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ABSTRACT

ULTRASONIC ENHANCED SOIL WASHING

by
Chu-Feng Wei

Soil washing is an ex-situ process employing chemical and physical extraction and separation techniques to remove a broad range of organic, inorganic, and radioactive contaminants from soils. This research investigates the enhanced soil washing of a high level Polycyclic Aromatic Hydrocarbons (PAHs) contaminated coal tar soil by the application of ultrasound energy coupled with surfactant (soap) emulsions and attempts to optimize pollutant removal from contaminated soils. The non-ionic surfactant, octyl-phenyl-ethoxylate, was used as the surfactant.

Using bench-scale experiments, the magnitude of the ultrasonic enhancement was evaluated by changing the process parameters, such as ultrasonic power density, Dwell (extractor residence time), surfactant concentration, solvent ratio (liquid/soil w/w ratio), pH, and temperature. Experimental results show that the ultrasonic power density was the main contributing factor for the removal of PAHs. In general, the enhancement of removal efficiency due to ultrasound reached up to 40% to 60% when compared with that without ultrasound. The optimum condition with ultrasound was obtained at a solvent ratio of 25 with 750 Watts power density, 30 minutes dwell time, and 1% concentration of surfactant solution. The removal efficiency can be further improved by increasing the pH of the surfactant solution.

ULTRASONIC ENHANCED SOIL WASHING

by
Chu-Feng Wei

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This thesis is dedicated to my parents.

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CHAPTER 1

INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) are ubiquitous environmental pollutants that are suspected to be carcinogenic. Chemical analysis studies show that PAHs appear in a large number of industrial processes, mainly due to high temperature treatment of coal tar and pitch as well as Products of Incomplete Combustion (PIC) or pyrolysis of organic material [1]. Remediation of soil contaminated with PAHs is a problem requiring an immediate and economical solution, especially in New Jersey with many Superfund sites needing cleanup. As part of an overall treatability study [2], air stripping, leaching, bioremediation, and surface flooding flotation are being investigated as potential remediation alternatives. Soil washing is the most appropriate for treating non-complex soils which contain at least 50% sand and gravel, such as coastal sandy soils and soils with glacial deposits.

Soil washing has been practiced as a means for removing contaminants from soil since the early 1970s when the EPA funded and operated a crude soil washer, the "Beach Cleaner". Today, soil washing is a commercially available method for treating excavated soil and dredge sediments that are contaminated with toxic and other hazardous pollutants.

Soil washing is a method of treatment based on extraction using water, or water plus additives, such as surfactants, chelating agents (e.g., EDTA), acids, and alkalis. The removal efficiency is highly dependent on physical and chemical characteristics of the soil, the contaminants, the spatial distribution of pollutants within the soil, and the soil washing additives. Superfund Innovative Technology Evaluation (SITE) [2] Program reported removal efficiencies for residual metals and hydrocarbons can be up to 90 to 98% when heat and surfactants were added to the washwater.

Soil washing can be also used to remove Volatile Organic Compounds (VOCs) and other materials with a relatively high vapor pressure or water soluble quotient. Up to 90-99% removals of VOCs can be achieved by simple water washing. However, removal rates for semi-volatile organic materials tend to be lower, on the order of 40 to 90%, and the addition of surfactants to the washwater is often required to aid in the washing and/or separation.

Ultrasonic cleaning is an industrial method for the removal of oil, grease, and other contaminants from solid surfaces. Ultrasound is applied to the cleaning of manufactured parts in the metals and electronic industries. It is also combined with the chemical action of a solvent-surfactant on the contaminant to increase the speed and quality of the cleaning [3]. The velocity of sound in water is typically 1500 m/s; ultrasound spans the frequency of roughly 15 kHz to 1 MHz, associated with acoustic wavelengths of 10.0-0.15 cm. The ultrasonic effect is based on cavitation, which is the formation of microscopic vapor bubbles in the rarefied zones of the ultrasonic wave. The bubbles quickly collapse under the compression part of the wave, causing minute but highly energetic scrubbing action on the solid surface [4].

The great majority of industrial cleaners operated in the frequency range from 18 to 44 kHz. This is the optimum range in terms of technological efficiency, economy of the process, and safety considerations. The lower frequency range (18 to 22 kHz) is used for the removal of contaminants having a high adhesion to the surface (scale, pickup, polymer films); the higher range (40 to 44 kHz) is used for cleaning in the case of contaminants that are weakly bound to the surface (grease and machining contaminants).

There are limited reports showing good removal efficiency of PAHs, especially on 4-6 rings of PAHs and contaminated soil containing high silt and clay fraction. Also, to the best of our knowledge there was no systematic work carried out to develop information on the important variables that can affect the efficiency of ultrasonic enhancement of contaminant removal from soil. In this study, we attempted to quantify

application of ultrasonic energy which will enhance soil washing and to qualify the enhancement effect of applying ultrasonic energy to a soil washing with surfactant. Then quantify the enhancement due to ultrasonic cleaning. This research study is designed to demonstrate that ultrasonic energy can:

1. Improve process performance, i.e. remove contaminants to lower residual concentrations by increasing the percentage removed due to application of ultrasound by 20% or more with 95% confidence.
2. Improve process economics, e.g., 50% to 66.6% reduction in treatment (residence) time and surfactant usage at the same removal efficiency (with and without ultrasound).
3. Enhance existing process, e.g., treat silt and clay fraction.
4. Determine the effect of the process parameters to optimize soil washing process.

CHAPTER 2

LITERATURE REVIEW AND BASIC CONCEPT OF ULTRASONIC CLEANING

2.1 Different Alternatives to Clean-up Soil Contaminated with PAHs

Coal tar products, derived from the carbonization of bituminous coal, are the most important sources of work place PAH emissions. The PAHs are a group of chemical compounds that are strongly suspected of exhibiting carcinogenic effects in humans. The soil contaminated with PAHs can be cleaned not only by soil washing or soil flushing, but also by bioremediation, chemical treatment, solvent/chemical extraction, stabilization/solidification, thermal desorption, thermal destruction, or vacuum vapor extraction.

Soil flushing is an in situ process that uses water, with additives, or gaseous mixtures to accelerate the mobilization of contaminants from a contaminated soil for recovery and treatment. The process accelerates one or more of the same geochemical dissolution reactions that alter contaminant concentrations in groundwater systems [2]; adsorption/desorption, acid/base, and biodegradation. A variety of site conditions can limit the use of soil flushing. Soil with pockets of low hydraulic conductivity may limit effectiveness. Pipes and underground utilities may limit the effectiveness of flushing of sites contaminated with underground storage tanks. Soil flushing is less effective where the contaminants are relatively insoluble or tightly bound to the soil, and in situations where there is lack of an adequate supply of process water.

The objective of the desorption procedure is to separate PAHs from the bulk-sample matrix in as high a yield as possible, with a minimum of co-extraction of other compounds present in the sample [1]. The various methods that are available for desorption of PAHs from filters or adsorption trap may be divided into solvent/chemical extraction and thermal desorption.

The principle of solvent extraction is to selectively dissolve contaminants from the sample matrix with a suitable solvent. Some of the reported [5] major deficiencies are: length of treatment, decomposition of PAHs during extraction, and low recovery at low PAHs concentrations.

Thermal methods of extraction of PAHs, such as sublimation, have generally received only limited attention [1]. These methods may offer certain advantages over conventional solvent extraction, e.g., no further clean-up is required before the analysis of PAHs in airborne particulate, and no need of large volumes of solvents. However, in the case of highly sorptive matrices such as coal fly ash [6] or carbon black [7], even after numerous extractions, the extraction recoveries of some PAHs may be very low. This may lead to serious underestimation of PAHs concentrations if the recoveries are not determined otherwise.

Thermal desorption is an ex-situ means to physically separate volatile and some semivolatile contaminants from soils, sediments, sludges, and filter cakes [8]. It is applicable to organic wastes, but not for treating metals and other inorganics. Depending on the specific thermal desorption venter selected, this technology heats contaminated matrix between 100 - 550 °C to drive off water and volatile contaminants. The primary technical factor affecting thermal desorption performance is the maximum bed temperature achieved. Since the basis of the process is physical removal from the matrix by volatilization, bed temperature directly determines which organics will be removed.

Many PAHs can be removed from the environment by microbial degradation. Some bioremediation technologies biodegrade creosote-contaminated materials through aerobic bacteria that use the contaminants as their carbon source. Davis et al., 1993 [9] determined the ability of selected lignin-degrading fungi to remediate soil contaminated with creosote found at a wood-treating facility. The depletion of 3-ring (85-95%) and 4-ring (24-72%) analytes of PAHs after 56 days was greater in the fungal treatment than in control treatments in all cases. This technology usually needs a long treatment time and

large quantity of microbes and nutrients to biodegrade PAHs, and the intermediate products of PAHs during treatment are unknown.

Soil washing has been selected as a remedial application at 23 Superfund National Priorities List (NPL) sites and at one other, lower priority CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act) site. None of these applications involve the separation and recovery of volatile contaminants, but, instead, involves the treatment of soils for semivolatile, Polynuclear Aromatic Hydrocarbons (PAHs), dioxins, pesticides, and heavy metals contamination. The amount of soil to be washed at these sites ranges from 1,400 to 150,000 m³ [2].

The status of soil washing application has been reviewed in recent publications [10]. Following is a summary of that publication:

- The Heijmans process (Netherlands) extracts organics and metals from excavated soil. The organic pollutants are then separated from the wash liquid by air flotation, and the metal impurities by precipitation.

- The HWZ process (Netherlands) extracts organics and metals from excavated soil. The metals are separated from the wash liquid by precipitation, and the organics by carbon adsorption.

- The Harbauer process (Germany) extracts organics and metals from excavated soil. The impurities are separated from the wash liquid by air flotation followed by carbon adsorption.

- The TAUW process (Netherlands) removes Cadmium from soil by in-situ acid leaching. The metal is separated from leachate by on-site ion exchange.

2.2 The Application of Surfactant in Soil Washing

Soil washing is an ex-situ physical/chemical separation technology where excavated soil is pretreated to remove large objects and soil clods and then washed with fluids to remove contaminants. For soil washing, to be effective, contaminants should be transferred to the

wash fluids or concentrate the contaminants in a fraction of the original soil volume using size separation techniques. In either case, soil washing must be used in conjunction with other treatment technologies.

Soil washing systems usually consist of six distinct process units: pretreatment, separation, coarse-grained (>200 mesh or > 74 micron) treatment, fine-grained (<200 mesh or <74 micron) treatment, process water treatment, and residuals management. Particle size distribution has a direct effect on the ability of a soil washing system to separate contaminants from the major soil mass. In general, the higher percentage of sand and gravel in the soil or sediment the more effective the soil washing. Contaminated fines and sludges resulting from the process require additional treatment, e.g., incineration, low-temperature thermal desorption, bioremediation, or landfilling.

Surficial contamination of sand and gravel fractions is due to forces of adhesion and compaction. It can be removed from the coarse fraction by abrasive scouring or scrubbing actions. This washing step is sometimes enhanced by adding chemicals to the washing fluid. After washing steps, the coarse soil fraction may be washed again to further remove residual contaminants and additives. The spent and rinsing fluids are treated to remove the contaminants prior to recycling back to the treatment units.

An essential part of a soil washing process is the extraction, in which the soil is brought in contact with washing fluid by mechanical agitation. The shearing action achieved by vigorous agitation is needed to dislodge the contamination from the soil particles, and to enhance the solubilization of contaminants in the washing fluids.

Due to the possibility of metabolic degradation of some PAHs, an interest has emerged in incorporation of surfactants into bioremediation process at contaminated sites. Because of slowing desorption of surfactant, soil-bound PAH may be promoted when applying surfactant to contaminated soil. Putchá and Domach, 1993 [11] employed fluorescence spectroscopy and quenching experiments to investigate micelle-naphthalene interaction and the dynamics of biodegradation in the presence and absence of micelles. In

the absence of micelles, naphthalene was observed to have degraded within three days and intermediates were detected. Micelles protected naphthalene against copper quenching and also suppressed biodegradation.

The application of surfactants in oil-spill cleanup is a relatively recent idea. Rickabaugh et al., 1986 [12] performed bench-scale batch shaker experiment on soil washing with 14 different surfactants on soil contaminated with chlorinated hydrocarbons (CHC). The surfactants in this study included a blend of nonionic-anionic and nonionic-cationic, as well as anionic and nonionic surfactants. Results showed that the removal efficiency with 2% surfactant solutions is much higher than that of 0.5% solutions. The removal efficiencies of blended surfactants were much better than that for the anionic or nonionic surfactants.

Nash, 1987 [13] performed in-situ soil flooding of soils contaminated with hydrocarbons (HC) and chlorinated hydrocarbons (CHC). He determined the success of various surfactants in laboratory screening and soil-column tests similar to Rickabaugh et al., 1986 [12] and scaled up to pilot scale study. Nash, 1987 [13] reported measurable contaminant removal, and some of the samples even showed no removal in contaminant concentrations. The low removal was most likely due to surfactant dilution by heavy rains that occurred during three days of surfactant application. The increase in the contaminant concentrations of some of the treated samples was due to variation in the site; moreover, the initial values used were not representative of all points in the site.

Peters et al., 1992 [14] summarized a surfactant screening/flooding research program in which 22 surfactants were screened for their effectiveness in mobilizing the organics from a soil contaminated with No. 2 diesel fuel prior to bioremediation. Results indicated that the anionic surfactants generally provided the best removal of Total Petroleum Hydrocarbons (TPHs) from the diesel-contaminated soil where approximately 60,000 gal of No. 2 diesel fuel leaked into the surface environment. These 22 surfactants were used to examine the removal of alkanes in the C12 to C19 range. Three surfactants,

two anionic and one nonionic, removed 80 to 90% of the C12 to C19 alkanes. They claimed that the performance of the anionic surfactants was the best.

Liu et al., 1991 [15], studied the solubilization of PAHs sorbed onto soil. They compared the solubilization of anthracene, phenanthrene and pyrene in water-soil suspensions with 9 nonionic and anionic surfactants. For a soil-water mass ratios between about 1:7 to 1:2, greater than 0.1% by volume surfactant dose was required to initiate solubilization. With surfactant doses of 1% by volume resulted in 70-90% solubilization. The most effective surfactant is the nonionic octyl- and nonyl-phenyl ethoxylates with 9 to 12 ethoxylate units.

For the laboratory treatment of contaminated soil, it is possible to achieve a target level of separation by adjusting the concentration of additives, increasing the wash liquid to soil ratio, or repeated washing treatments. However, for industrial operation, the disposal of the wash and rinse liquids, which contain the additives as well as the impurities is a problem. GHEA Associates [10] invented a novel separation process to cost-effectively clean, wash, and rinse liquids and also to have a good recovery of the surfactants for repeated use. This method can isolate the impurities as highly concentrated fraction, which is thereby amenable to reclamation or disposal at low cost, due to volume reduction.

The ability of surfactants to act as mediators between hydrophobic chemicals and water is related to the structure of the surfactant molecule, which contains a hydrophilic part, referred to as the “head”, and a hydrophobic part, referred to as the “tail”. The attractive forces between the surfactant tail and the non-polar organic compounds, and the surfactant head and the water molecules contributes to solubilization of organic compounds in water.

Another property of surfactant molecules which may be related to solubilization is aggregation to sub-micron droplets, referred to in the art as “Micelles” (Figure 2.1). In a water environment, the surfactant molecules constituting the Micelle are oriented with

hydrophilic heads towards the water, i.e., outwards, and the hydrophobic tails towards the interior is hydrophobic micro-environment, capable of retaining organic solutes.

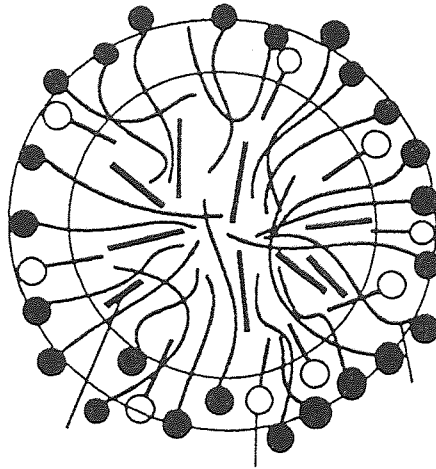


Figure 2.1 Micelle (aggregation of surfactant molecules)

Anionic and cationic surfactants have an adsorptive affinity towards counter-ion solutes due to electrostatic forces. Nonionic surfactant have solvating and adsorptive properties due to their polarity, and also due to the formation of hydrogen bonds and the presence of Van Der Waals forces.

A low interfacial tension requires optimal electrolyte concentration and salinity of the solution, as well as optimal alkyl chain length of the surfactant. It has shown that the point at which the interfacial tension is at or near its minimum is at the surfactant concentration where the most surfactants are found at the interface. This point is called the critical micelle concentration (CMC). The CMC can be defined as the concentration of a micelle at which the rate of increase of electrical conductance with an increase in concentration stabilizes or proceeds at a much slower rate. The CMC is dependent on factors such as surfactant concentration, structure of the oil phase, time, and temperature. Therefore, CMC is unique for a given field condition [16].

It is important to distinguish that although all amphiphilic molecules are surface active and can be expected to be in excess at interfaces, not all amphiphilic compounds are commonly referred to as surfactants. Though perhaps an over simplification, a good deal of insight into the properties of micelles can be gained by thinking of them in terms of the "oil drop model". The micelle is pictured as a 3-4 nm diameter droplet of oil with an ionic or polar coating. Micelle formation occurs above a critical concentration of surfactant monomers, referred to as the critical micelle concentration (CMC), which is different for every surfactant. CMCs typically range between 0.1 and 10 nM. In a micelle, the individual monomers are oriented with their hydrophilic moieties in contact with the aqueous phase and their hydrophobic moieties tucked into the interior of the aggregate.

2.3 Ultrasound Applications

Sir John Thornycroft and Sidney Barnaby observed a severe vibration and excessive slippage of the screw propeller of destroyer H.M.S [4]. A solution to the problem was found by increasing the surface area of the propeller and decreasing its angular velocity. The bubbled formation on the moving propeller resulted in reduced vibration. This was the first report on phenomenon known as "cavitation", which occurs both in turbulent flow and ultrasonic irradiation of liquids.

Loomis is the first chemist to recognize the unusual effects of intense sound waves traveling through a liquid, known as sonochemistry [4]. A renaissance in sonochemistry took place in the 1980's, evidence by the growing number of publications on usefulness of sonochemistry. Suslick [3] stated that even though ultrasound showed up in such varied uses as medical imaging and self-focusing cameras, it is extremely useful in controlling chemical reaction and creating unusual materials.

Ultrasonic cleaning works by providing shear forces to remove the material adhered to a surface. This shear force is developed by cavitation due to the formation of microscopic vapor bubbles in the low pressure (rarefied) part of the ultrasonic waves.

Ultrasound waves, like all sound waves, consists of cycle of compression and expansion. Compression cycles exert a positive pressure on the liquid, pushing the molecules together; expansion cycles exert a negative pressure, pulling the molecules away from one another. During the expansion cycle a sound wave of sufficient intensity can generate cavities. Once a cavity has experienced a very rapid growth caused by either low- or high-intensity ultrasound, it can no longer absorb energy as efficiently from the sound waves. Without this energy input, the cavity can no longer sustain itself. The liquid rushes in and the cavity implodes. For each cycle of sound, then, the cavity expands a little more than it shrinks. The growing cavity can eventually reach a critical size where it will most efficiently absorb energy from the ultrasound.

Collapse of these bubbles in the compression part of the wave creates very minute, but high, energy movements of the solvent that results in localized high shear forces. Ultrasonic energy also develops these minute “cavities” around the particles. These “cavities” or areas of low pressure provide a sink of low concentration or partial pressure of the contaminant into which adsorbed material will desorb.

The chemical effect of ultrasound derive from the creation, expansion, and collapse of small bubbles that result when a liquid is irradiated by ultrasonic waves. This ultrasonic process generates cavities which creates intensive heat in certain spots within the liquid, yet the cool surrounding liquid quench the hot spots quickly in less than a millionth of a second, therefore the formation and violent collapsing of small bubble or cavities in the liquid as a result of pressure changes is achieved.

The implosion of cavities establishes unusual environment for chemical reactions [4]. The gases and vapors inside the cavity are compressed, generating intense heat that raises the temperature of the liquid immediately surrounding the cavity and create local hot spots. The temperature of the imploding cavity can not be directly measured by physical thermometer, because the heat is dissipated too fast to be measured. Suslick and his co-workers [3] found an alternative way that enabled them to measure these temperatures. It

is by observing the rate at which well-known chemical reactions take place. More precisely, the temperature is related to the negative inverse logarithm of the rate of the reaction. If the rates of several different reactions are measured in an ultrasound environment, the temperature from cavity implosion can be calculated.

During the cavitation collapse, Suslick et. al. [17] found out the intense heating of the bubbles occurs. These localized hot spots had temperatures around 5000 °C, pressures of about 500 ATMs, and lifetimes of a few microseconds.

It is possible that new reactions can be initiated, and exist ones intensified by the application of ultrasound energy. Boucher [18] reviewed these possibilities, examined the relevant mechanisms, and investigated potential synergistic effects.

2.4 Ultrasound Enhanced Soil Washing

Ultrasound, sound frequencies greater than 20 kHz, has long been used in the Chemical Process Industries (CPI) to clean mechanical parts, weld plastic materials, make emulsification, and to remove valuable products from mined materials. It can be also used in dissipating airborne dust in mines; bagging and loading facilities because lighter particles in an ultrasonic field will travel farther than heavier ones. Its application in environmental remediation can provide the function of removing clods or breaking up contaminant level small to be treated conventionally.

All the contaminants may be classified as soluble or insoluble according to the nature of their interaction with the surfactant. Higher frequencies are preferred for the removal of soluble contaminants that are weakly bounded. However, the flow velocities in this case will be increased due to the greater absorption of acoustic energy. The use of lower frequencies for the removal of insoluble contaminants with strong adhesion to the surfaces is preferred, because of the higher intensity of cavitation. The reduction in thickness of the boundary layer at the boundary with the solid is the principal factor for agitation.

Ultrasonic washing is generally combined with the chemical action of a solvent on the contaminants. To increase the speed and the quality of washing, it would be suitable to combine a high chemical activity on the part of the liquid with the maximum net effect in the cavitation destruction of the contaminant film. However, this combination is not always possible. The physical properties of a chemically active liquid can provide unfavorable in a number of cases from the point of view of its erosive activity. The selection of fluids for ultrasonic washing, particularly in the removal of cavitation-resistant film that is strongly bonded to the clean surface, is required to choose surfactants whose erosive activity is the greatest from the liquids that are chemically active.

The extraction step of soil washing is carried out in a mechanically agitated vessel. The agitation will provide sufficient power to maintain the soil in a suspended state and in bulk motion. Hence it will achieve an enhanced mass transfer by operating in the convective flow regime. To examine the ultrasonic enhancement effect, high shear mechanical agitators will not be employed.

The extraction step will be followed by a water rinse. The rinse procedure will be standardized to attain essentially complete removal of the solubilized contaminant from the void volume in the soil matrix.

Chilingarian et. al. [19] employed an extraction method for tar sand. They used sodium silicate and sonication at low temperature and ambient atmosphere. This process utilized the principle of membrane-mimetic chemistry. A 20/1 solvent ratio (which means the ratio of sodium silicate solution to tar sand) was added to the sonication reactor agitating with a mixer rotating at 320 rpm above the sample. The tar sand was sonicated for 6 hours. The solution was at 50 °C and pH was 12.2 (fresh sodium silicate has pH = 12.3). They used the gravity of the bitumen in the tar sand. It had an average value of 8° API. After treatment, the bitumen had an average gravity of 15° API for a 95% cumulative recovery (based on carbon content).

Previous studies had focused on soil washing techniques based on either using different agents or different processes. There was no systematic work on the ultrasonic enhancement of contaminants removal from soil by soil washing. The development of an ultrasonic enhanced soil washing process requires a comprehensive, well-designed experimental program, with the results carefully analyzed on the basis of known ultrasonic cleaning mechanism. The goal of this study is to examine the potential of ultrasonic energy to enhance soil washing and to optimize conditions.

CHAPTER 3

EXPERIMENTAL APPROACH

3.1 Experimental Material

3.1.1. Soil

A coal tar contaminated soil, obtained from a Superfund site, was used to investigate the enhancement of the soil washing process by application of ultrasound energy. A large quantity of soil was excavated, and screened before it was shipped to the NJIT Research Center. The soil was air dried, mixed for homogenization, sieved through US #4 (4.75 mm) and retained in US #200 (0.075 mm).

Sieve analysis is a necessary index test for soils, especially coarse soils, to determine relative proportions of different sizes of particles. Sieve analysis will provide information on the predominant constituents of soil, such as gravel, sand, silt, or clay, and ability of its constituents in controlling the engineering properties. The results of sieve analysis of the soil is described in Table 3-1. The soil used is a well-graded sand with silt (16% finer than US # 200 sieve). It had a moisture content of 2%. The total organic content of the soil was 16%. The extractable organics of the soil which is extracted from Soxhlet extraction method is 5%. The sieved soil was collected in the capped barrel and stored in the cold room kept at 4°C.

Table 3-1 Sieve analysis of soil

Sieve No.	Diameter (mm)	% Passing
4	4.75	99.96
10	2	87.85
20	0.85	71.19
40	0.425	59.86
70	0.212	38.71
200	0.075	16.43

3.1.2. Surfactant

In this study, a nonionic surfactant, octyl-phenyl-ethoxylate, was used as the washing additive. The term surfactant covers surface-active compounds, in which interfacial and solution behavior leads to the following key surface-active properties: emulsification/de-emulsification, wetting/rewetting, foaming/defoaming, dispersing, detergency, and solublizing. Particularly, surfactant is applied to hydrophobic organic compounds for the purpose either dissolving, emulsifying or dispersing the organic compounds in a water environment. Octyl-phenyl-ethoxylate, a non-ionic surfactant with a CMC of $2-3.3 \times 10^{-4}$ moles manufactured by Union Carbide, was used as the surfactant in this study.

3.1.3 Ultrasound Source

A laboratory bench scale ultrasound enhanced soil washing apparatus was provided by US-EPA. Two different types of ultrasound energy sources were used. One source was 1500 Watts probe type of Ultrasonic device (Sonics & Materials Inc. Model VC1500, 220 Volts, Power 1500 Watts, Frequency 20 kHz). The other ultrasound energy source was a 1000 Watts transducerized tank containing groups of "Vibra-Bar" which are permanently bonded to the tank bottom (Crest Ultrasonics Corporation, Model 4G-500-6, 120 Volts, Power 1000 Watts, Frequency 40-90 kHz).

3.2 Experimental Design

Four major and two minor variables (factors) were identified that appeared to have significant contributions to the removal efficiency. Following were the variables:

Treatment Time (Dwell): The cleaning time for soil washing (using conventional agitation) is 15 to 30 minutes. Therefore we used 5, 15 and 30 minutes as treatment times.

Surfactant Concentration: The typical range used in conventional soil washing process is 100 to 1000 ppm. The Ghea soil washing process, used higher concentrations (up to 4%), depending on the soil size distribution and contaminants levels [10]. In this study,

depending on the soil size distribution and contaminants levels [10]. In this study, surfactant concentrations, 0.01%, 0.1%, 1%, were used. They are about 50 and 5 times greater than the CMC at 1% and 0.1% of surfactant concentration respectively. At 0.01% of surfactant concentration, it has only half of CMC.

Solvent Ratio (liquid/soil weight ratio): The usual range of solvent ratio is 4/1 to 10/1. However, due to high PAH concentration in the soil, there was no removals of PAHs at 3/1, 4/1, and 5/1 solvent ratios. Therefore, we used the following solvent ratios: 10/1, 25/1, and 50/1.

Ultrasonic Power Density: We set the following ultrasonic power densities: 0% power (stir only), 50% (750 Watts) and 80% (1200 Watts).

For the experimental design, each factor was considered in a factorial design at three levels (low, medium, and high) for the above four variables. In the case of power, three levels were no power (using mechanical agitator), lower power and high power. Following are the two minor factors.

pH Effect: The pH range for experiment was from pH 1 to pH 13. The pH value was determined by pH meter (ORION, Model SA 720). Since the 0.1% surfactant solution had a pH value of 5.3 to 5.7, it was adjusted by adding HCl or NaOH solution.

Temperature: The temperature of probe type of ultrasound during treatment can not be controlled. Therefore we adjusted the temperature by freezing or heating the surfactant solution to 4 °C, 20 °C, 50 °C and 80 °C before rinsing the contaminated soil.

Full factorial for four major factors at three levels results in 81 experiments. The order of 81 individual runs was randomized and assigned a number to eliminate possible bias. Once all 81 experiments were completed, the selected PAHs' concentrations were determined. Since the PAHs have very similar characteristics, we only chose 12 significant compounds of interest, listed in Table 3-2, to determine removal efficiency.

Table 3.2 Target Analytes of PAHs

Compound	Mass
Naphthalene	128
Acenaphthylene	152
Acenaphthene	154
Fluorene	166
Anthracene	178
Fluoranthene	202
Pyrene	202
Chrysene	228
Benzo(k)fluoranthene	252
Benzo(a)pyrene	252
Indeno(1,2,3-cd)pyrene	276
Benzo(ghi)perylene	276

The removal efficiency for each compound and each run was then calculated. The removal efficiency was computed from the differences in concentration of each PAH before and after treatment. Then the 27 experiments with no power were compared with 27 experiments with medium power (750 Watts) to determine the enhancement due to ultrasound.

3.3 Experimental Procedure

Soil was homogenized again for each experiment. Figure 3.1 is the flow chart of this experimental procedure.

The experimental process mainly consisted of an extraction step followed by a water rinse. The extraction was carried out with a surfactant solution (solvent), followed by the rinse with distilled water. The extraction and the rinse were carried out in an ultrasonic cell equipped with a heater and a mechanical stirrer. Experimental procedure is described in the following section:

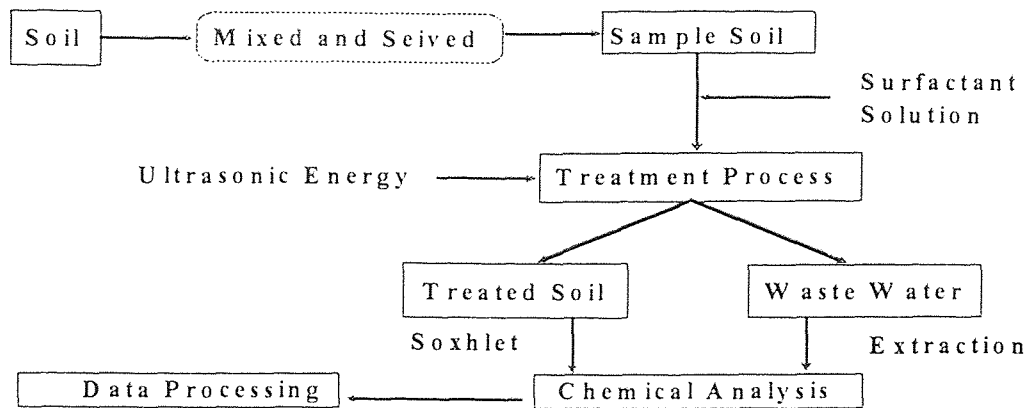


Figure 3.1 Shows the experimental procedure.

Sample Soil

Soil specimens weighing 50.0g, 20.0g, and 10.0g were placed in 600 mL stainless beaker and pre-wetted by adding either 500.0 mL of various concentration of surfactant solution (which were used in the treatment, 0.01%, 0.1%, and 1.0%) or distilled water directly into the beaker to yield the desired Liquid : Soil Ratios (also termed Solvent Ratio) of 10:1, 25:1, and 50:1 soaking for 10 minutes.

Ultrasonic Treatment

The Sonicator was set at the 50% (750 Watts) and 80% (1200 Watts) power output. For the zero power experiment a mechanical stirrer was used (Soil Mixer Lightnin Model & Staco Energy Variable Autofomer, Type 3PN1010 operating at 120 Volts). The stirring speed was kept at the lowest setting to avoid strong shearing force. Since the probe type of ultrasound generated enough convection of soil slurry, it did not need stirring.

The stainless container with soil slurry was then kept inside the wooden cabinet that houses the ultrasonic probe at the top. The aerosolizing action produced by the sonicator probe dipping about 1 inch into the soil/surfactant solution kept the soil in suspension. The ultrasound treated soil slurry was allowed to set for 30 minutes after treatment time.

The top portion of solution was decanted to avoid re-deposition of PAHs. The remaining portion of treated soil slurry was then placed in the Buchner funnel with vacuum line adding Whatman #40's 11.0 cm filter paper to separate soil from solution. The remaining soil left on the filter paper was then rinsed through with additional 300 mL of distilled water to avoid re-deposition of the PAHs. The treated soil portion was then kept under a fume hood and air-dried over night for further analysis.

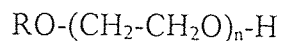
Chemical Analysis -- Soil Sample Preparation

Either 5.0 g each of treated soil (which was dried over night) or untreated soil (as base line) sample were mixed with 5.0g anhydrous sodium sulfite ($\text{Na}_2\text{S}_2\text{O}_3$) and placed in the extraction thimble (internal diameter 33 mm \times external length 94 mm, Whatman). The contaminants were extracted using methylene chloride (CH_2Cl_2) as solvent in the Soxhlet extractors (Pyrex). Added 0.25 mL 2000 ppm of hexachlorobenzene (C_6Cl_6) as surrogate standard into soil. The Soxhlet extraction lasted for 16 hours. The Kuderna-Danish (K-D) apparatus (Kontes, Vineland, NJ) was used to concentrate the extraction solution to 10.0 mL. EPA Method 3540A was employed for extracting PAHs from soil samples.

Chemical Analysis -- Aqueous Sample Preparation

The water/surfactant portion of the treated soil was transferred to a 2 liter funnel (Pyrex). Added 0.25 mL of 2000 ppm of hexachlorobenzene as surrogate standard into the funnel. EPA Method 3510 was employed for liquid-liquid extraction. Added 60 mL of methylene chloride to the separate funnel to extract PAHs from wash water for three times. The collected methylene chloride portion with PAHs was then concentrated by Kuderna-Danish (K-D) apparatus to 10.0 mL.

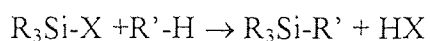
The emulsion in liquid portion had to be eliminated before GC/MS chemical analysis as the emulsion may block, damage separation column, or contaminate instrument. Alkyl ethoxylate (AE) surfactants consisted of an aliphatic hydrocarbon chain connected to a block of one or more ethoxylate groups.



R represents alkyl chain length of 12 to 15 carbons

n represents ethoxylated chain length of 1 to 20

Schmitt et al. [20] used reverse-phase chromatographic conditions to separate AE by alkyl chain length, and normal-phase chromatographic conditions to separate AE by ethoxylate chain length. Fendinger et al. [21] stated that ethylene oxide groups can be cleaved by reaction with hydrobromic acid to form alkylbromides. Because the cleavage reaction products formed are independent of ethoxylate chain length, the number of analyzed is reduced. However, it has to be kept at 100°C for 4 hours for the reaction to occur. Another way to cleave the structure of the surfactant is by silylation [22]. It is the most versatile currently available technique for enhancing GC performance by blocking protic sites. It reduces the dipole-dipole interactions and increases volatility. The general reaction with alkyl ethoxylate surfactant is given by:



This reaction occurs at 60°C after 20 minutes. Therefore, the silylation was performed on liquid portion before GC/MS analysis.

To 1 mL of PAH extract from soil analysis. 10 µL 4000 ppm of internal standard solution was added before GC/MS analysis. To 0.5 mL of wash water solution with 10 µL 4000 ppm of internal standard solution, and 0.5 mL of silylation solution, and 0.5 mL of methylene chloride were added and placed in a capped vial to extract some PAHs from emulsion part into methylene chloride part. The small vials were placed in the oven kept at 60°C for 20 minutes. A 1 µL portion from these small vials was used for GC/MS analysis.

GC/MS Analysis and Conditions

All the samples were analyzed by Varian Saturn II Ion Trap GC/MS equipped with 8200 Auto sampler using full scan to qualify PAHs compounds and SIM (Selective Ion Monitoring) technique to quantify PAHs concentrations. The column used for GC is DB - 5 30 m × 0.25 mm ID and 1 μm film thickness silicone-coated fused-silica capillary column (manufactured by J&W Scientific). The linear velocity for GC was 40 cm/sec. Figure 3.2 shows the typical resolution and retention time of each PAH peak. Figure 3.3 shows one example about how to auto integrate the area of PAH compound and match its spectrum.

A minimum of five calibration standards were prepared for each set of analysis. One of the calibration standards was at a concentration near, but above, the method detection limit (MDL). The others were corresponding to the range of the concentrations found in real samples but did not exceed the working range of the GC/MS system. Each 1 mL aliquot of calibration standard was spiked with 40 ppm of the internal standard solution prior to analysis. All standard solutions were purchased from Ultra Scientific Inc. and were provided with certificate of analysis.

Chromatogram Plot
Comment: STD 300PPM
Scan: 1800 Seg: 1
Plotted: 600 to 3000

C:\SOIL19\SS1902

Date: 06/16/95 13:58:13

Group: 0 Retention: 24.29 RIC: 1312
Range: 1 to 3333

Masses: 40-207
100% = 124745

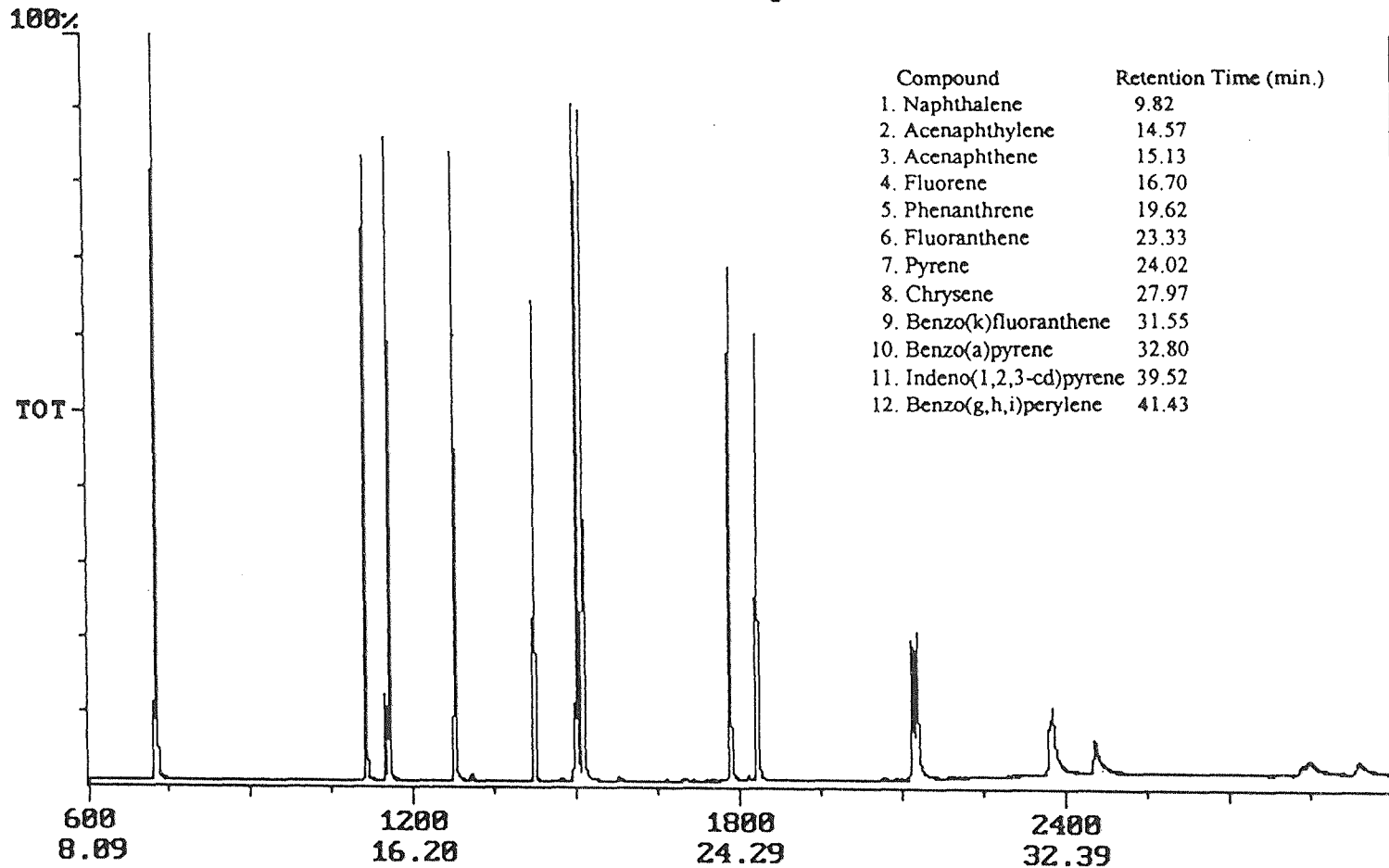
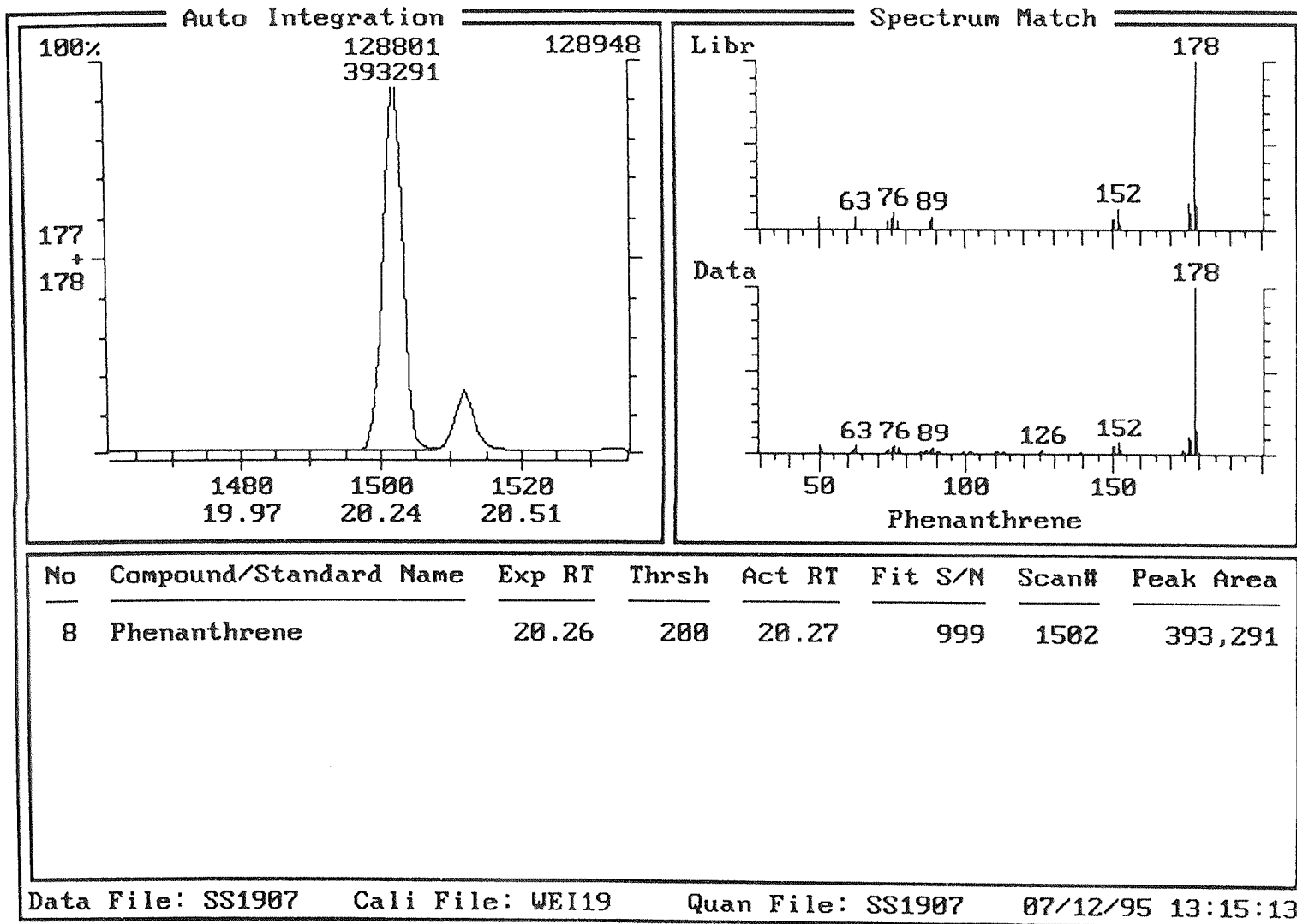


Figure 3.2 Gas Chromatogram of 12 PAHs



Calculations complete -- any key to continue
 Figure 3.3 Auto Integration and Spectrum Match

3.4 Quality Assurance/Quality Control (QA/QC)

An environment data acquisition measurement involves planning, sampling, analysis and finally reporting. Systematic as well as random errors are encountered at each step and the purpose of QA (Quality Assurance) QC (Quality Control) is to identify, measure and control these errors. QA/QC measures are necessary during the field sampling as well as laboratory procedures.

QA refers to the activities for which assurance can be obtained that a certain quality standard at a stated confidence level. QC refers to procedures that lead to statistical control of the measurement process and provides the desired accuracy of the measurement. Therefore, QC consists of specific technical procedures (e.g., running blanks or spike samples) to assess and control the measurement process, and QA refers to the management process that implements effective QC.

3.4.1 QA/QC Objectives

Precision objectives for all the listed methods were presented as RPD (Relative Percentage Difference) of duplicates.

Accuracy objectives for PAHs measurements were given as percentage recovery range of laboratory matrix spikes. Accuracy objectives for temperature measurements were absolute deviations in °C. Accuracy objectives for pH measurements were absolute deviation in pH units.

Table 3.3 QA Objectives for Precision, Accuracy

Measuremen	Matrix	Method	Units	Precision	Accuracy
PAHs	soil	EPA-8270	ug/kg	≤25	60-140
PAHs	water	EPA-625	ug/L	≤25	60-140
Temperature	water	Thermometer	°C		±2
pH	water	pH meter	pH units		±2

The required containers, preservation techniques, and holding time are listed in the Table 3.4.

Table 3.4 Required Containers, Preservation Techniques, and Holding Time

Measurement	Type	Preservation	Holding Time
PAHs	Glass, and Teflon-lined septum	Cool to 4 °C, protect from light	7 days until extraction, 40 days after extraction
pH	Glass	None required	Analyze water immediately
Temperature	Glass	None required	Analyze water immediately
Power Density	Glass	None required	Analyze water immediately

For general acceptable accuracy and precision, the following procedures were performed. A reagent blank, a matrix spike, and a matrix spike duplicate were analyzed for each analytical batch (up to 10% samples of batch). To determine acceptable accuracy and precision limits for surrogate standards the efficiency and recovery of preparative extraction procedure and instrument condition were evaluated according to the following procedures. The percent recovery of surrogate in each analyzed sample and blank was calculated. Once all the samples were analyzed, the average percent recovery for surrogate was calculated.

3.4.2 Calculation of Data Quality Indicators

EPA method 8270 was employed to determine the 12 PAHs listed above (Table 3.2). The surrogate standard was hexachlorobenzene. Quantification was by internal calibration. The internal standards were Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, and Chrysene-d12. The semi-volatile internal standards with corresponding analytes assigned for quantification are listed in the Table 3.5. Acceptance criteria for surrogate recovery is determined by control charts, but must be within 60-140 percentage range.

Table 3.5 Internal standards with corresponding analytes assigned for quantification

Naphthalene-d8	Acenaphthene-d10	Phenanthrene-d10	Chrysene-d12
Naphthalene	Acenaphthene	Anthracene	Chrysene
	Acenaphthylene	Fluoranthene	Benzo(k)fluoranthene
	Fluorene	Pyrene	Benzo(k)pyrene
	Hexachlorobenzene		Indeno(1,2,3-cd)pyrene
			Benzo(ghi)perylene

3.4.3. Internal Quality Control

Samples: Ten percent (or at least one) of the extraction samples was run in duplicate for each analytical batch. There was one split sample for each analytical batch. For each task (i.e., power density, dwell, surfactant concentration, etc.), 10% of the samples were run in replicate. Replicate sample means two soil samples treated with same washing condition (i.e., power density, dwell, surfactant concentration, etc.) but separate chemical analysis. Duplicate sample means same sample same extraction procedure but chemical analysis (GC/MS) was ran twice. Split sample means same soil sample was used to run two extractions followed by GC/MS analysis.

Blanks: One laboratory blank was run through the extraction procedures for each analytical batch to control any false positive arising from PAHs contamination.

Spikes: Ten percent of runs was spiked with matrix spike standard that contained four PAHs compounds listed previously in this QA Project Plan. Spiked samples were run for PAHs analysis with each analytical batch. All samples, blanks, standards were spiked with surrogate and internal standards.

Others: All calibration standards were purchased from ULTRA Scientific. Standard solution was gravimetrically prepared and all weights were traceable through NIST Test No. 732/221797. Initial calibration was performed by running five different concentration standard solutions (i.e., 500 to 0.1 ug/ml) to a minimum corresponding to instrument detection limit.

3.4.4 Calculation

For each treatment condition, the control efficiency, E, was calculated from the following equation:

$$E = C_{\text{out}} / C_{\text{in}}$$

The removal efficiency, X, was calculated from the following equation:

$$X = (1 - C_{\text{out}} / C_{\text{in}}) \times 100\%$$

where C denotes concentration.

A. Precision

Precision with respect to the analytical systems was assessed by the initial replicate samples. In addition duplicates were run on a routine basis to ensure continuing attention to precision. The requirements for precision varied with the parameter being tested. Precision was calculated by the relative percentage difference (RPD) between duplicate samples.

$$R. P. D. = \frac{D_1 - D_2}{(D_1 + D_2) / 2} * 100\%$$

where D₁ and D₂ are the measured values of an analyte in the two replicate samples.

B. Accuracy

Accuracy was assessed by the frequent use of matrix spikes. Accuracy requirements varied according to the parameter being tested. Accuracy was computed as follow:

where %R = percentage recovery, S = measured concentration in spiked aliquot, U = measured concentration in un-spiked aliquot, C_{sa} = actual concentration of spike added.

C. Mass Balance

A mass balance was calculated according to the following expression:

(Mass of PAHs in treated soil + Mass of PAHs in water portion)

Mass Balance = -----

Mass of PAHs in untreated soil

The acceptance criteria for the mass balance was set between 50 and 150 percent. The specific equation for calculating the influent and effluent masses in term of measured quantities is given in Chapter 4 Experimental Result of this thesis.

CHAPTER 4

RESULTS AND DISCUSSIONS

The results can be carried out from 81 experiments plus 9 replicate runs. There was an increase in the sample temperature due to the application of ultrasound energy. The rise in temperature was proportional to dwell time. In general, the rising range of temperature was about 5 °C to 10 °C if treating with sonication for 5 minutes; and the temperature rose up to 15 °C to 20 °C and 25 °C to 30 °C if treatment with sonication for 15 minutes and 30 minutes each.

The probe type ultrasound source was much better than the tank type (by comparing two tests involving to ultrasound sources set at 750W power level) in transmitting the ultrasound energy to the container with contaminants. The reason for that is the ultrasonic energy of probe type directly transmitting to soil, but the ultrasonic energy of tank type is transmitting to water bath and then to soil. Application of external pressure to the soil/solvent slurry with the probe type of ultrasound drastically increased the reflection. This observation eliminated the possibility of applying the ultrasound energy to a container filled with fluid/soil suspension. The above test with external pressure was conducted to determine if the aerosolizing action and cavitation (and not the resonance) were the main reasons for enhancement in removal efficiency. One disadvantage of selecting the probe type source was that the system temperature can not be controlled during the experiment. The other difficulty was the variation of frequency.

4.1 pH Effect

Initial results showed that the solution pH (if between 2-11) does not contribute to the removal efficiency, i.e., there is no influence of pH on the removal efficiency of the ultrasound enhanced soil washing process as shown in Figure 4.1. It is no need to adjust the pH value of surfactant solution while varying the other parameters. At pH values equal or greater than 12, removal of Anthracene increased up to 80%. The condition for pH factor was applied 750 Watts energy of ultrasound to 50/1 solvent ratio containing 0.1% surfactant concentration for 30 minutes.

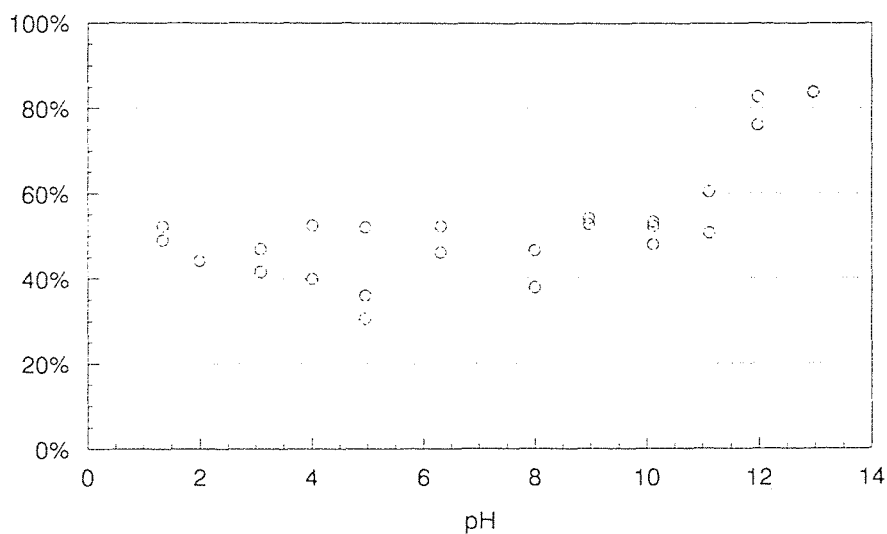


Figure 4.1 Removal efficiency of anthracene with pH

The use of the sonicator with probe type does not require a mechanical stirrer to keep the soil in suspension. The aerosolizing action at the tip of the probe provided ample convective current to ensure adequate soil mixing.

Figure 4.2 shows the removal efficiency of Naphthalene versus pH. The solution pH values varied from pH 1 to 13. Naphthalene removal efficiency can reach between 60 to 80% for pH = 2 - 11 while pH = 12 and 13 slightly increase removal efficiency (ca. 85 - 90%).

Figure 4.3 illustrates the removal efficiency of Chrysene for various pH values. For pH values between 4 and 11, removal efficiency of chrysene is between 40 to 60%. Removal efficiency of Chrysene decreased by 20% at pH values of 2 and 3, yet at pH 1 it was back to 40 - 60% range. Again, removal efficiency dramatically increased 20% for pH = 12 or higher.

To determine ultrasonic enhanced soil washing, we compared removal efficiencies for sonication treatment with traditional soil washing (stir only). The removal efficiency w/wo sonication for different PAHs at pH = 2 are plotted in Figure 4.4, where the ultrasonic enhancement was between 5 to 20%. The PAHs concentration of untreated soil varied in the range of 10 - 15%.

For pH = 12, the overall removal efficiency of soil washing with sonication was higher than 80%, where ultrasonic enhancement was observed. Figure 4.5, shows a comparison of soil washing process with or without sonication and with or without surfactant. Under strong alkaline condition, removal of PAHs using ultrasound energy without surfactant was comparable to soil washing with stirring for 0.1% surfactant solution. Enhanced Removal efficiency (removal efficiency by stir w/ surfactant subtract from removal efficiency by sonication w/ surfactant) is ca. 20% for most PAHs.

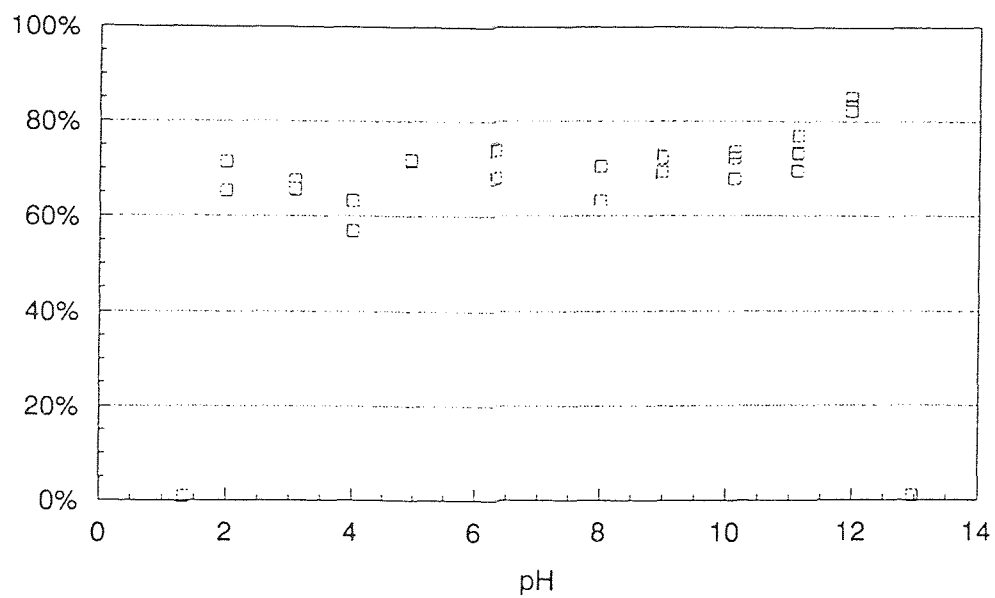


Figure 4.2 Removal efficiency of Naphthalene with pH

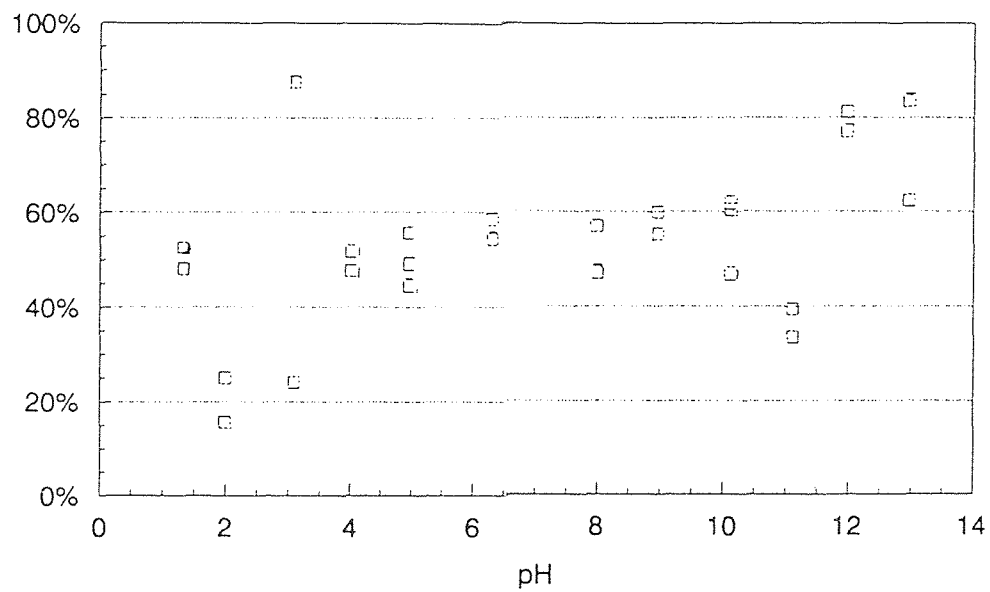


Figure 4.3 Removal efficiency of chrysene

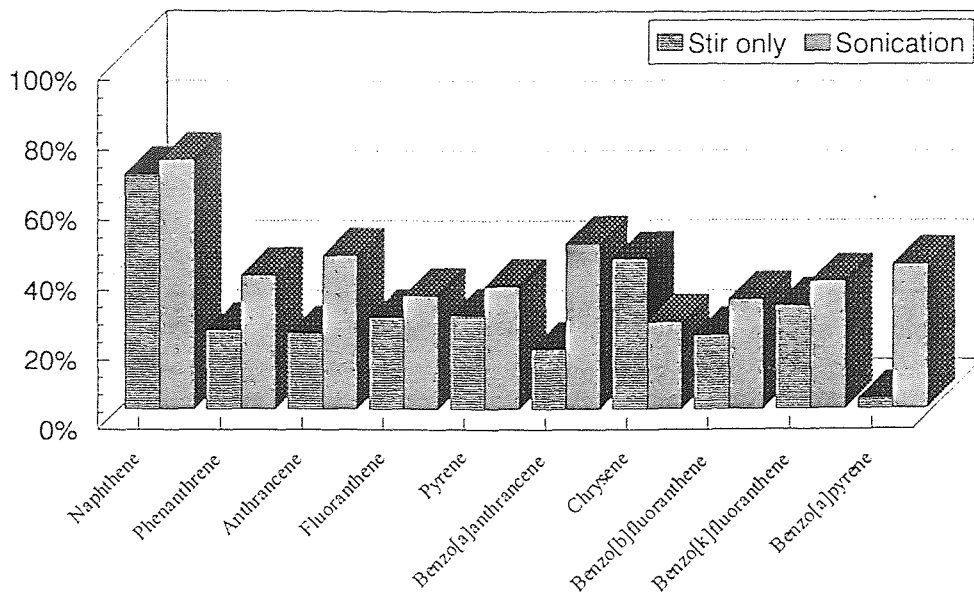


Figure 4.4 Removal efficiency of w/wo sonication at pH = 2

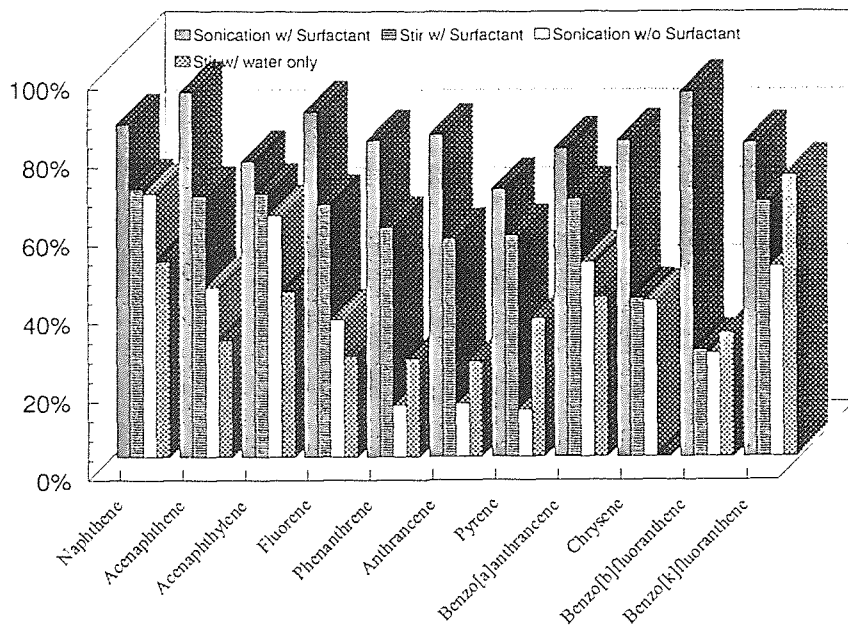


Figure 4.5 Comparison of soil washing process

4.2 Ultrasound Effect

The four main parameters at 3 levels produced 81 experiments, i.e. 3^4 , with removal efficiencies for 12 PAHs, following procedure was adopted to analyze the data. For each variable (e.g., Dwell) three plots were made: 1) with lowest values of other three variables (e.g., 0% power density - stir, 10/1 solvent ratio, and 0.01% surfactant concentration), 2) middle values of other three variables, and 3) highest values of other three variables. One variable with other 3 parameters kept at the same low, medium, and high levels resulted in 12 plots.

The density seems to be the factors with highest contribution for ultrasound enhancement. It is difficult to observe any removal for three variables which are power density, surfactant concentration, and solvent ratio set at lowest level (shown in Appendix A.1, A.2, and A.3). When the variables are in medium range, only solvent ratio showed different removal efficiencies (shown in Appendix Figure A.4, A.5, and A.6). Under highest power density (1200 Watts), surfactant concentration should not be too low, otherwise, it still results low removals (shown in Appendix Figure A.7, A.8, and A.9).

A. Treatment Time (Dwell)

Compare Appendix Figure A7, and A.13. There is almost no removal when the surfactant concentration was under 0.01%. Above 0.1% of surfactant concentration, the removal efficiency of 15 minutes of treatment time was as good as that of 30 minutes when applying ultrasound energy. The enhancement of ultrasound was 40-60% compared to stir only. Ultrasound enhancement show the removal heavier PAHs (the mass is heavier than pyrene whose molecular weight is 178). Results show that longer dwell gets better

removal efficiency under high surfactant concentration and solvent ratio for both with and without sonication.

B. Surfactant Concentration

Compare Appendix Figure A.14, A.15 and A.16. Apply 750 Watts sonication to 50/1 solvent ratio with 0.01% and 0.1% surfactant concentration, there was no removal of PAHs for 5 minutes treatment. But for 15 and 30 minutes treatment, the better removals on 25/1 and 10/1 of solvent ratio were shown for 0.1% surfactant concentration. The 1% surfactant concentration had a high removal efficiency of PAHs up to 95% for 50/1 of solvent ratio. It is difficult to remove the mass heavier than Fluorene (M.W. = 178) with low surfactant concentration (e.g., 0.01% or 0.1%), however, the medium mass PAHs (molecular weight is between 154 and 228) were removed when applying mechanical stirring. Therefore, at low surfactant concentration, the treatment time is not important, and ultrasonic enhancement was not observed.

C. Power Density

Compare Appendix Figure A.17 and A.18. There was not much difference of removal efficiency for all treatment time and surfactant concentrations for 10/1 and 25/1 solvent ratios where the power density has no contribution. At 50/1 of solvent ratio, the 750 Watts of ultrasound had better removal efficiency than 1200 Watts. That is, high soil loading, ultrasonic power density was very important; while for higher surfactant concentration or solvent ratio, high power density was not necessary. Ultrasonic power density becomes important at high soil loading; while higher surfactant concentration or solvent ratio, high power density is not necessary.

D. Solvent Ratio

Compare Appendix Figure A.19 and A.20. For 5 minutes of treatment time at 100 Watts power density, 25/1 of solvent ratio had better removal efficiency for all surfactant concentration; but for 30 minutes of Dwell, a 50/1 solvent ratio had better removal efficiency. Overall, for lower solvent ratio, treatment time is not important, and ultrasonic enhancement is not observed. Lower solvent ratio obtains lower removal efficiency and ultrasonic enhancement is not observed.

E. Temperature

Compare Appendix Figure A.21 and A.22 illustrate temperature effect on PAH removal for stir and 50% power (750 Watt) under different temperature at four different temperature points. The sonication can enhance overall removal efficiency by 40% - 60% when compared with zero power. Lowest surfactant solution temperature (4 °C) and highest surfactant solution temperature (80 °C) had better removals on PAHs.

Analysis of all 12 plots (Appendix Figure A.1 through A.12) shows that 750 Watts power with 30 minutes dwell time, with 1% surfactant concentration produced the best removal efficiency (shown in Appendix Figure A.10, A.11, and A.12). Appendix Figure A.13 shows a plot of removal efficiency for various solvent ratio while keeping power, dwell time and surfactant concentration at the optimum levels. It indicated that the most economical removal efficiency was obtained at a solvent ratio of 25/1 with 750 Watts power, 30 minute dwell time, and 1% surfactant concentration. Meegoda and Ratnaweera [23] showed that a surfactant works best for oils when the surfactant weight is more than 50% the weight of the contaminants or a surfactant to contaminant ratio of 0.5. For the above optimum combination, soil had 3.2 grams of contaminants and has added 5.0 grams

of surfactants or surfactant to contaminant ratio of 1.6. The next lowest surfactant to contaminant ratio was 0.625, for a solvent ratio of 10 with 750 Watts power, 30 minute dwell time (shown in Appendix Figure A.13).

4.3 QA/QC Result

A. Precision:

Tables 4.1 and 4.2 show RPD data for soil and water sample respectively. There were five data point for each replicate, duplicate, and split (water matrix has no split sample) samples in both soil and water matrixes. As shown in Table 4.1, the average RPD for each species varied from 5.15% to 57.69%. The global average for replicate, duplicate, and split were 20.45%, 10.16%, and 21.38% respectively; while the overall RPD for soil samples was 17.33%.

Table 4.1 Precision data for soil samples

Species	Replicate	Duplicate	Split	Average
Naphthalene	13.78%	6.69%	14.50%	11.66%
Acenaphthene	12.84%	12.31%	15.14%	13.43%
Acenaphthylene	22.81%	11.20%	20.41%	18.14%
Fluorene	12.12%	7.64%	13.36%	11.04%
Phenanthrene	17.75%	14.30%	29.31%	20.45%
Anthracene	16.34%	7.48%	18.88%	14.23%
Fluoranthene	20.19%	5.15%	25.41%	16.92%
Pyrene	21.79%	7.14%	22.29%	17.07%
Benzo[a]anthracene	41.94%	11.26%	18.15%	23.78%
Chrysene	18.05%	13.49%	23.38%	18.30%
Benzo[b]fluoranthene	29.41%	8.91%	57.69%	32.00%
Benzo[k]fluoranthene	21.09%	10.53%	21.94%	17.85%
Benzo[a]pyrene	17.04%	10.85%	21.48%	16.46%
Benzo[ghi]perylene	23.46%	10.49%	9.20%	14.38%
Indeno(1,2,3-d)pyrene	18.20%	14.94%	9.61%	14.25%
Global	20.45%	10.16%	21.38%	17.33%

Chemical analysis of PAHs in water matrix was performed in replicate and duplicate in order to calculate RPD. The overall RPD for water samples was 12.83%.

Table 4.2 Precision data for water samples

Species	Replicate	Duplicate	Average
Naphthalene	18.29%	21.94%	20.11%
Acenaphthylene	6.79%	6.06%	6.82%
Fluorene	15.21%	4.28%	9.75%
Phenanthrene	4.41%	2.45%	3.43%
Anthracene	7.64%	2.60%	5.12%
Fluoranthene	19.67%	9.51%	14.59%
Pyrene	13.45%	7.14%	10.30%
Benzo[a]anthracene	8.06%	16.03%	12.05%
Chrysene	15.21%	13.41%	14.31%
Benzo[k]fluoranthene	23.14%	14.30%	30.89%
Benzo[a]pyrene	9.79%	42.89%	26.34%
Global	12.88%	12.78%	12.83%

B. Accuracy:

The calculated spike recovery values are listed in Table 4.3. 10 Ng (10 ppm) each PAHs was spiked into three soil (Soxhlet Extraction) and three water samples (Liquid-Liquid Extraction). It is blank spike. The global recovery (average for species) ranged from 75.53% to 116.46% for soil samples and 78% to 98% for water samples. Table 4.3 lists the average of three spike samples of both soil and water matrix samples.

C. Surrogate Recovery

Surrogate recovery of hexachlorobenzene was calculated and listed in Table 4.4. It provides data for five different classes i.e. blank, spike, untreated, soil, and water. The overall average recovery was 90.88%.

D. Mass Balance

The mass balance calculations were performed and results are listed in Table 4.5. The average mass balance for Naphthalene was lower than acceptable value due to volatility of it. The low mass balance value for Acenaphthene and Indeno(1,2,3-cd)pyrene was due to low concentration in untreated samples (less than 3 ppm) and below detection limit concentration in water samples.

Table 4.3 Spike Recovery

Species	Soil	Water
Naphthalene	98.55%	93.76%
Acenaphthene	104.28%	106.00%
Acenaphthylene	104.33%	111.08%
Fluorene	112.78%	110.48%
Phenanthrene	75.53%	78.67%
Anthracene	102.38%	68.41%
Fluoranthene	100.97%	106.85%
Pyrene	106.62%	102.14%
Benzo[a]anthracene	78.42%	64.19%
Chrysene	104.29%	70.49%
Benzo[k]fluoranthene	116.46%	95.44%
Benzo[a]pyrene	100.74%	53.79%
Hexachlorobenzene	109.46%	76.55%
Global	94.90%	81.75%

Table 4.4. Surrogate Recovery

Sample Source	Surrogate Recovery
Blank	91.98%
Spike	86.51%
Untreated Sample	99.12%
Soil Sample	92.71%
Water Sample	84.08%
Global	90.88%

Table 4.5 Mass balance

Compound	Average
Naphthalene	47.87%
Acenaphthene	61.08%
Acenaphthylene	92.89%
Fluorene	77.89%
Phenanthrene	82.88%
Anthracene	102.70%
Fluoranthene	102.28%
Pyrene	96.84%
Benzo[a]anthracene	67.39%
Chrysene	88.53%
Benzo[b]fluoranthene	69.54%
Benzo[k]fluoranthene	84.54%
Benzo[a]pyrene	88.47%
Benzo[ghi]perylene	93.94%
Indeno(1,2,3-cd)pyrene	65.47%
Global	77.26%

CHAPTER 5

CONCLUSION AND FUTURE WORK

There was an increase in the sample temperature due to the application of ultrasound energy. The temperature increased with higher soil loading (e.g., 10/1) and longer treatment time. The probe type ultrasound source was much better than the tank type in transmitting the ultrasound energy to the container with contaminants. Test results showed that ultrasound energy supplied by a 1500 Watts probe operating at 50% power rating applied for 30 minutes to a container carrying 20 grams of coal tar contaminated soil with 1% surfactant in 500 ml can enhance the soil washing process by more than 100%. The experimental design suggested that the optimum operation condition was at a solvent ratio of 25 with 750 Watts power, 30 minute dwell time, and 1% surfactant concentration. It also appears that for heavily coal tar contaminated soils with ultrasound energy it needs surfactant to contaminant ratio of more than 0.625 and a solvent ratio greater than 10 to obtain near perfect removal efficiency.

Several experiments were performed to determine the ultrasonic effect on the enhancement in soil washing. The process requires continuous experiment study before scale-up to commercial operation. The following conclusions can be drawn.

1. The removal efficiency of ultrasonic enhancement effect can reach up to 40% to 60% better than the removal efficiency of 0% power (stir only).
2. The higher pH, temperature, power density of sonication, surfactant concentration, solvent ratio, and treatment time, values provide better removal efficiency of PAHs.
3. From experimental results, the power density of sonication is the most important factor among all variables in ultrasound cleaning. Under the same ultrasonic power density, the concentration of surfactant solution should be far higher than CMC value for

higher removal efficiencies. If the surfactant amount is enough to catch the contaminants in soil, the variable of solvent ratio becomes the most important factor.

4 The optimum condition in this research is obtained at a solvent ratio of 25 with 750 Watts power density, 30 minutes dwell time, and 1% concentration of surfactant solution.

5. The removal efficiency can be further improved either by adding alkaline solution into the surfactant solution or by raising the temperature of surfactant solution.

It is proposed to develop a statistical model using a multi-variable regression analysis. The equation is to be considered as following:

$$y = \sum_{i, j, k, l = 0}^4 \beta_{ijkl} A^i B^j C^k D^l$$

Where $i + j + k + l = 0$ intercept

1 main effects (A, B, C, D)

2 quadratic effects (A^2 , AB, etc.)

3 cubic effects (A^3 , A^2B , ABC etc.)

4 four factor interactions (ABCD)

and β_{ijkl} are constants calculated from the regression analysis.

From this statistical modeling, it is possible to determine the optimum condition to operate the process and to get the most economic way to treat the contaminated soil. Also, it is important to consider soil washing as a continuous flow operation.

APPENDIX

REMOVAL EFFICIENCY OF PAHs

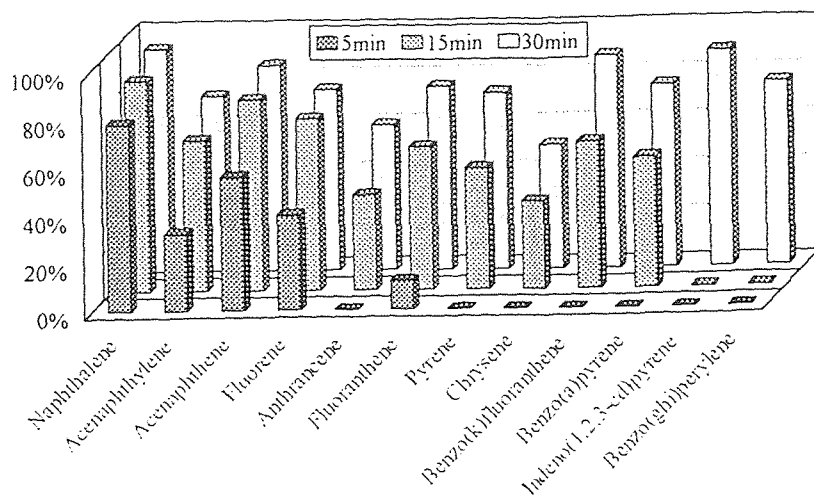


Figure A.1 Removal efficiency when stir w/ 0.01% surfactant conc. & 10/1 solvent ratio

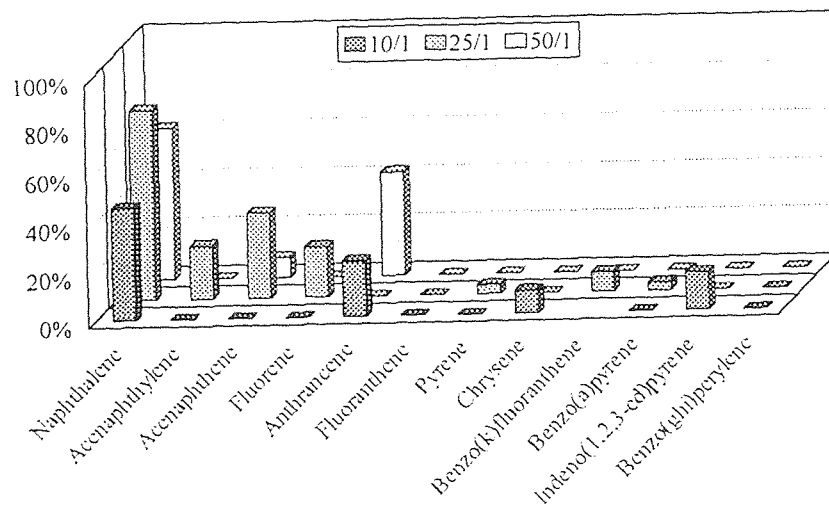


Figure A.2 Removal efficiency when stir w/ 0.01% surfactant conc. for 5 min.

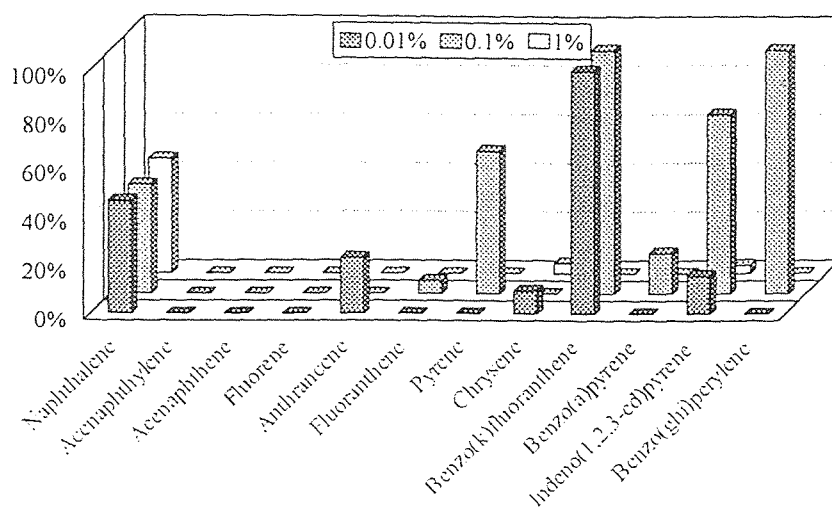


Figure A.3 Removal efficiency when stir w/ 10/1 solvent ratio for 5 min

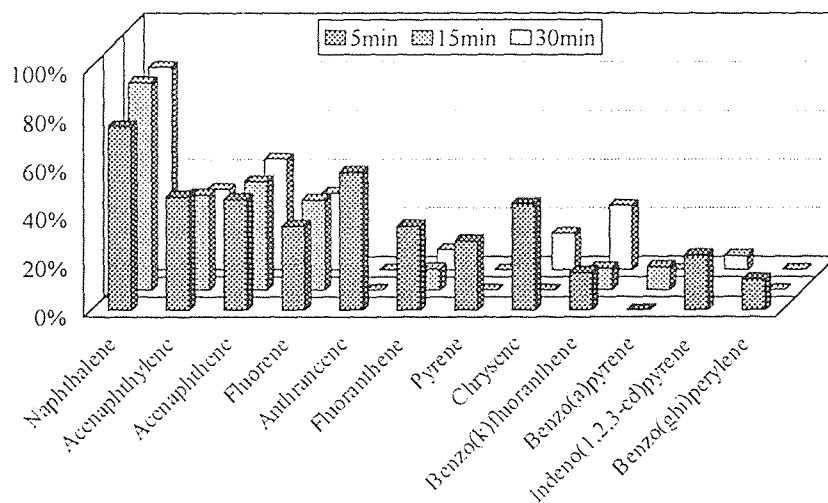


Figure A.4 Removal efficiency when 750W sonication w/ 0.1% surfactant conc. & 25/1 solvent ratio

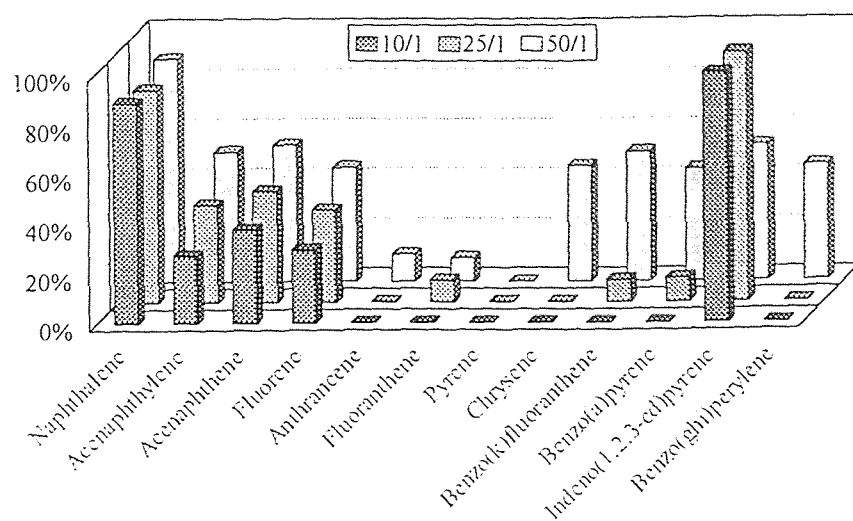


Figure A.5 Removal efficiency when 750W sonication w/ 0.1% surfactant conc. for 15 min.

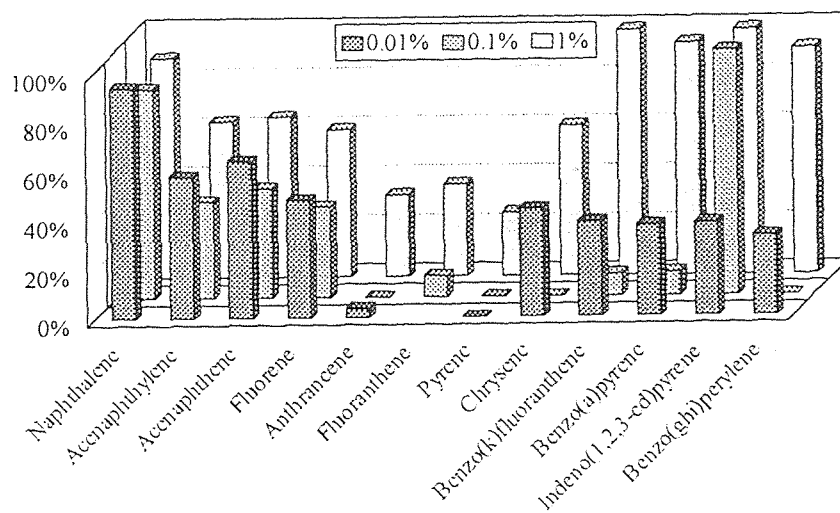


Figure A.6 Removal efficiency when 750W w/ 25/1 solvent ratio for 15 min

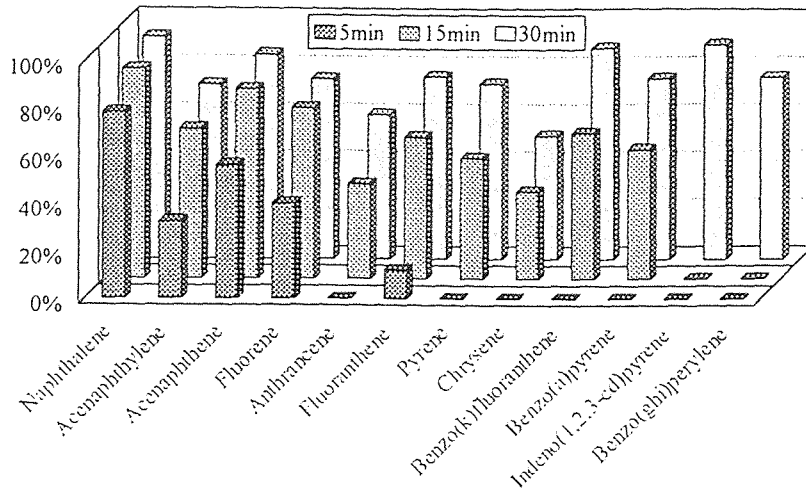


Figure A.7 Removal efficiency when 1200W sonication w/ 1% surfactant conc. & 50/1 solvent ratio

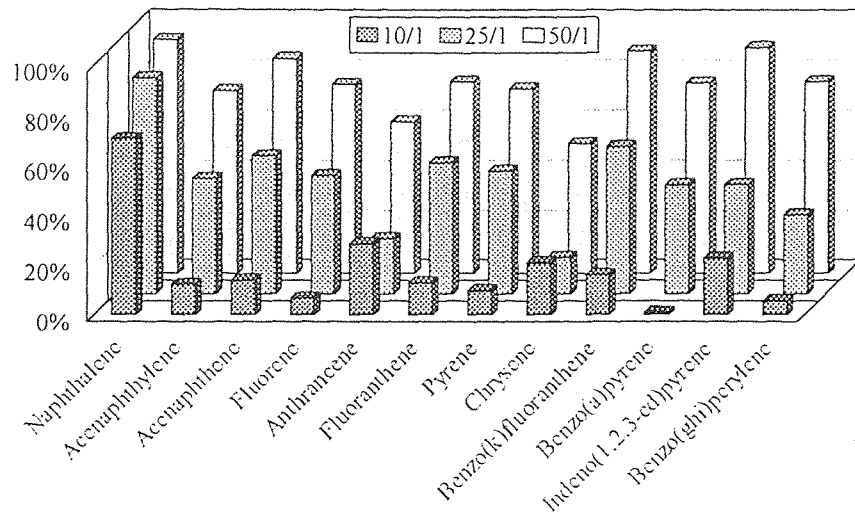


Figure A.8 Removal efficiency when 1200W sonication w/ 1% surfactant conc. for 30 min

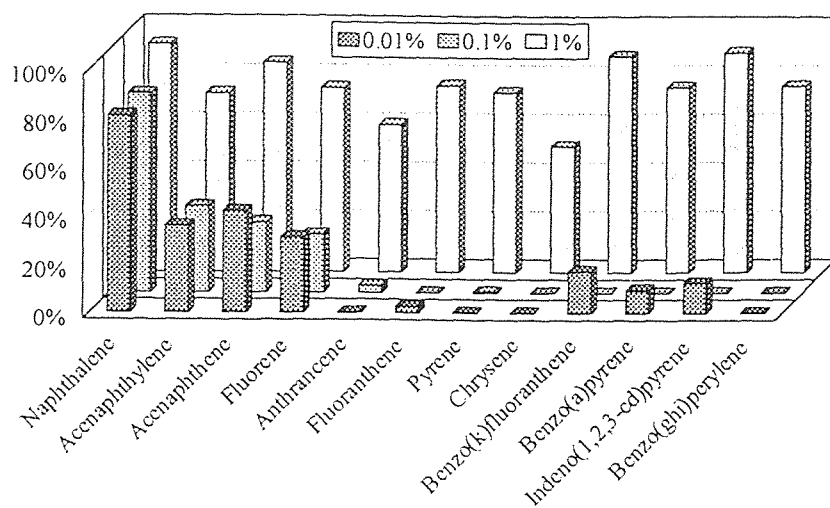


Figure A.9 Removal efficiency when 1200W w/ 50/1 solvent ratio for 30 min

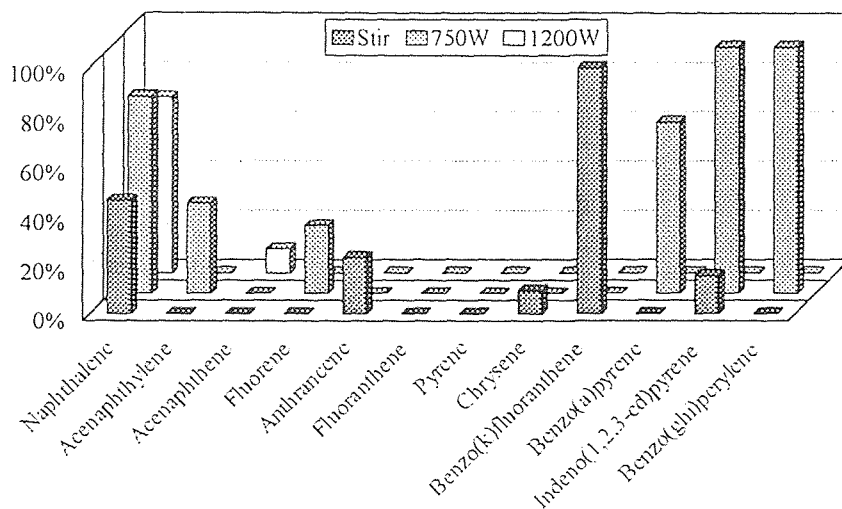


Figure A.10 Removal efficiency w/ 10/1 solvent ratio and 0.01% surfactant conc. for 5 min

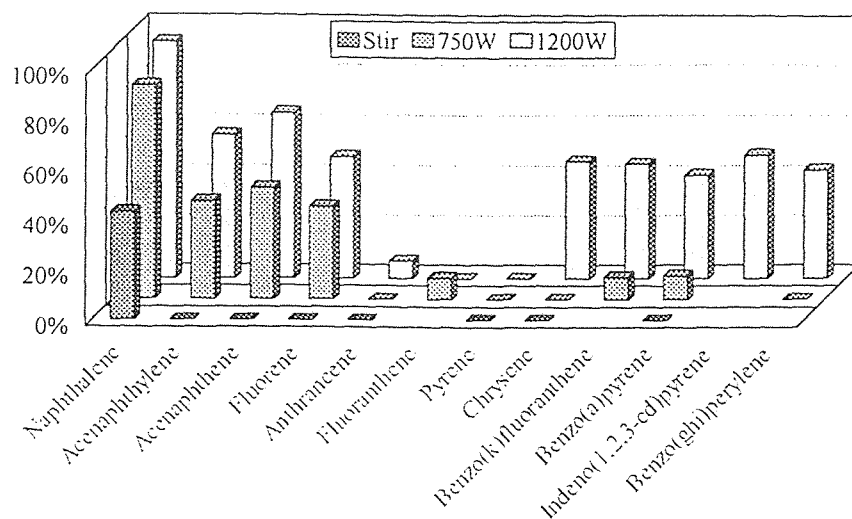


Figure A11 Removal efficiency w/ 25/1 solvent ratio and 0.1% surfactant conc. for 15 min

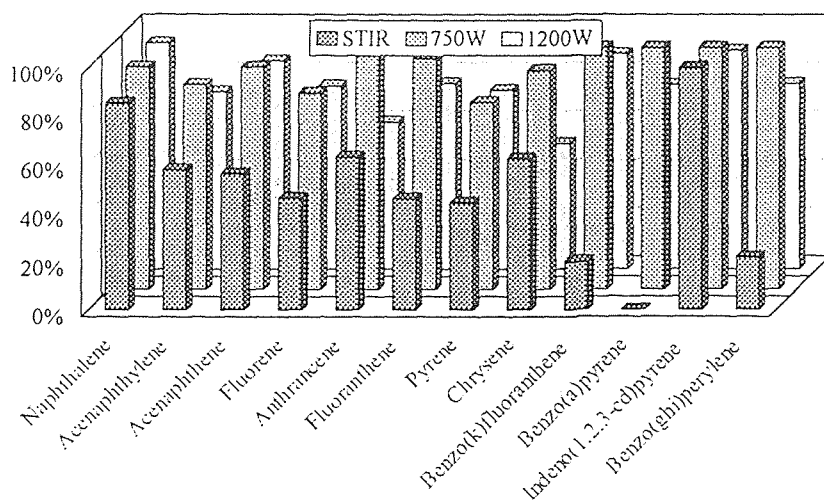


Figure A.12 Removal efficiency w/ 50/1 solvent ratio and 1% surfactant conc. or 30 min

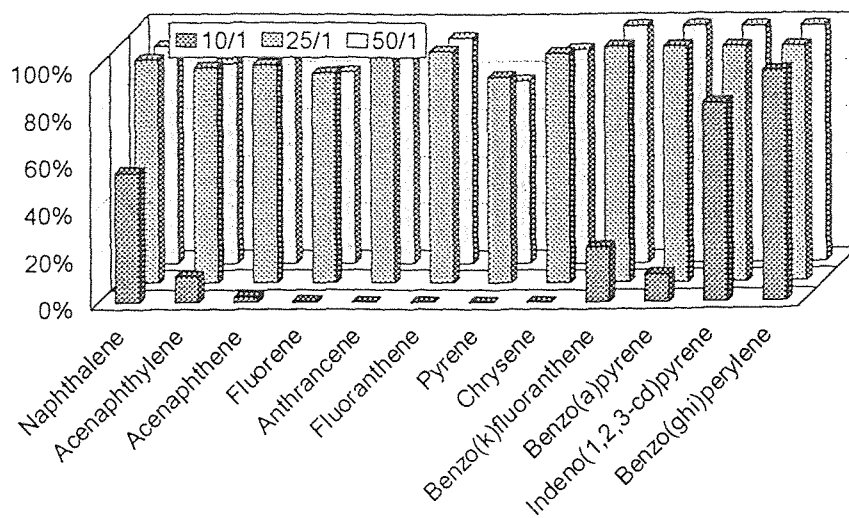


Figure A.13 Removal efficiency when 750W w/ 1% surfactant conc. or 30 min

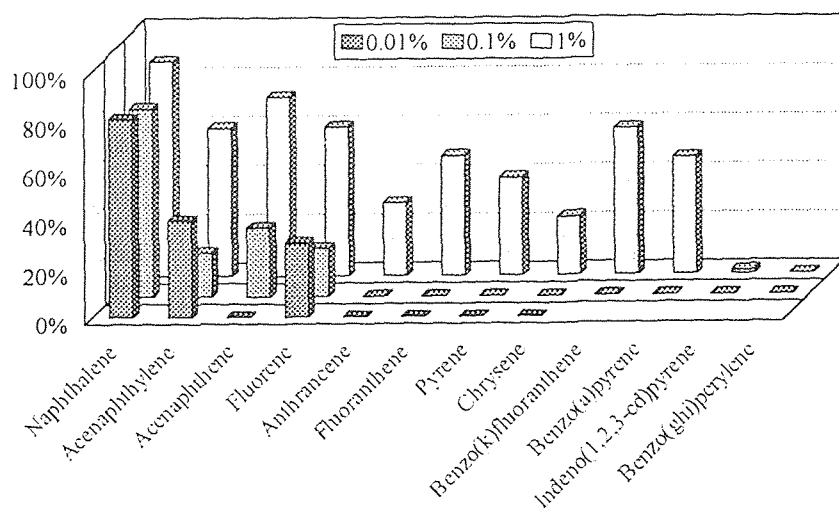


Figure A.14 Removal efficiency when 750W w/ 50/1 solvent ratio for 5min

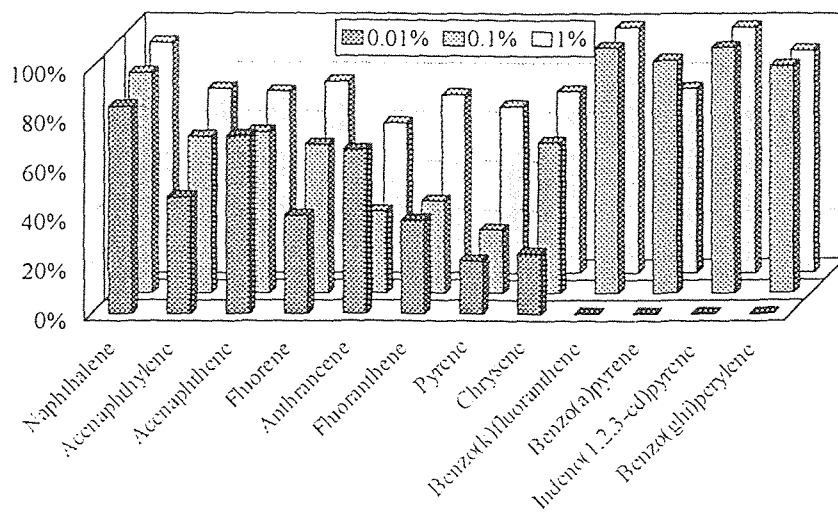


Figure A.15 Removal efficiency when 750W w/ 50/1 solvent ratio for 15min

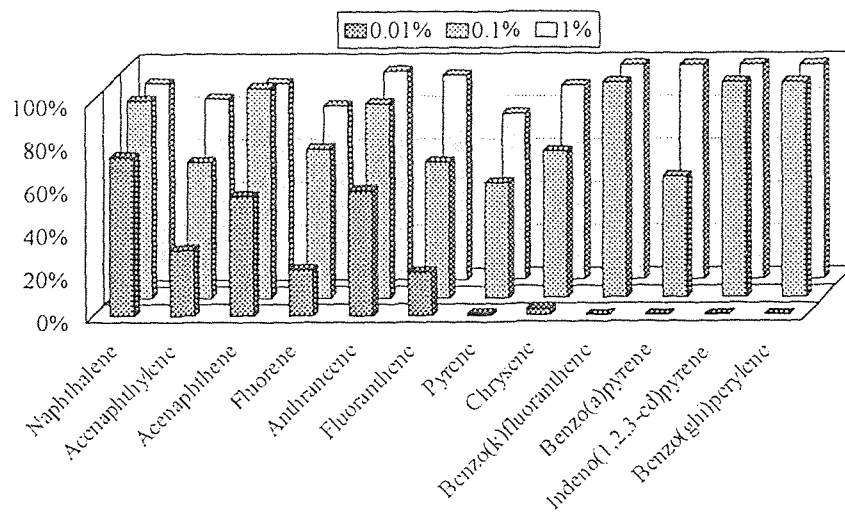


Figure A.16 Removal efficiency when 750W w/ 50/1 solvent ratio for 30min

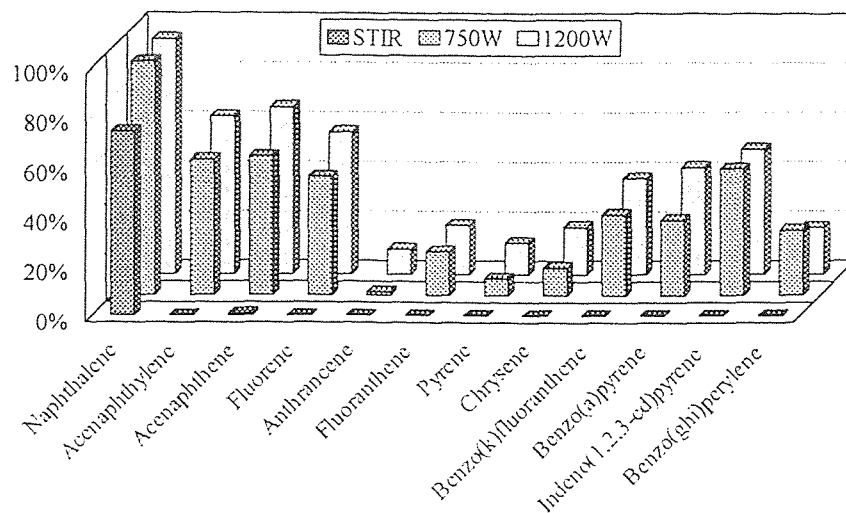


Figure A.17 Removal efficiency w/ 25/1 solvent ratio and 0.01% surfactant conc. for 30 min

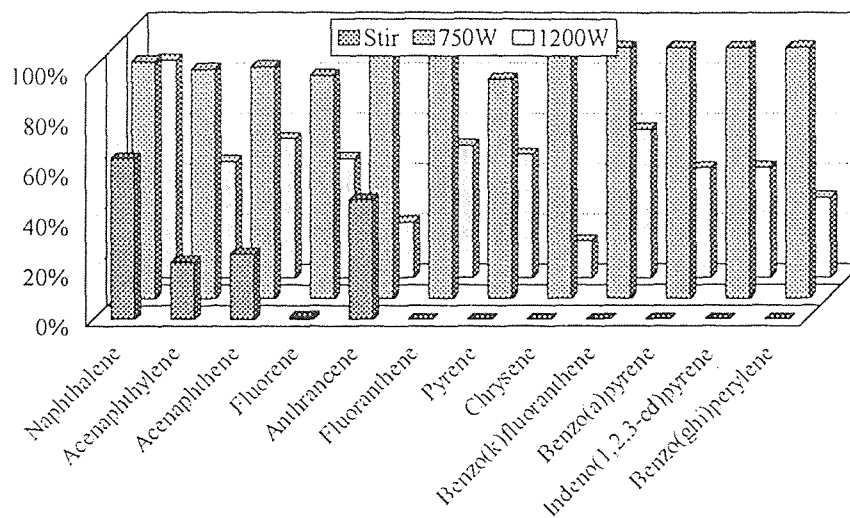


Figure A.18 Removal efficiency w/ 25/1 solvent ratio and 1% surfactant conc. for 30 min

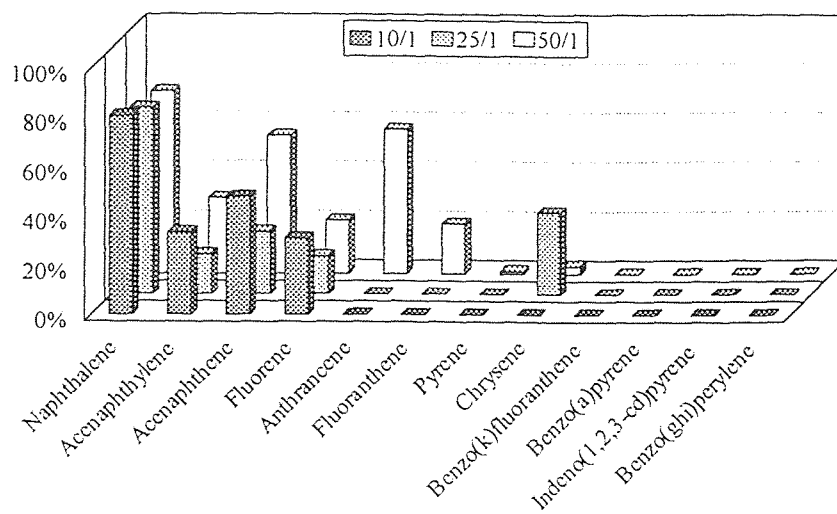


Figure A.19 Removal efficiency when 1200W sonication w/ 0.01% surfactant conc. for 30 min

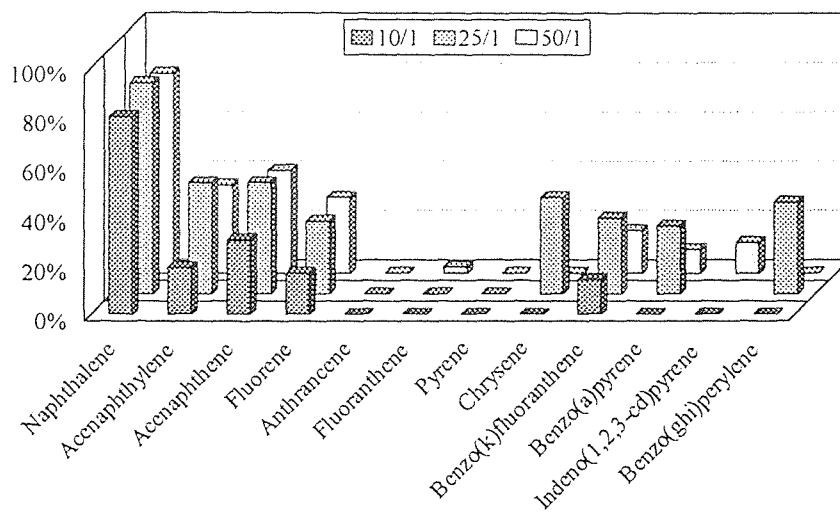


Figure A.20 Removal efficiency when 1200W sonication w/ 0.1% surfactant conc. for 30 min.

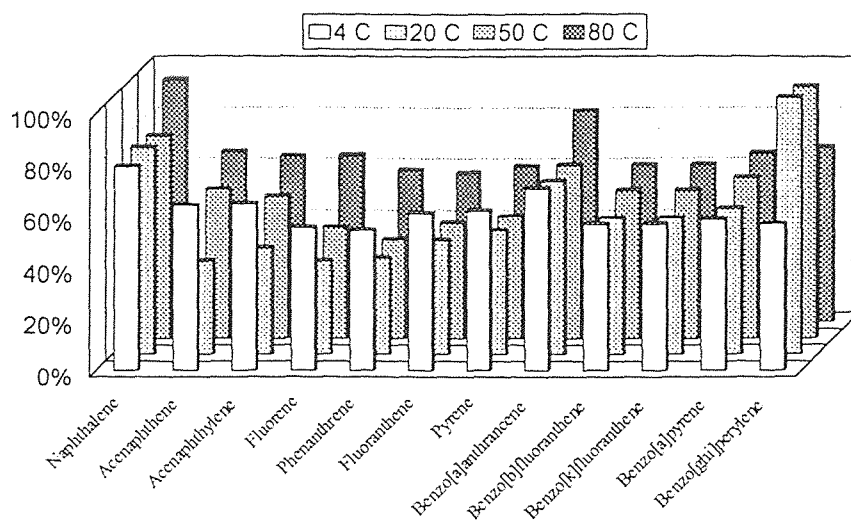


Figure A.21 Temperature effect on PAH Removal when 750W sonication w/ 25/1 solvent ratio 1% surfactant conc. for 30 min.

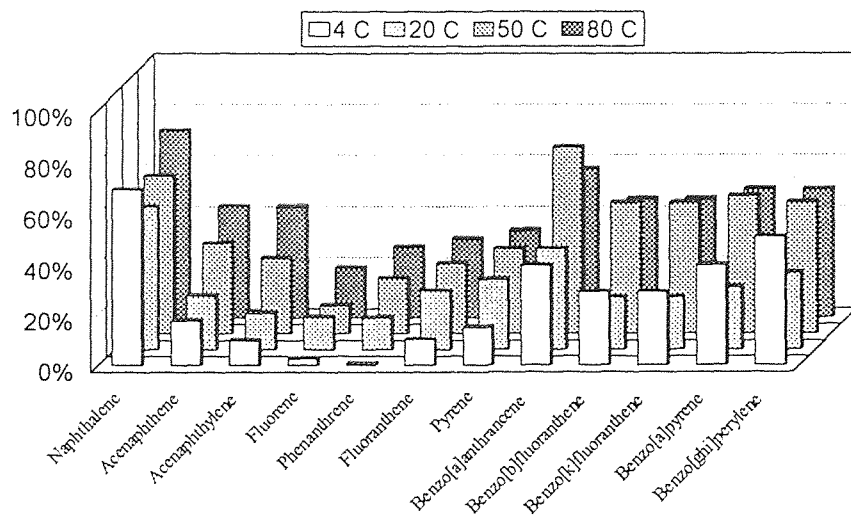


Figure A.22 Temperature effect on PAH Removal when stir w/ w/ 25/1 solvent ratio 1% surfactant conc. for 30 min

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