

**Surfactant Enhanced Removal of Petroleum Products
from a Contaminated Soil with Sand and Clay
Components**

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of

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ABSTRACT

Surfactant Enhanced Removal of Petroleum Products from a Contaminated Soil with Sand and Clay Components

Xujun Li

The growing energy demand leads to the increasing use of petroleum products. Contaminations caused by uncontrolled release of oil bring risks to the environment. In this study, SDS (sodium dodecyl sulfate), AOT (sodium dioctyl sulfosuccinate) and Brij 35 (polyoxyethylene lauryl ether) are the surfactants selected as washing solutions to remove engine oil from an artificially contaminated soil. The soil was formed using clean sand and montmorillonite clay with different ratios. Contaminated soil samples were formed by contaminating the artificial soil with engine oil which was the chosen petroleum product.

Both batch and column tests were conducted to investigate the desorption behavior of engine oil from the contaminated soil. The effects of surfactant type, surfactant concentration, soil composition and pH on desorption efficiency of engine oil were examined in batch experiments. The influences of washing volume and flow rate on oil removal efficiency were investigated in column tests. Distilled water was used as the control. The test results indicate that engine oil solubilization increases with the concentration of surfactants above CMC. In the engine oil removal process, nonionic

surfactant Brij 35 is more effective than surfactants SDS and AOT. Desorption efficiency of the residual engine oil by 0.6% Brij 35 is almost 20 times higher than that by distilled water. With the same washing volume, lower flow rate appears to be more desirable for oil removal from the contaminated soil.

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List of Abbreviations

AEO ₉	Aliphatic Polyethenoxy Ether
AES	Sodium Alcohol Polyethoxylated Ether Sulfate
AOT	Aerosol*OT
ATSDR	Agency for Toxic Substance and Disease Registry
Brij 35	Polyoxyethylene Lauryl Ether
CEC	Cation Exchange Capacity
CMC	Critical Micelle Concentration
EPA	Environmental Protection Agency
IFT	Interfacial Tension
LAS	Linear Alkyl Benzene Sulfonate
MSR	Molar Solubilization Ratio
NAPL	Non-Aqueous Phase Liquid
SDS	Sodium Dodecyl Sulfate
USDA	United States Department of Agriculture
VOC	Volatile Organic Compounds

List of Symbols

A	Section Area (cm ²)
D	Diameter (mm)
f_{oc}	Fraction of Organic Carbon Presented in Soil
H	Height (cm)
K	Hydraulic Conductivity (cm/s)
K_d	Distribution Coefficient (L/kg)
K_m	Micelle-water Partition Coefficient (M ⁻¹)
K_{oc}	Organic Carbon Normalized Partition Coefficient (L/kg)
L	Length (cm)
P	Partial Pressure of the Constituent (Pa)
P^0	Vapor Pressure of the Pure Constituent (Pa)
t	Time (s)
V	Outflow Volume (mL)
V_{pore}	Pore Volume (cm ³)

CHAPTER 1

INTRODUCTION

1.1 General remarks

The growing energy demand in the world leads to the increasing use of petroleum products. Contamination of soils due to uncontrolled releases of these products, such as aboveground oil spills and underground leaking storage tanks, is a common environmental problem. In the typical case of soil contamination by petroleum products, a fraction of the free phase oil can be removed by pumping or drainage as primary recovery. However, a significant fraction of the released petroleum products will also be trapped in the soil pores or on the soil particles. The petroleum products that remain within the soil may volatilize into the air or leak into groundwater. The transport of contaminated soil can cause further damage to the environment and bring potential risks to human beings due to their volatilization and their ability to contaminate ground water.

Various techniques have been used in the past for the remediation of petroleum contaminated soils. Mainly these include pump-and-treat technology, soil vapor extraction, thermal desorption, soil flushing and soil washing. It is now widely known that conventional pump-and-treat remediation technologies are ineffective and costly methods of aquifer restoration (MacDonald and Kavanaugh, 1994). Soil vapor

extraction & thermal desorption are only suitable for volatile organic compounds (VOCs). Hence, in-situ soil flushing and ex-situ soil washing could be the potentially viable strategy for the removal of complex petroleum products from the soil. Engine oil is the petroleum product chosen for this study.

The main components of engine oil are non-aqueous phase liquids (NAPLs). Surface-active agents (surfactants) that have a hydrophobic structural group together with a hydrophilic group were used to enhance the remediation of NAPLs from soils, for both in-situ and ex-situ operations (Abdul et al, 1990). Surfactants enhanced removal of residual NAPLs is recognized to occur via two general mechanisms: solubilization and mobilization. Surfactants can be used to enhance the dissolution of NAPLs into aqueous phase by solubilization or to reduce the interfacial tension between NAPLs and aqueous phase by mobilization (Chevalier, 2003).

The present studies attempt to investigate the potential of using surfactants in conjunction with soil flushing techniques for the removal of petroleum products within a soil with sand and clay components. A laboratory study was carried out to evaluate the feasibility of removing petroleum products from a contaminated soil using surfactant solutions with low concentrations.

Commercial engine oil was selected as a typical petroleum product because of its wide usage and its greater stability in the soil than other petroleum products. The soil sample was mixed in the lab by fine sand and montmorillonite with different ratios. Two anionic surfactants sodium dodecyl sulfate (SDS), sodium dioctyl sulfosuccinate (AOT) and one non-ionic surfactant polyoxyethylene lauryl ether (Brij

35) were used in this study. Both batch and column tests were conducted to investigate the adsorption & desorption behavior of selected engine oil in surfactant-water-soil system. In batch tests, the effects of surfactant type, surfactant concentration, soil composition and pH on removing petroleum products from soil were studied in detail. In column experiments, washing volumes and flow rates were adjusted to compare the removal efficiency of oil from the soil.

1.2 Objective of the study

The objectives of this study are listed below.

1. Select an effective surfactant with a low concentration that can combine with soil flushing/soil washing in the remediation of petroleum products from a soil contaminated by engine oil which is the chosen petroleum product.
2. Investigate the mechanisms of surfactant-enhanced removal of engine oil from the contaminated soil composed of sand and clay in varied proportions.
3. Determine the effects of soil environment, such as soil composition and pH, in the surfactant enhanced petroleum product removal process.
4. Examine the washing capacity of surfactants and study the effects of washing volumes & flow rates on the desorption characteristics of engine oil contaminated soil in the column tests.

1.3 Thesis outline

This study is organized as follows:

Chapter 2 gives a brief review of some technologies related to surfactant enhanced

site remediation and provides correlative properties of surfactants & transport principles of petroleum products in the subsurface.

Chapter 3 contains the experimental methods, materials and operations involved in this study. Both batch and column experiments are conducted to study the effects of surfactant type, surfactant concentration, soil composition, pH, flow rate and washing volume on removing petroleum products (contaminants) from a contaminated soil.

Chapter 4 discusses the results connected to batch & column tests and analyzes the factors that influence the petroleum product (engine oil) removal efficiency from the soil.

Chapter 5 includes the thesis conclusion, contribution and the recommendations for future work.

CHAPTER 2

BACKGROUND INFORMATION

2.1 Remediation technologies for NAPL-contaminated soils

The environment problems have got increasing concern during last few decades. Consequently, the assessment and remediation of contaminated site in subsurface systems become one of the major research areas in the environmental and earth sciences. Improper disposal and uncontrolled releases of NAPLs, such as aboveground oil spills and underground storage tanks leaking, are sources of persistent pollutants in the subsurface environment (Chevalier, 2003). NAPLs contaminants which are found in some area have a very high risk of influencing people's health if there is no proper remediation.

Various in-situ and ex-situ techniques are used in practice to remediate the NAPLs contaminated sites, such as soil vapor extraction, soil flushing, chemical treatment, bioremediation, thermal desorption, physical separation and soil washing. For less volatile petroleum mixtures, soil flushing & soil washing are effective source control treatment technologies.

2.1.1 Soil flushing treatment technology

In-situ soil flushing is the extraction of contaminants from the soil with water or other suitable aqueous solutions. Compared with soil washing which involves

excavating the contaminated soil and treating it at the surface in a soil washer, soil flushing involves an injection/recirculation process in place. A schematic of in-situ soil flushing system is shown in Figure 2-1

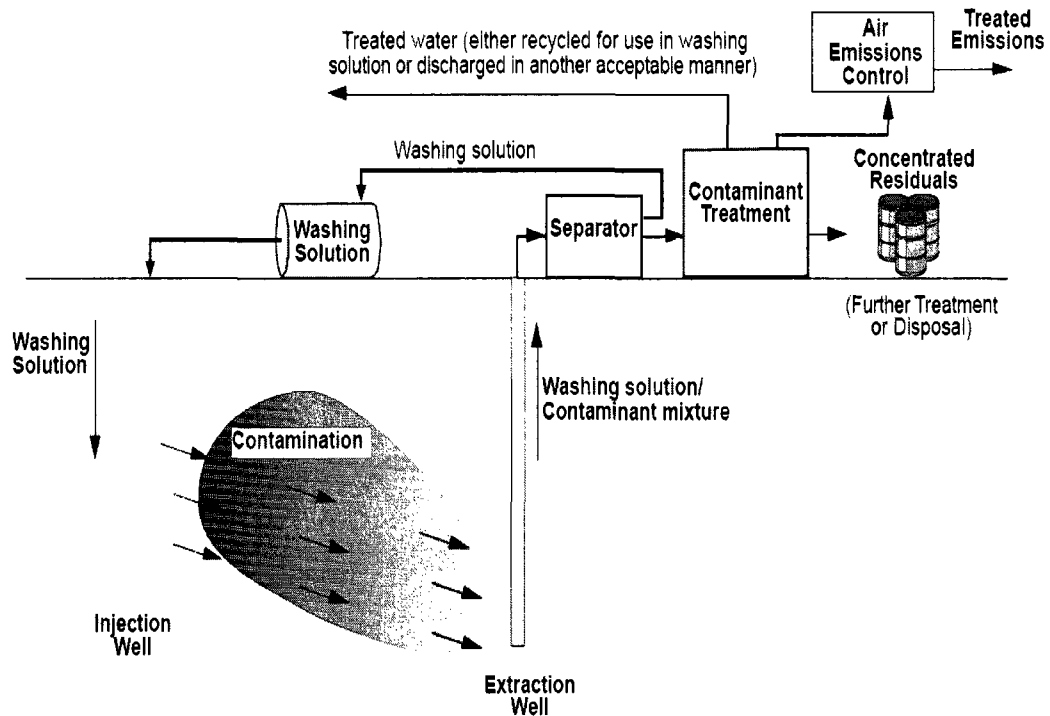


Figure 2-1 Schematic of an In-Situ Flushing System (USEPA, www.epa.gov accessed on Feb 8th 2009).

The flushing process first begins with the drilling of injection and extraction wells into the ground where the contamination has been found. Then the flushing solution is pumped into the injection wells. The solution passes through the soil, picking up contaminants as it moves towards the extraction wells. The solution-contaminant mixture is pumped out of the ground through the extraction wells (Lee, 2007). Recovered flushing fluids should be collected and treated, as

appropriate, to meet applicable regulatory standards.

Surfactant enhanced flushing involves injecting a solvent mixture (e.g., water plus a surfactant) into the soil to extract NAPLs (contaminants). Surfactant enhanced flushing can be applied to soils to dissolve either the source of contamination or the contaminant plume emanating from it. The separation of surfactants from recovered flushing fluid for reuse in the process is a major factor in the cost of soil flushing. Residual flushing additives in the soil may be a concern and should be evaluated on a site-specific basis (Federal Remediation Technologies Roundtable, <http://www.frtr.gov/>).

2.1.2 Soil washing treatment technology

In contrast to soil flushing, soil washing is a type of ex-situ treatment. It “scrubs” soil to remove and separate the portion of the soil that is most polluted. This reduces the amount of soil which needs further cleanup. The wash water may contain other ingredients (leaching agent, surfactant or pH adjustment) to assist in the removal of NAPLs. A simple schematic of ex-situ soil washing process is shown in Fig. 2-2.

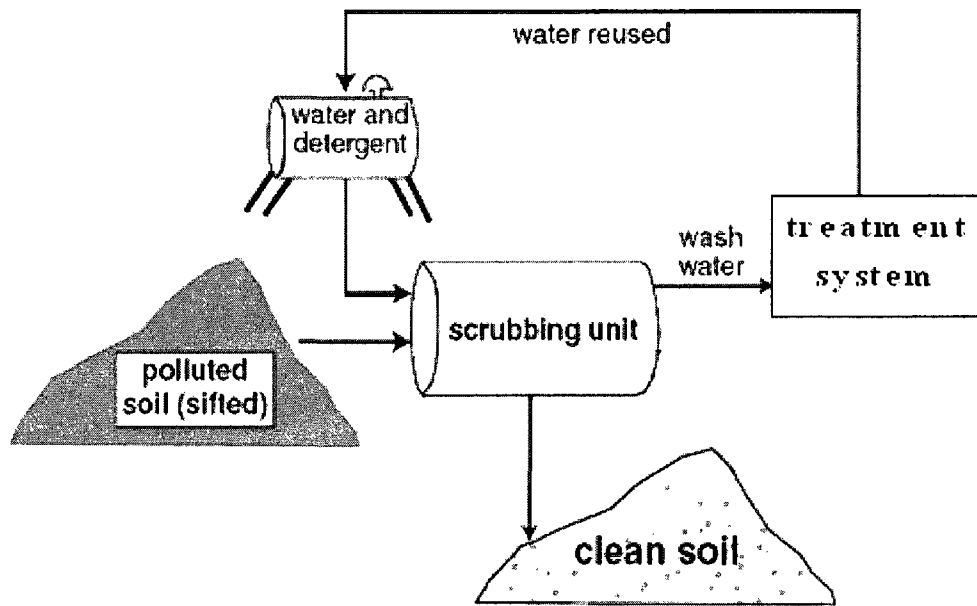


Figure 2-2 Schematic of ex-situ soil washing process (USEPA, www.epa.gov accessed on Feb 8th 2009).

Soil washing is not often used for soils with different types of contaminants such as a mixture of metals and NAPLs. Similarly, in-situ flushing is not applicable when many different types of contaminants are encountered. It is also not applicable to highly heterogeneous soils that have low permeability (Dupont and Marve, 2001).

The flowing factors may influence the applicability and effectiveness of the soil washing process (Federal Remediation Technologies Roundtable, <http://www.frtr.gov/>):

- Complex contaminant mixtures (e.g., metals with organics) make the choice of washing fluid difficult.

- High humic content in soil may require pretreatment.
- The aqueous stream will require treatment at demobilization.
- Additional treatment steps may be required to address hazardous levels of washing solvent remaining in the treated residuals.
- Low permeability or heterogeneous soils are difficult to treat. The efficiency of extraction depends on the hydraulic conductivity of the soil. Soils with high permeability have better results (greater than 1×10^{-3} cm/s) in soil washing (Dupont and Marve, 2001).

The selection of a surfactant depends on its performance in mobilizing and solubilizing the contaminants besides its toxicity & cost considerations.

2.2 Surfactants

2.2.1 Introduction

Surfactants (surface active agents) are chemical agents with structures that can alter the property at the solution interface. Figure 2-3 illustrates a typical surfactant molecule structure, which consists of a hydrophilic (water-loving) head and a hydrophobic (water-hating) tail.

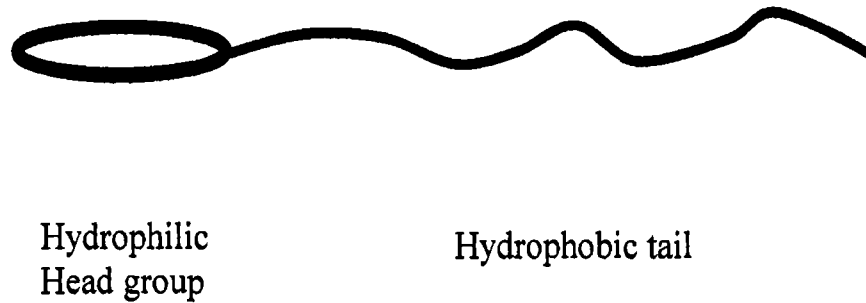


Figure 2-3 Surfactant molecule structure.

The hydrophilic head group often includes anion or cation as a counter charge balancing ion. The hydrophobic portion of a surfactant molecule is typically a long hydrocarbon chain, with strong affinity to NAPLs. This amphiphilic nature leads to the accumulation of surfactant monomers at NAPL-water interfaces, with the hydrophobic tail embedded in the NAPL and the hydrophilic head facing toward the aqueous phase (See Figure 2-4). The molecular weight of surfactants generally used in environmental remediation area ranges from 200 g/mol to 2000 g/mol (AATDF, 1997).

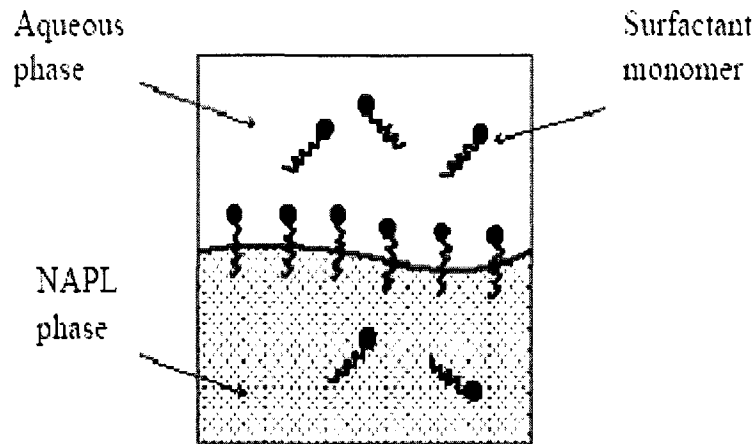


Figure 2-4 Surfactant accumulation at the NAPL-water interface (AATDF, 1997).

The common classification of surfactants given below is based on the nature of the hydrophilic part. It is described by Myers (1999).

1. Anionic: The hydrophilic group carries a negative charge. Typically it contains one or more of the following head group: carboxyl, sulfonate or sulfate.
2. Cationic: The hydrophilic group has a positive charge like quaternary ammonium halides.
3. Non-ionic: The hydrophilic group has no charge. It owes its water solubility to the highly polar groups. Example: Polyoxyethylenated alkylphenols.
4. Zwitterionic: The hydrophilic group has both a negative and a positive charge on the principal chain. Example: sulfobetaines, sultaines.

2.2.2 Mechanism of surfactant enhanced removal of NAPL

A surfactant molecule that exists as a single unit is called a surfactant monomer.

With increase of surfactant concentrations, monomer concentration increases up to the

concentration at which micelles form. Critical micelle concentration (CMC) denotes this minimum concentration (Rosen, 1978). At concentrations at or above the CMC, the number of monomers remains constant and the excess surfactant molecules aggregate to form micelles (Lee, 2007). The process of micelle aggregation is shown in Figure 2-5.

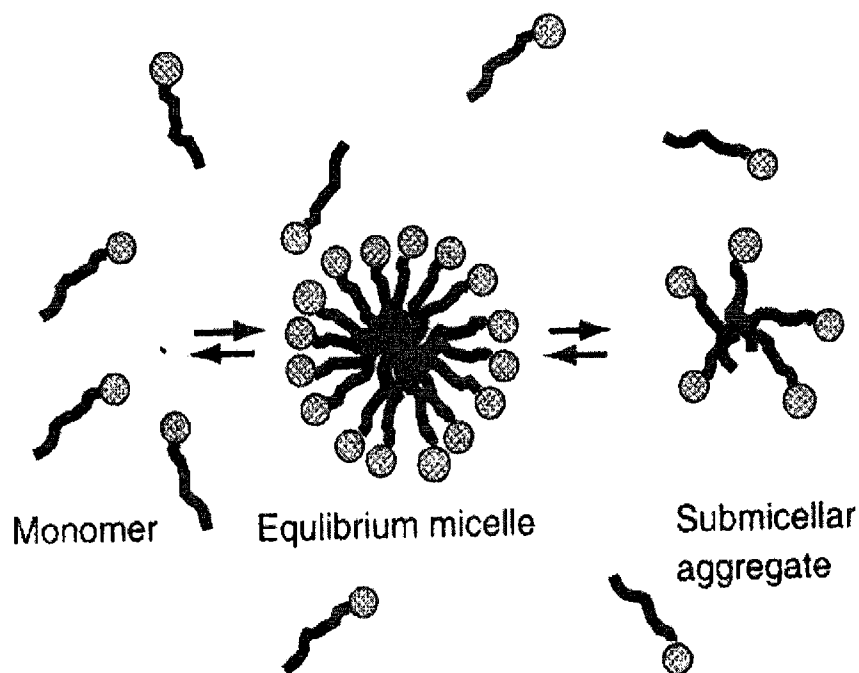


Figure 2-5 Surfactant micellization (Myers, 1999).

Micelles in aqueous solutions will have their hydrophobic tail pointing toward the interior of the micelle and the hydrophilic head oriented toward the aqueous solution. The hydrophobic nature inside of the micelle makes it a friendly place for NAPL to reside (Lee, 2007).

This NAPL removal mechanism is defined as solubilization. It improves NAPL recovery by increasing the aqueous solubility of NAPL which relies on high surfactant concentrations to provide adequate contaminant recovery. The other mechanism assisting contaminant removal is mobilization. Mobilization occurs mainly by reducing interfacial tension (IFT) between the NAPL and surfactant (see Figure 2-6).

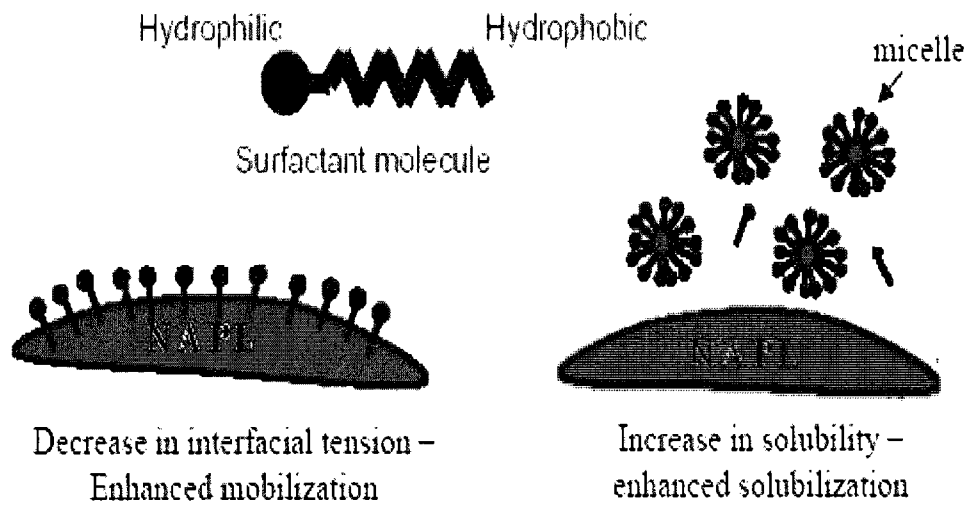


Figure2-6 Mobilization versus solubilization of NAPL by surfactant (Lee, 2007).

Organic compounds can be trapped in soil pores due to capillary forces that exist in soil, which is called residual NAPL. These capillary forces are proportional to the interfacial tension at the NAPL-water interface (West and Harwell, 1992). During surfactant enhanced aquifer remediation, surfactants accumulate at the NAPL-water

interface, and the interfacial tension (IFT) is reduced between the two-phases because of amphiphilic nature of surfactant (Lee, 2007).

The influence of surfactant concentration on IFT and NAPL solubility is illustrated in Figure 2-7.

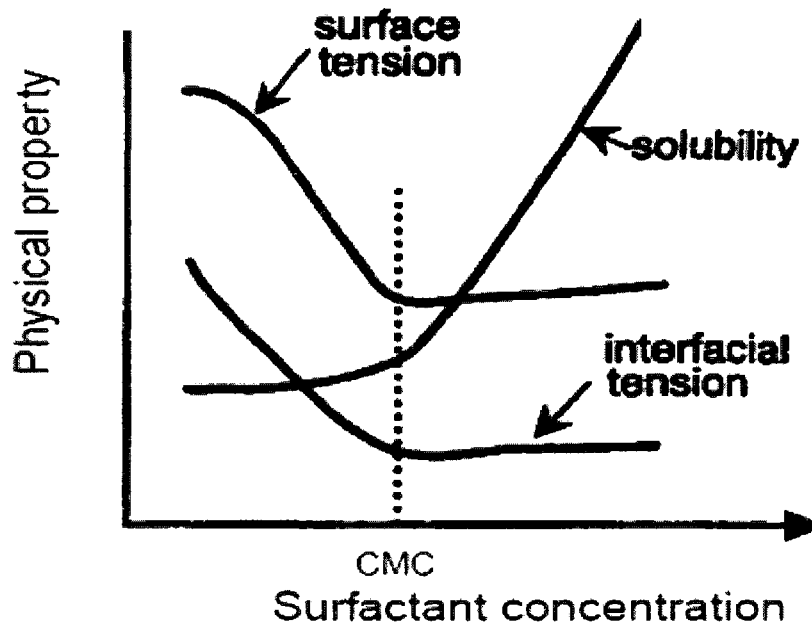


Figure 2-7 Parameters' relationship in surfactant system (Longino and Kueper, 1995).

Increasing surfactant concentrations, and hence increased costs, are required to promote higher degrees of NAPL solubility above the CMC. For NAPL mobilization, the IFT will not change very much after the CMC.

2.3 Petroleum products

Subsurface contaminants can be classified into several types: synthetic organic compounds, naturally occurring organic compounds, inorganic compounds. Most

synthetic organic compounds encountered at contaminated sites are hardly soluble in water. As a result, they can exist in the subsurface as NAPLs. Many NAPLs are highly persistent in the subsurface and can not be removed in a reasonable time period by the conventional pump-and-treat technique. This persistence may be caused by slow dissolution kinetics of NAPLs, slow diffusion of the contaminants from low permeability zones (which have accumulated pollutants over decades) or resistant desorption of the contaminants by the aquifer material (Teutsch et al, 2001).

Petroleum products usually contain aromatic hydrocarbons and halogenated compounds. Table 2-1 shows the physical & chemical properties of some aromatic hydrocarbons in petroleum products. For the present study, engine oil was the chosen petroleum product. It is termed as light non-aqueous phase liquid (LNAPL) as its specific gravity is less than water. Details of the engine oil characteristics are discussed in Chapter 3.

Table 2-1 Physical & chemical properties of some aromatic compounds (Fiorenza et al, 2002)

Compound	Vapor pressure (mm Hg, 20°C)	Solubility (mg/L)	Henry's law constant (dimensionless)	log K_{oc} (at 20-25°C)
Aromatic gasoline hydrocarbons				
Benzene	95.2	1,750	0.22	1.58
Toluene	30.0	515	0.26	2.13
Ethylbenzene	10.0	152	0.32	1.98
m. p. o-xylene mixture	7.0	198	0.29	2.38

The physical & chemical properties listed in table above indicate that the petroleum products have low water solubility. Hence, it is easy for them to be trapped in the soil. Further, their low Henry's constants lead to their partitioning more into the liquid phase rather than into the air.

The aromatic hydrocarbons and halogenated compounds released from petroleum products are considered as hazardous substance by ATSDR (Agency for Toxic Substances and Disease Registry) and can cause harmful health effects. Some of these NAPLs have been recognized as priority contaminants at many sites. The transport of NAPL contaminants can cause further damage to the environment and bring potential risks to human beings.

2.4 Fate and transport of NAPL in soils

2.4.1 Introduction

In general, NAPLs are distinguished in terms of NAPL density greater than or less than water. LNAPLs are those NAPLs with densities lighter than water, whereas DNAPLs are the NAPLs with densities greater than water.

Concern about NAPLs exists because of their persistence in the subsurface and their ability to contaminate large volumes of water. A greater understanding of the transport and dissolution of NAPLs is necessary if cost-effective techniques for control and cleanup of these contaminants are to be achieved.

2.4.2 NAPL pathways in the subsurface soil

The migration of these NAPL contaminants depends primarily on the quantity released, the physical properties of the surface and the structure of the soil through which the contaminant moves (Yong et al, 1992).

When the liquid contaminant is released below the ground surface, it percolates downward to the unconfined groundwater surface. When the release involves small quantities, the contaminant may be held locally, in the void spaces of the soil and may not reach the saturated zone. The extent of movement in both the vertical and lateral directions depends on both the porosity and the permeability of the soil.

2.4.3 Transport of NAPL between the three phases

The fundamental principles involving contaminants transport between the three phases (solid, liquid and gaseous) are demonstrated by Figure 2-8. The chemical properties that affect NAPL transport may include: 1. volatility; 2. relative polarity; 3. affinity for soil organic matter or organic contaminants; 4. density and viscosity.

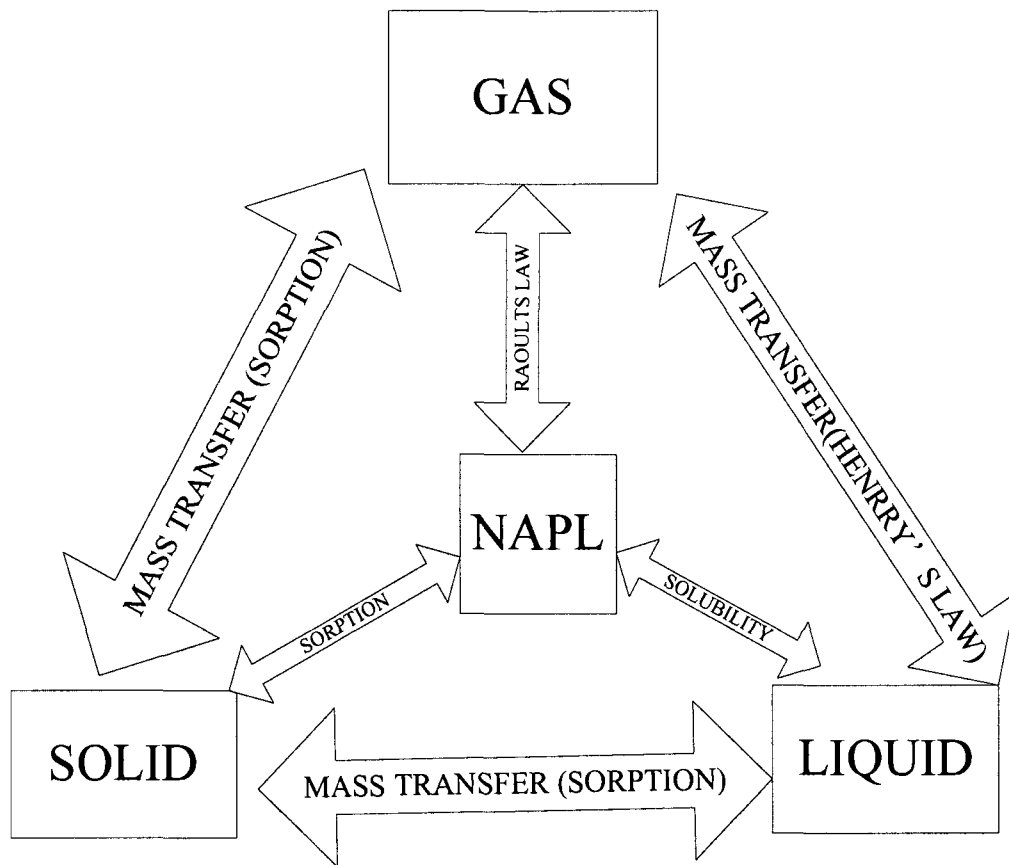


Figure 2-8 Processes involved in partitioning of NAPLs into solid, liquid and gaseous phases.

2.4.4 Raoult's law

At equilibrium between NAPLs and the vapor phase, the equilibrium partial pressure of a component is directly related to the mole fraction and its pure vapor pressure. Raoult's law can be written as

$$P = xP^0 \quad (2.1)$$

Here:

P = partial pressure of the constituent

x = mole fraction of the constituent

P^0 = vapor pressure of the pure constituent

Raoult's law is applicable under the following conditions:

1. Equilibrium conditions exist
2. The mole fraction of a constituent is greater than 0.9

2.4.5 Adsorption

In the water/soil system, sorption is recognized as one of the important factors in the determination of the fate of NAPLs. Aqueous concentrations of hydrophobic hydrocarbons in natural water systems are highly dependent on adsorption/desorption equilibrium with sorbents present in the systems. Studies suggest that the sorption of NAPLs is governed by the organic content of the substrate.

The dominant mechanism of organic adsorption is the hydrophobic bond established between a chemical and a natural organic matter in natural soil/water system. The extent of sorption can be reasonably estimated if the organic carbon content of the soil is known by using the expression $K_p = K_{oc} f_{oc}$, here f_{oc} is the fractional organic carbon content of the soil and K_{oc} is the proportionality constant for the specific NAPL between organic carbon and water. K_p is the partition coefficient for NAPL between soil and water (Yong et al, 1992).

Several main factors that influence the value of K_{oc} are listed as follows:

- Temperature
- pH
- Particle size distribution and surface area
- Salinity
- Dissolved organic matter
- Water content

2.4.5.1 Freundlich Isotherm

The Freundlich Equation is frequently used to describe the sorption of reactive solute onto the soil matrix. It is given (Lagrega et al, 2000) as:

$$S=k.C_e^n \quad (2.2)$$

$$0 < n < 1$$

Here S is the amount of NAPL solute retained by the soil, in mg/kg, C_e is the NAPL equilibrium concentration in the aqueous phase, in mg/L, k is Freundlich coefficient, and the parameter n is dimensionless.

2.4.5.2 Langmuir Isotherm

The Langmuir isotherm is a combination of the adsorption and desorption rate equations (Lagrega et al, 2000):

$$S = \frac{abC_e}{1 + bC_e} \quad (2.3)$$

In this equation, S is the concentration of NAPL adsorbed in the soil, C_e is the equilibrium concentration of solute in the aqueous phase, a is an empirical constant and b is the saturation coefficient.

2.5 Previous studies on surfactant enhanced remediation of soil

In the previous studies, surfactants are shown to have significant potential for enhancing the remediation of contaminated soil and groundwater. Some investigations have been conducted on the surfactant enhanced remediation of organics (Harwell, 1992, Chevalier, 2003).

Duffield et al. (2003) studied the mechanism of surfactant (Triton X-100) enhanced mobilization of light white mineral oil within a porous media. In this research, column studies were conducted to determine the changes of solution surface tension under different flushing conditions.

Zhu et al. (2005) made a detailed study to evaluate the feasibility of in situ remediation of a loess soil (a type of soil in China) site contaminated with diesel oil. Surfactant LAS (linear alkyl benzene sulfonate), SDS (sodium dodecyl sulfate), AEO₉ (aliphatic polyethenoxy ether) and AES (sodium alcohol polyethoxylated ether sulfate) were selected in this study. The effects of surfactant type and concentration on oil solubilization were investigated.

2.6 Summary

In this chapter, some background materials related to surfactants and NAPL contaminated soil remediation have been reviewed. In Section 2.1, in-situ soil flushing and ex-situ soil washing are introduced as two main technologies that can be combined with surfactants to remove NAPL, such as petroleum mixtures, from soils and effectively control the source of pollution. Section 2.2 describes some general characteristics of surfactants. The molecular structure of a typical surfactant, the common classification of surfactants and the mechanism of surfactant enhanced removal of NAPL from soil have been discussed. In Section 2.3, several typical petroleum products and their potential risks have been introduced. Section 2.4 contains information about fate and transport of NAPL in soils. This section includes NAPL pathways in the subsurface soil and the transport of NAPL between three phases. Raoult's Law has been proposed to explain the equilibrium between NAPL and its vapor phase. Also, Freundlich Isotherm and Langmuir Isotherm have been reviewed for the study of the distribution of NAPL between liquid and solid phase. Section 2.5 is about previous studies on surfactant enhanced remediation of soil.

Previous studies have given an indication that surfactants can enhance the NAPL removal. However, some other factors, such as the texture of soil, pH and temperature, can also influence the effectiveness of surfactant-based remediation of soil

contaminated by NAPLs. Importantly, the role of surfactants in site remediation remains unclear. In the next chapter, both batch and column tests will be set up and conducted to investigate the factors that can affect the effectiveness of surfactant and select an effective and economical surfactant for the removal of engine oil from a contaminated soil.

CHAPTER 3

EXPERIMENTAL DESIGN AND MATERIALS

3.1 Introduction

The experiments in this study are performed using both batch and column tests to select effective and economical surfactants for the removal of engine oil from an artificially contaminated soil. Engine oil is chosen as an indicator of petroleum pollutants because of its wide usage and its greater stability in the soil matrix than other petroleum products like gasoline. SDS, AOT, Brij35 are chosen as surfactants in this study. All chemicals used in this study are reagent grade. A Lambda 40 UV/VIS spectrometer (PerkinElmer Instruments) is used to detect the concentration of engine oil. Photometric accuracy of this device is ± 0.003 A.

In batch tests, soil samples were prepared by mixing sand and montmorillonite soil with the ratio of 5:1 by weight. And at the end of batch tests, the ratio of sand: clay was changed to some different values to examine the effect of soil composition on surfactant effectiveness. In column tests, the soil samples were mixed with sand and clay with a ratio of 9:1. All soil samples in both batch and column tests were contaminated by engine oil with the ratio of engine oil: soil samples=160mg: 40g.

The overall experimental design is shown in Figure 3-1.

equals 420-149 μm (U.S. standard), and this type of sand is between medium sand (500-250 μm) and fine sand (250-100 μm) according to USDA (United States Department of Agriculture) soil textural classification system. The diameter of montmorillonite clay soil is around 63 μm . The soil samples mixed by sand and montmorillonite (5:1 in batch and 9:1 in column) in this study can be classified as loamy fine sand, which may contain 70-90% fine sand, 0-30% silt, and 0-15% clay (<http://soils.usda.gov/technical/aids/investigations/texture/> accessed in Jan, 2009). The soil is air dried for 24 hours before usage. The characters of soil components are shown in table 3-1.

Table3-1 Characteristics of Sand and Montmorillonite

Name	Sand	Montmorillonite
CEC(meq/100g)	0	1.05 (meq/g) ⁽¹⁾
pH in water	6.7	3.7
Particle size	149-420 μm	63 μm

(1) Kuppa and Manias, 2005

3.3 Surfactant characteristics

Surfactant SDS (sodium dodecyl sulfate), AOT (dioctyl sodium sulfosuccinate) and Brij 35 (polyoxyethylene lauryl ether) are used to represent anionic (SDS and AOT) and non-ionic (Brij 35) surfactants, respectively. All the surfactants are obtained from Fisher Scientific Canada. As most soil surfaces are negatively charged, cationic surfactants are not chosen in this soil remediation study. The properties of

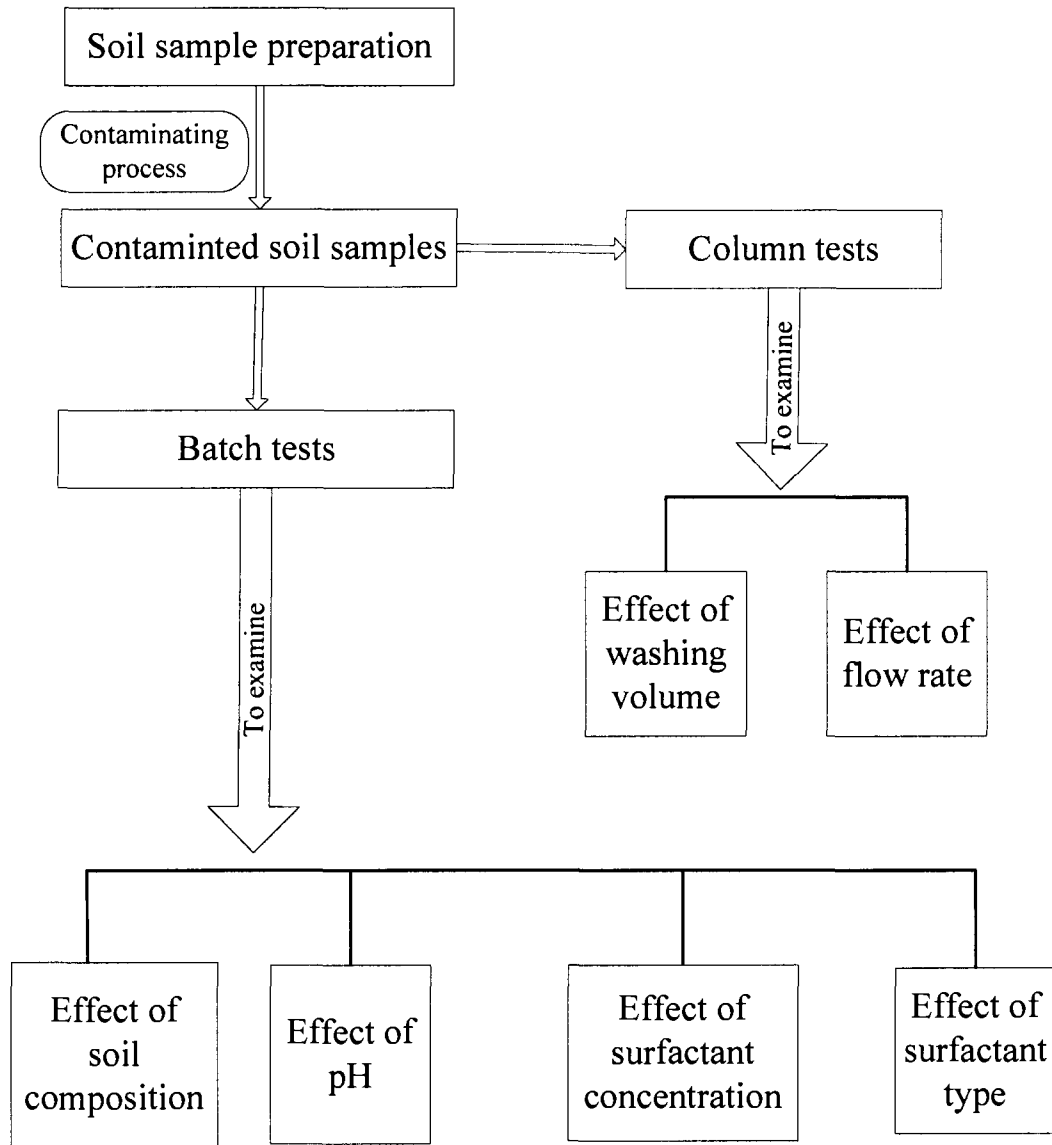


Figure 3-1 Flowchart of experimental process.

3.2 Soil preparation

The soil sample used in batch tests is a mixture of uniformly mixed sand and montmorillonite clay with a ratio of 5:1 by weight and the ratio of sand: clay in column tests is 9:1. Both sand and montmorillonite soil are purchased from Fisher Scientific Inc, Canada. The size of sand used here corresponds to mesh 40-100 which

surfactants used in this study are listed in Tables 3-2 to 3-4 and the chemical structures of these surfactants are shown in Figures 3-2 to 3-4.

Anionic surfactants:

1. SDS

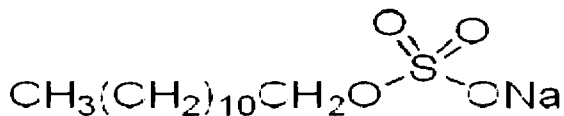


Figure 3-2 Chemical structure of SDS

Table 3-2 Properties of SDS (Fisher, 2008)

Product Name	Sodium Dodecyl Sulfate (Certified)
Categories	Anionic Surfactant
Molecular Formula	$\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$
F.W.(g)	288
Appearance	White powder
CMC(mg/L)	2100 ⁽²⁾
Specific gravity	0.4
Water solubility	10% in water

(2) Zhu et al. 2005

2. AOT

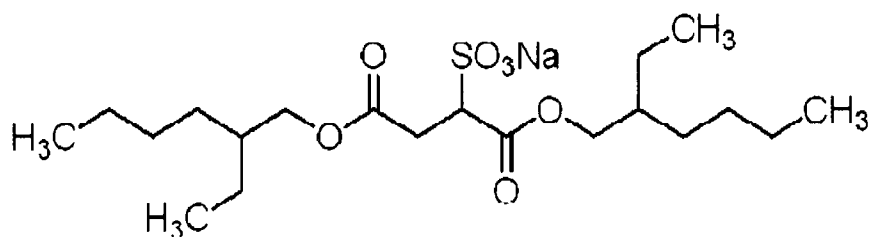


Figure 3-3 Chemical structure of Aerosol* OT.

Table 3-3 Properties of AOT (Fisher, 2008)

Product Name	Aerosol* OT Solution ,75%(w/w)
Ingredient	Sodium Dioctyl Sulfosuccinate, Ethyl Alcohol, Acetone
Categories	Anionic Surfactant
Primary Ingredient Formula	$(C_9H_{17}O_2)_2CH_2CHSO_3Na$
F.W.(g)	444
Appearance	Viscous Colorless liquid
CMC(mg/L)	1065.6 ⁽³⁾

(3) Mandal and Pal. 2000

The hydrophilic group of these two anionic surfactants (SDS and AOT) is the sodium sulfite anion ($NaSO_3^-$) and the hydrophobic groups are their respective hydrocarbon chains.

Non-ionic surfactant:

1. Brij 35

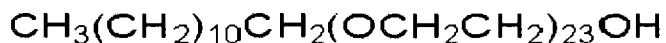


Figure 3-4 Chemical structure of Brij 35.

Table 3-4 Properties of Brij 35 (Fisher, 2008)

Product Name	Brij 35, 30% (w/w) Aqueous Solution
Ingredient	Polyoxyethylene Lauryl Ether
Categories	Non-ionic Surfactant
Molecular Formula	$(CH_2CH_2O)_{23} C_{12} H_{26} O$
Appearance	Viscous Colorless liquid
F.W.(g)	1198
CMC(mg/L)	120 ⁽⁴⁾

(4) Sanchez-Camazano et al. 2003

The hydrophilic group of the non-ionic surfactant Brij 35 is $-(\text{OCH}_2\text{CH}_2)_{23}\text{OH}$ and the hydrophobic group is the hydrocarbon chain. The oxygen in $-(\text{OCH}_2\text{CH}_2)_{23}\text{OH}$ can form hydrogen bonds with the H (hydrogen) in water, that enhances the solubility of functional group $-(\text{OCH}_2\text{CH}_2)_{23}\text{OH}$ in water.

3.4 Contaminant characteristics

The target contaminant in this study is engine oil which is selected because of its wide usage and great stability. Its low water solubility and low volatility also permit safe laboratory work. The oil is purchased from Canadian Tire Canada and its properties are listed in table 3-5.

Table 3-5 Properties of engine oil

Property	Value
Density(pound/gallon)	7.11
Kinematic Viscosity @ 40° C (cSt)	70.8mm ² /s
Average molecular weight	500
Specific gravity	0.854
Flash point(°C)	238

3.5 Experiment procedure

Batch and column experiments were conducted to investigate different parameters involved in the surfactant-enhanced removal of oil from contaminated soil. The soil samples were artificially contaminated in the laboratory.

3.5.1 Soil contamination process

Engine oil was added to clean soil samples at a ratio of 160mg oil: 40g soil. After preparatory blending with a stirring rod, the contaminated soil was thoroughly mixed by a vortex mixer for 10 minutes at high speed in batch tests. In column experiments, the soil contamination process for each column was similar. The gravimetric measurements were done with an electrical balance which had a detection limit of 0.1mg. All the newly contaminated soil was kept at room temperature for 24 h before usage to obtain adsorption equilibrium.

3.5.2 Batch experiments

Batch tests were operated at a room temperature of $24 \pm 1^\circ\text{C}$. Three different surfactants (SDS, AOT and Brij 35) at different concentrations were used as washing solutions to desorb engine oil from artificially contaminated soil. Four parts are included in batch experiments. The flowchart of batch test is shown in Figure 3-5.

1. For each type of surfactants, solutions at different concentrations under and above CMC were made to study the effect of surfactant concentration in oil desorption process.
2. The test results of three surfactants from part 1 were compared to determine the effect of surfactant type on oil desorption efficiency.
3. The ratio of sand: montmorillonite in clean soil samples was changed from 5:1 to 9:1, 1:1 and 1:4 (by weight). The ratio of engine oil: clean soil sample was kept

the same value as mentioned earlier. 1.2% SDS and 0.6% Brij 35 were selected as washing solution to study the effect of soil composition on the desorption of oil from contaminated soil.

4. 50% NaOH and 1mol/L NaOH were added to adjust the pH value in soil and surfactant solution system. The effect of pH for surfactant on oil desorption efficiency was determined. pH was measured and controlled by a pH meter which was purchased from Fisher Scientific Inc.

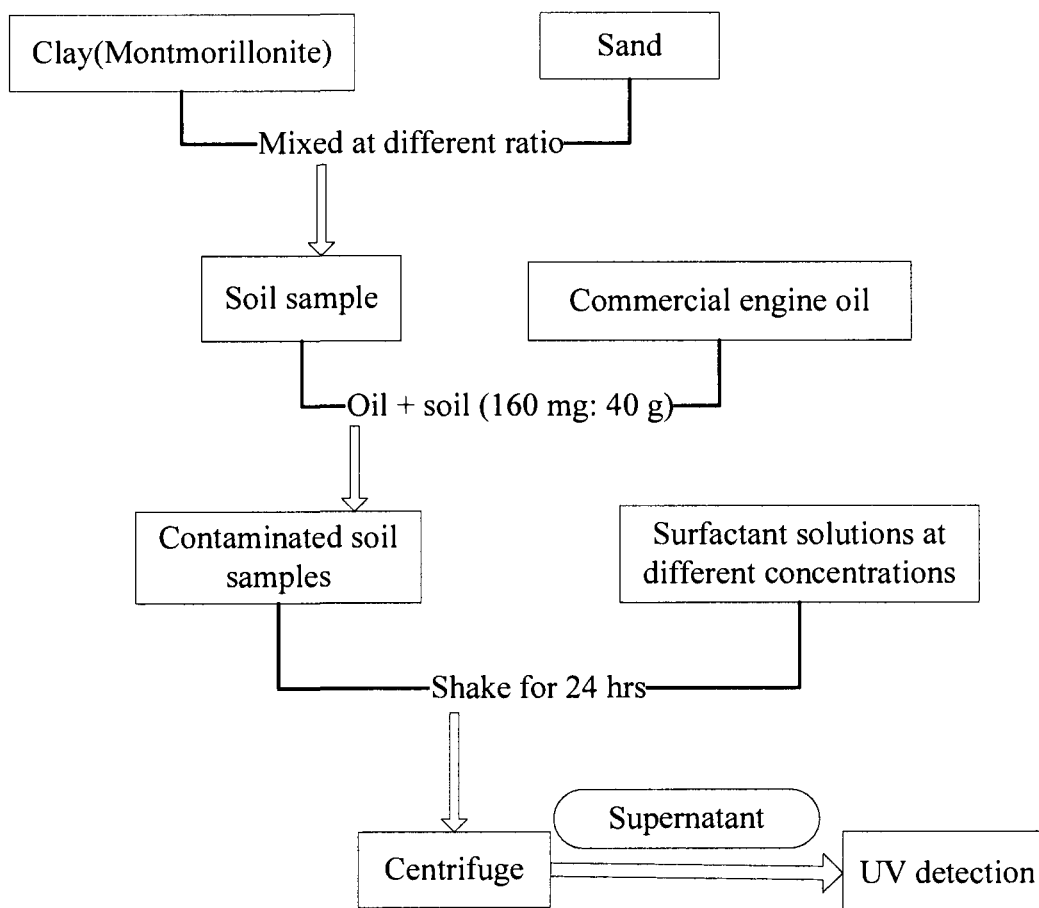


Figure 3-5 Flowchart of batch test.

3.5.2.1 Batch operation

In batch tests, contaminated soil samples (4.0g) were weighed and placed in capped centrifuge tubes (50mL). 40mL aliquots of various surfactant solutions ranging in concentration from 0.01% to 1.2% were added in each tube. The mixtures of contaminated soil sample and washing solution were placed on the wrist action shaker at a speed of 10 for 24 h to obtain desorption equilibrium and then allowed to rest for 1 hour. Following this, samples were centrifuged at 1500rpm for 30mins to separate the solid and aqueous phases. The supernatants were taken out by pipet.

After standardization of the instrument, the aqueous phase oil concentrations in the supernatant were measured using the Lambda 40 UV/VIS spectrometer at a wavelength of 275nm. The batch samples were measured three times and the reported values denote the average oil concentrations for the three measured concentrations.

3.5.3 Column experiments

3.5.3.1 Column setup and parameters

All soil column experiments were conducted at room temperature ($24\pm 1^\circ\text{C}$). The experimental set-up is shown in Figure 3-6 and Figure 3-7.

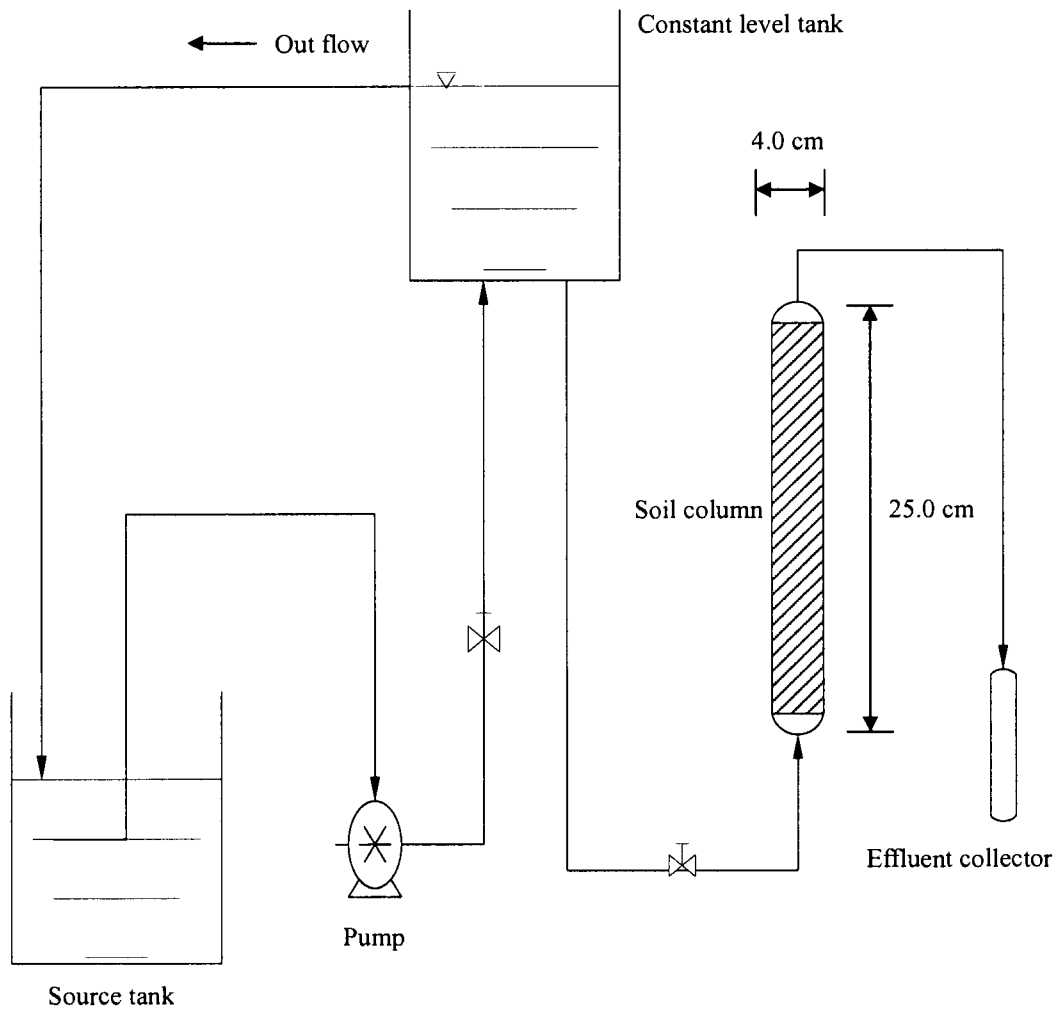


Figure 3-6 Schematic set-up of column test.

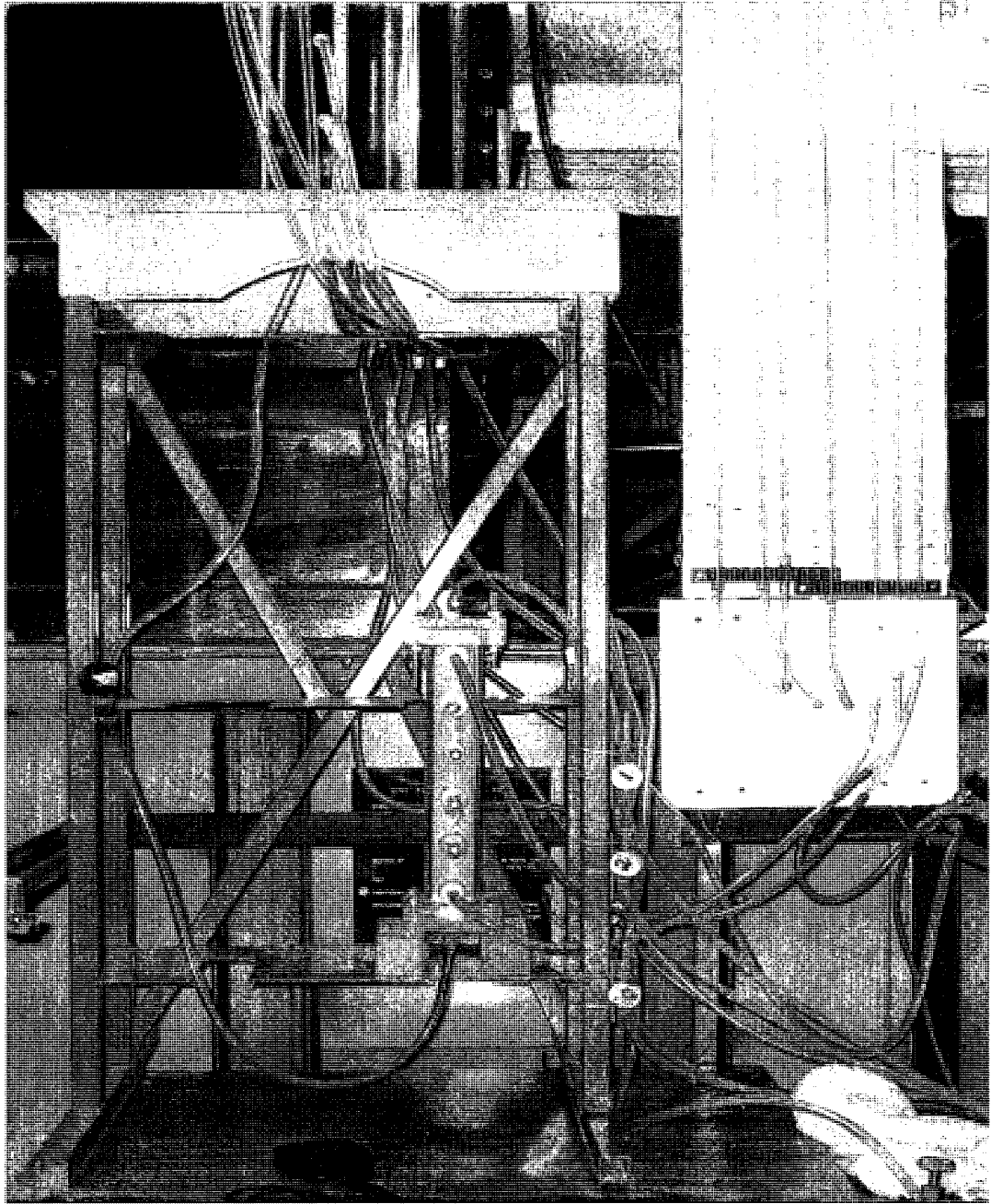


Figure 3-7 Column setup.

The internal diameter of the plexiglas column, which was measured by Vernier Caliper, is 40.0mm and the length of the column is 25.0cm. The column was also equipped at both the top and bottom with sandy disk filters with a pore size of $2\mu\text{m}$. This sandy disk filters out oil-surfactant fluid mixture and supports the soil particles.

It also allows injected fluid to spread radially and evenly, thereby promoting uniform fluid delivery.

The soil sample for each column was separately prepared with the ratio of sand: clay=9:1 (oil: clean soil =160mg: 40g). New contaminated soil was mixed thoroughly in a big plastic box using a stirring rod and then rested for 24h before usage. The soil mixture was packed into the column by tapping against the plexiglas wall after each 2cm layer added, to make the soil inside the column uniform and tight.

The other columns were prepared in the same way with the same amount of soil mixture. A peristaltic pump and a high level container were used to maintain a constant flow through the column. The valves on the pipes were used to adjust the flow rate.

3.5.3.2 Column experiment operation

A series of column experiments were conducted to investigate the effects of washing volume and flow rate on the removal efficiency of engine oil by the surfactant which was selected for batch tests.

The surfactant solution or distilled water was pumped from the source tank and passed through the soil column. The column effluent was collected after every pore volume (void volume) passed through the column. All the samples of effluent were measured using the UV spectrophotometer at least twice and the results averaged. The oil removal efficiency can be calculated by the sample concentration value and the known initial amount of oil.

3.5.4 Detection of oil concentration in distilled water

In this study distilled water was also used as a type of washing solution in both batch and column tests to compare its oil removal efficiency with the selected surfactants. As oil is almost insoluble in pure water, it is difficult to detect the oil concentration in water directly. The procedure of measuring oil concentration washed off by pure water needs an extra operation. That is the oil extraction process. In this study, HPLC grade n-hexane was chosen as an organic solvent to extract the oil washed off by distilled water. The extraction process is presented as follows:

A. In batch experiments:

1. The mixture of contaminated soil sample and distilled water was put into a centrifuge after desorption equilibrium.
2. After centrifugation, 20mL supernatant was transferred into a clean centrifuge tube with a measuring pipette.
3. 5mL n-hexane was added into the supernatant (20mL) mentioned above.
4. The liquid mixture in the centrifuge tube was capped and shaken for 10 minutes to make sure that the oil extraction into the n-hexane was complete.
5. The oil concentration in the upper liquid layer (n-hexane) was measured after standardizing the UV device.
6. The original oil concentration in distilled water can be calculated.

B. In column tests, a similar extraction method can be performed.

3.6 Summary

In this chapter, experimental materials and design processes have been presented. Section 3.1 presents an overall introduction to this chapter. Section 3.2 introduces the components of soil used in this study. Section 3.3 & Section 3.4 present the characteristics of three selected surfactants and the contaminant (engine oil). Section 3.5 presents the main content of this chapter and it explains the procedure used in the experiments. In this part, the soil contamination process is described. Operation and experimental set-up of batch and column tests are described in detail and a brief explanation of the oil extraction process is presented. The next chapter is dedicated to the discussion and analysis of the experimental results from this chapter.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 General remarks

In this study, distilled water, ionic (SDS and AOT) and non-ionic surfactants (Brij 35) were used to remove engine oil from the artificially contaminated soil. The temperature for all experiments was in the range of 24 ± 1 °C. All the experimental samples (batch & column) were measured twice to three times and the reported data denotes the average of the measured values.

4.2 Batch experiments

In this section, the effects of surfactant concentration, surfactant type, soil composition and pH on oil desorption from contaminated soil are discussed. The results of the batch tests are the average of samples measured three times.

4.2.1 Effect of surfactant concentration

Surfactant concentration is an important factor that affects the desorption efficiency of oil from contaminated soil. The batch results of the three selected surfactants tested at different concentrations are shown in Figures 4-1 to 4-3.

Related details of data such as initial pH values of surfactants before they have been added to the soil samples and the figures of standard curves are listed in

Appendix B.

As mentioned earlier, in batch experiments the ratio of oil: clean soil is 160mg: 40g and contaminated soil: washing solution is 4g: 40mL. After calculation, the initial amount of engine oil (M_i) in every 4g contaminated soil equals 153.8mg. The concentration of oil desorbed from soil into aqueous phase (mg/L) is plotted against the initial surfactant concentration (%). The oil removal efficiency can be calculated using the amount of oil desorbed from solid phase into aqueous phase (M_a) divided by the amount of initial oil in contaminated soil samples (M_i). And M_a equals the oil concentration in aqueous phase multiply the volume of washing solution. The oil concentration in aqueous phase has been measured three times for each sample. The error bars from Figures 4-1 to 4-3 stand for the relative standard deviation values at correlative points and it is found that the maximum relative standard deviation value is < 5%. For the sample with oil concentration higher than 150mg/l, the relative standard deviation value ranged from 3% to 1%.

4.2.1.1 Surfactant SDS

The results of oil desorption by surfactant SDS are shown in Table 4-1 and Figure 4-1.

Table 4-1 Desorption of engine oil by SDS solutions [SDS CMC is at 2,100mg/L]

SDS C %(w/w)	Oil Concentration(mg/L)	Desorption efficiency
0.2	77	2.0%
0.3	152	4.0%
0.6	296	7.7%
0.9	431	11.2%
1.2	558	14.7%
1.5	561	14.8%

Calculation details for Desorption efficiency= (Oil concentration × Washing volume)/
Initial amount of oil in contaminated soil sample.

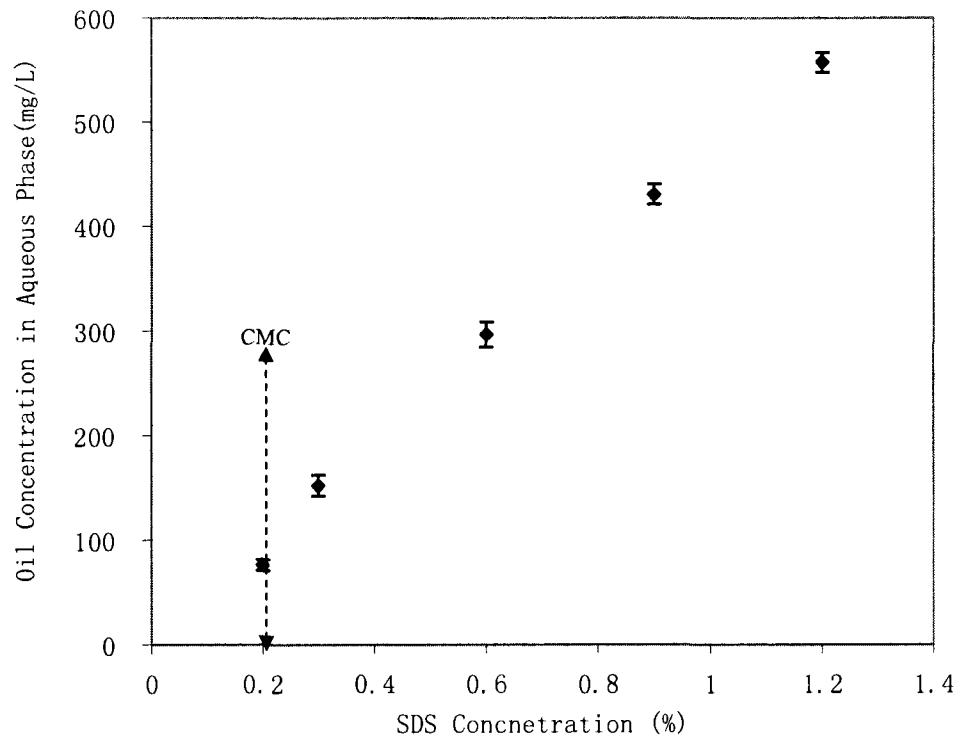


Figure 4-1 Desorption of engine oil by SDS solutions.

The results of oil desorption with SDS show that the oil concentration in aqueous phase increases with the concentration of surfactant SDS. The oil desorption efficiency did not be enhanced significantly when the SDS concentration reached 1.2%. From a cost perspective, the concentration of 1.2% could be considered as the optimal concentration for surfactant SDS to remove engine oil in this case.

4.2.1.2 Surfactant AOT

Table 4-2 shows the results of oil desorption by surfactant AOT solution at different concentrations.

Table 4-2 Desorption of engine oil by AOT solutions [AOT CMC is at 1,065mg/L]

AOT C %(w/w)	Oil Concentration(mg/L)	Desorption efficiency
0.1	151	3.9%
0.2	178	4.6%
0.4	239	6.2%
0.6	292	7.7%
0.8	265	6.9%

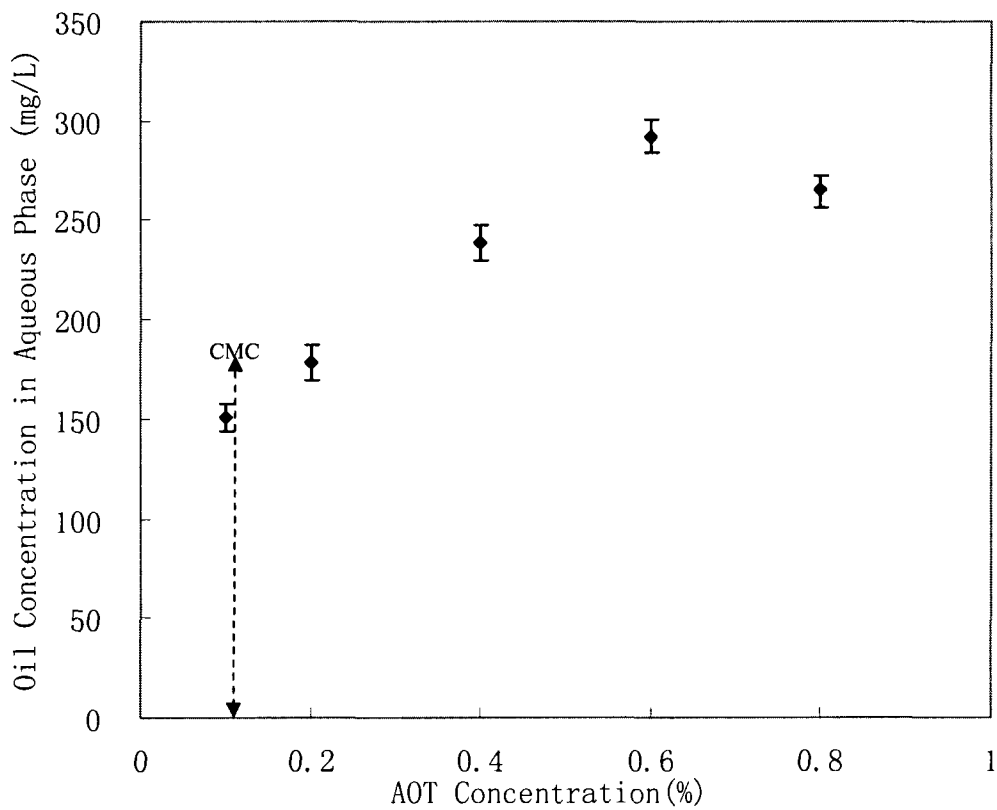


Figure 4-2 Desorption of engine oil by AOT solutions.

The test results above indicate that oil desorption efficiency does not increase with the concentration of AOT when the AOT concentration > 0.6%. Therefore, 0.6% can be considered as the optimal concentration for AOT to remove oil in this study.

4.2.1.3 Surfactant Brij 35

Brij 35 is a non-ionic surfactant and the main data collected from the batch tests are listed in Table 4-3. Figure 4-3 shows the relationship between the concentration of Brij 35 and the concentration of engine oil desorbed from contaminated soil.

From the figure and data collected, it can be seen that 0.6% is the best concentration for surfactant Brij 35 to desorb the engine oil from the contaminated soil sample in this study.

Table 4-3 Desorption of engine oil by Brij 35 solutions [Brij 35 CMC is at 120mg/L]

Brij 35 %(w/w)	Oil Concentration(mg/L)	Desorption efficiency
0.01	196	5.1%
0.1	302	7.9%
0.3	493	12.8%
0.5	618	16.1%
0.6	700	18.4%
0.8	698	18.4%

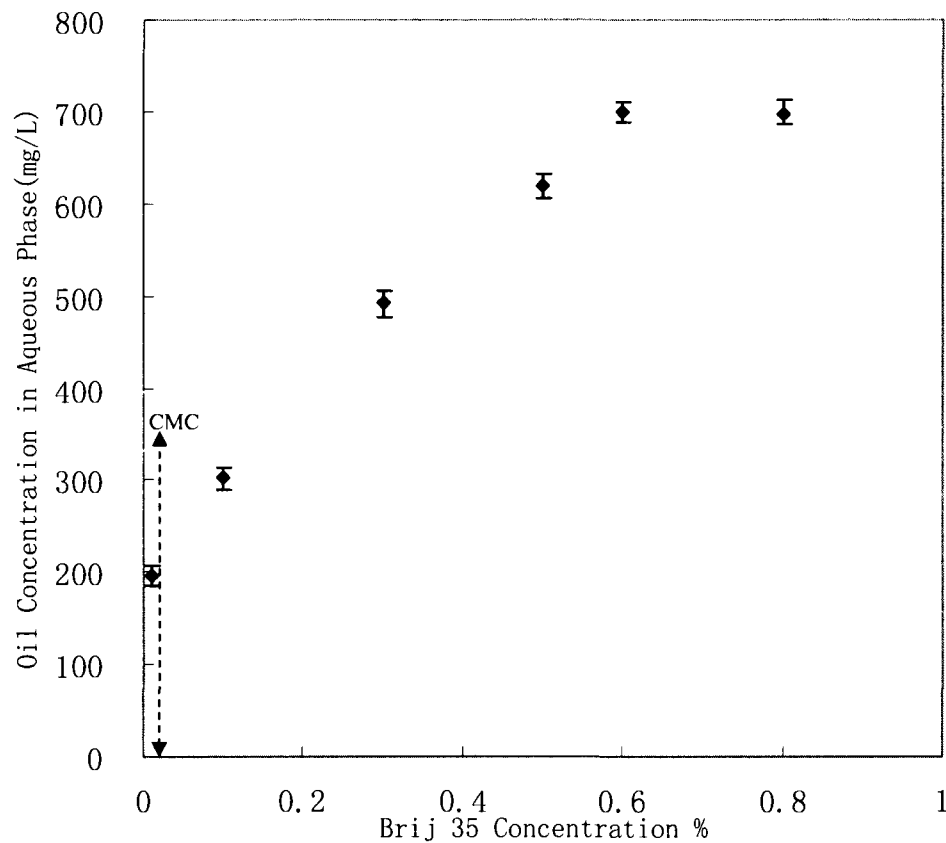


Figure 4-3 Desorption of engine oil by Brij 35 solutions.

CMC is defined as the critical micelle concentration beyond which micelles are formed. Figures 4-1 to 4-3 indicate that the concentration of oil removed into the aqueous phase tends to be higher with increased surfactant concentrations above their CMC. As mentioned in Chapter 2, the concentration of micelles increases as the surfactant concentration increases above its CMC. The existence of micelles can noticeably enhance the solubility of an oil in the aqueous phase.

The CMC values of SDS and AOT are 2100mg/L and 1065mg/L (Chapter 3). CMC is an important factor to evaluate the effectiveness of a surfactant. Generally, a

surfactant with lower CMC may be applied preferentially in the oil removal process. The batch results of the two ionic surfactants demonstrate that surfactant SDS achieved a better desorption efficiency of oil from contaminated soil than surfactant AOT. There could be two reasons for this: Firstly it may be attributed to their chemical configuration. The hydrophilic functional group (NaSO_3^-) of AOT is in the middle of its hydrophobic chain and the hydrophilic functional group of SDS is at the end of its hydrophobic chain. The effectiveness decreases with the position of hydrophilic functional group starting from the end and moving towards the middle of its hydrophobic chain (Fu et al, 2001). Secondly, in batch tests the pH range of the soil solution was from 4.3 to 5.0. The weak acid environment may decrease the effectiveness of surfactant AOT more than SDS. Also, loss of surfactants occurs as some of them get adsorbed onto the soil.

4.2.2 Effect of surfactant type

Table 4-4 summarizes the batch tests results of oil desorption by the three surfactants at their optimal concentrations.

Table 4-4 Oil desorption results by different surfactants.

Surfactant	Optimal concentration (%) w/w	Ratio of surfactant conc. to its CMC	Desorption efficiency
SDS	1.2	5.7	14.7%
AOT	0.6	5.6	7.7%
Brij 35	0.6	50	18.4%

At equilibrium, the concentration of aqueous phase oil which is desorbed by distilled water is 38mg/L and the engine oil desorption efficiency is 1%. Figures 4-1 to 4-3 show that the highest aqueous concentrations of desorbed engine oil by SDS, AOT and Brij 35 were 558mg/L, 292mg/L and 700mg/L respectively. The corresponding desorption efficiencies of oil are 14.7, 7.7 and 18.4 times greater than that by pure water. The optimal washing concentrations for the surfactants generally occurred at specific concentrations above their CMC.

From the above tests results, the non-ionic surfactant Brij 35 shows better oil desorption efficiency than the two anionic surfactants. That might be because the non-ionic surfactant is not influenced by the ionic interactions of the soil solution.

4.2.3 Effect of soil composition

The objective of this part of the study is to examine the effect of soil composition on engine oil desorption from contaminated soil. Four types of different soils (sand plus montmorillonite mixtures) were prepared and contaminated with oil in the lab. The compositions of the prepared soil samples No.1-4 were 9:1; 5:1; 1:1; 1:4 (ratios of sand: montmorillonite). The soils were washed using SDS and Brij 35 surfactant solutions at their optimal concentrations of 1.2% (w/w) and 0.6% (w/w), respectively. The process of oil spiking of the soils was as described above for the batch tests.

The test results for 1.2% SDS solution are listed in Table 4-5. The oil desorption results by 0.6% Brij 35 solution are shown in Table 4-6.

Table 4-5 Oil desorbed by 1.2% SDS from soil samples No.1-4.

Soil Sample No.	1	2	3	4
Sand: montmorillonite ratio	9:1	5:1	1:1	1:4
Oil concentration (mg/L)	1390	558	152	79
Oil desorption efficiency %	36.6	14.7	4.0	2.1

Table 4-6 Oil desorbed by 0.6% Brij 35 from soil samples No.1-4.

Soil Sample No.	1	2	3	4
Sand: montmorillonite ratio	9:1	5:1	1:1	1:4
Oil concentration (mg/L)	1780	700	182	95
Oil desorption efficiency %	46.8	18.4	4.8	2.5

Oil is adsorbed mainly by van der Waals forces and not through ionic interaction with the soil particles. The results shown in Figure 4-4 indicate that engine oil desorption efficiency is enhanced as the ratio of sand in the soil increases. The results show that the non-polar oil molecules interact mainly with the montmorillonite and not the sand particle surfaces. Under the same soil conditions, the oil desorption efficiency by non-ionic surfactant Brij 35 is better than anionic surfactant SDS.

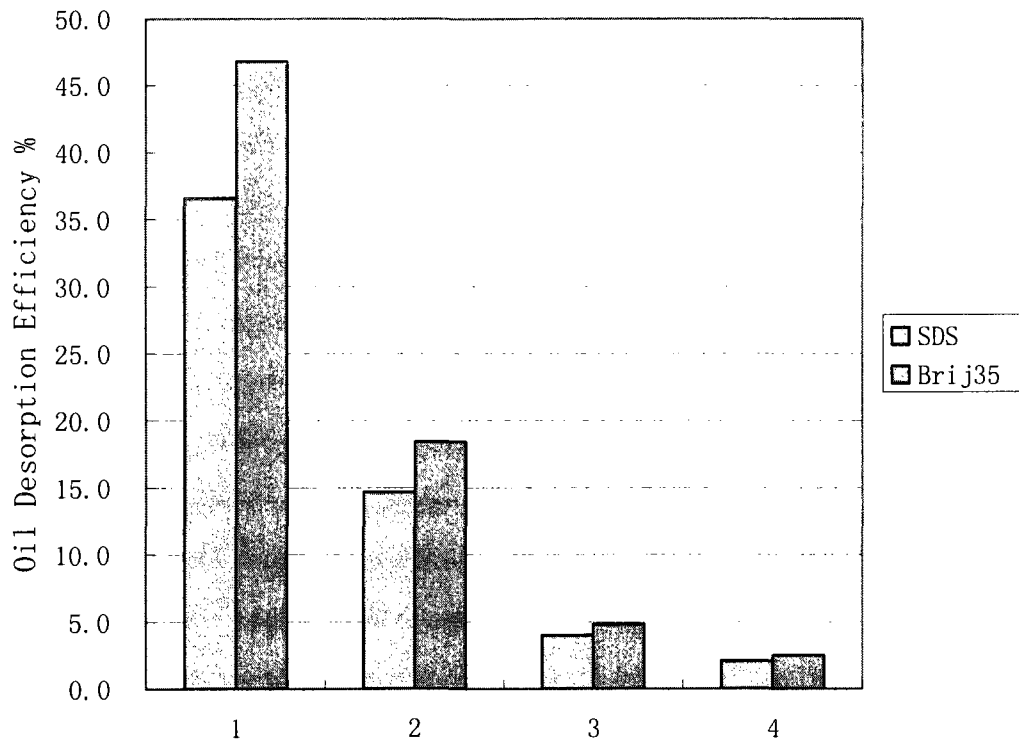


Figure 4-4 Effects of soil composition on engine oil desorption process with 1.2% SDS and 0.6% Brij 35 surfactant solutions. The x axis labels stand for soil samples No.1-4 with composition sand: montmorillonite= 9:1; 5:1; 1:1; 1:4, respectively.

4.2.4 Effect of pH

To know the effect of pH in the oil desorption process, a few tests were performed. As the original range of pH value in soil solution was weakly acidic (4.3-5.0), 50% (w/w) and 1mol/l NaOH solutions were added to keep the pH in the

range of 6.7-7.0. The surfactants used here were 1.2% SDS, 0.6% AOT and 0.6% Brij 35 and the volume in each case was 40mL respectively.

The detailed results are shown in Tables 4-7 to 4-9.

Table 4-7 Effect of pH on the oil desorption process with 1.2% surfactant SDS.

1.2% SDS	pH range 4.3-5.0	pH range 6.7- 7.0
Oil concentration (mg/L)	558	625
Oil desorption efficiency	14.7%	16.4%

Table 4-8 Effect of pH on the oil desorption process with 0.6% surfactant AOT.

0.6% AOT	pH range 4.3-5.0	pH range 6.7- 7.0
Oil concentration (mg/L)	292	470
Oil desorption efficiency	7.7%	12.4%

Table 4-9 Effect of pH on the oil desorption process with 0.6% surfactant Brij 35.

0.6% Brij35	pH range 4.3-5.0	pH range 6.7- 7.0
Oil concentration (mg/L)	700	729
Oil desorption efficiency	18.4%	19.2%

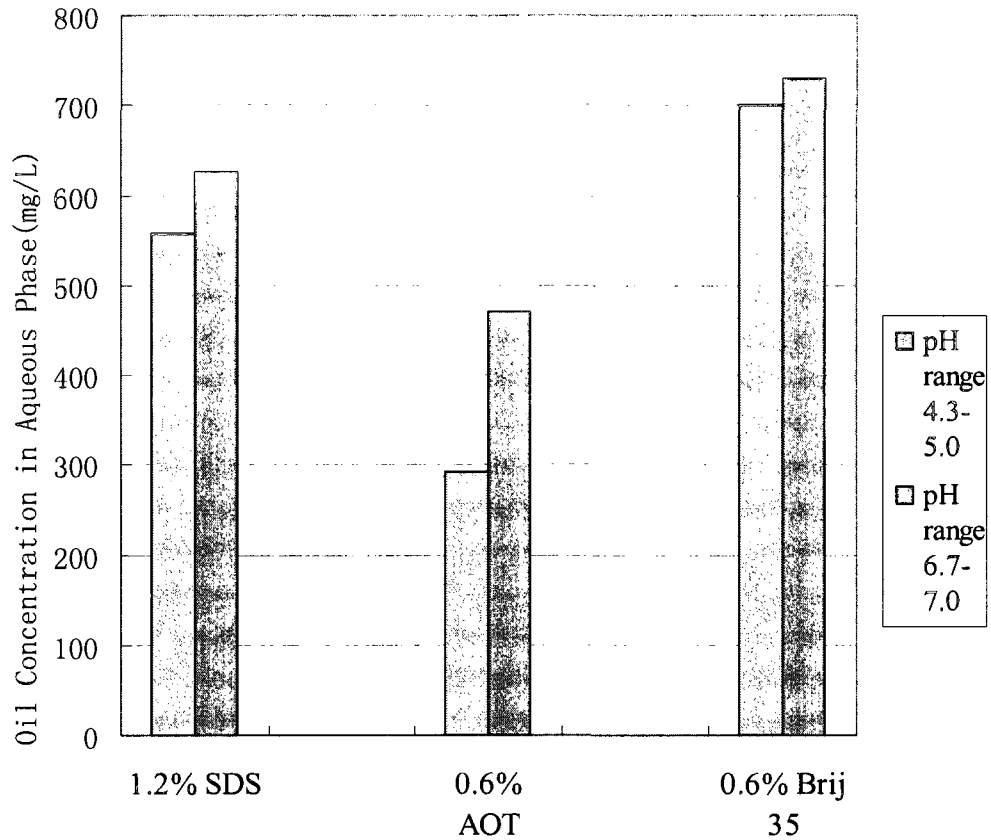


Figure 4-5 Effect of pH on the oil desorption process by 1.2% SDS, 0.6% AOT and 0.6% Brij 35 respectively.

The results (Figure 4-5) indicate that the pH value did not affect non-ionic surfactant Brij 35 significantly in the oil desorption process. Lower pH may decrease the oil removal efficiency of anionic surfactants, especially for AOT. That's because the non-ionic surfactant is not involved in the ionic interaction in the solution while the anionic surfactants could be affected by the H^+ concentration in the environmental system.

4.2.5 Examination of surfactant enhanced oil removal through a study of the pollutant partition process

Under sorption-desorption equilibrium conditions, engine oil will partition between two different phases. This can be quantified in terms of the distribution coefficient (K_d). In a soil water system, K_d represents the partition of a chemical (engine oil) between soil and water and K_d is usually expressed as the ratio of solute to soil and to the solution. The equation is:

$$K_d = \frac{C_s}{C_e} \quad (4.1)$$

where C_s (mol/kg) is the chemical (oil) concentration in the solid phase; C_e (mol/L) is the chemical (oil) concentration in solution at equilibrium.

In the presence of a surfactant, K_d can also be described by Equation (4.2) (Jafvert, 1991):

$$K_d = [C]_s / ([C]_w + [C]_{mic}) \quad (4.2)$$

where $[C]_{mic}$ (mol/L) is the mole of solute (oil) in micelles per liter of solution, $[C]_w$ (mol/L) is the concentration of solute (oil) dissolved by water, $[C]_s$ (mol/kg) is the solute (oil) concentration in soil.

When surfactants exist in solution, another important parameter is the micelle-water partition coefficient (K_m). This indicates the partition of NAPL between the surfactant micelles and the water phase (Zhou and Zhu, 2005). The partition coefficient expressed in concentration units is defined by Equation (4.3) (Almgren, et al 1979):

$$K_m = \frac{[C]_{mic}}{[S]_{mic}[C]_w} \quad (4.3)$$

where $[S]_{mic}$ (mol/L) is the concentration of surfactant in micellar form per liter of solution, and K_m (M^{-1}) is the partition coefficient.

Sorption to soils often correlates with the organic carbon content of the soil as the sorption process approaches equilibrium (Jafvert et al, 1995):

$$K_{oc} = \frac{[C]_s}{[C]_w f_{oc}} \quad (4.4)$$

Here, K_{oc} is the organic carbon normalized partition coefficient, and f_{oc} (organic carbon / soil) is the fraction of organic carbon present in the soil.

Combining eqs (4.2), (4.3) and (4.4) results in the following equation

$$K_d = K_{oc} f_{oc} / (1.0 + K_m [S]_{mic}) \quad (4.5)$$

The above equation shows that the values of K_d correlate with K_m . For the same oil-contaminated soil, we can assume K_{oc} and f_{oc} are constants (Zhu, et al 2005). For the same surfactant level, increased desorption of NAPL would occur under the conditions of higher values of K_m and lower values of K_d . In contrast, lower K_m and higher K_d values would result in decreased desorption of oil from the soil surfaces.

To quantify the effectiveness of surfactant in solubilizing the test compounds (engine oil), the molar solubilization ratio (MSR) is introduced. The MSR is defined as the number of moles of organic compound solubilized per mole of surfactant added to solution (Attwood and Florence, 1983). The increase in solubilize concentration per unit increase in micellar surfactant concentration is equivalent to the MSR. And in the presence of excess hydrophobic organic compound, the MSR value can be

obtained from the slope of the curve formed when the solubilize concentration is plotted against surfactant concentration (Edwards, et al 1991):

$$MSR = C_e / C_{surf} = (C_1 - C_{cmc}) / (C_{1surf} - CMC) \quad (4.6)$$

where C_{surf} is the surfactant concentration in solution, C_{cmc} (mol/L) is the apparent solubility of organic compound at CMC, C_1 (mol/L) is the apparent solubility of organic compound, when surfactant concentration equals C_{1surf} , and C_{1surf} (mol/L) is the surfactant concentration which is greater than the CMC.

An expression for the value of K_m provided by Edwards (1991) is:

$$K_m = \left(\frac{1}{C_{cmc} V_m} \right) \frac{MSR}{1 + MSR} \quad (4.7)$$

Here, V_m is the molar volume of water (0.01805L/mol at 25°C).

For our case, in the presence of excess oil, the correlations between concentration of engine oil and the surfactant concentration in solution are shown in Figures 4-6 to 4-8. The data related to the tests are provided in Appendix Tables B4-1 to B4-3. (Average molecular weight of oil is 500).

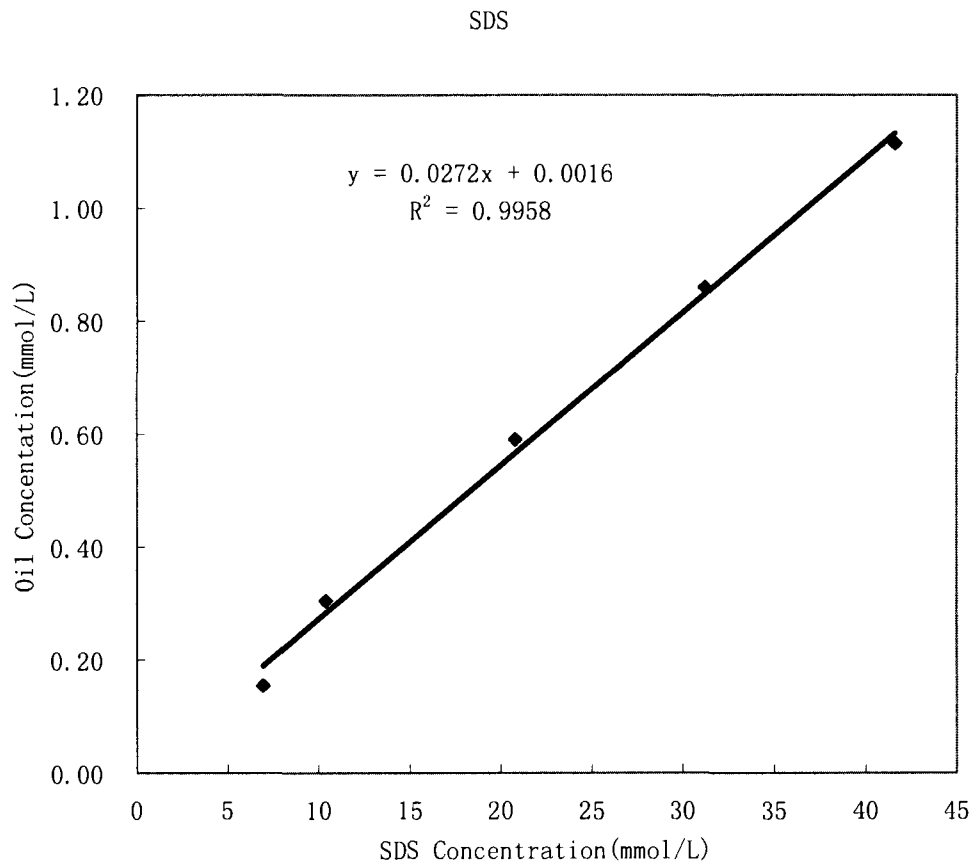


Figure 4-6 Determination of engine oil MRS in SDS solutions.

For SDS, MSR is 0.0272 and at CMC (7.28mmol/L) C_{cmc} equals 0.20mol/L, $K_{mSDS} = 7.34 \times 10^3$. (R^2 is the square of the sample correlation coefficient in the case of simple linear regression.)

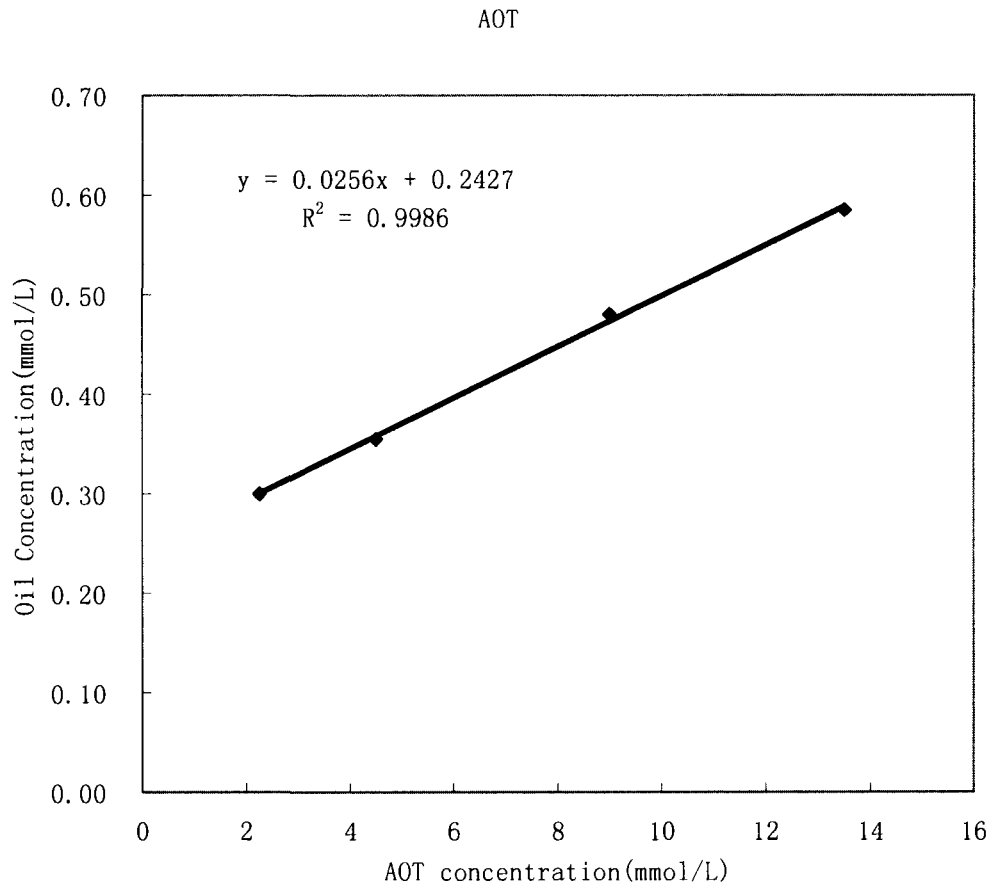


Figure 4-7 Determination of engine oil MRS in AOT solutions.

For AOT, MSR is 0.0256 and at CMC (2.40mmol/L) C_{cmc} equals 0.30mmol/L,

$$K_{mAOT} = 4.61 \times 10^3.$$

Brij 35

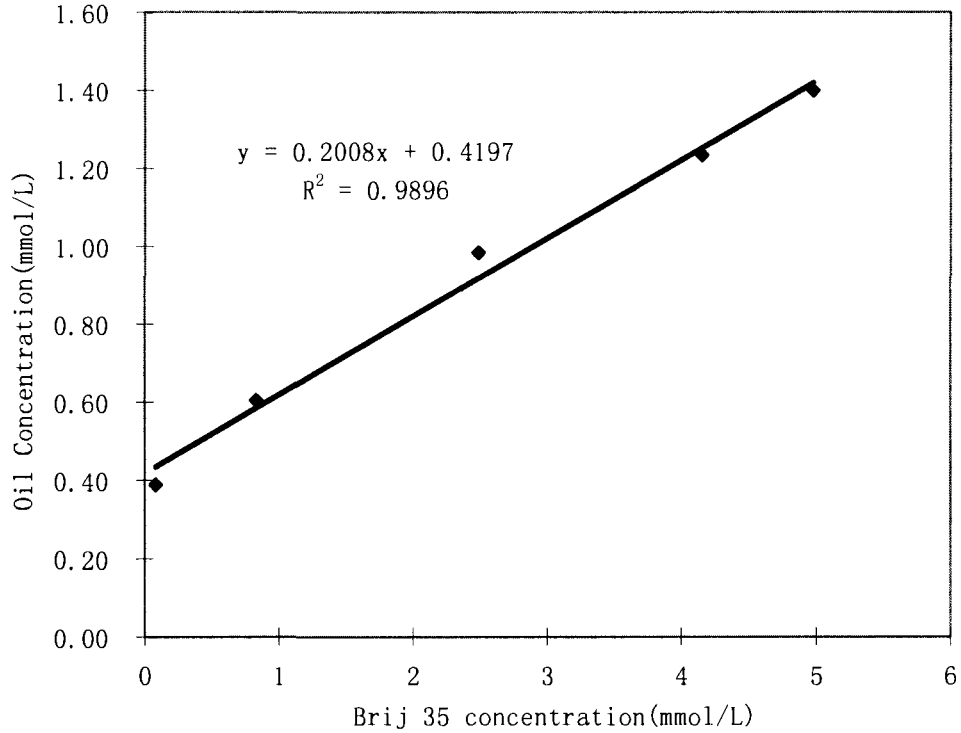


Figure 4-8 Determination of engine oil MRS in Brij 35 solutions.

For Brij 35, MSR is 0.2008 and at CMC (0.10mmol/L) C_{cmc} equals 0.44mmol/L,

$$K_{mBrij\ 35} = 21.1 \times 10^3.$$

Comparing the results, it is clear that $K_{mBrij\ 35} > K_{mSDS} > K_{mAOT}$ and from the Equation 4.5 we can see that $K_{dBrij\ 35} < K_{dSDS} < K_{dAOT}$. As discussed earlier in this section, the surfactant which provides the higher value of K_m and lower value of K_d has a better oil removal efficiency. So the result of this study is that Brij 35 has the

best oil removal efficiency from contaminated soil compared to the other surfactants tested.

4.3 Column studies

The effects of washing volume and flow rate on oil removal from contaminated soil are discussed in this section. The results of batch tests showed that non-ionic surfactant Brij 35 had a better oil removal efficiency than the other two surfactants. In column studies, surfactant Brij 35 was therefore selected to make washing solutions. Distilled water was used as the control. The samples from the column experiments were measured twice as described above for the batch tests, and the data listed in this report are averaged values of the two measurements.

4.3.1 Oil removal efficiency comparison between water and Brij 35 solution

In batch experiments three surfactants were used to remove engine oil from contaminated soil (sand-montmorillonite mixture). The results indicated that surfactants could enhance the removal of engine oil compared to pure water. However, the conditions of batch experiments, which are similar to soil washing techniques, are a little different from those (soil flushing techniques) in the field where the soil is stationary and not mixed with water. Although the influence of factors such as surfactant type and concentration can be provided by batch tests, there are still some other factors that can affect the removal of oil like washing volume and the flow rate of the washing solution. To reproduce field conditions, column studies were therefore

conducted.

Oil removal from soil columns were evaluated with distilled water and surfactant solution. The batch tests established that Brij 35 at a concentration of 0.6% had the best effectiveness for oil removal of the three surfactants tested. Consequently, in column studies 0.6% Brij 35 was selected to compare oil removal efficiency to distilled water.

The effects of washing volume and flow rate were studied in this section. The hydraulic conductivity of the soil in the column was measured and determined to be $(5.98 \pm 0.09) \times 10^{-3} \text{cm/s}$ (See appendix A). The pore volume (void volume) of the packed soil in each column was calculated to be 125 cm^3 . Table 4-10 lists some relevant details pertaining to the column studies.

Table 4-10 Column properties

Extraction Agent	Mass of soil (g)	Bulk density(g/cm^3)	Flow rate (mL/min)
Distilled water	419.6	1.34	10
0.6% Brij 35	419.6	1.34	10
0.6% Brij 35	419.6	1.34	5
0.6% Brij 35	419.6	1.34	30

In column tests, the first part was to compare the oil removal efficiency by distilled water and by 0.6% Brij 35. The flow rate was equal to 10mL/min, the total amount of oil in one column (W_{oil}) was $419.6\text{g} \times \frac{40}{1000+40} = 16.1\text{g}$, and the pore

volume (V_{pore}) was 125 cm^3 . Tables C-1 to C-2 provide the data related to the column tests.

Figure 4-9 shows the relationship between the amount of oil removed and the volume of washing solution. It is clear that Brij 35 appears to be much more effective for removal of oil compared to pure water under the same conditions.

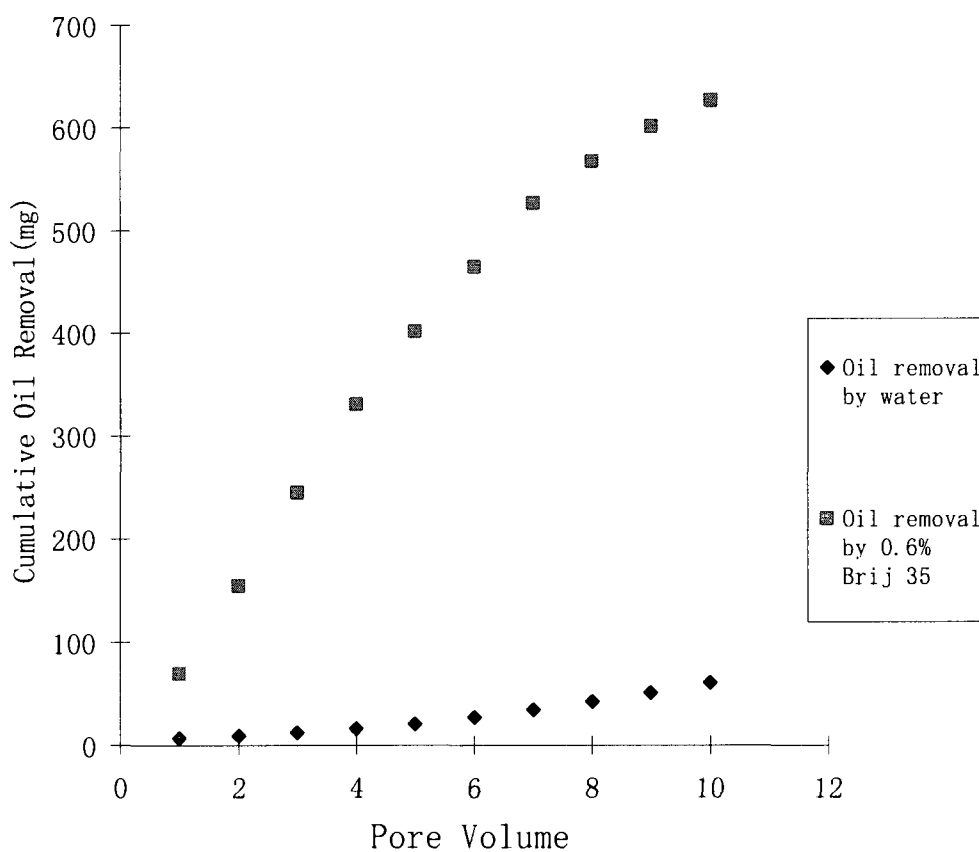


Figure 4-9 Oil removed by distilled water and 0.6% Brij 35 at a flow rate of 10mL/min.

Batch experimental results indicated that the addition of anionic and non-ionic surfactants can enhance desorption of oil from contaminated soil. The enhancement

by 0.6% Brij 35 was noted to be 18.4 times higher than by distilled water. In column studies, the cumulative amounts of oil removed by distilled water and 0.6% Brij 35 were 56.6mg and 601.7mg at 10 pore volumes respectively. The column tests also demonstrate that surfactant solution can enhance the oil removal from contaminated soil compared to pure water. Since the oil concentration in 0.6% Brij 35 effluent of this column test is 199 mg/L after 10 pore volumes (see Table C-2), the oil left in the column soil can still be removed by continuing soil flushing process.

4.3.2 Effect of flow rate

The flow rate is an important factor that affects the oil removal effectiveness in the column tests. In this part of the study, the flow rate was varied over a range of 5mL/min to 30mL/min using 0.6% Brij 35 as washing solution. The time of washing varied from 250 minutes to 42 minutes. One pore volume was equal to 125mL.

Figures 4-10 to 4-12 illustrate the oil removal results at different flow rates. Tables C-2 to C-4 provide the data related to the tests. The general trend of the oil removal curves for the three different flow rates was found to be similar in this study. The quantity of engine oil removed is primarily related to the quantity of the washing solution and oil removal increases with increased volume of washing solution.

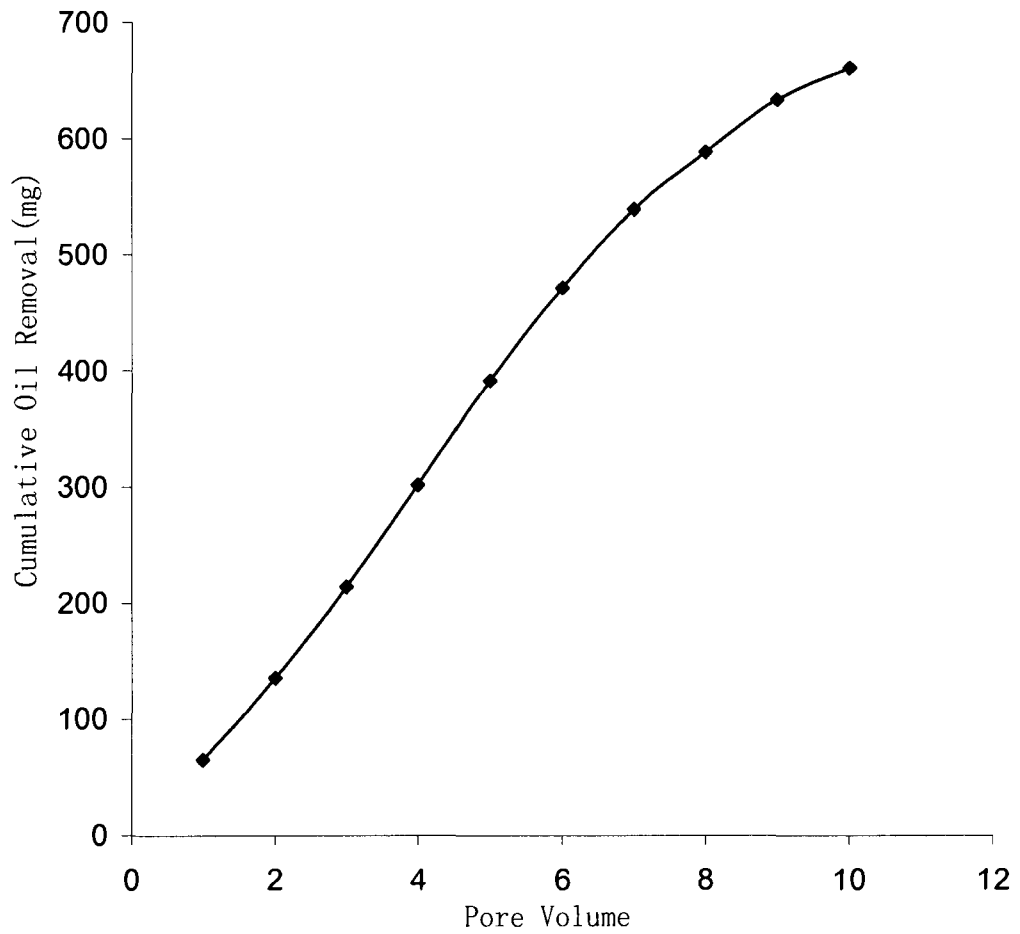


Figure 4-10 Oil removal by 0.6% Brij 35 at a flow rate of 5mL/min.

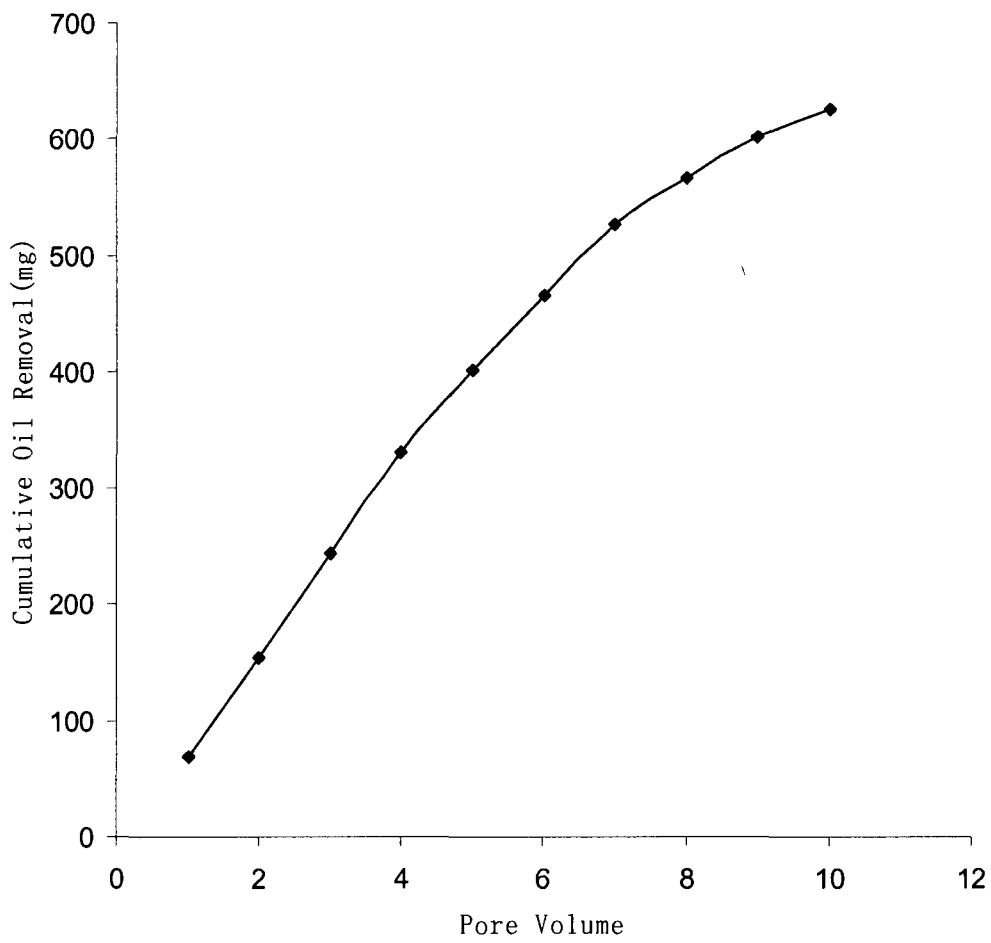


Figure 4-11 Oil removal by 0.6% Brij 35 at a flow rate of 10 mL/min.

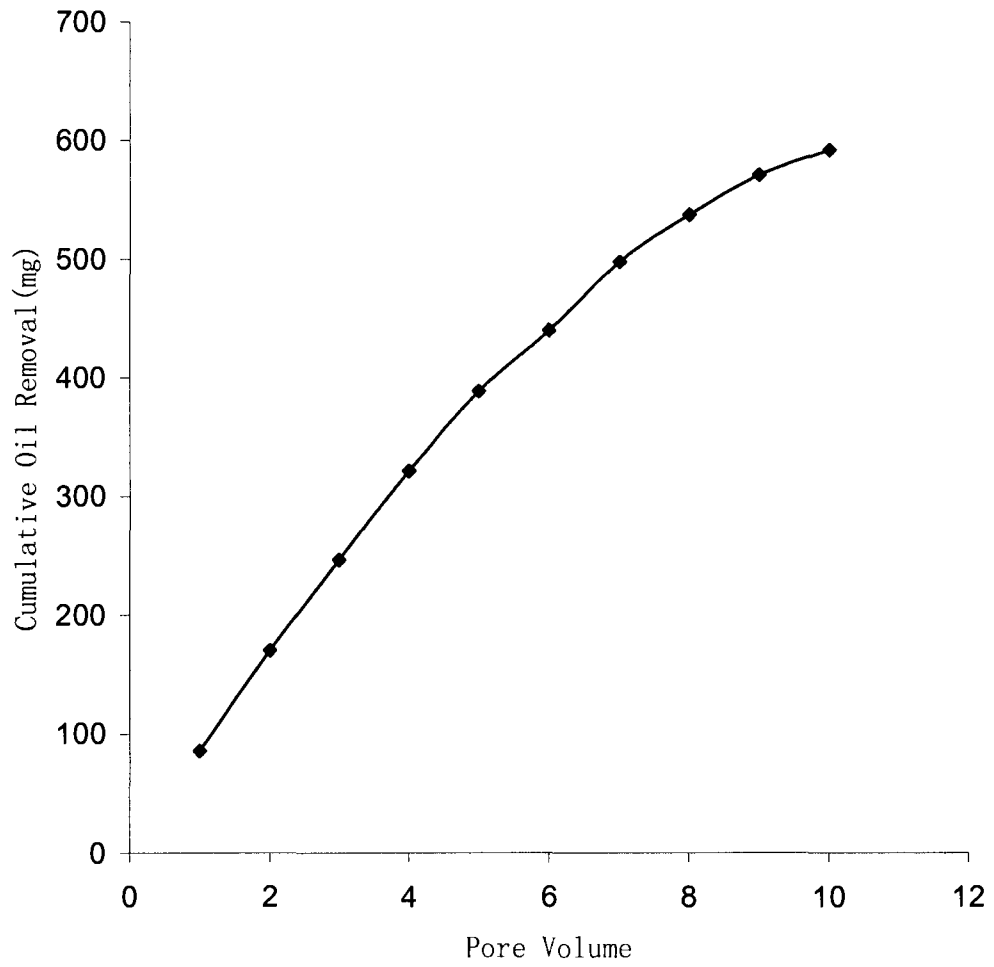


Figure 4-12 Oil removal by 0.6% Brij 35 at a flow rate of 30mL/min.

Oil Removal by Different Flow Rate

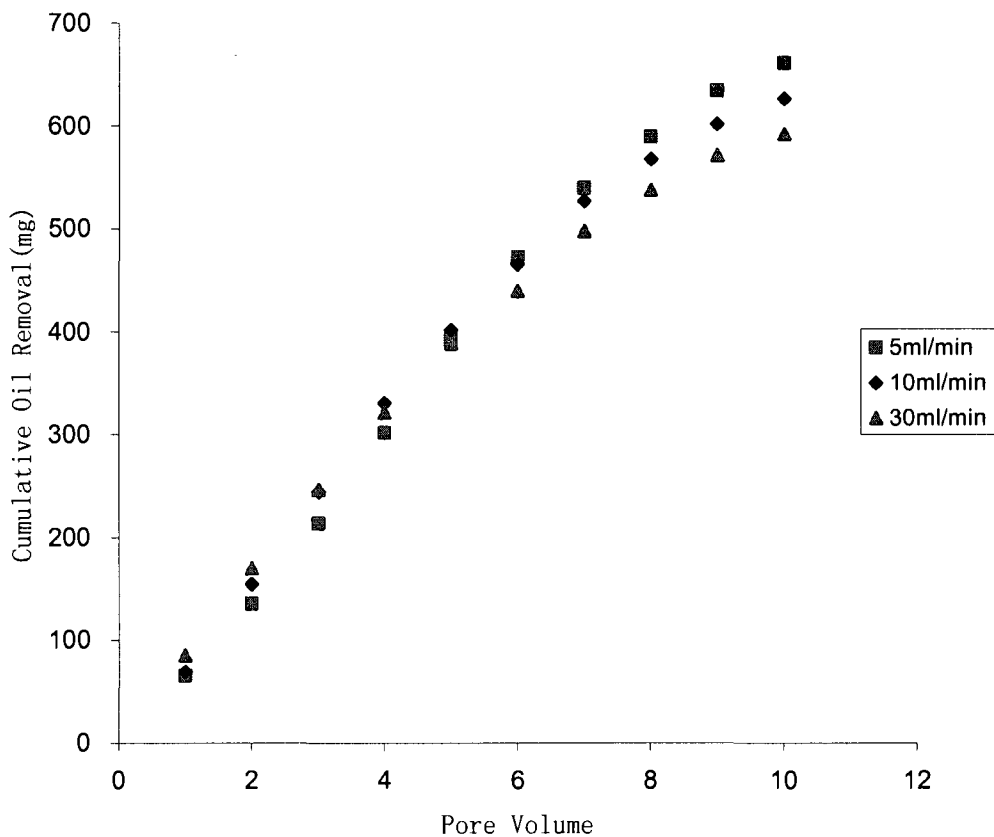


Figure 4-13 Cumulative oil removal by 0.6% Brij 35 at three different flow rates.

Figure 4-13 illustrates the cumulative oil removal at different flow rates with 0.6% Brij 35 solution. It indicates that flow rates did not significantly affect engine oil removal at the beginning of the tests, but with increasing washing volume, lower flow rates appear to be more desirable for oil removal. At the lowest flow rate 5mL/min, the engine oil removed is 661.0mg after 10 pore volumes. While at the highest flow rate 30mL/min, the engine oil removed is 592.4mg in the same condition. With the

same washing volume, the washing duration at the flow rate of 5mL/min is 250mins and the washing duration at the flow rate of 30mL/min is 42mins. The results represent that higher oil removal efficiency at a lower flow rate may contribute to the more sufficient contact between the washing solution and the contaminated soil due to longer washing time.

Generally, the results demonstrate that the removal of oil mainly depends on the volume of the washing solution. With the same amount of washing solution, lower flow rates tend to improve oil removal efficiency mainly due to the longer contact time between the surfactant and the oil-soil mixture. Higher flow rates are recommended when there is some requirement for a short treatment time or the pore volume is small.

4.4 Summary

In this chapter, experimental results and factors that influence the tests results are discussed. Section 4.1 is a brief remark about the experiments. The main results of the batch tests are presented in Section 4.2.

In Section 4.2, the effects of surfactant concentration and surfactant type on oil desorption efficiency are analyzed. The tests results indicate that the concentration of oil removed into the aqueous phase tends to be higher with increased surfactant concentration above the CMC. The major factors of the soil system that influence the oil desorption process, such as soil composition and soil pH, are also discussed in this section. Engine oil desorption efficiency was shown to be enhanced with increasing sand ratio in the soil (sand-montmorillonite mixture). The pH of the soil does not

affect the non-ionic surfactant noticeably because the non-ionic surfactant is not involved in the ionic interactions in the soil solution. At the end of this section, oil desorption efficiencies by the three surfactants are compared. Some empirical equations are used to calculate the K_d (distribution coefficient) and K_m (micelle-water partition coefficient) values of engine oil in the presence of the three surfactants individually. The results demonstrate that the non-ionic surfactant Brij 35 has the best effectiveness in the oil removal process from the soil compared to the other surfactants tested.

Section 4.3 presents the results from column tests. Under the same conditions, 0.6% (w/w) Brij 35 and distilled water were used as washing solutions to compare their oil removal efficiency for oil-contaminated soil. Also, the effects of flow rates (5mL/min, 10mL/min and 30mL/min) were studied. The results demonstrate that the oil removal efficiency mainly depends on the volume of washing solution. With the same washing volume, lower flow rates appear to be more desirable for oil removal. To determine the specific requirements for oil removal from a given soil, the column experiment results can be further verified by changing the flow rate and washing volume to determine the exact trend needed to maximize oil removal.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Concluding remarks

The present study was undertaken to evaluate the potential of three different surfactants to enhance the remediation of a commercial petroleum product (engine oil) from contaminated soils of different compositions (sand-montmorillonite mixtures) in order to select the effective and economical surfactants for the NAPLs removal process. Both batch and column experiments were performed in the lab to investigate the sorption/desorption behavior of the petroleum product using a soil-surfactant aqueous solution system, and the major factors which could affect the oil removal efficiency, such as soil composition, pH, flushing flow rates and washing volumes. Commercial engine oil was selected as a typical petroleum product because of its wide usage and good stability. Two anionic surfactants (SDS and AOT) and one non-ionic surfactant (Brij 35) were used in this study as surfactants in the soil washing solutions.

5.2 Summary of research findings

1. Batch tests indicated that all three of the surfactants used in this study can enhance the removal of commercial engine oil from soil. The efficiency of

desorption of engine oil was determined to be high and ranked as follows: Brij 35 (18.4%) > SDS (14.7%) > AOT (7.7%). Compared to distilled water alone (1%), desorption efficiencies with surfactants are almost 7 to 18 times higher.

2. Batch tests also showed that the non-ionic surfactant Brij 35 at the lower concentration (0.6%) was the optimal surfactant for oil removal of the three surfactants tested. Batch test results indicated that the best concentrations for SDS, AOT and Brij 35 to desorb oil from the same contaminated soil were respectively 1.2%, 0.6% and 0.6%. As the unit prices of these three surfactants are similar, based on a cost perspective, the surfactant that has the highest oil desorption efficiency at the lowest concentration could be considered as the optimal one. The experimental results and the analysis according to empirical equations proved that the non-ionic surfactant Brij 35 at 0.6% is more effective in oil removal.

3. Soil composition can affect the desorption of oil from contaminated soil. From the batch test results, it was readily observed that surfactant enhanced oil desorption from soil was significantly less effective with increasing of montmorillonite content in the soil. For the soil with the lowest clay content (sand: montmorillonite= 9:1), the oil desorption efficiency with 0.6% Brij 35 is 46.8%. For the soil with the highest clay content (sand: montmorillonite= 1:4), the oil desorption efficiency with 0.6% Brij 35 is 2.5%. The results confirmed the fact that sandy soils are more suitable for surfactant remediation than clay soils. This

is likely because clay sorption reduces surfactant effectiveness (Lee, et al 2001).

4. Batch tests also demonstrated that the pH of the soil environment affected surfactant enhanced oil desorption from contaminated soil. Desorption with the anionic surfactants SDS and AOT was more affected by the pH value than desorption with the non-ionic surfactant Brij 35. This is because the non-ionic surfactant Brij 35 was not involved in ionic interactions with the soil particles in the soil solutions.

5. The effects of flow rate and the washing capacity of surfactants were examined in the column tests. The results demonstrated that oil removal mainly depended on the volume of the washing solution. With the same amount of washing solution the lower flow rate had better oil removal efficiency due to its longer contact time with the soil mixture. At the lowest flow rate 5mL/min, the oil removed is 661.0mg after 10 pore volume. At the highest flow rate 30mL/min, the oil removed is 592.4mg under the same conditions. The washing time at the lowest flow rate is five times longer than that at the highest flow rate.

This study investigated the factors which affect the surfactant enhanced petroleum product (engine oil) removal efficiency from soil, such as soil composition (ratio of sand: clay), pH, flushing flow rates and washing volumes. The application of the non-ionic surfactant Brij 35, which has not been used widely before, was also

studied, and it was found to be a more effective and economical surfactant, which has the highest oil desorption efficiency (18.4%) at the lowest concentration (0.6%), for common engine oil removal from soil.

5.3 Recommendations for future work

1. There are some other factors that affect surfactant enhanced NAPLs removal efficiency of oil, such as temperature and contaminant aging. These factors could be studied in future work.
2. The column experiments can be further verified by repeating the tests with a wider range of flow rates and washing volumes to achieve specific requirements.
3. Future research should include studies related to the cost effectiveness of the contaminant removal process involving natural soils.
4. The oil removal efficiency under field conditions may be slightly different from that measured in laboratory experiments due to the existence of other factors influencing oil removal from natural soils. In general, no single technology can remediate an entire site because of the multiple contaminants in the soil matrix (Diane, 1998). In field remediation, surfactant enhanced soil flushing or soil washing should be combined with some other treatment technologies according to the specific conditions at the site.

5. The fertilizer solution containing N, P, K could be added to the remediated site to promote the growth of microorganisms in the soil after the surfactant enhanced soil flushing or soil washing process.

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APPENDIX A

A. Measurement of soil hydraulic conductivity (Hillel, 1980, Jury et al, 1991)

1. Procedure

- 1) Measure the diameter (D) and length (L) of column.
- 2) Pack exactly the same amount of contaminated soil as those in the column experiments.
- 3) Sandy disk filters are placed at both top and bottom of the column.
- 4) Install the experimental setup shown as in Figure 3-7 in Chapter 3.
- 5) Record the height (H) between the water surface of the container and the top of the column.
- 6) Collect the outflow in a graduated cylinder and record the outflow vs. time at 25mL intervals.
- 7) After the time interval for 25mL outflow remains constant for five consecutive readings (this indicates that steady state flow condition is attained) begin the hydraulic conductivity (K) test.
- 8) Record the test time (t) and outflow volume (V).
- 9) Calculate K by the flowing equations:

$$q = -K \frac{H}{L} \tag{1}$$

$$q = Q/A \tag{2}$$

$$Q = V/t \tag{3}$$

$$A = \pi (D/2)^2 \quad (4)$$

2. Experimental results and calculations

Table A-1 Parameters of column installation.

Diameter (D) mm	Section area (A) cm ²	H (cm)	L (cm)	H/L
40.0	12.56	81	25	3.24

Table A-2 Soil hydraulic conductivities.

No.	V (mL)	t (s)	Q=V/t (mL/s)	q=Q/A (cm/s)	K (cm/s)
1	500	2020	0.2475	0.0197	6.08x10 ⁻³
2	700	2897	0.2416	0.0192	5.93x10 ⁻³
3	900	3739	0.2407	0.0192	5.93x10 ⁻³

The hydraulic conductivity can be calculated as the average of the following three values:

$$K = (6.08 \times 10^{-3} + 5.93 \times 10^{-3} + 5.93 \times 10^{-3}) / 3 = 5.98 \times 10^{-3} \text{ cm/s}$$

Standard

$$\text{deviation} = \sqrt{\frac{1}{(N-1)} \sum_{i=1}^N (x_i - \bar{x})^2} = \sqrt{\frac{(6.08 - 5.98)^2 + (5.93 - 5.98)^2 + (5.93 - 5.98)^2}{2}}$$

$$\times 10^{-3} = 0.09 \times 10^{-3} \text{ cm/s}$$

The range of the hydraulic conductivity can be expected to be $(5.98 \pm 0.09) \times 10^{-3} \text{ cm/s}$.

B. Measurement of pore volume (Jury et al, 1991)

$$V_{\text{pore}} = (W_{\text{sat}} - W_{\text{dry}}) / \rho_{\text{water}}$$

Table A-3 Calculation of pore volume.

W_{sat} (g)	W_{dry} (g)	ρ_{water} (g/cm ³)	V_{pore} (cm ³)
1598.8	1473.6	1	125

($w_{\text{soil}} = 419.6$ g in each column)

Bulk density of soil in each column = $419.6/V = 419.6/(\pi r^2 L)$

$$= \frac{419.6}{3.14(2.0)^2 25} = 1.34 \text{g/cm}^3$$

APPENDIX B

RESULTS OF BATCH EXPERIMENTS

B1. Surfactant SDS

Table B1-1 Initial pH value of SDS solutions with concentration ranging from 0.2% to 1.5%.

SDS Conc.	0.2%	0.3%	0.6%	0.9%	1.2%	1.5%
Initial pH	6.21	6.20	6.15	6.10	6.02	6.00

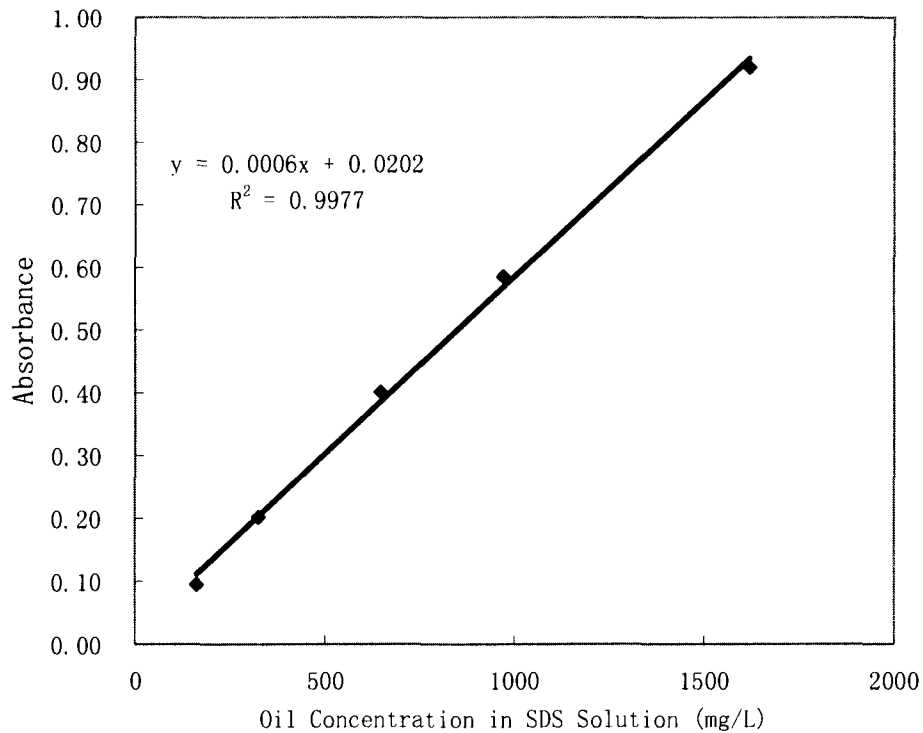


Figure B1-1 Standard curve of oil concentration vs. absorbance in SDS solutions

B2. Surfactant AOT

Table B2-1 Initial pH value of AOT solutions with concentration ranging from 0.1% to 1.2%.

AOT Conc.	0.1%	0.2%	0.4%	0.6%	0.8%	1.2%
Initial pH	6.30	6.35	6.38	6.22	6.32	6.02

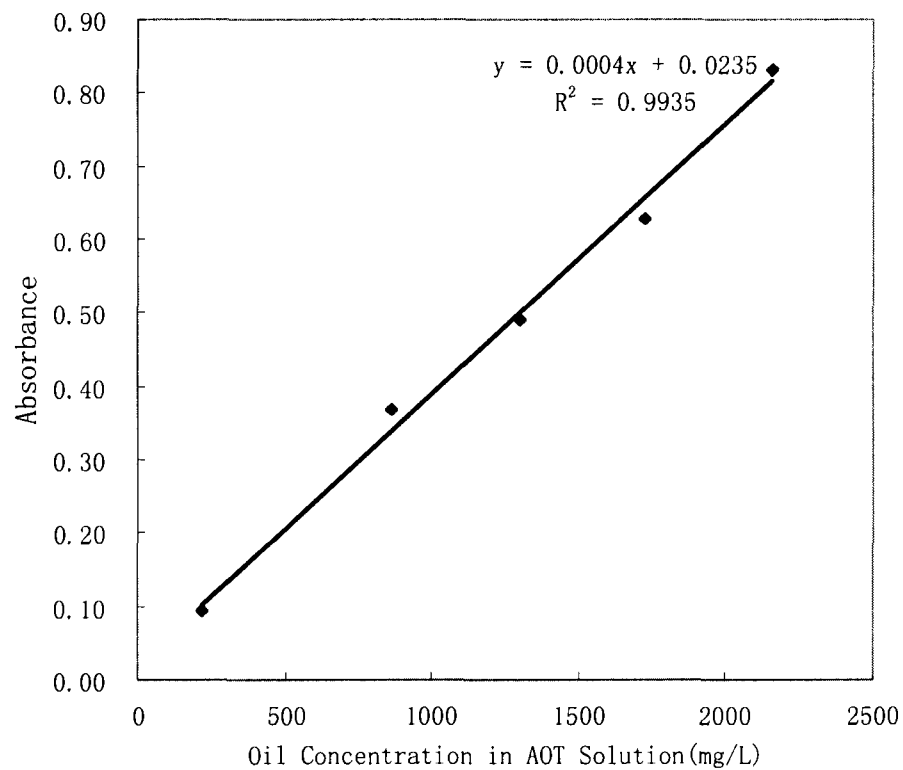


Figure B2-1 Standard curve of oil concentration vs. absorbance in AOT solutions

B3. Surfactant Brij 35

Table B3-1 Initial pH value of Brij 35 solutions with concentration ranging from 0.01% to 1.2%

Brij 35 Conc.	0.01%	0.1%	0.3%	0.5%	0.6%	0.8%	1.2%
Initial pH	6.31	6.22	5.89	5.38	5.39	5.33	5.30

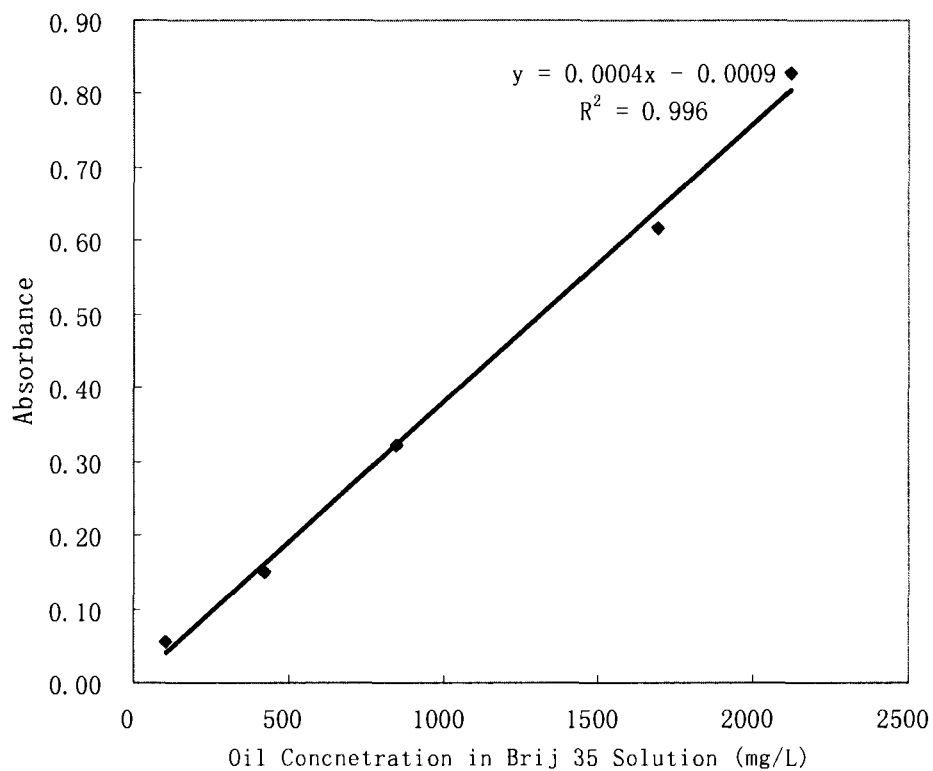


Figure B3-1 Standard curve of oil concentration vs. absorbance in Brij 35 solutions

B4. Analysis of surfactants efficiency with experimental equations

Table B4-1 Determination of engine oil MRS in SDS solutions

Concentration of SDS in solution (mmol/L)	Concentration of Oil in solution (mmol/L)
6.93	0.15
10.40	0.30
20.80	0.59
31.20	0.86
41.60	1.12

Table B4-2 Determination of engine oil MRS in AOT solutions

Concentration of AOT in solution (mmol/L)	Concentration of Oil in solution (mmol/L)
2.25	0.30
4.50	0.36
9.00	0.48
13.50	0.58

Table B4-3 Determination of engine oil MRS in Brij 35 solutions

Concentration of Brij 35 in solution (mmol/L)	Concentration of Oil in solution (mmol/L)
0.08	0.39
0.83	0.61
2.49	0.99
4.15	1.24
4.98	1.40

APPENDIX C

RESULTS OF COLUMN EXPERIMENTS

Table C-1 Average data of engine oil removal from column by distilled water

Flow rate: 10mL/min

No.	Pore volume ($V_{\text{pore}} \text{ cm}^3$)	Oil concentration $C_{\text{oil}} \text{ (mg/L)}$	Oil removed (mg)	Cumulative removal (mg)
1	1	57	7.1	7.1
2	2	67	8.4	15.5
3	3	60	7.5	23.1
4	4	50	6.3	29.3
5	5	43	5.4	34.8
6	6	47	5.8	40.6
7	7	39	4.9	45.5
8	8	39	4.8	50.3
9	9	31	3.8	54.2
10	10	19	2.4	56.6

Calculation details for Cumulative removal of No. $n = V_{\text{pore}} \sum_n C_{\text{oil}}$

Table C-2 Average data of engine oil removal from column by 0.6% Brij 35

Flow rate: 10mL/min

No.	Pore volume ($V_{\text{pore}} \text{ cm}^3$)	Oil concentration $C_{\text{oil}} \text{ (mg/L)}$	Oil removed (mg)	Cumulative removal (mg)
1	1	556	69.6	69.6
2	2	679	85.0	154.6
3	3	721	90.2	244.8
4	4	686	85.8	330.6
5	5	568	71.1	401.7
6	6	507	63.5	465.2
7	7	493	61.7	526.9
8	8	324	40.5	567.5
9	9	274	34.3	601.7
10	10	199	24.8	626.6

Table C-3 Average data of engine oil removal from column by 0.6% Brij 35

Flow rate: 5mL/min

No.	Pore volume ($V_{\text{pore}} \text{ cm}^3$)	Oil concentration $C_{\text{oil}} \text{ (mg/L)}$	Oil removed (mg)	Cumulative removal (mg)
1	1	522	65.3	65.3
2	2	560	70.1	135.4
3	3	629	78.7	214.1
4	4	703	87.9	302.0
5	5	720	90.1	392.1
6	6	639	79.9	472.0
7	7	539	67.5	539.5
8	8	396	49.6	589.1
9	9	358	44.8	634.0
10	10	216	27.1	661.0

Table C-4 Average data of engine oil removal from column by 0.6% Brij 35

Flow rate: 30mL/min

No.	Pore volume ($V_{\text{pore}} \text{ cm}^3$)	Oil concentration $C_{\text{oil}} \text{ (mg/L)}$	Oil removed (mg)	Cumulative removal (mg)
1	1	685	85.8	85.8
2	2	678	84.8	170.6
3	3	609	76.2	246.8
4	4	599	74.9	321.8
5	5	538	67.4	389.1
6	6	406	50.9	440.0
7	7	463	58.0	498.0
8	8	316	39.5	537.5
9	9	269	33.7	571.2
10	10	169	21.2	592.4