Remediation of a heavy metal and PAH-contaminated sediment by a rhamnolipid foam

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ABSTRACT

Remediation of a heavy metal and PAH-contaminated sediment by a rhamnolipid foam

Ali Alavi

Industrial contaminants have long term and sometimes irreversible adverse effects on humans, animals and the ecosystem. As a result attention has been focused on the effects of these contaminants. One of the concerning environmental issues these days is contaminated sediments. The presence of aquatic organisms in sediments makes them important in the well-being and health of these organisms. If sediments become contaminated, they can pose a threat to sediment dwelling habitants and through these microorganism that can be spread even to humans. Nowadays a major concern that government regulators and related industry can face is the protection and investigation of the quality of aquatic sediments. A protection that can be done through different pathways includes remediation.

An investigation was made into evaluating the capability of a rhamnolipid biosurfactant (JBR425) in the form of a foam for treatment of polycyclic aromatic hydrocarbon (PAH) contaminated fresh water sediments that also have elevated levels of Pb, Zn and Ni. Studies commenced by evaluating foam characteristics followed by performing column tests. To do this, dewatered non-dried sediments were put in a column and the biosurfactant was injected in the form of a foam or a liquid solution. The pressure gradient was monitored during flushing tests to avoid possible problems due to high pressure. Foam quality of the rhamnolipid varied between 85% and 99% with stabilities from 15 to 43 min. PAH and metal removal were then evaluated for sediment samples from sector 103 of the Port of Montreal in Montreal, Quebec with different initial concentrations of target contaminants. Among PAHs, pyrene; benz(a)anthracene and chrysene had concentrations above thresholds according to Quebec Sediment Quality Criteria. Highest removal for PAHs was obtained by a 99% quality foam produced by 0.5% rhamnolipid solution after 20 pore volumes. Removal efficiency (due to mobilization) for the biosurfactant foam was 44.6% of pyrene, 30% of benz(a)anthracene and 37.8% of chrysene while total removal efficiency (mobilization + volatilization) for the biosurfactant foam was 56.4% of pyrene, 41.2% of benz(a)anthracene and 45.9% of chrysene. With biosurfactant liquid solution at the same pH as above mentioned foam (pH 6.8), maximum removal (mobilization) was 31.4% of pyrene, 20.5% of benz(a)anthracene and 27% of chrysene. Here no volatilization of PAHs was observed. Deionized water (DI) did not remove any PAH. For metals, highest removal was achieved using 0.5% rhamnolipid foam (99% quality, pH 10.0). These were 53.3% of Ni, 56.8% of Pb and 55.2% of Zn. Removal efficiencies were reduced between 11% - 13% for metals when a 0.5% rhamnolipid solution was used. DI water removed only 16% for both Pb and Ni individually and 17% of Zn at pH 10.0. From these analyses, lower pH (6.8) rhamnolipid showed higher removal efficiencies for PAHs while it was not as successful for metals. As for metals, pH 10 was proven to be the best. It is concluded that, rhamnolipid foam could be a non-toxic and effective method of remediating PAH and heavy metal contaminated soil/sediments. Further efforts will be required to optimize the performance of the foam.

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To my parents and little sister

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List of Abbreviations

ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
CAD	Confined aquatic disposal
CCME	Canadian Council of the Ministries of the Environment
CDF	Confined disposal facilities
CEC	Cation Exchange Capacity
CEPA	Canadian Environmental Protection Act
CMC	Critical Micelle Concentration
DC	Direct Current
DDT	Dichloro Diphenyl Trichloroethane
DI	Deionized Water
EPA	Environmental Protection Agency (U.S.)
FEL	Frequent Effect Level
HAC	Heterocyclic Aromatic Compound
HPAH	High-molecular-weight PAH
HPLC	High Performance Liquid Chromatography
LOI	Loss on Ignition
LPAH	Low-molecular-weight PAH
MNR	Monitored Natural Recovery
MSDS	Material Safety Data Sheet
NRCC	National Research Council of Canada
OECD	Organization for Economic Cooperation and Development
PAH	Polycyclic Aromatic Hydrocarbon

List of Abbreviations (Continued)

PCB	Polychlorinated Biphenyl
PCDD	Polychlorinated dibenzodioxins
PCDF	Polychlorinated dibenzofuran
PCP	Pentachlorophenol
PEL	Probable Effect Level
UV	Ultra Violet
VOC	Volatile Organic Carbon

List of Symbols

A	column cross-section, *cm*^{2}
C_f	final concentration of sediment contaminant, *mg/kg* dry sediment
C_i	initial concentration of sediment contaminant, *mg/kg* dry sediment
D	column diameter, *cm*
k	permeability, *cm/s*
K	hydraulic conductivity, *cm/s*
K_{oc}	organic carbon partition coefficient
K_{ow}	octanol-water partition coefficient
L	column length, *cm*
L	head loss, *cm*
μ	viscosity, *kg/cm.s*;
q	foam flow rate, *cm*^{3}*/s*
Q	liquid flow rate, *cm*^{3}*/s*
t	time, *s*
V	volume of water, *cm*^{3}
W_w	wet weight of the sample, g
$W_{d,105}$	dry weight of the sample at 105ºC, g
$W_{d,550}$	dry weight of the sample at 555ºC, g
Δh	difference in water level between inflow and outflow, *cm*
ΔP	pressure drop, *kPa*.

Chapter One

Introduction & Background

1.1 Introduction

Humans have been introducing different substances known to have toxic properties into the environment throughout the years. What can be a matter of concern is their degree of toxicity that greatly varies and as a result can make them a danger not only to human health but also to other living organisms. Many of these substances after being released into the ecosystem, either immediately or gradually, come into contact with soil, sediments, water or air. In an aquatic system, bottom sediments play a major role in contamination distribution as they are able to absorb different contaminants and when strong currents occur, sediments may easily let contaminants free. Two major sources of contamination related to bottom sediments are heavy metals and organic compounds that can be found together or individually. Metals are naturally present in the soil with a fairly low concentration (Forstner, 1995).

As a result of industrialization and anthropological activities, the concentration of heavy metals have been augmented in a way that they can interfere with natural ecosystems and pose a significant threat to the health of humans and other species. "Skin lesions, liver and urological problems, different cancers, gene mutations and intoxications leading to death are all results of heavy metal poisoning. Heavy metals like lead (Pb), cadmium (Cd), copper (Cu), nickel (Ni), chromium (Cr), mercury (Hg), zinc (Zn) and iron (Fe) are of major concern" (Mulligan, 2005). Among these, all except iron and chromium are listed as priority pollutants by the U.S EPA (Cameron, 1992). Alongside heavy metals, organics also play an important role in polluting the environment. Among the organic chemicals, most important categories are organic aqueous wastes (pesticides), organic liquids (solvents from dry cleaning), oils (lubricating, hydraulic, fuel and automotive oils) and at last organic sludges (paint, different tars). Most of the major soil and sediment pollution cases related to organics are usually caused by accidental leaks and spills, left over residues in industrial containers and old chemicals. Beside these, minor pollutants regarding organics include improperly managed landfills (lack of enough liners, leachate collectors, etc), chemicals used in photography (solvents) and maintenance shops. To conclude this category of contaminants; herbicides, household cleaners and automotive products can also be taken into account (LaGrega et al., 2001). "Low solubility in water and high interfacial tension with water are two major characteristics of organic contaminants which are reasons for the lower efficiency during in-situ remediation" (Mulligan and Eftekhari, 2003).

Mulligan et al. (2001c) indicated that "Remediation technologies for contaminated soil include pump-and-treat techniques, thermal extraction for volatile metals (Cd, As, Hg,...), vitrification, electronics, solidification/stabilization, chemical oxidation, soil washing and bioremediation". Treating heavy metal contaminated sediments as well as those with organic contamination, poses a difficult problem since heavy metals cannot be fully removed by either thermal decomposition procedures or by microbial degrading techniques. As a solution for the heavy metals, any method in which metals are immobilized can be beneficial as they are bound to soil-sediment constituents. On the other hand, the organic contaminants that are not water-friendly or hydrophilic, must be transferred through the liquid phase in a manner that their bioavailability increases (for bioremediation) or they can be flushed more easily. To overcome the present problems, one of the ways to perform remediation on organic and heavy metal-contaminated soil or sediments is the application of surfactants as the main extracting agent in soil-sediment flushing techniques (Mulligan et al., 1999a; Shi et al., 2004; Ningning et al. 2008). Mulligan et al. (2001c) performed a surfactant-enhanced remediation of contaminated soil along with batch experiments and demonstrated the effectiveness of biodegradable surfactants (e.g., surfactin, a rhamnolipid and sophorolipid) to remove heavy metals from oil-contaminated soils.

A promising and new way of using surfactants is their usage under the form of foam (a mixture of surfactant and a gas such as air). Many researchers have been evaluating the usage of surfactant foam in soil flushing (Chowdiah et al., 1998; Rothmel et al., 1998; Mulligan and Eftekhari, 2003; Mulligan and Wang, 2004) but it is important to perform enough investigations on this issue for sediments. Mulligan and Eftekhari (2003) performed column tests using a rhamnolipid (JBR425) biosurfactant and Triton X-100 to investigate removal efficiency of pentachlorophenol (PCP) in soil. Mulligan and Wang (2004) continued using the rhamnolipid (JBR425) biosurfactant foam to remove nickel and cadmium from a column packed with sandy soil.

The present study focuses on the investigation of the foamability of JBR425 (mixed rhamnolipid) at different concentrations with different pH values, evaluation of foam characteristics such as foam stability and quality, and the pressure built-up during foam passing through the sediment column and finally assessment of the rhamnolipid (JBR425) biosurfactant foam for treatment of polycyclic aromatic hydrocarbon (PAH) contaminated fresh water sediments that have elevated levels of lead, zinc and nickel. Biosurfactant solution and pH-adjusted deionized water were also used for comparison.

1.2 Thesis content

This thesis consists of six chapters as follows:

- Chapter One is the background and introduction to the subject and also provides an outline of the thesis chapters as well as study objectives.
- Chapter Two consists of the literature review regarding other researchers findings on sediment associated pollution problems, their importance and effect on the environment, heavy metals and organic pollutants specially in this case polycyclic aromatic hydrocarbons (PAHs), surfactants and biosurfactants and finally foam technology.
- Chapter Three is a review of sediment remediation techniques. In this chapter different techniques are compared and discussed.
- Chapter Four demonstrates materials and method used along with the experimental setup. All lab experiments and procedures performed on sediments are explained here.
- Chapter Five presents the results achieved from each set of the experiments in this study. Data analysis is performed in this chapter.
- Chapter Six gives the concluding part of this study with some recommendations for future work.

1.3 Objectives

In this project the objectives are:

- To evaluate the foamability of JBR425 (mixed rhamnolipid) at different concentrations with different pH values
- To determine the effect of the parameters that effect foam stability and quality and the pressure build-up during foam passing through sediment column.

- To determine the effectiveness of biosurfactant foam in the remediation of heavy metal/organic contaminated sediments by performing column experiments.
- To determine the influence of parameters such as biosurfactant solution pH on the removal efficiency of JBR425.

Chapter Two

Literature Review

2.1Contaminants and the Environment

2.1.1 Overview

As society has begun to realize the long term and sometimes irreversible adverse effects of industrial contaminants, attention has been focused on the effects of these contaminants on humans, animals and ecosystem health (Beck et al., 1995). Contaminants come into contact with our surrounding environment each and every day. Some of these substances are added directly from residential, commercial or industrial sources through soil, runoffs, stacks and many other different pathways. Nowadays a major concern that government regulators and industry can face is environmental protection. Protection can be done through remediation and reclamation of contaminated sites (Alexander, 1995). Domain of the group of contaminants is very vast and they can affect different angles of the environment. Spills from petroleum distillates are the most common type of contamination that effects soils (Cookson, 1995). This soil contamination can be passed to underground water, making it contaminated as well. Lack of regulatory guidelines and ignorance has resulted in thousands of contaminated sites (Amatya et al, 2000). Industrial runoffs leaving plants, if not treated enough prior to entering the rivers or lakes, can add chemicals to the environment which in certain incidents can be costly towards human health and that of wildlife. The same thing exists for the agricultural runoffs that if left untreated, might bring pesticides and loads of nutrients into our water bodies. Not only are contaminants carried by water, considered as matters of concern; but also those that are stripped off to the air from the stack of plants or the exhausts of cars must be closely watched and regulated since humans and animals might be affected through inhalation. These air contaminants are also able to land in lakes and rivers far from their points of origin making the water system contaminated. In such cases, sediments, can play the role of contaminants reservoir. This completely shows the need and importance of contaminated sediment regulatory methods.

According to Health Canada (2010), substances that, when accidentally or deliberately are introduced into the environment may be problematic or harmful to people, wildlife and plants are considered as “environmental contaminants”. These contaminants are available everywhere; from soil, sediments and underground water to air and even drinking water reservoirs. In its more general form, when contaminants are introduced into the environment, they can be referred to as pollution.

2.1.2 Common Contaminants in the Environment

According to the US Environmental Protection Agency, among all of the environmental contaminants known to scientists, these listed in this paragraph are the most common that can pose threats of different level. As described earlier, these contaminants have their effects which can depend on the concentration of the contaminant released (possibly a chemical), mixture of chemicals or an individual chemical and finally the physical characteristics of the disposal site. The most common contaminants, which can be released into waterways, soil and sediment include metals, petroleum hydrocarbons, solvents, biological wastes, oil and grease, caustic agents, acids, phenols and cyanide (EPA, 2008). Now we must add the 6-most common air pollutants according to US Environmental Protection Agency to our list to make it referable for the environment as a whole. They are ozone, particulate matter, carbon monoxide, nitrogen oxides, sulfur dioxide and lead (EPA, 2010b).

2.1.3 Sediments

When rocks undergo erosion through physical and chemical weathering, they become broken to coarse grains and clay minerals that can be much easily transported by air and water and finally become deposited into rivers, lakes and seas. The result of this deposition is formation of sediments in water systems. Besides these minerals, soil organic matter that has been degraded by microorganisms alongside a variety of materials that has been discharged by anthropological activity are also released into water columns and added to the matrix of sediments. Generally, larger particles, when being discharged into waters, are transported by water currents at the bottom and near the shoreline while lighter particles that disperse further, will settle at the bottom and merge with other particles. Sediments are primarily categorized into brackish, marine and freshwater sediments (Mulligan et al., 2010).

2.1.4 Sediments place in aquatic ecosystem

Why is sediment contamination important?

Sediments can be a suitable site of living for both autotrophic and heterotrophic organisms. As a result, they are considered to be essential elements of aquatic ecosystems. Autotrophic organisms are those that synthesize food from simple inorganic substances (e.g., carbon dioxide, nitrogen, and phosphorus) and they get their energy from sunlight (Mulligan, 2002). “Green plants, such as algae, bryophytes (e.g., mosses and liverworts), and aquatic macrophytes (e.g., sedges, reeds, and pond weed), are the major autotrophic organisms in freshwater ecosystems”(McDonald and Smorong, 2006).

In contrast, heterotrophic organisms consume, degrade or transform those substances synthesized by autotrophic organisms (Mulligan, 2002). They also can utilize or decompose other organisms whether autotrophic or heterotrophic. “Bacteria, epibenthic and infaunal invertebrates, fish, amphibians, and reptiles, beside these organisms, birds and mammals” are considered among heterotrophic members of aquatic food cycles. Sediments can be the proper place for aquatic ecosystem inhabitants to live and grow. The hard sediments, laid at the bottom of the sediment layers, that mostly are made of gravel, boulders, cobbles and bedrock, can be a supporting media for some algae to attach and grow on them. Softer sediments that are made of sand, clay and silt can provide a good environment for aquatic plants and macrophytes to root and grow. They also can contain necessary minerals and nutrients. Doing these, sediments support autotrophic organisms in aquatic ecosystems.

Meiobenthic and prolific bacterial groups are also among the organisms sheltered and supported by freshwater sediments. Bacteria are considered very important components of aquatic ecosystems as by degrading organic materials, they release considerable amount of nutrients to the water column. As a result, bacteria are considered the primary heterotrophic components of aquatic environments. The fact that sediments uphold primary productivity by supporting both autotrophs and heterotrophs is very essential because both green plants and bacteria are considered to be the foundation of food webs. These two big families provide food for a vast majority of other aquatic habitants.

Not only in soft sediments, reside many invertebrates and benthic fish (this is how sediments provide a place to live for aquatic organisms), but also these invertebrates use bacteria, plants or organisms that are as well bound to the sediments. Since invertebrates are consumed by many different aquatic organisms like fish, mammals and birds, they are important members of aquatic systems. Therefore, sediments are of high importance to many wildlife organisms because of their place in food webs in terms of the production of aquatic invertebrates. In terms of providing habitat for water creatures, sediments have proven to have the major role. For this, we can refer to the fact that fish use sediments for spawning and incubation of their eggs. Furthermore, many young fish hide in the sediments from predators. Therefore, sediments have the essential duty of maintaining the structure and function of aquatic ecosystems (McDonald and Smorong, 2006).

2.1.5 Contaminated Sediments

One of the concerning environmental issues these days is contaminated sediments. As explained above, the presence of aquatic organisms on and inside sediments makes them important for their well-being and health. If sediments become contaminated, they can pose a threat to sediment dwelling habitants (Ingersoll et al., 1995). Threats can be of different types and intensities, e.g. damaged reproduction of fish and other invertebrates, declined rate of aquatic organism growth, contaminants bioaccumulation in aquatic plants or animals and even death. Smaller aquatic organisms are located at the base of food webs.

If they get contaminated through these steps, they can die due to the toxicity of the sediments so larger organisms at top of the food web lose their food (EPA, 1999), if they survive the contamination, they easily can transmit it to bigger members of the food chain including terrestrial animals and human. This is how fish, benthic organisms, birds and mammals can be touched by the impacts of contaminated sediments through the connections of food webs. Anything that disturbs the bottom sediments like a boat propeller, a boat anchor or even a storm, can cause resuspension. Resuspension is the reason that sediments can be directly problematic.

Not only can human life be harmed by contaminated sediments indirectly but also through direct ways. This can be achieved through direct exposure to contaminated sediments via recreational activities, swimming in waters that have contaminated sediments and more. As it is seen here, contaminated sediments in aquatic environments are potential hazards to any related organisms, whether sediment-dwelling and any species that depends on them or terrestrial organisms and humans (Ingersoll et al., 1995; EPA, 1999).

2.1.6 Major Contaminants of Sediments

According to the US Environmental Protection Agency, among all known types of environmental contaminants, these listed here are found in sediments. They include 1) nutrients like phosphorus and nitrogen compounds such as ammonia, 2) bulk organics, a type of hydrocarbons that take oil and grease as an example, 3) halogenated hydrocarbons such as PCBs and DDT, 4) polycyclic aromatic hydrocarbons (PAHs) that include a wide variety of hydrocarbon chemicals and finally 5) Metals, e.g. lead, cadmium, manganese, iron, zinc and many more (EPA, 1999).

2.2 Heavy Metals

2.2.1 Overview

Heavy metals have been used in industry over decades and without using them most of the industrial activities cannot be accomplished. They are easily found in the earth's crust and mantle. These metals are used as catalysts in oil refineries, as corrosion inhibitors in pipelines and ship making and as stabilizers in plastic making industries. They are also used to produce batteries and pigments. As mentioned here, if heavy metals are not used, chemical and metallurgical processes will not complete (O'Neil, 1993;Weiner, 2000).

According to Cameron (1992) heavy metals by definition are the elements having a density more than 5 g/cm^3. They include a group of 38 elements but what usually is referred to as heavy metals is a group of 12 elements used and discharged by different industries. Those include: cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, molybdenum, nickel, tin and zinc. The metalloids, boron and selenium, are also in this list. The US Environmental Protection Agency has a list of 128 priority pollutants, both organic and inorganic. Elements that are listed are antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium and zinc. From this group, cadmium, copper, lead, mercury, nickel and zinc are considered to have the highest potential hazards to animals, humans and plants (EPA, 2008).

The major sources of heavy metal contamination are (1) industrial and urban aerosols, such as those introduced to our environment by metal ore refining, fuel combustion, metal (iron, copper, etc.) melting and fabricating plants and etc.; (2) liquid and solid wastes from humans, some animals and of course industry; (3) mining wastes; and (4) industrial and agricultural chemicals. The major heavy metal introductions to our food cycle are through plant's subsequent uptake, absorption by soil particles and adsorption and displacement by freshwater/marine sediment through waterways. As a result, the fate and transport of heavy metals has elevated priority in human health issues (Cameron, 1992).

2.2.2 Cation Exchange Capacity (CEC)

In soil and sediments, critical concentrations of metallic contaminants that are proven to show toxic effects on biota and the environment can correlate with the cation exchange capacity (CEC) of the holding matrix as having a higher CEC is interpreted to having more toxic effects. Cation exchange capacity (CEC) of a sediment/soil is its ability to exchange cations with the surrounding system and is one of the important properties. Different sediments/soils have different levels of CEC. It ranges from 1 meq to <100 meq/100 g of solid phase. When the solid phase has a large surface area, e.g., clays, then they usually have a high CEC value. This is what determines the elements migration rate in soil/sediment profiles (Cameron, 1992).

2.2.3 Heavy Metal Effects

Since heavy metals are not biodegradable and their high values can cause serious problems like cancer for living organisms, they are a matter of high concern by the environmental authorities. Among them, lead (Pb), cadmium (Cd) and mercury (Hg) are of higher toxicity (Manahan, 2003). Long term exposure to toxic heavy metals, can cause liver damage, lung disease, fragile bones and blood problems (Weiner, 2000). Heavy metals can bioaccumulate in animals, fish, plants and humans (Harrison et al., 1996), besides, as reported by Weiner (2000), some heavy metals seem to be the major reason behind some specific cancers. Cancer cases that can be attributed to environmental causes probably account for more than 60% of all cancers, although the environment in this level, not only involves air, soil, sediments and water, but also has food, drink, living habits, drugs and occupational exposure in its domain (Zakrzewski, 2002). Since heavy metals in certain limits are known to be dangerous to our health, guidelines have been arranged to standardize the usage and release of these useful but at some limits harmful agents in our surrounding environment (Section 2.2.5).

2.2.4 Heavy Metals in Sediments

As discussed above, heavy metals are among the major contaminants that aquatic sediments can absorb. Many of these metals naturally exist in Earth crust. The concentration of those metals that naturally exist, is referred to as ‘background level’. Concentrations of many heavy metals are often above this limit which is a result of anthropological activities. Researchers do not unanimously agree on the dangerous level of heavy metals that may pose hazards to their surrounding ecosystem. This might come from the fact that, the bioavailability of heavy metals in sediments cannot be defined by a dry weight normalization. After a lot of research, it was found that “dry weight metal concentrations that elicit toxicity can vary by one or more orders of magnitude among different sediments” (Di Toro et al., 1990).

Metals are available in aquatic sediments under different forms. They include “soluble free ions, soluble organic (low molecular- weight humic) and inorganic complexes, easily exchangeable ions, precipitates of metal hydroxides, precipitates with colloidal ferric and manganic oxyhydroxides, insoluble organic complexes, insoluble sulfides, and residual forms” (Gambrell et al., 1976). Free metallic ions are considered to have the highest toxicity among different types of metals (Lee and Jones, 1984).

There is a relation between metal concentration in sediments and that in sediment’s pore water (interstitial water). It is largely a factor of metal desorption/precipitation processes. Different materials are in competition with metals to become sorbed on aquatic sediments. It must be taken into account that high concentrations of organic matter, increase complexation and solubility of metals (Salomons, 1985) as a result, metals tend to get sorbed to sediments having a higher organic content.

2.2.5 Heavy Metals and Sediments Quality Criteria

As explained earlier, since sediments are a major component of aquatic environments and various organisms depend on sediments for both food and shelter, availability of hazardous materials in sediments can be harmful to all species related directly or indirectly to sediments. In order to assess this hazard, the relationship between sediment contaminants and possible occurrence of biological effects must be understood. This can be achieved by arranging necessary information and limiting contaminant's concentration under the form of a guideline. Sediment quality guidelines scientifically demonstrate the relationships between environmental and biological hazards with chemical concentrations in the ecosystem.

These guidelines are prepared from toxicological test results in accordance with the protocol established by the Canadian Council of Ministers of the Environment. According to the Canadian Sediment Quality Guideline, one of the important thresholds that must not be passed over is one that is referred to as the Probable Effect Level or PEL. Above this level, adverse biological effects can happen. Like many other environmental quality guidelines, a lot of different applications have been linked to sediment quality guidelines. These guidelines can be used as objectives or potential targets for different provincial and/or national hazardous materials inspection, assessment or management programs.

Table 2.1- Freshwater Sediment Quality Guideline for Heavy Metals

Metals and metalloids	PEL (mg/kg)*, Quebec[1]	PEL (mg/kg)*, Canada[2]
Arsenic	17	41.6
Cadmium	3.5	4.2
Chromium	90	160
Copper	200	108
Lead	91	112
Mercury	0.49	0.70
Nickel	N/D[3]	N/D[3]
Zinc	310	271

*Based on kg of dry-weight sediment

1 - Environment Canada and Ministère du Développement durable, de l'Environnement et des Parcs du Québec, 2007

2- CCME, 2002

3 - CCME has not established a threshold like other contaminants in this study, according to Canadian Sediment Quality Criteria, this value for Ni can be compared with other jurisdictions values that have determined thresholds above which adverse effect can be observed (similar to a PEL value), the range here is taken from MacDonald et al. (2000) and is in the range between 33 to 75 mg/kg dry sediment.

Not only can they be referred to as benchmarks at international debates and symposiums on reduction of environmental hazards emission or while preparing annual reports on cleanliness of sediments of one specific area, but also on the utility of environmental regulations. Although there are too many possible applications for these quality guidelines, but one sole usage is probably more applied than the others and that is the routine screening tool in assessing the danger of environmental contaminants in sediments of a specific site. Using the sediment quality guidelines, experts can better decide what to do and what not to do in each case study (CCME, 2001).

2.3 Organic Compounds

2.3.1 Overview

As awareness towards environment cleanliness increases day by day, important polluting agents are organic. They can be produced through anthropological activities e.g., use of pesticides, use of different fuels in industry and transportation. It is normally done by lack of management or human errors. Some organics may create by-products or residues that can be even more harmful than the original organic substances themselves and could persist in the environment for ages. The number of dangerous organic compounds is pretty large. The most famous organic pollutants include polychlorinated biphenyls (PCB), chlorinated pesticides (e.g., DDT), polycyclic aromatic hydrocarbons (PAH) as well as the polychlorinated dibenzodioxins (PCDD) and the dibenzofurans (PCDF) have high stability and toxicity so as a result can be considered as ecologically high relevant compounds. The original source of many of these contaminants is known to be petroleum hydrocarbons (Amlinger, 2004).

2.3.2 Polycyclic aromatic hydrocarbons (PAHs)

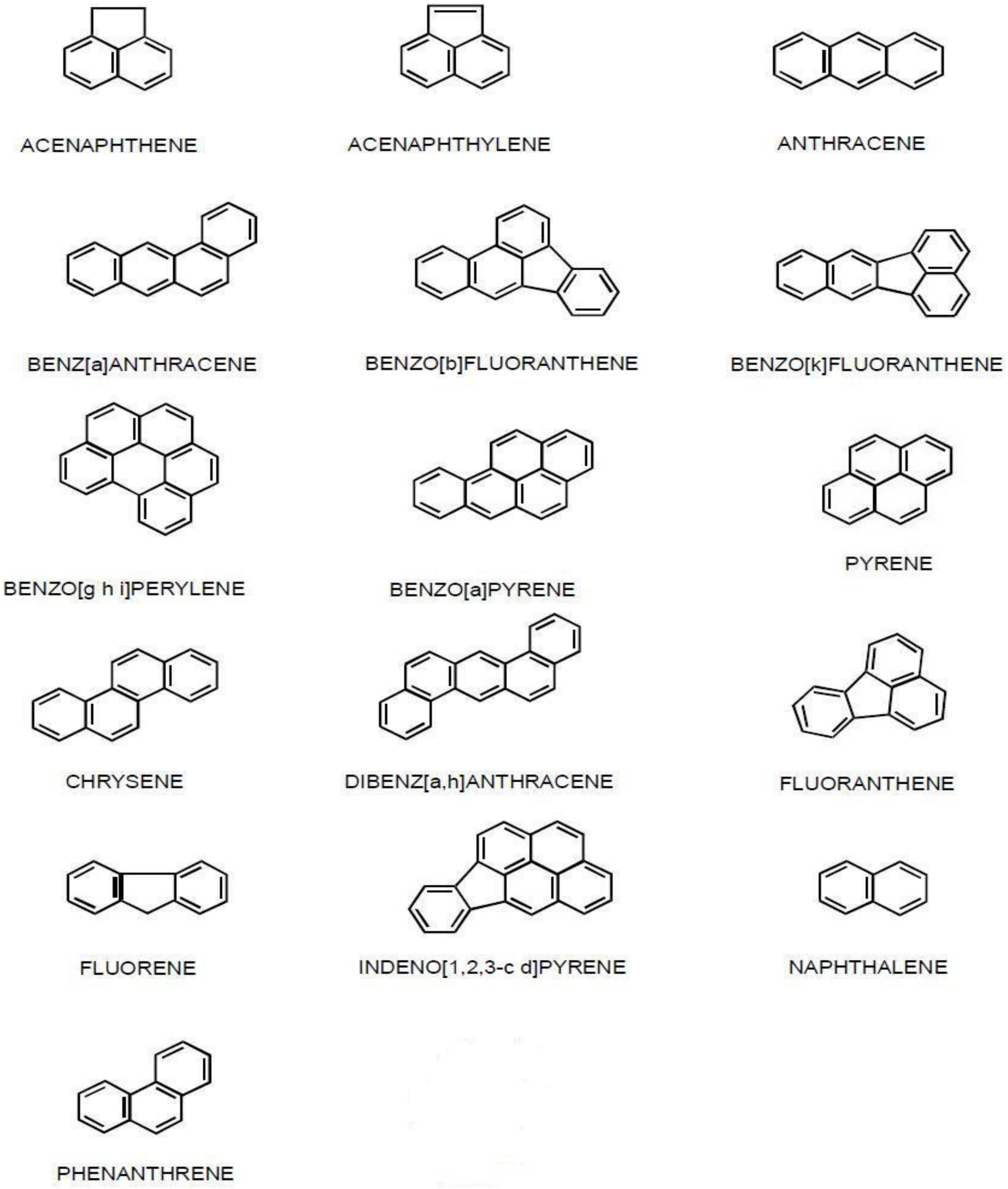
Polycyclic aromatic hydrocarbons or PAHs contain fused benzene rings that are only made up of carbon and hydrogen atoms with a minimum number of two rings. They can be categorized into two main groups according to their weight: 1) low molecular weight polycyclic aromatic hydrocarbons or LPAHs that consist of less than four rings and 2) high molecular weight aromatic hydrocarbons or HPAHs (CEPA, 1994). These are made of four or more rings. PAH derivatives are PAHs that are branched or have an alkyl or a radical on any of their rings. If any carbon atom on a PAH molecule is replaced by either a nitrogen, oxygen or sulfur atom they will be called heterocyclic aromatic compounds (HACs). At room temperature, pure PAHs are crystalline like substances that may be colored as well. Their physical properties changes according to their molecular weight and stereochemistry. “They have very low to low water solubilities, and low to moderately high vapor pressures” (CEPA, 1994). Table 2.2 presents the basic physical and chemical characteristics for the EPA’s 16 priority pollutant PAHs.

Table 2.2 - EPA’s 16 priority-pollutant PAHs and selected physical–chemical properties (adapted from ATSDR, 2005)

Polycyclic aromatic hydrocarbons*	**Number of rings**	**Molecular weight (g/mole)**	**Solubility (mg/L)**	**Vapor pressure (mm Hg)**
Naphthalene	2	128.17	31	8.89E−02
Acenaphthene*	3	154.21	3.8	3.75E−03
Acenaphthylene	3	152.20	16.1	2.90E−02
Anthracene	3	178.23	0.045	2.55E−05
Phenanthrene	3	178.23	1.1	6.80E−04
Fluorene*	3	166.22	1.9	3.24E−03
Fluoranthene*	4	202.26	0.26	8.13E−06
Benzo(a)anthracene*	4	228.29	0.011	1.54E−07
Chrysene*	4	228.29	0.0015	7.80E−09
Pyrene	4	202.26	0.132	4.25E−06
Benzo(a)pyrene*	5	252.32	0.0038	4.89E−09
Benzo(b)fluoranthene*	5	252.32	0.0015	8.06E−08
Benzo(k)fluoranthene*	5	252.32	0.0008	9.59E−11
Dibenz(a,h)anthracene*	6	278.35	0.0005	2.10E−11
Benzo(g,h,i)perylene*	6	276.34	0.00026	1.00E−10
Indeno[1,2,3-cd]pyrene*	6	276.34	0.062	1.40E−10

* US EPA has classified these PAHs as probable human carcinogens (NTP, 2005).

Their octanol-water partition coefficients (K_{ow}) are relatively high (CEPA, 1994). This means PAHs have a higher tendency to get absorbed into organic phase rather than water phase besides they have this high potential (relatively high K_{oc}) to get adsorbed on particulate matter whether in water or in the air (NRCC, 1983; Slooff et al., 1989). Figure 2.1 presents the chemical structure of the 16 EPA's priority-pollutant PAHs.



ACENAPHTHENE

ACENAPHTHYLENE

ANTHRACENE

BENZ[a]ANTHRACENE

BENZO[b]FLUORANTHENE

BENZO[k]FLUORANTHENE

BENZO[g h i]PERYLENE

BENZO[a]PYRENE

PYRENE

CHRYSENE

DIBENZ[a,h]ANTHRACENE

FLUORANTHENE

FLUORENE

INDENO[1,2,3-c d]PYRENE

NAPHTHALENE

PHENANTHRENE

Figure 2.1 The chemical structure of EPA's 16 priority-pollutant PAHs (adapted from Bruzzoniti et al., 2010)

PAHs can be present in the environment in the form of very complex compounds which makes them more challenging and hard to characterize and measure. Their analysis usually is through using gas chromatography technique coupled with mass spectrometry (GC-MS), or recently by using high performance liquid chromatography (HPLC) with ultraviolet (UV) and fluorescence (Fl) detectors (U.S. EPA, 1982; Bjørseth and Ramdhal, 1985; Slooff et al., 1989; Tardif and Chiu, 1992). Large amounts of polycyclic aromatic hydrocarbons are generated via human activities like incomplete combustion processes, use of wood preservatives especially creosote, forest fires and even volcanic eruptions (CEPA, 1994; Nikolaou et al., 2009).

2.3.3 Fate and Transport of Sediment-bound PAHs in Aquatic Environments

Only some of the PAHs that have fewer aromatic rings and basically are lighter, volatilize from water or even soil while the majority of polycyclic aromatic hydrocarbons are non-volatile and they have a low solubility in water. In aquatic ecosystems, PAHs can easily adsorb to particulate matter and sediments. Bottom sediments are considered to be the most important environmental sink for polycyclic aromatic hydrocarbons (Payne et al., 1988; Vandermeulen, 1989). As mentioned before, PAHs are bound to particulates in water systems (Harrison et al., 1975; Wakeham et al., 1980; Germain and Langlois, 1988). When PAHs are bound to suspended matter with higher organic content and when they are high in concentration on suspended solids, they are more persistent. The major processes that govern the fate of PAHs in water columns include volatilization, hydrolysis, photolysis, biodegradation and adsorption to suspended matter that is followed by sedimentation (NRCC, 1983; Eisler, 1987; Slooff et al., 1989). In the aspect of biodegradation of sediment-bound PAHs, again LPAHs have smaller half-lives than HPAHs, e.g. biodegradation half-life of naphthalene (a two-ring PAH) ranges from 0.3 to 129 days while it is from 0.3 to 58 years for benzo alpha pyrene (B[*a*]P) (a five-ring PAH) (Herbes and Schwall, 1978). From these it can be concluded that sediment-bound polycyclic aromatic hydrocarbons are relatively stable. According to NRCC (1983) when PAHs accumulate in freshwater invertebrates, the rate of elimination is much lower than that of uptake. This results in longer PAH half-lives in invertebrates. In places like harbors that the exchange of water with open sea is limited, PAHs can accumulate more in sediments (Bakker et al., 2000; Anyakora et al., 2005). This shows that in such areas physical and mechanical factors have important roles in PAH distribution in sediments (Yim et al., 2007). When partial resuspension of sediments occurs, then PAHs can be subjected to transport pathways (Windsor and Hites, 1979; Larsen et al., 1986). "The final fate of PAH is generally sedimentary deposition, after transport in the water column, as reported for material collected in sediment traps" (Zaghden et al., 2007).

2.3.4 PAHs Toxicity and Carcinogenicity

Sediment-bound polycyclic aromatic hydrocarbons have been proven to cause adverse biological effects. Those related to benthic invertebrates include lower diversity, abundance and decreased growth rate, while other behavioral and physiological changes have been observed among other species (Environment Canada, 1998, Appendices I– XIX). The most common acute toxicity of sediment-bound PAHs is mortality. PAH toxicity is a function of the type of organism, route of exposure and molecular weight and chemical structure. Usually, LPAHs are categorized as acute-toxic but non-carcinogenic to aquatic species while HPAHs are considered to be non-acutely toxic to aquatic organisms while some are potential carcinogens (Neff 1979; Moore and Ramamoorthy 1984; Goyette and Boyd 1989). The reason behind higher toxicity of low molecular weight PAHs (LPAHs) is that LPAHs have higher water solubility which higher molecular weight PAHs (HPAHs) do not have (Duffus, 1980; Uthe, 1991). According to Canadian Council of Ministers of the Environment (CCME, 1999), from previous experiments it has been documented that PAH toxic levels in sediments are equal to or even higher than the PELs, which clearly states that when PAHs concentrations are above PELs, effects are more likely to happen. From these it can be interpreted that sediment quality guidelines (as once indicated before for heavy metals) are very useful to assess toxicological effects of sediment-bound PAHs and to decide the necessity of performing remediation.

Table 2.3 – Comparison between PAHs Canadian PELs and Quebec's PEL & FEL

PAHs	PEL (mg/kg)*, Canada[1]	PEL (mg/kg)*, Quebec[2]	FEL (mg/kg)*, Quebec[2]
Naphthalene	0.391	0.39	1.2
Acenaphthylene	0.128	0.13	0.34
Phenanthrene	0.515	0.52	1.1
Anthracene	0.245	0.24	1.1
Pyrene	0.875	0.88	1.5
Benzo*(a)*anthracene	0.385	0.39	0.76
Chrysene	0.862	0.86	1.6
Benzo*(a)*pyrene	0.782	0.78	3.2

*Based on kg of dry-weight sediment

1- CCME, 1999

2 - Environment Canada and Ministère du Développement durable, de l'Environnement et des Parcs du Québec, 2007

In Quebec, to have better management of dredged sediment disposal into bodies of water, it was needed to determine a contamination threshold which is high enough meaning that any disposal with contamination above this limit without further analysis is illegal. "Since the PEL is not a high enough threshold for this type of decision, a new reference value has been derived: the frequent effect concentration (FEL), or the concentration above which adverse effects are anticipated for the majority of benthic species" (Environment Canada and Ministère du Développement durable, de l'Environnement et des Parcs du Québec, 2007). Table 2.3 presents Canadian Sediment's Quality Criteria values for PAHs (PEL) and also Quebec's Sediment Quality Criteria values for PAHs (both PEL and FEL).

2.4 Surfactants & Biosurfactants

2.4.1 Surfactants

Surfactants have been induced in soil and sediment washing, flushing, and pump-and-treat technologies to increase the solubilization of sorbed and highly hydrophobic contaminants including heavy metals, petroleum-based organics and PAHs (Mackay and Cherry 1989) because surfactants have the unique ability to increase solubility (Ishikawa et al., 2002) , lowering surface tension, detergency power, wetting and foaming capabilities (Tadros, 1984; Holmberg et al., 2002; Mulligan, 2005). Their more specific and desirable properties are: 1) having strong solubilizing tendency, 2) surface tension reduction and 3) having small CMC. Surfactants have also been used in industry as adhesives, wetting, de-emulsifying, penetrating, flocculating and foaming agents (Mulligan and Gibbs, 1993). According to Rosen (1989), the ability to decrease surface tension corresponds to the effectiveness of a specific surfactant. This is a measure of the surface free energy for each unit of area needed to displace a molecule from the bulk to the surface. Surfactants can be divided into different groups based on their various physical or chemical characteristics. Depending on their electrical charge, they can be categorized into four different groups including anionic, cationic, nonionic and zwitterionic (those containing both anionic and cationic groups, also known as amphoteric). These descriptions are typically constructed on the basis of the surfactants molecules, specifically their head groups (hydrophilic head). Whenever the surfactant concentration exceeds a certain level in any aqueous solution, surfactant develops an aggregate called micelle. This certain concentration or level is referred to as CMC or critical micelle concentration (Holmberg et al., 2002; Chang et al., 2006). In other words, CMC is also defined as the minimum required concentration that the micelle formation starts (Becher, 1965). Practically, the CMC is also the maximum value of surfactant monomers observed in water and this CMC value is correlated with temperature, pH, hardness of the water being used and most importantly the type of the surfactant. As it has been previously observed, nonionic surfactants generally have lower CMCs than ionic ones (Rosen, 1989), which means less surfactant is needed to lower the surface tension in comparison with ionic surfactants. Figure 2.2 demonstrates the relationship between the CMC and other influencing factors.

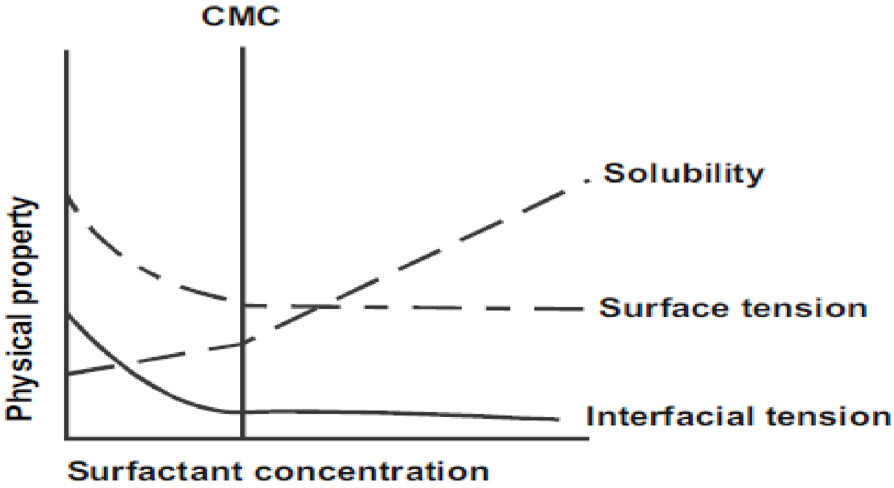


Figure 2.2 Relationship between CMC and surfactant physical property (adapted from Mulligan, 2005)

It is understood from this figure that all these parameters are defined as functions of surfactant concentration. In aqueous solutions, micelles consist of two parts; interior and exterior. Since the head of each of the surfactant molecules is considered a hydrophilic substance they are always oriented towards the water phase while the hydrophobic tails are pointed to the center of the micelles (Lange, 1999; Mulligan, 2005; Chang et al., 2006). This can clearly describe why the solubility of the hydrophobic organics is enhanced in the solution when surfactant-based micelles are present and those organics can be dissolved in the hydrophobic interior section of the micelles (Mulligan, 2005; Chang et al., 2006). This fact that organics can be dissolved more easily in aqueous solutions via being trapped by the interior of the surfactants is called solubilization. The degree of organic solubilization depends on the concentration and type of the surfactants. In order to choose an efficient surfactant many factors must be taken into account including production costs, energy costs (how much they can decrease energy consumption compared to other methods), charge-type, adsorption and physiochemical behavior and finally solubility (Mulligan and Gibbs, 1993). One problem with synthetic surfactants is that they themselves can become an environmental issue as their biodegradability is not always possible (Shi et al., 2004). One way to overcome this problem is using biodegradable biosurfactants (Scheibenbogen et al., 1994).

2.4.2 Biosurfactants

Biosurfactants are microbial-derived surface active agents that can lower surface and interfacial tension of liquids (Georgiou et al., 1992). The word surfactant is a contraction of SURFace ACTive AgeNT and literally means active at the surface (Tadros, 1984). As stated above, biosurfactants are produced by a variety of microorganisms (Banat et al, 1991) like bacteria (Yoon et al., 2003), yeast (Nielsen et al., 2003; Mulligan, 2005) and fungi (Paraszkiewicz et al., 2002). Like synthetic surfactants, these are amphiphilic molecules with hydrophilic and hydrophobic domains (Tsujii, 1988; Mulligan, 2005). The hydrophilic part can be a carbohydrate, amino acid, cyclic peptide, carboxylic acid, phosphate or alcohol. The hydrophobic portion is constructed of long carbon chains which can be fatty acids, hydroxy fatty acids or α-alkyl-β-hydroxy fatty acids (Mulligan, 2005).

The combination of these hydrophobic and hydrophilic portions facilitates the absorption of hydrocarbons into living cells (while present to utilize them as their carbon source). Owing to their surface active properties, microbial surfactants can accumulate at interfaces, form micelles, lower surface tension, and enhance the solubilization of poorly soluble compounds in water (Singh et al., 2007).

2.4.2.1 Types of Biosurfactants

In addition, biosurfactants can also be categorized into several broad groups according to their chemical basis. These groups are: glycolipids, lipopeptides, lipopolysaccharides, phospholipids, and fatty acids/neutral lipids (Biermann et al., 1987; Fiechter, 1992). As it was mentioned earlier in this text, according to Rosen (1989) nonionic surfactants generally have lower CMCs than the ionic ones and it is found that most of the biosurfactant groups are either anionic or neutral according to their molecular structures. The exception here is those containing $–NH_3$ (amine) groups that make them cationic (Mulligan, 2005).

2.4.2.2 Advantages of Biosurfactants

Biosurfactants have major advantages over synthetic surfactants such as: biodegradability, low toxicity, hydrocarbon biodegradation in aquatic environment, sediment and soil remediation & flushing, pesticide degradation, heavy metal decontamination, emulsifiers in cosmetics and personal care products, pharmaceuticals and many more (Mulligan, 2005). Interest in using biosurfactants has been steadily increasing in recent years due to their diversity, environmentally friendly nature, possibility of large-scale production, selectivity, usability under extreme conditions and potential applications in environmental protection (Banat et al., 2000; Rahman et al., 2002). Biosurfactants can be helpful in a vast number of industries like petroleum, agriculture, food, textile, paint and many more (Kosaric and Cairns, 1987).

Biosurfactants have been involved in enhanced oil recovery and crude oil transportation (Hayes et al., 1986). According to Harvey et al. (1990), biosurfactants have been feasible in releasing oil from sandy beaches in Alaska after the disaster of Exxon-Valdez tanker and spill of huge amounts of oil into the ocean. The type of biosurfactant used for Exxon-Valdez was found to be three times more effective than water alone in releasing oil from the beaches in Alaska. Both surfactants & biosurfactants while combined with hydroxide can be useful in enhanced oil recovery, a process that is referred to as alkaline flooding.

In petroleum exist acidic components like carboxylic acids, components from the phenol family and asphaltene. When placed under basic conditions, these acidic substances can lead to hydrolysis and the formation of surfactant products (Peru and Lorenz, 1990). The largest group of biosurfactants on which the most research has been performed till this date is glycolipids, which includes the sophorose-, rhamnose-, trehalose-, sucrose-, and fructose-lipids (Miller, 1995). In the present study, the rhamnolipid biosurfactant has been used and studied as the cleansing agent.

2.4.3 Rhamnolipids

The major rhamnolipid generating microorganism is a bacteria called *Pseudomonas aeruginosa* (Hitsatsuka et al., 1971; Guerra-Santos et al., 1984 & Lee et al., 2004). This bacteria has widely been studied and up to seven homologues have been discovered (Abalos et al., 2001). At first rhamnolipids were isolated from *Pseudomonas aeruginosa* by Jarvis and Johnson. They briefly described rhamnolipids as derivatives made from rhamnose structural units (Jarvis and Johnson, 1949). Surface tensions of 29 mN/m are characteristic of these compounds (Guerra-Santos et al., 1984). *Pseudomonas aeruginosa* can produce rhamnolipids from a large group of substrates which include C11 and C12 alkanes, citrates, glycerol, glucose, fructose, pyruvate, succinates and mannitol (Robert et al., 1989; Lee et al., 2004), corn oil (Linhardt et al., 1989), soybean oil (Lang and Wullbrandt, 1999) and olive oil (Robert et al., 1989).

Pseudomonas aeruginosa can produce four different rhamnolipids by changing the length of the carbon chain (fatty acid) or number of the monosaccharide (in this case rhamnose) rings (molecules with either one or two rings have been observed). Rhamnose is another name for 6-deoxymannose (Jneil Biosurfactant Co., 2004). Surfactant activity is derived from the combination of rhamnose rings and the carboxylic acids at both ends of the molecule that surround the hydrophobic alkyl chain. Figures 2.3 to 2.6 show the chemical structure of these 4 different rhamnolipid molecules:

R1

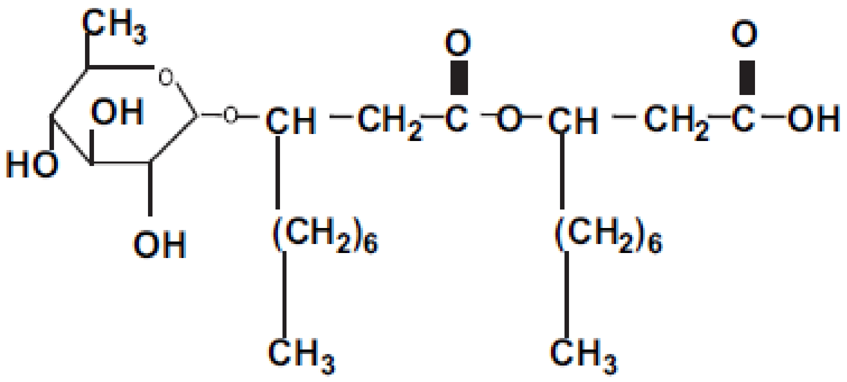


Figure 2.3- Structure of R1 rhamnolipid (adapted from Tsujii, 1998)

R2

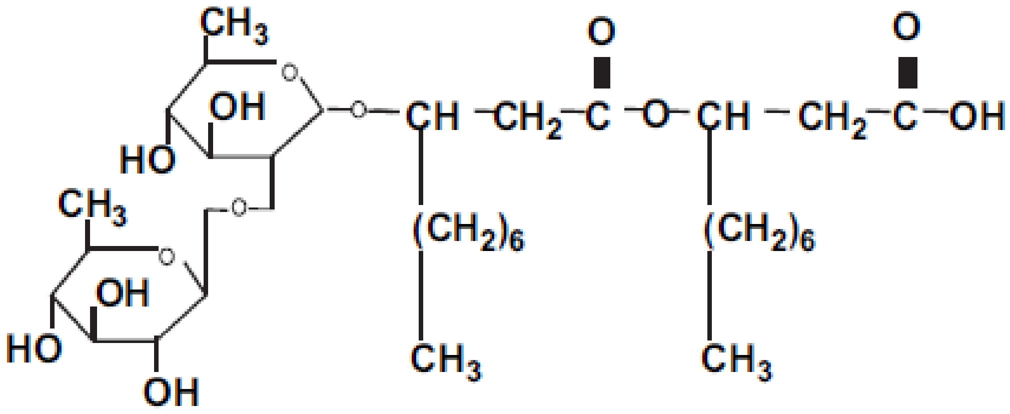


Figure 2.4- Structure of R2 rhamnolipid (adapted from Tsujii, 1998)

R3

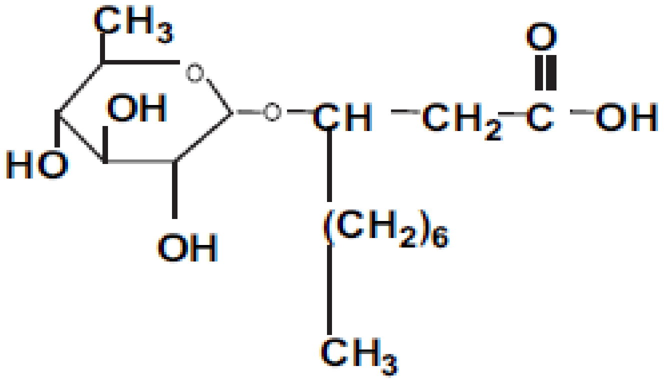


Figure 2.5- Structure of R3 rhamnolipid (adapted from Tsuji, 1998)

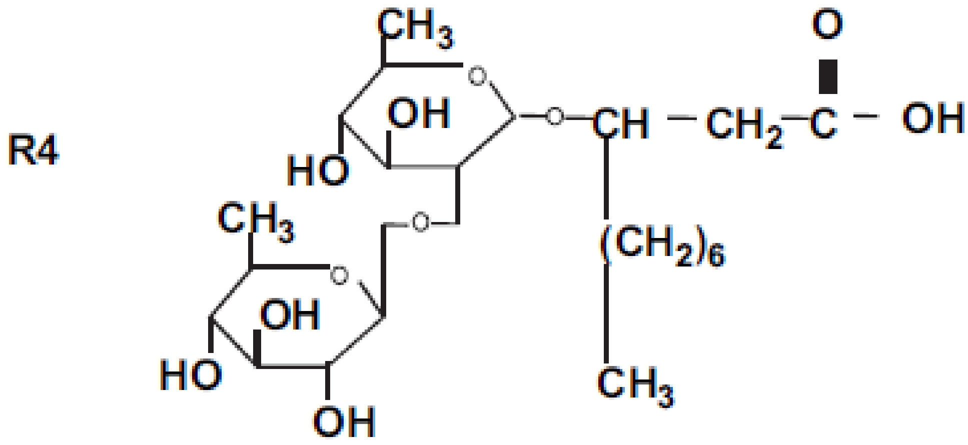


Figure. 2.6 Structure of R4 rhamnolipid (adapted from Tsujii, 1998)

2.4.3.1 Rhamnolipids Properties and Applications

These molecules are soluble in water for 100% and also are fairly soluble in polar solvents such as alcohols, glycols and glycol ethers but not in mineral oil. Between the pH range of 1-5, the carboxylic group on these molecules can provide them a nonionic feature which can be useful while dealing with nonionic substances. Rhamnolipids show very good stability in waters as hard as 500 ppm and also exhibit fine activity in salty waters (Jeneil Biosurfactant Co., 2004). As indicated earlier, surface tensions of 29 mN/m are characteristic of these molecules (Guerra-Santos et al., 1984). Another benefit of using rhamnolipids is their tendency to produce foam depending on their concentration and the pH. Rhamnolipids can make foam at concentrations as low as 0.05% to 0.1%. This foaming property of rhamnolipids is directly a function of pH. Their foam profile changes when the used pH increases. At a pH of 5, fast foaming can be observed but it is not stable. When the pH goes up to 7, foam develops more slowly but it is stable for more than 3 hours. If pH still increases to be equal to 9, fairly stable foam appears. Rhamnolipids are so sensitive to low pH that when pH drops to 2, their rhamnose rings will completely degrade. One last important thing to mention about rhamnolipids is their biodegradability (Jeneil Biosurfactant Co., 2004).

Rhamnolipids have been studied for years for their different characteristics. Among their applications, important ones include corrosion inhibition, emulsification, lubricity & wetting in metalworking fluids, causing detergency in cleansers and finally capability in enhancing (bio)remediation of contaminated soil, sediments and water. The effectiveness of using rhamnolipids as the enhancers of organic contaminants bioremediation has been reviewed and not all the results were satisfactory. Majority of these researches, were focused on low soluble hydrocarbons. According to Maier and Soberon-Chavez (2000) application of rhamnolipid can be beneficial for the removal of many organic substances including: octadecane, hexadecane, n-paraffin and phenanthrene in liquid systems while it has the same value and effect in treating pristine, tetradecane, hexadecane, creosote and other hydrocarbons in soil matrix. Beal and Betts (2000) found out that rhamnolipid increased the solubility of hexadecane more than 12.5 fold while Noordman et al. (2002) found rhamnolipids to be effective on hexadecane degradation but when the process is rate-limited. Deschenes et al. (1994) showed that rhamnolipids can enhance the solubilization of four-ring PAHs much better than the three-ring PAHs but despite all these they figured out that high molecular weight PAHs cannot be biodegraded even when the biosurfactant is added. Rhamnolipids are anionic biosurfactants that can also be used in the removal of heavy metals from soil and sediments. Their feasibility for heavy metal removal from soil and sediments was demonstrated in batch washes (Mulligan et al., 1999a, 2001b). Among metals in general, cations of lowest to highest affinity for rhamnolipids are $K^+ < Mg^{2+} < Mn^{2+} < Ni^{2+} < Co^{2+} < Ca^{2+} < Hg^{2+} < Fe^{3+} < Zn^{2+} < Cd^{2+} < Pb^{2+} < Cu^{2+} < Al^{3+}$.

These affinities were approximately the same or higher than those that organic acids have for metals. This shows how capable rhamnolipids are in metal remediation (Mulligan, 2005). Rhamnolipids were added to heavy metal contaminated sediments (Mulligan et al., 2001b) and also to soil samples with oil and heavy metal contamination (Mulligan et al., 1999a). Around 80%-100% of Cd^{2+} and Pb^{2+} were removed from artificially contaminated samples. Due to the ability of biosurfactants to produce foam, metal-biosurfactant complexes can be removed by adding air to initiate foaming and then biosurfactant can be recycled by decreasing the pH to acidic (close to 2) to cause precipitation.

Another example of using rhamnolipids in a metal contaminated environment is their usage on mining ores which has lead to speed up the process of metal extraction from the ores (Dahr Azma and Mulligan, 2004). With respect to their ability in generating foam, rhamnolipid effectiveness in treating penthachlorophenol (PCP) contaminated soil has been examined by Mulligan and Eftekhari (2003). They observed an excellent rhamnolipid foam stability and a 99% foam quality.

Using foam has this advantage that in soil/sediments experiments while performing in-situ or column tests, foam would cause a lower pressure than a normal liquid so as a result fewer problems like heaving or channeling can be recorded and also smaller values of biosurfactant are needed. While foam quality increases, hydraulic conductivity decreases and when they go below that of water, biosurfactant higher viscosity causes the biosurfactant to provide a better mobility control within soil/sediments during in-situ applications (Mulligan and Wang, 2004). From this it is understood that rhamnolipid foam can be a beneficial, environmental friendly, cost-effective and non-toxic way of remediating hydrocarbons, heavy metals or mixed contaminated soil or sediments. In section 2.5 (foam technology), foams will be discussed from a closer look.

To understand rhamnolipids' capability in in-situ remediation of contaminated soil and sediments, whether it is for heavy metals or organics, column tests must be done. As shown by Noordman et al. (1998), and Noordman et al. (2000), rhamnolipids must not attach to the soil/sediments particles. It was understood that to avoid biosurfactant adsorption on media particles as much as possible, interfacial hydrophobic adsorption of biosurfactant aggregates to media (soil/sediments) must be limited and that can be achieved under one condition and that is the consumption of biosurfactant (rhamnolipid) at concentrations higher than the CMC. According to Herman et al. (1995), using dosages lower than the CMC concentration of biosurfactant will lead to mineralization of hydrocarbons which are encircled by surfactant monomers while concentrations higher than CMC enhance the hydrocarbon's mobilization.

2.5 Foam Technology - Overview

"Foam is a non-equilibrium dispersion of gas bubbles in a relatively smaller volume of liquid" (Durian and Weitz, 1994). One of the important building blocks of a liquid-based foam is surface-active agents. Liquid foams carry the characterization of solids, liquids and gases. Foams can be able to support shear elastically, as a result they can be considered as solid. Having the ability to flow and deform in whatever they are poured into, they are considered as liquid and finally they are gas-like as they are very compressible (Durian and Weitz, 1994).

In a simple word, when the rate of bubble production is higher than that of bubble rupturing, foaming occurs. The larger part of foams is made of gas. This causes the bulk density to approach near the density of gases rather than surfactants. Since they have low density, they have a large surface area for a fixed amount of foam (Myers, 1999). True foaming happens when the thickness of liquid between two bubbles becomes too small (lamella) instead of bubbles breaking down (Ghildyal et al., 1988). During formation and destruction of foams, many processes take place including: liquid run-over from interfacial thin films; liquid can get redistributed along the foam generating column; gas can diffuse from smaller into larger bubbles; liquid may naturally drain from the foam matrix (Vardar, 1998). According to Myers (1999) foams can be classified morphologically into two categories: (1) kugelschaum or foams that contain spherical bubbles and (2) polyederschaum that refers to foams with polyhedral-shape bubbles with very thin lamellar films.

When enough liquid is present, such a foam would resemble “the random close-packed structure formed by hard spheres” and with less liquid, depending on bubble sizes distribution, the bubbles will be distorted from their initially spherical shapes to either distorted sphere or polyhedral (Durian and Weitz, 1994). The continuous phase of foams can consist of only liquids or liquids with dissolved components. Two general classes of foams are presented in Figure 2.7. The relationship between foaming capability of a specific surfactant and its chemical formula is so complicated.

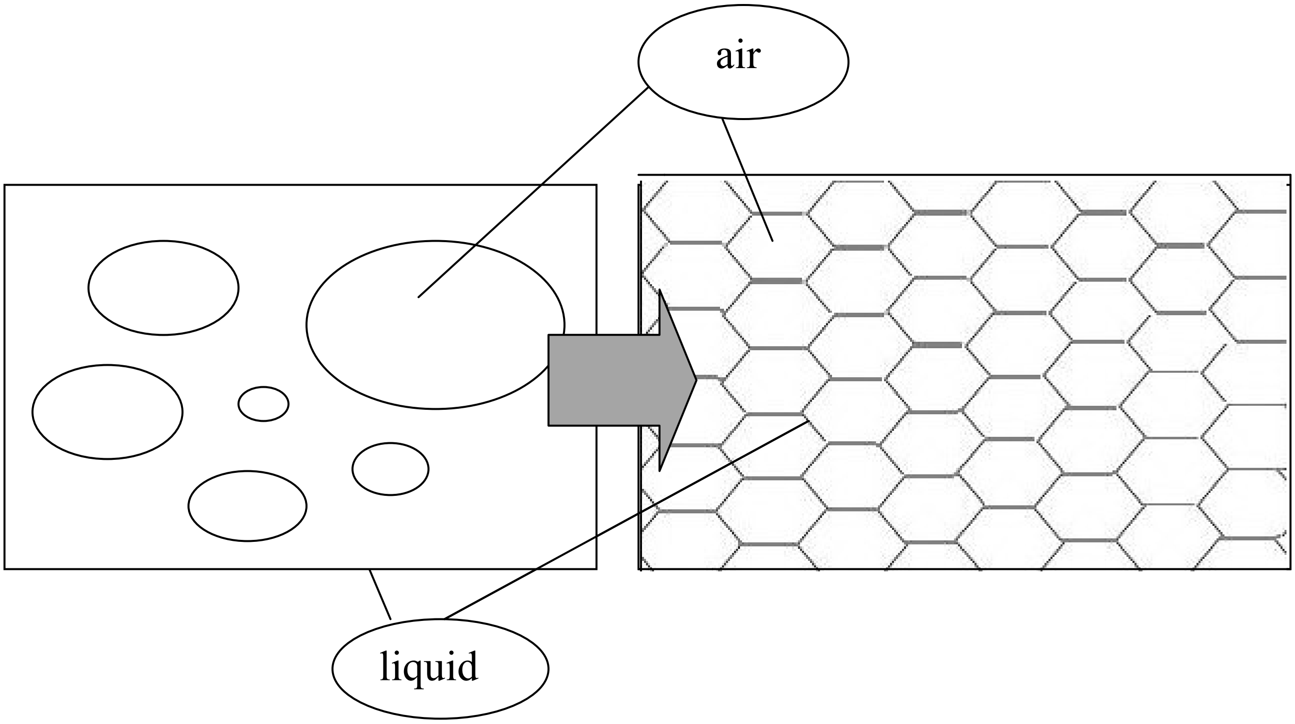


Figure 2.7 Two general morphological classes of foams (adapted from Myers, 1999)

What is usually found is that when the surfactant concentration increases to a maximum level, close to critical micelle concentration (CMC), then the amount of produced foam increases as well (Myers, 1999). In aqueous solutions, surface activity is related to those molecules that contain both hydrophobic (lipophilic) and hydrophilic characteristics. When such molecules (e.g. surfactants) are placed at an interface, the hydrophobic section of the molecule is repelled out of the solution as the attraction between water molecules is much stronger than its attraction to both hydrophilic-hydrophobic parts of the surfactant molecule all together. This naturally induced positive adsorption at the liquid-vapor interface, decreases the surface tension of the main solvent (Thomas et al., 1977). Figure 2.8 presents surfactant molecules placement in foam clusters when applied in foam production.

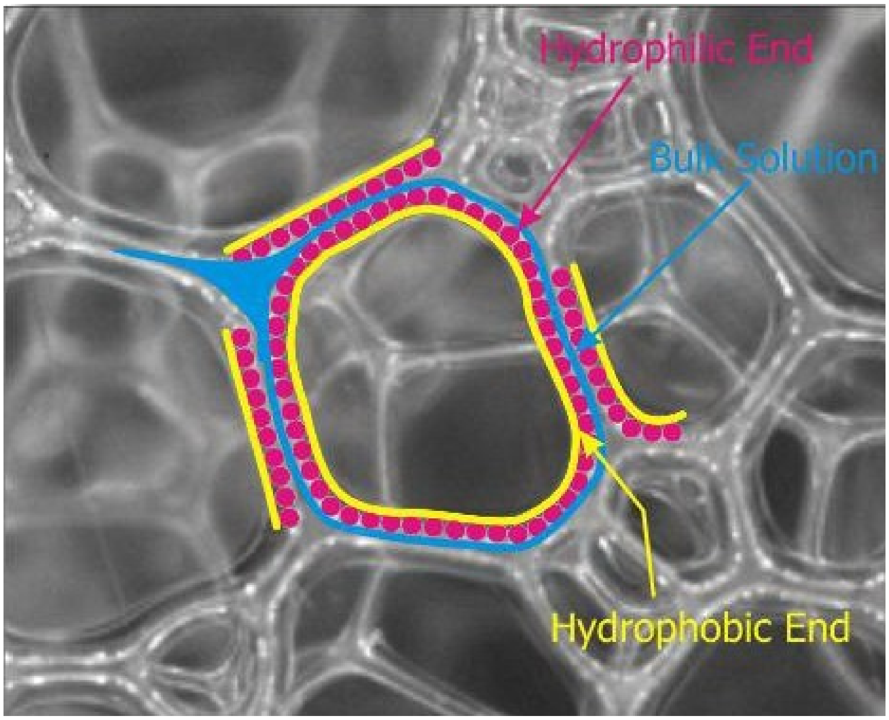


Figure 2.8 Surfactants incorporated in the foam structure (adapted from D-foam Inc., 2005)

2.5.1 Characteristic Properties of Foams

If the foams are considered to be homogeneous, then their physical structure and to some extent their behavior can be formulated. The fashion under which gas and liquid are mixed together, particularly the amount of both of these alternatives, defines many foam properties, including its physical structure. To express the value of the gas content of a foam, the term ‘Foam Quality’ is used. It is defined as :

$$\text{Foam Quality} = \frac{\text{Gas Volume}}{\text{Total Foam Volume}} \qquad \text{Eq. 2-1}$$

‘Expansion Factor’ is another factor that is used to explain the foamability of a solution. It is defined as :

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

The reason that foams are compressible is the existence of gas inside them. As a result of this compressibility both the expansion factor and the foam quality are related to pressure. Another important characteristic of foams is the ‘stability’. “Stability of a foam refers to the ability of the foam to resist bubble breakdown” (Chowdiah et al., 1998). It is defined by measuring the required time for the drainage of half of the liquid volume of the foam. Another important parameter regarding foams and their behavior is ‘foam effective viscosity’ which is shown by $\mu_{(foam)}$. The effective viscosity is 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 has a direct relationship with the change in value of soil permeability (Chowdiah et al., 1998). Figure 2.9 illustrates a set-up normally used to investigate the terms related to foam behavior.

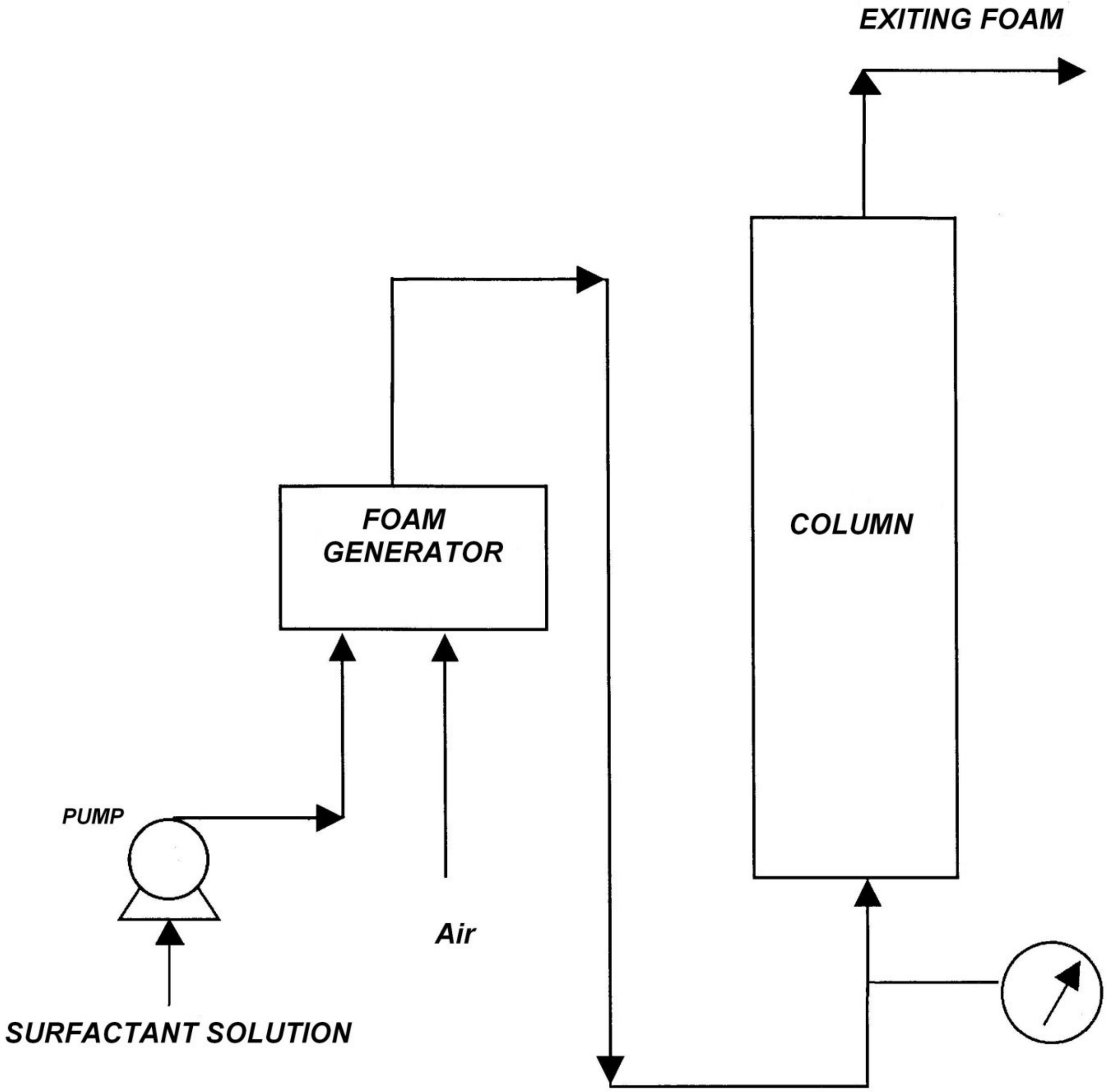


Figure 2.9 Schematic of apparatus for foam generation analyses

2.5.2 Foam Technology in Soil-Sediment Remediation

As explained earlier, use of a surfactant in foam production is essential. Its major role is to adsorb at the air-water interface so that the surface tension becomes decreased. Since foams have larger liquid surface area compared to air-liquid interface when foams do not exist, using them can be a good auxiliary technology in remediation of soil and sediments (Chowdiah et al., 1998). As the main factor in remediation techniques, surfactants can be used in soil washing and contaminant mobilization and also to initiate biodegradation of strongly-bound organic contaminants like PAHs. However, their usage is not free of problems like contaminant spreading into soil and reaching underground water (Peters et al., 1992). Using foam technology as a remediation method is more amenable to containment than are solutions of different surfactants (Kilbane et al., 1997). It must be remembered that the type of surfactant needed and the formulation of the foam are all related to the characteristics of the specific contaminated site that requires remediation. These can be surfactant adsorption onto soil/sediment particles therefore loss of the surfactant (Allred et al., 1994), loss or decrease of surfactant ability to produce foam (foamability) as a result of contaminant dissolution (Minnsieux, 1974) and finally the required pressure under which foam must be injected into soil/sediment contaminated zone (Peters, 1994). The most important issue regarding foam injection is to avoid heaving and channeling in the soil under treatment. To avoid this, injection pressure must be limited to 1 psi/ft (22.6 kPa/m) of depth (Chowdiah et al., 1998).

Chapter Three

Review on Sediments Remediation Techniques

3.1 Overview

In order to clean up contaminated sediments and avoid the release of contaminants into the aquatic ecosystem, different techniques have been applied throughout the years. Remediation methods can be classified as physical, chemical or biological remediation techniques. Also these technologies can be categorized as in situ or ex situ remediation methods. In situ refers to those treatments that take place in a sediment's original location without excavating them while ex situ refers to those treatments that must be followed on sediments that are taken out of their initial place. Remediation can be performed either off-site or on-site (Soesilo and Wilson, 1997). Many of the available sediment remediation technologies can also be used for soils, but the treatments that are only specific to sediments are limited. It is important to note that sometimes a combination of these methods must be applied to achieve better remediation either for sediments or soils. In this chapter, those sediment remedial technologies that have been mostly used, are being briefly reviewed.

3.2 Remediation Technologies

3.2.1 In Situ Containment Technologies

3.2.1.1 Capping

One of the major contaminated sediment remediation techniques is capping. It is done by using a clean material, e.g. sediment, gravel or sand to cover the sediments that are of concern for their contamination. In recent years, new caps that contain geotextile mats, organoclay liners or other permeable or impermeable materials are often used. In order to slow down the movement of contaminants through the caps, sometimes materials like organic carbon can be utilized. Capping can be helpful in risk reduction depending on contaminants type and the surrounding environment. That can be done in the following ways: 1) physical isolation of the contaminated sediments from the overlying water; 2) contaminated sediments can get stabilized and protected from erosion so in this case contaminants transport becomes minimum and 3) chemical isolation of the sediments contaminants from the overlying water can be achieved. There can be three different capping designs: 1) conventional, that is made of sand or other natural materials directly on the contaminated sediments. Sand caps usually are used in waterways with low velocity; 2) armored, that is basically a stone layer or riprap over a conventional cap. This is used in high velocity waterways; and 3) composite capping which is constructed of many layers of sand, rock and geotextile. It is used for sediments that are too contaminated (EPA , 2010a).

3.2.1.2 Resuspension

This is a phenomenon that can occur either naturally or artificially. Artificial sediment resuspension can be achieved through fishing with dragnets, dredging, constructions under water and any other physical device, e.g. water jets. When sediment organic matter degrades, bacteria consume the dissolved oxygen in a way such that sediments will go under anaerobic conditions. Organic matter retains sediment contaminants and when it is degraded, contaminants can be released. Using water jets is the simplest and easiest technique that can change the sediments into aerobic while suspends the lightest particles (organic particles). Since organic particles have lower settling velocities and grain size than inorganic particles their dispersion height and the time that they remain dispersed is much longer. In this step, organic matter can be skimmed or filtered from the water column (Mulligan et al., 2010).

3.2.2 Removal Technologies

3.2.2.1 Dredging

Sediment dredging is a useful tool to take out contaminated sediments without doing any further action like dewatering or draining. When dredging is done, a certain amount of water from the aquatic system is also removed. The water must be treated prior to release back into the water body while contaminated sediments may be disposed of in a landfill or a confined disposal facility. If sediments are very contaminated, they usually get treated by stabilization in advance of getting dumped in a landfill. Dredging can be either mechanical or hydraulic. In mechanical dredging, a bucket is applied to collect the sediment and then deposit it in a container but in hydraulic dredging, “the sediment is loosened with some form of cutter head and sucked into a holding tank” (EPA, 2010a). The water content of the mechanically dredged sediments is about the actual water content of the sediments in their original place while the hydraulically dredged sediments look like a thin slurry with only 10 to 20 percent solids. Whether dredged sediments need to be disposed of or go to a treatment facility, they all must be dewatered as much as possible. Silt curtains are used to enclose the dredging area so that minimum resuspension occurs. These curtains have certain devices to help them stay afloat and they also can extend to the bottom and get attached to the bottom sediments via anchors. Dredging is usually applied when low currents are available. During dredging, turbidity must be monitored as a precaution for resuspension (EPA, 2010a).

3.2.2.2 Excavation

Excavation is usually applied for those sediments that are partially dewatered in their place. ”Typically a coffer dam is built in the area to be excavated and the sediments are removed with conventional construction equipment” (EPA, 2010a). Since the sediments are dewatered in advance, excavated sediments have less water in comparison with dredged sediments. When dealing with smaller water systems, the option of diverting water from the contaminated sediments area is available so sediments can be excavated more easily and then can be replaced by cleaned sediments (EPA, 2010a).

3.2.3 Disposal Technologies

Generally there are three types of confined disposal facilities (CDFs) available for the disposal of contaminated sediments (Anchor Environmental Inc., 1999):

- Confined aquatic disposal (CAD);
- Near-shore confined disposal; and
- Upland.

3.2.3.1 Confined Aquatic Disposal (CAD)

For this system, it is necessary that the contaminated sediments be confined in a natural depression, a berm-like area or a pit. There are usually two variations of CADs: 1) Pit CAD, contaminated sediments fill a natural depression or an excavated pit then the whole system is capped. This way a CAD is produced which resembles a pit; 2) Near-shore CAD, alongside the shoreline a toe berm is constructed then contaminated sediments are placed behind the berm. Again the whole system is capped (Anchor Environmental Inc., 1999).

3.2.3.2 Near-Shore Fill

A near-shore confined disposal facility is an underwater fill alongside the shoreline. It is a berm near the shore, constructed of clean materials. The upper layer of the area is made with clean sediments or fill materials until it is above the water level and the lower layer of the area between shoreline and the berm is where the contaminated sediments must be placed. The sediments are normally dredged using a hydraulic dredge (Anchor Environmental Inc., 1999).

3.2.3.3 Upland/Landfilling

This is a good way to dredge contaminated sediments and take them as far as possible from the aquatic system. Usually sediments that are hard to treat or not so cost-effective to get treated are chosen to be disposed of in a landfill (Anchor Environmental Inc., 1999; EPA, 2010a). In order to stop possible leachate from the landfills, they must follow construction standard regulations that in their case the major one is establishing liners and a specific leachate collection system. If these systems are not designed, groundwater can become contaminated by landfill leachate. Typically there are two types of landfilling options: 1) Monofill, a landfill is designed only for contaminated sediments, or 2) Municipal landfill, in which the sediments are dumped into an existing landfill with other solid wastes (Anchor Environmental Inc., 1999).

3.2.4 Treatment Technologies

Generally the treatment technologies are considered to be the least cost-effective procedures for the remediation of contaminated sediments. The reason is the usual lower amount of contaminants in comparison with the larger volumes of sediments that must get remediated. If these conditions are changed in a way that sediment volumes become low and contaminants become high in concentration, treatment technologies can become much more cost-effective. Treatment technologies can be categorized into three different groups: physical; chemical; and biological (Anchor Environmental Inc., 1999; Mulligan et al., 2010).

3.2.4.1 Physical Treatment

The aim of physical treatments is to dewater sediments so by doing this sediment handling and contaminant separation from sediments will become improved. There are two types of dewatering systems:

- Belt Press: this is considered the most economical type of mechanical dewatering technology. It works by passing the sediment through a conveyor that squeezes the water out.
- Additives: to absorb the free water, additives like cement or fly ash can be added to the sediment. Adding the additives, both the strength of the sediment and also the unit weight are increased. If sediment contaminants are common to one grain size then the physical separation technologies can be applied, e.g. if the contaminant is only associated with the silt and clay fractions of the total sediment, then this fraction can be broken off via a separation process. **Physical separation process** options include:
- Hydrocyclones: typical “cone-shaped vessels with a cylindrical section containing a tangential feed entry port and axial overflow port on top and an open apex at the bottom. They can fairly accurately separate sediments into coarse- and fine-grained portions” (EPA, 1994).
- Grizzly and Vibrating Screens: larger size particles can be screened out by running the sediment through screens or grizzlies (EPA, 1994).

Sediment (Soil) Washing: This technology results in separation and amount reduction of the contaminants associated with solid phase. After the excavation of either soil or sediments, this technique can be applied on site. Prior to the washing step, solids must be sieved to get rid of any big and coarse particle. Sediments or soils are washed by water while being shaken or stirred in a shaker (Mann, 1999).

Solvent Extraction: is similar to soil washing, but uses a solvent rather than water based wash solution. In order to treat contaminated sediment/soil, contaminants (metals, organic compounds) need to be more soluble. To achieve this target, amendments like salts, acids, chelating agents and surfactants are applied to better extract these contaminants and increase the level of desorption from solid particles into the extracting solvent. Organic compound sorption onto sediments/soil is strong, so by lowering surface or interfacial (between non-polar and polar liquids) tensions via (bio)surfactant addition, their dissolution is achieved more easily (Mulligan et al., 2001b). The use of surfactants in soil-sediment remediation has been discussed in section 2.4 of this text (Surfactants and Biosurfactants). At the end when treatment goals are met, sediment and solvent mixture (slurry) go through a dewatering step then the washing solution is treated by either sedimentation and/or flocculation.

3.2.4.2 Chemical Treatment

The primary focus of chemical treatment technologies is to stabilize the contaminant in the sediment body so that the contaminant cannot be released easily into the surrounding environment. These processes include:

Thermal Treatment (Cement Plant): Dredged sediments might be applicable as raw material for making cement. In this process (kiln process) the raw material must reach a very high temperature to become semi-molten. As a result, organics are destroyed and heavy metals become immobilized in the clinker at the bottom of the kiln, so they are not available for leaching. This process can only be applicable for fresh water sediments as marine sediments have higher salinity and can make cement weak (Anchor Environmental Inc., 1999).

Stabilization: In this method, sediments are passed through a pug mill and then a stabilizing agent is added to the sediments. Agents can include lime, fly ash and Portland cement. The mixture controls how the sediment is placed and cured. “A flowable type mix would be poured into its disposal site or temporary holding area and allowed to cure. A dry mix would be spread as soil and compacted with earth moving equipment”. No matter what process is taken, the final product is a material stronger and less leachable than the raw sediments (Anchor Environmental Inc., 1999).

Low Temperature Thermal Desorption: This technology is commercially available. In this method, sediments are heated to 200 to 600ºF to volatilize water and organic compounds.

Hazleton Maxi-Clone/Maximstrip Air Stripping: Sediments that are dredged hydraulically are screened to ½ inch then passed through a series of Maxi-Clones. “Volatiles are stripped from the slurry and sediment in each Maxi-Clone”. To enhance the process, oxidizing agents like ozone or peroxides can be added to the system (Anchor Environmental Inc., 1999).

Slurry Aeration/Oxidation: In this technology, aeration tanks are used. Dredged sediment is placed in those aeration tanks at about 10 to 20 percent solids and then treated in batch, semi-continuous, or continuous mode. Like the previous treatment, here again oxidizing additives can be added to the system to enhance the oxidation. It is necessary to inject the ambient air for

VOCs stripping and for maintaining solids in suspension, a mixer is applied. At the end, vapors are trapped and treated (Anchor Environmental Inc., 1999).

Vitrification: The basics of this technology are the same as those for the soil remediation. Insertion of electrodes into dredged soil (sediment) and application of a high current to immobilize the whole matrix and then solidify when cooled down. As a result of the very high temperatures, organic contaminants will degrade and heavy metals melt and immobilize. Since fuels values are not high and reversely moisture content is so high this method can be costly (Mulligan et al., 2010).

Electrokinetic Remediation: in this technology, electrodes are inserted into contaminated sediments, then a low DC current or a low potential gradient is applied. As a result, ions start to migrate towards their corresponding electrodes and accumulate at the surface. They can be recovered by other methods like plating. During this procedure, pH monitoring is essential (Mulligan et al., 2010).

3.2.4.3 Biological Treatment

In these technologies, microbiological processes are used to transform or degrade contaminants to a less toxic or non-toxic state. They are costly and there can always be uncertainties about their efficiencies. Biological treatment options include:

- Bioslurry Treatment: Anaerobic or aerobic activated sludge processes.
- Land Treatment (including phytoremediation): In this technology, sediments are combined with amendments and placed on a treatment area which includes leachate collection. “The soil and amendments are mixed using a windrow composter, conventional tilling equipment, or other means to provide aeration. Moisture, heat, nutrients, oxygen, and pH can be controlled to

enhance biodegradation. Other organic amendments such as wood chips, potato waste, or alfalfa are added to composting systems" (Anchor Environmental Inc., 1999).

3.3 Monitored Natural Recovery (No-Action Alternative)

Monitored natural recovery (MNR) is a way to reduce the risk of contaminated sediments. It uses natural processes to destroy or minimize the toxicity or bioavailability of sediment-bound contaminants. To get the best results out of MNR process, it is mandatory to identify and evaluate the natural processes that reduce risk as sometimes the results can be something significantly in a different direction. "Natural processes that can reduce risk include the following, in order of preference:

- Processes that convert contaminants to less toxic forms (e.g., biodegradation)
- Processes that bind contaminants more tightly to the sediment (e.g., sorption)
- Processes that bury contaminated sediment beneath clean sediment (e.g., sedimentation)"

MNR can be very useful where the water has relatively slower currents and is deep. MNR can be a recommendation for sensitive environments depending on the type of sediment-bound contaminants. It can be an environment (like a wetland) where sediment disturbance can cause irreversible damage to the whole system. While the ecosystem is being monitored, during the MNR, it is for being further ensured that the necessary conditions for a successful MNR have not been changed. For this purpose, different tests must be performed on water, sediments and tissues of fish, birds and other bottom dwelling invertebrates. Advantages of the MNR (no-action alternative) include the minimized risk of contaminant spread and low cost (Southerland et al., 1993; EPA, 2010a).

Chapter Four

Experimental Materials and Methods

4.1 Introduction

In this chapter, the experimental materials and all the methods and setup used during the measurements are introduced. Experimental materials include sediment samples, biosurfactant JBR425 (mixed rhamnolipids), and as for the contaminants measurement, a mixture of 16 PAHs as well as all the individual PAH standards were used. Solutions of HCl (1 N) and NaOH (1 N) were used to adjust the required pH for biosurfactant solutions. Millipore deionized water was also utilized in order to dilute solutions, wash vessels and perform as a control solution.

The experimental setup, which will be presented in this chapter, gave better results compared with others tested regarding the uniformity of the wet biosurfactant foam generated. The use of foam technology in remediating PAH contaminated sediments studied through column tests, is considered an open system nearing the basics of soil flushing procedures. The sizes of all tubings, fittings and columns were chosen by trial and error in a way to assure the best uniformity, quality and stability for the produced biosurfactant foams.

4.2 Experimental Materials

4.2.1 Sediment Samples

The contaminated sediments were dredged prior to the lab experiments. Sediments are from the port of Montreal, sector 103 at the Saint Lawrence River in Montreal, Quebec, Canada. Sector

103 of the Montreal harbor is located on the North bank of the St. Lawrence River which is approximately 15 km downstream of downtown Montreal (Appendix A). This part of St-Lawrence has been the site of industrial activities for over 100 years, including oil and metal refining industries. These sediments were used since it was believed that the concentration of organic compounds (especially PAHs) and heavy metals were relatively high. To determine particle size, a Horiba particle size analyzer (LA-95V2) was used at the lab.

Table 4.3 Result of Sediment Particle Size Analysis

Fraction	Size (μm)	Percentage
Coarse Sand	500.00 – 840.90	4.3
Medium Sand	250.00 – 420.45	11.3
Fine Sand	125.00 – 210.00	30.7
Very Fine Sand	62.50 – 105.11	31.1
Coarse Silt	31.25 – 52.56	13.9
Medium Silt	15.63 – 26.28	3.4
Fine Silt	7.81 – 13.14	4.0
Very Fine Silt	3.91 – 6.57	0.01
Clay	0.98 – 3.28	0.0
Colloid	0.01 – 0.82	1.4

A slurry of sediments was prepared by mixing one spatula size of sediments with Millipore deionized water then it was fed to the Horiba particle size analyzer. Results are presented in Table 4.1. After completing the particle size analysis, Milli-Q deionized water (Millipore, Laval, Canada) was added to a sample of sediments which was acquired to be prepared for further tests on sediment physical and chemical properties. Sediment-water suspensions were shaken on a wrist action shaker (BURRE, Pittsburgh, PA, USA) at 60 oscillations/min for 24 hours. In this point, samples were placed in centrifuge tubes. Centrifugation started at 4500 rpm and lasted for 15 minutes to separate solid and liquid phases. It was done using a Damon/IEC Division Centrifuge, Model # HNS, made by Needham HTS Company, Massachusetts, USA. After this stage, sediments were air dried under a fume hood (Hamilton, Fisher Scientific) prior to measure their other physical and chemical characteristics. Data recorded here were in triplicate and did not vary more than 5%. The average results are presented in Table 4.2. All the procedures followed to capture these data are listed in the Methods section of this chapter.

Table 4.2 Characteristics of Sediment Samples

Parameter	Value
CEC (meq/100g)	12
Hydraulic Conductivity (cm/s)	0.00163
Water Content (%)	44.1
Loss On Ignition (LOI) (%)	2.7

4.2.2 JBR425

The rhamnolipid biosurfactant (JBR425) was the surfactant used in this study. It was obtained from Jeneil Biosurfactant Co., USA. The major outstanding properties of this surfactant that motivated us using it for this research were high molecular weight, low CMC and its ability to produce high quality foams. The supplied surfactant solution was a 25% w/v viscous active liquid. It was used to prepare fresh dilute rhamnolipid solutions with concentrations 0.5%, 1.0% and 1.5% that were needed to measure biosurfactant CMC, ability to produce foam, stability, quality of the produced foam and finally it was applied as the major factor in remediation experiments.

As it was mentioned before (Section 2.4) four different rhamnolipids can be produced by bacteria *Pseudomonas aeruginosa* only by changing the length of the carbon chain or number of the monosaccharide (in this case rhamnose) rings (molecules with either one or two rings have been observed). Rhamnose is another name for 6-deoxymannose sugar. Rhamnolipids are glycosides of rhamnose and β-hydroxydecanoic acid (Jeneil Biosurfactant Co., 2004). Two strains of rhamnolipid were present in the mixture that was purchased. These were RLL or R1 and RRLL or R2. Figure 4.1 shows the chemical structure and name of these two rhamnolipids. According to Jeneil Biosurfactant Co. (2004) these have been the products of a controlled fermentation at which the molar ratio of R2/R1 was 0.9 to 1. Final product in this process is called JBR480 which has more than 80% pure biosurfactant. The actual product used in this study (JBR425) which is made from JBR480 by the supplier, has more than 20% active biosurfactant solution and is considered very biodegradable. Its effect on the environment is very low and it has low toxic characteristics and does not irritate the skin (Jeneil Biosurfactant Co., 2004).

R1

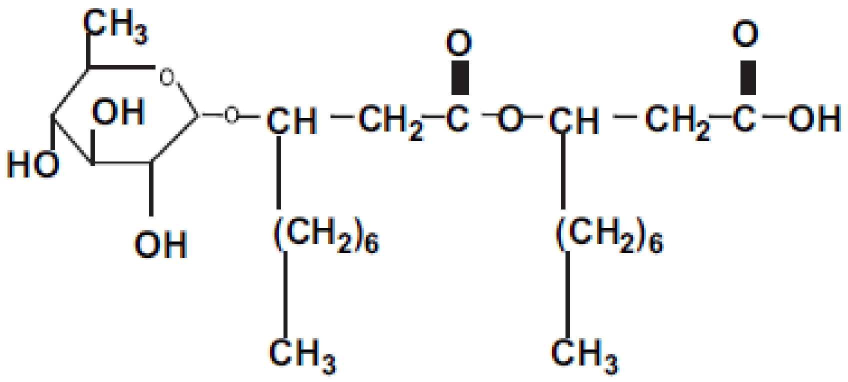


Figure 4.1A - Structure and name of RLL or R1 rhamnolipid (adapted from Tsuji, 1998)
α –L-rhamnopyranosyl-β-hydroxydecanoyl-β-hydroxydecanoate (Jeneil Biosurfactant Co., 2004)

R2

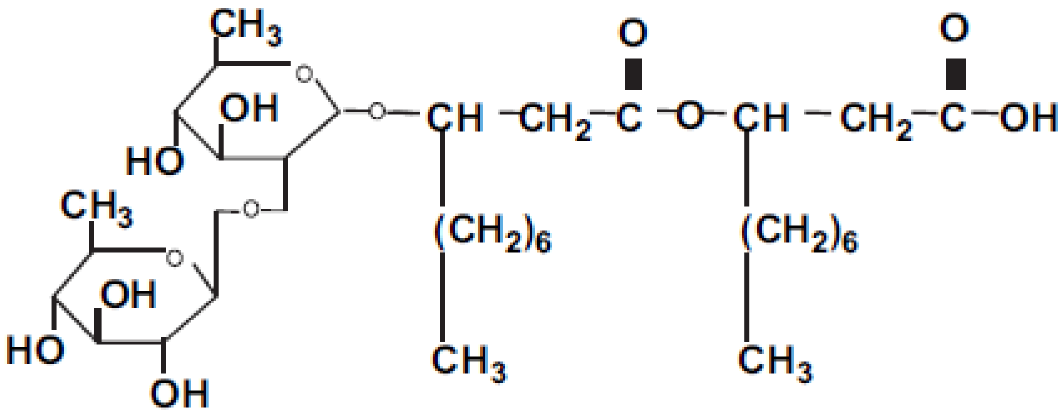


Figure 4.1B – Structure and name of RRLL or R2 rhamnolipid (adapted from Tsuji, 1998)
2 - O - α – L - rhamnopyranosyl- α – L- rhamnopyranosyl- β -hydroxydecanoyl-β-hydroxydecanoate (Jeneil Biosurfactant Co., 2004)

Several tests (Organization for Economic Cooperation and Development, OECD) done by the manufacturer and independent laboratories (OECD 209ASRIT,OECD301Dand OECD202) showed that the degree of biodegradability and toxicity of JBR425 meet the EPA requirements

(Jeneil Biosurfactant Co., 2004). The critical micelle concentration (CMC) was found to be 0.035 g/L through conductivity measurement at various dilutions (DahrAzma and Mulligan, 2004). This value is equivalent to 0.003% rhamnolipid. Therefore, for all experiments, a concentration above the CMC was used to ensure the formation of micelles. The fact that JBR425, in an aqueous solution, has got a very low CMC interprets into the capability of this biosurfactant to show high surface activity at low concentrations.

It is characterized by low interfacial tension for water and hydrocarbon mixtures while it has also a low surface tension for water and other electrolyte solutions. As indicated earlier in this text, surface tensions of 29 mN/m are characteristic of these molecules (Guerra-Santos et al., 1984). Other properties and applications of rhamnolipids have been mentioned in the literature review, section 2.4. The properties of JBR425 according to its product Material Safety Data Sheet (MSDS) are sorted in Table 4.3.

Table 4.3 Properties of biosurfactant JBR425 (Jeneil Biosurfactant Co., 2004)

Parameter	Value
Type	Anionic biosurfactant
Formula	$C_{26}H_{48}O_9$, $C_{32}H_{58}O_{13}$
pH (1% suspension)	6.5 – 7.5
Specific Gravity @ 25°C	1.05-1.06 mg/ml
Appearance and Odor	Amber, Soapy liquid
CMC[1]	0.03 g/l

(1) Mulligan et al., 2001b

4.2.3 PAH Standards

A mixture of the EPA 16 priority pollutant PAHs as well as all 16 individual-PAH standards were purchased from Sigma-Aldrich Canada. After measuring PAHs concentration in advance of the remediation experiments, four PAHs that had concentrations above Quebec threshold for freshwater sediments were chosen. Those PAHs include naphthalene, pyrene, benzo (α) anthracene and chrysene. Table 4.4 shows some physical and chemical properties of these four PAHs.

Table 4.4 Physical – Chemical properties of target PAHs

PAHs	**Molecular weight (g/mole)**	**Solubility (mg/L)**	**Density (g/cm^3)**	**Melting Point (^{o}C)**	**Boiling Point (^{o}C)**	**Vapor pressure (mm Hg)**
Naphthalene	128.17	31	1.14	80.26	218	8.89E−02
Pyrene	202.26	0.132	1.271	145-148	404	4.25E−06
Benzo*(a)*anthracene	228.29	0.011	1.19	158	438	1.54E−07
Chrysene	228.29	0.0015	1.274	254	448	7.80E−09

Source: ATSDR, 2005

4.3 Experimental Methods and Setup

4.3.1 Determination of Sediment Cation Exchange Capacity (CEC)

The cation exchange capacity (CEC) of sediment samples from sector 103 Saint Lawrence River was measured in the lab. For each sediment sample, triplicate measurements were performed. A sample of 5.00 g of dried sediments was weighed using a digital scale with an accuracy of 0.01 g and was placed in centrifuge tubes, then 20 ml of 1 M potassium acetate ($KC_2H_3O_2$) was added to each sediment sample. Samples were capped and shaken well for 5 minutes. After being shaken, tubes were opened and the sides of the centrifuge tubes were washed with distilled water for not losing any solid particle. The tubes were centrifuged for 15 minutes at 3000 rpm. The clear supernatant was not needed and it was discarded.

Again 20 ml of $KC_2H_3O_2$ (1 M) was added to each sediment sample, and then they were centrifuged for 15 minutes at 3000 rpm. At this point again, the supernatants were discarded. A volume of 20 ml methanol was added to each of the centrifuge tubes. They were shaken well to resuspend the sediments. Centrifuging for 15 minutes at 4500 rpm was performed and again the clear supernatant was discarded. Here, the steps from methanol addition to centrifugation at 4500 rpm were repeated. Now 25 ml of 1 M ammonium acetate ($NH_4C_2H_3O_2$) was added to the sediments in centrifuge tubes, they were shaken well and centrifuged for 15 minutes at 3000 rpm.

The supernatants at this stage were all collected in a 100 ml beaker. Another ammonium acetate addition and centrifugation at 3000 rpm for 15 minutes was completed and the supernatants were collected and added to the previous one in the 100 ml beaker. Atomic Absorption Spectrometry was applied to detect the concentration of potassium ions (K^+). Using this value, CEC can be determined in meq/100 g of dry sediment or $cmoles^+/kg$ of dry sediment (Rhoades, 1982; Spectrum Analytic Inc., 2010).

The data collected and the calculations are presented in Table 4.5.

Table 4.5 Experimental Data and Calculations for Sediment CEC

Sediment Sample	[K$^+$] in supernatant (ppm)	[K$^+$] Mass (mg)	CEC (meq/100g dry sediment)
1	484	24.2	12.4
2	460.2	23	11.8
3	464.1	23.2	11.9

The CEC of the sediment sample was calculated by finding the average of the three CEC values from Table 4.5

CEC = (12.4 + 11.8 + 11.9) / 3 = 12 meq/100 mg dry sediment

4.3.2 Determination of Sediment Hydraulic Conductivity

Laboratory methods nowadays can let us have reproducible and quite accurate values of hydraulic conductivity if determined carefully by conducting experiments in the laboratory. Some level of disturbance most of the time accompanies the collection of the samples. For these reasons, it is extremely hard to characterize the hydraulic conductivity of an aquifer, or even a small portion, by means of laboratory measurements. These methods can only be done on small samples. Hydraulic conductivity can be measured directly with permeameters. Two commonly used permeameters are shown in Figure 4.2 depicts a constant-head permeameter in which steady upward flow through the sample is established. Darcy's equation can be applied directly in this case to compute K,

$$K = QL / \Delta h\ A \qquad \text{Eq. 4-1}$$

$$Q = V/t \qquad \text{Eq. 4-2}$$

The total head loss through the permeameter is indicated by the difference in elevation level between the inflow and outflow water levels. In a permeameter that is properly designed, "the head loss through the retaining screens and the inflow and outflow plumbing is negligibly small" and the head loss through the sample is almost equal to the difference in water level between inflow and outflow.

Some constant head permeameters are equipped with piezometer taps located in the test section and the difference in piezometric head is presented by water level difference in the two applied piezometers. This difference reflects the head loss between the two piezometer taps, regardless of the head loss in the remainder of the system (McWhorter and Sunda, 1977).

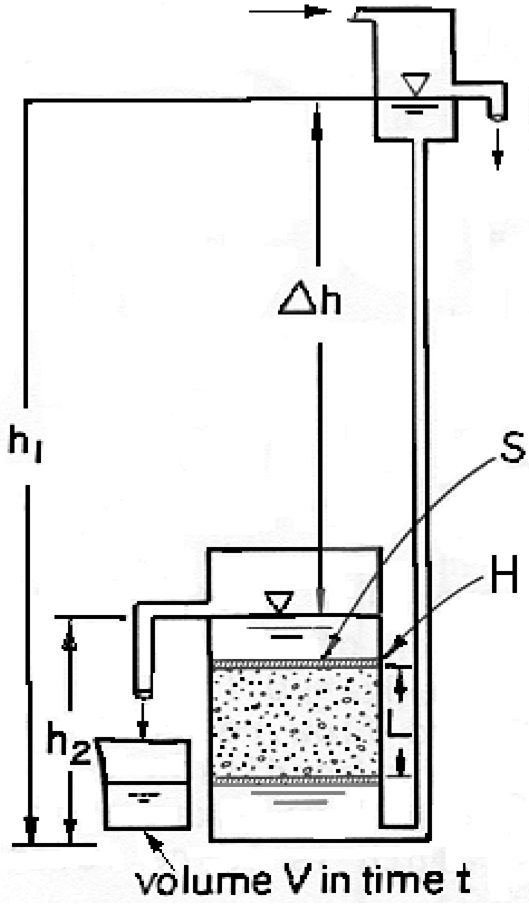


Figure 4.2 Constant head-permeometer to determine hydraulic conductivity (adapted from: McWhorter and Sunda, 1977).

4.3.3 Determination of Water Content

The water content of sediment samples from sector 103 Saint Lawrence River was measured in the lab. It was tested according to the ASTM method D2216. For each sediment sample, triplicate measurements were performed. Porcelain crucibles were taken and weighed using a digital scale accuracy of 0.01 g. Sediment samples were placed in those mentioned previously weighed porcelain crucibles and the wet weight of each sample was measured using the same digital scale with an accuracy of 0.01 g. Then the samples were placed in the oven under a temperature of 105ºC for a minimum of 18 h. After that, the oven dried samples were kept in the desiccators to avoid any absorption of humidity while cooling. At the end of this step, the dry weight was recorded.

Water content was calculated according to the following equation:

$$\textbf{Water Content} = [\, W_w - W_{d(105^{\circ}C)})] / W_w * 100\% \qquad \text{Eq.4-3}$$

W_w : Wet weight of the sample, g

$W_{d(105^{\circ}C)}$: Dry weight of the sample at 105ºC, g

The final water content value was calculated as the average of the three replicates.

4.3.4 Determination of Loss on Ignition (LOI)

LOI was tested according to the ASTM methods D2216 and D2974-00. The same oven-dried sediment samples (on triplicate) were placed into an incinerator for ignition at 550ºC for 4h. Then the samples were placed in desiccators while cooling to prevent any possible humidity absorption. The weights of the samples were recorded using a digital scale accuracy of 0.01 g. LOI was calculated using the following equation:

$$LOI = [\, W_{d(105^{o}C)} - W_{d(550^{o}C)} \,] / W_{d(105^{o}C)} * 100\% \qquad \text{Eq.4-4}$$

$W_{d(105^{o}C)}$: Dry weight of the sample at 105ºC, g

$W_{d(550^{o}C)}$: Dry weight of the sample at 550ºC, g

The final LOI value is the average of the triplicate readings for each sample.

4.3.5 Sediment preparation for column experiments

Prior to initiating the main remediation experiment, sediment samples had to be prepared for the column test. At first both crude sediments and dry sediments; were taken from the bulk to be prepared for column experiments. When proceeded, it was observed that using dry sediment samples for a column test has a negative point while measuring the concentration of PAHs. Only some of the PAHs that have fewer aromatic rings and basically are lighter, volatilize from water or even soil while the majority of the polycyclic aromatic hydrocarbons are non-volatile (Payne et al., 1988). Since some low molecular weight PAHs are either volatile or semi-volatile, they can be evaporated, so based on this fact, wet sediments as they were acquired from buckets containing dredged sediments, were chosen to be applied. To continue, wet sieving was carried out to get rid of stones, debris, wood or anything that could make sediments more heterogeneous. The use of water in this step was to facilitate sediment passing through the sieves. An 8”-brass Cole-Parmer sieve with a U.S. standard mesh size of 60 (that lets through particles < 250μm) was applied. To start, sediments were mixed with water to make a suspension and after that they were placed on top of the sieve. The sieving stopped when water coming out of the sieve was no longer turbid. Sediments were collected from the receiving pan and the receiving pan was rinsed with water not to lose smaller particles. Here sediments were placed on a standard size Whatman paper filter and were filtered for 30 min. At this point, wet sediments were ready to be placed in the columns.

4.3.6 Column Experiments and Foam Parameters

For column tests, all experiments were conducted at ambient temperature (23.0±0.2 °C). The experimental setup is shown schematically in Fig. 4.2. As mentioned by Selim et al. (1996), column tests are considered open systems and they have this principal advantage over batch systems in that the contaminants are being removed continuously while in batch system they stay and accumulate in the system. Experiments were performed in three different stages. In phase (I), characteristics of the produced foam were investigated. These parameters include foam quality and stability. In phase (II), possible pressure build-up in the system was evaluated to see if column experiments can be done without problems caused by high pressure. In this phase, effects of different factors on the induced pressure were investigated. Finally the main part (Phase III) was the remediation experiments.

A Plexiglass column (L=25 cm, D= 2.5 cm) with a circular porous stone plate was used to generate foam through mixing the biosurfactant solution and air. This porous medium was attached to a one-hole rubber stopper that was carefully fitted and sealed in the mouth of the foam generation column. A Masterflex (Cole-Parmer) binary pump was used to feed different concentrations of the biosurfactant solution (0.5%, 1% and 2%) while aluminum standing flow meters (Fisher Scientific, Oakville, Canada) were applied to monitor the flow of the fluids. To make higher quality foams, biosurfactant and air flow rates were changed. From a 3-way valve placed after the foam generating column, foam exiting the column was sampled for stability-quality tests after reaching a steady and uniform state in terms of bubble size and appearance. In each stability-quality test, three 50 ml samples of the generated foam were taken and left until all of the bubbles collapsed. As previously discussed (Chapter 2), foam stability and quality are the two major factors with which characteristics and efficiency of the foam can be evaluated.

The volume of total gas in the foam per total foam volume at atmospheric pressure was calculated to indicate the foam quality. The required time that half of the generated foam collapsed was referred to as the foam stability. For this a regular wrist watch with chronometer was used. When both quality and stability of the generated foam were tested and it was found that the foam was ready to start the remediation experiments, the three-way-valve was turned towards the sediment column. The sediment column, made from plexiglass (L=20 cm, D=3 cm), was placed after the foam generation column (Fig. 4.3).

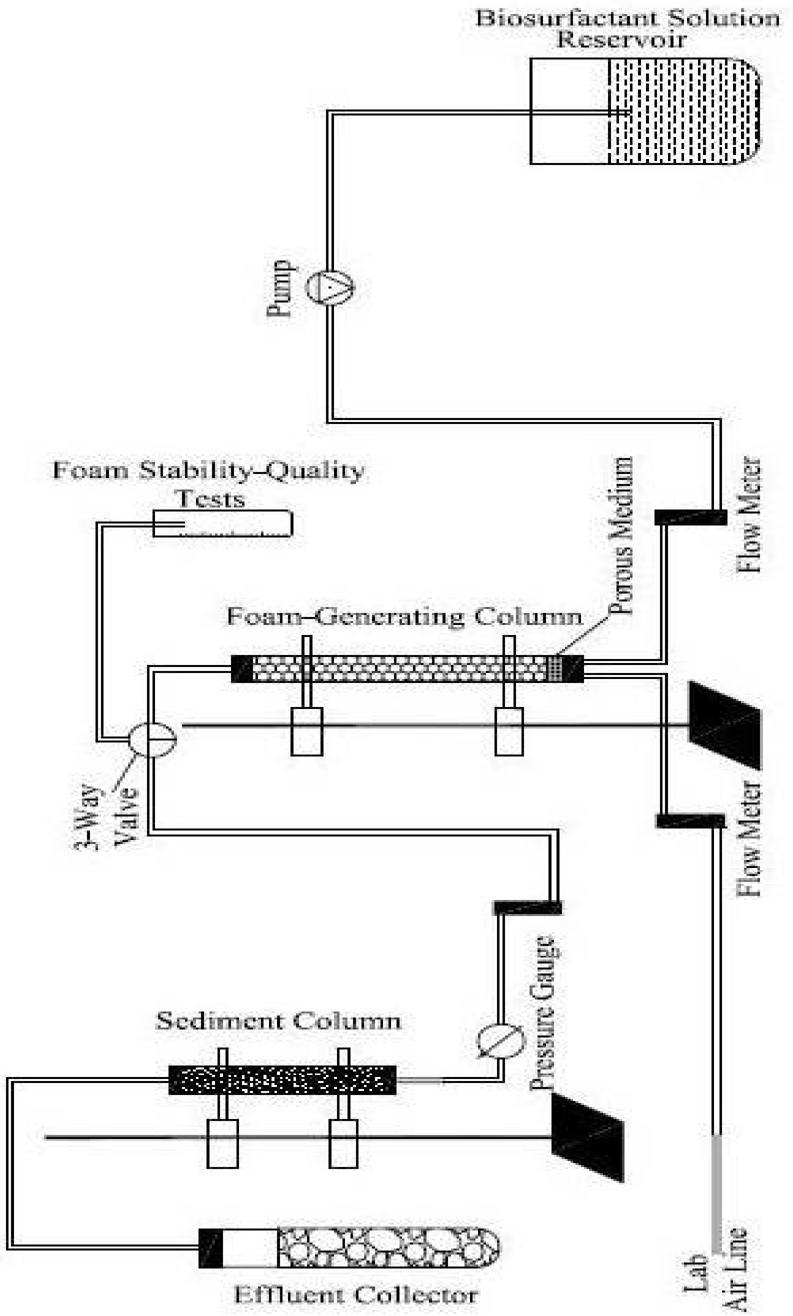


Figure 4.3 Schematic of the Experimental Setup

4.3.7 Pressure Gradient

A digital traceable manometer (Fisher Scientific, Oakville, Canada) was installed upstream of the sediment column to monitor the inlet pressure. In order to avoid possible problems due to higher pressure like heaving and channeling, the pressure gradient must not exceed 22.6 kPa/m (Chowdiah et al., 1998). That is the reason monitoring pressure gradient in soil/sediment flushing and remediation tests is very important and since using the flushing agent under the form of foam induces lower pressure than its own liquid form, using foams for soil/sediments remediation looks to be promising. The pore volume of sediment samples was measured by saturating the sediment column by pumping water into the sediment column at a pressure gradient close to zero. Here the water volume used to saturate the sediment column is equal to its pore volume. Foam quality, flow rate and concentration of the biosurfactant solution were all involved in inducing different pressures in the sediment column. To find pressure gradients, pressure values were divided by the sediment column length. Foam with the highest quality (99%) and lowest concentration and flow rate was used to investigate the PAH and metal removal efficiencies.

4.3.8 Remediation Experiments

The sediment was packed as uniformly as possible. The total weight of the sediment was approximately 32 g (32.0±2 g) at each experiment. To find the PAH concentration after the remediation experiments, foam samples were collected at the end of the sediment column and according to the number of pore volumes passed through the contaminated sediments. These samples, were left to collapse completely prior to HPLC analysis. All studies were conducted at various initial pH values (6.8, 8.0, and 10.0) while maintaining a 0.5% rhamnolipid solution and a foam quality of 99%. The pH value was adjusted by adding 0.1 N NaOH and HCl. All chemicals were purchased from Fisher Scientific. The reason behind using a 0.5% rhamnolipid, which was lower than others, was to avoid 1) high pressure gradient caused by higher concentration; 2) plugging of the column caused by dispersion of fine materials and finally 3) possible formation of viscous emulsions (Rothmel et al., 1998). Beside of all these facts, results from previous experiments (Mulligan and Eftekhari, 2003; Wang, 2003) suggested using a 0.5% rhamnolipid for the remediation experiments. Characteristics of all sediment contaminants including concentrations of heavy metals and PAHs before remediation analyses are listed in Table 4.6. PAH and metal contents slightly vary as sediments are not homogenous.

Table 4.6 Concentration of sediment contaminants prior to remediation

Parameter	Value
Heavy metal content (mg/kg dry sediment)	
Pb	149.7
Ni	217.0
Zn	363.0
PAHs content (mg/kg dry sediment)	
Pyrene	2.0
Benz(a)anthracene	1.1
Chrysene	1.8

To observe the benefits of biosurfactant foam in sediment/soil remediation, columns were also flushed by biosurfactant solutions at different pH. Deionized (DI) water with adjusted pH was used as control. Columns flushed by the rhamnolipid foam were chosen to evaluate the PAH mass balance at the end of the experiments. To evaluate metal removal efficiency of rhamnolipid foam and solution as well as DI water with adjusted pH, sediment samples were taken out from the flushed column, left to dry at 105 °C for 48 h then ground with a mortar and pestle followed by sieving to collect smaller particles (< 250μm) that have higher metal content, and analyzed (in triplicate) for heavy metal concentrations using the Niton XRF analyzer.

4.3.9 Analytical Methods

The PAHs from the sediment samples in this study were extracted using a modification of EPA Method 3550A (EPA, 1994). A solid sample taken from the sediment was put in a centrifuge tube that had been previously weighed. Using an ultrasonic bath sonicator (Model 8510, Branson, CT, USA), a sample was extracted twice every 10 min with dichloromethane as the solvent. The extracted solution was collected by centrifugation for 40 min at 4500 rpm. The remaining sediment was dried and weighed in order to measure the net mass of the sampled sediment (by subtraction of the net tube mass from the total mass). The extracted solution was volatilized at a temperature of 50^{o}C and acetonitrile was added as an exchanging solvent as well as to adjust the volume.

The PAH concentrations were determined using a modification of EPA method 610 (EPA, 1984) based on HPLC-UV-Fluorescence detection of PAHs. The HPLC used was an Agilent 1200 series with a quaternary pump and a Supelcosil LC-PAH (Supelco, Inc. Bellefonte, PA) reverse-phase C18 column (25 cm × 4.6 mm, 5 μm) specific for PAH analysis. The mobile phase was acetonitrile : water 60:40 (v/v), at a flow rate of 1 mL/min. A solvent gradient was applied. It started from 60% acetonitrile, went up gradually to 100% and came back to 60% acetonitrile. PAH detection wavelengths were 254 nm for UV while they were 260 and 420 nm for fluorescence excitation and emission wavelength respectively. The removal efficiency of PAHs was determined by comparing PAH content in the effluent with PAH initial values. The results are presented in next chapter (Chapter 5). After flushing tests, sediments were taken out and extracted yet again using dichloromethane (EPA 3550A) to investigate possible volatilizations. Results are presented as percent removal of PAHs. Heavy metal concentrations were analyzed using a Niton XRF analyzer purchased from Thermo Scientific, MA, USA. Prior to using this instrument, samples were air dried for 48 hours under the fume hood and then were ground using mortar and pestle. Dry-sieving of samples was performed afterwards (smaller particles <250 μm collected). The removal efficiency of heavy metals was found by calculating the metal concentration difference before and after flushing tests with biosurfactant foam and solution and multiplying by 100%. Results are presented in next chapter (Chapter 5) as percent removal of heavy metals.

Chapter Five

Results and Discussion

5.1 Overview

As previously mentioned, lab experiments were divided into three different phases. Phase (I) was performed to investigate foam characteristics like foam quality and stability using different concentrations (0.5%, 1.0% and 2.0%) of the JBR425 biosurfactant (rhamnolipid) under different pH conditions (original-rhamnolipid-pH or 6.8, 8.0 and 10.0). Phase (II) experiments were conducted to evaluate the pressure gradient build-up along the sediment column. In this chapter, the effect of different factors such as JBR425 concentration, pH, flow rate and foam quality were analyzed. The final phase (Phase III) was performed to investigate decontamination and remedial efficiency of the JBR425 foam. In this project, control experiments were also performed for comparison.

All results in accordance with these three phases of experiment are discussed and demonstrated in this chapter. It must be mentioned that, all data recorded were in triplicate and the data average values are presented. The range of the presented data was presented as the data average ± 5% of the data, as the difference was either equal to or smaller than 5% of the average data.

5.2 Foam Parameters (Phase I)

As mentioned in Chapter Four, different concentrations of the JBR425 biosurfactant solution (0.5%, 1% and 2%) were prepared in the lab from the 25% original solution, which was purchased from a supplier (Jeneil Biosurfactant Co.), using Milli-Q deionized water (Millipore, Laval, Canada) each under three different pH conditions (6.8, 8.0 and 10.0). The 25% solution had an original pH of about 6.8. From this solution, three dilutions were made to prepare 0.5%, 1.0% and 2.0% of JBR425 all with a pH value of about 6.8. After this step, two new solutions with adjusted pH were prepared at the same concentration (8.0 and 10.0). The pH adjustment was performed using 0.1 N NaOH and 0.1 N HCl (Fisher Scientific). These solutions were applied to assess the foamability of the specified biosurfactant and to check its characteristics such as foam quality and stability. During the pH adjustment process, it was observed that when the pH of rhamnolipid solution (regardless of its concentration) reached a specific value (pH 6.2), the biosurfactant solution started to precipitate. With a precipitated biosurfactant solution, foam generation is unlikely and besides it may not be as efficient for sediment remediation.

From the results of these experiments, it was observed that JBR425 foams can be generated at concentrations as low as 0.5% and possibly even lower (this was not investigated). Regardless of the concentration and pH of the biosurfactant solution, high quality foams (from 85% to 99%) were produced and it was observed that pH has no significant effect on biosurfactant foam quality or stability. The time that foams took to fully collapse was 2 hours to 4 hours. These foams had stabilities of 16 minutes to 42 minutes. Again it must be mentioned that all experiments were performed in triplicate and the observed variation between data was less than 5%. These data are presented in the following sections.

5.2.1 Foam Quality Effect

According to observed data, different characteristics of generated foam can be in correlation with each other. Different conditions may affect different characteristics. When data from the experiments are plotted, the relationships between foam stability, quality, biosurfactant concentration and pH become more clear. Figures 5.1, 5.2 and 5.3 display these relationships.

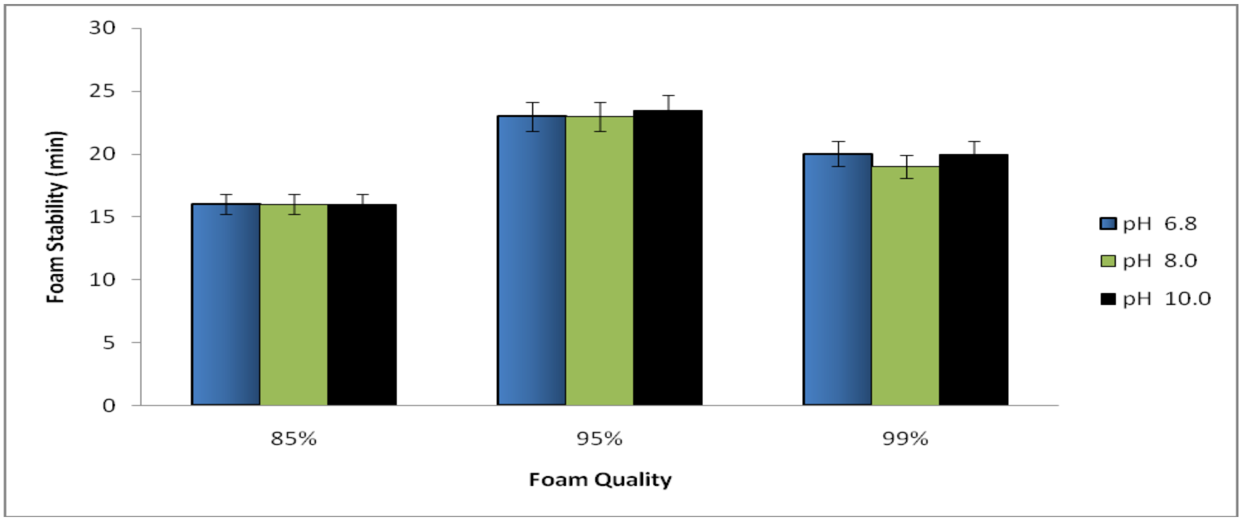


Figure 5.2. 0.5% JBR425 Foam Stability and Quality at Different pH Conditions

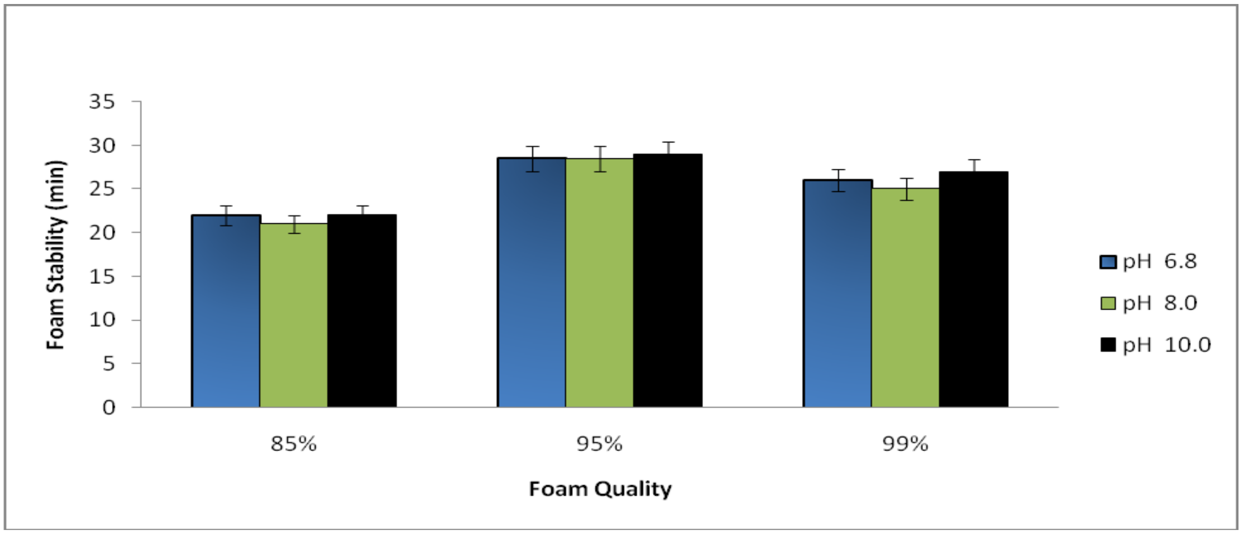


Figure 5.2. 1.0% JBR425 Foam Stability and Quality at Different pH Conditions

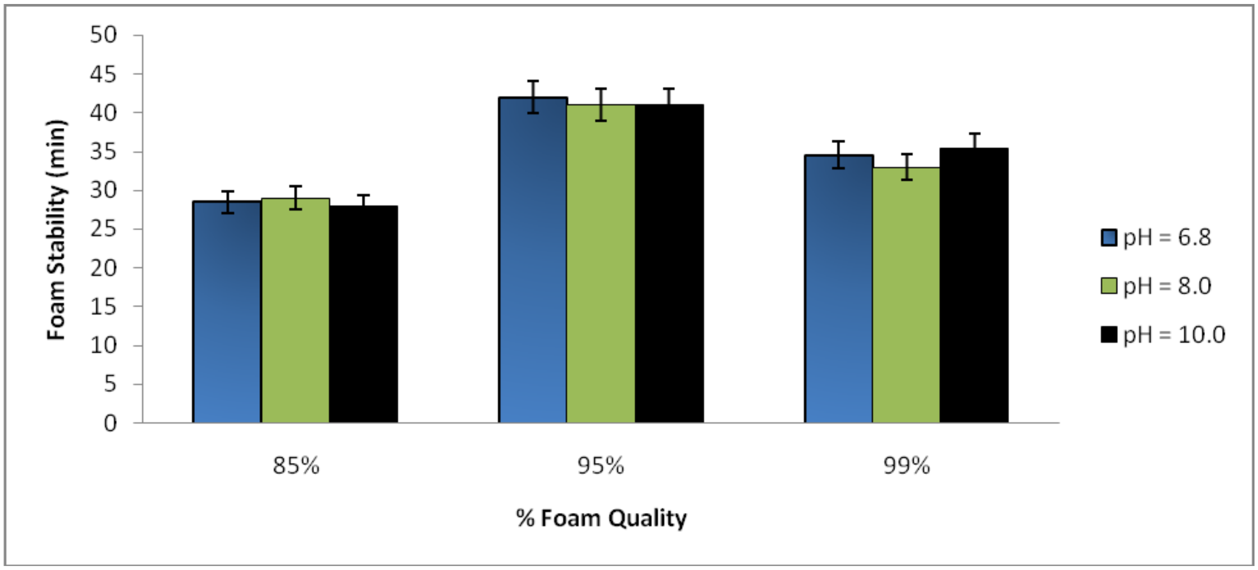


Figure 5.3 2.0% JBR425 Foam Stability and Quality at Different pH Conditions

The common fact among Figures 5.1, 5.2 and 5.3 is the increase of foam stability when the foam quality increases from 85% to 95% and also the descending state of the data for foam stability when foam quality continues to grow. As a more numeric example, in Figure 5.1, for the foam produced by 0.5% JBR425 solution under pH conditions equal to its original (pH 6.8), foam stability increased from 16 to 23 minutes when the foam quality increased from 85% to 95% and then when foam quality goes from 95% to 99%, the stability decreased from 23 minutes to 20 minutes. From these it is observed that foam quality and stability are inseparable and that foam quality has a clear effect on foam stability. The reason could be behind this fact that when a foam is higher in quality, it has larger air portion or in other words it has larger bubbles that have thinner liquid films. This would force the capillary flow to diminish and as a result rupturing lamellar film between adjacent bubbles. Also if the size distribution of gas bubbles within a foam is too heterogeneous, then very large bubbles might affect others when breaking causing lower foam stability.

5.2.2 Solution Concentration Effect

It is crystal clear that foam stability is in direct relation with biosurfactant solution concentration. According to observed data from the experiments and also Figures 5.4, 5.5 and 5.6, at a constant pH value, when biosurfactant solution concentration increased, foam stability did also increase. For example, when pH value was equal to 6.8 (Figure 5.4), for a 99% quality foam, by increasing solution concentration from 0.5% to 2.0%, the stability increased from 20 minutes to 34.5 minutes.

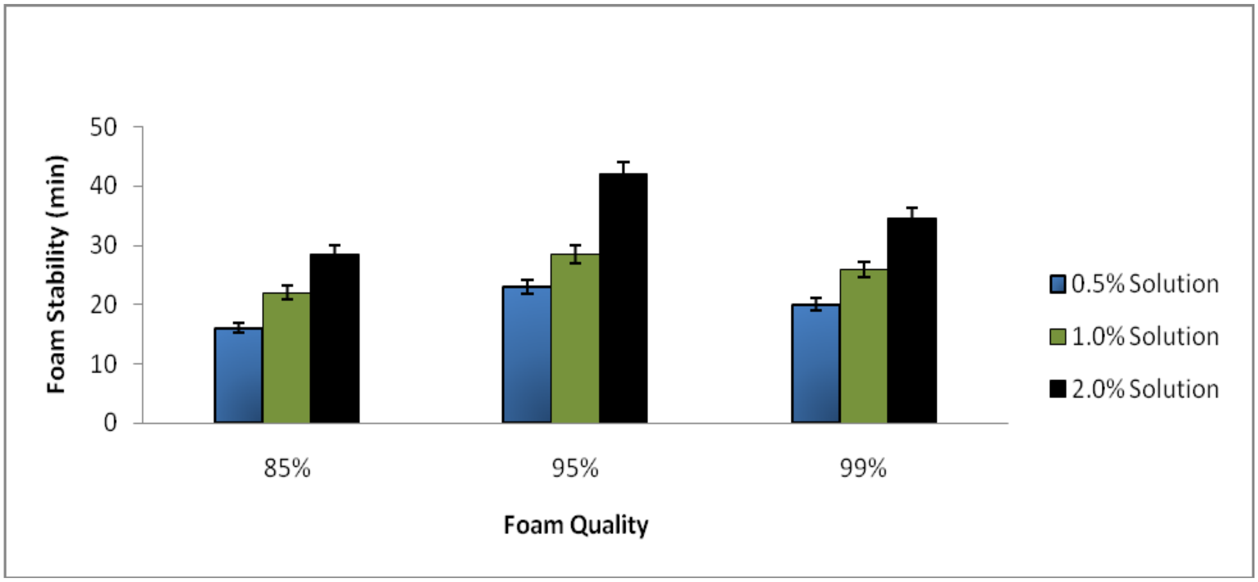


Figure 5.4 Foam Stability and Quality at Different Concentration at pH 6.8

It is interesting that for the same pH conditions (pH 6.8), when having a foam quality of equal to 95%, by adding to the biosurfactant solution concentration, the increase in foam stability is bigger than two other foam qualities. The reason possibly could be more homogeneous distribution of air bubbles throughout the foam, as a result, fewer big bubbles rupture and less lamellar films would be destroyed.

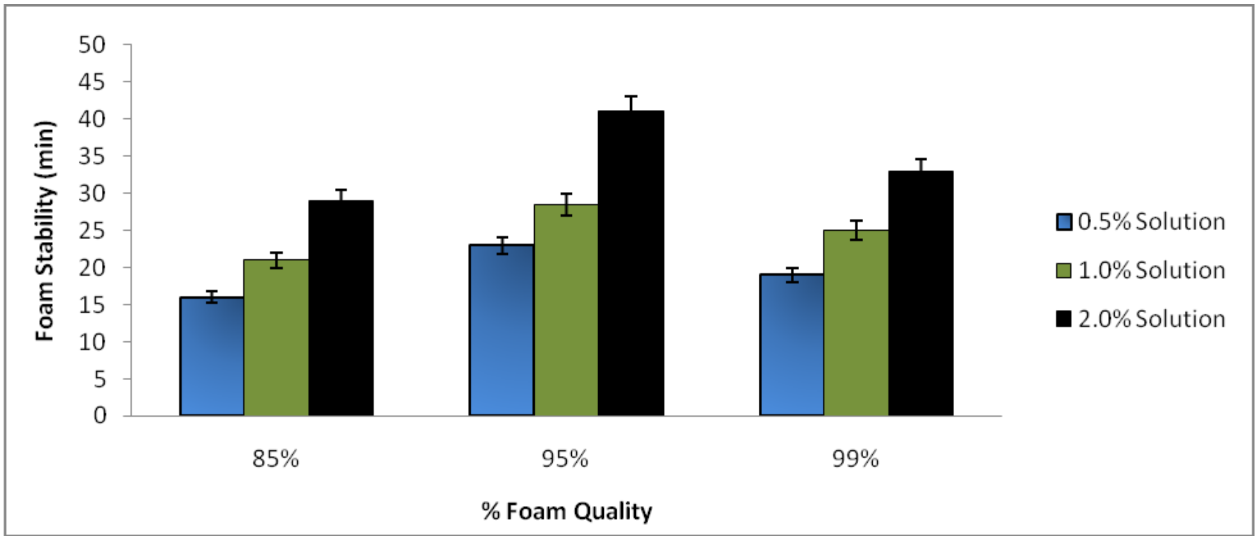


Figure 5.5 Foam Stability and Quality at Different Concentrations at pH 8.0

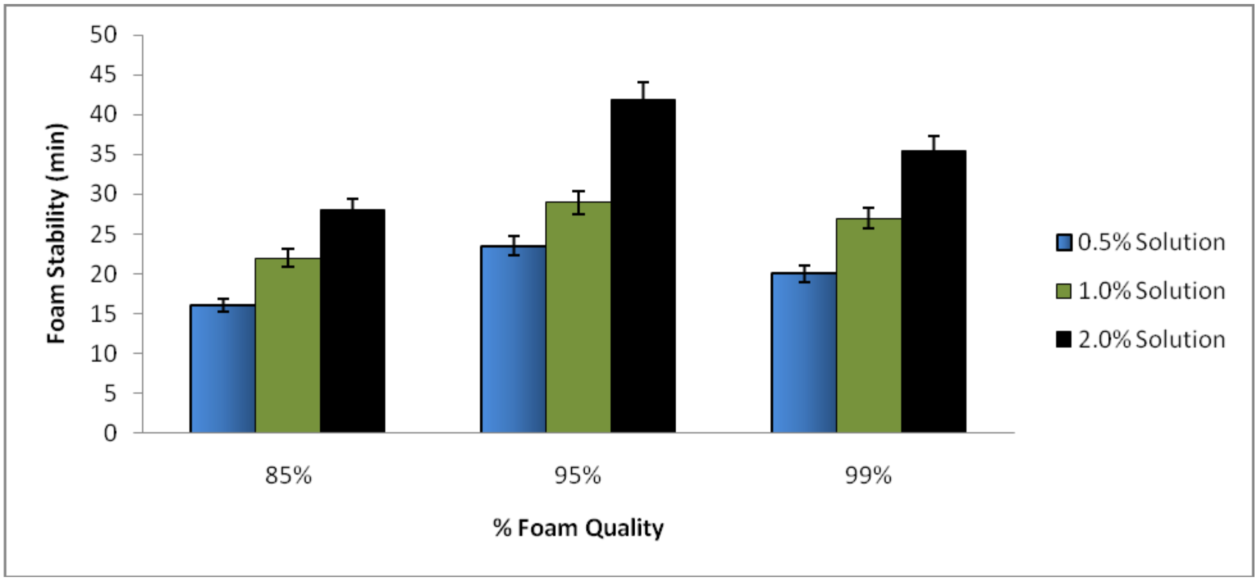


Figure 5.6 Foam Stability and Quality at Different Concentrations at pH 10.0

According to Wang (2003), from a theoretical point of view, as long as the biosurfactant solution concentration increases, the generated foam stability is also increased until reaching a threshold. At this point, the foam stability, in contrast with what it was performing, will start descending with any addition to solution concentration. The reason might be the high mass of the produced foam. It is certain that 2.0% of foam concentration does not have such a limit.

5.2.3 Solution pH Effect

Figures 5.1, 5.2 and 5.3 indicate that the pH of the biosurfactant solution has no significant effect on major foam characteristics like quality and stability, e.g. for a foam made from a 1.0% JBR425 solution (Figure 5.2), when foam has a quality of 85%, under different pH conditions (6.8, 8.0 and 10.0), the corresponding foam stabilities are 22, 21 and 22 minutes respectively. At the end of this part, from all observed results and data, it can be comprehended that biosurfactant concentration and foam quality have an effect on foam stability while biosurfactant solution pH does not have any apparent influence.

5.3 Pressure Gradient Build-up in the Sediment Column (Phase II)

Investigation of a foam induced pressure gradient along the sediment column under various conditions like different foam qualities (85%, 95% and 99%), different foam flow rates (10 ml/min, 15 ml/min, 20 ml/min and 30 ml/min) and finally different JBR425 biosurfactant concentrations (0.5%, 1.0% and 2.0%) are the major goals in this section (Phase II). For a constant flow rate of 10 ml/min, for a 0.5% concentrated foam, the pressure gradient increased from 0.35 kPa/cm to 3.8 kPa/cm when the foam quality decreased from 99% to a value of 85%. Again for a constant foam quality of 99% (the same concentration as the previous example), when the flow rate changed from 10 ml/min to 30 ml/min, the increase in the pressure gradient was from 0.35 kPa/cm to 1.4 kPa/cm. When biosurfactant concentration is doubled, it was observed that the increase in pressure gradients was not that significant (when all other foam factors such as quality and flow rate remained the same). From this and from previous studies (Wang, 2003) it can be concluded that foam concentration has no significant influence on building up the pressure gradient along a sediment or soil column. As previously mentioned, all the experiments in this Phase (II) were also performed in triplicate and the data obtained from them did not vary by more than 5%. The data are presented in Tables 5.1 and 5.2, for a 0.5% and 1.0% concentrated foam, respectively. Similar results for a 2.0% JBR425 foam was observed (data not shown).

Table 5.1 Pressure buildup in Sediment column as a function of foam quality & flow rate- 0.5% rhamnolipid (JBR425)

	Flow Rate (ml/min)	**10**	**15**	**20**	**30**
PRESSURE ($kPa.cm^{-1}$)	***Foam Quality 99%***	0.35	0.85	1	1.4
	Foam Quality 95%	1.6	2.4	3.3	5.6
	Foam Quality 85%	3.8	4.7	5.3	6.4

Table 5.2 Pressure buildup in Sediment column as a function of foam quality & flow rate - 1% rhamnolipid (JBR425)

	Flow Rate (ml/min)	**10**	**15**	**20**	**30**
PRESSURE ($kPa.cm^{-1}$)	***Foam Quality 99%***	0.7	1.3	1.6	1.9
	Foam Quality 95%	1.8	2.7	4.1	6.2
	Foam Quality 85%	4.3	5.1	5.8	7.2

5.3.1 Foam Quality Effect

Figures 5.7 and 5.8 present various pressure gradients observed with a constant foam flow rate while foam quality is changed. When foam flow rate remained constant, it was observed that by lowering the foam quality value, the induced pressure along the column was being increased. For example, while foam flow rate was being kept constant, at foam qualities around 85% (the lowest in this experiment) for either of the concentrations, maximum pressures were observed. Conversely while the same foam under the same conditions reached qualities as high as possible (in this experiment 99%), the lowest pressures were recorded. From this it is clearly concluded that for maintaining the pressure gradient as low as possible along the sediment column to perform the column tests without experiencing any problems due to high pressure like heaving and channeling, higher foam qualities must be applied.

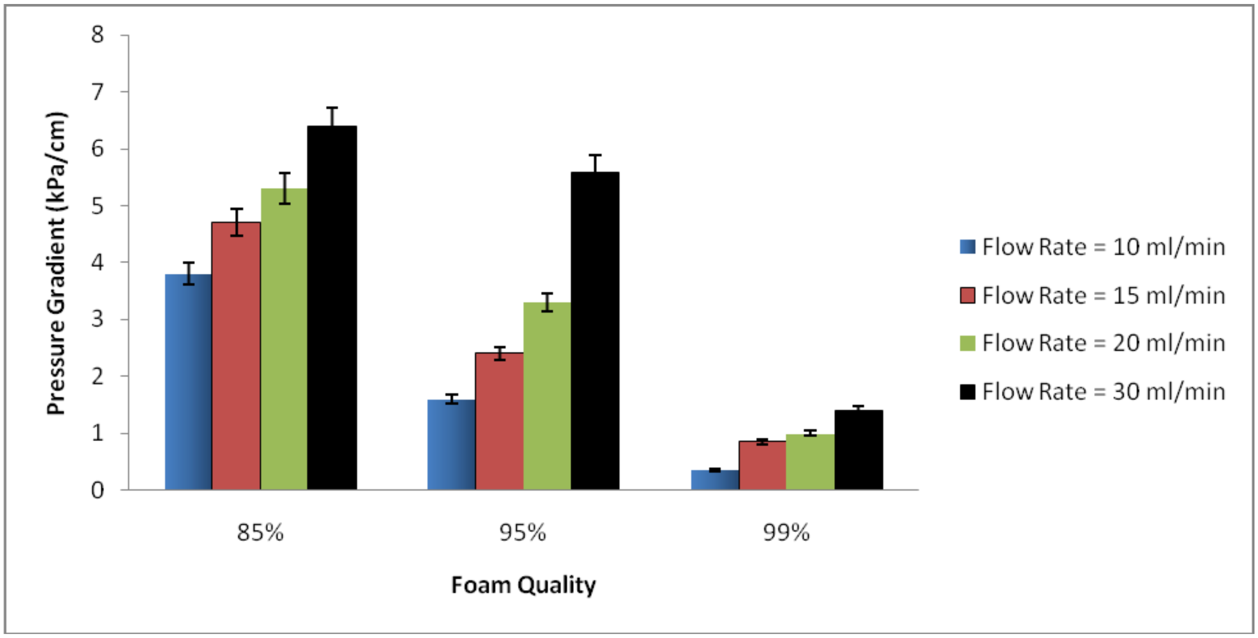


Figure 5.7 Effect of Foam Quality on Pressure Gradient (JBR425 Concentration = 0.5%)

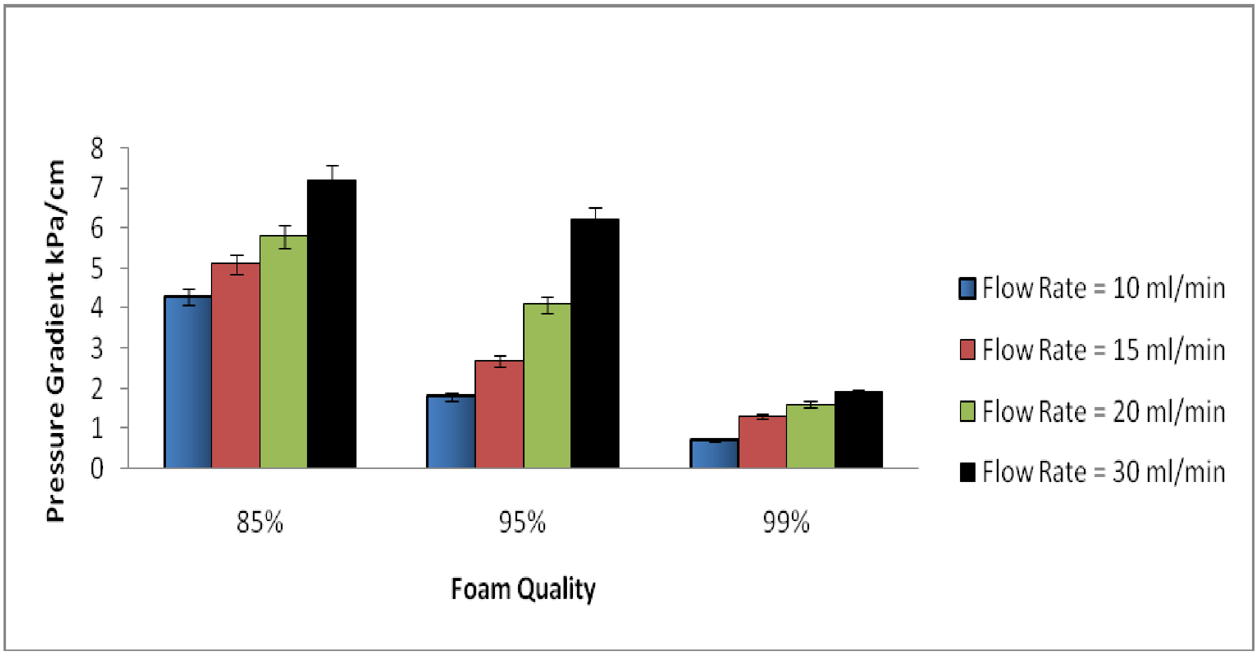


Figure 5.8 Effect of Foam Quality on Pressure Gradient (JBR425 Concentration = 1.0%)

According to these data, it is understood that no matter what flow rate was used, all of the foams exhibited lower pressures inside the sediment column when the qualities increased. When foam quality increases, generally the size of foam bubbles become larger and since the foam structure is dependent on the quality of the foam (Chowdiah et al., 1998), the lower pressures at higher qualities can be linked to a possible change in the structure of the biosurfactant foam.

The bubbles of the 85% foam were more spherical than the bubbles of the 99% quality foam and also the 85% quality foam bubbles were smaller than those from the 99% quality foam. Based on what Chowdiah et al. (1998) described, when performing a column experiment, the exiting foam texture is dependent on both the entering foam quality and flow rate. In this experiment, it is believed that when foam was injected into the sediment column, the bubbles ruptured and by passing through the porous sediments, the foam structure reformed again in a novel way and transferred into a coarser foam while exited at the end of the process.

5.3.2 Flow Rate Effect

Figures 5.9 and 5.10 show various pressure gradients observed with a constant foam quality value while foam flow rate was being changed. As it is seen, when foam flow rate increased, the pressure gradient build-up was also increased, e.g. for a 0.5% concentrated foam that had a foam quality of 95%, when the foam flow rate increased from 10 to 30 ml/min, it was noted that the pressure gradient build-up was increased from a value of 1.6 kPa/cm to a higher value of 5.6 kPa/cm. The same increase happened when the foam flow rate was doubled. From Tables 5.1 and 5.2, it can be realized that the highest value of pressure gradient was recorded at the foam flow rate of 30 ml/min.

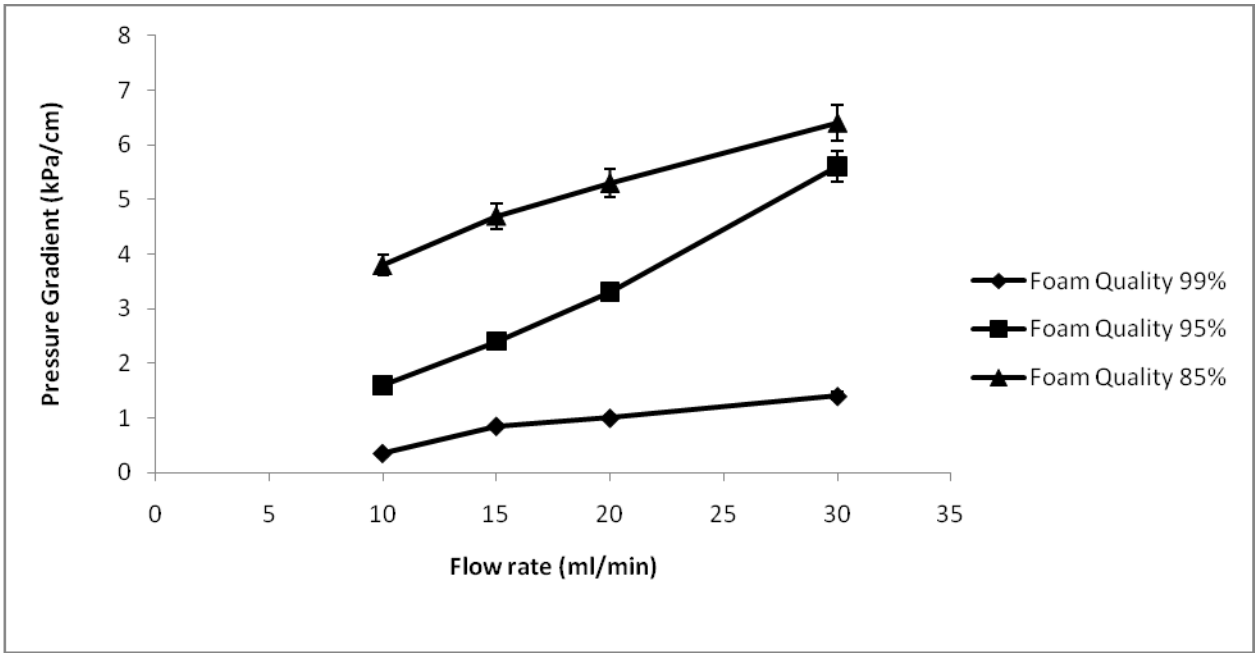


Figure 5.9 Pressure Build-up in Sediment Column vs. Foam Flow Rate (0.5% concentration)

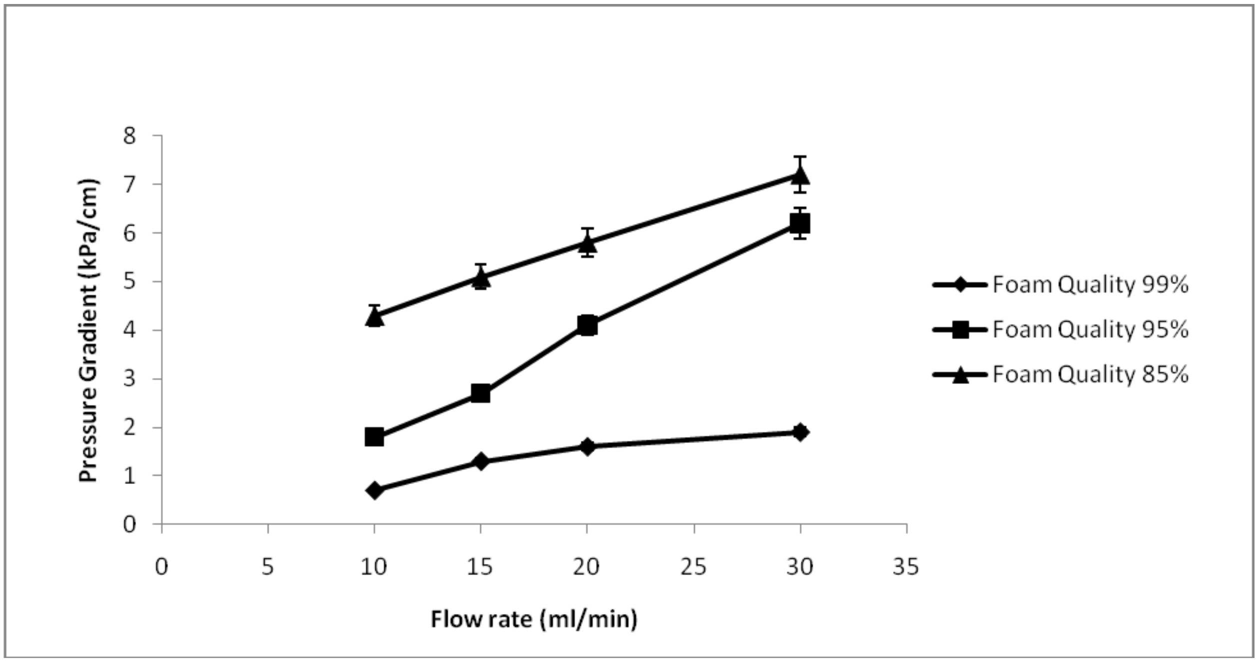


Figure 5.10 Pressure Build-up in Sediment Column vs. Foam Flow Rate (1.0% concentration)

Another way to describe the pressure gradient build-up increase with the increase in foam flow rate is based on the theory of foam specific viscosity that states when all foam characteristics remain the same, the pressure gradient increase will be proportional with the foam flow rate increase (Eq. 2-3). Here use of a control solution to monitor pressures caused versus fluctuations of the flow rate can be interesting.

5.3.3 Solution Concentration Effect

Figures 5.11 to 5.14 show that changing the JBR425 biosurfactant solution concentration does not have any significant effect on the pressure gradient build-up along the sediment column. Since any addition to the biosurfactant concentration will lead to an increase in its binding effect which will end in the sediment column plugging due to either formation of viscous emulsions or dispersion of finer materials, from the theory it is expected to see even higher pressure gradient build-up in the sediment column.

It must not be forgotten that the solution concentration effect is much smaller than foam quality effect and the foam flow rate effect. From all these experiments, it can be concluded that to commence remedial experiments (Phase III), the highest quality biosurfactant foam with the lowest flow rate possible and also low concentration must be chosen. This way not only does the pressure gradient build-up remain the lowest possible but also it becomes more practical budget wise as a smaller mass of the JBR425 biosurfactant is being consumed to make 0.5% foam rather than a 1.0% foam and also when a higher quality foam is chosen (such as a 99% quality foam over a 90% quality foam), the JBR425 consumption is lowered by an order of 10.

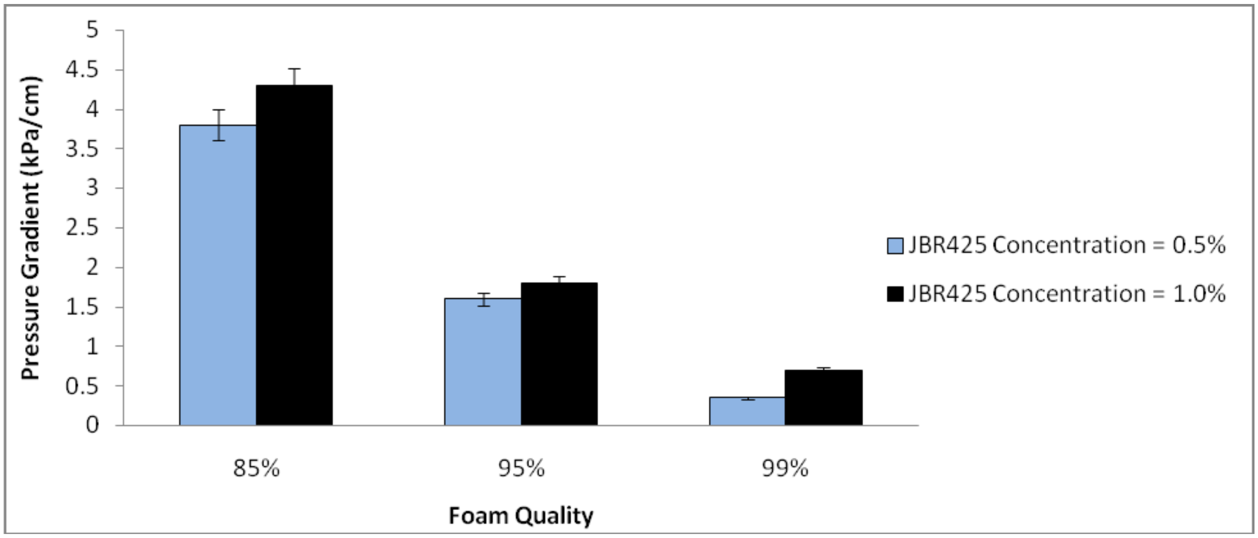


Figure 5.11 Effect of JBR425 Concentration on Pressure Gradient
(Foam Flow Rate = 10 ml/min)

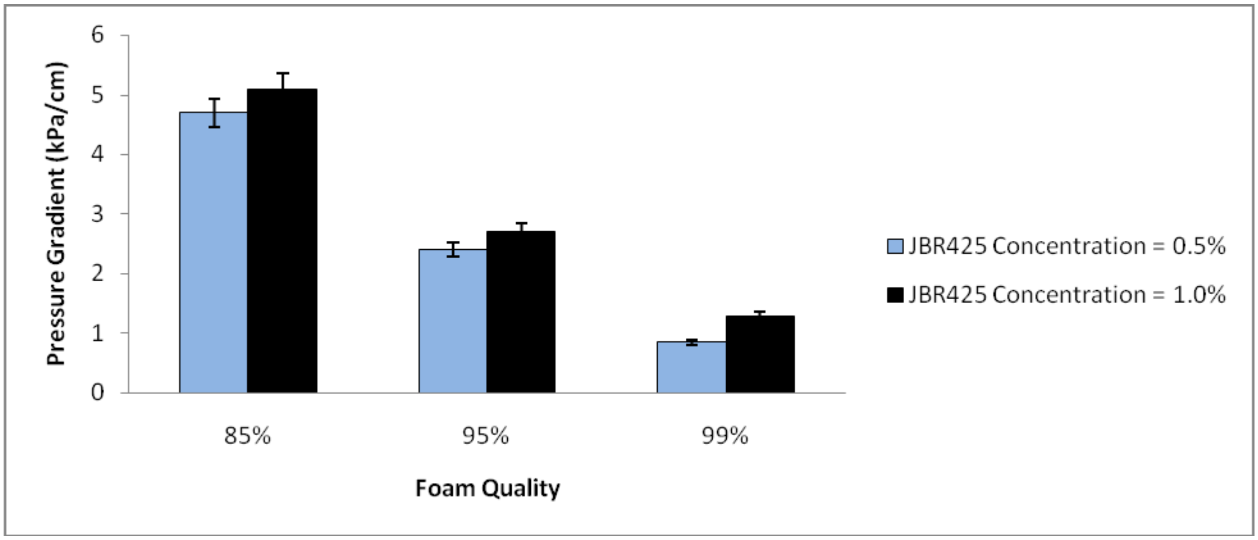


Figure 5.12 Effect of JBR425 Concentration on Pressure Gradient
(Foam Flow Rate = 15 ml/min)

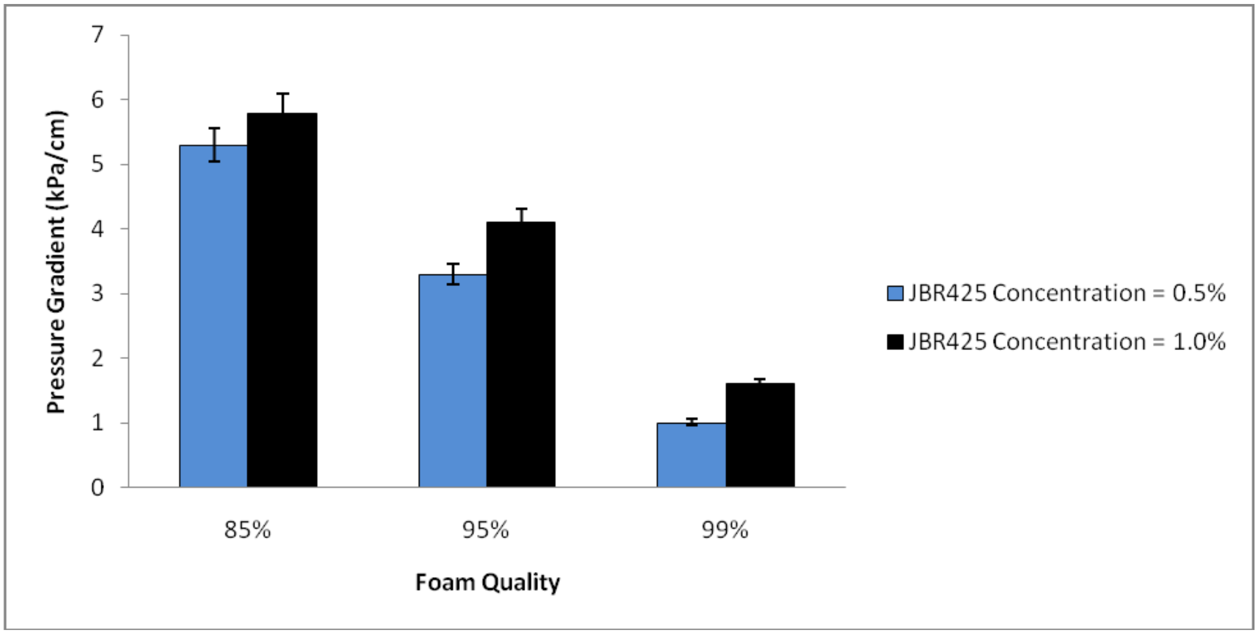


Figure 5.13 Effect of JBR425 Concentration on Pressure Gradient
(Foam Flow Rate = 20 ml/min)

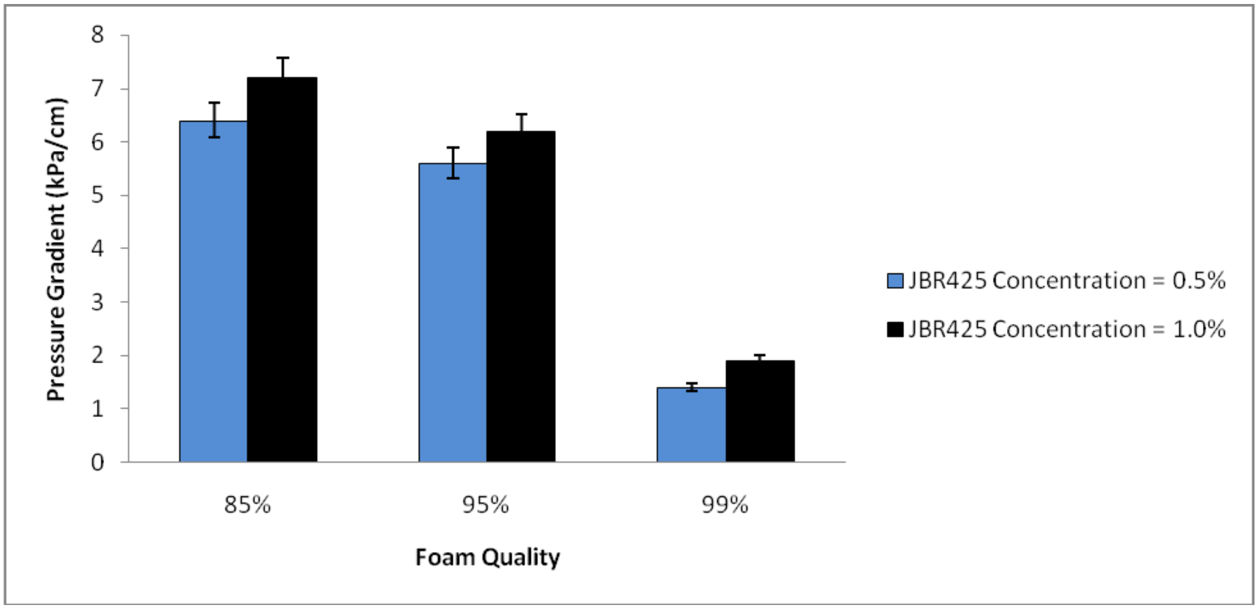


Figure 5.14 Effect of JBR425 Concentration on Pressure Gradient
(Foam Flow Rate = 30 ml/min)

5.4 Remedial Experience (Phase III)

In this part of the project, after investigating the generated biosurfactant foam, the remediation experiments began. The basis of this last section of the experiments (Phase III) was on the utilization of JBR425 biosurfactant foam generated at the lab in order to perform the sediment column flushing. The remedial agent here (JBR425 foam) was applied under a concentration of 0.5% and at three different pH values (6.8, 8.0 and 10.0). Foam samples were taken individually at the end of the sediment column based on the pore volumes passed. Foam with the highest quality (99%) and lowest flow rate was used to investigate the PAH and metal removal efficiencies.

5.4.1 PAHs Removal Efficiency

To find the PAH removal efficiency of the JBR425 biosurfactant (rhamnolipid) foam generated at the laboratory, foam samples were taken individually at the exit of the sediment column based on the pore volumes passed. The sediment was packed as uniformly as possible. The total weight of the sediment was approximately 32 g (32.0±2 g) for each experiment. A series of flushing experiments was performed on sediment samples using 0.5% JBR425 (rhamnolipid) biosurfactant foam and 0.5% rhamnolipid biosurfactant solution with different pH values (6.8, 8 and 10). At the end, deionized water with adjusted pH was also used as a control. It was found that the best removal efficiency for PAHs (pyrene, benz(a)anthracene and chrysene) was when a 0.5% rhamnolipid foam with a pH of 6.8 was used for 20 pore volumes.

5.4.1.1 Removal Efficiency by JBR425 Foam

To determine the removal efficiency of the JBR425 (rhamnolipid) foam under different pH values, the results of the observations are presented in Figure 5.15, 5.16 and 5.17. As it can be seen in Figure 5.15, pyrene had a stronger tendency to be remediated by 0.5% JBR425 foam at pH 6.8 rather than the two other PAHs present in the matrix. It is understood from Figure 5.15 that the maximum concentration of different PAHs was observed in the exiting foam at or after the 12th pore volume. Pyrene had a maximum concentration at pore volume 13, while it was pore volume 16 for chrysene and 12 for benz(a)anthracene. The removal percentages of these PAHs by 0.5% JBR425 foam were 44.6%, 30.0% and 37.8% for pyrene, benz(a)anthracene and chrysene, respectively.

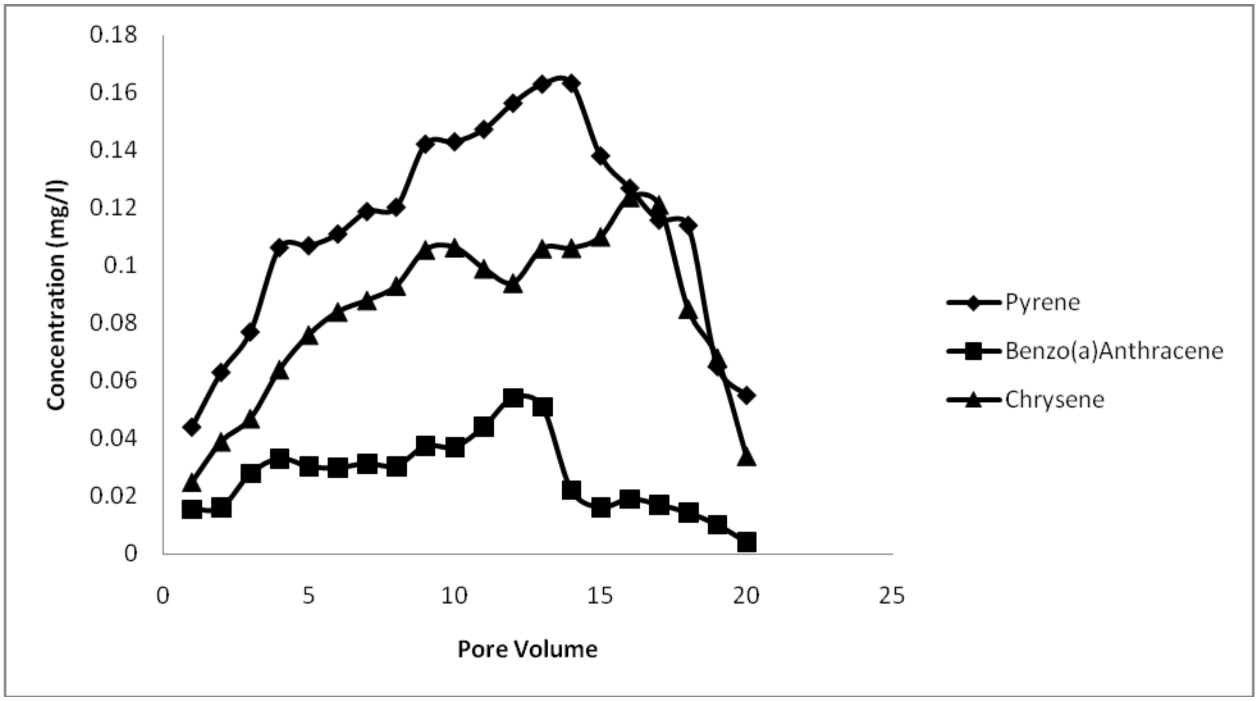


Figure 5.15 PAH Removal Efficiencies by 0.5% JBR425 foam (pH 6.8)

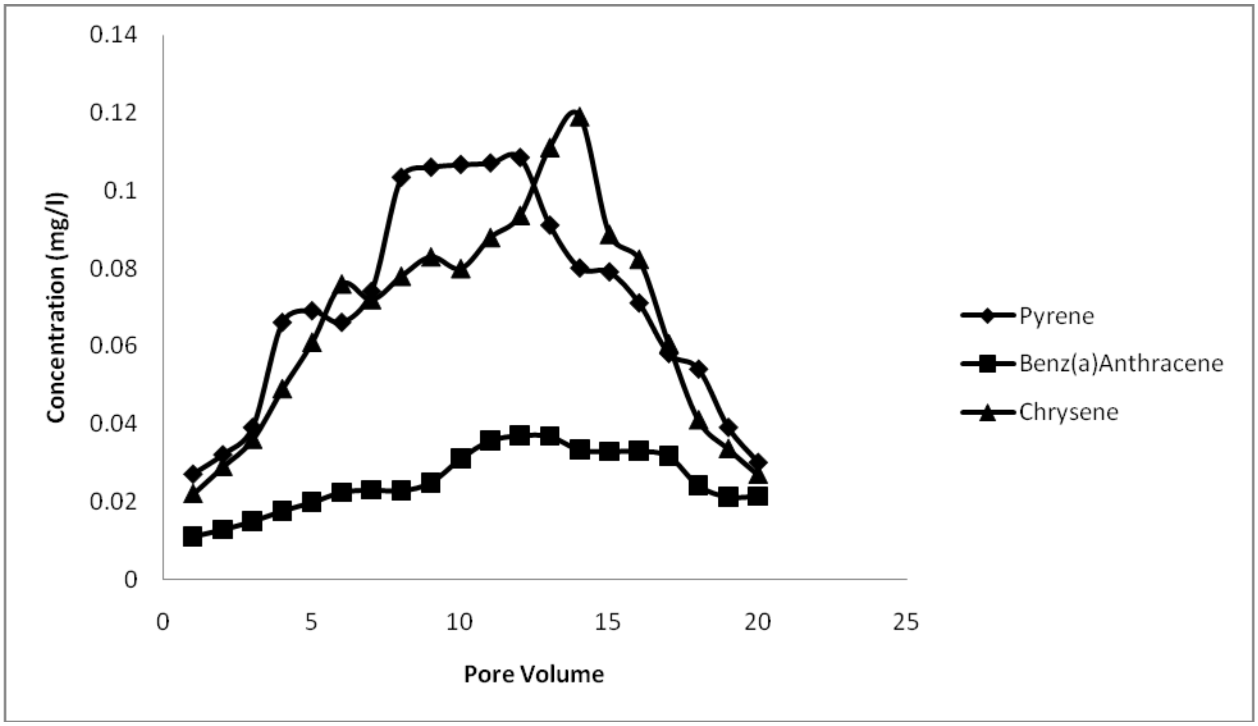


Figure 5.16 PAH Removal Efficiencies by 0.5% JBR425 foam (pH 8.0)

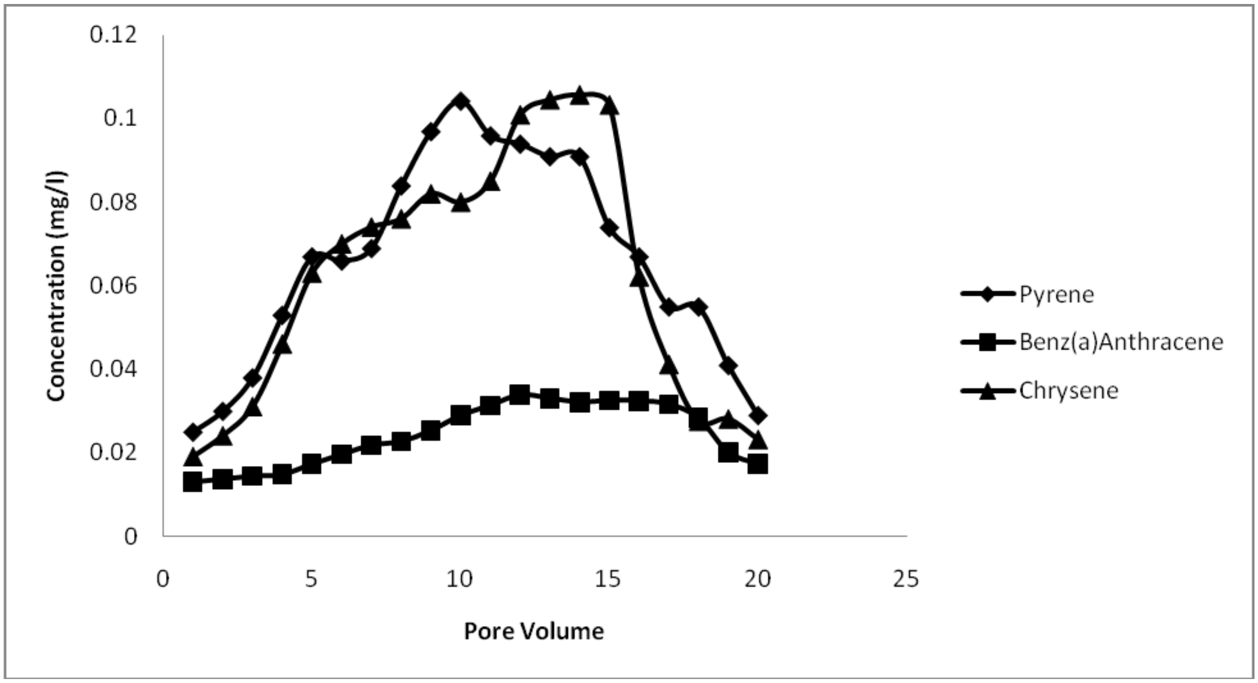


Figure 5.17 PAH Removal Efficiencies by 0.5% JBR425 foam (pH 10.0)

As shown in Figures 5.16 and 5.17, the pH of the JBR425 had an effect on the removal efficiency in a way that when pH increased, the removal efficiency decreased. This change is not that significant between more alkaline pHs (8.0 and 10.0), it was mostly observed when pH increased from 6.8 to 8.0. All the data related to these experiments are gathered in Table 5.3.

Table 5.3 PAH Removal Efficiencies by 0.5% JBR425 foam at Different pH

PAH	% Removal by 0.5% JBR425 Foam					
	Mobilization			Mobilization + Volatilization		
	pH 6.8	pH 8.0	pH 10.0	pH 6.8	pH 8.0	pH 10.0
Pyrene	44.6%	37.7%	36.4%	56.4%	47.5%	46.8%
Benz(a)A	30.0%	26.3%	23.9%	41.2%	33.0%	31.0%
Chrysene	37.8%	31.7%	29.7%	45.9%	39.1%	37.1%

At a pH value equal to 6.8, the highest removal efficiency that was only a result of mobilization of the PAHs by biosurfactant was 44.6% of pyrene, 30% of benz(a)anthracene and 37.8% of chrysene while total removal efficiency (mobilization + volatilization) for the biosurfactant foam was 56.4% of pyrene, 41.2% of benz(a)anthracene and 45.9% of chrysene. The accumulative removal (mobilization) of PAHs by 0.5% JBR425 foam at a pH value of 6.8 is presented in Figure 5.18.

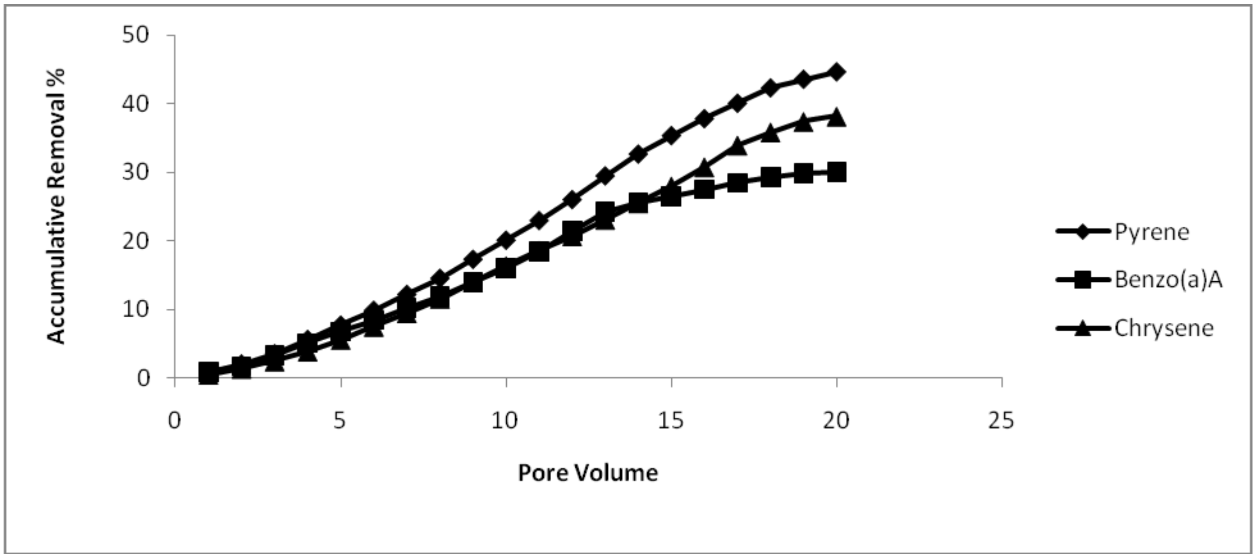


Figure 5.18 PAH removal efficiencies by 0.5% rhamnolipid foam (pH 6.8)

5.4.1.2 Removal Efficiency by JBR425 Solution

To better show the benefits of using a biosurfactant foam, biosurfactant liquid solution at the same pH values as the foam (pH 6.8, 8.0 and 10.0) was also applied and again solution with a pH value of 6.8 reached maximum removal (mobilization) of 31.4% for pyrene, 20.5% for benz(a)anthracene and 27% for chrysene after flushing the contaminated sediment column for 20 pore volumes. No significant change in the PAH mass balance was observed. From this, it could be concluded that when JBR425 (rhamnolipid) solution was used, these 4-ring PAHs have relatively higher tendencies to sorb on to the solid media and are harder to volatilize, no significant volatilization of PAHs was observed. Results presenting PAH removal efficiencies by 0.5% JBR425 solution are presented in Table 5.4 while those results recorded from the column experiments are presented in Figures 5.19 to 5.21.

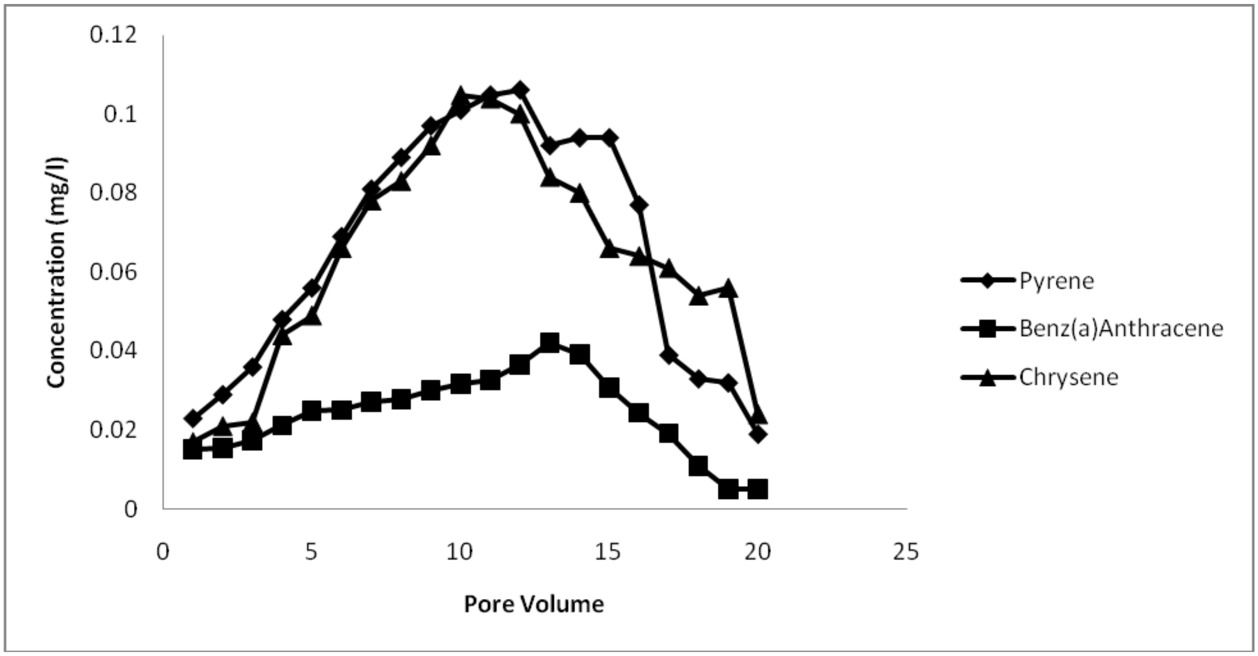


Figure 5.19 PAH Removal Efficiencies by 0.5% JBR425 Solution (pH 6.8)

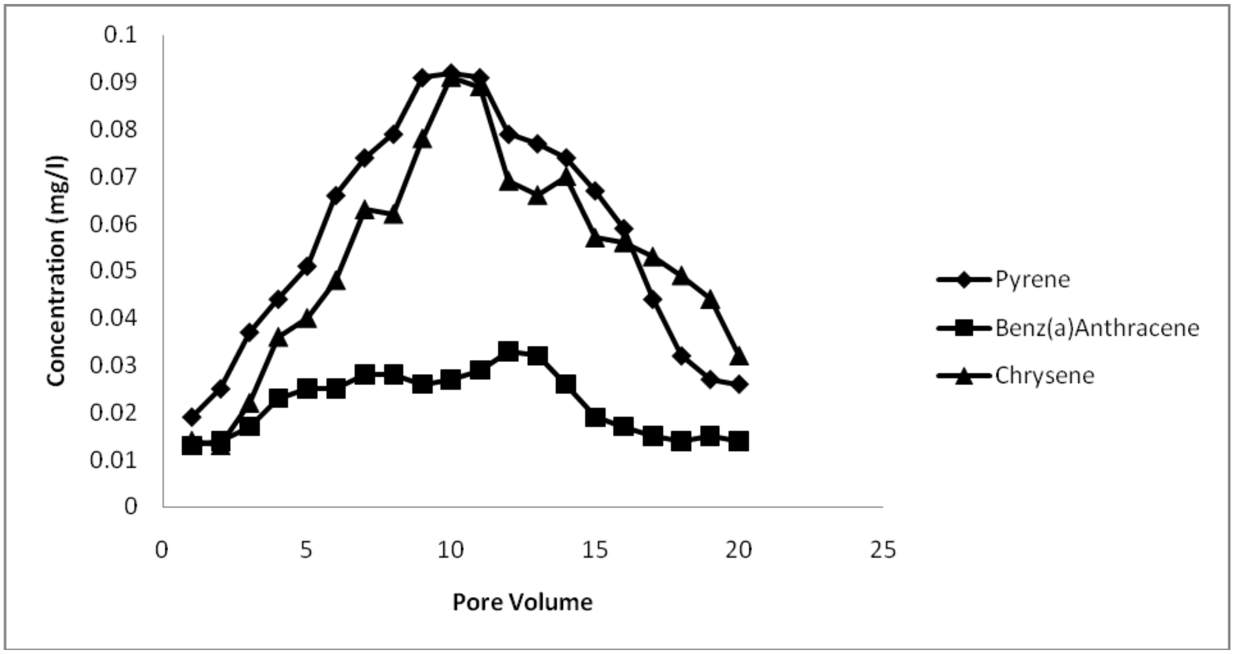


Figure 5.20 PAH Removal Efficiencies by 0.5% JBR425 Solution (pH 8.0)

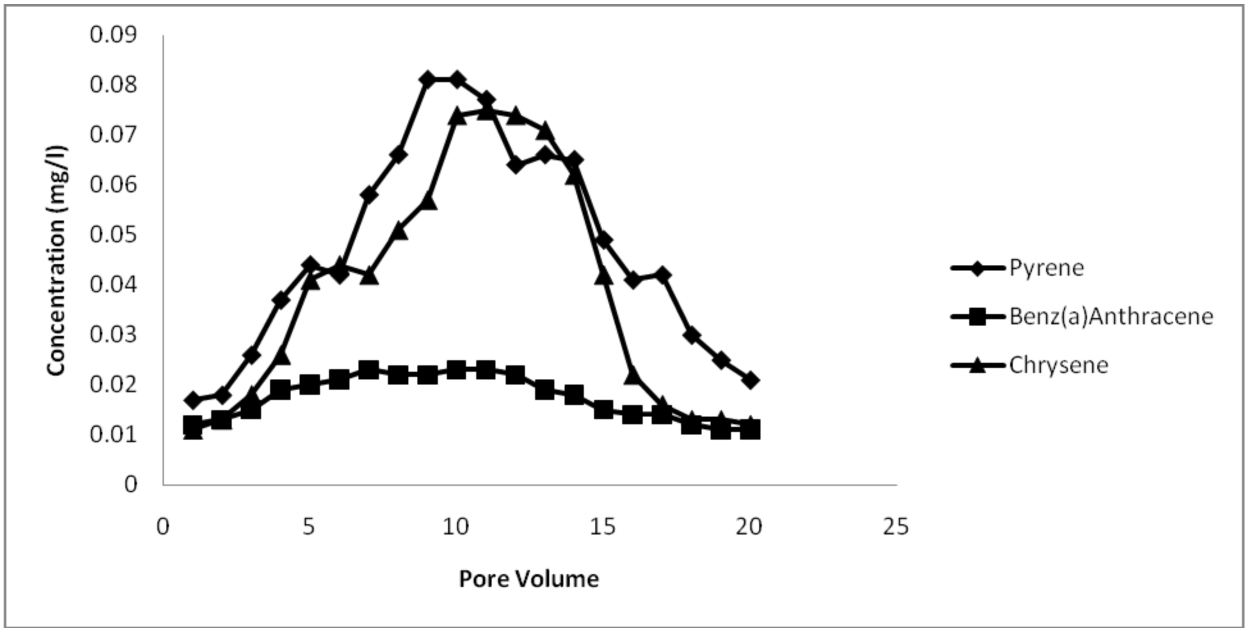


Figure 5.21 PAH Removal Efficiencies by 0.5% JBR425 Solution (pH 10.0)

Table 5.4 PAH Removal Efficiencies by 0.5% JBR425 Solution at Different pH values

PAH	**% Removal by 0.5% JBR425 Solution**					
	Mobilization			**Mobilization + Volatilization**		
	pH 6.8	**pH 8.0**	**pH 10.0**	**pH 6.8**	**pH 8.0**	**pH 10.0**
Pyrene	31.4%	25.5%	21.4%	34.8%	27.5%	23.3%
Benz(a)A	20.5%	16.2%	12.8%	21.6%	17.7%	13.6%
Chrysene	27.0%	24.4%	19.6%	29.5%	25.5%	20.5%

When a comparison between PAH removal efficiencies by 0.5% JBR425 biosurfactant under different pH values (6.8, 8.0 and 10.0) is done, regardless of application of a 99% quality foam or biosurfactant solution, as mentioned earlier, it can be noted that the pH of the JBR425 has an influence on the removal efficiencies. As when higher pH is applied, a smaller PAH removal efficiency was observed. After the application of biosurfactant solution to make a comparison with foam and better present the benefits of foam in contaminated sediment/soil remediation, again extractant agent with a pH of 6.8 showed maximum removal. As a result to demonstrate the comparison between foam and solution, these removal efficiencies are presented only for pH value of 6.8 and as it is seen in Table 5.5, the 0.5% JBR425 biosurfactant foam had the highest removal for PAHs.

Table 5.5 Comparison between PAH Removal Efficiencies by 0.5% JBR425 Foam and Solution at pH 6.8

PAH	**% Removal by 0.5% JBR425 Biosurfactant (pH 6.8)**			
	Mobilization		**Mobilization + Volatilization**	
	Foam	**Solution**	**Foam**	**Solution**
Pyrene	44.6%	31.4%	56.4%	34.8%
Benz(a)A	30.0%	20.5%	41.2%	21.6%
Chrysene	37.8%	27.0%	45.9%	29.5%

5.4.2 Heavy Metals Removal Efficiency

To find the heavy metal removal efficiency of the JBR425 biosurfactant (rhamnolipid) foam generated at the laboratory, after the remediation experiments sediment were sampled 3 times each for the top, mid and bottom section of the sediment column. The sediment was earlier packed as uniformly as possible. The total weight of the sediment was approximately 32 g (32.0±2 g) for each experiment. A series of flushing experiments was performed on sediment samples using 0.5% JBR425 (rhamnolipid) biosurfactant foam and 0.5% rhamnolipid biosurfactant solution with different pH values (6.8, 8 and 10). At the end, deionized water with adjusted pH was also used as control. It was found that the best removal efficiency for heavy metals (nickel, lead and zinc) was when a 0.5% rhamnolipid foam with a pH of 10.0 was used for 20 pore volumes.

5.4.2.1 Removal Efficiency by JBR425 Foam

To give an idea about the removal efficiency of the JBR425 foam under different pH values for heavy metals present in the matrix of the contaminated sediments, results of the experiments are presented in Figure 5.22. For heavy metals, the highest removal efficiency was achieved using a 0.5% rhamnolipid foam (99% quality, pH 10.0). The removals were 53.3% of Ni, 56.8% of Pb and 55.2% of Zn (Fig 5.22). It is understood that rhamnolipid has an affinity for these metals in this range: Pb > Zn > Ni and when the pH was more alkaline, the morphology of rhamnolipids changes from micelles to larger aggregates (Ishigami et al., 1987) but we still can see better removal which can be due to better solubility of metals at that pH.

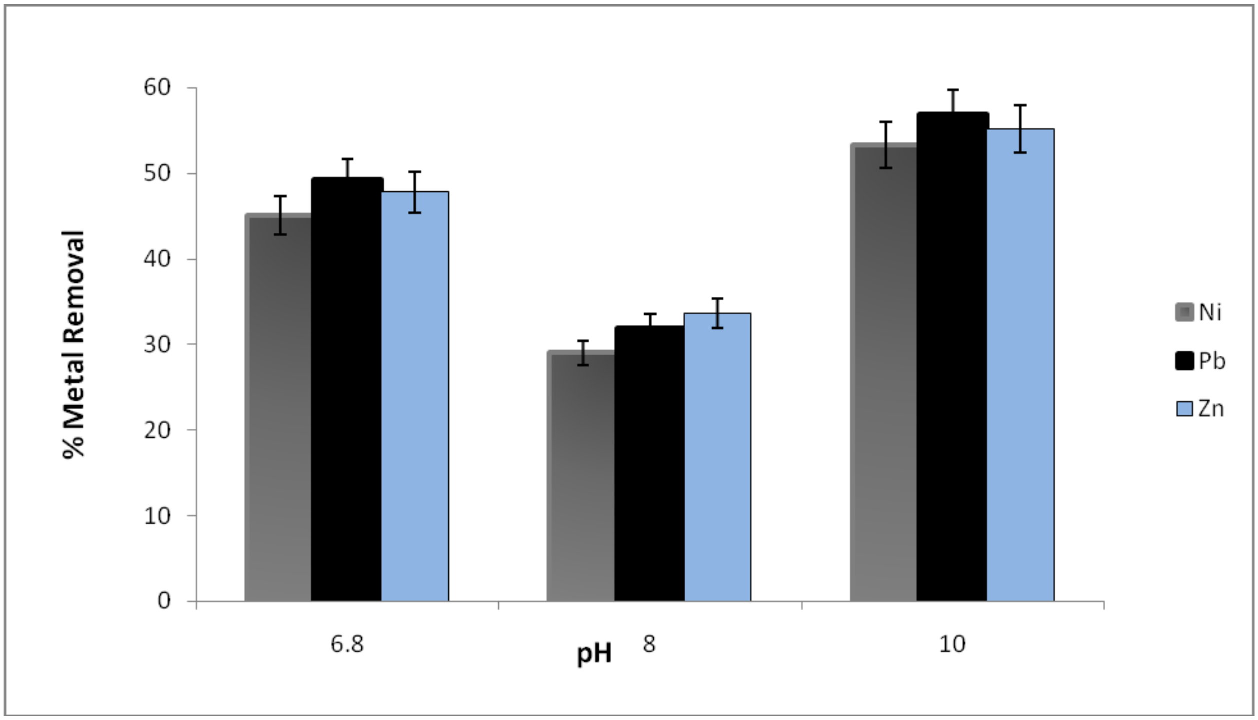


Figure 5.22 Effect of pH on Metal Removal capability of 0.5% JBR425 (rhamnolipid) foam

5.4.2.2 Removal Efficiency by JBR425 Solution

To better show the benefits of using a biosurfactant foam, biosurfactant liquid solution at the same pH values as the foam (pH 6.8, 8.0 and 10.0) was also applied and again solution with a pH value of 10.0 reached maximum removal of 42.2% for Ni, 44.5% for Pb and 41.8% for Zn after flushing the contaminated sediment column for 20 pore volumes. After a simple comparison between removal efficiencies related to foam and solution, it is notable that removal efficiency of JBR425 foam at a pH value of 10.0 was higher for all the target heavy metals present than that of the same biosurfactant without foam generation. For instance, over 11% more of Ni, 12.8% more of Pb and 13% more of Zn were removed by JBR425 foam than JBR425 solution under the same conditions. The possible reason behind the higher removal rate of the JBR425 foam can be this fact that biosurfactant gains more surface contact areas so as a result and in comparison with the JBR425 solution, the remedial capability of the extractant agent increases.

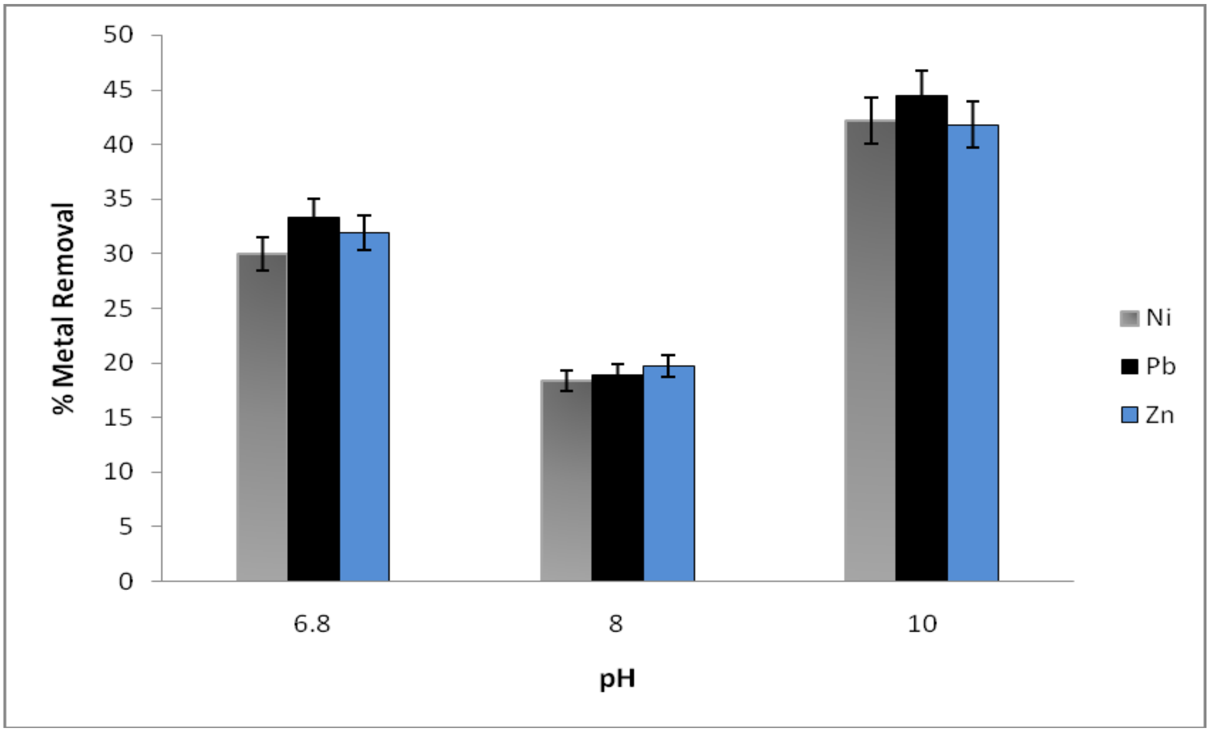


Figure 5.23 Effect of pH on Metal Removal capability of 0.5% rhamnolipid solution

5.4.3 Control Experiments

In order to see the differences that applying a biosurfactant can cause in a remediation experiment, control experiments were carried out by using deionized water (DI) with adjusted pH values. Deionized water (DI) with adjusted pH did not remove any PAHs but for heavy metal analysis, DI water removed 16% of Pb, 16% of Ni and 17% of Zn at pH 10.0 (Fig 5.23). In addition, the foam showed a higher removal than the JBR425 rhamnolipid solution and deionized water. Therefore, both the surface activity of the biosurfactant and the higher surface area of the foam were effective for heavy metal removal.

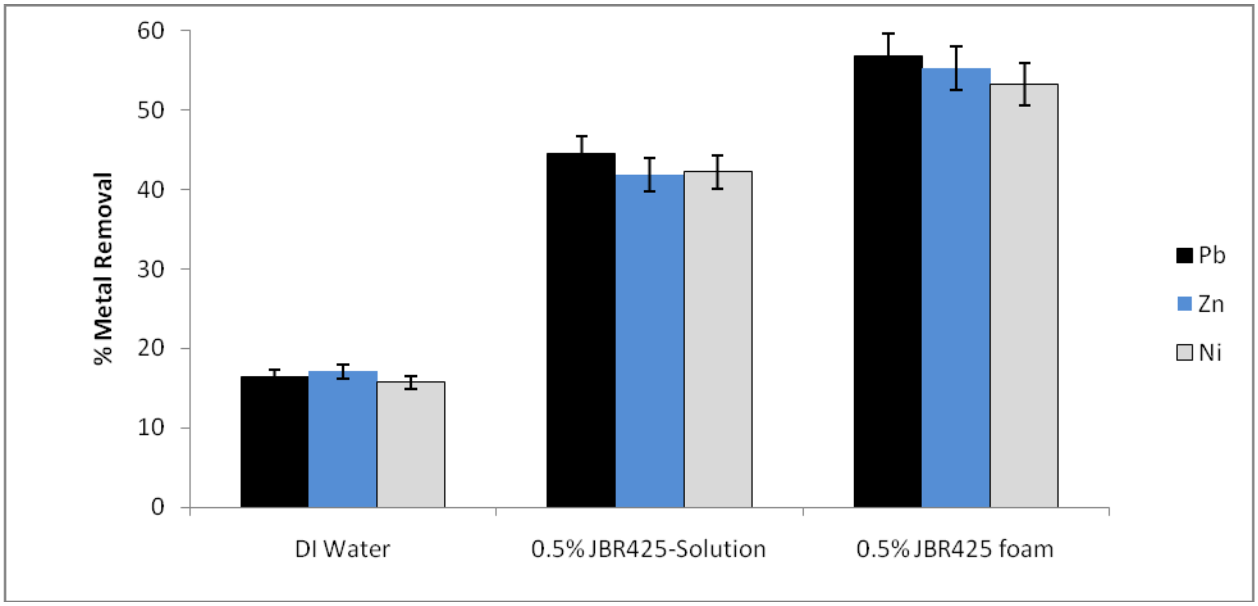


Figure 5.24 Comparison of metal removal capability between DI water, JBR425 (rhamnolipid) solution and foam (pH 10.0)

5.4.4 Hazard of Remediated Samples

After performing the remediation of PAH and heavy metal contaminated sediments, this question can come in mind that whether the remediation was successful or are the sediments clean enough? To clarify this aspect about remediated sediments, comparisons must be done to demonstrate the state of contamination before and after remediation and also to show the concentration difference with what is an acceptable level by the environmental authorities. This is what must be done for each of the contaminants remediated individually. The concentration before and after the remediation experiment as well as the acceptable levels are presented in Table 5.6. According to the data from this table, it is noted that all target PAHs were remediated successfully which means that if the sediment had only these contaminants, at this point, it was free of hazardous contaminants and it can be dumped into open-water or used as a liner in a municipal landfill, but the point is not that all the contaminants are fully removed in this experiment. Among target heavy metals, Ni reaches a final concentration which was above the acceptable level. In this case it can be suggested that the sediment sample be remediated again or washed by a hazard free chemical solvent like an acid or a base to lower the value of Ni within the sediment.

Table 5.6 Comparison of Contaminants Pre and Post Remediation Values with Acceptable Levels

Contaminant	**C_i** [1]	**C_f** [2]	**PEL** [3]	**FEL**
Pyrene	2.2	0.96	0.88	1.5
Benz(a)A	0.77	0.45	0.39	0.76
Chrysene	1.9	1.03	0.86	1.6
Ni	216	100.9	ND [4]	ND
Pb	149.7	64.7	91	150
Zn	363.0	162.6	310	770

1. **C_i** is the initial concentration (pre-remediation) of the contaminant (mg/kg dry sediment)
2. **C_f** is the final concentration (post-remediation) of the contaminant (mg/kg dry sediment)
3. Environment Canada and Ministère du Développement durable, de l'Environnement et des Parcs du Québec, 2007 (units are in mg/kg of dry sediment)
4. CCME has not established a threshold like other contaminants in this study, according to Canadian Sediment Quality Criteria, this value for Ni can be compared with other jurisdictions values that have determined thresholds above which adverse effect can be observed (similar to a PEL value), the range here is taken from MacDonald et al. (2000) that is equal to 75 mg/kg dry sediment

Chapter Six

Conclusions and Recommendations

6.1 Conclusions

Sediments consist of a heterogeneous matrix containing inorganic and organic components. As a result of their unique structure, they can be a sink for any environmental pollutant that is dumped into the aquatic ecosystem. Organic contaminants (PAH) and heavy metals such as Ni, Pb and Zn are potentially considered among sediment pollutants. Among remediation techniques, those that do not allow the sediments to be released again in the system so that they can be taken up by the biota and fauna, and those that have a higher removal efficiency are preferred by the authorities. As previously discussed in Chapter Two, gradual and excessive exposure to certain sediment contaminants can cause threats to sediment dwellers at the beginning specially those smaller aquatic organisms that are based at the bottom of the food web. If they get contaminated through these steps, they can die due to the toxicity of the sediments, so that larger organisms at top of the food web lose their food (EPA, 1999), if they survive the contamination, they easily can transmit it to bigger members of the food chain including terrestrial animals and human. As it is reminded here, sediment contamination can be costly to humans and the environment so it must be taken seriously. Ways of not introducing the contaminants must be established. Contamination monitoring procedures as well as different modern and modified remedial technologies must be created, analyzed and while the best removal efficiencies are known, they need to be introduced to the municipalities and environmental sectors. Since biosurfactant foam technology has been thought of as a promising and emerging method, in remediation of organic (especially for PAHs) and heavy metal contaminated sediments, it was investigated by performing column experiments. Although the effect of other materials in the sediments matrix on the remedial efficiency of biosurfactant foam has been assumed to be null, the results and observations present considerations that can be helpful while a biosurfactant foam is being applied for sediment flushing. From the performed experiments, starting from the premier steps, the following conclusions can be achieved.

6.1.1 Characteristics of the Generated Foam

It is observed that JBR425 foams can be generated at concentrations as low as 0.5% and regardless of the concentration and pH of the biosurfactant solution, high quality foams (from 85% to 99%) can be produced. They can have stabilities of 16 minutes to 42 minutes and these are enough to be applied in a sediment/soil remediation application. It is also noted that biosurfactant solution concentration and the quality of generated foam can affect foam stability while pH has no effect.

6.1.2 Pressure Gradient Build-up in the Sediment Column

This part of the experiments showed that biosurfactant foam quality and flow rate have an influence on inducing pressure in the sediment column. Increasing flow rate or decreasing the foam quality will lead to an increase in the pressure gradient build-up, which is not favored and can lead to problems in sediment/soil flushing such as channeling and heaving. Also theoretically, any addition to concentration of the biosurfactant foam (from 0.5% to 2.0%) would increase the pressure gradient, however in contrast, it appears that the change of biosurfactant solution has no significant effect on the pressure build-up. To perform a potentially efficient biosurfactant foam remediation of the contaminated sediments or soil, foam has to be relatively low in stability but high in quality to result in the minimum pressure gradients in the order of 0.2 kPa/cm. Also low concentration and low flow rate are two other factors to take into account to be able to finalize the remediation experiments as economically as possible by consuming less biosurfactant and a smaller need to perform any biosurfactant recycling that may contribute to the costs of the project.

6.1.3 PAH Removal Efficiencies

The results of this study show that biosurfactant foam technology can be applied in remediation of PAH contaminated sediments/soils that also have elevated levels of mixed heavy metal contamination. The main reasons behind using a biosurfactant foam in remediation of contaminated soil/sediments is due to the decreased hydraulic conductivity and affinity with the mixed metal and hydrocarbon contaminants. It is understood that these analyses are based on lab scale bench tests and it is probable that results of the actual field experiments, if performed under the same conditions, may be different. The efficiency of the biosurfactant foam is based on various alternatives such as the chemistry of the biosurfactant used, its concentration, resident time, different type of contaminants whether they can affect each other like development of heavy metal-organic complexes that may be harder to mobilize and finally the characteristics of the sediment/soil.

The maximum removal percentages (only due to mobilization) of these PAHs were achieved by 0.5% JBR425 foam with an unadjusted pH value (pH 6.8). Those were 44.6%, 30.0% and 37.8% for pyrene, benz(a)anthracene and chrysene respectively. From the experiments, the role of the biosurfactant pH in mobilizing different PAHs was demonstrated. Shifting the biosurfactant solution pH to more alkaline zones can lead to lower removal efficiency of PAHs.

Since air and biosurfactant solution are injected simultaneously, even in a heterogeneous matrix such as sediments, the flooding efficiency of the biosurfactant flushing would become more enhanced which leads to higher removal efficiency due to both mobilization and induced volatilization of the PAHs. According to this, the total maximum removal percentages that are due to mobilization and volatilization of these PAHs were achieved again by 0.5% JBR425 foam with an unadjusted pH value (pH 6.8). These were 56.40%, 41.20% and 45.90% for pyrene, benz(a)anthracene and chrysene respectively. Also it can be concluded that biosurfactant foam remediation seems to be more efficient than application of biosurfactant solution in soil/sediment flushing experiments.

6.1.4 Heavy Metal Removal Efficiencies

The results of this part of the study, as explained above, show that biosurfactant foam technology can be applied in remediation of PAH contaminated sediments/soils that also have elevated levels of mixed heavy metal contamination. For heavy metals, the highest removal efficiency was achieved using a 0.5% rhamnolipid foam (99% quality, pH 10.0). The removals were 53.3% of Ni, 56.8% of Pb and 55.2% of Zn. It is understood that rhamnolipid has an affinity for these metals in this range: Pb > Zn > Ni and when the pH was more alkaline, the morphology of rhamnolipids changes from micelles to larger aggregates (Ishigami et al., 1987) but still better removal can be notable which may be a result of heavy metals better solubility at that pH. Dahrazma et al. (2008) reported the co-existence of larger aggregates with micelles that have a radius of gyration (R_G) of 17 Ǻ which can also be a reason behind the removal of heavy metals by rhamnolipid at more basic pH. The removal by DI water was only 16% for Pb, 16% for Ni and 17% for Zn at a pH value of 10.0. Since the JBR425 foam showed a higher removal efficiency than the JBR425 biosurfactant solution and deionized water, it seems to be promising to apply these type of biosurfactant under the form of foam in remediation of heavy metal contaminated soil/sediments. It must be noted that, both the higher surface area of the foam and also surface activity of the biosurfactant were effective for the removal of heavy metals.

To conclude here, it must be mentioned again that biosurfactant foam technology seems to be an effective and non-toxic method to be applied on contaminated sites with either type of contamination (organic and inorganic). The use of biosurfactants as mentioned earlier in Chapter Two, is environmentally friendly as they themselves are products of bacteria and can get biodegraded more easily than other synthetic surfactants. Though it was observed from these studies that this technology can be applied for remediation of contaminated sediments through column tests, but one important thing that can affect the efficiency of foam must always be taken into consideration and that is the particle size distribution of the sediment/soil sample that influences the hydraulic conductivity of the solid matrix. When the clay percentage in a soil or sediment sample is relatively high then the soil becomes a clay soil. Low porosity of clays may affect the efficiency of this technique and as a result lower removal efficiencies are achieved. In this case, other methods can be applied.

6.2 Recommendations

- To better follow the flow of foam within a column during flushing tests and to make sure that the interactions between contaminated solid particles (whether soil or sediments) and the biosurfactant foam are all sufficiently done, there must be a method to trace the flow path of foam inside a column. One thing that can be helpful here would be the application of a tracer inside the column.

- Application of the biosurfactant foam under different salinity and pH conditions can also be investigated to see the possible effect of biosurfactant under different salinities on the removal of various kind of contaminants specially PAHs and PCBs.
- The presence of different contaminants at the same time may make it hard to perform the remediation experiments. Sometimes these contaminants can produce hard-to-mobilize complexes that have very low water solubility and tend to get sorbed on the solid particles. In this case, use of the biosurfactant foam technology can be a good opportunity to investigate whether they can gain good removal efficiencies through application of different biosurfactants.
- Another interesting subject can be the use of a mixture of two or three different biosurfactants on a heavy metal and PAH contaminated sediment. This way, results can be compared with what were drawn in this experiment and the better technique will outstand.

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Appendix

Appendix A

Cells A, B & C of Montreal Harbor's Sector 103

Figure A.1 - Cells A, B & C of Montreal Harbor's Sector 103 (Source: www.Google.ca, 2010)