INTEGRATED NANO ZERO VALENT IRON AND BIOSURFACTANT AIDED REMEDIATION OF PCB-CONTAMINATED SOIL

by

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ABSTRACT

Polychlorobiphenyls (PCBs) have been identified as environmental hazards for many years. Due to historical issues, a considerable amount of PCBs were released deep underground in Canada. In this research, a nanoscale zero valent iron (nZVI)-aided dechlorination followed by biosurfactant enhanced soil washing method was developed to remove PCBs from soil. During nZVI-aided dechlorination, the effects of nZVI dosage, initial pH level and temperature were evaluated, respectively. The results showed that the nZVI dosage of 7.5 g nZVI/kg led to the maximum PCB dechlorination rate. Adding more nZVI could cause particle aggregation, and thus, lower the PCB dechlorination rate. A pH level of 5 was selected for PCB dechlorination before soil washing. The results also indicated that the temperature changes could positively influence the dechlorination process. In the soil washing process, results showed that the presence of nano iron particles played a key role in PCB removal. The crude biosurfactant was produced using a bacterial stain isolated from the Atlantic Ocean and was applied for soil washing. The soil washing results indicated that a higher concentration of the biosurfactant solution led to an increased solubilization of PCBs. The overall removal rate of PCBs using the biosurfactant solution with a concentration of 0.5% was 80%. The study has led to a promising technology for PCB-contaminated soil remediation.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS, NOMENCLATURE OR ABBREVIATIONS

ATSDR	Agency for Toxic Substances and Disease Registry.
BCD	Base Catalyzed Decomposition.
BNZVI	bimetallic particles.
CAS	Chemical Abstracts Service.
CCME	Canadian Council of Ministers of the Environment.
CMC	carboxymethyl cellulose.
CMC	critical micelle concentration.
CREAIT	Core Research Equipment & Instrument Training.
DCE	dichloroethylene.
DEW	Distant Early Warning.
DND	Department of National Defence.
FCSAP	Federal Contaminated Sites Action Plan.
FCSI	Federal Contaminated Sites Inventory.
GC-ECD	Gas Chromatograph-Electron Capture Detector.
GC-MS	Gas Chromatograph-Mass Spectrometer.
H	height.
HTTD	high temperature thermal desorption.
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry.
IS	international standard.
LDL	lower detection limit.
LLME	liquid liquid micro extraction.
LTTD	low temperature thermal desorption.
NFESC	National Facilities Engineering Services Center.
NL	Newfoundland and Labrador.
nZVI	nano zero-valent iron.
OD	outside diameter.
ORP	oxidation-reduction potential.
PCBs	polychlorinated biphenyls.

PCDDs	polychlorinated dibenzodioxins.
PCDFs	polychlorinated dibenzofurans.
POPs	persistent organic pollutants.
RREL	Risk Reduction Engineering Laboratory.
S/S	Solidification/Stabilization.
SEM	scanning electron microscopy.
SIM	selected-ion monitoring.
SPE	solid phase extraction.
SVOCs	semi-volatile organic compounds.
SWE	subcritical water extraction.
TCE	trichloroethylene.
TIC	Total ion current.
VC	vinyl chloride.
VOCs	volatile organic compounds.
XRD	X-ray Diffraction.

A	cross-sectional area of permeameter.
D_b	bulk density (g/cm^3).
D_p	particle density (g/cm^3).
K_T	coefficient of permeability at temperature T, cm/sec.
L	length of specimen in cm.
Q	volume of discharge in cm^3.
t	time for discharge in sec.
V_s	Volume of the solids (cm^3).
V_t	Total volume of the sample (cm^3).
W_s	Oven dried mass of the sample (g).
W_s	Oven dried mass of the sample (g).
Δh	hydraulic head difference across length L, in cm of water.

LIST OF APPENDICES

CHAPTER 1 INTRODUCTION

1.1 Background

As family members of chlorinated hydrocarbons, polychlorinated biphenyls (PCBs) are a group of manmade chemicals which were first synthesized in 1881 and commercialized in North American industries from the 1930s to the late 1970s (Pal et al., 1980; CCREM, 1986; Tanabe, 1988). Although never manufactured in Canada, PCBs have been imported and widely used in hundreds of industrial and commercial applications (e.g., electric insulators, plasticizers for adhesives, lubricants, hydraulic fluids, sealants, cutting oils, flame retardants) due to their non-flammability, electrical insulating properties, as well as chemical stability at high temperature and low vapor pressures (CCME, 1999; NSC, 2004).

These compounds did not exist in nature. After synthesis, they were found in the environment in 1966 (Jensen, 1966). Since then, PCBs were so widely discovered in the global environment that trace concentrations were detected even in remote areas such as the atmosphere of the Arctic and the Antarctic, the hydrosphere and biosphere (Tanabe, 1988). The widespread presence of PCB wastes in the environment was historically attributed to the leakage from electrical transformers, spills during transportation, emissions from waste incinerators, application of wastes to land, improper disposal and storage, and some other pathways (CCME, 1999).

Exposure to PCBs can lead to cancer and a variety of serious non-cancer health effects on different systems including immune system, reproductive system, nervous system and endocrine system in animals. There are also show supportive evidences

showing that PCBs have potential to cause carcinogenic and non-carcinogenic effects in humans (Erickson, 1997). Canada restricted the use of PCBs in 1977 and prohibited the import of PCBs in 1980 (Strachan, 1988; Barrie et al., 1992). Current legislation allows PCB-containing electrical equipment manufactured before 1980 to remain in use until the end of their service life; however, strict maintenance and handling procedures, and regulatory control by governments are required to prevent any release into the environment (CCREM, 1986).

Prior to restriction coming into force, about 1.2 million metric tonnes of PCBs were produced globally from 1929 to 1977 (Tanabe, 1988; WHO, 1993); and more than half of them were produced by Monsanto Co. in the U.S. under the trade name Aroclor (CCREM, 1986). Until importation was banned, approximate 40,000 tons of PCBs were imported into Canada. Over 24,000 tons can be accounted for in still-in-use electrical equipment and in storage awaiting permanent disposal. The remaining 16,000 tons are assumed to have been dispersed into the environment; hence resulting in traces of PCBs being found throughout Canada (CCREM, 1986).

Canadian Council of Ministers of the Environment (CCME) has published an environmental guideline about soil quality for the protection of environment and human health in 1999. The guideline has been designed for PCBs in four types of land uses (Table 1.1): agricultural, residential/parkland, commercial, and industrial. In 2005, a 15-year program named "The Federal Contaminated Sites Action Plan" (FCSAP) was established to reduce environmental and health risks from contaminated sites in Canada. The FCSAP listed over 22,000 contaminated sites (Table 1.2) within Canada; 364 of them are identified as PCB-contaminated sites, and these are mainly abandoned military sites

and Distant Early Warning (DEW) Line stations. With the support of the Government of Canada, more than 13,000 sites, including 115 PCB-contaminated sites, were remedied by August 2014. For the remaining 249 PCB-contaminated sites (Table 1.3), 216 of them require further remedial actions and 33 of them are still under suspicion or assessment (FCSAP, 2014).

As specified in the Federal Contaminated Sites Inventory (FCSI), PCB-contaminated sites are recognized in all the provinces and territories throughout Canada. Among the 341 PCB-contaminated sites, 131 of them are located in the province of Newfoundland and Labrador (NL) (Table 1.4); which has the severest PCB-contaminated situation compared with other provinces and territories. In fact, most of these sites are contaminated as a consequence of inappropriate handling, storage and disposal. For instance, Five Wing Goose Bay, located in central Labrador, which served as a military base for the Air Force since World War II (now operated by Canadian Force Command within the Department of National Defence, DND), has been contaminated with a significant amount of PCB wastes for years. This contamination can be attributed to the oil leaks from the tanks and cracked pipelines, the containment management and the waste disposal practices in the past (Zhang et al., 2012).

Federal and provincial governments, as well as associated industries, have been obliged to endeavour research efforts and provide financial support for site identification, remediation, and long term monitoring. In 1988, the federal government enacted strict PCB waste storage regulations and announced its federal PCB Destruction Program. Meanwhile, PCB contamination was becoming a rising concern in NL. Since 1994, the number of PCB-contaminated sites has been reduced under provincial jurisdiction. The

largest-scale cleanup of PCB-contaminated soil in Canadian history was undertaken in the Saglek area of northern Labrador and approximately 20,000 cubic meters of PCB-contaminated soil were evacuated in the remediation project from 1997 to 2004 (CSMWG, 2005). By August of 2014, however, only 45 contaminated sites have completed their remediation activities (Table 1.5). The large amount of remaining untreated sites and the revived problems in the treated sites are still risking the provincial ecosystems and environment in NL. The preliminary assessment process estimates the volume of free products could be among 15-20 million litres and the majority of the PCB pollutants are deep underground (AMEC, 2008).

Industries have been making efforts to solve individual problems and/or processes related to site remediation practices in NL during the past years. Among the existing technologies, incineration and landfill were frequently applied. However, the remediation was usually long-term and costly, and the exhaust could cause secondary pollution (FCSAP, 2014). There is a shortage of effective technologies to treat and remove PCB contaminants from soils and sediments. This situation has hindered the efforts to effectively protect the environments of this region. Therefore, it is desired that innovative technologies that can enhance the efficiencies and effectiveness of remediation of PCB-contaminated sites be developed within an NL context.

1.2 Research Challenges

PCBs are known as very stable compounds and have a long half-life. It can take years and even decades to restore the contaminated sites. Nano-scale zero-valent iron (nZVI) particles have been widely applied in removing chloridized hydrocarbons including PCBs due to their extraordinarily reductive property (Mikszewski, 2004; Cook,

2009). Some recent research has revealed that nZVI particles are effective in the transformation of a large variety of environmental contaminants, while they are inexpensive and non-toxic (Zhang, 2003). nZVI may chemically reduce PCBs effectively through reductive dechlorination, allowing the pollutant to be readily biodegradable after treatment. Wang and Zhang (1997) have developed an efficient method of synthesizing nanoscale iron particles that can rapidly and completely dechlorinate PCBs in the subsurface. Studies by Mueller and Nowack (2010) have shown that nZVI as a reactive barrier is very effective in the reduction of chlorinated methane, chlorinated ethane, chlorinated benzenes and other polychlorinated hydrocarbons. Varma (2008) has successfully applied nZVI in soil columns with a wide range of plant phenols as additives, which allows greater access to the contaminant and creates less hazardous waste in the manufacturing process. The application of nZVI to the contaminated soil could enhance the dechlorination of PCBs; nevertheless, higher chlorinated biphenyls require much longer time than lower ones to be completely dechlorinated. Biphenyls as the final product of PCBs are still environmental and health hazards which need further treatment. A time-saving technology that can completely degrade PCBs in the soils or remove PCBs from the soils is consequently in demand.

Soil washing has been applied to effectively and rapidly remove soil contaminants. This technology provides a closed system that remains unaffected by external conditions (Chu and Chan, 2003), and the system permits the control of the conditions (e.g. additive concentration) under which the soil particles are treated (Urum et al., 2003). Soil washing is cost-effective and often combined with other remediation technologies. Solvents are critical for soil washing and selected on the basis of their

ability to solubilize specific contaminants, and on their environmental and health effects (Feng et al., 2001). However, although soil washing can provide a high efficiency when extracting contaminants from the soil, there is still some limitations when dealing with PCBs. One of the constraints is that PCBs have low water solubility – 0.0027-0.42 ng/L (UNEP, 1997); they are soluble in organic or hydrocarbon solvents, oils and fats. When applying soil washing technology, PCBs tend to stay in the soils instead of flushing with solvents or water. Since high-chlorinated biphenyls are less water-soluble than low-chlorinated ones and PCBs often preferentially adhere to the clay or silt fraction of the soils (Lyons et al., 2013), removal of the high-chlorinated biphenyls in clayey or silty soils will become extremely difficult. It is thus very hard to find an appropriate washing solvent for PCB removal from soil.

Biosurfactants are surface-active compounds from biological sources, usually extracellular, produced by bacteria, yeast or fungi (Zhang et al., 2008). Compared with chemical surfactants, biosurfactants have been applied in contaminated soil remediation due to the advantages of low toxicity, high specificity, biodegradability and biocompatibility, and functionality under extreme conditions (Qin et al., 2009; Amaral et al., 2010; Xia and Yan, 2010). Applying biosurfactants as the solvents in soil washing systems to treat PCB-contaminated soil has the following benefits: 1) it would effectively enhance solubilization of PCBs in the washing solution, leading to increased removal efficiency; and 2) it could stimulate microbial activity that enhances biodegradation of PCBs which are soil bound (Xia and Yan, 2010). However, although the application of biosurfactants with soil washing can significantly increase the solubility of PCBs that increase the extraction efficiency (Amaral et al., 2010), PCBs that dissolved in the

washing solution need to be further treated before being released into the environment. As persistent organic pollutants, PCBs are hard to degrade, leading to costly and complex post-treatment processes before discharge (Xia and Yan, 2010). In addition, larger volumes of washing solution may be needed when additives like biosurfactants are used. A high biosurfactant concentration in the washing solution can cause foaming problems and inhibit the ability to remove PCBs from the soil (USACE, 2010). Increasing attention has been received on the combination of different technologies in recent years. These technologies can be applied in sequence to enhance the cost effectiveness (Gomes et al., 2013). Effective dechlorination approaches which can be integrated with soil washing and facilitate PCB biodegradation are thus desired.

1.3 Objectives

This research is essential for the applications to the removal of PCBs from the subsurface in NL. It aims to combine nanotechnology and an existing soil washing system with biosurfactants as the solvent to better cleanup the PCB-contaminated sites in NL. Since higher chlorinated biphenyls have lower aqueous solubilities than lower chlorinated ones, biosurfactant-aided soil washing could have higher removal efficiencies on lower chlorinated biphenyls than that on higher ones (Shiu and Mackay, 1986). Therefore, the sequence of the combined technologies would be better started with nZVI-aided dechlorination and followed by biosurfactant-aided soil washing. Through the experimental study of various factors (one factor at a time) affecting PCB dechlorination (nZVI dosage, pH, and temperature) and soil washing effectiveness (nZVI and concentrations of biosurfactant solution), the research output is expected to generate environmentally friendly and

economically/technically feasible solutions for helping solve the challenging site contamination problem in NL.

1.4 Structure of the Thesis

This thesis is composed of five chapters. Chapter 2 presents a comprehensive review on PCB properties and remedial strategies for PCB-contaminated soil. The strengths of nanotechnology and biosurfactant washing are summarized. The extent and scope of different applications are discussed. In Chapter 3, the methodology of the two-step experiment is introduced. It includes experimental materials preparation, detailed experimental design and sample analysis. Chapter 4 shows the treatment results of nZVI-aided dechlorination combined with biosurfactant-aided soil washing. Treatment efficiencies of each examined PCB congener are detected. Effects of nZVI dosage, pH, temperature, and biosurfactant concentration are discussed to obtain selected operation conditions for a better remediation performance. Finally, conclusions of this research are drawn along with the recommendations for future work in Chapter 5.

Table 1.1 Soil Quality Guidelines for Polychlorinated Biphenyls (mg/kg)

	Land use			
	Agricultural	Residential/ parkland	Commercial	Industrial
Guideline	0.5[a]	1.3[b]	33[b,c]	33[b,c]
SQG_{HH}	NC[d]	NC[d]	NC[d]	NC[d]
Limiting pathway for SQG_{HH}	ND	ND	ND	ND
Provisional SQG_{HH}	NC[e]	NC[e]	NC[e]	NC[e]
Limiting pathway for provisional SQG_{HH}	ND	ND	ND	ND
SQG_E	1.3	1.3	33	33
Limiting pathway for SQG_E	Soil and food ingestion	Soil and food ingestion	Soil contact	Soil contact
Provisional SQG_E	NC[f]	NC[f]	NC[f]	NC[f]
Limiting pathway for provisional SQG_E	ND	ND	ND	ND
Interim soil quality criterion (CCME 1991)	0.5	5	50	50

Notes: NC = not calculated; ND = not determined; SQG_E = soil quality guideline for environmental health; SQG_{HH} = soil quality guideline for human health.

[a]Data are sufficient and adequate to calculate only an SQE_E, which is greater than the interim soil quality criterion (CCME 1991) for this land use. Therefore, the interim soil quality criterion is retained as the soil quality guideline for this land use.

[b]Data are sufficient and adequate to calculate only an SQG_E, which is less than the existing interim soil quality criterion (CCME 1991) for this land use. Therefore, the SQG_E becomes the soil quality guideline and supersedes the interim soil quality criterion for this land use.

[c]In site-specific situations where the size and/or the location of commercial and industrial land uses may impact higher level consumers, the soil and food ingestion guideline is recommended as the SQG_E.

[d]There is no SQG_{HH} at this time.

[e]The is no provisional SQG_{HH} at this time.

[f]Because data are sufficient and adequate to calculate an SQG_E for this land use, a provisional SQG_E is not calculated.

(Source: Canadian Environmental Quality Guidelines, Canadian Council of Ministers of the Environment, 1999)

Table 1.2 Federal Contaminated Sites Classification

Classification Type	Suspected	Active	Closed	Total
Total	3,022	6,141	13,429	22,592
High Priority for Action	0	751	860	1,611
Medium Priority for Action	0	1,950	1,060	3,010
Low Priority for Action	0	1,567	696	2,263
Insufficient Information	0	250	330	580
Not a Priority for Action	0	562	2,060	2,622
Site(s) not yet Classified	3,022	1,061	8,423	12,506

(Source: http://www.tbs-sct.gc.ca/fcsi-rscf/classification-eng.aspx)

Table 1.3 Federal PCB-Contaminated Sites Classification

Classification Type	Suspected	Active	Closed	Total
Total	33	216	115	364
High Priority for Action	0	79	11	90
Medium Priority for Action	0	76	12	88
Low Priority for Action	0	33	10	43
Insufficient Information	0	6	3	9
Not a Priority for Action	0	15	56	71
Site(s) not yet Classified	33	7	23	63

(Source: http://www.tbs-sct.gc.ca/fcsi-rscf/classification-eng.aspx?qid=1250966)

Table 1.4 Province or Territory Classified Federal PCB-Contaminated Sites

Province or Territory	Number of Sites
Alberta	9
British Columbia	50
Manitoba	5
New Brunswick	11
Newfoundland and Labrador	128
Northwest Territories	7
Nova Scotia	40
Nunavut	43
Ontario	37
Prince Edward Island	5
Quebec	17
Saskatchewan	5
Yukon	5
Total Number of Sites Inside Canada	362
Total Number of Sites Outside Canada	2
Total	364

(Source: http://www.tbs-sct.gc.ca/fcsi-rscf/cen-eng.aspx?dataset=prov&sort=name&qid=1250968)

Table 1.5 Federal PCB-Contaminated Sites Classification in NL

Classification Type	Suspected	Active	Closed	Total
Total	19	64	45	128
High Priority for Action	0	14	5	19
Medium Priority for Action	0	30	1	31
Low Priority for Action	0	16	2	18
Insufficient Information	0	0	1	1
Not a Priority for Action	0	3	31	34
Site(s) not yet Classified	19	1	5	25

(Source: http://www.tbs-sct.gc.ca/fcsi-rscf/classification-eng.aspx?qid=1250974)

CHAPTER 2 LITERATURE REVIEW

2.1 Properties of PCBs

PCBs are a group of synthetic nonpolar aromatic hydrocarbons which consist of 209 possible congeners. Each congener contains 1 to 10 chlorine atoms attached to two connected benzene rings. The general chemical structure is shown below.

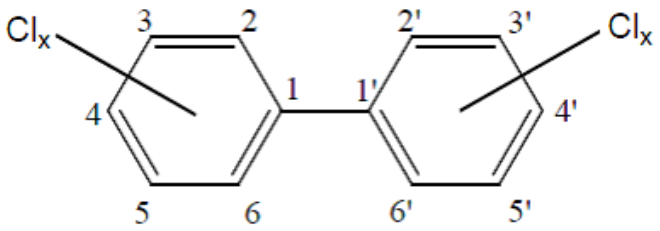

Figure 2.1 General Chemical Structure of PCBs
(Source: http://www.scilogs.com/maniraptora/journal-club-pcbs-cause-birds-to-sing-a-different-tune/)

The chemical formula of PCBs could be represented by $C_{12}H_{(10-x)}Cl_x$, where x = 1~10; thus, PCBs can be classified by different degrees of chlorination (Erickson, 1997). Congeners with the same number of chlorines are referred to as "homolog" (e.g., monochlorobiphenyl, trichlorobiphenyl and decachlorobiphenyl). Homologs with different chemical structures are referred to as "isomers". Appendix A shows the chemical identity of PCB congeners and homologs that are summarized by ATSDR (Agency for Toxic Substances and Disease Registry) and USEPA (United States Environmental Protection Agency). Most congeners possess no odor and no taste. Lower chlorinated biphenyls are clear to pale yellow crystals, while highly chlorinated congeners display deeper yellow.

Table 2.1 Industrial Trade Names of Popular PCB Mixtures in Different Countries

United States	Japan	France	Italy
Aroclor, Askarel, Bakola 131,Therminol, Asbestol, Noflamol, Saf-T-Kuhl, Hydol	Kanechlor Santotherm Pyroclor	Phenoclor Pyralène	Apirolio Fenclor
Former Czechoslovakia	**United Kingdom**	**Former USSR**	**Germany**
Delor	Aroclor Askarel	Sovol Sovtol	Clophen

(Source: http://tabemono.info/report/former/pcd/2/2_2/e_1.html)

130 out of 209 congeners were used in commercial PCBs. Thus, commercial PCBs were produced and used as complex mixtures, which contain many isomers of different homologs, from the 1930s to the 1970s. These mixtures are clear viscous oily liquids; the higher degree of chlorination they have, the more viscous they appear. PCB mixtures were marketed under different names in different countries. Table 2.1 lists the industrial trade names of popular PCB mixtures in different countries. Among these trade names, Aroclor is the most common one manufactured by Monsanto Company in U.S. and sold in both North America and the United Kingdom.

The physical and chemical properties of PCBs vary widely across the class (Erickson, 1997). As the chemical structure in Figure 2.1 shows, the substitution of hydrogen by chlorine may happen in most of the positions except position 1 and 1'. Position 4 and 4' are called *para* positions, position 3, 3', 5 and 5' are called *meta* positions, and position 2, 2', 6 and 6' are called *ortho* positions. There are two extreme cases of the configuration of the two connected benzene rings. One is called planar configuration in which case the two benzene rings are in the same plane; the other is nonplanar configuration in which case the benzene rings are at a 90° angle to each other. The number of chlorines, their positions on the connected benzene rings, and the planarity of the configuration would influence and determine the physical and chemical properties of PCBs. However, all PCB congeners or mixtures have low water solubilities and low vapor pressures compared with other chemicals. By comparison within all PCB congeners or mixtures, when the degree of chlorination increases, vapor pressure and water solubility will decrease while the melting point and lipophilicity will increase (Erickson, 1997; Fiedler, 1997). The water solubility of Aroclor was found to be in the range of

0.0027-0.42 ng/L (UNEP, 1997); on the contrary, it can easily dissolve in most organic solvents, oils and fats (Erickson, 1997). Some other physical and chemical properties have been addressed by Shiu and Mackay (1986), and Metcalfe et al. (1988). The density of PCBs ranges from 1.182-1.566 kg/L under room temperature, and they are non-flammable and have a high flash point (170-380℃). Crucially, some characteristics such as high electrical insulating property, high thermal conductivity and extreme chemical stability became the reasons that commercial PCBs were widely and extensively applied in hundreds of industrial products. For instance, PCBs were ordinarily used as dielectric fluids in capacitors and transformers; as heat transfer and hydraulic fluids; as lubricating and cutting oils; as plasticizer in paints, adhesives, sealants, plastics and rubber products; as additives in pigments, dyes and carbonless copy paper; and as flame retardants.

PCBs were never manufactured in Canada but only imported. Before the manufacture of PCBs was banned in the U.S. in 1977, tens of thousands of the imported PCBs were released into the environment through illegal use and dumping, unexpected leaks from electrical transformers, inappropriate storage and disposal, as well as municipal or industrial incineration (ATSDR, 2000). Since they are hard to degrade, PCBs may stay for years or decades once entered into the environment; thus, are classified as persistent organic pollutants (POPs). Due to their low vapor pressure, high viscous and lipophilic properties, PCBs are found to mainly exist in soils and sediments, organisms, and hydrosphere. Although PCBs are not easily evaporated, detectable level of PCBs has been measured in the atmosphere that resulted from volatilization of lower chlorinated biphenyls. Furthermore, the atmosphere was proved to be the primary route for global transport of PCBs (Erickson, 1997; ATSDR, 2000). Until the end of 1960s,

PCBs were recognized to occur in many environmental (e.g., air, drinking water, soil, sediment and solid waste) and biological samples (e.g., human blood, milk, animal tissues and fish) (Jensen et al., 1969; Jensen, 1972; Hutzinger et al., 1974).

The toxic effects of PCBs started to gain public attentions since the Yusho incident happened in western Japan in 1968. More than 14,000 people were poisoned through ingestion of a commercial brand of rice oil, which was contaminated by PCBs and some other chlorinated chemicals. A similar mass food poisoning incident called Yucheng occurred in Taiwan ten years later. It was reported as being a consequence of consumption of one kind of rice cooking oil contaminated by heat-degraded PCBs and related chemical compounds, and at least 2,000 people were affected from 1979 to 1981 (Erickson, 1997; UNEP, 1997). The ingestion of contaminated food is one primary pathway for PCB exposure, but not the only one. Other possible pathways include the inhalation of contaminated vapors and dermal contact with PCB products. In fact, workers in PCB manufacturing plants were the first to report toxic effects via exposure to high concentrations of PCBs in the air (Jones and Alden, 1936). Dealing with PCB-containing equipment such as old transformers and capacitors could provide extremely high dermal contact potential (Kimbrough, 1987). Numerous of studies have been conducted to investigate the toxicology of PCBs, and the findings revealed that toxic effects were directly in relation to their structures (NRC, 1979). Although sufficient evidence has indicated that PCBs are carcinogenic to animals, there is still lack of data proving that they can cause cancer to human beings (Safe, 1994). Moreover, both individual congeners and PCB mixtures exhibit a series of chronic toxicological effects on the immune system, reproductive system, nervous system and endocrine system.

Symptoms of health effects include acne and rashes on the skin, irritation of nose and lungs, gastrointestinal discomfort, changes in the blood and liver, depression and fatigue, and even unusual skin color on newborn babies (ATSDR, 2000).

With in-depth studies carried out, more and more adverse effects were discovered. As mentioned previously, tens of thousands of PCB contaminants have been released into the environment, and the majority of the PCBs were found existing in soils and sediments. Regardless of the fact that the use, storage and disposal of PCBs are regulated by federal and provincial governments; effective techniques and approaches for PCB-contaminated soil remediation are much more desired.

2.2 Current Remedial Strategies for PCB-contaminated Soil

Numerous PCB treatment technologies have been researched, developed and even applied to real sites since there is a rising concern among the public. Many technologies can be applied in-situ, whereas certain amounts of technologies are designed for ex-situ treatment. Some conventional physical, chemical and physiochemical remedial processes have been demonstrated to be quite effective for the removal of particular congeners or mixtures; however, these processes normally require relatively high energy cost. To better define our research scope, the popular technologies in the past few decades as well as emerging technologies have been reviewed in this chapter.

2.2.1 Physical/Chemical Treatment Technologies

1) Excavation and Incineration

Excavation and incineration, as a conventional treatment technology, is one of the most frequently applied ex-situ technologies and has the ability to destruct contaminants like PCBs, pesticides and similar chemicals (Rahuman et al., 2000). The contaminated

soil is excavated and then transferred into an incinerator with an inside temperature higher than 1 000 °F (537.8 °C). The presence of oxygen and enough residence time are required to achieve complete combustion and destruction (Dàvila et al., 1993; Rahuman et al., 2000). This technology has the ability to destroy PCBs and significantly reduce the high PCB concentration in soil. However, the great input of energy did not shorten the residence time of PCBs; very long residence time is always necessary for the PCBs to get completely destructed. In addition to the economic and time factor, another concern is exhaust from incineration. Since PCBs are not easy to destruct, the undestroyed PCBs may form dioxin-like pollutants or furans in the off-gas. Hence, the extensive off-gas has to be collected and treated before it is released into the surrounding environment (Magar, 2003).

2) Landfill Disposal

After the manufacture and use of PCB were regulated in 1979, landfilling became a very common method for PCB-contaminated soil containment. In this way, the PCB-containing wastes are well isolated from the environment so that the relevant human and ecological risks will be significantly reduced (Dàvila et al., 1993). Even though landfill disposal is inexpensive, the PCBs will not be destroyed but retained in the disposal site. Only a little natural degradation may occur in a long period of time. Also, long-term monitoring should be implemented on the disposal sites just in case any leakage happens underground (Dàvila et al., 1993; Hartig et al., 1999).

3) Solidification/Stabilization (S/S)

Solidification/Stabilization is a technology that is capable of solidifying and stabilizing the PCB contaminants by addition of a binding agent such as cement or

alternative binding materials. The S/S process converts the PCBs into an insoluble, less mobile and less toxic solid matrix instead of destroying them (Wiles, 1987; Trussell and Spence, 1994). In practice, it is not frequently applied for heavily contaminated PCB wastes. High concentrations of PCBs may interfere with the setting of cement and other binding agents due to the hydrophobic characteristic of PCBs. As a result, when the solid matrices are crushed and proceed to landfill disposal after the S/S process, the potential for PCB leaching is high. Moreover, some reports indicate that a portion of the PCBs may be discharged into the air during the heating and mixing with the cements; thus, the off-gas after S/S treatment is required to be collected and treated before it is released to the environment (Paria and Yuet, 2006).

4) Vitrification

Vitrification is a method similar to solidification; in contrast, the PCB-contaminated soil is heated to a temperature higher than 2,200 °F (1,204 °C); after melting, the contaminated wastes will be rapidly cooled down to form glass-like products. It has been proven that the volume of the contaminated soil through vitrification could be distinctly decreased at least 20% (Jackson and Boulding, 1996; Rahuman et al., 2000). This technology has the advantage of immobilizing and destroying PCBs; however, the cost of vitrification is much higher than other technologies because a huge amount of energy is essential to achieve the heating temperature. In the meantime, it is difficult to measure the effectiveness of the treatment. Thus, this technology has only been tested in a few sites but has not been widely used after 1990s.

5) Thermal Desorption

Thermal desorption is proven to be an effective approach to physically separate volatile and semi-volatile contaminants from the soil waste matrices (Dàvila et al., 1993). In general, oxygen or air in the heating chamber should be removed or pumped out and filled with inert gas before desorption, because extremely toxic and carcinogenic by-products like polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) may possibly form through PCB combustion (Risoul et al., 1999; Zhao et al., 2012). As the desorption process is a physical phenomenon and only transfer the contaminants from solid phase to gas phase, the contaminants are not destructed. As a consequence, thermal desorption is usually combined with other techniques such as incineration, S/S and chemical dehalogenation.

6) Solvent Extraction

Since organic contaminants usually have high solubility in chemical solvents, the technology of solvent extraction is developed and applied to remove these contaminants from soils and sediments. The extraction is an ex-situ physical process using chemical solvents as extractants to collect and concentrate the contaminants (e.g., PCBs) in a single phase; it can clearly reduce the volume of contaminants needed to be treated accordingly. No contaminant has been created or destroyed through this process. The extracted contaminants are only transferred from the solid phase (soil) to the liquid phase (solvent); therefore, they should be destroyed by other techniques such as incineration and chemical dehalogenation. Although solvent extraction can effectively separate the PCBs from the contaminated soil, some limitations were also found out. Higher clay content in the contaminated soil could reduce the extraction efficiency because PCBs can easily be adsorbed onto the soil particles. Hence, a longer contact time or extraction time is

required. In addition, the soil containing higher clay content and organic matter may form aggregates that are very tight and difficult to break, which results in a relatively low extraction efficiency (Dàvila et al., 1993).

7) Base Catalyzed Decomposition (BCD)

The BCD process is a chemical dehalogenation and catalytic hydrogenation process during which the halogen atoms in the organic contaminants are stripped from the molecules and replaced by hydrogen atoms. BCD has been developed by EPA's Risk Reduction Engineering Laboratory (RREL) in collaboration with the National Facilities Engineering Services Center (NFESC) since 1990; it mainly targets the chlorinated organic contaminants such as PCBs, dioxins and furans in the liquids, sludge, soils and sediments (Dàvila et al., 1993). BCD is an efficient and inexpensive treatment technology for heavily contaminated soils. As a matter of fact, it is essential to monitor the BCD process properly and frequently when dealing with high concentration of PCBs, because incomplete dechlorination of higher chlorinated PCBs may result in an increase of lower chlorinated congeners. This could lead to the formation of PCDDs and PCDFs, which will cause a rising concern (Rahuman et al., 2000). Therefore, a complete dechlorination reaction must be ensured in BCD treatment. In addition, factors like high moisture content, high clay content and existence of co-contaminants may reduce the efficiency of BCD process.

8) Soil Washing

Soil washing is considered to be one of the innovative and effective technologies for the cleanup of many organic and inorganic pollutants at many Superfund sites in Northern Europe and the U.S. It basically uses liquids/washing fluids (such as water) to

mechanically mix, wash and rinse the soils to get rid of the contaminants. The washing fluids are then separated from the soil-water mixture and handled by conventional wastewater treatment technologies. Similar to solvent extraction, the contaminants are neither destroyed nor immobilized through the washing process. They are only transferred from the solid phase to the liquid phase; thus, soil washing is regarded as a media transfer technology (Dàvila et al., 1993; EPA, 2001).

Unlike solvent extraction, washing fluids used in soil washing are usually water or water with some additives, while solvent extraction utilizes chemical solvents to extract the contaminants from soil (Dàvila et al., 1993). Detergents/surfactants and acid are two types of additives commonly added to washing fluids. They are capable of desorbing the majority of the contaminants, including PCBs and some other hydrophobic contaminants, from the soil (Anderson, 1993; Griffiths, 1995; Billingsley et al., 2002; Occulti et al., 2008). However, one of the shortcomings of adding these agents is that it could result in a greater volume of washing fluid. Furthermore, surfactants with a high level of concentration are recognized to cause foaming problems that may dramatically affect the washing efficiencies (Deshpande et al., 1999; Shi and Chen, 2013).

2.2.2 Biological Treatment Technologies

1) Bioremediation

Bioremediation makes use of microorganisms to break down organic compounds such as petroleum products, solvents and pesticides in contaminated soil or groundwater (Dàvila et al., 1993). Microorganisms have the ability to degrade complex organic compounds into simpler ones, or completely mineralize them. Bioremediation of PCBs can be generally summarized into two pathways: anaerobic reductive dechlorination and

aerobic oxidation (Gomes et al., 2013; Magar, 2003; Dàvila et al., 1993; Passatore et al., 2014). Anaerobic reductive dechlorination is an energy-yielding process in which PCBs act as electron acceptors and can be altered into less chlorinated forms/congeners (Passatore et al., 2014). Aerobic oxidation, also known as biphenyl degradation, involves the presence of oxygen to accomplish ring cleavage and complete mineralization of PCBs. Aerobic bioremediation usually takes place at a faster rate than anaerobic bioremediation. In practice, PCBs can be degraded anaerobically, aerobically, or through the combination of the two (Magar, 2003; Passatore et al., 2014; Gomes et al., 2013). From the research of Harkness et al. (1993), Borja et al. (2005) and Pieper (2005), aerobic bacteria tend to biodegrade lower chlorinated biphenyls, usually those with less than five chlorines, while PCB with higher chlorine content always show great resistance to oxidative degradation. On the contrary, molecules of higher chlorinated biphenyls could be partly degraded through reductive dechlorination under anaerobic conditions; the final products in the anaerobic environment are usually biphenyls. Because of this, PCBs with higher chlorine content can be completely mineralized by sequential anaerobic-aerobic treatment (Dàvila et al., 1993; Gomes et al., 2013). A number of experiments have been conducted (Haluska et al., 1995; Fava and Piccolo, 2002; Komancová et al., 2003) to explore the biodegradability of commercial PCB products (e.g., Aroclors) through aerobic oxidation/degradation. As most of the congeners in commercial products contain less than four chlorines in their molecules, the results show significant mass decreases in commercial products. Even so, an observation from these studies indicates that the aerobic biodegradation is limited and influenced by the position of chlorines and the bacteria strains (Haberl and Bedard, 1990; Magar, 2003; Furukawa and Fujihara, 2008;

Gomes et al., 2013). Anaerobic reductive dechlorination could follow different substitution pathways according to the physical, chemical and biological characteristics of each contaminated site and different anaerobic bacteria could selectively dechlorinate PCB congeners in their own pattern (Passatore et al., 2014). Quensen et al. (1990), Ye et al. (1992), Natarajan et al. (1997), Cho et al. (2001), Bedard et al. (2007) and Kim et al. (2008) have done much research to seek the pathways of many different bacteria. Their studies demonstrate that the molar concentration of PCBs is not decreased by the process of reductive dechlorination but the toxicity of PCBs is reduced, especially those dioxin-like congeners; consequently, they are ready for aerobic oxidation. Bioremediation is suitable for both in situ and ex situ treatment. In situ treatment allows the soil to be decontaminated in its original place. There is no need for excavation and transportation of the soil and thus, this process will benefit for the cost saving. Compared with in situ treatment, ex situ bioremediation has shorter biodegradation time since the soil is homogenized and continuously mixed (Dàvila et al., 1993). In recent years, many approaches have been attempted to enhance bioremediation such as to solubilize PCBs and make them transportable across the cell membrane, to regulate the production of PCB degrading enzymes and to genetically engineer the enzymes (Wilken et al., 1995; Abramowicz and Olson, 1995). Although the enhanced strategies are successful in lab-scale and pilot-scale experiments, comprehensive field-scale research is necessary to promote bioremediation.

2) Phytoremediation

Phytoremediation is a biologically remedial technology that depends on the use of various green plants and associated bacteria to extract, transfer, remove, degrade and/or

detoxify contaminants in the soil, sediment, wetland and groundwater (Gomes et al., 2013; Salt et al., 1998; Huesemann et al., 2009). The concept of plants being used for environmental remediation was raised a few decades ago. Now, phytoremediation has been developed into a promising, cost-effective and environmentally friendly approach according to the interdisciplinary research conducted in previous years (Salt et al., 1998). The contaminants capable of being treated include metals, pesticides, explosives, fuels, VOCs and semivolatile organic compounds (SVOCs) (Salt et al., 1998; Susarla et al., 2002; Gomes et al., 2013). When dealing with PCBs, three principle mechanisms are involved: I) Phytoextraction – PCBs are absorbed and accumulated in stems and leaves tissues; II) Phytodegradation – PCBs are transformed or degraded by a series of enzymatic reactions; and III) Rhizoremediation – Microbial activity is enhanced by the release of secondary metabolites in the root zone which could further enhance the biodegradation of PCBs. A number of experiments have been performed in laboratories and greenhouses to investigate the remediation efficiencies of plants in the last decade. Singer et al. (2003), Zeeb et al. (2006), Shen et al. (2009), and Chen et al. (2010) tested the remediation effect of many different kinds of plants on PCB-contaminated soil in greenhouses and they found that most of the plant candidates were able to extract PCB from soil and translocate them from their roots to their shoots; however, their results revealed microbial degradation provided the primary contribution to the PCB removal rather than plants uptake (Singer et al., 2003; Zeeb et al., 2006; Shen et al., 2009; Chen et al., 2010). In practice, phytoremediation offers several benefits over many other remedial technologies. The operational cost of the treatment is relatively low because no energy-consuming equipment is needed in this process or related maintenance. Also, the yield of

biomass during phytoremediation could be made use of as bioenergy, which is renewable and substantial. This technology is accepted by the public as a green technology and it is believed that there is no or limited negative environmental impact due to the in situ nature of the phytoremediation process (Salt et al., 1998; Aken et al., 2009; Gomes et al., 2013). At the same time, however, the technology endures some drawbacks. One major limitation is that the uptake, translocation and degradation process of PCBs by plants and associated bacteria are quite slow, which could always lead to incomplete decomposition of the contaminants. Meanwhile, the toxic metabolites could be potentially released into the surrounding area; and thus, become a threat to the environment (Gomes et al., 2013; Sylvestre, 2013). To overcome this obstacle, two strategies are developed. One way is to cultivate transgenic crops through the metabolism of which the PCB mineralization can be speeded up, the other way is to genetically modify the associated bacteria so that the biodegradation of PCBs can be accelerated. Many transgenic plants are produced until now, but no one has been applied in the real field. What the researchers concern is the potential risk of horizontal gene transfer to the related wild plants. Hence, additional research is needed to assess the risk of using transgenic plants before any application in the field (Sylvestre, 2013; Aken et al., 2009).

2.2.3 Advantages of Soil Washing for PCB Removal

Compared with remediation technologies, soil washing shows a simple and rapid treatment approach that is able to remove various contaminants from soil. Soil washing system provides a closed system that remains unaffected by external conditions (Chu and Chan, 2003). The enclosed design without discharge is also more environmentally friendly. The low cost of soil washing can easily compete and substitute the thermal

treatments such as thermal desorption, vitrification and incineration. The process requires no combustion thus limits generating more toxic by-products such as PCDDs and PCDFs (Kaštánek and Kaštánek 2005). With the present of surfactants, the interaction and emulsification will increase the solubilization of PCBs from soil; thus, shorten the treatment time (Shin et al., 2004) which is a superior feature in comparison with bioremediation or phytoremediation. Billingsley et al. (2002) examined the PCB removal aided by eight different chemical surfactants (including anionic and nonionic surfactants). Seven of these surfactants exhibited higher than 60 percentage removal efficiencies, and the highest removal was even showed to be 89 percent. Zhu et al. (2012) have done experiments to investigate the removal of PCBs by a surfactant called polyoxyethylene lauryl ether (Brij35). Results showed that a 90 percent removal rate was achieved. By adjusting the composition of washing fluid, soil washing technologies can treat a broad range of influent contaminant concentration. Less chemical consumption of soil washing is able to reduce the cost and the toxicity leading to a more sustainable treatment. With the higher removal efficiency of contaminants and low adsorption of surfactants onto the soil (Zhu et al., 2012), the soil washing technology is able to provide reusable soil.

2.3 Nano-aided Dechlorination

2.3.1 nZVI

Nanotechnology requires the material particles not only to be on the “nano” scale, which means the particle diameter should fall between 1 and 100 nanometer (nm); but also to own novel physical, chemical or biological properties and functions that different from materials on a large scale (Watlington, 2005). In the past decade, this technology has made contributions to materials development in magnetic, electronic and

optoelectronic, biomedical and pharmaceutical, cosmetic, energy, catalytic, and many other applications. Also, it offers a number of direct and indirect benefits for environmental protection. For instance, it can be used to protect the environment in the aspects of pollution prevention, sensing and detection, as well as treatment and remediation (Watlington, 2005). Nanoparticles, which have miniature sizes and innovative surface coatings, are very reactive materials and have properties to enable both chemical reduction and catalysis that are effective for pollution mitigation (Karn et al., 2009). The nanoscale materials explored for environmental remediation include nanoscale zeolites, metal oxides, carbon nanotubes and fibers, enzymes, bimetallic nanoparticles, and titanium dioxide. Among these, nanoscale zero-valent iron (nZVI) is currently one of the most studied and widely used.

Compared with granular iron, nZVI particles have much larger surface areas with 2-5 nm particles giving 142 m^2/g (Taghizadeh, 2013), which is approximately 30 times greater than that of granular iron. The large surface area provides a large fraction of stepped surface and it makes the nZVI particles significantly reactive and effective. Li et al and Müller et al's studies have discovered that the reaction rates of nZVI are 10 to 1 000 times faster and the sorption capacity is much higher than granular iron (Li et al., 2006; Müller and Nowack, 2010). Due to their extraordinarily reductive property, they are effective in the transformation and reduction of different inorganic perchlorate compounds and metals (e.g., Cr(Ⅵ), As(Ⅲ), Pb(Ⅱ), Cu(Ⅱ) and Ni(Ⅱ)). They are also able to rapidly and extensively remove chlorines from chlorinated organic hydrocarbons (e.g., PCB, TCE, PCE and pesticides) in contaminated soils (Zhang, 2003; Mikszewski,

2004; Cook, 2009). To mitigate PCB contamination, reductive dechlorination is preferred to chemical or biological oxidation, since oxidation would possibly result in the generation of dioxin-like products (such as PCDDs and PCDFs) (Jackman et al., 1999; Mikszewski, 2004).

2.3.2 Reactions of nZVI with Chlorinated Hydrocarbons

Zero valent iron, as a moderate reducing agent, will react with dissolved oxygen, water and possible contaminants if existing in an aqueous media. These redox reactions with nZVI usually result in an increase of the pH and a decrease of the oxidation-reduction potential (ORP) (Müller and Nowack, 2010). In addition, the reaction with oxygen will lead to an anaerobic environment and the reduction of water will yield hydrogen. The dechlorination of chlorinated organics has been extensively studied by Matheson and Tratnyek (1994), Orth and Gillham (1995), Farrell et al. (2000), as well as Deng and Hu (2002). The reaction taking place in this process is as follows:

$$Fe^0 + \mathrm{R-Cl} + H_3O^+ \rightarrow Fe^{2+} + \mathrm{R-H} + Cl^- + H_2O$$

This reduction reaction occurs when electron at the iron surface are transferred to degrade the chlorinated compounds. According to Deng and Hu (2002), surface-bound Fe^{2+} is also capable of reducing chlorinated compounds (Deng and Hu, 2002). There are two pathways for the chlorinated hydrocarbons to be degraded by nZVI (Karn et al., 2009). One pathway is hydrogenolysis through sequential dechlorination, namely, one chlorine atom is removed in each step (Watlington, 2005; Karn et al., 2009). For example, trichloroethylene (TCE) is degraded to dichloroethylene (DCE), then to vinyl chloride (VC), and finally to ethene and ethane (Tratnyek et al., 2003; Cook, 2009). The other pathway is beta-elimination, in which the formation of partially dechlorinated products is

avoided (Watlington, 2005; Karn et al., 2009). In other words, the TCE is directly reduced to ethane; meanwhile some transient itermediates like chloroacetylene and acetylene are produced during the process (Karn et al., 2009; Müller and Nowack, 2010). The latter pathway is described in 70-90 percent of the reactions with nZVI; therefore, it is believed that chlorinated hydrocarbons are degraded primarily through beta-elimination when in direct contact with the nZVI particles (Karn et al., 2009; Tratnyek et al., 2008).

2.3.3 Applications of nZVI-aided Soil Remediation

Although there are not many studies of nZVI-aided PCB dechlorination in soil, some encouraging results are obtained from laboratory experiments. Wang and Zhang (1997) studied and compared PCB dechlorination by synthesized nZVI particles and commercial iron powders, as well as pure nano iron particles and nanoscale palladized iron particles at ambient temperature (Wang and Zhang, 1997). Their results showed that freshly synthesized nZVI particles were comparatively more reactive than commercial iron powders; complete dechlorination of PCB mixtures were observed within 17 hours in the presence of nanoscale Pd/Fe bimetallic particles, while the PCBs were partial dechlorinated within the same time period in the presence of pure nZVI particles. Wang and Zhang explained that was possible because pure nZVI particles tend to agglomerate and adhere to the soil surfaces, and thus, their mobility underground is limited. Lowry and Johnson's (2004) research demonstrated that the nZVI particles were able to dechlorinate PCBs to lower chlorinated congeners, but no completion of PCB dechlorination was noted in their experiments (Lowry and Johnson, 2004). Yak et al. utilized nZVI and subcritical water extraction (SWE) to dechlorinate and transport PCBs under 250 ℃ temperature and 10MPa pressure from soils and sediments. The results

revealed that the PCBs with higher chlorine content were completely degraded into lower chlorinated congeners which were almost dechlorinated into biphenyls thereafter (Yak et al., 1999). In the research of Varanasi et al. (2007), 95% destruction efficiency was achieved when a 300 ℃ high temperature was applied. Besides temperature, pH is another key factor that could have much influence on PCB dechlorination. Experiments conducted by Wang et al. (2012) revealed that acid environment could result in a higher dechlorination rate.

In situ applications of nZVI particles form a mixture with water prior to being injected as slurry into the subsurface contaminated plume (Zhang, 2003; Watlington, 2005). On the other hand, the nZVI slurry can also be employed in ex situ reactors for the treatment of soil, sediment and solid waste (Mikszewski, 2004; Zhang, 2003). Field scale tests have been carried out on the degradation of several chlorinated organics such as PCE, TCE, DCE and TCA; however, few studies have been performed at contaminated sites regarding PCB dechlorination. Lowry et al. (2004) tested PCB dechlorination aided by micro and nano scale ZVI. Micro ZVI particles did not show any dechlorination activity but nZVI did. They also reported that chlorines at *para* and *meta* positions are more preferred for substitution than those at *ortho* positions. Since the lifetime and mobility are limited in subsurface, the nano iron particles have been modified and tested. A metallic catalyst doped nZVI particles, as called bimetallic particles (BNZVI), were used to improve the performance of pure nZVI. As mentioned earlier, Wang and Zhang (1997) have synthesized a type of Pd/Fe nano particles which showed a higher dechlorination rate than nZVI particles. Similar to Pd/Fe, other bimetallic particles such as Ag/Fe and Ni/Fe were synthesized and tested in other studies as well (Xu and Zhang,

2000; Schrick et al., 2002). A field contaminated by PCBs, PCE and TCE was treated by carboxymethyl cellulose (CMC) stabilized nano iron particles in California. The assessment results indicated that the reducing power of nZVI was all consumed after two weeks and a reduction of 87% of PCB concentration was observed in one of the monitor wells during the testing (He et al., 2010). Emulsified ZVI has been developed by the researchers at the NASA Kennedy Space Center and the University of Central Florida to enhance the mobility of nZVI particles. The water-in-oil emulsion is formed by mixing nZVI particles, a biodegradable surfactant and food grade oil together. A field employment of EZVI was performed and demonstrated to significantly and substantially reduce the TCE in both soil and groundwater (Quinn et al., 2005; Hara et al., 2006). The nZVI aided reduction technology has shown a great achievement in the treatment of PCE, TCE, and other chlorinated ethenes; nevertheless, studies on nZVI aided PCB dechlorination remain insufficient. Hence, feasibility of nZVI particles on PCB reduction should be of consideration in current research.

2.4 Biosurfactant-aided Soil Washing

Soil washing systems provide a closed system that remains unaffected by external conditions (Chu and Chan, 2003). It is cost-effective and often combined with other remediation technologies. Additives are critical for soil washing and selected on the basis of their ability to solubilize specific contaminants, and of their environmental and health effects (Feng et al., 2001). Although soil washing can provide a high efficiency when extracting contaminants from the soil, there are still some limitations when dealing with PCBs. One of the constraints is that as PCBs have low water solubility: 0.0027-0.42 ng/L (UNEP, 1997), they are soluble in organic or hydrocarbon solvents, oils and fats. When

applying soil washing technology, PCBs tend to stay in the soils instead of flushing with solvents or water. Since the higher chlorinated biphenyls are less water-soluble than the lower chlorinated ones (Lyons et al., 2013), removal of the high-chlorinated biphenyls in soil will become extremely difficult. It is thus very hard to find an appropriate washing solvent for PCB removal from soil.

2.4.1 Biosurfactants

Biosurfactants are surface-active compounds, and usually are metabolic products or membrane components produced by different types of bacteria, yeasts and fungi when growing on water-insoluble substrates. Since they behave similarly to chemical surfactants, thus, are called biologically produced surfactants (Falatko and Novak, 1992; Mulligan and Gibbs, 1993; Zhang et al., 2008).

Biosurfactants are comprised by a large variety of chemical structures, within which lipids are the major components. The hydrophobic/lipophilic portions of lipids are always the hydrocarbon tails of one or more fatty acids which may be saturated or unsaturated and may contain cyclic structures or hydroxyl functions. The hydrophilic/water-soluble part of a biosurfactant may be from the phosphate portions of phospholipids, a carbohydrate of glycolipids, or a carboxylate group of fatty acids (Georgiou et al., 1992; Zhang et al., 2012).

Same as chemical surfactants, biosurfactants are capable of modifying the interface between polar and nonpolar phases such as oil and water phases or air and water phases by mediating their surface tension. Moreover, biosurfactants can enhance desorption of contaminants like petroleum hydrocarbons from soil, improve the

solubilization in liquid phase, and further increase the concentration of nonpolar compounds in the aqueous solution.

According to their composition, biosurfactants can be classified into glycolipids; fatty acids; neutral lipids and phospholipids; lipopeptides and lipoproteins; and polymeric or particulate biosurfactants (Zhang et al., 2012). Most of the biosurfactants are either negatively charged or neutral. The negative charge usually results from the presence of carboxylate, phosphate or sulphate groups, while amine functions exists in the minority cationic biosurfactants (Cooper, 1986; Cameotra and Bollag, 2003). Different types of biosurfactants and their microbial origin were summarized by Zhang et al. (2012) and shown in Appendix B.

In aqueous solution, surfactants tend to aggregate and form micelles as the concentration reach above the Critical Micelle Concentration (CMC). At this point, a sudden change appears in the solution properties including surface tension, osmotic pressure, viscosity, density and electrical conductivity (Margaritis et al., 1979; Motin et al., 2012). The micelle formation occurs above CMC which affects the solubility of a biosurfactant (West and Harwell, 1992). CMC is, thus, used to estimate the efficiency of a biosurfactant.

Fifty-five novel biosurfactant producers belonging to the genera of *Alcanivorax, Exiguobacterium, Halomonas, Rhodococcus*, *Bacillus*, *Acinetobacter*, *Pseudomonas, and Streptomyces* have been isolated from North Atlantic Canada by Zhang's group at the NRPOP Lab (Cai et al., 2014). These producers are capable of generating biosurfactants in diverse substrates including industrial wastes with facile procedures (Muthusamy et al., 2008). Also, the cold adapted microorganisms are enabled to produce biosurfactants at

low temperature and thus having potential of being applied under diverse conditions including the cold and harsh environments (Cai et al., 2014).

Some of the fifty-five isolated strains can greatly reduce surface tension, stabilizing emulsion, and producing flocculant. Because of the highest yield, the *Bacillus* sp. bacterial strain was selected to generate biosurfactants in this study.

Surfactin, as an acidic biosurfactant produced by Bacillus subtilis, has been well studied and proved to be most potent in the group of lipopeptides and lipoproteins. Their common structure is shown in Figure 2.2. Structure indicates that surfactin consists of 3-hydroxyl-13-methyl-tetradecanoic acid amidated to the N-terminal amine of a heptapeptide. The molecule exhibits excellent surface active properties which are probably attributed to the ionizable side chains of glutamic and aspartic acids (Georgiou et al., 1992).

2.4.2 Advantages of Biosurfactant-aided Soil Washing

Compared with chemical surfactants, biosurfactants have been applied in contaminated soil remediation due to the advantages of low toxicity, high specificity, biodegradability and biocompatibility, and functionality under extreme conditions (Qin et al., 2009; Amaral et al., 2010; Xia and Yan, 2010).

The application of biosurfactants in hydrocarbons-contaminated soil washing is to enhance desorption and slubilization of the pollutants and to increase their mobility in soils. In the studies of biosurfactants, rhamnolipids and surfactin showed a higher removal efficiency of petroleum hydrocarbons (Franzetti et al., 2010). The removal rate could reach up to 80% by adjusting the contact time and biosurfactant concentration. Rhamnolipids show their advance in soil washing: the amount of removed crude oil by

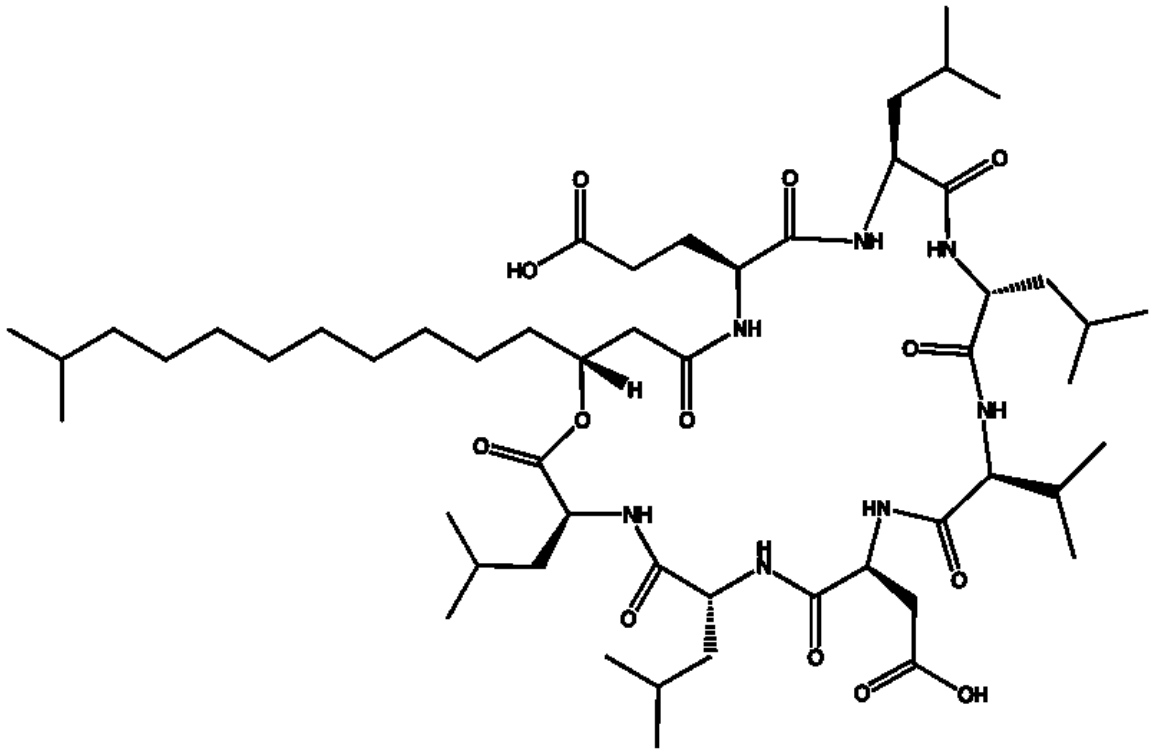

Figure 2.2 Chemical Structure of Surfactin
(Source: Georgiou et al., 1992)

rhamnolipids from the coastline in Alaska after the Exxon Valdez tanker spill were 3 times more than by water alone (Harvey et al., 1990).

The mobilization of oil in soil can be enhanced even the concentrations of biosurfactant are below the CMC (Bustamante et al., 2012). At this concentration, biosurfactants can reduce the surface and interfacial tension between air/water and soil/water systems. The reduced interfacial force would increase the contact angle thus reduce the capillary force that holds oil and soil together. When the concentration of biosurfactant is higher than CMC, the solubilization process dominates (Zhang et al., 2012). Biosurfactants tend to form micelles, which can absorb the hydrophobic oil inside the micelles by hydrophobic ends of biosurfactant molecules and maintain the mobility of micelles by exterior hydrophilic ends. As a result, the solubility of oil is significantly increased.

The low interfacial tension and low CMC property of biosurfactants indicate their great potential as substitutes of traditional chemical surfactants which are usually utilized as additives in soil washing (Georgiou et al., 1992). Several studies have indicated a higher treatment effectiveness of biosurfactant compared to that of chemical surfactant: 10% increase of hydrocarbons was released from soil by rhamnolipids compared with the same concentration of sodium dodecyl sulfate (Dyke et al., 1993); the solubility of PAHs in biosurfactant solution was achieved 5 times higher than chemical surfactant (Cameotra and Bollag, 2003).

A wider applicability of biosurfactants is generally over recognized chemical surfactants: 1) the various structures of biosurfactants can perform a wide variety of physic-chemical properties thus can be adapted to many environmental conditions.

Biosurfactant BL-86, which is generated from the growth of *Bacillus licheniformis* 86, has a composition of lipopeptides (Horowitz et al., 1990). This biosurfactant was tested and appeared to be very stable in the pH level from 4.0 to 13.0, a temperature range from 25 to 120 °C and salinity from 0 to 30% NaCl equivalence. A similar composition can be found in JF-2, which is still active at a temperature up to 75 °C after 140 hours (Lin et al., 1994). Its strong tolerance was also determined in acidic condition. 2) Biosurfactants has lower toxicity than chemical surfactants. The generation of biosurfactant is natural and the process is considered to be non-toxic, whereas most of the synthesized surfactants produced from petroleum have non-negligible toxicity. The synthesis process of sodium dodecylbenzene sulfonate could also generate the corrosive and toxic chemical byproducts (Zhang et al., 2012). Biosurfactants should be much favored when dealing with environmentally sound applications.

The remediation of hydrocarbons by applying biosurfactants could further result in the increase of contaminants' biodegradability (Ron and Rosenberg, 2002). There are two mechanisms for the enhancement of biodegradation: 1) to enhance the substrate bioavailability for microorganisms, and 2) to increase the hydrophobicity of the cell surface thus increase the contact of contaminants. Biosurfactant can also enhance the hydrocarbon biodegradation by reducing the hydrocarbon and water interfacial tension, increasing the surface areas of insoluble compounds, and leading to the increase of mobility and bioavailability of hydrocarbons (Mulligan and Gibbs, 2004; Zhang et al., 2012).

Although limited studies have been documented, applying biosurfactants as the additives in soil washing of PCB-contaminated soil has the following benefits: 1) it would

effectively enhance the solubilization of PCBs in the washing solution, leading to increased removal efficiency; 2) it could stimulate microbial activity and enhance the biodegradation of PCBs which is soil bound (Xia and Yan, 2010). However, although the application of biosurfactants with soil washing can significantly increase the solubility of PCBs that increase the extraction efficiency (Amaral et al., 2010), PCBs that dissolved in the washing solution need to be further treated before releasing into the environment. As persistent organic pollutants, PCBs are hard to be degraded, leading to the costly and complex post-treatment processes before discharge (Xia and Yan, 2010). In addition, a high biosurfactant concentration in the washing solution can cause foaming problems and inhibit the ability to remove PCBs from the soil (USACE, 2010). Effective dechlorination approaches which can be integrated with biosurfactant-aided soil washing and facilitate PCB biodegradation are thus desired.

2.5 Summary

To cleanup soils contaminated by PCBs has been a challenging task since last century. Conventional physical/chemical remedial technologies such as incineration and landfill disposal have been frequently used, but these solutions are disruptive and unsustainable (Agarwal et al., 2007). Thermal desorption, solvent extraction and soil washing as media transfer technologies are able to transfer the PCBs from the contaminated soil to a liquid phase without destroying them. Contrastingly, bioremediation and phytoremediation are environmental friendly technologies which have the ability to destruct PCBs into non-toxic forms. However, the complete destruction usually takes years to decades; thus, bioremediation and phytoremediation are not suitable for heavy contamination. In fact, increasing attention has been received on the

combination of different technologies in recent years. These technologies are generally applied in sequence and many bench scale studies were conducted to improve PCB removal from the contaminated soil such as thermal desorption and catalytic hydrogenation (Aresta et al., 2008), surfactant washing and photocatalytic treatment (Occulti et al., 2008), Pd coated iron and an aerobic bacterium (He et al., 2009), as well as soil washing and TiO_2 photocatalytic degradation (Zhu et al., 2012). Among these studies, no one has tried to combine nanotechnology with biosurfactant-aided soil washing. In this study, an nZVI-aided dechlorination followed by biosurfactant-aided soil washing approach was tested and the corresponding remediation efficiency was investigated. Theoretically speaking, the application of nZVI to the biosurfactant-aided soil washing system could enhance the dechlorination of PCBs and thus: 1) further increase the solubility of PCBs in the washing water, leading to increased remediation efficiency; and 2) resulting in a solution free of PCBs which could be easily treated through the following biological processes.

CHAPTER 3 METHODOLOGY

3.1 nZVI-aided PCB Dechlorination

3.1.1 Materials

1) Soil

Soil used in this research was fine sands purchased from a local company City Sand & Gravel Ltd., St. John's, NL.

2) PCBs

Commercial PCB products are no longer manufactured and traded in Canada. The contaminants used in this study were in the form of transformer oil obtained from Newfoundland Power Inc., St. John's, NL. The overall PCB concentration in the transformer oil was measured to be 120 ppm by Maxxam Analytics.

3) nZVI particles

NANOFER STAR, one kind of commercialized air-stable nano iron powders, was purchased from NANO IRON, s.r.o., Czech Republic.

4) Other materials and chemicals

Other materials and chemicals used in this experiment include: Anhydrous sodium sulfate (ACS reagent); Hexane (CHROMASOLV® Plus, for HPLC, ≥ 95%); Acetone (CHROMASOLV® Plus, for HPLC, ≥ 99.9%); Supelclean™ Sulfoxide SPE Tube (PE frit, bed wt. 3 g, volume 6 mL); Biphenyl-d_{10} (99 atom % D); EPA 525, 525.1 PCB Mix (500 μg/mL each component in hexane, analytical standard); Barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$, ACS reagent, ≥ 99.0%); Magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$,

ReagentPlus®, ⩾99.0%); and Sulfuric acid concentrate (0.1 *M* H_2SO_4 in water (0.2N)). All these were purchased from Sigma-Aldrich Canada Co., ON, Canada.

3.1.2 Experimental Design

3.1.2.1 PCB-contaminated soil preparation

The soil was dried at room temperature for one week and passed through a 2 mm stainless steel sieve to remove any coarse sand and gravel particles as well as to improve the homogeneity before use. Then soil characterization was conducted. After characterization, PCB-contaminated soil was prepared in two 20 L-stainless steel trays. Each tray was filled with 10 kg of soil and 2 L of transformer oil. The soil and oil were mixed thoroughly until it reached a homogenous phase. The trays were then covered with tin foil and stored for one week. After that, the oil in the tray was drained off until there was no fluid in soil, and the soil was ready for nZVI treatment.

3.1.2.2 Air stable nZVI powder activation

Before any experiment, the surface character and crystal structure of these commercial nZVI particles were examined by scanning electron microscopy (SEM) and X-ray Diffraction (XRD) respectively in the Core Research Equipment & Instrument Training Lab (CREAIT) at Memorial University.

For the activation, the air stable nano powder of nZVI was mixed with deionized water at a ratio of 1:4. The mixture was then activated by a Branson Sonifier™ brand digital ultrasonic homogenizer for 2 mins at 50% amplitude (Figure 3.1). The treated mixture was sealed and stored at room temperature for two days before dechlorination experiments.

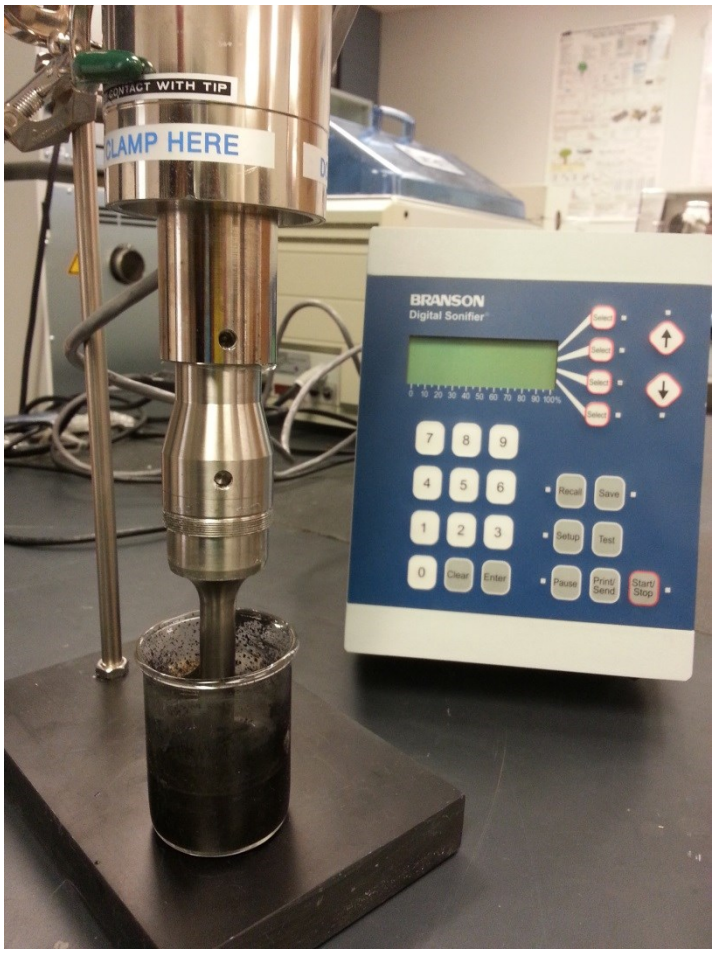

Figure 3.1 nZVI Activation by Ultrasonic Disruptor

3.1.2.3 Effect of nZVI dosage

The effect of the dosage of the commercial nZVI prticles on PCB dechlorination was investigated. nZVI dosages of 5, 7.5, 10, 12.5 and 15 g per kg PCB-contaminated soil were tested. For each dosage, activated nZVI slurry was transferred into a 500 mL wide neck amber glass bottle with 200 g PCB-contaminated soil; and 30 ml deionized water was added as well. The solid and liquid phases were thoroughly mixed and each bottle was covered with a solid-top cap. The homogenous mixture was then stored at room temperature and let the reaction between nZVI particles and PCBs last for 75 days. The soil was sampled at the 1^{st} and the 75^{th} days. The concentrations of different PCB congeners in soil were monitored and analyzed using Agilent 7890A/5975C Gas Chromatograph-Mass Spectrometer (GC-MS). The corresponding congener dechlorination rates were calculated. The selected nZVI dosage for PCB dechlorination was then determined.

3.1.2.4 Effect of pH

The nZVI dosage was selected and the effect of pH on the PCB dechlorination was further investigated. Since there has been a hypothesis stating that protons are essential to the dechlorination and are consumed in the reaction, acidic condition might enhance the dechlorination extent (Varanasi et al., 2007). Hence, this experiment was designed to verify this hypothesis. The experimental procedure was similar to that stated in Section 3.1.2.3. The only difference was to adjust the pH of the homogenous mixture after adding nZVI and deionized water to the contaminated soil. Sulfuric acid was used to achieve different levels of pH. The effect of pH at 2 and 5 were examined through

monitoring the PCB concentrations in soil. The pH for the following experiment was then selected.

3.1.2.5 Effect of temperature

The nZVI dosage and pH were selected, and the effect of temperature on PCB dechlorination was investigated. The experimental procedure was the same as stated in Section 3.1.2.3. The soil mixture after mixing was stored at ovens with different temperatures (0 ℃, 35 ℃ and 100 ℃), respectively, for the whole reaction period. Through monitoring PCB concentration after the reaction under each temperatures, its effect on PCB dechlorination was determined.

3.1.3 Sample Analysis

3.1.3.1 Soil physiochemical characterization

A series of soil properties including particle size distribution, soil pH, bulk density, particle density, pore space, cation exchange capacity, hydraulic conductivity and moisture content were measured. The methods for measuring these properties were listed in Table 3.1 and the detailed procedure was described below. Metal substances in soil were determined using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) by the CREAIT Lab at Memorial University.

1) Particle size distribution

Sieve analysis is usually used for measuring the distribution of particle size. It is generally conducted by shaking the sample in a set of IS sieves until the amount retained on each sieve becomes more or less constant.

2) Soil pH

Soil pH was measured following the EPA Method 9045D:

i. Put 20 g of soil in a 50-mL beaker, add 20 mL of reagent/distilled water. Cover the suspension and continuously stir for 5 min.

ii. Let the soil suspension stand for about 1 hr to allow most of the suspended clay to settle out from the suspension, and then measure the pH of the suspension by using a bench top pH meter.

3) Bulk density, Particle density and Pore space

Bulk density represents the density of the oven dried soil as a whole, which includes solids and pore space. Particle density represents the weight of dry soil per unit volume of the soil solids; the pore space is not included in the volume measurement. In other words, the pore space of a soil is that portion of the soil volume occupied by air and water. It can be calculated based on the values of bulk density and particle density. The bulk density and particle density were measured by using volume replacement method with procedure as follows:

i. Weigh 50 g (W_s) of the dry sand and use a funnel to quantitatively transfer to a 100 mL graduated cylinder.

ii. Carefully tap the cylinder 4 times to settle the sand. Read the volume (V_t) and record on the data sheet. Calculate the bulk density by the equation below:

$$D_b = W_s/V_t$$

Where:

D_b = bulk density (g/cm^3);

W_s = Oven dried mass of the sample (g);

V_t = Total volume of the sample, pore volume + solid volume (cm^3).

iii. Transfer the sand to a container.

iv. Add approximately 60 mL of water to the 100 mL graduated cylinder. Record the exact water volume (V_w) (assume the density of water is 1 g c/m^3).

v. Transfer the 50 g of sand from step 3 back into the cylinder. Stir to remove the trapped air.

vi. Read and record the volume (V_w'). Note the difference in the volume and that in step iv, which is the volume of the sand particles (V_s).

vii. Calculate the particle density by dividing the weight of the sand (50 g) by the volume of the sand particles:

$$D_p = W_s/V_s$$

Where:

D_p = particle density (g/cm^3);

W_s = Oven dried mass of the sample (g);

$V_s = V_w' - V_w$ = Volume of the solids (cm^3).

viii. Calculate the pore space by the following equation:

$$PS = [1 - (D_b/ D_p)]$$

4) Cation exchange capacity (CEC)

The CEC represents the amount of cations a soil sample can hold in an exchangeable form. CEC can be determined by using $BaCl_2$ compulsive exchange method which is developed by Gillman and Sumpter (1986). The detailed procedure is shown below:

i. Weigh each 30 mL centrifuge tube to the nearest mg.

ii. Add 2 g of soil, 20 mL of 0.1 *M* $BaCl_2 \cdot 2H_2O$ to the tube, cap it, and shake the tube for 2 hours.

iii. Centrifuge the tube at about 10,000 rpm and decant carefully.

iv. Add 20 mL of 2 m*M* $BaCl_2 \cdot 2H_2O$ to the tube, cap it, and shake it for 1 hour. Shake it vigorously at first to disperse soil pellet.

v. Centrifuge it again at 10,000 rpm and discard supernatant.

vi. Repeat steps iv. and v. twice. Before the third centrifugation, obtain slurry pH.

vii. After the third decantation of 2 m*M* $BaCl_2 \cdot 2H_2O$, add 10 mL of 5 m*M* $MgSO_4$ to the tube and shake it gently for one hour.

viii. Determine conductivity of the 1.5 m*M* $MgSO_4$ solution. If the conductivity of the sample solution is not 1.5x this value, add 0.100 mL increments of 0.1 *M* $MgSO_4$ until it is (keep track of the amount of 0.1 *M* $MgSO_4$ added).

ix. Determine the pH of the solution.

x. Add distilled water, with mixing, until the solution conductivity is the same as that of the 1.5 m*M* $MgSO_4$ solution.

xi. Wipe outside of the tube, dry and weigh.

xii. Calculate the CEC:

a.) Total solution (mLs) [assumes 1 mL weighs 1 g] = final tube weight (g) - tube tare weight (g) - 2 g [weight of soil used]

b.) Mg in solution (meq) = total solution (mLs) x 0.003 (meq/mL) [1.5 m*M* $MgSO_4$ has 0.003 meq/mL]

c.) Total Mg added (meq) = 0.1 meq [meq in 10 mLs of 5 m*M* $MgSO_4$] + meq added in 0.1 *M* $MgSO_4$ [mLs of 0.1 *M* $MgSO_4$ x 0.2 meq/mL (0.1 *M* $MgSO_4$ has 0.2 meq/mL)]

d.) CEC (meq/100g) = (c - b) x 50 [Total Mg added - Mg in final solution; 50 is to convert from 2 g of soil to 100 g]

5) Hydraulic conductivity

This parameter was tested following the ASTM D2434-68(2006) method which is developed according to the Darcy's Law. The apparatus used here is permeameter. A scheme of the device used is shown in Figure 3.2. The procedure is stated below:

i. Measure the inside diameter of upper and lower chambers. Calculate the average inside diameter of the permeameter (D).

ii. Mix the soil with a sufficient quantity of distilled water to prevent the segregation of particle sizes during placement into the permeameter. Add enough water so that the mixture flowed freely.

iii. Use a scoop to pour the prepared soil into the lower chamber and a tamping device to compact the layer of soil. Repeat the compaction procedure until the soil is within 2 cm of the top of the lower chamber section.

iv. Continue the placement operation of the upper chamber and secure the cap firmly with the cap nuts.

v. Measure the sample length at four locations around the circumference of the permeameter and compute the average length. Record it as the sample length.

vi. Adjust the level of the funnel to allow the constant water level in it to remain a few inches above the top of the soil.

vii. Connect the flexible tube from the tail of the funnel to the bottom outlet of the permeameter and keep the valves on the top of the permeameter open.

viii. Place tubing from the top outlet to the sink to collect any water that may come out.

ix. Open the bottom valve and allow the water to flow into the permeameter.

x. As soon as the water begins to flow out of the top control (deairing) valve, close the control valve, letting water flow out of the outlet for some time.

xi. Close the bottom outlet valve and disconnect the tubing at the bottom. Connect the funnel tubing to the top side port.

xii. Open the bottom outlet valve and raise the funnel to a convenient height to get a reasonable steady flow of water.

xiii. Allow adequate time for the flow pattern to stabilize.

xiv. Measure the time it takes to fill a volume of 750 – 1,000 mL using the graduated cylinder, and then measure the temperature of the water. Repeat this process three times and compute the average time, average volume, and average temperature. Record the values as t, Q, and T, respectively.

xv. Measure the vertical distance between the funnel head level and the chamber outflow level, and record the distance as Δh.

xvi. Repeat step xii. and xiii. with different vertical distances.

xvii. Calculate the permeability, using the following equation:

$$K_T = QL/At\Delta h$$

Where:

K_T = coefficient of permeability at temperature T, cm/sec;

L = length of specimen in cm;

t = time for discharge in sec;

Q = volume of discharge in cm^3 (assume 1 mL = 1 cm^3)

A = cross-sectional area of permeameter = $(\pi/4)\cdot D^2$

Δh = hydraulic head difference across length L, in cm of water.

Table 3.1 Soil Properties Measurement and Their Corresponding Detection Methods

Properties	Method
Particle size distribution	Sieve analysis
Soil pH	USEPA 9045D
Bulk density, Particle density and Pore space	Volume replacement method
Cation exchange capacity	$BaCl_2$ Compulsive Exchange Method
Hydraulic conductivity	ASTM D2434-68(2006)
Moisture content	ASTM D2216-10
Metals	ICP-MS

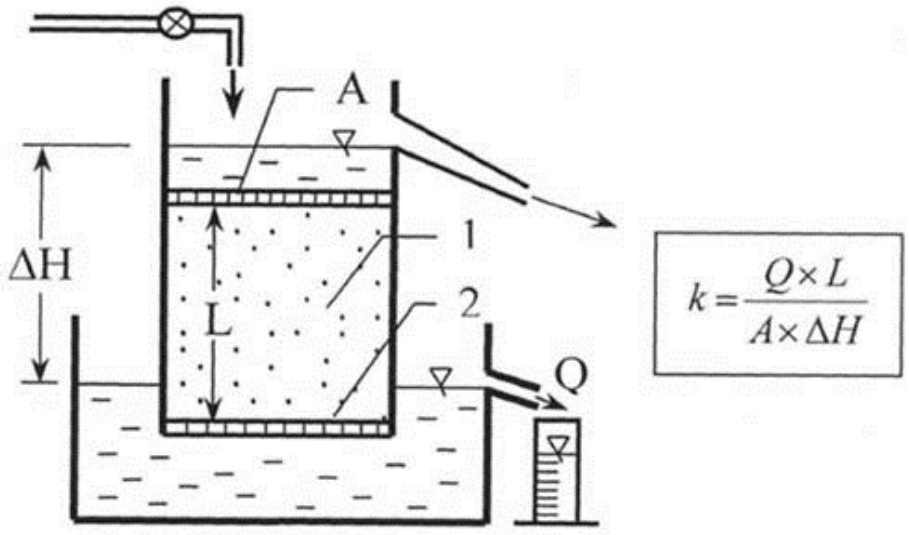

Figure 3.2 A Scheme of a Measurement Test-Stand in the Constant-Head Method
(Source: Sobolewski, 2005)

6) Moisture content

Moisture content of the soil was determined following ASTM D2216-10 method. A test specimen is dried in an oven at a temperature of 110 ± 5°C for at least two hours to a constant mass. The loss of mass due to drying is considered to be water. The water content (%) is calculated through dividing the mass of water by the total mass of the original specimen.

3.1.3.2 Analysis of PCB in soil

Soil samples were taken at the 1st and 75th days to estimate the change of PCB concentrations. The PCBs in each soil sample were first extracted into the solvent phase through ultrasonic extraction. Then, the extracts were cleaned up and concentrated by conducting solid phase extraction (SPE). Finally, the concentrates were examined by GC-MS. All the samples were treated and analyzed in duplicates. The detailed methodology is described as follows.

1) Ultrasonic extraction

EPA method 3550B was used as a guide for ultrasonic extraction. A modification of the method was conducted to achieve a better testing performance. Two grams of soil sample was transferred to a 30 mL beaker. Two grams of anhydrous sodium sulfate was added to the sample and the solution was well mixed. Two surrogates, 500 µL 10 ppm biphenyl-d_{10} and 200 µL 10 ppm EPA 525, 525.1 PCB Mix, were spiked to the sample. A hexane solvent of 9.3 mL was immediately added to the matrix in order to bring the final volume to 10.0 mL. This was followed by disrupting the sample with a Branson Sonifier^{TM} brand ultrasonic probe for 2 minutes at 50% amplitude. After ultrasonic extraction, 1 mL extract was filtered by glass wool and ready for SPE cleanup.

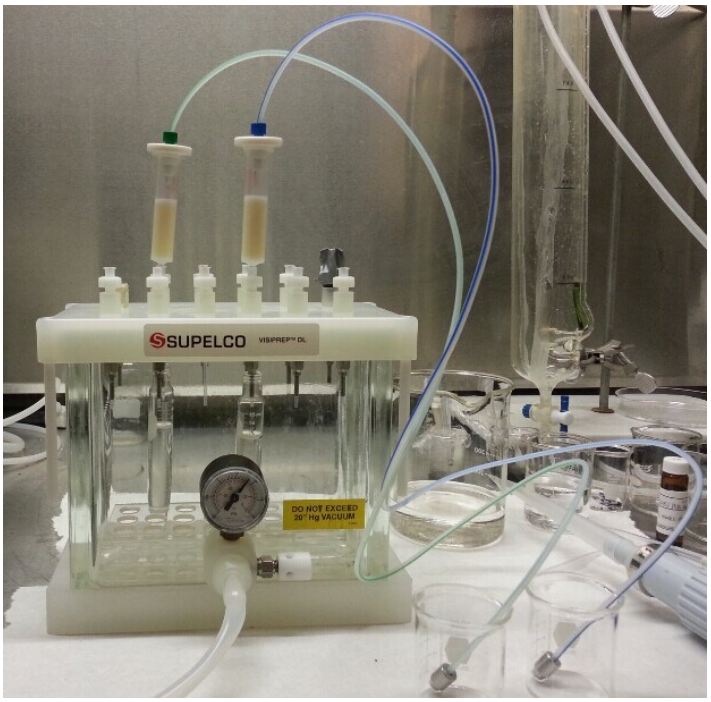

Figure 3.3 Setup of SPE Assembly

2) SPE cleanup

Supelclean Sulfoxide SPE cartridges purchased from Sigma-Aldrich were used for transformer oil cleanup. The SPE normal procedure of conditioning, loading, washing and elution was followed. The conditioning was accomplished by eluting 10 mL of acetone to remove residual moisture from the supelclean sulfoxide cartridges. This was followed by adding 20 mL of n-hexane to equilibrate the cartridges. The pre-treated 1 mL sample was loaded onto the cartridge and washed with 5.5 mL of n-hexane. Elution was done with 13 mL of n-hexane. The eluate was concentrated to 1 mL by gentle air blow. The cleanup extracts were transferred into GC vials ready for analysis. The setup of SPE is shown in Figure 3.3.

3) GC-MS analysis

Instrumental analysis was performed using an Agilent 7890A/5975C gas chromatograph – mass spectrometer (GC-MS) equipped with an Agilent 7693 autosampler. GC conditions were set up based on EPA method 8082A. A few adjustments were made to ensure no PCB congener was retained in the column. The GC conditions applied are listed as follows:

- Column -- DB-5MS UI, 30 m x 0.53 mm ID, 1.5 μm film thickness;
- Carrier gas -- He, 16 psi;
- Injector temperature – 225 °C;
- Type of injector – splitless;
- Detector temperature – 300 °C;
- Initial temperature – 100 °C, hold 2 min;

- Temperature program – 100 °C to 160 °C at 15 °C/min, followed by 160 °C to 300 °C at 5 °C/min;
- Injection volume – 2 μL;
- Final temperature – 300 °C.

Total ion current (TIC) chromatogram was acquired to examine the changes of PCBs in soil samples. The analysis of each congener and its surrogate was carried out in selected-ion monitoring chromatogram (SIM). The ratio of sample congener response to standard congener response was defined as the relative concentration, which was used in the results and discussion.

3.2 Biosurfactant-aided Soil Washing

3.2.1 Materials

1) Biosurfactants

A *Bacillus* sp. bacterial strain isolated from the Atlantic Ocean (Cai et al., 2014) was cultured to generate biosurfactants in the NRPOP Lab. After culturing and extraction, the crude biosurfactants were separated from the media and characterized through testing the critical micelle concentration (CMC). These crude biosurfactants were then ready for use.

2) Other materials and chemicals:

Other materials and chemicals include Chloroform (CHROMASOLV® Plus, for HPLC, ≥ 99.9%); Methanol (CHROMASOLV®, for HPLC, ≥ 99.9%); Ammonium sulfate ($(NH_4)_2SO_4$, ReagentPlus®, ≥99.0%); Sodium chloride (NaCl, BioXtra, ≥99.5% (AT)); Iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, BioReagent, ≥99%); Monopotassium

phosphate (KH_2PO_4, ⩾ 99%); Dipotassium hydrogenphosphate (K_2HPO_4, ⩾ 99%); Sucrose (BioXtra, ⩾ 99.5%); Select yeast extract; Zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$, BioReagent); Manganese(II) Sulfate Tetrahydrate ($MnSO_4 \cdot 4H_2O$, BioReagent); Boric acid (H_3BO_3, BioReagent, ⩾99.5%); Copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, BioReagent, ⩾ 98%); Sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$, ACS reagent, ⩾ 99%); Cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, BioReagent); EDTA (Ethylenediaminetetraacetic acid, ACS reagent); Nickel(II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, BioReagent); and Potassium iodide (KI, BioXtra, ⩾99.0%). All of them were purchased from Sigma-Aldrich Canada Co., ON, Canada.

3.2.2 Experimental Design

3.2.2.1 Batch-scale washing system design and setup

The experimental setup used to perform soil washing experiments consists of a washing fluid reservoir, a soil column, a peristaltic pump and an effluent collection system. The peristaltic pump contains variable speed drives that can run from 0.4 to 85.0 ml/min. The soil column is made of glass to avoid any interference from phthalate esters when contacting with plastic materials, and with a cylindrically diameter of 19 mm and 15 cm in length. The column was packed with 25 g of nZVI-treated soil and the outlet end of the column was fitted with glass beads and glass wool to prevent soil loss during washing. The system assembly is shown in Figure 3.4.

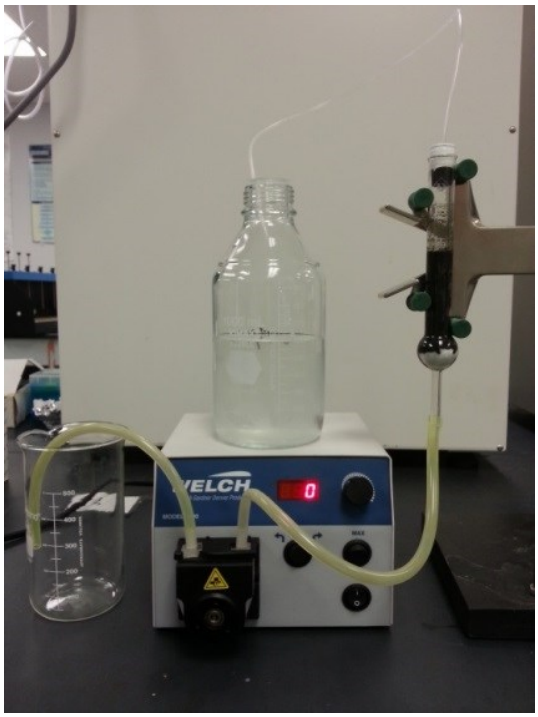

Figure 3.4 Soil Washing System Assembly

3.2.2.2 Biosurfactant production and washing fluid preparation

The bacteria used to generate biosurfactant were isolated from the Atlantic Ocean recently. Till now, no commercial biosurfactant products associated with this strain were available. Thus, biosurfactants need to be produced before conducting washing experiments. For the media and cultivation conditions, a medium modified from Peng et al. (2007) was used, which contains the following composition (g/L): sucrose (10), KH_2PO_4 (3.4), K_2HPO_4 (4.4), $(NH_4)_2SO_4$ (10.0), $FeSO_4 \cdot 7H_2O$ (2.8×10^{-4}), NaCl (2.2), $MgSO_4 \cdot 7H_2O$ (1.02), yeast extract (0.5), and 0.5 mL of trace element solution including (g/L): $ZnSO_4 \cdot 7H_2O$ (2.32), $MnSO_4 \cdot 4H_2O$ (1.78), H_3BO_3 (0.56), $CuSO_4 \cdot 5H_2O$ (1.0), $Na_2MoO_4 \cdot 2H_2O$ (0.39), $CoCl_2 \cdot 6H_2O$ (0.42), EDTA (1.0), $NiCl_2 \cdot 6H_2O$ (0.004) and KI (0.66). Cultivations were performed in 1 L Erlenmeyer flasks containing 750 mL medium at 30°C, and stirred in a rotary shaker for 7 days. Enriched culture medium after 7 days was centrifuged at 10 000 rpm for 10 min, and the supernatant layer was extracted using chloroform-methanol (1:2) on a magnetic stirrer for 8 hours. The solvent layer was separated from the aqueous phase and the solvent was removed by rotary evaporation at 40°C and 60 rpm under reduced pressure.

3.2.2.3 Effect of nano iron particles on soil washing

Parallel experiments were conducted to investigate the effect of nano iron particles on soil washing treatment. Both of the PCB-contaminated soil samples treated with 7.5 g/kg and without nZVI particles were loaded into the washing columns respectively, to test whether the presence of nano particles would have any effect on soil washing. Twenty-five grams of the soil was washed with deionized water in a down flow mode for 1.5 hours at a steady flow rate controlled by the peristaltic pump. The change of

PCB concentrations in soil was determined by measuring each soil sample before and after washing.

3.2.2.4 Effect of biosurfactant concentration on soil washing

The CMC of the resulting crude biosurfactants was determined through measuring the surface tension in accordance with ASTM D1331-14 method.

The surface tension of a crude biosurfactant solution was measured by using Du Noüy Tensiometer to determine CMC. The method procedure is described below.

i. Attach the ring to the lever arm.

ii. Fill a wide mouth clear glass jar (55 mm OD x 48 mm H) with a minimum depth of 1.0 cm biosurfactant solution.

iii. Place the glass jar on the sample table. Raise the sample table assembly until the ring is immersed approximately 5 mm into the liquid. Ensure that the ring is roughly centered in the test jar. Lower the sample table assembly until the ring is just below the surface of the solution.

iv. Use the fine adjustment screw, continue lowering the table until the ring is just within the surface of the solution, with the index reading still at approximately zero.

v. Gradually increase the torsion of the wire while slowly lowering the table; this balance of forces will keep the index reading at zero even as the surface of the solution is distended by the removal of the ring. Continue this step until the solution film breaks, and the ring breaks free.

vi. The scale reading at the breaking point of the solution film is the force of the pull exerted on the ring, or the apparent surface tension.

The CMC value of the crude biosurfactants was estimated by the surface tension curve over a wide concentration range. They were determined by noting the concentrations at which the surface tension reaches the minimum.

After the CMC of the crude biosurfactants was determined, 25 g of the PCB-contaminated soil pre-treated by nZVI particles under selected dosage, pH and temperature was loaded into the washing column. The crude biosurfactants were diluted into different concentrations (0.25%, 0.5% and 3%) with deionized water and injected in the column as the washing fluid. The soil was washed in a down flow mode for 3 hours at a steady flow rate controlled by the peristaltic pump. The washing effluents were sampled at 0, 10, 20, 30, 60, 90, 120 and 180 minute of washing to investigate the change of PCB concentration with time. The change of PCB concentration in soil was determined by measuring the soil sample before and after washing. After the experiment, an concentration of biosurfactant solution was then selected for the following experiment.

3.2.3 Sample Analysis

3.2.3.1 Analysis of PCB in water

The PCB concentration in liquid phase was analyzed using modified Liquid-Liquid Micro-Extraction (LLME) (Zheng et al., 2012) followed by the GC-MS analysis. For modified LLME, 25 μL of 10 ppm biphenyl-d_{10} and 10 μL of 10 ppm EPA 525, 525.1 PCB Mix were spiked as surrogates to each 10 mL water sample (25 ng/L biphenyl-d_{10} and 10 ng/L EPA 525, 525.1 PCB Mix aqueous solution), which was treated by vortex mixing for 10 sec. This was followed by adding 500 μL of hexane and the vortex mixing for 1 min. The water sample was then centrifuged at 4,000 rpm for 5 min. Ten μL of

extract was transferred to micro vials for GC analysis. Conditions for GC-MS analysis were the same as those stated in nZVI dechlorination experiments.

3.2.3.2 Analysis of PCB in soil

PCB concentration in soil was determined following the methodology described in Section 3.1.3.2.

3.3 QA/QC Plan

Four PCB congeners with high abundance in the transformer oil were set as the target analytes. Each analytical method was calibrated using the standards of PCB congeners with different concentration levels (10, 5, 2, 1, 0.5, and 0.2 ppm), and the linearity was determined. Each sample was analyzed for three times so as to determine the PCB recovery and the repeatability of analytical methods. The results were listed in Table 3.2.

Results in Table 3.2 indicated that the analytical methods show good linearity with all the coefficients of the calibration curves using available standards higher than 0.999. The recoveries were in the range between 72% and 82% which were acceptable (Anastassiades et al., 2009). The repeatability was good with all RSD lower than 9%. All the analytical data shown in PCB dechlorination and soil washing experiments were averages generated from duplicated analysis.

Table 3.2 Linearity, Recovery and Repeatability of the Analytical Methods

Congener	GC-MS Linearity (0.2-10 ppm)	Soil Sample Recovery (%)	Repeatability RSD (%)
Penta-17.8	N/A	N/A	8.82
Penta-18.7	>0.999	72.2	0.64
Penta-20.0	N/A	N/A	8.34
Hexa-20.8	>0.999	81.6	5.52

(N/A: Congener standard unavailable)

3.4 Health and Safety Plan

A PCB management plan, as an operational guideline, was developed and implemented for the purpose of storing PCBs and managing the disposed wastes containing PCBs in the lab. The Department of Health and Safety (DHS) provides campus compliance assistance with PCB management based on the PCB Regulations (SOR/2008-273), which have been widely applied across Canada. The plan specifies the researcher's responsibilities, requirements in laboratory PCB usage, storage and disposal, as well as the spill control. The plan was stated below.

I. Laboratory Researcher Responsibilities

The PI and relevant students are responsible for notifying DHS prior to the use of PCBs in the NRPOP Lab. A DHS representative will then set up an appointment to discuss the precautions and safeguards with the PI.

II. Laboratory Usage Requirements

The laboratory must meet the following PCB usage requirements:

i. The use of sample should be recorded in a usage sheet, with the information of date, names of students and the supervisor, and the PCB quantity.
ii. All the sampling, manipulating and analytical pretreatment activities must be conducted in Fume Hood.
iii. Nitrile gloves should be worn while taking samples. Double Gloves are recommended. Gloves should be changed between different samples to eliminate the chance of cross-contamination.
iv. Lab coat and mask should be worn during the experiments.

v. The fume hood should be cleaned up by applying solvent rinse after experiments to prevent the accumulation of PCBs.

III. Laboratory Storage Requirements

The PCB Regulations (SOR/2008-273) can be used to guide the storage of material containing PCBs. The requirements apply to a solid or liquid product containing PCBs in a concentration of 50 mg/kg or higher (s. 18 (1)) that is in an amount equal to or greater than 100 L if the material is a liquid, or in an amount equal to or greater than 100 kg if the material is a solid; or that is in a lesser amount if the material contains 1 kg or more of PCBs.

Laboratory must meet the following storage requirements:

i. Only authorized person are allowed to access the PCB-contaminated samples.
ii. PCB-contaminated samples should be labelled clearly with the WHMIS labels.
iii. All the PCB samples and wastes should be stored in a secondary containment area such as refrigerators and labeled with the information including the user name, concentration of PCBs, date, MSDS information and protective requirements.
iv. The storage should be inspected at least once every 30 days to ensure that there is no leakage from the container.
v. Doors to storage sites, fencing and other security barriers enclosing storage sites shall be labeled with the Act's certificate of approval number on a sign with 50 millimetres or larger letters and Environment Canada's non-serialized, black and white "ATTENTION PCB" label, measuring 150 millimetres by 150 millimetres, or a reasonable alternative.

IV. Disposal/Request Waste Pickup

The wastes include surplus samples, extracted samples and wastes generated from analytical processing. Any waste contaminated with PCBs at a concentration over the regulatory limit must be treated as a hazardous waste. The analytical processing wastes (pipettes, gloves, kimwipes, weighing dishes, filters, and etc.) and surplus samples should be placed in a zip-lock bag. The liquid waste should be collected in a sealed bottle. The containers should be marked with the WHMIS labels together with the information such as the first date of waste deposed. The request for laboratorial PCB wastes disposal can be completed by forwarding DHS a Hazardous Waste Disposal form. PCB wastes must be sent to a certified disposal facility within nine months.

V.Spill control

The appropriate spill kits will be kept in the lab at all times. In case of a spill, the chemical spill cleanup procedures will be followed and the waste will be collected and stored in a sealed and labeled bag or bottle. An accident investigation report should be completed for every accident which occurs in the NRPOP Lab and DHS should be notified in the meantime.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Method Modification for Analyzing PCBs in Soil and Water

Transformer oil is a liquid that electrically insulates and removes heat from transformers. As a result, PCBs are added to the liquid due to their high flame resistance and electron insulating ability (Erickson and Kaley, 2011). Transformer oil contains a large amount of hydrocarbons (alkanes and aromatic hydrocarbons) and can significantly interfere with the analytic results of PCBs. As shown in Figures 4.1 and 4.2, the high organic content resulted in a baseline wander, thus the analytes could not be effectively isolated and quantified. As a result, the cleanup step was required for sample preparation. There are two cleanup methods that are commonly applied to remove oil from the PCB-containing extracts prior to instrumental analysis. One is oxidation/reduction which usually employs sulfuric acid/permanganate as the oxidizing agent to eliminate any interference caused by the transformer oil (Gill et al., 1995; Dmitrovic et al., 2002); the other is SPE cleanup which can effectively separate the PCBs from the transformer oil by applying different types of adsorbents (Dmitrovic et al., 2002; Motladiile, 2012). Compared with oxidation/reduction, SPE has been used more frequently since it requires less solvent amount, lower cost and time for analysis, and better recoveries and accuracies (Cadocinicov, 2004). Various adsorbents including alumina, florisil, silica gel and sulfoxide have been widely studied during the past decades. Among these adsorbents, sulfoxide has shown reasonable recoveries for all PCB congeners while other adsorbents have selectivity to certain PCB congeners (Motladiile, 2012). Therefore, a Supelclean™ Sulfoxide SPE Tube was applied to clean up the PCB-containing extracts in

this study. The detailed cleanup procedure is described in Section 3.1.3. From Figures 4.1 and 4.2, it can be seen that the tube, which acts as a chromatography column, can effectively separate PCBs from transformer oil; and thus, the extract contained less transformer oil reduced the baseline wander from TIC spectra. In SIM spectra, straight baseline and higher response of targeted compounds were observed after SPE cleanup, leading to a more confident analytic method with enhanced accuracy and higher sensitivity. Additionally, the extract after cleanup would reduce the risk of GC column contamination.

4.2 nZVI-aided PCB Dechlorination

4.2.1 Soil Characterization

Before the nZVI-aided PCB dechlorination experiments, basic soil properties including particle size distribution, soil pH, bulk density, particle density, pore space, cation exchange capacity, hydraulic conductivity and moisture content of the purchased plain soil were measured. The results are shown in Tables 4.1 and 4.2. The plain soil used in this research was mainly composed of sand, which was suitable for soil washing. The bulk density, particle density, pore space, hydraulic conductivity and moisture content are physical properties which can be greatly influenced by soil composition and particle size distribution. The pH of the soil was slight alkalinity, which could result in a higher CEC value. In an environmental context, CEC stands for the ability of soil adsorbing contaminants. The pH and CEC are two important chemical properties which could affect the soil remediation process, thus need to be examined before remediation.

Metal substances of the plain soil sample were characterized by ICP-MS. Table 4.3 displays the analytical results. It is noticed that a high concentration of iron was

present, which was of 33.6 g per kg soil. The addition of nZVI for PCB dechlorination thus would not much influence the composition of soil.

4.2.2 Analysis of PCB Concentrations in the Original Spiked Soil

The concentrations of PCBs in the spiked soil sample were evaluated before conducting the dechlorination and soil washing experiments. Four PCB congeners were selected as analytes due to their high abundances in the transformer oil, namely Penta-17.8, Penta-18.7, Penta-20.0 and Hexa-20.8. The former parts of the names represent the numbers of chlorine atoms in the congener compounds while the latter ones are their corresponding retention times (minutes) in the MS spectra (Figure 4.3). The average response ratios of PCBs to their corresponding surrogates are listed in Table 4.4.

4.2.3 nZVI Characterization and Activation

The commercial nZVI particles were characterized by SEM and XRD prior to their applications in PCB dechlorination in soil. Figure 4.4 shows the SEM image of nZVI particles. It can be seen that the majority of the particles were nearly spherical in shape and uniform in size. The particle size was in the range of 20-100 nm with an average particle size of 50 nm.

Figure 4.5 displays the XRD pattern of the nZVI particles and it proved that there were crystal iron particles existed in the commercial product. The 2θ values of the peaks were compared with the standard data for iron and its oxides such as magnetite and α-Fe. Apparent peak at the 2θ of 44.9° indicates the presence of α-Fe, while other apparent peaks show the presence of iron oxides.

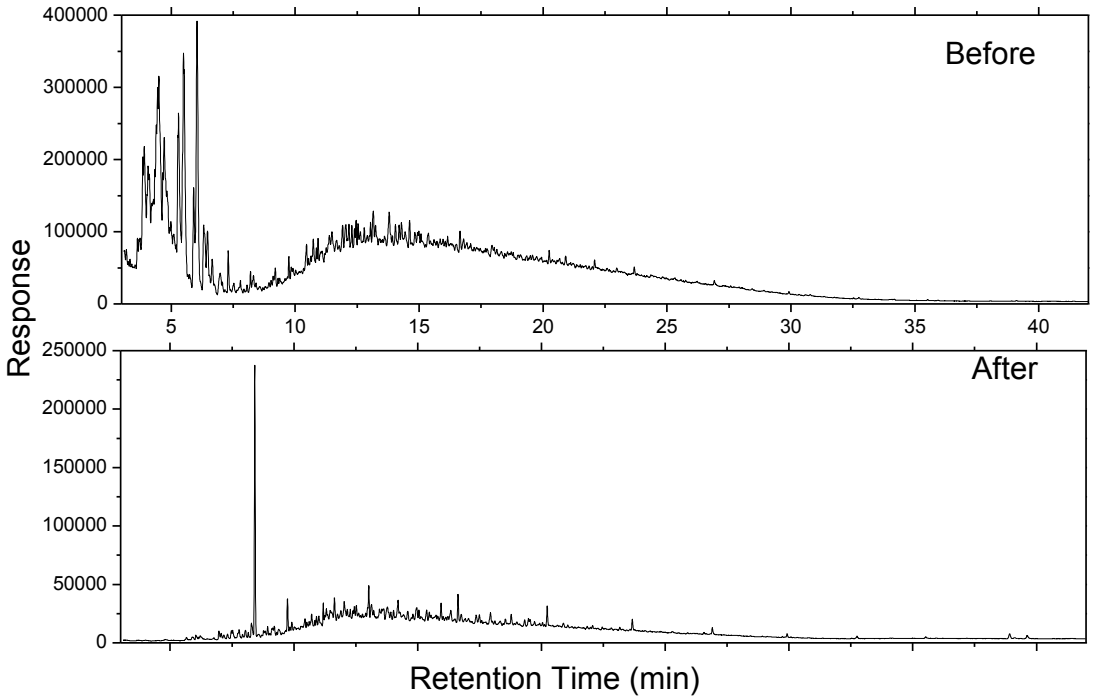

Figure 4.1 The GC-MS TIC Spectra of PCBs in Transformer Oil before and after SPE Cleanup.

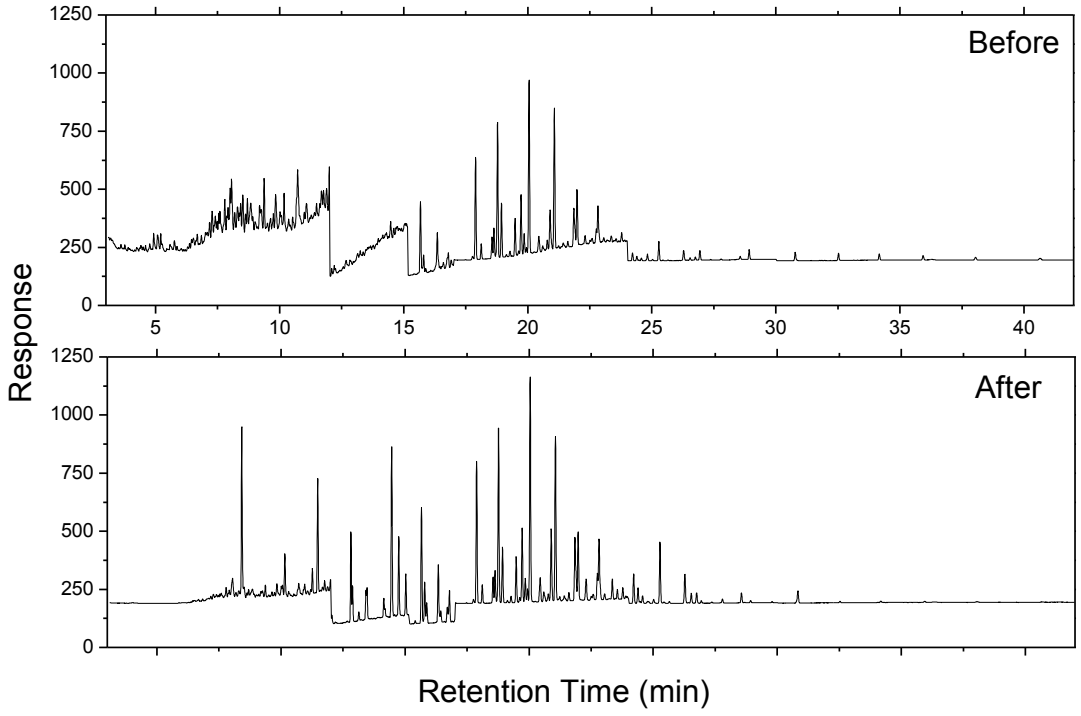

Figure 4.2 The GC-MS SIM Spectra of PCBs in Transformer Oil before and after SPE Cleanup.

Table 4.1 Soil Properties

Properties	Results
Soil pH	7.53
Bulk density	1.78 g/cm^3
Particle density	2.71 g/cm^3
Pore Space	34.3%
Moisture content	0.069%
Cation Exchange Capacity	95.22 cmol/kg
Hydraulic conductivity	0.024cm/s

Table 4.2 Soil Particle Size Distribution Determined by Sieve Analysis

Particle	Diameter (mm)	Size Distribution (%)
Gravel	> 2.0	4.5
Sand	0.05-2.0	92.5
Silt	0.002-0.05	2.5
Clay	< 0.002	0.5

Table 4.3 Metal Substances in the Soil Sample Determined by ICP-MS

Metals	Concentration in soil (mg/kg)
Arsenic	5.306
Barium	643.918
Cadmium	0.146
Chromium	16.815
Copper	13.727
Iron	33,562.114
Lead	17.681
Mercury	< LDL
Nickel	9.142
Selenium	< LDL
Thallium	0.444
Uranium	1.675
Vanadium	46.084
Zinc	71.958

Note: LDL = lower detection limit

Table 4.4 The Initial Relative Concentrations of PCBs in the Spiked Soil

Analytes	Surrogate	Response Ratio
Penta-17.8	2,2',3',4,6-pentachlorobiphenyl	0.384
Penta 18.7	2,2',3',4,6-pentachlorobiphenyl	0.551
Penta-20.0	2,2',3',4,6-pentachlorobiphenyl	0.736
Hexa-20.8	2,2',3',4,6-pentachlorobiphenyl	0.262

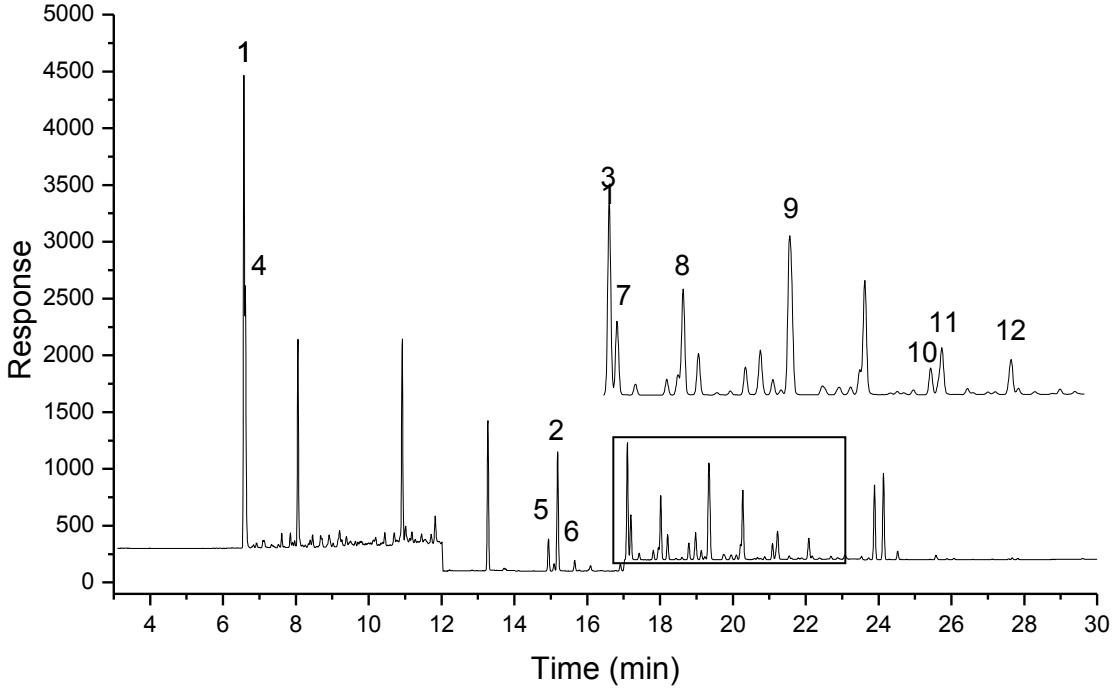

Figure 4.3 GC-MS SIM Spectra of PCBs in Contaminated Soil Sample Spiked with Bipenyl-d10 and EPA 525,525.1PCBs Standard: 1. Biphenyl-d10. 2. 2,2',4,4'-tetrachlorobiphenyl. 3. 2,2',3',4,6-pentachlorobiphenyl. 4. Biphenyl. 5. Tetra-15.6. 6. Tetra-16.3. 7. Penta-17.8. 8. Penta-18.7. 9. Penta-20.0. 10. Hexa-20.8. 11. Hexa-21.8. 12. Hexa-22.8.

The air stable nZVI powder was mixed with deionized water at a mass ratio of 1:4. The slurry solution was then activated by the intensive ultrasound irradiation. Temperature increase was observed during the irradiation, indicating the collision of nZVI particles was significantly enhanced. The air stable film of iron oxide outside of each nZVI particle was thus removed and the activated iron was released. The initial redox potential of the slurry solution was 360 mV and the value was deceased to -300 mV after the activation. The activated nZVI slurry was then mixed with the PCB-contaminated soil.

4.2.4 Natural Attenuation of PCBs

The changes of PCB concentrations in the contaminated soil were tracked on the 1st, 15th and 45th day, respectively, during the natural attenuation process. As depicted in Figure 4.6, the concentrations of all the four congeners did not change significantly within the 45-day period. It illustrated that the dechlorination rates of PCBs during the natural attenuation process was extremely slow. It also proved that the PCBs were not able to be degraded without any additional treatment.

4.2.5 Effect of nZVI Dosage

The performance of PCB dechlorination using different nZVI dosages is shown in Figure 4.7. The trends of the PCB dechlorination rate versus nZVI dosage were similar based on the results of all the four congeners. The overall PCB dechlorination rate was first increased as nZVI dosage increased from 5 to 7.5 g/kg, indicating the increase of nZVI dosage can accelerate the dechlorination of PCBs. The overall dechlorination rate of PCBs was then decreased when the nZVI dosage increased higher than 7.5 g/kg. The maximum dechlorination rates of Penta-17.8, Penta-18.7, Penta-20.0 and Hexa-20.8

during 75 days period were 36.3%, 20.3%, 18.9% and 32.9%, respectively. The results indicated that when choosing 7.5 g/kg as the nZVI dosage, the highest dechlorination rates were achieved in all four congeners. Adding more nZVI particles had shown a negative influence on PCB dechlorination. This was possibly due to the particle aggregation formed during mixing (Müller and Nowack, 2010). Besides the nZVI aggregation, the biotransformation from higher chlorinated biphenyls to lower ones may also affect the PCB dechlorination rate under multiple nZVI dosages. Based on the experimental results, the nZVI dosage of 7.5 g/kg with the best PCB dechlorination performance was selected for the following treatments.

4.2.6 Effect of pH Level

The mechanism of nZVI aided PCB dechlorination was summarized in Section 2.3.2. Generally, soil pH can affect the dechlorination of PCBs. Therefore, two levels of pH were selected to evaluate the effect of pH on PCB dechlorination. The result is shown in Figure 4.8. After 75 days monitoring, the average dechlorination rates of Penta-17.8, Penta-18.7, Penta-20.0 and Hexa-20.8 at pH of 2 were 10.8%, 8.9%, 5.0% and 5.6%, respectively; while their average dechlorination rates at pH of 5 were 11.9%, 11.8%, 6.8% and 6.2%, respectively. The dechlorination rates of each PCB congener were higher at pH of 5 than those at pH of 2. Previous studies have shown that an acid environment with more protons could accelerate the PCB dechlorination (Varanasi et al., 2007). The results of this study led to a different conclusion. It might be because in this case, the protons were sufficient at pH of 5 so that pH was not a dominating effect on PCB dechlorination anymore. In addition, the addition of H_2SO_4 would have more interference with the mass transfer of PCBs from the soil to the iron (Fe) surface (Varanasi et al.,

2007). The pH of 5 was thus selected to be the initial pH condition in the following experiments.

4.2.7 Effect of Temperature

The effect of temperature on PCB dechlorination after 75 days period was investigated with results shown in Figure 4.9. The PCB dechlorination was greatly enhanced when the temperature increased from 0 to 100 ℃. As the temperature increased, the PCB dechlorination of Penta-17.8 improved the most, with a rate change from 10.1% to 34.2%. The dechlorination rates of Penta-18.7, Penta-20.0 and Hexa-20.8 were enhanced from 11.3% to 32.2%, from 9.8% to 29.4%, and from 13.7% to 28.8%, respectively. These results showed that a temperature increase would enhance the mobility of PCBs from the soil to the iron surfaces, and thus, accelerate the dechlorination reaction (Varanasi et al., 2007).

4.3 Biosurfactant-aided Soil Washing

4.3.1 Effect of nZVI Particles on Soil Washing

The effect of the nZVI particles on PCB removal during the soil washing treatment was investigated. Figure 4.10 showed the results. Although the insolubility of PCBs makes their distribution negligible in water phase, the PCBs in the transformer oil could be flushed out of the column due to the high flow rate during direct soil washing without using any biosurfactants. As shown in Figure 4.10, after 1.5 hours of operation, about 18% to 30% of PCBs in the congeners were removed by direct washing of the non-nZVI treated soil.

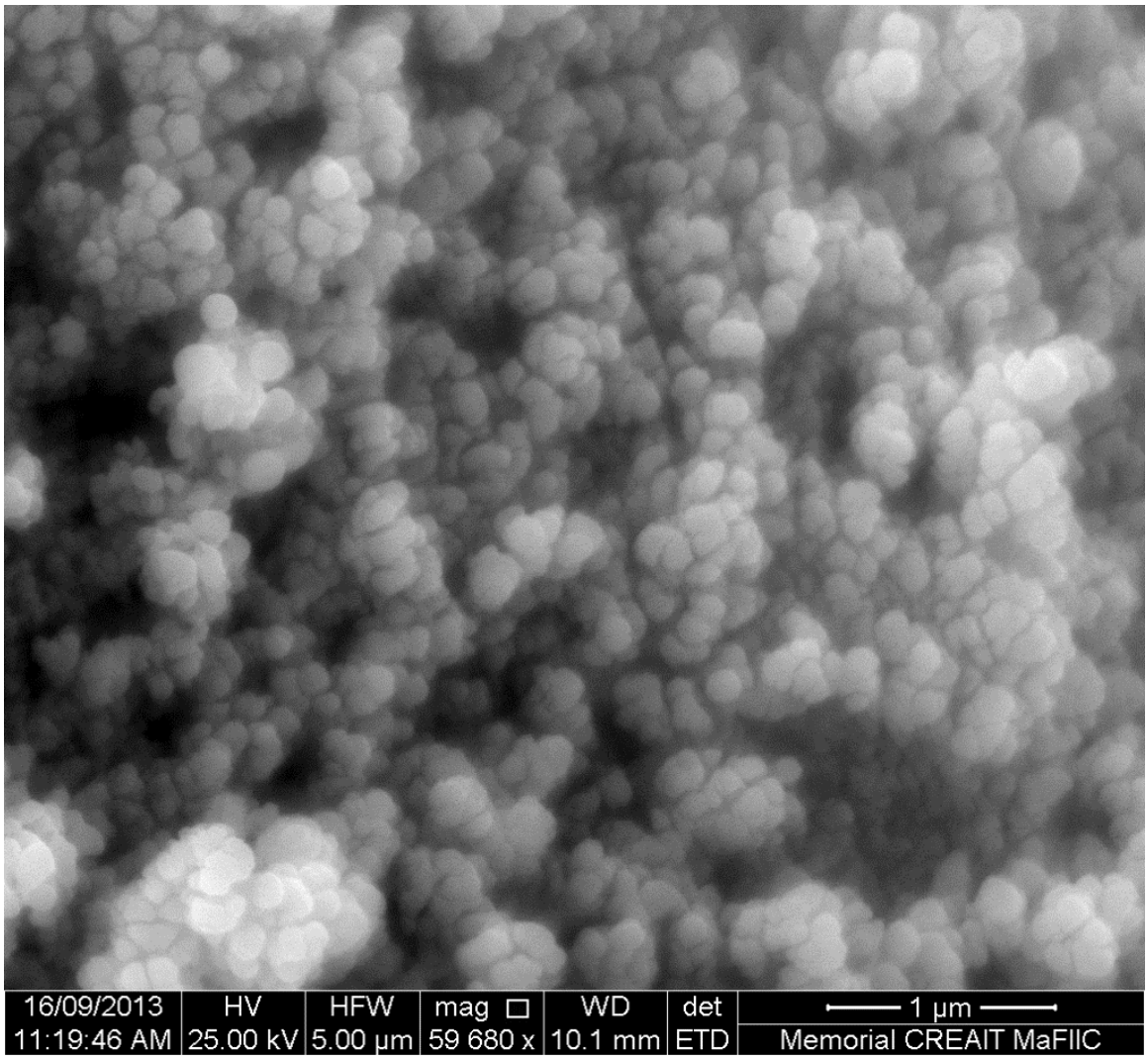

Figure 4.4 SEM Image of the Commercial nZVI Particles

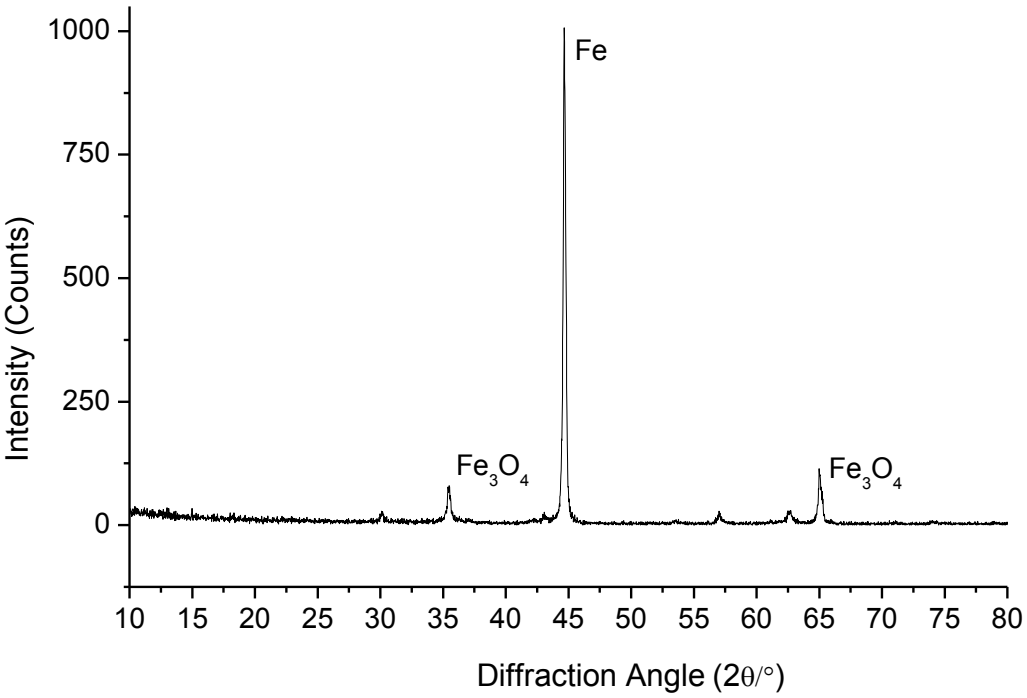

Figure 4.5 XRD of the nZVI Particles

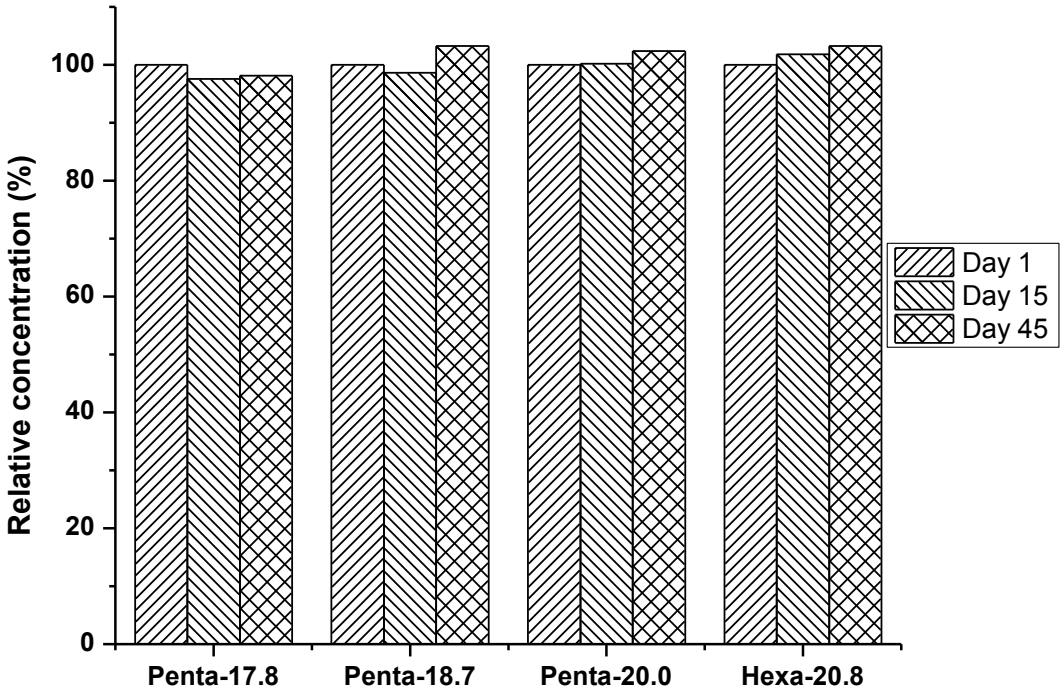

Figure 4.6 Natural Attenuation of PCBs in Contaminated Soil

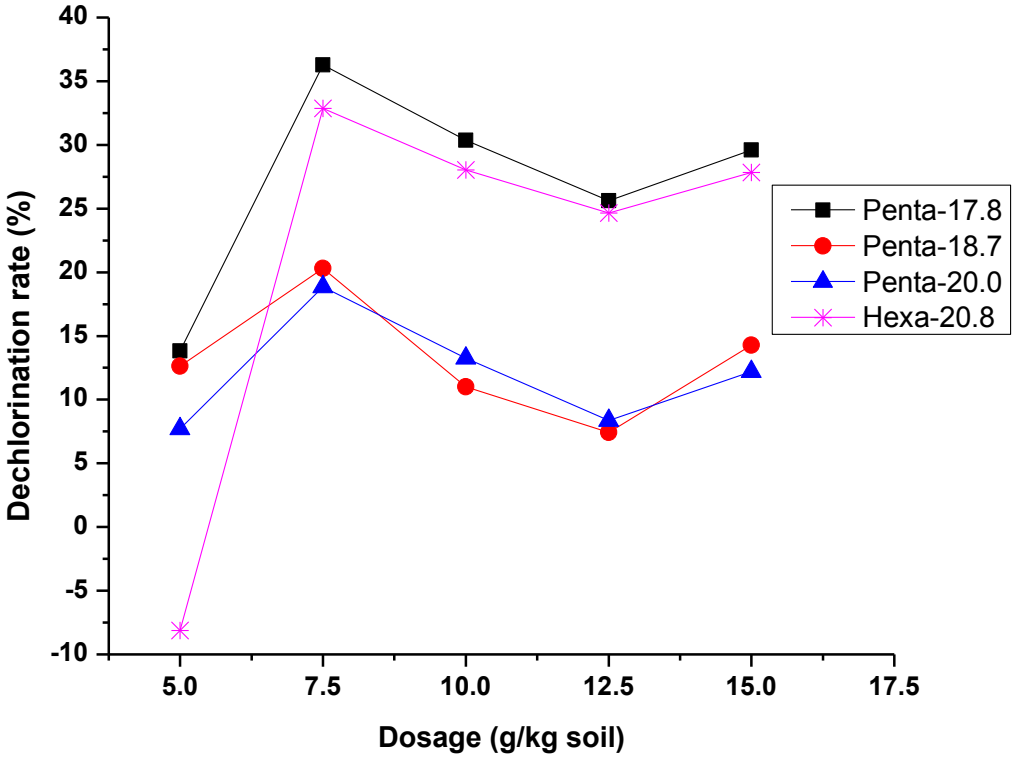

Figure 4.7 Effect of nZVI Dosage on PCB Dechlorination in the Contaminated Soil

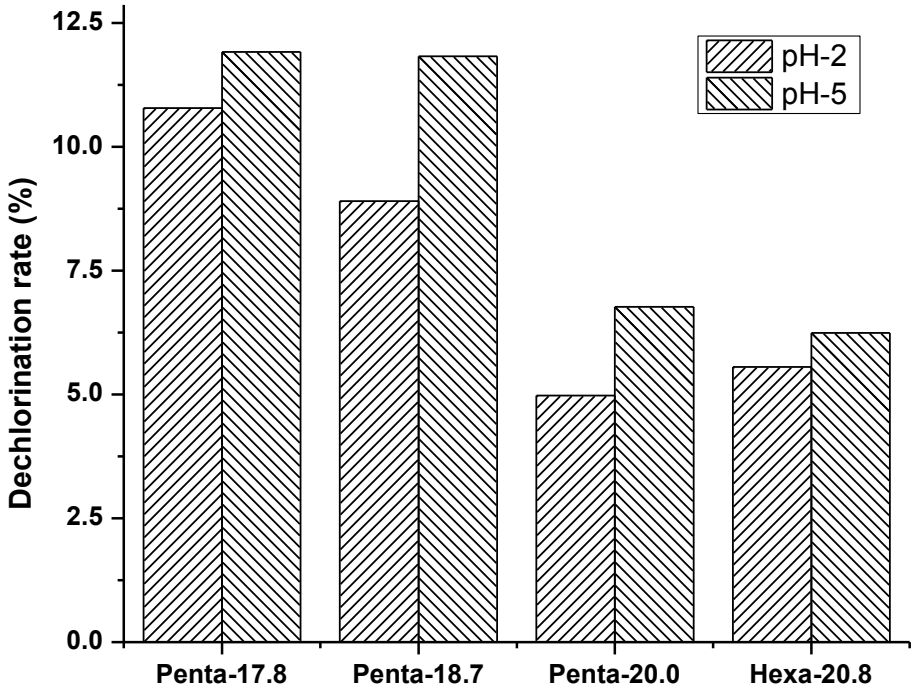

Figure 4.8 Effect of pH on PCB Dechlorination in the Contaminated Soil

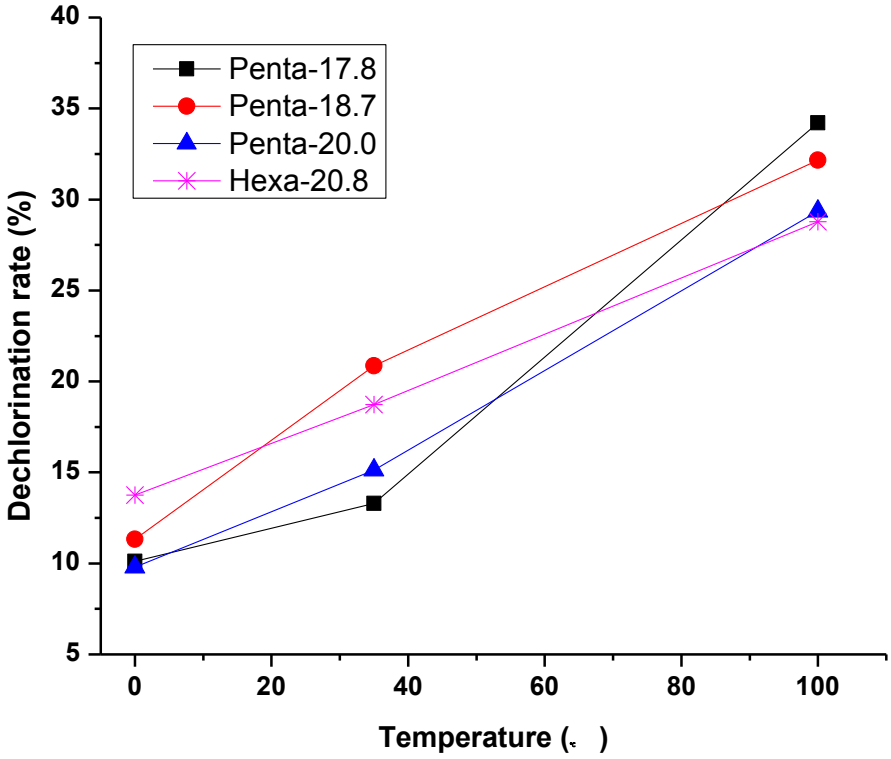

Figure 4.9 Effect of Temperature on nZVI-Aided PCB Dechlorination

After the nZVI aided dechlorination, a red color was observed in the treated soil, implying the formation of ferric hydroxides or ferric oxides. It indicated that the nZVI particles were transferred to their oxidative forms after the reaction. During washing of the nZVI treated soil, the PCB concentration of each congener was significantly decreased. In Figure 4.10, the removal rates of PCBs after washing were between 60% and 62% in the nZVI treated soil. It was illustrated that the treatment by the nZVI particles greatly enhanced the soil washing efficiency. Besides, the presence of nano-scale ferric oxides in the system plays a key role in PCB removal (Hendraningrat and Torsæter, 2014). The contaminated soil trapped a certain amount of transformer oil, and the oil droplets were blocked by the pore throat of soil due to the high interfacial tension between oil and soil (Roustaei et al., 2013). With the presence of nano-scale ferric oxides, the interfacial tension would be reduced and the mobility of oil droplets would be increased (Hendraningrat and Torsæter, 2014). As a result, more oil droplets were desorbed from the soil, resulting in an increased effectiveness of soil washing. This experiment confirmed that the combination of the nZVI-aided dechlorination and soil washing is reasonable and feasible.

4.3.2 CMC of the Crude Biosurfactant

The surface tension of a series of biosurfactant solutions with different biosurfactant concentrations was tracked. The trend of surface tension versus biosurfactant concentration was shown in Figure 4.11. The value of surface tension was decreased sharply till the biosurfactant concentration reached 0.01%. When the biosurfactant concentration was higher than 0.01%, the surface tension changes became

relatively stable. Therefore, the CMC of the crude biosurfactant was determined to be 0.01%.

4.3.3 Effect of Biosurfactant Concentration on Soil Washing

The nZVI treated soil sample was washed by crude biosurfacant solutions. The concentration of crude biosurfactant in the washing fluid was set as 3%, 0.5% and 0.25%. The initial flow rate of the column washing fluid was set within the range of 18-20 mL/min. The results of relative PCB concentrations (the ratio of sample congener response to standard congener response) in column effluent were shown in Figures 4.12 (a) - (c). The elution of PCBs was started at 10 min. The PCB concentrations in effluents were sharply increased and reached their peaks at 15 - 45 min. Steep declines were followed by the peaks and the gentle deduction appeared in the final stage.

The overall PCB removal rates after washing of the nZVI treated soil were examined. As shown in Figure 4.13, the higher concentration of the crude biosurfactant solution was used, the higher the removal rate achieved. The maximum removal rate was found when using 3% crude biosurfactant and 90% of the total four PCB congeners were removed from the soil. The final removal rates using 0.5% and 0.25% crude biosurfactant solutions were 80% and 75%, respectively. The PCB removal rates using all the three crude biosurfactant solution were higher than 75%, indicating the promising effectiveness of biosurfactant-aided soil washing. Compared with the performance of using the 3% biosurfactant solution, the crude biosurfactant solution with concentrations of 0.5% and 0.25% were more cost-effective. Figure 4.12 (b) and (c) showed that, the 0.5% crude biosurfactant solution could remove the majority of the four PCB congeners within 60 minutes; which is faster than the solution with the biosurfactant concentration of 0.25%.

Therefore, 0.5% was selected as an appropriate biosurfactant concentration for further applications.

The SIM spectrum shows the removal of almost all the PCBs in the soil sample after washing. As shown in Figure 4.14, the peaks of PCBs were almost disappeared after washing with 0.5% crude biosurfactant solution, only the peaks of surrogates were left. Besides, the contents of the transformer oil that generated the baseline wander were also removed. As a consequence, the crude biosurfactant solution was able to remove almost all the organic components including PCBs in transformer oil unselectively.

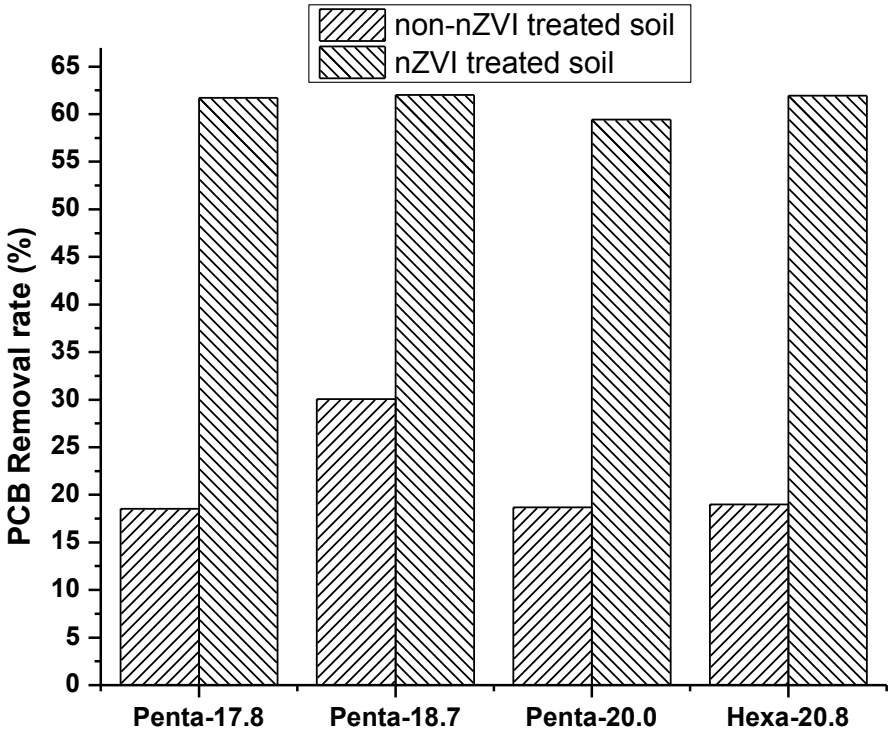

Figure 4.10 Effect of the nZVI Particles on PCB Removal during Soil Washing

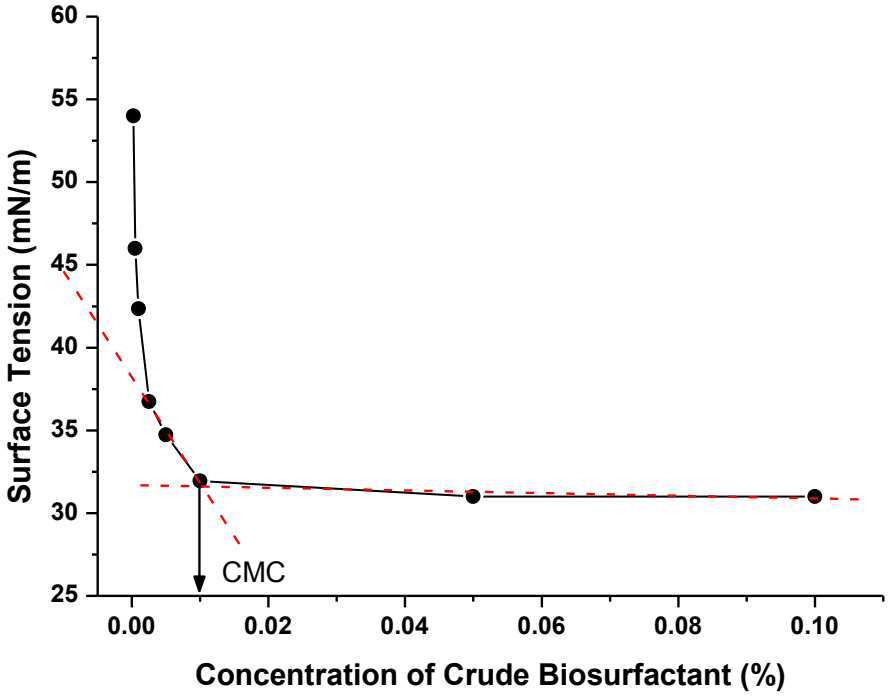

Figure 4.11 CMC of the Crude Biosurfactant

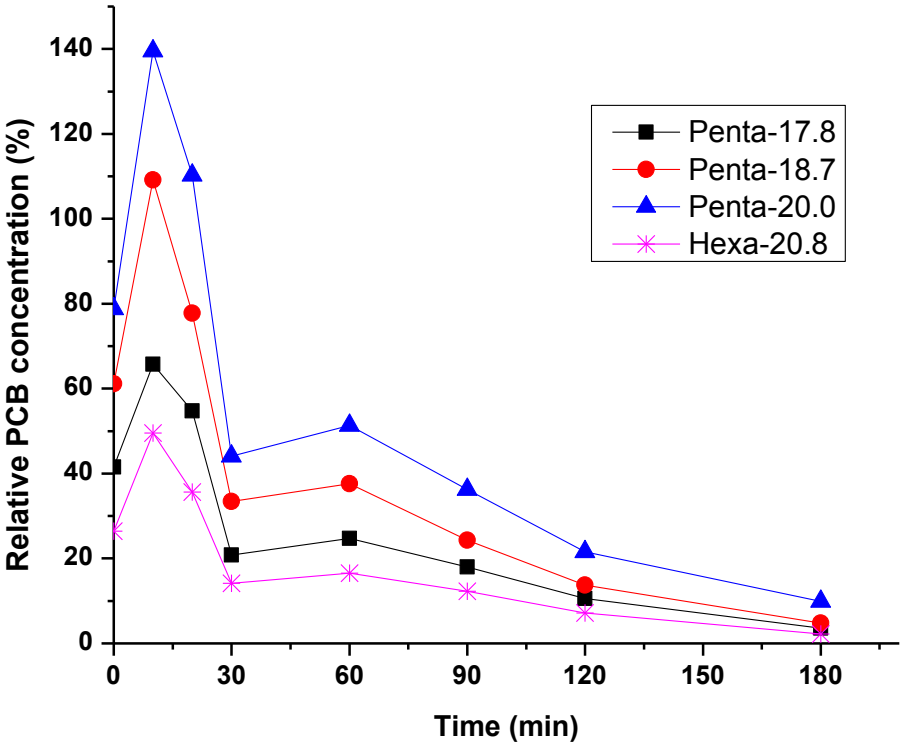

Figure 4.12 - (a) Relative Concentrations of PCBs in Washing Effluent with 3% Crude Biosurfactant Solution

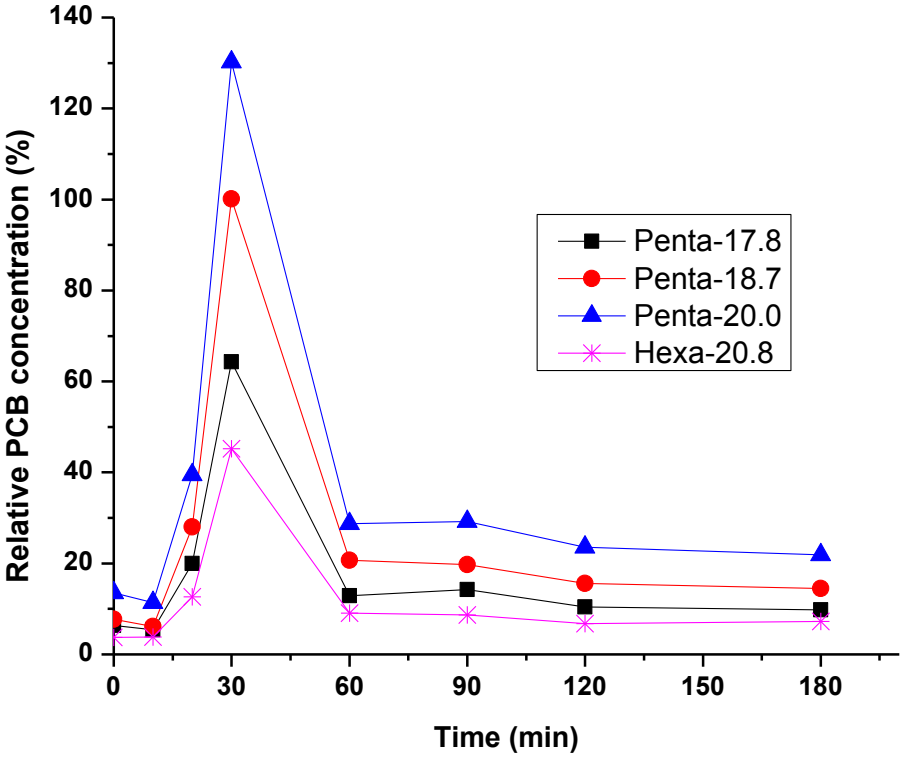

Figure 4.12 - (b) Relative Concentrations of PCBs in Washing Effluent with 0.5% Crude Biosurfactant Solution

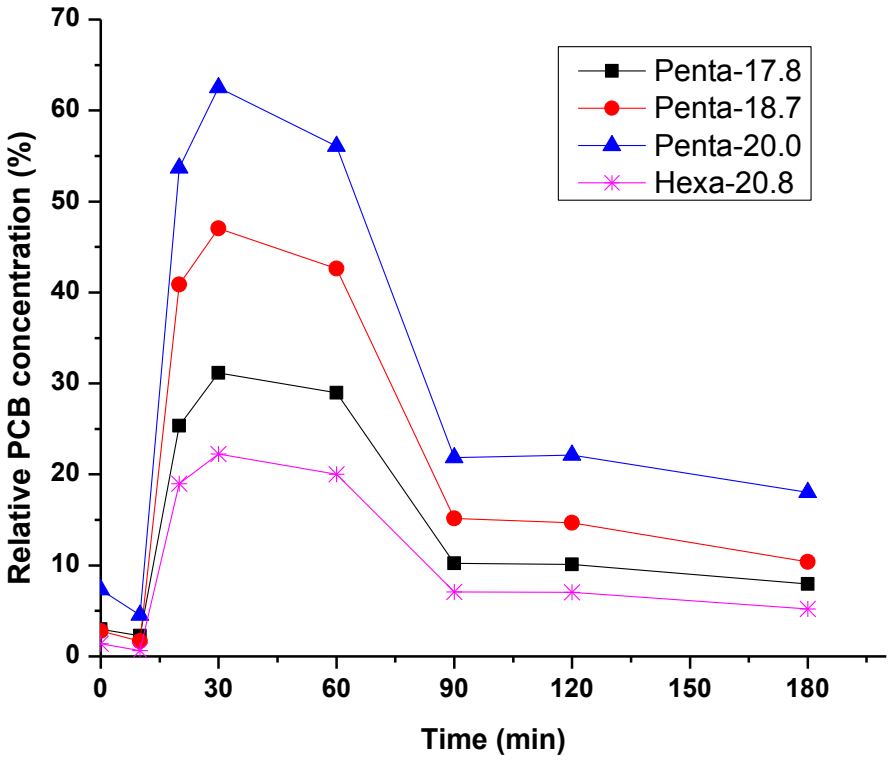

Figure 4.12 - (c) Relative Concentrations of PCBs in Washing Effluent with 0.25% Crude Biosurfactant Solution

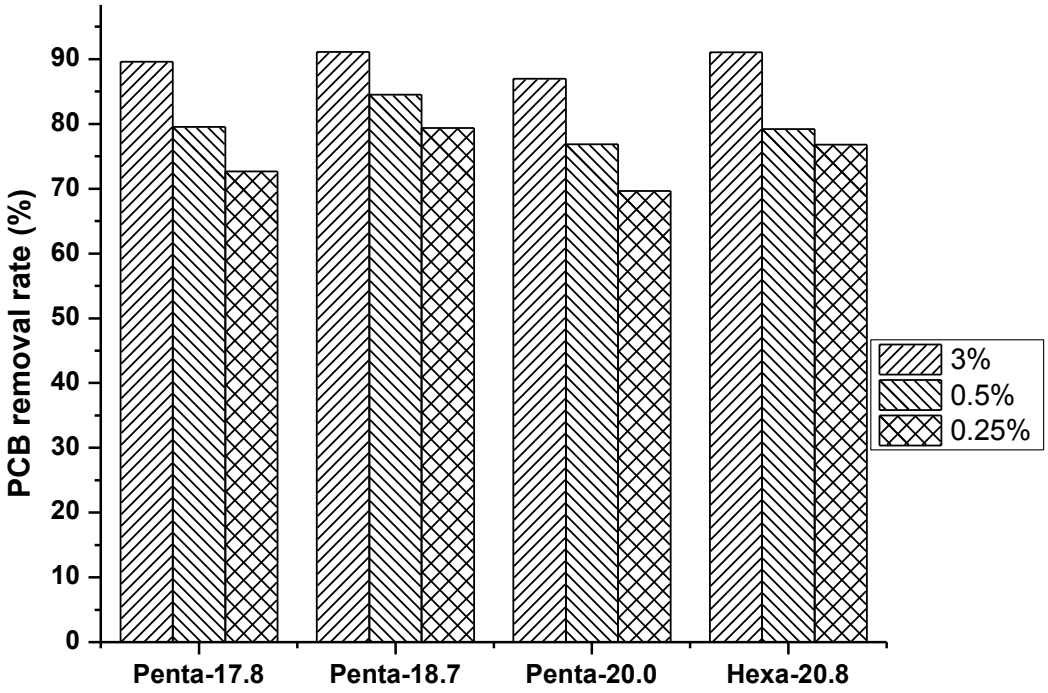

Figure 4.13 The Washing Efficiencies of PCBs in the nZVI Treated Contaminated Soil by Different Concentrations of Crude Biosurfactant Solution

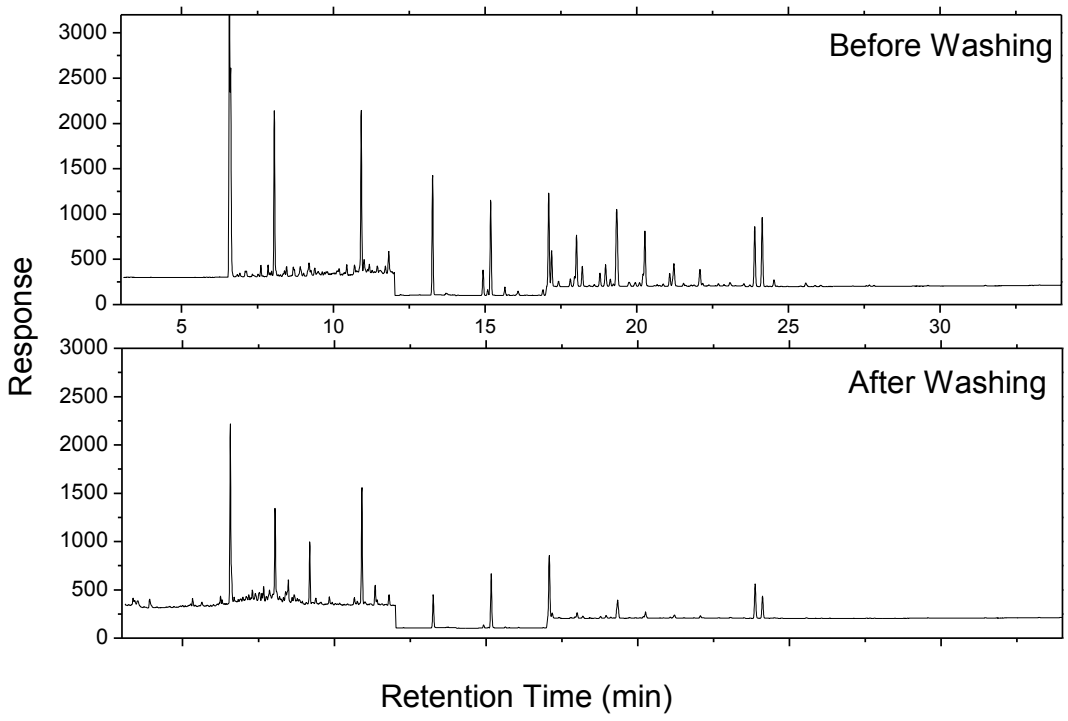

Figure 4.14 GC-MS SIM Spectra of PCBs in the Contaminated Soil before and after Washing by 0.5% Crude Biosurfactant Solution

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

PCBs have been identified as environmental hazards for many years. Due to historical issues, a considerable amount of PCBs can be found deep underground in Canada, such as Happy Valley Goose Bay in Newfoundland and Labrador. To remediate PCB contaminations, this research has focused on the development of a two-step treatment consisting of nZVI-aided dechlorination followed by biosurfactant-based soil washing technology to remove PCBs from soil. The contaminated soil was prepared by mixing the plain soil with PCBs contained transformer oil. Four most abundant PCB congeners were selected and examined as target PCBs to evaluate the effectiveness of nZVI and biosurfactants.

The analyses of PCBs in the soil phase and in the water phase were pre-treated through ultrasonic extraction and liquid-liquid micro-extraction, respectively. The extracts were analyzed by GC-MS. The PCBs were quantified by SIM spectra. A SPE cleanup step has been applied after ultrasonic extraction of soil which showed increased method accuracy and MS response.

In nZVI-aided dechlorination, the effects of nZVI dosage, initial pH and temperature on PCB transformation were evaluated one at a time, respectively. The selected dosage of nZVI was 7.5 g/kg soil. Adding more nZVI particles could have negative influence on PCB dechlorination, since the aggregates could be easily formed as the nZVI dosage increases. An environment with pH lower than 5 did not much influence the removal rates of PCBs, indicating the presence of sufficient protons in the system.

The results showed that the lower pH would actually inhibit the dechlorination by the presence of H_2SO_4, which has an effect on the reduction of mass transfer. An improvement of dechlorination was observed as the temperature increased, since higher temperature would accelerate the dechlorination reaction.

The presence of nZVI particles in the soil washing system plays a key role in PCB removal. They can greatly enhance the soil washing efficiency because the interfacial tension between the oil phase and the soil phase would be reduced and the mobility of oil droplets would be increased.

The crude biosurfactant was produced for the soil washing and its CMC was determined as 0.01%. Consequently, the levels of crude biosurfactant concentration in the washing fluid were set as 0.25%, 0.5% and 3%. The results indicated that the concentrations of PCBs in the effluent were affected by the concentration of biosurfactant, the flow rate and the total volume of washing fluid. Higher biosurfactant concentration could increase the solubilization of PCBs from soil phase to liquid phase. The overall PCB removal rates using all the three crude biosurfactant concentrations (3%, 0.5% and 0.25%) were 90%, 80% and 75%, respectively, indicating the promising effectiveness of this biosurfactant. Compared with the 3% biosurfactant solution, the crude biosurfactant concentration of 0.5% and 0.25% were more cost-effective. The 0.5% crude biosurfactant solution could remove the majority PCBs within a shorter time than the solution with a concentration of 0.25%. Therefore, 0.5% was recommended as an appropriate biosurfactant concentration for furture application.

In conclusion, this study was able to provide a promising treatment technology for PCB-contaminated soil remediation.

5.2 Recommendations

Since this proposed preliminary research did not tackle the interaction effects among different factors, they would be evaluated through using design of experiment in future studies. This would be followed by using response surface methodology to optimize the factor combinations to give the best results. Secondly, it is recommended that various temperature conditions could be examined in soil washing for the harsh environments in the North Atlantic and Artic regions; since the change of temperature is able to affect the formation of CMC, the viscosity of washing solution and transformer oil, and the adsorption and desorption process of PCBs in soil. The internal mass transfer and emulsification inside the column would be evaluated for a better understanding of the performance of biosurfactant and nZVI in the treatment processes. The purification of crude biosurfactant is quite important. The removal of insoluble particles would lead to a better performance of soil washing. At last, the recovery of biosurfactant and nZVI should be considered in the whole treatment process to illustrate the applicability in the field. The toxicity of nZVI to the microbes in the subsurface should be evaluated and the effect of nano iron particles on the transport and fate of PCBs underground should be investigated in future.

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APPENDICES

Appendix A: Table of Chemical Identity of PCB Congeners and Homologs

Congener No.	CAS No.[a]	IUPAC[b] Name
	92-52-4	Biphenyl
	1336-36-3	Polychlorinated biphenyl (PCB)
	27323-18-8	Monochlorobiphenyl
1	2051-60-7	2-Chlorobiphenyl
2	2051-61-8	3-Chlorobiphenyl
3	2051-62-9	4-Chlorobiphenyl
	25512-42-9	Dichlorobiphenyl
4	13029-08-8	2,2'-Dichlorobiphenyl
5	16605-91-7	2,3-Dichlorobiphenyl
6	25569-80-6	2,3'-Dichlorobiphenyl
7	33284-50-3	2,4-Dichlorobiphenyl
8	34883-43-7	2,4'-Dichlorobiphenyl
9	34883-39-1	2,5-Dichlorobiphenyl
10	33146-45-1	2,6-Dichlorobiphenyl
11	2050-67-1	3,3'-Dichlorobiphenyl
12	2974-92-7	3,4-Dichlorobiphenyl
13	2974-90-5	3,4'-Dichlorobiphenyl
14	34883-41-5	3,5-Dichlorobiphenyl
15	2050-68-2	4,4'-Dichlorobiphenyl

	25323-68-6	Trichlorobiphenyl
16	38444-78-9	2,2',3-Trichlorobiphenyl
17	37680-66-3	2,2',4-Trichlorobiphenyl
18	37680-65-2	2,2',5-Trichlorobiphenyl
19	38444-73-4	2,2',6-Trichlorobiphenyl
20	38444-84-7	2,3,3'-Trichlorobiphenyl
21	55702-46-0	2,3,4-Trichlorobiphenyl
22	38444-85-8	2,3,4'-Trichlorobiphenyl
23	55720-44-0	2,3,5-Trichlorobiphenyl
24	55702-45-9	2,3,6-Trichlorobiphenyl
25	55712-37-3	2,3',4-Trichlorobiphenyl
26	38444-81-4	2,3',5-Trichlorobiphenyl
27	38444-76-7	2,3',6-Trichlorobiphenyl
28	7012-37-5	2,4,4'-Trichlorobiphenyl
29	15862-07-4	2,4,5-Trichlorobiphenyl
30	35693-92-6	2,4,6-Trichlorobiphenyl
31	16606-02-3	2,4',5-Trichlorobiphenyl
32	38444-77-8	2,4',6-Trichlorobiphenyl
33	38444-86-9	2,3',4'-Trichlorobiphenyl
34	37680-68-5	2,3',5'-Trichlorobiphenyl
35	37680-69-6	3,3',4-Trichlorobiphenyl
36	38444-87-0	3,3',5-Trichlorobiphenyl

37	38444-90-5	3,4,4'-Trichlorobiphenyl
38	53555-66-1	3,4,5-Trichlorobiphenyl
39	38444-88-1	3,4',5-Trichlorobiphenyl
	26914-33-0	Tetrachlorobiphenyl
40	38444-93-8	2,2',3,3'-Tetrachlorobiphenyl
41	52663-59-9	2,2',3,4-Tetrachlorobiphenyl
42	36559-22-5	2,2',3,4'-Tetrachlorobiphenyl
43	70362-46-8	2,2',3,5-Tetrachlorobiphenyl
44	41464-39-5	2,2',3,5'-Tetrachlorobiphenyl
45	70362-45-7	2,2',3,6-Tetrachlorobiphenyl
46	41464-47-5	2,2',3,6'-Tetrachlorobiphenyl
47	2437-79-8	2,2',4,4'-Tetrachlorobiphenyl
48	70362-47-9	2,2',4,5-Tetrachlorobiphenyl
49	41464-40-8	2,2',4,5'-Tetrachlorobiphenyl
50	62796-65-0	2,2',4,6-Tetrachlorobiphenyl
51	68194-04-7	2,2',4,6'-Tetrachlorobiphenyl
52	35693-99-3	2,2',5,5'-Tetrachlorobiphenyl
53	41464-41-9	2,2',5,6'-Tetrachlorobiphenyl
54	15968-05-5	2,2',6,6'-Tetrachlorobiphenyl
55	74338-24-2	2,3,3',4-Tetrachlorobiphenyl
56	41464-43-1	2,3,3',4'-Tetrachlorobiphenyl
57	70424-67-8	2,3,3',5-Tetrachlorobiphenyl

58	41464-49-7	2,3,3',5'-Tetrachlorobiphenyl
59	74472-33-6	2,3,3',6-Tetrachlorobiphenyl
60	33025-41-1	2,3,4,4'-Tetrachlorobiphenyl
61	33284-53-6	2,3,4,5-Tetrachlorobiphenyl
62	54230-22-7	2,3,4,6-Tetrachlorobiphenyl
63	74472-34-7	2,3,4',5-Tetrachlorobiphenyl
64	52663-58-8	2,3,4',6-Tetrachlorobiphenyl
65	33284-54-7	2,3,5,6-Tetrachlorobiphenyl
66	32598-10-0	2,3',4,4'-Tetrachlorobiphenyl
67	73575-53-8	2,3',4,5-Tetrachlorobiphenyl
68	73575-52-7	2,3',4,5'-Tetrachlorobiphenyl
69	60233-24-1	2,3',4,6-Tetrachlorobiphenyl
70	32598-11-1	2,3',4',5-Tetrachlorobiphenyl
71	41464-46-4	2,3',4',6-Tetrachlorobiphenyl
72	41464-42-0	2,3',5,5'-Tetrachlorobiphenyl
73	74338-23-1	2,3',5',6-Tetrachlorobiphenyl
74	32690-93-0	2,4,4',5-Tetrachlorobiphenyl
75	32598-12-2	2,4,4',6-Tetrachlorobiphenyl
76	70362-48-0	2,3',4',5'-Tetrachlorobiphenyl
77	32598-13-3	3,3',4,4'-Tetrachlorobiphenyl
78	70362-49-1	3,3',4,5-Tetrachlorobiphenyl
79	41464-48-6	3,3',4,5'-Tetrachlorobiphenyl

80	33284-52-5	3,3',5,5'-Tetrachlorobiphenyl
81	70362-50-4	3,4,4',5-Tetrachlorobiphenyl
	25429-29-2	Pentachlorobiphenyl
82	52663-62-4	2,2',3,3',4-Pentachlorobiphenyl
83	60145-20-2	2,2',3,3',5-Pentachlorobiphenyl
84	52663-60-2	2,2',3,3',6-Pentachlorobiphenyl
85	65510-45-4	2,2',3,4,4'-Pentachlorobiphenyl
86	55312-69-1	2,2',3,4,5-Pentachlorobiphenyl
87	38380-02-8	2,2',3,4,5'-Pentachlorobiphenyl
88	55215-17-3	2,2',3,4,6-Pentachlorobiphenyl
89	73575-57-2	2,2',3,4,6'-Pentachlorobiphenyl
90	68194-07-0	2,2',3,4',5-Pentachlorobiphenyl
91	68194-05-8	2,2',3,4',6-Pentachlorobiphenyl
92	52663-61-3	2,2',3,5,5'-Pentachlorobiphenyl
93	73575-56-1	2,2',3,5,6-Pentachlorobiphenyl
94	73575-55-0	2,2',3,5,6'-Pentachlorobiphenyl
95	38379-99-6	2,2',3,5',6-Pentachlorobiphenyl
96	73575-54-9	2,2',3,6,6'-Pentachlorobiphenyl
97	41464-51-1	2,2',3,4',5'-Pentachlorobiphenyl
98	60233-25-2	2,2',3,4',6'-Pentachlorobiphenyl
99	38380-01-7	2,2',4,4',5-Pentachlorobiphenyl
100	39485-83-1	2,2',4,4',6-Pentachlorobiphenyl

101	37680-73-2	2,2',4,5,5'-Pentachlorobiphenyl
102	68194-06-9	2,2',4,5,6'-Pentachlorobiphenyl
103	60145-21-3	2,2',4,5',6-Pentachlorobiphenyl
104	56558-16-8	2,2',4,6,6'-Pentachlorobiphenyl
105	32598-14-4	2,3,3',4,4'-Pentachlorobiphenyl
106	70424-69-0	2,3,3',4,5-Pentachlorobiphenyl
107	70424-68-9	2,3,3',4',5-Pentachlorobiphenyl
108	70362-41-3	2,3,3',4,5'-Pentachlorobiphenyl
109	74472-35-8	2,3,3',4,6-Pentachlorobiphenyl
110	38380-03-9	2,3,3',4',6-Pentachlorobiphenyl
111	39635-32-0	2,3,3',5,5'-Pentachlorobiphenyl
112	74472-36-9	2,3,3',5,6-Pentachlorobiphenyl
113	68194-10-5	2,3,3',5',6-Pentachlorobiphenyl
114	74472-37-0	2,3,4,4',5-Pentachlorobiphenyl
115	74472-38-1	2,3,4,4',6-Pentachlorobiphenyl
116	18259-05-7	2,3,4,5,6-Pentachlorobiphenyl
117	68194-11-6	2,3,4',5,6-Pentachlorobiphenyl
118	31508-00-6	2,3',4,4',5-Pentachlorobiphenyl
119	56558-17-9	2,3',4,4',6-Pentachlorobiphenyl
120	68194-12-7	2,3',4,5,5'-Pentachlorobiphenyl
121	56558-18-0	2,3',4,5',6-Pentachlorobiphenyl
122	76842-07-4	2,3,3',4',5'-Pentachlorobiphenyl

123	65510-44-3	2,3',4,4',5'-Pentachlorobiphenyl
124	70424-70-3	2,3',4',5,5'-Pentachlorobiphenyl
125	74472-39-2	2,3',4',5',6-Pentachlorobiphenyl
126	57465-28-8	3,3',4,4',5-Pentachlorobiphenyl
127	39635-33-1	3,3',4,5,5'-Pentachlorobiphenyl
	26601-64-9	Hexachlorobiphenyl
128	38380-07-3	2,2',3,3',4,4'-Hexachlorobiphenyl
129	55215-18-4	2,2',3,3',4,5-Hexachlorobiphenyl
130	52663-66-8	2,2',3,3',4,5'-Hexachlorobiphenyl
131	61798-70-7	2,2',3,3',4,6-Hexachlorobiphenyl
132	38380-05-1	2,2',3,3',4,6'-Hexachlorobiphenyl
133	35694-04-3	2,2',3,3',5,5'-Hexachlorobiphenyl
134	52704-70-8	2,2',3,3',5,6-Hexachlorobiphenyl
135	52744-13-5	2,2',3,3',5,6'-Hexachlorobiphenyl
136	38411-22-2	2,2',3,3',6,6'-Hexachlorobiphenyl
137	35694-06-5	2,2',3,4,4',5-Hexachlorobiphenyl
138	35065-28-2	2,2',3,4,4',5'-Hexachlorobiphenyl
139	56030-56-9	2,2',3,4,4',6-Hexachlorobiphenyl
140	59291-64-4	2,2',3,4,4',6'-Hexachlorobiphenyl
141	52712-04-6	2,2',3,4,5,5'-Hexachlorobiphenyl
142	41411-61-4	2,2',3,4,5,6-Hexachlorobiphenyl
143	68194-15-0	2,2',3,4,5,6'-Hexachlorobiphenyl

144	68194-14-9	2,2',3,4,5',6-Hexachlorobiphenyl
145	74472-40-5	2,2',3,4,6,6'-Hexachlorobiphenyl
146	51908-16-8	2,2',3,4',5,5'-Hexachlorobiphenyl
147	68194-13-8	2,2',3,4',5,6-Hexachlorobiphenyl
148	74472-41-6	2,2',3,4',5,6'-Hexachlorobiphenyl
149	38380-04-0	2,2',3,4',5',6-Hexachlorobiphenyl
150	68194-08-1	2,2',3,4',6,6'-Hexachlorobiphenyl
151	52663-63-5	2,2',3,5,5',6-Hexachlorobiphenyl
152	68194-09-2	2,2',3,5,6,6'-Hexachlorobiphenyl
153	35065-27-1	2,2',4,4',5,5'-Hexachlorobiphenyl
154	60145-22-4	2,2',4,4',5,6'-Hexachlorobiphenyl
155	33979-03-2	2,2',4,4',6,6'-Hexachlorobiphenyl
156	38380-08-4	2,3,3',4,4',5-Hexachlorobiphenyl
157	69782-90-7	2,3,3',4,4',5'-Hexachlorobiphenyl
158	74472-42-7	2,3,3',4,4',6-Hexachlorobiphenyl
159	39635-35-3	2,3,3',4,5,5'-Hexachlorobiphenyl
160	41411-62-5	2,3,3',4,5,6-Hexachlorobiphenyl
161	74472-43-8	2,3,3',4,5',6-Hexachlorobiphenyl
162	39635-34-2	2,3,3',4',5,5'-Hexachlorobiphenyl
163	74472-44-9	2,3,3',4',5,6-Hexachlorobiphenyl
164	74472-45-0	2,3,3',4',5',6-Hexachlorobiphenyl
165	74472-46-1	2,3,3',5,5',6-Hexachlorobiphenyl

166	41411-63-6	2,3,4,4',5,6-Hexachlorobiphenyl
167	52663-72-6	2,3',4,4',5,5'-Hexachlorobiphenyl
168	59291-65-5	2,3',4,4',5',6-Hexachlorobiphenyl
169	32774-16-6	3,3',4,4',5,5'-Hexachlorobiphenyl
	28655-71-2	Heptachlorobiphenyl
170	35065-30-6	2,2',3,3',4,4',5-Heptachlorobiphenyl
171	52663-71-5	2,2',3,3',4,4',6-Heptachlorobiphenyl
172	52663-74-8	2,2',3,3',4,5,5'-Heptachlorobiphenyl
173	68194-16-1	2,2',3,3',4,5,6-Heptachlorobiphenyl
174	38411-25-5	2,2',3,3',4,5,6'-Heptachlorobiphenyl
175	40186-70-7	2,2',3,3',4,5',6-Heptachlorobiphenyl
176	52663-65-7	2,2',3,3',4,6,6'-Heptachlorobiphenyl
177	52663-70-4	2,2',3,3',4,5',6'-Heptachlorobiphenyl
178	52663-67-9	2,2',3,3',5,5',6-Heptachlorobiphenyl
179	52663-64-6	2,2',3,3',5,6,6'-Heptachlorobiphenyl
180	35065-29-3	2,2',3,4,4',5,5'-Heptachlorobiphenyl
181	74472-47-2	2,2',3,4,4',5,6-Heptachlorobiphenyl
182	60145-23-5	2,2',3,4,4',5,6'-Heptachlorobiphenyl
183	52663-69-1	2,2',3,4,4',5',6-Heptachlorobiphenyl
184	74472-48-3	2,2',3,4,4',6,6'-Heptachlorobiphenyl
185	52712-05-7	2,2',3,4,5,5',6-Heptachlorobiphenyl
186	74472-49-4	2,2',3,4,5,6,6'-Heptachlorobiphenyl

187	52663-68-0	2,2',3,4',5,5',6-Heptachlorobiphenyl
188	74487-85-7	2,2',3,4',5,6,6'-Heptachlorobiphenyl
189	39635-31-9	2,3,3',4,4',5,5'-Heptachlorobiphenyl
190	41411-64-7	2,3,3',4,4',5,6-Heptachlorobiphenyl
191	74472-50-7	2,3,3',4,4',5',6-Heptachlorobiphenyl
192	74472-51-8	2,3,3',4,5,5',6-Heptachlorobiphenyl
193	69782-91-8	2,3,3',4',5,5',6-Heptachlorobiphenyl
	31472-83-0	Octachlorobiphenyl
194	35694-08-7	2,2',3,3',4,4',5,5'-Octachlorobiphenyl
195	52663-78-2	2,2',3,3',4,4',5,6-Octachlorobiphenyl
196	42740-50-1	2,2',3,3',4,4',5,6'-Octachlorobiphenyl
197	33091-17-7	2,2',3,3',4,4',6,6'-Octachlorobiphenyl
198	68194-17-2	2,2',3,3',4,5,5',6-Octachlorobiphenyl
199	52663-75-9	2,2',3,3',4,5,5',6'-Octachlorobiphenyl
200	52663-73-7	2,2',3,3',4,5,6,6'-Octachlorobiphenyl
201	40186-71-8	2,2',3,3',4,5',6,6'-Octachlorobiphenyl
202	2136-99-4	2,2',3,3',5,5',6,6'-Octachlorobiphenyl
203	52663-76-0	2,2',3,4,4',5,5',6-Octachlorobiphenyl
204	74472-52-9	2,2',3,4,4',5,6,6'-Octachlorobiphenyl
205	74472-53-0	2,3,3',4,4',5,5',6-Octachlorobiphenyl
	53742-07-7	Nonachlorobiphenyl
206	40186-72-9	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl

207	52663-79-3	2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl
208	52663-77-1	2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl
209	2051-24-3	Decachlorobiphenyl

Note:

a. Chemical Abstracts Service (CAS) Registry Number.

b. The International Union of Pure and Applied Chemistry.

(Source: ATSDR, 2000; USEPA, 2003)

Appendix B:Table of Different Types of Biosurfactants and Their Microbial Origin

Biosurfactant type	Producing Species	Reference
1. Glycolipids		
Rhamnolipids	Pseudomonas aeruginosa	Edward and Hayashi, 1965
	Pseudomonas spp.	Lang and Wagner, 1987
Trehalolipids	Rhodococcus erythropolis	Rapp et al., 1979
	Nocardia erythropolis	Margaritis et al., 1979
	Nocardia spp. SFC-D	Kosaric et al., 1990
	Mycobacterium spp.	Cooper et al., 1989
Sophorolipids	Torulopsis bombicola	Gobbert etal., 1984
	Candida (Torulopsis) apicola	Hommel et al., 1987
	Torulopsis petrophilum	Cooper and Paddock, 1983
Glucolipids	Marine bacterial strain MM1	Cooper et al., 1989
2. Fatty acids, neutral lipids, and phospholipids		
Fatty acids	Corynebacteria lepus	Cooper etal., 1978
Neutral lipids	Nocardia erythropolis	MacDonald et al., 1981
Phospholipids	Thiobacillus thiooxidans	Beeba and Umbreit, 1971
3.Lipopeptides and lipoproteins		
Peptide -lipids	Bacillus licheniformis	Yakimov et al., 1995,
Surfactin	Bacillus subtilis	Arima etal., 1968
Subtilisin	Bacillus subtilis	Bernheimer and Avigad, 1970

Viscosin	Pseudomonas fluorescens	Neu et al., 1990
Gramicidins	Bacillusbrevis	Marahiel etal., 1977
Polymixins	Bacilluspolymyxa	Suzuki etal., 1965
Viscosin	Pseudomonas fluorescens	Nue et al., 1990
4. Polymeric biosurfactants		
Emulsan	Acinetobacter calcoaceticus	Rosenberg et al., 1979
Alasan	Acinetobacter radioresistens	Barkay etal., 1999
Biodispersan	Acinetobacter calcoaceticus	Rosenberg etal., 1988
Mannan-lipid-protein	Candida, tropicalis	Kappeli et al., 1984
Liposan	Candida lipolytica	Cirigliano et al., 1984
Carbohydrate-protein-lipid	Debaryomyces polymorhpis	Singh and Desai, 1989
	Pseudomonas. fluorescens	Desai etal., 1988
PS-33	*Rhodococcus* spp.strain No. 33	Nue et al., 1992
5. Particulate Biosurfactants		
PM factor	Pseudomonas marginalis	Burd and Ward, 1996
Vesicles and fimbriae	Acinetobacter calcoaceticus	Kappeli and Finnerty, 1979
Whole cells	Variety of Bacteria	Rosenberg, 1986

(Source: Zhang et al., 2012)