	53.4	3.5	42.6	43.8	1.5	58.1	60.4	3.1	80.5	81.6	1.3
			56.0			43.3			63.9			83.0		
			54.8			45.5			59.2			81.1		

Table A12 Diesel removal efficiency on real soil and artificial soil

Surfactant concentration		Artificial soil			Real soil		
		%Removal	Avg.	SD	%Removal	Avg.	SD
DI		42.4	40.5	2.6	25.3	25.8	2.1
		37.5			28.1		
		41.5			24.0		
TW80	CMC_m	45.4	44.4	1.5	27.7	28.6	1.1
		45.1			28.4		
		42.7			29.8		
	CMC_a	60.5	60.4	3.3	29.9	32.7	2.9
		57.1			35.6		
		63.7			32.7		
	CMC_{rs}	-			35.6	37.0	1.6
					36.7		
					38.7		
TS15	CMC_m	44.5	46.7	2.9	27.0	27.2	1.1
		45.6			28.5		
		49.9			26.3		
	CMC_a	62.9	65.2	2.9	36.5	37.8	1.3
		64.2			39.2		
		68.4			37.8		
	CMC_{rs}	-			48.1	47.7	0.5
					47.1		
					47.8		

Table A13 CMC_a of TW80 and TS15 on real soil and artificial soil with the same soil composition as real soil

Soil composition	**TW80**			**TS15**		
	mg/L	**Avg.**	**SD**	**mg/L**	**Avg.**	**SD**
Real soil	6552	6391	228	3335	3285	69
	6229			3236		
Artificial soil using Kaolin as clay	1893	1965	103	1050	1027	32
	2038			1004		
Artificial soil Montmorillonite as clay	5623	5751	181	10525	10773	352
	5879			11022		

Table A14 Effect of rinsing on Diesel removal efficiency

Surfactant		No Rinse			Rinse		
		%Removal	Avg.	SD	%Removal	Avg.	SD
DI		42.4	40.5	2.6	57.1	54.7	2.4
		37.5			54.5		
		41.5			52.4		
TW80	CMC$_m$	45.4	44.4	1.5	61.6	61.5	2.8
		45.1			64.2		
		42.7			58.6		
	1x CMC$_a$	60.5	60.4	3.3	73.9	73.7	0.7
		57.1			72.9		
		63.7			74.2		
	10x CMC$_a$	68.2	70.0	2.2	78.1	79.1	1.8
		69.3			77.9		
		72.5			81.1		
TS15	CMC$_m$	44.5	46.7	2.9	67.5	66.1	1.4
		45.6			66.0		
		49.9			64.8		
	1x CMC$_a$	62.9	65.2	2.9	75.9	73.7	1.9
		64.2			72.3		
		68.4			72.9		
	10x CMC$_a$	76.2	78.3	1.8	77.6	79.8	2.1
		79.3			80.2		
		79.4			81.7		

Table A15 Effect of L/S ratio and shaking speed on diesel removal efficiency using TW80 at 30 min

L/S ratio (mL/g)	Shaking speed	%Removal	Avg.	SD
3:1	50	56.2	54.8	1.9
		55.6		
		52.6		
	100	66.7	68.8	2.2
		68.7		
		71.1		
	200	73.9	73.7	0.7
		72.9		
		74.2		
4:1	50	60.3	60.2	1.1
		61.2		
		59.1		
	100	69.8	70.4	1.1
		69.7		
		71.7		
	200	71.7	70.7	0.9
		69.9		
		70.6		
5:1	50	67.3	67.0	1.8
		68.6		
		65.1		
	100	71.6	71.9	1.1
		71.0		
		73.2		
	200	74.9	74.2	1.5
		75.2		
		72.5		

Table A16 Effect of L/S ratio and shaking speed on diesel removal efficiency using TS15 at 30 min

L/S ratio (mL/g)	Shaking speed	%Removal	Avg.	SD
3:1	50	59.4	56.5	3.6
		57.5		
		52.5		
	100	65.5	69.7	3.7
		72.4		
		71.2		
	200	75.9	73.7	1.9
		72.3		
		72.9		
4:1	50	59.0	61.3	2.0
		62.6		
		62.3		
	100	75.5	72.5	3.3
		73.2		
		69.0		
	200	70.6	72.2	1.5
		72.3		
		73.6		
5:1	50	70.3	70.7	0.9
		70.0		
		71.7		
	100	75.1	74.1	3.6
		77.1		
		70.2		
	200	70.6	73.5	1.5
		72.3		
		73.6		

Table A17 Effect of time on diesel removal efficiency using TW80 and TS15 with L/S ratio 3:1 (mL/g) at 100 rpm

Time	TW80			TS15		
(min)	%Removal	Avg.	SD	%Removal	Avg.	SD
3	64.44	63.39	2.45	62.04	63.71	1.63
	65.13			65.30		
	60.59			63.79		
5	67.03	64.02	3.24	65.04	66.17	1.22
	64.44			66.01		
	60.59			67.46		
10	67.03	66.73	2.15	63.82	67.01	3.26
	64.44			66.88		
	68.72			70.33		
15	65.67	65.68	0.52	68.25	68.35	1.52
	66.21			69.91		
	65.17			66.88		
20	64.22	66.55	2.25	71.07	67.02	4.10
	66.70			67.12		
	68.72			62.87		
30	66.75	68.85	2.17	65.46	69.70	3.73
	68.72			72.45		
	71.08			71.20		
45	70.81	67.17	3.15	69.05	70.55	2.71
	65.36			68.92		
	65.35			73.68		
60	66.86	68.22	1.29	72.94	70.31	2.31
	68.35			68.60		
	69.44			69.40		

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