Biosurfactant Enhanced Remediation of Heavy Metal Contaminated Soil

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ABSTRACT

Biosurfactant Enhanced Remediation of Heavy Metal Contaminated Soil

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Pollution is the most serious of all environmental problems and poses a major threat to the health and well being of millions of people and global ecosystems. Heavy metals in the environment are a source of some concern because of their potential reactivity, toxicity, and mobility in the soil. Multireaction models (MRMs) could be used basically to present the metal fate and transport in the subsurface. A number of remediation technologies have been developed for the remediation of heavy metal contaminated soils. The specific technology selected for treatment of a metal-contaminated site will depend on the metal speciation and other site-specific characteristics. Soil flushing, an in-situ process, can be used to remove metals from the soil by water or additives. The use of biosurfactants to enhance remediation of contaminants has recently received increasing interest, though research in this area has been limited.

In this study, column experiments were conducted in three main phases. The first phase was to investigate the main parameters that influence the foam quality and stability. Foam generated by a rhamnolipid solution displayed high qualities from 90% to 99% and stabilities varied from 17 to 41 minutes. The second phase was carried out to study the pressure gradient build-up in the soil column with foam flowing through under different conditions (flow rate, foam quality, biosurfactant solution concentration), which varied from 0.3 kPa/cm to 6.6 kPa/cm. In the third phase, the biosurfactant (JBR425, mixed rhamnolipids) foam enhanced removal of heavy metals (Cd, Ni) from the contaminated soil was investigated. The soil was characterized as a sandy soil contaminated with Cd (1706 ppm) and Ni (2010 ppm). Best results were obtained from foam generated by the 0.5% rhamnolipid solution with an initial pH value of 10 after 20-pore-volume flushing, which removed 73.2% of the Cd and 68.1% of the Ni. Removal efficiencies by foam generated from chemical surfactant Triton X-100 were investigated as comparisons, which removed 64.7% of the Cd and 57.3% of the Ni. Rhamnolipid and Triton X-100 solutions (0.5%) without foam and distilled water with adjusted pH values were also used to flush through the contaminated soil column as controls.

This research shows that rhamnolipid foam may be an effective, non-toxic means for the remediation of heavy metal contaminated sites even though experiments were conducted in idealized conditions. However, as a promising innovative technology, few investigations have been done, thus, further experiments are required before this technology can be used for larger in-situ applications.

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I would like to express my thanks to Dr. Catherine N. Mulligan, my supervisor, for her knowledgeable suggestions and continued support towards the culmination of this research.

Special thanks to Mr. Ronald Parisella, the Environmental Engineering lab instructor, for his help in conducting the laboratory work.

To my parents, sisters and brothers

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List of Abbreviations

AEC	anion exchange capacity
CEC	cation exchange capacity
CGA	colloidal gas aphron
CMC	critical micelle concentration
CTAB	cetyltrimethylammonium bromide
DOM	dissolved organic matter
DPC	diphenylthiocarbazone
EDTA	ethylenediamine tetra-acetic acid
EPA	Environmental Protection Agent U. S.
HLB	hydrophilic-lipophilic balance
ISV	in situ vitrification
LMMEUF	ligand-modified micellar-enhanced ultrafiltration
MRM	multireaction model
NAPLs	non-aqueous phase liquids
PAHs	polynuclear aromatic hydrocarbons
PCBs	polychlorinated biphenyls
RE	removal efficiency
SDS	sodium dodecyl sulfate
SOM	soil organic matter
S/S	solidification and stabilization

List of Symbols

A	column cross-section, cm^2
b	dimensionless parameter
C	solute concentration in solution, mg/L
$f(C)$	isotherm expression as a function of concentration C, mol/L
k	hydraulic conductivity, cm/s
k_1, k_2, k_3, k_4, k_5 and k_6	reaction rate coefficients, h^{-1}
k_b	reaction rate coefficient, h^{-1}
k_{ce}	reaction equilibrium constant
k_d	linear distribution coefficient, ml/g
k_f	distribution coefficient, l/kg or ml/g
k_s	associated rate coefficient, h^{-1}
L	column length, cm
n	nonlinear parameter
m	nonlinear parameter
ΔP	pressure drop, kPa
ρ	soil bulk density, g/cm^3
q	flow rate, cm^3/s or ml/s
S	amount of solute retained by the soil, $\mu g/g$ or mg/kg or $mmol/kg$
S_e, S_1, S_2, S_3 and S_i	five phases representing solute retained by the soil matrix

List of Symbols (Continued)

S_{max}	maximum sorption capacity or total amount of available sites per unit soil mass, *μg/g or mmol/kg of soil*
Γ	a local isotherm equation
μ	viscosity, *kg/cm.s*
ω	measure of the bond strength of molecules on the matrix surface, *ml/g*
ξ	empirical affinity coefficient, dimensionless
θ	soil water content, cm^3/cm^3
X	total amount of solute, $\mu g/cm^3$

Chapter One

Introduction & Background

1.1 Introduction

Heavy metals are natural components of the environment, but are of concern because they are being added to soil, water, and air in increasing amounts from a variety of sources such as mines, metal processing and smelting, paint manufacturing, metal pipe, batteries, military activities, and domestic effluents. They pose a persistent problem at many contaminated sites, and a significant threat to the human health and ecological systems. Some of the effects of metal poisoning include skin lesions, birth defects, cancer, learning disabilities, liver and kidney dysfunction, even death. Typically metals are relatively immobile in surface systems as a result of precipitation or adsorption reactions (Evanko and Dzombak, 1997). For this reason, remediation activities at metal contaminated sites have focused on the solid-phase sources of metals, contaminated soils, sludges, wastes, or debris.

A number of remediation technologies have been developed for heavy metal contaminated soils, such as thermal extraction for volatile metals (e.g. mercury, arsenic and cadmium as well as their compounds can be evaporated at 800 °C), electronics, solidification/stabilization, vitrification, chemical oxidation, soil washing, and bioremediation (Mulligan et al., 2001a). The specific technology selected for treatment of a metal contaminated site will depend on the form of the contamination and other site-specific characteristics. Another important consideration is that the chosen method does not leave toxic residues which must be subsequently removed (Roundhill, 2001). One or more of these approaches are often combined together for more cost-effective treatment (Evanko and Dzombak, 1997).

Soil flushing, an in-situ process, can be used to remove metals from the soil using water or additives. Chemical treatment involves addition of extraction agents that interact with the contaminant and leach it from the soil (Evanko and Dzombak., 1997). Mulligan et al. (2001a) have demonstrated the feasibility of surfactant-enhanced remediation of contaminated soil, and batch washing experiments were also carried out to evaluate the feasibility of using biodegradable surfactants (e.g., surfactin, a rhamnolipid and sophorolipid) to remove heavy metals from oil-contaminated soils, or sediments (Mulligan et al., 1999; Mulligan et al. 2001b). Column experiments showed that surfactant foam could also be used as a fluid to enhance soil remediation (Eftekhari, 2000).

In this project, column experiments were conducted to investigate the foamability of JBR425 (mixed rhamnolipids) at different concentrations with different pH values, the foam characteristic parameters such as foam quality and stability, and the pressure gradient build-up in the soil column during foam passing through the column. Then, surfactant foam enhanced removal of heavy metals (Cd, Ni) from the contaminated soil under different pH values was investigated. Removal efficiencies by foam generated from conventional nonionic surfactant Triton X-100 was investigated as a comparison. Surfactant solutions without foam and distilled water with correspondent pH values were also flushed through the contaminated soil column as controls.

1.2 Thesis Contents and Structure

This thesis consists of seven chapters as follows:

- Chapter One gives an introduction to the subject and an overview of the thesis contents and structure as well as research objectives.

- Chapter Two reviews the literature concerning the background knowledge of soil environment, pollution and heavy metals, surfactants and biosurfactants, and the foam technology.

- Chapter Three discusses the fate and transport processes of heavy metals in the soil environment. Basic models and a multireaction model (MRM) of such processes are described.

- Chapter Four reviews and evaluates the remediation technologies for the heavy metal contaminated soils. Examples of previous research on surfactant enhanced remediation of heavy metal contaminated soils are demonstrated.

- Chapter Five presents all materials and the experimental setup used in this investigation. All processes and procedures before and after each test are explained in this chapter.

- Chapter Six summarizes the results obtained from different experiment phases in this project. Data and results are analyzed and discussed.

- Chapter Seven presents the conclusions of this study with some important inferences made from different stages of this study and the results obtained. In addition, recommendations about the future development of this promising innovative technology are made.

1.3 Research Objectives

The overall objectives of this research are listed below:

- Evaluate the feasibility of biosurfactant-enhanced remediation of heavy metal contaminated soil;

- Investigate the biosurfactant foam technology in the remediation of heavy metal contaminated soil;

- Investigate the parameters that effect the foam quality and stability, and the pressure gradient build-up in the soil column to guarantee the success of the application of the biosurfactant foam technology;

- Investigate the influence of parameters such as initial pH values on the removal efficiencies;

- Compare the removal efficiencies (RE) by biosurfactant (JBR425, mixed Rhamnolipids) with chemical surfactants (Triton X-100);

- Discuss the overall augmentation and applicability of foam-biosurfactant flushing technology for in field full-scale applications.

Chapter Two

Literature Review

2.1 Soil Environment

Soil contains solids, liquids, and gases. Soil solids consist of a mixture of weathered minerals and varying amounts of organic matter, ranging in size from gravels to fine clays (Table 2.1) (Wild, 1993).

Table 2.1 Size Classifications of Soil Particles According to the U. S. Department of Agriculture System

Soil Particles	Diameter (mm)
Gravels	>2.0
Very Coarse Sand	1.0-2.0
Coarse Sand	0.5-1.0
Medium Sand	0.1-0.5
Fine Sand	0.05-0.1
Silt	0.002-0.05
Clay	<0.002

(Adapted from Wild, 1993)

Soil structure and composition are a function of various physical, chemical and biological processes that are constantly at work changing soils over geologic time (Pierzynski et al., 1993). Soils can be contaminated as a result of spills or direct contact with contaminated waste streams such as airborne emissions, process solid wastes, sludges, or leachate from waste materials. The solubility of metals in soil is influenced by the chemistry of the soil and groundwater (Evans, 1989; Sposito, 1989). Factors such as pH, cation exchange capacity (CEC), and complexation/chelation with organic matter directly affect solubility (Evanko and Dzombak, 1997).

For soil physical properties, we are concerned primarily with the composition and arrangement of solids, moisture content, temperature, particle and bulk density, as well as hydraulic conductivity. The arrangement of soil solids determines the amount of open volume, or pore volume. Soil structure describes the size, shape, arrangement and degree of development of soils into structural units. It can influence the contaminant mobility by limiting the degree of contact between groundwater and contaminants. Soil moisture influences the chemistry of contaminated soil. The amount of dissolved minerals, pH and redox potential of the soil water depends on the soil moisture content.

Mineral solubility, soil reactions (pH), cation and anion exchange, buffering effects, and nutrient availability are major chemical properties of soils. These are determined primarily by the nature and quality of the clay minerals and organic matter present (Pierzynski et al., 1993; Eftekhari, 2000). Carbon is present in all soils in the form of organic matter, which is made up of humic substances and biochemical compounds. Soil organic matter contents vary from less than 1% in coarse-textured soils and soils of arid regions to nearly 100% in some poorly drained organic soils (Pierzynski et al., 1993). Organic matter influences soil physical, chemical, and biological properties. On the beneficial side, they can adsorb organic chemicals such as pesticides, and trace element pollutants such as lead, cadmium, and copper, which will reduce the contamination of surface and ground waters, however, on the detrimental side, high levels of trace elements may be toxic to plants, and possibly to animals and humans consuming foods grown in the contaminated soils.

2.2 Contaminants

2.2.1 Overview

Pollution is the most serious of all environmental problems and poses a major threat to the health and well being of millions of people and global ecosystems. A widely used definition of pollution is " the introduction by man into the environment of substances or energy liable to cause hazards to human health, harm to living resources and ecological systems, damage to the structures or amenity, or interference with legitimate uses of the environment" (Holdgate, 1979). Some scientists make a distinction between contamination and pollution. Contamination is used for situations where a substance is present in the environment, but not causing any obvious harm while pollution is reserved for cases where harmful effects are apparent (Alloway and Ayres, 1997).

In all cases of pollution events, the common characteristics include:

1) the pollutant;
2) the source of the pollutant;
3) the transport medium (air, water or soil); and
4) the target (the organisms, ecosystems or items of property affected by the pollutant).

A simplified model of environmental pollution (Alloway and Ayres, 1997; Holdgate, 1979) is shown in Figure 2.1.

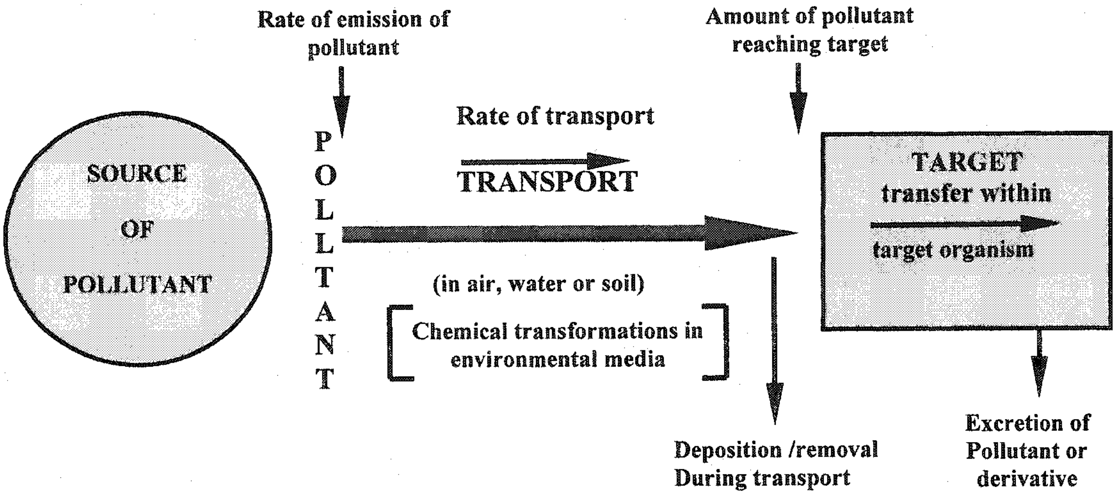


Figure 2.1 A Simplified Model of Environmental Pollution (from Holdgate, 1979; Alloway and Ayres, 1997))

2.2.2 Contamination Classification

Pollution is commonly categorized as either point source or non-point source. Point source pollution is from direct, concentrated discharges such as sewage effluents. On the other hand, non-point source pollution is usually less concentrated and diffuse in its entry to the environment, and therefore, much more difficult to control and regulate.

Pollutants are basically of two types: primary pollutants, which exert harmful effects in the form in which they enter the environment, and secondary pollutants, which are synthesized as a result of chemical processes, often from less harmful precursors, in the environment (Alloway and Ayres, 1997). The common classification of pollutants and typical examples and the most possible medium that would be impacted are listed in Table 2.2.

Table 2.2 Classification of Pollutants and the Impacted Medium

Pollutant Category	Examples	Medium Impacted		
		Soil	Water	Air
Nutrients	Nitrogen and phosphorus in commercial fertilizers, manures, sewage sledges, municipal solid waste	x	x	x
Pesticides	Insecticides, herbicides, fungicides	x	x	x
Hazardous substances	Fuels, solvents, volatile organic compounds	x	x	x
Acidification	Acid precipitation, acid mine drainage	x	x	
Salinity and sodicity	Road salt, saline irrigation water	x	x	
Trace elements	Cationic metals, oxyanions	x	x	
Sediments	Soil lost via water erosion	x	x	
Particulates	Soot, soil lost via wind erosion, volcanic dusts		x	x
Greenhouse gases	Carbon dioxide, methane, nitrous oxide, chlorofluorocarbons			x
Smog-forming compounds	Ozone, secondary products of fuel combustion			x

(Adapted from Pierzynski et al., 1993)

2.3 Heavy Metals

2.3.1 Overview

Heavy metals have found industrial, agricultural and military uses for several centuries of time (Roundhill, 2001). As a result they are now widely dispersed in the environment in a range of different forms, which are a source of some concern because of their potential reactivity, toxicity, and mobility in the soil (Selim and Amacher, 1996). "Heavy metals" is a general collective term applying to the group of metals and metalloids with an atomic density greater than 6 g/cm^3 (Alloway and Ayres, 1997). Although it is a loosely defined term, it is widely recognized and usually applied to the elements such as cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn) which are commonly associated with pollution and toxicity, and are included on the EPA's list of priority pollutants (Cameron, 1992; Mulligan et al., 2001b). Sources of heavy metals in the environment and factors influencing their distribution, reactivity, mobility, and toxicity are numerous.

Although heavy metals differ widely in their chemical prosperities, they are used widely in electronics, machines and the artifacts of everyday life as well as " high-tech" applications. Consequently, they tend to reach the environment from a vast array of anthropogenic sources as well as natural geochemical processes (Alloway and Ayres, 1997). Sources of metals include domestic and industrial effluents, the atmosphere, runoff and lithosphere (Mulligan et al., 2001b).

Heavy metals in soils are present in many different physicochemical forms. The potential toxicity of metals in the surrounding environment, either added as pollutants or naturally occurring depends on their total concentrations in the soil, soil solution, and exchangeable forms. The chemical behavior of metals is primarily governed by retention and release reactions of solute with the soil matrix. The sorption behavior of Zn, Cu, Ni, and Cd in soils varies from soil to soil and is influenced by soil properties, such as pH, organic matter, clay and amorphous hydrous oxide contents, and cation exchange capacity (McBride, 1989). The sorption process thus affects metal availability to plants and leachability to ground and surface waters (Singh and Oste, 2001).

2.3.2 Cadmium

Cadmium, a highly toxic non-essential element, with the symbol of Cd, has an atomic number of 48, an atomic weight of 112.41, and falls in Group IIB of the Periodic Table. It is usually found as a mineral combined with other elements such as oxygen (cadmium oxide), chlorine (cadmium chloride), or sulfur (cadmium sulfate, cadmium sulfide).

Cadmium is found naturally in small quantities in air, water, and soil. Similar to other metals, cadmium does not break down and can accumulate over time. The main sources of cadmium in the environment include (Callahan et al., 1979; Peterson and Alloway, 1979; Smith et al., 1995; Alloway and Ayres, 1997; Evanko and Dzombak, 1997):

1. metal processing and smelting;
2. battery, coating and plating, and paint manufacturing;
3. cadmium-containing fertilizers, sewage sludge and wastes;
4. waste hauling and disposal activities; and
5. burning household or industrial waste and burning coal or oil, car exhausts.

Cadmium emissions to the environment are normally transported continually between the three main environmental compartments, air, water and soils. Cadmium is much less mobile in soils than in air and water. The major factors governing cadmium speciation, adsorption and distribution in soils are pH, soluble organic matter content, hydrous metal oxide content, clay content and type, presence of organic and inorganic ligands (Callahan and Alloway, 1979), and competition from other metal ions.

Cadmium accumulates in the kidneys of mammals and can cause kidney dysfunction, especially for young children. A serious case of Cd poisoning occurred in the Jintsu Valley in the Toyama Prefecture in Japan, where the river water was contaminated by Zn and Cd from Pb-Zn mining and smelting. After the Second World War, it was found that more than 200 elderly women who had several children had developed kidney damage and skeletal deformities (Alloway and Ayres, 1997).

2.3.3. Nickel

Nickel, with the symbol of Ni, has an atomic number of 28, an atomic weight of 58.70, and falls in Group X of the Periodic Table. Nickel ores occur primarily in the form of the oxides, silicates and sulfides and the ore is usually associated with other sulfide, silicate or arsenide minerals. About 84% of all nickel produced is used in alloys (Bodek et al., 1988). These alloys have important uses such as in the making of metal coins and jewelry and in industry for making items such as valves and heat exchangers. Nickel metal, nickel (II) sulfate, nickel (II) chloride and nickel (II) cyanide are used in electroplating. Other uses of nickel are in batteries and as catalysts.

Nickel combined with other elements occurs naturally in the earth's crust, is found in all soils, and is also emitted from volcanoes. Nickel is also found in meteorites and in lumps of minerals known as sea floor nodules on the floor of the ocean. The earth's core is believed to contain large amounts of nickel. Nickel is released into the atmosphere during nickel mining and by industries that convert scrap or new nickel into alloys or nickel compounds or by industries that use nickel and its compounds. These industries also may discharge nickel in wastewater. Nickel also is released into the atmosphere by oil-burning power plants, coal-burning power plants, and trash incinerators (ATSDR, 1997; USEPA, 1999; USEPA, 2003).

Exposure to nickel may be through breathing air, drinking water, eating food, smoking tobacco or skin contact with soil, water, and metals containing nickel as well as with metals plated with nickel. The most common adverse health effect of nickel in humans is an allergic reaction to nickel, though a small amount of nickel is probably essential for humans. It has been determined that some nickel compounds are carcinogenic to humans and that metallic nickel may possibly be carcinogenic to humans (USEPA, 1986; IARC, 1987; ATSDR, 1990). The most serious effects of exposure to nickel, such as cancer of the lung and nasal sinus, have occurred in people who have breathed nickel dust while working in nickel refineries or in nickel processing plants (USEPA, 1986).

2.4 Surfactants & Biosurfactants

2.4.1 Surfactants

Surfactants (surface active agents) are organic chemical wetting, cleaning and disinfecting agents (Gutcho, 1977), and they are frequently used in detergents and food products that alter the properties of solution interfaces (Strbak, 2000). They also can be added to washing water to assist in the solubilization, dispersal and desorption of contaminants from excavated soils or sediments in a washing unit for subsequent return of the cleaned soils to their original site (Mulligan et al., 2001b).

At room temperature, the surface tension of water is approximately 72 mN/m. It is the highest surface tension of any biologically relevant liquid, and results primarily from the effects of the hydrogen bonding. Many surfactants can reduce surface tension to approximately 25 ± 5 mN/m depending on concentration and surfactant type (Myers, 1999). Surfactants achieve these effects by acting as a bridge between two materials meeting at the surfaces. As amphiphilic (both loving) molecules, typically, surfactants consist of a strongly hydrophilic (water loving) group (polar group), the "head" of the molecule, and a strongly hydrophobic (water fearing) group (nonpolar group), which is the "tail" (Figure 2.2). The hydrophilic portion causes surfactants to exhibit high solubility in water, while the hydrophobic portion prefers to reside in a hydrophobic phase such as NAPL (non-aqueous phase liquid). Surfactant monomers will form spheroid or lamellar structures with organic pseudo-phase interiors. This coincides will lower the surface and interfacial tensions (Figure 2.3) (Mulligan et al., 2001c). The minimum concentration at which this occurs is called the critical micelle concentration (CMC) (Rosen, 1979).

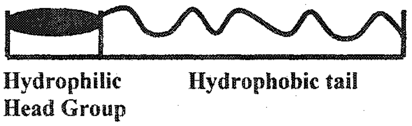


Figure 2.2 Basic Surfactant Molecular Structure

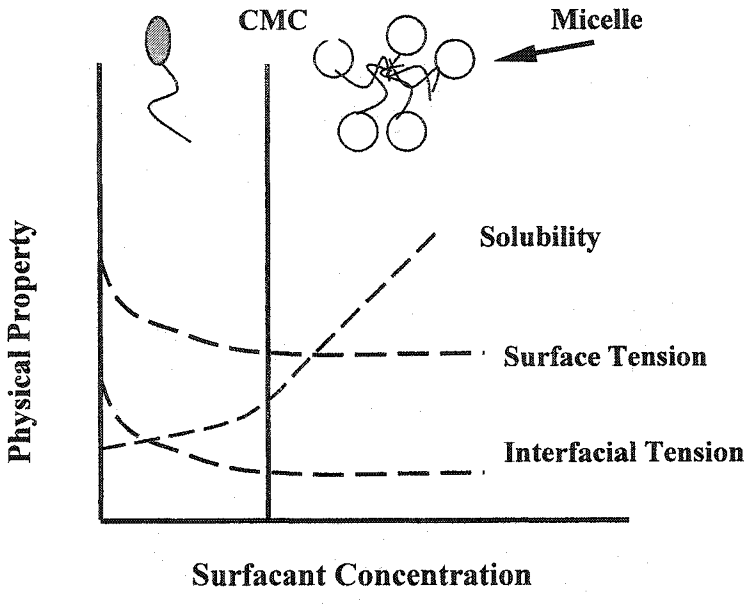


Figure 2.3 Schematic Diagram of the Variation of Surface Tension, Interfacial and Contaminant Solubility with Surfactant Concentration (Mulligan et al., 2001c)

The most useful chemical classification of surfactants is based on the nature of the hydrophile; subgroups are defined by the nature of the hydrophobe. The general groups of the surfactants are defined as follows (Myers, 1999):

1. Anionic, with the hydrophilic group carrying a negative charge such as carboxyl ($RCOO^-M^+$), sulfonate ($RSO_3^-M^+$), or sulfate ($RSO_4^-M^+$);
2. Cationic, with the hydrophile bearing a positive charge, as for example, the quaternary ammonium halides ($R_4N^+X^-$);
3. Nonionic, where the hydrophile has no charge but derives its water solubility from highly polar groups such as polyoxyethylene ($-OCH_2CH_2O-$), sugars or similar groups.

4. Amphoteric (and Zwitterionic), in which the molecule has, or can have, a negative and a positive charge on the principle chain (as opposed to a counter ion, M^+ or X^-) such as the sulfobetaines, $RN^+(CH_3)_2CH_2CH_2SO_3^-$.

Cationic, anionic and nonionic surfactants are particularly used for soil washing or flushing (Mulligan et al., 2001c). They can be used in mixtures or with additives such as alcohol and/or salts such as sodium chloride. Polymers or foams can also be added to control the mobility of the contaminants (Mulligan et al., 2001c). Additions of surfactants can have two beneficial effects: 1) a decrease in the aqueous activity coefficient for the dissolved nonionic organic compound and 2) formation of micelles in the aqueous phase.

Besides low surface tension and low critical micelle concentration (CMC), economic considerations can often be almost as important as surface activity in selecting a surfactant for a given application. Surfactants must be recovered and reused for the process to be economical (Mulligan et al., 2001c). Numerous studies demonstrate the feasibility of surfactants enhanced recoveries of non-aqueous liquids (NAPLs). Surfactant enhanced remediation of heavy metal contaminated soils also has been demonstrated.

2.4.2 Biosurfactants

Biosurfactants, surface active agents produced by bacteria or yeast, are potentially useful, particularly due to their anionic nature, low toxicity, biodegradability and excellent surface active properties (Mulligan et al., 2001b).

Biosurfactants range in chemical structure from simply fatty acids (soaps) to complex cyclic peptides, glycolipids, and proteins, and most of them are lipids, which are grouped as glycolipids, lipopeptides, lipopolysaccharides, phospholipids, and fatty acids. Rhamnolipids belong to the glycolipids group, which is the largest and best-studied group. Some of the major types are listed in Table 2.3. Most of these compounds are either anionic or neutral. Only a few are cationic such as those containing amine groups (Mulligan et al., 2001c).

Table 2.3 Classifications and Microbial Origin of Biosurfactants

Surfactant Class	Microorganism
Rhamnolipids	*Pseudomonas aeruginosa*
Lipopeptides	*Arthrobacter sp.* *Bacillus pumilis* *Bacillus subtilis* *Bacillus licheniformis* *Pseudomonas fluorescens*
Lipopolysaccharides	*Acinetobacter calcoaceticus* *Pseudomonas spp.* *Candida lipolytica*
Phospholipids	*Thiobacillus thiooxidans* *Corynebacterium alkanolyticum*
Fatty acids	*Penicillium spiculisporum* *Corynebacterium lepus* *Arthrobacter parafineus* *Talaramyces trachyspermus*

(Adapted from Mulligan and Gibbs, 1993; Banat ,1995 and Mulligan et al., 2001c)

Biosurfactants include classes of molecular structures quite different from synthetic surfactants while having effects on surface and interfacial tension within the same range. Biosurfactants as a class contribute significantly to the repertoire of available surfactants but do not present radically different effects on surface or interfacial tensions. Critical micelle concentrations of biosurfactants (a measure of its efficiency) range from 1 to 2000 mg/L. Surface and interfacial tensions (measure of effectiveness) of good biosurfactants are less than 30 and 1 mN/m, respectively (Mulligan and Gibbs, 1993). The contributions of biosurfactants to expanding the surfactant repertoire are in extending the possibilities for selection of the hydrophilic-lipophilic balance (HLB), emulsion or foam stability, production technology, and, especially, biological and environmental compatibility (Gerson, 1993).

Microbial surfactants exhibit high specificity and are consequently suited to new applications. Effective physicochemical properties (low interfacial tensions and critical micelle concentrations) and temperature stability are characteristic of these compounds. Other advantages include biodegradability, reduced toxicity, and a broad range of structures (Mulligan and Gibbs, 1993). As with the selection of synthetic surfactants, each application has special considerations that ultimately lead to the selection of the most appropriate surfactant. Selection of biosurfactants for a particular application proceeds along similar lines, but allows greater flexibility while maintaining lower toxicity and greater biodegradability (Gerson, 1993).

2.4.3 Extraction Mechanisms

It has been shown that surfactants could be used potentially for environmental remediation of heavy metals from soil, though research in this area has been limited. It is possible that surfactants can be used as extractants for transferring metal ions from an aqueous to an organic phase (Roundhill, 2001). The possible mechanisms for the extraction of heavy metals by surfactants are ion exchange, precipitation-dissolution, and counterion binding (Rosen, 1979).

The first mechanism for enhanced heavy metal removal from soil surface is ion exchange. This process takes place when a negatively charged ion adsorbed onto a subsurface is replaced by negatively charged surfactant ions from solution. Since micelles are not directly involved in ion exchange (monomers are), exchangeable ions will increase linearly below the CMC and remain relatively constant above CMC (Nivas et al., 1996; Doong et al., 1998).

The second mechanism for enhanced heavy metal removal from soil surface is counterion binding. For ionic micelles, the interfacial region between the aqueous solution and the micelle contains the ionic head groups, the stern layer of the electrical double layer pertaining to these groups, more than one half of the counterions associated with the micelle, and water. Nivas et al. (1996) suspected that precipitating cations (e. g. Ca^{2+}, Ba^{2+}) would be attracted to the surfactant micelles to promote dissolution of precipitated heavy metals when the concentration of surfactant exceeds the CMC, thereby enhancing the removal of chromium from soil.

For the third mechanism, it is possible that the surfactants precipitate with the cations of insoluble mineral phased by heavy metals and then could enhance dissolution of the heavy metal ions. Anionic surfactants also can interact with a negatively charged surface.

They associate with multivalent surface cations or are precipitated. Siffert et al. (1992) interpreted the adsorption of anionic surfactant such as dodecylsulfate, dodecylbenzenesulfate and dodecylbenesulfonate at minerals qualitatively as precipitation at mineral surface. Illic et al. (1996) found that on Ni- and Cu-montmorillonite, dodecylsulfate (DS-) forms ion pairs with the cations on the soil surface. In all cases, DS- is not bound above the CMC, but metal ions are mobilized from the surface, either by solubilization of the precipitates or by formation of mixed micelles. For Ca- and Pb-montmorillonite, DS- is precipitated as $Me(DS)_2$. Also, when CMC is exceeded, the precipitates are solubilized in the micelles of the bulk solution.

2.5 Foam Technology

Foams consist of thousands of tiny bubbles. They may be formed either by dispersion or condensation processes. In the former process, the incipient disperse gas phase is present as a bulk or condensed phase. Small volumes of the future dispersed phase are introduced into the liquid by agitation or converted into gas by some mechanism such as heating, or pressure reduction. In the case of condensation, the gas phase is introduced at the molecular level and allowed to "condense" within the liquid to form bubbles (Myers, 1999).

Foam always has a definite structure because of the forces involved in its formation and stabilization, Early investigators proposed the classification of foams into two morphological classes: (1) the "kugelschaun" or spherical foams consisting of widely separated spherical bubbles, also called gas emulsions; and (2) "polyederschaum" or polyhedral foams consisting of bubbles that are nearly polyhedral in shape, having narrow lamellar films of very low curvature separating the dispersed phase (Myers, 1999). The continuous phase of foams may consist entirely of liquid components or a mixture of various liquids and solutes (Figure 2.4).

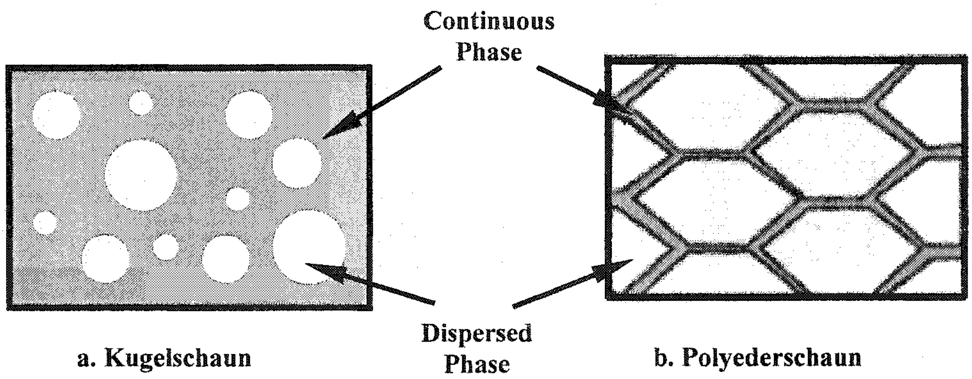


Figure 2.4 The Two General Classes of Foams (Myers, 1999)

The relationship between the foaming power of a surfactant and its chemical structure can be quite complex. The correlation is further complicated by the fact that there is not necessarily a direct relationship between the ability of a given structure to produce and its ability to stabilize that foam. It is usually found that the amount of foam produced by a surfactant under a given set of circumstances will increase with its bulk concentration to a maximum, which occurs somewhere near the critical micelle concentration (CMC). Obviously, the lower the surface tension of the solution, the greater will be the surface area that can be expected to be developed by the input of a given amount of work (Myers, 1999). Expansion factor is a parameter used to describe the foamability of a solution. It is defined as:

$$Expansion \quad Factor = \frac{Foam \quad Volume}{Liquid \quad Volume} \qquad \text{Eq. 2-1}$$

A primary characteristic of foams is that they have very low densities because they consist mainly of air bubbles. Aqueous foam with bubble diameters of about 1 cm and lamellar thickness of 10^{-3} cm will have a density of approximately 0.003 g cm^{-3} (Myers, 1999). Related to the low density of foams is the characteristic that they will have a large surface area for a given weight of foam. The gas content of foam is defined as the foam quality, which is a term defined as:

$$Foam \quad Quality = \frac{Gas \quad Volume}{Total \quad Foam \quad Volume} \qquad \text{Eq. 2-2}$$

Foams can be prepared that have a lifetime (persistence) of minutes, days, or even months, even though they are inherently unstable systems and have an ultimate tendency to collapse. Foam stability is defined as the stability of the foam to resist bubble breakdown. In static foam it is sometimes quantified by the time required for the drainage of half of the liquid volume (time of half-drainage) (Chowdiah et al., 1998). The overall question of foam stability and bubble coalescence requires the consideration of both the static and dynamic aspects of bubble interactions.

Another important parameter of foam is the effective viscosity. The effective viscosity was calculated as:

$$\mu_{(foam)} = \frac{kA}{q_{(foam)}} \frac{\Delta P}{L} \qquad \text{Eq. 2-3}$$

where μ = viscosity, *kg/cm.s*; k = permeability, *cm/s*; q = flow rate, cm^3/s; A = column cross-section, cm^2; L = column length, *cm*; ΔP = pressure drop, *kPa*. The effective viscosity of a foam is useful for characterizing foam flow under various conditions. It was observed that it increases with the increase of soil permeability (Chowdiah et al., 1998).

Equipment setup as in Figure 2.5 is usually used to investigate the foam characterizations and the influencing parameters on them.

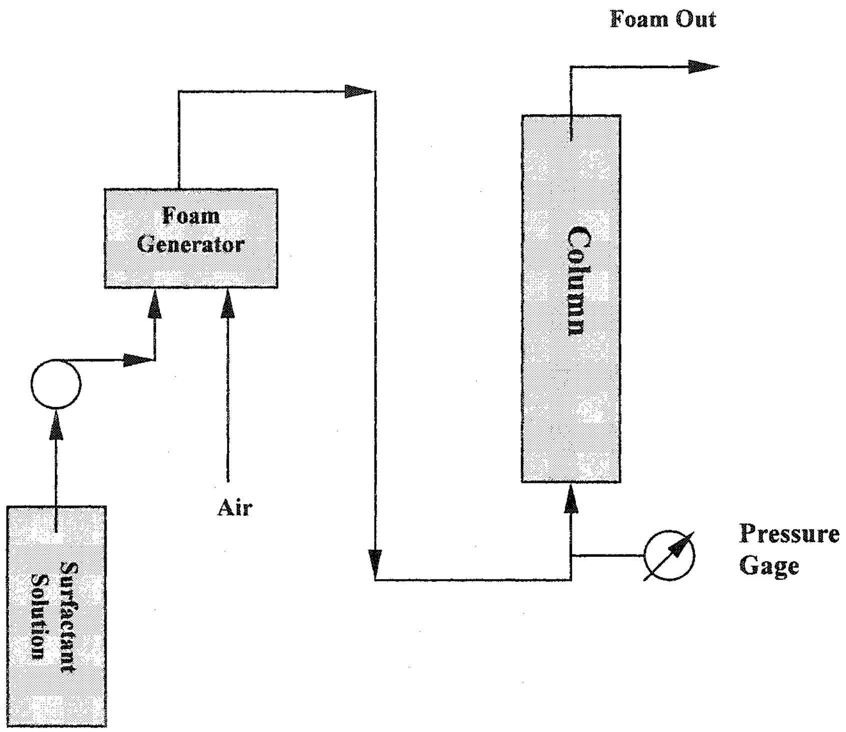


Figure 2.5 Schematic of Apparatus for Foam Flow Experiments (Modified from Chowdiah et al., 1998)

Chapter Three

Fate and Transport of Heavy Metals in Soils

3.1 Influence of Soil Properties on Metal Mobility

Soil is a dynamic system, as described in Chapter Two, subject to short-term fluctuation such as variations in moisture content, pH and redox conditions and also undergoing gradual alterations in response to changes in management and environmental factors. Contamination exists in three forms in the soil matrix: solubilized contamination in the soil moisture, adsorbed contamination on the soil surfaces, and contamination fixed chemically as solid compounds (Evanko et al., 1997). Chemical and physical properties of the contaminated soils will influence the form of the metal contaminant, its mobility, bioavailability and the technology selected for remediation (Gerber et al., 1991; Evanko et al., 1997). The soil reaction is the preeminent factor controlling the chemical behavior of metals and many other important processes in the soil.

Soil pH is considered the master variable concerning metal behavior in soil systems (McBride, 1994) and is the most important factor affecting the metal speciation in the soil. Soil has several mechanisms that serve to buffer pH to varying extent, including hydroxyaluminium ions, CO_2, carbonates and cation exchange reactions. However, even with these buffering mechanisms, soil pH differs significantly due to localized variations within the soil. Soil pH values generally range between 4.0 and 8.5, and are affected by the changes in redox potential that occur in soils. Reduction conditions generally cause a pH increase, and oxidation brings about a decrease. Metal cations are most mobile under acidic conditions while anions tend to sorb to oxide minerals in this pH range. Generally, the mobility of heavy metal cations increases as pH decreases. Solubility of metals may increase at higher pH due to binding with dissolved organic matter (DOM) (Allen and Yin, 1996).

Soil organic matter (SOM) content varies considerably in the amount and type from different soils. Organic matter, particularly humic materials, can complex metals and affect their removal from solution (Ali and Dzombak, 1996). Humic materials contain carboxylic and phenolic functional groups that can complex with metal ions. The organic components of soils and waters react with metal oxyhydroxide and clay minerals to form combinations of widely diverse chemical and biological stabilities. SOM can sorb /chelate metals and may have a greater impact on soils with low inorganic cation exchange capacity (CEC). McBride (1994) proposed the following order for the chelation of metals by SOM based on Paul electronegativities:

$$Cu^{2+} > Ni^{2+} > Pb^{2+} > Co^{2+} > Ca^{2+} > Zn^{2+} > Mn^{2+} > Mg^{2+}$$

Clay minerals affect greatly both the physical and chemical properties of the soils. They rarely exist in pure form in soils, and they usually have humic colloids and hydrous oxide precipitates linked to them. The combined organo-mineral colloids complex plays a very important role in controlling the concentrations of ions in the soil solution. Due to their comparatively large surface area and permanent surface negative charge, clays are also important ion exchange materials for metals and often contain the majority of contamination.

3.2 Fate and Transport Mechanism

The fate and transport of heavy metal in soils depend significantly on the chemical form and speciation of the metal (Allen and Torres, 1991). While the various metals undergo similar reactions in a number of aspects, the extent and nature of these reactions varies under particular conditions. Generally, heavy metals in soils can be grouped into five fractions: exchangeable, carbonate, Fe-Mn oxide, organic, and residual fractions. The presence of hydrous metal oxides of Fe, Al, Mn can strongly influence metal concentration because these minerals can remove cations and anions from solution by ion exchange, specific adsorption and surface precipitation. The most important chemical processes affecting the behavior and bioavailability of metals in soils are those concerned with the adsorption of metals from the liquid phase to the solid phase. These processes decide the concentrations of metal ions and complexes in the soil solution. Several different mechanisms can be involved in the adsorption of metal ions, including cation exchange, specific adsorption, organic complexation and co-precipitation.

3.2.1 Cation Exchange

Most heavy metals exist mainly as cations in the soil solution, and their adsorption, therefore, depends on the density of negative charges on the surfaces of the soil colloids. All other factors being equal, surfaces with a greater number of charged sites per unit surface area will be able to bind greater quantities of dissolved ions. Surfaces with a high density of negatively charged sites (cation exchangers) will selectively bind positively charged ions while those with a high density of positively charged sites will be selective for anions (Sumner and Miller, 1996). Cation exchange capacity (CEC) refers to the concentration of readily exchangeable cations on a mineral surface and is often used to indicate the affinity of soils for uptake cations such as metals. The CEC of mineral soils can range from a few to 60 meq/100 g, but in organic soils it may exceed 200 meq/100 g (Alloway, 1990). Anion exchange capacity (AEC) indicates the affinity of soils for uptake of anions, and is usually significantly lower than the CEC of the soil, owing to the greater number of negative charges on the colloid surfaces.

3.2.2 Specific Adsorption

Specific adsorption involves the exchange of heavy metal cations and most anions with surface ligands to form partly covalent bonds with lattice ions. It results in metal ions being adsorbed to a far greater extent than would be expected from CEC of a soil. Specific adsorption is strongly pH dependent and is related to the hydrolysis of the heavy metal ions. The metals most able to form hydroxy complexes are specifically adsorbed to the greatest extent. In addition to being adsorbed on mineral surfaces, heavy metal ions also can diffuse into minerals such as goethite, Mn oxides, illites, smectites and some other minerals. Adsorption comprises three different steps: first, surface adsorption; second, diffusion into the mineral particles and third, adsorption and fixation at positions within the mineral particles (Alloway, 1990).

3.2.3 Co-precipitation

Co-precipitation is defined as the simultaneous precipitation of a chemical agent in conjunction with other elements by any mechanism and at any rate. The types of mixed solid commonly formed included clay minerals, hydrous Fe and Mn oxides and calcite in which isomorphous substitution has occurred.

3.2.4 Organic Complexation

In addition to being involved in cation exchange reactions, solid-phase humic substances such as humic acids also adsorb metals by forming chelate complexes. Low-molecular-weight organic ligands, not necessarily humic in original, can form soluble complexes with metals and prevent them from being adsorbed or precipitated. Carboxyl groups play a predominant role in metal binding in both humic and fulvic acids. The maximum amount of any given metal that can be bound is found to be approximately equal to the number of carboxyl groups (Alloway, 1990).

3.3 Reaction and Transport Models

As described above, heavy metals in soils can be involved in a series of complex chemical and biological interactions including oxidation-reduction, precipitation and dissolution, volatilization, and surface and solution phase complexation. To predict the fate of heavy metals in soils, one must account for retention and release reactions of the various species in the soil environment.

3.3.1 Freundlich Equation

Sorption of heavy metals to pure mineral components is often investigated as a function of pH, resulting in the well-known adsorption edge plots exhibiting a steep increase in metal sorption with increasing pH (Sparks, 1995). With soil materials, however, it is much more difficult to vary the equilibrium pH over a wide range without creating problems due to dissolution of soil components or precipitation of heavy metals. Therefore, heavy metal sorption to soil materials is more often studied in terms of adsorption isotherms, in which metal sorption is measured as a function of solution concentration at fixed pH and background electrolyte concentration (Grolimund et al., 1995; Sauve et al., 2000; Kretzschmar and Voegelin, 2001).

The Freundlich equation (Eq. 3-3) is perhaps the simplest approach for quantifying the behavior of retention of reactive solute with the soil matrix (Selim et al., 1996).

$$S = k_f C^b \qquad \text{Eq. 3-3}$$

Where S is the amount of solute retained by the soil, in $\mu g/g$ or mg/kg; C is the solute concentration in solution in mg/l; k_f is the distribution coefficient in l/kg or ml/g; and the parameter b is dimensionless and typically has a value of $b<1$. The distribution coefficient describes the partitioning of a solute species between solid and liquid phases over the concentration range of interest and is analogous to the equilibrium constant for a chemical reaction.

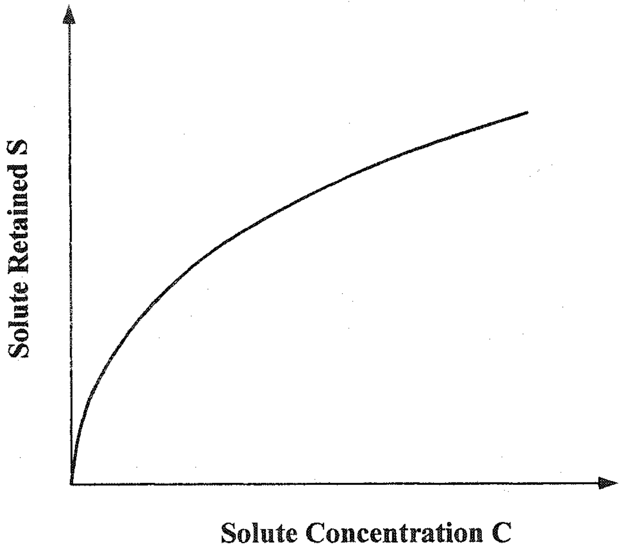


Figure 3.1 Nonlinear Isotherm of the Freundlich Retention Equation

For the case b = 1, the Freundlich equation is often referred to as the linear retention equation:

$$S = K_d C \qquad \text{Eq. 3-4}$$

where K_d is the linear distribution coefficient (*ml/g*).

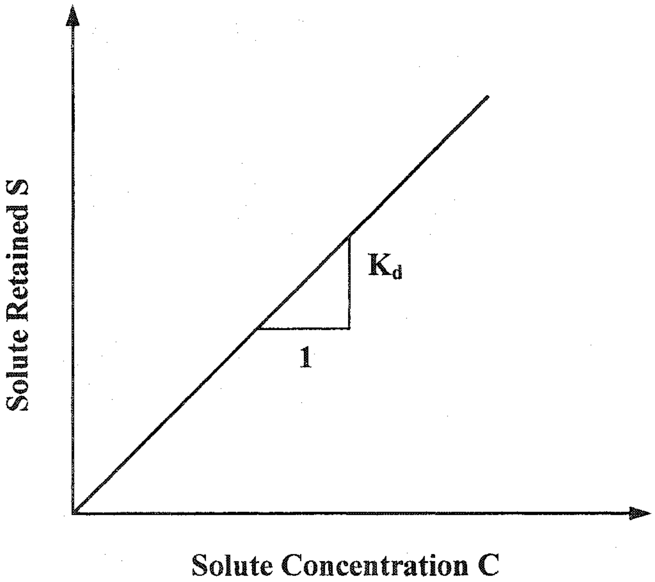


Figure 3.2 Linear Retention Isotherm for the Freundlich Equation (in case of b = 1)

Often complex retention processes can at least in part be described by relatively simple models such as the Freundlich equation. Therefore, the Freundlich parameters K_f and b are best regarded as descriptive parameters in the absence of independent evidence concerning the actual retention mechanisms.

A logarithmic representation of the Freundlich equation (Eq. 3-5) is frequently used to represent the experimental data. So, the slope of the best-fit curve provides the nonlinear parameter b and the intercept K_f in the equation, a linear representation of data in the log form is achieved (Figure 3.3).

$$\log S = K_f + b \log C \qquad \text{Eq.3-5}$$

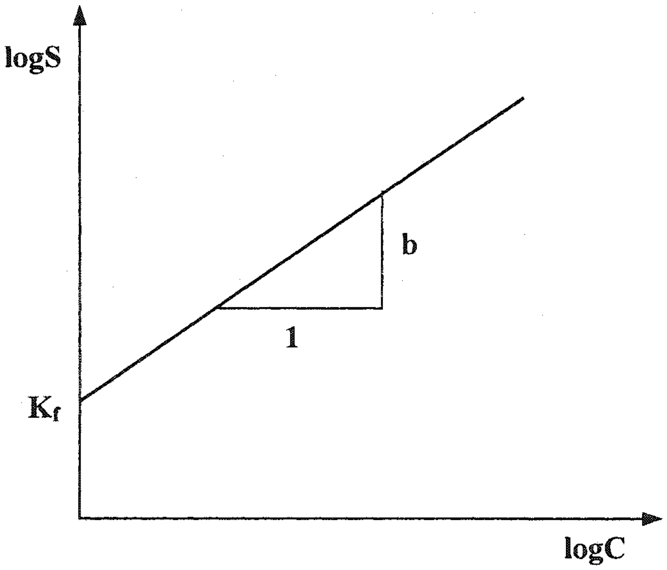


Figure 3.3 Logarithmic Representation of the Freundlich Equation

3.3.2 Langmuir Equation

The Langmuir isotherm is the oldest and most commonly used for soils (Selim et al., 1996). A major advantage of the Langmuir equation over linear and Freundlich types is that a maximum sorption capacity, which may be regarded as a measure of the amount of available retention sites on the solid phase, is incorporated into the formulation of the model. The standard form of the Langmuir equation is:

$$\frac{S}{S_{\max}} = \frac{\omega C}{1 + \omega C} \qquad \text{Eq.3-6}$$

where S_{max} and ω are adjustable parameters. Here ω (ml/g) is a measure of the bond strength of molecules on the matrix surface and S_{max} ($\mu g/g$ of soil) is the maximum sorption capacity or total amount of available sites per unit soil mass.

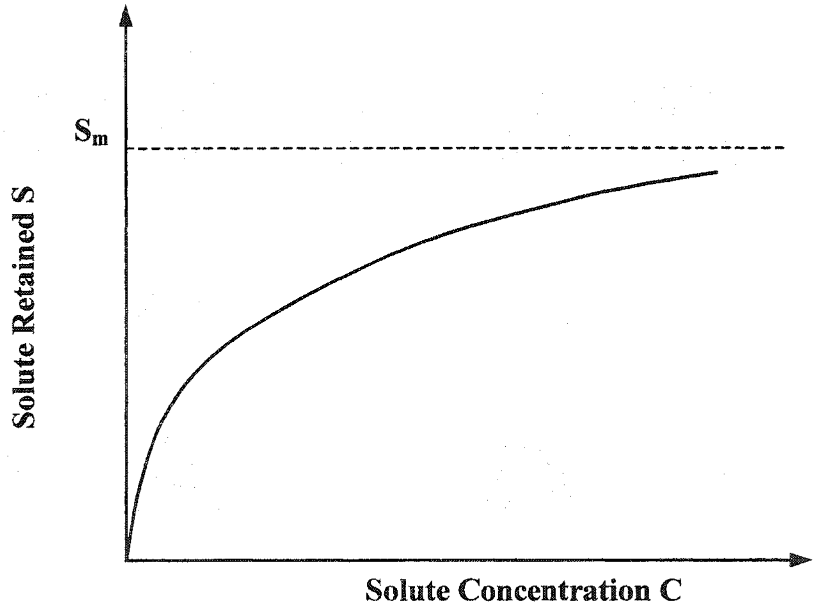


Figure 3.4 Nonlinear Langmuir Retention Isotherm

3.3.3 General Isotherm Equation

The description of heavy metal sorption in soils often remains empirical, such as the Freundlich model described above. As a result, "a general isotherm equation" describing the affinity of different binding sites on the surface of soils was proposed (Selim et al. 1996,Weber and DiGiano, 1996):

$$\frac{S}{S_{\max}} = \int_0^{\infty} w(\zeta)\Gamma(\zeta, C)d\zeta = f(C) \qquad \text{Eq.3-8}$$

where *f(C)* is a closed form isotherm expression as a function of concentration *C* (*mmol/l*). The terms *S* and S_{max} denote the amount of solute sorbed and the maximum sorption capacity (*mmol/kg*), respectively. The function $w(\xi)$ is equivalently defined as a weighting function, and ξ is an empirical affinity coefficient (dimensionless). The function Γ is a local isotherm equation and is often represented by the Langmuir equation:

$$\Gamma(\zeta, C) = \frac{\zeta C}{1 + \zeta C} \qquad \text{Eq.3-9}$$

A major advantage of the general isotherm formulation is that it can be used to drive several commonly known isotherm reactions, including the Freundlich and Langmuir isotherms (Papelis and Um, 2001).

3.3.4 Kinetic Retention Model

A number of empirical models have been proposed to describe kinetic retention of solutes in the solution phase. The earliest model is the first-order kinetic reaction first incorporated into the classical (convective-dispersive) transport equation by Lapidus and Amundson (1952):

$$\rho \frac{\partial S}{\partial t} = k_f \theta C - k_b \rho S \qquad \text{Eq.3-10}$$

where S is the amount of solute retained by the soil (*mg/kg*), C is the solute concentration in solution (*mg/l*), k_f and k_b are the forward and backward reaction rate coefficients (h^{-1}), respectively, ρ is the soil bulk density (g/cm^3), and θ is the soil water content (cm^3/cm^3). This type of reaction is fully reversible where the magnitudes of the rate coefficients dictate the extent of the kinetic behavior of the reaction (Hinz et al., 1994).

3.3.5 Multireaction Model

As described in Chapter Two, the soil solid phase is made up of different constituents. Moreover, heavy metal species are assumed to react at different rates with different sites on matrix surfaces. Therefore, a multireaction kinetic approach is used to describe heavy metal retention kinetics in soils. Such models are empirical in nature and are based on the assumption that a fraction of the total sites reacts rapidly or instantaneously with the solute whereas the remaining fraction of sites reacts slowly with solute in the soil solution. Nonlinear equilibrium (Freundlich) and first- or nth-order kinetic reactions are the associated processes (Hinz et al., 1994; Selim et al., 1996; Selim and Amacher, 2001). A schematic representation of the multireaction models (MRMs) is shown in Figure 3.6.

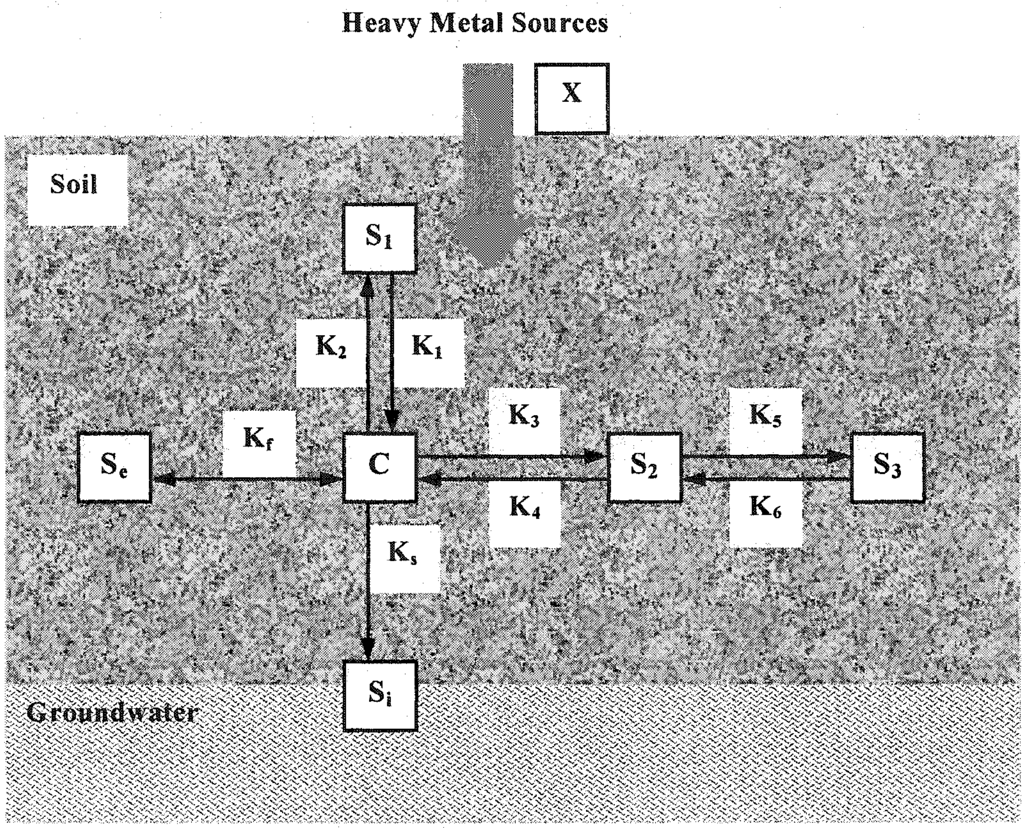


Figure 3.5 A schematic representation of the multireaction model MRM (Modified from Selim et al., 1996)

In this model, we consider the solute to be present in the soil solution phase (C) and in five phases representing solute retained by the soil matrix as S_e, S_1, S_2, S_3 and S_i. We further assume that S_e, S_1, and S_2 are in direct contact with the solution phase and are governed by concurrent type reactions. Here we assume S_e is the amount of solute that is sorbed reversibly and is in equilibrium with C at all times (Selim et al., 1996). The governing equilibrium retention/release mechanism is that of the nonlinear Freundlich as discussed previously. The retention/release reactions associated with S_1 and S_2 in direct contact with C are reversible processes of the nonlinear kinetic type:

$$S_e = k_f C^b \qquad \text{Eq. 3-11}$$

$$\frac{\partial S_1}{\partial t} = k_1 \frac{\theta}{\rho} C^n - k_2 S_1$$ Eq. 3-12

$$\frac{\partial S_2}{\partial t} = k_3 \frac{\theta}{\rho} C^m - k_4 S_2$$ Eq. 3-13

These two phases (S_1 and S_2) may be regarded as the amounts sorbed to surface of soil particles such as surface complex of Al and Fe oxide minerals or other types of surfaces. Moreover, these phases may be characterized by their kinetic sorption/desorption interaction with the soil solution. Thus, any solute whose retention/release behavior in soils can be described by such a model is susceptible to leaching in the soil. In addition, the primary difference between these two phases not only lies in the difference in their kinetic behavior, but also on the degree of nonlinearity, as indicated by the parameters n and m.

The multireaction model also considers irreversible solute removal via a retention sink term Q, to account for possible irreversible reactions such as precipitation and internal diffusions among others (Selim et al., 1996). We express the sink term as a first-order kinetic process:

$$Q = \rho \frac{\partial S_i}{\partial t} = k_s \theta C$$ Eq. 3-14

where k_s is the associated rate coefficient (h^{-1}).

The multireaction model also includes an additional retention phase (S_3) governed by a consecutive reaction with S_2 (Selim et al., 1996). This phase represents the amount of solute strongly retained by the soil that reacts slowly and reversibly with S_2 and may be a result of further rearrangements of the solute retained on matrix surface. Thus, inclusion S_3 in the model allows the description of the frequently observed very slow release of solute from the soil. The reaction between S_2 and S_3 was considered to be of the first – order type:

$$\frac{\partial S_3}{\partial t} = k_5 S_2 - k_6 S_3 \qquad \text{Eq. 3-15}$$

where k_5 and k_6 (h^{-1}) are the reaction rate coefficients. If a consecutive reaction is included in the model, then Eq.3-13 must be modified to incorporate the reversible reaction between S_2 and S_3. As a result, the following equation (Eq. 3-16) must be used in place of Eq.3-11. The above reactions are nonlinear in nature and represent initial-value problems that must be solved approximately using numerical methods. The initial conditions are that of a given initial solute concentration and assume no solute is retained at time zero.

$$\rho \frac{\partial S_2}{\partial t} = k_3 \theta C^n - \rho (k_4 + k_5) S_2 + \rho k_6 S_3 \qquad \text{Eq.3-16}$$

For a given bulk volume within the soil, the total amount of solute X ($\mu g/cm^3$) for a species i may be expressed as:

$$X = \theta C + \rho S \qquad \text{Eq. 3-17}$$

where S is the amount of solute retained by the soil ($\mu g/g$ of soil), C is the solute concentration in solution ($\mu g/cm^3$), θ is the volumetric soil water content (cm^3/cm^3) and ρ is the soil bulk density (g/cm^3).

Consider all the fractions and kinetic factors, and incorporate the mass balance equation, Eq. 3-17 can be expressed as:

$$\frac{\partial X}{\partial t} = \theta\frac{\partial C}{\partial t} + \rho\left(\frac{\partial S_1}{\partial t} + \frac{\partial S_2}{\partial t} + \frac{\partial S_3}{\partial t} + \frac{\partial S_e}{\partial t} + \frac{\partial S_i}{\partial t}\right) \qquad \text{Eq. 3-18}$$

Incorporate Eq.3-16 in Eq.3-17, we can get

$$\frac{\partial X}{\partial t} = \theta(C + k_1C^n + k_3C^m + \rho k_2C + \frac{\rho}{\theta}k_fC^b) + \rho(k_5S_2 - k_2S_1 - k_4S_2 - k_6S_3) \qquad \text{Eq. 3-19}$$

The nonlinear parameters *b*, *n* and *m* are considered to be less than unity and $n \neq m \neq b$.

For the case $b = n = m = 1$, the retention reactions are of the first-order type and the problem becomes a linear one. Then the Eq.3-18 can be rewritten as Eq.3-19.

$$\frac{\partial X}{\partial t} = k\theta C + \rho(k_5S_2 - k_2S_1 - k_4S_2 - k_6S_3) \qquad \text{Eq. 3-20}$$

where k is taken as a comprehensive partioning coefficient.

Assessing the movement and fate of contaminants in the subsurface, as the above paragraphs indicate, is not easy work. Accurate descriptions of the transport mechanisms, transformation processes and various interrelated factors that affect these processes are needed. The MRMs could be used basically to express the fundamental processes of the contaminant fate and transport in the subsurface. However, further research and experiments should be conducted to incorporate the various aspects of site characteristics.

Chapter Four

Soil Remediation Technology Review

4.1 Overview

The physical and chemical forms of the metal contaminants in soils strongly influence the selection of the appropriate remediation treatment approach. Several technologies exist for the remediation of heavy metal contaminated soils. Generally, these remediation technologies are classified into three categories: physical treatments, chemical treatments, and biological remediation technologies. In addition to the above classification, site remediation technologies can also be classified into in situ and ex situ treatments, depending on the placement of the technology. In situ treatment is the method of treating soil and groundwater contamination where they are found without excavating the overlying soil; all of the treatments take place in the subsurface. Ex situ treatment, on the other hand, refers to site remediation that occurs not in its original place; the remediation can take place either on-site or off site (Soesilo and Wilson, 1997). As is usually the case, a combination of one or more of these approaches is often used for more cost-effective treatment of a contaminated site.

This chapter gives an overview of the existing and emerging remediation technologies along the three major classifications of physical, chemical and biological treatments. Examined within each group of remediation technologies are in situ and ex situ technologies. Finally, some successful previous laboratory and pilot-scale studies of surfactant/biosurfactant enhanced remediation of heavy metal contaminated soils are demonstrated.

One point to be noted is that the classification scheme offered in this chapter is intended only for streamlining the discussion. In reality, more than one technology may be needed to achieve the cleanup goals at a site according to the specific site characteristics. In some cases, it is very difficult to group one technology exactly into one of the three categories, in such cases, the major remediation processes are considered for classification.

4.2 Remediation Technologies

4.2.1 Physical Treatments

4.2.1.1 Isolation

Isolation technologies attempt to prevent the further transport of contaminants by containing them within a designated area. These technologies can be used to prevent further contamination of groundwater when other treatment options are not physically or economically applicable for a site. Contaminated sites may also be isolated temporarily in order to limit transport during site assessment and site remediation. Subsurface barriers are designed to isolate contaminated soil and water by controlling the movement of groundwater at a contaminated site (Rumer and Ryan, 1995).

Vertical barriers are commonly installed upstream, downstream, or completely surrounding the site to restrict the lateral flow of groundwater. They are often limited to depths achievable with backhoe excavation technology for trenches, to about 9 m (Evanko and Dzombak, 1997). Slurry walls are the most common type of vertical barrier due to their low relative cost. Other available vertical barriers include grout curtains and sheet piles. Horizontal barriers also may be used in conjunction with vertical barriers at sites where a natural aquitard is not present, to control the downward migration of contaminants by lining the site without requiring excavation of the contaminated matrix. Technologies for the construction of horizontal barriers are under investigation (Evanko and Dzombak, 1997).

4.2.1.2 Immobilization

Immobilization technologies are designed to reduce the mobility of contaminants by changing the physical or leaching characteristics of the contaminated matrix. A variety of methods are available for immobilization of metal contaminants, including those that use chemical reagents and/or thermal treatment to physically bind the contaminated soil or sludge. Most immobilization technologies can be performed ex situ or in situ. The aqueous and solid phase chemistry of metals is conducive to immobilization by these techniques. In situ processes are preferred due to the lower labor and energy requirements, but implementation in situ will depend on specific site conditions.

Solidification and stabilization (S/S) immobilization technologies are the most commonly selected treatment options for metal contaminated sites (Conner, 1990). S/S seeks to immobilize contaminants within the contaminated matrix by mixing soil with a binder. Leachability testing is typically performed to measure the immobilization of contaminants. Solidification involves the formation of a solidified matrix that physically binds the contaminated material. Stabilization, also referred to as fixation, usually utilizes a chemical reaction to convert the waste to a less mobile form. The general approach for solidification/stabilization treatment processes involves mixing or injecting treatment agents to the contaminated soils. The dominant mechanism by which metals are immobilized is by precipitation of hydroxides within the solid matrix (Shively et al., 1986). S/S technologies are not useful for some forms of metal contamination, such as species that exist as anions (e.g., Cr(VI), arsenic) or metals that don't have low-solubility hydroxides (e.g., mercury). S/S may not be applicable at sites containing wastes that include organic forms of contamination, especially if volatile organics are present. Pretreatment, such as air stripping or incineration, may be used to remove the organics and prepare the waste for metal stabilization/solidification (Smith et al., 1995).

Ex situ S/S contaminants are physically bound or enclosed within a stabilized mass (solidification), or react with the stabilizing agent to reduce their mobility (stabilization). In situ S/S techniques use auger/caisson systems and injector head systems to apply S/S agents to in situ soils. In situ S/S treatment appears to have been applied less frequently than ex situ techniques mostly due to concerns about uniformity of treatment and long-term reliability. These limitations are being reduced, however, through advances in chemical reagent delivery systems for large-diameter auger drilling devices. In situ S/S is less labor and energy intensive than ex situ processes that require excavation, transport and disposal of the treated material. In situ S/S also is preferred if volatile or semi volatile organics are present because excavation would expose these contaminants to the air.

Vitrification involves the insertion of electrodes into the soil which must be able to carry a current and then to solidify as it cools (Mulligan et al., 2001a). It is most applicable to sites containing low-volatility metals with high glass solubility, and therefore appears to be well suited for treatment of lead, chromium, arsenic, zinc, cadmium and copper wastes.

Vitrification may be performed ex situ or in situ, although in situ processes are preferred due to the lower energy requirements and cost. Typical stages in ex situ vitrification processes may include excavation, pretreatment, mixing, feeding, melting and vitrification, off-gas collection and treatment, and forming or casting of the melted product. The energy requirement for melting is the primary factor influencing the cost of ex situ vitrification. In situ vitrification (ISV) involves using an electric current to melt soil or other earthen materials at extremely high temperatures (1,600 to 2,000 ^{o}C or 2,900 to 3,650 ^{o}F), thereby immobilizing most inorganics and destroying organic pollutants through pyrolysis. The main requirement for in situ vitrification is the ability of the soil melts to carry current and solidify as it cools.

4.2.1.3 Physical Separation

Physical separation is an ex situ process that attempts to separate the contaminated material from the rest of the soil matrix by exploiting certain characteristics of the metal and soil. Physical separation techniques are available that operate based on particle size, particle density, surface and magnetic properties of the contaminated soil. These techniques are most effective when the metal is either in the form of discrete particles in the soil or if the metal is sorbed to soil particles that occur in a particular size fraction of the soil. Physical separation often is used as a form of pretreatment in order to reduce the amount of material requiring subsequent treatment. Several techniques are available for physical separation of contaminated soils including screening, classification, gravity concentration, magnetic separation, and froth flotation.

Screening separates soils according to particle size by passing the matrix through a sieve with particular size openings. Smaller particles pass through the sieve and leave larger particles behind, however, the separation is not always complete. Screening may be performed as a stationary process or with motion using a wet or dry process stream (Smith et al., 1995).

Classification involves separation of particles based upon the velocity with which they fall through water (hydroclassification) or air (air classification). Hydroclassification is more common for soil separation and may be performed using a non-mechanical, mechanical or a hydraulic classifier.

Gravity concentration relies on gravity and one or more other forces (centrifugal force, velocity gradients, etc.) that may be applied to separate particles on the basis of density differences. Gravity concentration may be achieved through the use of a hydrocyclone, jig, spiral concentrator, or shaking table.

Magnetic separation subjects particles to a strong magnetic field using electromagnets or magnetic filters and relies on differences in magnetic properties of minerals for separation. Low intensity wet magnetic separators are the most common magnetic separation devices. This process can recover a wide variety of minerals and is particularly successful for separating ferrous from nonferrous minerals (Allen and Torres, 1991).

Froth flotation uses air flotation columns or cells to remove particles from water. In this process, air is sparged from the bottom of a tank or column that contains slurry of the contaminated material. Some metals and minerals attach to the air bubbles due to particular surface properties, such as hydrophobicity. Froth flotation can be used to remove metals that attach to air bubbles, or to remove other minerals while the metal remains in the slurry.

4.2.1.4 Extraction

Metal contaminated sites can be remediated using techniques designed to extract the contaminated fraction from the rest of the soil, either in situ or ex situ. Metal extraction can be achieved by contacting the contaminated soil with a solution containing extracting agents (soil washing and in situ soil flushing) or by electrokinetic processes. The contaminated fraction of soil and/or process water is separated from the remaining soil and disposed of or treated.

Electrokinetic remediation technology is one of the innovative technologies for soil remediation, it involves passing a low intensity electric current between a cathode and an anode imbedded in the contaminated sites (Mulligan et al., 2001a). This technology is most applicable to saturated soils with low ground-water flow rates and moderate to low permeability. The efficiency of metal removal by this process will be influenced by the type and concentration of contaminant, the type of soil, soil structure, and interfacial chemistry of the soil.

Water and/or chemical solutions also can be added to enhance the recovery of metals by this process. Positively charged metal ions migrate to the negatively charged electrode, while metal anions migrate to the positively charged electrode. Electrokinetic treatment concentrates contaminants in the solution around the electrodes. The contaminants are removed from this solution by a variety of processes, including electroplating at the electrodes, precipitation/coprecipitation at the electrodes, complexation with ion exchange resins, or by pumping the water from the subsurface and treating it to recover the extracted metals (Smith et al, 1995).

Pyrometallurgical technologies use elevated temperature extraction and processing for removal of metals from contaminated soils. Soils are treated in a high-temperature furnace to remove volatile metals from the solid phase. Subsequent treatment steps may include metal recovery or immobilization. Hydrometallurgical treatment requires a uniform feed material for efficient heat transfer between the gas and solid phases and minimization of particulates in the off-gas. This process is usually preceded by physical treatment to provide optimum particle size. Hydrometallurgical processes usually produce a metal-bearing waste slag, but the metals also can be recovered for reuse (Evanko and Dzombak, 1997).

Hydrometallurgical treatment is usually performed offsite because few mobile treatment units are available. This technology is most applicable to large volumes of highly contaminated soils (metal concentrations of 5%-20%, especially when metal recovery is expected). Low metal concentrations can be processed, especially for mercury since it is easy to volatilize and recover (Smith et al., 1995).

In situ soil flushing is the extraction of contaminants from the soil with water or other suitable aqueous solutions. The extraction solution is injected into or sprayed onto the contaminated area to mobilize the contaminants usually by volatilization. After being contacted with the contaminated material the extractant solution is collected using pump-and-treat methods for disposal or treatment and reuse. Similar extracting agents are used for in situ soil flushing and soil washing, including acids/bases, chelating agents, oxidizing/reducing agents and surfactants/cosolvents. Also, water can be used alone to remove water-soluble contaminants such as hexavalent chromium. The applicability of in situ soil flushing technologies to contaminated sites will depend largely on site-specific properties, such as hydraulic conductivity, that influence the ability to contact the extractant with contaminants and to effectively recover the flushing solution with collection wells (NRC, 1994). This technology has been applied for a limited number of projects, mostly for soils containing organic forms of contamination (NRC, 1994), and limited information is available on the application of this technology to metal contaminated sites.

Soil washing is an ex situ process that scrubs excavated soils to remove contaminants by chemical or physical treatment methods in aqueous suspension. Physical treatment is achieved by particle size separation technologies adapted from mineral processing to concentrate the contaminant in a particular size fraction (Allen and Torres, 1991). Based on the tendency of many organic and inorganic contaminants to bind to clay, silt, and organic soil particles, washing processes that separate fine clay and silt particles from the coarser sand and gravel soil particles effectively separate and concentrate the contaminants into a smaller volume of soil that can be further treated or disposed of. Chemical treatment involves addition of extraction agents that react with the contaminant and leach it from the soil. The liquid containing the contaminants is separated from the soil resulting in a clean solid phase.

4.2.2 Chemical Treatment

Chemical and/or biological processes can be used to alter the form of metal contaminants in order to decrease their toxicity and/or mobility. They convert hazardous contaminants to nonhazardous or less toxic compounds that are more stable, less mobile, and/or inert. The three types of reactions that can be used for this purpose are oxidation, reduction, and neutralization reactions. Changing the oxidation state of metals by oxidation or reduction can detoxify, precipitate, or solubilize the metals (NRC, 1994). Chemical neutralization is used to adjust the pH balance of extremely acidic or basic soils and/or groundwater. This procedure can be used to precipitate insoluble metal salts from contaminated water, or in preparation for chemical oxidation or reduction.

Chemical treatment also may be used to solubilize contaminants from the most contaminated fraction of the soil. It is performed in an aqueous slurry of the contaminated material to which an extracting agent is added. The extraction is performed in a mixing vessel or in combination with the physical treatment stage. The type of extractant used will depend on the contaminants present and the characteristics of the soil matrix. Many processes manipulate the acid/base chemistry of the slurry to leach contaminants from the soil (Tuin and Tels, 1990). However, if a very low pH is required concerns about dissolution of the soil matrix may arise. Chelating agents (e.g., EDTA) selectively bind with some metals and may be used to solubilize contaminants from the soil matrix (Elliot et al., 1989). Oxidizing and reducing agents (e.g., hydrogen peroxide, sodium borohydride) provide yet another option to aid in solubilization of metals since chemical oxidation/reduction can convert metals to more soluble forms (Assink and Brown, 1989). Recently, batch tests conducted by Mulligan et al. (1999; 2001b; 2001c) demonstrated the feasibility of using surfactants and biosurfactants to enhance soil washing to remove heavy metals from soils and sediments.

The primary problem associated with chemical treatment is the nonspecific nature of the chemical reagents. Oxidizing/reducing agents added to the matrix to treat one metal will also target other reactive metals and can make them more toxic or mobile (NRC, 1994; Evanko and Dzombak, 1997). Also, the long-term stability of reaction products is of concern since changes in soil and water chemistry might reverse the selected reactions. In situ chemical agents must be carefully selected so that they do not further contaminate the treatment area.

4.2.3 Bioremediation

Bioremediation technologies are available for remediation of metal contaminated sites. These technologies are commonly used for the remediation of organic contaminants and are beginning to be applied for metal remediation, although most applications to date have been at the bench and pilot scale (Schnoor, 1997). Biological treatment exploits natural biological processes that allow certain plants and microorganisms to aid in the remediation of metals. These processes occur through a variety of mechanisms, including adsorption, oxidation and reduction reactions, and methylation (Means and Hinchee, 1994).

Bioaccumulation involves the uptake of metals from contaminated media by living organisms or dead, inactive biomass. Active plants and microorganisms accumulate metals as the result of normal metabolic processes via ion exchange at the cell walls, complexation reactions at the cell walls, or intra- and extra-cellular precipitation and complexation reactions. Adsorption to ionic groups on the cell surface is the primary mechanism for metal adsorption by inactive biomass. Accumulation in biomass has been shown to be as effective as some ion exchange resins for metal removal from water (Means and Hinchee, 1994).

Phytoremediation is an innovative technology that utilizes plants and their associated rhizospheric microorganisms to remove, contain, or degrade environmental contaminants located in the soil, sediments, groundwater, surface water, and even the atmosphere. This technology will likely be limited to use in shallow soils with relatively low levels of metal contamination. Potentially useful phytoremediation technologies for remediation of metals-contaminated sites include phytoextraction, phytostabilization and rhizofiltration (Jonathan, 1997).

Bioleaching is a way of using microorganisms to solubilize metal contaminants either by direct action of the bacteria, or as a result of interactions with metabolic products, or both. The microorganisms involved in bioleaching actually gain energy by breaking down minerals into their constituent elements. These can then be extracted easily. Bioleaching can be used in situ or ex situ to aid the removal of metals from soils. This process is being adapted from the mining industry for use in metals remediation.

Microbially mediated oxidation and reduction reactions can be manipulated for metal remediation. Some microorganisms can oxidize/reduce metal contaminants directly while others produce chemical oxidizing/reducing agents that interact with the metals to effect a change in oxidation state. Mercury and cadmium have been observed to be oxidized through microbial processes, and arsenic and iron are readily reduced in the presence of appropriate microorganisms (Evanko and Dzombak, 1997). The mobility of metal contaminants is influenced by their oxidation state. Redox reactions can therefore be used to increase or decrease metal mobility (Means and Hinchee, 1994).

Methylation involves attaching methyl groups to inorganic forms of metal ions to form organometallic compounds. Methylation reactions can be microbially mediated. Organometallic compounds are more volatile than inorganic metals and this process can be used to remove metals through volatilization and subsequent removal from the gas stream. However, organometallics are also more toxic and mobile than other metal forms and may potentially contaminate surrounding surface waters and groundwater (Means and Hinchee, 1994).

4.3 Surfactant Enhanced Remediation of Metal Contaminated Soils

The use of surface-active agents to enhance remediation of contaminants has recently received increasing interest (Abdul and Gibson, 1991, Doong et al. 1998). The addition of surfactant can enhance the solubilization of many hydrophobic organic compounds, such as polynuclear aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and chlorinated hydrocarbons by increasing the solubility of the contaminants via micellar solubilization (Edwards et al., 1991, Doong et al., 1998). Recently, it was reported that the addition of surfactant can enhance the remediation of subsurface chromium contamination (Nivas et al., 1996, Doong et al., 1998). Moreover, several researchers reported that surfactant in combination with a complexing agents has an even greater capability in extracting heavy metals from contaminated soils (Tondre et al., 1993; Doong et al., 1998; Mulligan et al., 2001b). Some previous studies related to surfactant/biosurfactant enhanced remediation of heavy metal contaminants are described below.

Beveridge and Pickering (1983) investigated the effect of a range of commercially available, water soluble surfactants on the uptake of Cu, Zn, Cd and Pb ions by three types of clay (kaolinite, illite, and montmorillonite) over the pH range 3-10. Results from batch equilibrium tests on clay suspensions indicated that the presence of surfactants of different types influenced metal ion uptake by clays to differing degrees. The adsorption of lead, cadmium, copper, and zinc was significantly reduced in the presence of small amounts of cationic surfactant, particularly with montmorillonite clays. One of the more promising aspects of the study involved the very low solution concentration (0.005% by weight) required to cause desorption.

Hessling et al. (1989) investigated the soil washing techniques for remediation of lead contaminated soils at battery recycling facilities. Three wash solutions were studied for their efficacy in removing lead from these soils: (I) tap water alone at pH 7, (2) tap water plus anionic surfactant in a 0.5% solution, and (3) tap water plus a 3: 1 molar ratio of EDTA (ethylenediamine tera-acetic acid) to toxic metals at pH 7-8. Tap water alone did not appreciably dissolve the lead in the soil. Surfactants and chelating agents such as EDTA offer good potential as soil washing additives for enhancing the removal of lead from soils.

The U.S. EPA conducted a series of laboratory bench-scale soil washing studies using water, EDTA, or a surfactant to treat soils from metal recycling sites (PEIAs, 1989; Royer et al., 1992). Soil washing did not remove significant quantities of lead. The lead was not concentrated in any particular soil from any of the soil fractions, but rather was distributed among the fractions. EDTA was more effective in removing lead than either the surfactant or water washes.

Simons et al. (1992) performed ligand-modified micellar-enhanced ultrafiltration (LMMEUF) experiments for metal ion separation by utilizing an amphiphilic ligand, solubilized in micelles, to selectively complex a target metal ion in a mixture of metal cations. The characteristic of anionic surfactants complexing and associating with metal cations has been applied to enhance the removal of metal ions.

Doong et al. (1998) investigated the addition of surfactants to remediate cadmium-contaminated soils. Anionic (sodium dodecyl surfate, SDS), nonionic (Triton X-I00, TX100) and cationic (cetyltrimethylammonium bromide, CTAB) surfactants were chosen to elucidate the extraction efficiency of surfactant. EDTA and diphenylthiocarbazone (DPC) were also added to enhance the extraction efficiencies of surfactant. Moreover, the pH effect was examined to determine the optimal surfactant system. They found that the addition of anionic and nonionic surfactants can enhance desorption rates of cadmium, lead and zinc but the addition of cationic surfactant decreased the desorption efficiency of heavy metals. The desorption efficiency was found to increase linearly with the increasing surfactant concentration below the CMC and remained relatively constant above the CMC. Moreover, they found the addition of EDTA could significantly enhance the desorption efficiency of heavy metals. The cationic surfactant was shown to be a more effective surfactant than anionic and nonionic surfactants in extracting heavy metals under acidic environment. However, the addition of DPC lowered the heavy metal removal by 2 to 4 times. Also, increasing the pH value can decrease the extraction capabilities of nonionic and anionic surfactant. The authors concluded that surfactants combined with complexing agents could be used effectively as chemical amendments to flush cadmium-contaminated soil by proper selection of the type and concentration of surfactant and complexing agent at different pH values.

Kornecki et a1. (1998) investigated the feasibility of using cationic surfactants to desorb lead (Pb) from contaminated soil using a two-phase test program. For nearly all the surfactants tested, increasing the surfactant solution concentration resulted in decreased pH and increased Pb desorption. Deionized water alone desorbed only 1% of the lead. Lead desorption using a 0.025 M surfactant solution was pH dependent. As the pH decreased, desorption of Pb increased. The researchers also compared the Pb extraction efficiency to that using EDTA. EDTA desorbed 94% to 97% of the lead and was not influenced by either solution pH or soil type.

Mulligan et al. (1999) conducted batch washes to investigate the feasibility of using biodegradable biosurfactants to remove heavy metals from an oil-contaminated soil with surfactin, a rhamnolipid and a sophorolipid. The soil contained 890 mg/kg of zinc and 420 mg/kg of copper with a 12.6% oil and grease content. Highest levels of zinc removal were obtained using 12% rhamnolipid (19.5% of the zinc) and 4% sophorolipid/0.7% HCl (15.8% of the zinc). Highest copper removal rates were achieved (greater than 25%) with 12% rhamnolipid or with 2% rhamnolipid /1% NaOH or 0.25% surfactin/1% NaOH. A series of five batch washes removed 70% of the copper with 0.1% surfactin/1% NaOH while 4% sophorolipid/0.7% HCl was able to remove 100% of the zinc. Sequential extraction procedures showed that the carbonate and oxide fractions accounted for over 90% of the zinc present in the soil and the organic fraction in the soil constituted over 70% of the copper. Sequential extraction of the soil after washing with the surfactin or rhamnolipid (both with 1% NaOH) indicated that these surfactants could remove the organically bound copper and that the sophorolipid with acid could remove oxide-bound zinc. The authors concluded that the results clearly indicated the feasibility of removing the metals with the anionic biosurfactants tested even through the exchangeable metal fractions were very low.

The research by Hatzinger (2001) was conducted to assess the use of surfactant colloidal gas apron (CGA) foams for the remediation of heavy metals in contaminated aquifers. The starting concentrations of the metals on the sand were 41.2 mg/kg for Pb, 8.6 mg/kg for Hg, and 13.0 mg/kg for Cd. Among the surfactant tested, Gemtek (plant surfactant mixture) and Ammonyx KP (oleyl dimethyl benzyl ammonium chloride) were the most effective agents for removal of all of the three metals. Gemtek solubilized 40% of the Pb, 61% of the Cd, and 38% of the Hg. The addition of ethylenediamine tetra-acetic acid (EDTA) to Gemetek further improved the extract efficiency of this surfactant, increasing removal efficiency for Pb and Cd to greater than 92%.

Mulligan et al. (2001b) used batch-washing experiments to evaluate the feasibility of using biosurfactant for the removal of heavy metals from sediments. Surfactin from *Bacillus subtilis*, rhamnolipids from *Pseudomonas aeruginosa* and sophorolipid from *Torulopsis bombicolla* were evaluated using a metal-contaminated sediment (110 mg/kg copper and 3300 mg/kg zinc). A single washing with 0.5% rhamnolipid removed 65% of the copper and 18% of the Zn, whereas 4% sophorolipid removed 25% of the copper and 60% of the zinc. Surfactin was less effective, removing 15% of the copper and 65% of the zinc. It was postulated that the metal removed by the biosurfactants occurs through sorption of the surfactant onto the soil surface and complexation with the metal, detachment of the metal from the soil into the soil solution and hence association with surfactant micelles. It was pointed out in the conclusions that heavy metal removal from sediments by biosurfactants is feasible and further research will be conducted.

Despite the successful demonstrations described above, the role of surfactants in the remediation of metal contaminated soil is quite site specific, depending on the pH, matrix of the soil, speciation of the metal, and organic content. Also the role of surfactant and complexing agent on the remediation of heavy metal contaminated soils still remains unclear. There are many further researches which should be conducted to improve the applicability and effectiveness of this emerging remediation technology.

Chapter Five

Experimental Materials and Methods

5.1 Introduction

In this chapter, the experimental materials and equipment setup used in the experiments are introduced.

Experimental materials included soil samples, and nonionic surfactant, Triton X-100, and biosurfactant, JBR425 (mixed Rhamnolipids), the target contaminants, Cd and Ni, in the forms of $Cd(NO_3)_2.6H_2O$ and $NiCl_2.6H_2O$, HCl (12 N, 6 N) used for digestions prior to AA analysis, and HCl (1 N) and NaOH (1 N) solutions used to adjust the pH values. Distilled water was also used for washing, diluting, and controls.

Foam biosurfactant technology in soil remediation was studied with column experiments, which are inherently open systems nearing soil flushing methods. The design of the system also considered the influence of the sizes of tubing and columns and connectors on the foam quality and stability, two significant foam characteristics. The effects of such parameters and the flow rate on the pressure gradient build-up in the soil column were also investigated. Finally, the removal efficiencies were tested and mass balances were checked.

5.2 Experimental Materials

5.2.1 Soil Samples

The soil sample was obtained near a building site. It was dried in an oven (LINDERG/BLUE) at 105 °C for 48 hours. The standard for completely dried is that the weight of the sample does not change over one hour interval, a minimum of 24 hours required. Large particles were crushed by mortar and pestle, and mixed with fine silica sands (in a ratio of 2:8). Consequently, sieve analyses were performed. A set of USA Standard Testing Sieves (Fisher Scientific Company, USA.) was used in this experiment. The particles that passed through the No. 200 sieve were discarded. Although they may contain a portion of the contaminants, they are not applicable for the column tests. All the analyses were performed in triplicate and did not vary more than 5%. The average results of the sieve analyses (per 500 g soil sample) were listed in Table 5.1. According to the ASTM (American Society for Testing and Materials) standard (D2487), the soil can be classified as sandy silt.

Table 5.1 Results from Sieve Analysis (per 500 g soil sample retained)

Sieve Size	**No. 50 Sieve (300 μm)**	**No. 100 Sieve (150 μm)**	**No. 200 Sieve (75 μm)**	**Total**
Retained Weight (g)	420.5	61.3	14.7	496.5
Percentage (after Sieving)	84.7%	12.3%	3.0%	100.0%

After sieve analysis, distilled water was added to the soil samples. Next, the suspensions were shaken on a wrist action shaker (BURRELL, Burrell, Pittsburgh, PA, USA.) at 60 oscillations/min for 24 hours, and then centrifuged at 3000 rpm for 15 minutes to separate the soil and the liquid, and this procedure was accomplished by an IEC HN-SII

Centrifuge, made by International Equipment Company in USA. Subsequently, the soil samples were dried again before analyzing their physical and chemical characteristics. All the data were triplicate and did not vary more than 5%. The average results were listed in Table 5.2. Specific procedures for such experiments are listed in the Appendix.

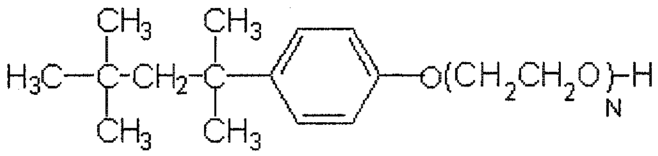
Table 5.2 The Characteristics of Soil Samples

CEC (1) (cmoles$^+$/kg)	7.92
Hydraulic Conductivity(2) (cm/s)	0.021
Organic Matter Content (3) (%)	0.96%

(1) See Appendix A.
(2) See Appendix B.
(3) See Appendix C.

5.2.2 Triton X-100

The nonionic surfactant, Triton X-100, was obtained from SIGMA Chemical Co., U.S.A. It is produced from octylphenol polymerized with ethylene oxide. The number ("-100") relates only indirectly to the number of ethylene oxide units in the structure. X-100 has an "average of 9.5" ethylene oxide units per molecule, with an average molecular weight of 625 (Sigma, 1993). The chemical structure of Triton X-100 is exhibited in Figure 5.1.



N = approx. 9.5

Figure 5.1 Chemical Structure of Triton X-100 (Sigma, 1993)

Triton X-100 is a nonionic detergent, 100% active ingredient, which is often used in biochemical applications to solubilize proteins. It has no antimicrobial properties and is considered a comparatively mild detergent, non-denaturing, and is reported in numerous references as a routinely added reagent used in the industrial and household detergent applications and in emulsifying agents (Sigma, 1993). Triton X-100 is employed in most industrial products to generate detergents for fine fabrics. These surfactants are also important ingredients of primary emulsifier mixtures used in the manufacture of emulsion polymers, stabilizers in latex polymers, and emulsifiers for agricultural emulsion concentration and wettable powders (Edwards et al., 1994). The properties of Triton X-100 from the Material Safety Data Sheet (MSDS) are listed as Table 5.3.

Table 5.3 Properties of Trixon-100 (Sigma, 1993)

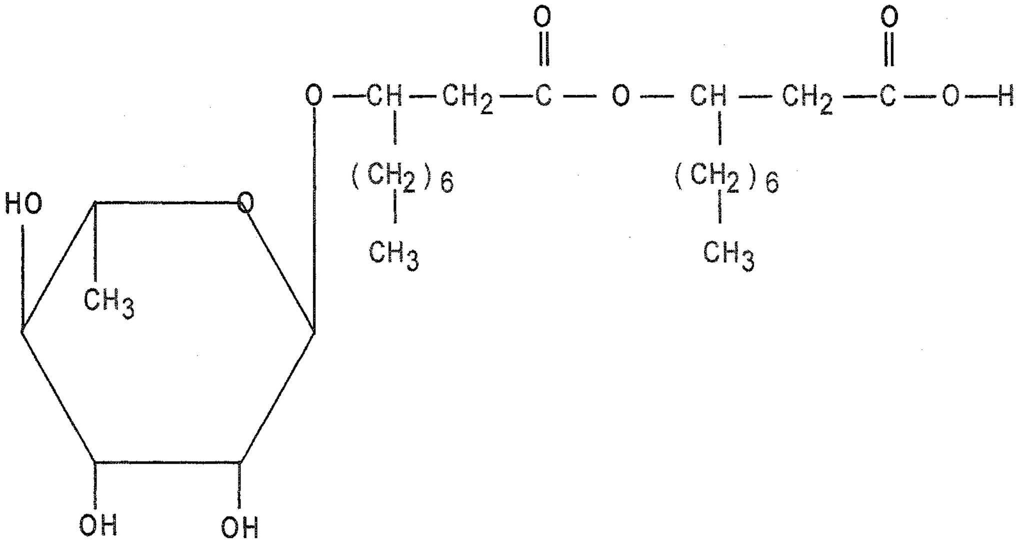
Product Name	Triton X-100
Type	Nonionic Surfactant
Formula	$C_8H_{17}C_6(OC_2H_4)_nOH$ (n = 9 –10)
Appearance and Odor	Colorless Liquid
Specific Gravity @ 25 °C	1.065 g/ml
pH (5% aqueous solution)	6.0 – 8.0
Viscosity (Brookfield) @ 25 °C	240 cps
Calculated HLB Value	13.5
CMC	0.22 – 0.24 mM

(1) Edwards et al., 1994

5.2.3 JBR425

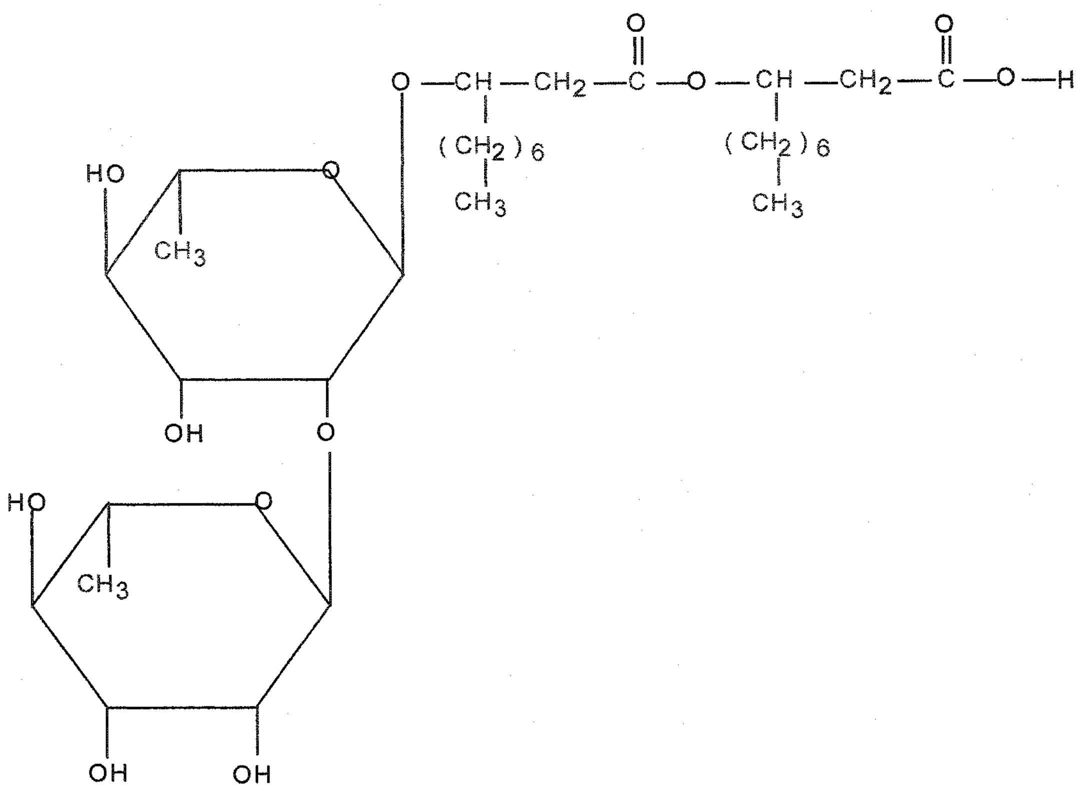
The biosurfactant, JBR425 (mixed rhamnolipids), was obtained from JENEIL Biosurfactant Co.

Chemically, rhamnolipids are glycosides of rhamnose (6-deoxymannose) and β-hydroxydecanoic acid. Two rhamnolipids, RLL (R1) and RRLL (R2) (Figure 5.2), are formed during controlled fermentation at an R2/R1molar ratio of 0.9 to 1 (Jeneil, 2001). The result, JBR480, is a >80% pure biosurfactant with excellent wetting and emulsification properties. JBR425 is a ready to use >20% active solution of JBR480, a readily biodegradable surfactant with a very low environmental impact (Jeneil, 2001). JBR425 is also of low toxicity and low skin irritation at use concentrations. As a cost effective alternative, JBR425 is an ideal choice for use in general and industrial formulated products.



RLL or R1
α-L-Rhamnopyranosyl-β-hydroxydecanoyl-β-hydroxydecanoate

Figure 5.2 Structure & Chemical Names of JBR425 (Jeneil, 2001)



RRLL or R2
2-O-α-L-Rhamnopyranosyl-α-L-rhamnopyranosyl-
β-hydroxydecanoyl-β-hydroxydecanoate

Figure 5.2 Structure & Chemical Names of JBR425 (Jeneil, 2001) (continued)

The general chemical and physical characteristics of JBR425, with the high degree of surface activity produced at very low concentrations, and ready biodegradability (biodegradability rate of >60% within the 28 day test cycle), indicates the use of JBR425 as a performance enhancing additive in a wide range of application areas, such as personal care products, detergents, textile manufacturing, industrial laundry supplies and pulp and paper processing and hydrocarbon recovery. In many applications, they are expected to be more effective than conventional surfactants in similar concentrations.

In aqueous solutions, JBR425 has a very low critical micelle concentration indicating the strong surface activity shown at low concentrations, characterized by low surface tension for water and electrolyte solutions with very low interfacial tensions for water/hydrocarbon systems. Like other surfactants, it can lower the air/water surface tension. For example, for distilled water the surface tension is lowered from 72 mN/m to around 30 mN/m in the presence of rhamnolipids (Zhang and Miller, 1992).

As described in Chapter Two, rhamnolipids can also be used to enhance soil flushing efficiency and the rate of adsorption of heavy metals from soil, which makes them preferable to remove heavy metals from soils to reduce the toxicity of soil. The most notable rhamnolipid surfactants that have been tested were found to release three times as much oil as water alone from beaches in Alaska after the Exxon Valdez tanker Spill (Mulligan et al., 2001b). The properties of JBR425 on the MSDS (Jeneil, 2001) are listed as Table 5.4.

Table 5.4 Properties of Biosurfactant JBR425 (Jeneil, 2001)

Product Name	JBR425
Type	anionic biosurfactant
Formula	$C_{26}H_{48}O_9$, $C_{32}H_{58}O_{13}$
Appearance and Odor	Amber, Soapy liquid
Specific Gravity @ 25 °C	1.05 - 1.06 mg/ml
pH (1% suspension)	6.5 – 7.5
CMC(1)	0.3 g/l

(1) Mulligan et al., 2001b

5.2.4 Contaminants

The target contaminants Cd and Ni, were added in the forms of $NiCl_2.6H_2O$ (Fisher Chemical, Fisher Scientific, New Jersey, USA) and $Cd(NO_3)_2.6H_2O$ (P. A., New Jersey, USA). They were dissolved with distilled water before being added into the soil samples.

5.3 Experimental Method and Setup

5.3.1 Soil Contamination

Metal salts were dissolved with distilled water (4000 ppm of Cd and 4000 ppm of Ni) and added together to the washed and dried soil sample (without adjusting the pH value) at the same time. The soil was left in the solution over two weeks, and then the suspension was shaken on a wrist action shaker (BURRELL, Burrell Scientific, Pittsburgh, P. A., USA) at 60 oscillations/min for 24 hours at a room temperature of 25 ± 0.2 °C, and subsequently centrifuged (IEC HN-SII Centrifuge, International Equipment Company, USA) at 3000 rpm for 15 minutes. Contaminated soil samples were dried and digested with 12 N and 6 N HCl and then the AA analysis was performed by an Atomic Absorption Spectrophotometer (PERKIN ELMER, AAnalyst 100, PerkinElmer Inc., ON, Canada) to measure the adsorbed metal concentrations. All the analyses were done in triplicate and results did not vary more than 10%. The average results were presented in Table 5.5.

Table 5.5 Soil Contamination Levels

Cd Concentration (mg Cd/ kg Soil)	Ni Concentration (mg Ni/kg Soil)
1706	2010

5.3.2 Column Experiments

A unique feature of the column experiments is that these methods are inherently open systems, as compared with batch methods, which are primarily closed systems. The solute is continuously added to the system and reaction products are continuously removed. While in batch tests, after all the reactants are added and mixed together, no additional amounts of reactants are added and products are allowed to accumulate. The only material removed from the system is that removed for analysis, and that is usually a very small fraction of the total. This unique feature produces special attributes for column methods that solve some of the problems associated with batch systems, but also involves some limitations as well. Perhaps the main advantage of these methods is the continual removal of reaction products that in batch reactors are allowed to accumulate. Furthermore, with these methods, the solid phase will react with a greater mass of solute (Concentration × flow velocity × time) than in batch reactors (concentration × volume) (Selim et al., 1996).

All column experiments were conducted at room temperature (25 ± 0.2 °C). A series of experiments were conducted to investigate different parameters involved in the biosurfactant foam technology in soil remediation. The experiments were done in three phases. The first phase was related to the foam parameters such as foam quality and stability. The second phase was carried out to measure the pressure gradient build up in the soil column under different conditions and to prepare for the next phase. The third phase involved the decontaminated efficiency of this technology.

5.3.2.1 Foam Parameters

Stability and quality are two of the most important characteristics of foam. As described in Chapter Two, the foam quality is defined as the ratio of total gas volume per total volume of foam, and the foam stability is measured as the time that half of the foam needs to collapse. The experimental setup for measuring such parameters and foam properties is shown schematically in Figure 5.3. Plastic columns (L = 25 cm, D = 2.5 cm) with metal end species were equipped with circular porous stone plates. The purpose of having the porous stone plates at the end of the column was to enable the foam generation in presence of surfactant solution and air. Two flow meters (flow meter I and flow meter II) (Cole Parmer, Niles, IL) were used to control the flow of the solution and the air before entering the foam generation column. A pump (MASTERFLEX, Cole-Parmer Instrument Company) was used to pump the surfactant solutions of different concentrations (0.5%, 1.0% and 1.5%). The flow rates of the surfactant solution and air could be varied independently in order to control the foam quality and generation rate.

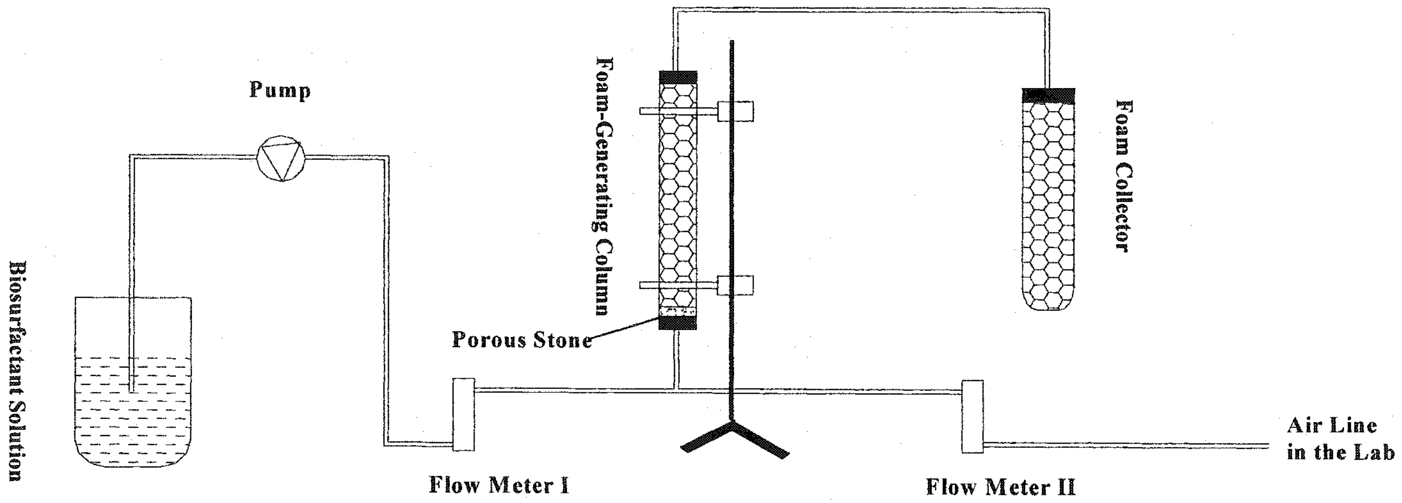


Figure 5.3 Schematic Setup of the Foam-Generating Column for Evaluating Foam Quality and Stability

The foam always exited the column at atmospheric pressure. After the foam reached a uniform and steady state in terms of bubble size and appearance, the foam exiting the column was taken as samples for quality and stability analyses. In each experiment, three 50 ml samples of the generated foam were taken and left until all of the bubbles collapsed. The time required for collapsing half of the foam was recorded as an indicator of the foam stability and the total liquid obtained from the collapsed foam per total volume of the foam sample was calculated to indicate the foam quality.

5.3.2.2 Soil Pressure Gradient

The pressure gradient developed in the soil column during the foam flow is one of the most important factors in using foams for soil remediation and soil flushing. From a physical perspective, to prevent problems due to channeling or soil heaving it is necessary to restrict injection pressure about 22.6 kPa/m of depth, corresponding to the weight of the soil overburden (Chowdiah et al., 1998). The effects of the surfactant concentration, the foam quality and the foam flow rate on the pressure build-up in the soil column were investigated in this stage. The set up of the experiments is shown in Figure 5.4.

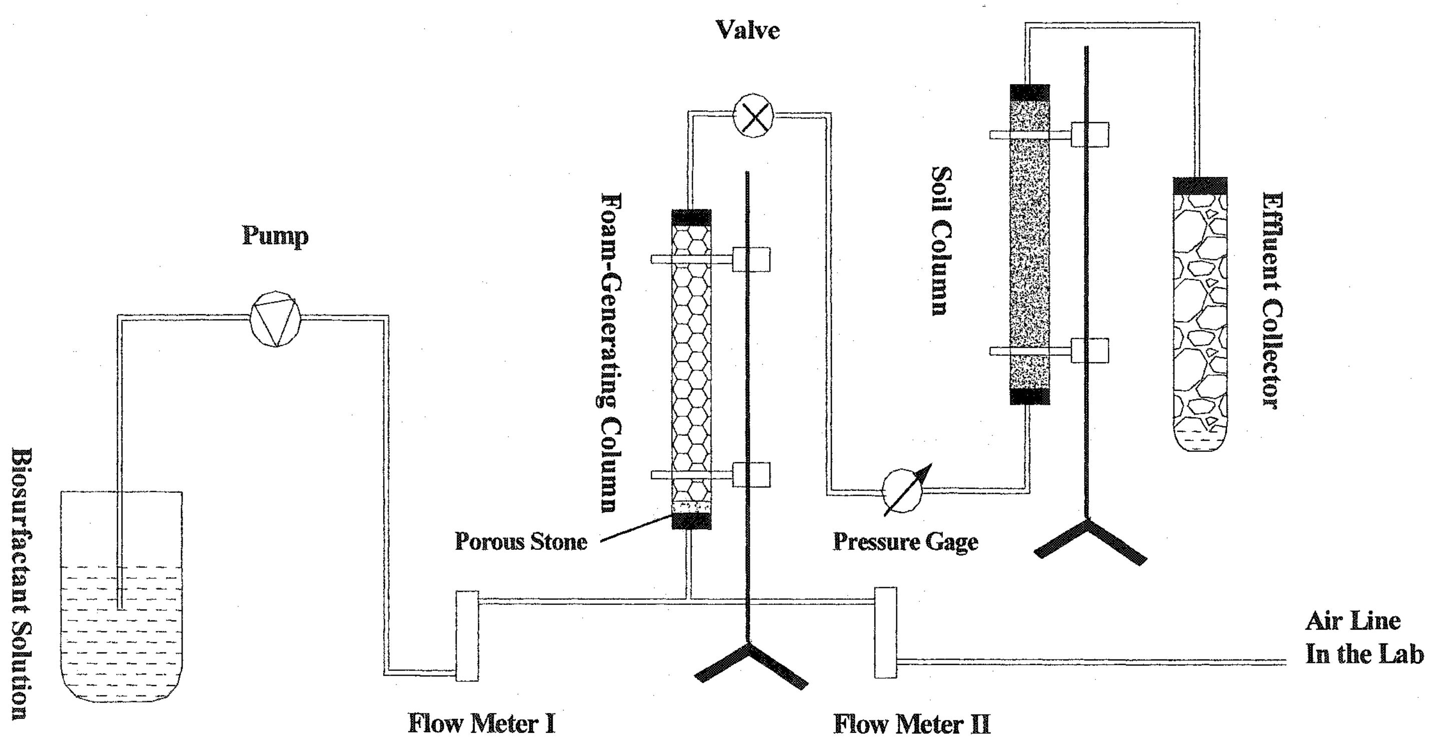


Figure 5.4 Schematic Setup of the Column Experiments for Soil Pressure Gradient and Remediation Tests

In this experiment, uncontaminated and dried soils were packed into another column (L = 25 cm, D = 4 cm) in 5 layers. The total weight of sand is about 430 g (430 ± 5 g). The plastic wall of the column was tapped continuously as the soil was added. The purpose of tapping and compacting was to pack the soil uniformly. The pore volume of the packed column which is an important parameter for the following experiments was measured for the soil sample and water was pumped into the column at a pressure gradient of close to zero to make it saturated. The volume of water needed to saturate the soil column was used to indicate the pore volume of the column.

Then the soil column was connected to the foam-generating column, and a two-way valve was used to control the foam flow. In all experiments, the foam flowed through the sand after the exiting foam reached steady conditions in terms of the pressure drop and the texture of the exiting foam, and the pressure was measured by the pressure gauge (CPW, Hydro-PAK, EDMONTON, Canada) before the pressure gradients were recorded.

Usually, the pressure gradient increase lasted a few hours. The exact behavior during this transient phase depends on several factors, including whether the soil pack was initially wet or dry, and whether there is a significant adsorption of the surfactant from the foam onto the sand or soil (Chowdiah et al., 1998).

5.3.3.3 Remediation Experiments

In this phase, the experimental setup was the same as in the second phase (Figure 5.4). Contaminated soils were compacted in the column as the same way described above.

Surfactant concentration is an important factor influencing the heavy metal removal efficiencies. It was found that metal removal efficiencies would increase linearly with the increasing surfactant concentration below critical micelle concentration (CMC), and remain relatively constant above the CMC (Doong et al., 1998). High concentrations of surfactant solutions (1 – 10%) often are required to overcome dilution and binding effects in order to be effective (Rothmel et al., 1998). It also has been observed that high surfactant concentrations can result in plugging of injection wells by the dispersion of fine materials or by the formation of viscous emulsions (Nash, 1987; Rothmel et al., 1998). Based on such points and also the results from the precedent experiments (discussed in Chapter Six), 0.5% rhamnolipid solution was chosen in this experimental phase.

All of the flushing studies were conducted by varying the initial pH values (6.8, 8.0, 10.0) of 0.5% rhamnolipid solutions. Foam generated by Triton X-100 with the same concentration and pH values was used for comparison. Surfactant solutions without foam generation were also pumped through the column. Distilled water with adjusted pH values were taken as controls. The pH value was adjusted by adding 1 N NaOH or 1 N HCl solutions. All of the experiments were performed in triplicate, and the average values were presented.

Flow rates less than 5 ml/min were used for measuring these properties and to prevent short-circuiting which results in inaccurate pore volume results. A pressure gauge installed upstream of the soil column measured the inlet pressure, and a valve was placed before the column to prevent injection of foam into soil before its uniformity and steady-state quality was reached. It also was used for taking foam samples before injection into the soil.

Foam exiting the soil column was collected for analyzing the metal concentration. Samples were taken according to pore volumes passed through the contaminated soil. Effluent for each sample was collected in containers. Foam samples were left to collapse for 24 hours and then transferred to centrifuge tubes.

All the samples were digested with 12 N and 6 N HCl and shaken at 60 rpm/min for 24 hours. Then AA analysis was performed to measure the concentration in the effluent. The removed metal amounts were calculated as concentration multiplied by volume, and the removal efficiency was calculated. All the samples were analyzed together to ensure that the metal concentrations were measured under the same conditions.

Columns flushed by the rhamnolipid foam were chosen to evaluate the mass balance after the experiments. At the end of the experiments, samples of soil were taken from the top, middle and bottom of the washed column to be analyzed for heavy metal concentrations. Soil samples were dried, weighed and digested with 6 N HCl, and then AA analyses were performed. The results were compared with the results from effluent analyses to check whether there was any metal missing.

Chapter Six

Results and Discussion

6.1 Overview

As described in Chapter Five, the main experiments were conducted in three phases. The first phase was related to the foam quality and stability under different biosurfactant concentrations (0.5%, 1.0%, 1.5%) with different pH values (6.8, 8.0, 10.0). The second group of experiments was performed to investigate the pressure gradient build-up in the soil column with different biosurfactant concentrations, pH values, foam qualities and foam flow rates (10 ml/min, 20 ml/min, 30 ml/min). The third phase involved the decontamination efficiencies of the biosurfactant foams. Other control experiments were also conducted to make comparisons, and the mass balance during the experiment was checked.

In this chapter, the results from the three groups of experiments are presented and discussed. All the data were in triplicate and the average values were presented. The data range was taken as an average ± standard deviation.

6.2 Foam Parameters

Different concentrations of biosurfactant under different pH values were investigated in the experiments for their ability to make foam. The stability and quality of the foam produced were evaluated. Three concentrations of surfactant (0.5%, 1.0% and 1.5%) were investigated. As described in Chapter Five, the solutions were adjusted to two other pH values at 8.0, and 10.0 with 1 N NaOH and 1 N HCl solutions. The original pH value for rhamnolipid solution is around 6.8, when it was adjusted to pH = 6.0, the biosurfactant began to precipitate and could not be used for foam generation.

Results from this study show that foams can be generated from low concentrations of biosurfactant solutions (0.5% or perhaps less). The three different concentrations of biosurfactant solutions all were able to generate high quality foams, from 90% to 99%. Stability of the generated foam varied from 17 minutes to 41 minutes. The time it took for the foam to collapse completely varied from 2 hours to 4 hours, and even much longer. All of the experiments were done in triplicate and did not vary more 5%. The average results are summarized in Table 6.1.

Table 6.1 Stability and Quality of Foam Generated by Different Rhamnolipid Concentration under Different pH Values

Rhamnolipid Concentration	**Solution pH Values**	**Foam Quality**		
		90%	95%	99%
		Foam Stability (minutes)		
0.5%	6.8	17	24	20
	8.0	18	24	17
	10.0	18	25	21
1.0%	6.8	26	31	29
	8.0	25	30	27
	10.0	26	31	28
1.5%	6.8	31	39	32
	8.0	32	39	33
	10.0	32	41	35

6.2.1 Effect of Foam Quality

The relationship between foam stability and foam quality at different conditions are clearly displayed in Figure 6.1, Figure 6.2, and Figure 6.3. From the curves, we can see that the foam stability first increases with the increase of foam quality (from 90% to 95%) and then decreases with an additional increase of foam quality (from 95% to 99%). For example, in Figure 6.1, for the foam produced by 0.5% rhamnolipid solution at pH = 8.0, the stability increases from 18 minutes to 24 minutes as the foam quality increased from 90% to 95%, and then as the foam quality increased from 95% to 99%, the foam stability decreased to 17 minutes. This indicates that foam quality has some significant effects on the foam stability. Highest foam stability was produced with the quality between 90% and 99%.

This is probably due to that higher quality foam consists of larger bubbles with thinner liquid films, which effectively diminish the capillary flow leading to the rupture of the lamellar film between the adjacent bubbles. Also the foam density is reduced. The 99% quality foam often has slugs of gas mixed in, which speeds the rupture of the bubbles, thereby decreased the foam stability.

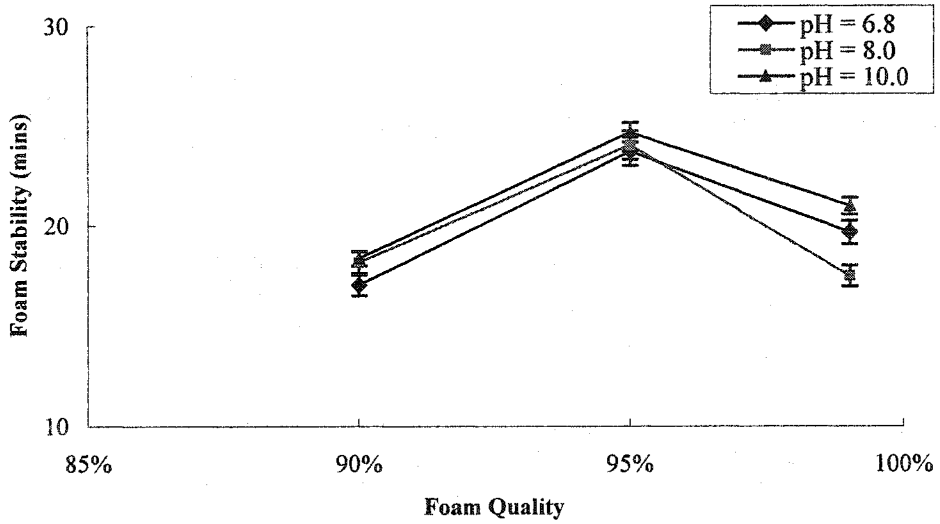


Figure 6.1 0.5% Rhamnolipid Foam Stability and Quality at Different pH Values

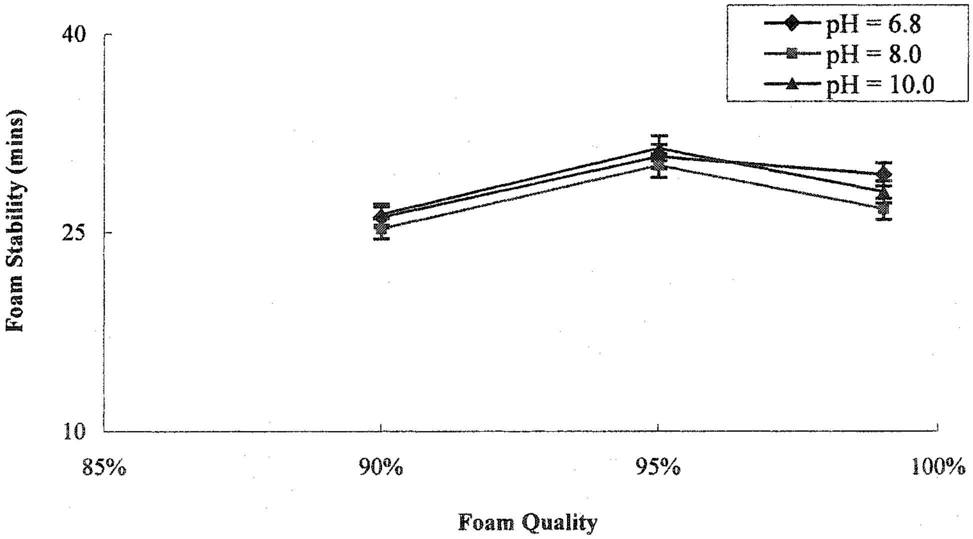


Figure 6.2 1.0% Rhamnolipid Foam Stability and Quality at Different pH Values

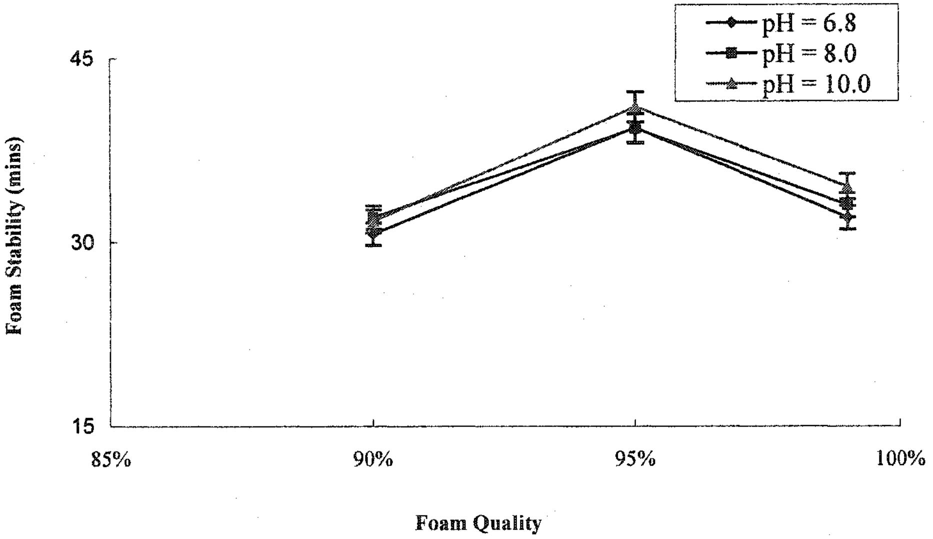


Figure 6.3 1.5% Rhamnolipid Foam Stability and Quality at Different pH Values

6.2.2 Effect of Solution Concentration

It is also apparent that the foam stability increases with the increase of the biosurfactant concentration (from 0.5% to 1.5%) (Figure 6.4, Figure 6.5, Figure 6.6). For example, as illustrated in Figure 6.5, when solution pH = 8.0, foam quality was 90%, the foam stability increased from 18 minutes to 32 minutes as the solution concentration increased from 0.5% to 1.5%. From the curves, we can conclude that solution concentration also has effects on the foam stability generated.

From a theoretical perspective, the increase of the foam stability will keep increasing with the increase of biosurfactant concentration until a threshold is reached, then the stability will decrease with the increase of the biosurfactant concentration, due to the increasing weight. Obviously, 1.5% is not such a threshold point.

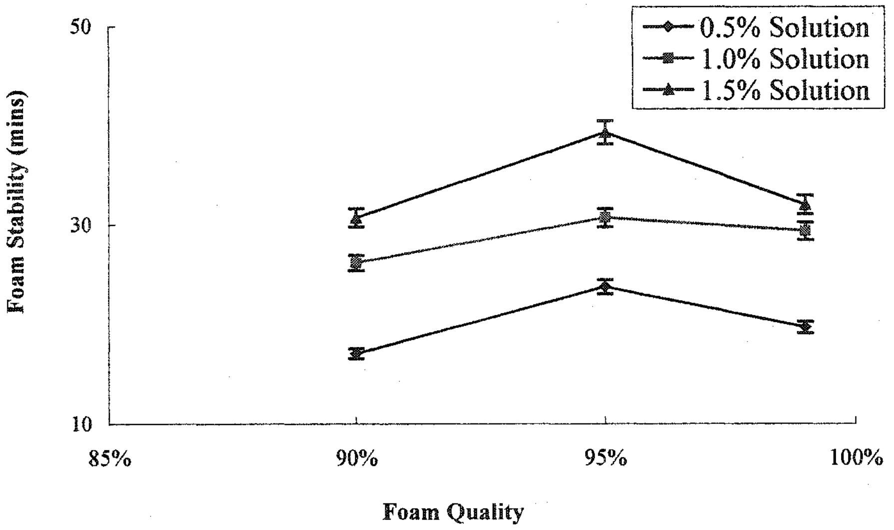


Figure 6.4 Foam Stability and Quality at Different Concentrations at pH = 6.8 (pH unadjusted)

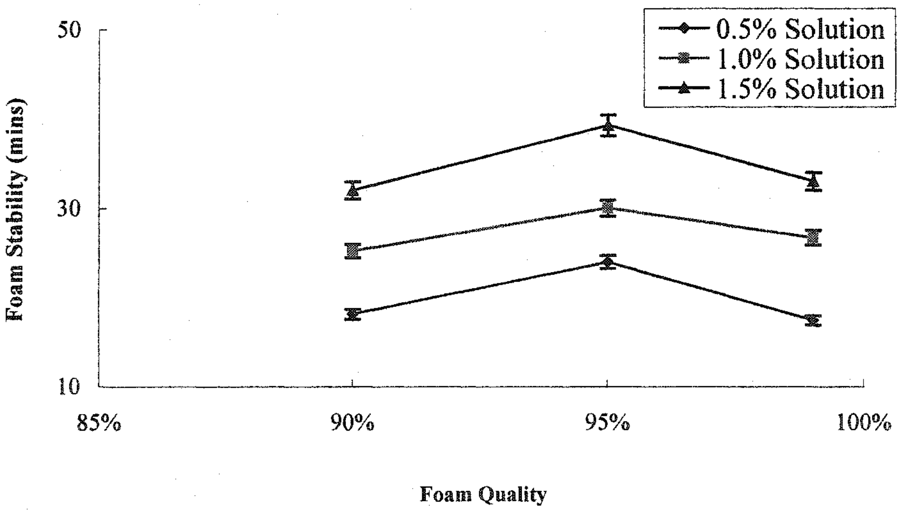


Figure 6.5 Foam Stability and Quality at Different Concentrations at pH=8.0

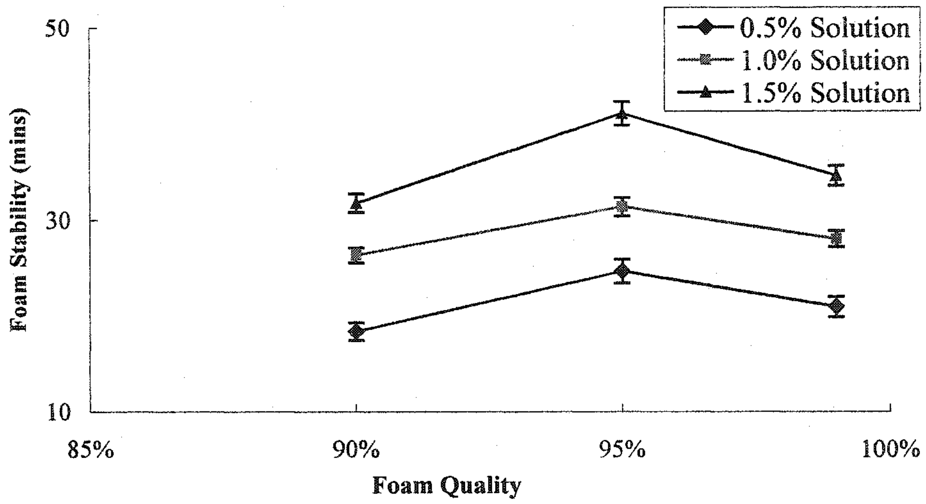


Figure 6.6 Foam Stability and Quality at Different Concentrations at pH=10.0

6.2.3 Effect of Solution pH Value

It is also obvious that the change of the solution pH values seems to have no significant influence on the foam stability and quality (Figure 6.1, Figure 6.2, Figure 6.3). For instance, in Figure 6.3, for the foam produced by 1.5% solution with different pH values, 6.8, 8.0 and 10.0, when the foam quality was 90%, the foam stability was 31, 32, and 32 minutes, respectively. It is very difficult to find out whether there is any effect of the solution pH values on the foam stability.

As Rothmel et al. (1998) concluded, foam stability does not appear to be dependent upon inherent properties such as HLB and CMC. According to the obtained results, we can conclude that the foam quality and concentration of surfactant solution have apparent effects on the foam stability while pH value of the surfactant solution has no obvious effects.

6.3 Pressure Gradient Build-up in the Soil Column

In this phase of the experiments, the pressure gradient build up in the soil column was investigated under different foam flow rates (10 ml/min, 20 min/ml, 30 ml/min), foam qualities (90%, 95%, 99%) and biosurfactant concentrations (0.5%, 1.0%, 1.5%).

The pressure gradient increased from 0.3 kPa/cm to 6.6 kPa/cm with the increase of the flow rate from 10 ml/min to 30 ml/min or with the decrease of foam quality from 99% to 90%. The change of the concentration of the biosurfactant solution (from 0.5% to 1.5%) had no significant influence on the pressure gradient build up in the soil column. All the experiments were in triplicate and did not vary more than 5%. The average results from this phase of experiments are summarized in Table 6.2.

Table 6.2 Pressure Gradients in the Soil Column by Different Foam Flow Rates with Different Foam Qualities

Rhamnolipid Concentrations	Foam Flow Rate (ml/min)	Foam Quality		
		90%	95%	99%
		Pressure Gradient (kPa/cm)		
0.5%	10	3.6	1.7	0.3
	20	5.0	3.0	0.7
	30	5.6	5.2	1.2
1.0%	10	3.9	1.8	0.4
	20	5.2	3.8	0.9
	30	5.8	5.4	1.3
1.5%	10	4.5	1.7	0.6
	20	6.1	4.7	1.2
	30	6.6	5.8	1.7

6.3.1 Effect of Foam Quality

Figure 6.7, Figure 6.8 and Figure 6.9 show the variation of observed pressure gradients with foam quality for foam generated at different concentrations of surfactant solution. At constant foam flow rates, a maximum pressure gradient was observed at qualities around 90%, and for foam with qualities greater than 95%, the pressure gradient drops sharply. In other words, there is a specific quality of foam by which the pressure in the soil drops dramatically for higher qualities.

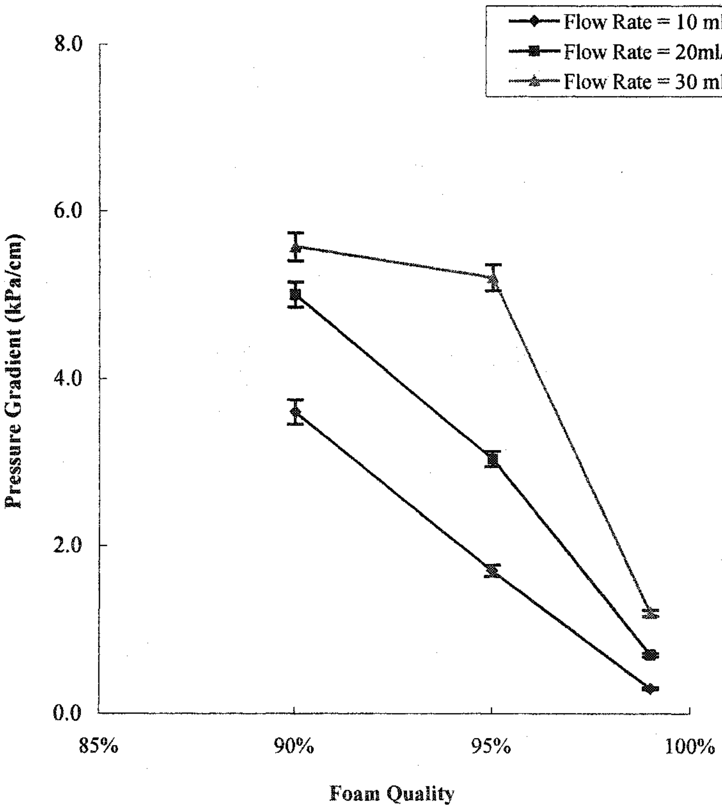


Figure 6.7 Effect of Foam Quality on Pressure Gradient at Rhamnolipid Concentration = 0.5%

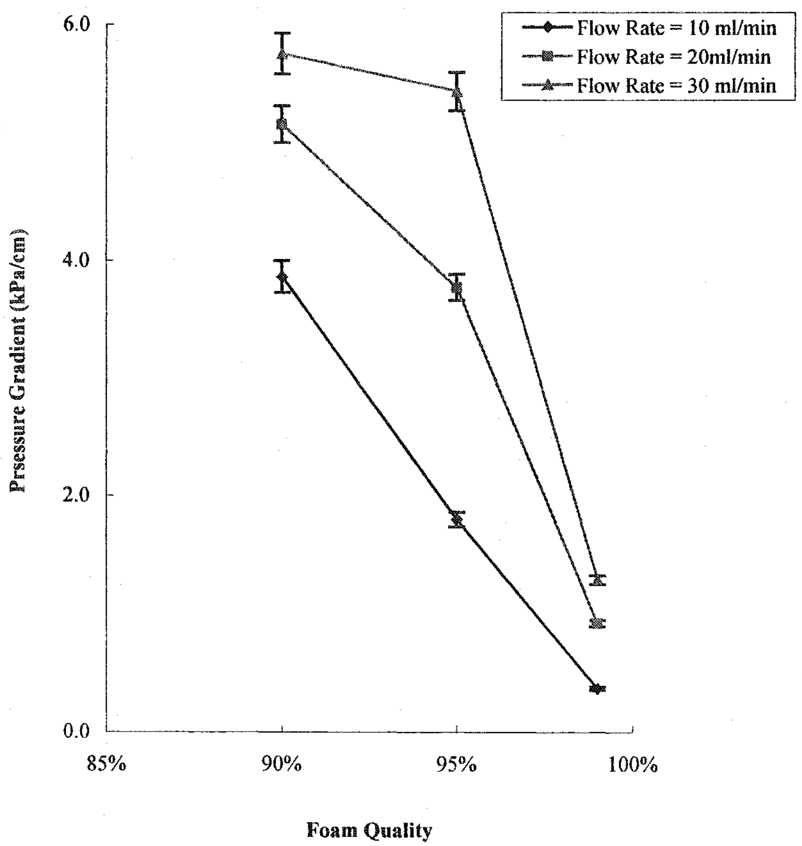


Figure 6.8 Effect of Foam Qualilty on Pressure Gradient at Rhamnolipid Concentration = 1.0%

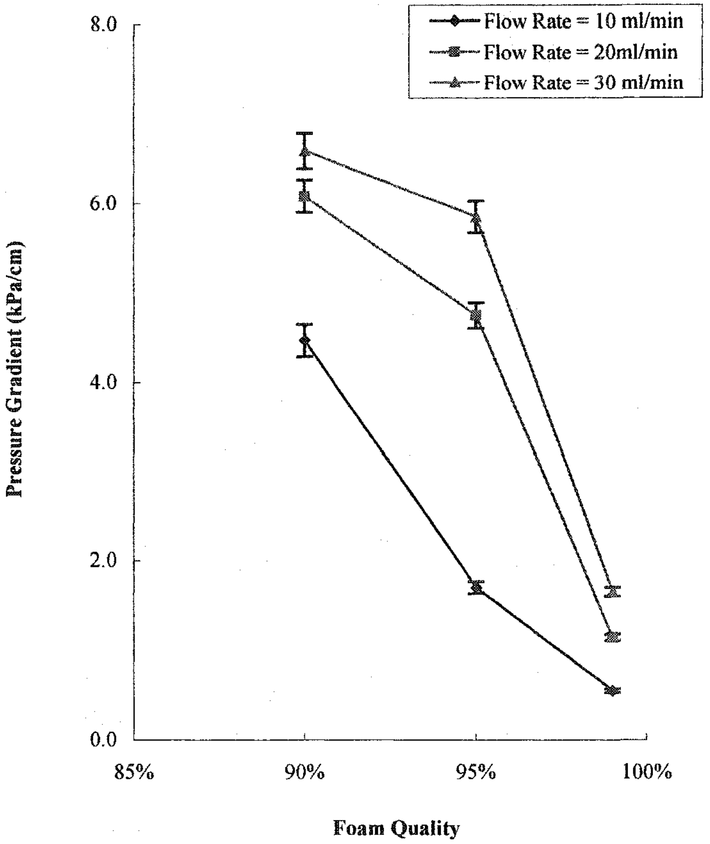


Figure 6.9 Effect of Foam Quality on Pressure Gradient at Rhamnolipid Concentration =1.5%

From the curves, a significant observation is that the observed pressure gradient decreased sharply with increasing quality. The decrease is indicative of a possible change in the structure of the foam. It has been demonstrated that the structure of the foam is dependent on the foam quality (Minnsieux, 1974; Chowdiah et al., 1998). In general, the bubble size of the foam was larger at higher quality. The 90% quality foam consisted of very fine, nearly spherical bubbles, while the 99% quality foam often had slugs of gas mixed in. Chowdiah et al. (1998) concluded that the texture of the foam exiting the column depended on both the injected foam quality and the flow rate. During the experiments, the significant differences observed in the texture were that the exiting foam was much coarser (even to slugs of gas and liquids), and broke down more quickly. This indicates that the mechanism of foam propagation involved breaking of the foam after it entered the column, with subsequent reformation within the soil.

Foam quality has a significant influence on foam flow and pressure in the soil. Higher quality foams exhibited lower pressure gradients during flow because the foam with a higher quality will collapse easier when passing through the soil column, thereby resulting in less pressure built up. The trend was most significant at qualities above 95%, and more dramatic for the stable aqueous foam used.

6.3.2 Effect of Foam Flow Rate

In Figure 6.10, Figure 6.11 and Figure 6.12, the effects of foam flow rate on the pressure gradients build-up in the column can be observed. It was noted that the pressure gradient build-up increased sharply with the increase of the foam flow rate. At constant foam quality, the maximum pressure gradient was observed at the foam flow rate of 30 ml/min. Theoretically, for foam with a specific viscosity, if all the other conditions are kept the same, the pressure gradient will increase proportionally with the flow rate (See Eq. 2-3, Chapter Two).

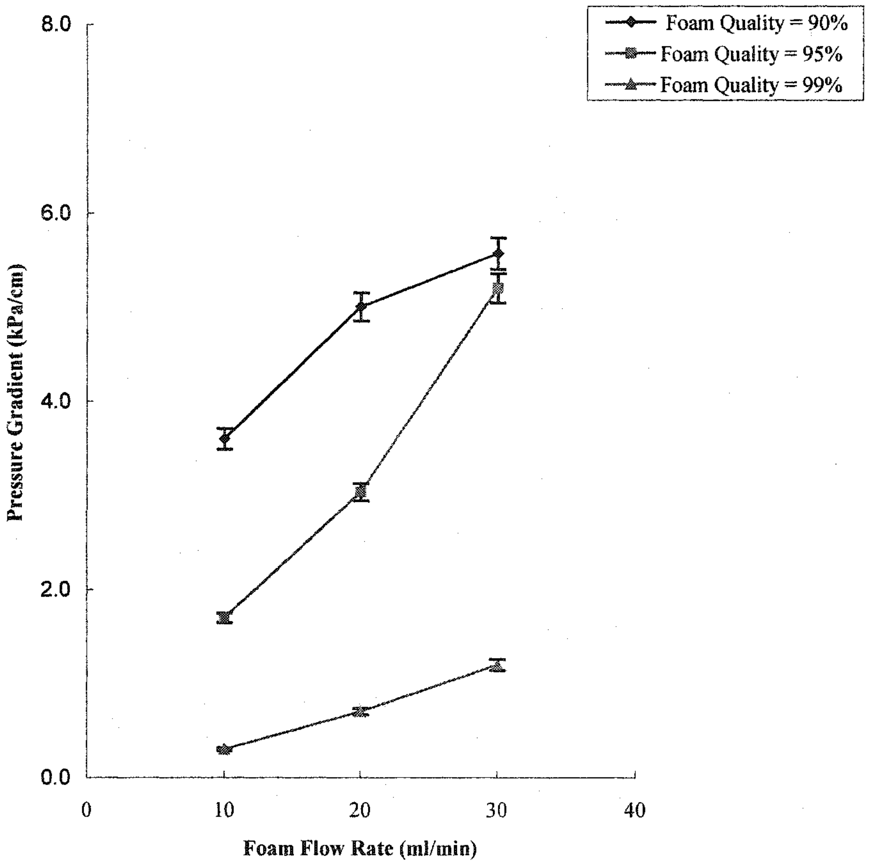


Figure 6.10 Effect of Foam Flow Rate on Pressure Gradient at Rhamnolipid Concentration = 0.5%

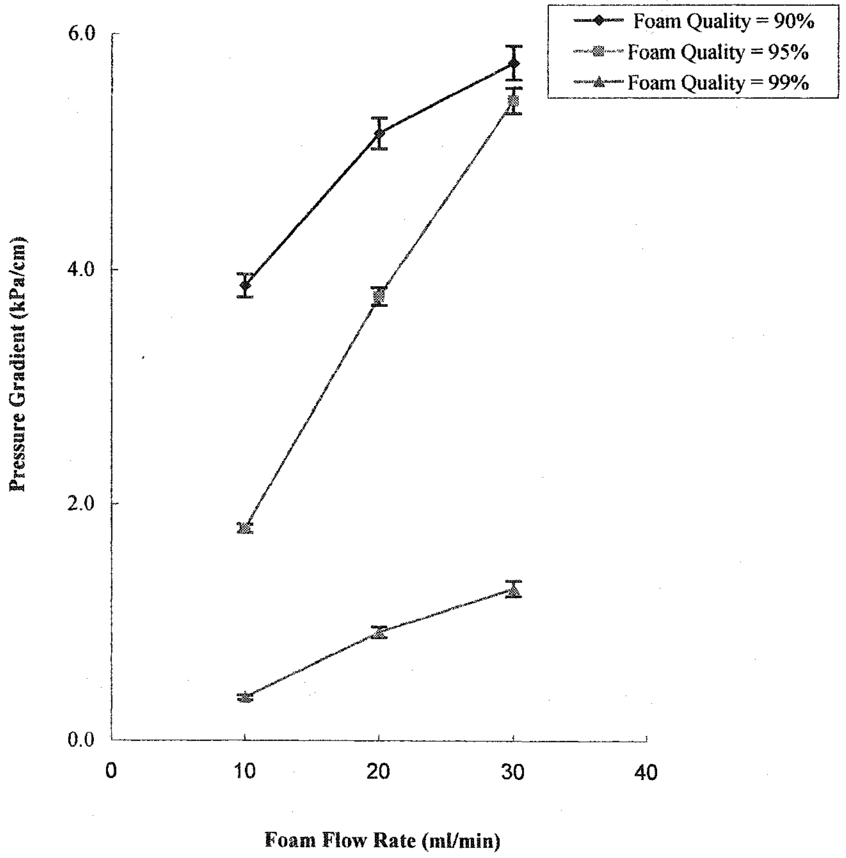


Figure 6.11 Effect of Foam Flow Rate on Pressure Gradient at Rhamnolipid Concentration = 1.0%

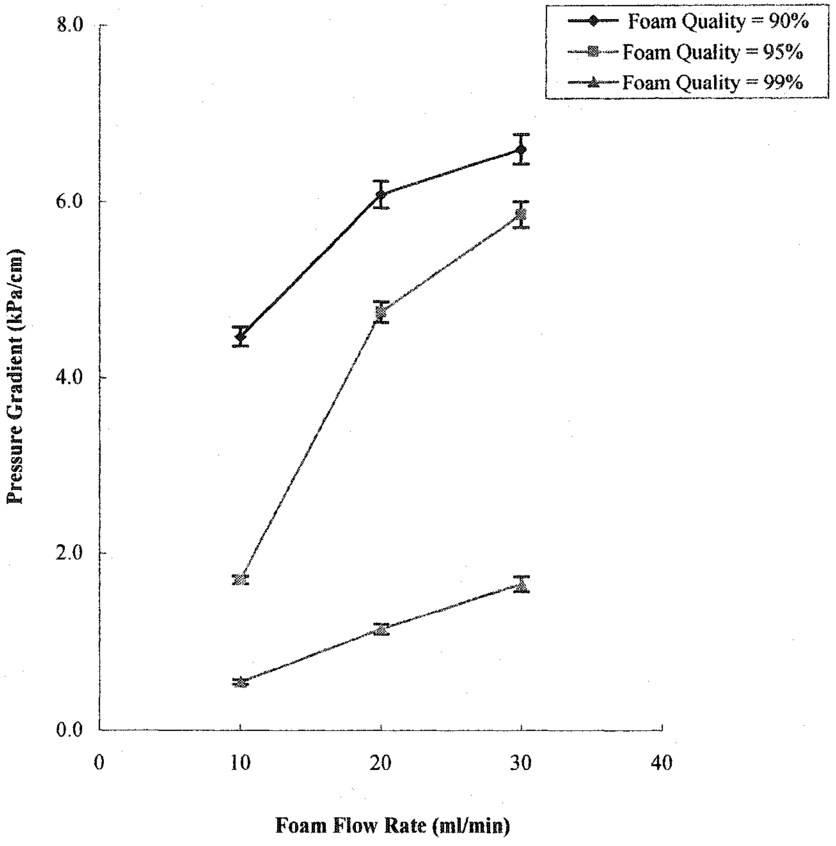


Figure 6.12 Effect of Foam Flow Rate on Pressure Gradient at Rhamnolipid Concentration = 1.5%

6.3.3 Effect of Solution Concentration

From Figure 6.13, Figure 6.14 and Figure 6.15, an observation is that the experimented biosurfactant solution concentrations (from 0.5% to 1.5%) have no significant influence on the pressure gradient build up in the soil column. This effect was much smaller compared with the effects of foam quality and foam flow rates, although theoretically, the pressure gradient will increase with the surfactant solution concentration, because it will increase the dilution and binding effects, which can possibly result in plugging of the column by the dispersion of fine materials or by the formation of viscous emulsions.

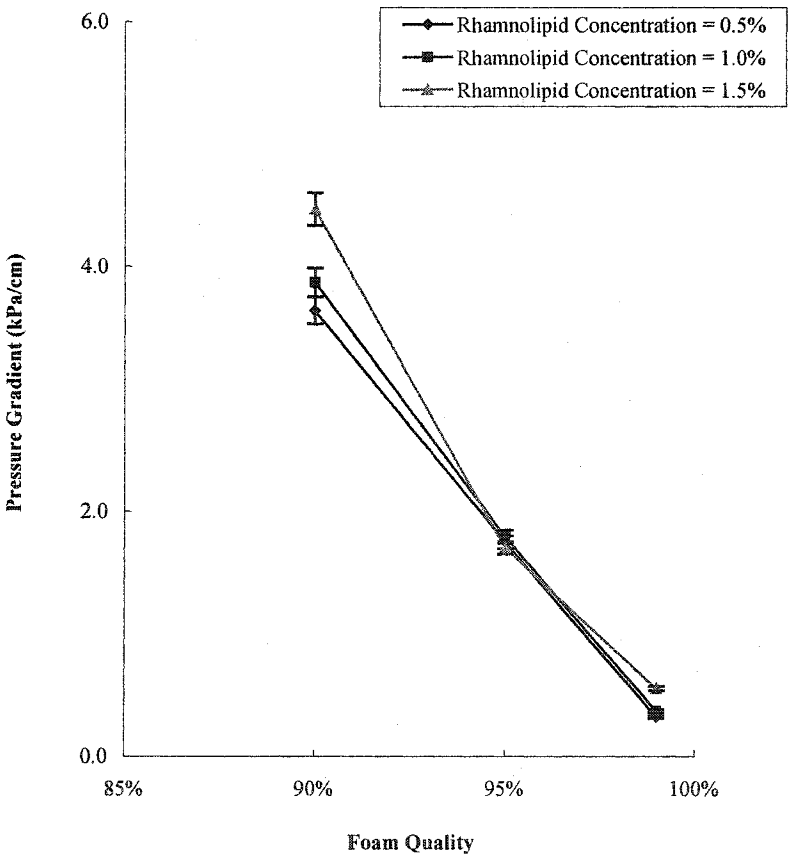


Figure 6.13 Effect of Rhamnolipid Concentration on Pressure Gradient at Foam Flow Rate = 10 ml/min

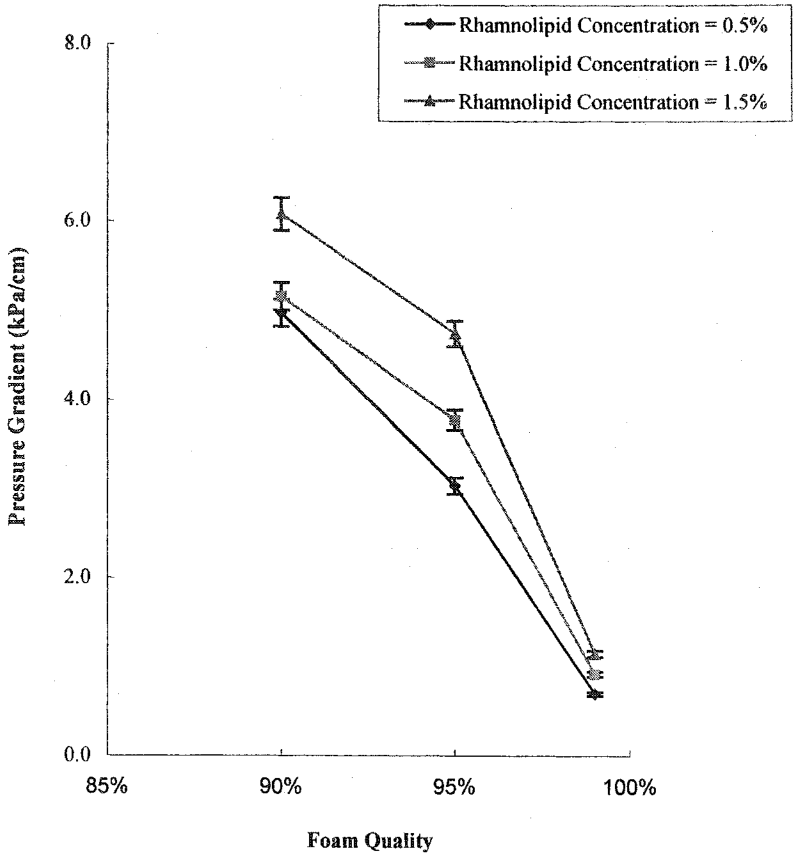


Figure 6.14 Effect of Rhamnolipid Concentration on Pressure Gradient at Foam Flow Rate = 20 ml/min

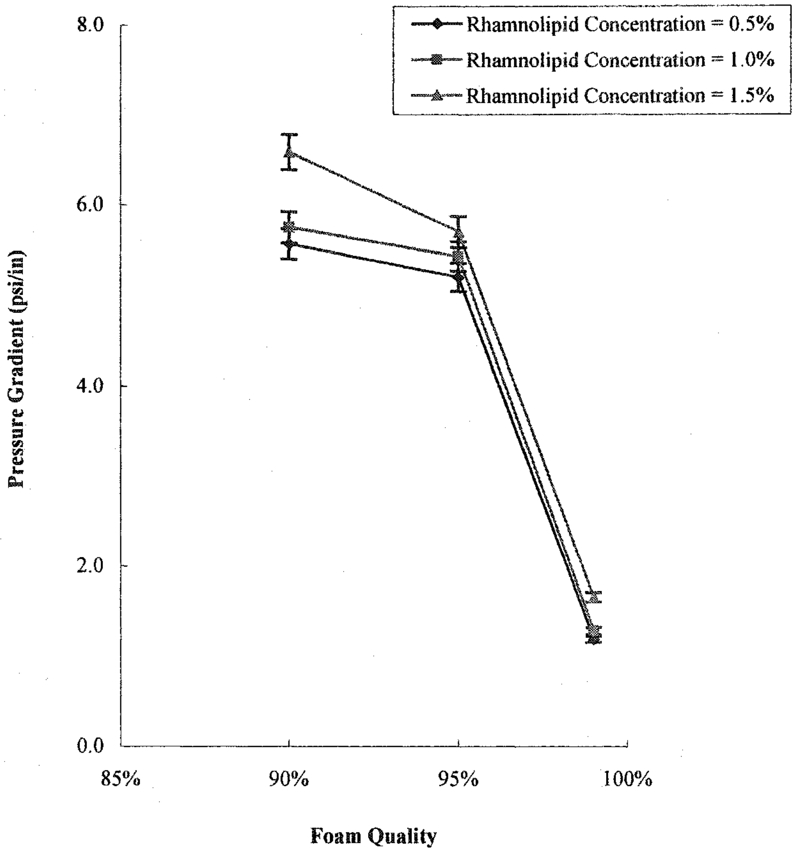


Figure 6.15 Effect of Rhamnolipid Concentration on Pressure Gradient at Foam Flow Rate = 30 ml/min

High quality foam from the biosurfactant solution with low concentration should be chosen for the further experiments in order to keep a lower pressure gradient in the soil column. It is also important to note that this will bring great economic effectiveness. For increasing the foam quality from 90% to 99%, usage of biosurfactant decreases by an order of 10, at the same time, decreasing the concentration of the biosurfactant solution from 1.5% to 0.5%, two thirds of the biosurfactant are saved. As discussed in Section 6.1, the foam generated from the biosurfactant solution with a concentration on order of 0.5% is stable enough to provide enough time for injection. A low flow rate should be chosen to reduce the pressure gradient in the soil column, to keep it below 0.2 kPa/cm.

6.4 Heavy Metal Removal Efficiencies

In this phase, experiments were carried out to investigate the metal removal efficiencies by different extractants at different pH values (6.8, 8.0, 10.0). Samples were taken separately according to pore volumes. The highest removal efficiency was obtained after rhamnolipid foam flushing through the soil column with an initial pH value of 10.0, which removed 73.2% of the Cd and 68.1% of the Ni after 20 pore volumes. All the experiments were done in triplicate and did not vary more than 10%. The average results (metal concentrations in the effluents) were used to calculate the metal removal efficiencies, which are summarized in Table 6.3 and Table 6.4.

Table 6.3 Cd Removal Efficiencies by Different Extractants (initial pH = 10)

Extractants	Pore Volume					
	1	3	5	10	15	20
	Removal Efficiency					
Distilled Water	6.1%	14.2%	16.5%	17.3%	17.5%	17.8%
Triton X-100 Solution	9.2%	35.0%	51.0%	51.7%	52.2%	52.8%
Triton X-100 Foam	14.7%	58.8%	64.0%	64.6%	65.1%	65.5%
Rhamnolipid Solution	10.5%	40.3%	58.2%	60.2%	61.1%	61.7%
Rhamnolipid Foam	15.6%	60.2%	68.1%	71.4%	72.8%	73.2%

Table 6.4 Ni Removal Efficiencies by Different Extractants (initial pH = 10)

Extractants	Pore Volume					
	1	3	5	10	15	20
	Removal Efficiency					
Distilled Water	5.2%	15.8%	17.9%	18.5%	18.6%	18.7%
Triton X-100 Solution	10.9%	32.1%	44.7%	45.0%	45.1%	45.2%
Triton X-100 Foam	15.7%	53.0%	56.5%	57.0%	57.2%	57.3%
Rhamnolipid Solution	12.7%	40.2%	47.2%	49.3%	50.3%	51.0%
Rhamnolipid Foam	16.0%	51.1%	62.3%	66.3%	67.5%	68.1%

6.4.1 Removal Efficiency by Rhamnolipid Foam

A series of experiments was performed using foam generated by 0.5% rhamnolipid solution at different pH values (6.8, 8.0, 10.0) to test the metal removal efficiency. The best removal rate, of 73.2% of the Cd and 68.1% of the Ni, was achieved by adjusting the initial solution pH value to 10.0, after 20-pore-volume flushing, which is shown in Figure 6.16. Probably, this could be the result of a combination of the enhanced metal solubility and rhamnolipid activity with the increase of the solution pH value.

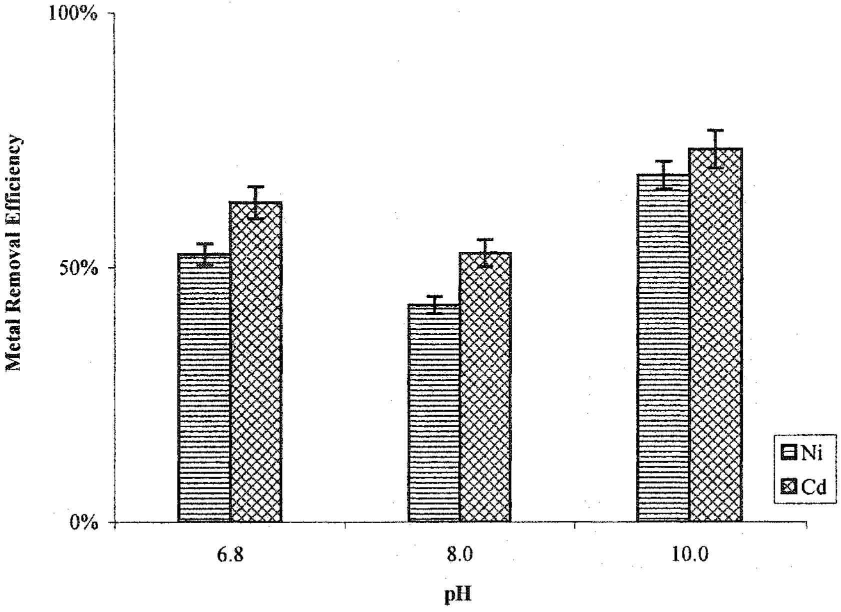


Figure 6.16 Metal Removal Efficiencies by Rhamnolipid Foam at Different Initial pH Values

Figure 6.17 illustrates the trend of metal removal efficiency as the foam flushing through the column. It can be observed that the metal removal efficiency increased sharply within the first 5 pore volumes. Then it increased slowly as more foam passing through.

It can also be observed that most metals were removed in the first 5 pore volumes of foam. For example, the first 5 pore volumes of foam removed 68.1% of the Cd while the total removal efficiency of Cd after 20 pore volumes of foam was 73.2%. This means that the first 5 pore volumes removed 93.1% of the total metal removed. This indicates that in the field applications, to save time and for economic efficiency, this technology could be used as a first flushing treatment in about 5 pore volumes, then other treatment methods could be used to enhance the metal removal efficiency. A combination with other technologies would be more effective in future development. This will be discussed in the following chapter.

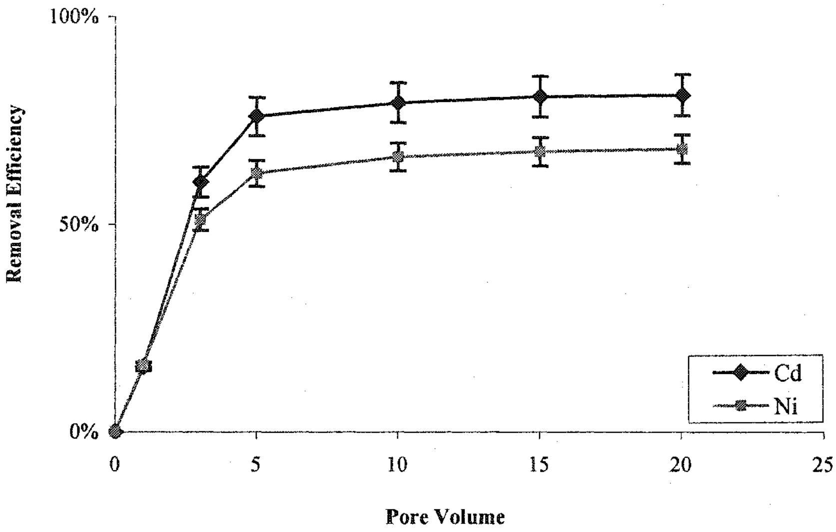


Figure 6.17 Metal Removal Efficiencies by Rhamnolipid Foam

6.4.2 Removal Efficiency by TritonX-100 Foam

Flushing experiments through the contaminated column also were conducted with another type of surfactant, Triton X-100, which is nonionic in nature, as introduced in Chapter Five. A 0.5% solution of Triton X-100 adjusted to pH 10.0 was used to generate foam and was injected into the column. Using this, 65.5% of the Cd and 57.3% of the Ni were removed. The results are illustrated in Figure 6.18.

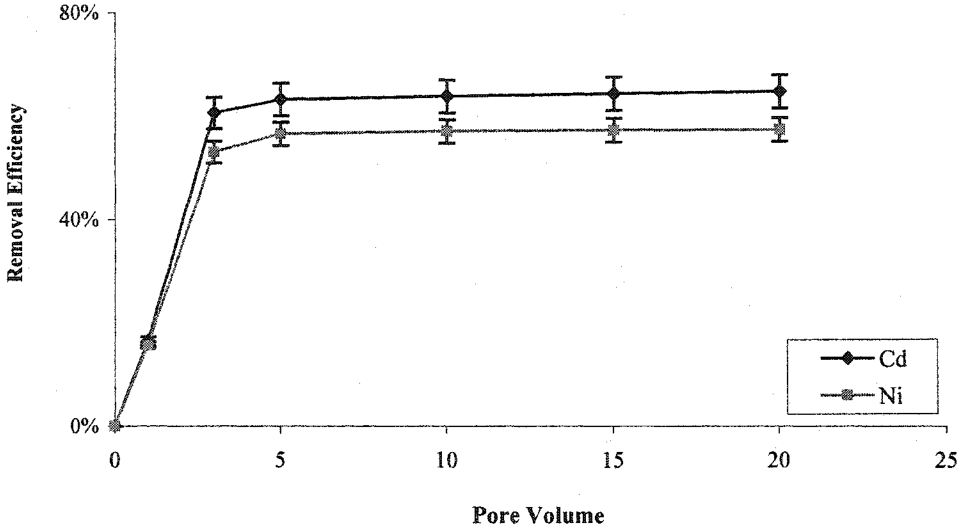


Figure 6.18 Metal Removal Efficiencies by TritonX-100 Foam

In Figure 6.19 and Figure 6.20, the metal extraction efficiencies of the foams generated by 0.5% rhamnolipid and Triton X-100 solutions are compared. Over 7% more of the Cd and 10% more of the Ni were removed by 0.5% rhamnolipid foam than by 0.5% Triton X-100 foam. A similar tendency in the curves indicates similar removal mechanisms by foams generated by the two tested surfactant solutions. The differences in metal removal efficiencies demonstrated that heavy metals (Cd, Ni) have stronger affinities for rhamnolipid than for Triton X-100, in other words, the rhamnolipid is more effective than the Triton X-100 in removing metals from soil.

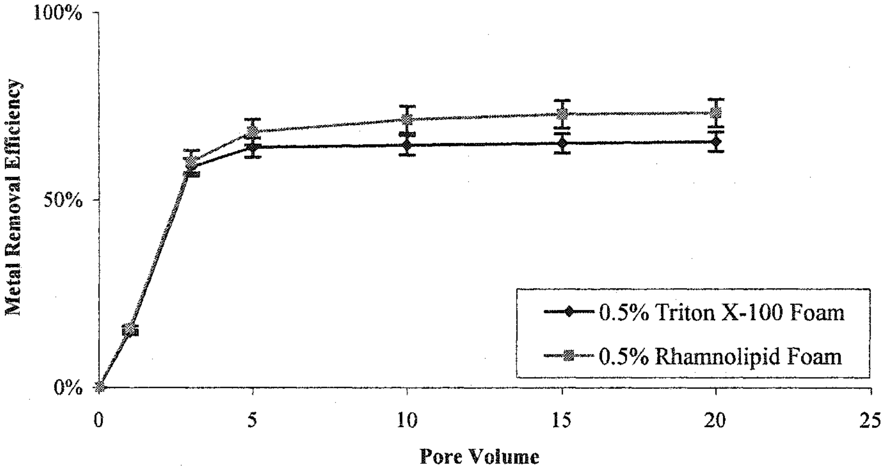


Figure 6.19 Cd Removal Efficiencies by Different Surfactant Foams

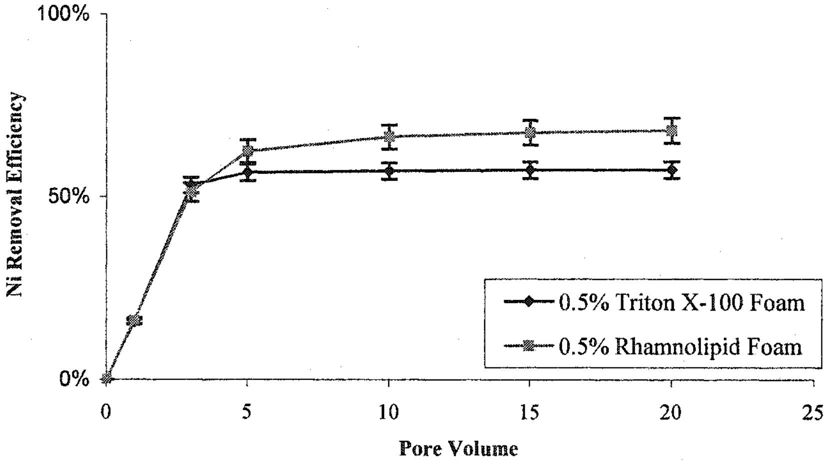


Figure 6.20 Ni Removal Efficiency by Different Surfactant Foams

1.4.3 Removal Efficiency by Surfactant Solutions

Surfactant solutions also were used to flush through the soil column without foam generation. After 20 pore volumes, a 0.5% rhamnolipid solution removed 61.7% of the Cd and 51.0% of the Ni, while a 0.5% Triton X-100 solution removed 52.8% of the Cd and 45.2% of the Ni. The results are summarized in Figure 6.21 and Figure 6.22.

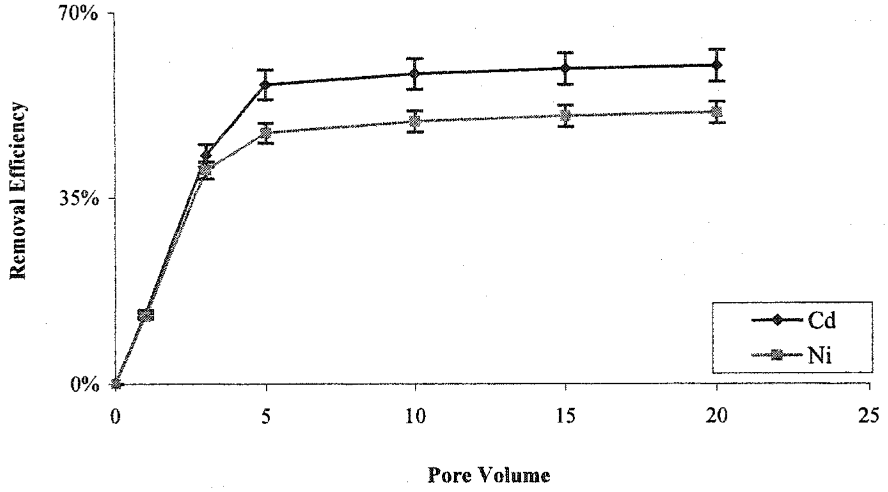


Figure 6.21 Metal Removal Efficiencies by 0.5% Rhamnolipid Solution

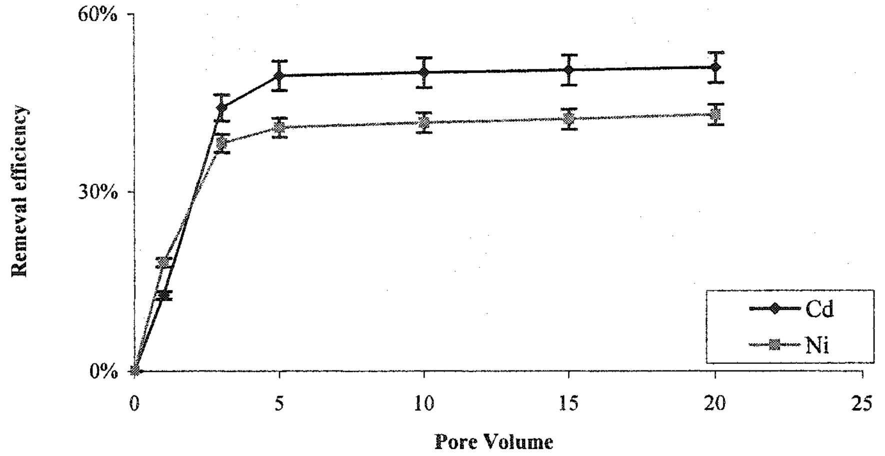


Figure 6.22 Metal Removal Efficiencies by 0.5% Triton X-100 Solution

As shown in Figure 6.23 to Figure 6.26, metal removal efficiencies by surfactant solutions and foam are compared. For example, over 11% more of the Cd and 17% more of the Ni were removed by rhamnolipid foam than rhamnolipid solution with the same concentration, while over 12% more of the Cd and 12% more of the Ni were removed by

Triton X-100 foam than Triton X-100 solution. Transfer from aqueous solution to foam greatly enhanced the metal removal efficiencies by the same concentration of both tested surfactants (rhamnolipid and Triton X-100). This increase is probably due to the greatly increased surface contact areas. As explained in the Chapter Two, in a foam with a quality of 95%, the volume is increased by 20 times, and the direct result is the increased surface area, which leads to the efficient contact of surfactant with the metals, and also the injection of surfactant and air at the same time effectively restrained channeling in the column.

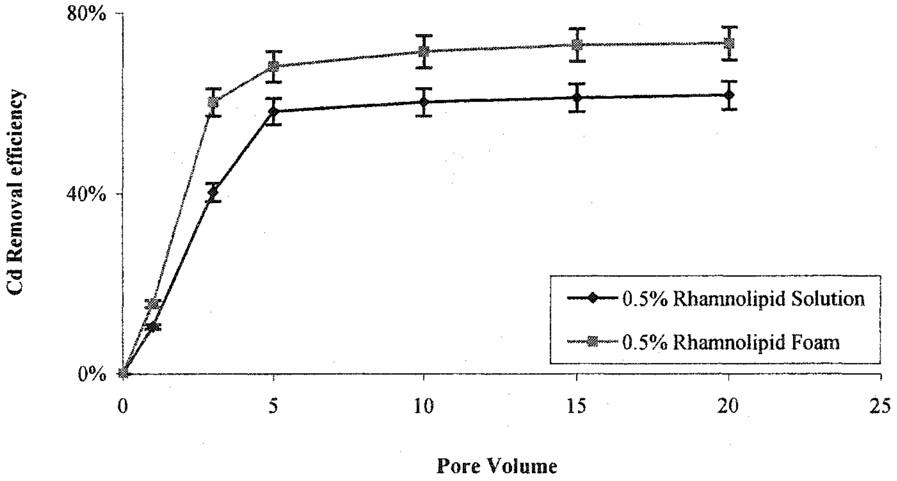


Figure 6.23 Cd Removal Efficiencies by 0.5% Rhamnolipid Solution and Foam

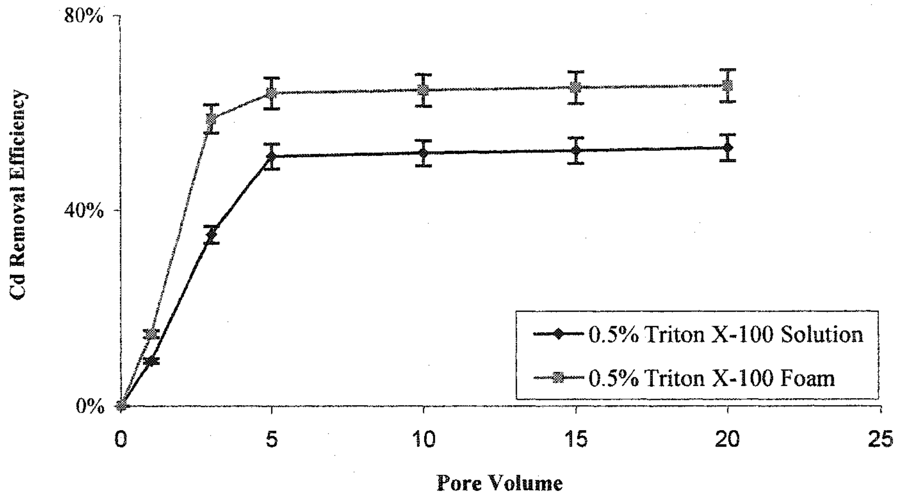


Figure 6.24 Cd Removal Efficiencies by 0.5% Triton X-100 Solution and Foam

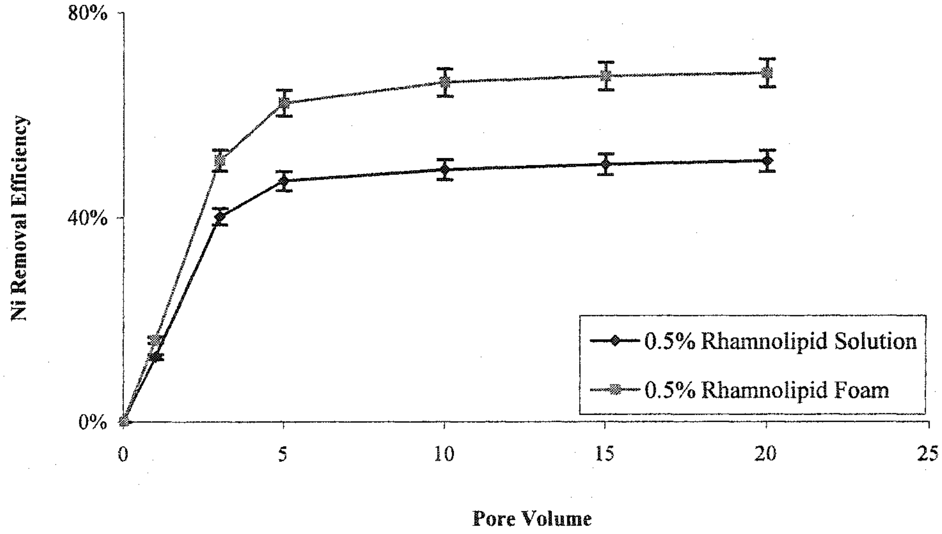


Figure 6.25 Ni Removal Efficiencies by 0.5% Rhamnolipid Solution and Foam

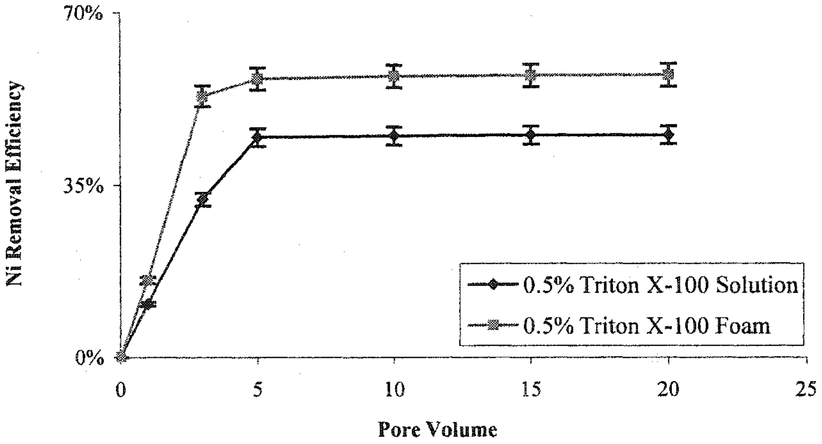


Figure 6.26 Ni Removal Efficiencies by 0.5% Triton X-100 Solution and Foam

6.4.4 Control Experiments

Control experiments were carried out with distilled water with correspondingly adjusted pH values. It was used to evaluate the metal removal efficiencies by using surfactants. Of which, distilled water (pH 10.0) removed 17.8% of the Cd and 18.7% of the Ni (Figure 6.27). It worked mainly as a physical dissolvent and removed the precipitated metal on the surface of the soil particles. These results were higher probably because a portion of the metals was not bound to the soil because it is an artificially contamination.

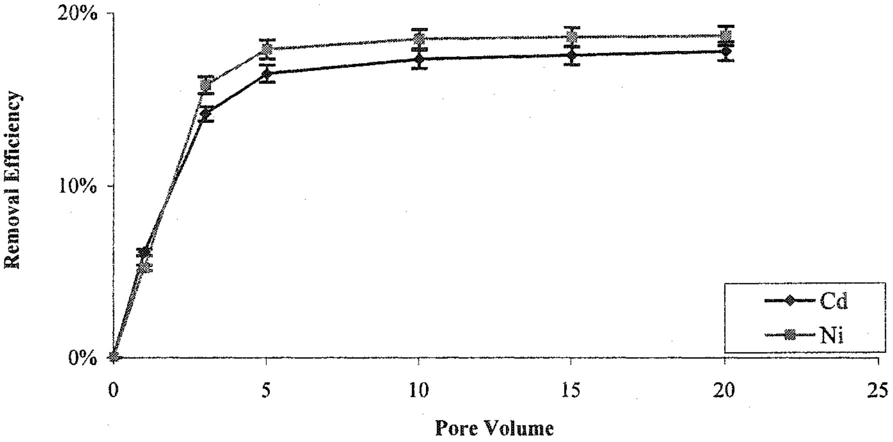


Figure 6.27 Control Experiment by Distilled Water (pH=10.0)

6.4.5 Mass Balance Check

Soil samples were taken from each of the chosen columns flushed by rhamnolipid foam after the experiments. AA analysis was performed to test the residual metal concentrations. The average results are shown in Table 6.5.

Table 6.5 Mass Balance Check

Metal	Removed	Residue	Total	Missing
Cd	73.2%	25.2%	98.4%	1.6%
Ni	68.1%	31.5%	99.6%	0.4%

From Table 6.5, it can be seen that the mass balances were good during the experiments, although 1.6% of the Cd and 0.4% of the Ni were not accounted for. For a reasonable explanation, the metal missing may be caused by the analytical and/or operation errors, which are unavoidable but expected during the experiments.

Chapter Seven

Conclusions and Recommendations

7. 1 Conclusions

Soil consists of heterogeneous mixtures of organic and inorganic components as well as a variety of soluble substances. It has long been regarded as a repository for society's wastes. Heavy metals, such as Cd, Cr, Ni, and Pb, are all potential soil pollutants. Gradually mobilized by biogeochemical processes, soil contaminants can pollute water supplies and impact food chains. As described in Chapter Two, excessive exposures to such contaminants can greatly damage human health, and can even cause death. Thus, it is of importance to study the fate and transport of such contaminants in the environment and to evaluate the feasibility of various technologies for remediating heavy metal contaminated sites.

As an emerging and promising technology for heavy metal removal, biosurfactant foam enhanced remediation of heavy metal contaminated soil was investigated in this project through column experiments.

Although this study was investigated in idealized conditions, the results illustrate some general considerations that are important for the use of foams for soil flushing during in situ applications. From the preliminary experiment results, the following conclusions can be drawn.

7.1.1 Foam Characteristics

This study showed that rhamnolipid solution with different concentrations (0.5%, 1.0%, 1.5%) could be used to generate high quality foam (up to 99%) with enough stability (from 17 minutes to 41 minutes) for soil flushing. Foam quality and biosurfactant solution concentration may effect foam stability, while the pH values of the solution seem to have no significant influence.

7.1.2 Pressure Gradient in the Soil Column

The flow of foam in the soil column and the flow characteristics are not predictable because of various influencing factors. Extensive experiments in which both the soil and the foam are involved have to be conducted.

It appears that both foam quality and flow rate have dramatic impacts on the pressure gradient build-up in the soil column. The change of the concentration of the biosurfactant solution (from 0.5% to 1.5%) had no significant influence on the pressure gradient build-up in the soil column, even though theoretically, it would increase the pressure gradient.

In general, the results indicate the need for foam that has relatively low stability but high foamability in order to achieve acceptable low-pressure gradients of the order of 1 psi/ft (0.2 kPa/cm). High quality foam from a biosurfactant solution with low concentration should be chosen for the further experiments, which will bring great economic effectiveness. A low flow rate should be chosen to reduce the pressure gradient in the soil column, to keep it below 0.2 kPa/cm.

7.1.3 Metal Removal Efficiencies

This study demonstrates that biosurfactant foam technology can be used successfully in remediation of heavy metal contaminated sites. This technology demonstrated promising results for soil contaminated with high levels of mixed metals (2 or more). Test results in field applications tend to vary more from those obtained in the lab scale bench tests, because the capacity of foam to extract and mobilize the metals from soil is a function of many parameters such as surfactant type and concentration, soil characteristics, and the resident time as well as type of metals.

Highest removal efficiencies were obtained by rhamnolipid foam with an initial pH value of 10.0, which removed over 73.2% of the cadmium and over 68.1% of the nickel from the contaminated soil. It was more effective than foam generated by Triton X-100 under the same conditions. The results also showed that rhamnolipid foams perform effectively at high pH values (10.0 or maybe more).

Biosurfactant foam technology seems to be more effective than conventional soil flushing by surfactant solutions without foam, which is due to the efficient contact and avoided channeling. The simultaneous injection of surfactant and air would enhance the flooding efficiency of surfactant flushing even in a heterogeneous porous medium, resulting in high removal efficiency. At the same time, it could be more cost effective because of the low usage of chemicals and surfactants.

The foam technology not only can be used in situ to enhance mobilization of heavy metals at industrial, military, or federal subsurface sites, as described in the literature review, but also be used as an effective technique for the treatment of soils contaminated with organic compounds such as NAPLs. It also probably to be a promising groundwater remediation technology. The use of biosurfactant foam technology could be an effective, non-toxic means of remediation, because biosurfactant are natural products and they may be more benign to biodegrading bacteria and be more biodegradable themselves, and, therefore, may be better candidates for the remediation of contaminated sites.

It is a promising technology but it is not a panacea for all-purpose operations. Though the experiments showed better results for flushing sandy soil with high hydraulic conductivity, it would not work well in contaminated soils such as clays with low porosity. Other new technologies are to be developed for such soils.

7.2 Recommendations

Although this study was conducted under idealized conditions, it does show the potential for the use of foams for mobilizing heavy metals. However, few investigations have been done, thus, further efforts need to be done before it can be used at larger scale of operations. Removal efficiency of contaminants from soils and sediments with natural heterogeneity, compatibility with other remediation technologies such as bioremediation, effectiveness of pulsed operation, and biosurfactant partitioning as well as the cost effectiveness of this technology need to be investigated with the development of in field applications.

Bioremediation represents the trend for the remediation of heavy metal contaminated sites. Efficient operation of an in-situ bioremediation process depends on the efficient delivery of oxygen, moisture and nutrient to the subsurface, good soil/liquid contact and good transfer of contaminants to the liquid phase (Chowdiah et al., 1998). The use of foam is being developed as a promising new medium to carry augmentations for such processes. Continued studies will involve further development and testing of the foam/biotreatment system as well as developing a predictive mathematical model for use in field remediation efforts.

A major concern in soil flushing is the need to contain treatment fluids at the remediation zone. This involves the use of an appropriate biosurfactant solution or solvent and can be used to dissolve or emulsify the contaminants and bring them to the surface for disposal /destruction or above the ground bioremediation (Vignon and Rubin, 1989; Luthy et al., 1994; Chowdiah et al., 1998). As a technology that could dramatically increase the solubilization of metal species, it could be applied in combination with the existing pump-and-treat systems. Foams display properties that are vastly different from the fluids that constitute the foam. The use of foam can provide a better control on the migration of contaminant-laden liquids, which can prevent the spreading of the contaminated zone.

In general, the role of surfactants in the remediation of metal contaminated soil is quite site specific, depending on the speciation of the metals, as well as matrix characteristics of the soil. The role of surfactant and complexing agent on the remediation of heavy metal-contaminated soils still remains unclear. Further research should be conducted to improve the applicability and effectiveness of this emerging remediation technology.

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Appendices

Appendix A

Determination of Soil Cation Exchange Capacity (CEC)

Materials

1. 15 g oven dried soil
2. 1 M Potassium acetate ($KC_2H_3O_2$)
3. Plastic, capped centrifuge tubes
4. Methyl alcohol (CH_3OH)
5. 1 M Ammonium acetate ($NH_4C_2H_3O_2$)
6. 100 ml beakers
7. Standard Potassium Solutions (5, 10, 20 ppm)
8. Atomic Absorption Spectrophotometer
9. Balances
10. Table top centrifuge

Procedure

1. Weigh 5 grams into a centrifuge tube. Prepare three samples.
2. Add 20 ml of 1 M potassium acetate to each tube. Stopper or cap the tubes, and shake intermittently for 5 minutes.

3. After shaking, remove the cap temporarily and rinse the sides of the tube with a squirt bottle (distilled water) to wash any soil on the sides of the tubes and/or the stopper down back down into the liquid.
4. Recap the tubes and place them into the centrifuge and centrifuge for 15 minutes at 3000 rpm. Discard the clear supernatant.
5. Add another 20 ml of 1 M potassium acetate, centrifuge again for 15 minutes. Discard the supernatant.
6. Add 20 ml methyl alcohol to the soil pellet and shake until the soil is resuspended.
7. Using the squirt bottle with distilled water, wash soil on the sides of the tubes and/or on the stopper back down into the liquid.
8. Centrifuge for 15 minutes on high setting. Discard the clear supernatant.
9. Repeat steps 6-8.
10. Add 25 ml of 1 M ammonium acetate to the soil pellet. Stopper or cap the centrifuge tube and shake until the soil pellet is resuspended.
11. Rinse the sides of the tube and/or the stopper to wash solid material back down into the liquid. Stopper or cap the tubes, then centrifuge for 15 minutes at 3000rpm.
12. Pour the clear supernatant into a clean 100 ml beaker.
13. Repeat steps 10-12, once again pouring the clear supernatant into the same beaker.
14. Measure the K concentration in the supernatant solution by using the atomic absorption spectrophotometer (AAS). Using the value for the concentration of K to determine the CEC of each soil in cmoles^+ /kg

Experiments Results

The experiment and calculation results are summarized in Table A.1.

Table A.1 Experimental Results and Calculations for the Soil CEC

Sample	$[K^+]$ by AAS (ppm)	$[K^+]$ in the Supernant (ppm)	$[K^+]$ Mass (mg)	CEC (cmoles$^+$/ kg)
1	5.55	277.5	16.65	8.54
2	4.98	249.0	14.95	7.66
3	4.92	246.0	14.76	7.57

Then the CEC of soil sample was taken as the average of the three values

$$CEC = \frac{8.54 + 7.66 + 7.57}{3} = 7.92 \text{ (cmoles}^+\text{/ kg)}$$

Standard deviation

$$STDEV = \sqrt{\frac{(8.54 - 7.92)^2 + (7.66 - 7.92)^2 + (7.57 - 7.92)^2}{2}} = 0.53 \text{ (cmoles}^+\text{/ kg)}$$

The range of CEC of the soil sample is: 7.92 ± 0.53cmoles$^+$ /kg.

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Appendix B

Measurement of Soil Hydraulic Conductivity

Materials

1. Soil Samples
2. Column
3. Graduated Cylinder
4. Timer
5. Flask
6. Ruler
7. Tubing

Procedure

1. Measure the column's diameter and length (L). Calculate the column section area F.
2. Pack the soil sample into the column; tap gently on the side of the column to pack the soil.
3. Install experimental setup as Figure B.1.
4. Collect the outflow into a graduated cylinder.
5. Record the outflow vs. time (at 10 ml intervals) until the time interval for 10 ml outflow remains constant for five consecutive intervals.
6. Calculate the hydraulic conductivity K using the equations listed as following.

$$q = \frac{Q}{t} \quad \text{Eq.B-1} \qquad v = \frac{q}{F} \quad \text{Eq.B-2}$$

$$i = \frac{h}{L} \quad \text{Eq. B-3} \qquad K = \frac{v}{i} \quad \text{Eq.B-4}$$

7. Reload the column, repeat steps 1-6, and repeat the experiment 3 times.
8. Calculate and present the hydraulic conductivity as the average of the 3 experiments.

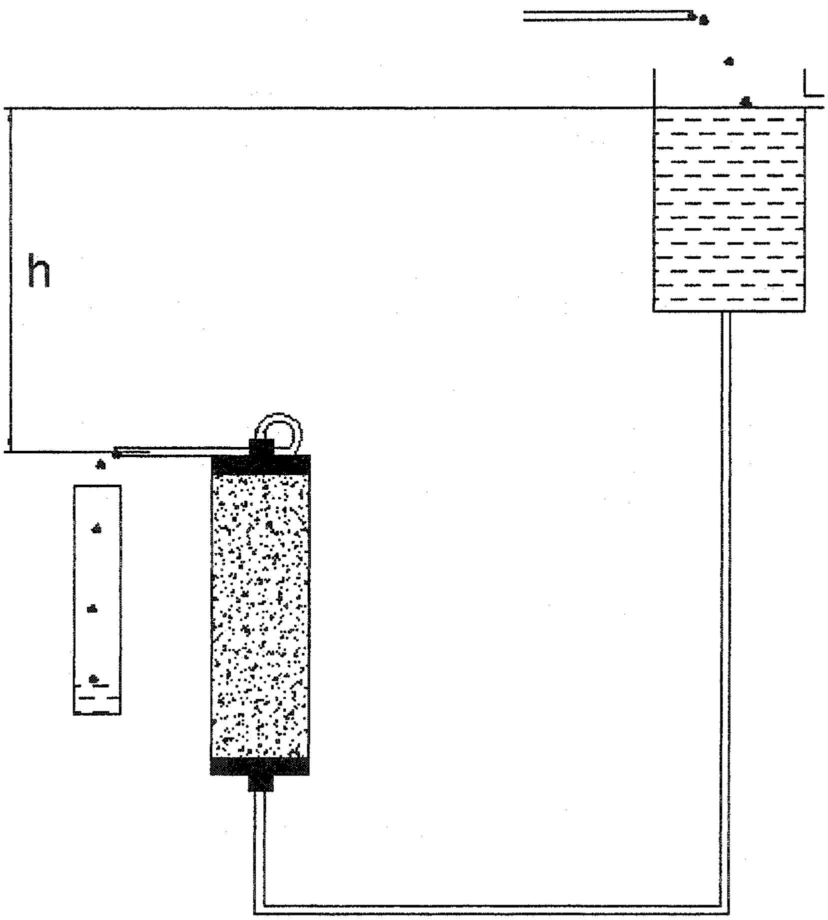

Figure B.1 Schematic Setup for Measuring Hydraulic Conductivity

Experiment and Calculation Results

The experiment and calculated results are listed in Table B.1, Table B.2.

Table B.1 Recorded Experimental Results for Soil Hydraulic Conductivity

Measurement No.	Column			Q (ml)	Time t (s)	h (cm)
	Length L (cm)	Diameter D (cm)	Section Area $F(cm^2)$			
1	25	4	12.56	10	44.35	20
2					49.13	
3					47.62	

Table B.2 Calculations for Soil Hydraulic Conductivity

Measurement No.	q=Q/t (ml/s)	v=q/F (cm/s)	i =h/L	Hydraulic Conductivity K= v/i (cm/s)
1	0.225	0.018	0.8	0.022
2	0.204	0.016		0.020
3	0.210	0.017		0.021

Then the hydraulic conductivity was calculated as the average of the three values,

$$K = \frac{K_1 + K_2 + K_3}{3} = \frac{0.022 + 0.020 + 0.021}{3} = 0.021\ (cm\,/\,s)$$

Standard deviation

$$STDEV = \sqrt{\frac{(0.022-0.021)^2 + (0.020-0.020)^2 + (0.021-0.021)^2}{2}} = 0.001(cm\,/\,s)$$

The rang of the hydraulic conductivity can be expressed as 0.021 ± 0.001 (*cm/s*).

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Appendix C

Measurement of Soil Organic Matter Content

Materials

1. Soil Samples
2. Crucibles
3. Balance
4. Dry desiccators
5. Muffle furnace
6. Oven

Procedure

1. Weigh crucibles.
2. Weigh soil samples (about 10 mg) into each crucible; Dry soil in 105°C oven for 48 hours.
3. Cool down soil in dry desiccators (30 minutes), weigh crucibles + dried soil.
4. Ash dried soil in 550 °C muffle furnace for 2 hours, leave the samples in the furnace overnight. Weigh soil as described above.
5. Calculate the soil organic matter content according to the following equation.

% Soil organic matter

= (Soil DW before ashing - DW after ashing) / Soil DW before ashing x 100%.

Experiment and Calculation Results

The experimental results and calculations were summarized in Table C.1.

Table C.1 Experimental Results and Calculations for Soil Organic Matter Content

Sample	Crucible Weight (g)	Total Weight Before Ashing (g)	Total Weight after Ashing (g)	Soil Weight (g)	Organic Matter Content
1	29.4771	39.9162	39.8142	10.4391	0.98%
2	30.3544	40.7488	40.6519	10.3944	0.93%
3	29.641	39.6941	39.5976	10.0531	0.96%

The organic matter content was calculated as the average of the three values.

$$Organic\ Matter\ Content = \frac{0.98\% + 0.93\% + 0.96\%}{3} = 0.96\%$$

Standard deviation

$$STDEV = \sqrt{\frac{(0.98\% - 0.96\%)^2 + (0.93\% - 0.96\%)^2 + (0.96\% - 0.96)^2}{2}}$$
$$= 0.02\%$$

The range of the organic matter content can be expressed as 0.96% ± 0.02%.

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