ABSTRACT

ANALYSIS AND MODELING OF ULTRASOUND TO DECONTAMINATE HEAVY METALS IN DREDGED SEDIMENTS

by
Ruvini Perera

Sediments contaminated with heavy metals due to past disposal practices threatens the environment and requires remediation. This research is an attempt to develop a technology to decontaminate heavy metals in the dredged sediments with an integrated set of processes using ultrasound. Acoustic cavitation caused by ultrasound energy can be used to remove chromium from the sediments. Two coupled processes were used to treat both coarse (Process#1) and fine (Process#2) fractions of the sediments. Full factorial experimental designs were carried out to evaluate the treatment technique and to statistically model and optimize the processes. The model for Process#1 had four contributing factors, namely power, soil-water ratio, vacuum pressure and dwell time, while Process#2 had power, soil-water ratio and dwell time as contributing factors. Removal efficiency was the dependent variable in both cases. The statistical analysis for Process#1 confirms that the chosen main factors significantly influence the removal efficiency and that a full quadratic model was adequate. The optimum removal obtained by the analysis was 97% with the factor levels at 1027.5 W power, 1:13 soil-water ratio, 18 psi vacuum pressure and 12 minutes of dwell time. The statistical analysis for the silt fraction in fines too, showed that a full quadratic model was adequate and the optimum removal of 99.4% can be obtained at factor levels at 1620 W power, 1:40 as soil to water ratio and 37 minutes of dwell time. The research showed that the proposed treatment technique is effective and economical for sediments with lower clay contents.

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by
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To my beloved parents

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CHAPTER 1

INTRODUCTION

1.1 Problem Statement

Harbors and waterways are routinely dredged to ensure safe navigable waters. Because of many of the waterways are located in industrial and urban areas, sediments are often contaminated with wastes from human activities. Ocean disposal of contaminated sediments has generated concern, and such operations may adversely affect water quality and aquatic organisms. The difficulty in finding suitable on land disposal sites for contaminated dredged sediment has resulted partial stoppage of dredging activities at some ports making them less competitive. The resulting economic impacts to the regions surrounding these ports have been severe. These sediments are contaminated both with high organic and inorganic concentrations. The existing disposal techniques have concentrated on sea disposal, artificial islands or disposal into lagoons for either containment or for long-term land reclamation, where the contamination levels of dredged sediments determine the end use.

Sediments contaminated with heavy metals require remediation. Heavy metal contamination is a common problem at many hazardous waste sites similar to heavy metals in dredged sediments. Once in the soil matrix heavy metals like chromium are absorbed making remediation difficult. Unlike many organic pollutants that can be eliminated or reduced by chemical oxidation techniques or microbial activity, heavy metals will not degrade. Chromium, Cadmium, Copper, Lead, Zinc and Mercury are the toxic metal contaminants.

These heavy metals adversely affect human health and, can cause variety of ailments including brain/neurological changes, liver and kidney damage and cancer.

Limited techniques have been used for remediation of heavy metal contaminated soils such as various soil washing techniques, chelating extractions, solidification, vitrification and land filling, which will be briefly discussed in Chapter 2. Soil excavation and handling in these technologies represents a very cumbersome and costly endeavor while landfills are scarce. Reuse of the contaminated sediments or deep sea dumping after decontamination will be the ideal solution for disposal of dredged sediments.

This is a laboratory study of application of ultrasound to decontaminate heavy metals (chromium) in dredged sediments. The dredged sediments from New York /New Jersey harbor are used in the demonstration study and chromium is selected as the metal contaminant for the quantitative evaluation of the treatment process.

1.2 Scope of Study

The reported study primarily embraces the optimization of chromium removal and development of a statistical model for removal efficiency.

The objectives of the study are:

- Understand the factors that contribute Ultrasound cleaning

- Selection of important parameters, which significantly influence the chromium removal efficiency

- Perform full factorial designs with the above parameters (factors) at various levels (factor levels) to evaluate the technology

- Critical examination of the results using the statistical analysis to determine the contributing parameters and their mutual interactions.

- Development of a statistical model to optimize the technology and to determine the maximum removal efficiency.

CHAPTER 2

LITERATURE REVIEW

2.1 Chromium

There are two types of chromium, natural and anthropogenic. Natural chromium in soil originated from the chromate mineral in magma upon exposure to the atmosphere and anthropogenic sources of chromium are generated from many industrial activities. The major industries processing chromium are the metallurgical, refractory and chemical manufacturing.

Trivalent chromium is considered to be more stable than hexavalent chromium, while the hexavalent form considered to be carcinogen. Hexavalent chromium is soluble in full pH range, but the trivalent chromium tends to precipitate as $Cr(OH)_3$ or be absorbed on soil surface, when pH is above 5.5.

The dominant species of chromium, which also indicates the potential hazard in soil, is controlled by the oxidation-reduction reaction of chromium in soils. In contaminated soil consisting clay, the cationic trivalent chromium is potentially attracted and absorbed by the negative charged sites on clay surface, while hexavalent chromium is present as an anion chromate, and is soluble in water and may precipitate as salt when the soil becomes dried.

2.2 Heavy Metal Remediation Methods in Soils/Sediments

Metals are natural constituents in soil. However as an adverse impact of unsafe waste disposal practices and the rapid industrialization, huge changes in the global budget of critical chemicals at the earth's surface has occurred.

Thousands of sites in the nation have been polluted with organic and inorganic contaminants resulting from various industrial activities including metal working, chemical processing, etc. Heavy metal contamination of soil is a common problem encountered at many of these hazardous waste sites and the sediments of many of the waterways that are located in and around industrial and urban areas, are contaminates with heavy metal wastes.

The difficulty in finding suitable disposal sites for increasing amounts of contaminated soils and contaminated dredged sediment has resulted the need to find effective and economical remediation technologies. Treatment of metal contaminated soil represents complex and challenging problems. Following is a brief discussion of remediation technologies for heavy metal contaminated soils and sediments.

2.2.1 Solidification/Stabilization and Landfilling

This method is well demonstrated and can be applied to the most common waste types including wastes with heavy metals. Metal wastes that cannot be eliminated by other means are usually stabilized and solidified in a suitable binder before disposal in landfills. Solidification/Stabilization reduces the mobility of metal contaminants by trapping or immobilizing the contaminants within the medium instead of removing them through chemical or physical treatment. The most common binder in containing heavy metal wastes is the Portland cement. Depending on the heavy metal ion, the mode of contaminant ranges from chemical fixation to physical encapsulation to produce a stable cement/waste solid matrix. Stability is defined by the amount of heavy metal leached under standard conditions.

The effects of the long term weathering, groundwater infiltration and physical disturbance can significantly affect the integrity of the stabilized mass and contaminant mobility. Finding the suitable disposal sites as landfills has become one of the major problems associated with this technology.

2.2.2 Vitrification

Vitrification is an innovative technology that converts the hazardous contaminated waste into chemically durable glass like product. This was first used to treat radioactive waste and was successfully demonstrated in bench and pilot scale studies by Pacific Northwest Laboratory (Bulet, et al. 1987). The study of Kamolponwijit W (1996) demonstrates the possibility of vitrifying chromium-contaminated soils. In the vitrification process, hexavalent chromium was reduced to trivalent chromium and incorporated into glass matrix of the vetrified products, which are physically and chemically similar to obsidian. The vetrified products are non-hazardous. The advantages of vitrification could be recognized by its long-term durability of waste, applicability to any kinds of wastes and soils, and volume reductions.

2.2.3 Heap Leaching

This method was originated with the precious metal mining industry and now being considered to use as remediation technology to treat heavy metals in soil. The contaminated soil will be left in heaps and a leaching solution is allowed to flow through the heap, which will dissolve the contaminants into the liquid phase. The leaching solution has to be treated separately to recover metals.

Hanson et. al.,(1993) studied the possibility of using this method with a laboratory scale column study. Experiments were carried out using a column instead of a heap to pile the contaminated soil and water was used as the leaching solution while chromium was selected as the contaminant. The study concluded the hexavelant chromium contaminated soils in arid climate (low in organics) could be decontaminated by heap leaching.

2.2.4 Soil Washing

This is one of the viable methods for removing undesirable heavy metals from soils with reasonable porosity. This method has been evaluated with increasing thoroughness during the past two decades. Soil washing is a chemical process that involves the separation of the contaminants from the soil fines by solubilizing or suspending them in a washing solution. In this technique the soil is vigorously mixed with the solvent, washed with water to remove the extraction solution in the soil. The metal rich wastewater will be treated separately to recover metals and solvents.

It's common to use an extraction solvent in the washing process, which are capable of desorbing the heavy metal contaminants from the soil into the solution.

These extraction solutions could be an acid, a base, a chelating agent, surfactant or some kind of alcohol. Several studies have been carried out to investigate the effectiveness of the different kinds of extraction solutions in the technique of soil washing. The ability to form stable metal complexes makes chelating agents like EDTA (ethylenediaminetetraacetic) and NTA (nitrilotriacetic acid) effective extractants for metal contaminated soils (Brown and Elliot, 1992; Elliot and Brown 1989).

It's shown that EDTA and NTA enhance the recovery of Chromium in soil washing when the EDTA/NTA concentration was above 1:1 ratio with the metal (Pitchel et al., 1997).

Metal removal efficiency during soil washing depends on soil characteristics (particle size), extractant chemistry, metal characteristics and processing conditions. Removal of metals like chromium is also a function of pH. Lower pH gives better recovery, but completely acidifing the soil is expensive due to its extensive buffering capacity and high acid strengths could destroy the soil structure.

2.2.5 Bioremediation

Bioreactors in the metal waste remediation are relatively a new concept. This has been used to treat chromium-contaminated wastes. The theory behind the treatment is to reduce the Cr(VI) to Cr(III) and immobilizes the contaminants by the means of bacteria. The study of Schieman.et al., (1998) reveals that providing calculated amounts of nutrients to a contaminated site would encourage bacterial growth and accelerate the rate of bacterial reduction of chromium. Bioremediation is still under investigation and should be studied in detail before implementing it as an effective solution in the metal waste remediation.

Ultrasound to treat dredged sediments eliminates most of the disadvantages of the above methods. Hence in this research ultrasound with sub-atmospheric pressures were applied to decontaminate method in dredged sediments.

CHAPTER 3

ULTRASOUND FOR SOIL DECONTAMINATION

Ultrasound refers to sound waves having frequencies in the range 16 kHz to 500 MHz, inaudible to the human ear, and can be transmitted through any medium with elastic properties, including water, gas-saturated water and aqueous particle suspensions. It is a form of mechanical energy, and its application to matter, under the right circumstances, can result in permanent physical changes. Ultrasound is widely used in industry for a variety of applications such as in medical imaging, cleaning metal parts, remove oxide films, oil, grease and other contaminants from solid surfaces and plastic welding, and even to remove contaminants from soils. As practiced today, the cleaning is done in batch processes where parts to be cleaned are placed in vats containing detergent solution to which ultrasound energy is applied. Ultrasonic tanks ranges in size from laboratory size to several thousand gallons. It is also possible to install submersible ultrasonic transducers into ordinary tanks or vats, thereby converting them into ultrasonic baths.

3.1 Mechanism of Ultrasound Application in Soil Decontamination

Ultrasonic waves have mechanical and chemical effects on a saturated soil medium. Studies of application of ultrasound in soil science are very few and are only in conceptual stages. Removing contaminants from soil using ultrasound is rather a new technology. Ultrasonic cleaning works by providing shear forces to remove the material adhering to a surface. The shear force is developed by cavitation.

Ultrasound causes high-energy acoustic cavitation- the formation, growth and implosive collapse of bubbles in liquid. Ultrasound waves consists 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 high intensity can generate cavities. In general a liquid is held together by attractive forces, which can be determined by surface tension 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 surface tension 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 the sound.

The growing bubble may eventually reach a critical size, where it absorbs energy most efficiently from ultrasound. This critical size depends on the frequency of the ultrasound wave. Once the bubble expands beyond the critical size, it can neither absorb the energy efficiently from the ultrasound waves, nor can survive without the energy input. Then the liquid rushes in and the bubble implodes. The gases and the vapor inside the bubble are compressed, generating intense heat that raises the temperature of the liquid immediately, in the surroundings of the bubble, creating local hot spots. These localized hot spots have temperatures of roughly 5000^0C, pressures of 500 atmospheres, and a lifetime of a few microseconds. Although the temperatures are extremely high in these, the region itself is so small that the heat dissipates quickly.

The number of cavitation bubbles collapsing per second may well be in millions. The cumulative effect of the bubble collapsing can be significant. In a solid-liquid system, these cavitational bubbles generate high differential fluid particle velocities, creating shear forces, which are capable of desorbing the contaminants from the soil particles and dispersing into the soil suspension by overcoming the forces binding the soil particles.

There has been no systematic work done in using ultrasound to remove contaminants in soils. To develop a technology to decontaminate sediments using ultrasound requires a well designed experimental program, with the results carefully analyzed on the basis of known ultrasonic cleaning mechanism. The objective of this study was to examine the potential usage of ultrasound energy to decontaminate heavy metals in dredged sediments. Ultrasound energy was applied to the contaminated soil in the slurry form and a sub-atmospheric pressure was applied to remove the contaminants from the slurry. This sub-atmospheric system was designed to extract fines with contaminants from Process #1 through US sieve #200, and the contaminated water from Process #2 through the porous stone.

3.2 Experimental Approach

The experimental approach of this study was an integrated process of multiple functions. It was designed to use a sonication coupled with extraction using sub-atmospheric pressure to remove contaminants. The flow chart followed explains the process in detail.

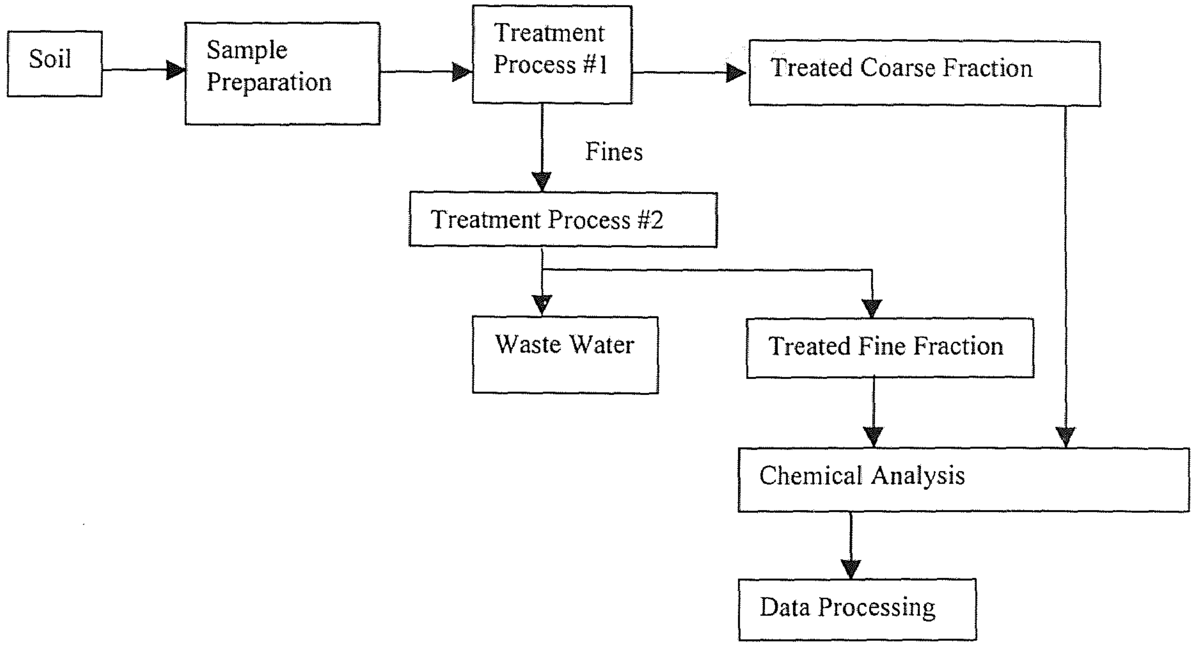

Figure 3.1 Flow Chart of the Experimental Approach

Treatment Process #1 is an attempt to separate fines from the bulk dredged suspension and removes them using sub-atmospheric pressure while cleaning the coarse particles, and treatment process#2 decontaminates fines and separates decontaminated fines from the contaminated water using a sub-atmospheric pressure as in process#1. Treating of the contaminated water was not investigated in this study. These processes will be discussed in detail under the experimental procedures in Chapter 4. Process variables that influence the treatment processes were selected according to the pre-experimental data. The number of experiments and the factors were designed based on the full factorial design for the statistical analysis.

3.2.1 Selection of the Ultrasound Source

Two sources of ultrasound, a probe type and an ultrasonic bath type, were investigated by Meegoda et.al., 1995. They revealed that probe type has higher intensity of local energy. However the disadvantage of the probe type is that the temperature of the system cannot be held constant during the experiment. Also it was noted the inability to vary the frequency. But when compared with the ultrasonic bath system, with all the disadvantages, still probe type is more effective because of its higher intensity. Therefore it was decided to use the probe type ultrasound in this study.

3.2.2 Selection of the Variables that Contribute to Ultrasound for Removal of Chromium in the Sediments

The following are the variables that could contribute to ultrasound for decontamination of sediment:

- Power
- Soil to water ratio
- Dwell time
- Solvent pH
- Ultrasonic frequency
- Suspension temperature
- Particle size distribution
- Probe insertion depth.
- Vacuum pressure

From the above factors only the most significant factors are chosen based on the following study. Previous study by Rajaratnam K (1997) reported that the solvent pH does not contribute significantly to the removal efficiency. The probe type ultrasound source used in this study has a power of 1500 W operating at 20 kHz, and there are no commercially available ultrasound sources at reasonable costs with the same power rating but with different frequencies. Therefore frequency was not considered as a factor in this research. It was noted that the increase in temperature due to ultrasound is proportional to the dwell time. Since with the probe type ultrasound source, temperature could not be controlled, it was decided to run the experiments at room temperature without temperature control. Raine and So (1994) reported that with decrease in particle size there must increase the number of particles, which will result the increase in cavitation in the system, however this effect – Particle size distribution- does not significantly affect the energy dispersion. Therefore particle sizes are not considered as a process variable in this study. Morra et.al.,(1991) observed that increase in energy depends on the depth of insertion, the width of the probe and the dimensions of the container. Based on that study it was decided to keep the factor probe insertion depth a constant.

Hence it was concluded that the critical factors which should be considered to be power, soil to water ratio, sonication time and vacuum pressure.

CHAPTER 4

EXPERIMENTAL DESIGN AND PROCEDURE

4.1 Experimental Design

The objective of the experiment design was to collect unbiased data that can be analyzed by statistical methods to obtain a valid, meaningful interpretation of data and conclusions. It is decided to perform a full factorial design for both process #1 and process #2, to obtain data for process evaluation and for the statistical analysis. The four factors power, soil to water ratio, sonication time and vacuum pressure are chosen to be the design variables in the experimental design. A series of experiments were performed to obtain the required range of levels for the each process variable in order to carry out the experimental design. These experiments were used to find the optimum removal efficiency. Each set had one varying factor while keeping the others constant.

The figures in Appendix A show the results of the above experiments for the Process #1. It could be seen that after 15 minutes of ultrasound energy, there was no significant change in the removal efficiency. Therefore the maximum value for the time was taken as 15 minutes. When considering power variation, it's seen that it is reasonable and economical to take 80% power input as the highest level. Similarly vacuum pressure levels were chosen as 5psi, 10psi and 15psi, while soil to water ratios were taken as 1:5, 1:10 and 1:15. Considering these results the levels of the process variables for the full factorial design of the Process #1 were selected as given in Table 4.1. Four factors at three levels produced 81 combinations.

In the experimental design, both the separation and the removal efficiencies were determined for all of the 81 experiments.

Table 4.1 Factor Levels of Process#1

Factors	Level 0	Level 1	Level 2
Power (%)	40	60	80
Soil-water ratio	5:1	10:1	15:1
Vacuum pressure (psig)	5	10	15
Sonification time (mins)	5	10	15

In order to streamline and maximize the output preliminary tests were conducted to investigate the optimum range of values to be used for the experimental design. Vacuum pressure was kept a constant, at the highest level (15 psi) to obtain high circulation of wastewater. The highest power level was chosen as 80% and a higher soil to water ratios and dwell times were selected compared to the Process #1, for better removal. The factor levels of the three parameters for the Process #2 are shown in Table 4.2. Three factors at three levels produced 27 combinations.

Table 4.2 Factor Levels for Process #2

Factors	Level 0	Level 1	Level 2
Power (%)	50	60	80
Soil-water ratio	10:1	25:1	50:1
Sonification time (mins)	30	60	90

The following is the experimental design for the Process#1. Process variables power, solvent-soil ratio, vacuum pressure and sonification time each having 3 levels (0, 1 and 2) were represented one treatment combination in the following order as given below.

4.1.1 Full Factorial Design for Process#1

(power, solvent-soil ratio, vacuum pressure, time)

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

Where for

Example: Treatment combination (0102) means;

Level 0 of power, which is 40%

Level 1 of solvent-soil ratio, which is 10:1

Level 0 of vacuum pressure, which is 5psi

Level 2 of time, which is 15 minutes.

The experimental order was randomized to get unbiased results as follows:

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

The experiments were carried in the above order of randomized form.

4.1.2 Full Factorial Design for the Process#2

(power, solvent-soil ratio, time)

020 021 022 010 011 012 000 001 002
120 121 122 110 111 112 100 101 102
220 221 222 210 211 212 200 201 202

4.2 Materials and Equipment

4.2.1 Soil Used

The contaminated soil used was dredged sediments from the New York/New Jersey metropolitan area, which was categorized as a material that failed to meet USEPA requirements for toxicity or bioaccumulation.

According to the data supplied by the Brookhaven National Laborotory in New York, this soil has water content of about 225%, and the pH is 8. It was heavily contaminated with organic as well as with inorganic compunds. The coarse fraction is considered as soils retained on US sieve #200 (0.075mm), and fines are considered as soils passing US sieve #200. Figure 4.1 shows the particle distribution of the soil.

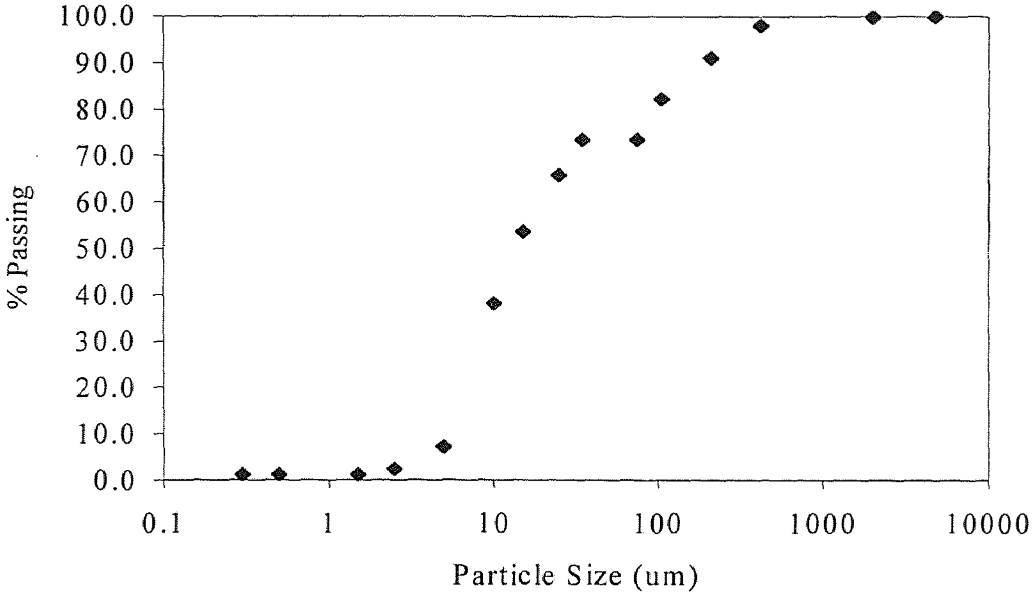

Figure 4.1 Particle Size Distribution of the Soil

4.2.2 Equipment Used

4.2.2.1 Ultrasound Source: Ultrasound energy was supplied using a 1500-Watts probe (Sonics & Materials Inc., Model VC1500, 220 Volts, Power 1500 Watts, Frequency 20 kHz). The power intensity meter controlled the actual power applied to the system.

4.2.2.2 Microwave: Microwave Digestion System- Model MDS-2100 from CEM Corporation was used for metal extraction from soil, in this study. The microwave energy was used to heat samples. This microwave device delivers approximately 950 Watts of microwave energy at a frequency of 2450 MHz at full power. This system is microcomputer controlled and monitors its operation.

4.2.2.3 Advanced Composite Vessels: Advanced Composite Vessels are designed for use inside the CEM microwave. The vessel consists of a chemically resistant liner and cover to contain, and isolate a sample solution. The materials of the vessel are transparent to microwave energy so that liquid and sample inside can absorb the maximum amount of incident microwave energy.

Specifications:

Vessel volume	100 ml
Maximum operating temperature	200^0C
Maximum operating pressure	200 psig

4.2.2.4 Atomic Absorption Spectrometry: Flame Atomic Absorption Spectrometry-Smith Heiftje 12 of Thermo Jarrel Ash Coporation was used for chromium analysis.

4.2.2.5 Other Experimental Apparatus: These will be discussed under the heading Experimental Procedure, relevant to each process in detail.

4.3 Experimental Procedure

4.3.1 Sample Preparation

Sample preparation was begun with the wet raw sediments. These sediments were highly contaminated with organics. Higher organic concentration is expected to give background errors in Atomic Absorption Spectrometry, which was used for the chromium analysis. Therefore, to have a better control over chromium it was decided to eliminate the organics from the sediment before applying ultrasound. This was achieved by keeping the sample in batches, in an oven at a temperature of 600^0 C for 36 hours. Then the sample was crushed manually to homogenize, and to avoid breaking coarse particles. Dried homogenized sediments were used as the input, material in Process #1.

4.3.2 Process #1

This process was designed to separate fines from the bulk dredged suspension and removes the using sub-atmospheric pressure while treating the coarse particles. Figure 4.2 shows the experimental apparatus specially designed to implement Process #1.

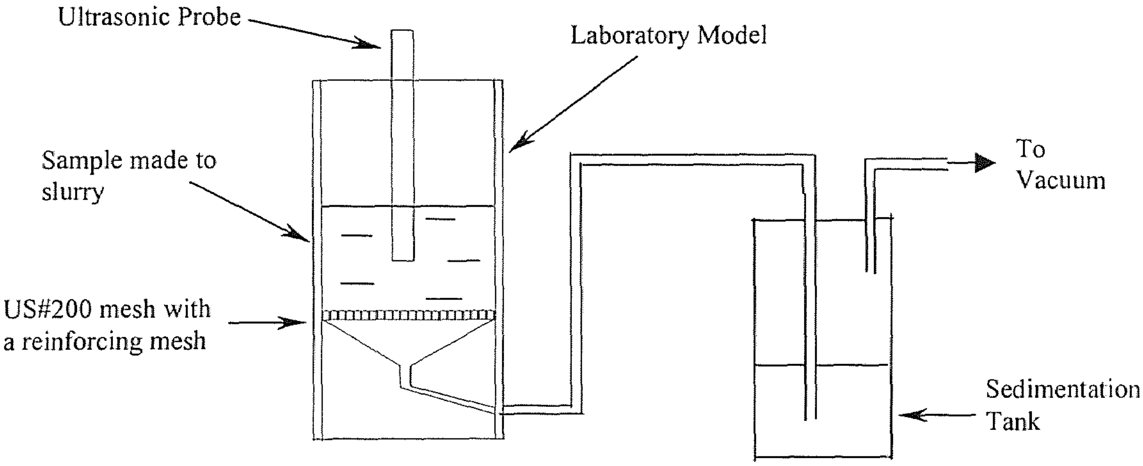

Figure 4.2 Laboratory Apparatus Setup for Process #1

Laboratory model was built as a cylindrical container separated into two parts with a US#200 mesh, which was used to separate the fines from coarse. The outlet of the model was connected to a vacuum through a sedimentation tank, which was used to collect fines and water. The ultrasound probe was dipped into the sample slurry.

The total volume of sediment slurry was kept constant (500mL) when performing experiments to evaluate Process #1. To find the initial chromium concentration, the prepared sediment sample was sieved using a US#200 sieve and the retained fraction, which was considered as the coarse fraction was used to determine the chromium concentration. The slurry was made with the measured amount of soil knowing the soil to water ratio and keeping the total volume constant at 500mL. The slurry was placed inside the container as shown in Figure 4.2, and ultrasound energy with the required power setting and the vacuum pressure with desired magnitude were applied for sonication given by the experimental design for each run. Water was added continuously to maintain the constant volume. At the end retained coarse was oven dried, measured, to find the separating efficiency, and was tested to determine final chromium concentration. The separated fines were used as the input for the porcess#2. Chromium analysis was performed by acid digestion of soil using the microwave method followed by Atomic Absorption Spectrometry analysis, which will be discussed in Chapter 5.

4.3.3 Process #2

This process attempts to decontaminate fines and to separate contaminated water using a sub atmospheric pressure. Figure 4.3 gives the laboratory set up for process#2.

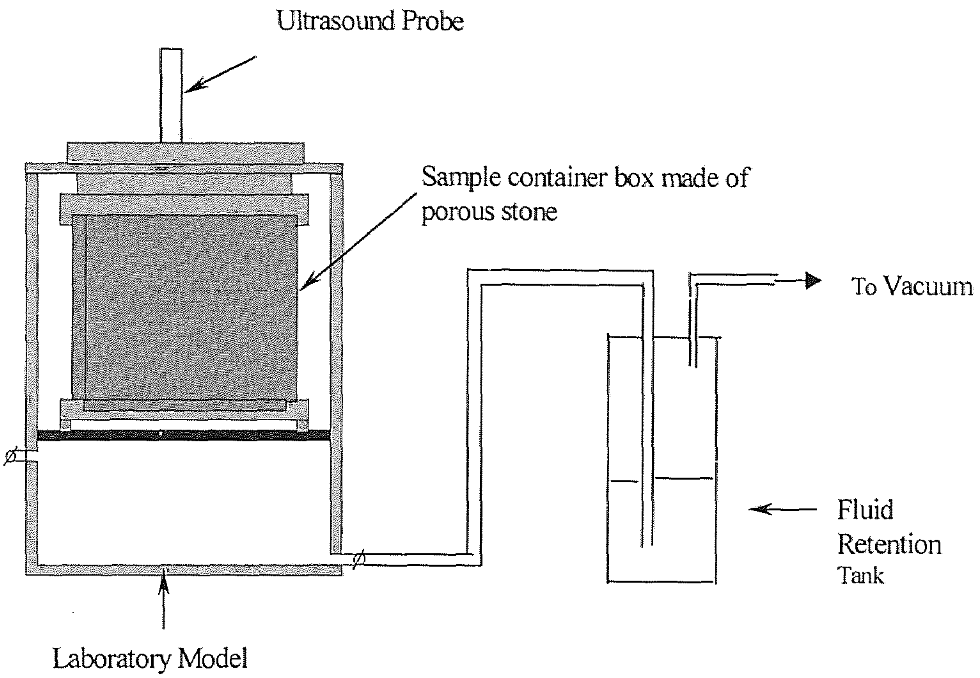

Figure 4.3 Laboratory Apparatus Setup for Process#2

A laboratory batch test module in the shape of a box was made of five porous stones as the sample container, where the ultrasound probe was dipped, and an outer box to apply vacuum pressure to the pores. The porous stones were used to separate the water from fines. The outlet of the outer box was connected to a third retention tank to collect wastewater, which was connected to the vacuum.

The collected fine sediments from process#1 were used as input to be treated in Process#2. These sediments were oven dried after process#1 and was tested for the chromium concentration after process #1, which was considered as the initial concentration for the Process #2.

The total volume of sediment slurry was kept as a constant (1000mL) during each experiment. The slurry was made with the measured amount of soil, each time according to the solvent to soil ratio, with 1000mL as total volume.

The slurry was placed in the batch device and ultrasound energy with the required power setting and the maximum vacuum pressure were applied for a required time period given by the experimental design. Water was added continuously to maintain the constant volume. At the end of the test the retained slurry was oven dried and determined the final chromium concentration. The Chromium analysis for the separated silt and clay fractions, was performed by acid digestion of soil using the microwave method followed by Atomic Absorption Spectrometry analysis. Twenty-nine experiments were run under similar conditions. For process#2 two additional experiments were conducted to explore the possibility of better treatment efficiency. They are as follows:

4.3.3.1 With pH Variation: Two experiments were conducted with sample slurry pH as 2 and 12. The original sample slurry pH was 8. Sodium hydroxide (NaOH) was added to make the slurry to increase the pH to 12 and Nitric acid was added to lower the pH to 2. Both these samples were run with 50% power, 50:1 solvent to soil ratio and ultrasound energy, applied for 60 minutes. The experiments were done as described above and the samples were oven dried. The chromium analysis was performed the same way and the results were compared.

4.3.3.2 With Chelating Agents: Ethylenediaminetetraacetic acid (EDTA) was used as the chelating agent. Two kinds of EDTA- with Sodium and without Sodium- were used in two separate experiments. The power output was 50%, solvent to soil ratio was 50:1 and the ultrasound was applied for 60 minutes. The experiments were carried out in the similar manner including the determination of chromium concentrations.

CHAPTER 5

ANALYTICAL PROCEDURE

The analytical procedure for the analysis of chromium in soil consists of two steps. The first is chromium extraction from soil using microwave digestion and the second is the analysis of chromium using the Atomic Absorption Spectrometry.

5.1 Sample Preparation for Chromium Analysis using Microwave Digestion

Sample preparation is a critical step in trace metal analysis by Atomic Absorption Spectrometry. Digestion methods have gained wide acceptance in preparing samples for trace metal analysis. Microwave digestion is often used in preference to heating in an open container. This method provides for acid extraction of soil following SW 846 method 0351 of EPA. Microwave heating is widely used with mineral acids such as Nitric acid that absorbs microwave energy and heat very rapidly. These digesters are similar to the microwave ovens used in cooking but having a corrosive resistant interior surface. The oven is programmable where times and power levels can be set before extraction, which allows to run two samples under the same conditions at two different times. For homogeneous distribution of energy the digesters are equipped with rotating turntable. Closed Teflon vessels, which are capable of withstanding internal pressures of 100-150psi, and can control pressure and temperature during microwave heating. Pressure relief valves were attached to vent manifold, to vent acid vapors, when the vials are heated. The great reduction of the testing time comes from combining the speed of microwave heating with the elevated temperature achieved in sealed Teflon containers.

The traditional method of sample digestion requires close and constant attention by the analyst to prevent the unintentional boiling of samples to dryness. It needs a longer time to insure complete digestion compared to microwave digestion. Less sample contamination, less venting of acid fumes, rapid and effective digestions of samples are the main advantages of microwave digestion over the traditional method.

5.1.1 Procedure

Nitric acid was used as the reagent according to the EPA method SW 846 - 0351. A 0.5grams of the sample was weighed into the vessel and 10ml of nitric acid was added. The vessels were placed in the turntable and vent tubes from vessels were connected to the collection vessel. A vessel, which was connected to pressure temperature sensors, was used with the most reactive sample.

<u>Program Variables.</u>

Power : 100%

Maximum Pressure : 200psi

Temperature :175C

Fan speed :100%

Ramp time : 5mins. 30 secs

Hold time : 4mins 30 secs

Number of vessels : 06

Volume per vessel :10ml

Sample weight :0.5g

Acid : Nitric

After running the heating program to completion the samples were left to cool to the room temperature. The solution in the vessels was then transferred into the Teflon tubes using pipettes. The extracted acid solution was diluted before the analysis.

5.2 Chromium Analysis using Flame Atomic Absorption Spectrometry

Atomic Absorption Spectrometry (AAS) has been the most widely used method for determination of single elements in analytical samples. This method is based on EPA SW 846-7190. This method is simple, rapid and applicable to large number of metals. In direct aspiration AAS, a sample is aspirated and atomized in the flame. A light beam from a hollow cathode lamp is directed through the flame into a monochramator, and onto the detector that measures the amount of absorbed light. The sensitivity is 0.04ug/ml and for wavelength 357.9nm. The maximum concentration is 5ug/ml.

5.2.1 Procedure

Instrumentation Parameters

- Reagent - Water
- Fuel - Acetylene
- Oxident - Nitrous Oxide
- Type of the flame - Fuel rich
- Chromium hollow cathode lamp

Fuel flow rate used was 4-5 l/min, the oxident flow rate was 10-12 l/min, the nebuliser intake was 4ml/min, the hollow cathode lamp was operated at 6 mA, and the wave length of the light used was 357.9 nm.

Calibration standards were made of 1ppm, 2ppm, 4ppm and 5ppm concentrations by diluting the stock metal solution. Standards were aspirated at the beginning with the blank. Diluted samples were aspirated followed by the standards. Concentration of the sample was found by using the dilution factor. If the concentration was found to be more than the highest standard concentration used, then the sample was diluted to get the concentrations within the range.

5.3 Determination of the Separation Efficiency

From the particle size analysis it's found that 28.91% was considered as coarse particles (retaining on US sieve #200). The percentage separation efficiency was calculated using the following equation.

$$\text{Separation Efficiency} = \frac{[\,W_f - (W - W_c)]}{W_f} * 100\ \% \quad \text{......................................}(5:1)$$

Where; W_f = Weight of the fines in the initial sample used

= Weight of the sample used * 71.09

W = Weight of the sample retained on the #200 mesh in the model, after Treatment

W_c = Weight of coarse fraction in the initial sample used

= Weight of the sample used * 28.91

5.4 Determination of the Removal Efficiency

The percentage removal efficiency was calculated using the following equation.

$$\text{Removal Efficiency} = \frac{(\text{Initial Concentration} - \text{Concentration after treatment})}{\text{Initial Concentration}} * 100\ \%$$

..............................(5:2)

CHAPTER 6

ANALYSIS OF THE RESULTS

6.1 Process#1

The series of experiments that were performed to obtain the required range of levels for the each process variable, produced the results in Appendix A. Except for solvent to soil ratio variation all the other experiments gave 100% separation efficiency. Figure 6.1 shows the separation variation in the solvent to soil ratio variation set of experiments.

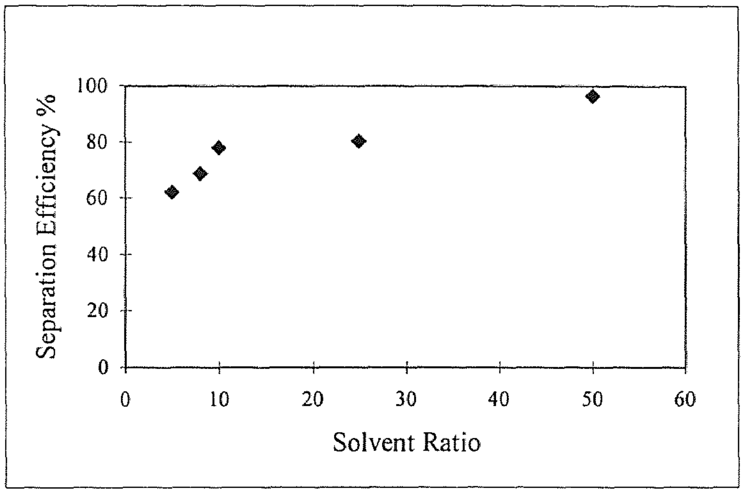

Figure 6.1 Separation Efficiencies for Varying Soil to Water Ratios with 60% Power, 10psig Vacuum Pressure and 6 minutes of Sonication

In the experimental design both the separation and the removal efficiencies were determined for all 81 experiments. Table B.1 in Appendix B shows experimental data for all the 81 experiments while the Appendix C elaborates the data in the following manner:

- One factor at three levels and remaining three factors at their lowest level

- One factor at three levels and remaining three factors at their middle level
- One factor at three levels and remaining three factors at their middle level

The above procedure gives 12 plots, which were reported in Appendix C. Figures C.1 to C.3 shows low removal levels because power, solvent to soil ratio, vacuum pressure and dwell time are at the lowest level. When soil to water ratio varies there seems to be an improvement which was almost as the removal efficiency as when power is 60% and all the other levels are in their lowest level as shown in figure C.2. When factors are at their lowest level except for one varying factor, the removal efficiencies are varying from lowest (19.96%) to the mid-level (70%). The lowest removal was obtained at 40% power, 5:1 solvent to soil ratio, 5psi vacuum pressure and 5 minutes of dwell time. From Figures C.9 to C.12 show higher removal efficiencies. That is because they are at the highest power level, which is 80% of power. The maximum removal efficiency (92.22%) was obtained when all the levels are at their highest level. Those are 80% power, 15:1 solvent ratio, 10 psi vacuum pressure and 15 minutes dwell time. In figure C.10, it can be seen even with the power at the mid-level (60%), when all the others factors are at their highest levels higher removal efficiency (89%) close to maximum could be obtained.

6.2 Process#2

It was found that process#2 separated fine fraction of the bulk sediment into silt and clay. For better interpretation of results both silt and clay concentrations were determined separately. The separation efficiency was 100% for all the Process #2 experiments.

Data representation in Process#2 follows the same as Process#1. Chromium removal of silt fraction of all the experiments were shown in Appendix D. It's seen that the removal efficiencies were very low when all the factors are at the lowest levels. It reached a maximum of 82% when all the factors were in their highest levels. But these factors are not significantly sensitive to the chromium removal efficiency.

Table B.2 and figure B.1 in Appendix B compares the removal efficiencies of clay and silt fraction for all 27 experiments. The removal efficiencies in the clay fraction were very low. Therefore, further investigations were performed at different pH levels and with chelating agents.

Table 6.1 shows the results obtained from the pH variation. It is seen that there is no significant change to the removal efficiency of the clay.

Table 6.1 Removal Efficiencies of Clay and Silt with the pH Variation

PH	Removal Efficiency %	
	Silt	Clay
2	61.00	-5.11
8	62.77	0.61
12	67.00	-36.8

Table 6.2 shows the variation with the chelating agent (EDTA) with and without Sodium. A crust was found to be formed with silt, when the sample was dried and also there was silt fraction in the sample without Sodium. Salt was found in the sample with Sodium. All these samples were tested separately for chromium removal.

Table 6.2 Removal Efficiencies of Clay and Silt with EDTA

EDTA	Removal Efficiency %	
	Clay	Silt
with Na	18.69	79.34
w/o Na	22.08	92.54

The results show that there are no significant changes in the removal efficiencies of clay fraction and the silt fraction even at different pHs or with chelating agents. It appears that the proposed technology is only applicable for soils without significant amount of clay. When the particle size decreases the removal becomes more difficult. It can be concluded although the clay fraction does not get treated by this method, its still safe to dispose clay fraction after Process #2, since the mobility of chromium is negligible. This is also concluded in a research of laboratory studies on remediation of chromium contaminated soils by Krishan and Canter (1999). They showed that soils with higher clay content were less amenable to chromium extraction than with soils with lower clay. Also Nelson et al., (1997) showed from a study of removal of heavy metals using chelating agents, that treating soils contaminated with chromium in trivalent state may not be necessary since the leachability of the metal may be minimal.

CHAPTER 7

STATISTICAL ANALYSIS OF THE EXPERIMENTAL DATA

7.1 Statistical Approach

The statistical approach has two aspects to any experimental problem. One is to design the experiments and the other to statistically analyze data. The objective of the statistical design of experiments performed is to collect the appropriate data that can be analyzed by statistical methods. In this study, statistical analysis was used to find a model, which could be used to predict the optimum removal efficiencies for each process. Statistical methodology is the preferred way of analysis when data are subject to experimental errors.

7.1.1 Design of Experiments

Two full factorial designs of experiments were used for Process#1 and Process#2 as mentioned in Chapter 4. For the Process#1 the most influential parameters for the removal of Chromium from the sediments, power, soil-water ratio, vacuum pressure and sonication time were chosen as the process variables (class) and each of the process variables is assigned with three levels. These three levels were based on the pre-experimental planning. Four classes and three levels produce 81 sets of data. For Process#2 the pre-determined process variables are power, soil-water ratio and time and each has three levels. Three classes and three levels produce 27 data. For both the processes the response variable is the removal efficiency.

7.1.2 Statistical Data Analysis

SAS/STAT version 6.09, a statistical computer software was used to analyze the data. It is a module of SAS (Statistical Analysis System) for statistical data analysis. SAS is an integrated collection of data management, analysis and reporting computer software package provided by the SAS Institute. General Linear Model (GLM) procedure and REREG-regression procedure are the two models used in this analysis from SAS/STAT module.

7.2 Statistical Analysis using the General Linear Model (GLM) Procedure

7.2.1 General Linear Model (GLM) Procedure

GLM procedure was used to find the dependence of the response variable to the process variables and the dependence of response variable to the interactions between the process variables. Even for an unbalanced design, GLM is the best choice for the statistical analysis. Once the dependence between the response variable and the process variables was found, an appropriate model can be chosen to estimate model parameters. This was done by using the regression procedure.

The following three effects were considered for Process#1:

- Main Effects

The main effects are:

- ☐ Power - (power)
- ☐ Soil-water ratio - (swratio)
- ☐ Vacuum pressure - (press)
- ☐ Dwell time - (time)

- Second Order Interaction Effects

The second order interaction effects are:

- ☐ (power*power)
- ☐ (power*swratio)
- ☐ (power*pess)
- ☐ (power*time)
- ☐ (swratio*press)
- ☐ (swratio*time)
- ☐ (press*time)

- Third Order Interaction Effects

Third order interaction effects are:

- ☐ (power*swratio*press)
- ☐ (power*swratio*time)
- ☐ (swratio*press*time)
- ☐ (power*press*time)

For Process#2:

- Main effects

The main effects are:

- ☐ Power - (power)
- ☐ Soil-water ratio -(swratio)
- ☐ Dwell time (time).

- Second Order Interaction Effects

The second order interaction effects are:

- ☐ (power*power)
- ☐ (power*swratio)
- ☐ (power*time)
- ☐ (swratio*time)

- Third Order Interaction Effect

Third order interaction effect is (power*swratio*time)

7.2.2 The Terminology

The terminology used are summarized below:

- ***Degree of Freedom (DF)***

The number of degrees of freedom (DF) of a statistic, can in general be defined as the number (N) of independent observations in the sample (the sample size) minus the number (k) of population parameters which can be independently, estimated from the sample observations, that is:

$$DF = N - k \qquad \text{(7.1)}$$

For ANOVA model in this study,

$$\text{Total } DF = N - 1; \qquad \text{(7.2)}$$

DF of each main effects, (ex; power) = Number of levels – 1 = 3-1 = 2

DF of each second order interactions, (ex; power*swratio) = 2*2 = 4

DF of each third order interactions, (ex; power* swratio*time) = 2*2*2 = 8

Thus with N=81, for four factors at three levels (3^4)

DF for the corrected total = N – 1 = 81 –1 = 80

DF for model = Sum of DF of all the sources which are used in this analysis = 64

DF for the error = DF of corrected total – DF of the model = 80 – 64 = 16

- ***Mean Square***

The mean square is defined as the ratio of sum of the squares to the degree of freedom.

$$\text{Mean Square} = \frac{\text{Sum of Squares(SS)}}{\text{DF}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (7.3)$$

- ***F-Test***

F- distribution gives the distribution of the relative inference for two independent samples using the variances. F-test is a test to test the variance explained by the model and the variance unexplained.

$$\text{F value} = \frac{\text{Mean square of model}}{\text{Mean square of error}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (7.4)$$

- ***Pr>F***

Pr>f is technically called the “p-value” or the observed significant level. The probability of obtaining at least or greater than F-value given that null hypothesis is true is called the p-value. It is the risk of wrongly rejecting the null hypothesis. Using 5% significance level, if the p-value or the Pr>F value of a given process variable is less than 0.05 (5%), then it can be concluded that the process variable has a significant influence on the response variable.

7.2.3 Evaluation of the GLM Procedure

7.2.3.1 Process#1: The results of the GLM procedure for the experimental data are given in Table E.1 and the summary is given in Table E.2 in Appendix E.

Conclusions from the statistical analysis are as follows:

- As for the overall model the value of Pr>F is 0.001which is less than 0.05 (5%). This is strong evidence that the factors as a whole influence the removal efficiency. The conclusion drawn from that is that the model is adequate for these data (Refer Table E.1).
- All the main effects have the value of Pr>F as 0.0001 which is less than 5%. That concludes all of the main effects individually influence the response variable, which is the removal (Refer Table E.2).
- For the second order interactions, its seen that only (power*press) with Pr>F value as 0.0141, (power*time) with Pr>F value as 0.0040 and (press*time) with Pr>F value as 0.0237 has the significant influence on removal (Refer Table E.2).
- In third order interactions, only (power*swratio*press) with Pr>F value as 0.0067 and (power*press*time) with Pr>F value as 0.0139 influence the removal (Refer Table E.2).
- As the overall conclusion from these informations, the model is adequate for these data and a full quadratic model is selected to find optimum operating conditions.

7.2.3.2 Process#2: In Process #2, the removal efficiencies of silt fraction and clay fraction were measured separately. After the process #2 treatment, it was found that the process has separated the silt and clay in the fine fraction and also in most of the experiments the chromium content in the clay fraction has increased while the silt fraction was treated. The other results were reported in the Chapter 6. The results of the GLM procedure for silt and clay fractions are given in Tables E.3 and E.4 in the Appendix E.

The information added from the above data is:

- As for the overall model of silt the value of Pr>F is 0.2691, which is not acceptable with the 95% confidence. The conclusion drawn from this is the model is adequate with a 75% confidence level. As for the clay is concerned the value of Pr>F is 0.8536 which is not acceptable and would not be considered as an adequate model (Refer Table E.3).
- In silt only solvent to soil ratio has a value of Pr>F value of 0.03750 which is less than 5%. That concluded the only factor that has a significant effect on the removal of chromium from silt. But in clay, all of the factors are not sensitive to removal (Refer Table E.4).
- All the second order interactions, the third order interaction and the other first order interactions are acceptable with in the same range of confidence levels for both the cases.

7.3 Regression Procedure (RSREG)

In this analysis we have used the Response Surface Method (RSM) for process optimization using the RSREG option in the SAS/STAT software. RSM is a set of mathematical and statistical tools for the modeling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize this response. The response surface analysis is done in the in the terms of the fitted surface using the method of least squares in parameter estimation.

From the evaluation of the GLM analysis, a full quadratic model is used for the parameter approximation in our analysis. REREG 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.

RSREG procedure does the following steps in the analysis:

1. Analysis of Variance (ANOVA) to determine the model fitting
2. Canonical analysis of response surface to characterize the response surface.
3. Ridge analysis to find the region of the factor levels that gives the optimum response

7.3.1 Analysis of Variance (ANOVA)

ANOVA techniques attempt to predict the value of a continuous, dependent variable given the value of one or more categorical independent variables using the least square method. ANOVA estimates the mean of the dependent variable for each level of the independent variable using the equation predicted with the estimated values. Also it gives the information about the adequacy of the model fitting in the form of an analysis of variance.

7.3.2 Canonical Analysis of Response Surface

Second order model which was used is shown in equation 7.5,

$$y = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} b_{ii} x_i^2 + \sum_{i,j=1}^{k} \sum_{j \neq i} b_{ij} x_i x_j$$

............................(7.5)

To optimize the predicted response the levels of x_1, x_2... x_k are found at the point where all the partial derivatives corresponding to the levels are equal to zero. This point is called the stationary point. The stationary point could be a minimum, a maximum or a saddle point. To find this characteristic of the stationary point Canonical analysis is used.

Canonical analysis is done by transforming the model into a new coordinate system with the stationary point as the origin and then rotate the axes of the system until they are parallel to the principal axes of the fitted response surface. This will eliminate all the cross product terms.

Writing the equation 7.5 in matrix notation;

$$\hat{y} = b_0 + x'b + x'Bx \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7.6)$$

Where

$$x = \begin{bmatrix} x_1 \\ x_2 \\ . \\ . \\ x_k \end{bmatrix} \qquad b = \begin{bmatrix} b_1 \\ b_2 \\ . \\ . \\ b_k \end{bmatrix} \qquad B = \begin{bmatrix} b_{11} & \frac{1}{2}b_{12} \ldots\ldots\ldots\ldots \frac{1}{2}b_{1k} \\ \frac{1}{2}b_{21} & b_{22} \ldots\ldots\ldots\ldots \frac{1}{2}b_{2k} \\ \ldots\ldots\ldots\ldots & \\ \frac{1}{2}b_{k1} & \frac{1}{2}b_{k2} \ldots\ldots\ldots\ldots b_{kk} \end{bmatrix}$$

b is a (k x 1) vector of the first-order regression coefficients and **B** is a (k x k) symmetric matrix whose diagonal elements are the pure quadratic coefficients.

If the new transformed model in the canonical form is

$$\hat{y} = \hat{y}_s + \lambda_1 w_1^2 + \lambda_2 w_2^2 + \ldots\ldots\ldots\ldots + \lambda_k w_k^2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7.7)$$

Where $\{w_i\}$ are the transformed independent variables and the $\{\lambda_i\}$ are the constants and are just the eigenvalues of matrix **B**. The nature of the stationary point can be determined by the sign and the magnitude of the eigenvalues. If all the eigenvalues are positive the stationary point is a minimum, if all are negative it's a maximum and if eigenvalues have different signs the stationary point is a saddle point.

The program provides the values of the eigenvalues, characterize the stationary point and gives the values of the response at the stationary point and all the corresponding values of the process variables at that point.

7.3.3 Ridge Analysis

When the stationary point is a saddle point, there is no unique maximum or minimum value for the response surface. Ridge analysis shows the direction in which the response surface increases. It computes the estimated response corresponding to the increasing coded radius from the stationary point of the new transformed system, as the origin. It also computes the corresponding values of the process variables to the response variable.

7.3.4 Evaluation of the Results from the RSREG Procedure

7.3.4.1 Process#1: The statistical analysis of the overall model using RSREG procedure is shown below. The parameter estimation is given in the Table E.5 in Appendix E.

Response Surface for Variable REMOVAL

Response Mean	0.649662
Root MSE	0.104949
R-Square	0.7192

Coefficient of Variation 16.1545

The Table E.6 in Appendix E show the analysis of variance for the overall model. The analysis which shows Pr>F is less than 5% for all the four main factors which indicates that the four factors have significant influence on the response variable (removal efficiency).

The canonical analysis results are shown in Table E.7 in Appendix E. The canonical analysis for the overall model clearly indicates that the stationary point is a saddle point as it has both the negative and positive eigen values. The largest component of the eigenvalue (|0.053278|), has the largest corresponding eign vector (0.848048) which is associated with time. The second largest eigen value is associated with water-soil ratio. Similarly third and fourth are vacuum pressure and the power. Therefore it can be stated that response surface is more sensitive to the factors according to the above order.

Ridge analysis shows the direction in which the optimum conditions can be achieved and that region is within the experimental region except the pressure factor, which in any case is very close to the maximum level taken in the experimental region. The ridge analysis data are given in Table E.8 in Appendix E with four factor variables.

From Table E.8 it is seen that even if the ridge analysis was done for a radius that exceeds the factor levels of the experimental range, it is realistic to take the optimum removal as 97%. This was obtained for 68.5% power, 12.9:1 solvent to soil ratio, 18psi vacuum pressure and 11.9 minutes.

From the overall statistical analysis the following findings are significant. All the main factors have a significant influence on the response variable. The full quadratic model is an adequate model.

7.3.4.2 Process#2: From the GLM statistical analysis and the results it can be seen that the factors are sensitive to the removal efficiency in silt, but not sensitive to the removal efficiency in clay, within the experimented range. Since the clay fraction has a very low acceptance, it was decided not to proceed with the further statistical analysis. Although it is with lower confidence level compared to the Process#1,the statistical analysis was proceeded further.

The results of the RSREG procedure of the statistical analysis for the overall model for silt were given below. The parameter estimation using the same procedure is given in Table E.9 in Appendix E.

Response Surface for Variable REMOVAL

Response Mean	0.653455
Root MSE	0.103544
R-Square	0.6409
Coefficient of Variation	15.8456

Table E.10 in Appendix E shows the analysis of variance for the overall model. The analysis shows that only soil to water ratio has a Pr>F value 0.0005 which is less than 5%. Other factors have a relative high Pr>F vales, which indicates that those factors are not sensitive to the removal efficiency within the experimental range.

The canonical analysis results for silt are given in Table E.11; shows that the stationary point is a saddle point because it has both negative and positive values in the eigen vectors. The largest component of the eigen value (|0.137101|), has the largest corresponding eigen vector (0.998097) which is associated with the soil to water ratio that says removal efficiency is most sensitive to the soil to water ratio within the experimental range. Similarly power is the second most important factor and then time. That is the order of factors that are sensitive to the removal efficiency.

Ridge analysis shows the direction which chromium removal could be optimized in silt. The ridge analysis data are given in Table E.12. As in Process #1, although the ridge analysis was done for a radius outside the factor levels of the experimental range, it is practical to take the optimum removal as 99.37%.

The optimum removal for silt fraction could be obtained with the process variables at 1620 W power, 40:1 solvent to soil ratio and with 38 minutes.

7.4 The Comparison between the Predicted and Observed values of the Response Variable (Removal Efficiency)

7.4.1 Process#1

The full quadratic model is:

$$Y_R = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_4 D + \beta_5 A^2 + \beta_6 BA + \beta_7 B^2 + \beta_8 CA + \beta_9 CB + \beta_{10} C^2 + \beta_{11} DA + \beta_{12} DB + \beta_{13} DC + \beta_{14} D^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7.8)$$

The response variable is denoted as Y and the four factors power, soil-water ratio, vacuum pressure and times are denoted by A, B, C and D respectively.

Please refer to the Table E.5 in Appendix E, for the all the parameter estimations. Figure 7.1 gives the comparison of the estimated and the predicted values using the model.

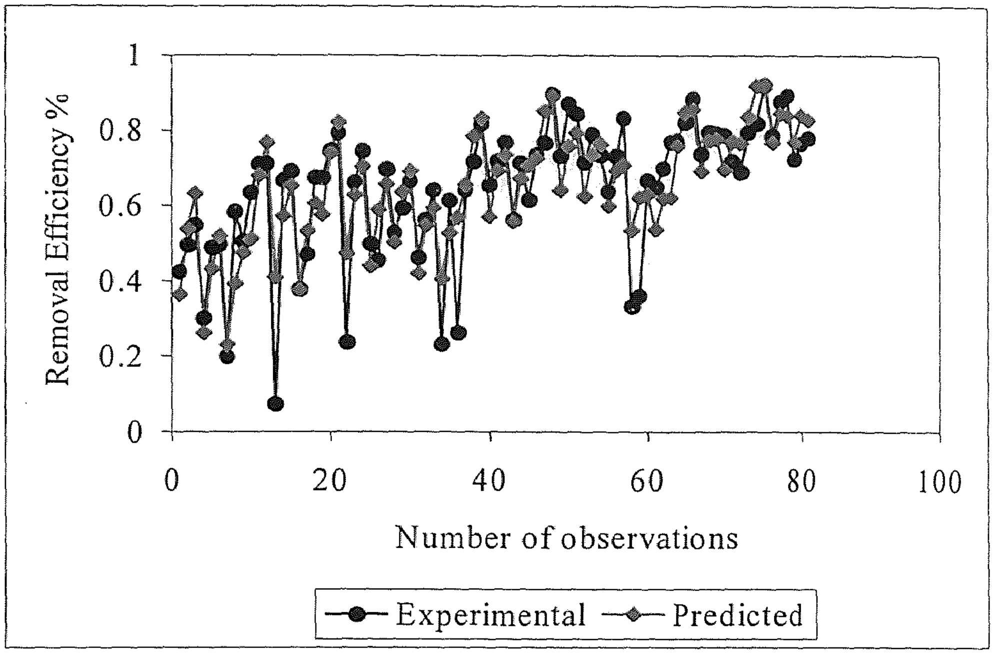

Figure 7.1 Comparison of Experimental and Predicted Values for the Removal Efficiency in Process #1

The comparison of the fitting parameters for the models using full quadratic regression shows that both experimental and the predicted values follow almost the same trend except for few points.

7.4.2 Silt in Process#2

The full quadratic model is:

$$Y_R = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_4 A^2 + \beta_5 BA + \beta_6 B^2 + \beta_7 CA + \beta_8 CB + \beta_9 C^2 \qquad \text{..................(7.9)}$$

The response variable is denoted as *Y* and the four factors power, soil-water ratio, and times are denoted by *A*, *B*, and *C* respectively. Please refer the Table E.9 for all the estimated parameters. Figure 7.2 gives the comparison of the experimental and predicted values for the removal efficiency in Silt.

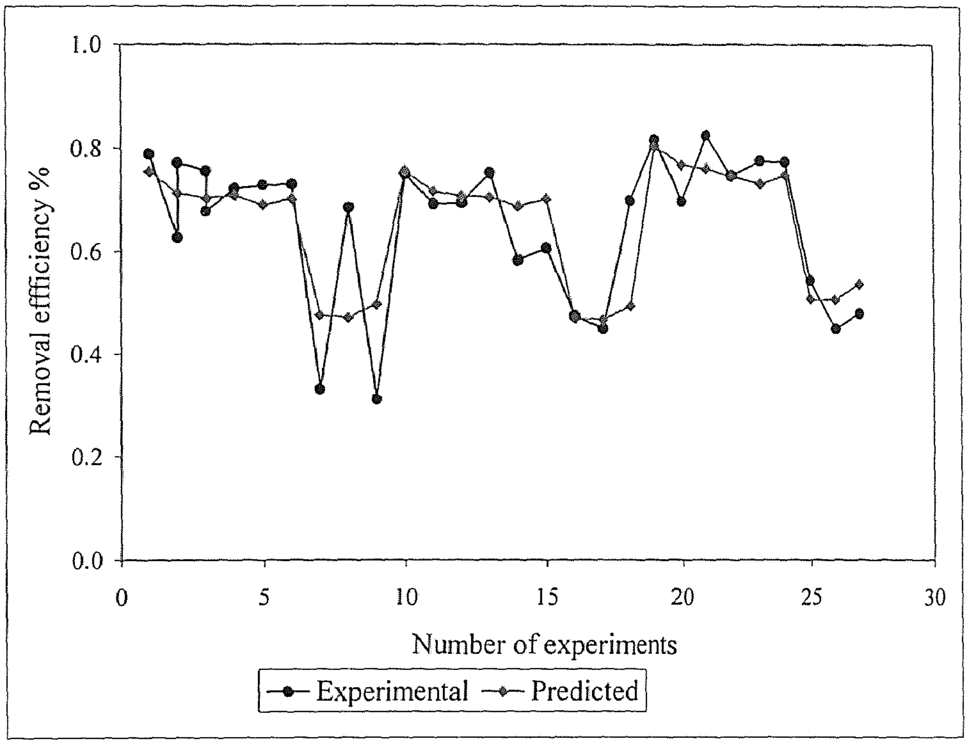

Figure 7.2 Comparison of Experimental and Predicted values for the Removal Efficiency in Silt in Process #2

Unlike the Process #1 the comparison of the fitting parameters for the models using a full quadratic regression, shows much variation in the values although both experimental and predicted values followed the same trend.

CHAPTER 8

SUMMARY AND CONCLUSIONS

From the baseline study its concluded that the most important factors contributing to the removal efficiency are power, soil to solvent ratio, vacuum pressure and sonication time and hence they were considered in the factorial design. Full factorial designs were performed for both Process #1 and Process #2.

In the Process #1, coarse fraction (retaining on US Sieve #200), of the bulk sediments was treated while separating the fine fraction (passing US Sieve #200) with the water. The experimental values give a maximum removal efficiency of 92% with 80% power, 1:15 soil to water ratio, 15 psi vacuum pressure and 15 minutes of sonication time. It was noted that higher separation efficiencies, up to 100% could be obtained in Process #1.

The General Linear Model Procedure in the statistical analysis of the data confirms, that the selected factors for the experimental design, power, soil to solvent ratio, vacuum pressure and sonication time have a significant influence on the removal efficiency. Since the third and fourth order interaction of factors could be considered as negligible, a full quadratic model was chosen for the regression analysis. From the analysis it can also be concluded that the overall model is acceptable with a 95% confidence level.

The canonical analysis reported that the stationary point for the data is a saddle point. As for the overall model the canonical analysis rank the order in which the removal efficiency is influenced by the four factors.

For Process #1 removal efficiency is most sensitive to sonication time, then to soil to water ratio followed by vacuum pressure and power. This order of sensitiveness is valid only for range of experimental values considered.

The ridge analysis shows the direction in which the removal can be optimized and the factor levels, which will give the maximum removal. The optimum removal that could be obtained according to this analysis is 97% and the relevant factor levels are 1027.5 watt power, 1:13 soil to water ratio, 18 psi vacuum pressure and 12 minutes of sonication time. Except for the vacuum pressure level, all the other factor levels are within the range of values used for the experimental design.

In the Process #2, it was expected to treat fine fraction of the bulk sediment, which was originally removed by Process #1 and, to separate them from water. Process #2 separated fines into silt and clay. Silt fraction was found to be treated while the clay fraction was not.

The General Linear Model Procedure for Process #2, the ANOVA model for clay fraction is highly insignificant with a Pr>F value as 0.8536, while for silt fraction is also insignificant, although at a comparatively smaller Pr>F value which is 0.2691. Based on the conventional acceptable level of Type I error risk of 5% or even 10%, the model for Process #2 is not acceptable to explain the chromium removal. Soil to water ratio was the only significant factor for the removal of chromium in silt with a Pr>F value as 0.0375. A revised ANOVA with soil to water ratio as the only factor would be the next step in the statistical analysis. Since the objective was to assess the importance if any, of the factors that enhances the ultrasound treatment, it can be concluded that, for Process #2 the selected factors, power, soil to water ratio and dwell time have no real effect in chromium removal. However this fact is valid only within the experimental range, used in the experimental design.

The canonical analysis ranks the factors in order of ability to influence the removal efficiency as soil to water ratio, power and time. It also showed that the stationary point for the data is a saddle point with no minimum or maximum. Ridge analysis gives the optimum removal that could be achieved as 99.37%, at 1620 watt power, 1:40 as the soil to water ratio and 38 minutes of sonication time. Both soil to water ratio and the sonication time is within the experimental range.

The General Linear Model Procedure for clay fraction says that the removal efficiency is not sensitive to any of the factors at an acceptable confidence level. This does not mean that these factors have no influence on the removal of chromium from the clay fraction. What that implies is, within the experimental range of levels, of the factors, removal efficiency is not sensitive to these factors. Varying pH of the slurry or using a chelating agent made no difference to the on the removal efficiency of the clay fraction within these factor levels.

Finally it is concluded that this method could be effectively use for the soils without clay fractions. When the particle size decreases the removal becomes more difficult. It can also be concluded, although the clay fraction does not get treated by this method, its still safe to dispose clay fraction after Process #2, since the mobility of chromium is negligible.

APPENDIX A

PRE-EXPERIMENTAL DATA FOR PROCESS #1

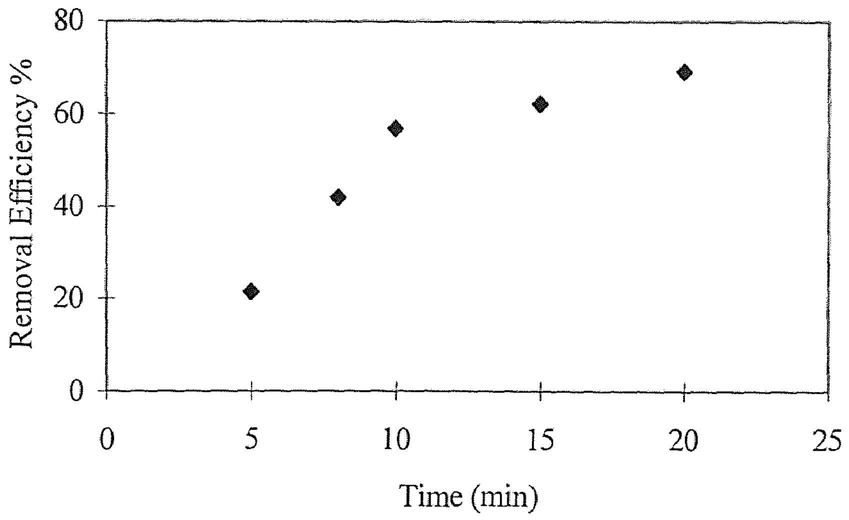

Figure A.1 Variation of Removal Efficiency with Time for 60% Power, 1:8 Soil-Water Ratio and 10psi Vacuum Pressure

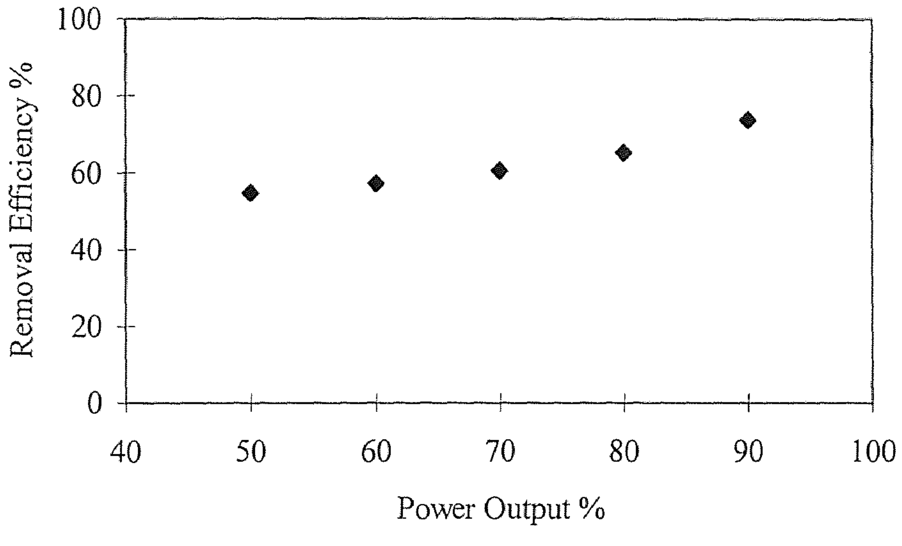

Figure A.2 Variation of Removal Efficiency with Power for 1:8 Soil-Water Ratio, 10 psi Vacuum Pressure and 6 minutes Time

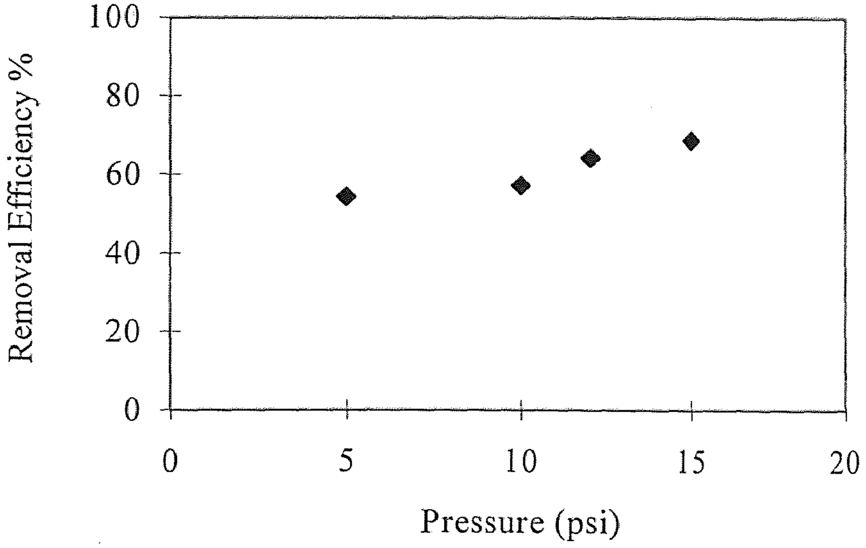

Figure A.3 Variation of Removal Efficiency with Vacuum pressure for 60% Power, 1:8 Soil-Water Ratio and 6 minutes Time

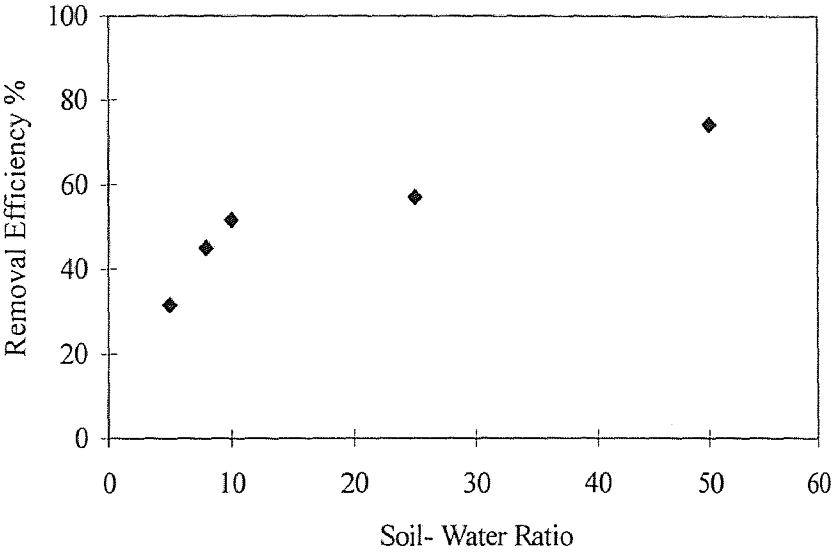

Figure A.4 Variation of Removal Efficiency with Soil-Water Ratio with 60% Power, 10psi vacuum Pressure and 6 minutes Time

APPENDIX B

EXPERIMENTAL RESULTS FOR PROCESS #1 AND PROCESS #2

Table B.1 Experimental Results for the Process #1

Power %	S-S ratio	V. Press (psi)	Time (mins)	Removal Efficiency (%)
40	5	15	5	42.45
40	5	15	10	49.52
40	5	15	15	55.02
40	5	10	5	30.11
40	5	10	10	48.93
40	5	10	15	49.94
40	5	5	5	19.96
40	5	5	10	58.53
40	5	5	15	50.57
40	10	15	5	63.70
40	10	15	10	71.30
40	10	15	15	71.37
40	10	10	5	7.42
40	10	10	10	67.04
40	10	10	15	69.43
40	10	5	5	37.81
40	10	5	10	47.14
40	10	5	15	67.67
40	15	15	5	67.72
40	15	15	10	74.79
40	15	15	15	79.54
40	15	10	5	23.70
40	15	10	10	66.39
40	15	10	15	74.75
40	15	5	5	49.95
40	15	5	10	45.64
40	15	5	15	69.87
60	5	15	5	52.96
60	5	15	10	59.60
60	5	15	15	66.70
60	5	10	5	46.24
60	5	10	10	56.49
60	5	10	15	64.36
60	5	5	5	23.15
60	5	5	10	61.69
60	5	5	15	26.27
60	10	15	5	64.29
60	10	15	10	71.96
60	10	15	15	81.89
60	10	10	5	65.73
60	10	10	10	72.19

Table B.1 Experimental Results for the Process #1 (Continued)

Power %	S-S ratio	V. Press (psi)	Time (mins)	Removal Efficiency (%)
60	10	10	15	77.09
60	10	5	5	56.45
60	10	5	10	71.55
60	10	5	15	61.72
60	15	15	5	73.91
60	15	15	10	76.90
60	15	15	15	89.91
60	15	10	5	73.50
60	15	10	10	87.31
60	15	10	15	84.71
60	15	5	5	71.84
60	15	5	10	79.25
60	15	5	15	73.74
80	5	15	5	64.05
80	5	15	10	73.58
80	5	15	15	83.50
80	5	10	5	33.32
80	5	10	10	36.14
80	5	10	15	66.96
80	5	5	5	65.18
80	5	5	10	70.14
80	5	5	15	77.10
80	10	15	5	77.69
80	10	15	10	82.50
80	10	15	15	88.72
80	10	10	5	74.08
80	10	10	10	79.79
80	10	10	15	79.43
80	10	5	5	78.95
80	10	5	10	72.10
80	10	5	15	69.27
80	15	15	5	79.77
80	15	15	10	82.13
80	15	15	15	92.22
80	15	10	5	78.88
80	15	10	10	87.91
80	15	10	15	89.54
80	15	5	5	72.58
80	15	5	10	76.76
80	15	5	15	78.31

Table B.2 Experimental Results for the Process #2

Power %	S-s ratio	Time (mins)	Number of experiment	Removal Efficiency(%)	
				Clay	Silt
50	50	30	1	11.88	78.84
50	50	60	2	7.30	62.77
50	50	60	2	8.30	77.20
50	50	90	3	12.36	75.68
50	50	90	3	0.00	67.80
50	25	30	4	7.58	72.25
50	25	60	5	3.03	72.86
50	25	90	6	3.82	73.00
50	10	30	7	0.07	33.17
50	10	60	8	4.86	68.49
50	10	90	9	0.00	31.20
60	50	30	10	0.00	74.98
60	50	60	11	0.00	69.29
60	50	90	12	0.00	69.41
60	25	30	13	3.22	75.40
60	25	60	14	14.82	58.39
60	25	90	15	0.00	60.70
60	10	30	16	0.00	47.46
60	10	60	17	0.00	45.01
60	10	90	18	4.75	69.98
80	50	30	19	0.00	81.70
80	50	60	20	0.00	69.75
80	50	90	21	0.00	82.54
80	25	30	22	0.65	74.81
80	25	60	23	10.10	77.64
80	25	90	24	0.00	77.39
80	10	30	25	0.00	54.39
80	10	60	26	4.73	44.96
80	10	90	27	2.75	47.96

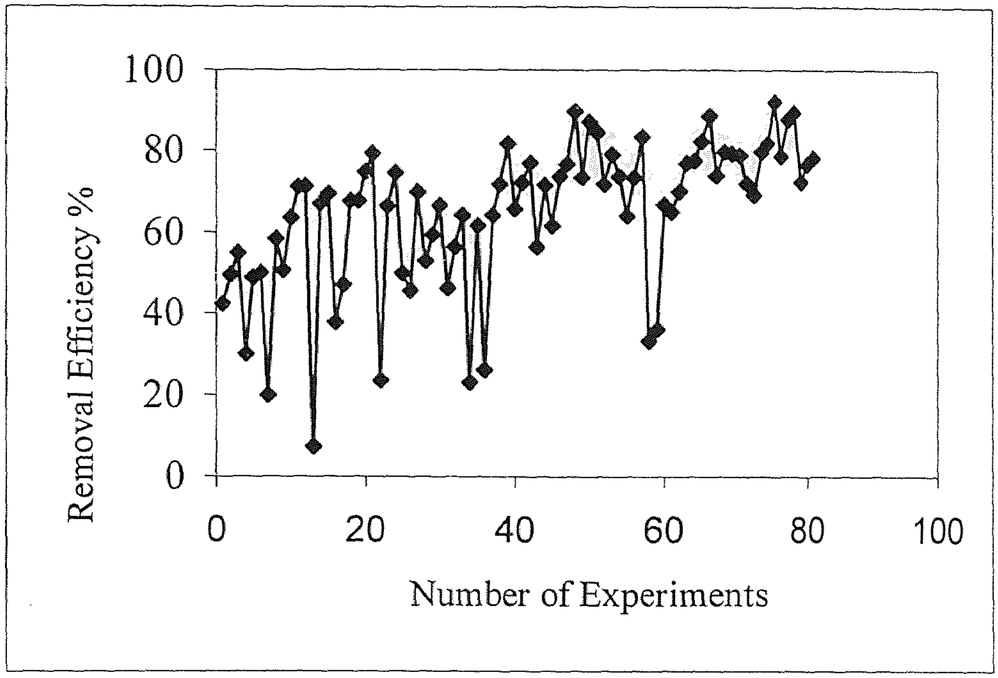

Figure B.1 Removal Efficiencies in Process #1

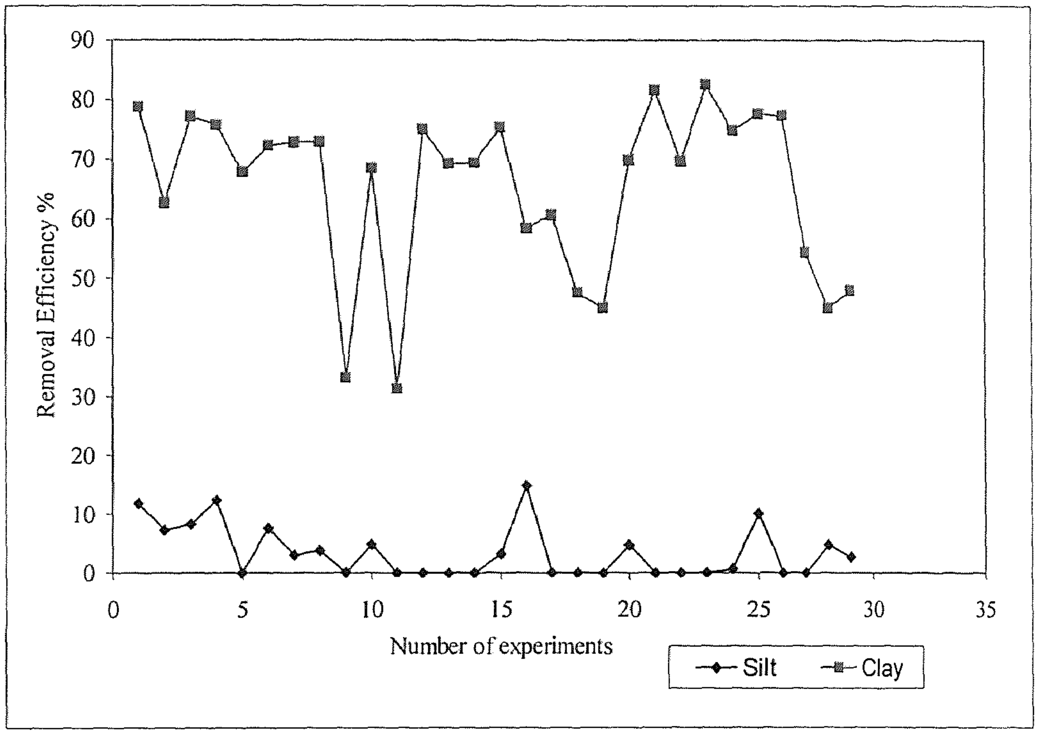

Figure B.2 Removal Efficiencies of Silt and Clay in Process #2

APPENDIX C

REMOVAL AND SEPARATION EFFICIENCIES OF PROCESS #1

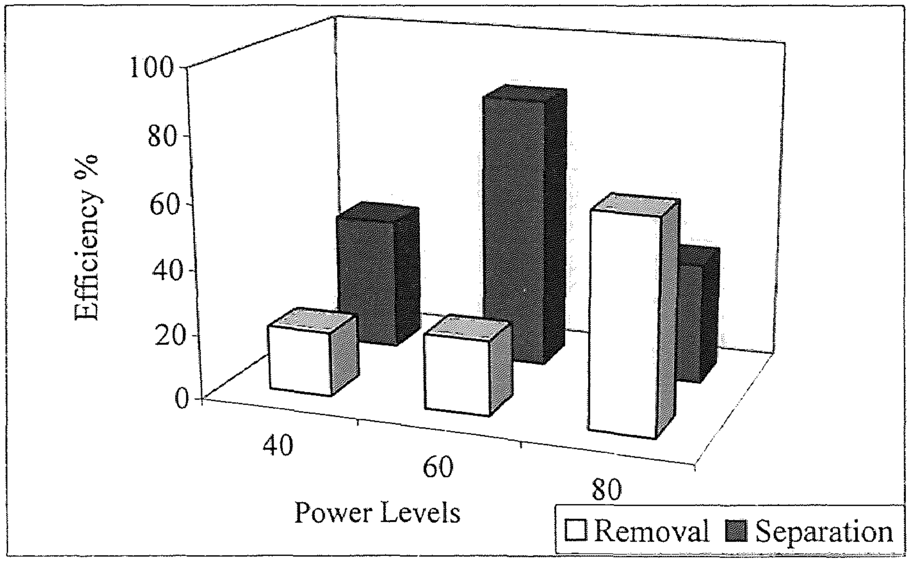

Figure C.1 Removal and Separation Efficiencies for Different Power Levels (1:5 Soil to Water Ratio, 5 psi Vacuum Pressure and 5 minutes Dwell Time)

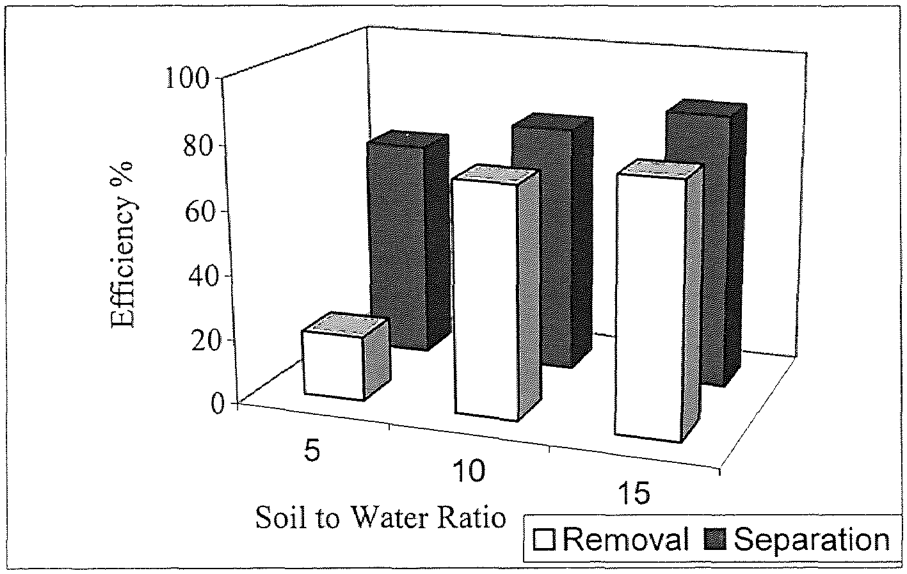

Figure C.2 Removal and Separation Efficiencies for Different Soil to Water Ratios (40% Power, 5 psi Vacuum Pressure and 5 minutes Dwell Time)

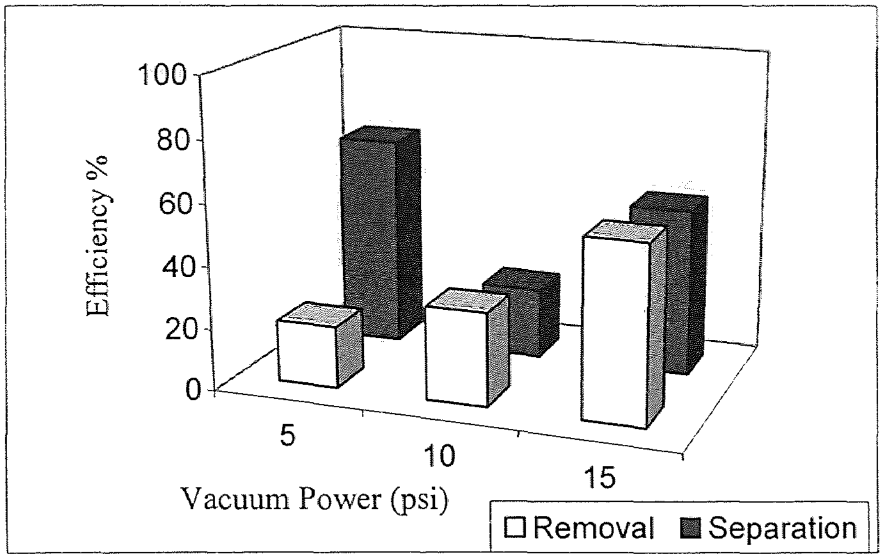

Figure C.3 Removal and Separation Efficiencies for Different Vacuum Pressure (40% Power, 1:5 Soil to Water Ratio and 5 minutes Dwell Time)

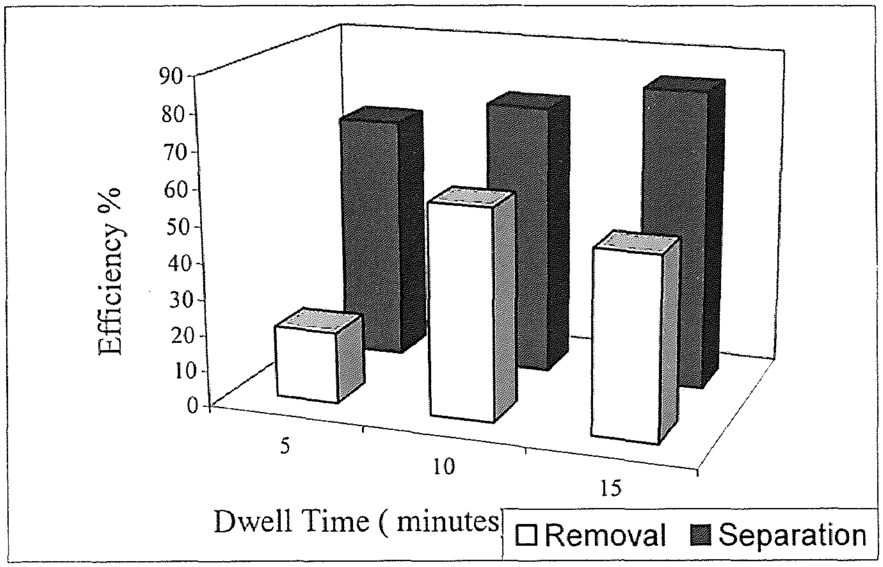

Figure C.4 Removal and Separation Efficiencies for Different Dwell Times (40% Power, 1:5 Soil to Water Ratio and 5 psi Vacuum Pressure)

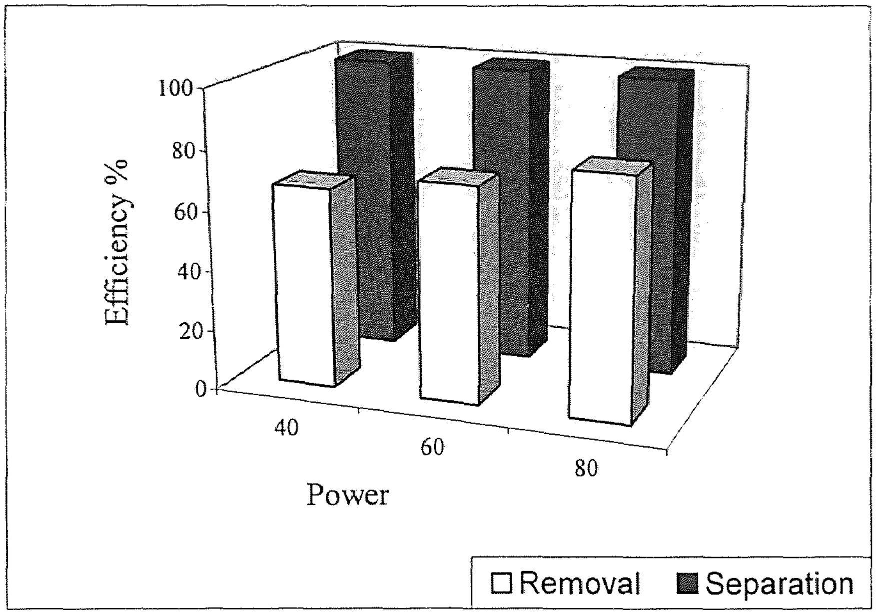

Figure C.5 Removal and Separation Efficiencies for Different Power Levels (1:10 Soil to Water Ratio, 10 psi Vacuum Pressure and 10 minutes Dwell Time)

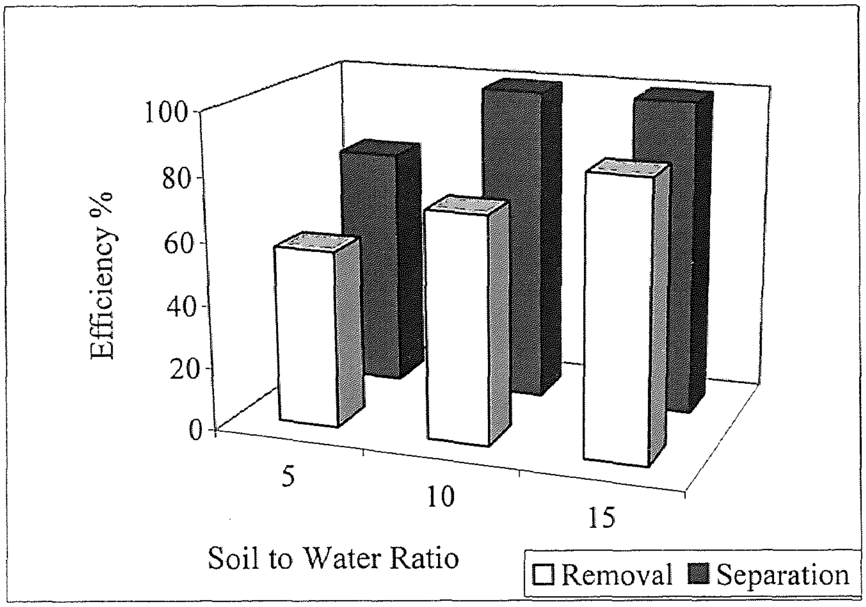

Figure C.6 Removal and Separation Efficiencies for Different Soil to Water Ratios (60% Power, 10 psi Vacuum Pressure and 10 minutes Dwell Time)

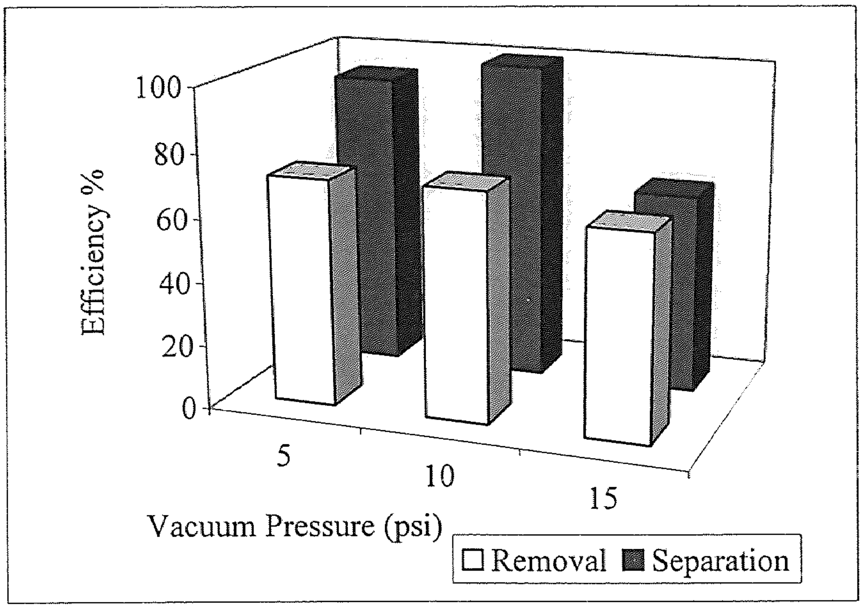

Figure C.7 Removal and Separation Efficiencies for Different Vacuum Pressures (60% Power, 1:10 Soil to Water Ratio and 10 minutes Dwell Time)

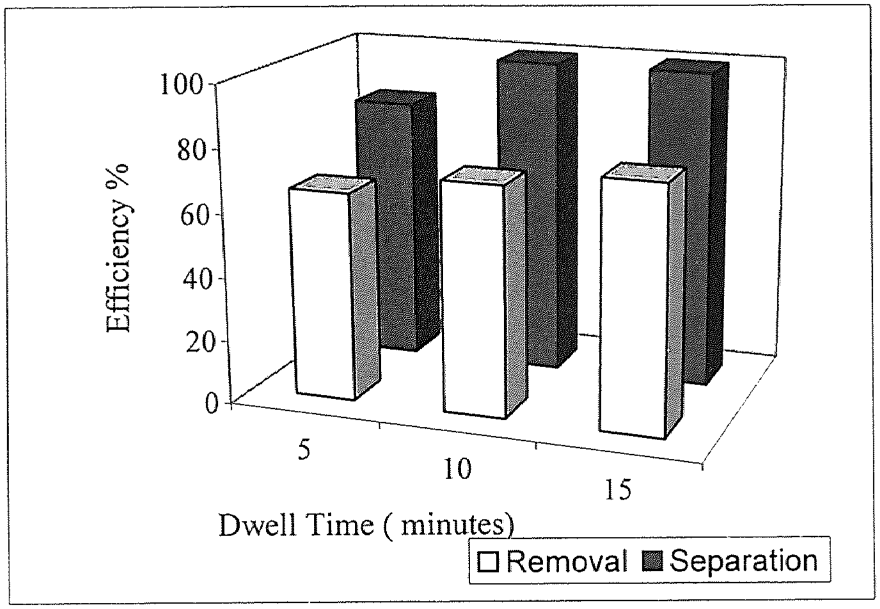

Figure C.8 Removal and Separation Efficiencies for Different Dwell Times (60% Power, 1:10 Soil to Water Ratio and 10 psi Vacuum Pressure)

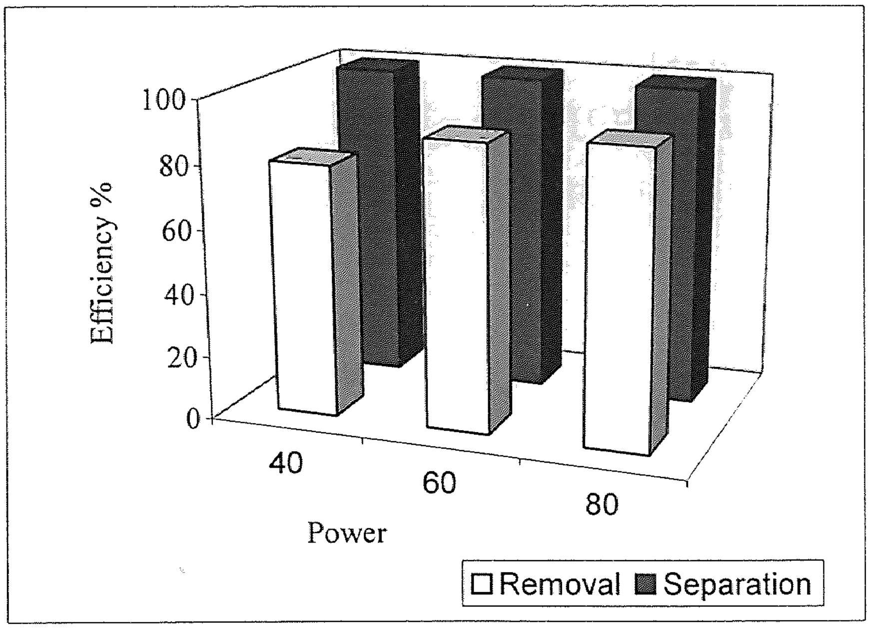

Figure C.9 Removal and Separation Efficiencies for Different Power Levels (1:15 Soil to Water Ratio, 15 psi Vacuum Pressure and 15 minutes Dwell Time)

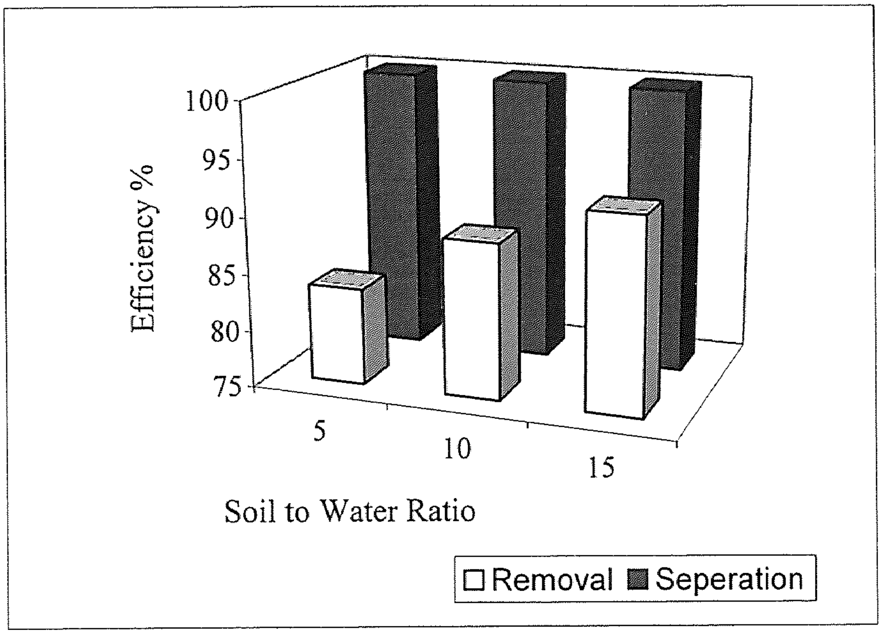

Figure C.10 Removal and Separation Efficiencies for Different Soil to Water Ratio (80% Power, 15 psi Vacuum Pressure and 15 minutes Dwell Time)

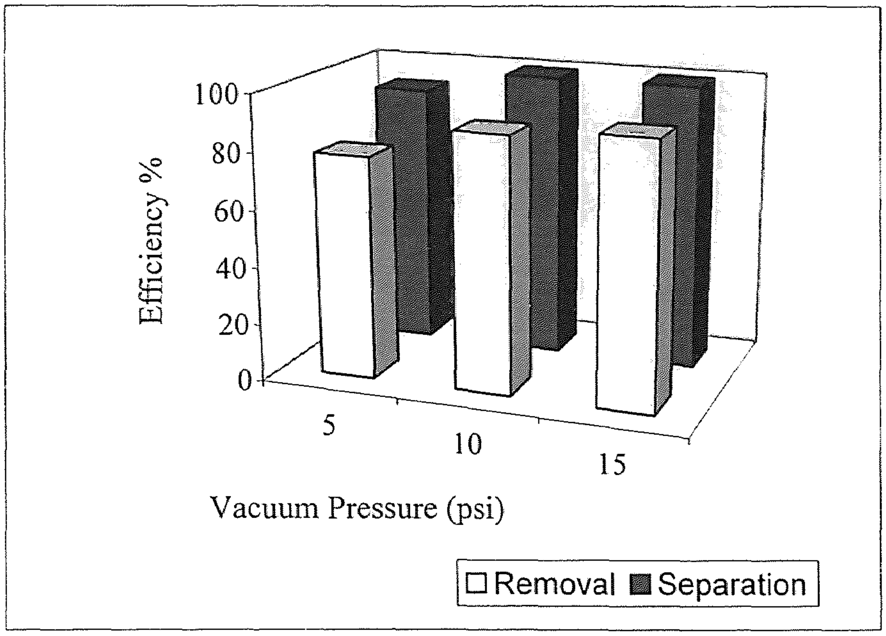

Figure C.11 Removal and Separation Efficiencies for Different Vacuum Pressures (80% Power, 1:15 Soil to Water Ratio and 15 minutes Dwell Time)

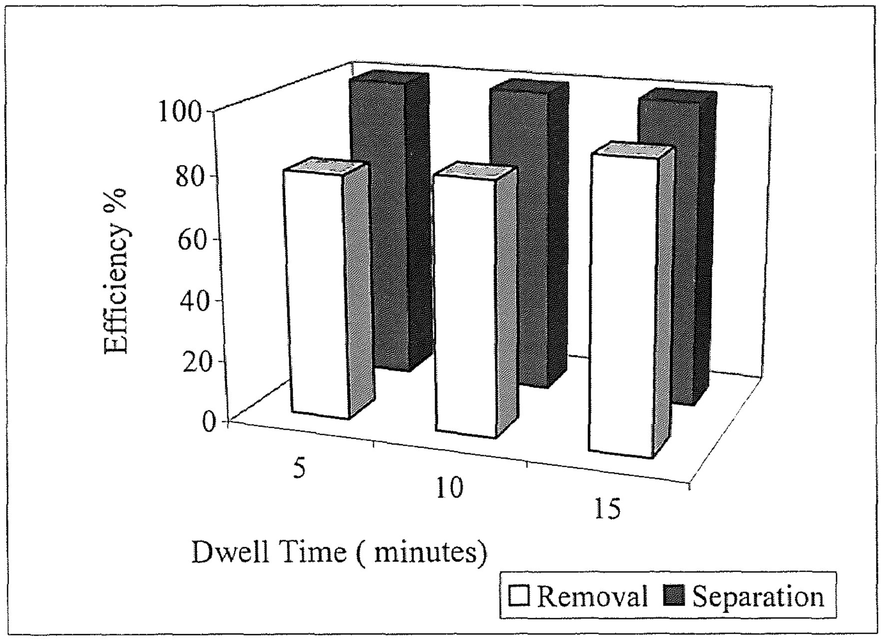

Figure C.12 Removal and Separation Efficiencies for Different Dwell Times (80% Power, 1:15 Soil to Water Ratio and 15 psi Vacuum Pressure)

APPENDIX D

REMOVAL EFFICIENCIES OF THE SILT FRACTION IN PROCESS #2

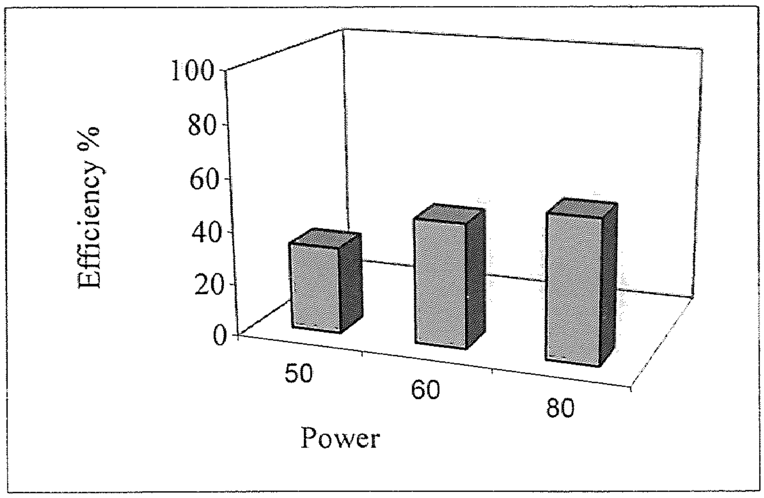

Figure D.1 Removal Efficiencies for Different Power Levels (1:10 Soil to Water Ratio and 30 minutes Dwell Time)

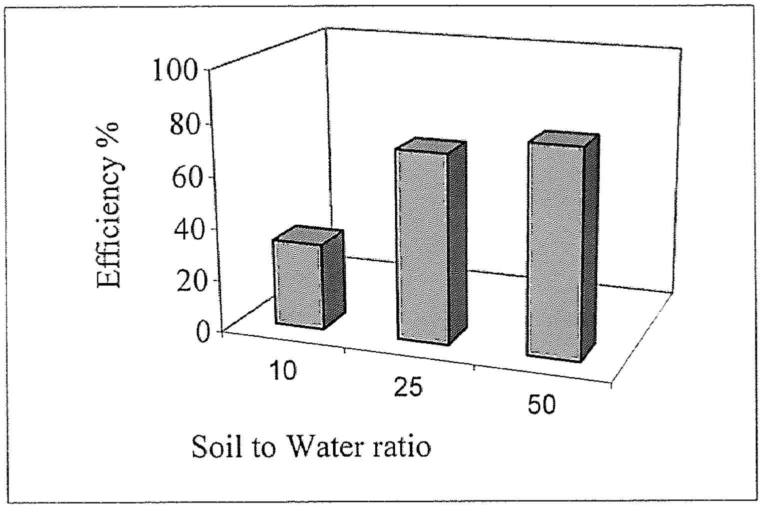

Figure D.2 Removal Efficiencies for Different Soil to Water Ratios (50% Power and 30 minutes Dwell Time)

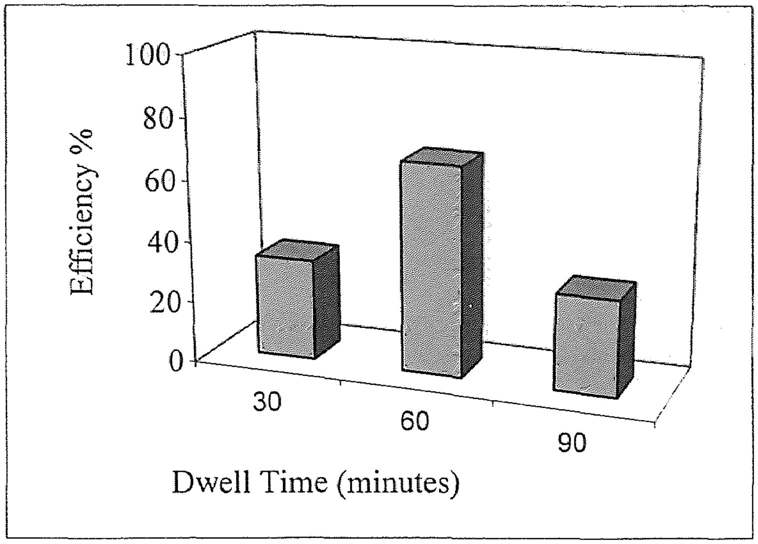

Figure D.3 Removal Efficiencies for Different Dwell Times (50% Power and1:10 Soil to Water Ratio)

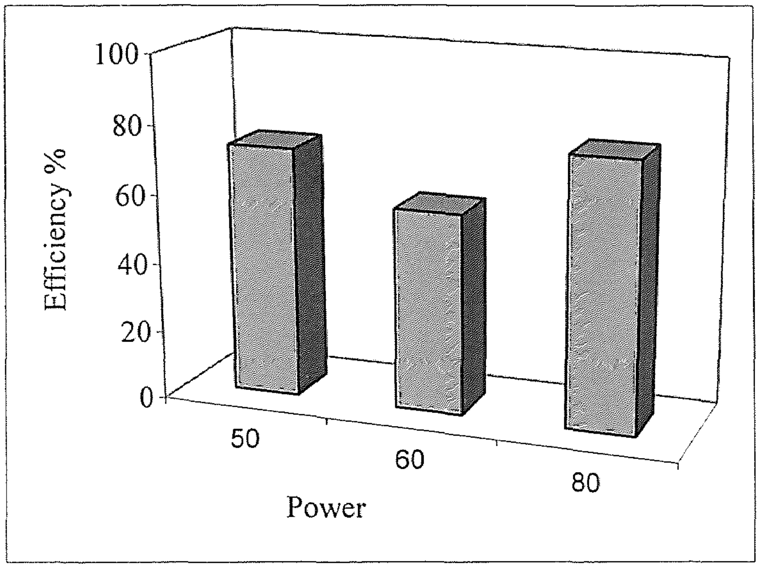

Figure D.4 Removal Efficiencies for Different Power Levels (1:25 Soil to Water Ratio and 60 minutes Dwell Time)

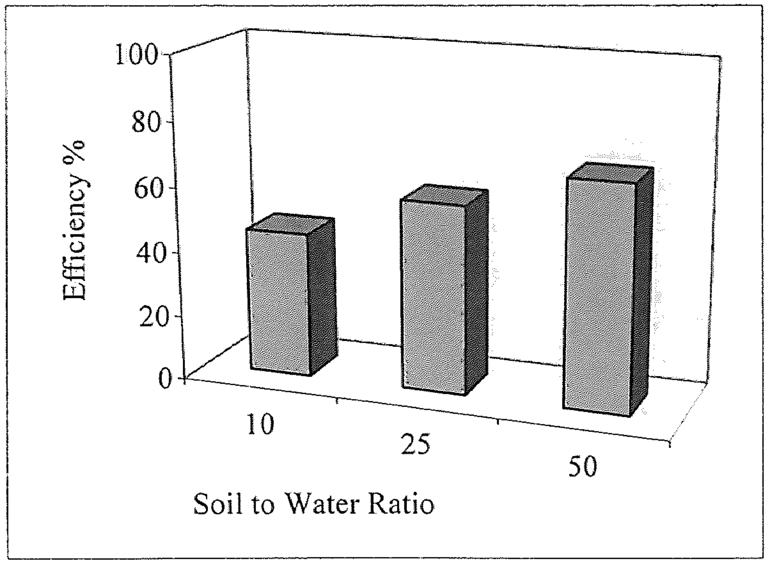

Figure D.5 Removal Efficiencies for Different Soil to Water Ratios (60% Power and 60 minutes Dwell Time)

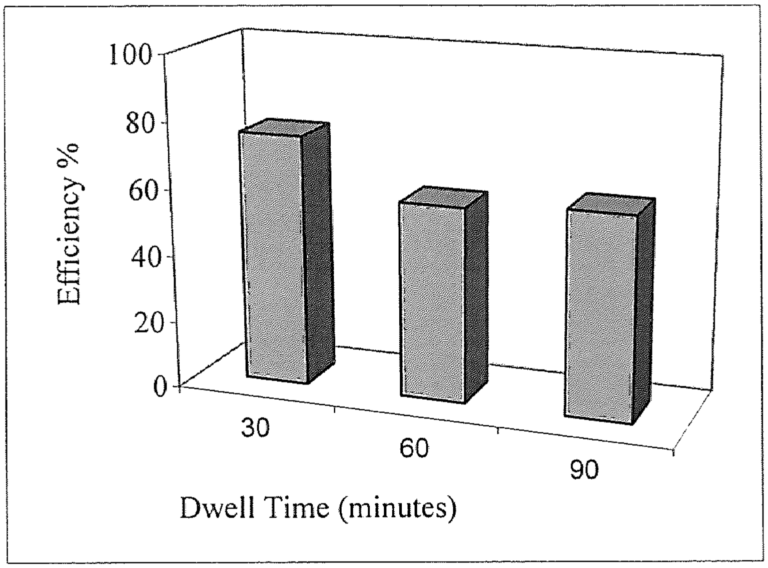

Figure D.6 Removal Efficiencies for Different Dwell Times (60% Power and 1:25 Soil to Water Ratio)

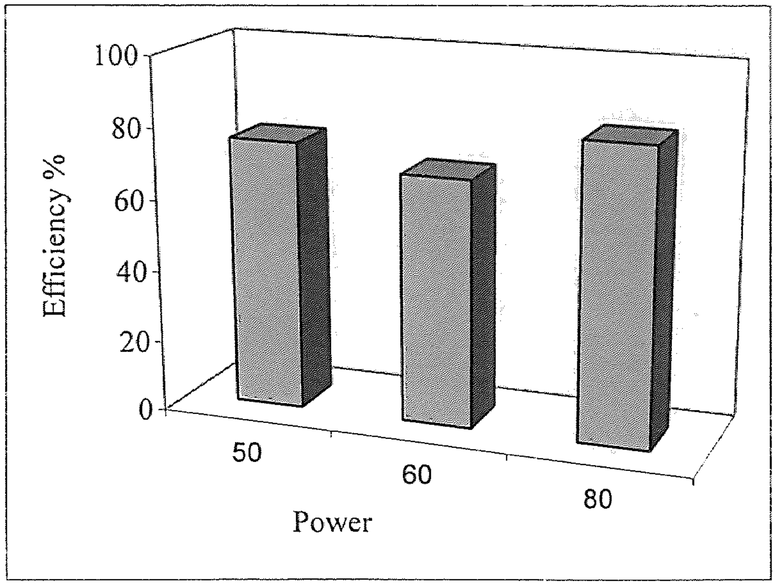

Figure D.7 Removal Efficiencies for Power Levels (1:50 Soil to Water Ratio and 90 minutes Dwell Time)

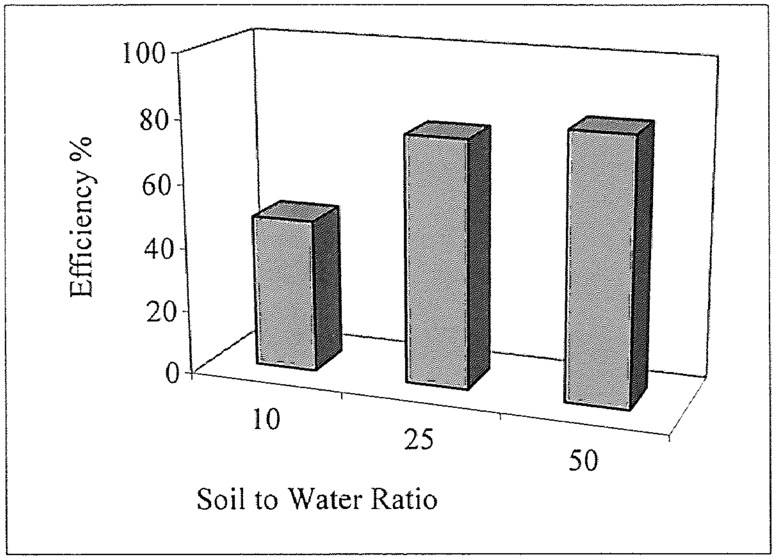

Figure D.8 Removal Efficiencies for different Soil to Water Ratios (80% Power and 60 minutes Dwell Time)

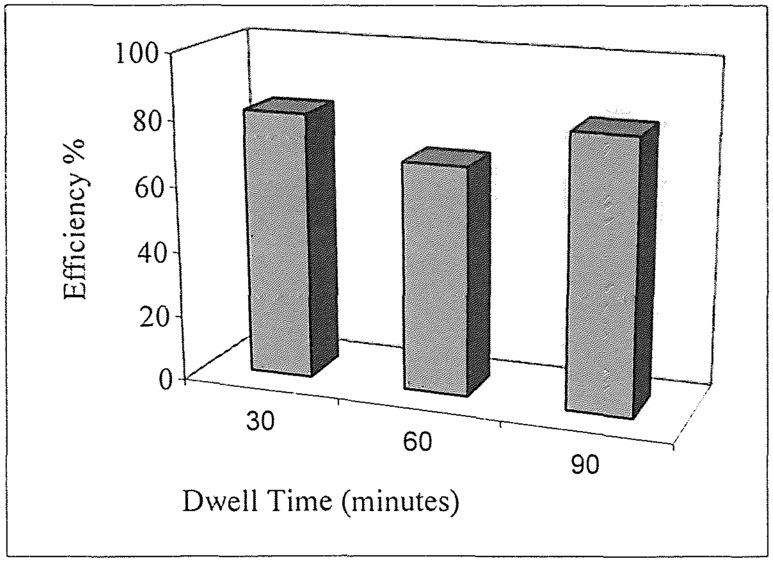

Figure D.9 Removal Efficiencies for different Dwell Times (80% Power and 1:50 Soil to Water Ratio)

APPENDIX E

RESULTS OF THE STATISTICAL ANALYSIS

Table E.1 Summary of GLM Procedure for Process#1

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	64	2.51639	0.03932	8.72	0.0001
Error	16	0.07211	0.00584		
Corrected Total	80	2.58852			

Table E.2 Results of the GLM Procedure for Process#1

Source	DF	SS	Mean Square	F Value	Pr > F
POWER	2	0.56861	0.28430	63.08	0.0001
RATIO	2	0.63026	0.31513	69.91	0.0001
PRESS	2	0.19354	0.09677	21.47	0.0001
TIME	2	0.39516	0.19758	43.84	0.0001
POWER*RATIO	4	0.03746	0.00936	2.08	0.1314
POWER*PRESS	4	0.07877	0.01969	4.37	0.0141
POWER*TIME	4	0.10705	0.02676	5.94	0.0040
RATIO*PRESS	4	0.01761	0.00440	0.98	0.4475
RATIO*TIME	4	0.00811	0.00202	0.45	0.7710
PRESS*TIME	4	0.06824	0.01706	3.79	0.0237
POWER*RATIO*PRESS	8	0.15298	0.01912	4.24	0.0067
POWER*RATIO*TIME	8	0.05722	0.00715	1.59	0.2053
RATIO*PRESS*TIME	8	0.07121	0.00890	1.98	0.1174
POWER*PRESS*TIME	8	0.13011	0.01626	3.61	0.0139

Table E.3 Summary of GLM Procedure for Silt and Clay in Process #2

Source	Model		Error		Corrected Total	
	Silt	Clay	Silt	Clay	Silt	Clay
DF	26	26	2	2	28	28
Sum of Squares	0.55378	0.04826	0.01352	0.00769	0.56729	0.055953
Mean Squares	0.02130	0.00186	0.00676	0.00384		
F Value	3.15	0.48				
Pr > F	0.2691	0.8536				

Table E.4 Results of the GLM Procedure for Silt and Clay in Process #2

Source	DF		SS		Mean Square		F Value		Pr > F	
	Silt	Clay	Silt	Clay	Silt	Clay	Silt	Clay	Silt	Clay
POWER	2	2	0.00957	0.00500	0.00479	0.00250	0.71	0.65	0.58540	0.60590
RATIO	2	2	0.34718	0.00392	0.17359	0.00196	25.69	0.51	0.03750	0.66220
TIME	2	2	0.00190	0.00505	0.00095	0.00252	0.14	0.66	0.87660	0.60380
POWER*RATIO	4	4	0.03118	0.01306	0.00779	0.00327	1.15	0.85	0.51340	0.60370
POWER*TIME	4	4	0.03550	0.00346	0.00887	0.00086	1.31	0.22	0.47550	0.90390
RATIO*TIME	4	4	0.02810	0.00786	0.00702	0.00197	1.04	0.51	0.54410	0.74450
POWER*RATIO*TIME	8	8	0.10035	0.01011	0.01254	0.00126	1.86	0.33	0.39670	0.89580

Table E.5 Parameter Estimation for Process #1

Parameter	Component	Parameter Estimate
β_0	INTERCEPT	-0.781622
β_1	POWER	0.01655
β_2	RATIO	0.052594
β_3	PRESS	-0.008935
β_4	TIME	0.072952
β_5	POWER*POWER	-5.1824E-05
β_6	RATIO*POWER	0.000057806
β_7	RATIO*RATIO	-0.001649
β_8	PRESS*POWER	-0.000179
β_9	PRESS*RATIO	0.000046222
β_{10}	PRESS*PRESS	0.001393
β_{11}	TIME*POWER	-0.000402
β_{12}	TIME*RATIO	-0.000247
β_{13}	TIME*PRESS	0.000263
β_{14}	TIME*TIME	-0.001626

Table E.6 ANOVA results for Process #1

Factor	Degrees of Freedom	Sum of Squares	Mean Square	F-Ratio	Prob > F
POWER	5	0.639606	0.127921	11.614	0.0000
SWRATIO	5	0.632893	0.126579	11.492	0.0000
PRESS	5	0.206711	0.041342	3.753	0.0047
TIME	5	0.456334	0.091267	8.286	0.0000

Table E.7 Canonical Analysis for Process #1

Eigenvalues	POWER	SWRATIO	PRESS	TIME
0.036817	-0.183774	-0.003100	0.978892	0.089380
-0.009647	0.818373	0.129751	0.201733	-0.522238
-0.041661	-0.156418	0.987319	-0.025361	-0.009609
-0.053278	0.521561	0.091417	0.020772	0.848048

Table E.8 Ridge Analysis for Process #1

Coded Radius	Estimated Response	Standard Error	Factor Values			
			POWER	RATIO	PRESS	TIME
0.00	0.69484	0.03498	60.00000	10.00000	10.00000	10.00000
0.20	0.72879	0.03464	62.28944	10.58976	10.37036	10.43292
0.40	0.76003	0.03366	64.49015	11.15531	10.87665	10.79790
0.60	0.78920	0.03224	66.42842	11.66398	11.56873	11.08971
0.80	0.81724	0.03081	67.87642	12.07727	12.46640	11.31320
1.00	0.84531	0.03035	68.72105	12.37838	13.51905	11.48528
1.20	0.87443	0.03253	69.05489	12.58528	14.64206	11.62579
1.40	0.90531	0.03870	69.04430	12.72791	15.77829	11.74856
1.60	0.93838	0.04901	68.81839	12.82954	16.90431	11.86119
1.80	0.97388	0.06288	68.45676	12.90477	18.01379	11.96767
2.00	1.01197	0.07972	68.00633	12.96236	19.10673	12.07018

Table E.9 Parameter Estimation for Silt in Process #2

Parameter	Component	Parameter Estimate
β_0	INTERCEPT	0.733259
β_1	POWER	0.022359
β_2	RATIO	0.125906
β_3	TIME	-0.005576
β_4	POWER*POWER	0.017704
β_5	RATIO*POWER	0.004734
β_6	RATIO*RATIO	-0.136520
β_7	TIME*POWER	0.001847
β_8	TIME*RATIO	-0.018234
β_9	TIME*TIME	0.015701

Table E.10 ANOVA for Silt in Process #2

Factor	Degrees of Freedom	Sum of Squares	Mean Square	F-Ratio	Prob > F
POWER	4	0.012792	0.003198	0.298	0.8754
SWRATIO	4	0.353206	0.088302	8.236	0.0005
TIME	4	0.006285	0.001571	0.147	0.9623

Table E.11 Canonical Analysis for Silt in Process #2

Eigenvalues	POWER	SWRATIO	TIME
0.018074	0.919680	-0.009071	0.392563
0.015912	-0.392357	-0.060986	0.917789
-0.137101	-0.015616	0.998097	0.059647

Table E.12 Ridge Analysis for Silt in Process #2

Coded Radius	Estimated Response	Standard Error	Factor Values		
			POWER	RATIO	TIME
0.00	0.73326	0.05770	65.00000	30.00000	60.00000
0.20	0.75388	0.05770	65.95387	33.76169	59.27725
0.40	0.76690	0.05630	68.42364	36.25253	56.97461
0.60	0.77766	0.05360	71.54692	37.25117	54.14784
0.80	0.78879	0.05093	74.61536	37.76223	51.59692
1.00	0.80091	0.05071	77.63053	38.10601	49.32119
1.20	0.81421	0.05592	80.62546	38.37106	47.28338
1.40	0.82878	0.06831	83.61835	38.59062	45.46106
1.60	0.84465	0.08767	86.61837	38.78011	43.84044
1.80	0.86185	0.11306	89.62985	38.94774	42.41186
2.00	0.88041	0.14371	92.65449	39.09833	41.16751
2.20	0.90032	0.17914	95.69248	39.23497	40.10037
2.40	0.92160	0.21910	98.74316	39.35973	39.20367
2.60	0.94425	0.26342	101.80533	39.47413	38.47065
2.80	0.96829	0.31203	104.87756	39.57929	37.89447
3.00	0.99371	0.36486	107.95829	39.67611	37.46821
3.20	1.02052	0.42188	111.04592	39.76531	37.18487

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