ABSTRACT

ANALYSIS AND MODELING OF ULTRASOUND ENHANCED SOIL WASHING PROCESS

by

Kamalavathany Rajaratnam

In this research, statistical analysis of data from ultrasound enhanced soil washing process was performed. The process was optimized using a statistical model. The model had four factors namely power, solvent:soil, surfactant, and dwell time as process variables. The percentage of removal efficiency was considered as the dependent variable. The results from two full and one partial factorial designs were analysed. Interactions up to third order were considered in the analysis, but the results from full factorial design showed that those of order higher than second had insignificant contributions to the removal of contaminants. Since the higher order interactions of process variables could be neglected, a quadratic model was used to optimize the process conditions. The analysis showed that the ultrasonic power density was the main contributing factor. The analysis results showed that for soil #1, optimum average removal of 83 % was obtained at 32% power, 42 solvent:soil, 0.69% surfactant con., and for a dwell time of 25.5 min. For soil #2, similar results were obtained with lower removal efficiency. The removal efficiency of individual PAHs produce similar conclusions for both soils. A partial factorial design was considered for soil #3 to drastically reduce the number of experiments. The statistical analysis showed that data for partial factorial design can be used to obtain meaningful results and had an optimal removal of 37.67% at 34.24% power, 32.62 solvent:soil, 0.89% surfactant con., and for dwell time of 11.33 min.

ANALYSIS AND MODELING OF ULTRASOUND ENHANCED SOIL WASHING PROCESS

by
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The author dedicates this thesis to her beloved parents

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CHAPTER 1

INTRODUCTION

1.1 Problem Statement

Organic contaminants such as petroleum hydrocarbons, coal tar, halogenated organic compounds are the primary sources for soil and ground water contamination commonly found in several federal and private sites. Soils can be contaminated from leaking underground storage tanks, chemical spills, toxic residues leaching from landfills, and nuclear wastes. The movement, transformation, and fate of these contaminants in the environment are of particular interest because many of these contaminants are suspected to be carcinogens or mutagens and are toxic to humans. Generally, the treatment technologies, which are available to treat contaminated soils, are categorized in three ways: physical, chemical and biological. Each of these treatment technologies is briefly described in chapter 2.

Low-permeability soils pose significantly higher technical challenges to in-situ as well as ex-situ remediation processes than high-permeability soils. This is because the low-permeability soils may accumulate greater amounts of nonconservative contaminants than equal volumes of high-permeability soils, as a result of large surface area. Coal tar is a residual product of coal gassification process. In the past, coal tar was used as a construction material, later it was found that coal tar contained carcinogens. In this study, coal tar contaminated soil, with Polycyclic Aromatic Hydrocarbons (PAHs), was used for the redemption process. Pasha are hydrophobic compounds. Since hydrophobic organic tend to sorb onto soil, PAHs are not readily amenable to remediation process by soil washing or microbial degradation. And also soil washing is ineffective on finer particles, high organic and hydrophobic organic contaminants. Therefore, in this research, ultrasound energy is used to overcome all the limitations associated with the soil washing technology .

1.2 Scope of Study

The study reported herein primarily embraces the optimization of the process of contaminants removal and development of mathematical modeling of removal efficiency.

The purpose of this research study is to demonstrate the following scopes:

- Understanding the modes of cleaning by surfactant and the selection of surfactant type, which could be more effective for removing PAHs by the soil washing process.
- Selection of important parameters, which significantly influence the energy dissipated into the soil-system by the ultrasound application.
- Critical examination of the results of statistical analysis for full factorial design carried out using general linear model procedure (GLM) for determining the effects of the interactions between the important parameters.

- Economization on the number of treatment combinations for partial factorial design by ignoring interactions (from third order) which are insignificant on removal of contaminants.

- Selection of an appropriate theoretical model from the GLM procedure and reanalyzes of the data using regression procedure (PROC REG) to determine the model parameters, optimization of the conditions and determination of the maximum removal efficiency.

- Conclusions

CHAPTER 2

LITERATURE REVIEW

2.1 Current Technologies for Remediation of Contaminated Soils

Contaminants migrating from unengineered facilities, accidental spills, and industrial operations threaten the nation's health and ground water supply. Such contaminants are often present in large volumes of soil underlying several acres of surface area. In view of the high cost of land, limited resources, and the fact that the contamination can occur in densely populated and industrialized areas, there exists a need for new, efficient and cost effective technologies of remediation for rapid reclamation and rehabilitation of such sites. The currently available technologies can be categorized as biological, physical, chemical and other methods (EPRI 1987; Ellis et al. 1985, 1989). These are summarized in Table 1.

2.1.1 Bioremediation

Bioremediation process, which is a biological technology, can be described as the use of microorganisms to transform hazardous chemicals (organic carbons) to less toxic and environmentally acceptable compounds that are naturally present in the environment. Bioremediation technology has been understood and implemented for decades in many areas such as composting for sludge and organic refuse, sludge activation and trickling filter for waste water treatment and anaerobic digestion for manures and organic sludges. Nutrients (nitrate, sulfate, phosphorus etc.,) and oxygen are usually supplied to enhance bioremediation process in which micro-organisms consume organic contaminants as energy source and nutrients as ingredients under favorable pH (5.5-8.5) and temperature (10-30 °C), (Grasso 1993, Boulding 1995). It is particularly well applicable to the cleanup of large areas of organic wastes due to its relatively low cost, its effectiveness in dealing with a wide range of toxic materials and its ecologically sound ability to provide a "final solution " to cleanup problems. On the other hand however, the bioremediation process will take a long time and for low permeability soils, it becomes ineffective to decontaminate.

2.1.2 Soil Washing

Soil washing is an ex-situ process that employs chemical and physical and separation process to remove organic, inorganic and radioactive contaminants including petroleum and radionuclides, heavy metals, polychlorinated biphenyls (PCBs), pentachlorophenol (PCP), pesticides, cyanides, creosole, semivolatiles and volatiles from the soil. Soil washing is a new technology, commercially proven (since 1982) method for treating excavated soil and dredged sediments that are contaminated with toxic or other hazardous pollutants. This process is capable of recovering a clean soil fraction and concentrating contaminants in a residual soil as a pretreatment step. It also facilitates the application of other remediation processes such as bioremediation, chemical treatment, solvent/chemical extraction, stabilization/solidification, thermal desorption, thermal destruction, vacuum vapor extraction etc. If the soils contain large proportion of sand and gravels, such as coastal sandy soils and soils with glacial deposits etc., the process will be more effective whereas for soils having a high silt and clay content, it is ineffective. And also, soils having a high cation exchange capacity tend to bind pollutants more tightly and reduce the ability of the soil washing process. Soil washing process is not effective for hydrophobic organic contaminants. Therefore, these type of soils are not amenable for soil washing techniques. Removal efficiency of contaminants from the contaminated soils is highly dependent on the physical and chemical characteristics, type of contaminants and the spatial distribution of pollutants throughout the soil. Soil washing process is also highly sensitive to site conditions. Since the soil washing has limitations, for the coal tar contaminated soil, ultrasound application was used to enhanced the soil washing technology.

2.1.3 Electrokinetics

Electrokinetic soil processing using low level DC currents is envisioned to be used for removal of organic and inorganic contaminants, to supply vital nutrients for the growth of micro-organism to speed up the processes of bioremediation and also form barriers to contain the contaminants. The electrokinetic technology was first used in geotechnical engineering work to remove water from clays, silts and fine sands by Leo Casagrande 1959; Gray and Mitchell 1967, Esrig 1968. In fine grained soil water system, generally, four electro kinetic phenomena can be identified as electro-osmosis, electrophoresis, streaming potential and migration potential.

Electro-Osmosis

The coefficient of permeability and therefore the rate of seepage through clay soils is very small compared to that of granular soils. However, the drainage can be increased by the application of external electric current for a wet soil mass. This phenomenon is a result of the exchangeable nature of the of the adsorbed cations in clay particles and the dipolar nature of the water molecules. When the direct current is applied to the soil, the cations start to migrate to the cathode, which consists of a perforated metallic pipe. Since the water is absorbed on the cations, it is also dragged along. When the cations reach the cathode, they release the water, and the subsequent build up pressure causes the water to drain out. This process is called electro-osmosis.

Electrophoresis

If a direct current (DC) is applied to the soil, charged particles are attracted electro-statically to one of the electrodes and are repelled from the other electrode. Negatively charged particles move toward the anode. This is due to moving electrical gradient particles. This is referred to as electrophoresis. Therefore, in electrophoresis, electrical gradient induces particle movement whereas in electro-osmosis, electrical gradient induces water flow through a continuous soil particle network.

Streaming Potential

When water is caused to flow through a soil under a hydraulic gradient, double-layer charges are displaced in the direction of flow. The result is an electrical potential difference proportional to the hydraulic flow rate, called the streaming potential, between the opposite ends of the soil mass. Streaming potentials of several tens of millivolts have been measured in clays.

Migration Potential

The movement of charged particles such as clays relative to a solution, as during gravitational settling, generates a potential difference. When an electric field is applied across a wet mass of contaminated soil, the contaminants migrate under the combined influences of hydraulic, electrical and chemical gradients. Although these transport processes are coupled and complex, they are the fundamental mechanisms of contaminant removal by electrokinetics. Recent studies provided a better understanding of the prevailing electrokinetic phenomena and demonstrated that the acid front generated by electrolysis at the anode advances and eventually flushes across the specimen by advection, migration and anions under electrical gradients constitute the mechanisms of removal of contaminants from soils. The factors influencing the acid/base profile across the porous medium would significantly affect the flow, the flow efficiency, and the extent of ion migration and removal in electrokinetic soil processing.

2.2 Modes of Cleaning by Surfactant Application to the Contaminated Soils

Surfactants are used for characterization and remediation of contaminated ground water and soil washing, and enhanced subsurface remediation. Surfactants (surface active compounds) are compounds having fundamental properties including an amphipatic structure, monolayer orientation at interfaces, and adsorption at interfaces (Duckes et.al.,). Surfactant compounds can satisfy the bond breaking and segregation requirements of the cleaning process. The primary functions of a surfactant in a detersive cleaning system are to promote cleavage of bonds between the contaminant and the soils substrate and to segregate the detached contaminant in the solution to prevent its redeposition throughout the remaining washing process.

Previous research has pointed out that the interfacial tension is at or near its minimum when the surfactant concentration produces the most surfactant at the interface. This point is called the critical micelle concentration (CMC). Surfactant possesses both polar and non-polar regions on the same molecule. If the strength of the surfactant solution is greater than the critical micelle concentration (CMC), surfactant molecules aggregate to form micelles. A micelle can be defined as an assembly of surfactant molecules having a non-polar hydrocarbon-like core surrounded by the polar entities of the surfactant molecules. Surfactant solutions may solubilize hydrophobic contaminants from the soil by reducing the work of adhesion between the contaminant and soil, resulting in desorption and incorporation of the organic compound within the aqueous phase surfactant micelle.

Surfactants can act as mediators between hydrophobic chemicals and water. The molecular structure of the surfactant contains a hydrophilic part, which is called head, and a hydrophobic part which is called tail. In a water environment, the surfactant molecules constituting the micelle are oriented with the hydrophilic heads towards water (i.e., outward) and the hydrophobic tails toward the interior which is an hydrophobic environment, capable of retaining organic solutes. If the contaminant is on the surface as a "liquid film," its removal process is called "roll up". This process can be summarized as follows:

1. Interfacial tension between the liquid contaminant and the solid surface are reduced by surfactant action.
2. Surface effects in the liquid contaminant cause the liquid to minimize its surface area (i.e., "roll up").
3. Batch "hydraulic currents" cause the liquid contaminant to detach from the surface, resulting in a cleaned surface.

However, if the contaminant is attached as an adherent insoluble solid (i.e., anthrance, Phenathrene etc.), "roll up" will not occur and the contaminant can only be detached from the substrate by solubilizing the interface boundary layer material of the adhering contaminant. Removal of adhering solid organic contaminants proceed as follows (Edward et.al.,).

1. Surfactant monomer in the wash bath preferentially sorbs on the contaminant surface. The Preferential sorption raises the concentration of monomer on the surface to a point where the contaminant melts or dissolves in the concentrated surfactant monomer interface zone.
2. This contaminant-surfactant liquid phase/film detaches from the soil substrate and disperses into the bath, due to mechanical action, as a miceller or microemulsion dispersion.

As mentioned above, in the cleaning process, mechanical action plays a major role with surfactant action in the bond cleavage process. Mechanical action and agitation participate in the process by inducing velocity gradients in the system. Therefore, the ultrasound application is helping in the following two ways:

1. Promotion of mass transfer of surfactant monomer between the bulk fluid phase and the soil substrate interface.
2. Induction of high fluid-solid shear stresses, which promote mechanical detachment and removal.

Surfactant can be classified as cationic, anionic or nonionic, depending on the nature of the hydrophilic group. They all can be converted from a hydrophilic state to a hydrophobic state by one of the following treatments:

1. Anionics are converted by reacting with a cationic surfactant or by reaction with metal ions (e.g., Al^{+++} or Fe^{+++}) to produce an insoluble organic salt.

2. Cationics are converted by reacting with an anionic surfactant to produce a water-insoluble hydrophobic-organic product.
3. Nonionics are converted by raising their temperature above their phase inversion temperature (PIT).

Having converted to the hydrophobic state, the surfactant and the hazardous hydrophobic contaminant can be removed by extraction.

Table 1: Summary of Current Technologies for Remediation of Organic Contaminated Soils

Treatment Technology	Techniques	Applicability	Advantages	Limitations	Reference
1) Biological Bioremediation (Aerobic/Anerobic)	Microorganisms degrade the contaminants in the presence of oxygen (aerobic)/nitrate or other terminal electron aspects (anerobic), nutrients under favorable pH and temperature.	In-situ and Ex-situ process Highly permeable soils	A cost-effective technology	For low permeability soils, this technique is not effective. Due to lower permeability and low solubility of oxygen in water, and difficulty in supplying oxygen.	Ward (1995), Boulding (1995), Grasso (1993)
2) Physical /Chemical					
Soil Vacuum Extraction	Air and contaminant could be extracted from unsaturated zone by injecting clean air.	Saturated highly permeable soils	Medium cost-effective	Vapors are impeded in soils.	Boulding (1995), Grasso (1993), EPA (1991)
Soil Washing (flushing)/Chemical Extraction	Using water as a solvent contaminants are extracted with the help of additives (surfactants or chelating agents).	Saturated highly permeable soils	Medium cost-effective	For low permeability soils, the contaminant mobility is decreased, the percolation and leaching are reduced.	EPA (1991), Grasso(1993)
Soil Washing with Ultrasound Enhancement	using water as a solvent contaminants are extracted with the help of the application of ultrasound energy and additives (surfactants).	Capable of removing contaminants in low permeability sediments	Medium cost-effective		Meegoda et al. (1996)
Electrokinetics	Water flow is induced by applying an electric field.	Saturated clays	Medium cost-effective	This process takes a long period of time because the solubility of most organics is very low.	Segall (1992a), H0. et al. (1995)

CHAPTER 3

ULTRASOUND ENHANCEMENT OF SOIL WASHING

3.1 Mechanism of Ultrasound Application

Ultrasound is sound pitched above 16kHz, beyond the normal range of human hearing. Ultrasound finds application in processing involving solid, liquid or gaseous media. It is important, therefore, to have an understanding of the basic physical and chemical effects that may be may created in various media by ultrasonic waves. Today, ultrasound is applied in hospitals for medical imaging, in industry for welding plastics, cleaning materials, for burglar alarms and vaporizers in the home, and removing contaminants from the contaminated soils. However, removing contaminants from soils by the application of ultrasound is a new technology. Because studies of ultrasonic applications in soil science are few and only in conceptual stages.

Ultrasonic waves have several mechanical, chemical and biological effects on a saturated soil medium. Their mechanical effect is popularly known as cavitaion. Cavitation is an important factor for determining dispersion and disaggregation in ultrasonic systems (Willard 1953). Cavitation is the rapid and repeated formation, and resulting implosion, of micro-bubbles in a liquid, resulting in the propagation of microscopic shock-waves. Ultrasound waves consist of compression and expansion cycles. Compression cycles form a positive pressure on the liquid, pushing the molecules together whereas expansion cycles form a negative pressure, pulling the molecules away from one another. During the expansion cycle, a source of waves of high intensity can generate cavities. Generally, liquid is held together by attractive forces, which can be determined by the tensile strength of the liquid. In order to develop a cavity, a large negative pressure associated with the expansion cycle of the sound wave is needed to overcome the tensile strength of the liquid. A bubble irradiated with ultrasound, however, continuously absorbs energy from alternating compression and expansion cycles of the sound wave. Due to the continuously absorbed energy, the bubbles can grow and contact each other, striking a dynamic balance between the vapor inside the bubble and the liquid outside. Cavity growth depends on the intensity of sound. High intensity ultrasound can expand the cavity in the negative pressure (expansion cycle) in which the cavity never has a chance to shrink during the positive pressure. In this process, therefore, cavities can grow rapidly in the course of a single cycle of sound.

The growing cavity may eventually reach a critical size where it will absorb energy most efficiently from the ultrasound. The critical size depends on the frequency of the ultrasound waves. Once a cavity expands beyond the critical to a low or high-intensity ultrasound, it can no longer absorb energy as efficiently from the ultrasound waves. And also, the cavity can no longer sustain itself without the energy input. The liquid rushes in and the cavity implodes. The gases and vapors inside the cavity are compressed, generating intense heat that raises the temperature of the liquid immediately surrounding the cavity and creates a local hot spot. Although the temperature of this region is extremely high, the region itself is so small that the and heat dissipates quickly. The number of cavitaion bubbles collapsing per second may well be in the millions. Thus, the cumulative effect can be significant. In a soil-liquid system, these cavitational bubbles generate high differential fluid particle velocities. Finally, the mechanism of ultrasound application is that cavities are formed by ultrasound waves. When these cavities implode, they generate differential fluid particle velocity, which is capable of dispersing contaminants from the soil particles into the soil suspension by overcoming the forces binding the soil particles. The velocity perturbations occur on a microscopic scale, and are capable of dislodging contaminants from the micro size particles in the system by overcoming the forces binding finer particles to medium size particles.

3.2 Soil Description

A coal tar contaminated soil, with Polycyclic Aromatic Hydrocarbons (PAHs), was obtained from a contaminated site (Superfund site) for the research. The soil was 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% (5% PAHs). A single batch of contaminated soil was homogenized and used for the study (Chu-Feng Wei, 1995). The coal tar contaminated soil was divided into three fractions namely soil #1, soil #2, and soil #3. The soil #1 is the fraction finer than US sieve #4 but retained on US sieve #200 (0.075mm). The soil #2 is the fraction finer than US sieve # 4 but containing sizes finer than sieve #200 and soil #3 is the fraction passing sieve #200.

3.3 Surfactant

In a recent study of solubilization of PAHs from soil-water suspensions with several nonionic and anionic surfactants, it was found that the most effective surfactants were non-ionic octyl and nonylphenyl-etheoxylates with 9-12 ethoxylate units (Lieu et. al., 1991). At soil-water mass ratio of 1:7 greater than 0.1% by volume surfactant dose was required to initiate solubilization and a dose of 1% by volume resulted in 70-90% solubilization. Furthermore, solubilization of PAHs in soil-water systems occurs at surfactant doses much greater than the clean water critical micelle concentration (CMC). Another study reported that 22 surfactants were involved in cleaning the diesel contaminated soil. Among the 22 surfactants, two anionic and one nonionic surfactant were found to be more effective. Of the nonionic surfactants, three were more effective (Meegoda et.al., 1995). Therefore, Octyl-phenyl-ethoxylate, a non-ionic surfactant with a CMC of $2\text{-}3.3\times10^{-4}$ moles/liter, was used as the surfactant in this study.

3.4 Polynuclear Aromatic Hydrocarbons (PAHs)

A wide range of polycyclic aromatic compounds are known that have benzene rings with common ortho positions. The parent compounds of this type are usually called polynuclear aromatic hydrocarbons. Two aromatic rings that share a pair of carbon atoms are said to be fused. Polynuclear aromatic hydrocarbons may be classified as ortho-fused and as ortho and peri-fused. Polyaromatic hydrocarbons are hydrophobic compounds readily sorbed onto soil. PAHs are formed by the heating of bituminous coal to high temperature with the absence of air. Much of the interest in polynuclear hydrocarbons has arisen because a considerable number of these substances have cancer producing properties. Some of the most powerful carcinogens are derivatives of 1,2-benz anthracene. For example, Benzo(a)pyrene is a carcinogen. Carcinogen is one that is cancer producing. It is converted in the liver to an epoxy diol that can induce mutations leading to the uncontrolled growth of certain cells. Some of the common PAHs and their physical properties are listed in Table 2. They are less dense than and highly insoluble in water.

Boiling points of these substances are found to increase fairly regularly with molecular weight.

Table 2 : Physical Properties of PAHs

PAHs compounds	Melting point (° C)	Boiling point (° C)
Benzene	5.5	80
Napthalene	80	218
Anthracene	216	
Fluoranthene		
Pyrene	150	
Chrysene	255	
Benzo(k)fluoranthene		
Benzo(a)pyrene		

3.5 Soil Washing with Ultrasound Enhancement

As mentioned in chapter 2, soil washing with the help of surfactants can efficiently remove contaminants from the coarser size fraction (i.e., sand and gravel). This is because in the coarser size fraction, soil-contaminant attachment is predominantly by physical Van der Waal forces. However, in the fine soil fraction (< 200 sieve or < 74 micron), because of chemical reactive clay/humus constituents (10 microns), strong chemisorption bonding causes attachment between contaminant and soil. The process can be further explained. Organic compounds that react with clay minerals can be categorized in the following ways:

1. Positively charged organic radicals (displace exchangeable cation in clay).
2. Uncharged polar organics (replace water of hydration in clay structure).
3. Uncharged nonpopular organic radicals (form only external surface Van der Waal attachments).

4. Negatively charged organic radicals (repelled and minimally sorbed).

The first two categories include most organic compounds on the EPA priority pollutants and acutely are in the list of hazardous substances. The aliphatics cover the third category. Aliphatics are found to form only physical Van der Waal attachments to external surfaces and consequently can be removed by surfactant action. The first two categories, which form chemically bound clay-contaminant complexes are immune to surfactant action. Therefore, for a better removal efficiency in contaminated fine soil fractions, significantly higher fluid-particle shear stresses than the encountered in conventional methods would be required. In this regard, ultrasonic application, providing cavitational excitation, would be able to accomplish the following: generate higher fluid particle shear stresses, achieve satisfactory cleaning levels, and minimize the need for surfactants in the cleaning process.

CHAPTER 4

EXPERIMENTAL DESIGN

The factors which contribute to the enhancement of soil washing by the application of ultrasound are listed below:

1. Power
2. Solvent to Soil ratio
3. Surfactant concentration
4. Sonification Time
5. pH
6. Suspension temperature
7. Probe insertion depth
8. Particle size distribution
9. Ultrasonic frequency

4.1 Selection of Ultrasound Source

The following conclusions were drawn from the initial tests (Meegoda et.al., 1995) in order to select the ultrasound source:

Two modes of producing ultrasound waves were investigated (a probe type source and an ultrasonic bath) to determine the best practical means of conducting the research. The probe-in-beaker approach was selected as the mode of choice because of the higher intensity of local energy of the source. However, a disadvantage of the probe type source is that the system temperature could not be held constant during the experiment. This was because of the heat generation in the soil/water mixture due to the application of ultrasound energy. The other consideration was the lack of frequency variation. Since the electrical power input to the probe is fixed at 20 kHz and 1500 Watts, the frequency could not be varied. No other commercial probes were identified that had variable frequency output. And also, Edwards and Bremner (1967), and Genrich and Bremner (1972) reported that probe type vibrators are now used almost exclusively for dispersion of soils by the ultrasonic-vibration technique because tank-type vibrators have proved unsatisfactory. Therefore, it was decided that the probe type ultrasound is to be used for the application of ultrasound, and the parameters temperature and frequency were eliminated from the statistical model.

4.2 Selection of Critical Factors which Influence the Energy Dissipated into the Soil-System by the Ultrasound Application

As previously mentioned, the factors which contribute to the enhancement of soil washing by the application of ultrasound are power, solvent to soil ratio, surfactant concentration, suspension temperature, sonification time, ultrasonic frequency, pH, probe insertion depth and particle size distribution. Initial tests were performed to determine the effects of pH and temperature. These initial tests were conducted using the ultrasonic bath which produces the ultrasonic waves.

4.2.1 The Effect of pH

Figure 1 shows the initial test results where removal efficiencies of 12 PAHs for different solvent pHs when the soil suspension was subjected to ultrasound energy at 50% power, 1% surfactant concentration, 30 minutes sonification and 25:1 solvent to soil ratio. The removal efficiency did not change when the soil suspension pH was between 2 and 10. However, when the soil suspension pH was 13, there was a significant improvement in the removal efficiency. At solvent pH of 13, the solution becomes an emulsion and it is extremely difficult to extract contaminants.

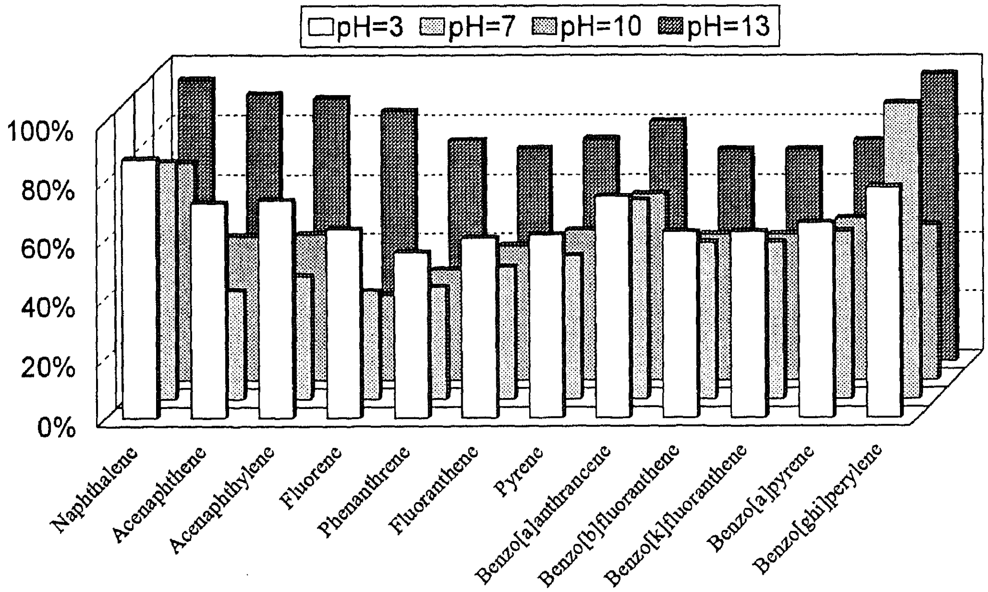

Fig. 1: Removal Efficiencies of 12 PAHs due to the Application of Ultrasound for Different Solvent pH Values

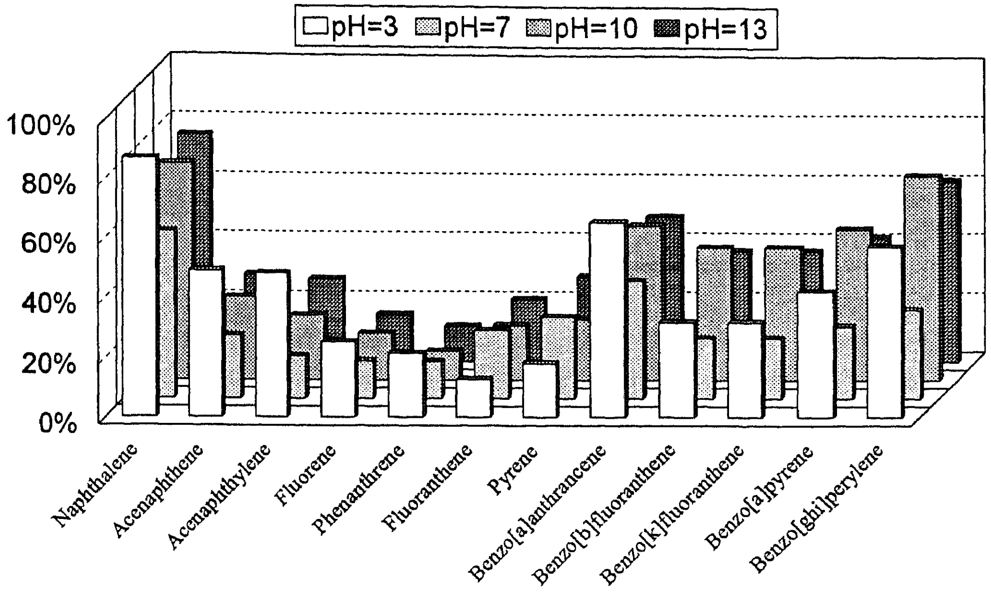

Fig. 2: Removal Efficiencies of 12 PAHs with Mechanical Stirring for Different Solvent pH Values

Figure 2 shows results similar to those of Figure 1 when the soil suspension was subjected to the mechanical stirring (no ultrasound application) at 1% surfactant concentration, 30 minutes time and 25:1 solvent to soil ratio. The removal efficiency did not change significantly, even when the soil suspension pH was 13.

The initial study, therefore, showed that if the solution pH was within the range of 2 to 10, solvent pH does not contribute to the removal efficiency. Therefore, it was decided to keep the pH between 6-7 during the ultrasound application and mechanical stirring in order to avoid the contribution due to solvent pH.

4.2.2 Temperature Effect

Figure 3 shows the removal efficiencies for 12 PAHs while applying ultrasound energy at 50% power 1% surfactant concentration, 30 minutes sonification and 25:1 solvent to soil ratio, and keeping a constant sample temperature. Figure 4 shows the removal efficiency for 12 PAHs while stirring a 1% surfactant concentration, 30 minutes time and 25:1 solvent to soil ratio, and keeping a constant sample temperature. When the suspension temperature was at 80° C, removal efficiency was quite high. One of the disadvantages of the probe type source is that the system temperature cannot be controlled during the experiment. It was also observed that the increase in temperature, due to ultrasound, is proportional to sonification time. When the removal efficiencies of 12 PAHs with and without ultrasound are compared for different solvent temperatures, results show that there is an increase in removal efficiency due to increase in solvent temperature.

However, for the rest of the research, it was decided to use probe type ultrasound source, and start the experiment at room temperature. Since the solvent temperature could not be controlled during the experiment, it was not considered as a factor for the rest of the research, except for the recording of the initial and final temperatures for each experiment.

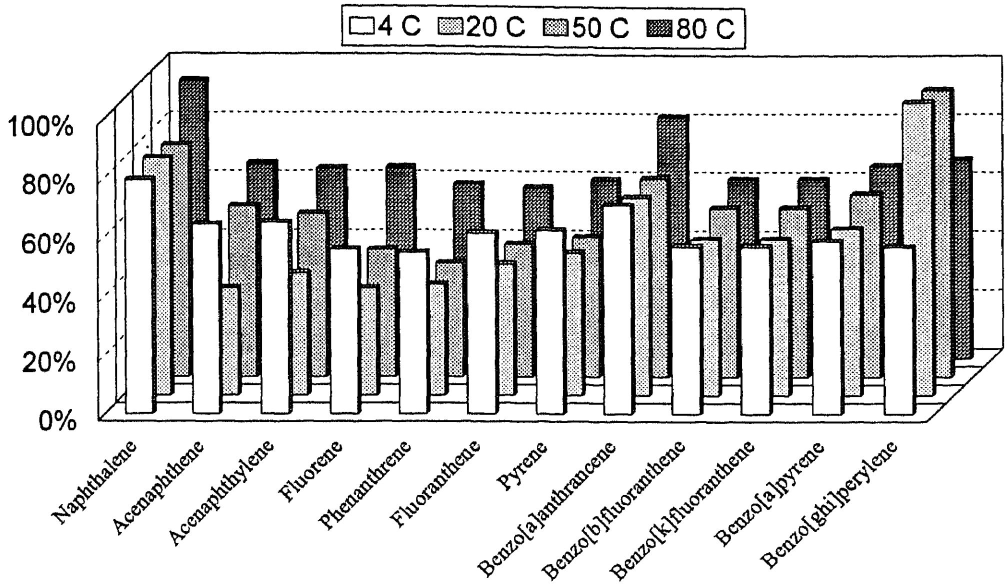

Fig. 3: Removal Efficiencies of 12 PAHs due to the Application of Ultrasound with Different Solvent Temperatures

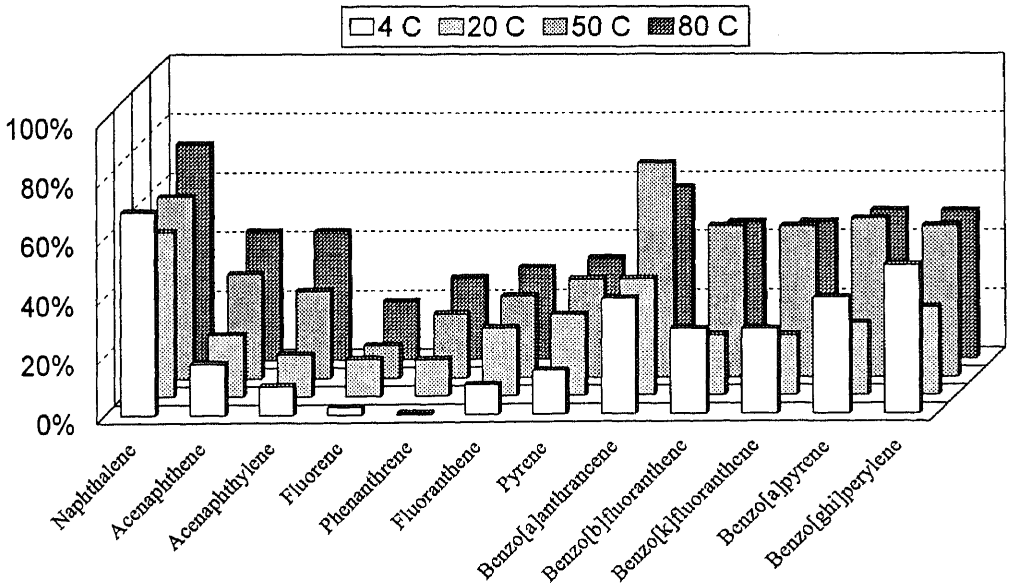

Fig. 4: Removal Efficiencies of 12 PAHs with Mechanical Stirring for Different Solvent Temperatures

4.2.3 Effect of Probe Insertion Depth

Morra et. al., (1991) observed that increasing the depth of probe insertion in their system increased power or energy dissipation into the system by 0.27W/mm. He also mentioned that this was because the increment of depth of probe increased the transmission of energy to the solvent solution. The increase in energy transmission depends on the depth of insertion, the width of the probe and the dimensions of the container. Therefore, for any comparative study, all the above should be used as standard measurements. Since it was decided to keep all the above constant, and the probe insertion depth factor was also eliminated from the list as a factor to be studied in order to minimize the variables.

4.2.4 Effect of Particle Size Distribution

Urick (1948), Buishy and Richerdson (1956), and Piotrowska (1971) have reported that the adsorption of ultrasonic waves, when they travel through Soil-Liquid suspensions, are affected by the particle size distribution of the soil. However, these tests have been conducted under high frequency ultrasound. When the average particle size decreases and the number of particles increases, cavitation may increase. Raine and So (1994) have reported that although decrease in particle size distribution must increase the number of particles and therefore, increasing cavitation to the system, this effect does not significantly affect the energy dissipation.

4.2.5 Effect of the Frequency of Ultrasound Source

The probe, used in the ultrasound application, has a 1500 W source operating at 20 kHz and there are no commercially available ultrasound sources with the same power rating but high frequency. Therefore, frequency was not considered as a factor in this research.

From the above discussion, of the nine factors, four of them, which are power, solvent to soil ratio, surfactant concentration, and dwell time, were identified as important. They influence the removal efficiency of the soil-system by the application of ultrasound.

4.3 Experimental Design

The baseline operation identified four variables (factors) which were included in the experimental design with three levels (low, medium and high except for ultrasound power density where the levels were: no power, low power and high power). The initial tests showed that power settings higher than 50% did not significantly improve the removal efficiency, hence, 50% power was selected as the maximum setting. Zero power with stirring was considered as the lowest level and used to compute ultrasound enhancement. Since the soil was heavily contaminated, a high solvent to soil ratio was required. Therefore, a solvent to soil ratio of 10:1 was considered as the lowest value. A solvent to soil ratio of 50:1 was selected as the maximum value for any ratio higher than that would be uneconomical and unpratical. For a probe type continuous treatment system, the treatment time is limited to about 30 minutes, as over 30 minutes of ultrasound overheats the system. Therefore, a treatment time of 30 minutes was used as the maximum. A surfactant concentration of 0.01 (below CMC value) was selected as the minimum and 1% (above CMC value) was selected as the maximum. Surfactant concentration above 1%

makes the treatment process uneconomical. These four factors with the three levels are shown in Table 3.

Table 3: Influence Factors and their Levels

Factors	Level 1	Level 2	Level 3
Power applied by ultrasound probe(%)	0	20	50
Solvent to Soil ratio	10	25	50
Surfactant concentration(%)	0.01	0.1	1.0
Sonification Time(min.)	5	15	30

Four factors at three levels produced 81 combinations. This is a complete (3^4) factorial design. For soil #1, which is the fraction finer than US sieve #4 but retained on US sieve # 200, and Soil #2, which is fraction finer than US sieve #4 but containing sizes finer than sieve #200, this complete factorial design was used. However, the full factorial design is achieved at a higher cost. The trade-off is between being able to economize on the number of treatment combinations in the experimental runs and the consequent sacrifice in ignoring certain effects (higher order interactions) which are no longer statistically estimable. A partial factorial design is more practical and economical if the higher order interactions have insignificant effects on the parameters. This indicates the technical constraints that can pinpoint the specific fractionally replicated design to be used. In this study, for soil #3, which is fraction finer than US sieve #200, a partial factorial design was conducted (1/3 of full 3^4) design which had 27 treatment combinations out of 81 possible in the complete (3^4) factorial. The choice of the particular factorial (i.e., if the number of levels are p and factors are n then, partial factorial will be $1/p^2$, $1/p^3$,.., and $1/p^m$, where m<n) is selected by which interactions are to be ignored. The set of generalized interactions confounded together are the "defining contrasts" of a factorial design. By using concepts and tools from finite geometry, one can construct the appropriate fractional replicated design for a given fraction (e.g., 1/3) of a given factorial (e.g., 3^4) corresponding to any given feasible set of "defining contrasts". Single replicated fractional designs with factors at two and three levels have been extensively tabulated in references (National Bureau of Standards, 1959), and (National Bureau of Standards, 1961). These have been reproduced in (Mclean et. al., 1984). Reference numbers (Patterson, 1976), (Box et. al., 1978) and (Franklin, 1984) are also related references.

4.3.1 Full Factorial Design for Soil #1 and Soil #2

Complete factorial design: 3^4 factorial (4 factors at 3 levels)

Factors = A, B, C & D,

Levels = 0, 1, 2 for each factor

Treatment combinations = (a, b, c, d)

a, b, c, d = 0, 1, 2 each

Total numbers of treatment combinations are 3^4 (= 81)

The full factorial design for soil #1 and soil #2:

Blocks

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
0000	0001	0002	1000	1001	1002	2000	2001	2002
1110	1111	1112	2110	2111	2112	0110	0111	0112
2220	2221	2222	0220	0221	0222	1220	1221	1222
1201	1202	1200	2201	2202	2200	0201	0202	0200
2011	2012	2010	0011	0012	0010	1011	1012	1010
0121	0122	0120	1121	1122	1120	2121	2122	2120
2102	2100	2101	0102	0100	0101	1102	1100	1101
0212	0210	0211	1212	1210	1211	2212	2210	2211
1022	1020	1021	2022	2020	2021	0022	0020	0021

The experimental order was randomized and resulted in the following:

0020	0021	0022	0010	0011	0012	0000	0001	0002
0120	0121	0122	0110	0111	0112	0100	0101	0102
0220	0221	0222	0210	0211	0212	0200	0201	0202
2022	2122	2222	2012	2112	2212	2002	2102	2202
2021	2121	2221	2011	2111	2211	2001	2101	2201
2020	2120	2220	2010	2110	2210	2000	2100	2200
1020	1010	1000	1021	1011	1001	1022	1012	1002
1120	1110	1100	1121	1111	1101	1122	1112	1102
1220	1210	1200	1221	1211	1201	1222	1212	1202

4.3.2 Partial Factorial Design for Soil #3

The partial factorial design was selected because it is economical and practical while giving similar results to the full factorial design.

Fractional factorial design (i.e., 1/3 replicate of 3^4 factorial) for the "defining contrasts":

H(1,1,1,1): corresponding to the four factor interaction ABCD. The corresponding design is a 1/3 replicate with all (=27) treatment combinations (a, b, c & d) satisfying:

$a+b+c+d = 0$ or multiple of $|3|$

The fractional factorial design for soil #3:

Blocks

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
0000	1110	2220	1101	2211	0021	2202	0012	1122
0111	1221	2001	1212	2022	0102	2010	0120	1200
0222	1002	2112	1020	2100	0210	2121	0201	1011

This is a useful design if all three and four factor interactions and some two factor interactions are negligible.

4.4 Experimental Procedure

The flow chart of the experimental procedure for the ultrasound enhanced soil washing is shown in Fig. 5.

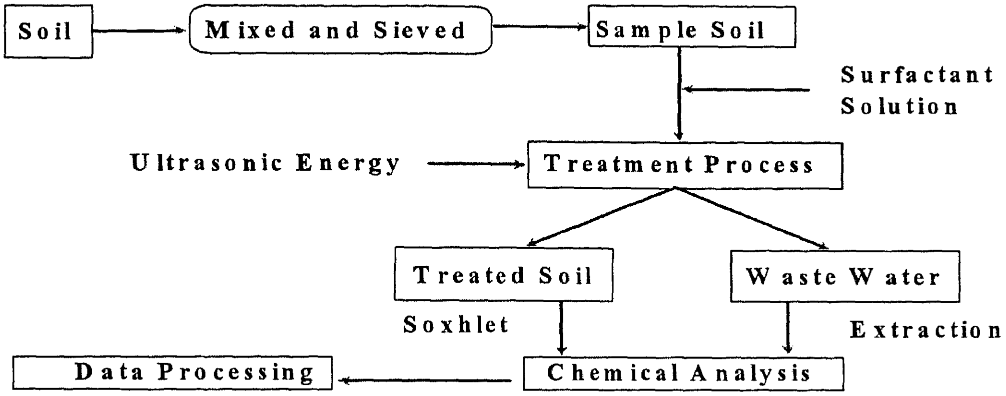

Fig. 5: Flow Chart for the Experimental Procedure

4.4.1 Preparation of Soil Suspension

Three levels of surfactant solutions (0.1 g, 1.0 g and 10.0 g of surfactant in 1000 mL of distilled water) were made. Initially, Soil specimens weighing 45.45 g, 19.19 g, and 9.80 g were placed in the containers and the various amounts of surfactant were added followed by the different amounts of water directly into the beaker to yield the desired solvent to soil ratios (i.e., 10:1, 25:1, and 50:1). The total solution volume was maintained at 500 mL for each experiment. Once the soil sample was thoroughly wetted with the water and surfactant solution, it was subjected to the ultrasound treatment.

4.4.2 Ultrasound Application to the Soil Suspension

The aerosolizing action produced by the sonicator probe dipping 4 cm into the soil/surfactant solution kept the soil in suspension. Since the sonication produced aerosolizing action, which stirred the system, no mechanical stirring was used with the sonicator. The probe type Sonicator was set at the 20% and 50% power output. However, for the 0% power, the mechanical stirrer was used. The container with soil slurry was kept inside the wooden cabinet that housed the ultrasonic probe at the top. The sonification time for soil suspension was set up at three levels, 5 minutes, 15 minutes and 30 minutes.

4.4.3 Filtration to Extract the Liquid Portion and Concentration

After the application of ultrasound to the soil suspension, it was transferred to the filtration system. The soil suspension was filtrated using whatman #40 filters. The vacuum was also used. The filtrated liquid portion was poured into a two liter funnel (Pyrex) in order to extract the PAHs from the wash water. EPA Method 3510 was employed for liquid-liquid extraction. A 0.25 mL solution of 2000 ppm of hexachlorobenzene in methylene chloride, as surrogate standard, and a 60 mL of methylene chloride were added for first time, into the funnel. After the first extraction of PAHs, the same procedure was repeated twice without hexachlorobenzene. The methylene chloride portion with PAHs was then concentrated in a Kuderna-Danish (K-D) apparatus in order to reduce the volume to 10.0 mL. This liquid-liquid concentrated portion was taken for the chemical analysis of PAHs in wash water.

4.4.4 Soxhlet Extraction for Soil Portion and Concentration

For the chemical analysis of PAHs in soils, treated soil slurry was allowed to air dry over night. EPA Method 3540A was employed for extracting PAHs from the soil. Soil #1 was treated according to EPA Method 3540A. Several ten gram samples of the untreated soil and the dried treated soil (base line) were weighed. Ten grams of sodium sulfate was added for each set and placed in an extraction thimble. These untreated and treated soil samples were then placed in Soxhlet Extraction for 16 to 18 hours followed by Kuderna-Danish (K-D) concentrate to 10 mL. However, it was found from the soil # 1 tests that addition of 10 grams of sodium sulfate to 10 grams of soil overdosed the extraction. Therefore, 5 grams of soil and 5 grams of sodium sulfate were used for soil # 2 and soil #3. The soil-liquid concentrated portion was taken for the chemical analysis of PAHs in soils.

Four factors at three levels produced 81 independent experiments. For better accuracy, in addition to the 81 runs, replicates, duplicates, and splits were also performed. Replicate sample means two soil samples treated with same washing condition (i.e., same power density, sonification time, surfactant concentration and solvent to soil ratio) and run chemical analysis separately. Duplicate sample means same soil sample, same extraction procedure but the chemical analysis (GC/MS) was run twice. Split sample means same soil sample was used to run two extractions followed by separate GC/MS analysis. According to the experimental design, 81 runs have to be performed. However, for the quality control, ten percent of samples were conducted in duplicate for each analytical batch. There was one split soil sample for each analytical batch. Ten percent of the samples were performed in replicate. This results in 8 or 9 duplicates, 8 or 9 replicates and 6 or 4 splits.

Therefore, the total number of experiments for soil #1, became as 103. In addition to 103 experiments, four extra tests, using 2%, 3%, 4% and 5% surfactants concentrations with 30 minutes of stirring for a solvent to soil ratio of 25:1, were performed. These data are not included in the statistical analysis. For soil # 2, in addition to the 81 experiments, 16 extra experiments were performed to achieve more accuracy. For soil # 3, 32 experiments were done. This is because in addition to 27 runs, rest of them are ten percentage of duplicate (2), ten percentage of replicate (2) and one split. This fractional factorial was to examine whether it is possible to produce a reasonable model with reduced experimental cost.

CHAPTER 5

ANALYTICAL PROCEDURE

The analytical procedure consists of the analysis of PAHs in soil and the analysis of PAHs in wash water for the mass balance calculation.

5.1 Chemical Analysis of PAHs in Soils

To 1.0 mL of concentrated solution, a 10 μL of 4000 ppm internal standard solution was added and placed in a capped vial. A 1 μL portion from these small vials was used for GC/MS analysis. All samples were analyzed by Varian Saturn II Ion-Trap GC/MS. EPA Method 3510A is used to isolate PAHs from liquid portion samples. An analyte was identified by comparing the sample mass spectrum with the mass spectra of standard compounds (standard reference spectra). When a compound is identified, the quantification of that compound was based on the integrated abundance of the SIM (selective ion monitoring) of the primary characterization as listed in EPA method 8270. Quantification was based on the internal standard technique. The internal standard was the one with the nearest retention time to that of a given analyte.

5.2 Chemical Analysis of PAHs in Wash Water

The chemical analysis of PAHs in wash water was performed for the mass balance. A mass balance will be calculated according to the following expression:

$$\text{Mass balance} = \frac{(\text{Mass of PAHs in treated soil} + \text{Mass of PAHs in water portion})}{(\text{Mass of PAHs in untreated soil})}$$

If the mass balance is in the range of 60 to 140 percent, then the test is considered successful (Chu-Feng Wei, 1995). The test results reported that the mass balance is in the range of 60 to 140 percent for all three soils. However, these results are not reported here.

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

$RO\text{-}(CH_2\text{-}CH_2O)_n\text{-}H$

R represents alkyl chain length of 12 to 15 carbons

n represents ethoxylated chain length of 1 to 20

Schmitt et. al., 1990, used reverse-phase chromatography to separate AE by alkyl chain length, and normal-phase chromatography to separate AE by ethoxylate chain length. Fendinger et al., 1995, stated that ethylene oxide groups can be cleaved by reaction with hydrobromic acid to form alkylbromide. Because the cleavage reaction products formed are independent of ethoxylate chain length, the number of analysis 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 (Blau and Halket, 1994). Presently, this is the most versatile technique available 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:

$$R_3Si\text{-}X + R'\text{-}H \rightarrow R_3Si\text{-}R' + HX$$

This reaction occurs in 20 minutes at 60° C. Therefore, the silylation was performed on the liquid portion before the GC/MS analysis. To 0.5 mL of wash water solution with 15 μL of 4000 ppm internal standard solution a 0.5 mL of silylation solution and o.5 mL of methylene chloride were added. Then, the mix was placed in a capped vial to extract some PAHs from the emulsion part into methylene chloride part. The small vials were placed in the oven at 60° C for 20 minutes. A 1 μL portion from these small vials was used for GC/MS analysis. The GC/MS analysis was the same as that for the analysis of PAHs in soil.

5.3 GC/MS Analysis

EPA Method 8270 was employed to determine the concentrations of 8 PAHs shown in Table 4. The GC/MS results were compared with the MS reference library to identify the compounds. The matrix spike compounds were the four PAHs listed in Table 5. The surrogate was Hexachlorobenzene. Quantification was by internal calibration. The internal standards were Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, Perylene-d12. The semi-volatile internal standards with corresponding analytes assigned for quantification are listed in Table 5. Acceptance criteria for surrogate recovery was not determined by control charts, but by maintaining at 60 - 140 percent range.

Table 4: Target Analytes

Species	Quantitative Mass
Acenaphthylene	152
Fluorene	166
Anthracene	178
Fluoranthene	202
Pyrene	202
Chrysene	228
Benzo(k)fluoranthene	252
Benzo(a)pyrene	252

Table 5: Internal Standards with Corresponding Analytes Assigned for Quantification

Acenaphthene-d10	Phenanthrene-d10	Chrysene-d12	Perylene-d12
Acenaphthene	Anthracene	Benzo[a]anthrancene	Benzo[b]fluoranthene
Acenaphthylene	Fluoranthene	Chrysene	Benzo[k]fluoranthene
Fluorene	Phenanthrene	Pyrene	Benzo[a]pyrene
	Anthracene-d10	Benzo[a]anthrancene-d12	Benzo[ghi]perylene

CHAPTER 6

ANALYSIS OF EXPERIMENTAL DATA

6.1 Determination of Removal Efficiency

The percentage removal efficiency R_m was calculated using the following equation:

$$R_m = 100 * \frac{(Initial\ concentration - Final\ concentration)}{(Initial\ concentration)} \%$$

The quantitative mass of each PAHs component and calculated removal efficiencies at different levels for all three soils (i.e., soil #1, soil #2 and soil #3) were calculated. However, these calculations are not shown in this thesis and are under the QA/QC report. Since EPA Method 8270 was employed to determine the concentrations of 8 PAHs as shown in Table 4, for the statistical analysis, only eight PAHs were used. Initial concentrations of 8 PAHs were shown in Table 6. Since it is necessary to examine the overall behavior of the removal efficiencies of all eight PAHs , it was decided to have one model for all eight PAHs . Therefore, the weighted average removal efficiency as dependent variable, removal efficiency in the statistical analysis. Rather than taking the average mean, the weighted average was used because each PAH has a different initial concentration which significantly affect the removal efficiency.

he weighted average percentage removal efficiency (R_w) is given by the following quation.

$$R_w = \frac{\sum_{i=1}^{8} (Initial\ concentration\ of\ each\ PAHs)_i * (R_m)_i}{\sum_{i=1}^{8} (Initial\ concentration)} \%$$

The weighted average removal efficiency calculations are also not reported here and are under the QA/QC report. These weighted average results were used in the statistical analysis in order to determine the residual conditions and develop a statistical model for the removal efficiencies in terms of four factors. However, each component of PAHs has different initial concentration and their characteristics are different in nature. In this regard, it was analysed to examine the behavior of the individual component also. Therefore, the results of the removal efficiency of each PAHs were also used in the statistical analysis.

Table 6: Initial Concentration of Eight PAHs

Species	Initial Concentrations (5 gm soil and 5 gm sodium sulfate)		
	Soil #1	Soil #2	Soil #3
Acenaphthylene	180.484	199.329	261.74
Fluorene	198.970	155.4245	323.55
Anthracene	470.439	383.9798	293.00
Fluoranthene	133.541	156.1011	188.12
Pyrene	239.662	236.2327	341.28
Chrysene	56.402	98.89417	405.44
Benzo(k)fluoranthene	60.789	29.47044	300.00
Benzo(a)pyrene	45.101	51.09164	384.13

6.2 Analysis of Data

6.2.1 Analysis of Data for Soil #1

For soil #1, 103 experiments were performed. In addition to 103 experiments, the extra four tests, which are 2%, 3%, 4% and 5% surfactants concentrations with 30 minutes of stirring for a solvent to soil ratio of 25:1, were also performed. These data are not included in the statistical analysis because they are not within the range of the experimental design. These additional data were needed to find the optimum conditions and for comparison with the ultrasound application. Removal efficiencies of Fluoranthene and Pyrene were plotted against the surfactant to soil ratio, by the application of ultrasound technique and mechanical stirring, shown in Fig. 6 and Fig. 7.

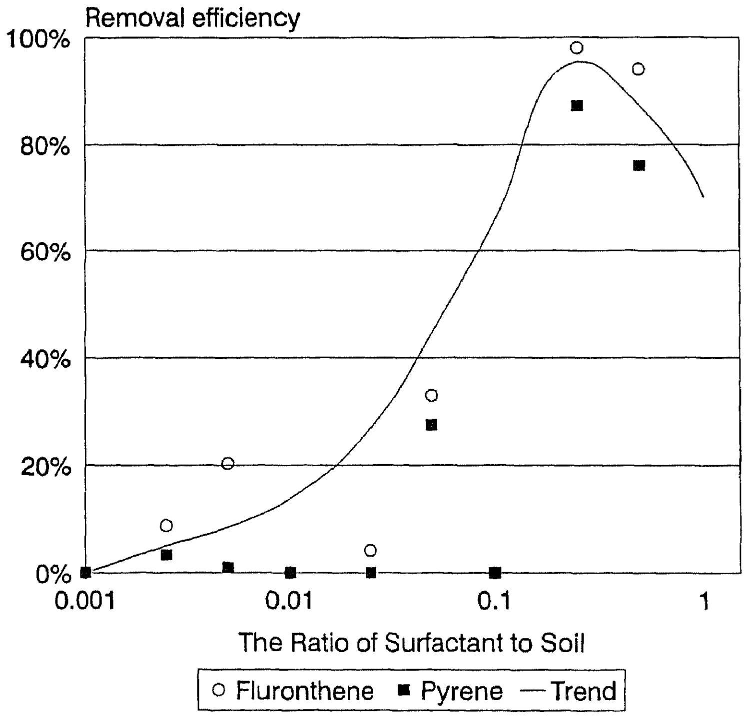

Fig. 6: The Removal Efficiency vs Surfactant to Soil Ratio for 50% Ultrasonic Energy Applied for 30 minutes

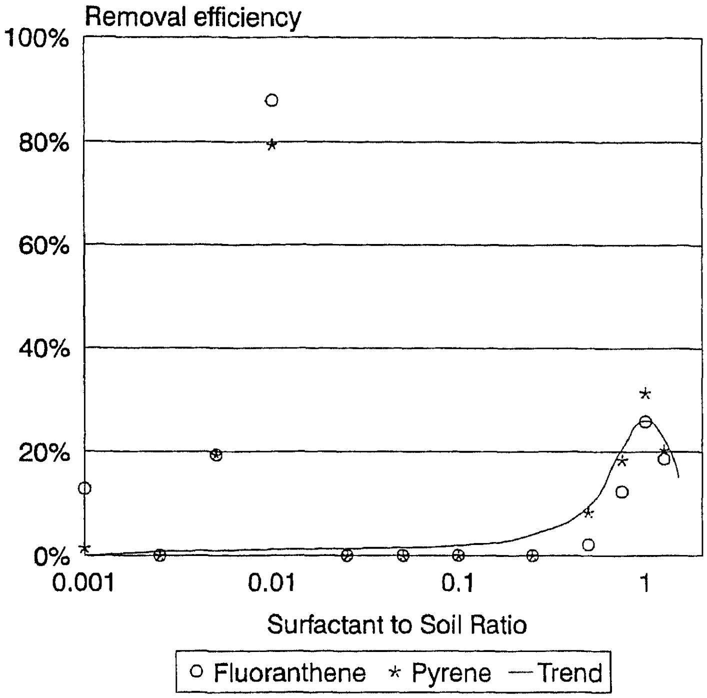

Figure 7: The Removal Efficiency vs Surfactant to Soil Ratio for Mechanical, Stirred Solvent for 30 minutes

However, out of 103 experiments 81 results were obtained (i.e., four factors with three levels). In order to present the data, the following procedure was used.

1. One factor at the three levels and other factors at their lowest level.
2. One factor at the three levels and other factors at their middle level.
3. One factor at the three levels and other factors at their highest level.

The above procedure gave 12 plots for 11 PAHs under different conditions for soil #1 and reported in Appendix A (Figures A.1 to A.12). Figures A.1 to A.3 show very little removal. This is because power, solvent to soil ratio and surfactant concentration are at lowest levels. However, Figure A.2 shows that three factors, which are solvent to soil ratio, surfactant concentration, and time, are at their lowest level, there is a significant improvement in removal efficiency with the variation of power. Figure A.9 indicates that the best removal efficiency could be obtained at 50% power, 1% surfactant concentration, 50:1 solvent to soil ratio, and 30 minutes sonification time. Figure A.10 confirms the above conclusion. Figure A.12 indicates that the lowest removal efficiency was obtained at 10:1 solvent to soil ratio whereas better removal efficiencies were obtained at 25:1 and 50:1 solvent to soil ratios. However, when the solvent to soil ratio was in the range of 25:1 to 50:1, the ultrasound application did not significantly improve the removal efficiency.

The following significant findings were reported by Meegoda et. al., (1996):

1. From Figures 6 and 7, a direct comparison between ultrasound application and mechanical stirring can be made. The ultrasound application produced 90% removal efficiency for 2 PAHs at the optimum surfactant to soil ratio of 0.25 by applying 750 Watts (50% power) for 30 minutes whereas for 2 PAHs, mechanical stirring produced 25% removal efficiency at the optimum surfactant to soil ratio of 1.0 (4% surfactant concentration) for the specified time of 30 minutes. In lay terms, the above translates to more than 300% enhancement with 75% less surfactant. This clearly demonstrates the applicability of the ultrasound process. Figure A.3 also confirms that the maximum removal efficiency could be obtained at the optimum surfactant concentration of 4% to 5%.
2. The best removal efficiency was obtained at 50% power, 1% surfactant concentration, 50:1 solvent to soil ratio, and 30 minutes of sonification. However, the solvent to soil ratio could be in the range of 25:1 to 50:1.

6.2.2 Analysis of Data for Soil #2

The analysis of data for soil #2 produced 12 plots of removal efficiency for 14 PAHs under different conditions, the plot are reported in Appendix B (Figures B.1 to B.12). Figures B.1 to B.3, do not show any removal due to low levels of power, solvent to soil ratio and surfactant concentration. Figure B.9 indicates that the best removal efficiency was obtained at a solvent to soil ratio of 50:1 with 50 % power (750 Watts), 30 minutes dwell time, and 1% surfactant concentration. Figure B.10 confirms the above conclusion, where the maximum removal efficiency is obtained at 30 minutes with 50% power, 1% surfactant concentration, and 50:1 solvent to soil ratio. There is no significant difference in removal efficiency between 5 and 15 minute treatment times but there is a substantial improvement with the 30 minute treatment time. Figure B.11 shows that with increasing surfactant concentration a progressively better removal efficiency was obtained. Figure B.10 shows the removal efficiency for soil washing with mechanical stirring (average 30%) and the removal efficiency for soil washing with ultrasound (average 90%).

The maximum removal efficiency could be obtained at 50% power, 1% surfactant concentration, 30 minutes dwell time and in the range of 25:1 to 50:1 solvent to soil ratio for soil #1 whereas for soil #2, the maximum removal efficiency could be achieved at 50% power, 1% surfactant concentration, 30 minutes dwell time and 50:1 solvent to soil ratio. Therefore, soil #2 requires more surfactant than soil #1. This is because soil #2 contains sizes finer than sieve #200 and therefore, the soil particles have larger surface area. More contaminants are captured in soil #2 than in soil #1. Table 6 shows the initial concentration levels for each soil with soil #3 highest and soil #1 lowest.

6.2.3 Analysis of Data for Soil #3

As described earlier, because of the fractional factorial, 27 experiments were selected to be used. Altogether 32 experiments were selected. The additional 5 experiments were for splits, duplicates and replicates. These results were presented in the Appendix C, Figures C.1 to C.6.

Figures C.1 and C.2 show more surfactant and less amount of soil improve removal efficiency. Figure C.3 demonstrates that when the surfactant concentration is low, even for the highest solvent to soil ratio, the removal efficiency does not improve significantly. This is more significant for soil #3 than for soil #1 and soil #2. Figure C.4 illustrates that increases of power improves removal efficiency significantly. When Figures C.1 to C.3 are compared, Figure C.3 shows that a good removal efficiency could be obtained at 20% power, 50:1 solvent to soil ratio, 15 minutes sonification time and 0.1% surfactant concentration. From the Figure C.6, the optimum removal efficiency could be expected at 50% power, 50:1 solvent to soil ratio, 1% surfactant concentration and 30 minutes time.

Soil #3 requires more surfactant the than other two types of soils to remove contaminants. The same conclusion was obtained from the soil #2. Therefore, soil # 3 confirms that when the particle size decreases, more surfactant is needed to remove contaminants. Since soil #3 has a lesser number of experiments (fractional factorial), Figures could not demonstrate this fact completely. However, the statistical analysis can produce reasonably optimum conditions.

CHAPTER 7

STATISTICAL ANALYSIS OF THE EXPERIMENTAL DATA

7.1 Statistical Approach

The detailed study carried out in the experimental design has shown that the main factors that need to be considered as influencial on the energy dissipated into the soil- water system, are power, solvent to soil ratio, surfactant concentration and time. Since the above four parameters are the most significant operating parameters, these were selected as processes variables (classes) in the statistical analysis. Each of these process variables were assigned in three levels. These four classes and three levels produce 81 sets of data. However, it is not necessary for a sample to contain exactly 81 data points. There can be more than 81 data points (i.e., repeated data) or less than 81 data points (i.e., missing data). The dependent variable used in this analysis is removal efficiency.

SAS/STAT version 6.0, a statistical program, was used in this study. There are several kinds of models, such as, Simple Regression, Multiple Regression, Polynomial Regression, Multivariate Regression, One-way Analysis of Variance (ANOVA), Main Effects Model, Factorial Model (with interaction), Nested Model, Multivariate Analysis of Variance (MANOVA), Analysis-of-Covariance Model, etc., can be used in the SAS/STAT program to analyze the data.

A complete factorial study is one in which several process variables (and settings of each) are identified as being variables of interest, and data are collected under each possible combination of settings of the process variables. The process variables are usually called factors or classes, and the settings of each variable, that are studied, are termed levels of the given factor or class.

For example, suppose there are four classes of interest namely, A, B, C and D. If A has 3 levels, B has 2, C has 2 and D has 4, a study includes samples collected under each of the class 3x2x2x4 different sets of conditions. This is called a 3x2x2x4 factorial study. In this study, in the cases of soil #1 and soil #2, the model was selected as the complete factorial model. It has 3x3x3x3 (81) different sets of conditions. However, for soil #3, the model was selected as the fractional factorial model.

7.2 Statistical Analysis Using General Linear Model Procedure

7.2.1 General Linear Model (GLM) Procedure

GLM procedure was used in this research to find the interactions between the process variables. For the unbalanced design, GLM procedure is the best of choice for the statistical analysis. However, GLM does not produce scatter plots. In addition to that, GLM allows only one model and fits the full model.

In the GLM procedure, three effects were considered in this study as described below:

(a) Main effects

The main effects are Power (POWER), Solvent to Soil ratio (WSRATIO), Surfactant concentration (SURFACT) and sonification time (TIME)

(b) Second Order Interaction Effects

The second order interaction effects are (Power*Power), (Power*Wsratio), (Power* Surfact), (Power *Time), (Wsratio*Surfact), (Wsratio* Time), and (Surfact* Time).

(c) Third Order Interaction Effects

Third order interaction effects are (Power*Wsratio*Surfact), (Power*Wsratio*Time), (Wsratio*Surfact*Time), (Power*Surfact*Time), and (Power*Surfact*Time).

7.2.2 Theoretical Background

The terminology used in this program is summarized below:

Degree of Freedom (DF)

In order to compute a statistical analysis, it is necessary to use observations obtained from a sample to estimate certain unknown population parameters. The number of degrees of freedom of a statistic which is generally denoted by DF, is defined as the number N of independent observations in the sample (i.e., the sample size) minus the number k of population parameters, which must be estimated from the sample observations. It can be written as:

$$DF = N - k$$

$$If \quad k = 1, \quad DF = N - 1$$

For example, consider soil #1, which has 103 observations (Refer Appendix D, Table D. 1).

No of observations N = 103

DF for corrected Total = N-1 = 103-1 = 102

Between treatment, Power = Levels-1 = 3-1 = 2

*Interactions, (Power*Wsratio) = (3-1)*(3-1) = 4*

*Interactions, (Power*Wsratio*Time) = (3-1)*(3-1)*(3-1) = 8*

DF for Model = Sum of DF of all sources which are used in this analysis

DF for error = Corrected Total -Model

Mean Square

$$Mean\ Square = \frac{Sum\ of\ Squares}{Degree\ of\ Freedom}$$

F-Test

It is important in some applications to know the sampling distribution of the difference in means $(\overline{X}_1 - \overline{X}_2)$ of two samples. Similarly, we may need the sampling distribution of the difference in variance $(S_1^2 - S_2^2)$. However, this distribution is rather complicated. Because of this, it is considered the statistic S_1^2/S_2^2. Its distribution, when the underlying true variances are equal, is the so called F-distribution.

For example, from the Table D. 1,

$$F = \frac{Mean\ Square\ of\ Model}{Error\ Mean\ Square}$$

Pr>F

"Pr > F" (technically called the 'P-value' or the 'observed significant level') is the probability of obtaining at least as great a F-ratio given that the null hypothesis is true. It is the risk of wrongly rejecting the null hypothesis that the postulated model is true. For a process variable, if the value of Pr > F is less than 5%, then it can be said that the process variable significantly influences the dependent variable.

7.2.3 Evaluation of the Results from the GLM Procedure

The statistical analysis results of one model (overall model), using GLM procedure, for soil #1, soil #2 and soil #3 are shown in Table D. 1 to Table D. 3 in Appendix D. A summary of these results is reproduced in Table 7. The results of the individual components of eight Polyaromatic Hydrocarbons (PAHs) are not reported here. However, those results also follow the same behavior.

The GLM procedure results add the following vital information:

1. Comparing the value of Pr > F for soil #1 (Refer Table 7), it was found that the value of Pr > F of all main effects except time are less than 5%. This suggests that main effects significantly influence the dependent variable, removal efficiency. Of the second order interactions, the value of Pr > F for (Power* time) is greater than 5%. Therefore, it would not significantly influence the dependent variable (removal efficiency). Of the third order interactions only (Power* Wsratio* Surfact) will influence the dependent variable. These results clearly indicate that the interactions between (Power*time), (Power*Wsratio*Time), (Wsratio*Surfact*Time), and

(Power*Surfact*Time) can be neglected in the regression procedure analysis in order to find the model parameters and also they agree with graphical results.

2. For soil #2, (Refer Table 7), the main effects significantly influence the dependent variable. However, the second order interactions and third order interactions do not influence the dependent variable.
3. For soil #3, of the main effects, only Power will influence the removal efficiency. Of the second order interactions, (Surfact*Time) will influence the removal efficiency.
4. Higher order interactions (3rd and 4th order) are not statistically significant and can be ignored, thus be absorbed error. This conclusion agrees with the experimental design, and therefore, the selection of partial factorial is appropriate for soil #3.
5. The higher order (from 3rd order) terms could be neglected from the GLM results, and therefore, the full quadratic model can be selected to find the model fitting parameters.

Table 7: Summary of the GLM Procedure Results for Overall Models of Soil #1, Soil #2 and Soil #3

Dependent Variable : Removal

Source	Degree of Freedom			Sum of Squares			Pr > F		
	Soil #1	Soil #2	Soil #3	Soil #1	Soil #2	Soil #3	Soil #1	Soil #2	Soil #3
Model	64	64	26	4.82991	3.34146	0.93878	0.0001	0.0043	0.2039
Error	38	32	5	0.49309	0.70140	0.05049			
Corrected total	102	96	31	5.32301	4.04282	0.98927			
					(Type I SS)				
Power	2	2	2	1.00047	1.56280	0.18966	0.0001	0.0001	0.0498
Wsratio	2	2	2	0.76713	0.11336	0.07366	0.0001	0.0910	0.2007
Surfact	2	2	2	0.70157	0.32330	0.03110	0.0001	0.0023	0.4467
Time	2	2	2	0.14871	0.23135	0.04704	0.0067	0.0105	0.3211
(Power*Wsratio)	4	4	4	0.32945	0.07377	0.13004	0.0005	0.5093	0.2347
(Power*Surfact)	4	4	4	0.18237	0.18162	0.08052	0.0155	0.1078	0.4037
(Power*Time)	4	4	4	0.05992	0.09102	0.05698	0.3461	0.4029	0.5403
(Wsratio*Surfact)	4	4	4	0.24320	0.10409	0.15590	0.0036	0.3352	0.1833
(Wsratio*Time)	4	4	1	0.25610	0.08670	0.04027	0.0026	0.4277	0.1774
(Surfact*Time)	4	4	1	0.16633	0.08907	0.10234	0.0231	0.4139	0.0544
(Power*Wsratio*Surfact)	8	8	0	0.45004	0.08298	0.00000	0.0009	0.8658	-
(Power*Wsratio*Time)	8	8	0	0.18101	0.18811	0.00000	0.1198	0.4062	-
(Wsratio*Surfact*Time)	8	8	0	0.16660	0.12022	0.00000	0.1559	0.7009	-
(Power*Surfact*Time)	8	8	0	0.17611	0.09302	0.00000	0.1311	0.8246	-

7.3 The Regression Procedure (PROC RSREG)

From the GLM procedure, it was found that the third order interactions are not significant. Therefore, the full quadratic model is appropriate to determine the model parameters. Although the other SAS/STAT procedures could be used to fit the response surface, PROC RSREG was selected for use in this analysis, as PROC RSREG is more specialized. The RSREG procedure is capable of estimating the parameters of the model of a complete quadratic response surface and analysis of the fitted surface in order to determine the factor levels at optimum response. In this procedure, if each factor variable is measured at three or more values, a quadratic response surface can be estimated by least-square regression. This program gives the predicted optimum value, if the surface shape is like a simple hill or valley. If the estimated surface is more complicated, or if the predicted optimum is far from the region of experiments, then the shape of the surface will be analyzed to indicate the directions in which the experiments should be analyzed.

The following steps are to be used in order to analyze the data:

1. Model fitting and analysis of variance to estimate the model parameters.
2. Canonical Analysis to investigate the shape of the predicted response surface.
3. Ridge Analysis to search for the region where the factors level is at the optimum response.

7.3.1 Model Fitting and Analysis of Variance

Model fitting and Analysis of Variance give the estimated parameters of the model by least-square regression. It also helps to know the information about the fitting in the form of an analysis of variance. If the estimated surface is a “hill," then peak will occur at the unique estimated point of maximum response. If it is a “valley“ or a “saddle” surface then there is no unique minimum or maximum.

7.3.2 Elucidation of Canonical analysis

The method of canonical analysis is to rewrite a fitted second degree equation in a form in which it can be easily understood. This can be achieved by a rotation of axes which removes all cross-product terms.

Consider a fitted second degree model,

$$y = b_o + \sum_{j=1}^{k} b_j x_j + \sum_{i \geq j}\sum b_{ij} x_i x_j$$

The above equation can be written in the other form

$$x = \begin{bmatrix} x_1 \\ x_2 \\ \cdots \\ x_k \end{bmatrix} \qquad b = \begin{bmatrix} b_1 \\ b_2 \\ \cdots \\ b_k \end{bmatrix} \qquad B = \begin{bmatrix} b_{11} & \frac{1}{2}b_{12} & \cdots & \frac{1}{2}b_{1k} \\ \frac{1}{2}b_{12} & b_{22} & \cdots & \frac{1}{2}b_{2k} \\ \cdots & & & \\ \frac{1}{2}b_{1k} & \frac{1}{2}b_{2k} & \cdots & \frac{1}{2}b_{kk} \end{bmatrix}$$

Therefore, the fitted equation is

$$y' = b_o + x'b + x'Bx$$

Let λ_1, λ_2, ...,λ_i, ...,λ_k be the eigen values of the symmetric matrix B, and m_1, m_2,...,m_i ,.....,m_k the corresponding eigen vectors. Therefore, by definition,

$$Bm_i = m_i \lambda_i \,, \qquad i = 1,2,\ldots,k.$$

If each eigen vector is standardized so that $m_i'm_i = 1$ and if the k x k matrix M has m_i for its ith column, then M is an orthonormal matrix and the k equations can be written simultaneously as:

$$BM = M\Lambda$$

Where Λ is a diagonal matrix whose ith diagonal element is λ_i. Multiplying by M', the following equation can get:

$$M'BM = \Lambda$$

However, $MM' = I$,therefore, y' can be written in the following form:

$$y' = b_o + (x'M)(M'b) + (x'M)M'BM(M'x)$$

Let $X = M'x \text{ and } \theta = M'b$, therefore, finally it will come as

$$Y' = b_o + \theta_1 X_1 + \ldots + \theta_k X_k + \lambda_1 X_1^2 + \ldots + \lambda_k X_k^2$$

The above form is called canonical form which eliminates cross-product terms by rotating the axes. The canonical analysis is able to analyze the overall shape of the curve and determine whether the estimated stationary point is a maximum, minimum or saddle point. In order to catergorise the stationary point, the eigen values are used. If the all eigen values are negative then the solution will be a maximum, and if they are all positive then the solution will be a minimum. If they have both signs (i.e., negative and positive) then it will be a saddle- point. If they contain zeros then it will be in a flat area.

7.3.3 Elucidation of Ridge Analysis

Ridge analysis is used to find the optimum response. Ridge analysis computes the estimated response (response variable) corresponding to the increasing coded radius which is from the center of the original design. It also computes the optimum of uncoded process variables (factors) corresponding to the increasing coded radii. If there is not a unique optimum of the response surface within the range of experimentation, the ridge analysis will help to indicate the direction in which further experimentation should be performed.

7.3.4 Evaluation of the Results from the PROC RSREG Procedure

The statistical analysis results of overall models, for soil #1, soil #2 and soil #3, using RSREG procedure, are shown in Table 8 to 14. The results of each PAH component are also shown in Appendix E, From Table E.1 to Table E.8. The canonical analysis, for the overall model of soil #1, clearly indicates that the directions of the principle orientation for the predicted response surface are along the axes associated with the four factors (Refer to Table 8 & 9). Since the eigen values have both signs (negative and positive), the stationary point is a saddle point. The first largest component of the eigen vector (0.966053) corresponding to the largest eigen values (-0.202102) is associated with power factor. The second largest eigen value (-0.175879) is associated with Surfactant. However, the influence of the both factors are approximately equal. Similarly third and fourth are solvent to soil ratio and time. This shows that the response surface is more sensitive when the power factor changes whereas it is not much sensitive when the time factor changes.

Once each PAH component is considered, for Acenaphthylene, the first significant factor is solvent to soil ratio. The second, third and fourth are surfactant, power, and time. Similarly, for Fluorene, the descending order of significant factors are power, solvent to soil ratio, surfactant and time (Refer Appendix E, from Table E.1 to E.8). The components of Fluorene, Anthrancene, Fluoranthene, Pyrene, Benzo(k)flouranthene and Benzo(a)pyrene behave the same way as the overall model.

Table 8: Canonical Analysis of Response Surface for Overall Models

Soil Type	Response Mean	Root MSE	R-Square	Sum of Residual Squares	Predicted Response Surface	Predicted Value at that Response Surface
Soil # 1	0.272018	0.144823	0.6533	1.845677	Saddle	0.417327
Soil # 2	0.369273	0.145181	0.5725	1.728353	Saddle	-0.383009
Soil # 3	0.320911	0.161306	0.5529	0.442331	Saddle	0.015446

For soil #2 and soil #3, since the eigen values are positive and negative, the stationary points are saddle points. However, for the overall model of soil # 2, when the solvent to soil ratio factor changes, the response surface is more sensitive. And also, most PAH components are significantly affected by power, surfactant, and solvent to soil ratio. For the overall model of soil # 3, when the surfactant factor changes, the response surface is more sensitive. Surfactant is the most significant factor for all PAH components (Refer Appendix E, from Table E.1 to E.8).

The individual components also mostly behave as the overall model. The canonical analysis also indicates that if the particles size decreases, the surfactant factor is more sensitive. More surfactant is required for the removal of contaminants in fine particles.

The analysis of variance, which gives the test of Prob > F, from the ridge analysis, indicates that all four factors are significantly influenced by the response variable for soil # 1 (Table 10). However, factors like power, solvent to soil ratio and surfactant are more significant than time. For soil #2, power is the more significant. Solvent to soil ratio is the least significant. The other two factors are also significant. Whereas for soil #3, power is the only significant factor. Once these results are compared with those used by the GLM procedure for the test of Prob >F, both give the same conclusion for soil #1, soil #2 and soil #3.

From all these procedures, it can be concluded that for soil #1, the significant factors are power, surfactant, and solvent to soil ratio. For soil #2, the significant factors are power, surfactant, solvent to soil ratio and time. For soil #3, the significant factors are power and surfactant.

For the overall model of soil #1, the canonical analysis indicates that the response surface has a saddle point and does not have a unique optimum. However, the ridge analysis indicates (Table 11) that maximum yields will result from relatively high reaction power, high reaction solvent to soil ratio, high reaction surfactant concentration and high reaction time. For individual components, the same behavior was found (Refer Appendix E, from Table E.9 to E.16).

Table 9: Canonical Analysis for Eigen Values and Eigen Vectors for Overall Models

Soil Type	Eigen Values	Eigen Vectors			
		Power	Wsratio	Surfactant	Time
Soil #1	0.015676	0.126266	0.406239	0.202592	0.882033
	-0.075594	0.222094	0.836934	0.192834	-0.461553
	-0.175879	0.038383	-0.282164	0.953915	-0.094640
	-0.202102	0.966053	-0.234295	-0.108712	-0.005414
Soil #2	0.076074	0.112757	0.005739	0.989918	0.085524
	0.002707	0.235799	0.154242	-0.110100	0.953145
	-0.039064	0.962022	-0.118746	-0.089100	-0.229072
	-0.077739	0.078726	0.980855	-0.000734	-0.178117
Soil #3	0.247629	0.160601	0.051572	0.918780	-0.356919
	0.105769	-0.166020	-0.236062	0.383134	0.877451
	0.029613	0.863741	0.402808	-0.058144	0.297181
	-0.088190	-0.447881	0.882814	0.075305	0.119881

Table 10: Ridge Analysis for Analysis of Variance for Overall Models

Soil Type	Factor	Degrees of Freedom	Sum of Square	Mean Square	F-Ratio	Prob> F
Soil #1	Power	5	1.188945	0.237789	11.338	0.0000
	Wsratio	5	1.301798	0.260360	12.414	0.0000
	Surfact	5	1.105782	0.221156	10.545	0.0000
	Time	5	0.448464	0.089693	4.276	0.0016
Soil #2	Power	5	1.668242	0.333648	15.830	0.0000
	Wsratio	5	0.142128	0.028426	1.349	0.2524
	Surfact	5	0.361785	0.072357	3.433	0.0072
	Time	5	0.283061	0.056612	2.686	0.0268
Soil #3	Power	5	0.325436	0.065087	2.501	0.0714
	Wsratio	5	0.202690	0.040538	1.558	0.2249
	Surfact	5	0.164848	0.032970	1.267	0.3228
	Time	5	0.203436	0.040687	1.564	0.2233

Table 11: Estimate Ridge of Maximum Response for the Overall Model of Soil #1 with four Factor Variables

Coded Radius	Estimate Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	0.65947	0.10186	25.0000	30.00000	0.50500	17.5000
0.1	0.67874	0.10210	26.0767	31.24530	0.53203	17.9482
0.2	0.69725	0.10178	27.0142	32.54440	0.55616	18.5188
0.3	0.71524	0.10103	27.8398	33.85012	0.57783	19.1952
0.4	0.73291	0.09996	28.5770	35.13530	0.59751	19.9582
0.5	0.75040	0.09864	29.2445	36.38694	0.61561	20.7898
0.6	0.76781	0.09713	29.8567	37.60062	0.63244	21.6749
0.7	0.78523	0.09547	30.4250	38.77655	0.64827	22.6016
0.8	0.80272	0.09374	30.9580	39.91717	0.66329	23.5605
0.9	0.82032	0.09199	31.4623	41.02579	0.67765	24.5446
1.0	0.83808	0.09029	31.9431	42.10589	0.69147	25.5485

For the overall model of soil #2, the canonical analysis indicates that the response surface has a saddle point and does not have a unique optimum. However, the ridge analysis indicates (Table 12) that maximum yields will result from relatively high reaction power, high reaction solvent to soil ratio, high reaction surfactant concentration, and high reaction time. For individual components, the same behavior was found (Refer to Appendix E, Table E.17 to E.24).

For the overall model of soil #3, the canonical analysis indicates that the response surface has a saddle point and does not have a unique optimum. However, the ridge analysis indicates (Table 13) that maximum yields will result from relatively high reaction power, high reaction solvent to soil ratio, high reaction surfactant concentration and lower time. For individual components, the same behavior was found (Refer to Appendix E, Table E.25 to E.30). This conclusion is quite different from those for soils #1 and #2.

Table 12: Estimate Ridge of Maximum Response for the Overall Model of Soil #2 with four Factor Variables

Coded Radius	Estimate Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	0.41446	0.104792	25.00000	30.00000	0.505000	17.5000
0.1	0.43356	0.104970	27.13489	30.22771	0.522956	17.9441
0.2	0.45270	0.104726	29.14686	30.43586	0.545375	18.4150
0.3	0.47201	0.103848	31.01215	30.62511	0.572620	18.8991
0.4	0.49169	0.102074	32.71246	30.79545	0.604726	19.3816
0.5	0.51189	0.099129	34.23949	30.94693	0.641344	19.8486
0.6	0.53281	0.094785	35.59681	31.08023	0.681818	20.2900
0.7	0.55458	0.088922	36.79795	31.19675	0.725353	20.7003
0.8	0.57733	0.081576	37.86217	31.29841	0.771172	21.0783
0.9	0.60118	0.073014	38.81027	31.38734	0.818621	21.4253
1.0	0.62621	0.063896	39.66179	31.46554	0.867194	21.7443

Model fitting parameters using the full quadratic regression for all soils (soil #1, soil #2 and soil #3) are shown in Table 14. However, for the individual components, these parameters are not reported in this thesis. The observed values of removal efficiencies and predicted values of removal efficiencies, which are obtained from the statistical analysis, are presented in the Figures 8, 9 and 10. And also, for the individual components, these Figures are presented in the Appendix F, from Figure 1 to Figure 24.

Table 13: Estimate Ridge of Maximum Response for the Overall Model of Soil #3 with four Factor Variables

Coded Radius	Estimate Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to soil ratio	Surfactant Concentration (%)	Time (min.)
0.0	0.084183	0.233198	25.00000	30.00000	0.505000	17.5000
0.1	0.096782	0.233243	27.07708	30.44855	0.505464	16.8634
0.2	0.111219	0.233261	28.82768	30.97088	0.521194	16.0676
0.3	0.128534	0.231850	30.10570	31.39208	0.557351	15.2548
0.4	0.149792	0.226971	30.99438	31.67994	0.603584	14.5476
0.5	0.175559	0.218181	31.68199	31.89257	0.651832	13.9289
0.6	0.206058	0.205724	32.26972	32.06711	0.700033	13.3633
0.7	0.241386	0.189948	32.80242	32.22056	0.747844	12.8298
0.8	0.281590	0.171322	33.30167	32.36118	0.795271	12.3171
0.9	0.326695	0.150604	33.77902	32.49340	0.842379	11.8183
1.0	0.376718	0.129212	34.24122	32.61980	0.889232	11.3296

The response variable (removal efficiency) is denoted as Y and the four parameters, which are power, solvent to soil ratio, surfactant concentration and time, are denoted as A, B, C and D respectively. For all three soils, the full quadratic model was fitted and expressed as follows:

$$\begin{aligned} Y_R &= \beta_o + \beta_1 A + \beta_2 B + \beta_3 C + \beta_4 D + \beta_5 A^2 + \beta_6 BA + \beta_7 B^2 + \beta_8 CA + \beta_9 CB + \beta_{10} C^2 \\ &\quad + \beta_{11} DA + \beta_{12} DB + \beta_{13} DC + \beta_{14} D^2 \end{aligned}$$

This can be written in the other form as:

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

Where, $0 \leq i+j+k+l \leq 4$ and $0 \leq i, j, k, l \leq 2$

Table 14: Comparing the Fitting Parameters for the Overall Model Using Full Quadratic Regression

Parameter	Components	Soil Type		
		Soil #1	Soil #2	Soil #3
β_o	Intercept	0.097884	0.021211	0.200585
β_1	Power	0.012684	0.005546	-0.003861
β_2	Wsratio	0.006415	0.013362	0.012049
β_3	Surfact	0.528132	0.006554	-0.370741
β_4	Time	-0.007017	0.002067	-0.008063
β_5	Power * Power	-0.000308	-0.60924E-04	0.44275E-04
β_6	Wsratio * Power	0.000138	0.23254E-04	0.000164
β_7	Wsratio * Wsratio	-0.000189	-0.000246	-0.000190
β_8	Surfact * Power	0.001931	0.001648	0.003494
β_9	Surfact * Wsratio	0.006320	0.001564	-0.001220
β_{10}	Surfact * Surfact	-0.671760	-0.015700	0.521892
β_{11}	Time * Power	0.71621E-04	0.000135	-0.47190E-04
β_{12}	Time *Wsratio	0.000239	0.95487E-04	-0.000136
β_{13}	Time *Surfact	0.008174	0.002749	-0.010272
β_{14}	Time * Time	-0.35132E-04	-0.90793E-04	0.000376

From the above results the following findings are significant:

1. From the ridge analysis, under optimum conditions, it can be observed that the highest removal efficiency could be obtained for soil #1 (Table 11) and lowest removal efficiency was obtained for soil #3 (Table 13). One of the reasons may be that soil #3 contains more finer particles than soil # 2, and soil #2 contains more finer particles than soil #1. Therefore, the amount of contaminants in soil #3 is larger than those of soil #2 and soil #1. Similarly, amount of contaminants in soil #2 is larger than soil #1.
2. Of the three soils, soil #1 requires a lesser amount of power and surfactant concentration than for soil #2 and soil #3. More finer particles need more surfactant to remove contaminants.

3. Ridge analysis shows that for all three soils, the optimum conditions do not fall within the experimental region. This indicates that additional experiments should be conducted in order to find the optimum conditions.

he comparison of the fitting parameters for the models using full quadratic regression Refer Table 14) shows that soil #1 and soil # 2 almost follow the same trend whereas soil 3 differs from soil # 1 and soil #2. Figures 8, 9 and 10 show the comparison between the bserved values and predicted values using the Procedure Regression analysis for the verall models of soil #1, soil #2 and soil #3.

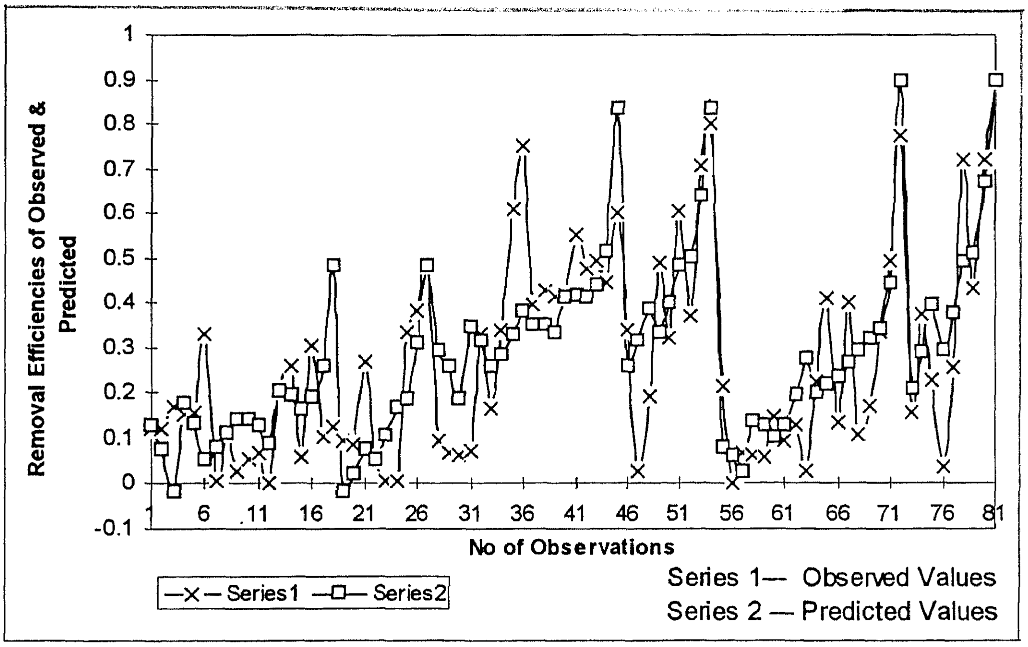

Fig. 8: The Comparison between the Observed values and Predicted Values Using Regression Procedure Analysis for the Overall Model, Soil #1

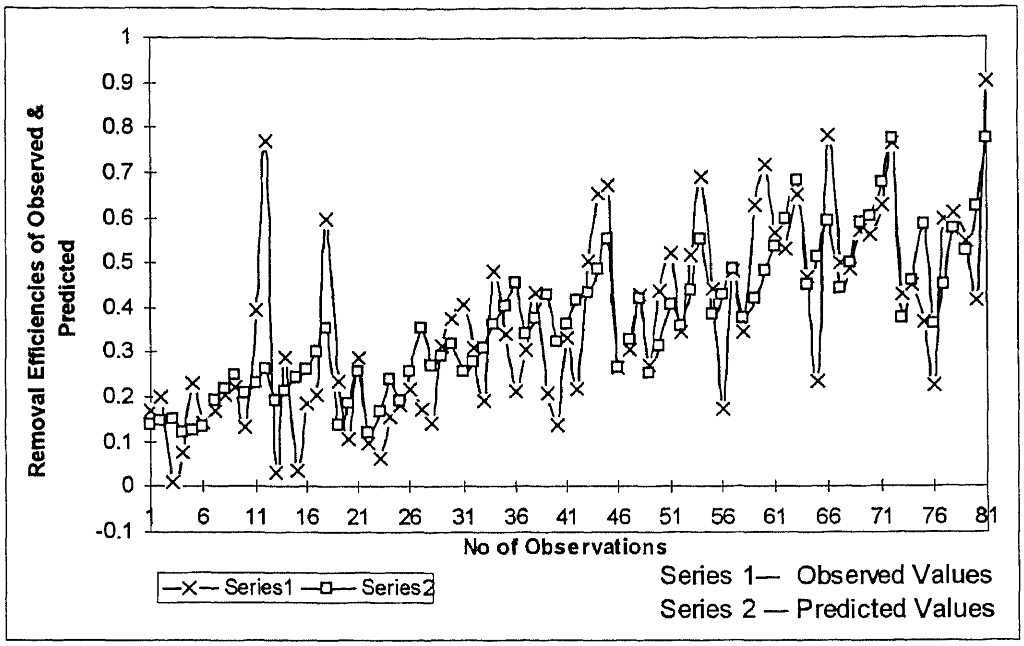

Fig. 9: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for the Overall Model, Soil #2

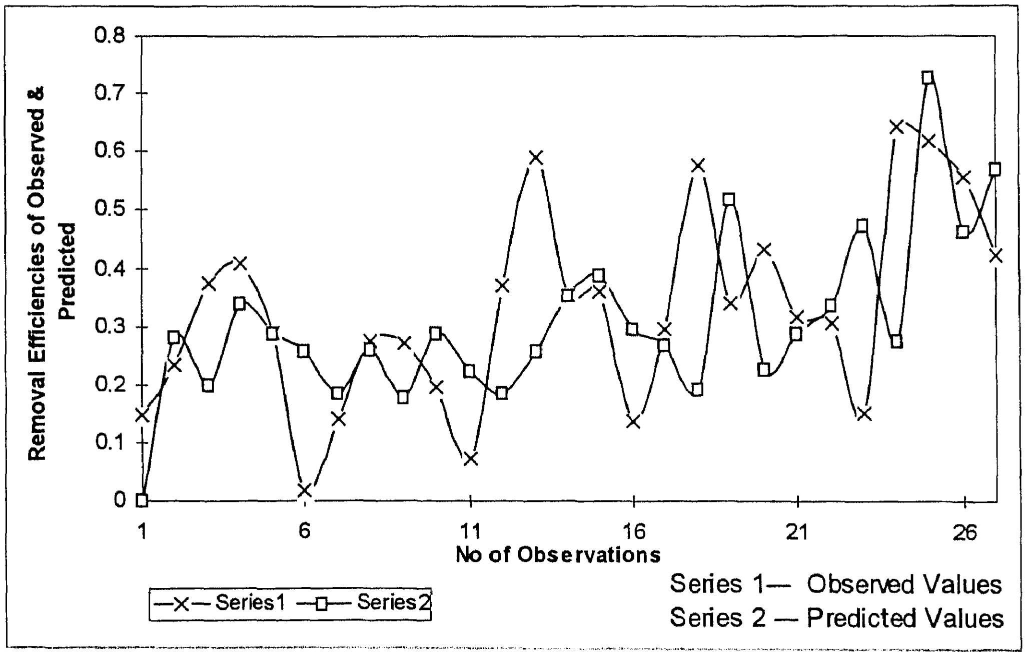

Fig. 10: The Comparison between the Observed values and Predicted Values Using Regression Procedure Analysis for the Overall Model, Soil #3

CHAPTER 8

SUMMARY AND CONCLUSIONS

- Although the probe type ultrasound source has disadvantages over the tank type, the system temperature cannot be held constant, the probe-in-beaker approach is appropriate for the application of ultrasound to the soil -suspension because of higher local intensity of the source.

- Base line operation was established to set the operating conditions under which the ultrasonic enhancement of the extraction is pronounced and reproducible. From the above study, it transpired that the contributing factors found during base line testing are the important factors: power, solvent to soil ratio, surfactant concentration, and sonification time. They were the most appropriate for the use in the factorial design and for the statistical analysis.

- In the cases of soil #1 and soil #2, a full factorial design was performed in order to analyze the interactions. The study showed that the third and fourth order interactions could be neglected. Therefore, in the case of soil #3, it became possible to perform a fractional factorial by neglecting the higher order interactions to economize on the number of the experimental runs.

- The mass balances for each set of experiments were checked by the analytical method. They were found to be in the range from 60 to 140 percent and therefore, the conclusion was that the tests were successful. Since EPA Method 8270 was employed to determine the concentrations of 8 PAHs, for statistical analysis, only 8 PAHs were considered.

- From the results of soil #1, ultrasound application produced 90% removal efficiency at the optimum surfactant to soil ratio of 0.25 at 50% power for 30 minutes whereas mechanical stirring produced 25% removal efficiency at the optimum surfactant to soil ratio of 1 (4% surfactant concentration) under similar conditions. Therefore, it can be concluded that the application of ultrasound energy can enhance soil washing with reduced surfactant dosages.

- From the procedure that was adopted to analyze the data without the statistical analysis, it showed that the maximum removal efficiency was obtained at 30 min. dwell time, 50% power, 1% surfactant concentration and 25:1 to 50:1 solvent to soil ratio for soil #1. Whereas for soil #2, the maximum removal efficiency was obtained at the same conditions except for higher solvent to soil ratio. Soil #2 required 50:1 solvent to soil ratio. Since soil #2 contained finer particles, it needed more surfactant to remove the contaminants. Soil #3 also agrees with the above conclusion.

- GLM procedure suggests that for the overall model of soil #1, power, solvent to soil ratio, and surfactant are the significant factors. For the overall model of soil #2, power, surfactant, and time are the significant factors. For the overall model of soil #3, power is the only significant factor. From these observations, it cannot be concluded that other factors are not important for soil #3. In order to come to a conclusion, it has to be compared with canonical analysis and ridge analysis. For higher order interactions (from third order), since the values of Pr>F are very high, they can be neglected. Therefore, the full quadratic model is complete enough for the regression analysis in order to find the model parameters. The individual components also confirm the conclusion.

- Canonical analysis reported that for all three soils, stationary points are saddle points. For the overall model of soil #1, the first largest component eigen vector corresponding to the largest eigen value is associated with power. This explains that the most significant factor is power. Similarly, for soil #2 and soil #3, the most significant factors are solvent to soil ratio and surfactant. Ridge analysis concluded same as the GLM. Therefore, it can be concluded that for the overall model of soil #1, the significant factors are power, solvent to soil ratio and surfactant. For soil #2, significant factors are power, solvent to soil ratio, surfactant and time. For soil #3, significant factors are power and surfactant. Most of the individual components also behave the same way as overall model.

- Although the canonical analysis indicates that the response surfaces have saddle points and do not have a unique optimum, the ridge analysis indicates that maximum yields will result from relatively high reaction power, high reaction solvent to soil ratio, high reaction surfactant concentration and high reaction time for the overall models of soil #1 and soil #2 and the individual PAHs of soil #1 and soil #2. However, for soil #3, the maximum yields will result in relatively high reaction power, high reaction solvent to soil ratio, high reaction surfactant concentration and low time.

Finally, it can be concluded that when the particle size decreases, more surfactant is needed to remove contaminants, and in such cases, surfactant concentration becomes more significant than others. The procedure, which is adopted to analyze the data without the statistical analysis, clearly indicated that the maximum removal efficiency could be obtained at the optimum condition of 50% power, 50:1 solvent to soil ratio, 1% surfactant concentration and 30 min. time. This is because the maximum design values are 50% power, 50:1 solvent to soil ratio, 1% surfactant concentration and 30 minute time. If the maximum design values are extended, then the optimum condition will increase. The ridge analysis also shows that for all three types of soils, the optimum conditions have not fall within the experimental region. This indicates that further experiments should be conducted in order to find the optimum conditions. For soil #3, time will decrease to get the maximum removal at optimum conditions. In order to conduct the further experiments, the power settings have to be increased beyond 50% and surfactant concentration has to be increased beyond 1%. Economically, it is not advisable to conduct further experiments in order to get the optimum conditions. Therefore, within the experimental range, the optimum conditions were selected as shown in Table 15.

Table 15: Maximum Removal at Optimum Conditions

Soil Type	Maximum Response (%)	Optimum Power (%)	Optimum Solvent to soil ratio	Optimum Surfactant (%)	Optimum time (min.)
Soil #1	83.808	31.9431	42.10589	0.69147	25.54845
Soil #2	62.621	39.6618	31.46554	0.867194	21.7443
Soil #3	37.6718	34.24122	32.6198	0.889232	11.3296

Future Research

Since the bench scale study showed that ultrasound can enhance the soil washing process at a reduced surfactant dosage, it is proposed to performed a pilot scale demonstration. This demonstration will be for a system with continuous treatment.

APPENDIX A

THE PLOTS SHOW THE VARIATIONS OF REMOVAL EFFICIENCIES WITH 12 PAHs AT DIFFERENT CONDITIONS FOR SOIL #1

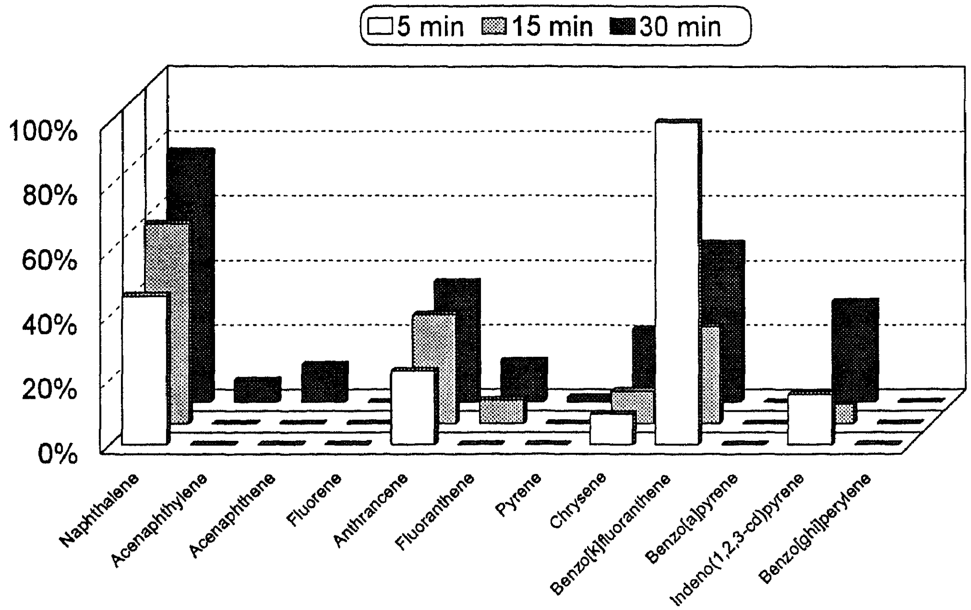

Fig. A.1: Removal Efficiencies of PAHs for Different Dwell Times
(0% Power, 10:1 Solvent to Soil Ratio, and 0.01% Surfactant Concentration)

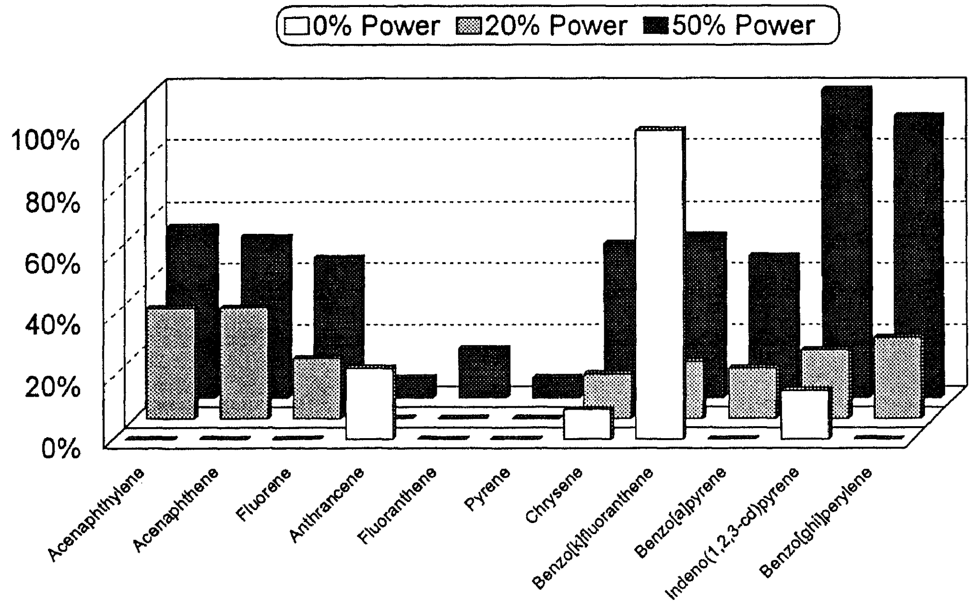

Fig. A.2: Removal Efficiencies of PAHs for Different Ultrasound Powers
(10:1 Solvent to Soil Ratio, 0.01% Surfactant Concentration, and 5min. Dwell Time)

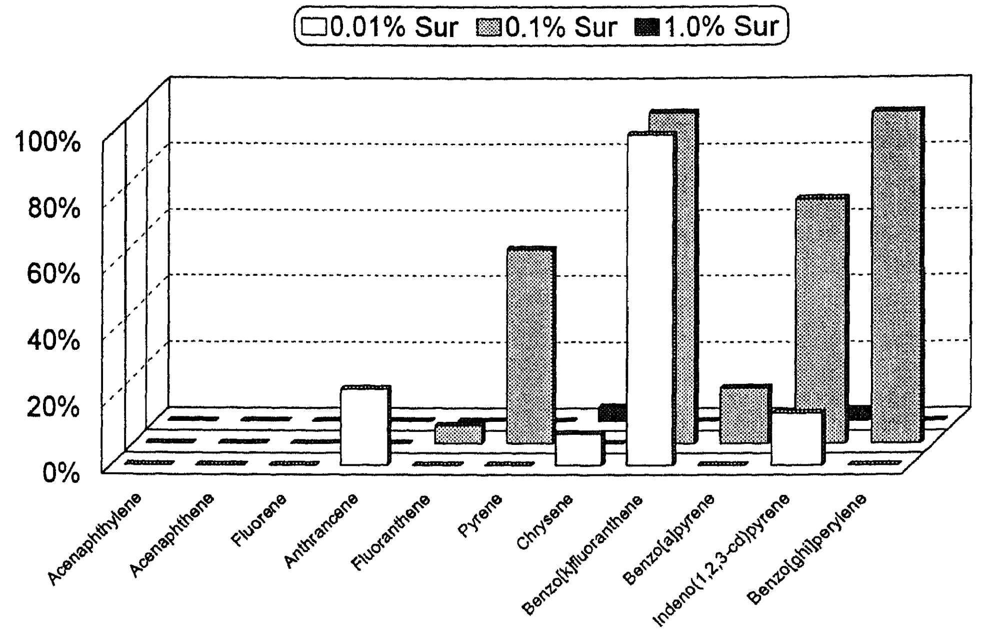

Fig. A.3: Removal Efficiencies of PAHs for Different Surfactant Concentrations (10:1 Solvent to Soil Ratio, 0% Power, and 5min. Dwell Time)

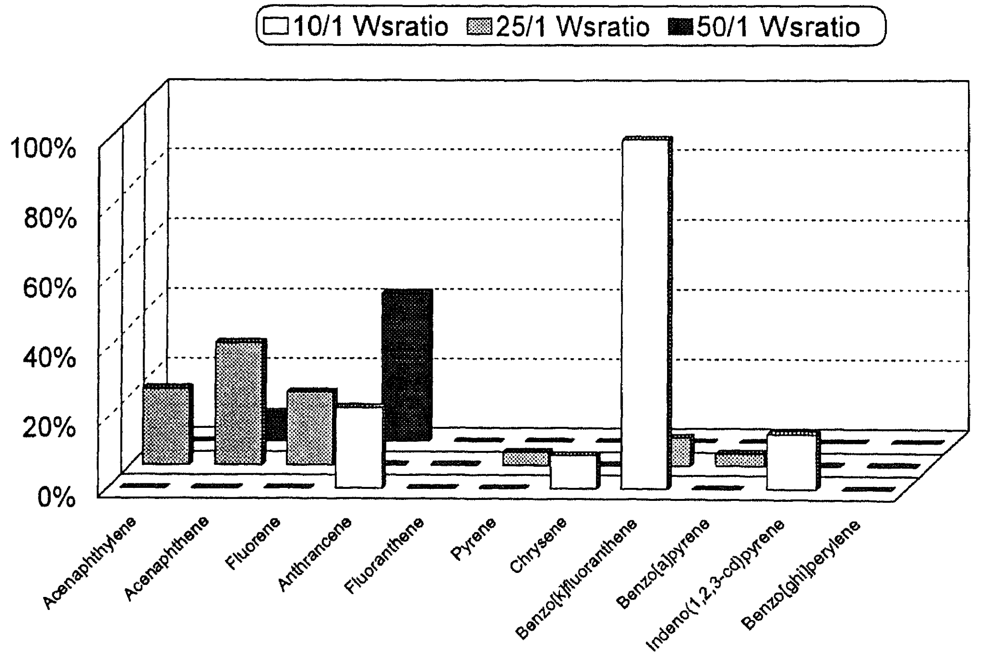

Fig. A.4: Removal Efficiencies of PAHs for Different Solvent to Soil Ratios (0% Power, 0.01% Surfactant Concentration, and 5min. Dwell Time)

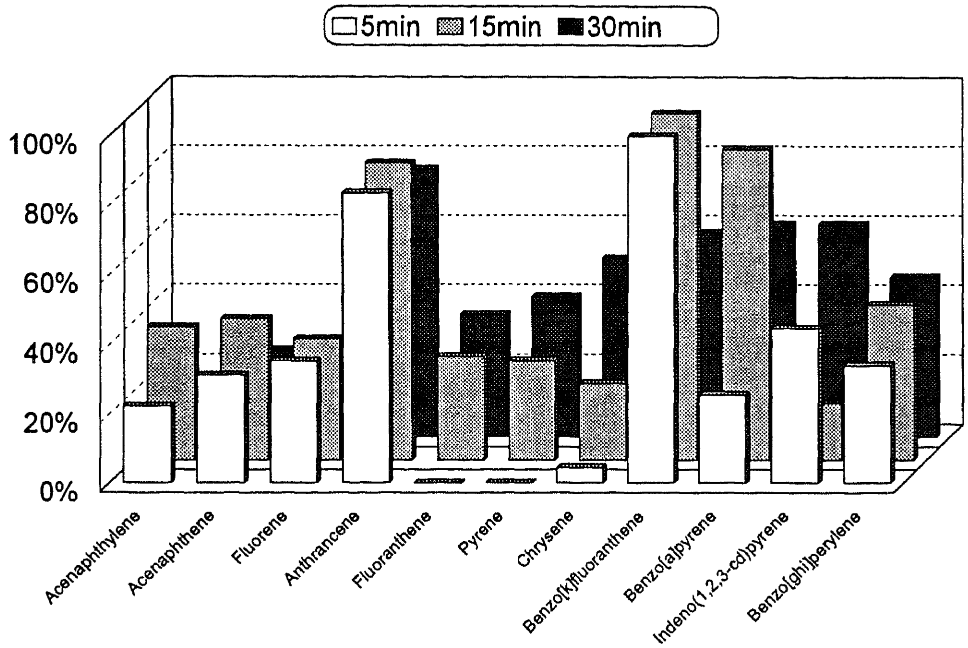

Fig. A.5: Removal Efficiencies of PAHs for Different Dwell Times
(20% Power, 25:1 Solvent to Soil Ratio, and 0.1% Surfactant Concentration)

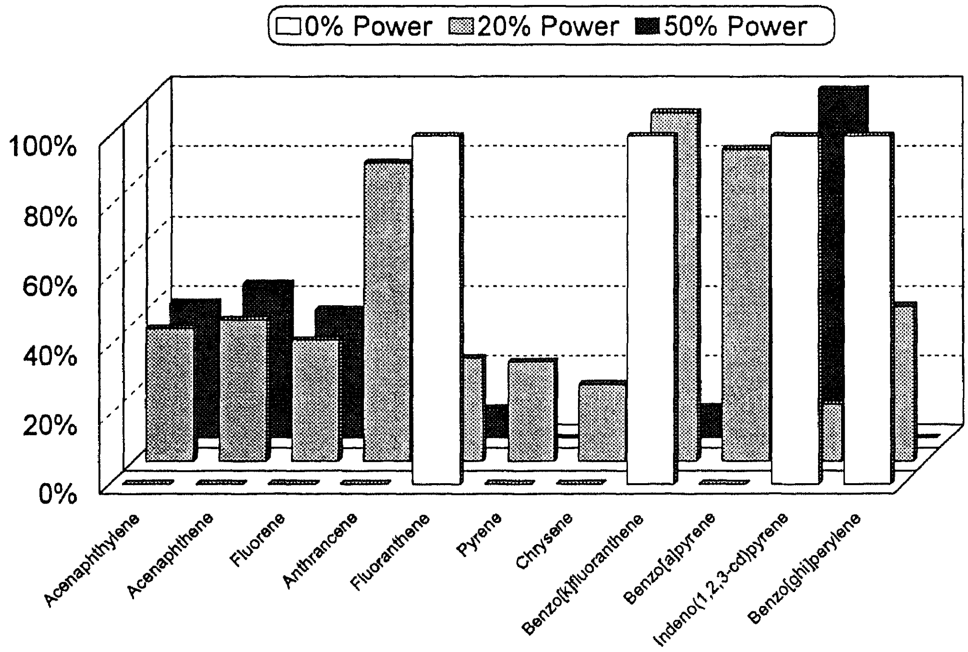

Fig. A.6: Removal Efficiencies of PAHs for Different Ultrasonic Powers
(25:1 Solvent to Soil Ratio, 0.1% Surfactant Concentration, and 15min. Dwell Time)

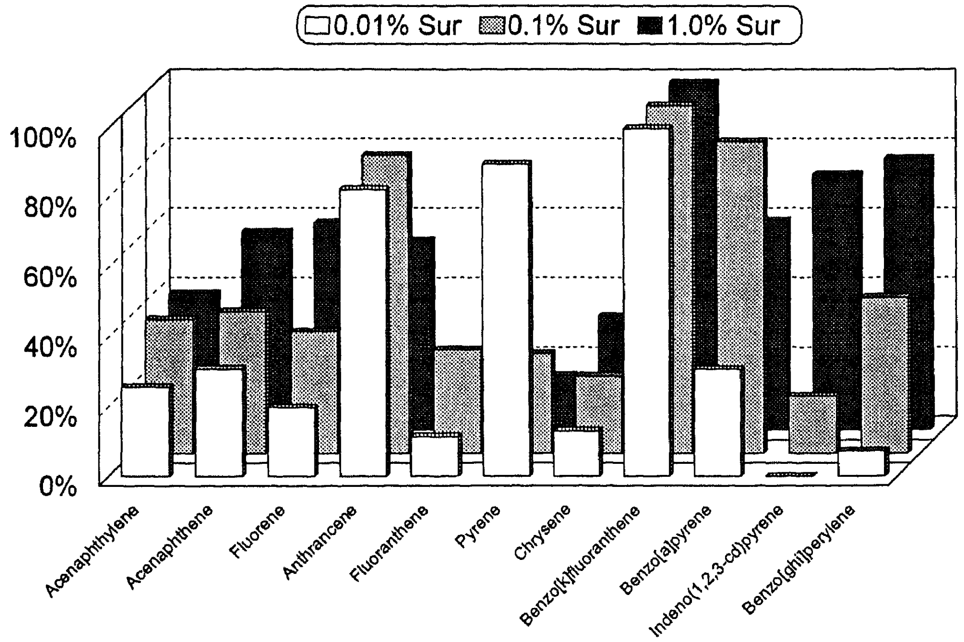

Fig. A.7: Removal Efficiencies of PAHs for Different Surfactant Concentrations (20% Power, 25:1 Solvent to Soil Ratio, and 15min. Dwell Time)

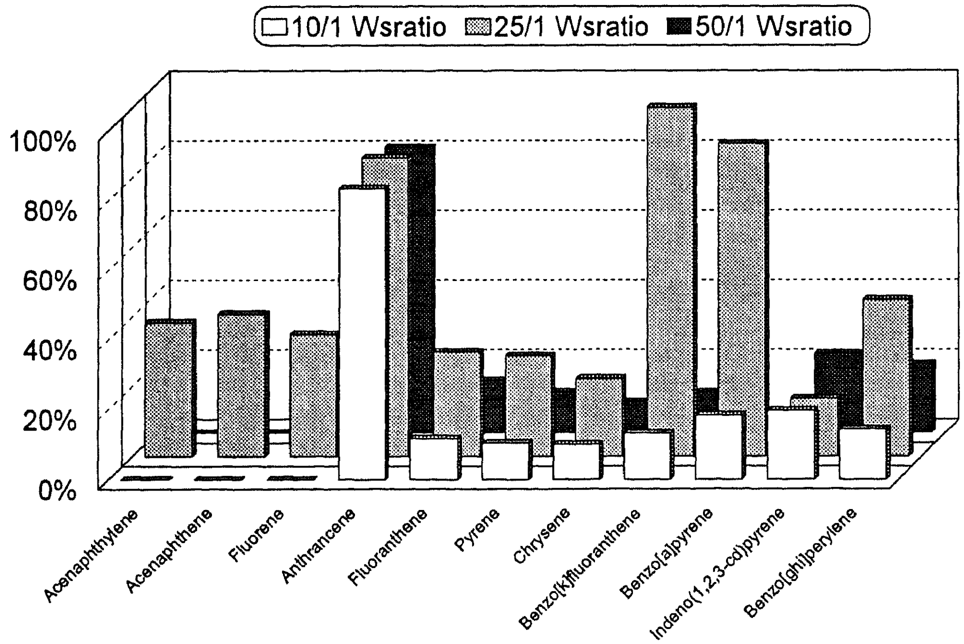

Fig. A.8: Removal Efficiencies of PAHs for Different Solvent to Soil Ratios (20% Power, 0.1% Surfactant Concentration, and 30min. Dwell Time)

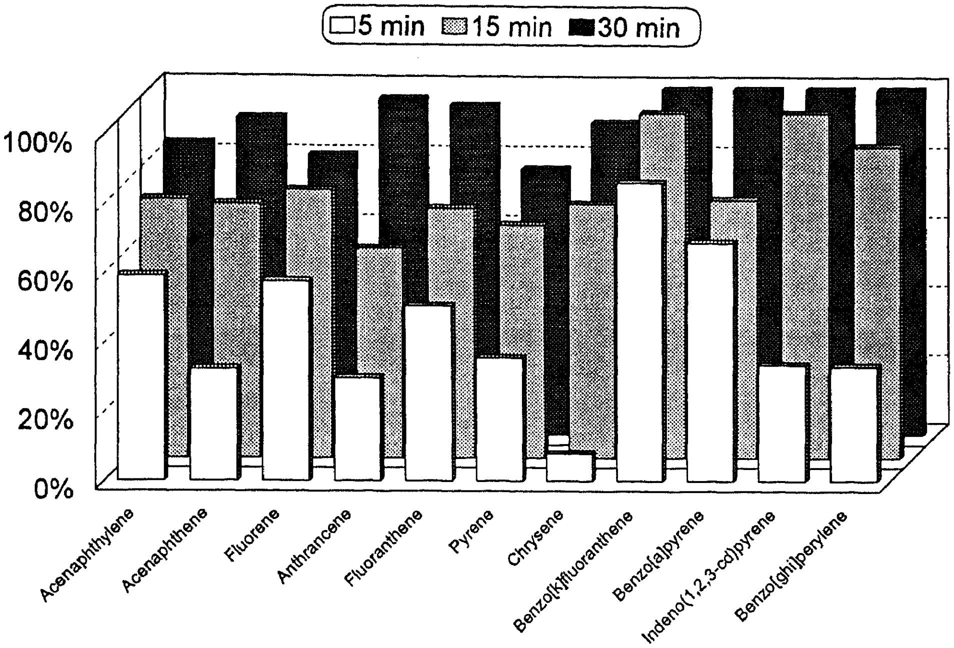

Fig. A.9: Removal Efficiencies of PAHs for Different Dwell Times
(50% Power, 50:1 Solvent to Soil Ratio, and 1% Surfactant Concentration)

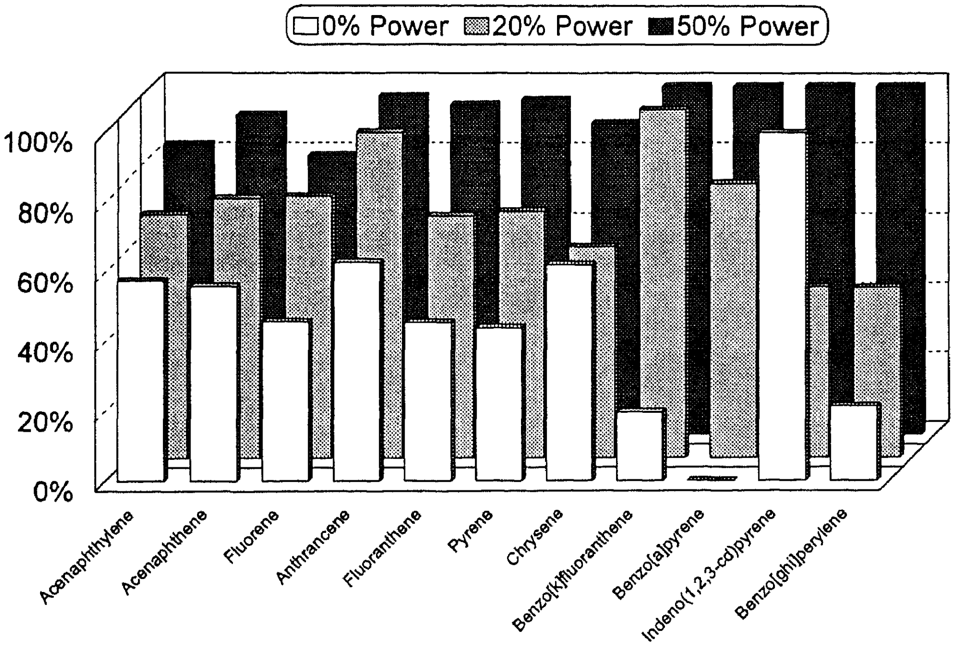

Fig. A.10: Removal Efficiencies of PAHs for Different Ultrasound Powers
(50:1 Solvent to Soil Ratio, 1% Surfactant Concentration, and 30min. Dwell Time)

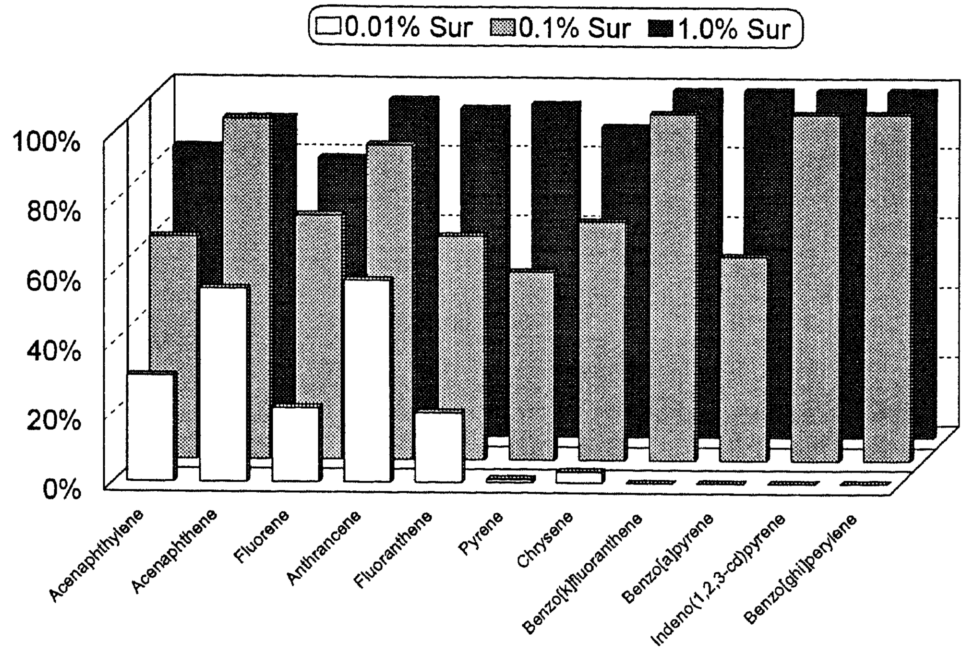

Fig. A.11: Removal Efficiencies of PAHs for Different Surfactant Concentrations (50% Power, 50:1 Solvent to Soil Ratio, and 30min. Dwell Time)

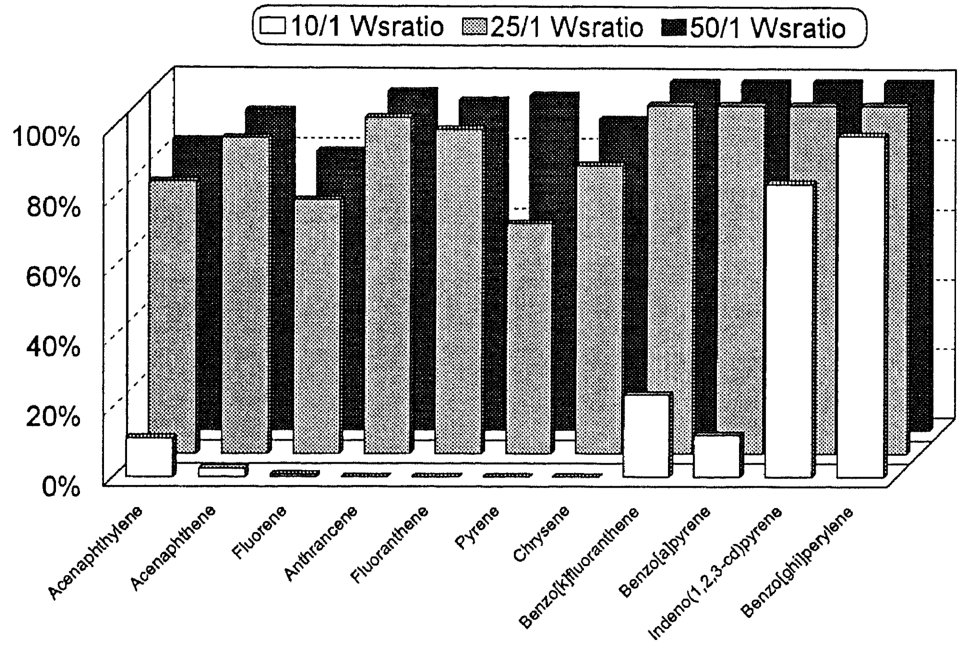

Fig. A.12: Removal Efficiencies of PAHs for Different Solvent to Soil Ratios (50% Power, 1% Surfactant Concentration, and 30min. Dwell Time)

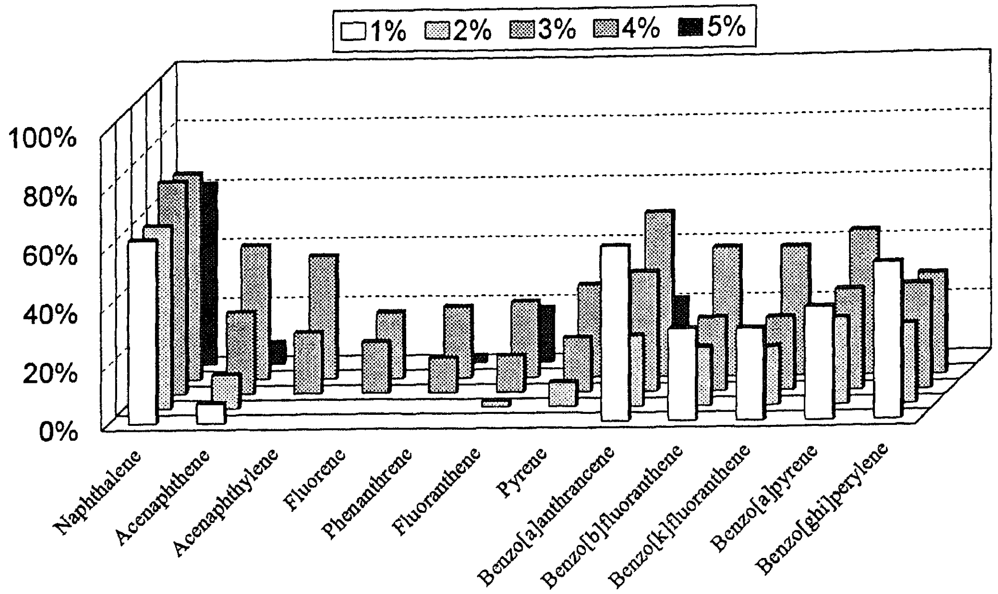

Fig. A.13: Removal Efficiencies of PAHs for Different Surfactant Concentrations (0 Power, 25:1 Solvent to Soil Ratio, and 30min. Dwell Time)

APPENDIX B

THE PLOTS SHOW THE VARIATIONS OF REMOVAL EFFICIENCIES WITH 11 PAHs AT DIFFERENT CONDITIONS FOR SOIL #2

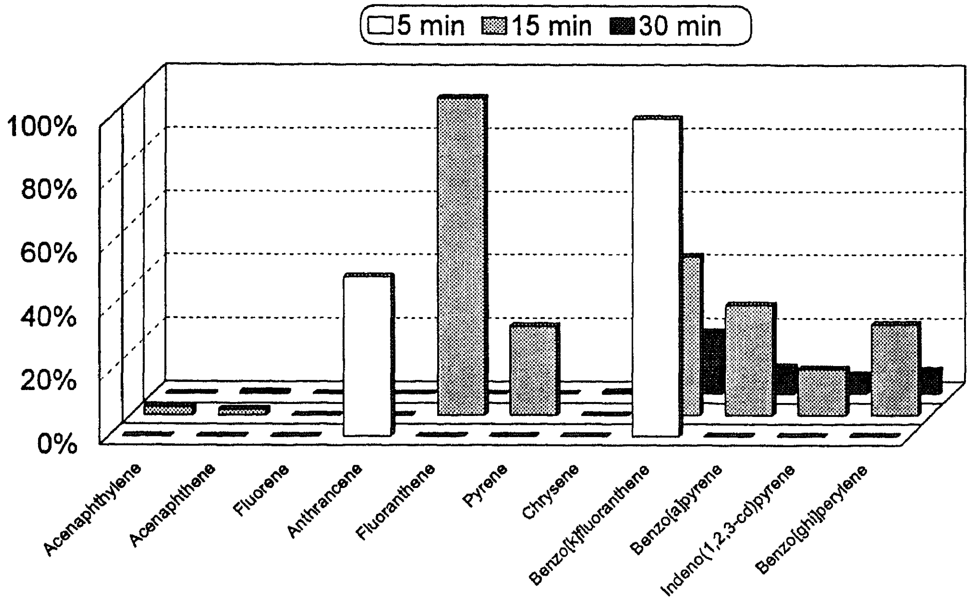

Fig. B.1: Removal Efficiencies of PAHs for Different Dwell Times
(0% Power, 10:1 Solvent to Soil Ratio, and 0.01% Surfactant Concentration)

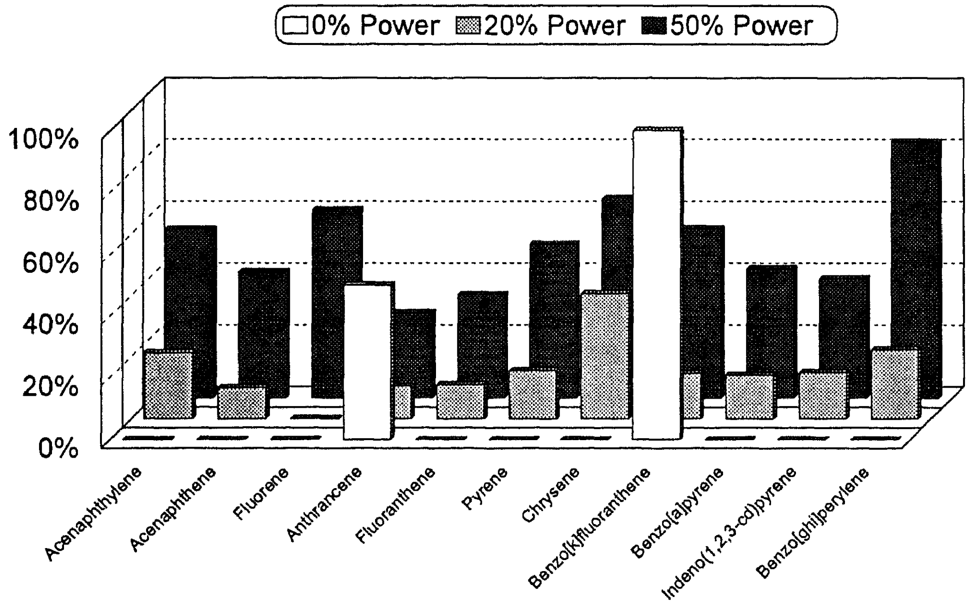

Fig. B.2: Removal Efficiencies of PAHs for Different Ultrasound Powers
(10:1 Solvent to Soil Ratio, 0.01% Surfactant Concentration, and 5min. Dwell Time)

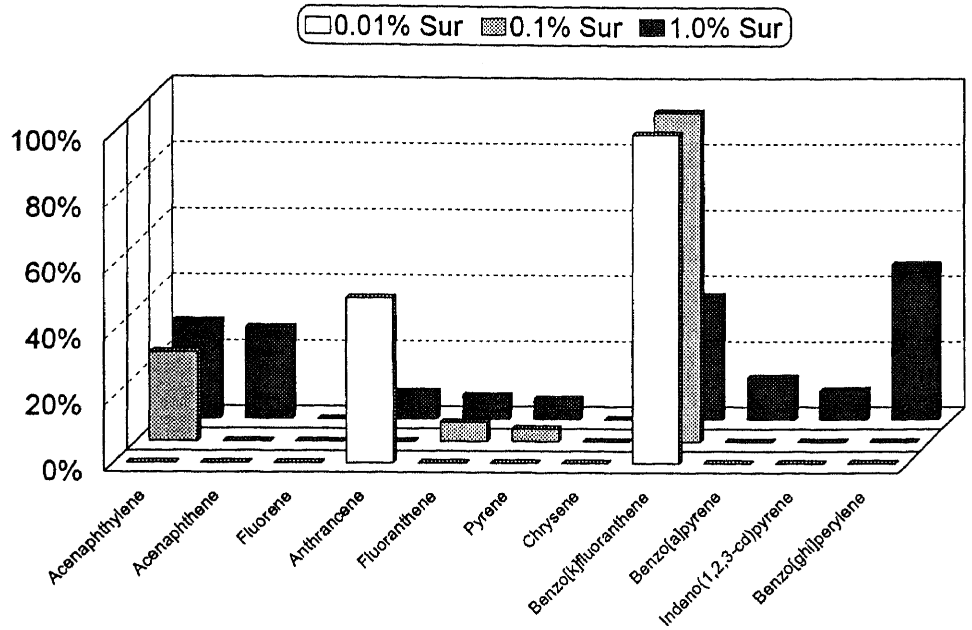

Fig. B.3: Removal Efficiencies of PAHs for Different Surfactant Concentrations (10:1 Solvent to Soil Ratio, 0% Power, and 5min. Dwell Time)

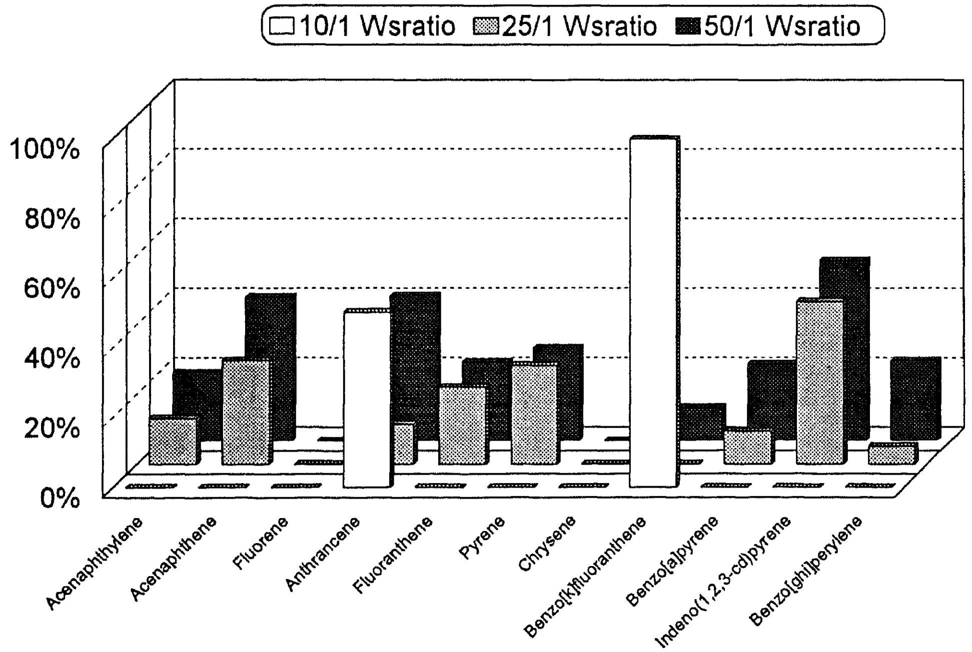

Fig. B.4: Removal Efficiencies of PAHs for Different Solvent to Soil Ratios (0% Power, 0.01% Surfactant Concentration, and 5min. Dwell Time)

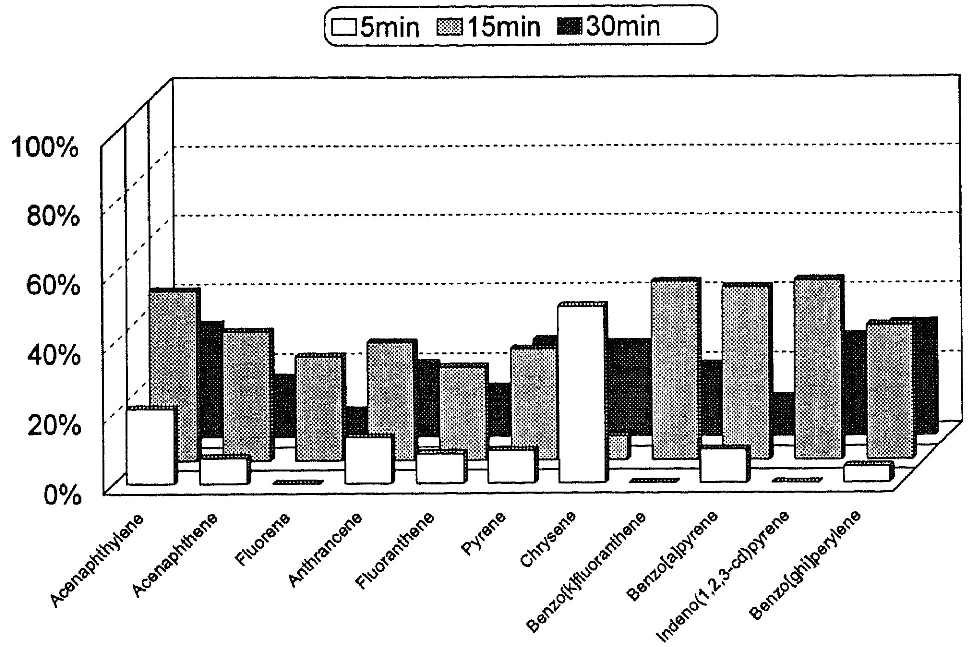

Fig. B.5: Removal Efficiencies of PAHs for Different Dwell Times
(20% Power, 25:1 Solvent to Soil Ratio, and 0.1% Surfactant Concentration)

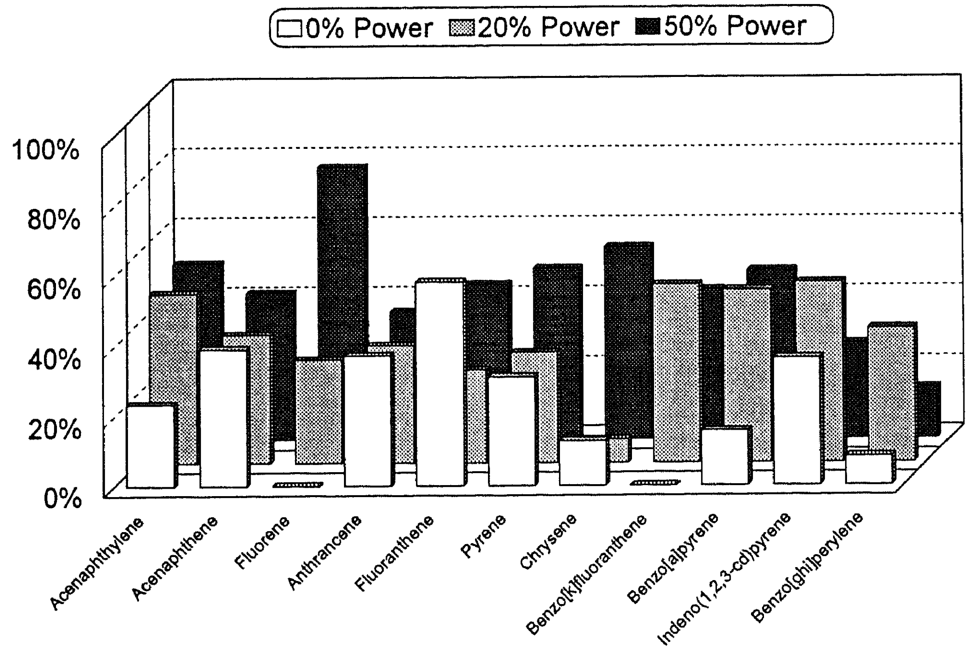

Fig. B.6: Removal Efficiencies of PAHs for Different Ultrasonic Powers
(25:1 Solvent to Soil Ratio, 0.1% Surfactant Concentration, and 15min. Dwell Time)

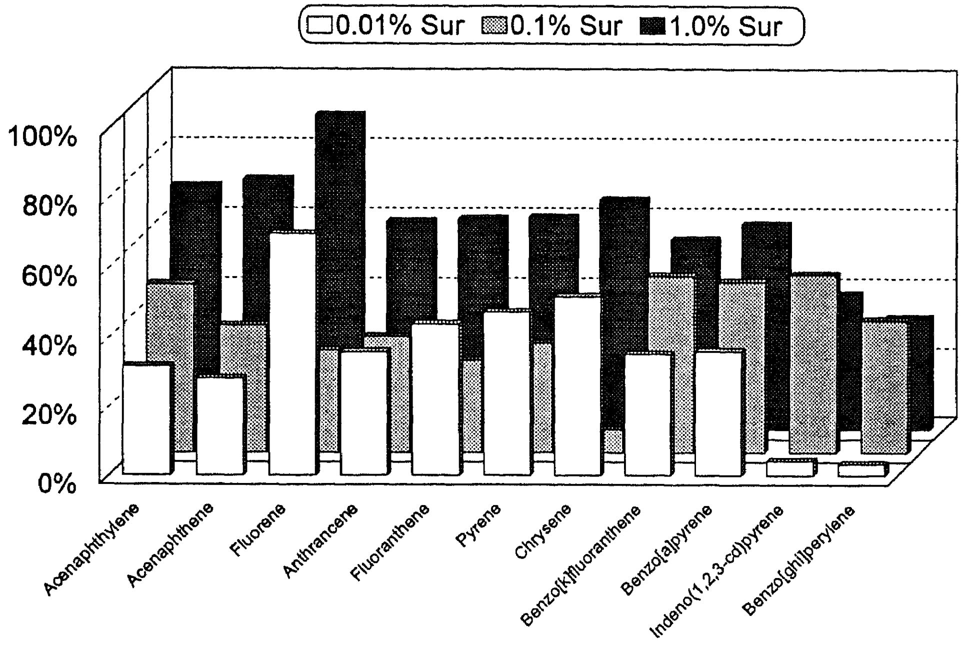

Fig. B.7: Removal Efficiencies of PAHs for Different Surfactant Concentrations (20% Power, 25:1 Solvent to Soil Ratio, and 15min. Dwell Time)

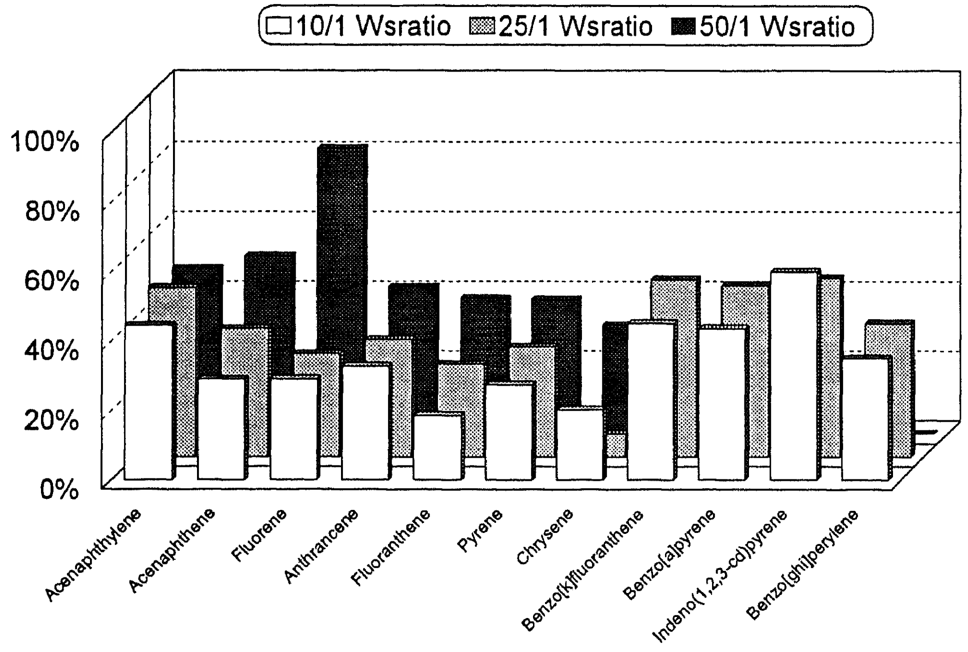

Fig. B.8: Removal Efficiencies of PAHs for Different Solvent to Soil Ratios (20% Power, 0.1% Surfactant Concentration, and 30min. Dwell Time)

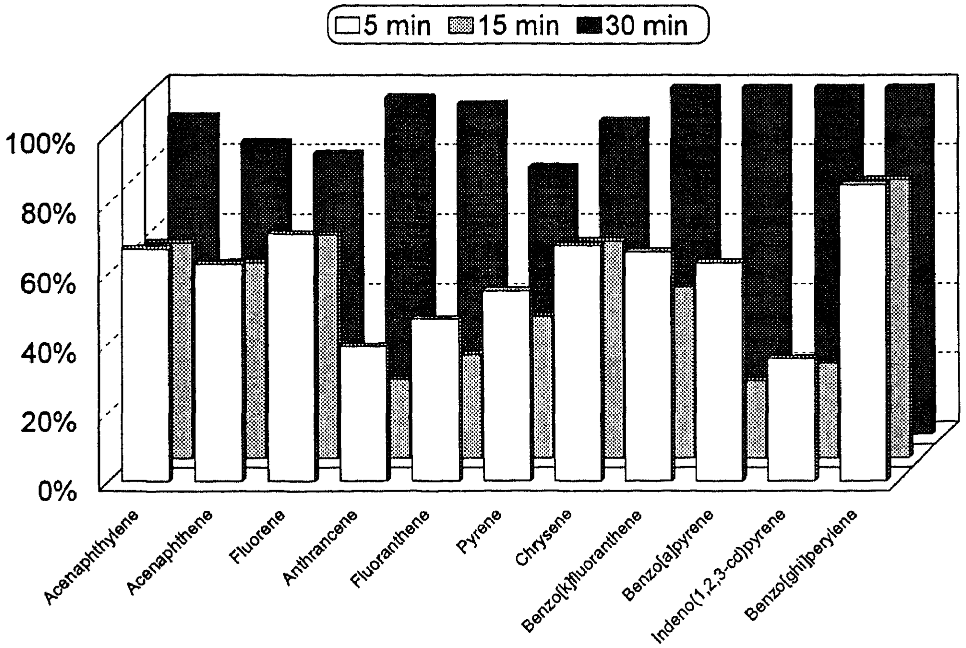

Fig. B.9: Removal Efficiencies of PAHs for Different Dwell Times
(50% Power, 50:1 Solvent to Soil Ratio, and 1% Surfactant Concentration)

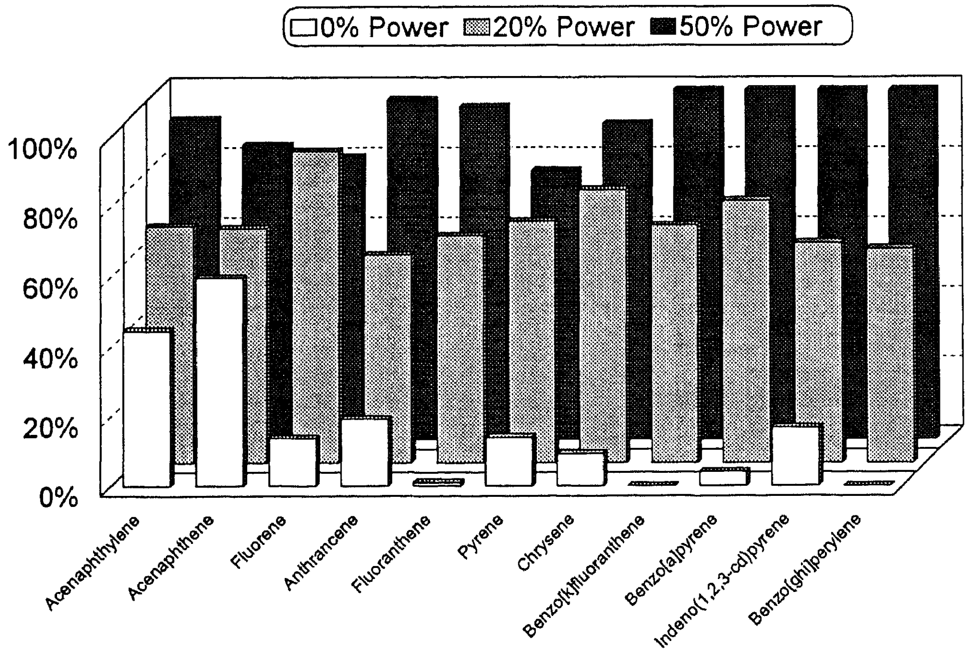

Fig. B.10: Removal Efficiencies of PAHs for Different Ultrasound Powers
(50:1 Solvent to Soil Ratio, 1% Surfactant Concentration, and 30min. Dwell Time)

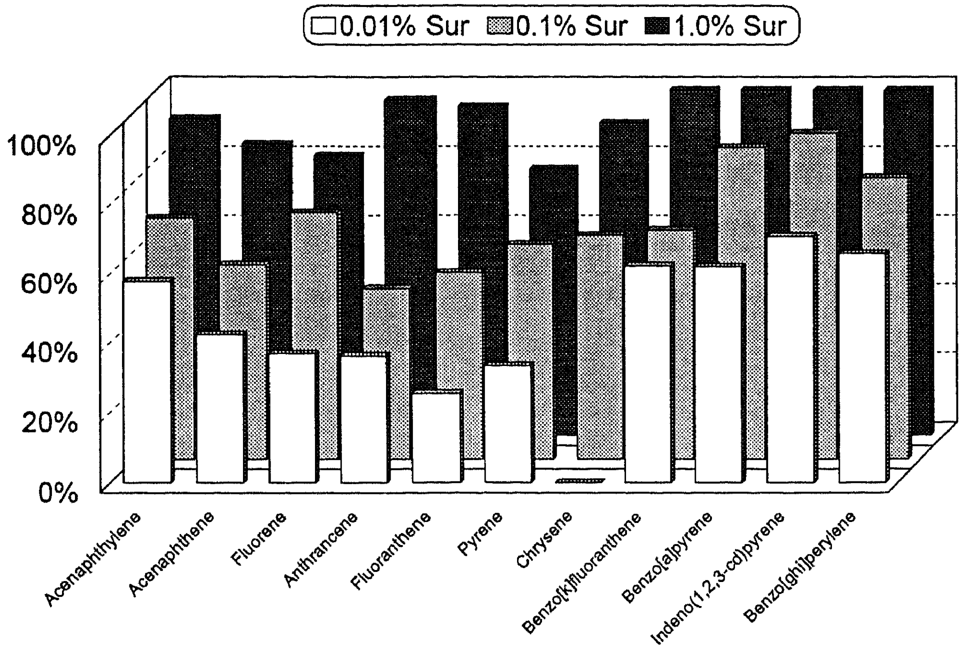

Fig. B.11: Removal Efficiencies of PAHs for Different Surfactant Concentrations (50% Power, 50:1 Solvent to Soil Ratio, and 30min. Dwell Time)

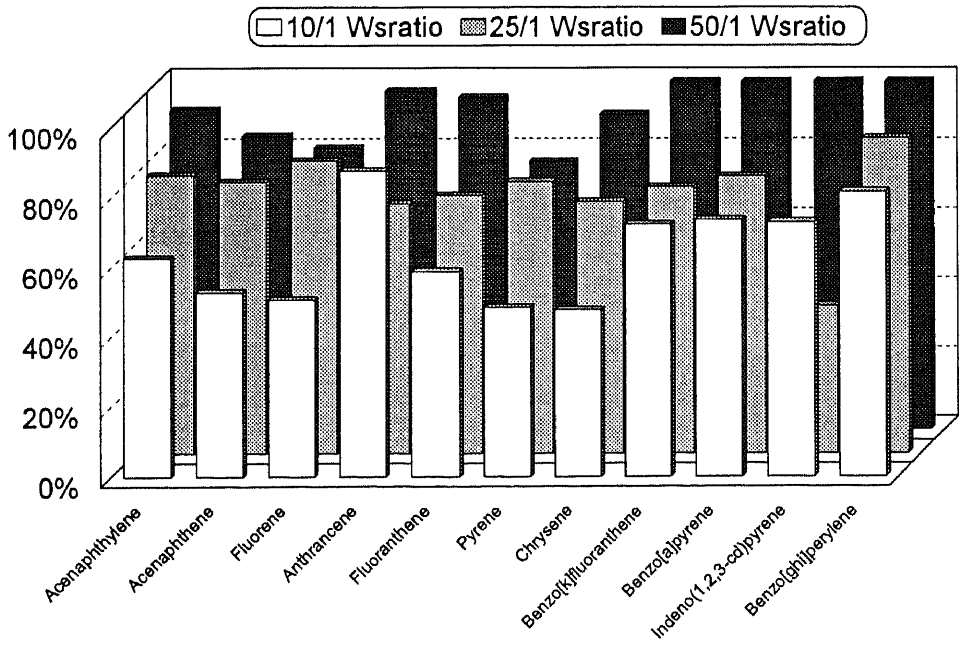

Fig. B.12: Removal Efficiencies of PAHs for Different Solvent to Soil Ratios (50% Power, 1% Surfactant Concentration, and 30min. Dwell Time)

APPENDIX C

THE PLOTS SHOW THE VARIATIONS OF REMOVAL EFFICIENCIES WITH 14 PAHs AT DIFFERENT CONDITIONS FOR SOIL #3

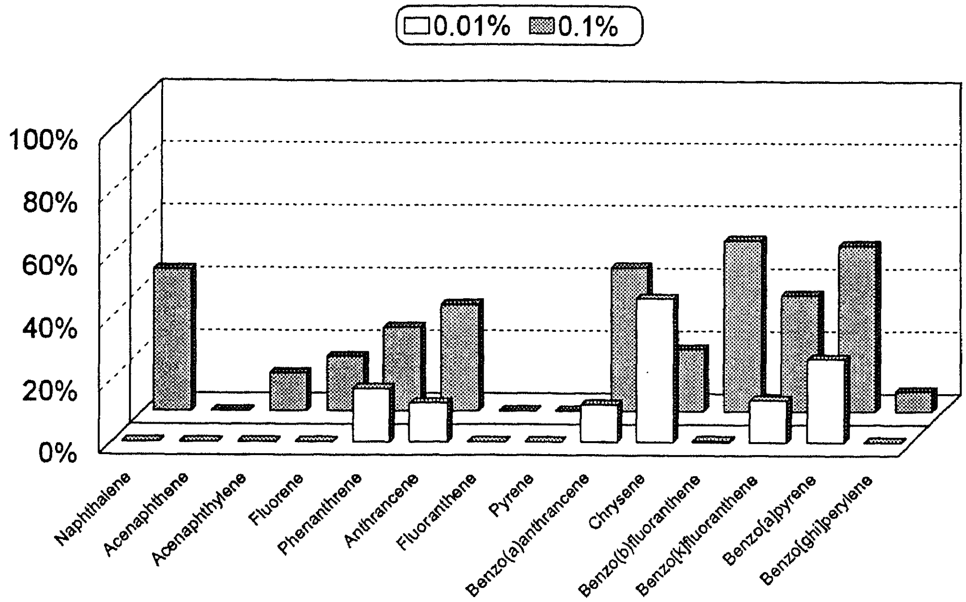

Fig. C.1: Removal Efficiencies of PAHs for Different Surfactant Concentrations (0% Power, 10:1 Solvent to Soil Ratio, and 15min. Dwell Time)

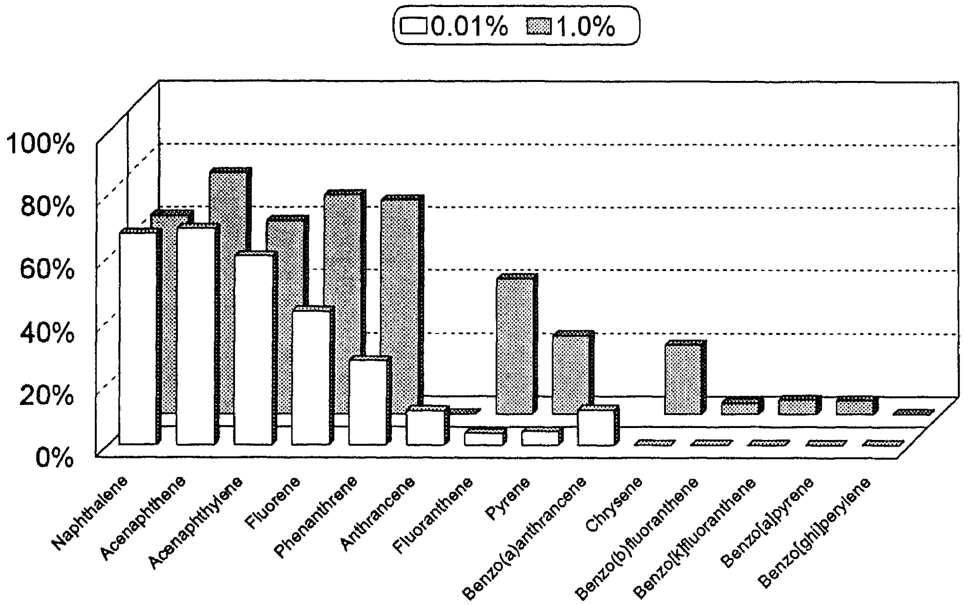

Fig. C.2: Removal Efficiencies of PAHs for Different Surfactant Concentrations (0% Power, 50:1 Solvent to Soil Ratio, and 5min. Dwell Time)

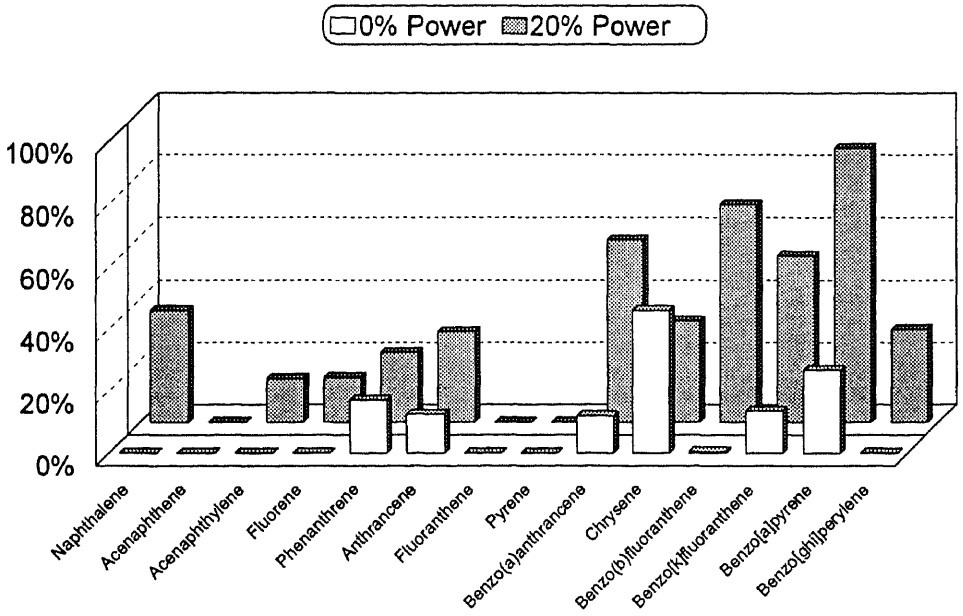

Fig. C.3: Removal Efficiencies of PAHs for Different Ultrasound Powers (10:1 Solvent to Soil Ratio, 0.01% Surfactant Concentrations, and 5min. Dwell Time)

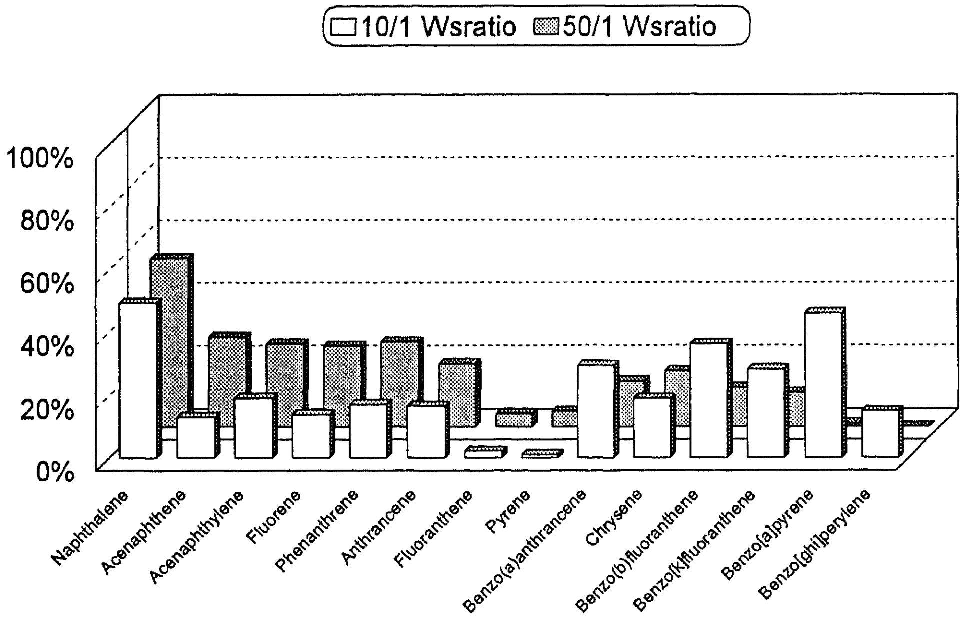

Fig. C.4: Removal Efficiencies of PAHs for Different Solvent to Soil Ratios (20% Power, 0.01% Surfactant Concentration, and 15min. Dwell Time)

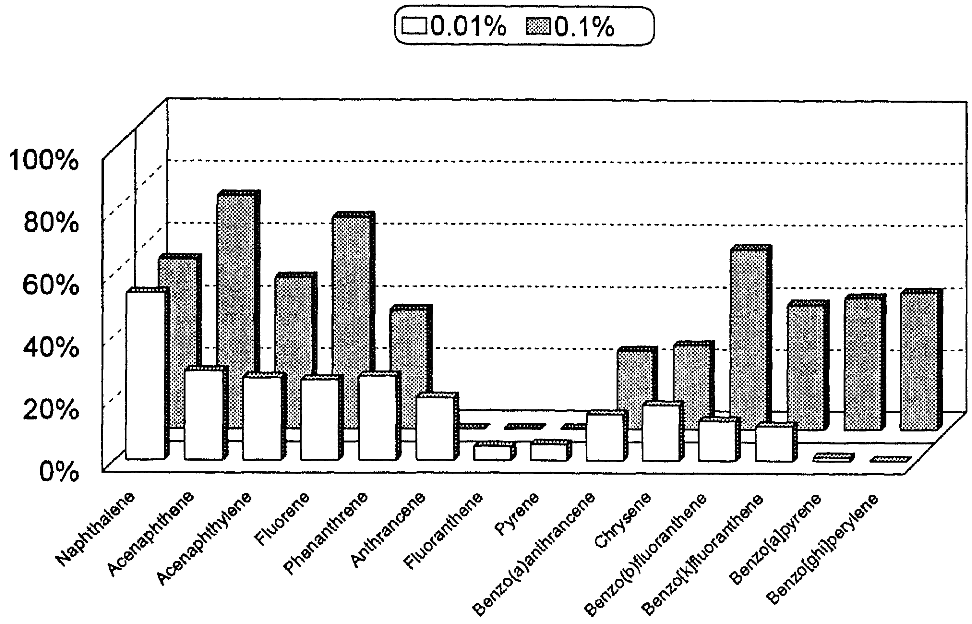

Fig. C.5: Removal Efficiencies of PAHs for Different Surfactant Concentrations (20% Power, 50:1 Solvent to Soil Ratio, and 15min. Dwell Time)

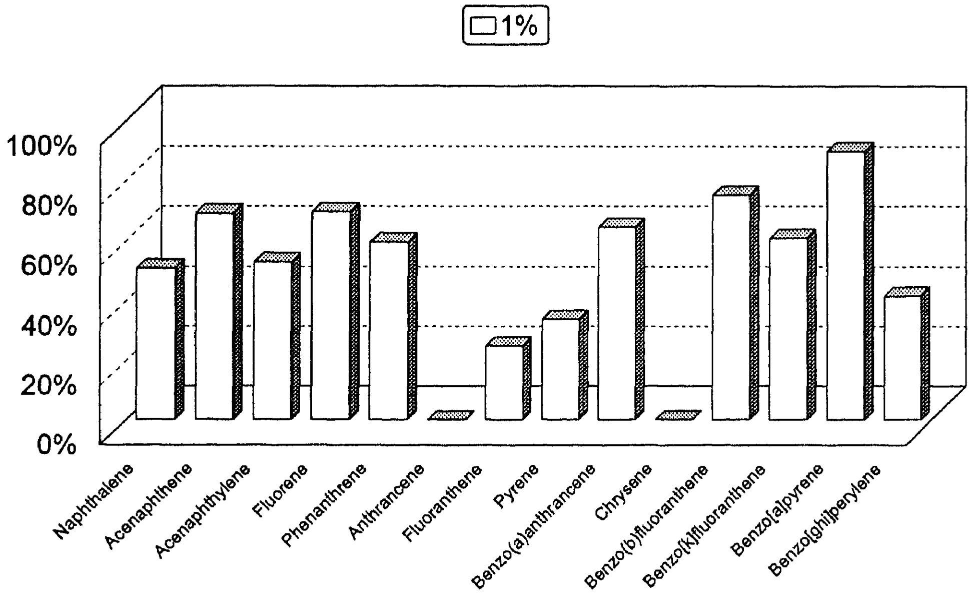

Fig. C.6: Removal Efficiencies of PAHs for 1% Surfactant Concentration (50% Power, 50:1 Solvent to Soil Ratio, and 30min. Dwell Time)

APPENDIX D

THE STATISTICAL ANALYSIS RESULTS OF OVERALL MODEL USING GLM PROCEDURE FOR SOIL #1, SOIL #2, AND SOIL #3

Table D.1: General Linear Models Procedure for Soil #1

Source	Degree of Freedom	Sum of Squares	Mean Squares	F Value	Pr > F
Model	64	4.829913	0.075468	5.82	0.0001
Error	38	0.493099	0.012976		
Corrected total	102	5.323012			
	R-Square	Coefficient of Variation	Root MSE	Removal Mean	
	0.907365	41.87715	0.11391	0.27202	
		Type I SS			
Source	Degree of Freedom	Sum of Squares	Mean Squares	F Value	Pr > F
Power	2	1.000475	0.500238	38.55	0.0001
Wsratio	2	0.767131	.383566	29.56	0.0001
Surfact	2	0.701568	0.350784	27.03	0.0001
Time	2	0.148714	0.074357	5.73	0.0067
(Power*Wsratio)	4	0.329447	0.082362	6.35	0.0005
(Power*Surfact)	4	0.182372	0.045593	3.51	0.0155
(Power*Time)	4	0.059923	0.014981	1.15	0.3461
(Wsratio*Surfact)	4	0.243201	0060800	4.69	0.0036
(Wsratio*Time)	4	0.256999	0.064250	4.95	0.0026
(Surfact*Time)	4	0.166329	0.041582	3.20	0.0231
(Power*Wsratio*Surfact)	8	0.450037	0.056255	4.35	0.0009
(Power*Wsratio*Time)	8	0.181012	0.022626	1.74	0.1198
(Wsratio. *Surfact*Time)	8	0.166600	0.020825	1.60	0.1559
(Power*Surfact*Time)	8	0.176106	0.022013	1.70	0.1311

Table D.2: General Linear Models Procedure for Soil #2

Source	Degree of Freedom	Sum of Squares	Mean Squares	F Value	Pr > F
Model	64	3.341416	0.052210	2.38	0.0043
Error	32	0.701402	0.021919		
Corrected total	96	4.042818			
	R-Square	Coefficient of Variation	Root MSE	Removal Mean	
	0.826507	40.09229	0.14805	0.36927	
		Type I SS			
Source	Degree of Freedom	Sum of Squares	Mean Squares	F Value	Pr > F
Power	2	1.562800	0.781400	35.65	0.0001
Wsratio	2	0.113362	0.056681	2.59	0.0910
Surfact	2	0.323298	0.161649	7.37	0.0023
Time	2	0.231352	0.115676	5.28	0.0105
(Power*Wsratio)	4	0.073770	0.018442	0.84	0.5093
(Power*Surfact)	4	0.181618	0.045405	2.07	0.1078
(Power*Time)	4	0.091020	0.022755	1.04	0.4029
(Wsratio*Surfact)	4	0.104091	0.026023	1.19	0.3352
(Wsratio*Time)	4	0.086698	0.021674	0.99	0.4277
(Surfact*Time)	4	0.089069	0.022267	1.02	0.4139
(Power*Wsratio*Surfact)	8	0.082984	0.010373	0.47	0.8658
(Power*Wsratio*Time)	8	0.188107	0.023513	1.07	0.4062
(Wsratio*Surfact*Time)	8	0.120222	0.015028	0.69	0.7009
(Power*Surfact*Time)	8	0.093024	0.011628	0.53	0.8246

Table D.3: General Linear Models Procedure for Soil #3

Source	Degree of Freedom	Sum of Squares	Mean Squares	F Value	Pr > F
Model	26	0.907505	0.034904	2.13	0.2039
Error	5	0.081763	0.016353		
Corrected total	31	0.989268			
	R-Square	Coefficient of Variation	Root MSE	Removal Mean	
	0.917351	39.84807	0.12788	0.32091	
		Type I SS			
Source	Degree of Freedom	Sum of Squares	Mean Squares	F Value	Pr > F
Power	2	0.189658	0.094829	5.80	0.0498
Wsratio	2	0.073655	0.036827	2.25	0.2007
Surfact	2	0.031103	0.015552	0.95	0.4467
Time	2	0.047036	0.023518	1.44	0.3211
(Power*Wsratio)	4	0.130042	0.032510	1.99	0.2347
(Power*Surfact)	4	0.080525	0.020131	1.23	0.4037
(Power*Time)	4	0.056978	0.014245	0.87	0.5403
(Wsratio*Surfact)	4	0.155898	0.038975	2.38	0.1833
(Wsratio*Time)	2	0.040266	0.040266	2.46	0.1774
(Surfact*Time)	1	0.102344	0.102344	6.26	0.0544
(Power*Wsratio*Surfact)	0	0.000000	-	-	-
(Power*Wsratio*Time)	0	0.000000	-	-	-
(Wsratio*Surfact*Time)	0	0.000000	-	-	-
(Power*Surfact*Time)	0	0.000000	-	-	-

APPENDIX E

THE STATISTICAL ANALYSIS RESULTS OF EIGHT PAHs COMPONENTS USING PROG RSREG PROCEDURE FOR SOIL #1, SOIL #2, AND SOIL #3

Table E.1: Eigen Values and Eigen Vectors by Canonical Analysis for Acenaphthylene Component

Soil Type	Eigen Values	Eigen Vectors			
		Power	Solvent to Soil Ratio	Surfactant Concentration	Time
Soil #1	0.089687	-0.019900	0.212593	0.938927	0.269861
	0.001782	0.050501	0.245117	-0.317327	0.914697
	-0.038606	0.939634	0.312351	-0.010767	-0.139316
	-0.106401	-0.337848	0.892837	-0.132683	-0.266637
Soil #2	0.022887	0.124305	0.147140	0.954166	0.229075
	-0.015821	0.700555	0.259383	-0.276406	0.604602
	-0.035277	-0.599798	0.717589	-0.113028	0.335459
	-0.057766	0.366078	0.629402	0.019767	-0.685163
Soil #3	0.453061	0.035084	-0.052064	0.993618	-0.093715
	0.137106	0.084811	-0.080540	0.086102	0.989397
	0.039294	0.581683	0.812953	0.023406	0.014278
	-0.048609	0.808221	-0.574378	-0.069012	-0.110031

Table E.2: Eigen Values and Eigen Vectors by Canonical Analysis for Fluorene Component

Soil Type	Eigen Values	Eigen Vectors			
		Power	Solvent to Soil Ratio	Surfactant Concentration	Time
Soil #1	0.046105	0.051270	0.291545	0.830595	0.471683
	0.002307	0.049111	0.196736	-0.537073	0.818802
	-0.083641	0.609174	0.725932	-0.125763	-0.293450
	-0.125121	0.789852	-0.591032	0.076474	0.144796
Soil #2	0.038664	0.057823	0.015169	0.923497	-0.378919
	0.001785	0.014358	0.175665	0.370414	0.911992
	-0.075922	0.000491	0.984325	-0.080569	-0.156882
	-0.191991	0.998223	-0.003890	-0.058783	0.008909
Soil #3	0.139016	0.157496	0.440951	-0.632243	0.617273
	0.075897	0.322098	0.794858	0.493536	-0.144487
	0.044011	0.197779	-0.297166	0.566878	0.742445
	-0.050365	0.912322	-0.292328	-0.187990	-0.216501

Table E.3: Eigen Values and Eigen Vectors by Canonical Analysis for Anthrancene Component

Soil Type	Eigen Values	Eigen Vectors			
		Power	Solvent to Soil Ratio	Surfactant Concentration	Time
Soil #1	0.045079	0.123204	0.206666	0.082314	0.967127
	-0.132947	0.036798	0.974505	0.044809	-0.216744
	-0.257051	-0.131572	-0.052940	0.988304	-0.056042
	-0.364416	0.982932	-0.069473	0.120296	-0.120611
Soil #2	0.084692	0.261254	-0.029362	0.952377	0.154475
	0.021638	0.673357	0.001534	-0.294648	0.678064
	-0.014870	-0.607003	0.470641	0.077930	0.635588
	-0.093394	0.331488	0.881835	-0.009368	-0.335253
Soil #3	0.207817	-0.028169	-0.274191	0.937838	0.210915
	0.113187	0.382213	0.562437	0.323852	-0.657797
	0.012979	0.915822	-0.142715	-0.095838	0.362929
	-0.031869	-0.119956	0.766888	0.079963	0.625380

Table E.4: Eigen Values and Eigen Vectors by Canonical Analysis for Fluoranthene component

Soil Type	Eigen Values	Eigen Vectors			
		Power	Solvent to Soil Ratio	Surfactant Concentration	Time
Soil #1	0.037711	0.687036	0.676722	0.189164	0.185058
	-0.057391	-0.633598	0.439546	0.116398	0.625942
	-0.091708	0.352710	-0.555015	-0.031849	0.752688
	-0.279925	-0.046156	-0.202001	0.974502	-0.086087
Soil #2	0.100676	0.958138	0.279733	-0.054241	-0.027896
	-0.008223	0.197054	-0.489908	0.769033	0.360206
	-0.047629	-0.052653	0.218216	-0.284101	0.932146
	-0.053976	-0.200919	0.796317	0.570029	-0.024033
Soil #3	0.305472	0.098505	0.092186	0.980634	-0.141968
	0.114897	-0.144176	-0.136988	0.167161	0.965663
	0.013275	0.926752	0.305473	-0.093169	0.197828
	-0.112444	-0.332626	0.937775	-0.041631	0.090576

Table E.5: Eigen Values and Eigen Vectors by Canonical Analysis for Pyrene Component

Soil Type	Eigen Values	Eigen Vectors			
		Power	Solvent to Soil Ratio	Surfactant Concentration	Time
Soil #1	0.063999	0.232896	0.847933	0.177051	0.442065
	0.005189	-0.136979	-0.427291	-0.004755	0.893665
	-0.106170	0.960797	-0.276098	0.020080	0.015364
	-0.259444	-0.062174	-0.149001	0.983985	-0.075536
Soil #2	0.119140	0.035407	-0.004399	0.995001	0.093278
	0.021525	0.057270	0.016337	-0.095120	0.993683
	-0.034189	0.996192	-0.056285	-0.030133	-0.059373
	-0.116833	0.055386	0.998271	0.004242	-0.019199
Soil #3	0.222100	0.167883	0.084642	0.955757	-0.226229
	0.127883	-0.048707	-0.130422	0.247088	0.958940
	0.006712	0.907673	0.363457	-0.159295	0.136581
	-0.152141	-0.381541	0.918545	0.010043	0.102961

Table E.6: Eigen Values and Eigen Vectors by Canonical Analysis for Chrysene Component

Soil Type	Eigen Values	Eigen Vectors			
		Power	Solvent to Soil Ratio	Surfactant Concentration	Time
Soil #1	0.041983	0.340315	0.653714	0.472033	0.483764
	-0.024149	0.846839	-0.017146	-0.043863	-0.529760
	-0.072583	0.273903	0.074613	-0.816323	0.503018
	-0.087923	0.303358	-0.752859	0.329967	0.481974
Soil #2	0.129378	0.033927	0.118260	0.964527	0.233564
	0.075315	-0.006083	0.051351	-0.240778	0.969202
	-0.111678	0.067473	0.989135	-0.104760	-0.078009
	-0.183403	0.997126	-0.070643	-0.027198	0.003245
Soil #3	0.191114	0.467247	0.212661	0.647487	-0.563219
	0.062134	0.847144	0.076893	-0.502758	0.153844
	-0.041154	0.227006	-0.262797	0.570142	0.744543
	-0.170143	-0.111781	0.937977	0.054154	0.323685

Table E.7: Eigen Values and Eigen Vectors by Canonical Analysis for Benzo(k)fluranthene Component

Soil Type	Eigen Values	Eigen Vectors			
		Power	Solvent to Soil Ratio	Surfactant Concentration	Time
Soil #1	0.128836	0.107024	0.142747	0.482954	0.857277
	-0.008175	0.139106	0.103425	0.842874	-0.509428
	-0.189424	0.236333	0.947876	-0.200329	-0.074480
	-0.444195	0.955689	-0.265440	-0.127230	-0.003435
Soil #2	0.224412	0.188485	0.118510	0.965310	0.136404
	0.096994	0.654702	0.647034	-0.249743	0.300567
	-0.007443	-0.642726	0.322933	-0.01229	0.694599
	-0.023249	0.350347	-0.680453	-0.075194	0.639208
Soil #3	0.264455	0.207652	0.048632	0.823060	-0.526391
	0.140713	-0.024739	-0.111139	0.544341	0.831101
	-0.003285	0.813204	0.540313	-0.123618	0.177425
	-0.123177	-0.543109	0.832673	0.104799	0.026543

Table E. 8: Eigen Values and Eigen Vectors by Canonical Analysis for Benzo(a)pyrene Component

Soil Type	Eigen Values	Eigen Vectors			
		Power	Solvent to Soil Ratio	Surfactant Concentration	Time
Soil #1	0.023674	0.081496	0.312889	0.502446	0.801877
	-0.050752	0.381945	0.716756	0.295006	-0.503339
	-0.119918	-0.036552	0.544171	-0.788154	0.285229
	-0.245494	0.919859	-0.303709	-0.198326	0.149288
Soil #2	0.184719	0.087150	-0.065101	0.992952	0.047033
	-0.011802	0.256985	0.545474	-0.024562	0.797379
	-0.037543	0.954698	-0.034087	-0.072452	-0.286601
	-0.089578	00.122126	0.834900	0.090514	-0.528993
Soil #3	0.408428	0.220644	0.052055	0.846117	-0.482383
	0.180157	-0.123672	-0.150325	0.516794	0.833686
	0.067273	0.862936	0.418446	-0.099583	0.265194
	-0.142076	-0.437450	0.894201	0.084224	0.044134

Table E.9: Estimate Ridge of Maximum Response for Soil #1 with four Factor Variables for Acenaphthylene Component

Coded Radius	Estimate Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	0.35605	0.12921	25.00000	30.00000	0.50500	17.50000
0.1	0.37642	0.12951	26.59936	30.98458	0.53299	17.71196
0.2	0.39725	0.12881	28.00863	31.91180	0.56556	17.96987
0.3	0.41879	0.12680	29.21414	32.77948	0.60216	18.26480
0.4	0.44125	0.12318	30.22332	33.58878	0.64199	18.58674
0.5	0.46483	0.11780	31.05799	34.34430	0.68421	18.92668
0.6	0.48967	0.11062	31.74564	35.05262	0.72811	19.27767
0.7	0.51591	0.10178	32.31317	35.72086	0.77314	19.63491
0.8	0.54362	0.09159	32.78391	36.35562	0.81893	19.99530
0.9	0.57287	0.08069	33.17689	36.96261	0.86523	20.35691
1.0	0.60372	0.07036	33.50719	37.54659	0.91184	20.71862

Table E.10: Estimate Ridge of Maximum Response for Soil #1 with four Factor Variables for Fluorene Component

Coded Radius	Estimate Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	0.42322	0.11716	25.00000	30.00000	0.50500	17.50000
0.1	0.44332	0.11743	26.58068	31.04721	0.53206	17.70636
0.2	0.46313	0.11687	27.94877	32.07967	0.56307	17.98599
0.3	0.48288	0.11525	29.11434	33.07819	0.59735	18.33135
0.4	0.50280	0.11239	30.10113	34.03341	0.63408	18.73086
0.5	0.52308	0.10820	30.93849	34.94378	0.67255	19.17253
0.6	0.54383	0.10266	31.65491	35.81230	0.71220	19.64605
0.7	0.56516	0.09587	32.27489	36.64388	0.wazzu 75262	20.14336
0.8	0.58715	0.08798	32.81819	37.44374	0.79356	20.65847
0.9	0.60985	0.07932	33.30028	38.21675	0.83483	21.18702
1.0	0.63330	0.07048	33.73313	38.96710	0.87630	21.72584

Table E.11: Estimate Ridge of Maximum Response for Soil #1 with four Factor Variables for Anthrancene Component

Coded Radius	Estimate Response (Removal efficiency)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	0.95164	0.19762	25.00000	30.00000	0.50500	.50000
0.1	0.97355	0.19809	25.54778	31.49443	0.52650	18.06603
0.2	0.99415	0.19783	26.01528	32.89314	0.54351	18.83295
0.3	1.01407	0.19711	26.43937	34.14181	0.55705	19.76191
0.4	1.03377	0.19610	26.83699	35.23598	0.56806	20.80328
0.5	1.05360	0.19489	27.21661	36.19737	0.57731	21.91550
0.6	1.07379	0.19357	27.58311	37.05350	0.58536	23.07046
0.7	1.09449	0.19224	27.93973	37.82859	0.59254	24.25089
0.8	1.11581	0.19102	28.28870	38.54150	0.59912	25.44658
0.9	1.13781	0.19006	28.63168	39.20630	0.60525	26.65145
1.0	1.16054	0.18952	28.96986	39.83343	0.61103	27.86189

Table E.12: Estimate Ridge of Maximum Response for Soil #1 with four Factor Variables for Fluoranthene Component

Coded Radius	Estimate Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	0.57744	0.15561	25.00000	30.00000	0.50500	17.50000
0.1	0.59834	0.15598	26.05105	31.19002	0.53230	18.00787
0.2	0.61910	0.15556	27.26018	32.50419	0.55380	18.50222
0.3	0.64007	0.15466	28.57561	33.87558	0.57177	18.96844
0.4	0.66143	0.15341	29.96623	35.27299	0.58752	19.40556
0.5	0.68331	0.15190	31.41241	36.68170	0.60181	19.81660
0.6	0.70576	0.15017	32.90101	38.09443	0.61511	20.20532
0.7	0.72884	0.14829	34.42281	39.50754	0.62769	20.57519
0.8	0.75255	0.14634	35.97112	40.91913	0.63973	20.92917
0.9	0.77694	0.14440	37.54092	42.32830	0.65138	21.26972
1.0	0.80202	0.14256	39.12839	43.73464	0.66270	21.59886

Table E.13: Estimate Ridge of Maximum Response for Soil #1 with four Factor Variables for Pyrene Component

Coded Radius	Estimate Response Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	0.44798	0.10957	25.00000	30.00000	0.50500	17.50000
0.1	0.46624	0.10980	25.75987	31.19854	0.53522	18.02406
0.2	0.48461	0.10945	26.52146	32.62164	0.55744	18.61026
0.3	0.50365	0.10878	27.25272	34.15082	0.57496	19.21543
0.4	0.52364	0.10792	27.95381	35.73291	0.58976	19.82365
0.5	0.54471	0.10691	28.63093	37.34446	0.60291	20.42963
0.6	0.56693	0.10580	29.28987	38.97419	0.61500	21.03180
0.7	0.59034	0.10462	29.93501	40.61607	0.62637	21.62989
0.8	0.61497	0.10343	30.56959	42.26660	0.63724	22.22408
0.9	0.64082	0.10230	31.19594	43.92359	0.64773	22.81469
1.0	0.66793	0.10130	31.81579	45.58557	0.65793	23.40211

Table E.14: Estimate Ridge of Maximum Response for Soil #1 with four Factor Variables for Chrysene Component

Coded Radius	Estimate Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	0.37133	0.12799	25.00000	30.00000	0.50500	17.50000
0.1	0.39109	0.12827	26.30287	31.01600	0.53539	17.88207
0.2	0.41152	0.12764	27.56410	32.09484	0.56455	18.29423
0.3	0.43267	0.12619	28.78688	33.21976	0.59276	18.73133
0.4	0.45454	0.12399	29.97500	34.37913	0.62024	19.18914
0.5	0.47717	0.12111	31.13223	35.56473	0.64713	19.66424
0.6	0.50056	0.11759	32.26210	36.77064	0.67355	20.15386
0.7	0.52474	0.11350	33.36777	37.99253	0.69959	20.65578
0.8	0.54970	0.10892	34.45201	39.22714	0.72531	21.16817
0.9	0.57547	0.10393	35.51726	40.47204	0.75077	21.68955
1.0	0.60203	0.09866	36.56565	41.72533	0.77602	22.21867

Table E.15: Estimate Ridge of Maximum Response for Soil #1 with four Factor Variables for Benzo(k)fluranthene Component

Coded Radius	Estimate Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	0.80821	0.24124	25.00000	30.00000	0.50500	17.50000
0.1	0.82426	0.24181	26.47398	31.33738	0.52174	17.87694
0.2	0.83915	0.24135	27.45078	32.42610	0.54891	18.60440
0.3	0.85485	0.23917	28.10977	33.19431	0.57878	19.54639
0.4	0.87232	0.23538	28.60986	33.77352	0.60795	20.56945
0.5	0.89192	0.23020	29.02964	34.25259	0.63604	21.62183
0.6	0.913946	0.22385	29.40463	34.67487	0.66325	22.68592
0.7	0.938370	0.21649	29.75223	35.06223	0.68981	23.75513
0.8	0.965276	0.20832	30.08184	35.42662	0.71589	24.82672
0.9	0.994694	0.19959	30.39900	35.77509	0.74160	25.89945
1.0	1.026640	0.19060	30.70716	36.11207	0.76703	26.97270

Table E.16: Estimate Ridge of Maximum Response for Soil #1 with four Factor Variables for Benzo(a)Pyrene Component

Coded Radius	Estimate Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	0.61107	0.18104	25.00000	30.00000	0.50500	17.50000
0.1	0.63053	0.18145	26.54573	30.76425	0.53342	17.97109
0.2	0.64935	0.18058	27.79478	31.64409	0.56361	18.52513
0.3	0.66786	0.17834	28.82684	32.57228	0.59432	19.15211
0.4	0.68628	0.17480	29.70157	33.51197	0.62497	19.84042
0.5	0.70476	0.17001	30.45995	34.44461	0.65533	20.57921
0.6	0.72338	0.16410	31.13008	35.36157	0.68531	21.35918
0.7	0.74222	0.15719	31.73166	36.25939	0.71490	22.17265
0.8	0.76132	0.14942	32.27893	37.13727	0.74411	23.01345
0.9	0.78073	0.14100	32.78239	37.99578	0.77296	23.87662
1.0	0.80047	0.13218	33.24999	38.83610	0.80148	24.75823

Table E.17: Estimate Ridge of Maximum Response for Soil #2 with four Factor Variables for Acenaphthylene Component

Coded Radius	Estimated Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	0.49493	0.11531	25.00000	30.00000	0.50500	17.50000
0.1	0.51783	0.11550	27.24208	30.23385	0.51940	17.89013
0.2	0.54052	0.11537	29.44355	30.47682	0.53518	18.30256
0.3	0.56300	0.11488	31.60162	30.72961	0.55242	18.73495
0.4	0.58532	0.11399	33.71342	30.99267	0.57120	19.18503
0.5	0.60748	0.11267	35.77613	31.26622	0.59158	19.65051
0.6	0.62953	0.11088	37.78697	31.55023	0.61361	20.12916
0.7	0.65148	0.10858	39.74333	31.84450	0.63732	20.61875
0.8	0.67337	0.10575	41.64283	32.14861	0.66274	21.11715
0.9	0.69522	0.10236	43.48344	32.46200	0.68986	21.62224
1.0	0.71706	0.09844	45.26352	32.78399	0.71867	22.13205

Table E.18: Estimate Ridge of Maximum Response for Soil #2 with four Factor Variables for Fluorene Component

Coded Radius	Estimated Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	0.57580	0.18383	25.00000	30.00000	0.50500	17.50000
0.1	0.60463	0.18419	27.30693	30.54717	0.51771	17.60986
0.2	0.63038	0.18406	29.50306	31.16650	0.53545	17.74033
0.3	0.65334	0.18307	31.53018	31.84807	0.55982	17.88875
0.4	0.67397	0.18052	33.32009	32.56186	0.59208	18.04275
0.5	0.69282	0.17548	34.82147	33.26066	0.63230	18.17878
0.6	0.71047	0.16712	36.02950	33.89979	0.67898	18.27051
0.7	0.72743	0.15508	36.98481	34.45635	0.72990	18.30104
0.8	0.74412	0.13964	37.74558	34.92955	0.78307	18.26663
0.9	0.76081	0.12176	38.36457	35.32993	0.83717	18.1721
1.0	0.77772	0.10352	38.88167	35.67062	0.89146	18.02561

Table E.19: Estimate Ridge of Maximum Response for Soil #2 with four Factor Variables for Anthrancene Component

Coded Radius	Estimated Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	0.36217	0.16424	25.00000	30.00000	0.50500	17.50000
0.1	0.37890	0.16448	26.92299	30.20658	0.52250	18.15275
0.2	0.39651	0.16410	28.76640	30.34074	0.54372	18.80466
0.3	0.41509	0.16286	30.52714	30.42519	0.56862	19.44251
0.4	0.43473	0.16050	32.20293	30.47442	0.59703	20.05752
0.5	0.45553	0.15676	33.79323	30.49810	0.62864	20.64433
0.6	0.47755	0.15141	35.29975	30.50292	0.66309	21.20033
0.7	0.50086	0.14430	36.72631	30.49367	0.69997	21.72502
0.8	0.52553	0.13539	38.07837	30.47383	0.73887	22.21938
0.9	0.55160	0.12478	39.36231	30.44595	0.77944	22.68534
1.0	0.57911	0.11284	40.58483	30.41192	0.82135	23.12528

Table E.20: Estimate Ridge of Maximum Response for Soil #2 with four Factor Variables for Fluoranthene Component

Coded Radius	Estimated Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	0.42666	0.17417	25.00000	30.00000	0.50500	17.50000
0.1	0.44230	0.17420	25.93030	29.38932	0.54087	18.11642
0.2	0.45787	0.17258	27.04593	28.81386	0.57591	18.70298
0.3	0.47346	0.16952	28.43338	28.31442	0.60934	19.25013
0.4	0.48919	0.16542	30.20881	27.95407	0.63971	19.73841
0.5	0.50533	0.16099	32.46334	27.80821	0.66488	20.13839
0.6	0.52223	0.15703	35.14407	27.91173	0.68318	20.42825
0.7	0.54027	0.15400	38.05136	28.21830	0.69501	20.61672
0.8	0.55977	0.15198	41.00554	28.64874	0.70217	20.73287
0.9	0.58091	0.15092	43.92236	29.14486	0.70635	20.80315
1.0	0.60383	0.15086	46.77842	29.67476	0.70865	20.84468

Table E.21: Estimate Ridge of Maximum Response for Soil #2 with four Factor Variables for Pyrene Component

Coded Radius	Estimated Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	0.37943	0.12529	25.00000	30.00000	0.50500	17.50000
0.1	0.39620	0.12550	27.09682	30.29991	0.52315	17.96709
0.2	0.41307	0.12513	28.99672	30.51669	0.54865	18.46818
0.3	0.43041	0.12367	30.61438	30.66707	0.58266	18.97047
0.4	0.44867	0.12046	31.90461	30.76641	0.62446	19.43689
0.5	0.46827	0.11503	32.89210	30.82984	0.67168	19.84623
0.6	0.48955	0.10725	33.64435	30.86999	0.72188	20.19799
0.7	0.51273	0.09735	34.22941	30.89550	0.77341	20.50195
0.8	0.53796	0.08587	34.69849	30.91172	0.82543	20.76914
0.9	0.56534	0.07384	35.08630	30.92183	0.87751	21.00861
1.0	0.59493	0.06336	35.41584	30.92779	0.92948	21.22708

Table E.22: Estimate Ridge of Maximum Response for Soil #2 with four Factor Variables for Chrysene Component

Coded Radius	Estimate Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	0.40741	0.15635	25.00000	30.00000	0.50500	17.50000
0.1	0.42932	0.15655	27.31322	30.53861	0.51173	17.78726
0.2	0.44848	0.15653	29.41300	31.15322	0.52648	18.25343
0.3	0.46588	0.15574	31.04586	31.78656	0.55529	18.93692
0.4	0.48306	0.15297	32.07374	32.34135	0.59781	19.70365
0.5	0.50135	0.14738	32.68563	32.79680	0.64668	20.40508
0.6	0.52148	0.13898	33.08576	33.18447	0.69726	21.01735
0.7	0.54378	0.12807	33.37743	33.53058	0.74804	21.55970
0.8	0.56840	0.11517	33.60827	33.85033	0.79859	22.05151
0.9	0.59545	0.10115	33.80191	34.15243	0.84884	22.50658
1.0	0.62496	0.08761	33.97116	34.44211	0.89880	22.93431

Table E.23: Estimate Ridge of Maximum Response for Soil #2 with four Factor Variables for Benzo(k)fluranthene Component

Coded Radius	Estimated Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	0.17033	0.16822	25.00000	30.00000	0.50500	17.50000
0.1	0.19415	0.16843	27.12933	29.68853	0.51820	18.02921
0.2	0.21940	0.16816	29.18493	29.59694	0.53870	18.54120
0.3	0.24667	0.16687	31.07648	29.69233	0.56743	19.01965
0.4	0.27656	0.16383	32.74146	29.91411	0.60364	19.45208
0.5	0.30962	0.15844	34.17258	30.20226	0.64532	19.83612
0.6	0.34625	0.15039	35.40281	30.51665	0.69041	20.17768
0.7	0.38673	0.13971	36.47618	30.83661	0.73743	20.48542
0.8	0.43126	0.12671	37.43144	31.15327	0.78549	20.76726
0.9	0.47995	0.11209	38.29816	31.46347	0.83408	21.02942
1.0	0.53288	0.09718	39.09780	31.76655	0.88293	21.27652

Table E. 24: Estimate Ridge of Maximum Response for Soil #2 with four Factor Variables for Benzo(a)Pyrene Component

Coded Radius	Estimated Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	0.34757	0.15797	25.00000	30.00000	0.50500	17.50000
0.1	0.37130	0.15820	27.22774	30.10326	0.51719	17.97204
0.2	0.39498	0.15800	29.34251	30.22952	0.53690	18.43076
0.3	0.41909	0.15681	31.24088	30.34436	0.56693	18.85387
0.4	0.44429	0.15357	32.80631	30.41247	0.60800	19.21270
0.5	0.47139	0.14733	34.00788	30.42150	0.65696	19.49540
0.6	0.50104	0.13784	34.91824	30.38354	0.70961	19.71440
0.7	0.53366	0.12543	35.63110	30.31527	0.76335	19.88905
0.8	0.56952	0.11087	36.21528	30.22841	0.81710	20.03430
0.9	0.60876	0.09546	36.71405	30.12991	0.87047	20.15979
1.0	0.65148	0.08176	37.15405	30.02380	0.92341	20.27158

Table E.25: Estimate Ridge of Maximum Response for Soil #3 with four Factor Variables for Acenaphthylene Component

Coded Radius	Estimated Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	-0.18560	0.23844	25.00000	30.00000	0.50500	17.50000
0.1	-0.16800	0.23874	25.77089	31.50172	0.50669	16.77118
0.2	-0.14835	0.23879	26.47485	32.77855	0.52361	15.92851
0.3	-0.12434	0.23446	26.78704	32.95965	0.60076	15.50140
0.4	-0.09186	0.22382	26.92112	32.86833	0.66395	15.31987
0.5	-0.05040	0.20902	27.03087	32.76607	0.72053	15.17218
0.6	0.00008	0.19066	27.13195	32.66208	0.77439	15.03652
0.7	0.05960	0.16940	27.22877	32.55770	0.82681	14.90678
0.8	0.12817	0.14641	27.32311	32.45324	0.87838	14.78046
0.9	0.20580	0.12402	27.41590	32.34878	0.92941	14.65630
1.0	0.29249	0.10703	27.50762	32.24435	0.98005	14.53361

Table E.26: Estimate Ridge of Maximum Response for Soil #3 with four Factor Variables for Fluorene Component

Coded Radius	Estimated Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	0.18927	0.21678	25.00000	30.00000	0.50500	17.50000
0.1	0.21116	0.21757	25.64622	31.41801	0.52927	16.95500
0.2	0.23460	0.21702	26.26980	32.79929	0.55476	16.40141
0.3	0.25962	0.21503	26.86994	34.13472	0.58155	15.83454
0.4	0.28624	0.21144	27.44380	35.41344	0.60973	15.24928
0.5	0.31448	0.20611	27.98671	36.62227	0.63942	14.64002
0.6	0.34436	0.19886	28.49225	37.74522	0.67077	14.00069
0.7	0.37594	0.18951	28.95228	38.76332	0.70390	13.32500
0.8	0.40926	0.17789	29.35725	39.65502	0.73894	12.60701
0.9	0.44438	0.16395	29.69693	40.39768	0.77592	11.84202
1.0	0.48138	0.14784	29.96172	40.97053	0.81478	11.02783

Table E.27: Estimate Ridge of Maximum Response for Soil #3 with four Factor Variables for Anthrancene Component

Coded Radius	Estimated Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	-0.06048	0.27400	25.00000	30.00000	0.50500	17.50000
0.1	-0.04301	0.27117	26.25687	28.79508	0.47537	17.70190
0.2	-0.02436	0.26522	27.25709	27.80819	0.43740	17.93085
0.3	-0.00388	0.25442	27.96272	27.14906	0.39080	18.11394
0.4	0.01912	0.23771	28.41857	26.85148	0.33830	18.19664
0.5	0.04524	0.21536	28.71342	26.84230	0.28359	18.17783
0.6	0.07487	0.18846	28.91867	27.02104	0.22893	18.08473
0.7	0.10825	0.15859	29.07506	27.31460	0.17511	17.94299
0.8	0.14552	0.12852	29.20366	27.67923	0.12228	17.76972
0.9	0.18677	0.10432	29.31549	28.08965	0.07035	17.57545
1.0	0.23203	0.09794	29.41662	28.53087	0.01917	17.36667

Table E.28: Estimate Ridge of Maximum Response for Soil #3 with four Factor Variables for Fluoranthene Component

Coded Radius	Estimated Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	-0.14979	0.21095	25.00000	30.00000	0.50500	17.50000
0.1	-0.13201	0.21130	25.95832	31.10203	0.51237	16.59234
0.2	-0.11194	0.21108	26.86348	31.95725	0.53263	15.65644
0.3	-0.08857	0.20911	27.61965	32.59693	0.57004	14.85139
0.4	-0.06075	0.20366	28.19889	33.05969	0.61888	14.25729
0.5	-0.02766	0.19418	28.6552	33.41434	0.67119	13.81821
0.6	0.01110	0.18095	29.04167	33.71054	0.72380	13.46756
0.7	0.05572	0.16444	29.38760	33.97371	0.77594	13.16775
0.8	0.10630	0.14534	29.70844	34.21671	0.82755	12.89916
0.9	0.16288	0.12482	30.01272	34.44650	0.87868	12.65106
1.0	0.22550	0.10521	30.30549	34.66718	0.92942	12.41713

Table E.29: Estimate Ridge of Maximum Response for Soil #3 with four Factor Variables for Pyrene Component

Coded Radius	Estimated Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	-0.02011	0.18401	25.00000	30.00000	0.50500	17.50000
0.1	-0.00425	0.18332	26.21808	30.89753	0.51828	16.62565
0.2	0.01423	0.18406	27.26887	31.58729	0.54006	15.71247
0.3	0.03581	0.18233	28.16677	32.13792	0.56992	14.83865
0.4	0.06087	0.17860	28.94741	32.59086	0.60625	14.04381
0.5	0.08971	0.17241	29.64289	32.97447	0.64709	13.33561
0.6	0.12251	0.16354	30.27735	33.30889	0.69080	12.70462
0.7	0.15942	0.15200	30.86786	33.60817	0.73625	12.13655
0.8	0.20053	0.13800	31.42619	33.88198	0.78274	11.61798
0.9	0.24590	0.12203	31.96048	34.13696	0.82984	11.13804
1.0	0.29557	0.10510	32.47643	34.37771	0.87731	10.68841

Table E.30: Estimate Ridge of Maximum Response for Soil #3 with four Factor Variables for Chrysene Component

Coded Radius	Estimate Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	0.29387	0.37858	25.00000	30.00000	0.50500	17.50000
0.1	0.31245	0.37629	26.68145	29.81131	0.48341	16.76207
0.2	0.331599	0.37364	28.62822	29.88550	0.46918	16.03867
0.3	0.35199	0.37188	30.72936	30.15322	0.46614	15.29005
0.4	0.37434	0.37126	32.82715	30.54892	0.47547	14.49829
0.5	0.39928	0.37058	34.79999	31.00922	0.49457	13.68092
0.6	0.42727	0.36845	36.61625	31.49124	0.51961	12.86202
0.7	0.45860	0.36402	38.29733	31.97536	0.54785	12.05368
0.8	0.49343	0.35696	39.87476	32.45484	0.57779	11.25883
0.9	0.53186	0.34728	41.37485	32.92814	0.60866	10.47668
1.0	0.57396	0.33517	42.81691	33.39548	0.64005	9.70544

Table E.31: Estimate Ridge of Maximum Response for Soil #3 with four Factor Variables for Benzo(k)fluranthene Component

Coded Radius	Estimated Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	0.18763	0.34263	25.00000	30.00000	0.50500	17.50000
0.1	0.20154	0.34280	27.47117	29.77993	0.51014	17.49304
0.2	0.21555	0.34304	29.63011	29.85514	0.53919	17.13017
0.3	0.23239	0.33885	30.89620	30.00344	0.58633	16.42624
0.4	0.25385	0.32911	31.73972	30.13202	0.63274	15.70224
0.5	0.28036	0.31461	32.43925	30.24860	0.67732	14.99652
0.6	0.31206	0.29581	33.07459	30.35892	0.72076	14.30415
0.7	0.34899	0.27314	33.67540	30.46562	0.76350	13.62047
0.8	0.39117	0.24717	34.25533	30.57003	0.80577	12.94262
0.9	0.43862	0.21884	34.82159	30.67291	0.84773	12.26884
1.0	0.49134	0.18987	35.37840	30.77470	0.88946	11.59799

Table E.32: Estimate Ridge of Maximum Response for Soil #3 with four Factor Variables for Benzo(a)Pyrene Component

Coded Radius	Estimated Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant Concentration (%)	Time (min.)
0.0	0.19524	0.54044	25.00000	30.00000	0.50500	17.50000
0.1	0.21639	0.53995	27.38998	29.56707	0.50410	17.74651
0.2	0.23770	0.54047	29.86707	29.47499	0.51469	17.90040
0.3	0.26129	0.53795	31.74318	29.63661	0.56893	17.30665
0.4	0.29155	0.52290	32.69719	29.78677	0.62533	16.53162
0.5	0.32971	0.49908	33.43426	29.91495	0.67523	15.82748
0.6	0.37595	0.46800	34.09680	30.03407	0.72220	15.15917
0.7	0.43030	0.43052	34.72342	30.14854	0.76762	14.51037
0.8	0.49279	0.38768	35.32955	30.26027	0.81211	13.87339
0.9	0.56343	0.34115	35.92275	30.37023	0.85601	13.24412
1.0	0.64223	0.29405	36.50722	30.47900	0.89950	12.62018

APPENDIX F

THE PLOTS SHOWS THE VARIATIONS OF OBSERVED REMOVAL EFFICIENCIES AND PREDICTED REMOVAL EFFICIENCIES WITH 81 CONDITIONS

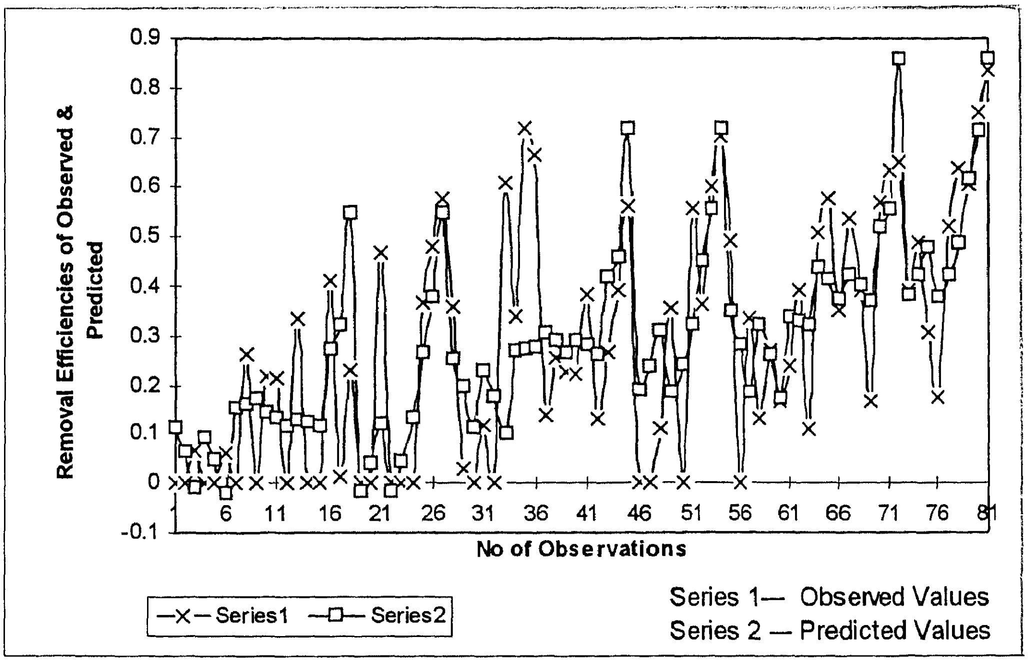

Fig. F.1: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for Acenaphthylene, Soil #1

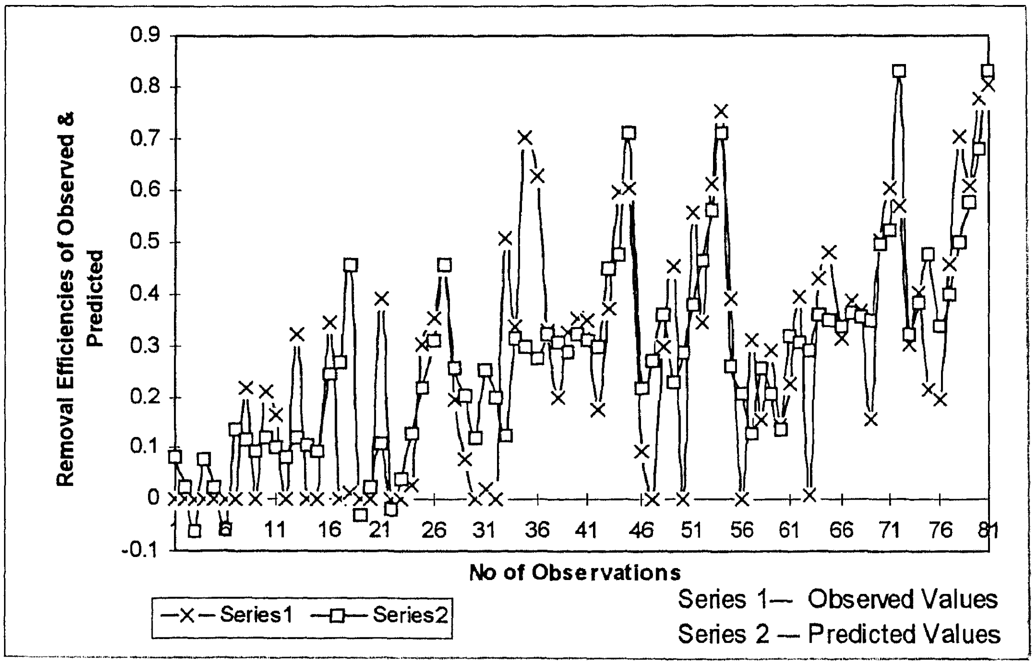

Fig. F.2: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for Fluorene, Soil #1

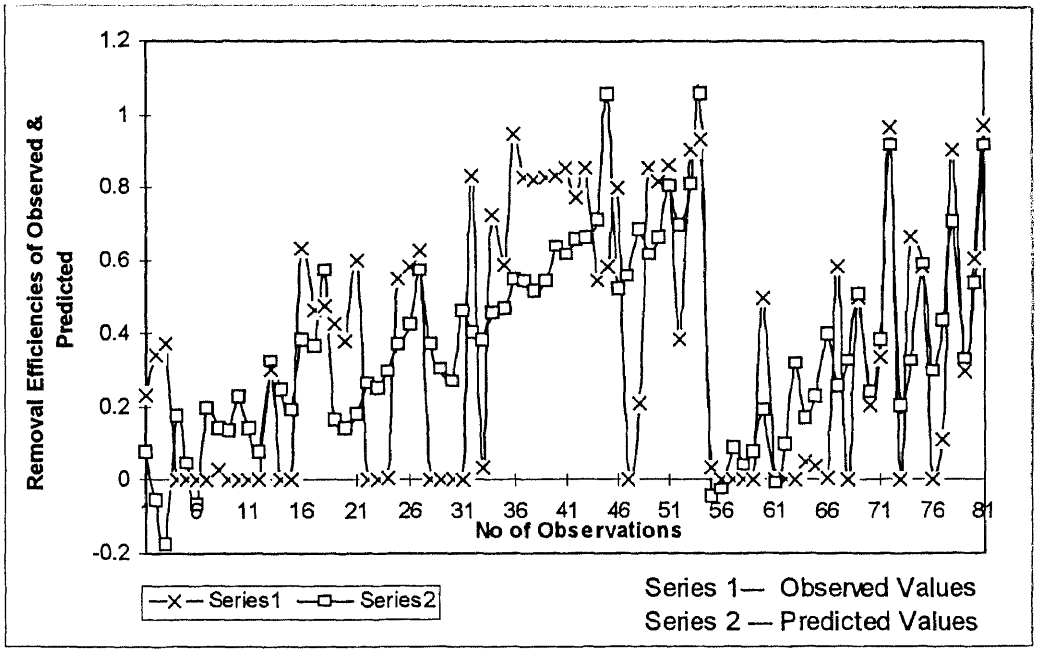

Fig. F.3: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for Anthrancene, Soil #1

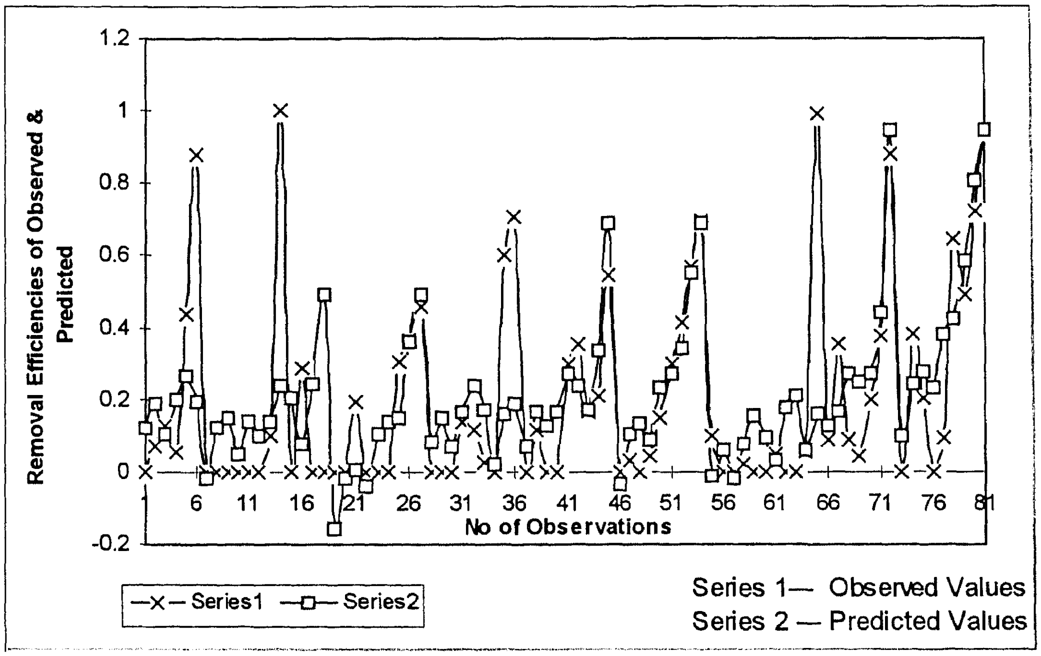

Fig. F.4: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for Fluoranthene, Soil #1

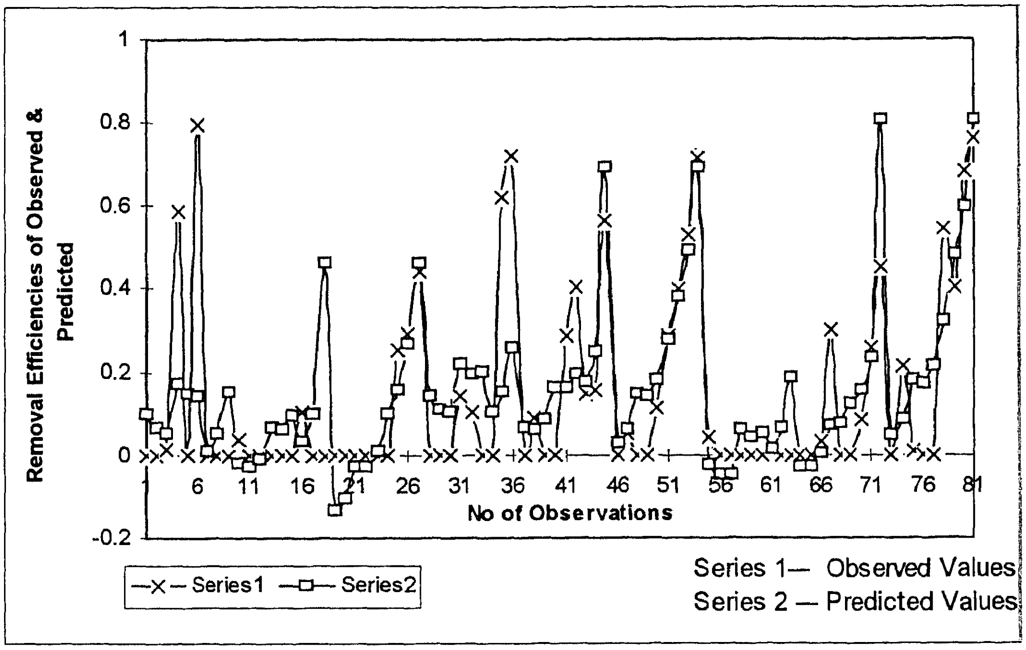

Fig. F.5: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for Pyrene, Soil #1

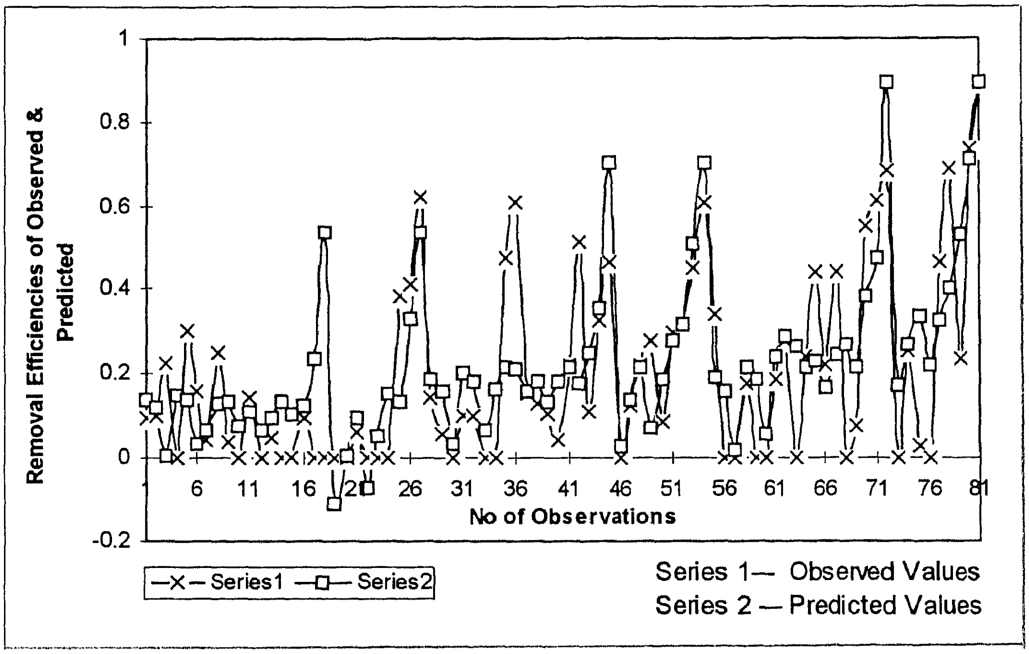

Fig. F.6: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for Chrysene, Soil #1

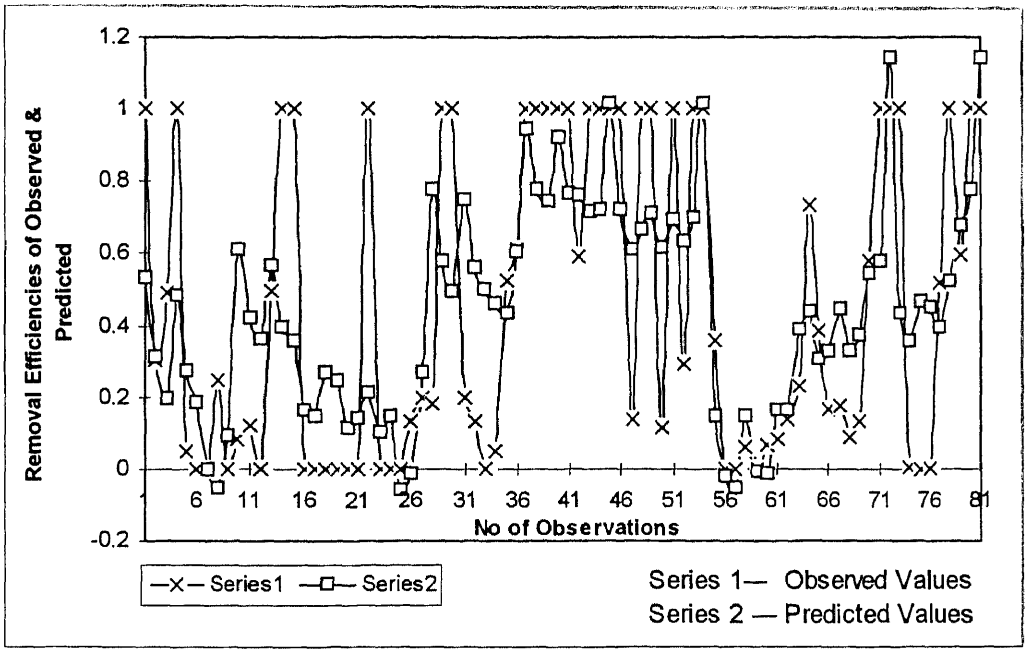

Fig. F.7: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for Benzo(k)fluoranthene, Soil #1

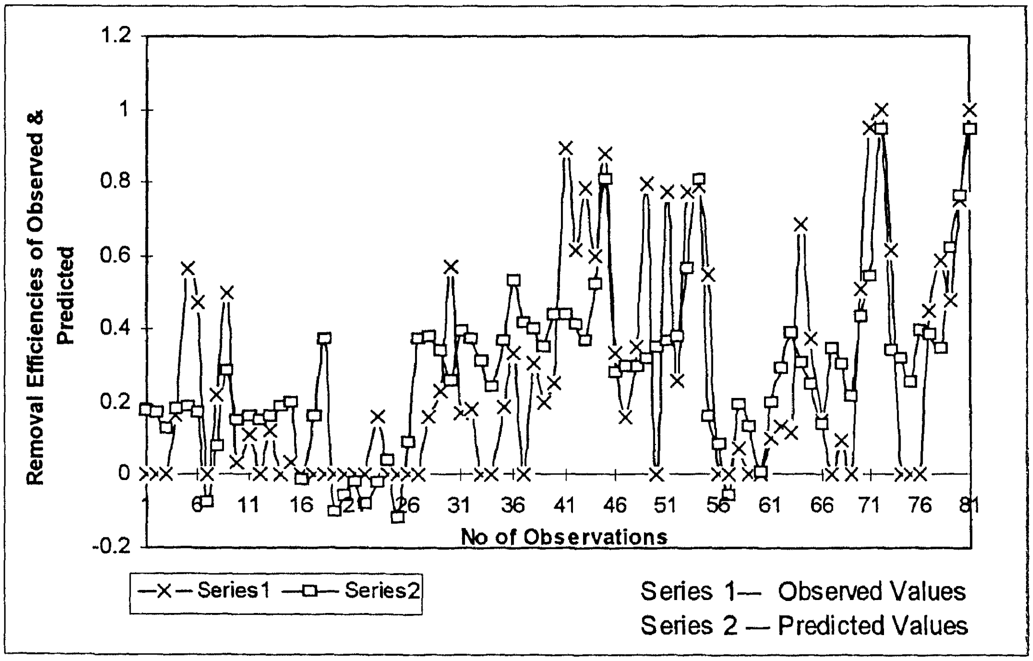

Fig. F.8: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for Benzo(a)pyrene, Soil #1

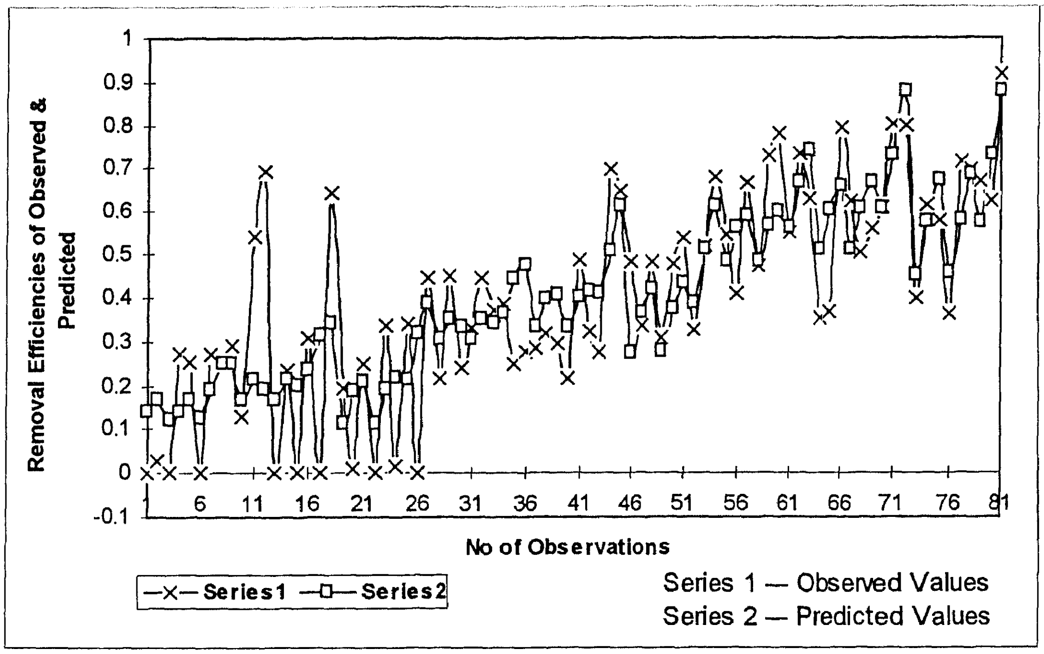

Fig. F.9: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for Acenaphthylene, Soil #2

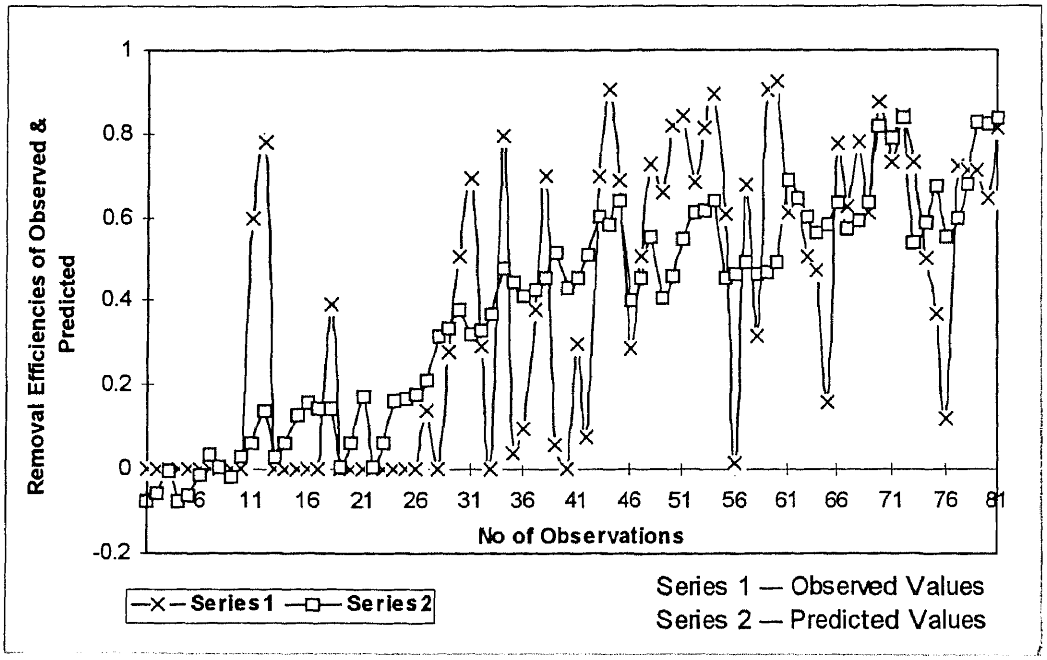

Fig. F.10: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for Fluorene, Soil #2

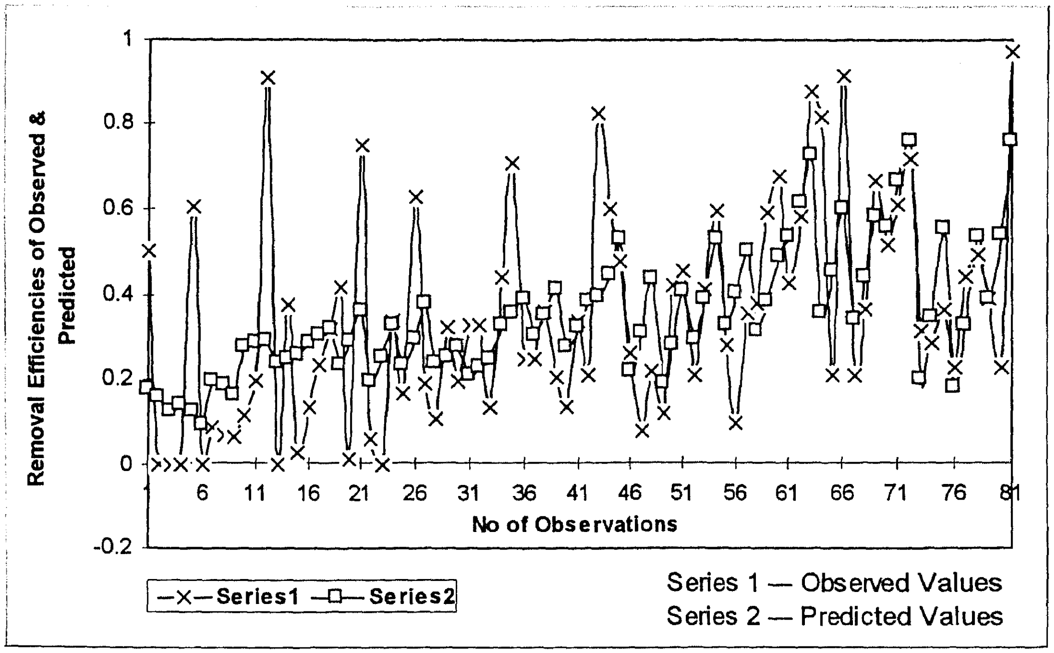

Fig. F.11: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for Anthrancene, Soil #2

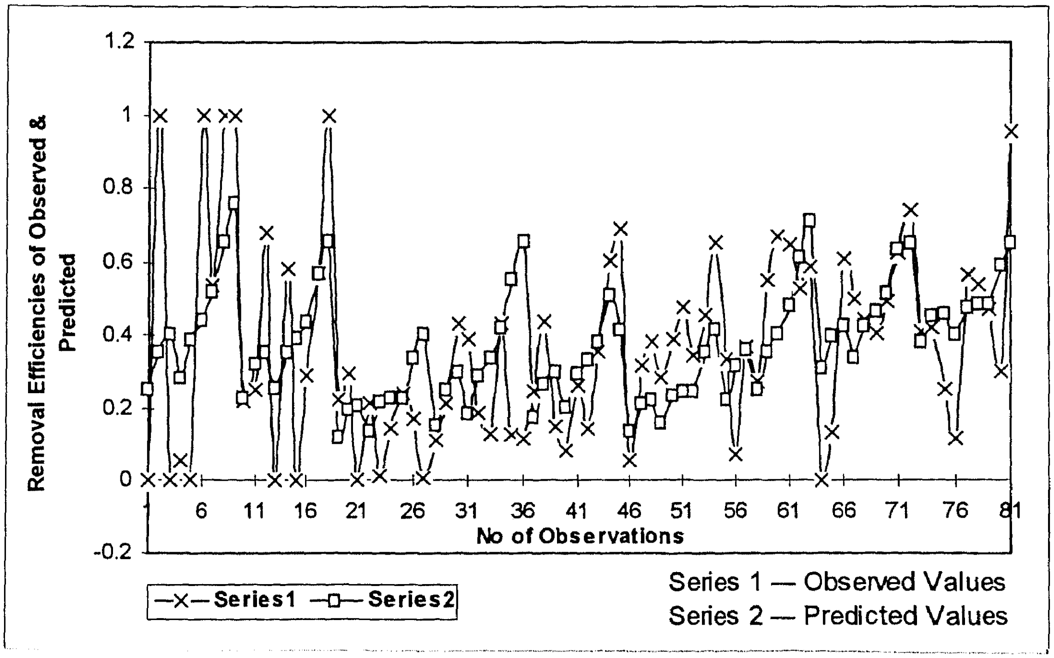

Fig. F.12: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for Fluoranthene, Soil #2

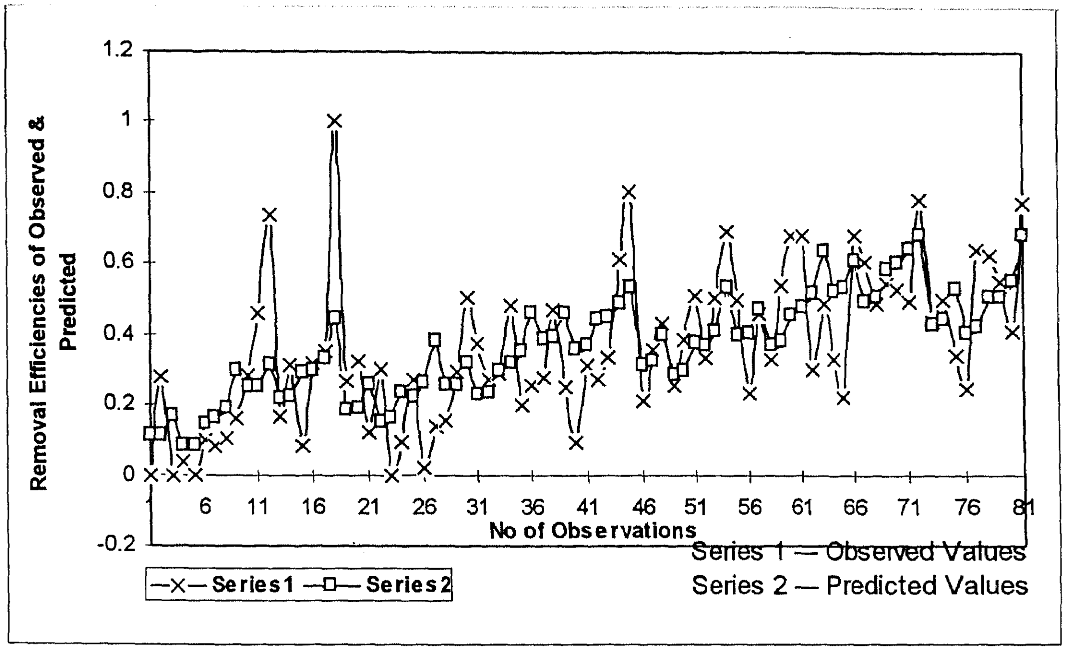

Fig. F.13: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for Pyrene, Soil #2

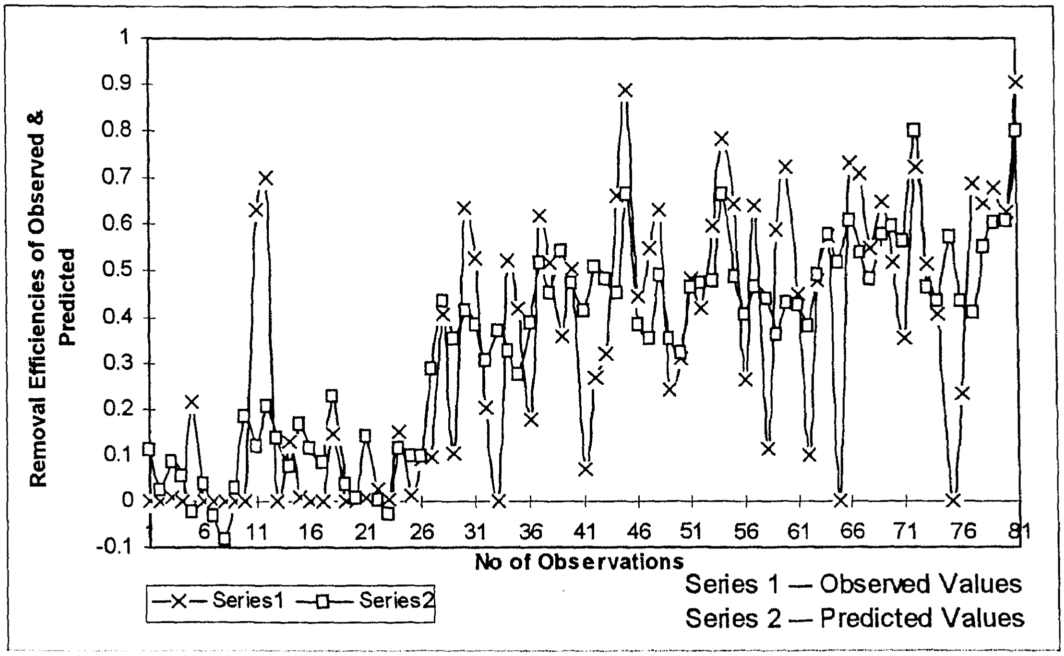

Fig. F.14: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for Chrysene, Soil #2

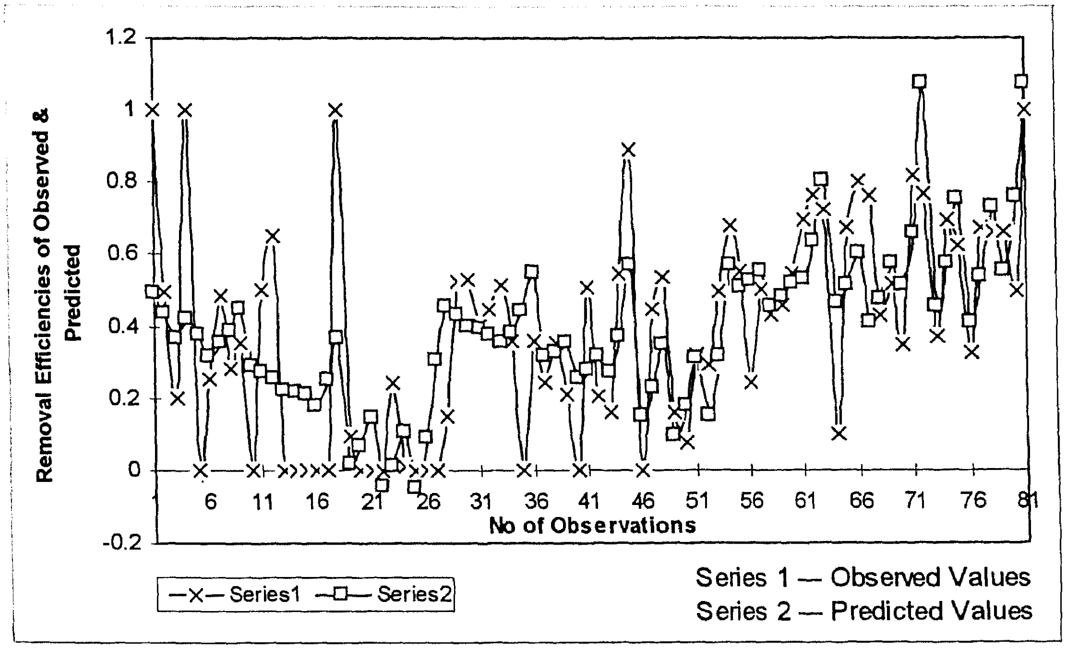

Fig. F.15: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for Benzo(k)Fluoranthene, Soil #2

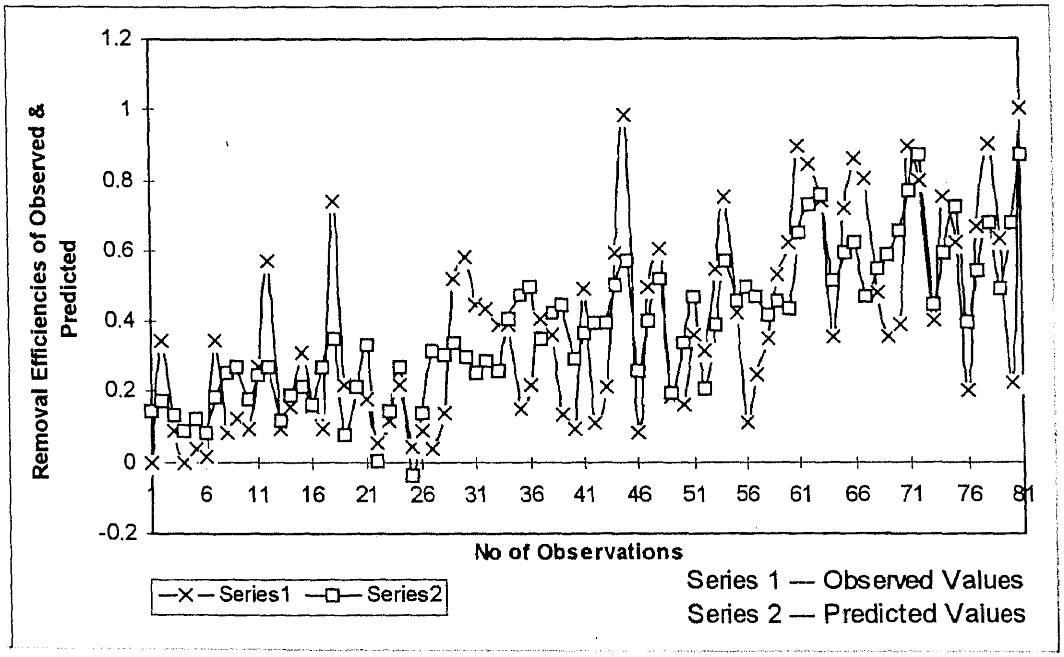

Fig. F.16: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for Benzo(a)pyrene, Soil #2

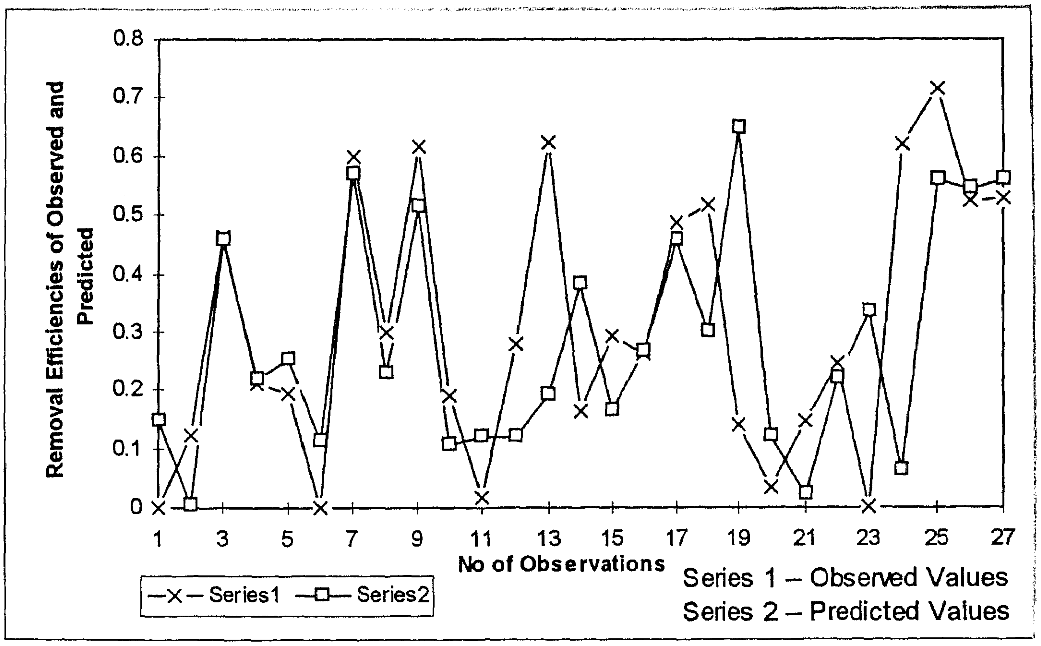

Fig. F. 17: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for Acenaphthylene, Soil #3

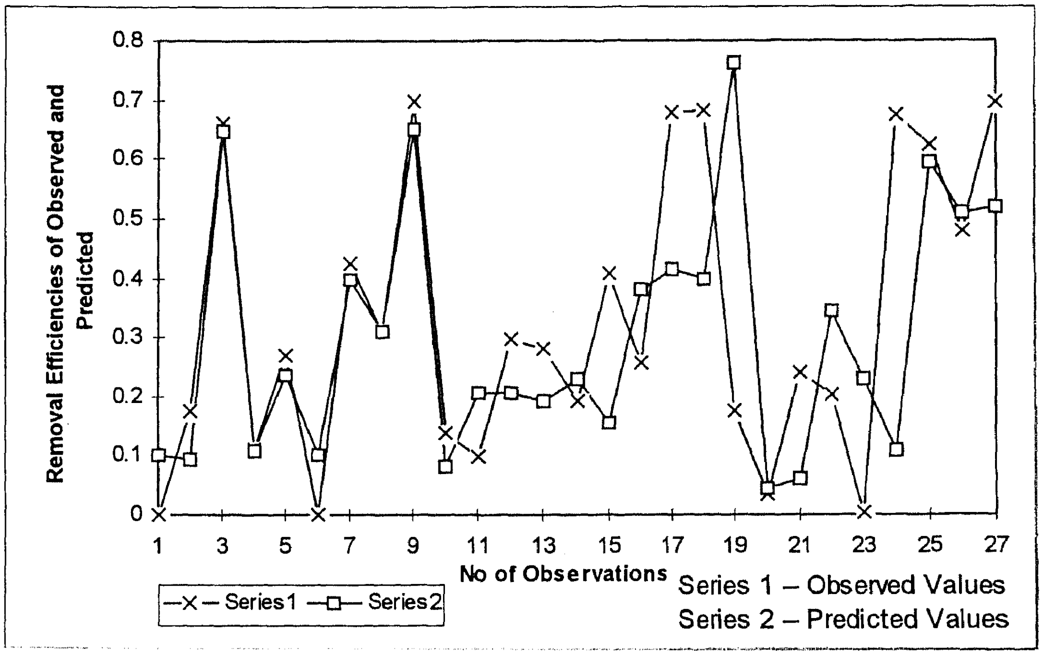

Fig. F. 18: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for Fluorene, Soil #3

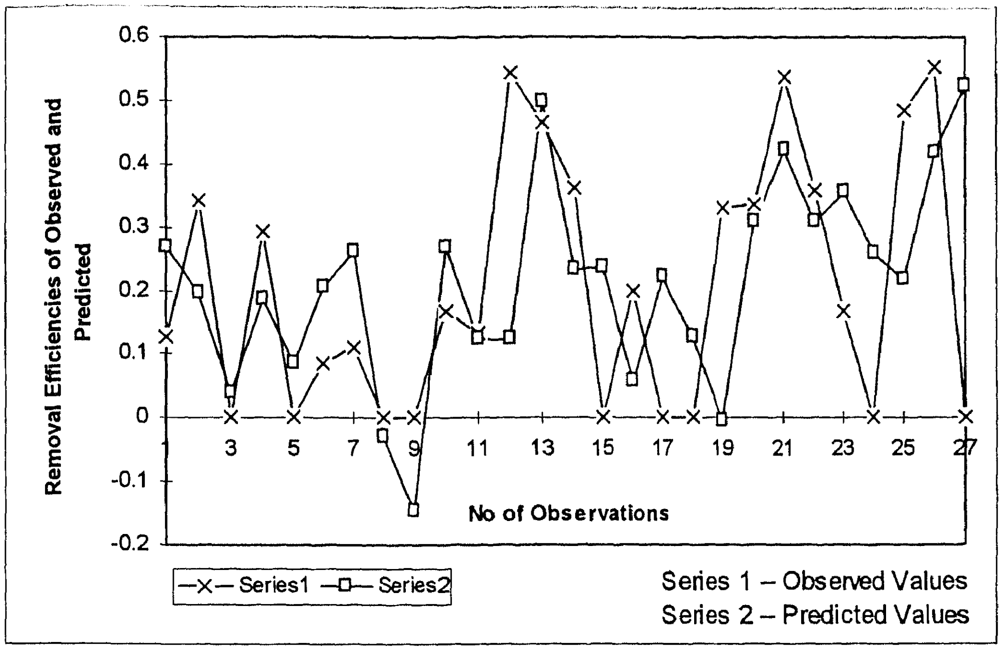

Fig. F. 19: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for Anthrancene, Soil #3

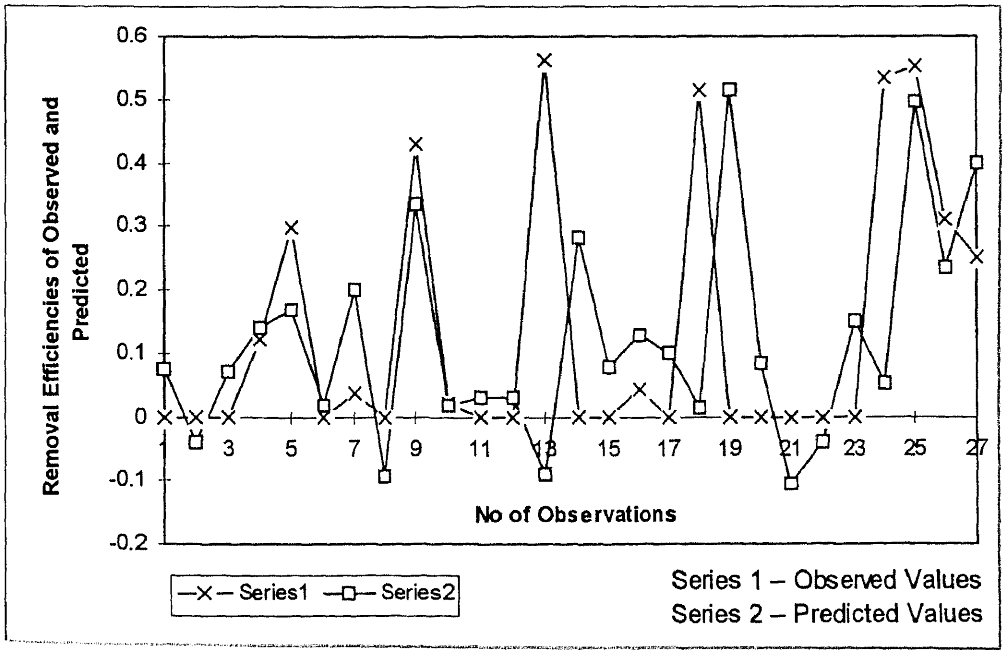

Fig. F. 20: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for Fluoranthene, Soil #3

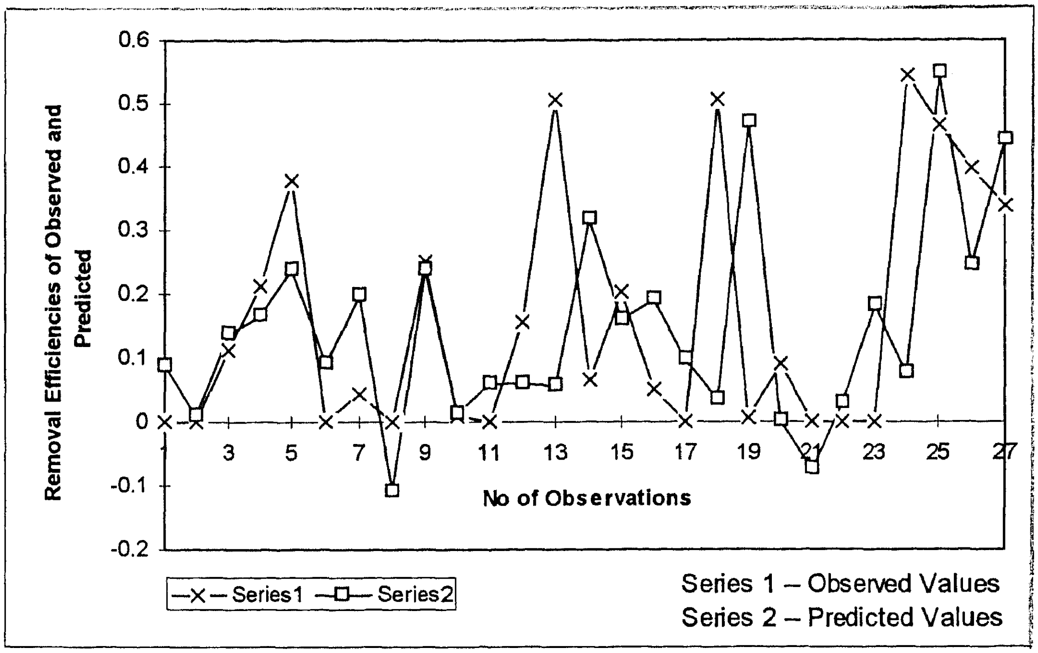

Fig. F. 21: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for Pyrene, Soil #3

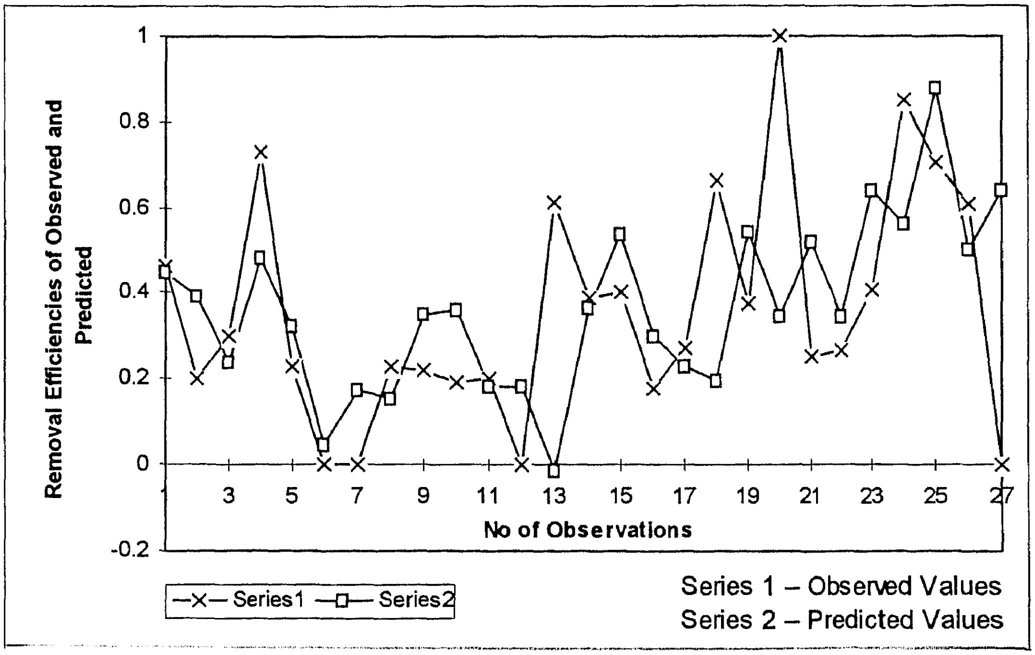

Fig. F. 22: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for Chrysene, Soil #3

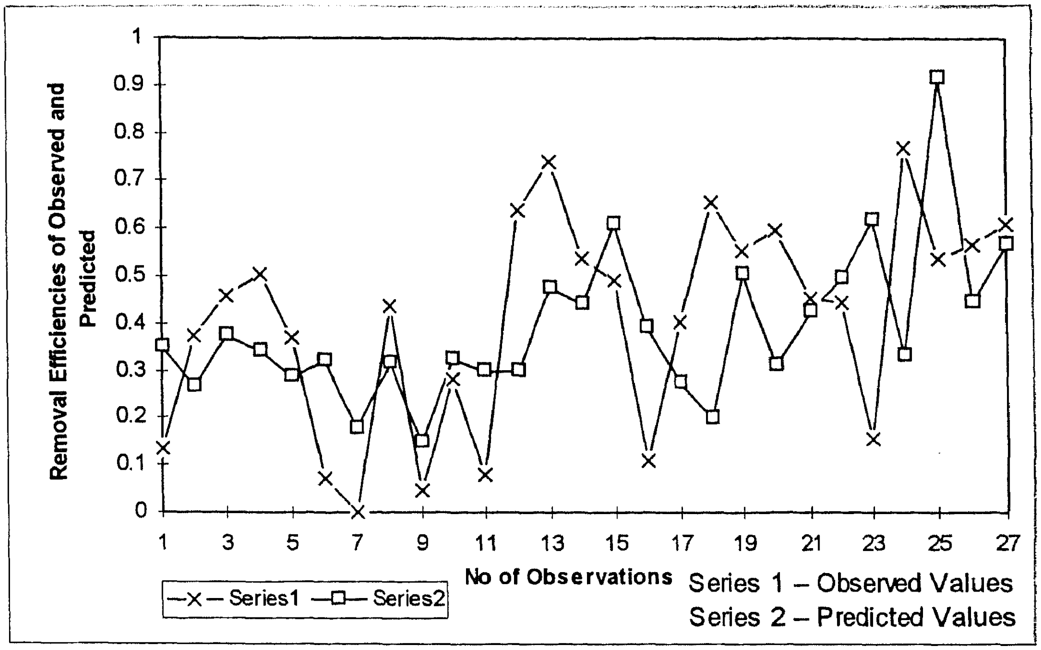

Fig. F. 23: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for Benzo(k)fluranthene, Soil #3

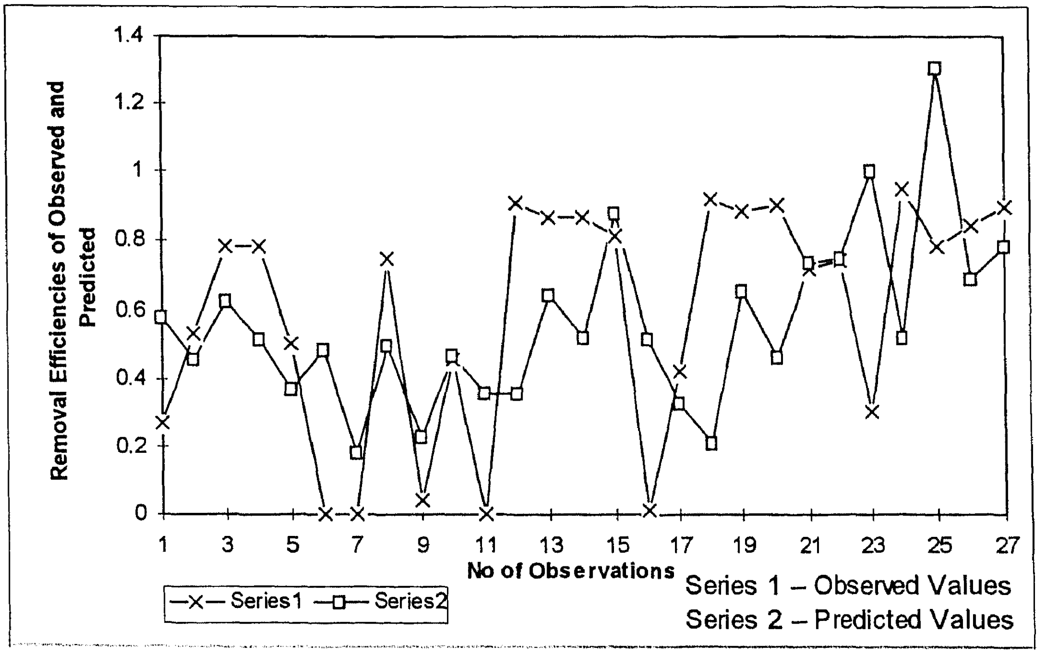

Fig. F. 24: The Comparison between the Observed Values and Predicted Values Using Regression Procedure Analysis for Benzo(a)pyrene, Soil #3

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