ABSTRACT

ULTRASOUND TO DECONTAMINATE ORGANICS IN DREDGED SEDIMENTS

by
Kanya Veerawat

In this research, it was attempted to decontaminate and separate dredged sediments contaminated with organic compounds by the application of ultrasound energy coupled with sub-atmospheric pressures. The decontamination and separation of contaminated sediments was achieved by integrated two processes. For Process 1, ultrasound energy was used to decontaminate the sandy fraction in dredged sediments, and sub-atmospheric pressure was used to separate and remove fines. For Process 2, ultrasound was again used to decontaminate fines with bulk fluid, and sub-atmospheric pressure was used to remove the contaminants with water. Process 1 was evaluated and found to have four variables contributing to its performance: power, solvent to sediment ratio, pressure, and sonication time. Process 2 was evaluated with and without surfactants. Process 2 without surfactant had three variables: power, solvent to sediment ratio, and sonication time, while Process 2 with surfactant had four variable contributing to its performance: power, solvent to sediment ratio, surfactant concentration, and sonication time. Both processes were optimized by analyzing experimental data using SAS statistical software. The percentage of removal efficiency was considered as the dependent variable. Statistical models were developed based on the experimental results to optimize the process conditions. Statistical analysis showed that Process 1 had 98% contaminant

removal efficiency at 58% power, 14:1 solvent to sediment ratio, 16-psi vacuum pressure, and 8 minutes of sonication time. Similarly, Process 2 without the surfactant had 99% contaminant removal efficiency at 75% power, 41:1 solvent to sediment ratio, and 95 minutes of sonication time. Process 2 with the surfactant had 99% contaminant removal efficiency at 57% power, 32:1 solvent to sediment ratio, 0.08% surfactant concentration, and 74 minutes of sonication time.

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by
Kanya Veerawat

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ULTRASOUND TO DECONTAMINATE ORGANICS IN DREDGED SEDIMENTS

by
Kanya Veerawat

5/12/99
Dr. Namunu Jay Meegoda, Thesis Advisor — Date
Associate Professor of Civil and Environmental Engineering
New Jersey Institute of Technology

5/13/99
Dr. John R. Schuring, Committee Member — Date
Professor of Civil and Environmental Engineering
New Jersey Institute of Technology

5/13/99
Dr. Robert Dresnack, Committee Member — Date
Professor of Civil and Environmental Engineering
New Jersey Institute of Technology

BIOGRAPHICAL SKETCH

Author: Kanya Veerawat

Degree: . Master of Science in Environmental Engineering

Date: May 1999

Undergraduate and Graduate Education:

- Master of Science in Environmental Engineering
  New Jersey Institute of Technology, Newark, NJ, 1996

- Bachelor in Environmental Engineering
  University of California at Riverside, Riverside, CA, 1997

Major: Environmental Engineering

The author dedicated this thesis to his beloved parents

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CHAPTER 1

INTRODUCTION

1.1 Problem Statement

Pollutants from industry waste, mining, agriculture, human, and other sources have contaminated surface water. These contaminants from the surface water were entrapped in the sediments over a long period of time and can adversely impact marine life, hence humans and the environment. An effort to clean up sediment contamination is on going since the 1960s. The NY/NJ Harbor Estuary Program has summarized and evaluated available data concerning toxic contamination in New York Harbor. Several chemicals including polychlorinated biphenyls, dioxin, pesticides, and metals were found at levels that exceed marine water quality, sediment quality, and/or fish tissue criteria (Pecchioli, 1994).

Dredged sediments from the Port of New York and New Jersey are mostly ocean disposed, or disposed in lagoons for either contaminants or for long-term land reclamation. Many containment facilities are almost full. Sites for additional capacity are scarce and expensive to construct. Due to the Ocean Dumping Act and lack of containment facilities, the disposal of nearly 7 billion tons of dredged sediments per year has become a major problem for the New York/New Jersey metropolitan area. New technologies for treating dredged sediments treatment are required so that dredged sediments can be de-watered, remediated, and disposed. The best remediation technology should decontaminate the dredged sediments so that sediments can be ocean dumped as clean material or used in construction. Ultrasound technology may be applied to decontaminated dredged sediments.

The contaminants such as organic compounds in the dredged sediments are usually attached to the clay and silt fractions, while the coarse fraction is essentially clean (van Rigt, 1993). Therefore, separating the coarse fraction from dredged sediment would reduce the volume that needs to be decontaminated. The application of ultrasound energy can remove organic compounds from dredged sediments. Application of ultrasound energy to soil slurry such as dredged sediments causes acoustic cavitation, which is sufficient to desorb contaminants from dredged sediments. Therefore, sonication coupled with extraction using sub-atmospheric pressure was evaluated in this study to decontaminate the contaminants from dredged sediments.

1.2 Scope of Study

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

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

- Implement application of ultrasound for decontamination of dredged sediments.
- Select the process parameters, which significantly influence the energy dissipated into the sediment-system by the ultrasound application.
- Develop a statistical model based on experimental results for each process for organic compounds.

- Critically examine of the results by statistical analysis for full factorial design carried out using general linear model procedure (GLM) for determining the effects of the interaction between the important parameters.
- Economize the number of treatment combinations for partial factorial design by ignoring interactions (from third order) which are insignificant on removal of contaminants.
- Select 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.

CHAPTER 2

LITERATURE REVIEW

2.1 Current Technologies for Remediation of Contaminated Dredged Sediments

Contaminants trapped in the sediments can adversely impact marine life, human, and the environment. To ensure safe, navigable waters, river and waterways must be dredged. The dredged sediments need to be de-watered, remediated, and disposed. The currently available technologies for remediation of contaminated dredged sediments can be categorized as biological, physical, and chemical treatment

2.1.1 Bioremediation

Bioremediation is a biological/chemical treatment where microorganisms are used to transform hazardous chemicals to less toxic and environmentally acceptable compounds. Bioremediation technology has been implemented in many area such as composting sludge, sludge activation, trickling filter for wastewater treatment, and anaerobic digestion for manures and organic sludges. Nutrients such as nitrate, sulfate, phosphorus, and oxygen are usually applied to enhance the bioremediation process (Grasso 1993, Boulding 1995). In-situ biological treatment provides destruction of the contaminants at the site and has harmless by-products, therefore reducing the cost associated with off-site transport and disposal/treatment of contaminant. However, bioremediation has limited applicability on certain types of compounds such as inorganic or synthetic compounds, and it also requires long treatment time.

2.1.2 Solidification/Stabilization

Solidification/stabilization techniques have been used for some time to treat sediments by excavated treatment. Solidification/stabilization treatment involves the addition of chemicals or cements to encapsulate contaminated sediments and/or convert them into less soluble, less mobile, or less toxic forms. Solidification reduces the amount of sediment being disturbed and decreasing the potential for contaminant release. It is one of the few techniques available to treat metals, although it is associated with volume increase.

2.1.3 Sediment Washing

Sediment washing is a physical/chemical treatment which mobilizes contaminants for extraction. Sediment washing for the treatment of contaminated sediments is an adaptation of mineral processing operations commonly used in the mining industry to separate slurries into sets of different-sized particles. Sediments are dredged/excavated and transported to facilities to be treated. The sediment washing equipment produces separated fractions of sand, organic debris, and silts and clays. The organic contaminants, and some heavy metals, are concentrated in the silt and clay fraction. The sediment washing process is very flexible and offers a wide variety of end uses for the recycled sediment which included: landfill cover, amended top soil blends, washed sand, plaster sand, clay liner soil, gravel, and road base material. Although no contaminants are destroyed during the sediment washing process, the volume of contaminated material (usually the silts and clays) is much smaller than the original sediment volume.

2.1.4 Thermal Desorption

Thermal desorption is a physical/chemical application, typically indirect, of heat to volatilize and remove the organic contaminants present in a solid matrix. A modified rotary-kiln incinerator was designed to indirectly heat sediments to temperatures up to 650 °C (Stern, 1994). Thermal desorption volatilizes contaminants and condenses, then into an oily residue of substantially less volume. However, this process is only applicable for treating organic compounds, not for treating metals and other inorganics. In addition, due to high water content of dredged sediments, thermal desorption is not a cost effective remediating technology for dredged sediments.

2.1.5 Solvent Extraction

Solvent extraction is the stripping and removal of organic contaminants from a solid or liquid matrix using the chemical and physical properties of a solvent or solvents. Solvent extraction is a process applicable to dredged/excavated sediments. This process separates organic contaminants and concentrates them as an oily residue. However, solvent extraction has limited full-scale application as a waste treatment technology and does not destroy contaminants, instead concentrating them in a greatly reduced volume for further destructive treatment.

2.2 Surfactant Application to the Contaminated Sediments

Surfactants are used for remediation of contaminated groundwater and contaminated soils. Surfactants are compounds having an amphipatic structure, monolayer orientation at interfaces, and adsorption interfaces. Surfactants act as de-bonding and segregating agents for 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 sediment substrate, to segregate the detached contaminant in the solution, and to prevent its redeposition throughout the remaining washing process. Surfactant solutions may solubilize hydrophobic contaminants from the sediment by reducing the work of adhesion between the contaminant and sediment, resulting in desorption and incorporation of the organic compound within the aqueous phase.

CHAPTER 3

ULTRASOUND TO DECONTAMINATE DREDGED SEDIMENTS

3.1 Mechanism of Ultrasound Application

Ultrasound is an acoustic wave with a frequency above 16 kHz, which is beyond the normal range of human hearing. Ultrasonic energy is applied to cleaning of manufactured parts in the metal and electronic industries to remove oxide films, oil, grease, and other contaminants from solid surfaces. In addition, ultrasound is also used for particle size analysis, where the ultrasound energy is used to disperse or de-aggregate soils and sediments (Reddi et al., 1994). In addition, ultrasound energy with a solvent was used as an extraction method (EPA method 3550, Hein et al., 1988). Therefore, it is important to know the basic physical and chemical effects that may be created in various media by ultrasonic waves.

Ultrasonic cleaning works by providing shear forces to remove the material adhering to a surface. This shear force is developed by cavitation. Ultrasound causes high-energy acoustic cavitation: the formation, growth and implosive collapse of bubbles in a liquid. Shock waves from cavitation in liquid-solid slurries produce high-velocity inter-particle collisions, the impact of which is sufficient to desorb contaminants from particles (Hein et al., 1988). The operating frequencies of the great majority of industrial cleaners range from 18 to 44 kHz. This is the optimum range for technological efficiency, economy of the process, and safety consideration. Higher frequencies are used for the removal of contaminants having a high adhesion to the surface such as smaller particles (clays and silts). Lower frequencies are used for cleaning of contaminants that are weakly bonded to the surface such as large particles (sand).

Rajaratnam (1997) studied the analysis and modeling of ultrasound to enhance soil-washing process. In that study, coal tar contaminated soils with PAHs were used. Three soil fractions were tested: coarse fraction, combination of coarse and fines, and fine fraction. The experimental analysis showed that ultrasound energy can enhance the soil washing process by 300%. Therefore, it is proposed to apply the ultrasound in this study to decontaminate dredged sediments.

3.2 Dredged Sediments Description

Table 3.1 shows the quantity and types of dredged material removed from NY/NJ harbors each year. Table 3.1 also shows that dredging of NY/NJ harbors annually produce 1.6 million tons of Category III dredged sediments with toxicity and bio-accumulation. Recently, the ocean Dumping Act prohibited Category III sediments from being ocean disposed due to high contaminant level. The dredged sediments in a slurry form need to be de-watered, remediated, and disposed.

Table 3.1 Types of Dredged Material Encountered in NY/NJ Ports

	Description	Disposal	Amount in million tons
Category I	Sediments that do not cause unacceptable toxicity or Bioaccumulation	Sediments can be ocean disposed	2.3
Category II	Material that shows some evidence of toxicity or bioaccumulation	Sediments may be disposed in the ocean with capping	3.1
Category III	Material that fails to meet federal criteria for toxicity or Bioaccumulation	Sediments not permitted for ocean disposal	1.6

Analysis of NY/NJ metropolitan area Category III sediments by the Brookhaven National Lab, NY, produced the following results:

Table 3.2 Analysis of Dredged Sediments on both Properties and Contaminant Concentrations

Analysis	Values
Water content	225%
Loss on Ignition	14%
Clay content	27%
Silt content	45%
PH	8.0
TOC	7.50%
Pesticides	~ 400 µg/kg
PCB (total)	~ 4,000 µg/kg
Dioxins	~ 5,000 µg/kg
Furans	~ 15,000 µg/kg
PAHs	~ 100,000 µg/kg
Chromium	~ 370 mg/kg
Lead	~ 600 mg/kg
TCLP Chromium	~ 0.03 mg/kg

There are two problems associated with cost effective disposal of dredge sediments: de-watering and decontamination. Due to the high water content (typically 200-500%) of dredged sediments, most of the economical treatment methods such as thermal desorption are not cost effective in remediating dredged sediments. The most promising treatment for Category III dredged sediments is solidification/stabilization. Solidification/stabilization is associated with volume increase and does not decontaminate the dredge sediments. Hence, a new technology is needed to treat Category III dredged sediments.

3.3 Application of Ultrasound to Decontaminate Dredge Sediments

Sediment can be decontaminated using ultrasound which efficiently remove contaminants from the coarser size fraction (i.e., sand and gravel) and concentrate the finer size fraction (i.e., silt and clay). This is because in the coarser size fraction, sediment-contaminant attachment is predominantly by physical Van der Waal forces. However, in the fine sediment fraction (< 200 sieve or < 75 µm), because of chemical reactive clay/humus constituents (10 µm), strong chemisorption bonding causes attachment between contaminant and sediment. 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. Nonpopular organic radicals without charge (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 pollutant list of hazardous substances and are immune to surfactant action. Therefore, for a better removal efficiency in contaminated fine sediment fractions, significantly higher fluid-particle shear stresses than those encountered in conventional methods would be required. The application of ultrasound energy will provide cavitational excitation, which then would be able to accomplish the following: (1) generate higher fluid particle shear stresses; (2) achieve satisfactory cleaning levels; and (3) minimize the amount of cleaning aids such as surfactants or solvents in the cleaning process.

CHAPTER 4

EXPERIMENTAL PROCEDURE AND DESIGN

4.1 Experimental Procedure

A multi-process treatment was developed where ultrasound is used to decontaminate dredged sediments. The flow chart of the experimental procedure is shown in Figure 4.1.

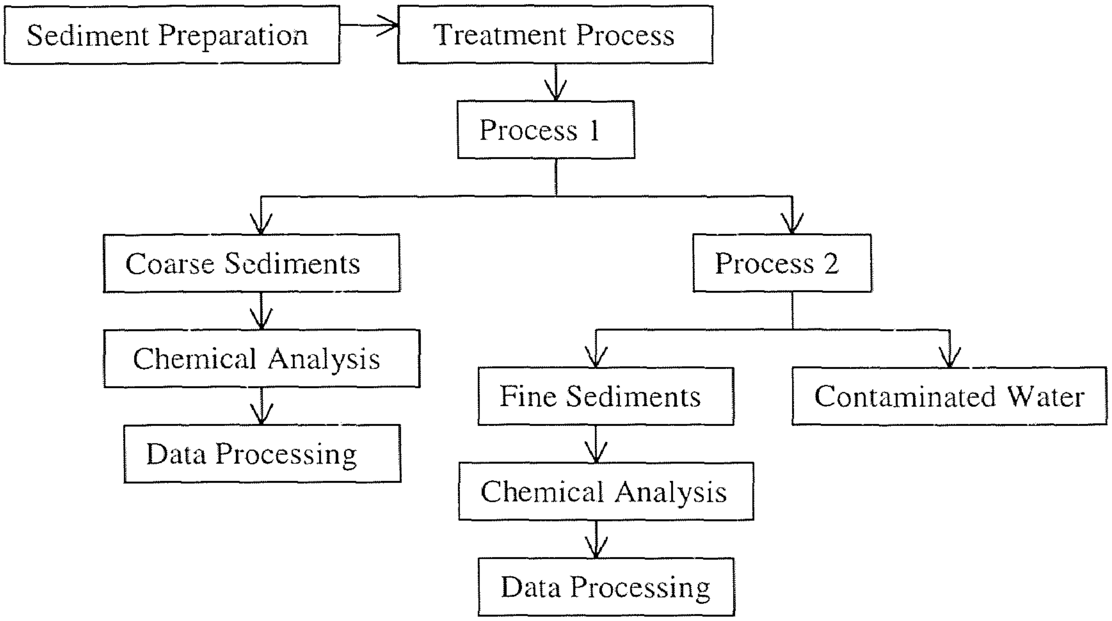


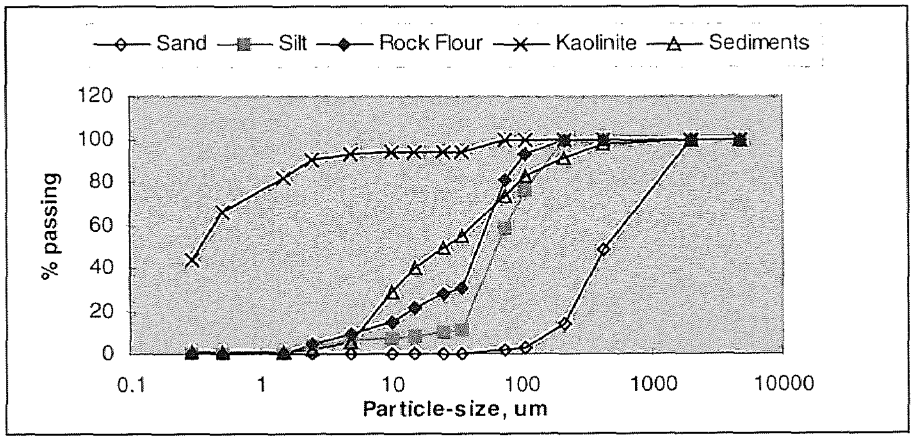
Figure 4.1 Schematic Flow Diagram for the Experimental Procedure

As stated before, sediments from NY/NJ harbor contain many different organic and inorganic compounds. To fully understand this treatment process and to optimize the process, a control environment is needed. Therefore, it was decided to use synthetic sediments contaminated with one organic compound, which had similar characteristics to those found in dredged sediments. Synthetic sediments (similar in size distribution to dredged sediments and contaminated with organic compound) were used to conduct the experiment to determine the process efficiency for organic compounds.

4.1.1 Preparation of Synthetic Contaminated Sediments

In order to design the synthetic dredged sediments, the particle-size of dredged sediments was characterized using a wet sieve analysis. The sieve sizes used in this analysis were 4, 10, 40, 70, 140, and 200. The sediments passing the # 200 sieve were then reanalyzed using the hydrometer test. The size distribution of NY/NJ harbor dredged sediments is shown in Figure 4.2. Sand, clay (such as kaolinite and rockflour), and silt were used to make up the synthetic dredged sediments. In order to obtain synthetic sediments with the same size distribution as dredged sediments, size distribution of sand, kaolinite, rockflour, and silt were also obtained using wet sieve analysis and hydrometer tests. The size distribution of sand, silt, rockflour, and kaolinite are shown in Figure 4.2.

Figure 4.2 Particle-Size Distribution from Wet Sieve Analysis and Hydrometer Test for Sand, Silt, Rockflour, Kaolinite, and Dredged Sediments.



After obtaining the particle-size of different samples, the design process of the synthetic dredged sediments was divided into two parts: particles retained on sieve # 200

After obtaining the particle-size of different samples, the design process of the synthetic dredged sediments was divided into two parts: particles retained on sieve # 200 (>75 μm) and particles passing sieve # 200. The two sample portions were combined and used as a synthetic dredged sediments for the laboratory experiments. The final compositions of sand, kaolinite, rockflour, and silt in the synthetic dredged sediments are shown in Table 4.1.

Table 4.1 Composition of Sand, Silt, Rockflour, and Kaolinite in Synthetic Dredged Sediments.

Particle-size	Sample	Percent of sample, %
> 75 um	Sand	2.60
	Silt	4.62
	Rock Flour	20.24
	Kaolinite	1.45
< 75 um	Rock Flour	71.09
Total		100.00

The wet sieve analysis and hydrometer test were used to analyze the particle-size of the synthetic dredged sediments, which are compared with the dredged sediments in Figure 4.3. Figure 4.3 shows that except for 1μm to 10 μm sizes range, a perfect match was obtained

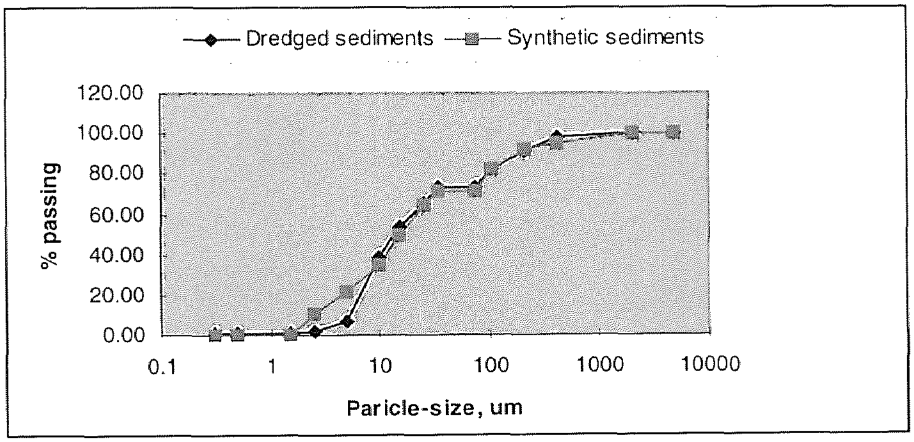


Figure 4.3 The Comparison of Wet Sieve Analysis and Hydrometer Test for Dredged Sediments and Synthetic Dredged Sediments.

4.1.2 Surfactant as Cleaning Agent

In the past few years, surfactants have been found to enhance performance of sediment washing operations. The washing process disperses the contaminated soil in a water/surfactant solution allowing the surfactant to strip the hycrocarbon contaminants from the sediment particles. 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 unites (Liu et. al., 1991). Rajaratnam (1997) investigated the use of surfactant to improve performance of soil washing. Octyl-phenyl-ethoxylate, a non-ionic surfactant, was used to investigate the relation between surfactant concentration and contaminant removal efficiency. The optimum removal efficiency was obtained at the optimum surfactant concentration of 4% to 5%. The same, Octyl-phenyl-ethoxylate was used as the surfactant in this study.

4.1.3 Selection of Ultrasound Source

The following conclusions were drawn from the initial test (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 (Rajaratnam, 1997). The probe-in-model approach was selected due to its 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 sediment/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. Edward and Bremner (1967), and Genrich and Bremner (1972) also 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. The ultrasonic probe, which is used in this study, is 1500-Watts probe (Sonics & Materials Inc.,) model VC1500, with 220 Volts and frequency of 20 kHz.

4.1.4 Selection of Organic Compound in Synthetic Dredged Sediments

p-Terphenyl was chosen as the contaminant for the synthetic dredged sediments. It was selected as its characteristic and physical properties are similar to PAHs, while being non-toxic and hazardous. p-Terphenyl has molecular weight of 230.31 g, melting point at 212 °C, and boiling point at 383 °C, while PAHs has molecular weight of 152.21-276.34 g, melting point at 93-278 °C, and boiling point at 270-496 °C.

The synthetic dredged sediments were mixed with p-terphenyl as described below. Synthetic dredged sediments were heated in an oven to 120 °C for 12 hours to remove water and volatile species. Since p-terphenyl is a solid at room temperature acetone/hexane mixture of 1:1 ratio by volume was used as a solvent. A 0.15 g of p-terphenyl was dissolved in 40 mL of acetone/hexane and then mix with 80 g of synthetic sediments. The sediment with organic solution was thoroughly mix using a mechanical mixer for 24 hours to assure p-terphenyl was dispersed evenly in the sediments. The homogenized sediments were left inside a fumed-hood over night to dry so that acetone/hexane could volatile into the atmosphere. Synthetic dredged sediments with contaminants were then used to perform experiments.

4.1.5 Treatment Process

Treatment process is divided into two parts: Process 1 and Process 2. The objective of Process 1 was to separate fines particles from the bulk dredged suspension and to remove them by using a sub-atmospheric pressure. The objective of Process 2 was to decontaminate fine particles and remove contaminants with water using a sub-atmospheric pressure.

a) Process 1 (separation of fines)

This process attempted to separate fines from the dredged suspension and remove them by using a sub-atmospheric pressure. Reddi et al. (1994) showed that there was size separation of soil due to the vibration produced by ultrasound. In this study, a similar experiment was used with an exception that the fine fraction was removed by the application of sub-atmospheric pressure. For Process 1, a cylinder tank model was developed with flexi-glass (9 inches height and 4 inches diameter) to use in this process. The schematic of the model for this process is shown in Figure 4.4. The above model was implemented with a # 200 mesh filter was placed at the bottom as shown, and it was connected to the sub-atmospheric pressure system to extract fines. The probe type ultrasound source was dipped into the center of the suspended sediments and the ultrasound energy was applied to the system while activating the vacuum system. The separated fine particles, contaminants, and water were collected in a sedimentation tank by vacuum system.

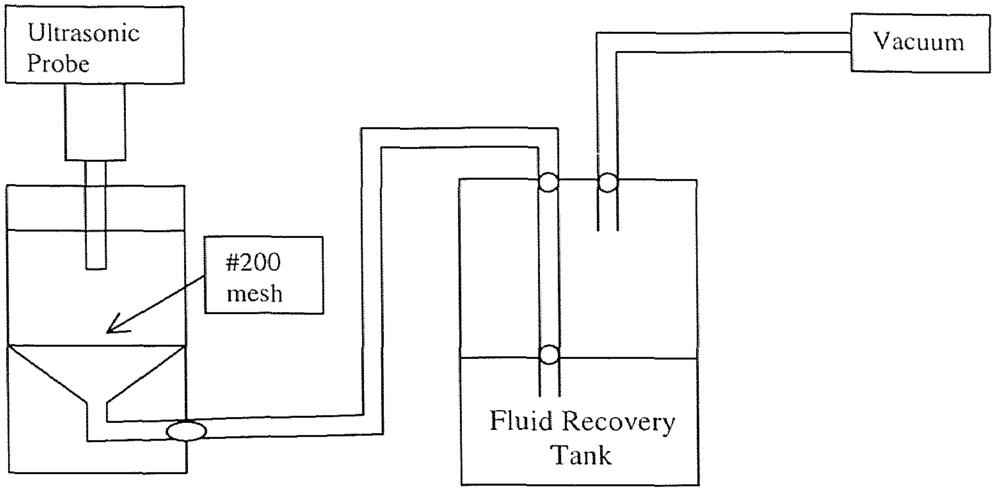


Figure 4.4 Schematic Diagram of Process 1

b) Process 2 (removal of contaminants)

This process was designed to decontaminate fines and to remove contaminants with water using a sub-atmospheric pressure. Meegoda et al. (1995) showed that ultrasound energy could enhance the soil washing process by more than 300%. The bench scale experimental design with one liter of soil slurry produced optimum removal of coal tar with the following process condition: 750 Watts power, 50:1 solvent to soil ratio, 30 minutes sonication time, and 1% surfactant concentration. In addition, ultrasound energy with a solvent was used as an extraction method (EPA method 3550, Hein et al., 1988). From these studies, it has been shown that ultrasound energy can remove hydrocarbons such as polycyclic aromatic hydrocarbons (PAHs). Compounds such as surfactants or solvents can keep the contaminants in the solution phase so that they do not re-absorb onto the soil.

Process 2 is essentially similar to EPA method 3550, although instead of solvents or surfactants, a sub-atmospheric pressure is used to extract contaminants that were desorbed from soil. A sub-atmospheric pressure is applied with fine filters to remove the fluid with contaminants during the application of ultrasound. The ultrasound probe is dipped into the center of the suspended sediments and the ultrasound energy is applied to the system while activating the vacuum system. The contaminants, and water are then collected in a fluid recovery tank by vacuum system.

For Process 2, a box model was developed with flexi-glass (7 inches*7 inches*10 inches height.) Five filtros porous ceramics (Ferro Corporation, Model Kellundite plates FAO-01, 4.5 inches*4.5 inches*1/4 inches thick, probable nominal particle retention 1 microns, maximum pore diameter 25 microns) were glued together to from a box. The box model was then used to separate contaminants and water from fine dredged sediments. The schematic of the model for this process is shown in Figure 4.5.

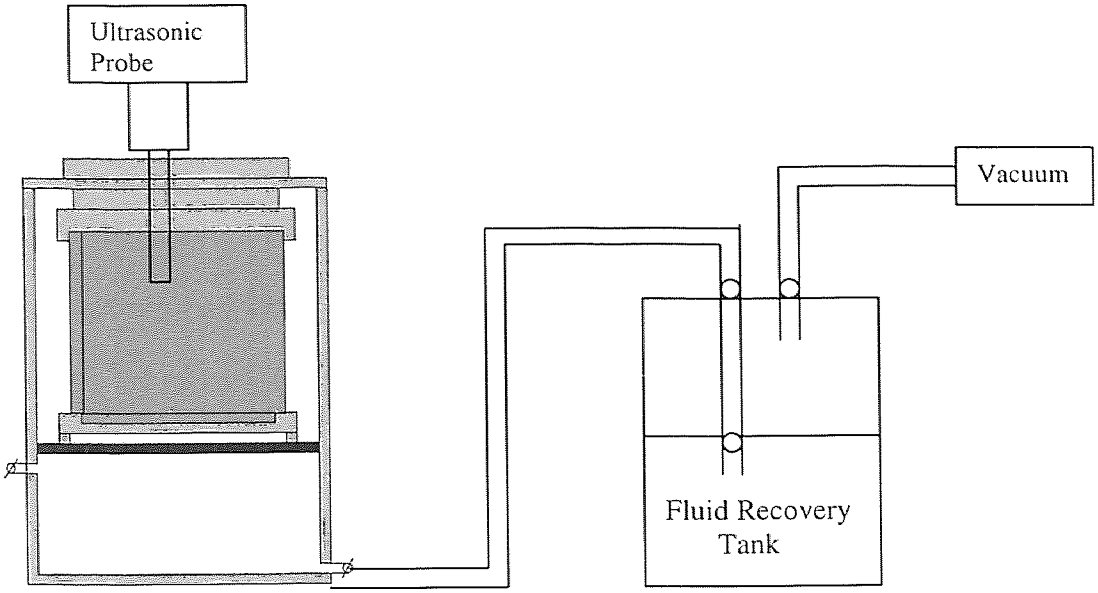


Figure 4.5 Schematic Diagram of Process 2

4.2 Selection of Important Factors which Influence the Energy Dissipated into the Sediment-System by the Ultrasound Application

The process factors, which contribute to the decontamination of sediment washing by the application of ultrasound, were identified and listed below:

1. Power
2. Solvent to Sediment ratio
3. Surfactant concentration
4. Vacuum pressure
5. Sonication time
6. pH

7. Suspension temperature
8. Probe insertion depth
9. Particle size distribution
10. Ultrasonic frequency

4.2.1 The Effect of pH

Rajaratnam (1997) observed that the removal efficiency did not change when the sediment suspension pH was between 2 and 10. However, when the pH of sediment suspension was 13, there was a significant improvement in the removal efficiency. At a pH of 13, the solution becomes an emulsion and it became extremely difficult to extract contaminants. Therefore, it was decided to keep the pH between 6-7 during the ultrasound application in order to avoid the contribution due to solvent pH, which is the pH range of dredged sediments from NY/NJ harbors.

4.2.2 Temperature Effect

Rajaratnam (1997) found that the removal efficiency of suspension temperature at 80 °C was higher when comparing with that performed at constant temperature. It was also observed that the increase in temperature, due to ultrasound, is proportional to sonication time. The results showed that there is an increase in removal efficiency due to increase in solvent temperature. However, in this research a probe type ultrasound source was used. One of the disadvantages of the probe type source is that the system temperature can not be controlled during the experiment.

Therefore, it was decided to use the 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.

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 0.27 W/mm. They provided an explanation stating that the above was due to increased transmission of energy to the solvent solution with higher depth of immersion. The energy transmission depends on the depth of insertion, the width of the probe and the dimensions of the container. Therefore, for a quantitative study, all the above should be kept constant. Since it was decided to keep all the above factors constant, the probe insertion depth factor was also eliminated from the list as a contributing factor to be studied.

4.2.4 Effect of Particle Size Distribution

Urick (1948), Busby and Richardson (1956), and Piotrowska (1971) have reported that the adsorption of ultrasonic waves, when they travel through sediment-liquid suspensions, are affected by the particle size distribution with suspension. However, these tests have been conducted with high frequency ultrasound. Raine and So (1994) reported that when the average particle size decreases and the number of particles increases, cavitation may increase. However, this effect does not significantly affect the energy dissipation.

4.2.5 Effect of the Frequency of Ultrasound Source

The probe type ultrasound source used in this study has a power rating of 1500-Watts and a operating frequency of 20 kHz. There are no commercially available ultrasound sources at reasonable costs with the same power rating but at high frequency. Therefore, frequency was not considered as a factor in this research.

From the above discussion, of the ten factors, five of them, which are power, solvent to sediment ratio, vacuum pressure, surfactant concentration, and sonication time, were identified as important process factors. That is, they influence the removal efficiency of the sediment-system by the application of ultrasound.

4.3 Experimental Design

4.3.1 Design Process Factors and Levels

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, and the settings of each variable that are studied are termed levels of the given factor.

The baseline operation identified five variables (factors) which were included in the experimental design with three levels (low, medium, and high). In Process 1, there are four process factors: power, solvent to sediment ratio, vacuum pressure, and sonication time. The four influence factors and levels for Process 1, Process 2 without the surfactant, and Process 2 with the surfactant is shown in Table 4.2, 4.3, and 4.4, respectively.

A preliminary experiment was performed for Process 1 to provide the range of treatment efficiencies at different factor variations. For solvent to sediment ratio variation, experiments were conducted at 60% power, 10 psi vacuum pressure, 5 min sonication time, and different solvent to sediment ratios of 5:1, 8:1, 10:1, and 15:1. For power variation, experiments were conducted at 10:1 solvent to sediment ratio, 10 psi vacuum pressure, and 5 min. sonication time, and different power at 40%, 50%, 60%, and 80%. For sonication time variation, experiments were conducted at 60% power, 10:1 solvent to sediment ratio, 10 psi vacuum pressure, and different sonication time at 3 min, 5 min, 7 min, and 10 min. For vacuum pressure variation, experiments were conducted at 60% power, 10:1 solvent to sediment ratio, 5 min sonication time, and different vacuum pressure at 5 psi, 10 psi, and 15 psi. The experimental result were tabulated and plotted and are presented in Appendix A. From the result of the preliminary experiments, ranges of four process variables were chosen. The range of factor levels chosen were: energy 40%-80%, solvent ratio 5-15, vacuum pressure 5-15 psi, and sonication time 3-9 minutes. Table 4.2 shows the summary of the influence factors and levels for Process 1.

Table 4.2 Influence Factors and Levels for Process 1

Factors	Level 0	Level 1	Level 2
Power applied by ultrasound probe (%)	40	60	80
Solvent to Sediment Ratio	5	10	15
Vacuum pressure (psi)	5	10	15
Sonication Time (minutes)	3	6	9

Table 4.3 Influence Factors and Levels for Process 2 without the Surfactant

Factors	Level 0	Level 1	Level 2
Power applied by ultrasound probe (%)	40	60	80
Solvent to Sediment Ratio	10	25	50
Sonication Time (minutes)	30	45	60

Experimental results from Process 1 have shown that vacuum pressure does not produce significant variation in removal efficiency and separation efficiency. Therefore, for Process 2, vacuum pressure was not considered as a process factor. However, since sub-atmospheric pressure is required to remove the contaminants and water, the full vacuum pressure were applied. All three levels for each influence factors for Process 2 without the surfactant were selected from the preliminary experiment to provide the range of treatment efficiencies. Since the sediment was heavily contaminated, a high solvent to soil ratio was required. A solvent to sediment ratio of 50:1 was selected as the maximum value since a higher ratio than that would be uneconomical and impractical. For a probe type continuous treatment system, the treatment time over 30 minutes of ultrasound would overheat the system. Therefore, a treatment time of 30 minutes, 45 minutes, and 60 minutes were divided into pulse mode with every 15 minutes the ultrasound would stop to let the probe cool off for 1 minute before start another interval. The experimental results from Process 2 without the surfactant was not sufficed due to low removal efficiencies. Therefore, Process 2 with the surfactant was conducted and the enhancement of the surfactant as cleaning agent was evaluated.

Table 4.4 Influence Factors and Levels for Process 2 with the Surfactant

Factors	Level 0	Level 1	Level 2
Power applied by ultrasound probe (%)	40	60	80
Solvent to Sediment Ratio	10	25	50
Surfactant concentration (%)	0.001	0.01	0.1
Sonication Time (minutes)	30	45	60

All three levels for each influence factors for Process 2 with the surfactant were the same as Process 2 without the surfactant, with the exception that surfactant concentration was introduced as the forth process factor. A surfactant concentration of 0.001% was selected as the minimum and 0.1% was selected as the maximum. Surfactant concentrations above 1% would make the treatment process uneconomical.

Four factors at three levels produced 81 combinations. This is a complete (3^4) factorial design. Three factors at three levels produced 27 combinations. Both Process 1 and Process 2 without the surfactant, a complete factorial design was used. 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 and give similar results to the full factorial design. This indicates the technical constraints that can pinpoint the specific fractionally replicated design to be used. In this study, for Process 2 with the surfactant, 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 is 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 from National Bureau of Standards, 1959 and 1961. These have been reproduced in McLean et. al., 1984, Patterson, 1976, Box et. al., 1978, and Franklin,

1984. The full factorial design and partial factorial design for Process 1, Process 2 with and without the surfactant is shown in Appendix B.

4.3.2 Preparation of Sediment Suspension and Ultrasonic Application

In order to make the sediment slurry, contaminated synthetic sediments were mixed with tap water. For Process 1, different solvent to sediment ratio was suspended in 500 mL of water. The total sediment solution was maintained at 500 mL throughout the treatment process by adding water when it was required. For Process 2, different solvent to sediment ratio was suspended in 1000 mL of water. The total sediment solution volume was also maintained at 1000 mL for Process 2 throughout the treatment process. Once the synthetic sediments were added to the solvent, it was subjected to the ultrasound treatment. For Process 2 with surfactant, the surfactant solution was made with water at three different concentrations: 0.001%, 0.01%, and 0.1%. The ultrasonic probe was dipped 7 centimeters into the sediment solution to keep the sediment in suspension for both Process 1 and Process 2.

4.3.3 Preparation of Sediment for Analysis

After the application of ultrasound to the soil suspension, sediment solution was transferred to the container. The soil suspension was allowed to settle and the separated water was removed. The soil was dried overnight for sediment analysis.

4.3.4 Ultrasound Extraction for Sediments Portion and Concentration

The EPA method 3550B was employed to extract p-terphenyl from the sediments. This extraction method is recommended for analyzing sediments with high concentration of organics (greater than 20 mg/kg). The method consisted of adding two grams of untreated sediment or treated sediment to two grams of sodium sulfate. Then it was mixed well and one mL of surrogate spiking solution (2-fluorobiphenyl) was added to the mixture and made total volume of sample 10 mL by adding acetone/hexane (1:1, v/v) solution. The acetone/hexane mixture served as solvent. The ultrasonic probe was used to extract the sample for 2 minutes at power of 50% set on pulse mode, meaning the ultrasonic probe was switched on and off for 2 minutes. However, it was found that adding of 2 g of sodium sulfate to 2 g of sediments in 10 mL of solution was not sufficient for extraction. Therefore, the above quantities were doubled and after the extraction with ultrasonic probe, the samples were concentrated using the Kuderna-Danish (K-D) method to 5 mL. One mL of extracted sample was then placed in a capped sample vial for the chemical analysis of p-terphenyl in sediments.

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. In a replicate sample, two soil samples are treated with same washing condition (i.e., same power density, sonication time, surfactant concentration and solvent to soil ratio) and chemical analysis are run separately. For a duplicate sample, the same soil sample and same extraction procedure are used, but the chemical analysis (GC/FID) is run twice. Split sampling means the same soil sample is used to run two extractions followed by separate GC/FID 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 4 or 6 splits.

CHAPTER 5

ANALYSIS OF EXPERIMENTAL DATA

5.1 GC/FID Analysis of p-Terphenyl in Sediments

A 1.0 mL of concentrated solution from extraction was used for analyzing concentration of p-terphenyl in sediments by GC/FID analysis. Hewlett Packard 5890 Series II Gas Chromatography was used for the analysis. The column used in the GC/FID was HP-5 crosslinked 5% PH ME Siloxane with 30m*0.32mm*0.25 μm film thickness. The GC/FID operating parameter is shown in Table 5.1. An auto sampler was used with the GC (HP Model #18596C). The initial temperature of GC/FID was 50 °C at the rate of 50 °C/min until it reached 75 °C, then the rate was changed to 10 °C/min until it reached 300 °C. The sensitivity of GC/FID was set at the lowest, the equilibrium time was 2 minutes, the injection temperature was kept at 3 °C above the oven temperature, and the total run time was 23.50 minutes per sample.

Table 5.1 Parameter of GC/FID

Parameter	Values
Auxilliary gas	≥ 20 mL/min
H_2	30 mL/min
Air	400 mL/min
Pressure at inlet	16.5 psi
Pressure at outlet	43.5 psi
Carrier gas	2.2 mL/min
Make up and carrier gas	23.5 mL/min
Total H_2	53.4 mL/min
Total air	423 mL/min
Flow rate	2.15 mL/min
Velocity rate	32.6 cm/sec
Initial temperature	50 °C
Detector temperature	320 °C

An analyze was identified by comparing the sample spectrum with the spectra of standard compounds (standard reference spectra). The chemical analysis of p-terphenyl in wash water was not performed for the mass balance, as wash water was too diluted to detect p-terphenyl concentrations by GC/FID.

5.2 Determination of Treatment Efficiency

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

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

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

$$S = \frac{(\text{Amount of fine fraction in sample - Amount of fine fraction remain}) * 100\%}{\text{Amount of fine fraction in sample}}$$

5.3 Analysis of Data

In order to present all the data, the following procedure was used.

1. Two factors at the three levels, one factor at its lowest level and the other factor at three different levels; this produces a graph for each level.
2. Two factors at the three levels, one factor at its middle level and the other factor at three different levels; produces a graph for each level.
3. Two factors at the three levels, one factor at its highest level and the other factor at three different levels; produces a graph for each level.

The above procedure gave 9 plots for p-terphenyl under different conditions for Process 1 and Process 2 with the surfactant. For Process 2 without surfactant, three graphs were generated.

5.3.1 Analysis of Data for Process 1

Figures C.1 to C.9 show the variations of removal efficiencies with p-terphenyl for different condition under different experimental settings for Process 1. Figures C.1, C.4, and C.7 show insignificant contaminant removal. This is due to low sonication time. The vacuum pressure does not have significant contribution to the removal efficiency by varying its value between 5 psi and 10 psi, but shows significant improvement at a vacuum pressure of 15 psi and 15:1 solvent to sediment ratio. Figure C.8 indicates that the lowest removal efficiency was obtained at 5:1 solvent to sediment ratio, and higher removal efficiencies were obtained at 10:1 and 15:1 solvent to sediment ratio. The power output also has significant contribution to removal efficiency, although, not as much as solvent to sediment ratio and sonication time.

Figures D.1 to D.9 show the variations of separation efficiencies with p-terphenyl at different experimental settings for Process 1. Figures D.1, D.4, and D.7 show low separation efficiencies at low solvent to sediment ratio (5:1) and (40%). At solvent to sediment ratio of 15:1, 100% separation efficiencies were obtained.

5.3.2 Analysis of Data for Process 2 without the Surfactant

Figures E.1 to E.3 shows the removal efficiency of dredged sediments without surfactant and had removal efficiencies range from 20% to 40%. The highest removal efficiency was obtained for 80% power, 50:1 solvent to sediment ratio, and at 60 minutes sonication time (Figure E.3). The separation efficiency for Process 2 was not plotted, as 100 % separation efficiency was obtained for all 27 experiments.

5.3.3 Analysis of Data for Process 2 with the Surfactant

Figures F.1 to F.5 shows the variation of removal efficiency for Process 2 with surfactant. Figures F.1 to F. 5 are not conclusive due to low removal efficiencies obtained with low surfactant concentrations (0.001% and 0.01%) with removal efficiencies ranged from 20% to 40%. Power and sonification time have equally significant effect on removal efficiencies, although they are secondary to the surfactant concentration. Solvent to sediment ratio does not have significant effect on removal efficiencies. The highest contaminant removal efficiency of 80% was obtained at 60% power, 25:1 solvent to sediment ratio, 0.1% surfactant concentration, and 60 minutes sonication (Figure F.9). The separation efficiency for Process 2 was not plotted, as 100 % separation efficiency was obtained for all 27 experiments.

CHAPTER 6

STATISTICAL ANALYSIS OF THE EXPERIMENTAL DATA

6.1 Statistical Approach

SAS/STAT version 6.0, a statistical program, was used for statistical analysis. The program can analyze data using several kinds of models including 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) and Analysis-of-Covariance Model.

6.2 Statistical Analysis Using General Linear Model Procedure

6.2.1 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 the GLM procedure, three effects were considered as described below:

a) Main effects

The main effects are power (Power), solvent to sediment ratio (Ratio), vacuum pressure (Press), surfactant concentration (Surfact), and sonification time (Time).

b) Second Order (Interaction) Effects

The second order (interaction) effects are (Power*Ratio), (Power*Press), (Power*Surfact), (Power*Time), (Ratio*Press), (Ratio*Press), (Ratio*Surfact), (Ratio*Time), (Press*Time), (Surfact*Time).

c) Third Order (Interaction) Effects

The third order (interaction) effects are (Power*Ratio*Press), (Power*Ratio*Time), (Ratio*Press*Time), (Power*Press*Time), (Power*Ratio*Surfact), (Ratio*Surfact*Time), (Power*Surfact*Time).

6.2.2 Terminology Used for Statistical Analysis

The terminology used in this program is summarized below:

a) Degree of Freedom (DF)

In order to perform a statistical analysis, it is necessary to use experimental observations to estimate 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) subtract the number k of unknown population parameters, which must be estimated from the sample observations. It can be written as:

$$\mathrm{DF} = \mathrm{N} - \mathrm{k}$$
$$\text{If } \mathrm{k} = 1,\ \mathrm{DF} = \mathrm{N} - 1$$

b) Mean Square

It is the ratio of sum of square to degree of freedom.

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

c) F-Test

It is important in some applications to know the sampling distribution of the difference in means (X_1-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, the S_1^2/S_2^2 statistic is considered. Its distribution, when the underlying true variances are equal, is called the F-distribution.

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

d) Pr > F

"Pr > F" (technically called the 'P-value' or the 'observed significant level') is the probability of obtaining at least as great as 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 the 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.

6.2.3 Evaluation of the Results from the GLM Procedure

The statistical analysis results of overall model using GLM procedure, for Process 1, Process 2 without the surfactant, and Process 2 with the surfactant are shown in Table 6.1.

Table 6.1 Summary of the GLM Procedure Results for Overall Models of Process 1, Process 2 w/o Surfactant, and Process 2 w/ Surfactant
Dependent Variable : Removal Efficiencies

Source	Degree of Freedom			Sum of Squares			Pr > F		
	Process 1	Process 2 w/o surfactant	Process 2 w/ surfactant	Process 1	Process 2 w/o surfactant	Process 2 w/ surfactant	Process 1	Process 2 w/o surfactant	Process 2 w/ surfactant
Model	64	26	26	4.7865	0.1374	0.8836	0.0004	0.1051	0.0078
Error	16	3	7	0.2319	0.0032	0.0363			
Corrected Total	80	29	33	5.0184	0.1406	0.9199			
					Type I SS				
Power	2	2	2	0.2340	0.0103	0.1209	0.0038	0.1151	0.0059
Ratio	2	2	2	0.6184	0.0059	0.0255	0.0001	0.2058	0.1554
Press	2	N/A	N/A	0.2259	N/A	N/A	0.0043	N/A	
Surfact	N/A	2	2	N/A	N/A	0.4518	N/A	N/A	0.0001
Time	2	2	2	1.8048	0.0309	0.1078	0.0001	0.0285	0.0080
Power*Ratio	4	4	4	0.2155	0.0309	0.0513	0.0253	0.1539	0.1396
Power*Press	4	N/A	N/A	0.0541	N/A	N/A	0.4699	N/A	N/A
Power*Surfact	N/A	N/A	4	N/A	N/A	0.0310	N/A	N/A	0.3006
Power*Time	4	4	4	0.1559	0.0319	0.0302	0.0689	0.0645	0.3117
Ratio*Press	4	N/A	N/A	0.6305	N/A	N/A	0.0002	N/A	N/A
Ratio*Surfact	N/A	N/A	2	N/A	N/A	0.0559	N/A	N/A	0.0383
Ratio*Time	4	4	2	0.1074	0.0130	0.0079	0.1683	0.1925	0.5006
Press*Time	4	N/A	N/A	0.1428	N/A	N/A	0.0871	N/A	N/A
Surfact*Time	N/A	N/A	2	N/A	N/A	0.0012	N/A	N/A	0.8923
Power*Ratio*Press	8	N/A	N/A	0.1767	N/A	N/A	0.2250	N/A	N/A
Power*Ratio*Surfact	N/A	N/A	0	N/A	N/A	0	N/A	N/A	-
Power*Ratio*Time	8	4	0	0.0609	0.0295	0	0.8206	0.1669	-
Ratio*Press*Time	8	N/A	N/A	0.1926	N/A	N/A	0.1845	N/A	N/A
Ratio*Surfact*Time	N/A	N/A	0	N/A	N/A	0	N/A	N/A	-
Power*Press*Time	8	N/A	N/A	0.1669	N/A	N/A	0.2541	N/A	N/A
Power*Surfact*Time	N/A	N/A	0	N/A	N/A	0	N/A	N/A	-

The GLM procedure results provided the following important information:

- Comparing the value of Pr > F for Process 1, it was found that the value Pr > F for all main effects (power, solvent to sediment ratio, vacuum pressure, and sonication time) was less than 5%. Therefore, main effects significantly influenced the dependent variable (removal efficiencies). Of the second order interactions, the values for Pr > F for (Power*Ratio) and (Ratio*Press) were less than 5%. Therefore, those second order parameters significantly influenced the removal efficiencies while other second order interactions had insignificant influence. None of the third order interactions influenced the removal efficiencies. These results indicated that the third and higher order interactions could be neglected in the regression analysis in order to develop a statistical model. In addition, these results were also consistent with conclusion obtained from data analysis in chapter 5.
- For Process 2 without the surfactant, sonication time was the only constituting factor, which significantly influenced the removal efficiencies. There were no second or higher order interactions with significant influence on the removal efficiencies.
- For Process 2 with the surfactant, power, surfactant concentration, and sonication time were the main factor that influenced the removal efficiencies. Of the second order interactions, only (Ratio*Surfact) influenced the removal efficiencies, and the third order interactions had no influence on the removal efficiencies.

- Higher order interactions (3rd and 4th order) are not statistically significant and can be ignored. This conclusion agrees with the experimental design in selecting partial factorial for Process 2 with the surfactant.

6.3 The Regression Procedure (PROC RSREG)

From the GLM procedure, it was found that the third order interactions are not significant. Therefore, a full quadratic statistical model is appropriate to model the process. The Regression Procedure provides 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 must 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 factor level is at the optimum response.

6.3.1 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 estimate point of maximum response. If it is a "valley" or a "saddle" surface then there is no unique minimum or maximum.

6.3.2 Elucidation of Canonical Analysis

The Canonical Analysis is able to analyze the overall shape of the surface to determine whether the estimated stationary point of the surface is a maximum, minimum, or saddle point. In order to categorize the stationary point, the eigen values are used. If all eigen values are negative then the solution will be 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 a flat area.

6.3.3 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 no 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.

6.3.4 Evaluation of the Results from the PROC RSREG Procedure

The statistical analysis results of overall models, for Process 1, Process 2 without the surfactant, and Process 2 with the surfactant, using RSREG procedure, are shown in Table 6.2.

Table 6.2 Canonical Analysis for Eigen Values and Eigen Vectors for Overall Models

Process	Eigen Values	Eigen Vectors				
		Power	Ratio	Pressure	Surfactant	Time
Process # 1	0.0680	0.8887	-0.2312	-0.3781		-0.1170
	0.0305	0.4382	0.3194	0.8400		-0.0174
	-0.0966	0.0134	0.8238	-0.3298		-0.4609
	-0.1409	0.1339	0.4073	-0.2064		0.8796
Process # 2 w/o surfactant	0.0456	0.2297	0.1475			0.9620
	-0.0177	0.4937	0.8342			-0.2458
	-0.0443	0.8388	-0.5314			-0.1188
Process # 2 w/ surfactant	0.0499	-0.0089	0.1823		0.0306	0.9827
	0.0008	0.2699	0.9029		-0.2961	-0.1556
	-0.1055	0.7999	-0.0434		0.5985	-0.0033
	-0.1157	-0.5359	0.3869		0.7437	-0.0998

For Process 1, 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 (0.8796) corresponding to the largest eigen values (-0.1409) is associated with sonication time. The second largest eigen vector (0.8238) is associate with solvent to sediment ratio. Similarly third and fourth are power and vacuum pressure, respectively. This shows that the response surface is more sensitive to sonication time changes whereas it is not that sensitive to vacuum pressures.

For Process 2 without the surfactant, since the eigen values were both positive and negative, the stationary points were saddle points. The significant factors for Process 2 without the surfactant were sonication time, power, and solvent to sediment ratio, respectively. The influence of both sonication time and power factors are approximately equal since their eigen values are very close.

For Process 2 with the surfactant, since the eigen values were both positive and negative, the stationary points were saddle points. The significant factors for Process 2 with the surfactant are surfactant, power, sonication time, and solvent to sediment ratio, respectively. The influence of both surfactant and power factors are approximately equal sine their eigen values are very close. The canonical analysis also indicated that if the particle size decreased, the surfactant factor is more sensitive. More surfactant is required for the removal of contaminants in fine particles.

The analysis of variance (Table 6.3), which gives the test of P > F, from the ridge analysis, indicated that all four factors significantly influenced Process 1. However, factors such as solvent to sediment ratio, vacuum pressure, and sonication time are more significant than power. For Process 2 without the surfactact, power and sonication time was more significant than solvent to sediment ratio. For Process 2 with the surfactant, surfactant concentration was the most significant contributor with power and sonication time equally important and solvent to sediment ratio was the least important contributor.

Table 6.3 Ridge Analysis for Analysis of Variance for Overall Models

Porcess	Factor	Degrees of Freedom	Sum of Square	Mean Square	F-Ratio	P > F
Process # 1	Power	5	0.3688	0.0738	3.119	0.0138
	Ratio	5	1.0810	0.2162	9.142	0.0001
	Pressure	5	0.6522	0.1304	5.516	0.0003
	Time	5	1.9302	0.3860	16.324	0.0001
Process # 2 w/o surfactant	Power	4	0.0329	0.0082	2.508	0.0745
	Ratio	4	0.0200	0.0050	1.521	0.2340
	Time	4	0.0455	0.0114	3.468	0.0262
Process # 2 w/ surfactant	Power	5	0.1440	0.0288	4.790	0.0053
	Ratio	5	0.0957	0.0191	3.181	0.0298
	Surfactant	5	0.4563	0.0913	15.172	0.0001
	Time	5	0.1416	0.0283	4.708	0.0058

For the overall model of Process 1, the canonical analysis indicated that the response surface had a saddle point and does not have a unique optimum. However, the ridge analysis indicates (Table G.1) that maximum for the overall model of Process 1 was at

98% removal efficiency with 58% power, 14:1 solvent to sediment ratio, 16 psi vacuum pressure, and 7.36 minutes of sonication time.

For the overall model of Process 2 without the surfactant, the canonical analysis indicates that the response surface had a saddle point and does not have a unique optimum. However, the ridge analysis indicates (Table G.2) that maximum yield for the overall model of Process 2 without the surfactant was at 99% removal efficiency with 75% power, 41:1 solvent to sediment ratio, and 95 minutes of sonication time.

For the overall model of Process 2 with the surfactant, the canonical analysis indicated that the response surface had a saddle point and does not have a unique optimum. However, the ridge analysis indicates (Table G.3) that maximum yields for the overall model of Process 2 with the surfactant was at 99% removal efficiency with 57% power, 32:1 solvent to sediment ratio, 0.08% surfactant concentration, and 74 minutes of sonication time.

Model fitting parameters using the full model regression for all process (Process 1, Process 2 without the surfactant, and Process 2 with the surfactant) are shown in Table G.1 to G.3. The response variable (removal efficiency) is denoted as Y and the three variables or four variables are denoted as A, B, C, and D respectively. For Process 1, the four variables are power, solvent to sediment ratio, vacuum pressure, and sonication time. For Process 2 without the surfactant, the three variables are power, solvent to sediment ratio, and sonication time. For Process 2 with the surfactant, the four variables are power, solvent to sediment ratio, surfactant concentration, and sonication time.

For Process 1 and Process 2 with the surfactant, the full quadratic model (four factors) was fitted and expressed as follow:

$$Y_R = \beta_0 + \beta_1A + \beta_2B + \beta_3C + \beta_4D + \beta_5A^2 + \beta_6AB + \beta_7B^2 + \beta_8CA + \beta_9CB + \beta_{10}C^2 + \beta_{11}DA + \beta_{12}DB + \beta_{13}DC + \beta_{14}D^2$$

For Process 2 without the surfactant, full triple model was conducted; the regression equation is expressed as follow:

$$Y_R = \beta_0 + \beta_1A + \beta_2B + \beta_3C + \beta_4A^2 + \beta_5AB + \beta_6B^2 + \beta_7CA + \beta_8CB + \beta_9C^2$$

The coefficient β for each expression were obtained and listed in Tables H.1 to H.3. From these tables the following conclusion can be drawn:

- From the ridge analysis, under optimum conditions, it can be observed that the high removal efficiency could be obtained for Process 1 and low removal efficiency was obtained for Process 2 with and without the surfactant. One of the reasons may be that Process 2 contains finer particles than Process 1, which as stated before, is more difficult to decontaminate. In addition, Process 2 with the surfactant has higher removal efficiency than process 2 without the surfactant as that surfactant significantly enhance the decontamination of dredged sediments during the application of ultrasound with sub-atmospheric pressure.
- Of the three experiments, process 1 requires lesser amount of power and sonication time than process 2 with and without the surfactant, which can be concluded that finer particles need more power, time, and surfactant to improve decontamination performance.
- Furthermore, additional experiments are required since the optimum condition from the statistical analysis do no fall within the experimental design.

Figures 6.1 to 6.3 show the comparison between the experimental removal efficiencies and the predicted removal efficiencies by using the Regression Procedure analysis for the overall models for Process 1, Process 2 without the surfactant, and Process 2 with the surfactant. Figures 6.1 to 6.3 show that experimental removal efficiencies are similar to the predicted removal efficiencies by using the Regression Procedure analysis. Therefore, it can be concluded that this experimental method is reliable and concur with the statistical analysis.

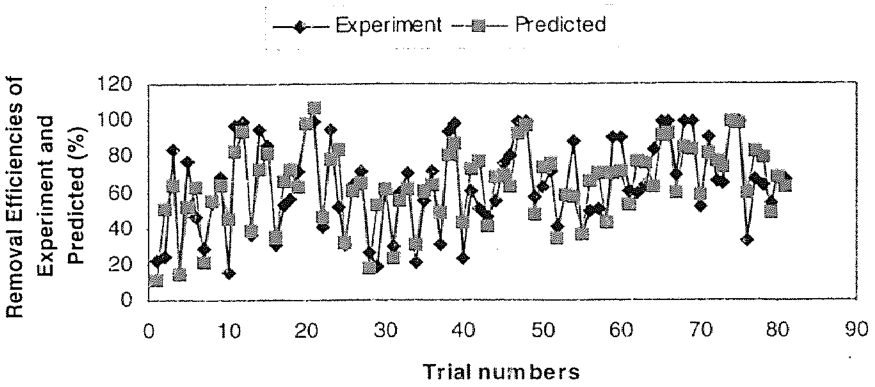


Figure 6.1 The Comparison between the Experiment Values and Predicted Values using Regression Procedure Analysis for the Overall Model, Process 1

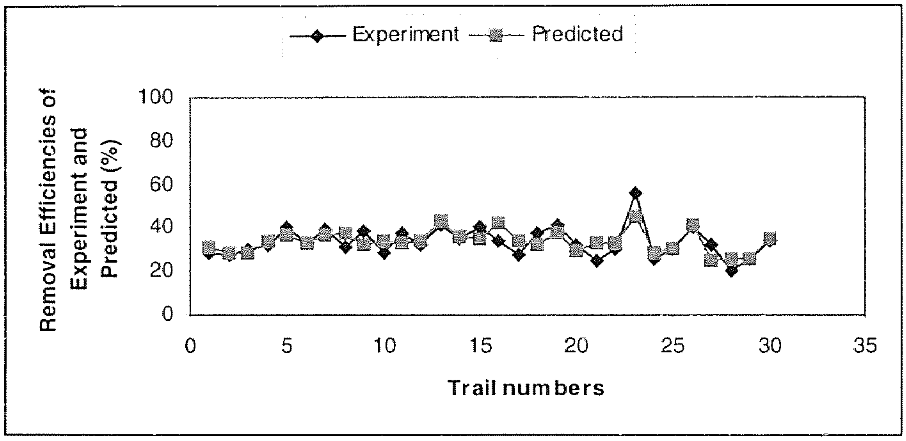


Figure 6.2 The Comparison between the Experiment Values and Predicted Values using Regression Procedure Analysis for the Overall Model, Process 2 without the Surfactant

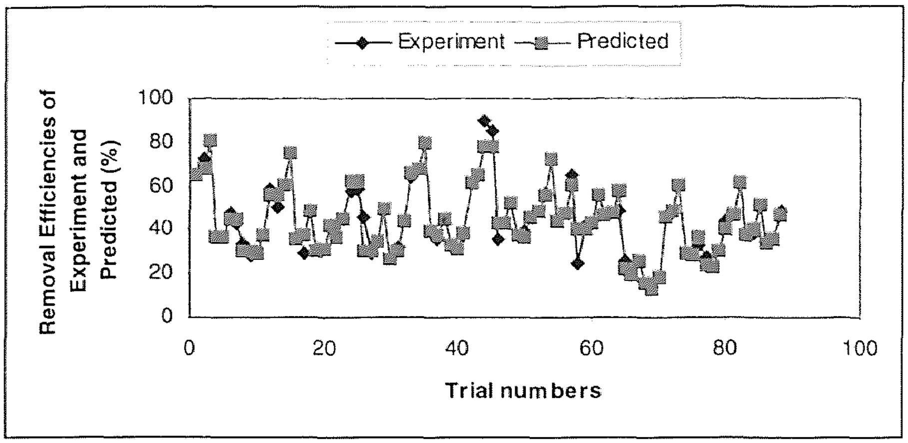


Figure 6.3 The Comparison between the Experiment values and Predicted Values using Regression Procedure Analysis for the Overall Model, Process 2 with the Surfactant

CHAPTER 7

SUMMARY AND CONCLUSIONS

The feasibility of using ultrasound with sub-atmospheric pressure to decontaminate dredged sediment was investigated. The effectiveness of treatment technology was evaluated based on contaminant removal efficiency. Process 1 (coarse fraction) produced high removal efficiencies and separation efficiencies at much shorter time than did Process 2 without surfactant. The decontamination of fine particles in Process 2 required more sonication time, higher solvent to sediment ratio, and also required surfactant in order to obtain high removal efficiencies. The vacuum pressure was used in Process 1 as one of the process factors, however, it was later removed since experimental results showed that it does not significantly contribute to removal or separation efficiency.

Based on the experimental results, a statistical model was developed to optimize the technology. The GLM procedure suggests that for the overall model of Process 1, sonications time, solvent to sediment ratio, vacuum pressure, and power are the significant factors. For Process 2 without the surfactant, sonication time is the only significant factor. For the overall Process 2 model with surfactant, surfactant concentration, sonication time, and power are the significant factors. Canonical analysis and ridge analyses were conducted to determine the factor levels at optimum conditions. From canonical analysis, it was observed that sonication time was the most significant factor for both Process 1 and Process 2 without the surfactant. For Process 2 with the surfactant, surfactant concentration was the most significant factor. Although the canonical analysis indicated that the stationary point is a saddle point, the ridge analysis gave the optimum condition for the overall processes. Table 7.1 lists the optimum operating condition for Process 1 and Process 2 with and without surfactant.

Table 7.1 Maximum Removal at Optimum Conditions

Process	Maximum Removal (%)	Optimum Power (%)	Optimum Solvent to sediment ratio	Optimum Vacuum pressure (psi)	Optimum Surfactant concentration (%)	Optimum Sonication time (min)
Process 1	98	58	14:1	16		8
Process 2 without surfactant	99	75	41:1			95
Process 2 with surfactant	99	57	32:1		0.8	74

Future Research

Since the bench scale study showed that ultrasound can decontaminate dredged sediment both with and without the application of surfactant, it is proposed to perform a pilot scale demonstration, which should include continuous treatment design and treatment of contaminated wash water.

APPENDIX A

PRELIMINARY EXPERIMENT RESULTS FOR PROCESS 1

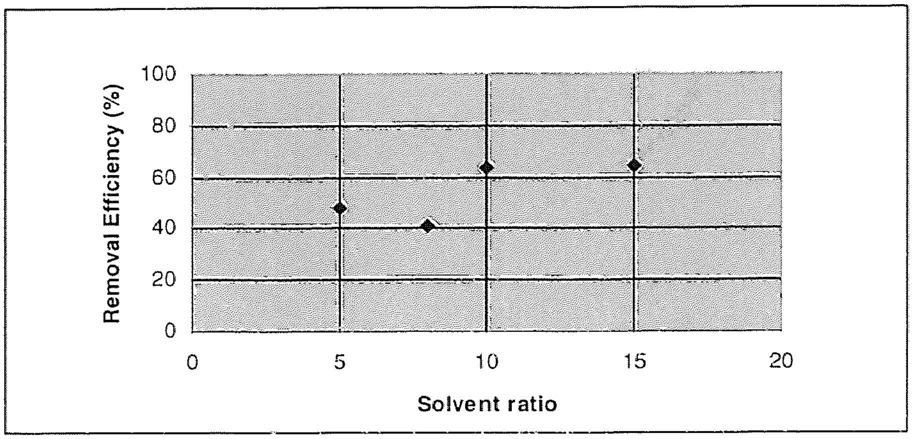


Figure A.1 Removal Efficiency of p-Terphenyl for Different Solvent to Sediment Ratio, at 60% Power, 10 psi Pressure and 5 min. Sonication Time

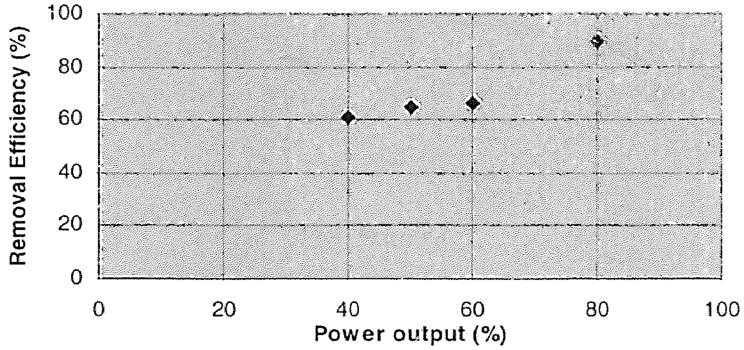


Figure A.2 Removal Efficiency of p-Terphenyl for Different Power Output, at 10:1 Solvent to Sediment Ratio, 10 psi Pressure and 5 min. Sonication Time

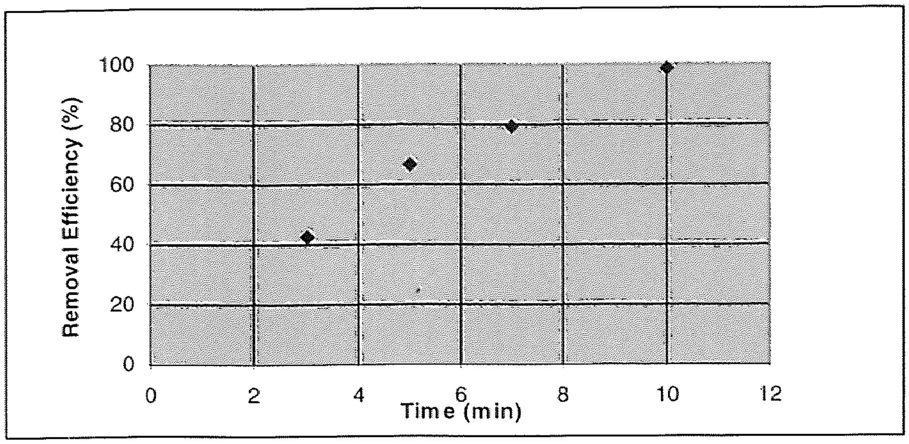


Figure A.3 Removal Efficiency of p-Terphenyl for Different Sonication Time, at 60% Power, 10:1 Solvent to Sediment Ratio and 10 psi Pressure

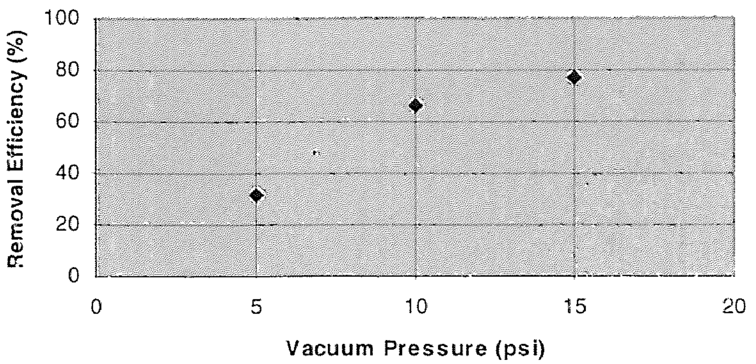


Figure A.4 Removal Efficiency of p-Terphenyl for Different Vacuum Pressure, at 60% Power, 10:1 Solvent to Sediment Ratio and 5 min. Sonication Time

APPENDIX B

FACTORIAL DESIGN FOR TREATMENT PROCESS

Appendix B.1 Full Factorial Design for Process 1

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 sediment:

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

Appendix B.2 Full Factorial Design for Process 2 without the Surfactant

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

Factors = A, B, C

Levels = 0, 1, 2 for each factor

Treatment combinations = (a, b, c)

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

Total numbers of treatment combinations are 3^3 (=27)

The full factorial design for process 2 without the surfactant:

Blocks

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
000	001	002	010	020	100	101	102	011
012	021	022	111	110	112	120	121	122
210	212	200	201	202	211	220	221	222

The experimental order was randomized and resulted in the following:

222 000 111 001 002 010 020 110 112

210 211 212 100 200 101 102 011 012

120 121 122 220 221 021 022 201 202

Appendix B.3 Partial Factorial Design for Process 2 with the Surfactant

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 process 2 with the surfactant:

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

The experimental order was randomized to minimize the experimental error and resulted in the following:

1200 1221 0021 1212 1110 1101 1122 0012 0000

0120 1020 0111 1011 0102 1002 2220 2010 2100

2022 0222 0210 2121 0201 2211 2001 2112 2202

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

APPENDIX C

THE PLOTS SHOW THE VARIATIONS OF REMOVAL EFFICIENCIES WITH P-TERPHENYL AT DIFFERENT CONDITION FOR PROCESS 1

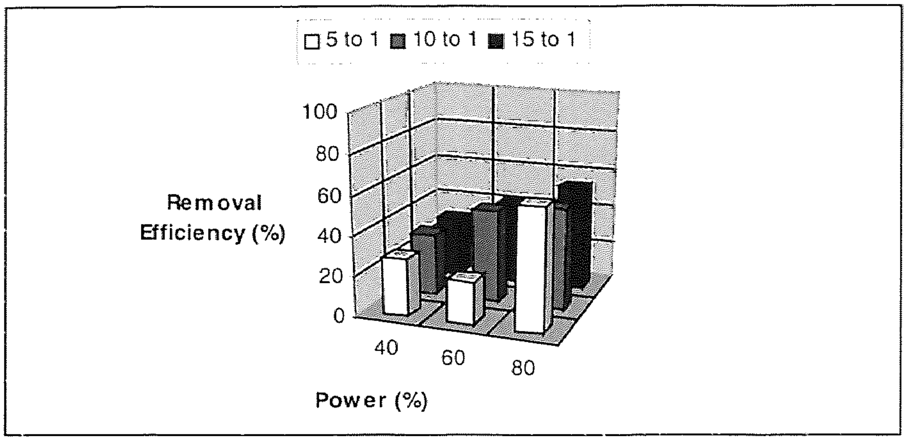


Figure C.1 Process 1, Removal Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 5 psi Pressure and 3 min. Sonication Time

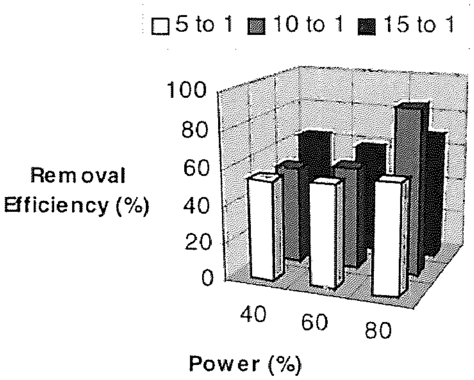


Figure C.2 Process 1, Removal Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 5 psi Pressure and 6 min. Sonication Time

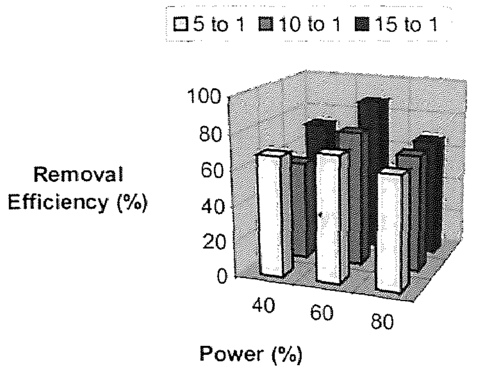


Figure C.3 Process 1, Removal Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 5 psi Pressure and 9 min. Sonication Time

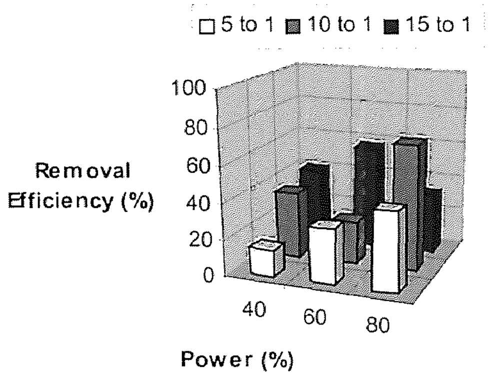


Figure C.4 Process 1, Removal Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 10 psi Pressure and 3 min. Sonication Time

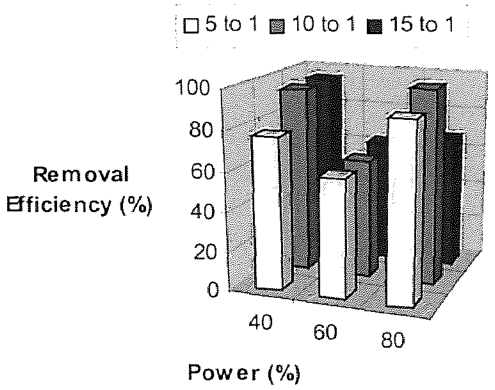


Figure C.5 Process 1, Removal Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 10 psi Pressure and 6 min. Sonication Time

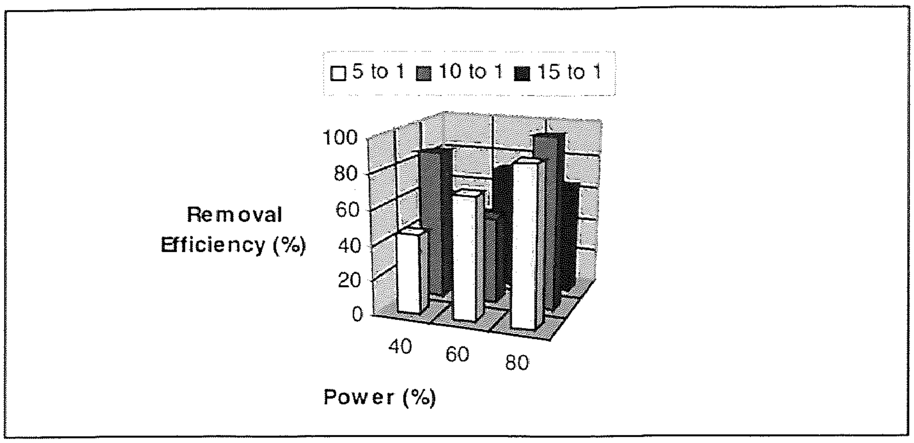


Figure C.6 Process 1, Removal Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 10 psi Pressure and 9 min. Sonication Time

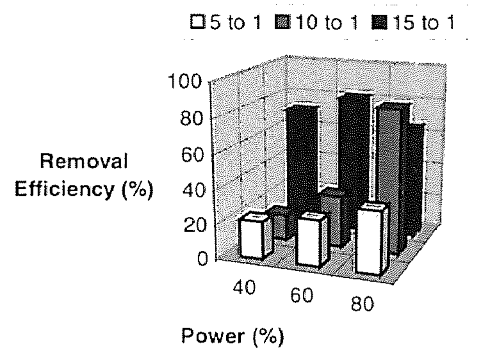


Figure C.7 Process 1, Removal Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 15 psi Pressure and 3 min. Sonication Time

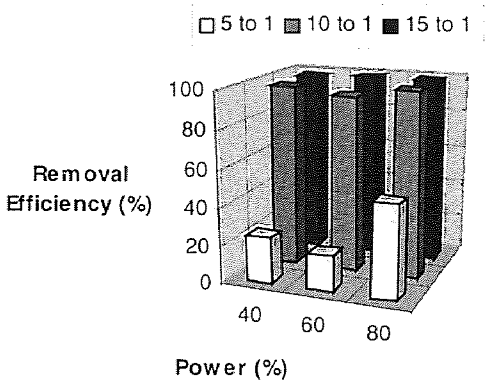


Figure C.8 Process 1, Removal Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 15 psi Pressure and 6 min. Sonication Time

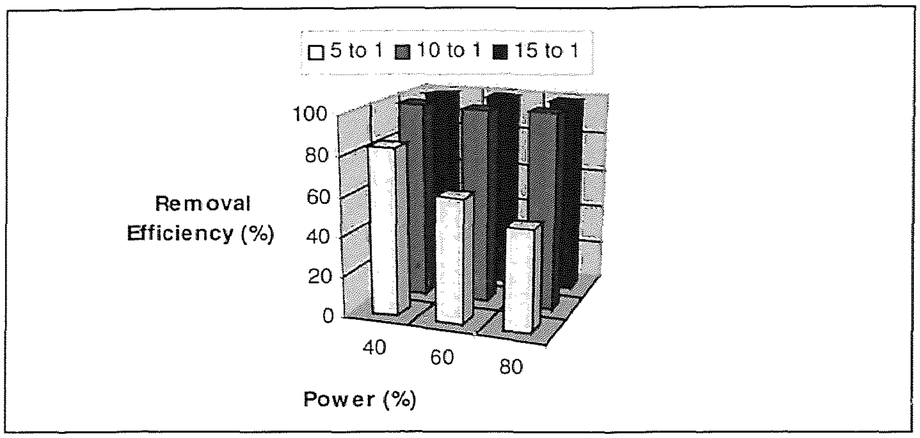


Figure C.9 Process 1, Removal Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 15 psi Pressure and 9 min. Sonication Time

APPENDIX D

THE PLOTS SHOW THE VARIATIONS OF SEPARATION EFFICIENCIES WITH P-TERPHENYL AT DIFFERENT CONDITIONS FOR PROCESS 1

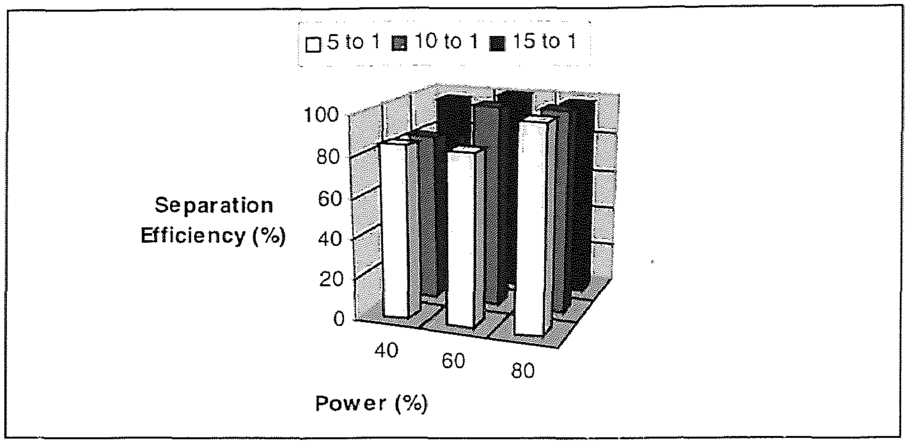


Figure D.1 Process 1, Separation Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 5 psi Pressure and 3 min. Sonication Time

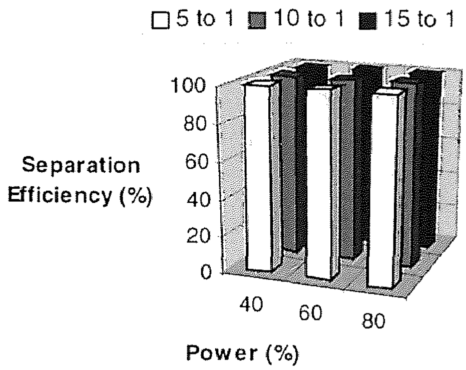


Figure D.2 Process 1, Separation Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 5 psi Pressure and 6 min. Sonication Time

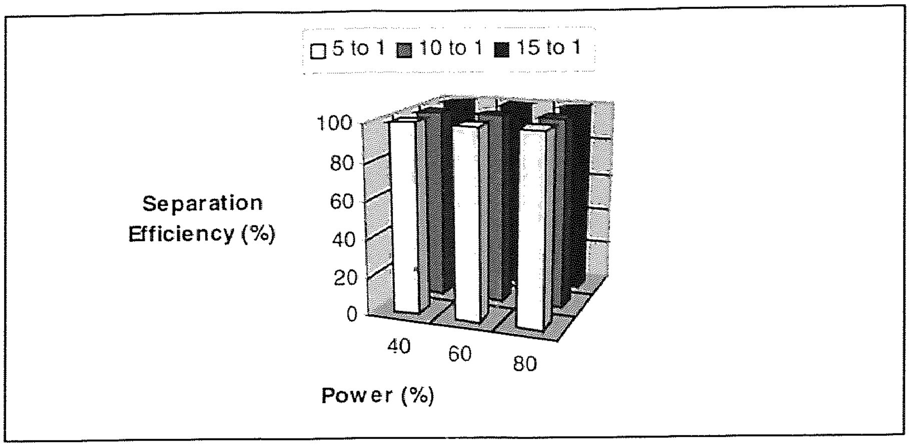


Figure D.3 Process 1, Separation Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 5 psi Pressure and 9 min. Sonication Time

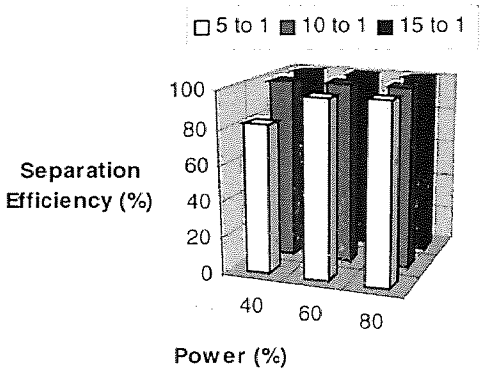


Figure D.4 Process 1, Separation Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 10 psi Pressure and 3 min. Sonication Time

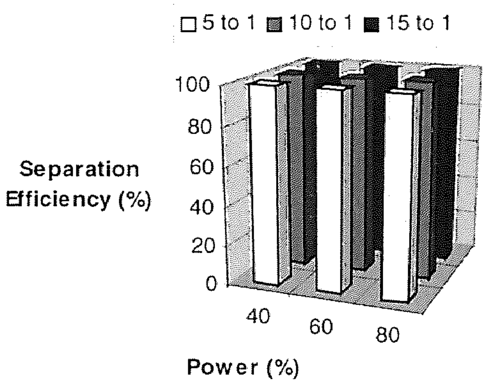


Figure D.5 Process 1, Separation Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 10 psi Pressure and 6 min. Sonication Time

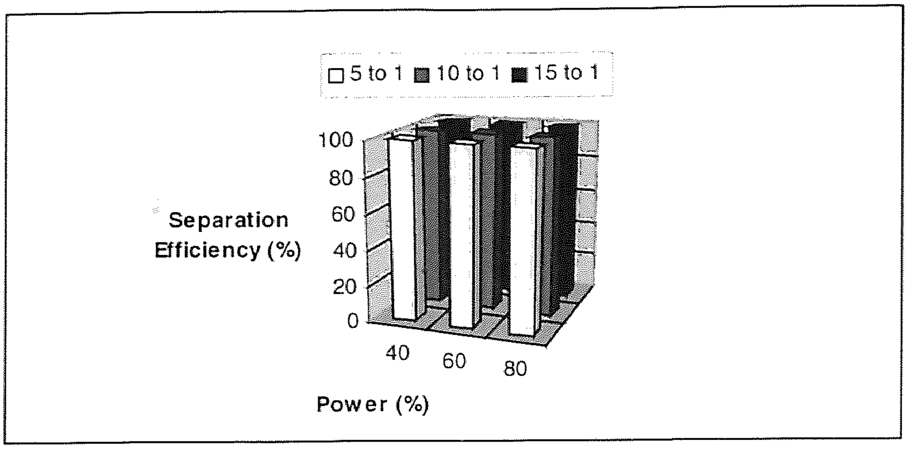


Figure D.6 Process 1, Separation Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 10 psi Pressure and 9 min. Sonication Time

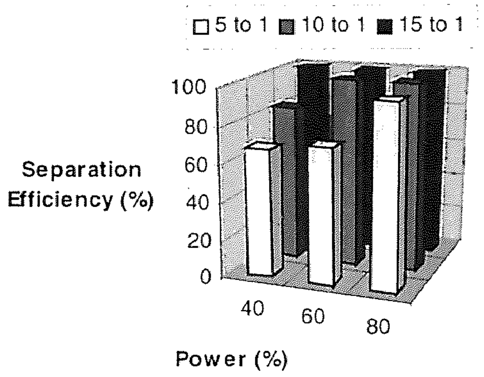


Figure D.7 Process 1, Separation Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 15 psi Pressure and 3 min. Sonication Time

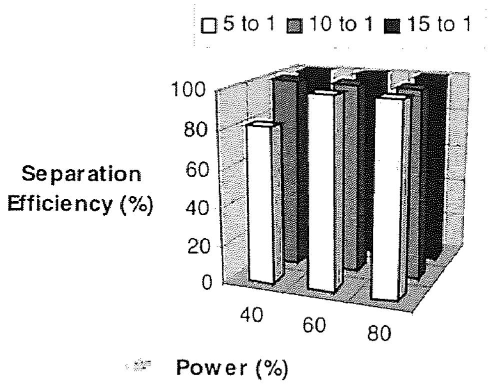


Figure D.8 Process 1, Separation Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 15 psi Pressure and 6 min. Sonication Time

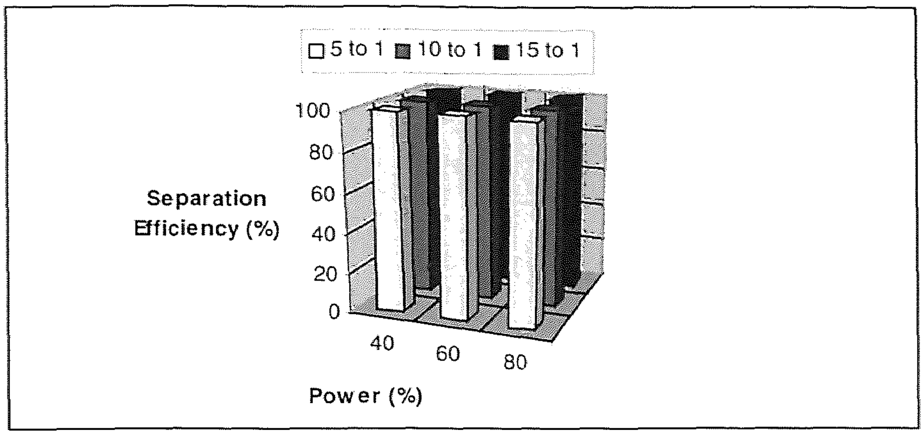


Figure D.9 Process 1, Separation Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 15 psi Pressure and 9 min. Sonication Time

APPENDIX E

THE PLOTS SHOW THE VARIATIONS OF REMOVAL EFFICIENCIES WITH P-TERPHENYL AT DIFFERENT CONDITIONS FOR PROCESS 2 WITHOUT SURFACTANT

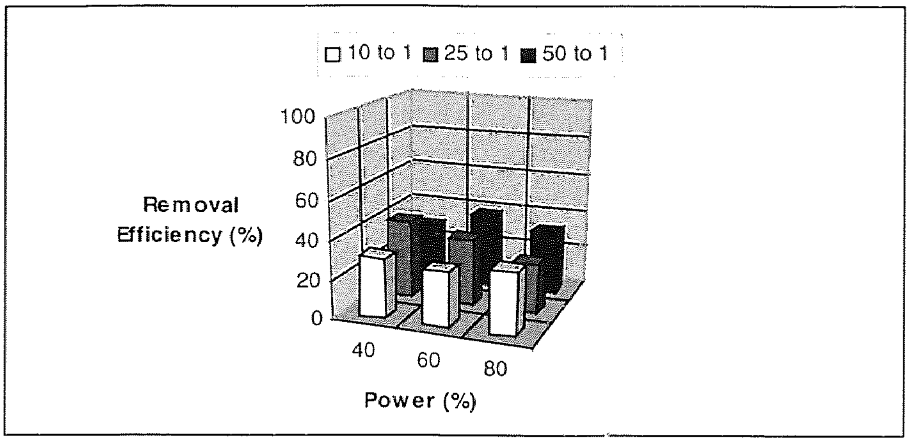


Figure E.1 Process 2 without Surfactant, Removal Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 30 min. Sonication Time

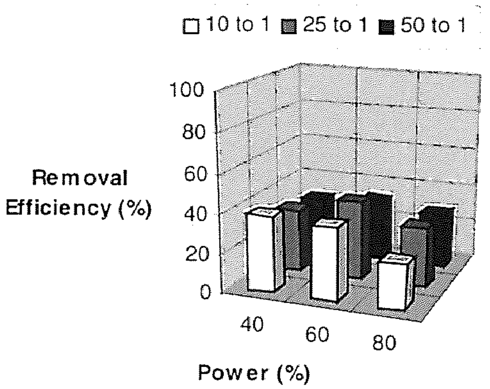


Figure E.2 Process 2 without Surfactant, Removal Efficiency of p-Terphynyl for Different Power and Solvent to Sediment Ratio, at 45 min. Sonication Time

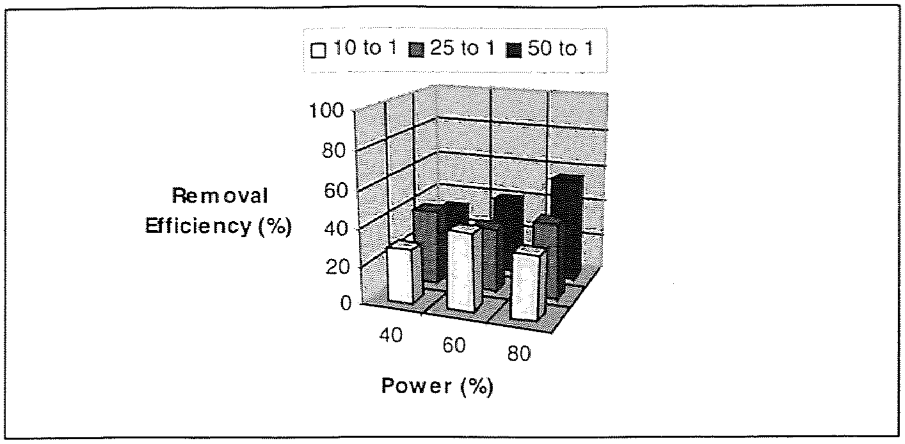


Figure E.3 Process 2 without Surfactant, Removal Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 60 min. Sonication Time

APPENDIX F

THE PLOTS SHOW THE VARIATIONS OF REMOVAL EFFICIENCIES WITH P-TERPHENYL AT DIFFERENT CONDITIONS FOR PROCESS 2 WITH SURFACTANT

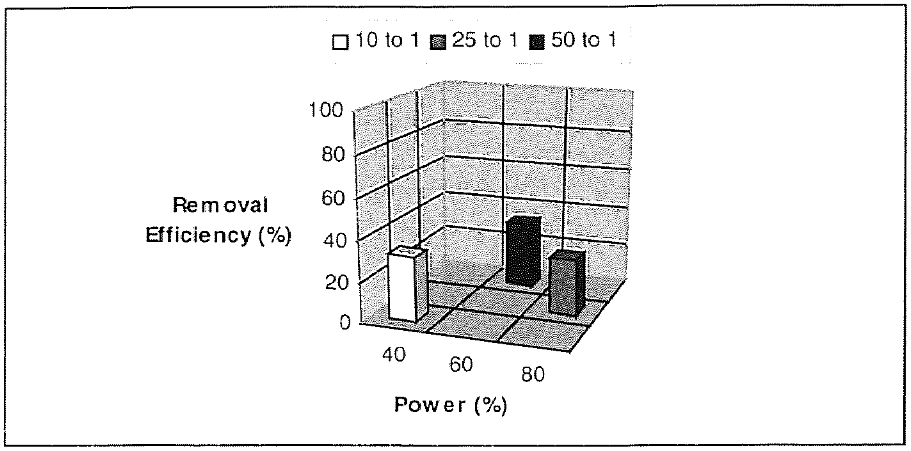


Figure F.1 Process 2 with Surfactant, Removal Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 0.001% Surfactant and 30 min. Sonication Time

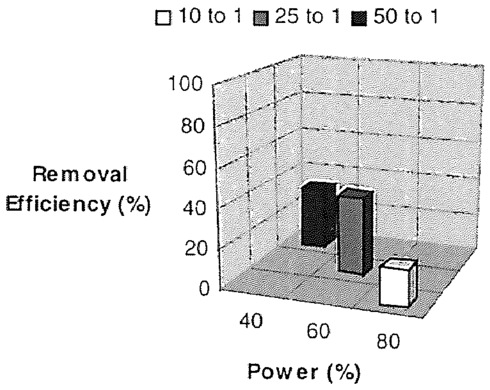


Figure F.2 Process 2 with Surfactant, Removal Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 0.001% Surfactant and 45 min. Sonication Time

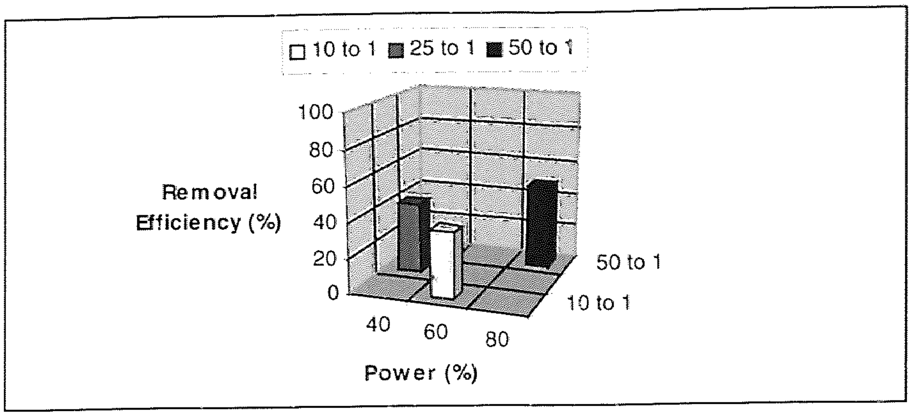


Figure F.3 Process 2 with Surfactant, Removal Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 0.001% Surfactant and 60 min. Sonication Time

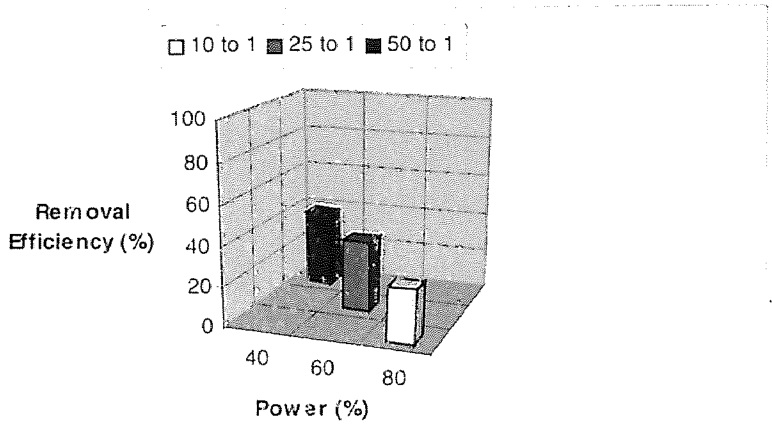


Figure F.4 Process 2 with Surfactant, Removal Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 0.01% Surfactant and 30 min. Sonication Time

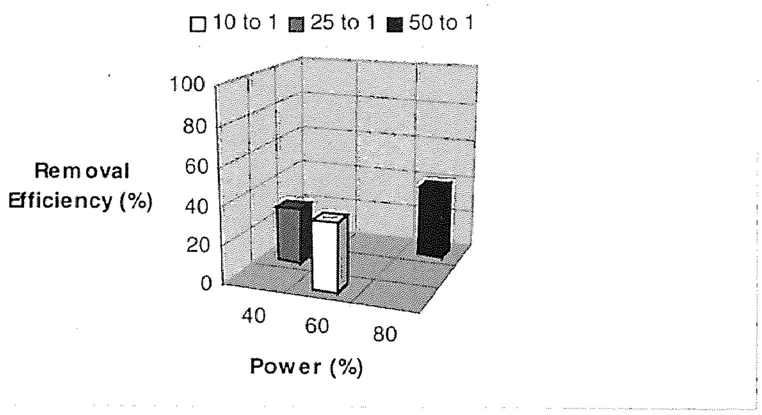


Figure F.5 Process 2 with Surfactant, Removal Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 0.01% Surfactant and 45 min. Sonication Time

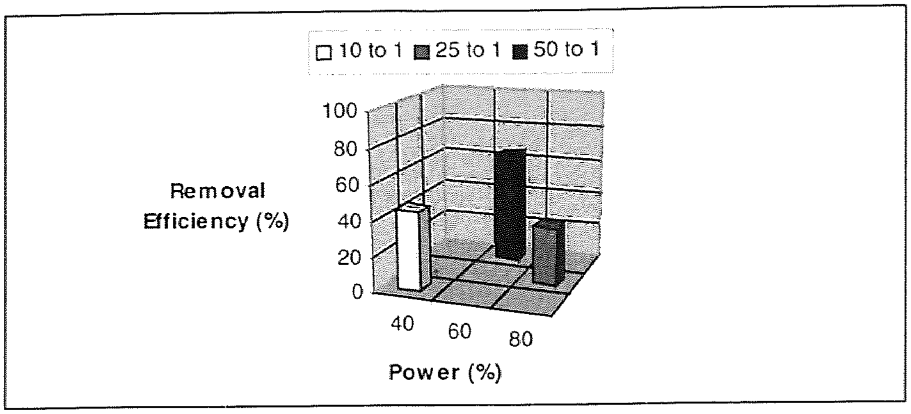


Figure F.6 Process 2 with Surfactant, Removal Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 0.01% Surfactant and 60 min. Sonication Time

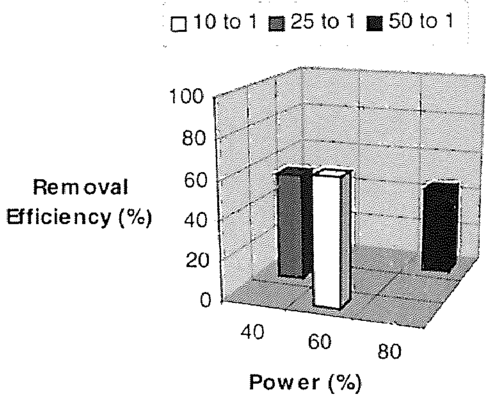


Figure F.7 Process 2 with Surfactant, Removal Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 0.1% Surfactant and 30 min. Sonication Time

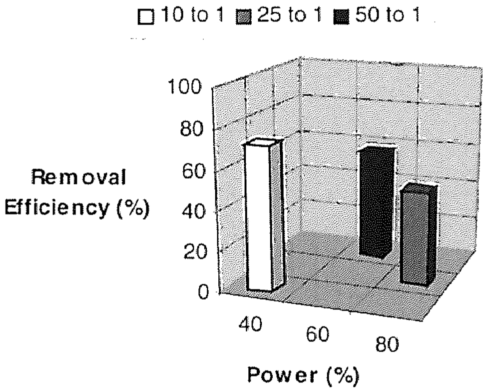


Figure F.8 Process 2 with Surfactant, Removal Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 0.1% Surfactant and 45 min. Sonication Time

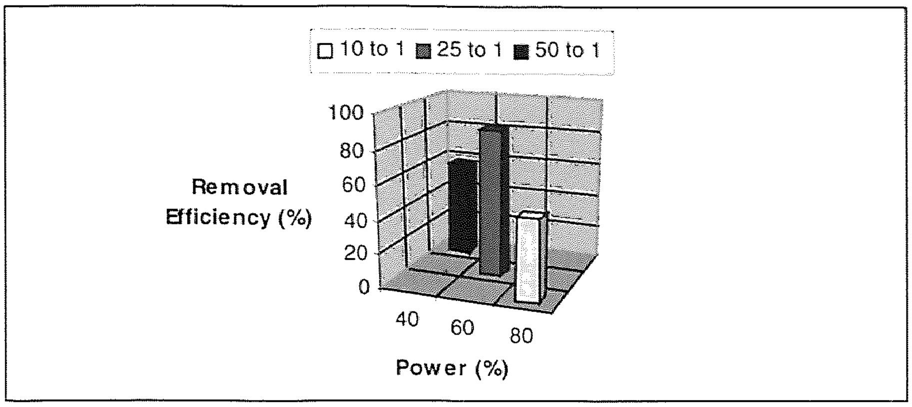


Figure F.9 Process 2 with Surfactant, Removal Efficiency of p-Terphenyl for Different Power and Solvent to Sediment Ratio, at 0.1% Surfactant and 60 min. Sonication Time

APPENDIX G

MAXIMUM RESPONSE FOR THE OVERALL MODEL

Table G.1 Estimate Ridge of Maximum Response for the Overall Model of Process 1 with Four Process Factors

Coded Radius	Estimate Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Pressure (psi)	Time (min)
0	0.7269	0.0513	60.00	10.00	10.00	6.00
0.1	0.7471	0.0511	60.56	10.23	10.19	6.23
0.2	0.7658	0.0508	61.16	10.47	10.44	6.43
0.3	0.7833	0.0501	61.76	10.71	10.76	6.59
0.4	0.8002	0.0493	62.34	10.94	11.14	6.73
0.5	0.8168	0.0484	62.84	11.18	11.56	6.83
0.6	0.8334	0.0473	63.25	11.41	12.00	6.92
0.7	0.8501	0.0463	63.51	11.64	12.47	6.99
0.8	0.8672	0.0455	63.59	11.87	12.94	7.05
0.9	0.8848	0.0452	63.43	12.10	13.42	7.10
1.0	0.9029	0.0456	62.97	12.33	13.91	7.15
1.1	0.9217	0.0469	62.16	12.57	14.39	7.21
1.2	0.9412	0.0493	60.98	12.81	14.87	7.26
1.3	0.9616	0.0527	59.47	13.04	15.32	7.31
1.4	0.9830	0.0569	57.70	13.26	15.74	7.36
1.5	1.0055	0.0620	55.77	13.47	16.13	7.41
1.6	1.0291	0.0676	53.73	13.66	16.50	7.46

Table G.2 Estimate Ridge of Maximum Response for the Overall Model of Process 2 without the Surfactant and Three Process Factors

Coded Radius	Estimate Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values		
			Power (%)	Solvent to Soil Ratio	Time (min)
0	0.3531	0.0300	60.00	30.00	45.00
0.1	0.3570	0.0300	60.02	30.49	46.45
0.2	0.3616	0.0298	60.26	30.88	47.92
0.3	0.3672	0.0294	60.60	31.23	49.38
0.4	0.3736	0.0290	60.98	31.56	50.84
0.5	0.3810	0.0285	61.38	31.88	52.29
0.6	0.3893	0.0281	61.80	32.20	53.74
0.7	0.3984	0.0279	62.23	32.50	55.19
0.8	0.4085	0.0279	62.66	32.81	56.64
0.9	0.4195	0.0284	63.10	33.11	58.09
1.0	0.4314	0.0294	63.54	33.42	59.54
1.1	0.4442	0.0310	63.98	33.72	60.99
1.2	0.4580	0.0334	64.43	34.02	62.43
1.3	0.4726	0.0365	64.88	34.32	63.88
1.4	0.4882	0.0404	65.33	34.62	65.32
1.5	0.5046	0.0450	65.78	34.92	66.77
1.6	0.5220	0.0502	66.23	35.21	68.21
1.7	0.5403	0.0560	66.69	35.51	69.66
1.8	0.5595	0.0624	67.14	35.81	71.10
1.9	0.5796	0.0693	67.59	36.11	72.55
2.0	0.6006	0.0768	68.05	36.40	73.99
2.1	0.6226	0.0848	68.50	36.70	75.44
2.2	0.6454	0.0932	68.96	37.00	76.88
2.3	0.6692	0.1022	69.41	37.29	78.32
2.4	0.6939	0.1116	69.87	37.59	79.77
2.5	0.7195	0.1214	70.33	37.89	81.21
2.6	0.7460	0.1317	70.78	38.18	82.66
2.7	0.7734	0.1425	71.24	38.48	84.10
2.8	0.8017	0.1536	71.70	38.78	85.54
2.9	0.8310	0.1653	72.15	39.07	86.99
3.0	0.8611	0.1773	72.61	39.37	88.43
3.1	0.8922	0.1898	73.07	39.66	89.87
3.2	0.9242	0.2027	73.52	39.96	91.32
3.3	0.9571	0.2160	73.98	40.25	92.76
3.4	0.9909	0.2297	74.44	40.55	94.20
3.5	1.0256	0.2439	74.90	40.85	95.65
3.6	1.0612	0.2585	75.36	41.14	97.09

Table G.3 Estimate Ridge of Maximum Response for the Overall Model of Process 2 with the Surfactant and Four Process Factors

Coded Radius	Estimate Response (Removal efficiency) (%)	Standard Error	Uncoded Factor Values			
			Power (%)	Solvent to Soil Ratio	Surfactant (%)	Time (min)
0	0.6132	0.0984	60.00	30.00	0.051	45.00
0.1	0.6276	0.0984	59.50	29.93	0.054	45.85
0.2	0.6413	0.0973	59.05	29.76	0.058	46.93
0.3	0.6549	0.0958	58.66	29.55	0.060	48.19
0.4	0.6685	0.0941	58.32	29.37	0.062	49.58
0.5	0.6826	0.0924	58.04	29.23	0.064	51.05
0.6	0.6973	0.0908	57.80	29.15	0.066	52.55
0.7	0.7126	0.0893	57.60	29.12	0.067	54.08
0.8	0.7287	0.0880	57.42	29.14	0.068	55.61
0.9	0.7457	0.0871	57.27	29.21	0.069	57.16
1.0	0.7635	0.0866	57.13	29.30	0.069	58.70
1.1	0.7821	0.0866	57.01	29.43	0.070	60.24
1.2	0.8017	0.0872	56.90	29.58	0.071	61.78
1.3	0.8222	0.0887	56.80	29.76	0.071	63.32
1.4	0.8437	0.0910	56.71	29.95	0.072	64.85
1.5	0.8660	0.0942	56.62	30.16	0.072	66.39
1.6	0.8894	0.0985	56.55	30.38	0.072	67.91
1.7	0.9137	0.1038	56.47	30.62	0.073	69.44
1.8	0.9389	0.1101	56.41	30.86	0.073	70.96
1.9	0.9652	0.1176	56.34	31.12	0.074	72.48
2.0	0.9924	0.1260	56.28	31.38	0.074	74.00
2.1	1.0205	0.1354	56.23	31.65	0.074	75.51
2.2	1.0497	0.1458	56.17	31.93	0.075	77.03

APPENDIX H

FITTING PARAMETERS FOR THE OVERALL MODEL USING FULL AND PARTIAL REGRESSION

Table H.1 Comparing the fitting Parameters for the Overall Model Using Full Quadratic Regression for Process 1

Parameter	Components	Process 1
β_0	Intercept	-0.529480
β_1	Power	-0.004442
β_2	Ratio	0.074990
β_3	Press	-0.042719
β_4	Time	0.271889
β_5	Power*Power	0.000143
β_6	Ratio*Power	-0.000369
β_7	Ratio*Ratio	-0.003287
β_8	Press*Power	-0.000146
β_9	Press*Ratio	0.004177
β_{10}	Press*Press	0.000589
β_{11}	Time*Power	-0.000776
β_{12}	Time*Ratio	-0.001615
β_{13}	Time*Press	0.001794
β_{14}	Time*Time	-0.014284

Table H.2 Comparing the fitting Parameters for the Overall Model Using Full Triple Regression for Process 2 without the Surfactant

Parameter	Components	Process 2 w/o surfactant
β_0	Intercept	0.754767
β_1	Power	0.002652
β_2	Ratio	-0.002313
β_3	Time	-0.022142
β_4	Power*Power	-0.000083
β_5	Ratio*Power	0.000070
β_6	Ratio*Ratio	-0.000060
β_7	Time*Power	0.000111
β_8	Time*Ratio	0.000049
β_9	Time*Time	0.000180

Table H.3 Comparing the Fitting Parameters for the Overall Model Using Full Quadratic Regression for Process 2 with the Surfactant

Parameter	Components	Process 2 w/ surfactant
β_0	Intercept	-0.039778
β_1	Power	0.026512
β_2	Ratio	-0.006947
β_3	Surfact	7.837032
β_4	Time	-0.015535
β_5	Power*Power	-0.000252
β_6	Ratio*Power	0.000139
β_7	Ratio*Ratio	-0.000038
β_8	Surfact*Power	-0.009072
β_9	Surfact*Ratio	-0.061563
β_{10}	Surfact*Surfact	-41.497692
β_{11}	Time*Power	-0.000043
β_{12}	Time*Ratio	0.000089
β_{13}	Time*Surfact	0.027834
β_{14}	Time*Time	0.000209

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