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ABSTRACT

ENHANCING THE BIOAVAILABILITY OF SORBED POLLUTANTS FROM SEDIMENTS USING ULTRASOUND

by
Rachel Mathew

Many organic compounds, that enter aquatic systems have a strong tendency to sorb onto particulate matter which may be present in suspension or as sediment. Numerous studies have shown that the sediment in aquatic systems concentrate contaminants several orders of magnitude greater than the concentration in the aqueous phase. Particulate associated contaminants in sediments are not easily bioavailable. Hence the efficacy of any treatment technology would be strongly undermined if the contaminants are not made available for microbial utilization. Sediment associated contaminants can be made biologically available to various microorganisms under certain conditions.

In this study, desorption studies were conducted by sonicating contaminated sediment obtained from Newton Creek in New York. After the sediment was characterized, experiments were conducted at various sonication energies and durations. Results indicate that sonication of the sediment suspensions significantly enhanced the release of organic matter into the soluble phase. Since microorganisms utilize organic matter only in the soluble phase, the rate and extent of biodegradation of organic matter can be consequently improved.

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**ENHANCING THE BIOAVAILABILITY OF SORBED POLLUTANTS
FROM SEDIMENTS USING ULTRASOUND**

by
Rachel Mathew

**A Thesis
Submitted to the Faculty of
New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
Master of Science in Environmental Engineering**

Department of Civil and Environmental Engineering

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APPROVAL PAGE

**ENHANCING THE BIOAVAILABILITY OF SORBED POLLUTANTS FROM
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This thesis is dedicated to
my family and friends.

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CHAPTER 1

INTRODUCTION

The toxicity and persistence of organic pollutants in aquatic sediments are dependent on the partitioning of the pollutant. A potential pollutant in an aquatic environment will partition itself among the water, sediment, atmosphere, and other biota that exist in the environment. If the pollutant sorbs onto the sediment or remains dissolved or dispersed in the water it persists in the aquatic environment and poses a potential risk to aquatic life. However, if it volatilizes from water, aquatic life will only be threatened by the portion that sorbed onto a sediment particle or dissolved in the water.

When considering the remediation of contaminated sediment, the contaminant should be available in the aqueous phase. One of the remediation alternatives considered for organic chemicals is bioremediation. To ensure effective bioremediation, the sorbed contaminants must be bioavailable to the microorganisms for biological breakdown of these contaminants. In other words, any biodegradable contaminant associated with the particulate phase has to be released into the soluble phase by desorption before it can be degraded by microorganisms (Mukherjee, 1992, Mukherjee et al., 1992).

Past research has shown that various characteristics of the contaminant and sediment, and the duration of contact of the contaminant with the sediment affect the bioavailability of the contaminant (Landrum et al., 1992, Harkey et al., 1994). Most work that assess the bioavailability of sediment associated contaminants, evaluates the toxicity of the contaminant (Harkey et al., 1994, Landrum et al., 1992, Liu et al., 1996, Segstro et al., 1995, Suedel et al., 1993, Swartz et al., 1990). These toxicity tests have been shown to be influenced by the bioavailability of the sediment associated with contaminants.

CHAPTER 2

RESEARCH OBJECTIVES

It is known that contaminants bound to sediment and associated with the particulate phase are not readily available for microbial degradation. Only when the contaminant is released from the particulate phase into the soluble phase through various metabolic pathways can it be utilized by microorganisms.

The objective of this research study was to evaluate the effect of sonication when used as a pretreatment process on the release of organic matter into the soluble phase. Considering that most organic contaminants bind preferentially to the organic matter in natural sediments, releasing the bound organic matter would result in a subsequent release of other sediment associated contaminants from the particulate phase. This achieves the goal of enhancing contaminant availability. To determine the influence of different experimental conditions the following tasks were performed:

- Studying the effect of sonication time on the release of organic matter. This study was conducted at a constant temperature of $10^{\circ}\text{C} \pm 5^{\circ}\text{C}$, and at an energy output of 750W and a frequency of 20 kHz..
- Studying the effect of sonication energy on the release of organic matter. This study was conducted at constant temperature and for a period of 60 seconds.

CHAPTER 3

BACKGROUND AND LITERATURE REVIEW

Assessing the persistence and compartmentalization of potentially toxic chemicals released into aquatic systems requires consideration of their interactions with sediments. Some chemicals sorb onto both suspended and settled sediments. To quantify the distribution of organic pollutants between the aqueous and particulate phases of aquatic systems, partition coefficients are used. In aquatic systems, partitioning between water and sediment or suspended solid particles is crucial because it influences the further transfer of the compound to the biota and ultimately to humans.

3.1 Partitioning

The partitioning of a chemical between water and a sediment can be depicted as

$$K_p = \frac{C_s}{C_w} \quad (3.1.1)$$

where K_p = sediment/ water partition coefficient (L/ kg)

C_s = amount of chemical sorbed per unit mass of sediment (mg/ kg)

C_w = amount of chemical in aqueous phase per unit mass of solution (mg/ L)

Only a fraction of the sorbed chemical will partition onto aquatic organisms. This fraction depends on the rate of desorption of the chemical and the duration of exposure. (Podoll et al., 1984).

3.1.1 Factors Influencing Partitioning

There are various parameters that affect partitioning and an overview of some of the key factors are detailed below. Most of the findings are derived from information collected by Versar (1984) in a study of selected contaminants at a Superfund site.

- *pH*

The adsorption of acidic compounds such as phenol and basic compounds such as amines onto sediment may be significantly affected by pH. Some organic acids bind strongly with clays particularly when the pH of the water is about 1 unit above the pK_a value of the acid (Lyman et al., 1982). However highly hydrophobic neutral organics are less affected by pH. Highly lipophilic molecules like PCBs, PAHs and aldrin are not expected to be affected by pH, since they have little tendency to ionize (Versar, 1984).

- *Temperature*

Ambient temperature affects the solubility of certain organic compounds, and therefore their adsorption to sediments. The effect of temperature on adsorption varies with the compound under consideration. Studies conducted by Lyman et al. (1982) indicate an 18 percent increase in adsorption coefficient with a temperature drop from 20°C to 5°C.

May (1980) developed quadratic equations that showed the relationship between temperature and solubility for a set of 12 PAHs. The solubility data at typical water temperatures indicated that decreased solubility at lower temperatures results in an increased affinity of compounds for the solid organic phase. Little information was available on the effect of temperature on solubility and partitioning behavior of PCBs.

- *Dissolved organic matter*

The concentration of organic matter dissolved in water affects the equilibrium partitioning of organic contaminants between sediments and water. A higher concentration of dissolved organic matter favors a greater equilibrium concentration of contaminant in the aqueous phase through two mechanisms: first through the increased solubility of organic contaminants in water of high dissolved organic material concentration, and then through the increased competition for sediment adsorption sites among the organic material present (Hassett et al., 1980). Experiments conducted by them show that the removal of dissolved organic matter from water samples had no effect on the solubility of aromatic hydrocarbons; however the solubilities of aliphatic hydrocarbons were significantly

affected. Their work concluded that the presence of dissolved organic matter has no effect on the partitioning behavior or solubilities of PAHs.

- *Sediment particle size*

This is a secondary factor in sediment/water partitioning because it characterizes the sediment in terms of its composition and the amount of surface area available for sorption. Variations in size fractions of sediments at a site may result in a difference in adsorption of organic compounds. The adsorption coefficient has been shown to increase by a factor of 10 with a 100 μm decrease in sediment particle size (Pavlou et al., 1979). The total surface of the sediments considerably affects the amount of contaminant being adsorbed. The variation in adsorption coefficients for pesticides on coarse and fine sediments was shown in experiments done by Karickhoff et al. (1979).

- *Dissolved inorganic compounds*

In most cases, dissolved inorganic compounds are not expected to affect sorption or partitioning of hydrophobic organic compounds onto sediment. An exception is the reduction of DDT sorption in the presence of metals because the presence of Fe II in soil of high organic content can facilitate reduction of DDT to DDE. However these reactions in sediments are not easy to quantify, because they occur only under anaerobic conditions and depend on the concentrations of metals or the reducing agents in water or sediment.

- *Redox potential (Eh)*

The redox potential, which is a measure of the oxidative state of a system, is more significant in affecting inorganics than it is for hydrophobic organics. The partitioning of PAHs and PCBs between sediment and water are not affected by Eh, although the DDT family shows an effect whose magnitude is difficult to quantify (Versar, 1984).

Summarizing the above discussion and information from literature, the unnormalized partition coefficient (K_d) may be expressed as a function of sediment organic carbon (OC), salinity (S), temperature (T), dissolved organic matter (D), sediment

particle size (P), and suspended particle matter (M) for most hydrophobic organic compounds. A form of this relationship is:

$$K_d = aOC + bS + cT^n + eD + fP^x + gM \quad (3.2.1.1)$$

where a, b, c, e, f, g, n, and x are compound specific proportionality constants. This expression is theoretical and will require modification as additional information is obtained.

3.2 Bioavailability

If a chemical is bioavailable, then it should elicit some response from an organism. The response is a function of duration of exposure and concentration of substrate. The Sixth Pellston Workshop committee defines bioavailable toxicant as the total concentration of toxicant released from a sediment to which aquatic organisms are exposed. When the degree of bioavailability results in a measurable biological response (e.g., mortality, bioconcentration) it is termed as the “bioavailable effect level” (Anderson et al., 1981).

Adams (1984) summarized the bioavailability of lipophilic organic chemicals is as it relates to three areas: (1) impact of organic carbon, (2) route of exposure, and (3) feeding habits of freshwater benthic invertebrates.

3.2.1 Bioavailability as a Function of Organic Carbon

The presence of organic carbon in sediments is the most important factor controlling the bioavailability of lipophilic organic chemicals. The use of organic carbon (OC) to predict the soil adsorption has become prevalent. Organic carbon is used to normalize the differences observed in soil partition coefficients (K_p) for a given chemical with different soils or soil fractions.

This relationship can be expressed as:

$$K_p = K_{oc} * F_{oc} \quad (3.1.1.1)$$

where K_p = the soil/ water partition coefficient (L/ mg)

K_{OC} = the organic carbon normalized

F_{OC} = fraction of organic carbon = % OC / 100

Various researchers have investigated into this relationship (Karickhoff et al., 1979, Hassett et al., 1980, Chiou et al., 1983, and Urano et al., 1984), and it has also been shown to be applicable to chemicals other than neutral organics. This equation can also be used to assess the bioavailability of chemicals in surface waters and sediment interstitial waters. In other words the bound and non-bound concentration of a chemical in water as a function of suspended particles can be assessed using the water solubility and the K_{OC} for the chemical. According to Adams (1984), for waters with a suspended solids of 250 mg/l and 4% OC, a chemical with a water solubility of 0.062 mg/l ($K_{OC} = 72,000$) is approximately 50% non-bound or available for uptake. As the concentration of suspended solids and OC change the amount of non-bound chemical also changes.

However, it is apparent that high values of K_{OC} are required to decrease the bioavailability of a chemical since most lakes and streams have a suspended solids level of around 250 mg/l and the OC level of these solids are usually less than 4 %. Sources of OC other than sediments and suspended solids in the water column can affect the bioavailability of the chemical and one such source is soluble organic carbon which occurs both in the water column and in the interstitial water.

3.2.2 Summary of Bioavailability Factors

- Organic carbon is the major factor controlling bioavailability of organic chemicals sorbed to sediments.
- Both DOC and TOC affect bioavailability. However particulate or TOC is the dominant factor for the water column, whereas DOC is important for interstitial water.
- Interstitial water seems to be the principal source of exposure for benthic organisms.
- Chemical concentrations of neutral organics in aquatic organisms and sediments can be normalized by the use of organic carbon.

CHAPTER 4

SONICATION AS A PRETREATMENT STEP

Studies of the nature and behavior of soil and organo-mineral complexes present in it, demand methods for dispersion of the soil particles without use of oxidants, acids and other chemicals, and minimize the degradation of primary particles as far as possible. The use of ultrasonic energy as a method towards physically dispersing soils and characterizing the nature and distribution of organic matter has been studied (Christensen, 1986, Christensen and Sorensen, 1985, Anderson et al., 1981). However, no standard method is in use, as yet (Christensen, 1985).

Factors which could affect the efficiency of dispersion include power output, treatment period, soil to water ratio, and specifications of the ultrasonic equipment (Edwards et al., 1967a; North, 1976). Once these factors are considered, the difference in studies which use ultrasonic energy would be the energy dissipated per ml of the soil suspension (Christensen et al., 1985). From all these studies, it is obvious that sonication is a viable technique to be used in the dispersion of soils. However, a question that arises with this is to decide on the duration of sonication. Results have shown that it depends upon the type of soil, and the time of sonication should not be extended much beyond the time required to achieve complete dispersion, so as to minimize degradation of primary particles (Edwards et al., 1967a). Edwards and Bremner have also shown that prolonged sonication leads to the degradation of primary particles. Gravel and sand size particles were reduced to clay size material.

Advantages of using this method include:

- simplicity of operation.
- speed of operation
- elimination of the use of chemicals and the consequent correction of results obtained
- no tendency of forming flocculated suspensions

- no need to remove organic matter or other aggregating agents and no dissolution of soil particles. Hence particle size analysis after dispersion is practically quantitative.

A study conducted by Liu et al., (1996), shows that sonication enhances the release of toxicants from sediment. In their study, the use of a surfactant (sodium ligninsulfonate) along with sonication enhanced the release of toxicants.

4.1 Ultrasonic Waves

A vibrating wave with a frequency above that of the upper frequency limit of the human ear is described as ultrasonic. Generally all frequencies above 16 k c/s are termed ultrasonic.

The wavelength usually determines the application for which ultrasonic power can be used, while the frequency required to produce a certain wavelength and the medium of propagation will decide the type of generator to be used.

The transmission of sound is dependent on particle vibration, each particle of the medium being displaced successively as the wave travels through the medium. Any material possessing elasticity can support the propagation of an acoustic wave, the elasticity providing a restoring force that tends to return each element of the material to its starting point. Because the wave takes a finite time to pass through a medium, there is a difference in phase between the orbital movements of particles at any two points (Crawford, 1955).

With the passage of an intense sound wave through a liquid, the phenomena most commonly associated with it is the production of cavitation. Early work (Willard, 1953) on the effects of ultrasonics in liquids concluded that the intensity of the propagated sound wave must reach a value where cavitation occurs and is responsible for the physical change produced.

4.2 Cavitation

The formation of cavities in a liquid and its subsequent collapse followed by intense hydraulic shocks is called cavitation. These cavities occur mainly due to excessive flow rates of the liquid past obstacles or through constrictions.

There are two kinds of cavitation bubbles. The first kind is a bubble containing gas previously dissolved in the liquid, like air, and forming a bubble of visible size, and the second is a bubble of much smaller sizes containing the vapor of the liquid in which cavitation is occurring.

Willard (1953) has conducted an exhaustive analysis of the conditions required for the production of cavitation, and the growth and decay of the bubble. Using a high intensity mercury arc lamp for illumination, with a lens and mirror system, the cavitation bursts were photographed. With this equipment, experimental results indicate that the full development of cavitation by ultrasonic energy is a step by step process, with each step dependent on the previous phase for its development. The liquid conditions and the three cavitation phases are designated as the pre-initiation condition of the liquid, the initiation phase of cavitation, the catastrophic phase of cavitation, the bubble phase of cavitation, and the post-cavitation phase of the liquid. The initiation and catastrophic phases are fundamental and can be produced in either degassed or aerated water, while the bubble phase can be produced only in aerated water. The three phases of cavitation are produced in an interval of a few milliseconds.

Willard (1953) has proposed that the mechanism are as follows.

- The pre-initiation condition requires the presence of weak spots in water. These are carried by the water streaming into the high intensity area of the sound field. The strength of the weak spots must be less than that of the homogenous water, since it has been shown that sonically available forces required to rupture water are far below the threshold level required theoretically. (Harvey et al., 1944)

- The initiation phase begins when a nucleus of low enough strength enters the high intensity area. The nuclei, which is composed of stabilized gas filled cavities in the liquid, can be expanded and contracted by the cyclic tension and compression in the surrounding water. As the nucleus moves toward the highest sonic concentration its volume oscillates with the frequency of the sound wave and gradually but continually grows larger. When the cavity reaches its resonant size the catastrophic phase will begin. However, if the water turbulence removes the cavity from the high intensity area it will collapse and no further effect is produced. The initiation phase is similar in aerated and degassed water.
- At the resonant size, when the catastrophic phase begins, the amplitude of vibration suddenly increases but stills varies at the sonic frequency. The small gas content prevents collapse in the case of a vapor filled cavity but the violent periodic vibration now radiates high amplitude shock waves. These shock waves along with the existing sonic waves open up lots of microcavities in the liquid surrounding them locally. These cavities are so minute as to be individually indistinguishable but are numerous and very dense. During this phase, the violently vibrating cavity streams continuously generate new microcavities. This phenomena continues for several milliseconds until the cavity passes out of the core. In degassed water, with the cessation of microcavities nothing further is visible, while in aerated water, the bubble phase occurs simultaneously with the catastrophic phase.
- The bubble phase is not necessary for the development of the other two phases, and relatively few bubbles are generated during a single cavitation burst .
- A post cavitation condition is experienced with aerated water where non-collapsing gas bubbles are present. These bubbles are then swept by the sonically induced liquid circulation.

4.2.1 Cavitation Erosion

The destructive action of smaller bubbles on solid surfaces immersed in an intense sound beam is very apparent. The erosion of surfaces by cavitation is considered to be caused by the forcing of the liquid under pressure into the pores of the material and its subsequent escape carrying small particles with it (Poulter, 1947). Assuming this theory of liquid penetration, the high pressure immediately surrounding the point at which cavities have collapsed forces the liquid into the pores of the solid. Then, during the low pressure part of the cycle, a liquid tension develops and the solid surrounding the pore is subjected to simultaneous pressure from within and on the outer surface. Under these conditions, small fragments of the solid can be expected to be forced off the surface and when done repetitiously, causes the erosion effect.

Lord Rayleigh (1917) calculated the velocity of contraction of a cavitation bubble:

$$v = \left(\frac{2}{3} \frac{P_o}{\rho} \left[\left(\frac{r_o}{r} \right)^3 - 1 \right] \right)^{0.5} \quad (4.2.1.1)$$

where P_o = hydrostatic pressure ($\text{kg m}^{-2} \text{s}^{-1}$)

ρ = density of the bubble (kg m^{-3})

r_o = initial radius of the bubble (m)

r = radius of the bubble at the particular instant (m)

CHAPTER 5

MATERIALS AND METHODS

Sediment samples obtained from Newton Creek, New York were stored in a plastic bag placed in a airtight PVC container at 4°C until characterization work began. To prevent drying of the sample with repeated exposure to the atmosphere, a small quantity of the sediment sample was placed in several small containers.

5.1 Sediment Characterization

The sample emanated a strong smell which was very petroleum like, and had a black, tar-like appearance. Characterization studies conducted include the measurement of Total Solids, Total Volatile Solids, Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), particle size, pH and color. All studies were conducted in accordance with procedures described in the Standard Methods (1989) using reagent grade chemicals.

5.1.1 Total Organic Carbon

The Total Organic Carbon (TOC) was estimated using a CHNS/O analyzer (Perkin Elmer, Model 2400, CT, USA). The analysis was performed when the combustion and reduction furnaces had attained temperatures of 925°C and 640°C respectively. The system was then purged with helium and oxygen gases. Before an actual sample run was made, blank runs which determine the C, H, and N signals and conditioner runs which equilibrate the analyzer's internal system with carbon dioxide, water vapor and nitrogen were conducted. When reproducibility of values were obtained, the samples were analyzed. Acetanilide was used as a conditioner to check the instrument's response.

5.1.2 Particle Size Analysis

The particle size of the sediment samples were measured using a Particle Size Analyzer (Malvern Instruments, Mastersizer X, UK) which was equipped with an automatic liquid sampler. The operation of this instrument involved aligning the lenses, measuring the background to account for electronic noise, and then adding the sediment suspension until a suitable obscuration value was obtained.

5.1.3 Chemical Oxygen Demand

The Chemical Oxygen Demand (COD) was determined using the Closed Reflux, Colorimetric Method described in the Standard Methods (1989). A HP 8453 UV-Visible Spectrophotometer was used to measure the absorbance of the samples at 600 nm and glucose standards were used for calibration. The COD of the supernatant obtained after centrifuging using a high speed centrifuge (Sorvall Instruments, Model RC – 28S, DE, USA) at 2000g for 30 minutes, was used as the soluble COD.

5.1.4 Total Solids and Total Volatile Solids

A clean evaporating dish was ignited at 550 °C for 1 hour in a muffle furnace. It was then cooled in a desiccator and weighed before use. 5 g of the sediment was weighed into the dish and placed in an oven at 103 °C - 105 °C for at least 1 hour. The dish was cooled in a desiccator and then weighed. The process was repeated until a constant weight was obtained.

The calculation is shown below

$$\text{mg of Total Solids/ g} = (A - B) / C \quad (5.1.4.1)$$

where A = weight of dried residue + dish, mg and

B = weight of dish, mg.

C = weight of sample used, g

The residue from above was ignited at 550 ° C for 20 minutes in a muffle furnace until constant weight was attained. The dish was then cooled in a desiccator and weighed. The process was repeated until a constant weight was attained.

The calculation is shown below.

$$\text{mg Volatile Solids/ g} = (A - B) / C \quad (5.1.4.2)$$

where A = weight of residue + dish before ignition, mg

B = weight of residue + dish after ignition, mg

C = weight of sample used, g

Based on the Total Volatile Solids concentration, a 0.25 % T V S sediment suspension was prepared. This was used to conduct all the required characterization work outlined above.

5.2 Procedure to Determine Soluble COD

In this study the organic carbon concentration of the sediment suspensions was the parameter whose change, if there was any, would be measured. The procedure involved measuring the soluble COD before and after sonication at various sonication energies and duration of contact. The particulate phase was separated from the soluble phase by centrifuging at a Relative Centrifugal Force (RCF) of 2000 g for 30 minutes. Previous work done (Smith et al., 1990, Pignatello, 1989) and actual experimentation helped in selecting a suitable RCF value and duration that would yield a relatively clear supernatant.

A 0.25 % TVS sediment suspension was prepared in a large glass bottle, by adding 25 grams of the sediment per liter of deionized water. This concentration was chosen by a trial and error procedure, and was selected since higher concentrations could not be measured for COD using a UV-Visible Spectrophotometer and lower concentrations did not yield consistent results. A magnetic stir bar was used to stir the suspension and keep the sediment particles from settling. At the beginning of the sonication experiments, 50 ml batches of the well mixed sediment suspension were poured into 100 ml beakers and

sonicated as described below. Previous experimentation showed that there was no significant release of organic matter after 120 seconds, and hence in this study, sonication was carried out in 30 second intervals within a 120 second time limit. The sample was cooled after sonication each time. After sonication the samples were thoroughly mixed, and the increased dispersion was visible to the naked eye.

25 ml of each sample was carefully poured into 50 ml disposable centrifuge tubes. Centrifugation of the samples were carried out in duplicates. The tubes were placed in the rotor symmetrically so as to keep it balanced, and the centrifuge was allowed to cool to 5°C once again to mimic sediment bed temperatures, before centrifugation was started. After centrifuging at a RCF of 2000 g for 30 minutes, the tubes were taken out and the supernatant was carefully poured out into clean glass conical flasks. The COD test was carried out immediately in duplicate and using blanks.

5.2.1 Sonication

Sonication experiments were conducted using a sonicator (Ultrasonic Processor, Model VC-1500). For optimum performance the sonicator was tuned at 50 % power output before the start of each experiment as per the manufacturer's instructions. Sonication experiments were conducted in a 100 ml beaker immersed in a larger cylindrical glass vessel containing ice, to maintain isothermal conditions around 10°C. This temperature was used to mimic best the sediment bed temperature.

To assess the influence of sonication time and output energy on the release of organic matter into the aqueous phase, 50 ml suspensions of the sediment at a fixed solids concentration of 25 g/l (0.25 % T V S), were sonicated for durations of 30, 60, 90 and 120 seconds at 30%, 40%, 50%, 60%, 70%, and 80% of the maximum output energy of 1500 W.

5.2.2 Centrifugation

After sonication, these suspensions were centrifuged at a Relative Centrifugal Force (RCF) of 2000g for 30 minutes to separate the particulate phase from the soluble phase. A high speed, refrigerated centrifuge was used (Sorvall Instruments, Model RC - 28S DE, USA). The supernatant was analyzed for soluble COD.

5.2.3 Quantification

To quantify the effect of the experimental variables selected, namely the sonication energy and time, on the efficacy of sonication in releasing organic matter, the change in concentration of the organic matter present in the aqueous phase, before and after sonication was used to calculate yields. The soluble phase referred to the supernatant obtained after centrifugation while the settled sediment particles represented the particulate phase. The concentration of organic matter in the soluble phase was measured as Chemical Oxygen Demand (COD).

The yield of organic matter into the soluble phase was calculated using the relation

$$\text{Yield \%} = \frac{\text{Soluble COD}}{\text{Total COD}} * 100 \quad (5.2.3.1)$$

This relationship has been used in studies done to quantify solubilization efficiencies for different pretreatment methods (Levine et al., 1992, and Mukherjee, 1992).

The total organic content of this system remained constant, inspite of the release of particulate and particulate associated organics into the aqueous phase or its conversion to soluble forms. The mass balance of organic carbon in the system was calculated as

$$\text{Organic}_{\text{Total}} = \text{Organic}_{\text{Particulate}} + \text{Organic}_{\text{Soluble}} = \text{Constant}$$

$$\Delta \text{Organic}_{\text{Soluble}} = - \Delta \text{Organic}_{\text{Particulate}}$$

CHAPTER 6

RESULTS AND DISCUSSION

This study involved selecting a parameter, which could be characterized or measured relatively easily, and whose change, if there was any, could also be measured. The organic carbon content of the sediment suspensions was the parameter chosen for this study. It was assumed that all the oxygen demand was due to organic carbon and that all the organic carbon was digested (Clark, 1990). As mentioned in the Materials and Methods section, the organic carbon concentration can be estimated stoichiometrically by using the COD test. The yield of organic matter into the soluble phase was calculated using the relation

$$\text{Yield \%} = \frac{\text{Soluble COD}}{\text{Total COD}} * 100 \quad (6.1)$$

This relationship has been used in studies done to quantify solubilization efficiencies for different pretreatment methods. (Levine et al., 1992, and Mukherjee, 1992)

Characteristics of the sediment are as shown Table 6.1.

Table 6.1 Sediment Characteristics

Parameter	Sediment Characteristics
Total Solids	0.65 g / g
Total Volatile Solids	0.094 g / g
Particle Size Distribution	256 μm
pH	7.8
Total Organic Carbon	4 %
Total COD	320 mg / l expressed as oxygen
Soluble COD	20 mg / l expressed as oxygen

Based on the TVS, a 0.25 % suspension of the sediment was sonicated. The result of varying sonication time and energy on soluble organic matter is depicted in Figures 6.1 and 6.2. The results of the particle size analysis is shown in Figures 6.3, 6.4 and 6.5.

At the start of the sonication experiments, most of the organic material in the sediment suspension was associated with the particulate phase. Hence any observed increase in organic carbon concentration after sonication was an indication of an increase in the bioavailability of organic matter in the sediment suspensions. The maximum output energy is 1500 W. It is observed that with an increase of sonication energy applied, there is an increase in the release of organic matter into the aqueous phase. Around 0 – 30 % output energy there is no appreciable effect, from 30 – 55 % output energy there is a gradual increase in the release of organic matter and around 70 % output energy a maximum effect is observed. However the phenomenon halts beyond this point.

At 50 % output energy and around 90 seconds, an optimum release of organic matter was observed. Beyond this there was no appreciable increase in the release of organic matter.

The particle size distribution in the original sediment sample was around 250 μm and fines of an average particle size of 11 μm existed in small quantities (2 %). After sonication at 50 % output energy for 30 seconds, there was a dramatic decrease in particle size to around 10 μm . When sonication time was increased there was no significant difference in the particle size distribution. This size reduction seems to be the result of the dispersion of the clay and silt particles which are present in large quantities in sediments and are held together by weak forces of attraction.

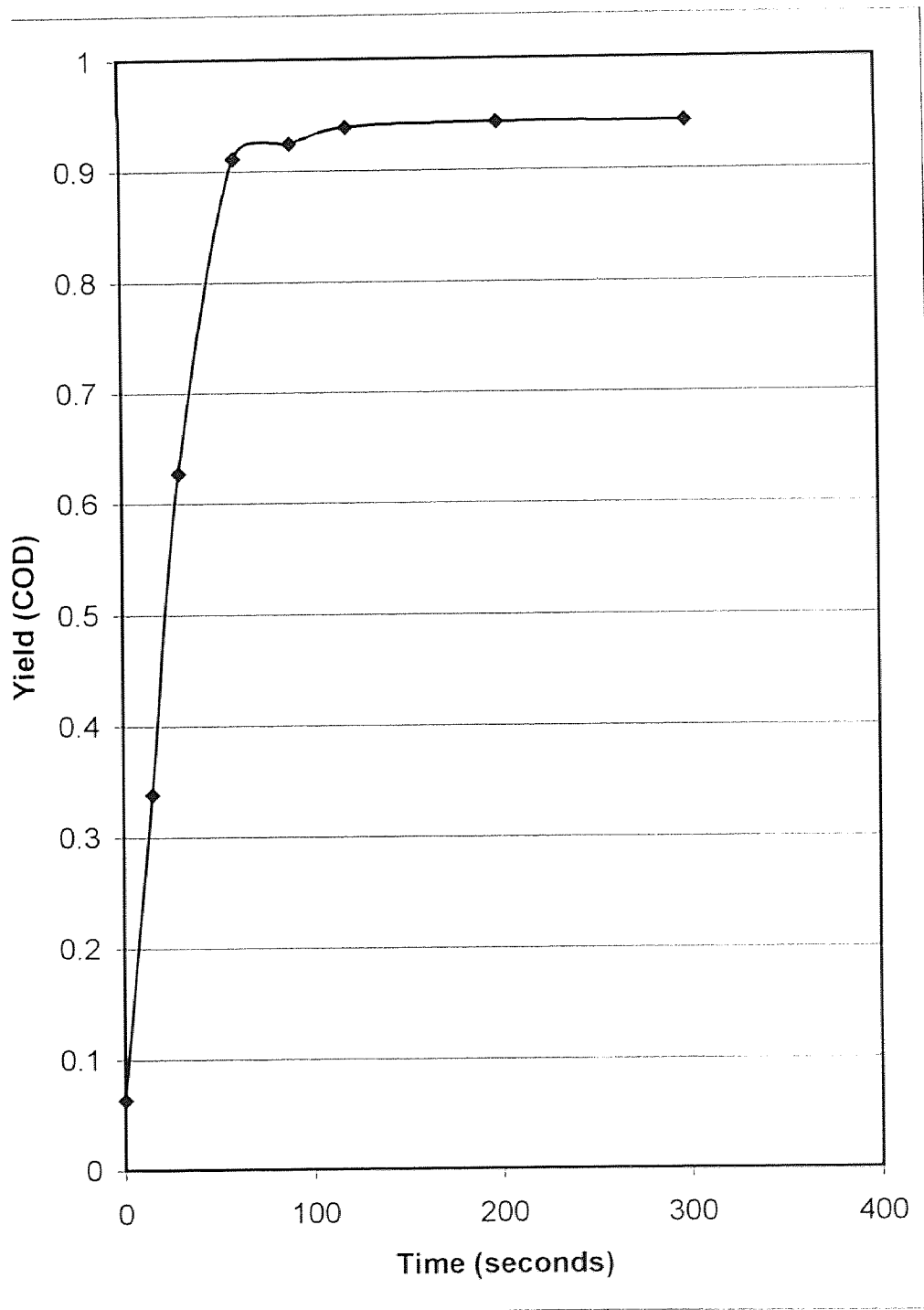


Figure 6.1: Yield (COD) vs Sonication Time

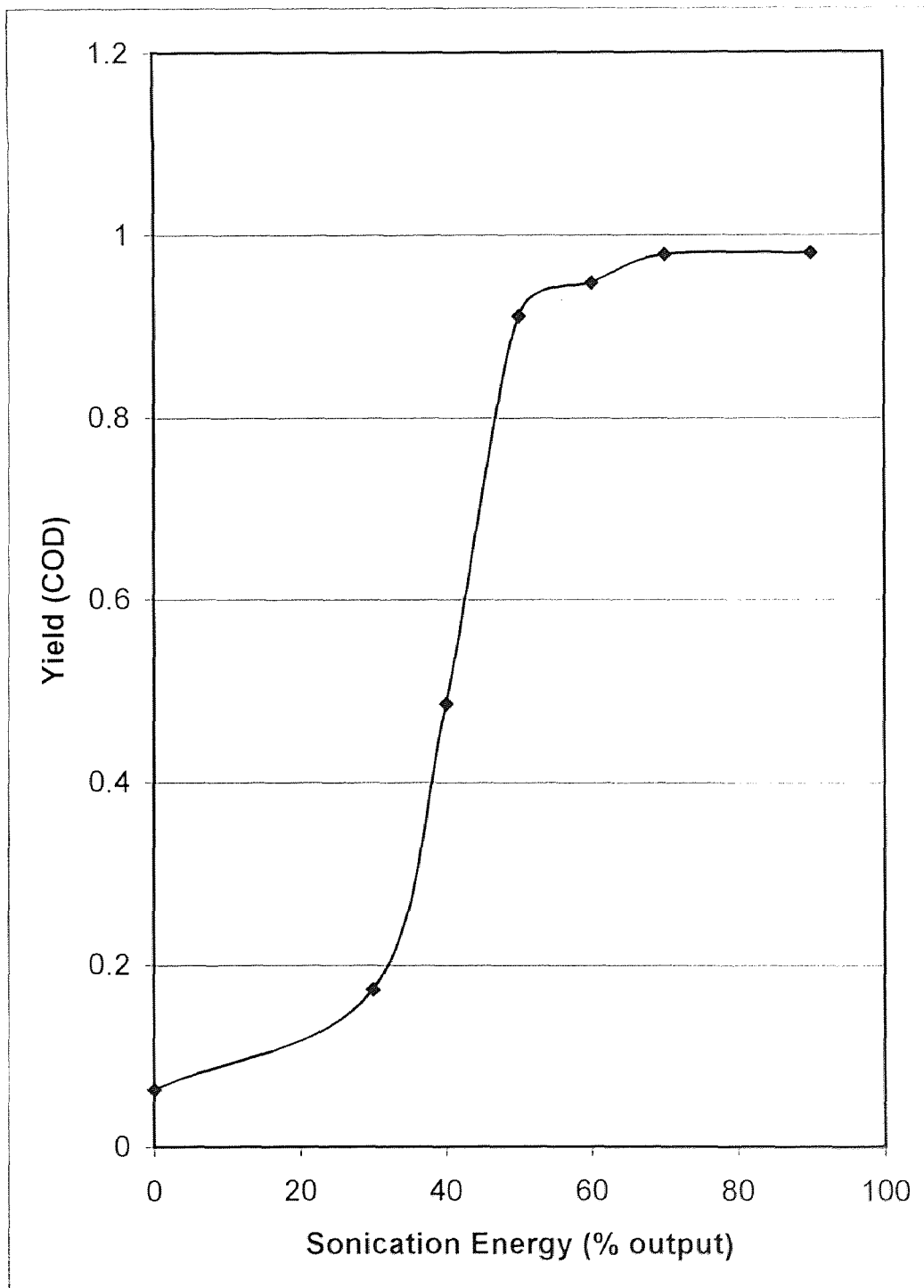


Figure 6.2: Yield (COD) vs Sonication Energy (% output)

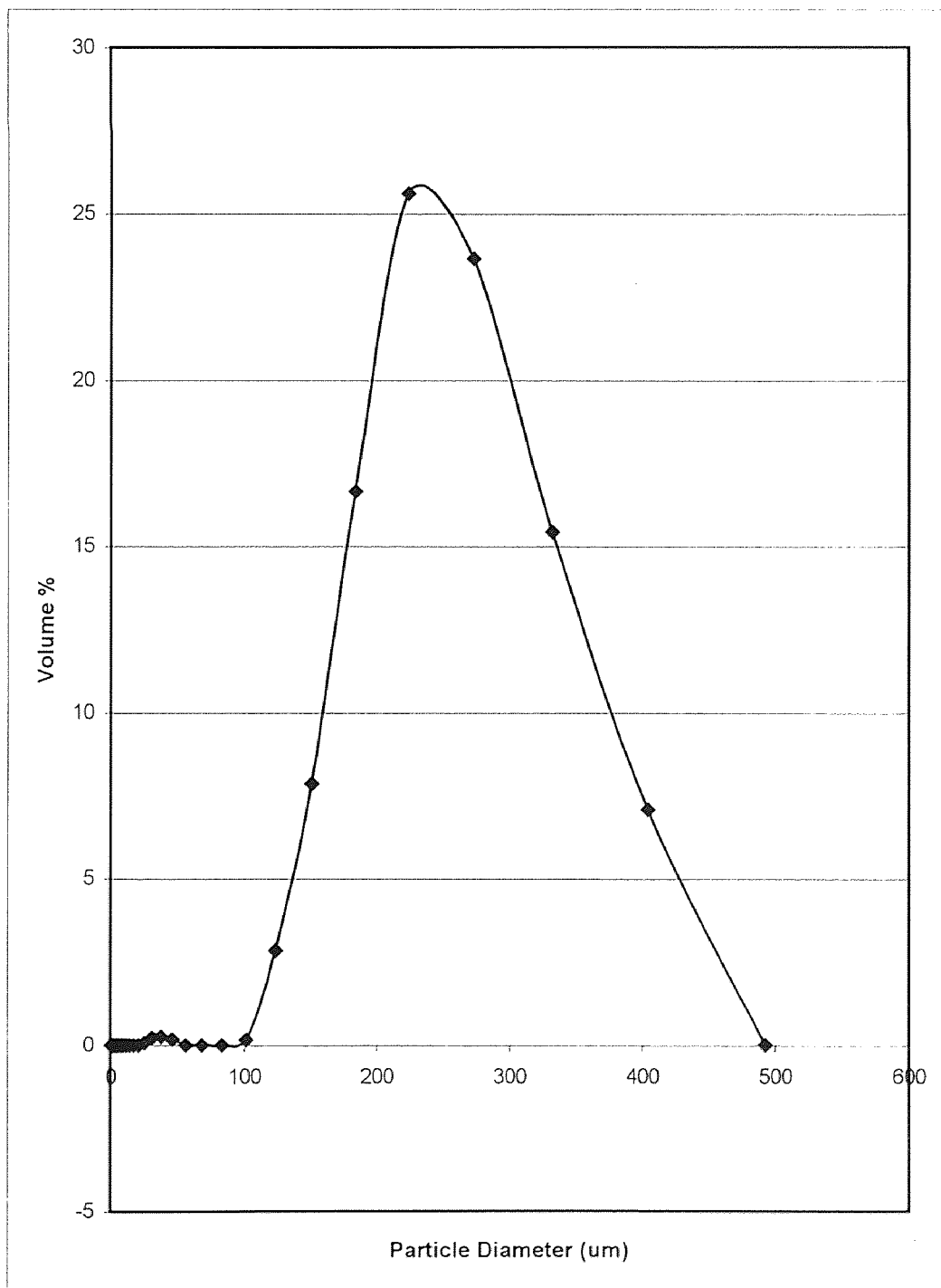


Figure 6.3: Particle Size before Sonication

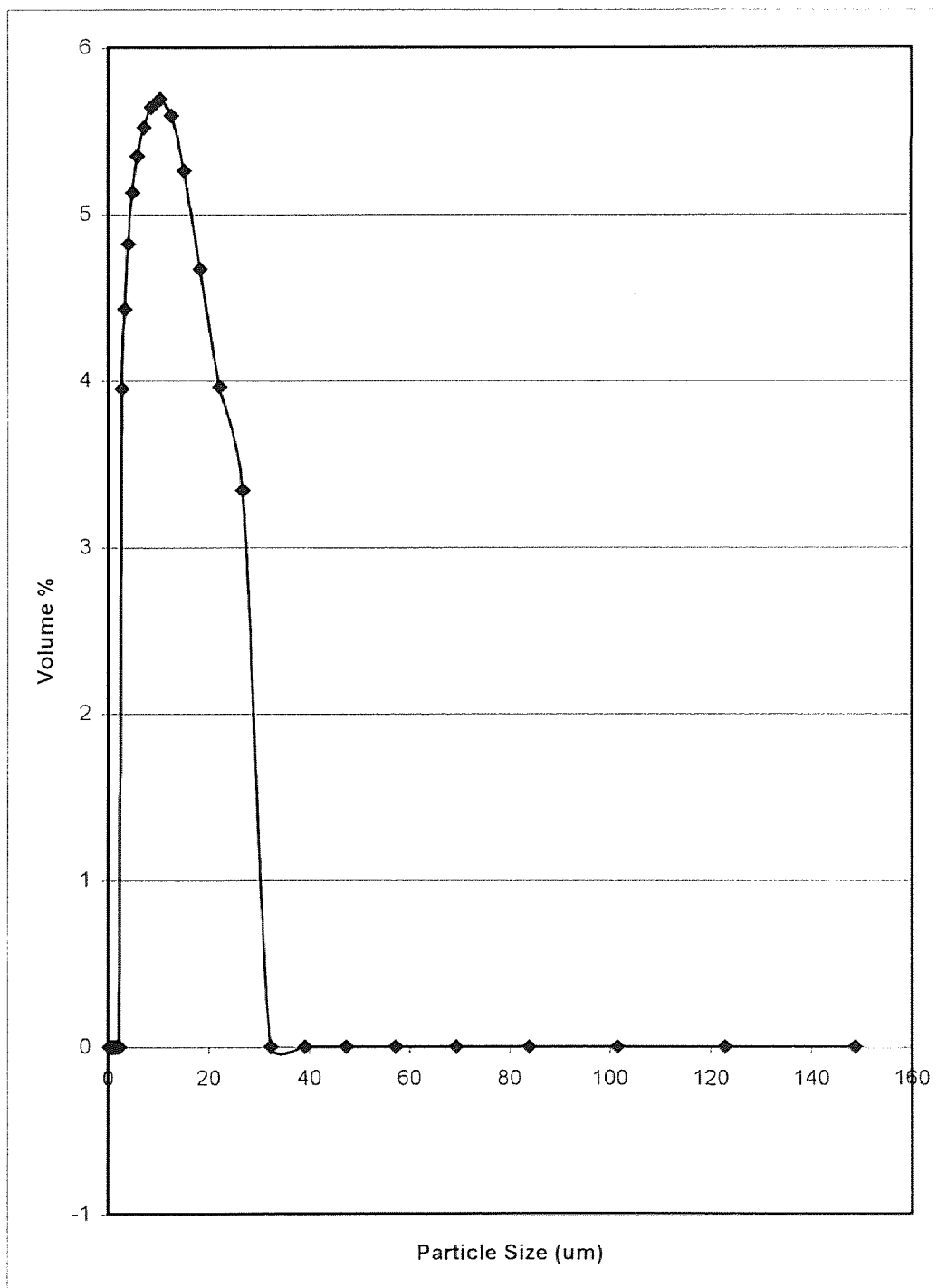


Figure 6.4: Particle Size after Sonication for 30 seconds

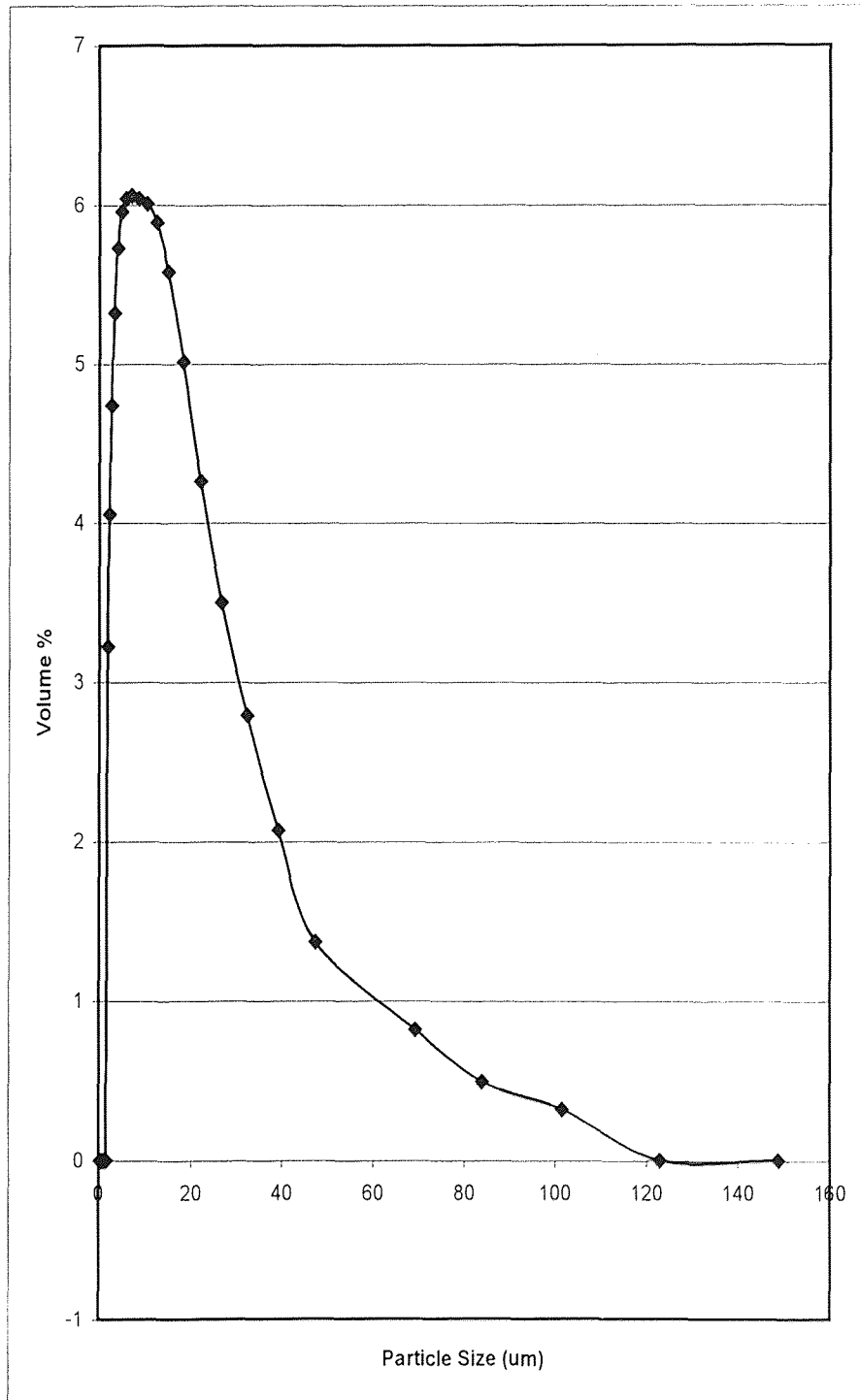


Figure 6.5 : Particle Size after Sonication for 60 seconds

CHAPTER 7

CONCLUSIONS AND SUGGESTIONS FOR FURTHER RESEARCH

7.1 Conclusions

At the start of the sonication experiments, most of the organic material in the sediment suspension was associated with the particulate phase. Hence any observed increase in organic carbon concentration after sonication was an indication of an increase in the bioavailability of organic matter in the sediment suspensions.

The release of the particulate associated contaminants can be explained by the alteration in particle size distribution during sonication. Since the clustered particulate matter is broken down and dispersed on application of sonication energy, the available surface area also increases, and any particulate organic matter released from the sediment or present in the sediment suspension is solubilized to a certain extent into the aqueous phase.

Thus the increase in soluble organic matter and the increased surface area available for biological activity would explain the enhancement of the bioavailability of organic matter associated with the particulate phase after sonication.

7.2 Suggestions for Further Research

Sediments are an important part of the aquatic environment providing food and a habitat for many aquatic biota. When sediments become contaminated, they become a source of contamination to overlying waters that may be relatively clean. There should exist a means to assess the quality of these sediments and associated contaminant concentrations, so that biota can be protected. Since pollutants tend to accumulate and concentrate on sediments, less sensitive analytical methods are required to analyze sediment samples as compared to water samples. Once this is done, the sediment quality can be used as an alternate indicator of the overlying water quality.

To develop a better understanding of a pollutant's sediment chemistry and bioavailability, data on various aspects such as total sediment, interstitial waters, particle size differentiation, depth profiles should be collected. A review of the uptake, release, complexation and degradation of pollutants in sediments, followed by an overall assessment of existing sediment quality, future expected trends in sediment quality, available remedial technologies for impacted sites and the usefulness of establishing sediment quality criteria are requirements.

There clearly exists a need for more research into the bioavailability of chemicals. The role of suspended sediments in alleviating the bioavailability of pollutants for bioconcentration needs to be understood well. For chemicals that sorb well, bioconcentration and toxicity are major concerns.

There exist various models which predict the partitioning of pollutants and their subsequent bioavailability. A significant impediment towards developing appropriate and predictive environmental models that describe the fate of pollutants, lies in the inability to describe sorption reactions properly. The ideas established in these models need to be validated using good laboratory and field studies.

APPENDIX A

DETERMINATION OF SOLUBLE COD

The sediment suspensions which were sonicated at various energies and durations were centrifuged, and the supernatant was analyzed for soluble COD. The results obtained were plotted as a function of varying sonication time and varying sonication energies. To demonstrate the effect of varying sonication times and energies on the Yield, which was measured as COD, graphs of the above mentioned variables were plotted as a function of the Yield.

The Yield was calculated using the relationship
$$\text{Yield (COD)} = \frac{\text{Soluble COD (mg/l)}}{\text{Total COD (mg/l)}}$$

As mentioned earlier the Total COD was found to be 320 mg/l.

Table A.1 Effect of Sonication Time on Yield

Sonication Time (seconds)	Soluble COD (mg/l)	Yield (COD)
0	20	0.0625
15	120.67	0.3377
30	200.57	0.6267
60	291.7	0.911
90	295.8	0.9243
120	300.4	0.9387
200	301.8	0.943
300	301.7	0.9428

Table A.2 Effect of Varying Sonication Energy on the Yield

Sonication Energy (% Total Output)	Soluble COD (mg/l)	Yield (COD)
0	20	0.0625
30	55.46	0.1733
40	155.46	0.4858
50	291.57	0.9111
60	303.13	0.9472
70	312.94	0.9779
90	313.54	0.9798

APPENDIX B

VARIATION OF PARTICLE SIZE DISTRIBUTION BEFORE AND AFTER SONICATION

The particle size distribution before and after sonication was measured using a particle size analyzer. The results are shown below. The particle size is expressed in μm and the volume % represents the percentage of the total number of particles that lie in that particle size range.

Table B.1 Particle Size Distribution Before Sonication

Particle Size (μm)	Volume %	Particle Size(μm)	Volume %
0.5	0	20.9	0
1.32	0	25.46	0.07
1.6	0	31.01	0.23
1.95	0	37.79	0.26
2.38	0	46.03	0.17
2.9	0	56.09	0
3.53	0	68.33	0
4.3	0	101.44	0.15
5.24	0	150.67	7.86
6.39	0	183.44	16.64
7.78	0	223.51	25.6
9.48	0	272.31	23.65
17.15	0	331.77	15.43

Table B.2 Particle Size Distribution After 30 Seconds Sonication

Particle Size (μm)	Volume %	Particle Size (μm)	Volume %
0.2	0	7.01	5.52
0.48	0	8.48	5.64
0.59	0	10.27	5.69
0.71	0	12.43	5.59
0.86	0	15.05	5.26
1.04	0	18.21	4.67
1.26	0	22.04	3.96
1.53	0	26.68	3.34
1.84	0	32.29	0
2.23	0	39.08	0
2.7	3.95	47.3	0
3.27	4.43	57.25	0
3.95	4.82	69.3	0
4.79	5.13	83.87	0
5.79	5.35	101.52	0

Table B.3 Particle Size Distribution After 60 Seconds Sonication

Particle size (μm)	Volume %	Particle Size (μm)	Volume %
0.2	0	7.01	6.06
0.48	0	8.48	6.04
0.59	0	10.27	6.01
0.71	0	12.43	5.89
0.86	0	15.05	5.58
1.04	0	18.21	5.01
1.26	0	22.04	4.26
1.34	0	24.54	3.1
1.52	0	26.68	3.5
1.84	0	32.29	2.79
2.22	3.22	39.08	2.07
2.7	4.05	47.35	1.37
3.27	4.74	69.3	0.82
3.95	5.73	83.87	0.48
4.79	5.96	101.52	0.32
5.79	6.04	122.87	0

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