Remediation of Salt- and Petroleum Hydrocarbon- Contaminated Soils using Ultrasound and Soil Washing

by

Xinyuan Song

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ABSTRACT

The mixed soil contamination of salts and petroleum hydrocarbons has become a worldwide concern since these pollutants can cause serious environmental and human health problems. An advanced remediation method - ultrasonic enhanced soil washing was evaluated for its ability of remediating such contamination. The impacts of five factors including initial total petroleum hydrocarbon (TPH) concentration, salinity, soil type, ultrasonic treatment time and soil washing flow rate were investigated through experimental design using orthogonal arrays, and the results indicated that all these factors could significantly affect the treatment performance. Two mechanisms of ultrasonic soil remediation of TPH were proved to be desorption and degradation. The combination of ultrasound and soil washing successfully enhanced the TPH removal and the best treatment efficiency at optimized conditions was 96.17 ± 3.56%. The application of soil washing in ultrasonic treatment greatly reduced the negative effect of salt.

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
CCME	Canadian Council of Ministers of the Environment
CAHs	Chlorinated aliphatic hydrocarbons
CEC	Cation exchange capacity
CFC	Chlorofluorocarbons
EC	Electrical conductivity
EPA	Environmental Protection Agency
ESP	Exchangeable sodium percentage
DCM	Dichloromethane
GC	Gas chromatograph
GC-FID	Gas chromatography – flame ionization detector
MDL	Method Detection Limit
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PCE	Perchloroethylene
PHCs	Petroleum hydrocarbons
SAR	Sodium adsorption ratio
SD	Standard deviation
RSD	Relative standard deviation
TCE	Trichloroethylene
TPH	Total petroleum hydrocarbons

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Chapter 1 Introduction

1.1 Background Information

Petroleum hydrocarbons and salts are two of the most common contaminants found at oil exploitation sites (Chaineau et al., 1995; Carty et al., 1997). The remediation of such contamination has received increasing interests worldwide since these pollutants could cause long-term environmental problems and potentially severe human health risks (Kirchmann and Ewnetu, 1998; CCME, 2008). After oil spills into soils, petroleum hydrocarbons tend to adsorb onto the surface of soil particles and enter the micropores of soil matrix, affecting soils by reducing soil permeability and water holding capacity (Cole, 1994; Alexander, 1999). Some of the petroleum hydrocarbons are even extremely toxic and carcinogenic to soil plants and animals (Miller and Herman, 1997). On the other hand, saltwater spills can make the contaminated soils to become saline or sodic and cause soil osmotic pressure, dispersion and drainage problems (Carty et al., 1997). Salts can also amplify the negative impacts of petroleum hydrocarbons on soils (Know and Sabatini, 2000).

Conventional remediation methods such as incineration, thermal desorption, soil washing, bioremediation and phytoremediation have been applied in many previous works (Delille, 2000; Knox and Sabatini, 2000; Hyman and Dupont, 2001; Onwudili and Willians, 2006). However, these methods are associated with many disadvantages such as high costs, insufficient treatment efficiencies and long treatment period, and can not well satisfy the soil cleanup criteria. Ultrasound is an advanced technology and has been proved effective for soil decontamination of recalcitrant contaminants such as petroleum hydrocarbons, salts and metals under various conditions (Feng and Aldrich, 2000; Kim and Wang, 2003; Mason et al., 2004; Collings et al., 2006). It could generate cavitation, heating and intense agitation within a liquid medium or suspension during the treatment process and its effect can reach the inner space of soil matrix which is usually inaccessible by other treatment methods (Abramov et al., 2009). The oscillating cavitational bubbles and shock waves introduced by ultrasound can lead to the breakage of solid particle aggregates, the appearance of erosion and fractures in contaminant films attached to solid particles and their detachment (Mason and Lorimer, 2002). Two of the major effects of ultrasound are degradation (direct oxidation) and desorption (Suslik, 1990; Little et al., 2002; Chung and Kamon, 2005; Collings et al., 2006).

A number of factors have been shown to affect the success of petroleum hydrocarbon removal using ultrasound, such as soil type, initial hydrocarbon concentration, salinity, energy level, and operation temperature (Feng and Alderich, 2000; Kim and Wang, 2003; Collings et al., 2006). Ultrasound is usually not a singly used remediation technique but integrated with several other treatment methods such as electrokinetic remediation and soil washing for better treatment effect (Chung and Kamon, 2005; Pham et al., 2009). Soil washing is a commonly used remediation technology which can remove contaminants of petroleum hydrocarbons and salts (Lyman et al. 1990). The combination of ultrasound and soil washing has been studied in many scientific researches. On the one hand, ultrasound was proved to be able to enhance soil washing by both accelerating and strengthening the treatment efficiency (Newman et al. 1997; Kim and Wang 2003; Mason et al. 2004; Kamalavathany 2007). On the other hand, soil washing could improve the reduction ability of ultrasound by enhancing transport of contaminants in solution (Kim and Wang 2003; Mason et al. 2004). However, few studies have been reported to investigate the effect of ultrasound combined with soil washing on the remediation of multiple contaminants especially petroleum hydrocarbons and salts. McMillan (2008) examined the effect of ultrasound on treating oil contaminated soil under saline condition. In his study, the existence of salt (sodium chloride) in the soil matrix was proved to significantly reduce the ultrasonic desorption of petroleum hydrocarbons from soils, but the effect of soil washing on ultrasonic treatment was not examined. In addition, although many previous studies have reported the effect of ultrasound on TPH desorption (Breitbach et al., 2002; Hamdaoui et al., 2003; Juang et al., 2006), most of the sorbates were selected as specific organic contaminants for mechanism investigations, and few studies were conducted to examine the desorption behavior of petroleum hydrocarbons fractions from different soils under the impact of ultrasound.

1.2 Objectives and Thesis Outline

The first objective of this thesis research is to investigate the relationship between sorbates (contaminants of petroleum hydrocarbons and salts) and sorbent (contaminated soils), through studying the impacts of soil type, salinity, and ultrasonic irradiation on the equilibrium of adsorption and desorption of petroleum hydrocarbons in soils. The investigation of adsorption and desorption will be helpful for better understanding of the experimental results from soil treatment by ultrasound and soil washing.

The second objective is to evaluate the ability of ultrasonic enhanced soil washing as an effective soil decontamination technique and find out the optimal operating conditions for this treatment process in order to provide useful information for future applications. The impacts of different factors including initial concentration of petroleum hydrocarbons in soil, salinity, ultrasonic treatment time, soil flushing rate and soil type on soil cleanup efficiency will be studied.

This thesis is structured as follows: in chapter 2, relevant literatures were reviewed and summarized; in chapter 3, the preparation of materials used in the experiments and the experimental design were described in detail; in chapter 4, the results of experiments and data analysis were provided; in chapter 5, the discussions of experimental results were presented, and in chapter 6, a summary of the research and suggestions for future research were provided.

Chapter 2 Literature Review

2.1 Soil Properties and Adsorption

2.1.1 Soil Properties

Soil has four physical components: inorganic solid, organic matter, water and air (Carty et al., 1997). The inorganic solid consists of primary and secondary minerals. Primary minerals such as quartz, mica and feldspars are extruded from molten lava therefore their compositions rarely change (McBride, 1994; Brady and Weil, 1996), and they are commonly found in the sand and silt fractions. Secondary minerals are those weathered particles of iron oxides and silicate clays. These minerals are usually found in the clay and a small fraction of silts (McBride, 1994; Brady and Weil, 1996). Based on grain sizes, soils can be classified into three groups: sand (from 0.05 to 2 mm), silt (from 0.002 to 0.05 mm) and clay (less than 0.002 mm) (Carty et al., 1997). Based on the proportions of sand, silt and clay in soil, soils can be divided into twelve texture categories, such as loam, silt and clay (Brady and Weil, 1996).

Surface area of soil particles is the most significant factor affecting physical and chemical kinetics in soil process. Increasing the surface area generally increases the porosity, adsorption capacity and biological activity (McBride, 1994; Brady and Weil, 1996). Sand and silt particles are relatively in large size with smaller surface areas and consist of minerals with a minimal functional electrical charge (Carty et al., 1997). On the contrary, clay particles with larger surface area and functional electrical charge play a very important role in physical, chemical and biological processes in soils (McBride, 1994). Comparing with sand and silt, the structure of clay is more complex with multiple layers and micropores within the soil matrix which means it have more sites for adsorption and entrapment of adsorbates (Carty et al., 1997). The desorption of chemicals from finer soil particles (i.e. clay) is more difficult than that from coarser soil particles.

Soil particles especially clays have charges or exchange sites on the surfaces where cations and water molecules can be attracted. In most of the clay particles, negative charges predominate because the original cations on the soil particles can be substituted by other cations with fewer valences and the loss of positive charges makes the soil particles negatively charged (Brady and Weil, 1996). Cations (such as sodium, magnesium, calcium and aluminum) with positive charges in the bulk solutions are attracted and assembled on the surface of soil particles and eventually form a monolayer of cations (Tan, 1993; McBride, 1994). The strengths of cation adsorptions on the surface of soil particles depend on the charges associated with the adsorbed cations (e.g., $Al^{3+}>Ca^{2+}>Mg^{2+}>K^{+}>Na^{+}$) (McBride, 1994). The cation exchanges make soil particles very sensitive and vulnerable to the influence of salts which can turn normal soils into saline (excessive salinity and sodium) or sodic (excessive sodium but low salinity) soils and consequently affect soil properties (Carty et al., 1997).

2.1.2 Adsorption and Partitioning

Once the organic matters enter the soil, there are several ways for their distributions (Xing, et al., 1996). For organic compounds with small molecular weights, they can be removed from the soil through volatilization (McGill, 1981). For semi-volatile and non-volatile compounds especially for crude oil with large amount of non-volatile and non-polar hydrocarbons, they are subject to either adsorption or partitioning on soil components (Alexander, 1999; Schwarzenbach, 2003). Factors influencing the persistence of organic matters in soil include the properties of soil (type, cation exchange capacity, salinity, organic content, etc.) and the properties of organic contaminant (concentration, polarity, charge, etc.).

Adsorption is a process of attraction of molecules from an adjacent gas or aqueous phase to an uncovered solid surface (Huang et al., 1997; Schwarzenbach, 2003). The attraction force can align the molecules into layers onto the existing surface. Organic molecules might be adsorbed weakly or strongly to the surfaces of organic polymers or the external surfaces of the mineral and organic soils (Alexander, 1999; Schwarzenbach, 2003). The strong interaction is an indication of chemical adsorption (i.e. ion exchange) while the weak interaction is an indication of physical adsorption caused by hydrogen bonding or van der Waals forces.

Partitioning is the process of distribution of organic molecules into aqueous solution or to soil organic matter (SOM) at equilibrium. The relative concentration of organic compound at equilibrium between soil and water system is described by the distribution coefficient K_d as the following equation:

$$K_d = \frac{C_s}{C_w} \qquad (2.1)$$

where C_s denotes the concentration of organic compound in the solid phase in equilibrium (mg/kg), C_w is the concentration of organic compound left in water at equilibrium (mg/L) (Xing et al., 1994; Alexander, 1999; Cornelissen, 2005). K_d (in L/kg or mL/g) is a quantitative characteristic of measuring the relationship between the sorbate and the sorbent.

The extent of sorption of many contaminants on soil is highly correlated to the amount of soil organic matter (SOM) (Cornelissen, 2005). Thus the normalized soil-water coefficient K_{ow} can also be described as in Equation 2.2:

$$K_{ow} = \frac{K_d}{f_{ow}} \qquad (2.2)$$

where f_{ow} denotes the fraction of organic carbon within the sorbent soil (Xing et al., 1994).

The distribution coefficient (K_d) tends to be influenced by other soil characteristics such as salinity, polarity and aromaticity of the soil (Xing et al., 1994; Brunk et al., 1997;

Scharzenbach, 2003). The presence of dissolved salts in water solution will lead to a decrease of solubility of organic compounds and therefore influence the distribution of the compounds between solid phase and water phase. The salinity compensated normalized partitioning coefficient can then be described as in Equation 2.3:

$$K_{ow,salt} = \left(K_{ow}\right)\left(10^{+K_s[salt]}\right) \qquad (2.3)$$

where K_S (in L/mol) is a salting constant and [salt] denotes the concentration of salt in the solution (mol/L) (Brunk et al., 1997).

2.1.3 Sorption Models

Adsorption and desorption data are most commonly represented by adsorption and desorption isotherms, which is a plot of the amount of adsorbate retained by a solid as a function of the concentration (liquid) or pressure (gas) of that adsorbate in the equilibrium gas or solution at certain temperature (McBride, 1994). Many models have been used to describe the interaction between the adsorbate and adsorbent, such as linear model, Freundlich model, Langmuir model, Temkin model, BET model and Elovich model etc. (Breitbach and Bathen, 2001; Hamdaoui et al., 2003; Ji et al., 2006; Juang et al., 2006).

Equation 2.1 is a linear adsorption model. The linear isotherm (constant partitioning) suggests a constant relative affinity of the adsorbate molecules for the adsorbent. This model is usually observed only at a situation of low range of adsorption (McBride, 1994). Many nonpolar organic compounds adsorbing at low concentrations follows this linear equation.

The Freundlich equation is an empirical adsorption model (Mohan and Karthikeyan, 1997) as shown in Equation 2.4. When n=1, the adsorption isotherm simply expresses the linear adsorption process; when n<1, the equation describes a cooperative adsorption process; when n>1, the equation expresses a normal Langmuir adsorption process which will be explained later.

$$C_s = \frac{q_e}{m} = KC_e^{\frac{1}{n}} \qquad (2.4)$$

where C_s denotes the equilibrium concentration of the organic compound in the solid phase (mg/kg), C_e denotes the equilibrium concentration of the organic compound left in water (mg/L), q_e denotes the amount of adsorption in equilibrium state, m denotes the mass of the adsorbent, K and n are empirical constants. Equation 2.4 can also be written as logarithmic equation as shown in Equation 2.5. The value of K and n can be calculated by plotting the value of log C_s versus log C_e.

$$\log C_s = \log K + (1/n) \log C_e \qquad (2.5)$$

The Langmuir equation assumes that there is no interaction between the adsorbate molecules and the adsorption only takes place in a monolayer on the solid surface

(McBride, 1994; Lowell et al., 2004). According to this theory, once an adsorbate molecule occupies a site on the solid surface, no further adsorption can take place at that site. Therefore a theoretical saturation adsorption maximum Q is reached and the adsorption stops. The Langmuir isotherm equation is presented as follows:

$$C_s = \frac{KQC_e}{1 + KC_e} \qquad (2.6)$$

where Q denotes the saturation adsorption capacity (mg/kg) and K denotes the adsorption equilibrium constant (L/mg) and it can be expressed as (McBride, 1994):

$$K = \frac{K_a}{K_d} \qquad (2.7)$$

where K_a denotes the rate of adsorption constant while K_d denotes the rate of desorption constant.

The linear Langmuir equation can be written as follows and Q and K can be obtained by plotting C_s/C_e versus C_e.

$$\frac{C_s}{C_e} = \frac{1}{KQ} + \frac{C_e}{Q} \qquad (2.8)$$

The Langmuir equation can often well describe chemical sorption and the adsorption is usually limited to monolayer. However sometimes the adsorbates can form multilayers during adsorption especially for physical adsorption where weak physical bonding (hydrogen bonding or iron-dipole attraction) is the major bonding force (McBride, 1994; Lowell et al., 2004). The BET equation developed by Brunauer, Emmet, and Teller takes this possibility into account. It is usually described as gaseous adsorption as shown in Equation 2.9.

$$\frac{V}{V_m} = \frac{C\,(P/P_0)}{(1 - P/P_0)\,[1 + (C - 1)\,P/P_0]} \qquad (2.9)$$

where V denotes the volume of the gas adsorbed, V_m denotes the volume of gas adsorbed at monolayer coverage, P denotes the equilibrium vapour pressure, P_0 denotes the saturation vapour pressure and C is a constant dependent on adsorption heat.

However, for adsorption of organics from solution to soil, the multilayer adsorption is not usually involved. The existence of water molecules in the solution can lead to a strong competition against the organic molecules if physical adsorption is the main process (McBride, 1994). The water molecules have the dual competitive advantage of usually being present greatly in excess of the organics and having a greater polarity than most organics. In this situation, the Langmuir equation may be more accurate in describing adsorption process than the BET model. Many studies had reported that the adsorption of organic compounds from vapour, aqueous and organic solvent phase onto solid surfaces can be well described by the Langmuir isotherm (Li et al., 2002; Ji et al., 2006; Juang et al., 2006).

2.2 Soil Contamination and Remediation in the Oil/Gas Industry

Two major soil contaminants during the process of exploitation of oil and gas are petroleum hydrocarbons and salts. If not being handled properly, the contaminated sites could cause consequential pollution to the environments and pose high risks to the human health. The crucial problem that needs to be solved for soil remediation within the oil and gas industry is to develop and choose a cost-effective and environmentally responsible method according to the specific situations of different contaminations.

2.2.1 Contamination and Remediation of Petroleum Hydrocarbons

Petroleum is a complex mixture of naturally occurring hydrocarbon molecules containing aliphatic (alkanes, cycloalkanes, alkenes and alkynes) and aromatic compounds (monoaromatics, diaromatics and polycyclic aromatics). It is primarily made up of carbon and hydrogen, with varying amounts of sulfur, nitrogen, oxygen and metals (Carty et al., 1997; Potter and Simmons, 1998; CCME, 2008). Generally the petroleum hydrocarbons contain approximately 85.3% of carbon, 12.2% of hydrogen, 3.6% of oxygen, 1.01% of sulfur and 0.22% of nitrogen by mass (McGill et al., 1981). The petroleum hydrocarbons are commonly released into the environments through accidental spills during transportation and storage of petroleum products (EPA, 2000; Nadim et al., 2000). It had also been found at soils contaminated with crude oil, drilling muds and brines generated from the exploitation at oilfield sites (Chaineau et al., 1995). It was reported that approximately 2 billion tons of petroleum is being produced and 8.8 million tons of oil is being spilled on land each year all over the world (Bartha, 1986).

This disturbance of oil contamination can lead to considerable changes of the physical and chemical properties of soils. Generally, as the molecular weight of the petroleum hydrocarbon increases, the boiling point increases, the volatility and solubility decrease (Cole, 1994). Therefore once the oil is spilled, the lighter hydrocarbons (volatile hydrocarbons) move fast and evaporate easily while the heavier hydrocarbons (semi-volatile and non-volatile) evaporate with less extent and adsorb on the soil particles with more extent (Cole, 1994; Carty et al., 1997). The petroleum hydrocarbons contaminated soils become "weathered" or "aged" when volatile hydrocarbons evaporate while the heavy non-volatile components stay within the soils after a long period of time. The longer these contaminants stay in the soils, the more they appear to resist desorption or degradation (Alexander, 2000).

With the existence of excessive amounts of petroleum hydrocarbons (e.g. more than 4 to 5% by weight) on the surface of the soil particles and within the soil pores, the porosity of the soils would greatly decrease (McGill et al., 1981). The contaminated soils may become less permeable and the water holding capacity may be reduced (Carty et al., 1997). This effect can also contribute to the toxicity of the oil contamination to soil plants by blocking soil pores and obstructing the movements of air and water to the plant roots (Trofimov and Rozanova, 2003). Many of the petroleum hydrocarbons especially polycyclic aromatic hydrocarbons (PAHs) have high toxicity to plant growth (Miller and

Herman, 1997). Petroleum hydrocarbons can directly kill plants on contact, slow the growth of the plants, inhibit seed germination or cause nutrients deficiency of the plants (McGill et al., 1981; Cole, 1994; Carty et al., 1997).

The most common treatment methods for soil remediation of petroleum hydrocarbon include physical, chemical and biological methods such as incineration, thermal desorption, solvent extraction, chemical oxidation and bioremediation, etc. Incineration is a physical remediation method which is capable of completely destroying petroleum hydrocarbons (up to 99.9% by weight reduction) (Leuser et al., 1990; Onwudili and Willians, 2006). However, the large cost of this method makes it unattractive for environmental applications (Onwudili and Willians, 2006). Thermal desorption is a similar physical treatment method which evaporate the petroleum hydrocarbons under extremely high temperature and pressure (Hyman and Dupont, 2001). Another physical treatment method – soil washing can transfer the contaminants from soil particles to washing solution (Bai et al., 1997). This method strongly depends on the soil types and can be ineffective when treating contaminated soils with large amount of clay particles (Griffiths, 1995; Hyman and Dupont, 2001). The large amounts of solvents can make it costly as well (Griffiths, 1995). Chemical methods like chemical extraction or oxidation had been proved effective but they are costly too (Vandermeer, 2005; Kulik et al., 2006). These methods usually strongly depend on many factors such soil types, moisture content and molecular weight of organic compounds. They can generate by-product or secondary pollutions as well. Bioremediation methods such as landfarming and composting had also been proved to be effective for remediation of petroleum hydrocarbons in many scientific researches (Delille, 2000; Aisablie et al., 2004). Generally these methods utilize the microbial organisms to remove or degrade hydrocarbon compounds in soils. Factors that influence the bioremediation process include soil moisture, temperature, pH, mineral nutrients and aeration condition etc. (Hyman and Dupont, 2001). Comparing with other treatment methods, bioremediations are more cost-effective and relatively green techniques generating less by-products or other contaminants (Hyman and Dupont, 2001; Marin et al., 2005). One problem of bioremediation methods is the poor bioavailability of the low soluble petroleum hydrocarbons for metabolisms by microorganisms (Amatya et al., 2002). The long period of treatment process (usually months to years) can be another disadvantage of bioremediations (Carty et al., 1997).

2.2.2 Contamination and Remediation of Salts

The oil and gas exploration and production process usually generate large quantities of drilling waste especially waste of produced water. It is estimated that approximately 20 to 30 bbl (billion barrels) per year around the world are being produced (Kharaka et al., 2005). The produced water contain large amount of dissolved salt and solids along with other contaminants such as heavy metals and hydrocarbons. The term used to express the extent of the salt dissolved concentration in soil is salinity which is usually measured by electrical conductivity (EC). Typically produced water has an EC around 200 dS/m comparing against seawater with an EC of about 50 dS/m and non-saline soil with an EC of about 4 dS/m (Rhykerd et al., 1995; Carty et al., 1997). Another similar term called total dissolved solids (TDS) which measures all the dissolved constituents regardless of an electrical charge is also used to describe salinity. TDS usually correlates with EC since most dissolved solids in soil solution are cations or anions. The TDS of produced water ranges from 3,000 mg/L to 380,000 mg/L while the TDS of drinking water is below 500 mg/L (Health Canada 1996; EPA 2000, Kharaka et al., 2005). The primary soluble salts that accumulate in soils consist of Na^+, Ca^{2+} and Mg^{2+} as cations and SO_4^{2-} and Cl^- as anions. Around 30 to 35% of the total ion content is sodium while around 50% of total anion content is chloride (Suleimanov, 2005). This makes NaCl the most common salt in produced water where the concentration of sodium chloride can reach up to 150,000 mg/L (Know and Sabatini, 2000; Tellez et al, 2002). This is also why the sodium chloride is an ideal surrogate chemical for scientific research on salt spills on soil.

Although salts are neither mutagenic nor carcinogenic, and they are generally not considered toxic to animals, they can still cause substantial adverse environmental impacts to soils and plants system. There are two primary impacts of salt contaminations on soil: the osmotic shock on plant growth and the destruction of soil physical structure. Osmotic potential is the force that balances the existence of water molecules between the plant roots and the soil (Carty et al., 1997). The high salinity lowers the free energy of water in soil solution and reduces the ability of the plant roots to extract water from the soil (McBride, 1994). Therefore the presence of excessive salts in soils reverses the osmotic gradient and leads to dehydration and nutrient deficiencies to the plants in soil (Know and Sabatini, 2000). The most obvious results will be wilting or death of plants.

Soil dispersion is the second major problem caused by salt spills. When divalent calcium and magnesium cations are adsorbed on the clay particles, they can balance the negative charges of clay particles and keep them neutral (Know and Sabatini, 2000). In this case, the soil can aggregate well and has abundant macropores. However, in the presence of excessive sodium cations which are monovalent, the clay particles will repel each other because they sense a similarly negative particle instead of sensing a neutral particle. The repulsion force will move apart the particles and lead to a soil swelling and diffusion (Brady and Weil, 1996; Carty et al., 1997). The movement of the clay particles into the soil macropores will greatly decrease the soil porosity and make the soil structure become impervious to water (Korphage et al., 2003).

The dispersive potential of soils is commonly discussed as soil sodicity which can be determined by the exchangeable sodium percentage (ESP). The definition of ESP is shown in the following equation (Brady and Weil, 1996):

$$\mathrm{ESP} = \frac{\text{Exchangeable sodium cations (cmol/kg of soil)}}{\text{Cation exchange capacity (cmol/kg of soil)}} \times 100\% \qquad (2.10)$$

Another measurement describing the competitive relationships between sodium and calcium plus magnesium cations adsorption onto clay cation exchange sites is called sodium adsorption ratio (SAR). The relationship is calculated as follows:

$$\mathrm{SAR} = \frac{\left[\mathrm{Na}^{+}\right]}{\sqrt{([\mathrm{Ca}^{2+}]+[\mathrm{Mg}^{2+}])/2}} \qquad (2.11)$$

According to Carty et al. (1997), the salt-impacted soils can be classified into four groups as follows:

Table 2.1 Salt-impacted soil classifications

EC>4 dS/m; ESP<15; SAR<13	Saline
EC>4 dS/m; ESP>15; SAR>13	Saline-Sodic
EC<4 dS/m; ESP>15; SAR>13	Sodic
EC<4 dS/m; ESP<15; SAR<13	Not saline or sodic

Unlike petroleum hydrocarbons, salts can not be degraded and therefore the remediation of salt-impacted soils is achieved only by removing salt ions from the soil. The most common remediation methods for cleaning excessive salts in soils are mainly divided into two ways: one is soil washing or flushing in physical or chemical way; the other way is bioremediation or phytoremediation using salt-tolerated microorganisms and crops (Carty et al., 1997; Alberta Environment, 2001; Greenberg et al., 2007). In terms of soil washing or flushing, water was the major solvent which was used to flush soluble salts out of the contaminated soils (Hyman and Dupont, 2001; Franzen, 2003). This method can provide a rapid solution to remediate salt contaminations, but it is very costly and often has limited effectiveness. Chemical amendments such as gypsum ($CaSO_4 \cdot xH_2O$) or calcium chloride are usually added to exchange the sodium adsorbed on the soils with the replacing cations like calcium, ammonium and potassium (Qadir et al., 1998; Knox and Sabatini, 2000). However, since the gypsum has extremely low solubility in water, it is very hard for the calcium to be available and therefore the process of remediation can be very slow, time-consuming and costly (Know and Sabatini, 2000; Alberta Environment, 2001; SOS Environmental, 2009). Amendments of bulking agents have also been used to change the bulk density, porosity and permeability of the soils and consequently enhance the efficiency of washing (Rechcigl, 1995; Sublette et al., 2005).

The phytoremediation method of salt-impacted soils uses the halophytic plants or halophilic bacteria which are usually very tolerant of high concentrations of salts (Nicholson and Fathepure, 2003; Greenberg et al., 2007; Zhang et al., 2008). Typically halophytic plants include barley, fescue, salt grass, wheat and seaweeds (Know and Sabatini, 2000). They are capable of surviving and even thriving in saline soils with EC of more than 16 mmhos/cm and in sodic soils with ESP of more than 15% (Carty et al., 1997). Comparing with chemical soil washing, the phytoremediation by halophytic plants causes less disturbance or toxicity to the topsoil (Carty et al., 1997). However, like soil washing, the process of phytoremediation takes extremely long period of time for treatment, usually from months to years (Knox and Sabatini 2000; Korphage et al., 2003).

2.2.3 Challenges of Remediation

The interactions between contaminants and soil particles are complex which could pose great challenges to provide an effective remediation method to clean up the mixed contaminants of petroleum hydrocarbons and salts. The contaminants are not only strongly adsorbed onto the surfaces of soil particles but also enter the soil pores within the soil matrix which make it extremely difficult for the complete decontamination (Alexander, 1999; Schwarzenbach, 2003). The attraction forces between contaminants and soils become stronger when the soil particles become finer or the amounts of water content and soil organic matters increase (Brady and Weil, 1996). Decontamination becomes even harder when contaminated soils become weathered after a long period of contacting time. The petroleum hydrocarbons can make the soil become hydrophobic and thus impede the salt leaching through water infiltration (Rhykerd et al., 1995). Furthermore, the challenge may be amplified by the existence of high concentration of salts which can affect the effectiveness of soil remediation by changing the physical properties of the soils (Carty et al., 1997; Greenberg et al., 2007). In order to improve the treatment abilities of the current remediation methods, a deeper understanding of the relationships and interactions between contaminants and soils is needed.

There are limited studies of soil remediation methods to deal with both petroleum hydrocarbons and salts contaminations. The most commonly used technologies include physical and chemical soil washing (Feng and Aldrich, 2000; Kim and Wang, 2003), chemical extraction (Hyman and Dupont, 2001), electrokinetic remediation (Pham et al, 2009), phytoremediation (Glick, 2003; Greenberg et al., 2007) and bioremediation (Rhykerd et al., 1995; Margesin and schinner, 2001; Zhu et al., 2004), etc. The limitations of these methods make them unsuitable to meet the requirements of being cost-effective and environmental benign under various conditions. Recently, ultrasonic technology has been utilized in many scientific studies and was proved effective to treat recalcitrant contaminants such as salts, metals and petroleum hydrocarbons under various conditions (Feng and Aldrich, 2000; Kim and Wang, 2003; Mason et al., 2004; Collings et al., 2006). The cavitation effect of ultrasound makes it a good alternative technology to potentially address the problems in a fast and effective way.

2.3 Remediation using Ultrasound

2.3.1 Ultrasound Principles

Ultrasound is defined as sound with its frequency higher than that to which the human ear can respond (usually above 20 kHz or 20,000 cycles per second) (Mason, 1990; Mason and Lorimer, 2002).The upper limit of ultrasonic frequency is not sharply defined but usually about 5 MHz for gases and 500 MHz for liquids and solids. The use of ultrasound within this frequency range can be generally divided into two categories: low intensity and high intensity ultrasound. The intensity of ultrasound has been defined as the amount of acoustic energy (Joules) flowing through per unit area (square centimeter) of the medium per unit time (second) and so the unit of sound intensity will be $J\bullet cm^{-2}s^{-1}$ or $W\bullet cm^{-2}$ (Thompson and Doraiswamy, 1999; Farmer et al., 2000). The low intensity ultrasound (usually with high frequency ranging from 2 to 10 MHz) carries non-destructive levels of sound energy which brings no chemical effect but physical effect to the medium (Mason and Lorimer, 2002). Typically it is used for analytical purposes in medicine and biology for medical imaging, diagnosis, scanning and material testing (Farmer et al., 2000; Raichel, 2000). The high intensity ultrasound which is also called power ultrasound carries high energy sound waves at low frequency between 20 and 100 kHz. It is more commonly used for surface cleaning, plastic welding, cutting, drawing in industry applications, mixing, emulsification, filtration and crystallization in processing application, and water disinfection and decontamination, air cleaning and land remediation in environmental protection (Mason and Lorimer, 2002; Mason, 2007a).

Sonochemistry was developed based on the process of acoustic cavitation which is defined as the formation, subsequence growth and implosive collapse of bubbles due to the sound wave through a liquid (Suslick, 1990). The formation of bubbles or cavities is a nucleated process that it usually happened at weak points in the liquid such as gas-filled crevices in suspended particulate matter or microbubbles remaining from previous cavitation events (Garcia and Castro, 2003). Unlike electromagnetic waves which can pass through vacuum, ultrasound waves must travel through mediums in alternating cycles of rarefaction (expansion) and compression which cause the molecules of the medium to oscillate around their mean position (Mason and Lorimer, 2002; Garcia and Castro, 2003). During the compression cycle, the molecules were pushed together with positive pressure, while during rarefaction they were pulled apart with negative pressure (Mason and Lorimer, 2002). During the rarefaction cycle, if the negative pressure generated by acoustic waves is sufficiently large to overcome the intermolecular forces that bind the liquid so that the average distance between molecules is greater than the critical molecular distance, the liquid will break down and the cavitation bubbles will be created (Suslick, 1990).

Since the mass transfer rate during rarefaction and compression is proportional to the surface area of the cavity which is slightly greater during rarefaction than during compression, the mass transfer in the cavity during rarefaction phase is larger than that during compression phase (Collings et al., 2006). Therefore after several cycles of rarefaction and compression, the cavity will grow. The growth of cavity depends on the intensity of the acoustic wave. The higher the intensity of the acoustic wave is, the faster the cavity grows. The importance of cavitation to sonochemistry is more embodied in the collapse of cavities than their formation and growth. When the bubble overgrow to a critical size that it can no longer efficiently adsorb any more energy from ultrasound, it can no longer sustain it self and implodes (Suslick, 1990). Then the surrounding liquid will enter very quickly that compress the gases and vapours pre-existed in the bubble. This will result in an instantaneous release of energy and generate highly localized temperature and pressure while the overall environment remains equivalent to ambient conditions (Gogate and Kabadi, 2009). The collapse happens so fast that the thermal energy can not be timely transported, thus it generates a short-lived, localized hot spot in the cold liquid that remains unaffected. The temperature of the hot spot was estimated to be about 5,000 °C which is similar to the surface of the sun while the pressure is estimated to be about 1,000 atmospheres (Suslick, 1990; Mason and Lorimer, 1991). The speed of the cooling down of the collapsed bubble was estimated to be greater than 109 °C /s (Suslick, 1990). The high temperature and pressure generated by ultrasound in the hot spot could provide stringent conditions for the effective execution of various physical and chemical reactions under ambient conditions (Mason and Lorimer, 2002; Gogate and Kabadi, 2009).

The cavity sustains its symmetric spherical shape during its collapse in homogeneous liquids. However, this is not the case when ultrasound was applied in heterogeneous liquid-solid system. When the cavity collapses occur near the solid particle which is several orders of magnitude larger than the cavity, symmetric cavitation is hindered by the asymmetric environment near the interface and the cavity collapses asymmetrically because the solid surface provides resistance to the liquid flow from that side (Suslick, 1990; Thompson and Doraiswamy, 1999). As the cavity collapses, high-speed microjets of liquid are formed directly towards the interface (Garcia and Castro, 2003). This had been proved by Lauterborn and Vogel (1984) using a high speed camera as shown in Figure 2.1 and the speed of the microjet had been estimated of 100 m/s (Suslick, 1990). This microjet can cause serious damage and generate microscopic pitting and erosion on the solid surface (Mason and Lorimer, 2002). Moreover, when the collapses occur away from the solid particle, it is still symmetrical and it generates shockwaves that lead to turbulence or microstreaming towards the soil particle (Thompson and Doraiswamy, 1999). The effects of high-speed microjet and turbulence can help to activate the solid surface area by disruption of the interfacial boundary layers for physical or chemical reactions, increase the mass and heat transfer to and from the layer. Therefore the cavitation effect can be widely applied for treating solids in suspension or slurry in many research areas, i.e. extraction, washing, homogenization, etc.

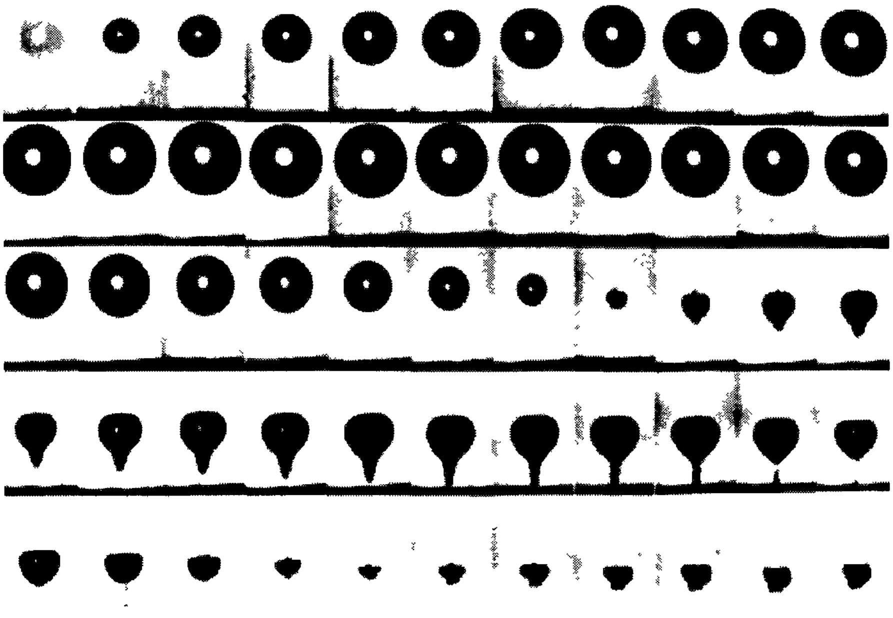

Figure 2.1 The formation of a microjet impact during cavitation near a liquid-solid interface; 75,000 frames per second (Lauterborn and Vogel, 1984)

Moreover, when ultrasound is applied to the aqueous solutions, the cavitation will also lead to the chemical degradation of components in the solution (Suslick, 1990; Thompson and Droaiswamy, 1999; Lim et al., 2007). The degradation can occur within the cavity, at the interface of the cavity or in the bulk solution (Thompson and Droaiswamy, 1999; Adewuyi, 2001). For volatile compounds, the chemical degradation mainly occurs in the cavity where pyrolysis is the dominant mechanism caused by the high temperature and pressure; while reactions of less-volatile or non-volatile compounds occur at the interface and in the bulk solution where sonolysis is the primary mechanism caused by radical reactions (Thompson and Droaiswamy, 1999; Mason and Lourimer, 2002). The sonication of water produces intermediate radicals such as hydrogen ($H\cdot$), hydroxyl ($HO\cdot$), hydroperoxyl ($HO_2\cdot$) and hydrogen peroxide (H_2O_2) with high oxidizing power in and around the cavitation bubbles, as shown in the following equations (Serpone, 1994; Suslick, 1999; Mason and Lourier, 2002):

$$H_2O \rightarrow H\cdot + HO\cdot$$

$$O_2 \rightarrow 2O\cdot$$

$$H\cdot + H_2O \rightarrow HO\cdot + H_2$$

$$O\cdot + H_2O \rightarrow 2HO\cdot$$

$$H\cdot + O_2 \rightarrow HO_2\cdot$$

$$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2$$

$$HO\cdot + HO\cdot \rightarrow H_2O_2 \qquad (2.12)$$

According to Adewuyi (2001), the majority of the degradation takes place in the solid-liquid interface region which has high hydroxyl concentration for radical oxidation. While in the bulk solution, hydroperoxyl and peroxide formed during the collapse of the cavity can diffuse to react with organic contaminants. These free radicals generated by sonic waves are capable of initiating or promoting fast reduction-oxidation reactions with the components in the aqueous phase and they had been proved to be very useful in the chemical degradation of contaminants in many scientific studies.

2.3.2 Application of Ultrasound in Environmental Remediation

Due to its great power to enhance and promote physical and chemical reactions and mass transfer, ultrasound has been growingly studied and applied in many areas for environmental protection and remediation (Adewuyi, 2001; Gogate and Kabadi, 2009; Pham et al., 2009). It had been widely used for degradation and disinfection in water treatment (Mason et al., 2003; Yazıcı et al., 2007), stabilization and dewatering of sludge in sewage treatment (Blume and Neis, 2004; Yin et al., 2004), agglomeration of smokes and aerosols in control of air-borne contamination (Hoffmann, 2000; Mason, 2007b) and removal of organic and inorganic contaminants from soil (Feng and Aldrich, 2000; Collings et al., 2006). Generally, the application of ultrasound as an advanced remediation technique causes two major effects to the removal of biological and chemical contaminants in soil and water. One is desorption which is a physical effect generated by the local turbulence and the liquid microjet, and another one is degradation which is a chemical effect generated by the direct oxidation reaction of the radicals.

2.3.2.1 Ultrasonic Desorption

Desorption of contaminants from soil particles is realized by breaking the physical bonds between the adsorbate and adsorbent (Lim and Okada, 2005). One of the conventional desorption methods for soil decontamination is soil washing which utilized water or other solvents to extract organic or inorganic contaminants from soil particles (Lyman et al., 1990; Mason and Lourimer, 2002). The pollutant materials existing at the surface or in the pores of soil particles dislodge and dissolve in the solvent, or adsorb onto finer soil particles (i.e., clay) which will be separated from the cleaned coarser particles (i.e., sand). The target contaminants of soil washing include semi-volatile organic compounds, petroleum and fuel residuals, heavy metals, PCBs, PAHs, and pesticides (Mbhele, 2008). Inorganic matters like soluble salts can also be washed out from contaminated soils. One of the shortages of soil washing is that it will require a large volume of solvent for treatment which leads to a big cost. By applying ultrasonic technique in soil washing, it will greatly reduce the volume of solvent needed for treatment, and moreover, increase the reduction efficiency and dramatically decrease the treatment time (Romdhane and Gourdon, 2001). There are two basic mechanical effects of ultrasonic enhanced desorption: surface cleaning and leaching (Mason and Collings, 2004). In terms of surface cleaning, the contaminants (i.e. organic hydrocarbons) adsorbed at the surface of solid particles are detached by the shear force generated by cavitation collapse and liquid turbulence. The bonds between contaminants and soil particles were easily broke when the solvent transfer high sonic energy to solid particle and the adsorbed contaminants. After dislodged from the soil particles, the contaminants can be flushed out or separated from the solid particles by other methods.

The other effect is ultrasonic leaching. The ultrasonic wave not only cleans the surface of solid particles but also penetrates into the soil matrix in which soluble contaminants can be trapped (Abramov et al., 2009). A model for understanding of leaching by Swamy and Narayayna (2001) was shown in Figure 2.2. The breakage of the aggregates of solid particles, the appearance of surface pits and micro-cracks of the solid particles could occur under the effect of high speed microjet caused by the ultrasonic cavitation (Mason and Lourimer, 2002; Garcia and Castro, 2003). The particle cracking makes it easier for the solvent or leaching reagent to enter the interior of the pores of the particles under the capillary forces by ultrasound and therefore increase the mass transfer of contaminants through the soil matrix. The fragmented long-chain or aromatic hydrocarbons desorbed more easily from the soil matrix than the long-chain or aromatic hydrocarbons due to the lower intermolecular forces between hydrocarbons and solid particles (Feng and Aldrich, 2002).

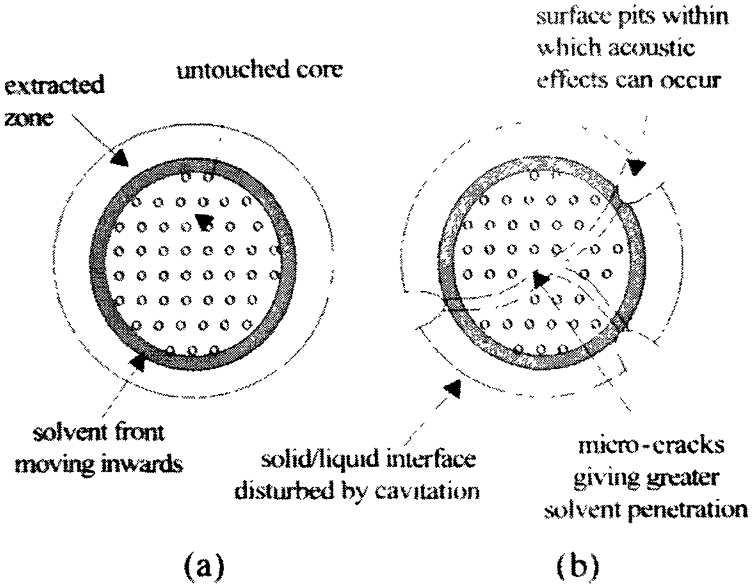

Figure 2.2 Contaminants leaching mechanism; (a) normal leaching; (b) ultrasonic leaching (Mason et al., 2004)

According to Rege et al. (1998), in the study of the desorption kinetics of phenol from activated carbon and polymeric resin, the diffusion coefficient and desorption rate in presence of ultrasound are 3-4 times larger than those in the absence of ultrasound.

Similar results were observed in many other studies (Breitbach et al., 2002; Hamdaoui et al., 2003; Ji et al., 2006; Juang et al., 2006). In the study of Juang et al. (2006), adsorption isotherm was used to study the adsorption ability of phenol on active carbon and the results showed that ultrasound enhanced the initial adsorption rate but reduced the adsorption capacity which might be due to the decrease of surface area and pore volume of carbons. In the works of Ji et al. (2006), ultrasound was proved effective to affect the extraction equilibrium and increased Geniposide extraction yield by 16.5%. The intraparticle diffusion coefficient and the external mass transfer coefficient increased with increasing ultrasonic intensity. It is believed that ultrasonic waves not only promote desorption of contaminants from solid particles but also increase the mass transfer of pollutants and solvent through the solid-liquid system (Breitbach and Bathen, 2001). According to Chung and Kamon (2005), as ultrasonic wave is applied to the solid-liquid suspension or slurry, the oscillating cavitation bubbles and shock waves decrease the liquid viscosity, increase the flow rate and mass transfer rate of liquid phase, as well as the porosity and permeability of solid phase and therefore increase the contaminant detachment efficiency. The degree of enhancement on pollutant removal can be affected by a plenty of factors which have been studied in many researches: sonication power, ultrasonic frequency and intensity, temperature, ultrasonic treatment time, water flow rate, soil particle size, initial hydrocarbon concentration, salinity, surfactant, etc (Feng and Aldrich, 2000; Farmer et al., 2000; Kim and Wang, 2003; Na, et al., 2007; Abramov et al., 2009).

2.3.2.2 Ultrasonic Degradation

The chemical effect of ultrasonic degradation of organic pollutant is an oxidation reaction that usually takes place at the interface or in the liquid phase. According to Hoffmann et al. (1996), the degradation caused by ultrasonic cavitation occurs through two distinct pathways: sonolysis by free radicals and pyrolysis under high pressure and temperature condition. The oxidants (hydrogen, hydroxyl and hydroperoxyl) generated by sonication of water can react with the organic pollutants and cause chemically and structurally changes of the pollutants. Long-chain or aromatic hydrocarbons with complex structure and large molecular weight can be broken down into fragment and simple hydrocarbons. The smaller fragment of hydrocarbons produced as degradation byproducts are supposed to have higher solubilities and bioavailabilities that it can be easier for them to be removed (Feng and Aldrich, 2000). For example trichloroethylene (TCE) and perchloroethylene (PCE) were reported to be ultimately degraded into chloride ion, water and carbon dioxide in the studies of Lim and Okada (2005) and Sáez et al. (2011). Many other organic pollutants that had been proved to be degradable by ultrasound in literatures includes chlorinated aliphatic hydrocarbons (CAHs), aromatic coumpounds, polychlorinated biphenyls (PCBs), poly aromatic hydrocarbons (PAHs), various phenols, chlorofluorocarbons (CFCs), pesticides and herbicides, etc (Adewuyi, 2001; Dewulf and Langenhove,2001; Peters, 2001; Little et al., 2002; Collings et al., 2006; Lim et al., 2007;).

2.3.2.3 Ultrasonic System Types

Various types of ultrasonic treatment systems were developed to deal with different situations. Basically they can be divided into two groups: static treatment system and flow-type treatment system (Thompson and Doraiswamy, 1999; Abramov et al., 2009). In lab experiments, static ultrasonic treatment systems such as probe system and ultrasonic bath system are more frequently used in sonochemical research in laboratory (Thompson and Doraiswamy, 1999). In ultrasonic bath systems, the ultrasonic transducers are attached to the bottom of the bath tank generating indirect sonication. The bath itself can be used as the reaction vessel or additional reaction vessels can be placed in the bath tank for receiving ultrasonic waves. Koparal et al. (2005) have used ultrasonic bath system to study the tar removal from sand. They proved that ultrasonic irradiation was more effective than traditional mechanical stirring to remove tar from sand. In the work of Ning et al. (2009), two groups of multiple transducers were placed in different dimensions in the ultrasonic tank for the study of oil sludge deoiling. However, the ultrasonic power of bath type ultrasound is relatively low comparing to the other treatment systems such as ultrasonic probe treatment system. Ultrasonic probes or horns are more commonly used reactor designs in many scientific researches (Na, S. et al., 2007; Ye et al., 2008; Shrestha, et al., 2009). Ultrasonic probes can be directly placed into the treating sample fluid for reaction. These reactors are typically recommended for lab scale work because the ultrasonic effect decreases exponentially on moving away from the probe and becomes ineffective at a distance of as low as 2-5 cm from the probe (Gogate et al., 2002). Therefore these probes cannot be used to effectively transmit ultrasonic energy throughout a large volume of fluid.

Ultrasound is usually not singly used remediation technique but integrated with several other treatment techniques in order to form an alternative treatment method to conventional treatment techniques for better treatment effect. For example electrokinetic remediation and soil washing had been applied with ultrasound in many scientific study and engineering projects (Kim and Wang, 2003; Chung and Kamon, 2005; Pham et al, 2009). Soil washing is a remediation technology currently being used at hydrocarbon contaminated sites. It removes contaminants by dissolving the liquid, sorbed, or vapor phase or by mobilizing contaminants existing as free product in soil pores and adsorbed to the soil (Lyman et al., 1990). Many researchers have used ultrasound to promote the process of soil washing, and the combination of ultrasonic treatment and soil washing can be called flow-type ultrasonic treatment (Newman et al., 1997; Kim and Wang, 2003; Mason et al., 2004; Kamalavathany, 2007; Abramov et al., 2009). Similar to static treatment system, the cavitation effect of ultrasound can cause two primary effect – surface cleaning and leaching out of more deeply entrenched material to the contaminated soils. Furthermore, the soil washing can improve the reduction ability of ultrasound by enhancing transportation of contaminants in solution. Technique of flow-type ultrasonic treatment system had been proved to have high efficiency and capable of being utilized in larger scale engineering applications. For example a company in Canada (Sonic Environmental Solutions Inc.) had developed a module that several ultrasonic probes directly contact the flow of the solution of contaminants soils (Mason et al., 2007b). The process incorporates soil washing with an organic solvent is capable of continues treatment of PCBs and reducing the contamination level from 910 ppm to <0.02 ppm (Mason et al., 2007b).

2.4 Summary

The soil contaminations of petroleum hydrocarbons and salts had became a worldwide concern due to their strong recalcitrations to remediation treatments and the high risks they may pose to the environment and human health. Conventional remediation techniques are not able to provide cost-effective and environmental benign means for cleaning up such mixed contamination. Ultrasound has been studied and used effectively in treating organic contaminations through ultrasonic desorption and degradation. However, only a few researches have considered the situations of mixed contaminations of petroleum hydrocarbons and salts while the results have shown the existence of salts in soil can strengthen the adsorption of hydrocarbons on soil particles and thus could greatly decrease the efficiency of ultrasonic remediation. Since soil washing is capable of not only removing and transporting petroleum hydrocarbons from soils but also reducing soil salinity by dilution and transportation, the combination of it with ultrasound have the potential to treat mixed contaminations of petroleum hydrocarbons and salts, and is thus examined in this thesis research.

Chapter 3 Materials and Methods

3.1 Soil Preparation

Two soils were used in the research experiments, including sand and silty clay loam. Commercially available sand (Ottawa standard sand, #30-40 sieve) was chosen to represent coarse grained material for comparison and is commonly used for laboratory based environmental research (Fine et al. 1997; Farmer et al. 2000; Feng and Aldrich 2000). The sand was characterized by visual observation as light brown medium grained sand.

The silty clay loam soil was collected in a forest within Prince George, BC, Canada. The soil was collected from B-horizon and was classified by visual observation as dense grey fine silt with some sand and gravel. It was screened using a #40 sieve to remove coarse organic debris and coarse particulates and was then dried in a laboratory oven at 60°C overnight to expel excessive moisture. The end results were workable, fine granular soil with homogenous soil conditions. The two soils were then thoroughly mixed at three different mixing ratios to represent three different soil texture types, including sand (with sand to silty clay loam mixing ratio of 100:0 v/v), sandy loam (with sand to silty clay loam mixing ratio of 70:30 v/v), and loam (with sand to silty clay loam mixing ratio of 40:60 v/v).

3.1.1 Soil Characterization

The main physical and chemical characteristics of soils were analyzed by BC Ministry of Forests (MOF) research branch laboratory in Victoria, BC. The analyzed parameters include soil texture, pH, conductivity, total carbon content, total nitrogen content, exchangeable cations, and effective CEC. Soil texture was analyzed using hydrometer and sieve analysis, and sample pH was measured using a lab pH meter, while conductivity was measured with a conductivity meter by saturated paste method. Total carbon and nitrogen were measured using an elemental analyzer. The exchangeable cations and effective CEC were analyzed by ICP spectrometer using a 0.1 N barium chloride extraction. ESP and SAR were calculated for each soil to assess initial salinity properties using the results for CEC and concentrations of Na^+, Ca^{2+}, and Mg^{2+}.

3.1.2 Crude Oil and Salt Spiking

The crude oil used in this study was obtained from Husky Energy light oil refinery in Prince George, British Columbia, Canada. It is called BC light oil crude and has a density of 0.8 g/mL at 15°C, 15% sulfur content, approximately 1% sediment/water content, and a salt concentration of 16-100 pounds per thousand barrels (Hughes, 2006). The salt used for spiking was sodium chloride (NaCl).

Spiking homogeneity is very essential for the statistical validity of the experimental data and for the study of concentration-dependent process (Northcott and Jones, 2000). Before experiments in this study, crude oil was measured out into a beaker and then diluted in hexane (Reid et al., 1998; Amellal et al. 2001). The hexane/crude solution was mixed thoroughly into the soil until the soil was completely saturated with hexane. The hexane was allowed to evaporate in the fume hood leaving the crude oil adsorbed evenly throughout the soil. Once the soil was dry, it was manually mixed again to assure even hydrocarbon distribution. The crude oil concentrations in the soils were subsequently determined by measuring the total petroleum hydrocarbons (TPH). The soil was spiked approximately 1 week before use and was stored in the fridge at 4°C.

Salt spiking was also conducted before each ultrasonic experiment. Certain amount of sodium chloride was dissolved in DI water before added to the soil samples (Feng and Aldrich, 2000). The soil and water mixture was stirred using a Fisher-Scientific magnetic stirrer for 5 minutes to achieve homogeneity. Then the stirrer was removed and rinsed with DI water. After that, salt spiking was completed and soil sample was ready for experiment.

3.2 Experimental Design

Experiments were designed to treat mixed contaminants of crude oil and salts using different types of ultrasonic treatments (flow-type and static type). The experiments can be divided in three parts:

The first part is desorption experiment on different soils with ultrasonic treatment in order to better understand the relationships and adsorption mechanisms between sorbate (petroleum hydrocarbons) and sorbent (contaminated soils). Soil desorption isotherms were obtained in the absence and presence of ultrasound. The impact of soil type on soil desorption was also studied.

The second part is the optimization of ultrasonic enhanced soil washing system (flow-type ultrasound treatment) by conducing orthogonal experiments. The impacts of five parameters on soil remediation efficiency were examined in the experiments, including initial concentration of petroleum hydrocarbons in soil, salinity, ultrasonic treatment time, soil flushing rate, and soil type.

The third part is to further examine the dynamic change of salinity and petroleum hydrocarbon concentration in soils during ultrasonic treatment process. The impact of salts on desorption of petroleum hydrocarbons was evaluated through such experiments.

3.2.1 Soil Desorption Experimental Design

Desorption experiments were designed to investigate the effect of soil type on oil desorption process in the absence and presence of ultrasound. Three types of soils including sand, sandy loam and loam with 7 different concentrations (0.2%, 0.4%, 0.8%, 1.2%, 1.6%, 2.0% and 2.5% by mass, respectively) of contaminant (crude oil) were prepared before the experiments were conducted. Five grams of each soil sample were added into a 40 mL glass vial with 30 mL DI water. Preliminary experiments were conducted to determine the time required for the aqueous/solid system to reach its equilibrium state. The desorption experiments without ultrasound were conducted using shaker, and the time for reaching equilibrium state was 24 hrs. For this type of desorption experiments, the glass vials with soils at different crude oil concentrations were placed in a shaker (New Brunswick Scientific C2 Platform shaker) for mechanical shaking at 250 rpm under ambient temperature for 24 hrs. The desorption experiments with ultrasound were conducted using ultrasonic probe, and the time for reaching equilibrium state was about 10 min. For this type of experiments, the glass vials were placed in a water bath with setup temperature at ambient temperature, and the ultrasonic probe was then inserted into the vial and vibrated for 10 min. The ultrasonic system used in the experiments was Misonix Sonicator 3000 with the ultrasonic vibration set at 20 kHz and power set at maximum (500-600 W).

After soil samples reached their steady states, the aqueous phase of soil solutions was separated through 20 min of centrifugation at 3000 rpm and then analyzed by GC-FID to determine the equilibrium concentrations (C^*) of crude oil in the solutions. The concentration of the retained crude oil on soil q^* can be calculated by the following equation:

$$q^* = q_0 - \frac{V}{m} C^* \qquad (3.1)$$

where q_0 denotes the initial concentration of adsorbate onto the soil; V denotes the volume of the aqueous solution; m denotes the mass of soil. Then the desorption isotherms of crude oil between solid phase and aqueous phase can be obtained.

3.2.2 Orthogonal Experimental Design

It is an important task to identify the major factors affecting ultrasonic enhanced soil washing process and their corresponding optimal levels for achieving higher system performance. However, when the number of investigated factors increases, a large number of experiments have to be carried out. In this study, the Taguchi method was used for experimental design in order to reduce the number of experimental runs.

Taguchi method can study large number of variables with only a small number of experiments by utilizing the design of orthogonal arrays (OAs) (Joseph and Piganatiells, 1988; Ross, 1996). The effects of interactions among multiple factors and the influence of individual factors on system performance can be effectively investigated by applying this technique (Ghani et al., 2004; Venkata Mohan et al., 2007). Analyses of the experimental data using signal-to-noise (S/N) ratio analysis and ANOVA can provide information about statistically significant factors and the corresponding optimal levels for each factor (Venkata Mohan et al., 2007).

Taguchi method has been broadly applied to many areas, such as material processing (Yang and Tarng, 1998; Ghani et al., 2004; Rosa et al., 2009), chemical engineering (Zhang et al., 2007; Chung et al., 2009) and biology (Kates et al., 1993; Liang, 2008). It has also been widely applied to environmental engineering studies. For example, Madaeni and Koocheki (2006) reported with positive results for optimization of a wastewater treatment system by using Taguchi method; Venkata Mohan et al. (2007) used Taguchi method to design experiments to evaluate the influence of biotic, abiotic and several other factors on soil bioremediation in bioslurry phase reactor. Some other related studies using Taguchi design method can be found in Urum et al. (2003), Wang et al. (2008), and Castorena-Cortés et al. (2009).

The experimental design approach of Taguchi method can be generally divided into the following steps as shown in Figure 3.1 (Ross, 1996):

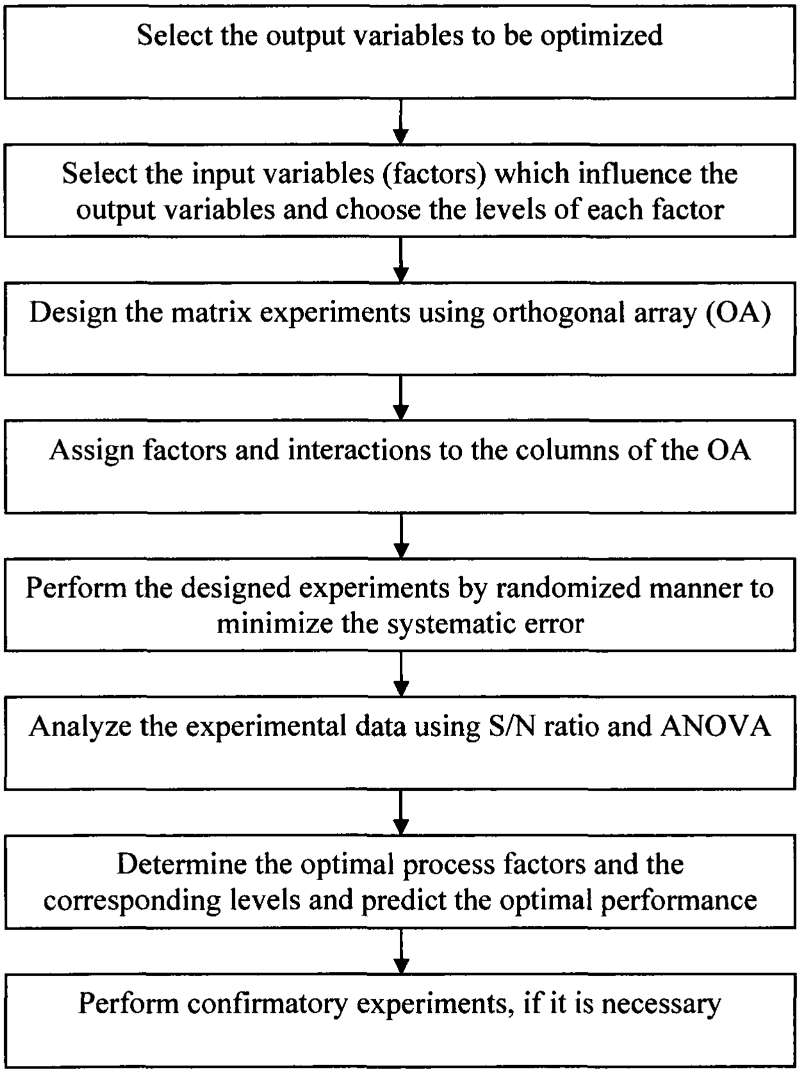

Figure 3.1 Experimental design procedures in Taguchi method optimization (Ross, 1996)

3.2.2.1 Taguchi Experimental Design Principles

There are two major tools used in Taguchi method: signal to noise (S/N) ratio and orthogonal arrays. S/N ratio was used as the quality characteristic of choice instead of standard deviation. It is a logarithmic function that is used to optimize the process and product design and reduce the sensitivity of system performance to sources of variations. The S/N ratio characteristics can be divided into three categories when the characteristics are continuous and can be used depending on different experimental goals:

Smaller the better (in this case the equation is used for undesirable characteristics such as carbon dioxide emissions):

$$\mathrm{S/N} = -10\log\sum_{i=1}^{n}\left(\frac{y_i^2}{n}\right) \qquad (3.2)$$

Larger the better (in this case the equation is used for desirable characteristics such as agricultural yield or treatment efficiency):

$$\mathrm{S/N} = -10\log\sum_{i=1}^{n}\left(\frac{1}{y_i^2}\right)/n \qquad (3.3)$$

Nominal is better (in this case a specific value is the most desirable for the characteristic such as length, depth or thickness. This means that neither a smaller nor a larger value is desirable):

$$\text{S/N} = 10\log\frac{\bar{y}^2}{s_y^2} \qquad (3.4)$$

where y_i denotes the observed data, n is the number of observations, $\bar{y}^2$ is the average of the observed data, s_y^2 is the variance of y. The unit of S/N ratio is decibels (dB). For each type of the characteristics, the higher the S/N ratio, the better the result is. Therefore the process optimization is to find the optimal levels of all the influencing factors that lead to the greatest S/N ratio. After S/N ratio analysis, statistical analysis of variance (ANOVA) can be conducted to verify whether the chosen factors are statistically significant to the entire process. The combination of S/N analysis and ANOVA would help find out the optimal levels of factors.

3.2.2.2 Influencing Factors

As shown in Figure 3.1, the first step of Taguchi experimental design procedures is to identify the important factors to be optimized. The treatment efficiency of ultrasonic enhanced soil washing can be influenced by many factors such as initial TPH concentration, salinity, soil type, ultrasonic treatment time, soil washing flow rate and others. The influencing factors are described below:

A. Initial TPH Concentration

The contamination of petroleum hydrocarbon on soil can affect the soil permeability and water holding capacity. The variation of the initial concentration of petroleum hydrocarbons in soil would affect the mixture status of soil, water and oil and consequently it might affect the treatment efficiency. Three levels of initial TPH concentrations were selected as 0.5, 1.0 and 2.0% (by weight).

B. Salinity

Soil salinity could affect the remediation effect by changing the soil structure. Previous studies had reported negative effects of salinity on TPH removal (Feng and Aldrich 2000; McMillan, 2008). However, in the presence of soil washing, the negative effect of salinity could be decreased since soil washing is capable of removing adsorbed salts from soil matrix. Thus three levels of soil salinity were used in the experiments, including 0 M (no salt), 0.4M, and 0.8M.

C. Soil Type

The adsorption and desorption of oil contaminants onto soils are highly related to soil types. Different soils have different properties such as surface areas, particle sizes and charges which can influence the remediation treatment efficiency. Three soil texture types were used in the experiments, including sand, sandy loam and loam.

D. Ultrasonic Treatment Time

Previous studies revealed that the maximum contaminant reduction could be achieved within a very short ultrasonic treatment time (i.e. 2 to 5 minutes), indicating that the duration of ultrasonic treatment will not have a significant effect on remediation efficiency (Feng and Aldrich 2000). However, after soil washing was added to the ultrasonic treatment system, the ability of oil desorption from soil and oil dilution in water might be increased which means the duration of ultrasonic treatment might be longer for better treatment. In this study, three levels of ultrasonic treatment time were selected (1 min, 5 min, 10 min) to examine the effect of sonication time on remediation effect when using soil washing.

E. Soil Washing Flow Rate

Results of many previous studies have shown that soil washing treatment it is an effective method for decontamination (Lyman et al., 1990). Many researchers had successfully combined soil washing with ultrasound for hydrocarbons reduction (Kim and Wang, 2003; Mason et al., 2007b). However limited studies have investigated its ability of handling mixed contaminations of petroleum hydrocarbons and salts. Since soil washing is capable of influencing the transportations of both organic and salt contaminants, it was combined with ultrasound in this research and expected to improve the overall treatment efficiency. Three different flow rates were selected in the experiments including 0.5 cm^3/s, 1.0 cm^3/s and 1.5 cm^3/s.

3.2.2.3 Orthogonal array and Experimental design

Five parameters including initial concentration of petroleum hydrocarbons in soil, soil salinity, ultrasonic treatment time, soil flushing rate and soil type were chosen as the examination factors in the experiments. Each parameter was set at 3 different levels (Table 3.1). In order to reduce the number of experiments and find out the optimal working conditions for the remediation process, orthogonal experiments were designed and utilized. The orthogonal experimental design is based on Taguchi method and used to determine the optimal process parameters and analyze the effects and significances of different parameters through least number of experiments (Ross, 1996; Venkata Mohan et al, 2007). Table 3.2 presents the results of Taguchi experimental design. There were 18 experimental runs and each run was replicated for 3 times to reduce the possibility of error and to achieve reasonable statistical results. After all the experiments, S/N ratio analysis and ANOVA were conducted to examine the validity of experiments.

Table 3.1 Influencing factors and levels in Taguchi experiment

Factors	Levels		
	1	2	3
(A) Initial TPH Concentration (% by mass)	0.5	1.0	2.0
(B) Salinity (M)	0	0.4	0.8
(C) Soil Type	Sand	Sandy Loam	Loam
(D) Ultrasonic Treatment Time (min)	1	5	10
(E) Soil Washing Flow Rate (cm^3/s)	0.5	1.0	1.5

Table 3.2 Taguchi (orthogonal array) L18 ($2^1 \times 3^7$) experimental design

Experimental Number	e[a]	e	A[b]	B[b]	C[b]	D[b]	E[b]	e

1	1	1	1[c]	1	1	1	1	1
2	1	1	2[c]	2	2	2	2	2
3	1	1	3[c]	3	3	3	3	3
4	1	2	1	1	2	2	3	3
5	1	2	2	2	3	3	1	1
6	1	2	3	3	1	1	2	2
7	1	3	1	2	1	3	2	3
8	1	3	2	3	2	1	3	1
9	1	3	3	1	3	2	1	2
10	2	1	1	3	3	2	2	1
11	2	1	2	1	1	3	3	2
12	2	1	3	2	2	1	1	3
13	2	2	1	2	3	1	3	2
14	2	2	2	3	1	2	1	3
15	2	2	3	1	2	3	2	1
16	2	3	1	3	2	3	1	2
17	2	3	2	1	3	1	2	3
18	2	3	3	2	1	2	3	1

[a] empty column; [b] corresponding influencing factors according to Table 3.1; [c] corresponding factor levels according to Table 3.1.

3.2.3 Time-Series Experiments

In order to better understand the effect of salts on the dynamic variation of hydrocarbon desorption from soil under the treatment of different processes, time-series experiments were designed and conducted. Three treatment processes including ultrasonic treatment (US), soil washing (SW) and ultrasonic enhanced soil washing (US+SW) were investigated. The control experiments were treatments without ultrasound or soil washing. Soil samples were saturated with DI water and let stand for certain treatment time followed by centrifugation same as other treatments. All the time serial experimental data were collected at treatment time of 0, 1, 2, 3, 4, 5, 7, and 10 min, respectively. EC and TPH removal were both selected as performance criteria. Table 3.3 summarizes the parameters with their corresponding levels designed for the experiments. Influencing parameters including initial TPH concentration, soil washing rate were set at constant levels based on the results from orthogonal experiments. Salt can cause the structure of soil especially silt and clay become tighter and less permeable and thus inhibits the oil contaminants from desorbing. Since the negative impact of salinity is stronger on fine soil particles such as silt and clay than on sand, loam soil was selected as experimental soil: 30 mL of loam soil (37.7g) was used as soil sample in each experiment.

Table 3.3 Summary of time-series experimental design

Parameters	Levels
Time (min)	0, 1, 2, 3, 4, 5, 7, 10
Salinity	No salt added (0 M), salt added (0.8 M)
Treatment System	ultrasonic treatment; soil washing; ultrasonic enhanced soil washing treatment; control

3.2.4 Sample Treatment Processes

Figure 3.4 illustrates the sample treatment process of ultrasonic enhanced soil washing system. The sample treatment involves several procedures including sample extractions and TPH GC-FID analysis which will be described in other section.

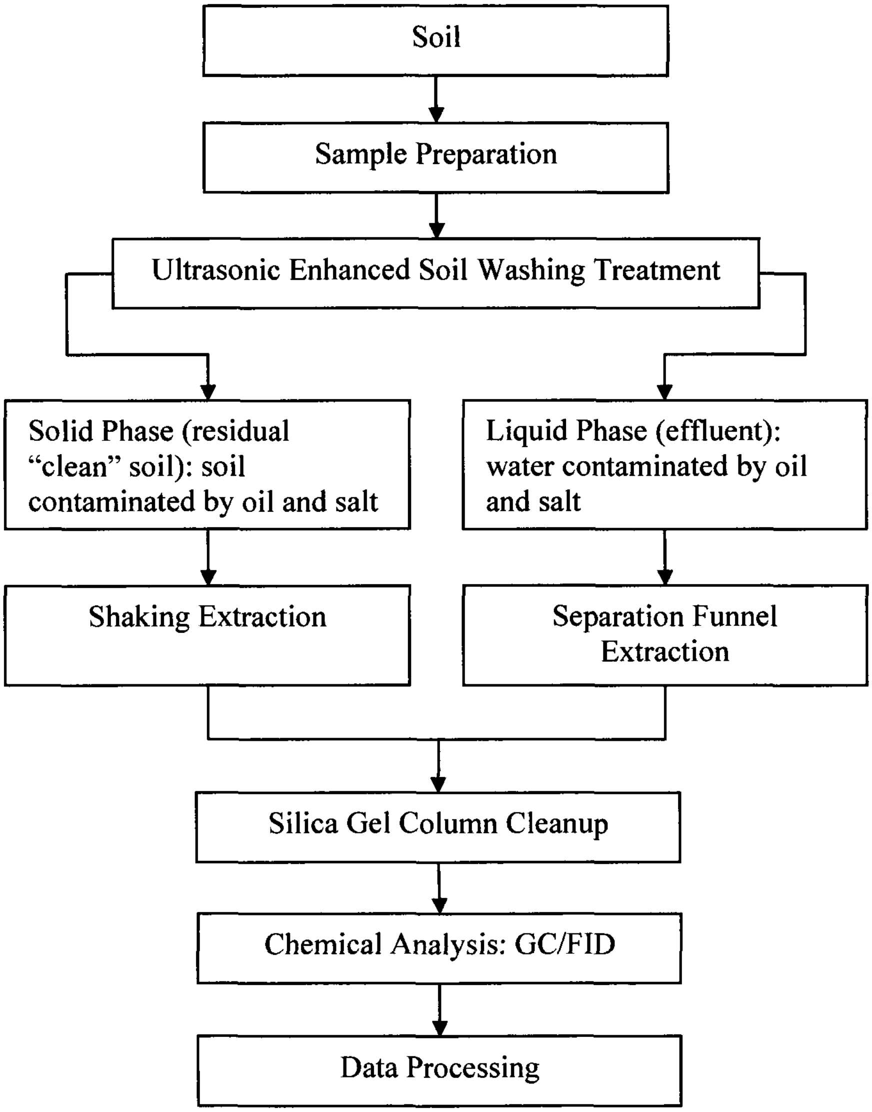

Figure 3.4 Flow chart of sample treatment for ultrasonic enhanced soil washing process

3.2.5 Ultrasonic Enhanced Soil Washing Treatment System

3.2.5.1 Reactor and Treatment System Design

The reactor for flow-type ultrasonic treatment experiments was designed for both soil washing treatment and ultrasonic treatment. The entire treatment system consists of two parts – a one dimensional soil washing chamber and an ultrasonic processor.

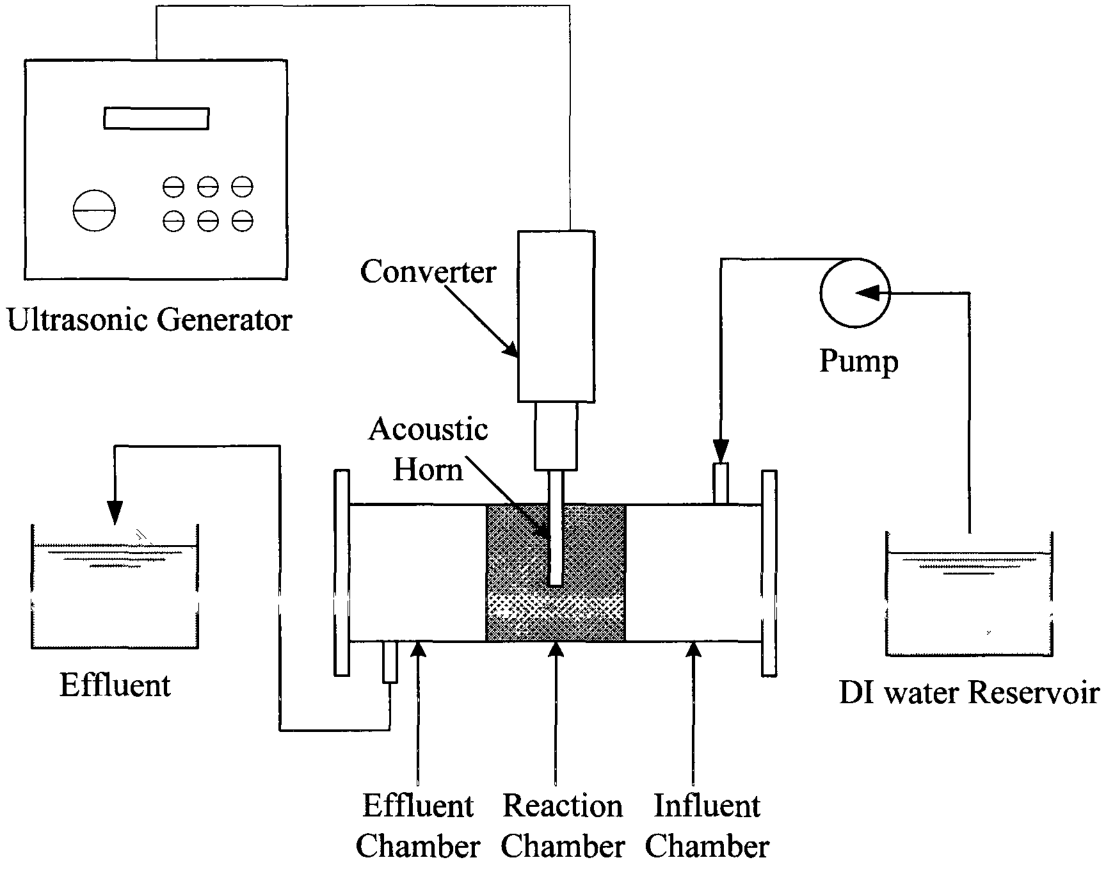

Figure 3.5 Ultrasonic enhanced soil washing treatment system design

The soil washing treatment chamber was made of a Plexiglas cylinder with an inside diameter of 5.0 cm and a total length of 20.0 cm. Figure 3.5 shows the design of the soil washing reactor. The influent chamber was 10.0 cm long and it was connected to a reservoir of deionized water which was pumped into the reactor to flush the PHC contaminants out of the soil samples in the reaction chamber. The continuous-flow pump used in the experiments was Simon Manostat Varistaltic Pump (Model No. 72-310-000) which can run from 24 to 720 rpm. The tubing used in the experiments was silicone lab tubing (4.8 mm inside diameter, Model 96400-25, Masterflex®, Cole-Parmer Instrument Co.) and it was connected to the apparatus using polyethylene-quick disconnects (Scienceware Co.). The reaction chamber was 5.0 cm long and it was the place where the soil washing treatment takes place. There is a hole with a diameter of ½ inch on the top of the reaction chamber where the ultrasonic probe was inserted for ultrasonic treatment. Between the reaction chamber and the other two chambers, woven wire mesh (stainless #120 mesh) were fitted to prevent soil losses during the soil washing treatment. After certain time of treatment, the effluent with contaminants flew out of the effluent chamber which was connected to a beaker.

The ultrasonic processor used in the experiments was Misonix Sonicator 3000 which was composed of three components: a generator, a converter and a standard acoustic horn. The generator converted the conventional 50/60 Hz alternating current at 110 V to a 20 kHz electrical energy at approximately 1500 V. The converter transformed the high-frequency electrical energy to mechanical vibration which was set at 20 kHz. The generator was set at maximum power (500-600 W output). The titanium acoustic probe was inserted with 3.75 cm into the reaction chamber from the hole and placed in the center of the soil samples. According to Mason (2002), the power intensity generated by the tip of the ultrasonic probe is equal to the electrical power divided by the surface area of the transducer tip. Thus the power intensity near the ultrasonic probe during the experiment was approximately:

$$I=\frac{P}{A}=\frac{550}{(\pi\times 1.27^2)}=109\mathrm{W/cm}^2$$

3.2.5.2 Treatment Procedures

Before each treatment, 30 mL of soil sample spiked with crude oil and salt (sodium chloride) was placed in the reaction chamber of the reactor. Sonic treatment was carried out by placing the ½-inch-diameter titanium sonic probe with 3.75 cm into the center of the soil specimen. The soil specimen was then saturated with DI water pumped from the DI water reservoir. Once the water level was maintained approximately 1 cm higher than the soil specimen, the soil specimen was applied with the ultrasonic waves at 20 kHz frequency; at the same time the DI water was kept being pumped into the reactor at a certain flow rate for soil washing. The DI water flew from the influent chamber through the soil specimen, and then carried the contaminants from the soil specimen and eventually flew out of the effluent chamber. The effluent was collected with a glass beaker. After a time period of T_{ul}, the ultrasonic treatment was stopped while the soil washing was still kept running for a certain time of T_{sw} to move all the "dirty" water into the beaker.

The soil washing treatment was then followed by extractions of PHCs from the "clean" soil specimen and the effluent. The effluent with washing water and fine soil particles were collected from the outlet and separated through centrifugation. The washing water without fines was then sent for liquid-liquid extraction (US EPA, 1996) before TPH analysis. The treated soil samples remaining in the reactor was then wet sieved through a stainless #120 mesh. The collected soil particles under this size were considered as detached particulates while those remaining in the sieve (sand) were retained for soil phase extraction (CCME, 2001) and TPH analysis. Figure 3.6 shows the setup of the ultrasonic enhanced soil washing treatment.

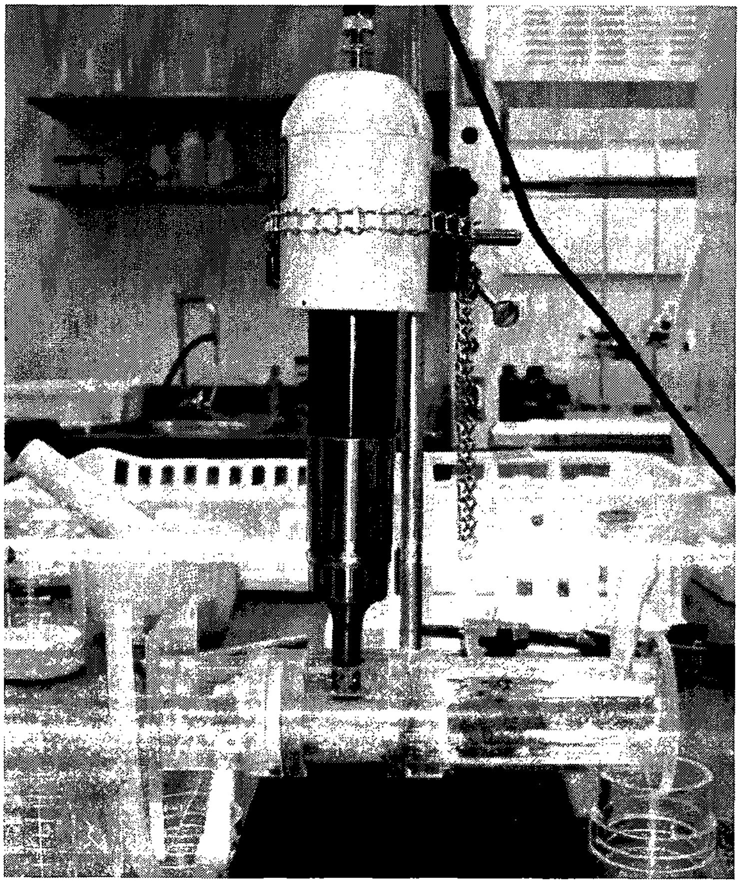

Figure 3.6 Ultrasonic enhanced soil washing treatment system set-up

3.2.6 Ultrasonic Treatment Systems

The ultrasonic treatment system consists of an ultrasonic generator, an acoustic horn, a glass beaker with contaminated soil sample and a temperature-controlled water bath, as shown in Figure 3.7. 30 mL of soil sample was measured and placed in a 300 mL glass beaker with 100 mL of DI water dissolved with certain amount of salt (sodium chloride). The sonic probe was placed 2.5 cm into the center of the sample. The frequency of the ultrasound is still 20 kHz and the ultrasonic power was set at maximum power (500-600 W output). The intensity of the ultrasound was approximately 109 W/cm^2.

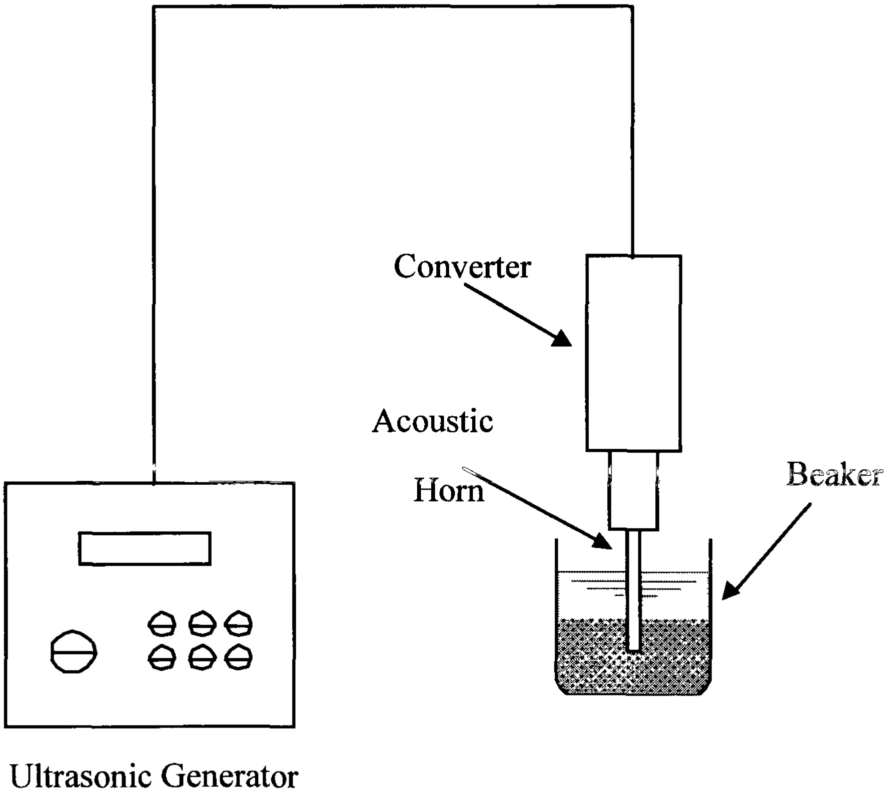

Figure 3.7 Ultrasonic treatment system design

In order to separate the water from the treated soil, the treated slurry was then poured into a 200 mL centrifuge bottle and centrifuged at 4,000 rpm for 30 min (Sorvall Legend X1 centrifuge, Thermo Scientific). The soil samples separated from the water will then be transferred to a 120 wide mouth glass jar and dried in an oven overnight before soil salinity test, sample extraction and TPH analysis.

3.3 Sample Extractions

3.3.1 Soil Extraction

Soils with residual crude were sampled to investigate the reduction of TPH concentration. Before sending for GC-FID analysis, soil extraction needed to be conducted. In this study, the soil extraction was completed using mechanical shaking method. According to Schwab (1999), mechanical shaking extraction is comparable in accuracy to the Soxhlet extraction which was the standard method for soil extraction as recommended by EPA (1996) and CCME (2001).

For the mechanical shaking method, 2 g (dry mass) of soil sample of each treated soil was weighed and collected into a 40 mL glass vial with a Teflon-lined cap. A volume of approximately 10 mL DCM (CCME, 2001) was added to the vial. The samples were then placed on a platform shaker (New Brunswick Scientific C2 Platform shaker) for 30 minutes of mechanical shaking at 250 rpm. After the mechanical shaking, the samples were allowed to settle for 10 min. The solvent extracts were then transferred into another set of vials, using a Finnpipette digital pipette. The samples were filled with another 10 mL of fresh solvent and the extraction procedure was repeated for two more times. In summary, a total of approximately 30 mL of solvent extracts was combined together in the 40 mL vials and then sent for Silica Gel Clean-up. Figure 3.8 shows how the mechanical shaking extraction works.

Figure 3.8 Mechanical shaking for soil extraction

3.3.2 Liquid Extraction

The effluents were also sampled to investigate the reduction of TPH concentration. The liquid extraction was carried out by using the separatory funnel liquid-liquid extraction (EPA, 1996). The organic compounds existing in the effluents were extracted from water by transferring 40 mL of sample from the graduated cylinder to the separatory funnel. 10 mL of DCM was then added into the separatory funnel which was sealed and shaken vigorously for 1-2 minutes with periodic venting to release excessive pressure. Once shaking was completed, the organic-phase layer and water-phase layer were separated for a minimum of 10 minutes. Then the solvent extract was collected in a set of 40 mL vials with a Finnpipette digital pipette. This extraction procedure was repeated two more times using fresh solvent of DCM. The 30 mL solvent extracts were then combined in the 40 mL vials. Figure 3.9 shows how the separatory funnel liquid – liquid extraction works.

Figure 3.9 Separatory funnel liquid – liquid extraction

3.3.3 Silica Gel Column Cleanup

According to the CCME Tier 1 Method-Reference Method for the Canada-wide Standard of Petroleum Hydrocarbons (CWS - PHC) in Soil (CCME, 2001), soil sample extraction was followed by silica gel cleanup which was intended to exclude moisture, particulate and unwanted polar organic compounds and improve the accuracy of analytical results by extraction (CCME, 2001). Since a national method has not been approved for water samples yet, the analysis of liquid sample extraction should be in accordance with the CCME Tier 1 method.

Glass column with a length of 30 cm and an inside diameter of 16 mm was prepared for each extract sample. A small amount of glass wool was placed at the bottom of the column followed by approximately 6.5 cm of 70-230 mesh silica gel (Fischer S286-1 activated at 110 °C for more than 12 hours). About 2.5 cm of 10-60 mesh ACS anhydrous sodium sulphate (S415-212 dried at 400 °C for 4 hours) was added at the top of the silica gel (CCME, 2001; Hughes 2005). The column was rinsed with approximately 15 mL 50:50 hexane / DCM. The extract sample was quantitatively transferred into a silica gel column. After the solvent level dropped below the top of the silica bed, another 20 mL of 50:50 hexane / DCM was added to elute the column. The clean extract were collected in an evaporating vessel and connected to a Yamato RE400 rotary evaporator to reduce extract volume to less than 2 mL. After that, the extract was quantitatively transferred into a 2 mL GC vial and then toluene was filled in to bring up the accurate final volume to 2 mL. The final extract samples were store at 4 °C before GC analysis. Figure 3.10 shows the operation for Silica Gel Cleanup procedure.

Figure 3.10 Silica gel clean-up of PHCs in soil

3.4 Sample Analysis

3.4.1 Hydrocarbon Analysis Using Gas Chromatograph

Samples with petroleum hydrocarbons were analyzed on a Varian CP-3800 Gas Chromatograph with flame ionization detector (GC-FID). The capillary column used was a Restek MXT-1 metal column with a length of 30 m and an inside diameter of 0.53 mm and a film thickness of 0.25 μm. 1.0 μL sample of TPH extract was injected into the injection port using a Varian CP 8400 Auto Sampler. Splitless injection mode was performed on the 1079 PTV injector and a split ratio of 10:1 was used after 0.7 minute of injection. Temperature of the injector was kept at 320 °C while temperature of the detector (FID) was kept at 350 °C during the analysis. The initial temperature of the capillary column was kept at 40 °C for 4 minute, then increased to 140 °C at a rate of 10.0 °C / min, and further increased to 340 °C at a rate of 20°C / min and held at 340 °C for 11 minutes. Thus the total run time for each sample was 35 minutes. The flow rate of the carrier gas (helium) was kept constant at 7.5 mL / min for the entire analysis. No pressure pulse was used for the injection.

Petroleum hydrocarbons were quantified by analyzing concentrations of CCME PHC fractions - F2 (PHCs from nC10 to nC16), F3 (PHCs from nC16 to nC34), and F4 (PHCs from nC34 to nC50) (CCME, 2001). A mixed analytical standard containing three straight-chain n-alkanes including decane (nC10), hexadecane (nC16), and tetratriacontane (nC34), was used for the calibration and to determine the response factor for TPH. Five different concentrations (i.e. 10, 25, 50, 100 and 250 ppm or µg per mL) of the mixed standard was prepared in toluene. Peak retention times were used to mark the beginning and the end of the F2, F3, and F4 fractions. The concentration of each fraction was calculated by integrating the area under the chromatogram from the apex of the nC10 peak to the apex of the nC16 peak, from the nC16 peak to the nC34 peak and from the nC34 peak to the nC50 where the chromatogram had returned to baseline. The integrated area data were converted into concentrations in mg/kg (ppm) by using the average response factor which was calculated using the response factors of each individual compounds (CCME, 2001). Figure 3.11 shows the setup for GC-FID TPH analysis procedure.

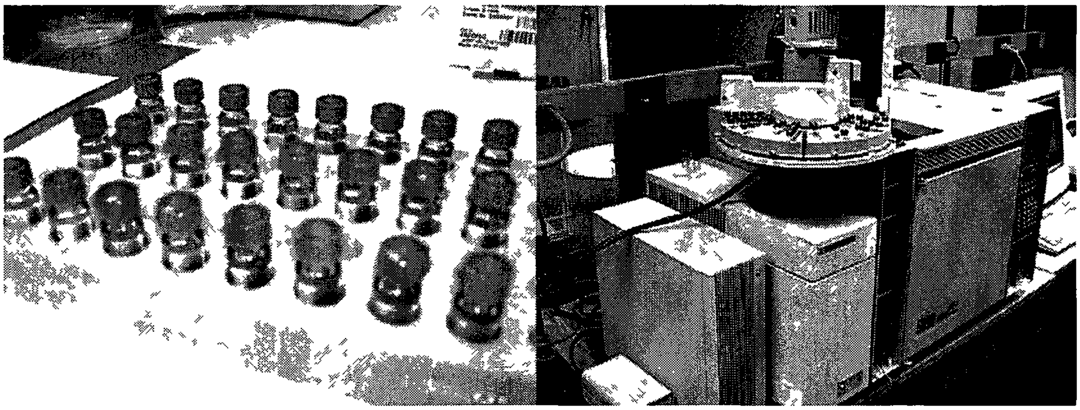

Figure 3.11 GC-FID analysis; left: analysis vials; right: GC-FID analyzer.

3.4.2 Salinity Analysis

Soil salinity was generally measured by the electrical conductivity (EC) of the soil samples. Fixed ratio extraction was used to extract soluble salts from soil samples to the water. The mixing ratio of air-dry soil to deionized water was 1:5. Air dry samples were weighed into 125 mL glass jars and sufficient deionized water was added to achieve desired ratio of 1:5. The glass jars were capped and shaken on the New Brunswick Scientific C2 Platform shaker for 1 hour and then allowed to settle for approximately 30 minutes. The suspensions in the glass jar were then vacuum filtered using filter paper (Fisher GF/A 1.6 m retention glass microfibre filter paper) (Carter and Gregorich, 2006). The solution was then measured for EC using an EC meter (VWR symphony

Conductivity Meter) with electrode (VWR symphony Two Cell Carbon Conductivity Probe). Before the measurement, the EC meter was calibrated using standard KCl solution to automatically adjust cell constant internal to the meter and all the measurements were automatically adjusted to 25 °C by the meter.

Chapter 4 Results and Analysis

4.1 Physical and Chemical Properties of Soils

The original soil samples were sent to the Analytical Laboratory of B.C. Ministry of Forests for the analysis of soil properties. The analysis results were listed in Table 4.1. The ESP and SAR values were calculated using exchangeable cation concentrations and CEC values according to Equations 2.10 and 2.11, respectively. The data for the two mixed soils (sandy loam and loam) were calculated using the data of sand and silty clay loam based on their mixing ratios.

According to the results listed in Table 4.1, those two soils mixed at ratio of 70/30 (sand/silty clay loam) and 40/60 (sand/silty clay loam) were classified into sandy loam soil and loam soil, respectively. Since silty clay loam was a natural soil collected in a forest while the sand was a purchased industrial product, the total carbon and total nitrogen of silty clay loam were all greater than those of sand. The exchangeable cation concentrations of silty clay loam were also greater than those of sand. The pH values of all the soils were approximately 7. The silty clay loam had an EC value greater than that of sand but less than 4 dS/m which means all these soils were not salt-impacted. The values of ESP and SAR of both sand and silty clay loam fit the relation as: EC < 4 dS/m, ESP <15, SAR<13 indicating that these two soils are neither saline nor sodic. Therefore they are clean and ready to be used in the following experiments (Carty et al., 1997).

Table 4.1 Soil properties of soil samples

Properties		Sand	Silty clay loam	Sandy loam	Loam
Soil composition (%)	Sand	100	7.8	72.4	44.7
	Silt	0	53.0	15.9	31.8
	Clay	0	39.2	11.7	23.5
Total Carbon (%)		0.06	1.15	0.39	0.71
Total Nitrogen (%)		0.002	0.084	0.027	0.051
Exchangeable Cation Concentration (cmol/kg)	Al^{3+}	0.007	1.286	0.391	0.774
	Ca^{2+}	0.040	0.150	0.073	0.106
	Mg^{2+}	0.021	0.300	0.105	0.188
	K^{+}	0.002	0.111	0.035	0.067
	Na^{+}	0.007	0.078	0.028	0.049
CEC (cmol/kg)		0.077	1.924	0.632	1.184
ESP (%)		8.4	4.0	4.4	4.1
SAR		2.8	11.5	6.6	9.0
pH		6.97	7.25	7.11	7.18
EC (dS/m)		1.2	1.5	1.3	1.4

4.2 Soil Desorption Properties

4.2.1 Effect of Soil Type on TPH Desorption

The results of desorption experiments are shown in Tables 4.2, 4.3 and 4.4, respectively. Three replications of treatments were conducted and the TPH concentrations were compared to insure the quality and precision of experimental data. The systematic errors were expressed by standard deviation (SD) and relative standard deviation (RSD) that were calculated using TPH concentrations of the three replications. SD was calculated as the square root of sum of variance while RSD was expressed in percentage and calculated as SD divided by average. According to the quality control standard in CCME Tier 1 laboratory methods (2001), the method detection limits (MDLs) for analysis of F2, F3 and F4 concentration is 200 mg/kg (CCME, 2001; McMillan, 2008). While the data quality objectives for laboratory precision require that repeated sample analysis with concentrations greater than 10 times the MDL must have a RSD less than 30% (CCME, 2001; McMillan, 2008).

Figure 4.1 shows the desorption isotherms of crude oil on those three soils in the absence of ultrasound. As shown in the figure, the desorption isotherm of crude oil on sand was much lower than that on the other two soils which means more oil was desorbed from sand into the water phase after reaching the steady state, therefore the crude oil adsorbed onto sand was the easiest to be desorbed after 24 hr of mechanical shaking. On the contrary, the crude oil adsorbed on loam has higher isotherm than the other two, indicating that it is the most difficult situation for oil to be desorbed from loam. The isotherm of crude oil on sandy loam was slightly lower than that on loam, thus the desorption ability of sandy loam is slightly stronger than that of loam. But comparing with sand, it is still very difficult for the oil on sandy loam to be desorbed. Therefore, for crude oil desorption on these three types of soil, the finer the soil particle is, the harder the hydrocarbon can be desorbed.

Figure 4.2 shows the desorption isotherms of crude oil on those three soils in the presence of ultrasound. Similar to the desorption isotherms in the absence of ultrasound, under the effect of 10 min of ultrasonic treatment, the desorption of crude oil on sand still showed the lowest isotherm indicating that sand is the easiest soil for crude oil to be desorbed from. On the contrary, the isotherm curve of loam was the highest and the isotherm curve of sandy loam lies between the other two, indicating that loam as the finest soil in this experiment was still the most difficult one to be cleaned by desorption and the desorption ability of sandy loam soil was still weaker then loam but stronger than sand. Therefore, under the effect of ultrasound, the desorption of crude oil from soil is still highly related to soil type: the finer the soil particle is, the harder the hydrocarbon can be desorbed. Moreover, comparing with the desorption isotherms in Figure 4.1, it can be found that under the effect of ultrasound, the desorption isotherms of all soils were lowered and the effect was more obvious on finer soils. The result of the further examination of the effect of ultrasound on desorption of crude oil can be found in the following paragraph.

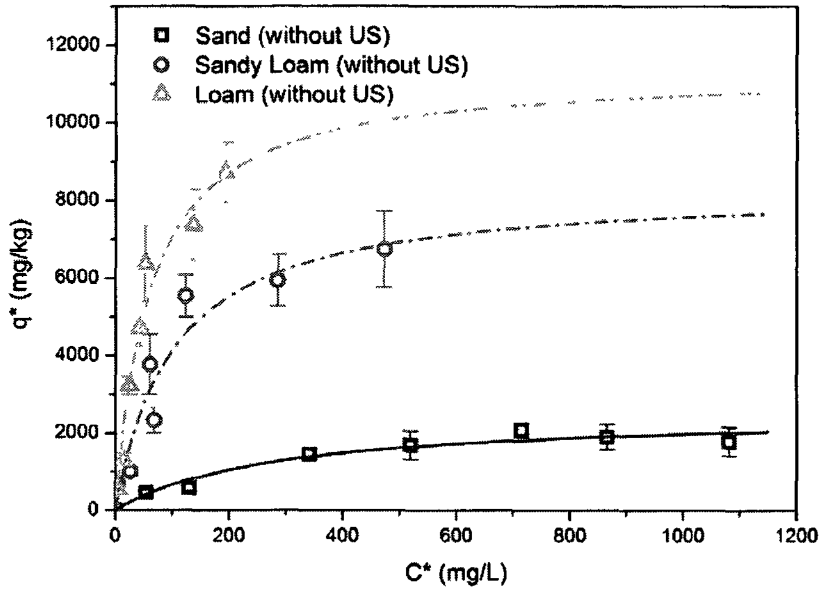

Figure 4.1 Desorptions of crude oil without ultrasound at 25 ° C

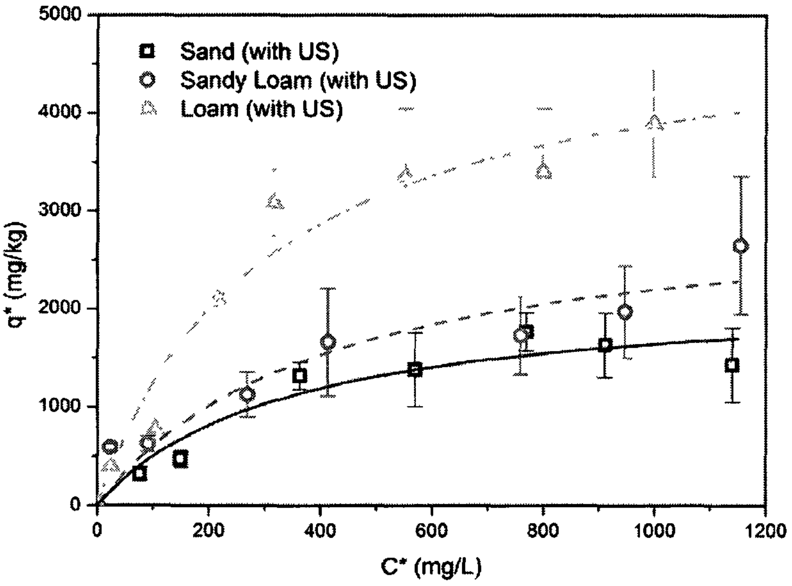

Figure 4.2 Desorptions of crude oil with ultrasound at 25 ° C

Table 4.2 Results of crude oil desorption from sand soil

Sand																	
Average TPH Concentration in Solution (shaking)						Average TPH Concentration in Solution (Ultrasonication)						Initial Average TPH Concentration in soil					
F2 (mg/L)	F3 (mg/L)	F4 (mg/L)	TPH (mg/L)	SD [a] (mg/L)	RSD [b] (%)	F2 (mg/L)	F3 (mg/L)	F4 (mg/L)	TPH (mg/L)	SD (mg/L)	RSD (%)	F2 (mg/kg)	F3 (mg/kg)	F4 (mg/kg)	TPH (mg/kg)	SD (mg/kg)	RSD (%)
12	28	14	54	8	13.8	25	39	12	76	14	18.3	177	450	149	775	103	13.3
30	72	29	131	28	21.4	54	72	24	149	19	12.5	325	713	328	1,366	114	8.3
97	166	78	341	81	23.8	134	181	47	363	50	13.8	974	1,714	803	3,491	189	5.4
114	291	114	519	34	6.5	200	291	80	570	42	7.4	1,104	2,640	1,056	4,800	526	11.0
172	386	157	715	65	9.1	277	400	92	769	56	7.3	1,594	3,251	1,530	6,374	267	4.2
208	468	191	866	54	6.3	346	446	118	911	80	8.8	1,703	3,689	1,703	7,095	455	6.4
270	562	249	1,081	96	8.9	433	581	125	1,140	131	11.5	1,902	4,383	1,985	8,269	521	6.3

[a] SD: standard deviation;

[b] RSD: relative standard deviation.

Table 4.3 Results of crude oil desorption from sandy loam soil

Sandy Loam																	
Average TPH Concentration in Solution (shaking)						Average TPH Concentration in Solution (Ultrasonication)						Initial Average TPH Concentration in soil					
F2 (mg/L)	F3 (mg/L)	F4 (mg/L)	TPH (mg/L)	SD (mg/L)	RSD (%)	F2 (mg/L)	F3 (mg/L)	F4 (mg/L)	TPH (mg/L)	SD (mg/L)	RSD (%)	F2 (mg/kg)	F3 (mg/kg)	F4 (mg/kg)	TPH (mg/kg)	SD (mg/kg)	RSD (%)
1	3	1	5	1	22.6	8	11	3	22	2	10.8	179	395	144	718	44	6.1
5	16	6	26	4	13.3	37	42	11	90	21	22.8	303	687	175	1,164	109	9.4
19	39	10	68	3	4.7	92	148	30	269	18	6.8	685	1,618	439	2,742	320	11.7
13	35	12	60	9	14.1	157	206	50	413	81	19.6	827	2,316	993	4,136	771	18.6
29	71	25	124	8	6.3	304	304	152	759	128	16.8	1,256	3,455	1,570	6,282	548	8.7
83	180	23	286	26	9.0	388	379	180	947	64	6.7	1,684	4,133	1,837	7,654	664	8.7
114	284	76	473	29	6.1	531	497	127	1,155	205	17.7	2,299	5,174	2,108	9,581	982	10.2

Table 4.4 Results of crude oil desorption from loam soil

Loam																	
Average TPH Concentration in Solution (shaking)						Average TPH Concentration in Solution (Ultrasonication)						Initial Average TPH Concentration in soil					
F2 (mg/L)	F3 (mg/L)	F4 (mg/L)	TPH (mg/L)	SD (mg/L)	RSD (%)	F2 (mg/L)	F3 (mg/L)	F4 (mg/L)	TPH (mg/L)	SD (mg/L)	RSD (%)	F2 (mg/kg)	F3 (mg/kg)	F4 (mg/kg)	TPH (mg/kg)	SD (mg/kg)	RSD (%)
2	4	1	6	2	37.8	11	11	3	24	3	12.9	114	309	119	542	133	24.6
4	8	2	14	2	11.9	42	45	17	104	16	15.0	362	738	292	1,392	167	12.0
6	12	6	25	5	18.8	101	91	24	216	20	9.4	676	1,959	743	3,378	234	6.9
14	23	6	43	3	7.3	123	149	44	316	23	7.3	995	2,837	1,145	4,977	482	9.7
15	28	9	52	13	25.5	221	254	77	552	82	14.8	1,401	3,668	1,601	6,669	972	14.6
32	70	36	137	13	9.5	327	351	120	799	38	4.7	1,802	4,505	1,884	8,191	911	11.1
37	107	50	194	14	7.3	429	439	130	998	109	10.9	2,273	5,238	2,372	9,883	767	7.8

4.2.2 Effect of Ultrasound on TPH Desorption

The isotherms of all the three types of soil showed the same shape in the absence and the presence of ultrasound. The relationships between C*/q* and C* shown in Figure 4.4, 4.6 and 4.8 were linear. Thus the desorptions of crude oil in the absence and presence of ultrasound can all be expressed by Langmuir equation in Equation 2.6 and 2.8.

Figure 4.3, 4.5 and 4.7 show the results of Langmuir curve fitting analyzed using Nonlinear Curve Fitting in OriginPro 8.0 (OriginLab Co.). It is obvious that all the isotherms of the soils treated by ultrasound were lower than those of the soils treated without ultrasound. The results indicate that ultrasound had promoted the oil desorption from all the soils. Ultrasound caused more oil desorption so the adsorbed amounts were decreased and the oil concentrations in solutions were increased. By comparing these three figures, it can also be found that the ultrasonic enhancement on desorption from fine soil (i.e. sandy loam and loam soil) is obviously more significant than that from the coarse soil (sand). In terms of sand soil, the bonding force between sorbent and sorbate is weak and the regular extraction by solvent water is strong enough to remove the adsorbed oil from sand. Thus the amount of desorbed oil by ultrasonic enhancement was small. On the contrary, the bonding forces between fine soils and oil are stronger. The fine soils have larger surface areas and micropore volumes for adsorption. Comparing to sand, more oil molecules can be adsorbed and trapped within the fine soils and they are difficult to be reached and extracted by solvent water. Under the cavitation effect of ultrasound, the sonic energy can be transported into the soil matrix and the bond between oil and soil particles can be easily broken. The works of Domingos et al. (1997) and Juang et al. (2006) had proved the ability of ultrasound to change the adsorbent's structure by decreasing its surface area and pore volume. Thus a large amount of adsorbed oil were desorbed under the influence of ultrasound leading to the result that the ultrasonic enhancements on desorption from fine soils are greater than that from sand soil.

Additionally, as shown Figure 4.5 and 4.7, , the experimental data of TPH desorption from sandy loam and loam soil in the absence of ultrasound didn't evenly distribute around the regression curves but concentrated at the left side of the curves. This might because that the initial TPH concentration on fine soils were not high enough. In order to obtain better data and fill up the right sides of the regression curves, higher TPH concentrations for saturation TPH adsorption on fine soils will be needed.

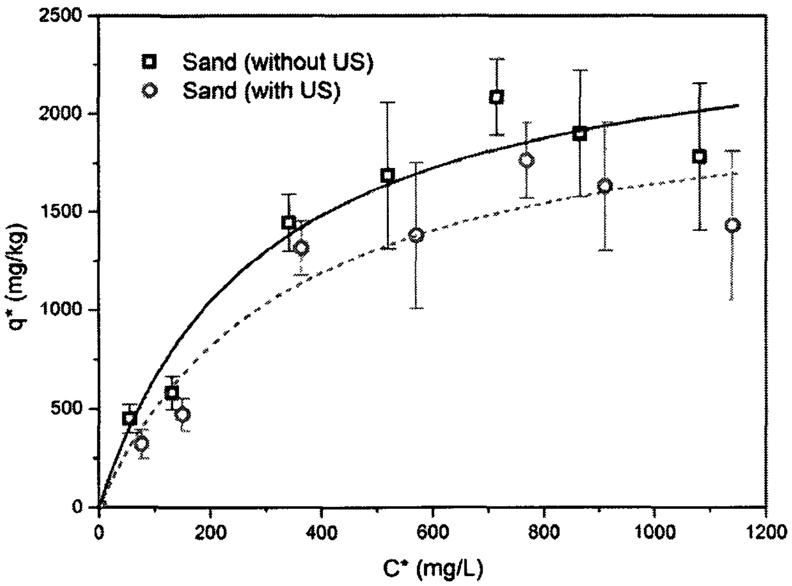

Figure 4.3 Effect of ultrasound on desorption isotherms of crude oil on sand at 25 ° C

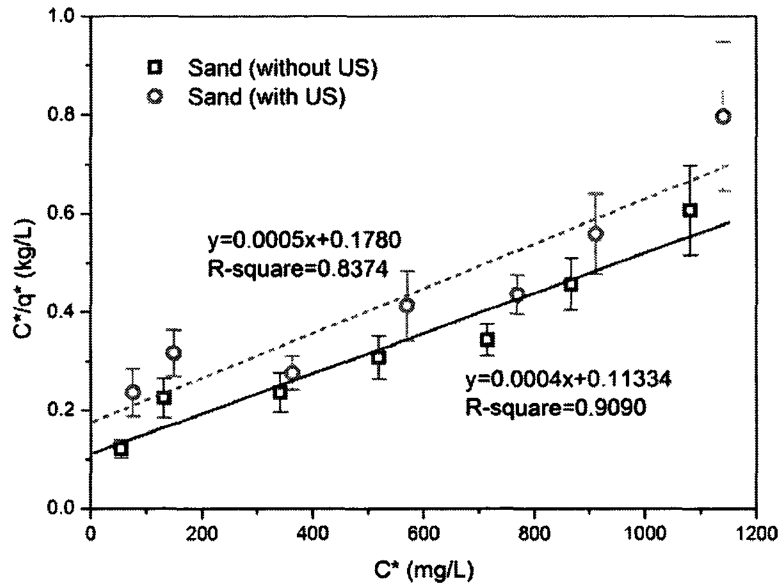

Figure 4.4 Linear Langmuir regression of desorption isotherms on sand at 25 ° C

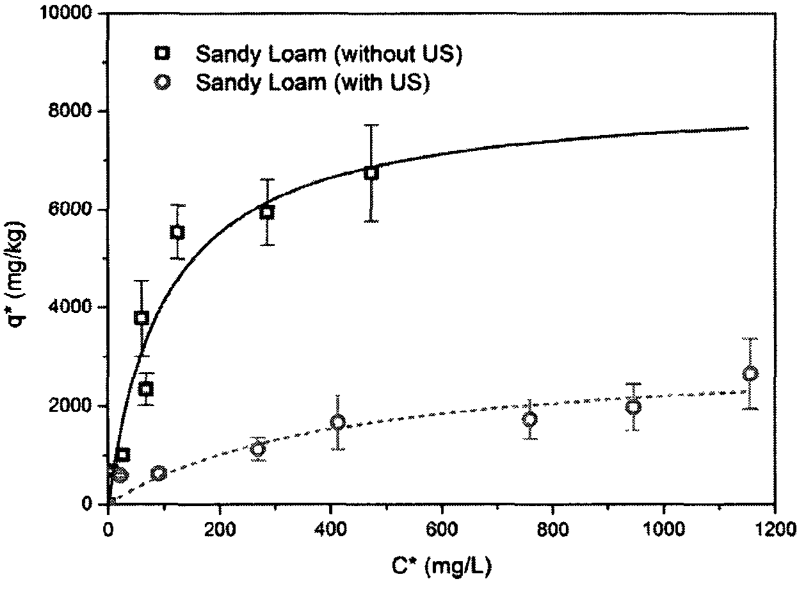

Figure 4.5 Effect of ultrasound on desorption isotherms of crude oil on sandy loam at 25 ° C

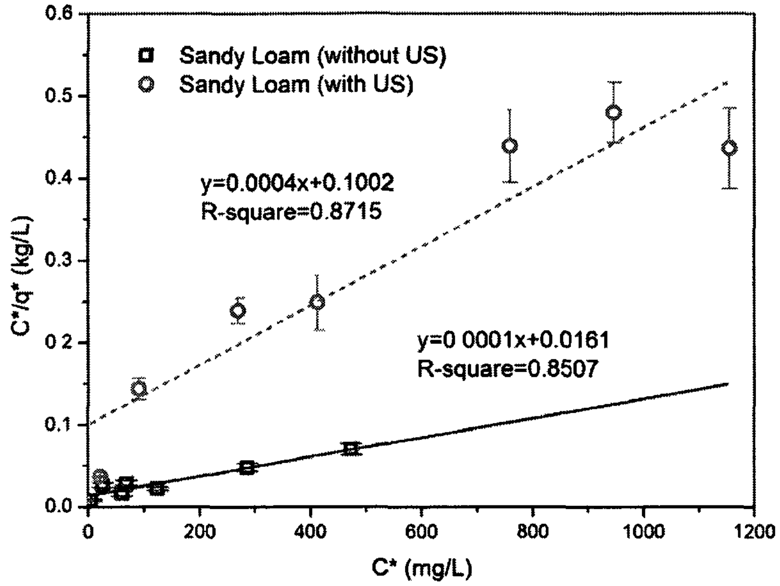

Figure 4.6 Linear Langmuir regression of desorption isotherms on sandy loam at 25 °C

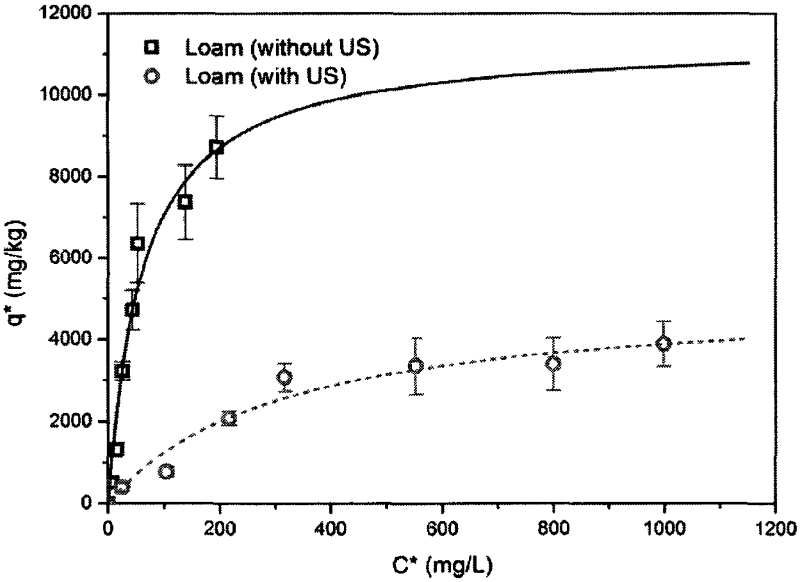

Figure 4.7 Effect of ultrasound on desorption isotherms of crude oil on loam at 25 ° C

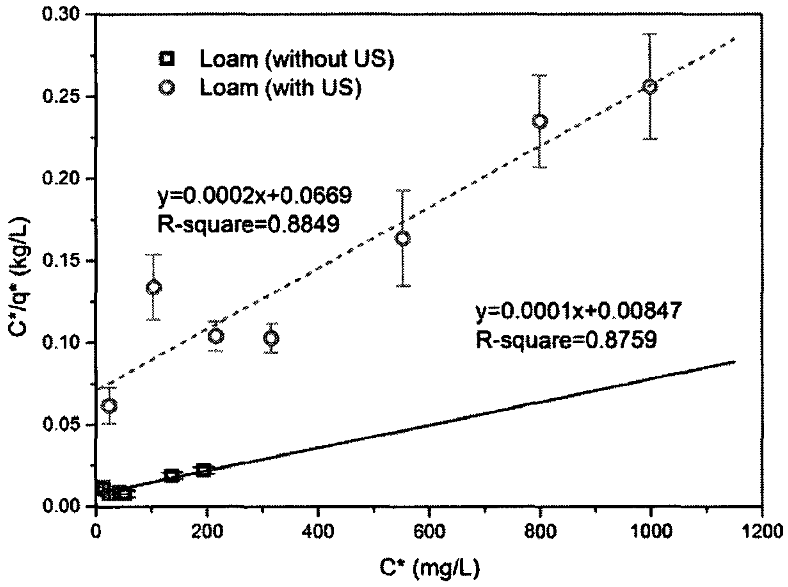

Figure 4.8 Linear Langmuir regression of desorption isotherms on loam at 25 ° C

The Langmuir equation assumes that there is no interaction between the adsorbate and the sorption is localized in a monolayer. Therefore, it is then assumed that once a hydrocarbon molecule occupies a site, no further sorption can take place at that site. Theoretically a saturation value is reached beyond which no further sorption can take place. The Langmuir constant K and the saturation adsorption capacity corresponding to monolayer coverage Q were obtained both from the linear regression and curve fitting. Table 4.5 lists the parameters of the Langmuir equation for different soils under different conditions. The results from Langmuir curve regression analysis have the higher correlation coefficients (from 0.8982 to 0.9622) than from linear regression (from 0.8375 to 0.9090); the F values of curve regression analysis (from 118.75 to 271.99) are also higher than those of linear regression analysis (from 35.18 to 60.93). Therefore the simulations of curve fitting were more accurate than the linear regression and the following discussions about the regression analysis will be focused on the results of curve regression.

Table 4.5 Parameters in the Langmuir regression equation and coefficients for desorption of crude oil under different conditions

	Without Ultrasound				With Ultrasound			
	Linear Regression		Curve Regression		Linear Regression		Curve Regression	
Sand	Q	2,205	Q	2,554	Q	2444	Q	2,197
	K	0.0025	K	0.0035	K	0.0036	K	0.0030
	R^2	0.8375	R^2	0.9507	R^2	0.909	R^2	0.9235
	F	60.93	F	271.99	F	31.92	F	168.78
	P	<0.001	P	<0.001	P	0.002	P	<0.001
Sandy Loam	Q	2,751	Q	8,340	Q	8859	Q	3,114
	K	0.0036	K	0.0098	K	0.0070	K	0.0024
	R^2	0.8715	R^2	0.9266	R^2	0.8507	R^2	0.8982
	F	35.18	F	128.8	F	41.70	F	118.75
	P	0.002	P	<0.001	P	0.001	P	<0.001
Loam	Q	5,263	Q	11,349	Q	1534	Q	5,090
	K	0.0028	K	0.0165	K	0.0770	K	0.0032
	R^2	0.8849	R^2	0.9622	R^2	0.8759	R^2	0.9576
	F	43.36	F	248.27	F	47.14	F	259.67
	P	0.001	P	<0.001	P	0.001	P	<0.001

Units: Q (mg/kg) and K (L/kg); R^2: correlation coefficient;
F: fisher test value; P: probability value, alpha=0.05

The changes of adsorption capacity in the absence and presence of ultrasound were shown in Fig 4.9. It is obvious to see that in the absence of ultrasound, the finer the soil was, the larger the original saturation adsorption capacity was (for sand, Q was 2254 mg/kg, while for loam, Q was 11349 mg/kg which was much higher than the former). However, in the presence of ultrasound, the equilibriums of the soils were all changed and reached to new levels. Comparing with the original equilibrium state without ultrasound, the saturation adsorption capacities of the soils treated with ultrasound had all decreased which means more oil molecules adsorbed on the soils were desorbed and entered the aqueous phase. The decrements of saturation adsorption capacity in loam (6259 mg/kg) and sandy loam (5226 mg/kg) were much higher than that in sand (357 mg/kg). Thus the effect of ultrasound was stronger on finer soils than granular soil.

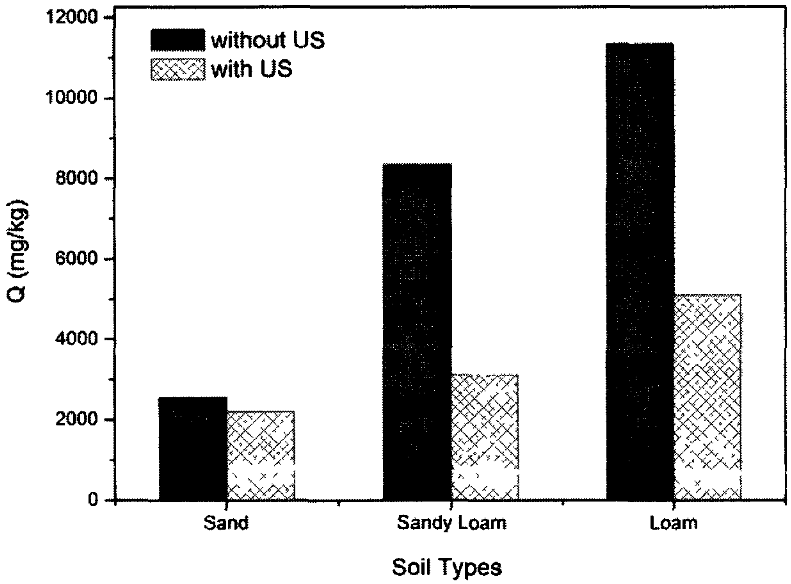

Figure 4.9 Effect of ultrasound on saturation adsorption capacity

The changes of adsorption equilibrium constant K was shown in Figure 4.10. According to Equation 2.7, K is the ratio of rate of adsorption constant to the rate of desorption constant. As K increases the adsorption/desorption equilibrium moves towards adsorption while as K decreases the equilibrium moves towards desorption. From Figure

4.10 it can be found that in the absence of ultrasound, K increases as the soil particles become finer (for loam K was 0.0165 L/mg, for sandy loam K was 0.0098 L/mg while for sand K was 0.0035 L/mg) indicating that when equilibrium was reached, the equilibrium moved towards adsorption thus more oil molecules were absorbed on the finer soils especially on loam. In the presence of ultrasound, the adsorption equilibrium constant decreases for all the soils which means that ultrasound helped to decrease the oil adsorption rate, increase the oil desorption rate, and therefore forced the adsorption/desorption to move towards desorption. The decrement on fine soils (from 0.0165 to 0.0032 L/mg) especially on loam was greater than that on granular sand (from 0.0035 to 0.0030 L/mg). Similar to the results of the changes of adsorption capacity, the changes of adsorption equilibrium constant also suggested that the effect of ultrasound was stronger on fine soils than granular soil.

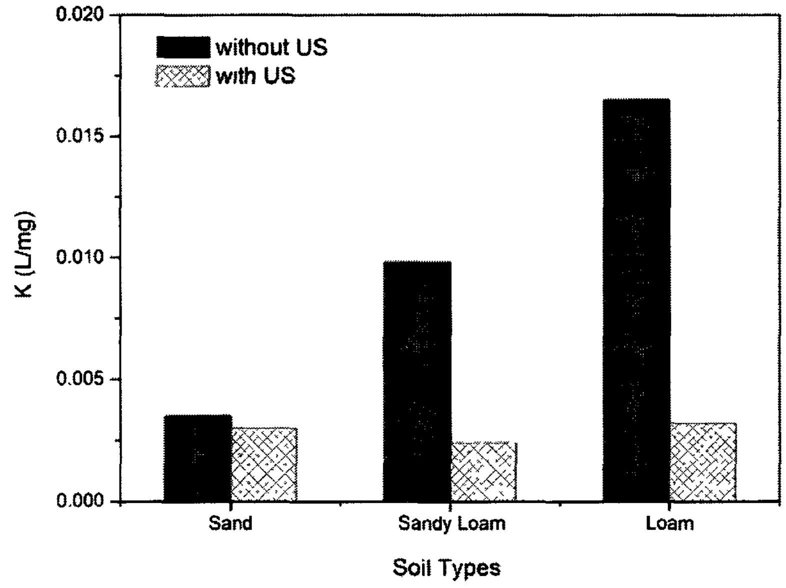

Figure 4.10 Effect of ultrasound on adsorption equilibrium constant

4.3 Orthogonal Experimental Results

The desorption experiment investigated the effect of ultrasound on TPH desorption from different soil types and the information acquired is useful for the study of the remediation of mixed contamination using ultrasound and soil washing. In order to systematically evaluate the ability of ultrasonic enhanced soil washing as an effective soil remediation technique, five influencing factors were selected for optimization of the technique. In order to investigate the change of the composition of TPH under the effect of treatment, the mass balance of both soil samples and TPH were first calculated. The experimental data was then analyzed by S/N ratio analysis and ANOVA.

4.3.1 Mass Balances

According to the results of the desorption experiments, fine soils with smaller particle sizes have larger adsorption capacity than coarse soils. Therefore, during a soil washing process, fine soil particles such as silt and clay which adsorb more contaminant (TPH) than coarse soils (sand) are usually separated from coarse soils and flushed out with washing solvent. In this way the coarse soil is cleaned while the finer soils carrying concentrated contaminants can be further separated through centrifugation and cleaned with further treatment method. In this thesis, in the experiments using ultrasonic enhanced soil washing, #120 sieve was used to keep sand and most part of the fine soils within the reaction chamber during treatment. In order to compare the TPH concentration changes on different fraction of soils (sand, fine soils) after being treated by ultrasound and soil washing, the mass of soil and TPH were calculated in fractions.

The soil particle sizes are very small especially for clay particles. In addition, under the irradiation of ultrasound the soil particles can be broken into even smaller pieces. Moreover, some of the soil particles might stay on the inside surface of the reactor or the sieve and became difficult to be removed. Therefore it is extremely difficult to completely transport and collect the test soils after the treatments. Additionally, the mass loss of soil can also cause the mass loss of TPH since some of the contaminants can be adsorbed on the lost soil particles. The mass loss of soil caused by incomplete transportation needs to be calculated and monitored in order to make sure the quality of experimental data.

For each experiment, the mass balance equation was established for different fractions of the test soil. In terms of experiments for sand soil (i.e. test #1, 6, 7, 11, 14 and 18 as shown in Table 3.2), since the sand used in these experiments was Ottawa standard sand which has a particle size between 0.420 to 0.595 mm (#30 to 40 sieve) while the # 120 mesh has an opening of 0.125 mm, the sand particles couldn't pass through the sieve. Since no fine soil particles such as silt or clay exists in sand soil, there was no fine soil particle in the effluent and therefore the mass balance equation can be described in Equation 4.1.

In terms of experiments for sandy loam and loam soil (i.e. test #2, 3, 4, 5, 8, 9, 10, 12, 13, 15, 16 and 17 as shown in Table 3.2), since the particle sizes for silt and clay were smaller than 0.05 mm, part of the fine soil particles could be flushed through #120 mesh and out of the reactor, while part of the fine soil particles could stay within the reaction chamber. The residual soil in the reaction chamber were separated into sand and fine soils by using #120 sieve; while the fine soils in effluent were separated from washing water by centrifugation. Therefore the mass balance equation for sandy loam and loam soil can be described using Equation 4.2. The soil distributions during treatment were shown in Figure 4.11.

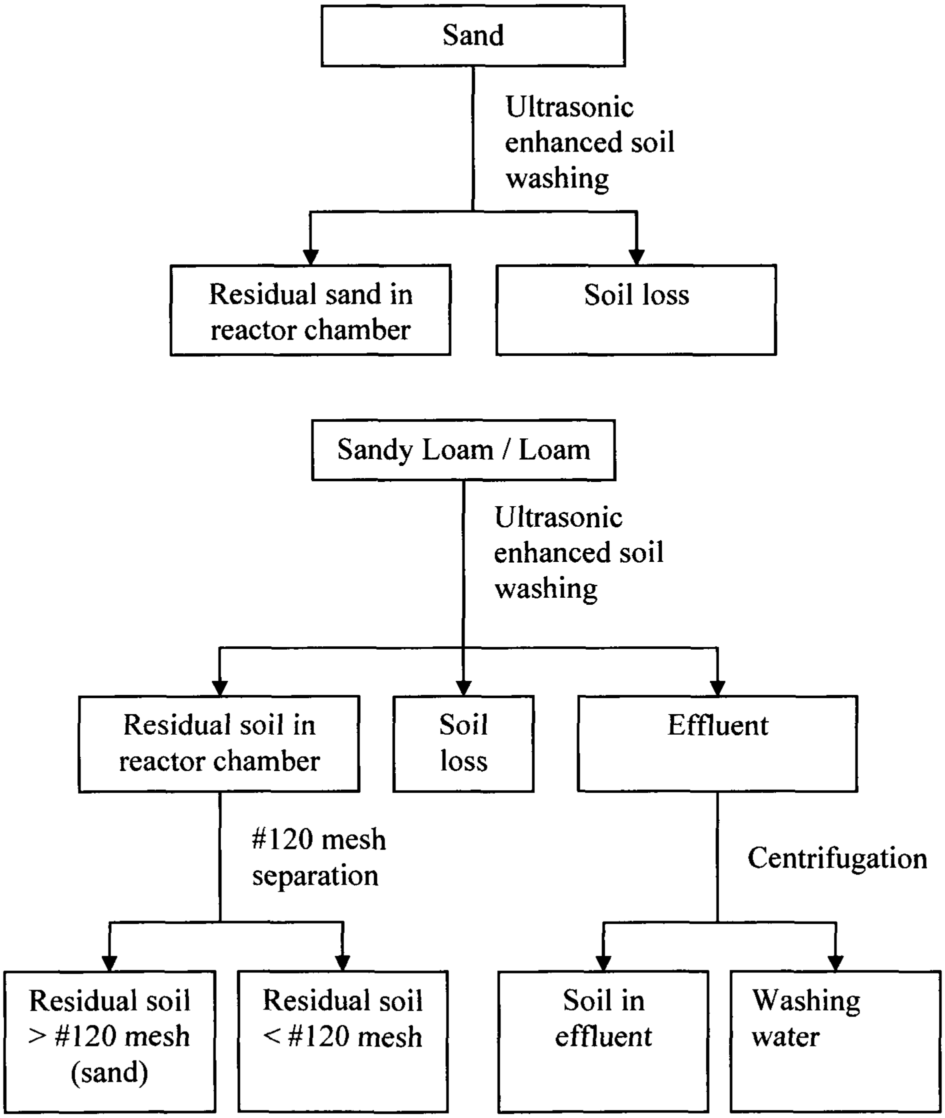

Figure 4.11 Soil distributions during ultrasonic enhanced soil washing treatment

The soil mass recovery representing the percentage of soils remaining after the treatment can thus be calculated according to Equation 4.3. The greater the soil mass recovery is, the less soil mass loss happen. Tale 4.6 lists the results of soil mass balance calculations for each orthogonal experiment. From this table it can be easily found that the soil recoveries of different treatments were between 93.4 and 98.5% while the average soil recovery was 96.0%.

$$\begin{aligned}\text{Mass of the original sand } (M_O) &= \text{Mass of the residual sand } (M_R) \\ &\quad + \text{Mass loss } (M_{loss})\end{aligned} \tag{4.1}$$

$$\begin{aligned}\text{Mass of the original soil } (W_O) &= \text{Mass of residual soil} > \#120 \text{ mesh } (M_{RS}) \\ &\quad + \text{Mass of residual soil} < \#120 \text{ mesh } (M_{RF}) \\ &\quad + \text{Mass of soil in effluent } (M_{LF}) \\ &\quad + \text{Mass loss } (M_{loss})\end{aligned} \tag{4.2}$$

$$\text{Soil Mass Recovery}(\%) = 1 - \frac{M_{loss}}{M_O} \times 100\% \tag{4.3}$$

The mass loss of TPH also occurred during the experiments which might be caused by the soil mass loss, the vaporization or oxidation of TPH, and the adhesion on the beaker when the effluent was collected. Similar to the soil mass balance, the mass balance equations of petroleum hydrocarbons are also varying for different types of soil. The TPH mass balances for sand, sandy loam and loam are shown in Equations 4.4 and 4.5, respectively. By summing up the masses of TPH in different fractions of the soil in the reaction chamber as well as those in the fine soils and washing water in the effluent, the mass of TPH loss can be calculated using Equations 4.4 or 4.5. The TPH recovery representing the percentage of TPH remaining after the treatment can then be calculated using Equation 4.6. Table 4.7 presents the results of TPH mass balance calculation for each orthogonal experiment. It is found that the TPH recoveries of different experiments were between 92.4 to 99.6% with an average TPH recovery of 97.3%. The results of both soil and TPH mass balance calculations indicates that after treated by ultrasonic enhanced soil washing, most of the soil and TPH were collected and kept while the mass loss of soil and TPH are small and can be considered negligible.

$$\begin{aligned}\text{TPH of original sand (O)} &= \text{TPH of residul sand (R)} \\ &\quad + \text{TPH of washing water (L)} \\ &\quad + \text{TPH loss } (\text{TPH}_{\text{loss}})\end{aligned} \tag{4.4}$$

$$\begin{aligned}\text{Original TPH on the soil(O)} &= \text{TPH of residual soil} > \#120 \text{ mesh (RS)} \\ &\quad + \text{TPH of residual soil} < \#120 \text{ mesh (RF)} \\ &\quad + \text{TPH of soil in effluent (LF)} \\ &\quad + \text{TPH of washing water (L)} \\ &\quad + \text{TPH loss } (\text{TPH}_{\text{loss}})\end{aligned} \tag{4.5}$$

$$\text{TPH Recovery (\%)} = 1 - \frac{\text{TPH}_{\text{loss}}}{\text{O}} \times 100\% \tag{4.6}$$

Table 4.6 Soil mass balance calculation for each orthogonal experiment

Exp No.	Rep No.	M_O	M_R			M_{RS}			M_{RF}			ML_F			Soil Recovery		
		M_O (g)	M_R (g)	SD (g)	RSD (%)	M_{RS} (g)	SD (g)	RSD (%)	M_{RF} (g)	SD (g)	RSD (%)	ML_F (g)	SD (g)	RSD (%)	Recov. (%)	SD (%)	RSD (%)
	Rep1		46.95			-	-	-	-	-	-	-	-	-	95.4		
1	Rep2	49.2	47.78	0.40	0.8	-	-	-	-	-	-	-	-	-	97.1	0.8	0.8
	Rep3		46.94			-	-	-	-	-	-	-	-	-	95.4		
	Rep1		-			34.20			5.00			2.61			96.3		
2	Rep2	43.4	-	-	-	33.40	0.46	1.4	4.99	0.05	1.1	2.92	0.15	5.6	95.2	1.0	1.0
	Rep3		-			33.11			5.11			2.59			94.0		
	Rep1		-			19.13			10.57			6.57			96.2		
	Rep2		-			18.95			11.10			7.02			98.3		
3		37.7		-	-		0.20	1.1		0.21	2.0		0.19	2.7		1.0	1.0
	Rep3		-			18.64			10.84			6.82			96.3		
	Rep1		-			33.56			4.89			2.57			94.5		
4	Rep2	43.4	-	-	-	32.60	0.40	1.2	5.20	0.24	4.7	2.91	0.19	7.0	93.8	0.3	0.3
	Rep3		-			32.90			5.49			2.48			94.2		
	Rep1		-			19.03			10.16			6.78			95.4		
5	Rep2	37.7	-	-	-	19.31	0.13	0.7	10.14	0.18	1.8	6.89	0.16	2.4	96.4	0.4	0.4
	Rep3		-			19.04			10.54			6.50			95.7		
6	Rep1	49.2	47.33	0.21	0.4	-	-	-	-	-	-	-	-	-	96.2	0.4	0.4
	Rep2		47.86			-	-	-	-	-	-	-	-	-	97.3		

	Rep3		47.59			-	-	-	-	-	-	-	-	-	96.7		
	Rep1		46.46			-	-	-	-	-	-	-	-	-	94.4		
7	Rep2	49.2	47.27	0.35	0.8	-	-	-	-	-	-	-	-	-	96.1	0.7	0.8
	Rep3		47.12			-	-	-	-	-	-	-	-	-	95.8		
	Rep1		-			33.26			5.79			2.71			96.2		
8	Rep2	43.4	-	-	-	32.81	0.19	0.6	6.13	0.14	2.4	2.49	0.09	3.5	95.5	0.3	0.4
	Rep3		-			32.94			5.96			2.55			95.5		
	Rep1		-			19.90			11.08			5.52			96.8		
9	Rep2	37.7	-	-	-	19.65	0.26	1.4	10.08	0.46	4.3	6.97	0.59	9.5	97.4	0.2	0.2
	Rep3		-			19.26			11.04			6.24			96.9		
	Rep1		-			19.39			10.67			5.75			95.0		
10	Rep2	37.7	-	-	-	19.39	0.19	1.0	10.80	0.08	0.7	5.99	0.10	1.6	96.0	0.5	0.6
	Rep3		-			18.98			10.84			5.88			94.7		
	Rep1		46.76			-	-	-	-	-	-	-	-	-	95.0		
11	Rep2	49.2	47.21	0.35	0.8	-	-	-	-	-	-	-	-	-	95.9	0.7	0.8
	Rep3		47.62			-	-	-	-	-	-	-	-	-	96.8		
	Rep1		-			34.33			5.95			2.45			98.5		
12	Rep2	43.4	-	-	-	33.45	0.36	1.1	5.63	0.13	2.3	2.27	0.07	3.1	95.3	1.3	1.4
	Rep3		-			33.77			5.72			2.34			96.4		
	Rep1		-			19.81			10.95			4.83			94.4		
13	Rep2	37.7	-	-	-	19.56	0.14	0.7	11.51	0.26	2.3	5.18	0.15	3.0	96.2	0.7	0.8
	Rep3		-			19.47			11.48			5.10			95.6		
14	Rep1	49.2	47.25	0.30	0.6	-	-	-	-	-	-	-	-	-	96.0	0.6	0.6
	Rep2		46.53			-	-	-	-	-	-	-	-	-	94.6		

	Rep3		46.89			-	-	-	-	-	-	-	-	-	95.3		
	Rep1		-			33.82			5.44			2.81			96.9		
15	Rep2	43.4	-	-	-	34.29	0.20	0.6	4.84	0.25	4.8	3.07	0.11	3.9	97.2	0.1	0.1
	Rep3		-			34.18			5.13			2.87			97.2		
	Rep1		-			33.33			5.68			3.13			97.1		
16	Rep2	43.4	-	-	-	33.05	0.12	0.4	5.16	0.22	4.1	3.52	0.16	4.8	96.1	0.4	0.4
	Rep3		-			33.27			5.27			3.37			96.6		
	Rep1		-			19.47			12.82			4.23			96.9		
17	Rep2	37.7	-	-	-	19.11	0.15	0.8	11.40	0.59	4.9	4.68	0.53	10.9	93.4	1.8	1.9
	Rep3		-			19.34			11.85			5.50			97.3		
	Rep1		46.92			-	-	-	-	-	-	-	-	-	95.4		
18	Rep2	49.2	47.33	0.20	0.4	-	-	-	-	-	-	-	-	-	96.2	0.4	0.4
	Rep3		47.36			-	-	-	-	-	-	-	-	-	96.3		

Table 4.7 TPH mass balance calculation for each orthogonal experiment

Exp No.	Rep No.	O (µg)	R (µg)	RS (µg)	RF (µg)	LF (µg)	L (µg)	Total Mass (µg)	TPH Recovery (%)	SD (%)	RSD (%)
1	Rep1	71,451	12,621	-	-	-	58,533	71,154	99.6	1.3	1.4
	Rep2		14,428	-	-	-	55,967	70,395	98.5		
	Rep3		13,726	-	-	-	55,117	68,843	96.4		
2	Rep1	193,027	-	23,440	10,560	10,164	139,732	183,896	95.3	1.6	1.6
	Rep2		-	24,815	13,858	9,365	141,817	189,855	98.4		
	Rep3		-	22,412	11,070	8,238	149,056	190,775	98.8		
3	Rep1	341,480	-	8,421	38,206	41,191	247,710	335,528	98.3	0.6	0.6
	Rep2		-	10,504	46,966	48,600	226,777	332,847	97.5		
	Rep3		-	8,629	42,161	44,397	235,246	330,433	96.8		
4	Rep1	58,547	-	4,898	3,207	3,152	45,790	57,046	97.4	0.6	0.6
	Rep2		-	6,677	4,804	3,311	43,120	57,911	98.9		
	Rep3		-	4,474	3,922	2,791	46,545	57,733	98.6		
5	Rep1	190,106	-	10,346	31,955	26,454	112,809	181,564	95.5	0.6	0.6
	Rep2		-	11,479	31,331	23,269	117,923	184,002	96.8		
	Rep3		-	11,216	32,475	22,666	117,448	183,805	96.7		
6	Rep1	367,401	63,202	-	-		294,509	357,710	97.4	0.2	0.2
	Rep2		54,220	-	-	-	302,114	356,334	97.0		
	Rep3		57,319	-	-	-	299,579	356,898	97.1		
7	Rep1	78,032	8,033	-	-		65,875	73,908	94.7	1.6	1.7
	Rep2		8,602	-	-	-	67,943	76,545	98.1		

	Rep3		6,794	-	-	-	69,917	76,711	98.3		
	Rep1		-	20,160	20,544	10,883	135,677	187,263	99.4		
8	Rep2	188,388	-	13,099	25,439	11,304	131,645	181,487	96.3	1.7	1.8
	Rep3		-	15,052	22,157	11,767	130,609	179,586	95.3		
	Rep1		-	12,093	57,141	35,829	204,296	309,359	97.5		
9	Rep2	317,377	-	11,706	58,927	46,610	183,888	301,132	94.9	1.5	1.6
	Rep3		-	11,247	52,255	34,005	215,277	312,784	98.6		
	Rep1		-	3,084	10,935	7,499	36,927	58,445	98.3		
10	Rep2	59,464	-	3,624	10,768	6,731	37,789	58,913	99.1	3.0	3.1
	Rep3		-	3,303	9,921	7,326	34,370	54,921	92.4		
	Rep1		7,449	-	-		225,885	233,335	98.1		
11	Rep2	237,899	8,403	-	-	-	223,102	231,505	97.3	1.4	1.5
	Rep3		5,953	-	-	-	219,533	225,486	94.8		
	Rep1		-	48,764	39,495	20,116	217,981	326,356	97.4		
12	Rep2	335,201	-	39,265	40,588	16,676	225,624	322,152	96.1	1.6	1.7
	Rep3		-	42,984	39,047	17,990	213,355	313,376	93.5		
	Rep1		-	7,838	10,275	3,795	32,593	54,501	98.3		
13	Rep2	55,458	-	7,493	8,806	3,586	34,700	54,585	98.4	0.5	0.5
	Rep3		-	7,691	7,989	3,241	36,192	55,113	99.4		
	Rep1		35,498	-	-		199,261	234,759	97.0		
14	Rep2	242,027	42,549	-	-	-	189,265	231,815	95.8	0.5	0.5
	Rep3		38,671	-	-	-	194,808	233,479	96.5		
15	Rep1	345,877	-	14,804	18,536	11,427	296,486	341,253	98.7	0.4	0.4
	Rep2		-	17,532	21,150	12,235	287,632	338,548	97.9		

	Rep3		-	15,652	19,863	11,027	291,644	338,187	97.8		
	Rep1		-	10,117	5,509	4,576	35,165	55,367	96.5		
16	Rep2	57,403	-	8,918	4,185	4,571	38,311	55,985	97.5	1.4	1.4
	Rep3		-	9,848	5,749	4,125	34,362	54,083	94.2		
	Rep1		-	16,986	30,352	17,222	128,929	193,488	98.1		
17	Rep2	197,320	-	14,029	28,450	24,288	122,694	189,461	96.0	1.2	1.2
	Rep3		-	14,527	26,120	19,690	134,868	195,204	98.9		
	Rep1		29,593	-	-		333,292	362,885	98.4		
18	Rep2	368,767	23,348	-	-	-	341,331	364,679	98.9	0.2	0.2
	Rep3		19,944	-	-	-	344,945	364,889	98.9		

4.3.2 Statistical Analysis

In order to keep the consistency of experimental results, the TPH removals were calculated using Equation 4.7. The S/N ratios were chosen as the optimization criterion. It was calculated using Equation 3.3. The larger the S/N ratio, the better the result is. The results of the orthogonal experiment using the ultrasonic enhanced soil washing treatment system were shown in Figure 4.12 and Table 4.8.

$$\text{TPH Removal (\%)} = \frac{\text{TPH in the liquid (L)}}{\text{Original TPH on the soil (O)}} \times 100\% \quad (4.7)$$

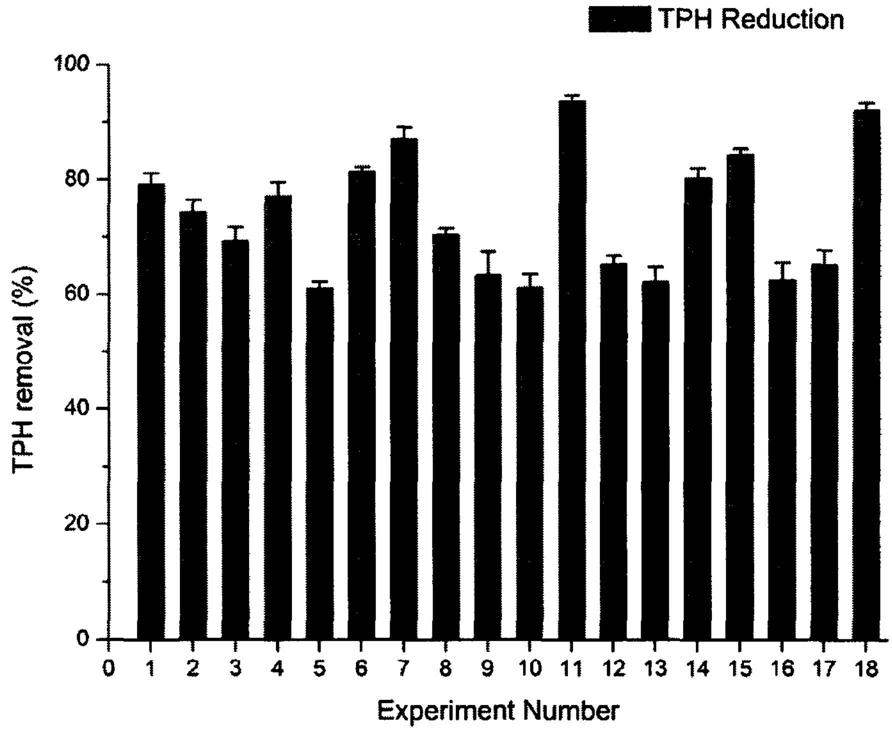

Figure 4.12 TPH removal for each orthogonal experiment

Table 4.8 Results of the orthogonal experiments

Exp. No.	TPH Conc. (%,w/w)	Salinity (Molarity)	Soil Type (sand/silt)	US Treatment Time (min)	SW flow rate (cm^3/s)	TPH Removal						S/N ratio (dB)
						Rep1 (%)	Rep2 (%)	Rep3 (%)	Average (%)	SD (%)	RSD (%)	
1	0.5	0	100/0	1	0.5	81.92	78.33	77.14	79.13	2.03	2.57	37.96
2	1	0.4	70/30	5	1.0	72.39	73.47	77.22	74.36	2.07	2.78	37.42
3	2	0.8	40/60	10	1.5	72.54	66.41	68.89	69.28	2.52	3.63	36.80
4	0.5	0	70/30	5	1.5	78.21	73.65	79.50	77.12	2.51	3.25	37.73
5	1	0.4	40/60	10	0.5	59.34	62.03	61.78	61.05	1.21	1.99	35.71
6	2	0.8	100/0	1	1.0	80.16	82.23	81.54	81.31	0.86	1.06	38.20
7	0.5	0.4	100/0	10	1.0	84.42	87.07	89.60	87.03	2.11	2.43	38.79
8	1	0.8	70/30	1	1.5	72.02	69.88	69.33	70.41	1.16	1.65	36.95
9	2	0	40/60	5	0.5	64.37	57.94	67.83	63.38	4.10	6.47	35.98
10	0.5	0.8	40/60	5	1.0	62.10	63.55	57.80	61.15	2.44	3.99	35.71
11	1	0	100/0	10	1.5	94.95	93.78	92.28	93.67	1.09	1.17	39.43
12	2	0.4	70/30	1	0.5	65.03	67.31	63.65	65.33	1.51	2.31	36.30
13	0.5	0.4	40/60	1	1.0	58.77	62.57	65.26	62.20	2.66	4.28	35.85
14	1	0.8	100/0	5	0.5	82.33	78.20	80.49	80.34	1.69	2.10	38.09
15	2	0	70/30	10	1.0	85.72	83.16	84.32	84.40	1.05	1.24	38.52
16	0.5	0.8	70/30	10	0.5	61.26	66.74	59.86	62.62	2.97	4.74	35.91
17	1	0	40/60	1	1.0	65.34	62.18	68.35	65.29	2.52	3.86	36.28
18	2	0.4	100/0	5	1.5	90.38	92.56	93.54	92.16	1.32	1.43	39.29

The experimental data shows that the TPH removals of contaminated soil were approximately between 61 to 94% and the average TPH removal was 73.9%. The experimental treatment with the highest TPH removal (93.67% in experiment #11) was conducted under the following conditions: 1.0% (w/w) of crude oil with no salt added on sand, 10 minutes of ultrasonic treatment with a soil washing flow rate at 1.5 cm^3/s.

The statistical analyses of the orthogonal experimental results include S/N ratio analysis and ANOVA. Table 4.9 and Figure 4.13 show the results of S/N ratio analysis while Table 4.10 shows the results of ANOVA. By comparing the ranges between the maximum and the minimum (Max-Min) of S/N ratio among the influencing factors in Table 4.9, the order of significances of the factors was determined as: Soil Type > Soil Washing Flow Rate > Salinity > Initial TPH Concentration > Ultrasonic Treatment Time.

Table 4.9 Results of the orthogonal experiment

Factors	Mean S/N ratio (dB)			
	Level 1	Level 2	Level 3	Max-Min
Initial TPH Concentration	36.84	37.16	37.36	0.52
Salinity	37.51	37.02	36.85	0.65
Soil Type	38.59	37.06	36.06	2.53
US Treatment Time	36.85	37.22	37.30	0.45
SW Flow Rate	36.57	37.34	37.49	0.92
	The total mean S/N ratio = 37.15 dB			

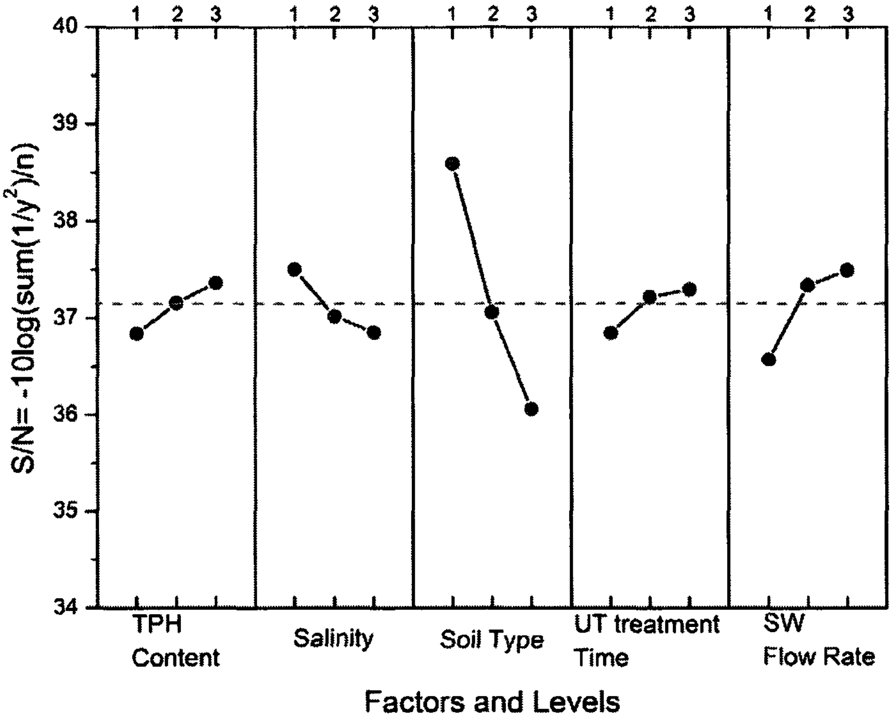

Figure 4.13 Effect of independent factors on TPH removal

It can be easily observed either from Table 4.9 or Figure 4.13 that the most significant influencing factor is soil type as it has the largest S/N ratio range value of 2.53. Sand with the largest particle size and the smallest surface area were much easier to be cleaned than the other two finer soils. Among the three soils, loam with 60% of fines was the most difficult one to be cleaned. As the percentage of fines in the soil increases, the difficulty of decontamination increases. The result was the same as the result of desorption experiment.

The second significant factor is soil washing flow rate with the second largest S/N ratio range value of 0.92. As the soil washing flow rate increases, the treatment was enhanced. The S/N ratio increased rapidly (S/N ratio from 36.57 to 37.34 dB) from 0.5 to 1.0 cm^3/s while the increment slowed down (S/N ratio from 37.34 to 37.49) from 1.0 to 1.5 cm^3/s. This result indicates that the treatment efficiency was enhanced by soil washing: as the soil washing flow rate increases, the treatment efficiency increases.

Salinity is the third significant influencing factor with S/N ratio range value of 0.65. It showed negative impact on the treatment since as the salinity increases the S/N ratio decreases. Comparing to soil type and soil washing flow rate, the less significant impact of salinity might be caused by the dilution of salt concentration and the transportation of salt by soil washing.

The other two factors have less significant impacts on the treatment (S/N ratio values for initial TPH concentration is 0.52; for ultrasonic treatment time is 0.45). The initial TPH concentration showed positive impact since as the initial TPH concentration increases, the S/N ratio increases. Usually the concentration of TPH showed negative impact on remediation since as the TPH concentration increases, the soil matrix become less permeable and more difficult to be remediated. However under the influence of ultrasound, the adsorbed and trapped oil contaminants can be easily extracted. The more oil existing in the soil matrix, the more oil molecules can be extracted by ultrasonic enhanced soil washing and thus the treatment efficiency increases as initial concentration increases.

Ultrasonication had positive impact on TPH removal, and the TPH removal increases as the duration of ultrasonic treatment increases. The increment of TPH removal from 5 to 10 min (S/N increased from 37.22 to 37.30) of treatment is less than that from 1 to 5 min (S/N increased from 36.85 to 37.22) of treatment, indicating that the treatment efficiency might reach a maximum value as the ultrasonic treatment time increases. Comparing to the results of many other studies on ultrasonic treatment time which were usually within 2 to 5 min for maximum treatment efficiency (Feng and Aldrich, 2000; McMillan, 2008), the treatment time for maximum treatment efficiency were increased to 10 min in this study due to the enhancement by soil washing.

The data of the orthogonal experiment was analyzed using ANOVA to verify the significances of the individual factors. S/N ratio was selected as response variable while initial TPH concentration, salinity, soil type, ultrasonic treatment time, soil washing flow rate were analyzed as fixed factors. The significance level was set at 0.05 which means the effect of independent factors will be considered significant when its probability value calculated from ANOVA was less than 0.05. The results were listed in Table 4.10. It is found that all the five factors considered in the experiment had statistically significant effects on the treatment efficiency at 95% confidence limit (Table 4.10). The percentage contribution was calculated for each individual factor as the ratio of the sum of squares of each factor to the total sum of squares. Comparing the contribution of each factor, it is obvious to find that the most significant influencing factor was soil type with contribution of 71.98%, followed by soil washing flow rate (12.82%), salinity (5.92%), ultrasonic treatment time (5.19%) and initial TPH concentration (2.95%). The result of ANOVA was consistent with the result of S/N ratio analysis except for the sequence of the significances of ultrasonic treatment time and initial TPH concentration. The slight difference might be caused by different analysis algorithms. ANOVA considered the effect of error to the accuracy of experiments and therefore it can provide the significance sequence of influencing factors by accurate mathematical estimation while for S/N ratio analysis can only provide rough comparisons between each factor. Therefore the result of significance sequence by ANOVA is more accurate.

Table 4.10 ANOVA of the orthogonal experiments

Factors	SS	d.f.	MS	F	P	Contribution (%)
Initial TPH Concentration	59.74	2	29.87	9.09	0.011	2.95
Salinity	119.98	2	59.99	18.25	0.002	5.92
Soil Type	1,457.44	2	728.72	221.69	<0.001	71.98
US Treatment Time	105.00	2	52.50	15.97	0.002	5.19
SW Flow Rate	259.65	2	129.82	39.50	<0.001	12.82
Error	23.01	7	3.29	-	-	1.14
Total	2024.82	17	-	-	-	100.00

SS: sum of squares; d.f.: degree of freedom; MS: mean of squares;

F: fisher test value= $MS_{parameter} / MS_{error}$; P: probability value; alpha=0.05

4.3.2 Optimization

According to the results of S/N ratio analysis and ANOVA, the optimal level of each influencing factor was obtained and listed in Table 4.11. As mentioned in chapter 3, the final steps in the orthogonal experiment are the predication of the optimal performance of treatment and the verification of enhancement using the optimal levels of the corresponding design factors. The estimated TPH removal can be calculated using the following equation (Yang and Tarng, 1998):

$$\hat{y} = \bar{y} + \sum_{i=1}^{o} (\bar{y}_i - \bar{y}) \qquad (4.8)$$

where $\hat{y}$ denotes the estimated TPH removal; $\bar{y}$ denotes the mean of TPH removal; $\bar{y}_i$ denotes the mean TPH removal at the optimum level of the i^{th} factor; o denotes the number of main factors that significantly affect the treatment. The calculation result using Equation 4.8 indicated that the TPH removal under the optimal condition should be 96.96%. In order to validate the result of optimization and verify the enhancement, a confirmation experiment was conducted under the optimal conditions listed in Table 4.11. The TPH removal was found to be 96.17 ± 3.56%, and the enhancement of treatment under the optimal condition was between 2.54 to 35.16% as compared with the TPH removal for each orthogonal experiment, which illustrate the validity of optimization and positive enhancement under optimal treatment condition.

Table 4.11 Optimal condition for ultrasonic enhanced soil washing treatment

Factors	Level	Value
Initial TPH Concentration (% w/w)	3	2.0
Salinity (M)	1	0
Soil Type (sand/silty clay loam)	1	100/0

US Treatment Time (min)	3	10
SW Flow Rate (cm^3/s)	3	1.5

4.4 Time-Series Experimental Results

For the time-series experiments, treatment time, salinity and treatment system were selected as the study factors. The corresponding levels for treatment time, salinity and treatment system are listed in Table 3.3. The other factors such as initial TPH concentration and soil washing flow rate were all set at constant levels based on the results of the orthogonal experiment, for example initial TPH concentration was set at 2.0% (by mass) while the soil washing flow rate was set at 1.5 cm^3/s. Loam instead of sand, was selected as the experimental soil which was used with a volume of 30 mL and a mass of 37.7 g in each experiment. This is because the effect of salinity of on oil desorption is highly related to soil type; the negative impact of salinity is much stronger on fine soil particles such as silt and clay than on sand. Therefore, in order to better investigate the relationship between salinity and the treatment of ultrasonic enhanced soil washing, loam soil with more fine soil particles were selected as experimental soil. For experiment added with salt, the salinity level was set at 0.8 M of sodium chloride. The results of time-series experiments with no salt addition are presented in Table 4.12 and Figure 4.14 while the results of experiments with salt addition are shown in Table 4.13 and Figure 4.15. Three replicates were completed for each experiment. The control experiments were treatments without ultrasound or soil washing. Soil samples were saturated with DI water and let stand for certain treatment time followed by centrifugation same as other treatments. The TPH removal of control group experiments were caused by stationary desorption and extraction during centrifugation.

As shown in Table 4.12, when no salt was added into the soil samples, the TPH removals of all the treatments increased with time. Approximately 31 to 61% of TPH was removed by ultrasonication alone and the enhancement of ultrasound was approximately 24 to 45% comparing with those from the control experiments with only 7 to 17% of TPH removal. Approximately 28 to 77% of TPH removal from loam soil was observed in the treatment of ultrasonic enhanced soil washing and the enhancement was approximately 22 to 60%. As compared with the treatment of using only ultrasound, the TPH removal of ultrasonic enhanced soil washing had been improved by 7 to 17%. Comparing with the treatment with ultrasound alone, the TPH removal of soil washing alone was lower (approximately 9 to 34%) and the difference was approximately 2 to 17% as compared with the results from the control experiments.

As shown in Table 4.13, the addition of 0.8M of salt to the soil samples appeared to restrict only the TPH removal from soil samples treated by ultrasound alone. The TPH removal by using ultrasound was approximately 16 to 38% while the TPH removal from control experiments was ranging from 5 to 14%, thus the enhancement of ultrasound was approximately 12 to 24%. Comparing with the experiments with no salt addition, the addition of salt showed a negative impact on the ultrasonic enhancement effect, decreasing the enhancement by 12 to 21%. In terms of the treatments of using soil washing or using both soil washing and ultrasound, the addition of salt appeared to just slightly decrease the TPH removal. For example, the TPH removals of soil washing alone and ultrasonic enhanced soil washing were approximately 5 to 29% and 17 to 70%, respectively, and the enhancements as compared with the TPH removal from control experiments were approximately 1 to 15% and 13 to 57%, respectively.

Table 4.12 Results of time–series experiments with no salt addition

Original TPH concentration (mg/kg)			8,418±704							
Soil Mass (g)			37.7							
EC (dS/cm)			1.4							
Time (min)			0	1	2	3	4	5	7	10
US	TPH in washing water (mg/L)	Rep1	0	1,122	1,574	1,767	1,883	1,978	2,046	1,999
		Rep2	0	887	1,376	1,483	1,569	1,684	1,893	1,914
		Rep3	0	946	1,572	1,559	1,601	1,860	1,885	1,780
		Aver.	0	985	1,507	1,603	1,684	1,841	1,941	1,898
		SD	0	100	93	120	141	121	74	90
		RSD	-	10.1	6.2	7.5	8.4	6.6	3.8	4.8
	Washing water volume (mL)		0	100	100	100	100	100	100	100
	Removal (%)		0.0	31.0	47.5	50.5	53.1	58.0	61.2	59.8
SW	TPH in washing water (mg/L)	Rep1	0	310	237	234	194	181	153	127
		Rep2	0	336	185	174	164	148	164	123
		Rep3	0	260	150	238	236	137	140	108
		Aver.	0	302	191	215	198	156	152	119
		SD	0	32	36	29	30	19	10	8
		RSD	-	10.5	18.7	13.7	15.0	12.1	6.4	6.7
	Washing water volume (mL)		0	90	180	270	360	450	630	900
	Removal (%)		0.0	8.6	10.8	18.3	22.5	22.1	30.3	33.9
US+SW	TPH in	Rep1	0	953	764	663	533	490	361	268

	washing water (mg/L)	Rep2	0	881	751	608	484	448	352	252
		Rep3	0	1,166	759	749	641	567	389	295
		Aver.	0	1,000	758	673	552	501	367	272
		SD	0	121	6	58	66	49	16	18
		RSD	-	12.1	0.7	8.6	11.9	9.8	4.4	6.5
	Washing water volume (mL)		0	90	180	270	360	450	630	900
	Removal (%)		0.0	28.4	43.0	57.3	62.7	71.1	72.9	77.0
Control	TPH in washing water (mg/L)	Repl	0	235	314	360	406	536	578	635
		Rep2	0	243	273	223	397	581	493	444
		Rep3	0	175	350	345	333	299	405	554
		Aver.	0	218	312	310	379	472	492	545
		SD	0	30	32	61	32	123	70	78
		RSD	-	13.9	10.2	19.8	8.6	26.1	14.3	14.4
	Washing water volume (mL)		0	100	100	100	100	100	100	100
	Removal (%)		0.0	6.9	9.8	9.8	11.9	14.9	15.5	17.2

Table 4.13 Results of time-series experiments with salt addition

Original TPH concentration (mg/kg)			9,058±763							
Soil Mass (g)			37.7							
Time (min)			0	1	2	3	4	5	7	10
US	Aver. EC(dS/cm)		17.09	17.45	17.58	17.89	17.93	17.88	17.95	17.93
	TPH in washing water (mg/L)	Repl	0	456	576	897	1,035	1,146	1,321	1,323
		Rep2	0	566	828	586	820	1,084	1,211	1,198
		Rep3	0	650	815	905	1,124	855	1,175	1,385
		Aver.	0	557	740	796	993	1,028	1,236	1,302
		SD	0	79	116	149	128	125	62	78

		RSD	-	14.2	15.7	18.7	12.9	12.1	5.0	6.0
	Washing water volume (mL)		0	100	100	100	100	100	100	100
	Removal (%)		0.0	16.3	21.7	23.3	29.1	30.1	36.2	38.1
SW	Average EC(dS/cm)		17.09	14.27	11.50	9.37	8.11	6.32	4.38	3.17
	TPH in washing water (mg/L)	Rep1	0	135	146	145	143	128	130	106
		Rep2	0	208	127	133	172	166	117	98
		Rep3	0	234	101	85	104	132	149	121
		Aver.	0	192	124	121	140	142	132	108
		SD	0	42	18	26	28	17	13	9
		RSD	-	21.8	14.8	21.2	19.8	12.0	9.9	8.6
	Washing water volume (mL)		0	90	180	270	360	450	630	900
	Removal (%)		0.0	5.1	6.6	9.6	14.8	18.7	24.3	28.5
US+SW	Average EC(dS/cm)		17.09	9.49	6.10	4.82	3.59	3.07	2.24	1.73
	TPH in washing water (mg/L)	Rep1	0	710	557	652	554	451	350	243
		Rep2	0	658	576	597	598	444	354	263
		Rep3	0	584	461	550	537	517	405	294
		Aver.	0	651	531	600	563	470	370	267
		SD	0	52	50	42	25	33	25	21
		RSD	-	7.9	9.5	7.0	4.5	7.0	6.7	7.9
	Washing water volume (mL)		0	90	180	270	360	450	630	900
	Removal (%)		0.0	17.2	28.0	47.4	59.3	62.0	68.2	70.3
Control	Average EC(dS/cm)		17.09	17.10	17.08	17.14	17.02	17.06	17.11	17.16
	TPH in washing water	Rep1	0	136	167	220	291	414	374	369
		Rep2	0	155	214	214	338	489	470	521
		Rep3	0	170	250	155	258	287	405	517

(mg/L)	Aver.	0	154	210	196	296	396	417	469
	SD	0	14	34	29	33	83	40	71
	RSD	-	9.2	16.0	15.0	11.2	21.0	9.6	15.1
Washing water volume (mL)		0	100	100	100	100	100	100	100
Removal (%)		0.0	4.5	6.2	5.8	8.7	11.6	12.2	13.7

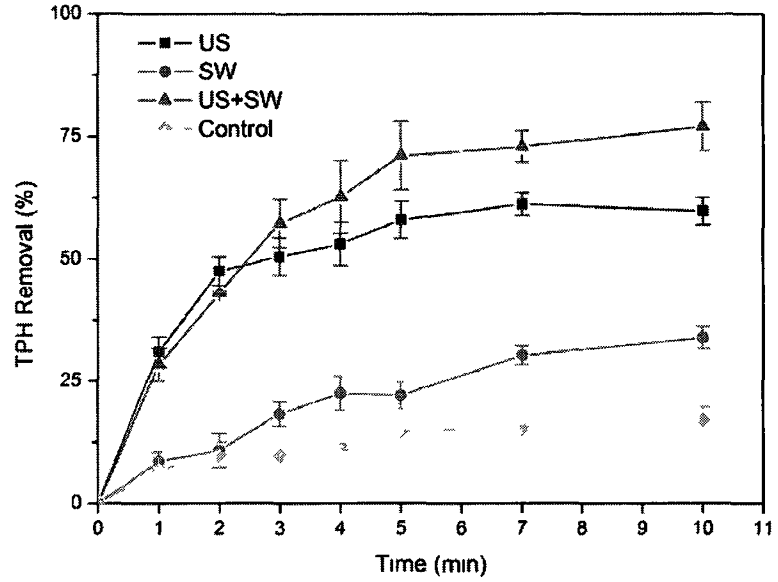

Figure 4.14 Average TPH removals versus treatment time with no salt addition

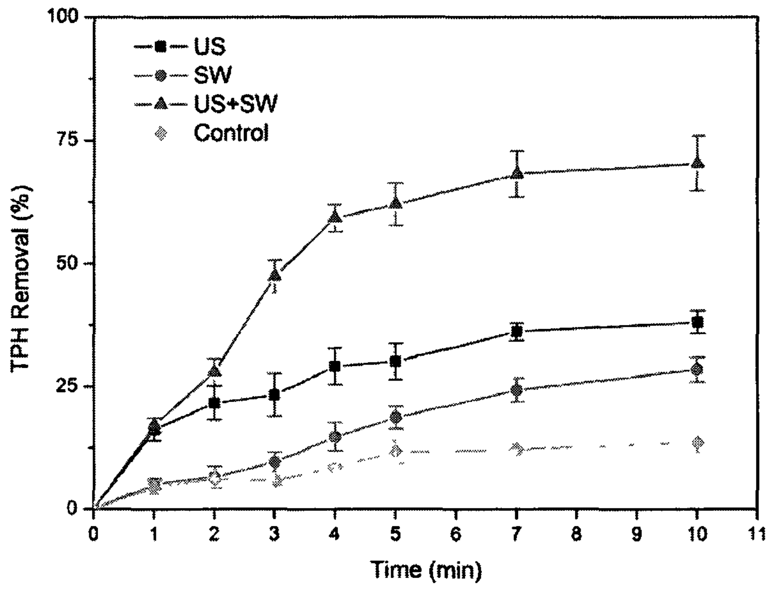

Figure 4.15 Average TPH removals versus treatment time with salt addition

The relationship between salinity and TPH removal can be analyzed through observing the dynamic changes of TPH removal and EC during each experiment as presented in Table 4.13 and Figures 4.14, 4.15 and 4.16. In terms of ultrasonic treatment alone (Figure 4.16), salt showed significant impact to impede the TPH removal (i.e. 12 to 21% decrement of removal efficiency). In terms of soil washing and ultrasonic enhanced soil washing (Figures 4.15 and 4.16), the salinities had been continually decreased during the treatment process from 17.09 to 3.17 dS/cm and from 17.09 to 1.73 dS/cm, respectively. The results implied that the salt in soil samples were kept being removed out of the remediation system and therefore the negative impact of salinity on TPH removal could be decreased. By comparing Figure 4.17 with Figure 4.18, it is found that the salinities in soil samples treated by ultrasonic enhanced soil washing decreased faster than those treated by soil washing alone, indicating that ultrasound can enhance the remediation treatment efficiency by accelerating the removal of salt from soil.

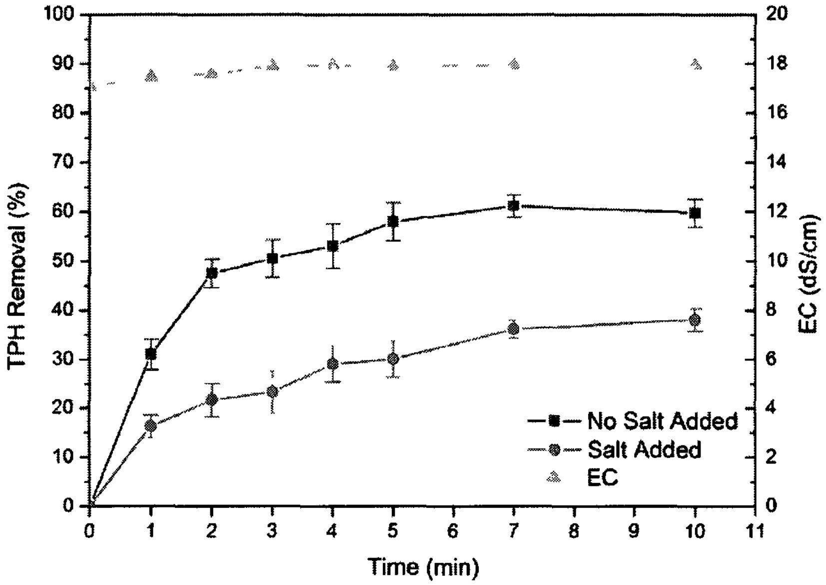

Figure 4.16 Soil TPH removal and EC change during treatment process by using ultrasound alone

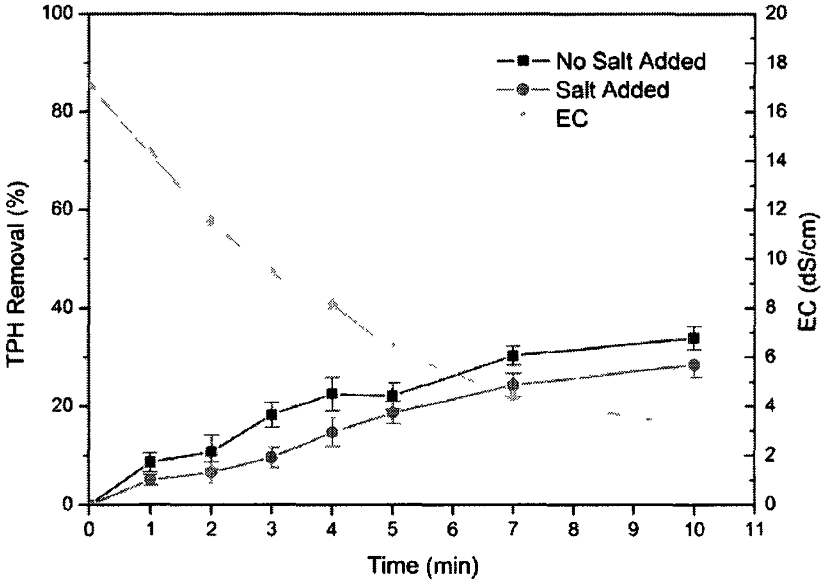

Figure 4.17 Soil TPH removal and EC change during treatment process by using soil washing alone

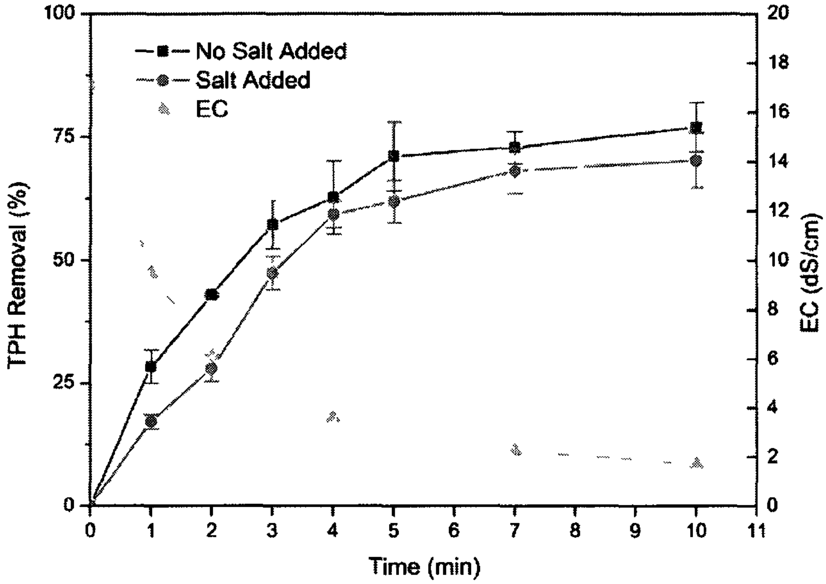

Figure 4.18 Soil TPH removal and EC change during treatment process by using both ultrasound and soil washing

Chapter 5 Discussions

5.1 Ultrasonic Desorption

As mentioned in the literature review in chapter 2.1, the adsorption and desorption process of adsorbate from soil particles are highly related to the soil properties such as grain size, surface area, porosity, etc. In this thesis study, sand and silty clay loam were mixed with different ratio (100:0, 70:30 and 40:60, v/v) in order to represent three different soil textures, including sand, sandy loam and loam. The abilities of soils to adsorb the crude oil molecules can be distinguished by studying the corresponding desorption isotherms as shown in Figure 4.1. Sand was associated with the lowest desorption isotherm which indicates that the adsorption of crude oil molecules on sand was the weakest. On the contrary, the adsorption on sandy loam was stronger and the adsorption on loam soil was the strongest. The large variation of adsorption capacity among different soils was mainly caused by different soil particle sizes. As compared with the coarse sand soil, the sandy loam and loam have smaller particle sizes associated with larger surface areas and pore volumes which could provide more spaces for adsorbates (oil molecules) to distribute and adsorb. This can also be found from the estimated maximum adsorption capacity of crude oil on each soil as presented in Table 4.5.

Desorption had been proved to be one of the most important mechanisms in soil remediation. The conventional desorption methods usually use water or chemical solvents to extract the contaminants from soil particles (Mason and Lourimer, 2002).

Desorption is a time consuming process and the contaminants removal is low especially when the treated soils are silt or clay. The results obtained from the pilot study of desorption experiments in this research proved that the maximum TPH desorption were acquired after 24 hours of mechanical shaking. As shown in Figure 4.14, 10 min of soil washing with DI water only accomplished with approximately 34% of TPH removal from the contaminated loam soil.

Results of the desorption experiments in the presence of ultrasound proved that ultrasound could greatly enhance the desorption of petroleum hydrocarbons from soils. Figure 4.14 shows that the treatment system could reach adsorption/desorption equilibrium after ultrasound was applied to the reactor for only 10 minutes. As compared with the 24 hr for maximum desorption through mechanical shaking, the time required to reach maximum desorption of TPH was greatly reduced through the application of ultrasound. This result indicates that in addition to increasing the desorption yield, ultrasound is also capable of accelerating the desorption. Moreover, Figure 4.2 illustrated that the ultrasound enhanced desorption was significantly affected by soil types. The orthogonal experiments (Figure 4.13 and Table 4.10) also demonstrated that soil type was the most significant factor among all the five selected factors affecting the performance of ultrasonic enhanced soil washing treatment process. As the soil particle size decreased, the TPH removal decreased. This conclusion agrees with the results of other studies. Study by Farmer et al. (2000) suggested that the ultrasonic energy needed to desorb the adsorbate was different for different soils, and more energy was required in the finer soil. Therefore under the same ultrasonic power application, fine soils could desorb less than coarse soils. For example, Feng and Aldrich (2000) reported a decrease in removal of diesel by ultrasound from approximately 98% to 77% when the soil particle size was decreased from 1 to 0.1mm; Na et al. (2007) also found that the removal of diesel was hindered by the decreased soil particle size, and they explained that the low desorption was due to the increasing surface area and capillary force in fine soils.

Additionally, it is very interesting to notice the different effects by ultrasound among the three soils. According to the results presented in Figures 4.3, 4.5 and 4.7, the desorption isotherms of all the soils in the presence of ultrasound were lower than those in the absence of ultrasound. The lowered sorption concentrations on soil particles indicate that part of the adsorbate (TPH) were desorbed and entered the liquid phase under the influence of ultrasound. Thus, ultrasound showed enhancement effect on the desorption of TPH. The enhancement of desorption by ultrasound on the fine soil (sandy loam and loam soil) was obviously greater than that on the coarse soil (sand). This phenomenon might be due to the different microstructures of the soils. As for sand matrix, the soil structure is simple and loose with comparatively small surface area for adsorption. The bonding force between sand particles and TPH molecules was so weak that the TPH molecules could be easily extracted by water with mechanical shaking (i.e. approximately 78% TPH desorbed by 24 hr of mechanical shaking). The amount of residual extractable TPH was too low thus although the ultrasound accelerated the desorption process, it did not show great enhancement effect on the TPH desorption (i.e. approximately 83% TPH desorbed after 10 min of ultrasound treatment).

On the contrary, since the finer soils especially the loam soil contained more silt and clay particles, their soil structures were more complex with multiple layers of micropores within the soil matrix (Carty et al., 1997). Thus the finer soils had larger surface area and micropore volumes which could provide more available sites for adsorption and more spaces for entrapment of TPH molecules. The TPH molecules were deeply entrapped within the soil matrix where it was very difficult for the solvent water to reach. The smaller particle size made the soil less permeable for water or other solvent and thus the diffusion of TPH molecules became more difficult. As a result, it is very difficult for desorption from fine soils. In fact, in engineering application of soil washing on desorption from fine soils, the treatment efficiencies are usually very low (Hyman and Dupont, 2001). However, the inextractable or inaccessible TPH within the finer soil matrix could be easily extracted by ultrasound. The ultrasonic power can be transmitted through the soil matrix and reach the interface. The oscillating cavitational bubbles and shock waves can lead to the breakage of soil matrix, the appearance of erosion and the detachment of adsorbed TPH molecules. Under the treatment of ultrasound, the fine soil could become more permeable and the mass transfer by diffusion could then be increased. In the works of Domingos et al. (1997) and Juang et al. (2006), ultrasound had been found to alter the adsorbent's structure by decreasing the BET surface area and pore volume. Therefore, as compared with soil washing or solvent extraction, the ultrasonic treatment can greatly enhance TPH desorption from fine soils, with TPH desorption from sandy loam being increased from approximately 30% (soil washing desorption) to 72% (ultrasonic desorption), and TPH desorption from loam being increased from approximately 12% (soil washing desorption) to 61% (ultrasonic desorption).

The great enhancement by ultrasound generally benefits from the concentrated high energy and the cavitation effect of ultrasound. Firstly, the desorption process is an endothermic process. When the sonic energy provided by ultrasound is high enough to overwhelm the bonding energy between the adsorbent and adsorbate, the adsorbed petroleum hydrocarbon molecules will be desorbed and enter the solvent (water) (Breitbach and Bathen, 2001). The cavitation bubble acted as energy transformer as the collapse of bubbles transformed the sonic energy into high temperature and pressure (Suslick, 1990; Mason and Lorimer, 1991). The high temperature could generate certain hot spots while the high pressure could help to form microjets of solvent and shock waves which can further create microscopic turbulence to break the bonds and accelerate the desorption of adsorbed hydrocarbon molecules. Moreover, the turbulence could enhance the leaching of the desorbed petroleum hydrocarbon molecules by generating surface pitting and micro-cracks onto and within the soil particles, as well as enhancing the internal and external mass transfer of hydrocarbon molecules.

Secondly, the ultrasonic cavitation affects the equilibrium between adsorption and desorption. According to experimental results presented in Table 4.5 and Figure 4.9, ultrasound showed negative impact on the saturation adsorption capacity Q. The Q values of all the soils were decreased due to the application of ultrasound. For example, Q_{sand} decreased from 2554 (with no ultrasound) to 2197 mg/kg (with ultrasound), $Q_{sandy\ loam}$ decreased from 8340 (with no ultrasound) to 3114 mg/kg (with ultrasound), and Q_{loam} decreased from 11349 (with no ultrasound) to 5090 mg/kg (with ultrasound) (Table 4.5). The decreased adsorption saturation capacity indicates that the amount of adsorbed petroleum hydrocarbon molecules that surpass the adsorption saturation capacity will be desorbed under the effect of ultrasound. This result might be caused by two reasons: one is that the ultrasonic cavitation could change some of the microstructures of soil particles.

According to the study by Juang et al. (2006) who used ultrasound to enhance the desorption of phenol on activated carbons, the ultrasound reduced the surface area and total pore volume by 5-7% and 14-17%, respectively. Since the complex soil matrix especially for fine soils can be destructed by ultrasound, some of the residual petroleum hydrocarbon molecules can no longer be adsorbed which causes the decrease of saturation adsorption capacity, thus the adsorption capacity of soil can be decreased. Another possible reason is that some of the sites for adsorption were occupied by the cavitation bubbles, and thus those replaced petroleum hydrocarbon molecules which were originally adsorbed on the soil particles were then released into the solvent, leading to reduced soil saturation adsorption capacity.

Lastly, it is very interesting to note the different desorption rates between different fractions of TPH. Either from the desorption experimental results presented in Tables 4.2, 4.3 and 4.4 or from the orthogonal experimental results presented in Table 5.1, it can be observed that as comparing with the TPH composition in the original soil, the TPH composition in the solvent water during the treatment process had been changed as the F2 fraction had been increased while the F4 fraction had been decreased. This can be explained by the properties of different fractions of TPH. As for the light fraction F2 (nC10-nC16), the hydrocarbons are small with high solubility, thus it is very easy for them to dissolve in the solvent water and to be flushed out from the soil matrix. On the contrary, as for the heavy fraction F4 (nC34 to nC50), their solubilities are lower which make them harder to dissolve in water but easier to be trapped in the soil matrix especially the fine soils. Thus, the light fractions of TPH are easier to be desorbed than the heavy fractions. A further discussion about the relationship between the desorption and degradation of different fractions of TPH can be found in the following paragraphs.

5.2 Ultrasonic Degradation

The cavitation effect generated by ultrasound is capable of degrading organic contaminants. The heavy fraction of petroleum hydrocarbons with complex structures and large molecules such as long-chain or aromatic hydrocarbons can be broken down by ultrasound into fragments and simple hydrocarbons with smaller molecules. The ultrasonic degradation could occur through pyrolysis within the cavitation bubbles and sonolysis at the interface or in the bulk solution (Hoffmann et al., 1996). Since most components in crude oil are semi-volatile or non-volatile hydrocarbons which are very difficult to be vaporized to enter the cavitation bubble, the degradation of these petroleum hydrocarbons are usually happened at the interface between the cavitation bubble and the bulk solution, or in the bulk solution. Therefore the main mechanism of ultrasonic degradation is sonolysis. The sonolysis is a radial oxidation reaction that the free radicals generated by ultrasound can attack the hydrocarbons and chemically change them into fragment and hydrocarbons with lower molecular weight through oxidation.

Crude oil is a complex mixture of different organic compounds. Since the heavy-fraction hydrocarbons can be degraded into light fraction hydrocarbons while light fraction of hydrocarbons can further be degraded into smaller fragments and CO_2, the composition of crude oil should have been changed during the ultrasonic remediation process. Figure 5.1 shows the GC chromatogram of petroleum hydrocarbons in soil and water after ultrasonic enhanced soil washing treatment. The x-axis denotes the chromatographic retention time while the y-axis denotes the signal intensity which was used for calculating TPH concentration. The concentration of extractable TPH was determined by integrating the peak area under the GC chromatogram, for example, the integration between nC10 to nC16 was used for determining F2 fraction, between nC16 to nC34 for F3 fraction, and between nC34 to nC50 for F4 fraction. The total TPH concentration was calculated by summing the concentrations of F2, F3 and F4. The large peak detected before nC10 (i.e. before retention time of 5 min) represents the mixture of extraction solvents (DCM, hexane, and toluene), therefore this peak area was not included in the TPH calculation. Since the curves of different analytical samples might overlap each other, in order to better differentiate them, the time and amplitude offset were both set up at 1%.

In Figure 5.1, the light blue chromatogram, representing the TPH concentration of the original soil before treatment, has the largest peak area than the other four curves. The chromatogram with the smallest peak area was the dark blue one which represents the TPH concentration of the residual sand (> #120 sieve) which was separated from residual fine soils by #120 sieve. The chromatograms representing TPH concentrations of the residual fine soils and the fine soils in the effluent were the red and the green chromatogram, respectively; they lie between the light blue and the dark blue chromatograms, while the green one has larger peak area than the red one. The pink chromatogram representing TPH concentration of the washing water separated from the fine soil by centrifugation lies in the middle near the green and red curves. This result illustrates that after the treatment of ultrasonic enhanced soil washing, the petroleum hydrocarbons were relocated to four different parts of the system. A great amount of the petroleum hydrocarbons were removed from the soil particles and flushed out of the reaction chamber with washing water, with one part of the petroleum hydrocarbons still being adsorbed on the fine soil particles in the effluent and the other part of the petroleum hydrocarbons being distributed to the washing water. The residual petroleum hydrocarbons were still adsorbed on the coarse soil (sand) and the fine soils (silt and clay). By comparing the red and the dark blue chromatograms, it is obvious that the residual sand in the reaction chamber contained less TPH than the residual fine soils in the reaction chamber, indicating that the coarse soil was mush easier to be cleaned than the fine soils.

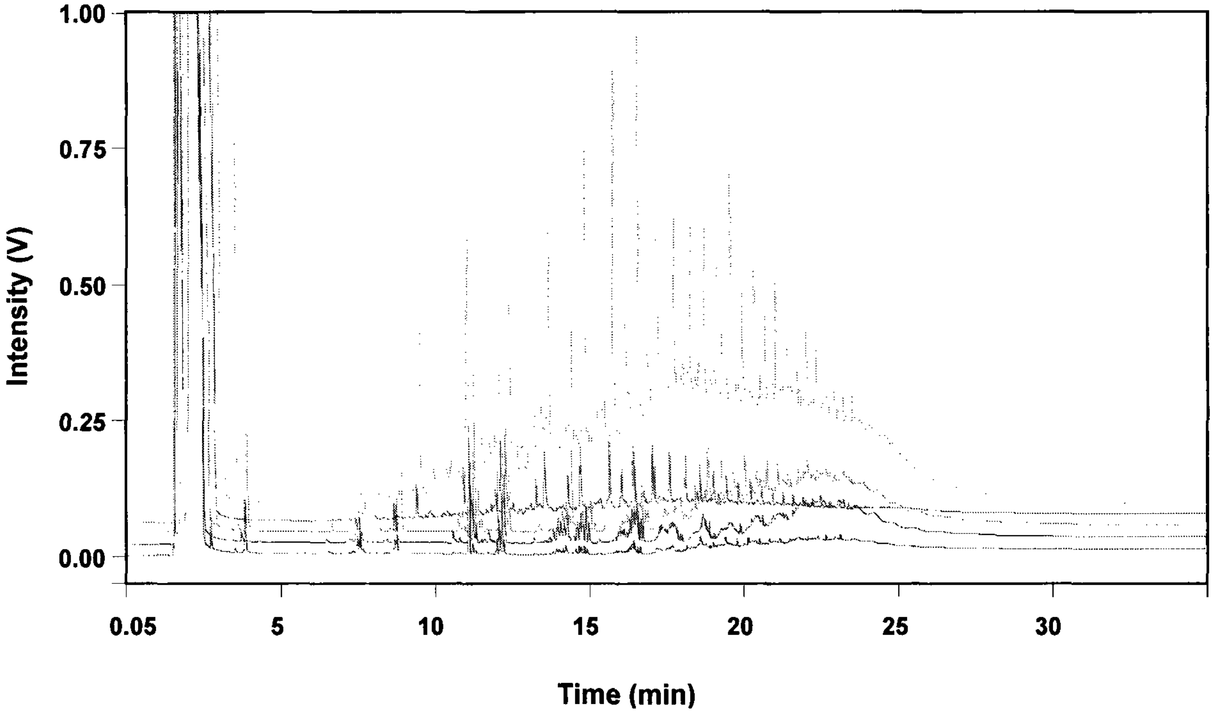

Figure.5.1 GC chromatogram of petroleum hydrocarbons after ultrasonic enhanced soil washing treatment (treatment conditions: initial crude oil concentration in soil of 2.0%, no salt, loam soil, 5 min of ultrasonic treatment, and 0.5 cm^3/s of soil washing flow rate), light blue curve representing TPH of original soil (O), pink curve representing TPH of washing water (L), green curve representing TPH of soil in the effluent (LF), red curve representing TPH of residual soil < #120 mesh (RF), and dark blue curve representing TPH of residual soil >#120 mesh (RS)

Comparing the TPH chromatogram for the original soil with the other four, it can be found that the TPH composition had changed. The percentage of different factions of TPH can be calculated using the experimental data presented in Appendix I, II, III, IV, V, and VI and the results were listed in Table 5.1. It is observed that in all the soils the F2 fraction was decreased while the F4 fraction was increased. However, in the soil washing water, the F2 fraction was increased while the F4 fraction was decreased. The F3 fractions in all the components were almost the same as that in the original soil. Such results might be due to two effects caused by the treatment of ultrasonic enhanced soil washing, namely desorption and degradation. Under the influence of ultrasound, the entrapped petroleum hydrocarbons were firstly desorbed from the soil particles and then degraded through radical oxidations at the interface between water and cavitation bubble or in the bulk solution. The complex heavy-fraction hydrocarbons were possibly broken down by ultrasound into smaller light-fraction hydrocarbons. Thus, F4 fraction might have been degraded into F2 and F3 fractions while F3 fraction might have been degraded into F2 fraction as well. Therefore the chromatogram of the TPH in the washing water shifted towards the left of the curve, indicating the existence of more light petroleum hydrocarbon fractions in the washing water. Since the heavy-fraction hydrocarbons especially F4 had less solubility and stronger bonding force to the soil particles, it was more difficult for F4 to be desorbed from the soil matrix than F2 or F3 fractions. Therefore more F2 and F3 fractions were removed out from the soil with the washing water, leading to the decrease of F2 fraction and the increase of F4 fraction concentration in the treated soil. Moreover, the short-chain hydrocarbons such as F2 fraction can be further degraded through pyrolysis within cavitation bubbles and transformed into CO_2 which will evaporate and cause the decrease of F2 fraction.

Further study of the mass balance of the TPH fractions in different components (Appendix VII, VIII, and IX) can better explain the ultrasonic degradation effect. Based on the results presented in Appendix VII, VIII, and IX, after the ultrasonic enhanced soil washing treatment, the total mass of F2 existing in different components were increased by approximately 15% as compared with the F2 mass in the original soil sample. On the contrary, the total mass of F3 and F4 fractions in the treatment system were decreased by approximately 9% and 3%, respectively. These results implied the existence of ultrasonic degradation during the treatment process.

Table 5.1 The percentage of TPH fractions in different components

Component	Percentage of TPH fraction (%)		
	F2 (nC10-nC16)	F3 (nC16-nC34)	F4 (nC34-nC50)
Original Soil	26.0	56.8	17.2
Soil washing water	37.3	50.8	11.9
Soil in the effluent	14.8	56.5	28.7
Residual soil >#120 mesh	17.5	52.2	30.3
Residual soil < #120 mesh	14.2	51.3	34.5

5.3 Salinity Effect and Soil Washing

The influence of salt on soil TPH removal was significant based on the S/N ratio analysis and ANOVA analysis of results obtained from the orthogonal experiments (Figure 4.13, Table 4.9 and 4.10). As the salinity was increased from 0 to 0.4 mol/L and from 0.4 to 0.8 mol/L, the negative impact on TPH removal were increased (i.e. S/N ratio was decreased from 37.51 to 37.02 and from 37.02 to 36.85, respectively) (Table 4.9). A further time-series experimental study of salinity effect was conducted and the results were shown in Figures 4.12 and 4.13. It was found that the TPH removals of all the treatments with the addition of 0.8 mol/L of salt (sodium chloride) were all lower than those with no addition of salt. For example, TPH removal was decreased from approximately 60% (with no salt addition) to 38% (with salt addition) for application of ultrasound alone, from approximately 34% (with no salt addition) to 29% (with salt addition) for application of soil washing alone, from approximately 77% (with no salt addition) to 70% (with salt addition) for application of both ultrasound and soil washing, and from 17% (with no salt addition) to 14% (with salt addition) for control experiments. More detailed comparisons among Figures 4.14, 4.15 and 4.16 illustrated that the effect of salinity on the treatment using ultrasound alone was more pronounced than that on the ultrasonic enhanced soil washing treatment or the treatment using soil washing alone.

In terms of the ultrasonic treatment alone (Figure 4.16), the existence of salt showed significant negative effect on reducing the TPH removal (i.e. decreased from approximately 60% to 38%). During the entire 10 min of ultrasonic treatment, the EC values were almost kept at approximately 18 dS/cm which indicated that the salt was maintained within the treatment system and it continuously affected the TPH removal by ultrasound. Similar negative effects of salinity on TPH desorption had been reported in many studies. For example, in the work of Hegemen et al. (1995), the increased salinity had been proved to increase the PAH adsorption by 22%; Brunk et al. (1997) observed a 55% increase of adsorption coefficient by increasing the ionic strength (salinity) from freshwater into seawater level. The salt effect can be well explained by the change of solubilities of the adsorbed TPH molecules caused by the salt concentration in the surrounding solution (Scharzenbach, 2003). The relationship was described using the empirical equation (i.e. Equation 2.4). According to this equation, as the salinity increases, the partitioning coefficient of TPH molecules will be increased which means more TPH molecules will be moved from the liquid phase to the solid phase. The TPH molecules may become less soluble, leading to the decrease of transport through water and the increase of trapping TPH molecules within the soil matrix (Brunk et al., 1997). Although ultrasound was supposed to enhance the TPH solubility and thus the transport of TPH molecules, its effect was weakened by the negative effect of salt existing in the surrounding solution.

In terms of the treatment using ultrasound combined with soil washing (Figure 4.17) as well as the treatment of using soil washing alone (Figure 4.18), the negative effects of salt on TPH removal were much smaller than that for treatment using ultrasound alone. This could be attributed to the effect of soil washing. With soil washing, the salt adsorbed together with TPH on the soil particles were desorbed and continually flushed out of the treatment system during the entire treatment process. In fact, it was observed that the EC values of soil treated by soil washing alone and by ultrasonic enhanced soil washing were decreased from 17.09 to 3.17 and 1.73 dS/cm, respectively. Hence the negative effect of salt was continually reduced during the soil washing process.

The experimental results proved the advantage of treatment combining ultrasound with soil washing. The combined process could not only decrease the inhibition effect of salinity on soil TPH removal, but increase the transport of TPH molecules. According to the experimental results of TPH removal by ultrasonic treatment alone (Figure 4.14), the duration of ultrasound showed little effect on the adsorption/desorption equilibrium which was reached within the first 2 to 5 min of ultrasonic treatment. Once the equilibrium was reached, the oil/water emulsion reached its maximum capacity and no more oil can be desorbed from soil. Additionally, the re-adsorption might have occurred right after the ultrasound was stopped which led to the decrease of TPH removal. However, as for the treatment of ultrasonic enhanced soil washing, the maximum treatment efficiency was reached at the end of 10 min of treatment. This slight difference might be caused by soil washing which could dilute the concentration of TPH by continuously flushing them out of the treatment system. Thus more petroleum hydrocarbon contaminants could be desorbed before the new equilibrium was reached, and the desorbed TPH were transported out of the system before being potentially re-adsorbed, which could prevent the decrease of TPH removal by re-adsorption.

Additionally, although the TPH removal difference between with and without soil washing treatment is significant, the increase of soil washing flow rate from 1.0 to 1.5cm^3/s did not lead to a rapid increase of TPH removal. This might be due to the insufficient contact time for ultrasound to take effect when the soil washing was too fast. When the washing was slow, the time-dependent process of the breakdown of contaminant/soil bond would allow more interaction of the contaminant/soil system to free the trapped contaminants in the soil pore spaces and the adsorbed contaminants on the surface of soil particles (Kim and Wang, 2003). So when soil washing flow rate is too fast, as it increases, the amount of desorbed contaminants in washing water per unit of time might decrease. Therefore, theoretically it is possible that the amount of TPH removal will reach its maximum at a soil washing rate and keep constant even the soil washing rate keep increasing.

Chapter 6 Conclusions

6.1 Research Summary

The first objective of this thesis research is to investigate the relationship and adsorption/desorption mechanisms between the petroleum hydrocarbon contaminants and soils. Soil desorption isotherms were obtained in the absence and presence of ultrasound. The impact of soil type on PHC desorption was also studied:

1) Desorption of TPH is highly related to the soil types. The highest desorption was found to be in sand, while the lowest desorption was found to be in loam.

2) The difference in desorption of TPH from different soil types were well explained by the soil physical properties such as particle size, surface area and pore volume. The attraction forces between the adsorbed TPH molecules and soil particles were stronger when the soil particle size decreased.

3) Ultrasound greatly enhanced the desorption of TPH from all the study soils. With the application of ultrasound, the TPH desorption from sand increased from approximately 78% to 83%, the TPH desorption from sandy loam increased from approximately 30% to 72%, and the TPH desorption from loam increased from approximately 12% to 61%.

4) Ultrasound could accelerate the TPH desorption and decrease the saturation adsorption capacity of TPH. For example, the time required for the soil/pollutant system to reach maximum desorption was reduced from 24 hr by using mechanical shaking to 10 min by using ultrasound. With ultrasound, Q_{sand} was decreased from 2554 to 2197 mg/kg, $Q_{sandy\ loam}$ was decreased from 8340 to 3114 mg/kg, and Q_{loam} was decreased from 11349 to 5090 mg/kg, respectively.

The second objective is to evaluate the effectiveness of ultrasonic enhanced soil washing as an effective soil decontamination technique and to investigate the optimal working conditions for this treatment in order to provide useful information for future applications. Five influencing factors including initial concentration of petroleum hydrocarbons in soil, salinity, soil type, ultrasonic treatment time and soil washing flow rate were examined through the design of orthogonal experiments:

1) The mass recoveries of soils and TPH in the mass balance calculations were approximately 96% and 97%, respectively. The results demonstrated the mass balance relationships and also proved the validity and accuracy of the experimental data.

2) The TPH removals of the treatment of ultrasonic enhanced soil washing were approximately between 61 to 94% and the average TPH removal was 73.9%.

3) All the five factors had shown statistically significant effects at 95% confidence interval while the most significant factors are soil type followed by soil washing flow rate.

4) The optimal condition for the treatment was estimated as: 2.0% w/w of initial TPH concentration, 1.0 M of Salinity, sand soil, 10 min of ultrasonication, and 1.5 cm^3/s of soil washing flow rate. The TPH removal working at the optimized working conditions was estimated to be 96.96%; the TPH removals of confirmation experiments at optimal conditions were 96.17 ± 3.56%.

The advantage of the combination of these two methods was evaluated by comparing with ultrasonic treatment and soil washing treatment alone:

1) Comparing with ultrasonic treatment (38 to 60%) and soil washing treatment (29 to 34% of TPH removal) alone, the combined treatment method with approximately 70 to 77% of TPH removal had significantly enhanced the treatment efficiency, especially when salt was added.

2) Two dominant mechanisms of the TPH removal by ultrasound had been proved to be desorption and degradation.

3) The increasing salt concentration was proved to greatly affect the TPH removal be decreasing solubilities and hindered the transportation of TPH.

4) The application of soil washing in ultrasonic treatment was proved effective in enhancing the mass transportation and preventing the re-adsorption of TPH on the soils. The negative effect of salt was reduced by the desalting through soil washing.

6.2 Limitations and Future Research

In the study of this thesis, the combined treatment method of ultrasonic enhanced soil washing had successfully enhanced the treatment process. Considering its cost-effectiveness and applicability in pilot scale experiment and large scale application, the combined treatment is of great advantages over others.

In the flow-type ultrasonic treatment, large amount of solvent (water) were introduced in order to enhance the mass transportation and solve the negative effect of salt. Comparing to soil washing, the cavitation effect generated by ultrasound had greatly increased the treatment efficiency; this means the combined treatment method had saved the cost of adding amendments such as chemical solvent or surfactant in order to enhance the treatment efficiency of soil washing to the same level as that of ultrasound; the ultrasound had also significantly accelerated the treatment process and shortened the treatment time which means it had saved the cost of large amount of washing water which is the biggest part of the cost in soil washing. Comparing to ultrasound treatment alone, the combined treatment holds higher treatment efficiency which was enhanced by increasing the mass transportation through soil washing; the ability of treating soils contaminated by mixed contaminants such as salts with petroleum hydrocarbons was increased by desalting through soil washing; this means it had saved the cost of other pretreatment of desalting before ultrasound.

Except for the cost on washing water, another was the cost on electricity used for generating ultrasound. Although the cavitation bubble generated extremely high temperature and pressure at the "hot spots" during the ultrasonic treatment, the temperature of the surrounding water and the soils were only raised up to approximately 40 or 50°C after 10 min of ultrasonication. Therefore the electricity power that needs to be supplied for and transferred into heating power plus the energy need for generating cavitation should not be a problem in the treatment cost.

As for applicability, the flow-type ultrasonic treatment had already been successfully applied in many pilot-scale and industrial-scale scientific researches (Mason et al., 2007b). Comparing to probe type ultrasonic treatment which is more suitable for bench-scale experiment, the flow-type treatment system is capable of being scaled up to handle heavier load of tasks under different conditions.

Due to time limit, the structure changes of different soils before and after ultrasonic treatment were not tested. In the future, the information about the changes of the microstructures of the adsorbent (soils) such as the surface area and pore volume will be very helpful to better understand the adsorption/desorption behavior of contaminants. In this study, the adsorbate was selected as the crude oil which is a complex mixture of many different chemical compounds in order to keep the consistency of the contaminants used in the experiment. However for further study, it is highly suggested to use single representative organic compound or specially selected groups of organic compounds to further study the mechanisms of adsorption and competitive adsorption which is very common when mixed contaminants exist as adsorbates.

In terms of the ultrasonic degradation, the fact itself was successfully proved by the calculation of the mass balance change of the fraction of TPH concentration. However, the chemical composition of the intermediate and the final products were not confirmed in this thesis. The following study can focus on the detection and identification of the products generated by ultrasonic degradation. During the ultrasonic treatment, the pH of the solution might have been being changed by the generation of radicals such as hydroxyl and chlorine radical. Thus the relationship between the pH change of the solution and the extent of degradation can also be interesting to be studied.

In order to improve the treatment process for higher treatment efficiency and shorter treatment time, the addition of amendments in washing water such as surfactant or chemical solvent can be considered; the combination with other treatment methods should be considered as well. For example the combination of ultrasound and electrolysis can be well applied in the remediation of metals or salts; the combination of ultrasound and ultraviolet radiation can be used for aqueous oxidation of organic contaminants, etc.

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APPENDIX

APPENDIX I The fractional and total TPH concentrations in the original soil (O) for each orthogonal experiment

APPENDIX II The fractional and total TPH concentrations in the liquid (L) for each orthogonal experiment

APPENDIX III The fractional and total TPH concentrations in the residual sand (R) for each orthogonal experiment

APPENDIX IV The fractional and total TPH concentrations in the soil < #120 mesh (LF) in the liquid for each orthogonal experiment

APPENDIX V The fractional and total TPH concentrations in the residual soil >#120 mesh (RS) for each orthogonal experiment

APPENDIX VI The fractional and total TPH concentrations in the residual soil <#120 mesh (RF) for each orthogonal experiment

APPENDIX VII Mass balance calculation of the F2 fractions of TPH for each orthogonal experiment

APPENDIX VIII Mass balance calculation of the F3 fractions of TPH for each orthogonal experiment

APPENDIX IX Mass balance calculation of the F4 fractions of TPH for each orthogonal experiment

APPENDIX I The fractional and total TPH concentrations in the original soil (O) for each orthogonal experiment

Exp.	F2 (mg/kg)			F3 (mg/kg)			F4 (mg/kg)			Total TPH (mg/kg)					
No.	Rep1	Rep2	Rep3	Rep1	Rep2	Rep3	Rep1	Rep2	Rep3	Rep1	Rep2	Rep3	Average	SD	RSD
1	314	236	301	942	818	771	235	504	235	1,491	1,559	1,307	1,452	106	7.3
2	1,089	1,115	886	2,333	3,081	2,531	618	888	801	4,041	5,084	4,218	4,448	456	10.3
3	2,838	2,646	2,047	4,939	5,821	4,339	1,164	1,578	1,801	8,941	10,046	8,187	9,058	763	8.4
4	359	325	327	766	812	666	246	329	218	1,370	1,466	1,211	1,349	105	7.8
5	1,526	1,295	1,221	2,758	2,998	2,833	695	973	830	4,979	5,265	4,884	5,043	162	3.2
6	2,590	2,148	1,489	4,462	3,997	4,183	1,002	1,114	1,418	8,055	7,259	7,089	7,467	421	5.6
7	321	381	384	956	1,086	783	259	382	206	1,535	1,850	1,373	1,586	198	12.5
8	1,445	1,007	1,078	2,599	2,459	2,528	669	698	539	4,713	4,164	4,145	4,341	263	6.1
9	2,707	1,978	1,969	5,330	4,474	4,759	1,330	1,230	1,477	9,367	7,683	8,206	8,418	704	8.4
10	555	326	383	1,020	798	807	314	351	178	1,889	1,475	1,368	1,577	225	14.3
11	1,170	1,195	1,039	2,625	2,823	2,908	621	879	1,246	4,416	4,897	5,193	4,835	320	6.6
12	2,433	2,089	1,781	4,255	4,695	4,006	1,040	1,239	1,632	7,728	8,023	7,419	7,724	247	3.2
13	523	341	363	798	735	842	233	331	247	1,555	1,407	1,451	1,471	62	4.2
14	1,987	1,205	1,122	2,791	2,676	2,432	610	812	1,122	5,388	4,693	4,677	4,919	332	6.7
15	2,520	2,237	1,596	4,803	4,534	4,331	1,052	1,163	1,672	8,376	7,934	7,599	7,970	318	4.0
16	331	306	320	727	879	712	212	325	154	1,270	1,511	1,187	1,323	137	10.4
17	1,694	1,299	1,359	3,236	2,957	2,624	871	960	703	5,801	5,216	4,685	5,234	456	8.7
18	2,408	2,171	2,155	4,461	4,160	3,951	983	1,119	1,077	7,852	7,451	7,183	7,495	275	3.7

APPENDIX II The fractional and total TPH concentrations in the liquid (L) for each orthogonal experiment

Exp.	F2 (mg/L)			F3 (mg/L)			F4 (mg/L)			Volume (mL)			Total TPH (mg/L)					
No.	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Aver.	SD	RSD
1	82	56	83	173	123	152	38	45	41	200	250	200	293	224	276	264	29	11.1
2	127	91	109	169	167	169	34	26	53	425	500	450	329	284	331	315	22	6.9
3	213	119	128	248	145	155	35	20	54	500	800	700	495	283	336	372	90	24.3
4	35	30	36	48	38	44	9	11	13	500	550	500	92	78	93	88	7	7.8
5	73	99	85	81	116	109	8	21	19	700	500	550	161	236	214	204	31	15.5
6	199	352	217	464	504	389	74	151	142	400	300	400	736	1,007	749	831	125	15.0
7	37	29	42	55	50	59	18	17	15	600	700	600	110	97	117	108	8	7.7
8	106	139	157	141	199	244	24	38	35	500	350	300	271	376	435	361	68	18.8
9	286	210	228	347	278	314	48	37	74	300	350	350	681	525	615	607	64	10.5
10	48	28	24	65	36	36	10	11	9	300	500	500	123	76	69	89	24	26.8
11	102	71	91	147	116	126	34	36	58	800	1000	800	282	223	274	260	26	10.1
12	255	245	219	330	329	280	37	71	110	350	350	350	623	645	610	626	14	2.3
13	60	39	46	65	44	63	5	17	12	250	350	300	130	99	121	117	13	11.2
14	279	185	227	325	218	299	60	71	123	300	400	300	664	473	649	596	87	14.6
15	148	173	165	189	221	233	33	49	87	800	650	600	371	443	486	433	47	10.9
16	29	28	25	35	39	34	6	10	4	500	500	550	70	77	62	70	6	8.8
17	139	176	162	158	192	193	26	41	31	400	300	350	322	409	385	372	37	9.9

18	211	210	224	278	279	276	67	80	75	600	600	600	555	569	575	566	8	1.5

APPENDIX III The fractional and total TPH concentrations in the residual sand (R) for each orthogonal experiment

Exp. No.	F2 (mg/kg)			F3 (mg/kg)			F4 (mg/kg)			Total TPH (mg/kg)					
	Rep1	Rep2	Rep3	Rep1	Rep2	Rep3	Rep1	Rep2	Rep3	Rep1	Rep2	Rep3	Average	SD	RSD
1	59	60	73	134	157	135	75	85	85	269	302	292	288	14	4.8
6	324	289	277	708	603	650	303	241	277	1335	1,133	1,205	1,224	84	6.8
7	32	39	29	99	83	71	43	60	44	173	182	144	166	16	9.7
11	26	37	26	89	82	66	44	59	33	159	178	125	154	22	14.2
14	188	208	165	413	483	437	150	224	223	751	914	825	830	67	8.0
18	125	98	106	355	272	232	151	124	83	631	493	421	515	87	16.9

APPENDIX IV The fractional and total TPH concentrations in the soil < #120 mesh (LF) in the liquid for each orthogonal experiment

Exp.	F2 (mg/kg)			F3 (mg/kg)			F4 (mg/kg)			Total TPH (mg/kg)					
No.	Rep1	Rep2	Rep3	Rep1	Rep2	Rep3	Rep1	Rep2	Rep3	Rep1	Rep2	Rep3	Average	SD	RSD
2	506	320	414	2,143	1,732	1,814	1,247	1,156	955	3,896	3,207	3,183	3,429	330	9.6
3	1,067	730	742	3,388	3,878	3,644	1,820	2,317	2,121	6,274	6,925	6,507	6,569	269	4.1
4	201	231	158	748	557	597	277	349	372	1,226	1,137	1,126	1,163	45	3.9
5	702	568	603	2,184	1,756	1,848	1,014	1,052	1,035	3,899	3,377	3,486	3,587	225	6.3
8	644	667	896	2,535	2,675	2,726	845	1,192	998	4,023	4,534	4,620	4,392	263	6.0
9	1,038	795	802	3,567	3,878	3,163	1,881	2,013	1,489	6,486	6,685	5,453	6,208	540	8.7
10	196	206	200	704	529	711	404	390	337	1,304	1,124	1,247	1,225	75	6.1
12	1,231	734	1,078	4,596	4,624	4,775	2,380	1,982	1,848	8,207	7,340	7,701	7,749	356	4.6
13	114	120	121	409	332	400	263	240	114	786	692	635	705	62	8.8
15	529	478	654	2,197	2,550	2,117	1,343	956	1,078	4,069	3,984	3,849	3,967	91	2.3
16	176	131	147	863	806	685	424	363	392	1,463	1,300	1,224	1,329	100	7.5
17	635	628	537	2,360	2,604	2,075	1,074	1,181	966	4,068	4,414	3,578	4,020	343	8.5

APPENDIX V The fractional and total TPH concentrations in the residual soil >#120mesh (RS) for each orthogonal experiment

Exp. No.	F2 (mg/kg)			F3 (mg/kg)			F4 (mg/kg)			Total TPH (mg/kg)					
	Rep1	Rep2	Rep3	Rep1	Rep2	Rep3	Rep1	Rep2	Rep3	Rep1	Rep2	Rep3	Average	SD	RSD
2	123	97	102	336	409	372	226	237	203	685	743	677	702	29	4.2
3	88	116	88	224	266	236	128	172	139	440	554	463	486	49	10.2
4	26	39	27	76	102	73	36	63	35	139	205	136	160	32	19.9
5	125	90	106	234	309	289	185	195	194	544	594	589	576	23	3.9
8	103	82	94	327	188	242	176	130	121	606	399	457	487	87	17.9
9	85	89	99	352	274	298	170	232	187	608	596	584	596	10	1.6
10	30	29	33	84	99	94	45	59	47	159	187	174	173	11	6.6
12	227	252	267	781	599	713	412	323	293	1,420	1,174	1,273	1,289	101	7.9
13	67	55	59	222	211	201	107	117	134	396	383	395	391	6	1.5
15	57	69	62	236	281	252	144	161	144	438	511	458	469	31	6.6
16	61	40	50	149	148	160	94	81	86	304	270	296	290	14	5.0
17	166	146	113	445	360	398	262	228	240	872	734	751	786	62	7.8

APPENDIX VI The fractional and total TPH concentrations in the residual soil <#120 mesh (RF) for each orthogonal experiment

Exp. No.	F2 (mg/kg)			F3 (mg/kg)			F4 (mg/kg)			Total TPH (mg/kg)					
	Rep1	Rep2	Rep3	Rep1	Rep2	Rep3	Rep1	Rep2	Rep3	Rep1	Rep2	Rep3	Average	SD	RSD
2	317	389	304	1,098	1,334	1,084	697	1,056	780	2,112	2,778	2,168	2,353	302	12.8
3	506	695	467	1,916	2,116	2,022	1,193	1,422	1,400	3,615	4,233	3,889	3,912	253	6.5
4	79	102	107	328	480	379	249	342	229	656	923	715	765	115	15.0
5	369	553	410	1,635	1,514	1,510	1,141	1,023	1,162	3,145	3,089	3,082	3,105	28	0.9
8	533	455	595	1,882	1,950	2,044	1,136	1,744	1,078	3,551	4,148	3,717	3,805	252	6.6
9	670	982	710	2,785	3,098	2,271	1,702	1,766	1,751	5,158	5,846	4,732	5,245	459	8.8
10	174	154	137	513	499	512	338	344	265	1,025	997	915	979	47	4.8
12	929	1,153	1,160	3,582	3,674	3,139	2,123	2,377	2,525	6,633	7,204	6,824	6,887	237	3.4
13	150	107	111	460	382	341	328	275	244	938	765	696	800	102	12.7
15	494	568	387	1,737	2,272	1,820	1,175	1,529	1,665	3,406	4,369	3,872	3,882	393	10.1
16	136	97	153	524	454	567	311	260	371	971	811	1,090	957	114	11.9
17	233	349	375	1,349	1,348	1,102	785	799	727	2,368	2,495	2,204	2,356	119	5.1

APPENDIX VII Mass balance calculation of the F2 fractions of TPH for each orthogonal experiment [a]

Exp. No.	$F2_{O}$ (µg)	$F2_{R}$ (µg)	$F2_{RS}$ (µg)	$F2_{RF}$ (µg)	$F2_{LF}$ (µg)	$F2_{L}$ (µg)	$F2_{total}$ (µg)	$F2_{total}$ /$F2_{O}$ (µg)
1	15,040	2,777				16,389	19,166	1.27
2	52,030		4,219	1,584	1,321	53,797	60,921	1.17
3	108,411		1,684	5,349	7,003	106,515	120,551	1.11
4	15,335		884	385	517	17,309	19,094	1.25
5	58,275		2,380	3,746	4,762	50,764	61,651	1.06
6	118,156	15,358				117,803	133,161	1.13
7	16,316	1,470				22,397	23,867	1.46
8	57,773		3,427	3,082	1,741	52,914	61,164	1.06
9	91,723		1,693	7,428	5,733	85,804	100,658	1.10
10	17,462		586	1,859	1,125	14,402	17,971	1.03
11	63,021	1,229				81,319	82,548	1.31
12	105,522		7,802	5,529	3,017	89,372	105,721	1.00
13	18,657		1,333	1,644	550	14,993	18,519	0.99
14	89,273	8,874				83,690	92,564	1.04
15	104,058		1,924	2,688	1,485	118,594	124,692	1.20
16	14,944		2,023	771	549	14,418	17,762	1.19
17	57,624		3,227	2,982	2,687	55,440	64,335	1.12
18	113,095	5,859				126,651	132,510	1.17
							Average	1.15

$F2_O$: mass of F2 fractions of TPH of the original soil;

$F2_R$: mass of F2 fractions of TPH of the residual sand;

$F2_{RS}$: mass of F2 fractions of TPH of residual soil >#120 mesh;

$F2_{RF}$: mass of F2 fractions of TPH of residual soil <#120 mesh;

$F2_{LF}$: mass of F2 fractions of TPH of soil in effluent;

$F2_L$: mass of F2 fractions of TPH of washing water;

for Exp 1, 6, 7, 11, 14 and 18, $F2_{total}$ is the sum of $F2_R$ and $F2_L$; for Exp 2, 3, 4, 5, 8, 9, 10, 12, 13, 15, 16, and 17, $F2_{total}$ is the sum of $F2_{RS}$, $F2_{RF}$, $F2_{LF}$ and $F2_L$.

APPENDIX VIII Mass balance calculation of the F3 fractions of TPH for each orthogonal experiment

Exp. No.	$F3_O$ (μg)	$F3_R$ (μg)	$F3_{RS}$ (μg)	$F3_{RF}$ (μg)	$F3_{LF}$ (μg)	$F3_L$ (μg)	$F3_{total}$ (μg)	$F3_{total}/F3_O$ (μg)
1	45,151	6,310				34,534	40,845	0.90
2	111,469		11,486	5,491	5,590	71,683	94,250	0.85
3	188,627		4,295	20,249	22,243	123,855	170,642	0.90
4	32,713		2,559	1,603	1,922	23,857	29,942	0.92
5	105,295		4,449	16,617	14,814	56,405	92,284	0.88
6	203,536	33,497				185,540	219,037	1.08
7	48,572	4,579				32,937	37,516	0.77
8	103,891		10,886	10,888	6,856	70,552	99,183	0.95
9	180,597		7,014	30,856	19,706	104,191	161,767	0.90

10	32,109		1,635	5,467	4,050	19,571	30,723	0.96
11	141,409	4,173				117,460	121,633	0.86
12	184,559		26,820	21,327	11,265	115,530	174,942	0.95
13	28,475		4,389	5,035	1,973	16,296	27,694	0.97
14	125,351	19,524				97,638	117,162	0.93
15	198,365		7,994	9,454	6,170	151,208	174,826	0.88
16	32,865		4,957	2,975	2,700	17,583	28,215	0.86
17	110,084		8,663	17,300	9,989	63,175	99,127	0.90
18	209,515	16,641				166,646	183,287	0.87
							Average	0.91

$F3_O$: mass of F3 fractions of TPH of the original soil;

$F3_R$: mass of F3 fractions of TPH of the residual sand;

$F3_{RS}$: mass of F3 fractions of TPH of residual soil >#120 mesh;

$F3_{RF}$: mass of F3 fractions of TPH of residual soil <#120 mesh;

$F3_{LF}$: mass of F3 fractions of TPH of soil in effluent;

$F3_L$: mass of F3 fractions of TPH of washing water;

for Exp 1, 6, 7, 11, 14 and 18, $F3_{total}$ is the sum of $F3_R$ and $F3_L$; for Exp 2, 3, 4, 5, 8, 9, 10, 12, 13, 15, 16, and 17, $F3_{total}$ is the sum of $F3_{RS}$, $F2_{RF}$, $F3_{LF}$ and $F3_L$.

APPENDIX IX Mass balance calculation of the F4 fractions of TPH for each orthogonal experiment

Exp. No.	$F4_{O}$ (μg)	$F4_{R}$ (μg)	$F4_{RS}$ (μg)	$F4_{RF}$ (μg)	$F4_{LF}$ (μg)	$F4_{L}$ (μg)	$F4_{total}$ (μg)	$F4_{total}/F4_{O}$ (μg)
1	11,260	3,534				7,609	11,143	0.99
2	29,528		7,735	3,485	3,253	14,253	28,725	0.97
3	44,442		2,442	12,608	11,946	17,340	44,335	1.00
4	10,500		1,210	1,219	712	4,625	7,765	0.74
5	26,537		3,518	11,593	6,878	5,640	27,629	1.04
6	45,709	14,347				29,451	43,798	0.96
7	13,145	1,984				10,540	12,524	0.95
8	26,724		5,846	6,574	2,285	12,211	26,917	1.01
9	45,057		3,386	18,857	10,390	14,301	46,934	1.04
10	9,892		864	3,608	2,325	2,954	9,751	0.99
11	33,470	2,047				27,106	29,154	0.87
12	45,119		14,141	12,638	5,834	13,079	45,692	1.01
13	8,326		2,116	3,596	1,271	1,304	8,288	1.00
14	27,403	7,100				17,933	25,033	0.91
15	43,455		4,885	6,395	3,771	26,684	41,735	0.96
16	9,594		3,136	1,763	1,327	3,165	9,391	0.98
17	29,612		5,096	10,069	4,547	10,314	30,026	1.01
18	46,157	7,092				39,995	47,087	1.02
							Average	0.97

$F4_O$: mass of F4 fractions of TPH of the original soil;

$F4_R$: mass of F4 fractions of TPH of the residual sand;

$F4_{RS}$: mass of F4 fractions of TPH of residual soil >#120 mesh;

$F4_{RF}$: mass of F4 fractions of TPH of residual soil <#120 mesh;

$F4_{LF}$: mass of F4 fractions of TPH of soil in effluent;

$F4_L$: mass of F4 fractions of TPH of washing water;

for Exp 1, 6, 7, 11, 14 and 18, $F4_{total}$ is the sum of $F4_R$ and $F4_L$; for Exp 2, 3, 4, 5, 8, 9, 10, 12, 13, 15, 16, and 17, $F4_{total}$ is the sum of $F4_{RS}$, $F4_{RF}$, $F4_{LF}$ and $F4_L$.