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INTEGRATION OF CHEMICAL OXIDATION AND BIOTREATMENT FOR REMOVAL OF TNT FROM EXPLOSIVES CONTAMINATED SOIL

By

Fangzhu Liu

A thesis
submitted to the Faculty of
Mississippi State University
in Partial Fulfillment of the Requirements
for the Degree of Master of Science
in Chemical Engineering
in the Department of Chemical Engineering

Mississippi State, Mississippi

May 2003

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INTEGRATION OF CHEMICAL OXIDATION AND BIOTREATMENT FOR REMOVAL OF TNT FROM EXPLOSIVE CONTAMINATED SOIL

By

Fangzhu LIU

Approved:

Mark E. Zappi
Professor of Chemical Engineering
(Major Professor)

R. Mark Bricka
Associate Professor of
Chemical Engineering
(Committee Member)

Chiang H. Kuo
Professor Emeritus of
Chemical Engineering
(Committee Member)

W. Todd French
Assistant Professor of
Chemical Engineering
(Committee Member)

Rebecca K. Toghiani
Associate Professor of Chemical Engineering
Graduate Coordinator of
Chemical Engineering

A. Wayne Bennett
Dean of the College of
Engineering

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Name: Fangzhu LIU

Date of Degree: May 10, 2003

Institution: Mississippi State University

Major Field: Chemical Engineering

Major Professor: Dr. Mark E. Zappi

Title of Study: INTEGRATION OF CHEMICAL OXIDATION AND BIOTREATMENT FOR REMOVAL OF TNT FROM EXPLOSIVE CONTAMINATED SOIL

Pages in Study: 162

Candidate for Degree of Master of Science

2,4,6-trinitrotoluene (TNT) is of environmental concern because it's a possible human carcinogen and it also remains potentially explosive. The Department of the Army (DA) estimates that there are 540,000 cubic meters (700,000 cubic yards) of explosives-contaminated soil at over 2,000 sites that require remediation. Biological treatment of TNT results in the production of the reduced intermediates (such as aminonitrotoluenes). When using chemical oxidation processes to treat TNT, 1,3,5-trinitrobenzene (TNB) is produced. The by-products of both biological and oxidation treatment processes are resistant to further treatment thus they require extensive treatment times. This study evaluated the use of biotic mechanisms that can be used to reduce TNT into aminodinitrotoluenes, which then are oxidized using Fenton's

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Reagent oxidation process. Integration experimental results showed that Fenton's Reagent was capable of degrading TNT, though not as fast as ADNTs. The optimal Fe^{2+}/H_2O_2 ratio appears to be less than 10:1. The TNT biodegradation rate was higher than the TNT oxidation rate and was biodegraded at a faster rate compared to the ADNTs. It was concluded that the integrated technology showed promise as an effective and innovative technology for treating TNT contaminated soil.

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DEDICATION

I would like to dedicate this thesis to my parents, Jianmin LIU and Yiyun Hu, and my Aunt BinXU. Without their enormous support and guidance throughout this whole process, I would never have come this far.

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First of all, I would like to thank Dr. Mark E. Zappi, my major professor, for the enormous time and effort he spent guiding and assisting me through the graduate program and thesis process. Expressed appreciation is also due to the other members of my thesis committee, Dr. Mark R. Bricka, Dr. Chiang H. Kuo, Dr. Todd French, and to Dr. Rebecca Toghiani, graduate program coordinator for the Dave C. Swalm School of Chemical Engineering. Sincere thanks are due to Mr. Rafael Hernandez for his valuable help in instrumental analysis. Last but not the least, I would like to thank Ian Tiang for his unparalleled help in the lab and through the thesis process.

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CHAPTER I

INTRODUCTION

Explosives

An explosive is a material that, under the influence of extreme thermal or mechanical shock, decomposes rapidly and spontaneously with the evolution of large amounts of heat and gas. Among explosives, there are two major categories: high explosives and low explosives (USEPA, 2002). High explosives can be further divided into initiating (or primary) high explosives and secondary high explosives. Under normal conditions, primary explosives will not burn, but they will detonate if ignited and can be extremely sensitive to mechanical shock. Their strength and brisance are inferior, but they are sufficient to detonate secondary high explosives. Because of their sensitivity, primary explosives are used in munitions for initiating and intensifying high-order explosions. Common primary explosives are lead azide, lead stiphnate, and mercury fulminate (Eveleth and Kollonitsch 1990).

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Secondary high explosives are much less sensitive to mechanical or thermal shock than primary high explosives. When set off by an initiating explosive, they explode with great violence. Examples of secondary high explosives are TNT (2,4,6-trinitrotoluene), nitroglycerine, RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine) and PETN (pentaerythritol tetranitrate). The most common secondary high explosives manufactured for military use since the turn of the century is TNT (Chaudhry, 1994).

TNT is a yellow, odorless solid that is manufactured because it does not occur naturally in the environment. The chemical structure of TNT is shown in Figure 1-1. TNT is only produced in the United States at military arsenals. TNT is used in military shells, bombs, and grenades (Rittmann, 1994). The physical and chemical properties of 2,4,6-trinitrotoluene are listed in Table 1-1.

TNT has been used either as the pure explosive or in binary mixtures (Gibbs and Popolato 1980). The most common binary mixtures of TNT are cyclotols (mixtures with RDX), octols (mixtures with HMX), amatols (mixtures with ammonium nitrate), and tritonals (mixtures with aluminum) (Eveleth and Kollonitsch 1990: Gibbs and Popolato 1980). In addition to military use, small amounts of TNT maybe used for industrial

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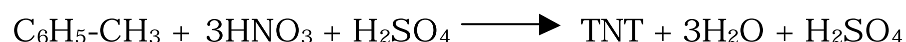
explosive applications, such as deep well and underwater blasting (HSDB 1994).

TNT Production

TNT was first produced on an industrial scale as early as 1891 by Germany. By 1901, it was adopted by basically all military powers as their key primary explosive (Kirk and Othmer, 1951). During World War I, the production of TNT was limited only by the amount of toluene available as a by-product of the coke industry (Kirk and Othmer, 1951). After 1940, toluene became readily available as a by-product of the petroleum industry, and thus, during World War ? , TNT was extensively manufactured (Kirk and Othmer, 1951).

Either a continuous or a batch process may be used to produce TNT, using toluene, nitric acid (HNO_3), and sulfuric acid as raw materials (USEPA, 2002). The production of TNT follows the same chemical process, regardless whether the batch or continuous method is used. The process flow chart for TNT production is shown in Figure 1-2. The overall chemical reaction may be expressed as:



$$C_6H_5\text{-}CH_3 + 3HNO_3 + H_2SO_4 \longrightarrow TNT + 3H_2O + H_2SO_4$$

The most common form of TNT production is a 3-stage process performed in a series of reactors, as shown in Figure 1-3. TNT is

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prepared by the nitration of toluene with a mixture of nitric and sulfuric acid (Fisher and Taylor 1983). Toluene is nitrated by using increasing temperatures and mixed-acid concentrations to successively introduce nitro groups to sequentially form mononitrotoluene (MNT), dinitrotoluene (DNT), and trinitrotoluene (Mark et al. 1980). Nitration can be accomplished in three separate steps or via continuous flow (Budavari et al. 1989). The mixed acid stream flows countercurrent to the flow of the organic stream. Numerous other compounds are also formed during the nitration of toluene, including unsymmetrical isomers of 2,4,6-trinitrotoluene, oxidation products (such as tetranitromethane, nitrobenzoic acid, and nitrocresol), and partially nitrated toluenes (Hamilton and Hardy 1974: Mark et al. 1980).

TNT manufacturing is controlled by the U.S. Army Armament Material Command (Gibbs and Popolato 1980). Army ammunition plants that have been involved in the production and storage of TNT include Shreveport (Louisiana), Anniston (Alabama), Crane (Indiana), Fort Wingate (New Mexico), Hawthorne (Nevada), Letterkenny (Pennsylvania), Lexington (Kentucky), McAlester (Oklahoma), Navajo (Arizona), Pine Bluff (Arkansas), Pueblo (Colorado), Red River and Lone Star (Texas), Savanna and Joliet (Illinois), Seneca (New York), Sierra (California),

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Tooele (Utah), Umatilla (Oregon), Weldon Springs (Missouri), West Virginia Ordnance Works (West Virginia), Radford (Virginia), and Volunteer (Tennessee) (Kraus et al. 1985; Army 1986).

TNT Toxicity

TNT contamination is a major environmental concern due to its toxicity and mutagenicity. TNT is not only a source of environmental contamination, but it also remains potentially explosive for years after it is produced (Won et al., 1976; Yinon, 1990; Collie et al., 1995). Some of the nitroaromatics and nitramines that have been found in the vicinity of munitions plants are known to be mutagenic, carcinogenic, or otherwise toxic to aquatic and terrestrial organisms (Won et al., 1974 and 1976; McCormick et al., 1976; Kaplan and Kaplan, 1982a). Human health concerns regarding exposure to TNT primarily arise from evidence linking occupational contact with liver damage, dermatitis, ocular disorders and gastrointestinal distress (Sittig, 1985). Exposure to TNT is known to cause rashes, skin hemmorages, and blood disorders (Kirk et al., 1993; Chaudhry, 1994). TNT is classified as an EPA class C Possible Human Carcinogen and many of its environmental degradation products have carcinogenic, mutagenic, and toxic properties (Roberts and Hartley, 1992).

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TNT Contamination

The Department of Defense (DoD) has numerous sites that contain environmental media that have been contaminated with explosives due to past military activities (DoD 1994). The Department of the Army (DA) estimates that there are 540,000 cubic meters of explosives-contaminated soil at over 2,000 sites that require remediation (Labat-Anderson, 1993; Georgia Institute of Technology, 1995).

TNT contamination has resulted from past disposal of manufacturing and demilitarization waste streams in landfills, waste pits, washout lagoons, and open burning grounds. Poor disposal techniques have generated numerous acres of TNT contaminated soil. For example, past disposal practices conducted at the former Nebraska Ordnance Plant (Mead, NE) have resulted with approximately 6,400 m^3 of contaminated soil (Li and Shea, 1997). The average U.S. munitions plant generated approximately 80,000 gallons of explosives contaminated wastewater and 250,000 lbs of solid waste per day (Tsai, et al., 1991).

In addition to munition plants, explosive waste was produced from load and pack operations and disposal of outdated stock via open burning and detonation. During load and pack operations, TNT was

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typically received by rail car, off-loaded, and moved via conveyor belt to shell loading facilities. TNT spilled from the conveyor belts and work areas was hosed to reduce explosive dust and to wash shells. These TNT saturated washwaters were disposed of through drainage ditches that flowed into lagoons, marshes, or other areas, generally with little to no treatment (Higson, 1992).

Overview of Current Treatment Technologies for TNT Contaminated Soil

Incineration

Incineration involves the supplying heat from fuel combustion or electrical input to cause the thermal decomposition of organic contaminants through cracking and oxidation reactions at high temperatures (usually between 1,400 - 3,000° F) (US Navy, 2002). It is a commercially available technology that has been selected or used as the remedial action at more than 150 Superfund sites (US CPEO, 2002). A typical incineration process is illustrated in Figure 1-4.

The current fully developed technology for treatment of explosives-contaminated soil is incineration. It is a well-developed technology (available from a wide range of vendors in many configurations) that can significantly reduce the volume of waste streams (US DOE, 2002). But,

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it is expensive ($350-$1,200 per cubic yard) and is generally not favored by the public (Zappi et al., 1995a). Incomplete combustion can result in the production of polycyclic aromatic hydrocarbons, carbon monoxide (CO), and nitrogen oxides (NO_x). Thus, the off-gas from the incinerator typically must be treated (Harvey, 1997). The problems with incineration have lead to the growth and further research on the bioremediation of TNT (Rittmann, 1994).

Biotreatment

Bioremediation uses microorganisms and plants to transform hazardous materials into more benign substances (Rittmann, 1994). Since the mid-1980s, bioremediation has been used at more than 100 locations to cost-effectively remediate hundreds of thousands of cubic yards of contaminated soil (Block, et al. 1993).

Removal of TNT using biological techniques has been reported by several research groups (Spain 1995). Both aerobic and anaerobic bacteria consortia and isolates are believed to utilize reductases that are responsible for TNT degradation (Bradley et al. 1994). The first fully-scale bioremediation project at a site containing explosives-contaminated soils became operational in 1995 (Craig et al., 1996).

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The reductive path for the biologically based removal of TNT is generally believed to be the stepwise aminization of the nitro groups until the molecule is fully reduced to triaminotoluene (TAT). Some research groups have reported that TNT coupling may occur at the 2-carbon and 6-carbon amino groups of two TNT molecules to form azoxytoluene dimmers (Greene et al. 1985). The reductive pathway for TNT degradation has been observed within aerobic soil slurries (Zappi et al. 1995a), anaerobic soil slurries (Funk et al. 1993b), composting units (Pennington et al. 1995), and phytocells (Best et al. 1997).

Overview of Current Treatment Technologies for TNT Contaminated Water

Explosives-contaminated process wastewaters can be subdivided into two categories: red water, which comes strictly from the manufacture of TNT, and pink water, which includes any wash water associated with load, assemble, and pack (LAP) operations or with the demilitarization of munitions involving contact with finished explosives. The United States stopped production of TNT in the mid-1980s, so no red water has been generated in this country since that date (Greene et al., 1985). However, the US still produces pink water because LAP activities continue as an integral part of military activities.

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GAC

Liquid-phase carbon adsorption is a fully developed technology in which wastewater is pumped through a series of vessels containing granular activated carbon upon which the dissolved contaminants adsorb onto the carbon. When the concentration of contaminants in the effluent from the bed exceeds a certain level, the carbon can be regenerated in place or removed and regenerated at an off-site facility, or removed and disposed (US DoD, 1994).

Granular-Activated Carbon (GAC) adsorption is commonly used for explosives-contaminated water treatment (Marvin and Harry, 2000). Most process waters found in the field are pink waters that were generated by LAP and demilitarization operations conducted during the 1970s (Maloney et al., 2002). GAC is effective, but the carbon columns are expensive and the explosive-laden GAC must periodically be transported off-site for regeneration or destruction by incineration (Mueller et al., 1993). Additionally, many GAC vendors are now refusing to accept spent GAC containing explosives due to safety concerns (personal communication with Dr. Mark Zappi, MSU, 2002).

Advanced Oxidation Processes (AOPs)

AOPs represent a group of chemical oxidation technologies that

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utilize the hydroxyl radical (OH·) as the primary oxidizing species responsible for contaminant degradation (Huang et al., 1993). Advanced chemical oxidation processes (AOP) generally use a combination of oxidation agents (such as H_2O_2 or O_3), irradiation (such as UV or ultrasound), and catalysts (such as metal ions or photocatalysts) as a means to generate hydroxyl radicals (Venkatadri et al., 1993). The hydroxyl radical is one of the most powerful oxidants next to elemental fluorine (Huang et al., 1993).

AOPs have also been evaluated for treating explosives contaminated groundwaters (Zappi et al. 1993). These processes have the ability to rapidly oxidize recalcitrant compounds and convert them to potentially less toxic and more readily biodegradable intermediate products (Huang, et al., 1993). Examples of AOPs evaluated or under evaluation by DoD for TNT removal include photocatalytic oxidation (Selby 1996), UV/peroxidation (AEC 1995), UV/ozonation (Hong et al. 1994), and peroxone oxidation (Zappi 1995b). AOPs are very aggressive treatment process due to the high reactivity of the hydroxyl radical, but the cost involved may be high and their operation usually requires highly trained labor.

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Table 1-1
Physical and Chemical Properties of 2,4,6-Trinitrotoluene
(Reference: Budavari et al., 1989)

Property	Information
Molecular weight	227.13
Color	Yellow
Physical state	Monoclinic needles
Melting point	80.1°C
Boiling point	240°C (explode)
Specific gravity	1.654
Odor	Odorless
Solubility:	
Water at 20°C	130 mg/L
Organic solvent(s)	Soluble in acetone and benzene; Soluble in alcohol and ether
Partition coefficients:	
Log K_{ow}	1.60 (measured)
	2.7 (estimated)
K_{oc}	300 (estimated)
	1,100 (measured)
Vapor pressure at 20°C	1.99 x 10^{-4} mmHg
Flashpoint	Explodes
Flammability and Reactivity	4.4
Conversion factors	1 ppm = 9.28 mg/m^3
	1 mg/m^3 = 0.108 ppm
Explosive temperature	464°F

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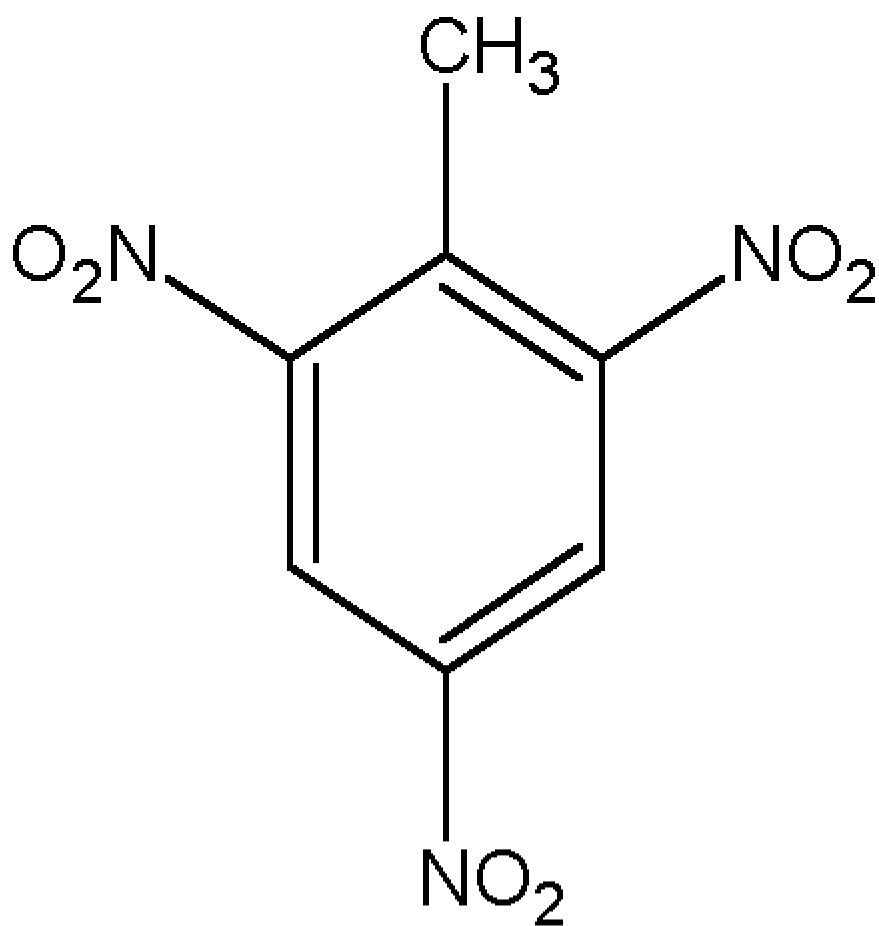

Figure 1.1. Chemical Structure of 2,4,6-Trinitrotoluene

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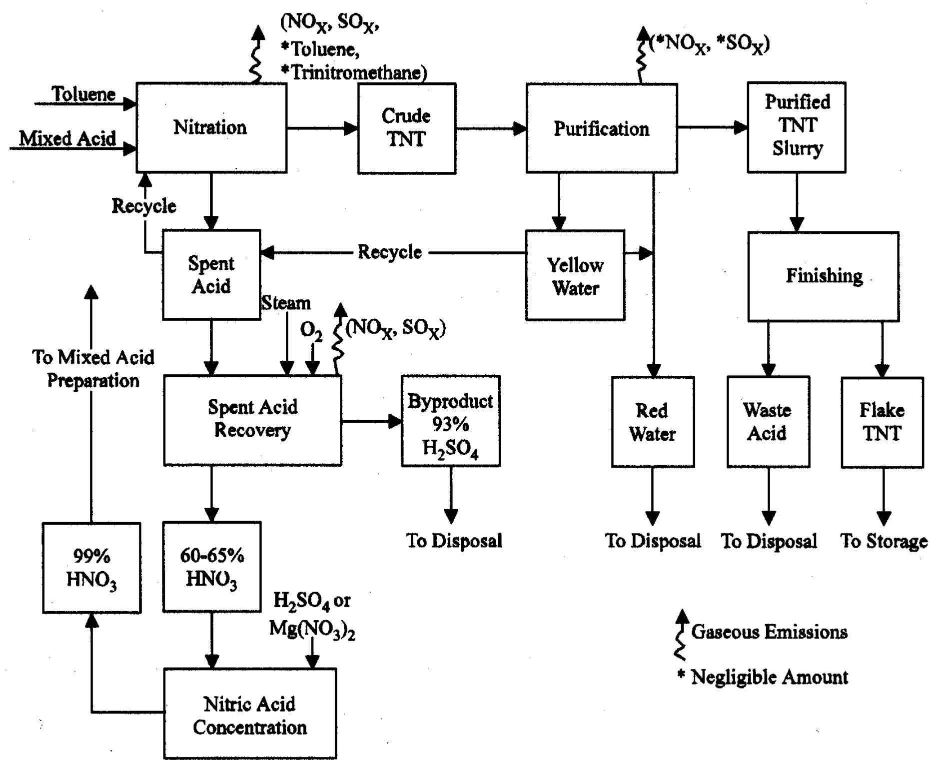

Figure 1.2. TNT Production

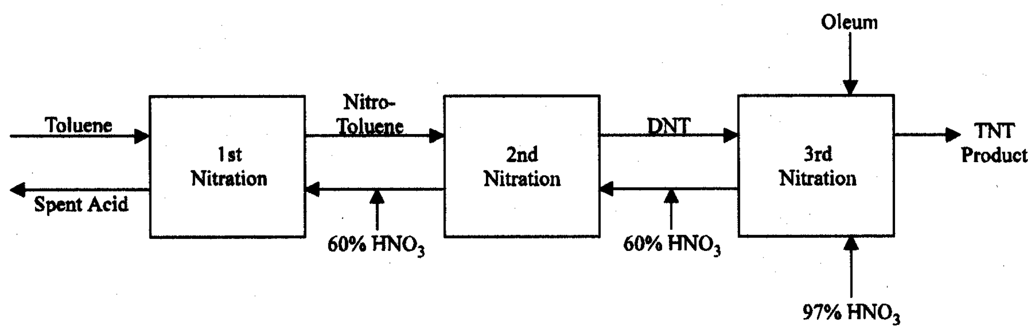

Figure 1.3. Nitration of Toluene to Form Trinitrotoluene

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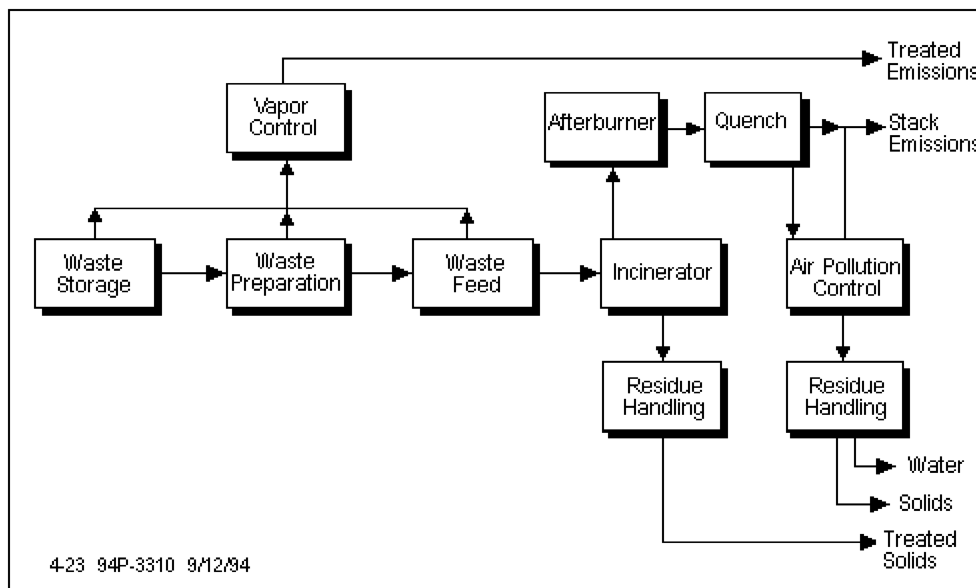

Figure 1.4. Typical Mobile/Transportable Incineration Process

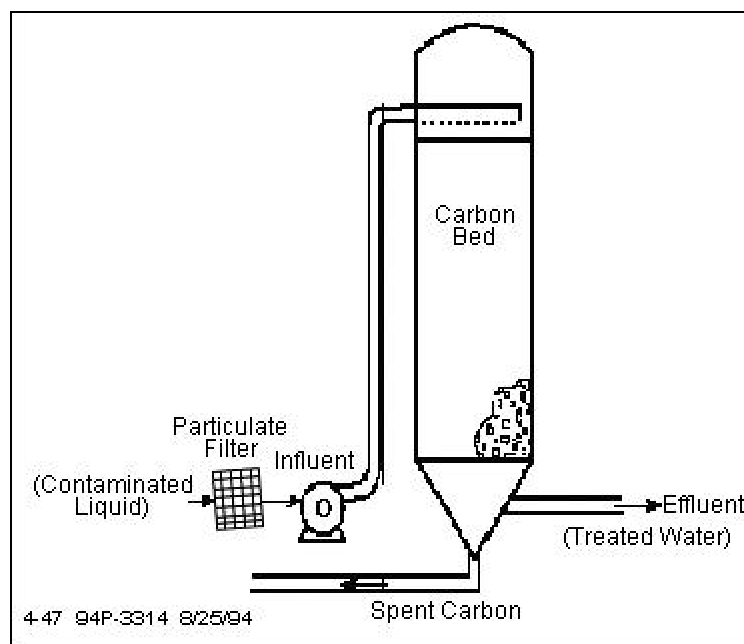

Figure 1.5. Typical Fixed-Bed Carbon Adsorption System

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CHAPTER II

LITERATURE REVIEW

Treatment of TNT contaminated soil has been a subject of many studies throughout the years (Spain 1995). Currently, the U.S. Army has deemed incineration to be the best means for remediating TNT contaminated soils (Major and Amos, 1993). Incineration is costly and the fact that most ash generated from incinerators must be treated as hazardous waste has led to a search for alternative treatment methods (Funk et al., 1996). The two current treatment alternatives are: bioremediation and advanced oxidation process (AOPs). Both biotreatment systems and AOPs have been or are being evaluated by DoD for treatment of explosives contaminated media (DoD 1994; ARO 1995). Unfortunately, neither process has been able to show high TNT mineralization yields. Both processes suffer from persistent by-products that hinder process acceptance by regulatory agencies (Hong et al., 1994; Weston Inc., 1988; Fleming, 2000). It is proposed that the integration of these two technologies has great potential to result in the development of a new and innovative technology that can effectively treat TNT in soils at

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greatly reduced costs. Presented in this chapter are discussions on some general aspects of both technologies toward treating TNT contamination alone, followed by examples of past studies that have evaluated the integration of these two technologies for treating various contaminants.

Bioremediation of TNT

Bioremediation has emerged as a potentially attractive, cost-effective alternative for the treatment of TNT-contaminated soils (Lenke et al., 2000). Although biotreatment technologies are less developed for explosives than for petrochemical wastes, there is substantial literature documenting the promise of biodegradation for treating TNT and other explosives in soil and water matrices (Enzinger, 1971; McCormick et al., 1976; Carpenter et al., 1978; Kaplan and Kaplan, 1982a-c; Fernando et al., 1990; Funk et al., 1993a,b; Boopathy et al., 1994a-c; Zappi, 1995a; Gilcrease and Murphy, 1995; Harvey, 1997). Studies present clear evidence that TNT can be degraded under aerobic and anaerobic conditions (McCormick et al., 1976; Spiker et al., 1992; Funk et al., 1993a,b; Collie et al., 1995; Manning et al., 1995; Funk et al., 1995). To date, a microbial pathway responsible for complete mineralization of TNT using aerobic or anaerobic consortia has not been fully demonstrated (Zappi et al., 1995a). TNT degradation has been shown to be a cometabolic process (Osmon and Klaumeier, 1974; Traxler et al., 1974;

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Won et al., 1974; Boopathy et al., 1994b; Boopathy et al., 1994c). Only few researchers have claimed TNT mineralization (Traxler et al., 1974; Fernando and Aust, 1990; Spiker et al., 1992; Boopathy et al., 1994a,b; Bradley et al., 1994). During treatment of TNT within most biotreatment systems, reduced by-products such as diaminonitrotoluenes (2,6-DANT & 4,6-DANT), dominate the required incubation times needed to properly remediate the soil (Harvey, 1997).

Fundamentals of TNT Biodegradation

Bioremediation is an engineered process that utilizes natural biochemical mechanisms that often results in the production of harmless end products. However, this tends not to be the case with TNT (Zappi et al., 1995a; Harvey, 1996). Biodegradation alters the molecular structure of TNT, and the degree of alteration determines whether biotransformation or mineralization has occurred. Biotransformation refers to the structural transformation of TNT into daughter compounds (by-products). Mineralization is the complete breakdown of TNT into cellular mass, carbon dioxide, water, and inert inorganic residuals. That is, biotransformation is partial degradation and mineralization is complete degradation, although degradation occurring does not infer mineralization.

Any form of living matter requires energy and carbon for growth and maintenance. Microorganisms degrade compounds to derive energy

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for cell growth and maintenance (LaGrega et al., 1994). The particular sources from which microorganisms derive their energy and cellular carbon provide a basis for their classification as shown in Table 2-1. Biological treatment of TNT contamination is the result of heterotrophic metabolism. Microorganisms use organized sequences of enzymatically catalyzed degradation reactions to obtain chemical energy from organic substrates; although, the exact mechanisms associated with the whole series of reactions are not fully defined by science to date.

Factors Affecting Biodegradation of TNT

For biodegradation of TNT to occur, several environmental factors must first be fulfilled. They are very crucial for the proper functioning of bioremediation. Sometimes, one of these factors can significantly affect or promote the activities of bioremediation in terms of rate and extent of pollutant removal.

Substrate Biodegradability:

From experience and research work, it has been shown that many synthetic organics are biodegradable, which makes biological treatment a technically plausible alternative. However, the literature is replete with cases where specific compounds have resisted biodegradation (LaGrega et al., 1994). Such compounds are termed recalcitrant or refractory. TNT

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falls into this category. TNT biodegradation rate is very slow, so biological treatment is generally considered inefficient if mineralization is the goal.

TNT has been proved amenable to biological treatment as summarized in recent reviews (Kaplan, 1992). The biodegradation pathways used always require co-metabolites and follow reductive, oxidative, or hydrolytic sequences.

Co-metabolism is an important example of a microbial community at work. It involves the transformation of one compound (the secondary substrate) by enzymes from microorganisms routinely degrading another compound (the primary substrate or co-metabolite). Molasses was found to be an effective carbon source that enhanced the TNT transformation rate significantly over other carbon sources studied (Boopathy et al., 1998). With this application, the secondary substrate was TNT. The microorganisms derive little carbon or energy from the secondary substrate (TNT); its degradation is serendipitous and fortuitous. The co-metabolite (molasses) induces the enzymes needed for transformation of the secondary substrate (TNT). Although the secondary substrate (TNT) typically does not enter the catabolic and anabolic pathways of the microorganism degrading the cometabolite, other microorganisms may be able to use the transformation products for substrate (LaGrega et al., 1994). In the case of TNT, the reductive pathway leads to the

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accumulation of amino derivatives (ADNTs and DANTs) and polymerized or conjugated products. Most studies indicate little evidence of measurable TNT mineralization (Kaplan, 1992). A microbial pathway responsible for complete mineralization of TNT using aerobic or anaerobic consortia has not been convincingly demonstrated to date (Zappi et al., 1995a). It is generally accepted that TNT transformation proceeds through the step-wise reduction of the 2- or 4- nitro group to nitroso- and hydroxylamino to amino-dinitrotoluene and diamino-nitrotoluene by a bacterial enzyme NADP-dependent PETN reductase under both aerobic and anaerobic conditions (Won et al., 1974; Kaplan and Kaplan, 1982c; Boopathy et al., 1994a). The proposed microbial TNT degradation pathway is shown in Figure 2.1. So far, only two authors have reported the complete reduction of TNT to triaminotoluene [TAT] (McCormick et al., 1976; Preuss et al., 1993).

<u>Bioavailability of TNT in Soil Environments</u>:

Bioavailability is defined as the ability of a compound to be freely transported across the cell membrane for intracellular metabolism and/or available for extracellular metabolism (Verschueren and Visschers, 1988). Contaminant interactions with soils are complex which influences their fate in biological systems. It is generally accepted that a contaminant must be in the aqueous phase to enter a microbial cell where it can be degraded (Mueller et al., 1993). Hence, the desorption of

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the contaminant from the soil surface to the bulk aqueous phase is one of the most important factors during the remediation of contaminants in soil-water systems (Edwards et al., 1991; Pennington et al., 1995; Volkering et al., 1995). Adding surfactant to the biotreatment system can increase the bioavailability of a contaminant (Pennel et al., 1993; Bury and Miller, 1993; Edwards et al., 1994; Zappi et al., 1995a). Harvey (1997) added a surfactant (Tween 80) to both biocell and bioslurry reactors. Both applications showed great increases in the bioavailability of TNT and the rate and extent of TNT biodegradation.

Nutrients:

Nutrients, rather than carbon or energy sources, may at times be the limiting chemicals for microbial cell synthesis and growth (LaGrega et al., 1994). The principle inorganic nutrients needed by microorganisms are N, S, P, K, Mg, Ca, Fe, Na, and Cl (LaGrega et al., 1994). Minor nutrients of importance include Zn, Mn, Mo, Se, Co, Cu, Ni, V, and W (Metcalf & Eddy, 1991). Phosphorus and nitrogen are referred to as macronutrients, because the synthesis of cellular tissue requires much more of these than the other nutrients (LaGrega et al., 1994). Theoretically, the optimum amount of nitrogen and phosphorus present in water should be based on a carbon: nitrogen: phosphorous (C: N: P) ratio similar to that stoichiometrically composing a typical bacterial cell. An approximate formula for the organic fraction of bacteria cell tissue is

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$C_{60}H_{87}O_{23}N_{12}P$ (Metcalf & Eddy, 1991). Therefore a C: N: P ratio of 100: 20: 2 is generally considered optimal. This ratio is often used as a starting point for soil bioremediation.

Moisture:

Biodegradation requires moisture for two reasons. One is that water is necessary for cellular growth (cellular tissue is 75%-80% moisture). The other is that water serves as a medium for the transport of the microorganisms to the substrate or vice versa. Biodegradation in soil systems can occur at moisture levels well below saturation. It is indicated that most bacteria fail to grow if the water content of the medium falls below 92% relative humidity (Singleton et al., 1978). However, it is generally accepted that the minimum moisture content necessary for treatment of wastes such as contaminated soil is 40% of saturation (LaGrega et al., 1994).

AOP Treatment of TNT

Advanced Oxidation Processes (AOPs) are defined as chemical oxidation technologies, which use hydroxyl radicals as the primary mechanism of waste treatment (Glaze, 1987). Commercial application of AOPs for contaminated media treatment in the United States has traditionally involved UV irradiation of hydrogen peroxide, ozone, or a combination of both (Zappi 1995b). AOPs tend to be much more

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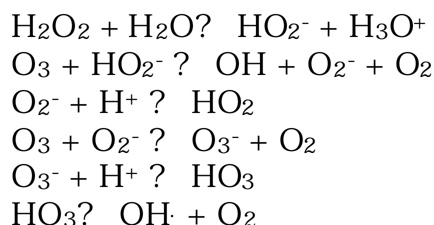
aggressive in terms of destruction of organic species than ozonation alone due to the higher reactivity of the hydroxyl radical toward complex organics (Sundstrom et al., 1986). The hydroxyl radical is stable over a wide pH range, up to pH 10 (Huang, et al., 1993). The hydroxyl radical reacts with organic chemical by three major mechanisms: hydroxy addition, hydrogen abstraction, and electron transfer (Wang, 1999). TNT oxidation pathway is shown in Figure 2.2. During TNT oxidation, 1,3,5-trinitrotoluene (TNB) has been observed to be one of the primary by-products of the incomplete oxidation of TNT (Burrow 1983; Himebaugh 1994; Peyton et al. 1994; Hong et al. 1994; Zappi 1995).

Peroxone

Peroxone technology involves using ozone in conjunction with hydrogen peroxide to produce hydroxyl radicals (Hong et al., 1994). It was developed for reducing the cost and increasing the aggressiveness of ozonation through the addition of small quantities of hydrogen peroxide (Langlais et al., 1991).

Langlais et al. (1991) presented the following mechanism for the formation of the hydroxyl radical during peroxone treatment:



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Peroxone has been successfully used for treatment of low-level organic contamination within groundwater matrices. Contaminants treated by peroxone include chlorinated solvents (Aieta et al., 1988), pesticides (Zappi et al, 1994), and explosives (Zappi et al, 1995b).

The U.S. Army Environmental Center and WES evaluated the technical and economic applicability of this process for the destruction of explosives contamination in groundwater (Zappi et al., 1993). Their results indicated that peroxone did result in explosives removals in excess of 90 percent, yet it was not successful in meeting the 2 ug/l TNB standard after 60 minutes of batch treatment. TNB appeared to be resistant to perxone treatment. Spanggord et al., (1997) investigated the reaction of peroxone with aminodinitrotoluenes. Their findings were that laboratory oxidation of ADNTs by peroxone proceeds rapidly to primarily mineralized products. Ozone in the peroxone system appeared to dominate the ADNT removal mechanism.

Fenton's Reagent

Fenton's Reagent is a term used for the reaction of hydrogen peroxide (H_2O_2) with ferrous iron (Fe^{2+}) to produce OH radicals. The oxidizing properties of this mixture of H_2O_2 and Fe^{2+} salts were first observed by Fenton at the end of the last century. But the identification of the hydroxyl radical as the oxidizing species didn't occur until forty

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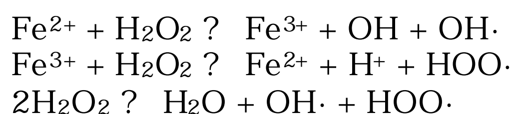
years later (Walling, 1975). Fenton's Reagent is recognized as one of the oldest and most flexible oxidizing reactions available (Li and Shea, 1997). Recently, considerable attention in the field of environmental research has been focused on Fenton's Reagent due to its proven ability to oxidize recalcitrant organic compounds (Sedlak and Andren, 1997). Fenton's Reagent is an effective technology for the treatment of TNT contamination in water and soils (Li and Shea, 1997; Brian et al., 1998). However, the build-up of trinitrobenzene (TNB) is of concern. Fleming (2000) conducted experiments on AOPs treatment for remediation of explosives contaminated soil. The results show that Fenton's Reagent was effective at degrading TNT to TNB, but TNB remained resistant to further treatment. The hydroxyl radical is formed according to the following equations:



$$Fe^{2+} + H_2O_2 \text{ ? } Fe^{3+} + OH + OH\cdot$$
$$Fe^{3+} + H_2O_2 \text{ ? } Fe^{2+} + H^{+} + HOO\cdot$$
$$2H_2O_2 \text{ ? } H_2O + OH\cdot + HOO\cdot$$

The major advantages of Fenton's Reagent as a hazardous waste treatment technology are: (1) there are no chlorinated organic compounds formed during the oxidation processes as is the case with chlorination; (2) both iron and H_2O_2 are cheap and nontoxic; (3) there is no mass transfer limitations associated with either reagent because of their homogeneous catalytic nature and high solubilities; and (4) there is

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no light involved as a catalyst, so reactor design is much simpler than those used with UV lighted systems (Huang et al., 1993).

The use of Fenton's Reagent recently has been shown to effectively oxidize a wide range of sorbed and biorefractory contaminants in soils and groundwater (Li and Shea, 1997). Under appropriate process conditions, adsorbed contaminants can be oxidized within hours, much faster than if they would desorb naturally and be removed via ground water advection. However, the mechanisms of this enhanced degradation of adsorbed contaminants have not been elucidated.

Li and Shea (1997) developed a study on the potential for remediating TNT-contaminated soil by direct Fenton's Reagent. Within 24 hours, the Fenton's Reagent oxidized TNT in a soil slurry (1:5 wt./vol. Soil: H_2O ratio) from 500 ppm to below 17.2 ppm (often a USEPA remediation goal for TNT-contaminated soil). TNB was identified as the key by-product from TNT oxidation, and it appeared to be resistant to further oxidation. Sherman et al., (1998) evaluated the treatment of TNT in water and soils using Fenton's Reagent. In solution, TNT was rapidly degraded after three sequential additions of H_2O_2 and Fe applied at a molar ratio of 25:15:1 (H_2O_2: Fe^{2+}: TNT) and a pH range between 2.5 and 3. After the 120 minutes reaction, the concentration of TNT had decreased by 98% (from 200 ppm to 0.31 ppm). A soil slurry of 100,000 ppm H_2O_2 and 1000 ppm Fe oxidized 95% of TNT in soils after 8 hours.

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Further treatments with 100,000 ppm H_2O_2 resulted in further TNT degradation, however 1 to 2% of TNT remained in an untreatable state on the soil surface.

Integration of the Biotreatment Technology and Chemical Technology in Treating Chemical Pollutants

The integration of biological and chemical treatments in order to improve the overall effectiveness of these stand-alone treatment technologies has been proven by several researchers. Wang (1999) performed a bench scale study to evaluate the effectiveness of using chemical oxidation processes to enhance the biotreatment potential of petroleum hydrocarbon (TPH) contaminated soils. Various candidate oxidation strategies were evaluated as chemical priming steps. Using packed soil column experiments, her results confirmed that all three types of proposed chemical oxidation processes (ozonation, peroxone, and Fenton's Reagent) successfully increased the biodegradation potential of the contaminants in previously biologically treated soils. The petroleum hydrocarbon contaminants, especially the high boiling point hydrocarbons, were treated using chemical oxidation primed bioremediation through the use of a pre-bio/oxidation/post-bio technique (Wang, 1999).

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Kemenade (1996) reported that 24 hour ozone pre-oxidation period followed by 5 days of biodegradation using an unacclimatized activated sludge in the soil phase achieved greater phenanthrene removal rates by Kemenade (1995) than either chemical or biological degradation alone. Experiments by Lee et al., (1992) indicated that PCP biodegradation was enhanced by the addition of Fenton's Reagent. They conclude that pretreatment with Fenton's Reagent before biological treatment was more effective than direct biological treatment alone for removing high concentrations of PCP (Lee et al., 1992).

Fenton's Reagent appeared to be effective as both a pre- and post-treatment for PAHs in soil and sandy matrices (Kelly et al., 1991). As a pretreatment, Fenton's Reagent's efficiently removed PAHs from the solid matrices by either degrading them into carbon dioxide or oxidizing them into more biodegradable compounds. As a post-treatment step, Fenton's Reagent removed a significant number of PAHs that were resistant to biological degradation (Kelley et al., 1991). They conclude that either pretreatment or post-treatment with Fenton's Reagent enhances the biodegradation of PAHs within soil matrices.

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Table 2.1. General Classification of Microorganisms by Sources of Energy and Carbon

Classification	Energy source	Carbon source
Autotrophic:		
Photoautotropic	Light	CO_2
Chemoaututropic	Inorganic oxidation-reduction reaction	CO_2
Heterotrophic:		
Chemoheterotrophic	Organic oxidation-reduction reaction	Organic carbon
Photoheterotrophic	Light	Organic carbon

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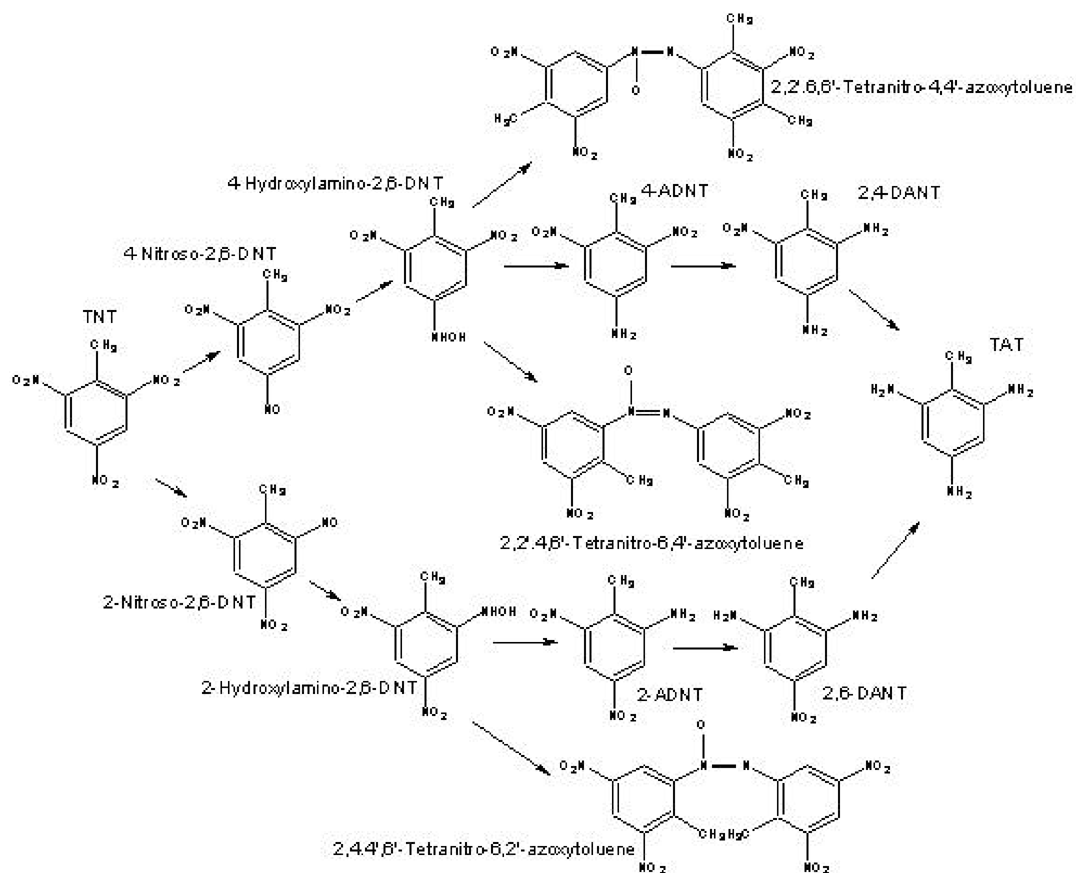

Figure 2.1. TNT Biodegradation Pathway

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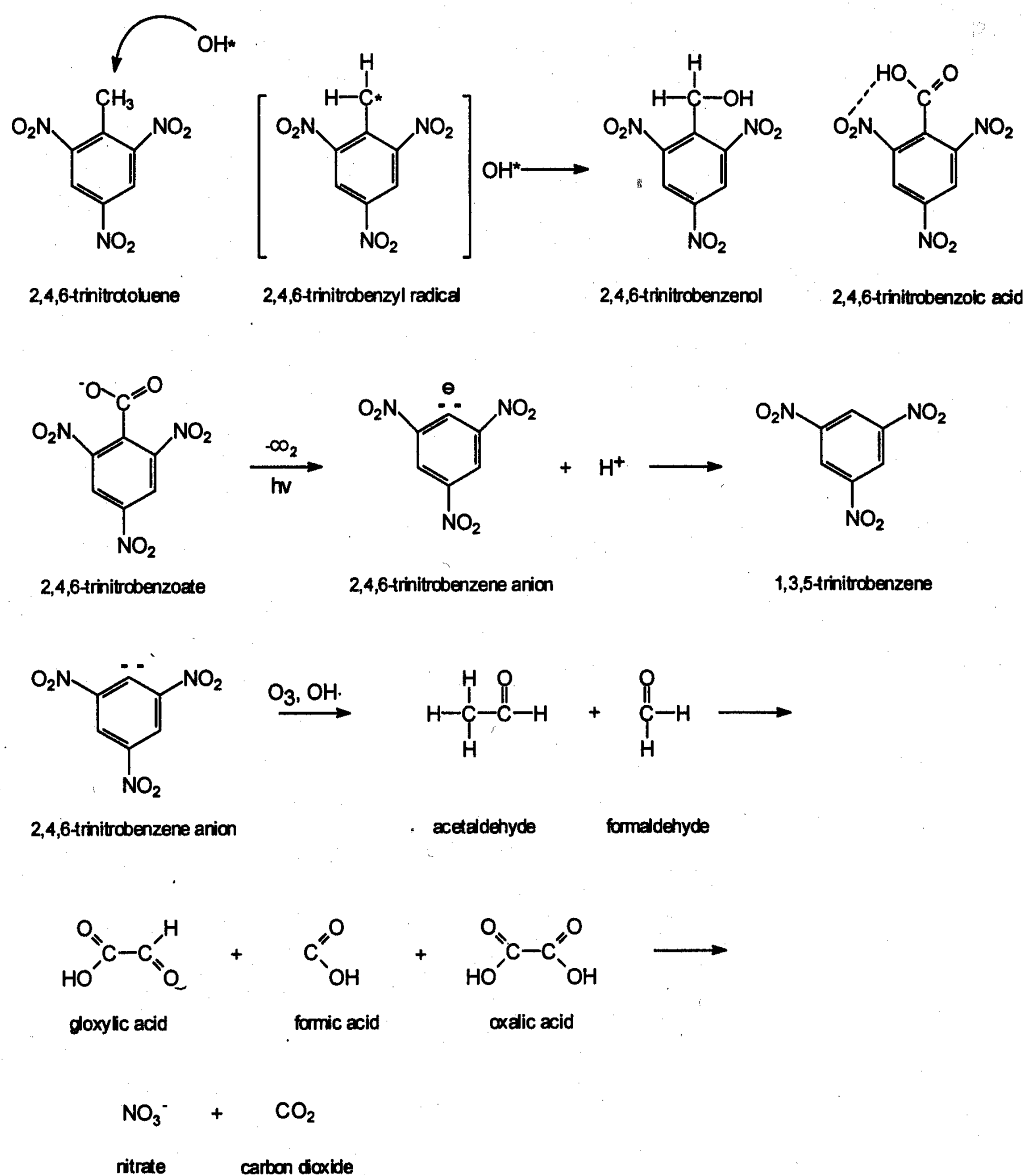

Figure 2.2. Proposed oxidation pathway for TNT and TNB during AOP treatment (reference: Zappi, 1995.)

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CHAPTER III

RESEARCH CONCEPT AND OBJECTIVE

Research Concept

Biological treatment of TNT will result in the production of the ADNTs or DANTs intermediates, which dominates the required incubation times to remediate the soil (Harvey, 1997). When using AOPs to treat TNT, oxidant-resistant products (such as TNB) are produced (Zappi, 1995). These by-products of incomplete TNT degradation require extensive treatment times (Hong et al., 1994). In summary, both treatment technologies have limitations associated with persistent by-products and/or slow degradation kinetics.

It is proposed that integration of the single mechanism treatment techniques discussed above (AOPs and biotreatment) could result in the development of a new and more aggressive treatment process than the use of any of these processes as stand-alone systems. ADNTs can be rapidly degraded by AOPs (Spanggord et al., 1997). So of primary interest are the use of biotic mechanisms that can be used to reduce TNT into aminodinitrotoluenes and diaminonitrotoluenes, which can then be

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oxidized using Fenton's Reagent oxidation process. This initial reduction step will eliminate the production of TNB, which is slow to degrade using chemical oxidation (Zappi, 1995).

A proposed integration mechanism is illustrated in Figure 3.1. In the first stage, one of the many well established biotic techniques can be used for conversion of the TNT into reduced metabolites via reductase-based co-metabolic mechanisms. As for the second stage, Fenton's Reagent can be applied to remove the reduced TNT by-products.

Objectives

The primary objective of this research is to examine the feasibility of using chemical priming as an enhancement to the bioremediation of TNT contaminated soils. The specific objectives were to:

1. Evaluate during the application of Fenton's Reagent would decreases in soil permeability occur.
2. Evaluate the fate of ADNT and TNT during the oxidation step using Fenton's Reagent under both buffered and non-buffered conditions.
3. Verify the effectiveness of selected biocell treatment conditions toward the biodegradation of TNT.
4. Optimize bioslurry treatment conditions toward the biodegradation of TNT.

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5. Optimize Fenton's Reagent Process toward both TNT and ADNT oxidation within soil matrices.
6. Determine overall effectiveness of applying both bioremediation and Fenton's Reagent on treating TNT contaminated soil comparing this results to each of the stand-alone technologies.

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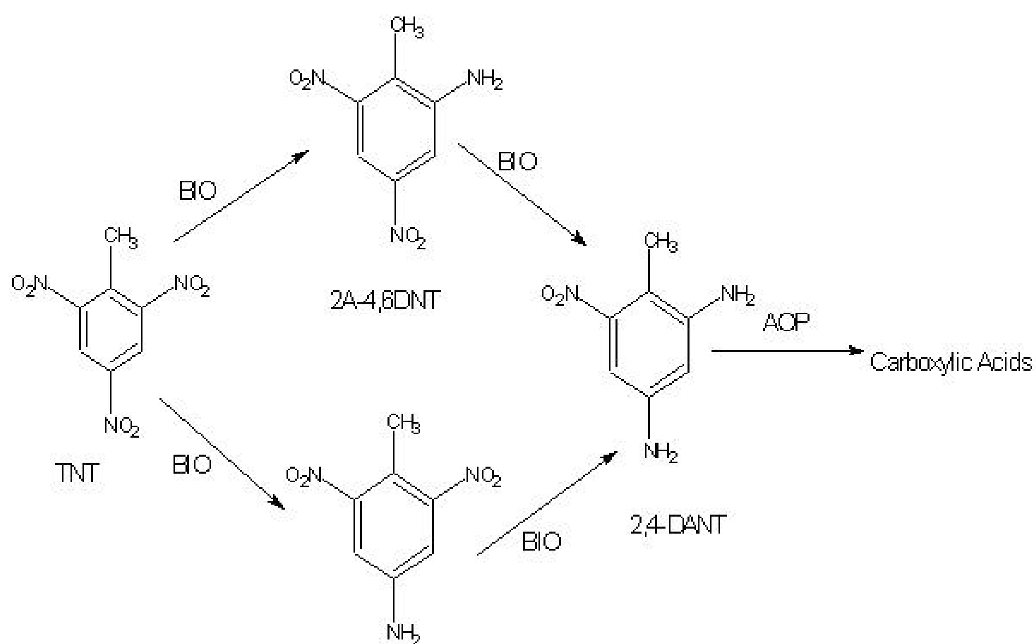

Figure 3.1. Proposed mechanism for the joint treatment of biological technology with AOP

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CHAPTER IV

MATERIALS AND METHODS

Materials

Soils

Two soil samples were used in this study. These soil samples were obtained from either an explosives contaminated site in Chattanooga, Tennessee (Volunteer AAP) or an explosive contaminated site in Weldon Springs, Missouri (Weldon Springs AAP). As a result of past military-related activities, these soils became contaminated with explosives compounds. Both soils were excavated by hand and placed into three 5-gallon plastic buckets, sealed, and transported to the laboratory, where they were stored until needed. Collection of the Chattanooga soil was performed during February 2000. Collection of the Missouri soil was done in 1998 by Dr. Mark Bricka during a field project conducted for the US Army of Engineers Waterways Experiments Station. Both soils were sieved manually with a US Standard No. 5 Sieve (4.0 mm) to remove sticks, rocks, and other debris. To accomplish this, wetted soil was manually pushed through the mesh sieve using a large plastic spoon.

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Sand (Control)

Common filter sand was purchased from a local store for use in evaluating potential hydraulic conductivity changes during application of Fenton's Reagent within porous media. The reason for the selection of filter sand was because it is homogeneous, clean, and has high K (hydraulic conductivity) eliminating problems caused by heterogeneity associated with real soils and lengthy experimental run times.

Nutrients

Ammonium nitrate (NH_4NO_3) and ammonium hydrogen phosphate ($[NH_4]_2HPO_4$) (both obtained from Fisher Scientific Company) were utilized as nitrogen and phosphorus sources during the biotreatment experimental phases.

Surfactant

Tween 80 (polyoxyethlene sorbitan ester) was used as the surfactant source because it is nonionic, and nontoxic, thus readily biodegradable. The sample used in this study was purchased from Baker Chemicals. It was successfully used in other studies involving the biodegradation of explosives (Harvey, 1997).

Bacteria Seeds

Anaerobic bacteria was obtained from the Tuscaloosa Waste Water Treatment Plant located in Tuscaloosa, Alabama. The actual source of

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the bacteria was an anaerobic digestor located on-site. It was used in the biocell experiments as the bacteria source.

Co-Metabolites

Molasses and sodium-acetate were both evaluated as cometabolites. Molasses (Grandma's Inc.) was purchased from Walmart and the sodium-acetate was obtained from Aldrich Chemical Company.

Hydrogen Peroxide

Hydrogen peroxide solutions were made from a 3% (w/w) hydrogen peroxide solution purchased from Fisher Scientific Inc. Solutions were formulated by diluting the original solution with distilled water (DI) water. Solutions were made freshly right before each experiment to prevent decomposition over time.

Iron Salt (Fe^{2+})

Iron salt serves as one of the components of Fenton's Reagent. Ferrous sulfate ($FeSO_4 \cdot 7H_2O$) was selected for use as the iron source. It is an inexpensive source of iron that is also soluble (Bigda, 1995). It was obtained from Fisher Scientific Inc.

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Soil Hydraulic Conductivity Experiments

The objective of this experiment was to evaluate if the Fenton's Reagent would change the soil hydraulic conductivity by forming Fe^{3+} (which is a non-soluble ion), which would precipitate and deposit onto the soil particles, and hence, decrease soil hydraulic conductivity. This was of concern because dramatic reductions in K would inhibit future remediation attempts because limited to no reagents will be able to be introduced into the soil mass.

A schematic of the permeameters used in these experiments is shown in Figure 3.1. The main body of the column was constructed using 12-inch long and 2 inch ID clear PVC pipe. Both ends of the column were capped with a 2-inch PVC union. The bottom end of the column reactor was reduced to ¼ inch NPT threads and a Quick-Connect TM was inserted to the bottom end of the reactor to connect the PVC union with the additive injection line (¼ inch Teflon tubing). The injection line was used as either a gas sparging line, solution pumping line, or drainage line depending on the stage of experimentation. The top end of the column was capped with a ½ inch Swagelok TM male connector upon which a ½ inch female connector could be attached. The female connector was connected to a ¼ inch PVC pipeline for transport of the off-gas to the ozone destruction unit during the ozonation stage of

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the experiments. Before loading the soil into the column, a piece of stainless-steel screen was inserted at the bottom of the column to support the contents of the column. On top of the screen, 1.5-inch layer of washed pea gravel was loaded to further support the contents and to provide distribution of injected solutions. This layer was overlaid with a non-woven geotextile fabric, which served as a filter to prevent soil fines from falling into the pea gavel layer and thus clogging the connector assembly. The geotextile was cut to tightly fit within the inside wall of the column. Three inches of soil was loaded on top of the geotextile. Taking where the geotextile was located within the column as the zero height line, 1-inch increments were marked with a laboratory marker pen on the outside wall of the column until the 9-inch point was reached. After all parts were assembled, leakage tests were performed with both water and air to ensure the proper fit of the system.

After the soil was loaded into the column, clean water was first pumped through the bottom until it reached the 9 inch mark, leaving 6 inches of water head above the surface of the soil. This water was allowed to soak for at least two hours to ensure that the soil was saturated. Then, the drainage line was connected to the outlet of the column reactor and the water in the column allowed to drain. At the moment the connector was connected, a timer was started to record the time required for the water level to drop from the 9-inch mark to 3-inch

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mark. This procedure was run in triplicate, and these data used to establish the baseline hydraulic conductivity of the soil. Next, a series of four injections of $FeSO_4$ solutions were pumped through the soil at concentrations of 1,000 ppm, 2,000 ppm, 4,000 ppm, and 5,000 ppm. These solutions were pumped each time until enough was added to bring the solutions to the 9-inch mark. Each time, the solutions were allowed to soak for 2 hours. This “soaking” period allowed the Fe^{2+} to diffuse into the soil matrix. Then, the iron solution was drained and the time required for H_2O level to drop from the 9-inch mark to the surface of the soil recorded. After each iron applications, the solutions of hydrogen peroxide pumped into column until the water level hit the 9-inch mark. The H_2O_2 solution was allowed to remain there for the H_2O_2 to react with the Fe^{2+} previously soaked into the soil. Then, the H_2O_2 solution was drained and the time required for the solution level to drop to the 3-inch mark was recorded. All runs were conducted in duplicate or triplicate.

Oxidation Evaluation Experiments

Liquid Phase Experiments

The fate of ADNT and TNT during reaction with oxidation species generated from Fenton’s Reagent was first examined in the liquid phase to assess their relative reactivity. A 250 ml amber glass flask was used as the reactor for these experiments. The contents in the flask were mixed

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using a magnetic stir plate with a stir bar for providing continuous mixing during the experiment. A burette was filled with 0.1N sodium hydroxide solution, which served as a buffering solution to control the pH of the reaction system at around pH=7. The pH was continuously monitored using a pH meter and small increments of a base solution (0.1N NaOH) added as needed.

Aqueous solutions of the test compounds (ADNT and TNT) were produced by dosing the pure chemicals in crystal form into distilled water and the solutions mixed for at least a week before use. This allowed for the complete dissolvtion of the chemicals into the water. The solutions were mixed within a 1000 ml amber flask, which was mixed continuously on a stir plate. $FeSO_4$ and H_2O_2 solutions were prepared on the day of experimentation. Because $FeSO_4$ will instantly react with H_2O_2, special attention was paid to the order of adding of the stock solutions. First, 50 ml of the prepared explosive solution and 50 ml of $FeSO_4$ solution were measured and poured into the amber reactor. Then, the stir plate was turned on to initiate mixing. Lastly, 50 ml of the hydrogen peroxide solution was added. The moment H_2O_2 was added, a timer was started to record the length of the experiment. At that point, NaOH was dropped into the reaction system to obtain the desired pH level. Samples were collected at test times of 5, 10, 15, 20, 25, and 30 minutes using a 50 ml beaker. These samples were analyzed for H_2O_2 and explosive

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concentrations. After sample collection, the H_2O_2 levels were determined, and then 0.5 ml of a saturated catalase solution added into the small sample beaker to cease the oxidation reactions. Post testing with catalase using HPLC indicated no interference with the HPLC (Zappi, 1995). Samples were filtered before analysis for explosives via HPLC. If complete degradation of the organics had occurred during the first 5 minutes (determined from HPLC analysis), then the test was rerun and samples collected more frequently over a tighter time range to gain a better understanding of the rate of degradation. Different combinations of reactant concentrations for each reactant were selected to see how they would impact explosives degradation. The experimental conditions were summarized in Tables 4.1. and 4.2.

Soil Phase Evaluation Experiments

The objective of this set of experiments was to see how the soil system change the Fenton's Reagent effectiveness towards oxidizing the explosives as compared to their relative performance in the liquid phase. Fenton's Reagent oxidation experiments were carried out using soil that had been previously biotreated to obtain a soil system containing both TNT and its biotransformation by-products. The reactors used in this study were amber 500 ml Erlenmeyer flasks mounted on a shaker table. Different dosages of Fenton's Reagent (listed in Table 4.3.) was applied to the reactors. These experiments were conducted in duplicate. In each

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application, the soil slurry was first soaked with the ferrous iron solution for 1 day, mixed well with the soil by stirring the contents with a spatula, and allowed to sit for one day giving the iron salt solution time to soak into the soil, then the hydrogen peroxide solution sequentially added as rapidly as possible while preventing foaming from spilling the flask contents over the top of the reactor. Each additional application was added when there was no hydrogen peroxide residual present from the previous step, which usually took about 2 days. The soil used in this testing was the Chattanooga soil.

Integration Experiments

The biocell reactors used in this study were composed of 1.8-liter stainless steel measuring cups covered with 9-inch ID pie trays to prevent light from entering the reactor. Each biocell was loaded with approximately 1,000 g of soil and 1,000 ml of distilled water poured into the reactor leaving about 1 inch of headspace within the measuring cup. Soil used in this set of study was obtained from Chattanooga, Tennessee. The TNT contamination level varied among buckets. Integration experiments performed on both high level contamination soil and low level contamination soil. With the high level contamination soil, nutrients and molasses were added on a weekly base. With the low level contamination soil, amendments were only added at the initial of the experiments. The objective was to determine if when treating mildly

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contaminated soils, the operations could be dramatically simplified, and once simplified, would these activities adversely impact the performance of the oxidation step or delay TNT conversion due to potential cometabolite/nutrient limitations.

Biocell reactors were set up to achieve the desired degree of conversion of TNT into intermediates (ADNTs and DANTs) within the soil, then the soil further treated with Fenton's Reagent to evaluate if this oxidation step had enhanced removal of the parent and by-products over further biotreatment (as determined from past MSU efforts). All testing conditions are listed in Table 4.3. For the high level contamination soils, this testing was done after the biotreatment phase. Several applications of Fenton's Reagent were performed on these biocell contents. For the low level contamination set of experiments, the soil post-biotreatment was divided into two beakers and the targeted Fenton's Reagent system applied into each of the two beakers.

During the biological step, the addition of nutrients and cometabolites was made in dissolved form by mixing the appropriate amounts of pure chemicals with distilled water. This was accomplished by first solublizing these components into 1000 ml distilled water in a beaker, then mixing the solution thoroughly into the wetted soil. Anaerobic digester sludge (from Tuscaloosa, Alabama) was added on a weekly base and mixed into the soil slurry using a spatula. Samples were

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collected once a week. Every time a sample was taken, the pH and ORP of the biocell contents were measured. After samples were taken, they were extracted using an Accelerated Solvent Extraction unit (ASE), and the extracts analyzed by HPLC for explosives and associated by-products. All tests were conducted in duplicate and all the analytical samples were collected in triplet.

Bioslurry Experiments

The objective of this set of experiments was to screen several candidate biological treatment strategies in order to optimize the biotreatment conditions for TNT degradation using an aerobic bioprocess. This allowed for a rapid comparison of the relative performance of aerobic versus anaerobic biotreatment. The soil-water slurries were formulated by combining 160 grams of contaminated soil (wet soil weight with a moisture content of 14%) with 300 ml distilled water to form a 30% (w/w) slurry that was added into 500 ml Erlenmeyer flasks. The flasks were placed on an orbital agitation table (Model 49235, Barnstead/Thermolyne) that was set at 250 rpm. Aeration was provided via agitation. All experiments were performed in duplicate at room temperature. The soil used in this testing was the Weldon Springs soil.

The experimental conditions performed using the shake flask systems are listed below:

a. Condition 1: Added distilled water (experimental control)

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b. Condition 2: Added distilled water, nutrients, cometabolite (sodium acetate), and bacterial seed (digester sludge)

c. Condition 3: Added distilled water, nutrients, cometabolite (sodium acetate), surfactant (Tween 80), and bacterial seed (digester sludge)

d. Condition 4: Added distilled water, nutrients, cometabolite (corn starch), and bacterial seed (digester sludge)

e. Condition 5: Added distilled water, nutrients, cometabolite (molasses), and bacterial seed (digester sludge)

Cometabolite, nutrients and surfactant were amended on a weekly base. ORP and pH were monitored every time a sample was collected for chemical analysis. Samples were centrifuged to separate the soil phase from the water phase. The liquid phase was filtered using a Gelman Glass Fiber filter (nominal 7 μm pore diameter) prior to HPLC analysis for explosives. The soil phase was extracted using a Dionex ASE extraction unit (discussed later), then extracts analyzed by HPLC.

Analytical methods

Moisture Content (MC)

Wet soil samples were dried in a laboratory oven set at 105°C for 12 hours. The calculation used to determine MC was:

$$MC\ (\%) = 100(W_{wet} - W_{dry})/W_{wet},$$

where,

W_{wet} = Total weight of wet soil, g

W_{dry} = Dry weight of the soil, g

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pH

pH measurements were performed using an Accumet Model 15 pH meter (Fisher Scientific). The pH meter was calibrated daily using standard buffer solutions of pH-4, pH-7, and pH-10 (Fisher Scientific). The pH probe was stored in pH 7.0 buffer when not in use.

Soil Extraction

An ASE 200 Accelerated Solvent Extractor (Dionex Corporation, USA) was used to extract the explosives from soil samples. The extraction conditions used with the ASE unit are listed below:

Solvent:	Acentonitrile
Oven Temperature:	100°C
Pressure:	1500psi
Oven Heat-up Time:	5 min
Static Time:	5 min
Flush Volume:	60% of extraction cell volume

Explosives Analysis

Explosive compounds were analyzed using a Hewlet Packard 6890 high performance liquid chromatograph (HPLC) equipped with a diode array detector. TNT and its transformation products were separated by HPLC on a reverse phase LC-8 column (flow rate 1.5 ml/min; mobile phase-18% of 2-propanol and 82% of deionized water). Soil and aqueous

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samples were prepared for analysis by adding acetonitrile to the concentrated sample. Before samples were injected into the HPLC, they were filtered using a Gelman AE Glass Fiber Filter, which helped to protect the various components of the HPLC system from clogged lines due to particulate blinding. This method generally followed those detail in the USEPA Method 8330 (USEPA, 1997).

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Table 4.1. TNT Liquid Phase Oxidation Experimental Conditions*

Condition	Fe^{2+}concentration	H_2O_2 concentration	pH Condition
1	30 ppm	100 ppm	Neutral
2	30 ppm	300 ppm	Neutral
3	30 ppm	900 ppm	Neutral
4	100 ppm	900 ppm	Neutral

*Performed in duplicate

Table 4.2. ADNT Liquid Phase Oxidation Experimental Condition*

Condition	Fe^{2+}concentration	H_2O_2 concentration	pH Condition
1	30 ppm	300 ppm	No pH adjustment
2	30 ppm	300 ppm	Neutral

*Performed in duplicate

Table 4.3. Soil Phase Oxidation Evaluation Experimental Condition*

Segment	Fe^{2+}concentration	H_2O_2 concentration
1	100 ppm	5000 ppm
2	100 ppm	20,000 ppm
3	2500 ppm	50,000 ppm
4	10,000 ppm	100,000 ppm

*Performed in duplicate

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Table 4.4. Integration Experiments Conditions*

Condition	Phase 1	Phase 2	
	Bioremediation	Fenton's Reagent Oxidation	
High Level Contamination	2% Molasses, 50 ppm Ammonium, 20 ppm Phosphate and 50 ml anaerobic digester sludge	2500 ppm Fe^{2+} /50,000 ppm H_2O_2	10,000 ppm Fe^{2+} /100,000 ppm H_2O_2
	2% Molasses, 50 ppm Ammonium, 20 ppm Phosphate and 100 ml anaerobic digester sludge	1,000ppm Fe^{2+}/ 100,000 ppm H_2O_2	10,000 ppm Fe^{2+}/ 100,000 ppm H_2O_2
Low Level Contamination	2% Molasses, 50 ppm Ammonium, 20 ppm Phosphate and 10 ml anaerobic digester sludge	100 ppm Fe^{2+}/ 5000 ppm H_2O_2	
		500 ppm Fe^{2+}/ 25000 ppm H_2O_2	

* Performed in duplicate

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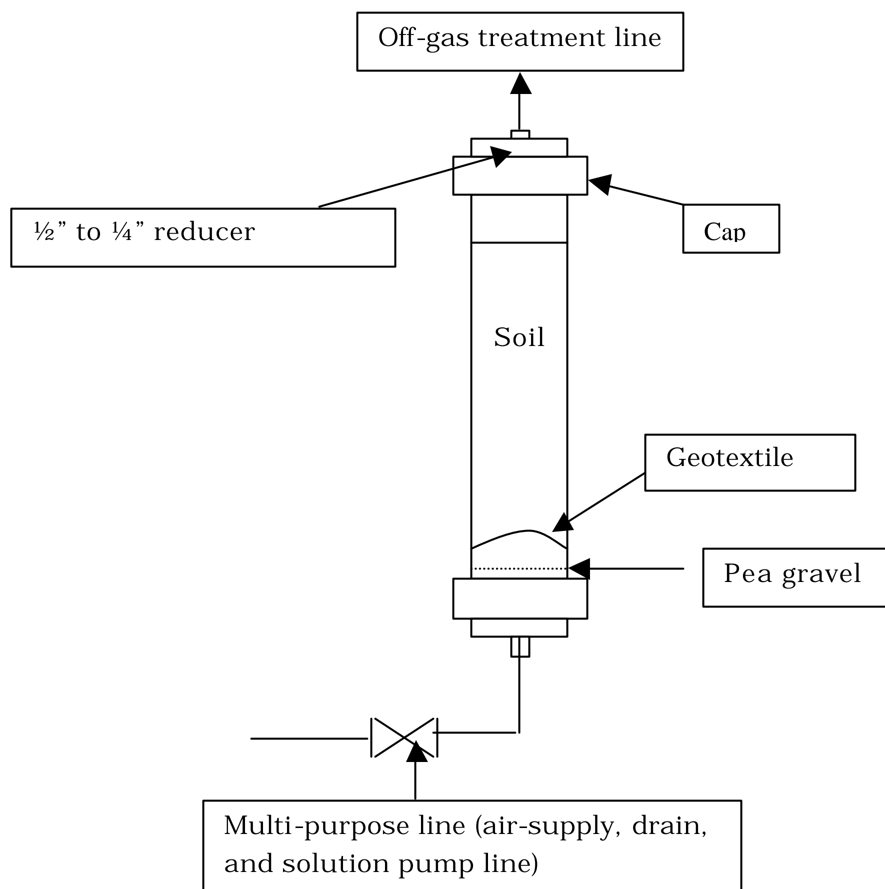

Figure 4.1. Schematic of Permeameter

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CHAPTER V

SOIL HYDRAULIC CONDUCTIVITY EXPERIMENTAL RESULTS

Hydraulic conductivity is the measure of how easily fluid flows through a material (for example, fractured rock, soil, or an aquifer media). The objective of this experiment was to evaluate if the Fenton's Reagent would change the soil hydraulic conductivity by forming Fe^{3+}, which is a non-soluble ion that would precipitate out; hence, decreasing soil hydraulic conductivity. Experiments were designed and carried out on the basis of Darcy's Law, which is expressed below:

$$Q = K i A \qquad (5\text{-}1)$$

where,
- Q = flow rate (cm^3/sec)
- K = hydraulic conductivity (cm/sec)
- *i* = hydraulic gradient (cm/cm)
- A = cross-sectional area of flow measured Perpendicular to the flow direction (cm^2)

The hydraulic gradient, *i*, describes the rate of change of headloss over the distance of water flow through the porous media. It is defined in algebraic form as:

$$i = (h_1 - h_2)/l \qquad (5\text{-}2)$$

where,
- h_1 = head at location 1 (cm)
- h_2 = head at location 2 (cm)
- l = length of sand column (cm)

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A permeameter is a simple device used to measure the hydraulic conductivity of a porous media (see Figure 5.1). Other than the parameters in Equation 5-2, all other parameters in Darcy's Law (*i*, A) are fixed values associated with the permeameter. The hypothesis for this testing was that by applying Fenton's Reagent, the soil hydraulic conductivity would decrease due to the formation of Fe^{3+}. By initially running clean water through the permeameter, a base line K is established, which served as a reference to calculate the percentage of change in K associated with the application of Fenton's Reagent.

Four sets of experiments were run using the same hydrogen peroxide concentration (1000 ppm) with increasing amounts of ferrous iron applied (1000 ppm, 2000 ppm, 3000 ppm, and 5000 ppm). As shown in Figure 5.2, the soil hydraulic conductivity decreased as the amount of iron added increased. The decrease is associated with the oxidation of the reduced iron into its insoluble form. With higher concentrations of ferrous iron, the hydraulic conductivity decreased incrementally as is shown in Figure 5.2.

The implication of this finding is that when applying Fenton's Reagent for the in-situ or surface added oxidation treatment of explosives contaminated soil, the soil hydraulic conductivity may very likely decease over the course of multiple applications. This proposes a potential hydraulic conductivity loss during oxidation treatment efficiency because

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the reduced K hinders the further delivery of additional oxidants into the soil matrix. This limitation becomes a critical limiting factor for the application of Fenton's Reagent.

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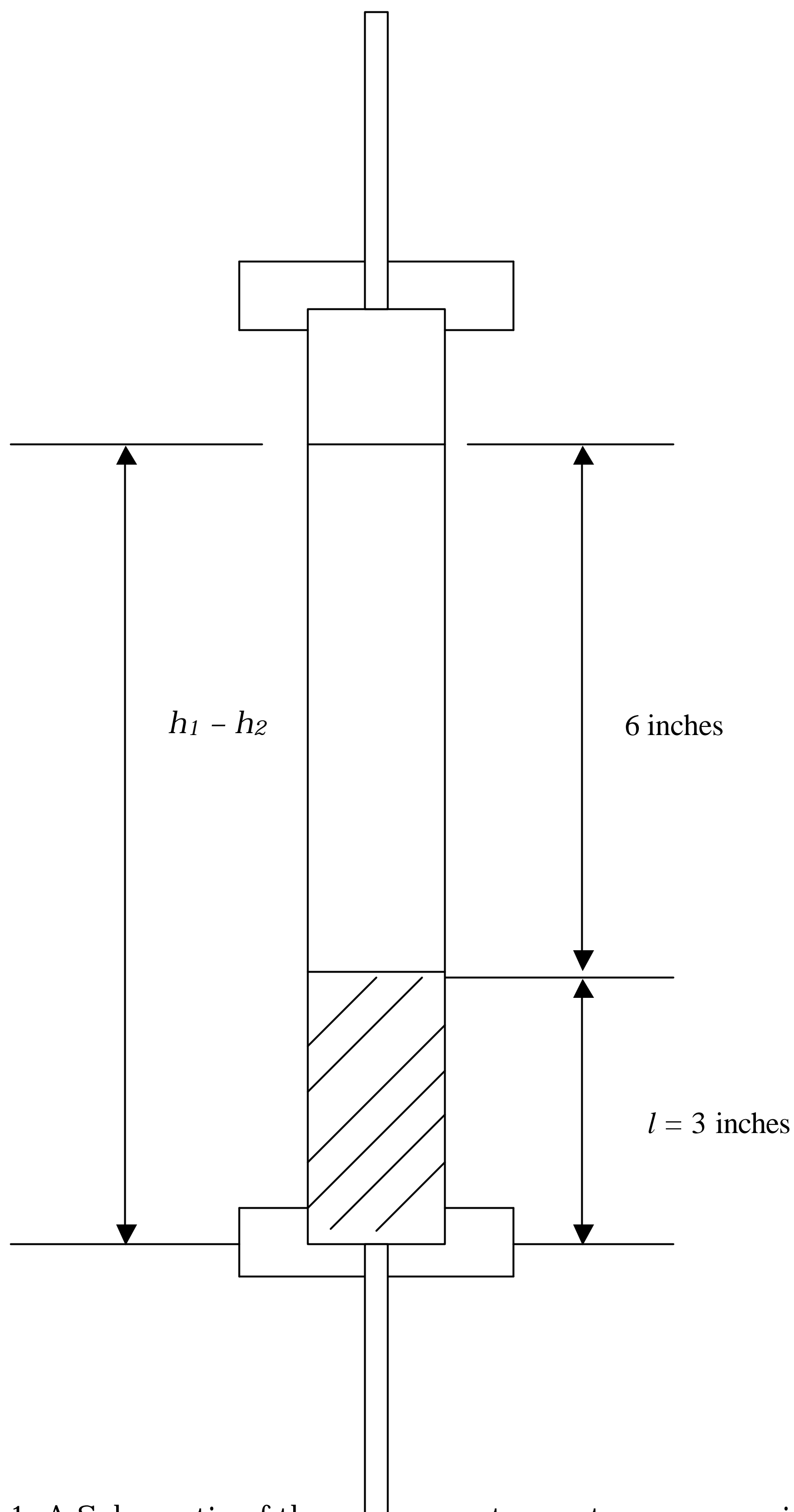

Figure 5.1. A Schematic of the permeameter system as associated key dimensions

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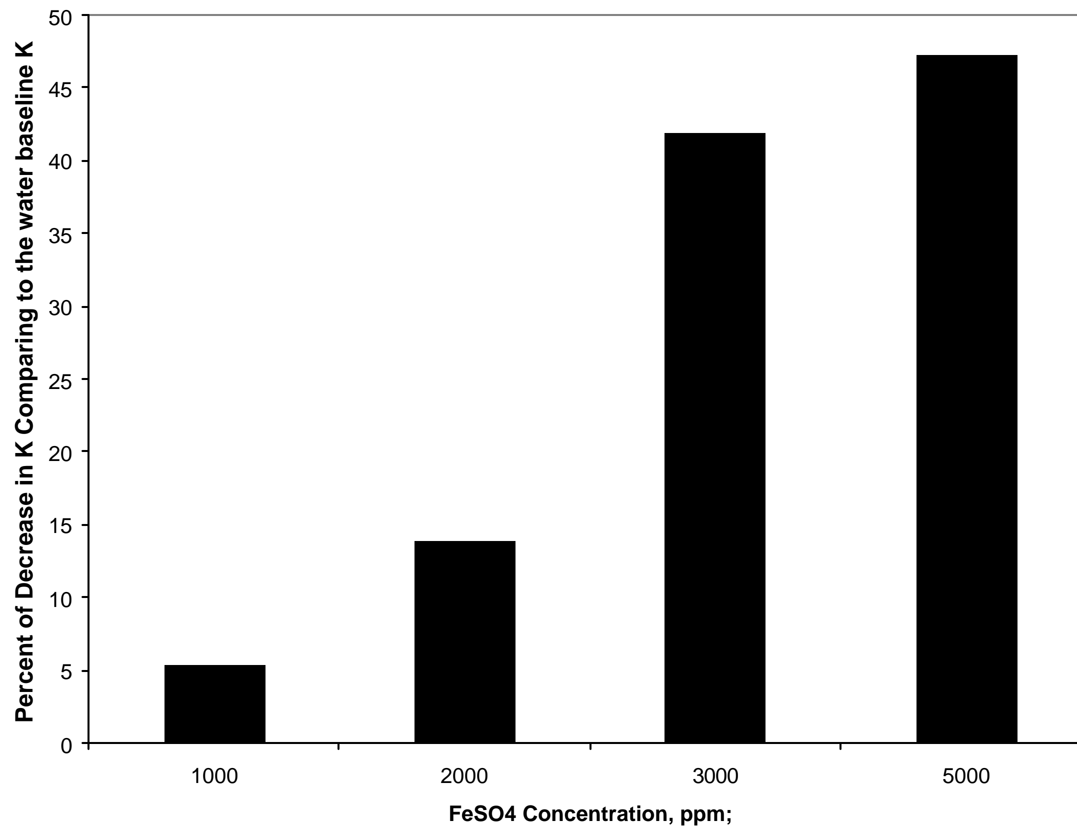

Figure 5.2. Effect Of Fenton's Reagent On Hydraulic Conductivity (Note: H_2O_2 concentration maintained at 1,000ppm)

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CHAPTER VI

OXDIATION EVALUATION EXPERIMENTAL RESULTS

Liquid Phase Oxidation Evaluation Experiments

When using advanced oxidation processes to degrade TNT, oxidant-resistant products, such as TNB, are produced (Hong et al., 1994). These by-products, derived from the incomplete degradation of TNT, require extensive treatment times for their subsequent removal (Zappi, 1995). In this study phase, aqueous TNT solutions were treated with Fenton's Reagent to determine the reactivity of this process toward TNT and to optimize the process dosing strategy toward the removal of TNT and its by-products. Additionally, one major category of biotransformation by-products of TNT is reduced nitrotoluenes (ADNTs and DANTs). These reduced by-products tend to dominate the required incubation times needed to bioremediate TNT contaminated soil (Harvey, 1997). Therefore, experiments were also conducted to evaluate the fate of ADNTs during oxidation using Fenton's Reagent with or without pH adjustment. The objective being that the relative reactivity of these by-products were of interest to prove the overall concept of our research hypothesis which is to first biodegrade TNT into its first-level

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amine by-products, which are believed to be more oxidizable compared to its parent compound TNT, while at the same time avoiding TNB formation. Hence, this approach may dramatically shorten reaction time.

For the various test conditions, all experiments were conducted in duplicate, with the averaged data plotted against time. Figures 6.1, 6.2, 6.3, and 6.4 present the results of this effort by plotting TNT fate, the formation of by-products, the consumption of H_2O_2, and the change of pH throughout the reaction. The applied H_2O_2 concentrations were varied: 100 ppm (Figure 6.1), 300 ppm (Figure 6.2), and 900 ppm (Figure 6.3). At the same time, the Fe^{2+} concentration was kept constant at 30 ppm dose. This was done to evaluate the effect of increasing H_2O_2 concentrations on TNT removal; thereby changing the H_2O_2: $Fe2^{+}$ ratio. In Figure 6.4, the Fe^{2+} concentration was increased to 100 ppm and the H_2O_2 concentration remained at 900 ppm. This was done to evaluate the effect of increasing the Fe^{2+} concentration on TNT removal using the higher H_2O_2 dose. The initial TNT concentration in all of the experiments was approximately 10 ppm and the pH was adjusted at neutrality.

Figures 6.1 and 6.2 both illustrate that within the first 5 minutes of reaction, over 30% of the TNT was removed through Fenton's Reagent oxidation using H_2O_2 concentrations of 100 ppm and 300 ppm, respectively. After the first 5 minutes, no further decrease in TNT concentration is observed. These data show that insufficient iron was

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available for the complete removal of TNT. The iron appears to be expended within five minutes of testing as witnessed by no more removal of the pollutants. TNB was generated as a by-product at the five-minute mark; however, no removal is noted beyond that time. These data show no reaction between TNT and the hydrogen peroxide, which agrees well with the observation reported by Zappi (1995). The H_2O_2 concentrations dropped gradually over the course of the reaction but were never completely depleted, which indicates that the rate limiting factor for this reaction is not hydrogen peroxide, but the ferrous iron. NaOH demonstrated fairly good pH adjusting capacity as the pH was held stable at around neutral throughout the reaction period for all of the tests.

Figure 6.3 shows that for the 900 ppm H_2O_2 dose, 10% of the TNT was removed during the first 5 minutes, and then remained at the same level beyond that period. This decrease was not as dramatic as those observed within Figures 6.1 and 6.2 (both achieved > 30% removal). Thus, this system was obviously less effective than the other two. This decrease in performance is further discussed later in this chapter.

Figure 6.4 shows that increasing the iron dose for the 900 ppm H_2O_2 dosed system yielded about 36% TNT removal during the first 5 minutes, and then, remained at this level throughout the remainder of the test. Increasing the Fe^{2+} concentration increased the amount of TNT

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removed, which further indicates that the limiting factor for this reaction is again the iron.

Table 6.1 summarizes the amount of TNT removed under these four different testing conditions studied. By comparing the data in Table 6.1, the optimal ratio of H_2O_2 to Fe^{2+} appears to be less than 10:1. Additionally, it can be seen that increasing H_2O_2 concentration within the optimal ratio provides no improvement. With increasing H_2O_2 concentrations, the amount of TNT reduced was decreased. This occurs because the excessive hydrogen peroxide acts as a radical scavenger consuming the free hydroxyl radicals (Hong et al., 1996). As with the other data, TNB formed within the first five minutes, then no change noted beyond that.

Figures 6.5 and 6.6 present the ADNT treatment data. As can be seen from these two graphs, ADNT was successfully removed within less than a minute with or without pH adjustment. The initial ADNT concentration was 10 ppm. These data indicate that this amino-nitrotoluene, which is a key by-product from the bioremediation of TNT, is much more reactive with the hydroxyl radicals than TNT. Thus, the hypothesis to biotreat TNT into amines first, which are then easily oxidized by Fenton's Reagent; hence, shortening overall treatment time appears to be valid within the liquid phase.

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Soil Phase Oxidation Evaluation Experiments

Natural soil material may reduce the effectiveness of Fenton's Reagent oxidation by competing with target contaminants for the OH· radicals or catalyzing excessive hydrogen peroxide decomposition (Li et al., 1997). Fenton's Reagent oxidation experiments were carried on reactors, which had been previously biotreated to obtain a soil system with both TNT and its biotransformation by-products (ADNTs) present. The objective of these sets of experiments was to see how the biostimulated soil system would change the effectiveness of Fenton's Reagent towards oxidizing the explosives as compared to their relative performance in the liquid phase (discussed above).

Fenton's Reagent was applied at 4 different dosing conditions. With each dosing condition, Fenton's Reagent was applied several times. These experiments were conducted in duplicate. In each application, the soil slurry was first soaked with the ferrous iron solution for 1 day, then the hydrogen peroxide solution sequentially added as rapidly as possible while preventing foaming from spilling the flask contents over the top of the reactor. Each application was added when no more hydrogen peroxide residual was detected in the slurry from the previous step, which usually took about 2 days.

Figure 6.7 is a plot of the averaged explosive concentrations versus time from the duplicate soil slurry oxidation experiments. The initial soil

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(previously biotreated) had approximately 16,000 ppm TNT and 7,500 ppm ADNTs present. After 18 applications of Fenton's Reagent, 62.5% of TNT and all the Total ADNTs were removed. These data agree well with the results from the liquid phase experiments in that ADNTs appear to be much more reactive than TNT.

The TNT and Total ADNTs oxidation degradation rates obtained under each dosing condition from Figure 6.7 are listed in Table 6.2. It is known from the previously performed liquid phase experiments that there appears to be an optimal dosing condition for the application of Fenton's Reagent. Several factors must be taken into consideration when optimizing a system of this type. The key factors are the pollutant concentration, the ratio of the ferrous iron to hydrogen peroxide, and the amount of H_2O_2 initially dosed. An excessive amount of H_2O_2 scavenges the free hydroxyl radical resulting in a less effective oxidation system. Generally speaking, there are lots of scavenging reactions competing for the hydroxyl radicals when using Fenton's Reagent to effectively treat soil. These scavenging effects may differ from soil to soil. Therefore, it is hard to generalize and apply an optimized treatment condition to a soil system without testing. Additionally, soil components may either enhance or decrease oxidation reactions depending on the type and level of each soil parameter impacting performance.

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As shown in Table 6.2, comparing the results for the first two dosing conditions, it can be seen that increasing hydrogen peroxide concentration, without changing the iron concentration, increased both the TNT and Total ADNT degradation rates. This illustrates that more hydrogen peroxide was needed to overcome the H_2O_2 scavenging reactions associated with the soil constituents. With a higher concentration of the iron salt and H_2O_2 (2,500 ppm Fe^{2+}/50,000 ppm H_2O_2), the highest TNT and Total ADNT degradation rates were observed. This is due to the increased amount of free hydroxyl radicals generated. But, when the hydrogen peroxide concentration reached a certain level (100,000 ppm), a decrease in the TNT degradation rate was observed. A possible explanation for this reduction in degradation rate is that at this H_2O_2 concentration, agglomerated soil particles were destabilized exposing new oxidizable material and adsorbed chemical species became solubolized, thus, greatly increasing oxidizer demand. In the lesser dosed systems, predominately freely solubolized reactants are oxidized.

The optimal Fenton's Reagent dosing condition among the four conditions tested for TNT oxidation in the soil phase appears to be 2500 ppm of Fe^{2+} and 50,000 ppm of H_2O_2 ($[Fe^{2+}]:[H_2O_2]$=20:1). According to the findings obtained from the liquid phase experiments, the 10,000 ppm Fe^{2+}/100,000 ppm H_2O_2 condition ($[Fe^{2+}]:[H_2O_2]$=10:1) should have performed the best. However, the difference between a dosing ratio of

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20:1 versus 10:1 is not considered significant. Upon review of the data presented in Figure 6.7, the rate of both TNT and ADNT removal is minimally impacted by dramatic increases in both hydrogen peroxide and iron salt. Increases in both reagents, while maintaining previously determined optimal dose ratios, did not dramatically improve performance. This suggests that in the soil phase, the oxidation of explosives using Fenton's Reagent is more mass transfer limited than kinetically limited. This is due to mass transfer limitations associated with desorption of the target pollutants from the soil particles.

Summary

These experiments clearly show that ADNTs are much more reactive than TNT. This finding clearly supports the research hypothesis that converting TNT to ADNTs results in a pollutant speciation much more conducive to chemical oxidation. Also, the liquid phase experiments clearly show the appearance of TNB as a by-product of incomplete TNT oxidation.

The soil phase experiments verified the results observed in the liquid phase experiments. The data strongly suggest that the removal of both TNT and ADNTs is mass transfer limited and not kinetically limited. This implies that either very high concentrations of Fenton's Reagent must be applied to overcome adsorption hindrances by oxidizing the sorptive bonds or lesser doses applied as the pollutants enter the liquid

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phase. The latter approach should reduce treatment costs, but require much larger remediation times.

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Table 6.1 TNT Removals under Different Testing Conditions in the Liquid Phase

[H_2O_2]	H_2O_2: Fe^{2+} Ratio	Amount of TNT Removed
100 mg/l	3.3:1	3 mg/l
300 mg/l	10:1	3.5 mg/l
900 mg/l	30:1	0.75 mg/l
900 mg/l	9:1	3.6 mg/l

Table 6.2. TNT and ADNT Removals under Different Testing Conditions in the Soil Phase

Fe^{2+}	H_2O_2	H_2O_2: Fe^{2+}	TNT degradation rate	ADNT degradation rate
100 ppm	5,000 ppm	50:1	137 mg/kg/d	110 mg/kg/d
100 ppm	20,000 ppm	200:1	189 mg/kg/d	140 mg/kg/d
2,500 ppm	50,000 ppm	20:1	233 mg/kg/d	156 mg/kg/d
10,000 ppm	100,000 ppm	10:1	130 mg/kg/d	48 mg/kg/d

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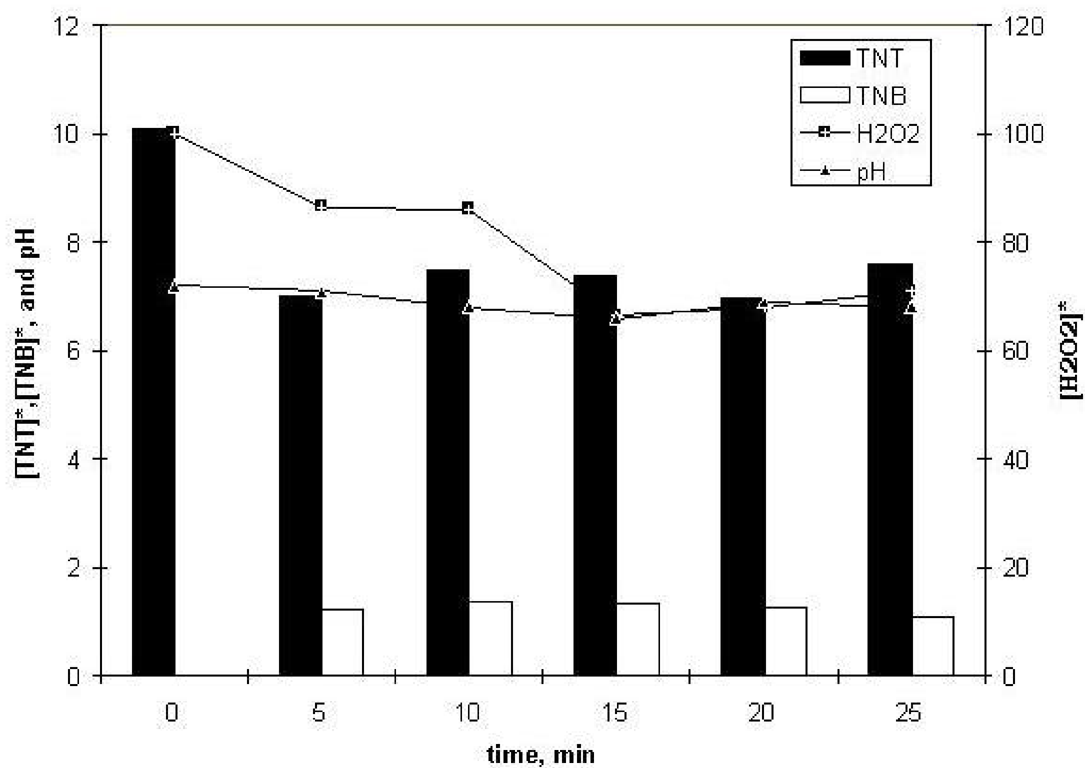

Figure 6.1. Oxidation of TNT using a H_2O_2: Fe^{2+} Ratio of 100 ppm: 30 ppm (Note: all concentrations are presented as mg/l and $[TNT]_0$=10 ppm)

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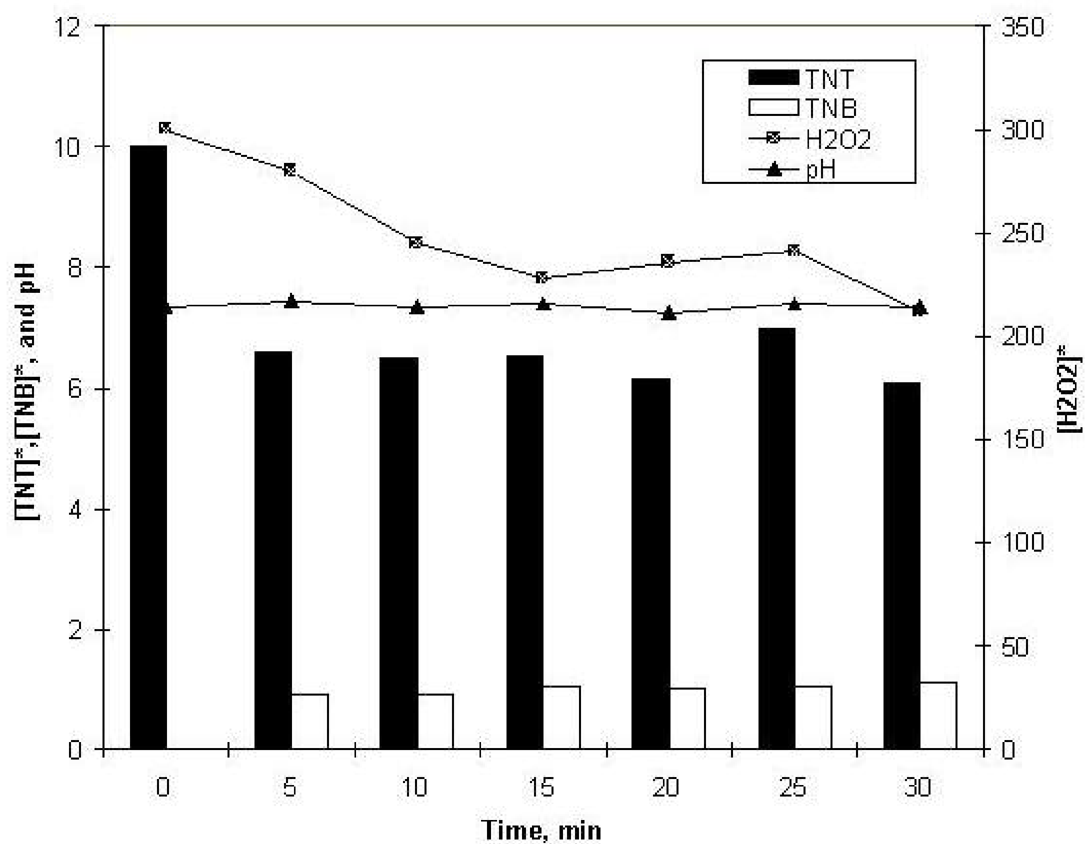

Figure 6.2. Oxidation of TNT Using a H_2O_2: Fe^{2+} Ratio of 300 ppm: 30 ppm (Note: All concentrations are presented as mg/l and $[TNT]_0$=10 ppm)

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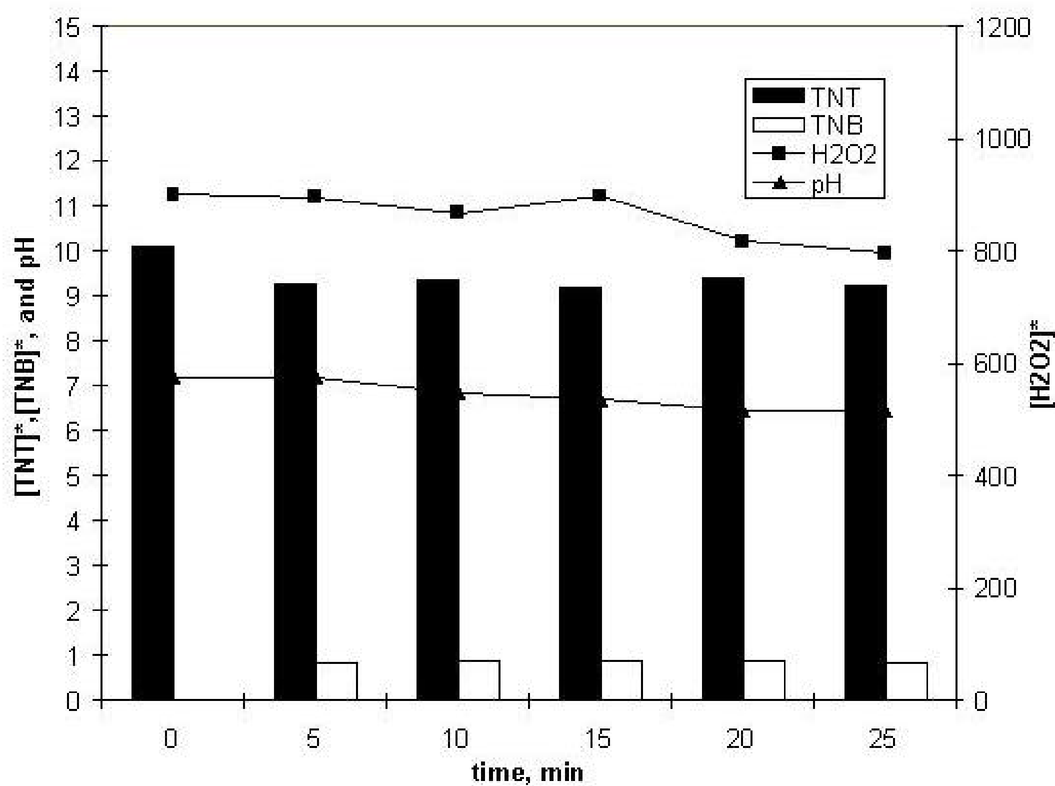

Figure 6.3. Oxidation of TNT Using a H_2O_2: Fe^{2+} Ratio of 900 ppm: 30 ppm (Note: All concentrations are presented as mg/l and $[TNT]_0$=10 ppm)

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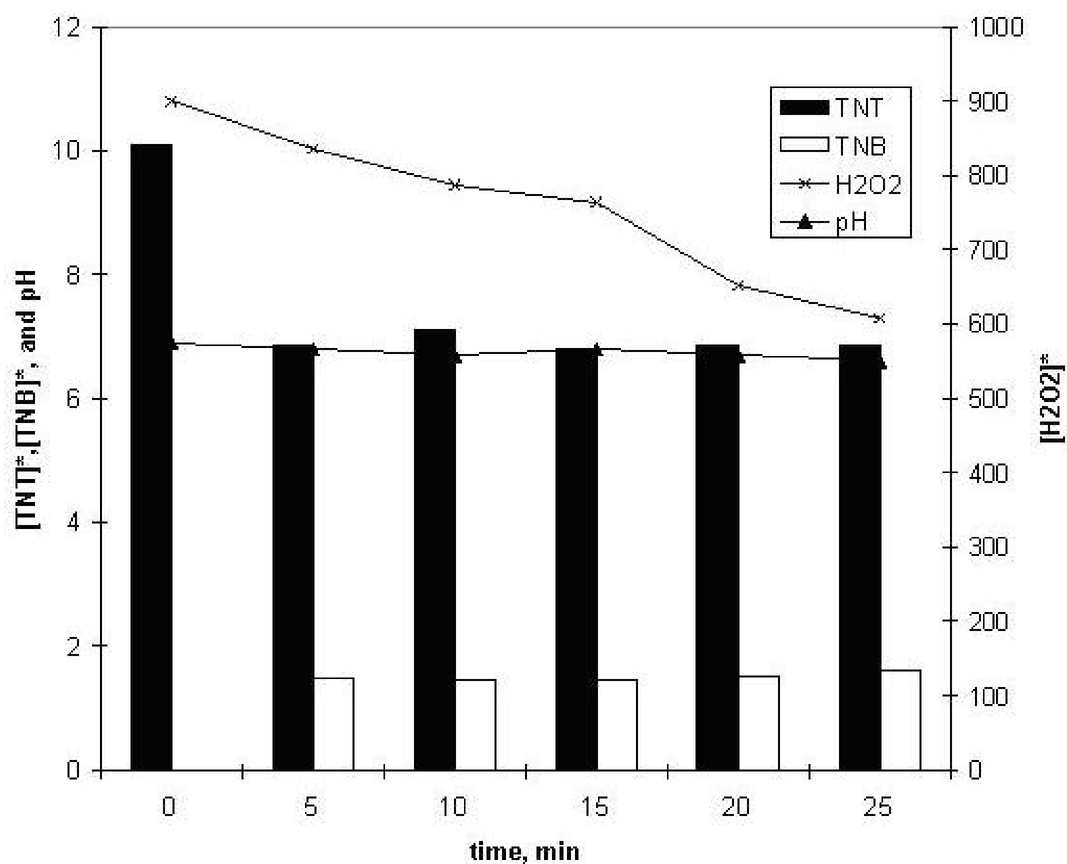

Figure 6.4. Oxidation of TNT Using a H_2O_2: Fe^{2+} Ratio of 900 ppm: 100 ppm (Note: All concentrations are presented as mg/l and $[TNT]_0$=10 ppm)

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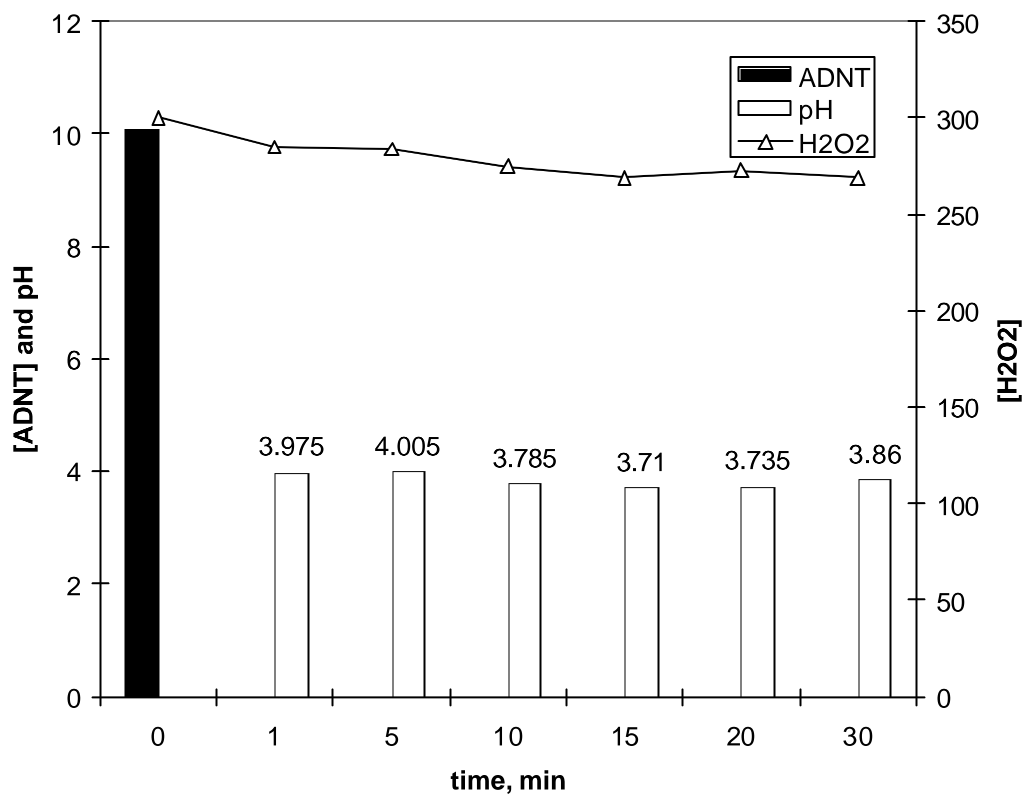

Figure 6.5. Oxidation of ADNT Using a H_2O_2: Fe^{2+} Ratio of 300 ppm: 30 ppm (Note: All concentrations are presented as mg/l and $[ADNT]_0$=10 ppm)

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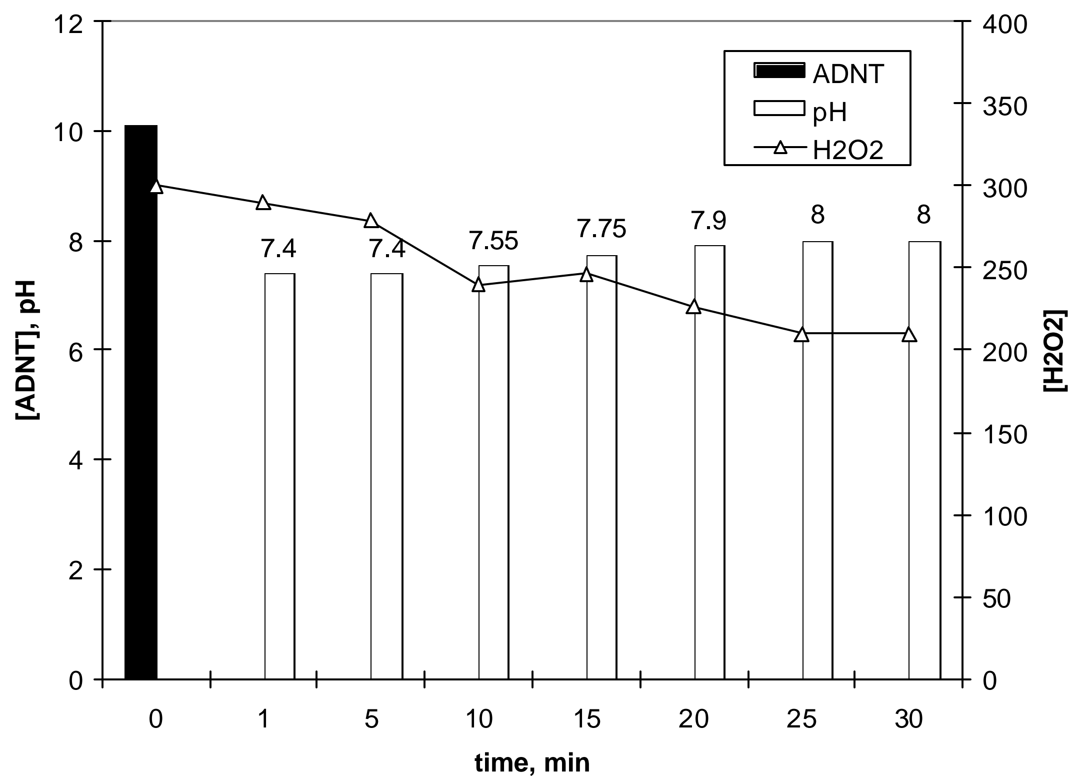

Figure 6.6. Oxidation of ADNT Using a H_2O_2: Fe^{2+} Ratio of 300 ppm: 30 ppm (Note: All concentrations are presented as mg/l and $[ADNT]_0$=10 ppm)

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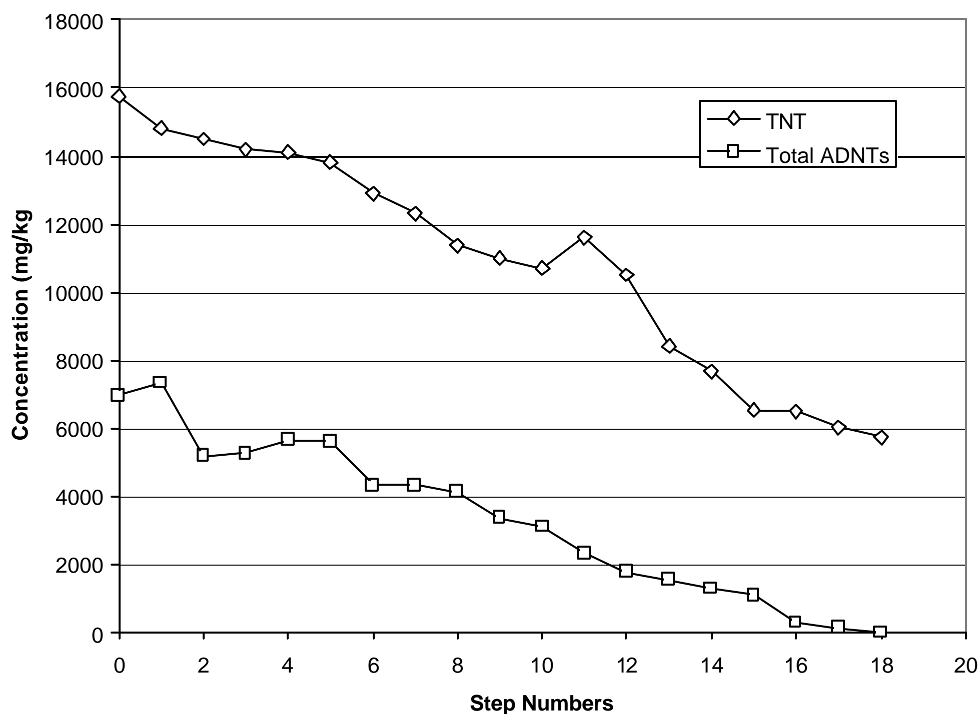

Figure 6.7. Plots of TNT and Total ADNTs Concentration Versus Time for the Soil Phase Oxidation Screening Experiments

Conditions:

1st through 4th application: 100 ppm Fe^{2+}/5,000 ppm H_2O_2
5th through 10th application: 100 ppm Fe^{2+}/20,000 ppm H_2O_2
11th through 16th application: 2500 ppm Fe^{2+}/50,000 ppm H_2O_2
17th through 18th application: 10,000 ppm Fe^{2+}/100,000 ppm H_2O_2

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CHAPTER VII

RESULTS OF INTEGRATION EXPERIMENTS

High Level TNT Contaminated Soil

This set of experiments was performed to evaluate the effectiveness of integrating biotreatment and AOP for improved treatment of TNT contaminated soil over either process as stand-alones. Experiments were conducted in duplicate and all the analytical samples analyzed in triplicate. Although they were integrated, the results are discussed separately from the biological step and oxidation step perspective. An illustration of the total integrated results will be shown at the end of the discussion as a summary of results.

Results of Biological Step

Figure 7.1 is a plot of E_h values versus time for the experiments performed in the biocell reactors. E_h is a measure of oxidation-reduction potential, which essentially measures the tendency of a substance to lose or accept electrons. TNT biotransformation proceeds through the step-wise reduction of the nitro groups to the amines. The more negative the E_h value, the deeper anaerobic conditions in the reactor. E_h values below

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–300 mV indicates methanogenic conditions, -200 mV indicates sulfate-reducing conditions, and –100 mV indicates nitrate-reducing conditions (also called anoxic) (Harvey, 1997).

For the biocell system maintained in this study, the molasses served as a cometabolite source that the microorganisms used for both growth and energy. The biocells were not continuously mixed allowing the bacteria within top layer of the water overlying the soil to consume the oxygen entering the water, thus, maintaining sub-aerobic conditions in the soil located at the bottom of the biocell.

The E_h values for the two conditions generally remained between a zero E_h and –60 mV over the course of the experiments, which indicates that anoxic conditions were maintained. E_h started off positive, then dropped gradually towards the negative range (-10 mV to –60 mV) within the first week.

Figure 7.2 is a plot of pH values versus time for the two biocell reactors. They generally behaved similar to each other, by first remaining at neutral conditions, then dropping to a pH of 4 by Day 41. This drop is likely due to organic acids produced during biodegradation of the molasses. The pH remained at approximately 4 for the remainder of the test period. These data, along with the E_h data, tend to indicate a lag time in the establishment of reduced conditions within the biocells. This lag is very likely attributable to a microbial lag that is common in start-up bioreactors.

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Figure 7.3 is a plot of percent TNT removed in the reactors versus time for the two biocell reactor systems. Both test conditions exhibited steady TNT disappearance with slight fluctuations seen at the initial stage of testing. This initial “data bounce” was likely due to the heterogeneity associated with the TNT contamination within the soil and soil fabric differences associated with this topsoil. Both biotreatment conditions yielded an overall TNT removal greater than 90%.

On Day 41, the amount of molasses and nutrients added weekly to the reactors seeded with the 50 ml digester sludge was doubled. This resulted in a dramatic decrease in the rate and extent of TNT removal over the remainder of the test. This trend shows that the bioactivity within the reactor was greatly stimulated when more cometabolite and nutrients were added. The depletion of the nutrients and cometabolite appeared to have been the limiting factor restricting the rate of TNT degradation. In the future, the amount and frequency of the addition of nutrients and molasses added to a bioreactor should be further evaluated to optimize the bioremediation process. This also shows that the adding the greater volume of bacteria seed (100 ml seed) to the bioreactors generally did not enhance TNT removal.

The calculated TNT biodegradation rates observed in both reactor sets are listed in Table 7.1. By comparing the rates obtained during the first 41 days of testing, it can be seen that increasing the amount of digester sludge added to the reactor appeared to very slightly increase

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TNT biodegradation rate. However, comparing the rate data from Day 41 to Day 64, the reactor system with lower seed volume, but higher molasses and nutrients levels (50 ml digester sludge), resulted in a much higher TNT biodegradation rate compared to the other reactor system (100 ml digester sludge level, but lower molasses and nutrients levels). This further illustrates that increasing the amount of the bacteria seed (from 50 ml to 100 ml) had little effect on change of the biodegradation rate compared to increasing the total supply of the nutrients and molasses fed into the reaction systems. Thus, it appears that the native soil bacteria are responsible for the bulk of the TNT removal observed.

Figure 7.4 is a plot of Total ADNT concentrations versus time for the two biocell systems. The rate of formation and rate of degradation of total ADNTs contribute to the net rate of change of Total ADNTs overtime. Initially, the net rates of change of Total ADNT were very similar for both of the two reactor systems. After Day 41, the rate of formation appeared to dominate the removal rate of ADNTs in both systems. On Day 41, the amount of molasses and nutrients added weekly to the reactors seeded with the 50 ml digester sludge was doubled, resulting in a dramatic increase in amount of Total ADNT formed over the remainder of the test. On Day 75, the reactors seeded with 100 ml digester sludge appeared to reach the turning point, and degradation of total ADNTs started dominating the overall change of Total ADNTs in this biocell set.

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The calculated net rates of change of Total ADNTs for both systems are listed in Table 7.2. When comparing the rate data over the first 41 days for the two reactor systems, it can be seen that increasing the amount of digester sludge added to the reactor slightly impacted the net rate of change of total ADNTs. The increase in the net rate of change of total ADNTs after Day 41 for reactor system seeded with 50 ml digester sludge also proves that the biotransformation within the reactor was greatly stimulated when more cometabolite and nutrients are available.

It was noticed that no DANT peaks was detected throughout this experiment, which is somewhat surprising because ADNT and DANT are both commonly formed as by-products during the TNT biodegradation process (Won et al., 1974; Boopathy et al., 1994a; Harvey, 1997). Two possible reasons for this are speculated and explained below. Firstly, it is believed that the reactors were not incubated long enough for a noticeable amount of DANT to be produced. Secondly, very low levels of DANT might have indeed been produced, but at levels below the analytical detection capability. Especially after the sample dilution procedure was performed during the sample preparation step (for the protection of the HPLC column). Harvey (1997) conducted similar study on biocell treatment of TNT contaminated soil. Under the same biological amendment condition, DANTs were produced in 21 days. The mass ratio of DANTs to TNT was approximately 3%. Base on this conversion ratio, approximately 900 ppm of DANTs were expected in our research.

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Although, it's hard to speculate on when and how much DANT should be produced with these soils due to differences associated with different soil sources and the native bacteria present within these soils.

Results of the Oxidation Step

Figure 7.5 is a plot of TNT concentration versus time for the two oxidation systems evaluated. The TNT concentrations in both systems fluctuated, but a clear overall disappearance trend is observed with both sets. The rates of oxidation for both systems are listed in Table 7.3. As can be seen, the higher H_2O_2 doses (Oxidation System II) provided a more rapid TNT degradation rate than the lower dosed.

Figure 7.6 is a plot of Total ADNTs concentration versus time for the two oxidation systems evaluated. The total ADNT concentrations in both systems slightly fluctuated with an overall disappearance trend occurring over the course of this test. In both sets, zero order removal is observed. The higher H_2O_2 doses (Oxidation System II) performed similarly towards degrading total ADNT as compared to the lower dosed system. The rate of total ADNT removal is minimally impacted by dramatic increases in both hydrogen peroxide and iron salt (as shown in Table 7.4). This suggests that in the soil phase, the oxidation of explosives using Fenton's Reagent is more mass transfer limited (hypothesized as adsorption limited) than reaction kinetics limited. This

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is due to mass transfer limitations associated with desorption of the target pollutants from the soil particles.

Table 7.3 also clearly shows that Total ADNTs were degraded at a much faster rate as compared to TNT within each oxidation system. This finding well supports the research hypothesis that converting TNT to ADNTs results in a pollutant condition much more conducive to chemical oxidation. Additionally, when comparing the biodegradation rate for TNT versus ADNT, clearly biological treatment does a better job with converting TNT to ADNT, and then biodegrading the ADNT, once it is formed. This will be further proven from the bioslurry experimental results, which will be presented in the next chapter.

Foaming problems occurred during the application of Fenton's Reagent as it generated oxygen gas. The biosurfactants generated from the biotreatment stage worsened the foaming problem. Sequential additions of H_2O_2 were used to ease the severity of the foaming problem and to enhance the effectiveness of the Fenton's Reagent treatment due to reactivity of the hydroxyl radicals. Also, with excessive amounts of H_2O_2, a glass rod was used to break the foaming bubbles. Slowly moving the glass rod along the inside wall of the reactor when adding the hydrogen peroxide was helpful in breaking the oxygen bubbles. This foaming problem associated with applying Fenton's Reagent to the soil system could cause future problems especially in a closed and highly mixed reactor.

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Summary

As shown in Figure 7.7, the integration experiments indicate effectiveness when jointly treating the high level TNT contaminated soil using both biological and oxidation processes (integrated processing). Biotreatment was carried out first until approximately 83% TNT removal was achieved, then Fenton oxidation was applied to the soil slurry to further treat the by-products accumulated from the previous biological treatment step.

TNT was degraded by Fenton's Reagent oxidation, but not as rapidly as with the ADNT compounds. The TNT biodegradation rate was higher than the TNT oxidation rate. These observations proves the proposed research concept of first treating the contaminated soil using biotreatment condition to convert TNT to more oxidizable chemicals; then, treat these more oxidizable by-products using the Fenton's Reagent Process.

Past studies conducted at MSU on biocell treatment of TNT contaminated soils show that in approximately 12 weeks, 90% of TNT and ADNTs (1000 ppm) were removed (Harvey, 1997). Though complete removal of TNT or its by-products was never achieved. Additionally, as mentioned earlier in the literature review section, TNB was generated as a by-product during the oxidation of TNT contaminated soils. The TNB in these soil slurries was found to be resistant to further treatment. 87% of TNB was removed after four cycles of slurrying yet complete removal was

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not achieved (Fleming, 2000). From the integrated treatment (biocell treatment followed by Fenton's Reagent oxidation) results obtained in this study, it can be seen that in 12 weeks, 93% of TNT and ADNTs (50,000 ppm) were removed. By-products were completely removed after multiple applications of Fenton's Reagent. Thus, that the integrated technology shows more effectiveness towards treating TNT contaminated soil comparing to these two stand-alone technologies in terms of remediating TNT contaminated soils.

Low Level TNT Contaminated Soil Screening Experiments

In this set of experiments, the previously evaluated biological conditions were applied toward TNT contaminated soil containing much lower TNT levels without the weekly addition of molasses and nutrients. The concept of only adding the amendments at the initiation of biotreatment was to determine if when treating mildly contaminated soils, would field operations be dramatically simplified, and once simplified, would these activities adversely impact the performance of the oxidation step or delay TNT conversion due to potential cometabolite/nutrient limitations.

Results of Biological Step

Figure 7.8 is a plot of E_h value versus time during the biological step. It can be seen that E_h started off at a positive range, dropped

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dramatically to the –500 mV range over the course of the test period. An extreme anaerobic methanogenic condition was achieved.

Figure 7.9 is a plot of pH value versus time during the biological step. It shows that pH remained at relatively neutral conditions throughout the test period.

Figure 7.10 is a plot of TNT concentrations versus time data for the biocells. It appeared that TNT concentrations rapidly declined from 390 ppm to below 50 ppm within the first 3 days, after which the reaction slowed and appeared to level off throughout the rest of the reaction period. The fact that no further TNT degradation was observed after Day 3 was likely due to the limitation of the nutrients and molasses, since they were added to the reactor only at the initiation of the experiments.

It was also noticed that no by-products of any kind were detected throughout this test. This was likely due to the low initial TNT concentration. The TNT/ADNT ratio obtained from the high level TNT contaminated soil experiments conducted previously was approximately 0.01. Based on this conversion ratio, approximately 3 mg/kg of ADNT was expected in these low level sets of experiments. After the sample dilution step during chemical analysis (for the protection of the HPLC column), the amount of ADNT in the diluted aqueous extract would be below the detection limit of the HPLC.

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Results of Oxidation Step

After the biotreatment step, the soil in the reactor was divided into two beakers. Different concentrations of Fe^{2+} and H_2O_2 (with the same ratio of 1:50) were applied into each beaker to see how effectively the two Fenton's Reagent formulations degraded TNT. Figure 7.11 shows that one application of Fenton's Reagent (Formula 1) removed 40% of the TNT, and one application of Fenton's Reagent (Formula 2) removed all the TNT. Apparently, increasing both the iron and hydrogen peroxide dosage, while keeping the same Fe^{2+}/H_2O_2 ratio, increased TNT removal achieved.

Summary

This test series performed on the low level contaminated soil showed that the integrated process was effective toward treating the low level TNT contaminated soil. The one time addition of molasses and nutrients during the biotreatment step approved to provide an acceptable condition if future oxidation is applied, while greatly reducing system operations complexity. With the higher doses of both the iron and hydrogen peroxide, complete removal of TNT was achieved through a single application of Fenton's Reagent.

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Table 7.1. Rates of TNT Biodegradation Within Biocell Reactors

	Day 1 to Day 41 (mg/kg/d)	Day 41 to Day 64 (mg/kg/d)
50 ml digester sludge	230	1090
100 ml digester sludge	280	472

Table 7.2. Net Rates of Change of Total ADNT Within Biocell Reactors

	Day 1 to Day 41 (mg/kg/d)	Day 41 to Day 64 (mg/kg/d)
50 ml digester sludge	124	996
100 ml digester sludge	104	394

Table 7.3. Comparison of TNT and Total ADNT Oxidation Rate under Different Oxidation Systems

	Oxidation System I	Oxidation System II
Overall TNT Oxidation Rate (mg/kg/d)	67	123
Overall ADNT Oxidation Rate (mg/kg/d)	953	1120

Table 7.4. Total ADNT Oxidation Rate under different Fenton's Reagent Doses for Oxidation System I

Oxidation System I	Total ADNT Oxidation Rate (mg/kg/d)
2500 ppm Fe^{2+}/50,000 ppm H_2O_2	1179
10,000 ppm Fe^{2+}/100,000 ppm H_2O_2	727

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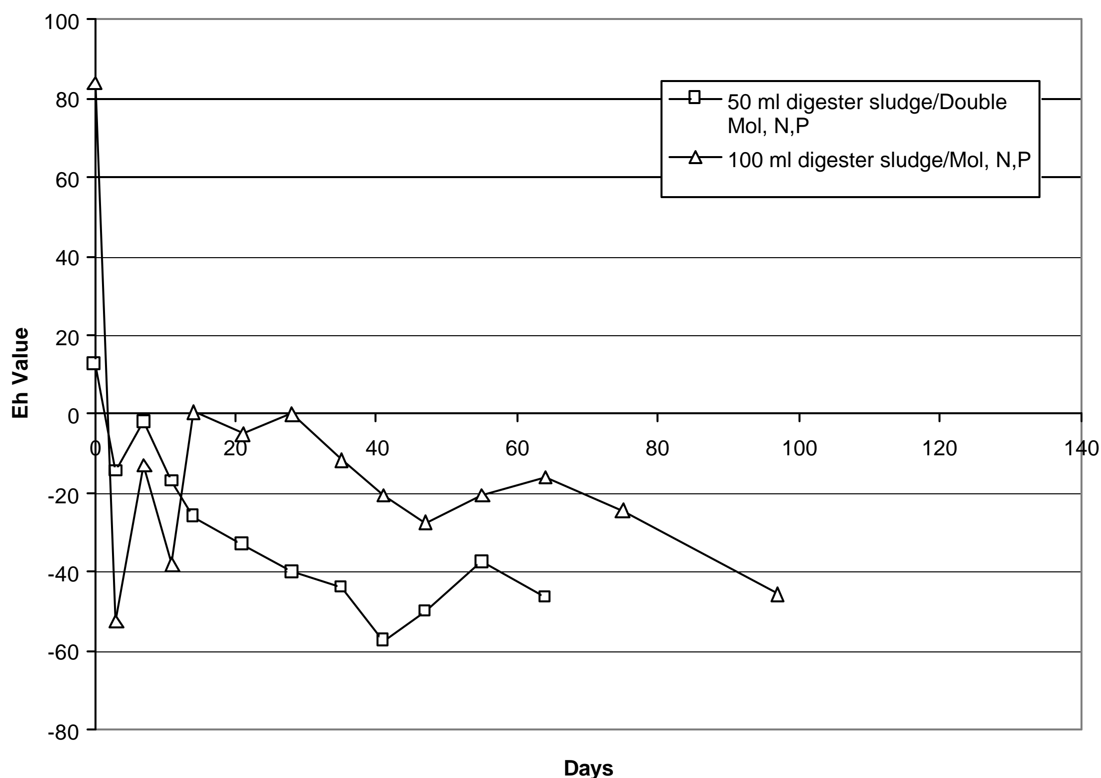

Figure 7.1. E_h Value in Biocell Reactors with Different Process Amendments (Note: double amount of addition of Mol/N/P started on Day 41)

Conditions:

✓ 50 ml digester sludge/Double Mol, N, P:
Seeded with 50 ml digester sludge
Day 0-Day 41 Molasses (2%)/N (50 ppm)/P (20 ppm)
Day 41-Day 64 Molasses (4%)/N (100 ppm)/P (40 ppm)
Amended on a weekly base

✓ 100 ml digester sludge/Mol, N, P:
Seeded with 100 ml digester sludge
Molasses (2%)/N (50 ppm)/P (20 ppm)
Amended on a weekly base

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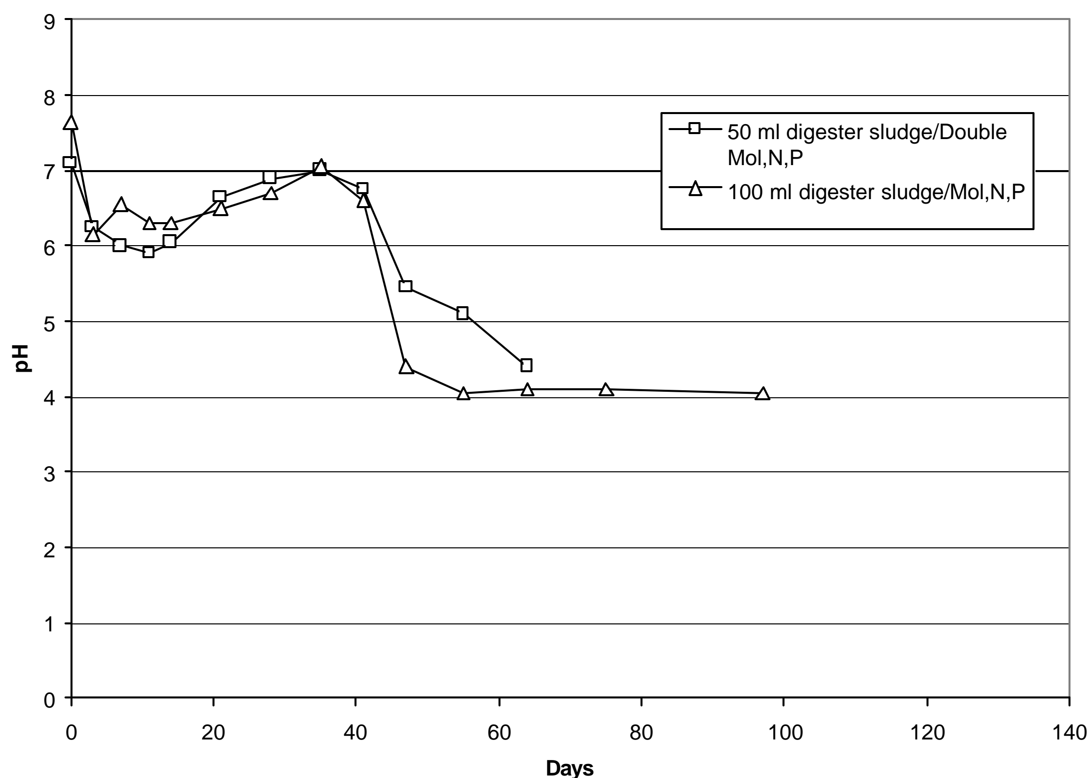

Figure 7.2. pH Value in Biocell Reactors with Different Process Amendments (Note: double amount of addition of Mol/N/P started on Day 41)

Conditions:

- ✓ 50 ml digester sludge/Double Mol, N, P:
  Seeded with 50 ml digester sludge
  Day 0-Day 41 Molasses (2%)/N (50 ppm)/P (20 ppm)
  Day 41-Day 64 Molasses (4%)/N (100 ppm)/P (40 ppm)
  Amended on a weekly base
- ✓ 100 ml digester sludge/Mol, N, P:
  Seeded with 100 ml digester sludge
  Molasses (2%)/N (50 ppm)/P (20 ppm)
  Amended on a weekly base

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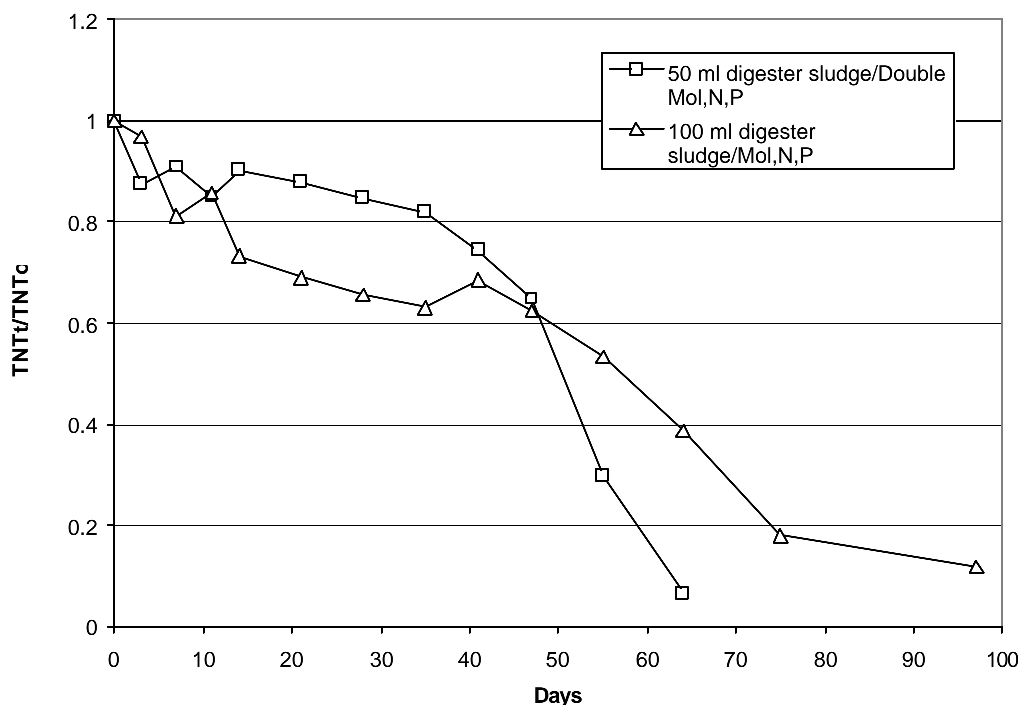

Figure 7.3. Disappearance of TNT in Biocell Reactors with Different Process Amendments (Note: double amount of addition of Mol/N/P started on Day 41)

Conditions:

- ✓ 50 ml digester sludge/Double Mol, N, P:
  Seeded with 50 ml digester sludge
  Day 0-Day 41 Molasses (2%)/N (50 ppm)/P (20 ppm)
  Day 41-Day 64 Molasses (4%)/N (100 ppm)/P (40 ppm)
  Amended on a weekly base
  $[TNT]_o$=36936 ppm
- ✓ 100 ml digester sludge/Mol, N, P:
  Seeded with 100 ml digester sludge
  Molasses (2%)/N (50 ppm)/P (20 ppm)
  Amended on a weekly base
  $[TNT]_o$=36419 ppm

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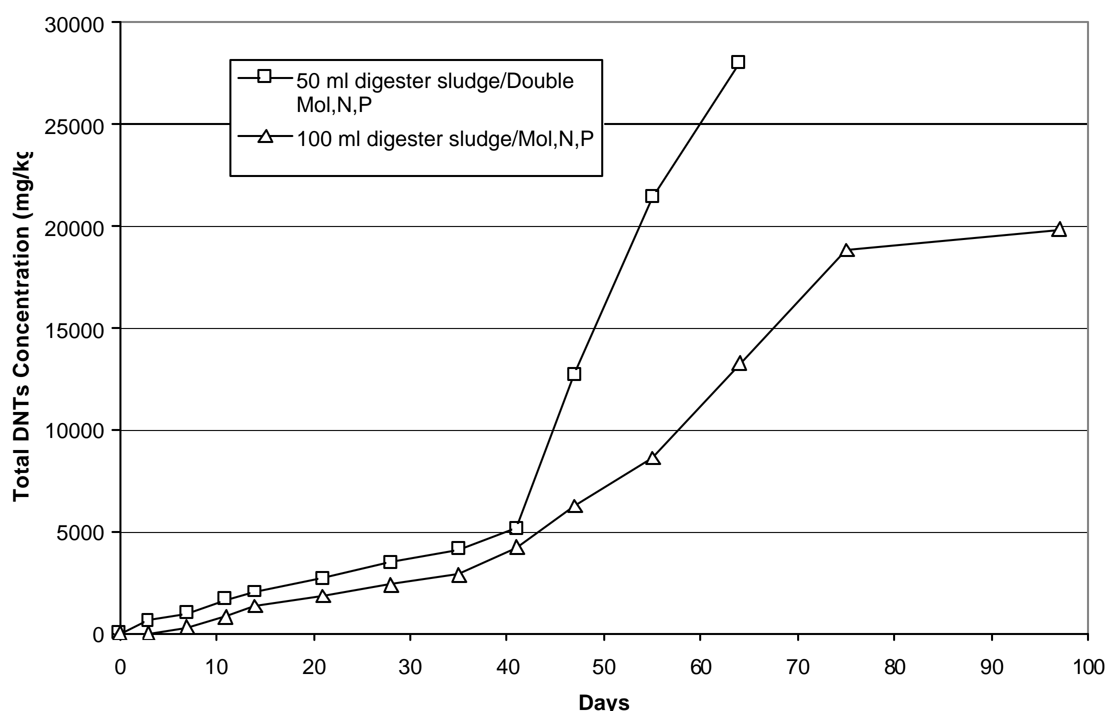

Figure 7.4. Formation and Disappearance of Total ADNTs in Biocell Reactors with Different Process Amendments (Note: double amount of addition of Mol/N/P started on Day 41)

Conditions:

- ✓ 50 ml digester sludge/Double Mol, N, P:
  Seeded with 50 ml digester sludge
  Day 0-Day 41 Molasses (2%)/N (50 ppm)/P (20 ppm)
  Day 41-Day 64 Molasses (4%)/N (100 ppm)/P (40 ppm)
  Amended on a weekly base
- ✓ 100 ml digester sludge/Mol, N, P:
  Seeded with 100 ml digester sludge
  Molasses (2%)/N (50 ppm)/P (20 ppm)
  Amended on a weekly base

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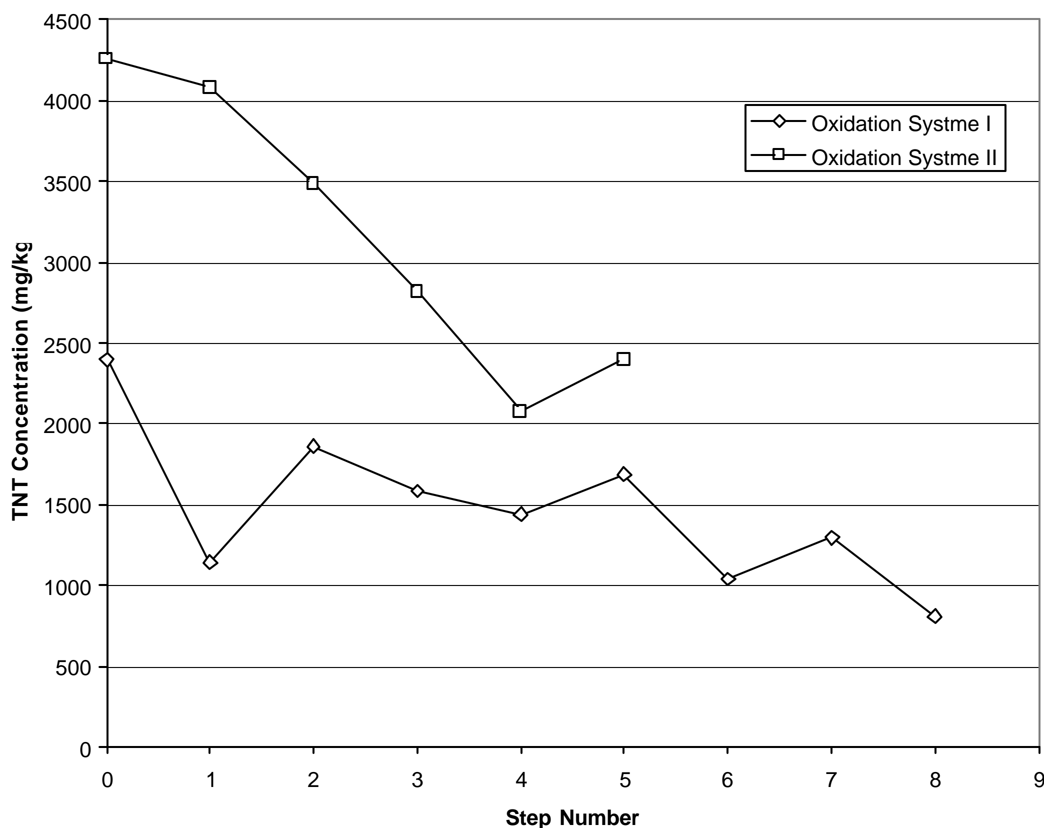

Figure 7.5. Disappearance of TNT During the Oxidation Phase of the Integration Treatment Experiments (I and II)

Conditions:

Oxidation System I:

1st ~ 4th application: 2500 ppm Fe^{2+}/50,000 ppm H_2O_2

5th ~ 8th application: 10,000 ppm Fe^{2+}/100,000 ppm H_2O_2

Oxidation System II:

1st ~ 2nd application: 1,000 ppm Fe^{2+}/100,000 ppm H_2O_2

3rd ~5th application: 10,000 ppm Fe^{2+}/100,000 ppm H_2O_2

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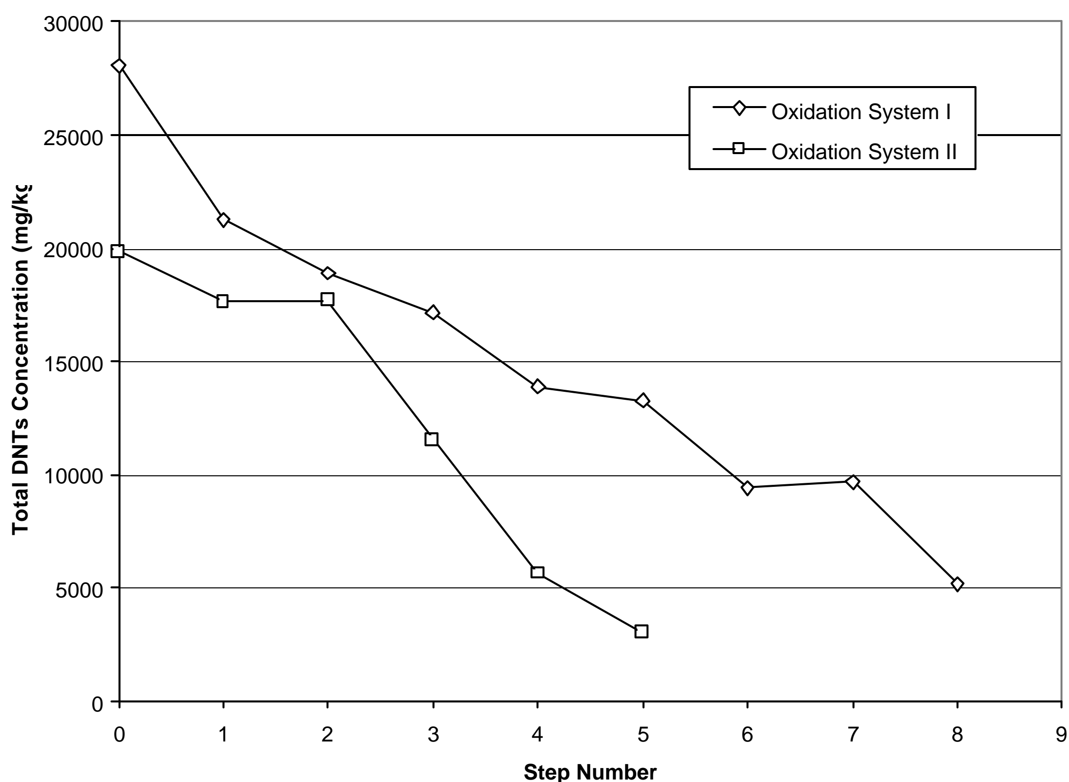

Figure 7.6. Disappearance of Total ADNTs During the Oxidation Phase of the Integration Treatment Experiments (I and II)

Notes:
Oxidation System I:
 1st ~ 4th application: 2500 ppm Fe^{2+}/50,000 ppm H_2O_2
 5th ~ 8th application: 10,000 ppm Fe^{2+}/100,000 ppm H_2O_2
Oxidation System II:
 1st ~ 2nd application: 1,000 ppm Fe^{2+}/100,000 ppm H_2O_2
 3rd ~5th application: 10,000 ppm Fe^{2+}/100,000 ppm H_2O_2

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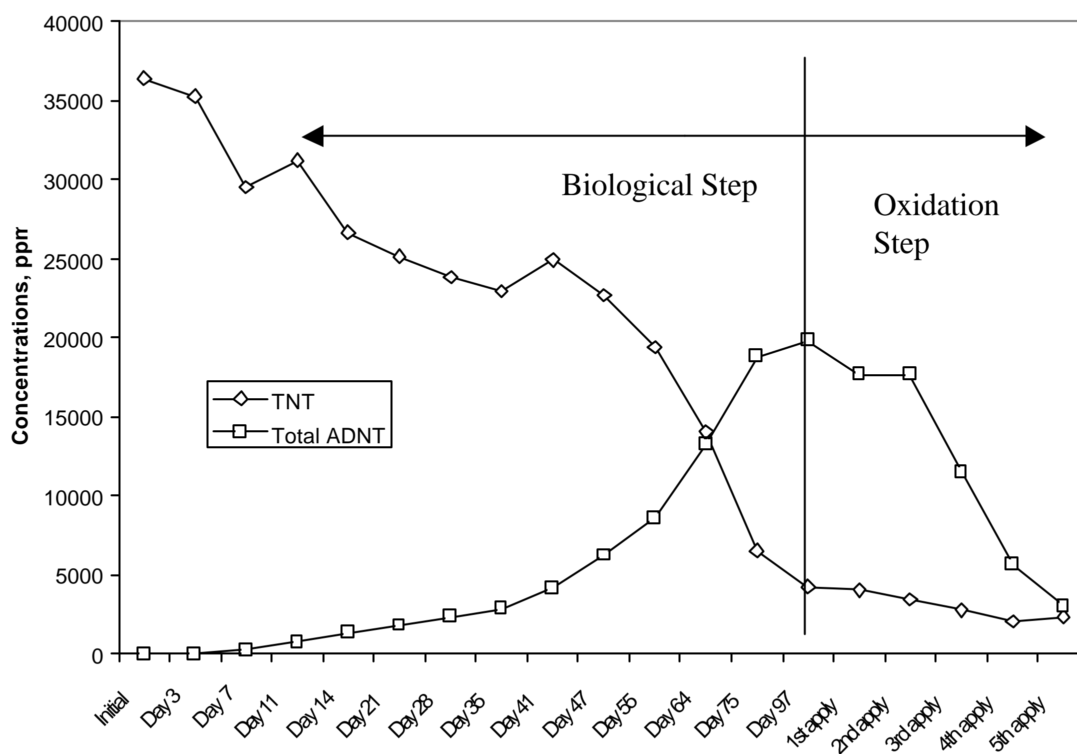

Figure 7.7. Plots of TNT and Total ADNT Concentration Versus Time for the Integration Experiments II

Conditions:

- ✓ Biological Step:
  Seeded with 100 ml digester sludge
  Molasses (2%)/N (50 ppm)/P (20 ppm)
  Amended on a weekly base
- ✓ Oxidation Step:
  1st through 2nd application: 1,000ppm Fe^{2+}/100,000 ppm H_2O_2
  3rd through 5th application: 10,000 ppm Fe^{2+}/100,000 ppm H_2O_2

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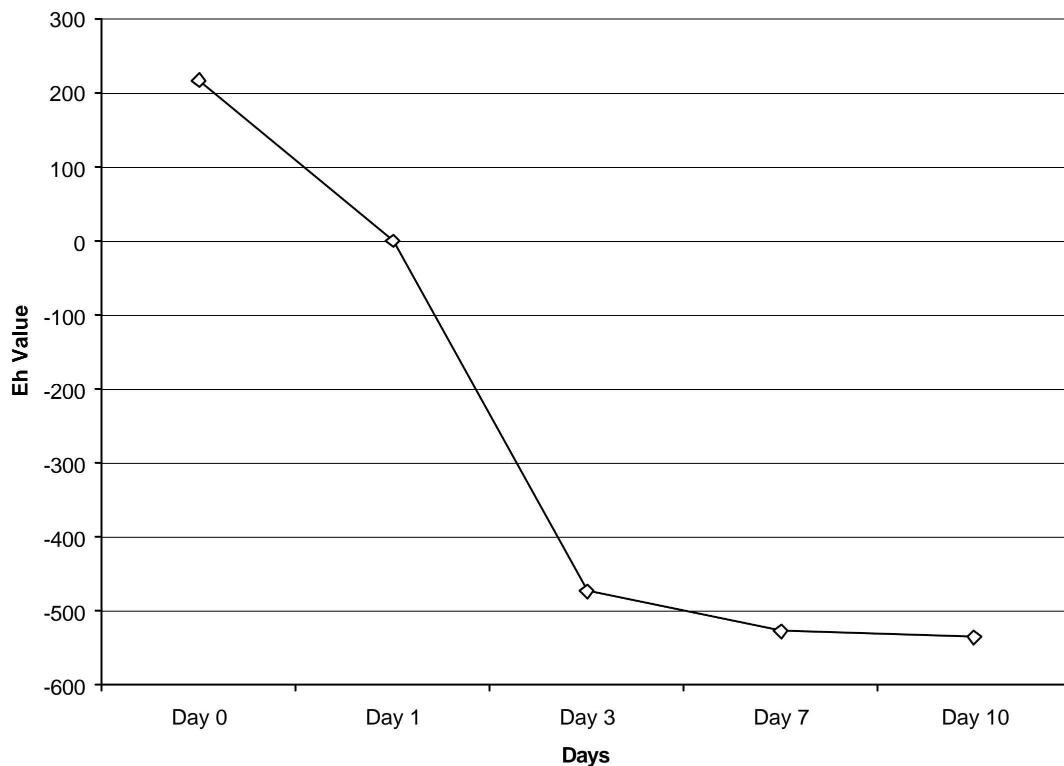

Table 7.8. E_h Value during the Biological Step of the Low Level Contamination Integration Experiment

Condition:

Seeded with 10 ml digester sludge
Molasses (2%)/N (50 ppm)/P (20 ppm)
Amended on a weekly base

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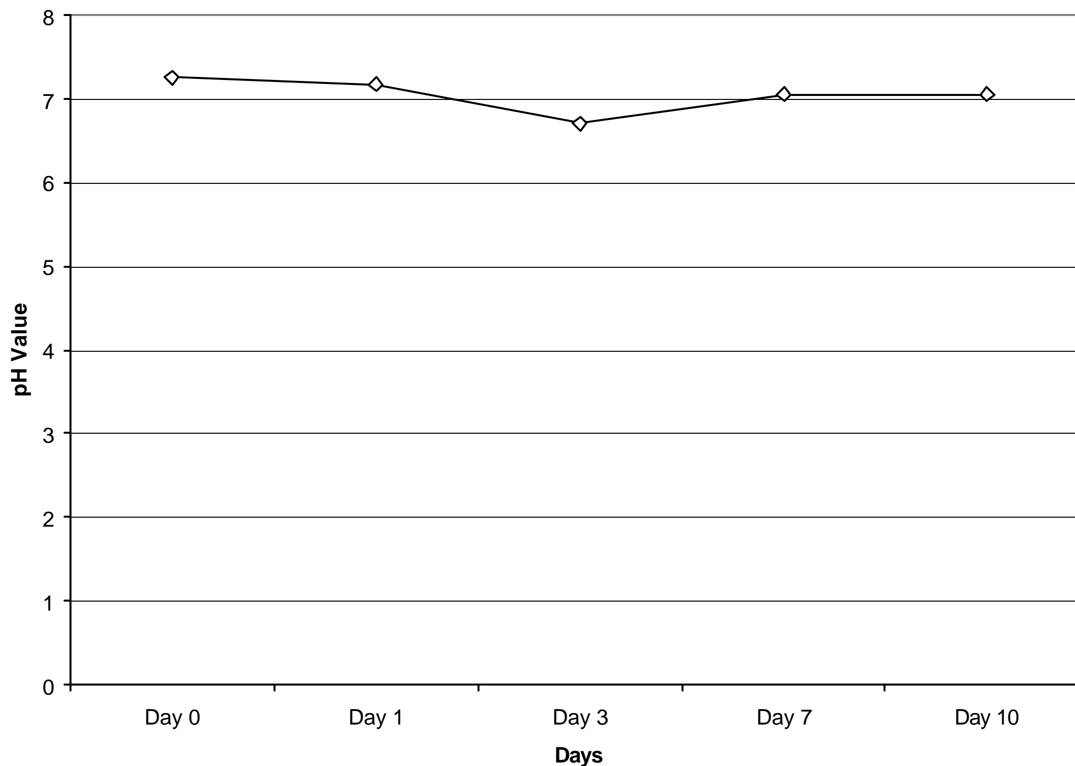

Table 7.9. pH Value during the Biological Step of the Low Level Contamination Integration Experiment

Condition:

Seeded with 10 ml digester sludge
Molasses (2%)/N (50 ppm)/P (20 ppm)
Amended on a weekly base

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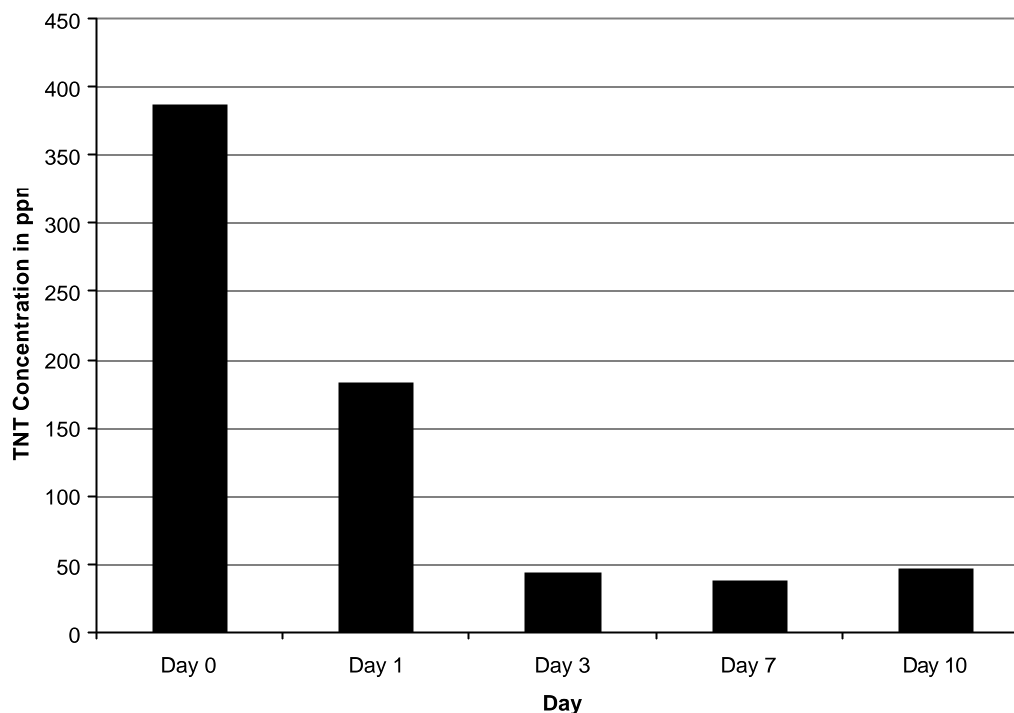

Figure 7.10. Low Level Contamination Experiments Bio-Phase Results

Condition:

Seeded with 10 ml digester sludge
Molasses (2%)/N (50 ppm)/P (20 ppm)
Amended on a weekly base

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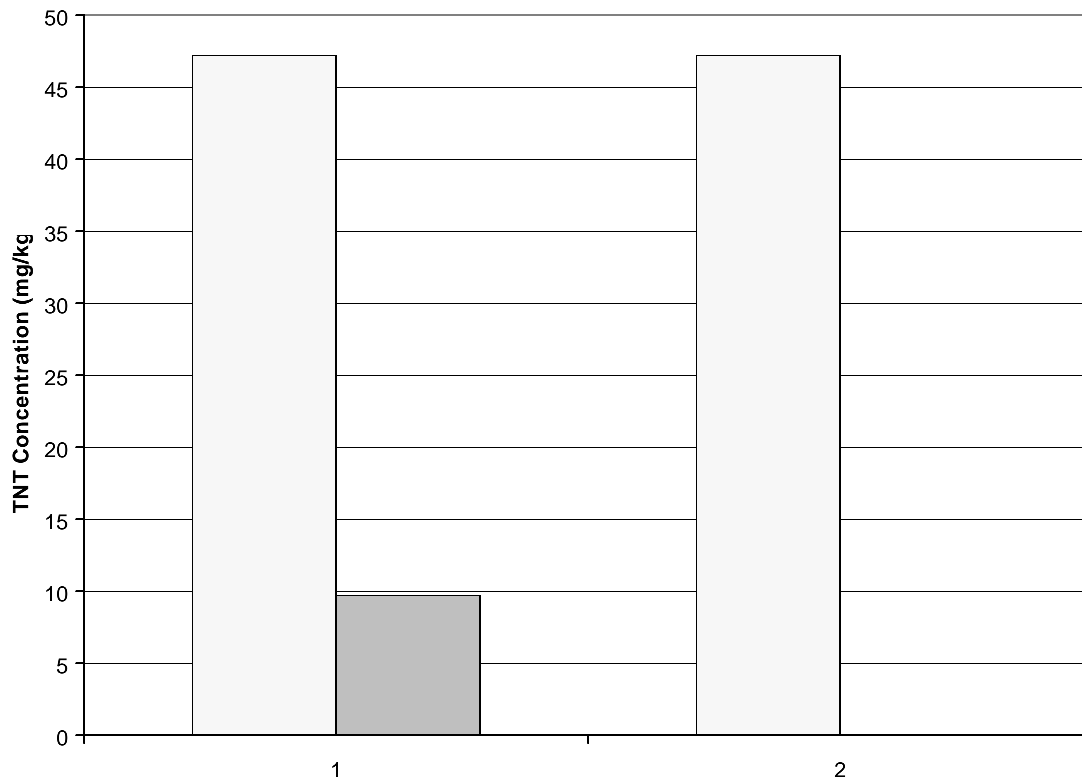

Figure 7.11. Low Level Contamination Experiments Oxidation-Phase Results after Pre-Biotreat Step

Conditions:

Formula 1: 100 ppm Fe^{2+}/5000 ppm H_2O_2
Formula 2: 500 ppm Fe^{2+}/25000 ppm H_2O_2

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CHAPTER VIII

BIOSLURRY EXPERIMENTAL RESULTS

The objective of this set of experiments was to screen several candidate biological treatment strategies in order to further optimize the treatment conditions for TNT biodegradation. These experiments were performed as an attempt to evaluate if other bioremediation strategies may provide better performance than the ones used in the integration experiments. Experiments were conducted in duplicate and all the analytical samples were analyzed in triplicate. The data will be presented as an average of each duplicate set for a given sampling event.

pH and E_h

Figure 8.1 is a plot of pH versus time for the experiments performed in the bioslurry shake flasks. All treatment conditions behaved similarly. The pH for the treatments with Na-acetate amended was slightly higher than the rest of the treatment conditions. No particular rationale for this slightly higher pH can be speculated.

Figure 8.2 is a plot of E_h values versus time. All treatment conditions behaved similarly. The E_h values remained positive, which indicates that aerobic conditions were maintained throughout the testing

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period. Therefore, any TNT and by-products removals will have to be attributed to aerobic-based reductases.

Soil Phase Results

Figure 8.3 is a plot of soil phase TNT concentrations versus time for the experiments performed in the bioslurry shake flasks. TNT concentrations in the control set remained relevantly constant throughout the course of the test, which indicated no loss of TNT due simply to the addition of oxygen. Clearly, all treatment process performed similarly towards biodegradation of TNT. TNT removal fluctuated with an overall downward disappearance trend. Apparently, aerobic treatment amended with numerous comatabolites is capable of TNT bioremediation. No clearly better performing co-metabolite emerges upon review of these data. By approximately 70 days, 80% of the initial TNT was removed from all of the amended flasks.

Figure 8.4 is a plot of soil phase TNB concentrations versus time for the experiments performed in the bioslurry shake flasks. It appears that TNB is not very biodegradable no matter the treatment condition employed during this test.

Figure 8.5 is a plot of soil phase total ADNT concentrations versus time for the experiments performed in the bioslurry shake flasks. ADNT concentration remained relatively constant throughout the test period. All testing conditions performed similarly. ADNT was initially rapidly

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removed during the first 20 days, and then appear to level off. Toward the end of the reaction, accumulation of the ADNT is observed, especially for the molasses/N/P amended flasks. The rate of formation and rate of degradation of ADNT contributes to the net rate of change of ADNT at any given time. At the initial stage of the test, degradation dominates the dynamics of ADNT rate within the flasks. Therefore, ADNT concentrations appeared to drop rapidly. At this point in time during this test, TNT levels are being reduced and ADNT begins to be formed as a result of this TNT degradation. Therefore, the rate of formation starts to increase over the rate of degradation to a balancing point resulting in a relatively constant level of total ADNTs observed over the remainder of the test, even to the point where some accumulation is observed.

TNT and ADNT biodegradation rates are listed in Table 8.1. As it can be seen that TNT was biodegraded at a must faster rate as compared to ADNT under each aerobic slurry flask biotreatment condition. ADNT are more resistant to biotreatment than TNT. A comparison of these rates to those obtained from the biocells is done later in this chapter.

Boopathy (2002) conducted similar work on aerobic shake flask biotreatment of TNT contaminated soil. Complete mineralization of TNT was reported. ADNT was produced as by-products, and then was removed completely. This was likely due to the lower initial

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contamination concentration (4000 mg/kg/d) comparing to those used in this study (30,000 mg/kg/d).

Liquid Phase Results

Figure 8.6 is a plot of liquid phase TNT concentrations versus time for the experiments performed in the bioslurry shake flasks. For the control and the starch and molasses amended systems, the TNT concentrations remain constant or show a slight downward trend. It can be seen that TNT concentration in the liquid phase increased at later period of the test for the Na-acetate/N/P treatment and Na-acetate/Tween80/N/P treatments. This build-up was likely due to that these two treatment created a condition more conducive to the production of bioemulsifiers which enhanced the desorption of the chemicals.

Figure 8.7 is a plot of liquid phase TNB concentrations versus time for the experiments performed in the bioslurry shake flasks. It can be seen that the Na-acetate/Tween80/N/P treatment behaved differently than the other systems towards the TNB level in the liquid phase. For these two systems, the TNB levels were clearly elevated over the other three systems. This observation indicates that TNB levels are impacted by the surfactant, resulting in a dramatic increase in TNB concentrations within the liquid phase. The Na-acetate/N/P treatment showed some level of increase in TNB concentrations within the liquid phase but not as

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dramatic as the treatment with the surfactant amendment. This difference in performance indicates that the surfactant is more effective in solubulize TNB than the bioemulsifier.

Figure 8.8 is a plot of averaged liquid phase Total ADNT concentration versus time for the experiments performed in the bioslurry shake flasks. It can be seen that Total ADNTs concentration in the liquid phase increased for the Na-acetate/N/P treatment and Na-acetate/Tween80/N/P treatments. This build-up was again likely due to that these two systems created a condition more conducive to the production of bioemulsifiers which enhanced the desorption of the chemicals into the aqueous phase. The Potato Starch/N/P treatment and Molasses/N/P treatment showed an overall Total ADNTs disappearance trend. The treatment condition with molasses amended performed the best in terms of degrading the Total ADNTs within the liquid phase.

Summary

From the soil phase results, it can be concluded that all treatment conditions showed effectiveness towards biodegrading TNT and Total ADNTs. None of these testing conditions clearly stand out. They all behaved similarly. Reactions were not carried longer due to the fact that there were only limited amount of soils present in the shake flask initially and after removing a number of samples from the flask, not enough soil was left for further treatment. It is speculated that with longer treatment

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times, complete removal of TNT would likely have been achieved; however, this testing was performed to evaluate the performance of various candidate co-metabolites with regard to TNT/ADNT removal. When comparing the biodegradation rate for TNT versus ADNT, clearly biological treatment does a better job with converting TNT to ADNT, and then degrading the ADNT, once it is formed.

From the liquid phase results, it can be seen that the treatment conditions with Na-acetate amending showed enhancement in the desorption of chemicals likely due to the production of bioemulsifiers. Tween80 showed a much greater enhancement in the desorption of TNB, which was attributed to its surfactant characteristic.

Comparisons with Biocell Treatments

TNT biodegradation rates under both the bioslurry condition and biocell condition are listed in Table 8.1. Two different soils were used for the bioslurry treatment and biocell treatment. Given its operation simplicity, biocells appear to be a much better option for the biotreatment step than bioslurry systems.

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Table 8.1. Rates Comparision between TNT and ADNT
(During the first 21 days of Bioslurry Test)

Test Conditions	TNT Biodegradation Rates (mg/kg/d)	ADNT Biodegradation Rates (mg/kg/d)
Na-acetate/N/P	1176	44
Na-acetate/Tween80/N/P	666	47
Potato/N/P	904	22
Molasses/N/P	350	25

Table 8.2. TNT Biodegradation Rates Comparision

	Test Conditions	Biodegradation Rates (mg/kg/d)
Bioslurry	Na-acetate/N/P	305
	Na-acetate/Tween80/N/P	253
	Potato/N/P	254
	Molasses/N/P	161
Biocell	50 ml sludge/Double Mol/N/P	539
	100 ml sludge/Mol/N/P	331

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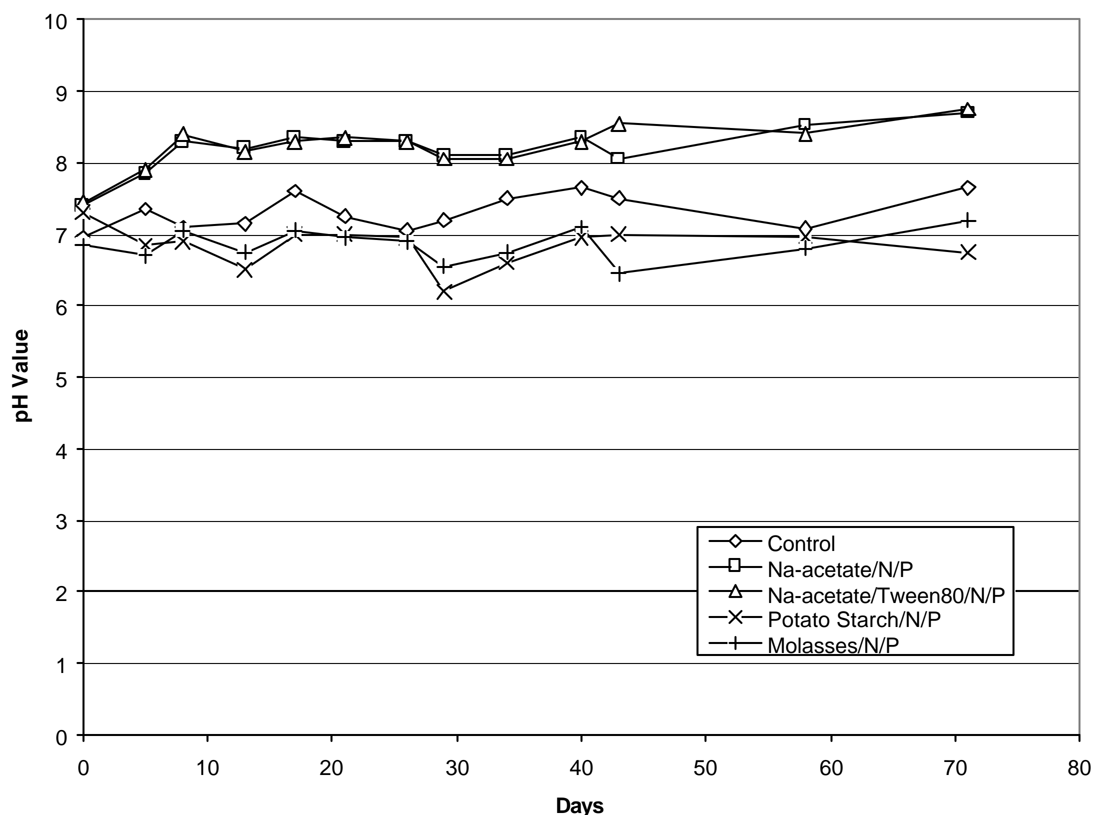

Figure 8.1. pH Values from the Bioslurry Experiments

Conditions:

- ✓ Control:
  Soil/Distilled Water
- ✓ Na-acetate/N/P:
  Na-acetate (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base
- ✓ Na-acetate/Tween80/N/P:
  Na-acetate (2%)/Tween80 (1%)/N (50 ppm)/P(20 ppm); amended on a weekly base
- ✓ Potato Starch/N/P:
  Patato starch (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base
- ✓ Molasses/N/P:
  Molasses (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base

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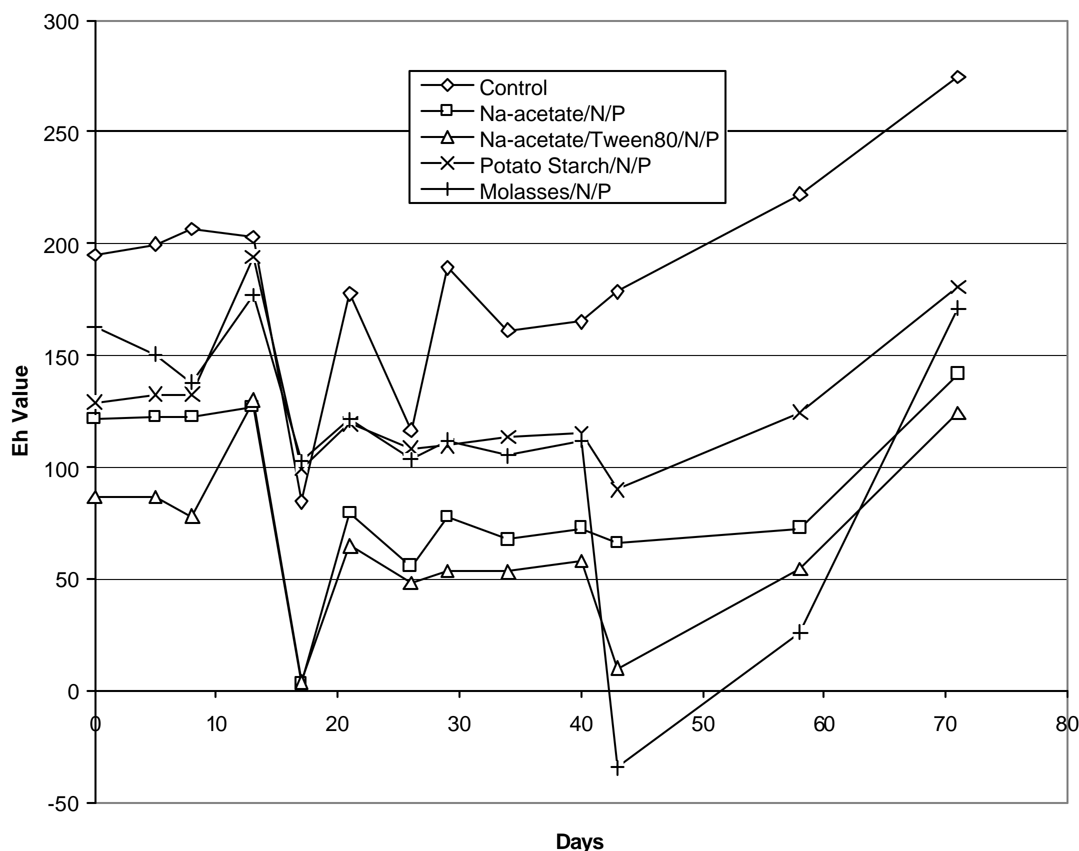

Figure 8.2. E_h Values from the Bioslurry Experiments

Conditions:

- ✓ Control:
  Soil/Distilled Water
- ✓ Na-acetate/N/P:
  Na-acetate (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base
- ✓ Na-acetate/Tween80/N/P:
  Na-acetate (2%)/Tween80 (1%)/N (50 ppm)/P(20 ppm); amended on a weekly base
- ✓ Potato Starch/N/P:
  Patato starch (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base
- ✓ Molasses/N/P:
  Molasses (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base

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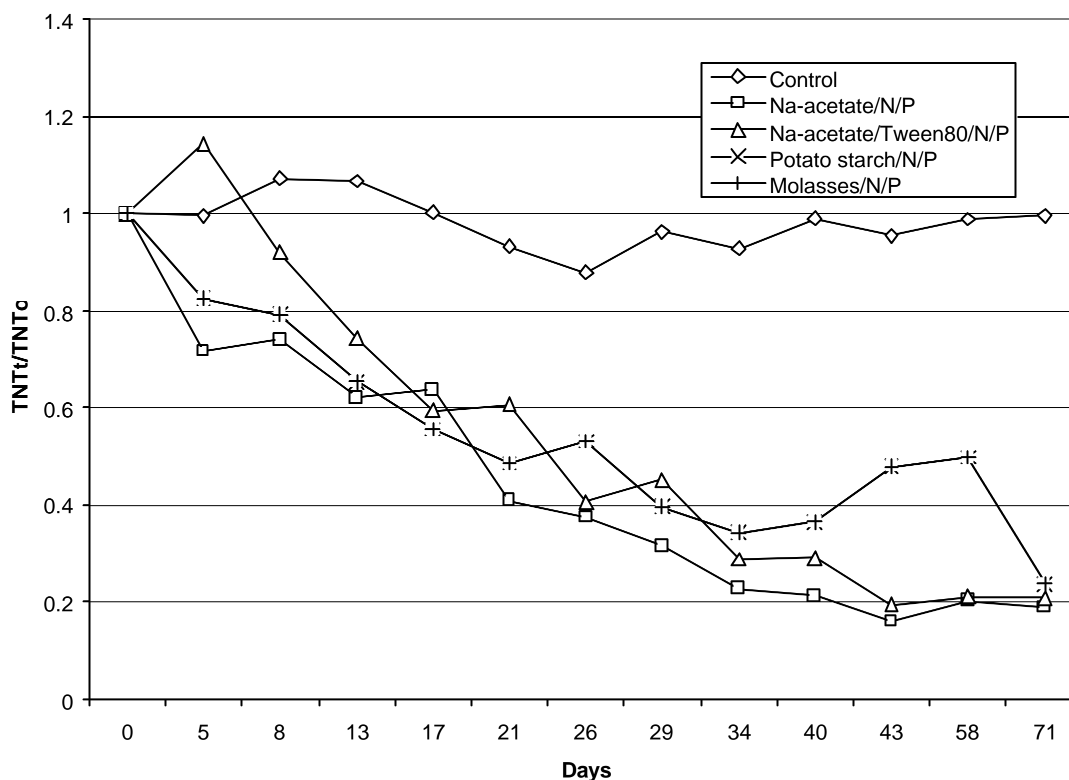

Figure 8.3. Soil Phase TNT Concentrations from the Bioslurry Experiments

Conditions:

- ✓ Control:
  Soil/Distilled Water; $[TNT_0]$= 29173 ppm
- ✓ Na-acetate/N/P:
  Na-acetate (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base; $[TNT_0]$= 41777 ppm
- ✓ Na-acetate/Tween80/N/P:
  Na-acetate (2%)/Tween80 (1%)/N (50 ppm)/P(20 ppm); amended on a weekly base; $[TNT_0]$= 35545 ppm
- ✓ Potato Starch/N/P:
  Potato starch (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base; $[TNT_0]$= 37007 ppm
- ✓ Molasses/N/P:
  Molasses (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base; $[TNT_0]$= 28761 ppm

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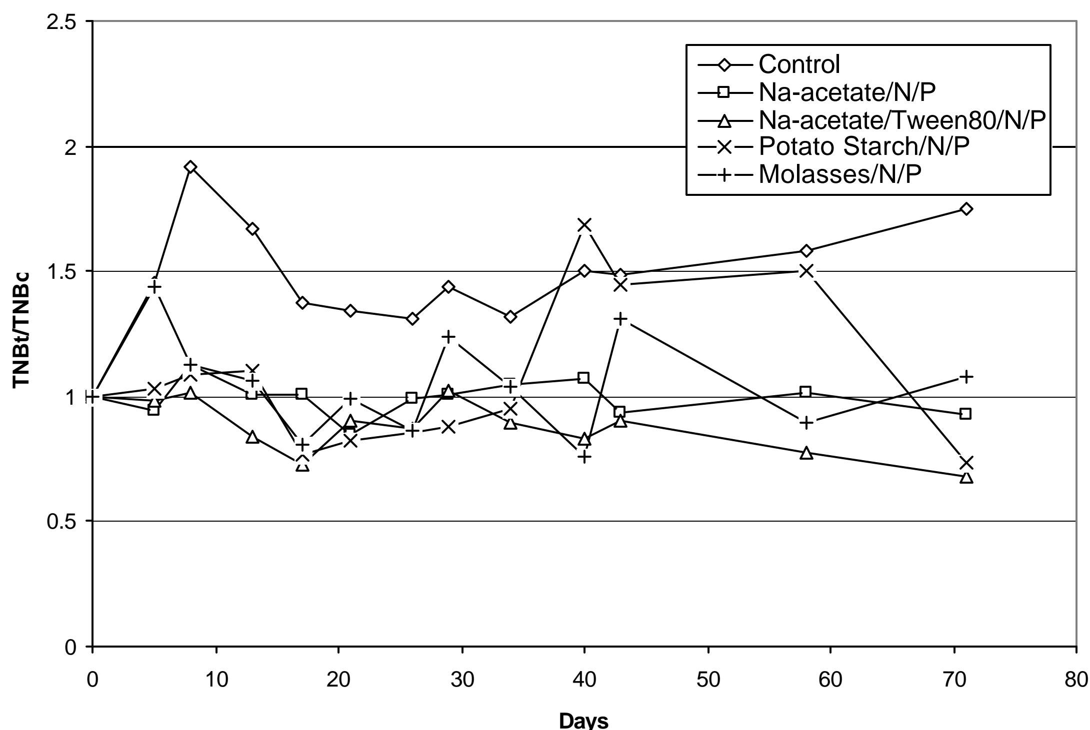

Figure 8.4. Soil Phase TNB Concentrations from the Bioslurry Experiments

Conditions:

- ✓ Control:
  Soil/Distilled Water; $[TNB_0]$= 34 ppm
- ✓ Na-acetate/N/P:
  Na-acetate (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base; $[TNB_0]$= 129 ppm
- ✓ Na-acetate/Tween80/N/P:
  Na-acetate (2%)/Tween80 (1%)/N (50 ppm)/P(20 ppm); amended on a weekly base; $[TNB_0]$= 125 ppm
- ✓ Potato Starch/N/P:
  Potato starch (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base; $[TNB_0]$= 43 ppm
- ✓ Molasses/N/P:
  Molasses (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base; $[TNB_0]$= 35 ppm

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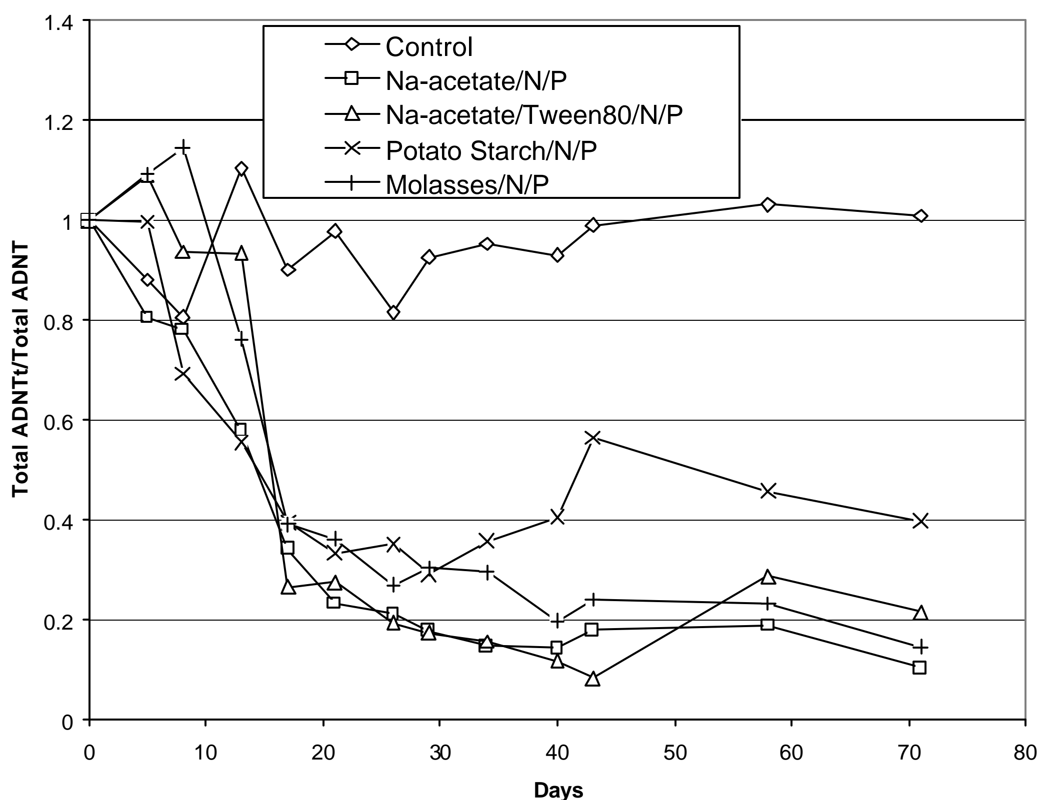

Figure 8.5. Soil Phase ADNT Concentrations from the Bioslurry Experiments

Conditions:

- ✓ Control:
  Soil/Distilled Water; $[ADNT_0]$= 619 ppm
- ✓ Na-acetate/N/P:
  Na-acetate (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base; $[ADNT_0]$= 1225 ppm
- ✓ Na-acetate/Tween80/N/P:
  Na-acetate (2%)/Tween80 (1%)/N (50 ppm)/P(20 ppm); amended on a weekly base; $[ADNT_0]$= 1384 ppm
- ✓ Potato Starch/N/P:
  Potato starch (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base; $[ADNT_0]$= 667 ppm
- ✓ Molasses/N/P:
  Molasses (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base; $[ADNT_0]$= 823 ppm

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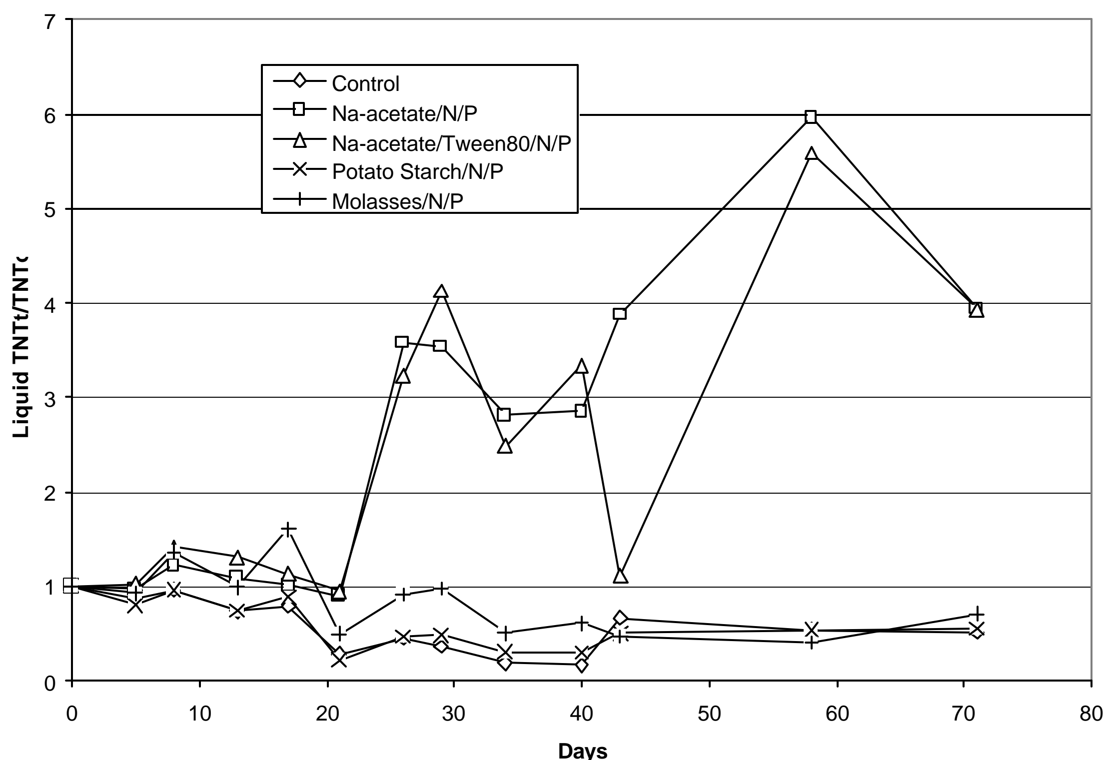

Figure 8.6. Liquid Phase TNT Concentrations from the Bioslurry Experiments

Conditions:

- ✓ Control:
  Soil/Distilled Water; $[TNT_0]$= 118 ppm
- ✓ Na-acetate/N/P:
  Na-acetate (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base; $[TNT_0]$= 46 ppm
- ✓ Na-acetate/Tween80/N/P:
  Na-acetate (2%)/Tween80 (1%)/N (50 ppm)/P(20 ppm); amended on a weekly base; $[TNT_0]$= 58 ppm
- ✓ Potato Starch/N/P:
  Potato starch (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base; $[TNT_0]$= 99 ppm
- ✓ Molasses/N/P:
  Molasses (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base; $[TNT_0]$= 51 ppm

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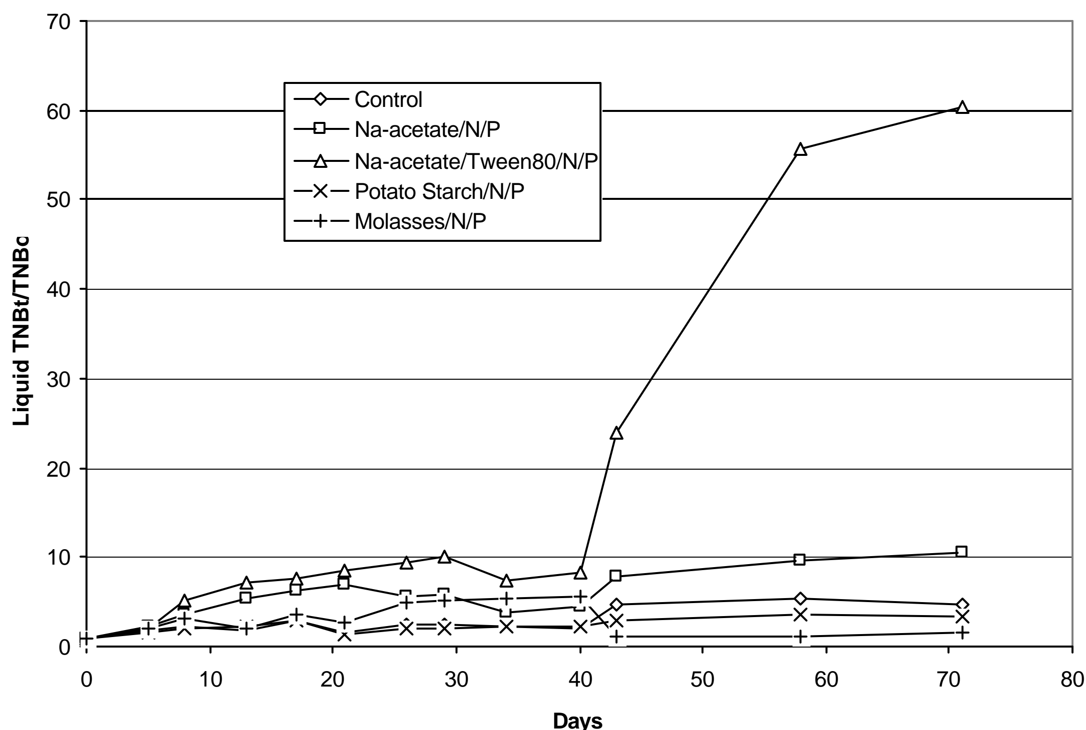

Figure 8.7. Liquid Phase TNB Concentrations from the Bioslurry Experiments

Conditions:

- ✓ Control:
  Soil/Distilled Water; [TNB_0]= 2.65 ppm
- ✓ Na-acetate/N/P:
  Na-acetate (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base; [TNB_0]= 3.8 ppm
- ✓ Na-acetate/Tween80/N/P:
  Na-acetate (2%)/Tween80 (1%)/N (50 ppm)/P(20 ppm); amended on a weekly base; [TNB_0]= 2.63 ppm
- ✓ Potato Starch/N/P:
  Potato starch (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base; [TNB_0]= 1.92 ppm
- ✓ Molasses/N/P:
  Molasses (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base; [TNB_0]= 0.70 ppm

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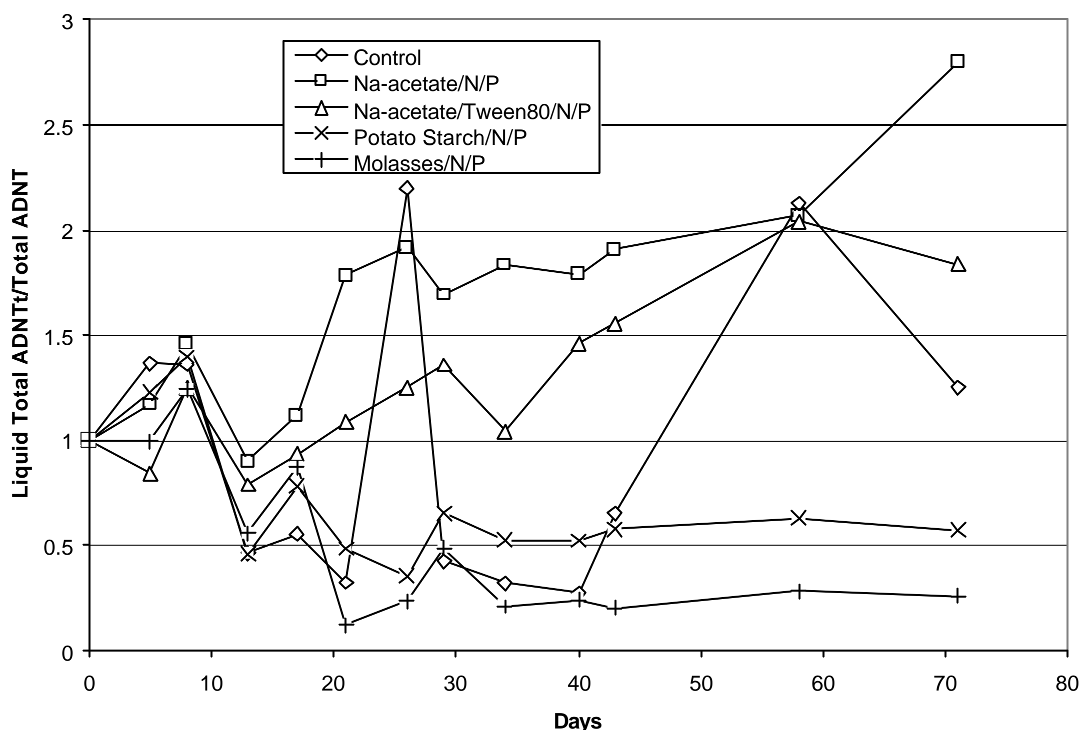

Figure 8.8. Liquid Phase ADNT Concentrations from the Bioslurry Experiments

Conditions:

- ✓ Control:
  Soil/Distilled Water; $[ADNT_0]$= 3.43 ppm
- ✓ Na-acetate/N/P:
  Na-acetate (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base; $[ADNT_0]$= 17.46 ppm
- ✓ Na-acetate/Tween80/N/P:
  Na-acetate (2%)/Tween80 (1%)/N (50 ppm)/P(20 ppm); amended on a weekly base; $[ADNT_0]$= 33.26 ppm
- ✓ Potato Starch/N/P:
  Potato starch (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base; $[ADNT_0]$= 3.16 ppm
- ✓ Molasses/N/P:
  Molasses (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base; $[ADNT_0]$= 8.98 ppm

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CHAPTER IX

CONCLUSIONS AND ENGINEERING SIGNIFICANCE

The results of this study provide sufficient evidence for the feasibility of Advanced Oxidation Process (AOP) enhanced bioremediation of TNT contaminated soil. Several conclusions can be made as an outcome of this investigation.

Soil Hydraulic Conductivity Experiments

Applying Fenton's Reagent to soil loaded in the permeameter decreased soil hydraulic conductivity due to the formation of Fe^{3+}. With higher concentrations of ferrous iron while remaining the same level of hydrogen peroxide, the hydraulic conductivity decreased incrementally. The implication of this finding is that when applying Fenton's Reagent for the *in-situ* or surface added oxidation treatment of explosives contaminated soil, the soil hydraulic conductivity may likely decrease over the course of the application. This proposes a potential loss in process effectiveness during oxidation treatment because the reduced K hinders the further delivery of additional oxidants into the soil matrix.

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This limitation could become a critical limiting factor for the multiple application of Fenton's Reagent into unmixed soil systems.

Oxidation Evaluation Experiments

The evaluation experiments conducted in both the liquid phase and the soil phase show that ADNTs are much more reactive than TNT. Under the same condition (initial pollutant concentration, Fenton's Reagent dosing concentration and pH), 100% of the ADNTs were successfully removed while only 30% TNT removal was achieved. The optimal H_2O_2/Fe^{2+} ratio appears to be less than 10:1. The liquid phase experiments clearly show the appearance of TNB as a by-product of incomplete TNT oxidation. The soil phase experiments verified the results observed in the liquid phase experiments. The data strongly suggest that the removal of both TNT and ADNTs is mass transfer limited (hypothesized as adsorption limited) and not kinetically limited. This implies that either very high concentrations of Fenton's Reagent must be applied to overcome adsorption hindrances by oxidizing the adsorptive bonds or lesser doses applied as the pollutants enter the liquid phase.

Integration Experiments

These integration experiments show that Fenton's Reagent was capable of degrading TNT, though not as fast as the Total ADNTs. The TNT biodegradation rate was higher than the TNT oxidation rate.

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Conversely, Total ADNTs were much more reactive with the oxidizing species than TNT. These observations proves the proposed research concept of first treating the contaminated soil using biotreatment condition to convert TNT to more oxidizable chemicals; then, treat these more oxidizable by-products using the Fenton's Reagent Process.

Foaming problems occurred during the application of Fenton's Reagent. This foaming problem associated with applying Fenton's Reagent to the soil system could cause future problems especially in a closed bio-slurry treatment systems.

Bioslurry Experiments

All tested treatment conditions performed similarly in biodegrading TNT. Under the same testing condition, TNT was biodegraded at a much faster rate as compared to Total ADNTs.

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APPENDIX

SUMMARY OF EXPERIMENTAL DATA

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Table A. 1. Results of Soil Hydraulic Conductivity Tests

$FeSO_4$ Concentration	Hydraulic Conductivity (K), sec^{-1}							
	Duplicate Experiment 1			Duplicate Experiment 2			Average	
	Ko, sec^{-1} (Before)	K_1, sec^{-1} (After)	Percent of Decrease	Ko, sec^{-1} (Before)	K_1, sec-1 (After)	Percent of Decrease	Percent of Decrease	Standard Deviation
1000 ppm	0.0268	0.0248	7.246	0.0152	0.0145	4.237	5.742	2.13
2000 ppm	0.0225	0.0193	14.607	0.0286	0.0248	13.043	13.825	1.10
3000 ppm	0.0144	0.0081	43.333	0.0286	0.0173	39.394	41.364	2.78
5000 ppm	0.0252	0.0137	45.600	0.0206	0.0105	49.080	47.340	2.46

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Table A.2. Liquid Phase Oxidation of TNT
Using a H_2O_2: Fe^{2+} Ratio of 100 ppm: 30 ppm

		Time, min	$[H_2O_2]$, ppm		[TNT], ppm		[TNB], ppm		pH	
Duplicate Experiment 1		0	100		10.1		0		7.0	
		5	85		7.26		1.31		6.9	
		10	81		7.71		1.24		6.8	
		15	77		7.87		1.25		6.5	
		20	68		7.33		1.17		6.7	
		25	63		7.90		1.28		6.8	
Duplicate Experiment 2		0	100		10.1		0		7.4	
		5	88		6.74		1.13		7.3	
		10	91		7.30		1.50		6.8	
		15	56		6.93		1.41		6.7	
		20	68		6.63		1.38		7.1	
		25	79		7.30		0.90		6.8	
Average	(Standard Deviation)	0	100	0.0	10.1	0.00	0	0.00	7.2	0.3
		5	86.5	2.1	7.00	0.37	1.22	0.13	7.1	0.3
		10	86	7.1	7.51	0.29	1.37	0.18	6.8	0.0
		15	66.5	14.8	7.40	0.66	1.33	0.11	6.6	0.1
		20	68	0.0	6.98	0.49	1.27	0.15	6.9	0.3
		25	71	11.3	7.60	0.42	1.09	0.27	6.8	0.0

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Table A.3. Liquid Phase Oxidation of TNT Using a H_2O_2: Fe^{2+} Ratio of 300 ppm: 30 ppm

	Time, min	$[H_2O_2]$, ppm		[TNT], ppm		[TNB], ppm		pH	
Duplicate Experiment 1	0	300		10.02		0		7.4	
	5	276		6.65		0.89		7.4	
	10	262		6.48		0.87		7.4	
	15	240		6.13		1.1		7.5	
	20	238		5.44		1.05		7.3	
	25	234		6.97		1.06		7.5	
	30	202		5.39		1.13		7.4	
Duplicate Experiment 2	0	300		10.03		0.		7.3	
	5	284		6.54		0.94		7.5	
	10	228		6.52		0.94		7.3	
	15	216		6.96		1.01		7.3	
	20	234		6.82		1.01		7.2	
	25	248		6.99		1.05		7.3	
	30	222		6.78		1.12		7.3	
Average / Standard Deviation	0	300	0	10.02	0.01	0.	0.00	7.35	0.07
	5	280	6	6.60	0.08	0.91	0.04	7.45	0.07
	10	245	24	6.50	0.03	0.90	0.05	7.35	0.07
	15	228	17	6.54	0.59	1.01	0.06	7.40	0.14
	20	236	3	6.13	0.98	1.03	0.03	7.25	0.07
	25	241	10	6.98	0.01	1.01	0.01	7.40	0.14
	30	212	14	6.08	0.98	1.12	0.01	7.35	0.07

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Table A.4. Liquid Phase Oxidation of TNT
Using a H_2O_2: Fe^{2+} Ratio of 900 ppm: 30 ppm

	Time, min	$[H_2O_2]$, ppm		[TNT], ppm		[TNB], ppm		pH	
Duplicate Experiment 1	0	900		10.1		0		7.2	
	5	874		9.45		0.79		7	
	10	836		9.53		0.81		6.8	
	15	892		9.14		0.76		6.7	
	20	860		9.62		0.79		6.5	
	25	860		9.16		0.73		6.5	
Duplicate Experiment 2	0	900		10.1		0		7.2	
	5	896		9.12		0.94		7.4	
	10	900		9.16		0.94		6.9	
	15	884		9.28		0.97		6.7	
	20	776		9.17		0.94		6.4	
	25	732		9.34		0.93		6.4	
Average / Standard Deviation	0	900	0	10.1	0.00	0	0.00	7.2	0.00
	5	886	16	9.29	0.23	0.86	0.11	7.2	0.28
	10	868	45	9.34	0.26	0.87	0.09	6.85	0.07
	15	898	6	9.21	0.10	0.86	0.15	6.7	0.00
	20	818	59	9.39	0.32	0.86	0.11	6.45	0.07
	25	796	91	9.25	0.13	0.83	0.14	6.45	0.07

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Table A.5. Liquid Phase Oxidation of TNT
Using a H_2O_2: Fe^{2+} Ratio of 900 ppm: 10 ppm

	Time, min	$[H_2O_2]$, ppm		[TNT], ppm		[TNB], ppm		pH	
Duplicate Experiment 1	0	900		10.1		0		7.1	
	5	886		7.26		1.39		6.9	
	10	808		7.3		1.4		6.9	
	15	795		6.9		1.42		6.7	
	20	725		6.9		1.59		6.8	
	25	708		6.8		1.6		6.7	
Duplicate Experiment 2	0	900		10.1		0		6.7	
	5	786		6.48		1.59		6.7	
	10	768		6.9		1.5		6.5	
	15	733		6.7		1.46		6.9	
	20	579		6.8		1.45		6.6	
	25	508		6.94		1.6		6.5	
Average / Standard Deviation	0	900	0	10.1	0.00	0	0.00	6.9	0.28
	5	836	71	6.87	0.55	1.49	0.14	6.8	0.14
	10	788	28	7.1	0.28	1.45	0.07	6.7	0.28
	15	764	44	6.8	0.14	1.44	0.03	6.8	0.14
	20	652	103	6.85	0.07	1.52	0.10	6.7	0.14
	25	608	141	6.87	0.10	1.60	0.00	6.6	0.14

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Table A.6. Liquid Phase Oxidation of ADNT without pH Adjustment
Using a H_2O_2: Fe^{2+} Ratio of 300 ppm: 30 ppm

	Time, min	$[H_2O_2]$, ppm		[ADNT], ppm		pH	
Duplicate Experiment 1	0	300		10		6.9	
	1	288		0		3.94	
	5	290		0		4.06	
	10	294		0		3.79	
	15	266		0		3.75	
	20	280		0		3.82	
	30	270		0		3.85	
Duplicate Experiment 2	0	300		10		6.9	
	1	282		0		4.01	
	5	278		0		3.95	
	10	256		0		3.78	
	15	272		0		3.67	
	20	266		0		3.65	
	30	268		0		3.87	
Average / Standard Deviation	0	300	0	10	0	6.9	0.00
	1	285	4	0	0	3.97	0.05
	5	284	8	0	0	4.00	0.08
	10	275	27	0	0	3.78	0.01
	15	269	4	0	0	3.71	0.06
	20	273	10	0	0	3.73	0.12
	30	269	1	0	0	3.86	0.01

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Table A.7. Liquid Phase Oxidation of ADNT with pH Adjustment
Using a H_2O_2: Fe^{2+} Ratio of 300 ppm: 30 ppm

	Time, min	[H_2O_2], ppm		[TNT], ppm		pH	
Duplicate Experiment 1	0	300		10		7.3	
	1	298		0		7.4	
	5	292		0		7.5	
	10	298		0		7.8	
	15	292		0		7.9	
	20	240		0		8	
	30	242		0		8	
Duplicate Experiment 2	0	300		10		7.4	
	1	282		0		7.4	
	5	187		0		7.6	
	10	195		0		7.7	
	15	160		0		7.9	
	20	180		0		8.0	
	30	177		0		8.0	
Average / Standard Deviation	0	300	0	10	0	7.35	0.07
	1	290	11	0	0	7.40	0.00
	5	278	74	0	0	7.40	0.07
	10	240	73	0	0	7.55	0.07
	15	246	93	0	0	7.75	0.00
	20	226	42	0	0	7.90	0.00
	30	210	46	0	0	8.0	0.00

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Table A.8. Soil Phase Oxidation Evaluation Results

Step Numbers	Duplicate Experiment I		Duplicate Experiment II		[TNT], ppm		[Total ADNT], ppm	
	[TNT], ppm	[Total ADNT], ppm	[TNT], ppm	[Total ADNT], ppm	Average	STD	Average	STD
0	15950	6699	15549	7228	15749	284	6963	374
1	14909	7888	14719	6770	14815	134	7329	791
2	14959	5497	14041	4866	14500	649	5181	446
3	14121	6508	14250	4011	14185	91	5259	1766
4	14185	5988	14013	5298	14099	122	5643	488
5	14134	5888	13485	5331	13809	459	5609	394
6	13614	4783	12157	3858	12886	1030	4320	654
7	12968	4497	11670	4166	12319	918	4332	234
8	11737	5137	10978	3088	11357	537	4112	1449
9	10519	3465	11467	3247	10993	670	3356	154
10	10119	3285	11268	2932	10693	812	3109	250
11	12583	2640	10610	2012	11596	1395	2326	444
12	12593	1852	8434	1699	10514	2941	1775	108
13	10547	1587	6276	1517	8411	3020	1551	49
14	7624	1384	7708	1186	7666	59	1285	140
15	6615	1176	6435	1000	6525	127	1088	124
16	6757	358	6242	228	6500	364	293	92
17	6932	196	5138	54	6035	1269	125	100
18	5968	0	5473	0	5720	350	0	0

Conditions:

1st through 4th application: 100 ppm Fe^{2+}/5,000 ppm H_2O_2

5th through 10th application: 100 ppm Fe^{2+}/20,000 ppm H_2O_2

1th through 16th application: 2500 ppm Fe^{2+}/50,000 ppm H_2O_2

17th through 18th application: 10,000 ppm Fe^{2+}/100,000 ppm H_2O_2

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Table A.9. Biological Step Results from Integration Experiment I

Days	Duplicate Experiment I				Duplicate Experiment II				Average					
	E_h	pH	[TNT], ppm	[Total ADNT], ppm	E_h	pH	[TNT], ppm	[Total ADNT], ppm	E_h	pH	[TNT], ppm	Std	[Total ADNT], ppm	Std
0	5	7.1	36690	0	20	7.1	37182	0	12	7.1	36936	348	0	0
3	-8	6.2	33320	627	-21	6.3	31286	614	-14	6.25	32303	1438	621	9
7	1	6	32273	830	-5	6	34886	1082	-2	6	33579	1848	956	178
11	-12	6.1	30081	1879	-22	5.7	32620	1455	-17	5.9	31350	1795	1667	300
14	-15	5.9	33247	2080	-37	6.2	33341	1963	-26	6.05	33294	66	2021	83
21	-26	6.6	33536	2765	-40	6.7	31310	2591	-33	6.65	32423	1574	2678	123
28	-35	7	32548	3598	-45	6.8	29960	3314	-40	6.9	31254	1830	3456	201
35	-37	7.3	32387	4235	-51	6.7	28125	4003	-44	7	30256	3014	4119	164
41	-60	6.9	27526	4897	-55	6.6	27390	5404	-57	6.75	27457	96	5150	359
47	-58	5.3	21898	11420	-42	5.6	25916	13975	-50	5.45	23907	2841	12697	1807
55	-40	5.1	12761	21194	-35	5.1	9141	21657	-37	5.1	10952	2560	21425	327
64	-45	4.4	2651	29747	-48	4.4	2141	26366	-46	4.4	2396	361	28056	2391

Condition:

Seeded with 50 ml digester sludge
Day 0-Day 41 Molasses (2%)/N (50 ppm)/P (20 ppm)
Day 0-Day 41 Molasses (4%)/N (50 ppm)/P (20 ppm)
Amended on a weekly base

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Table A.10. Biological Step Results from Integration Experiment II

Days	Duplicate Experiment I				Duplicate Experiment II				Average					
	E_h	pH	[TNT], ppm	[Total ADNT], ppm	E_h	pH	[TNT], ppm	[Total ADNT], ppm	E_h	pH	[TNT], ppm	STD	[Total ADNT], ppm	STD
0	72	7.8	33787	0	96	7.5	39052	0	84	7.65	36419	3723	0	0
3	-60	5.9	27873	0	-45	6.4	42680	0	-52	6.15	35277	10470	0	0
7	-1	6.6	29108	0	-25	6.5	29963	552	-13	6.55	39536	605	276	390
11	-21	5.9	32221	537	-55	6.7	30189	1056	-38	6.3	31205	1437	796	367
14	2	6.7	25925	1447	-1	5.9	27381	1223	0.5	6.3	26653	1030	1335	158
21	0	6.6	24366	1956	-10	6.4	25902	1702	-5	6.5	25134	1086	1829	180
28	2	6.8	22657	2459	-2	6.6	25034	2277	0	6.7	23846	1681	2368	129
35	-4	7	24600	2588	-19	7.1	21331	3182	-11	7.05	22965	2312	2885	420
41	-18	6.5	25972	3286	-23	6.7	23893	5104	-20	6.6	24932	1470	4195	1286
47	-21	4.2	22396	6525	-34	4.6	23000	5972	-27	4.4	22698	427	6248	391
55	-17	4	20293	7929	-24	4.1	18518	9298	-20	4.05	19405	1255	8613	968
64	-15	4.1	14671	11838	-17	4.1	13487	14673	-16	4.1	14079	837	13255	2005
75	-21	4.1	7234	17040	-28	4.1	5798	20616	-24	4.1	6516	1015	18828	2529
97	-36	4.1	4642	19906	-55	4	3870	19778	-45	4.05	4256	546	19842	91

Condition:

Seeded with 100 ml digester sludge
Molasses (2%)/N (50 ppm)/P (20 ppm)
Amended on a weekly base

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Table A. 11. Oxidation Step Results from Integration Experiment I

Step Numbers	Duplicate Experiment I		Duplicate Experiment II		[TNT], ppm		[Total ADNT], ppm	
	[TNT], ppm	[Total ADNT], ppm	[TNT], ppm	[Total ADNT], ppm	Average	STD	Average	STD
0	2651	29747	2141	26366	2396	361	28056	2391
1	1084	21776	1201	20767	1143	83	21271	713
2	2179	21503	1543	16289	1861	450	18896	3687
3	1460	17513	1710	16827	1585	177	17170	485
4	1393	14418	1492	13396	1443	70	13907	723
5	1742	14540	1630	12022	1686	79	13281	1780
6	714	8912	1367	9915	1040	462	9414	709
7	1369	11322	1224	8070	1297	103	9696	2300
8	783	5484	831	4863	807	34	5173	439

Conditions:

1st ~ 4th application: 2500 ppm Fe^{2+}/50,000 ppm H_2O_2

5th ~ 8th application: 10,000 ppm Fe^{2+}/100,000 ppm H_2O_2

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Table A. 12. Oxidation Step Results from Integration Experiment II

Step Numbers	Duplicate Experiment I		Duplicate Experiment II		[TNT], ppm		[Total ADNT], ppm	
	[TNT], ppm	[Total ADNT], ppm	[TNT], ppm	[Total ADNT], ppm	Average	STD	Average	STD
0	4642	19906	3870	19777	4256	546	19842	91
1	4502	18273	3658	17040	4080	597	17652	872
2	3481	17890	3486	17517	3484	4	17704	264
3	2084	13013	3553	10053	2818	1039	11533	2093
4	1745	6009	2407	5276	2076	468	5642	518
5	2413	3623	2382	2446	2398	22	3035	832

Conditions:

1st ~ 2th application: 1,000 ppm Fe^{2+}/100,000 ppm H_2O_2

3th ~5th application: 10,000 ppm Fe^{2+}/100,000 ppm H_2O_2

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Table A. 13. Biological Step plus Oxidation Step Results

Biological Step	Duplicate Experiment I			Duplicate Experiment II			E_h		pH		[TNT], ppm	
Days	E_h	pH	[TNT], ppm	E_h	pH	[TNT], ppm	AVG	STD	AVG	STD	AVG	STD
0	235	7.3	319	199	7.2	455	217	25	7.25	0.1	387	96
1	138	7.2	172	96	7.1	194	117	30	7.17	0.1	183	16
3	-486	6.5	38	-461	6.9	48	-473.5	18	6.7	0.3	43	7
7	-536	7.5	31	-518	6.6	45	-527	13	7.05	0.6	38	10
10	-549	7.3	53	-521	6.8	42	-535	20	7.05	0.4	47	8

Oxidation Step	Formula 1				Formula 2			
	Duplicate Experiment I	Duplicate Experiment II	AVG	STD	Duplicate Experiment I	Duplicate Experiment II	AVG	STD
	[TNT], ppm	[TNT], ppm			[TNT], ppm	[TNT], ppm		
Initial	49	45	47	2.8	48	47	47.5	0.7
Final	8.6	10.8	9.7	1.6	0	0	0	0.0

Condition:

- ✓ Biological Step: Seeded with 10 ml digester sludge
  Molasses (2%)/N (50 ppm)/P (20 ppm)
  Amended on a weekly base
- ✓ Oxidation Step: Formula 1: 100 ppm Fe^{2+}/5000 ppm H_2O_2
  Formula 2: 500 ppm Fe^{2+}/25000 ppm H_2O_2

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Table A. 14. Integration Experiments Initial Soil Characterization

<table>
<tr><td rowspan="7">High Level Contamination</td><td colspan="2"></td><td>[TNT], ppm</td></tr>
<tr><td rowspan="2">50 ml Sludge</td><td>Duplicate Reactor I</td><td>36690</td></tr>
<tr><td>Duplicate Reactor II</td><td>37182</td></tr>
<tr><td rowspan="2">100 ml Sludge</td><td>Duplicate Reactor I</td><td>33787</td></tr>
<tr><td>Duplicate Reactor II</td><td>39052</td></tr>
<tr><td colspan="2">AVG</td><td>36677</td></tr>
<tr><td colspan="2">STD</td><td>2179</td></tr>
<tr><td rowspan="4">Low Level Contamination</td><td colspan="2">Duplicate Reactor I</td><td>319</td></tr>
<tr><td colspan="2">Duplicate Reactor II</td><td>455</td></tr>
<tr><td colspan="2">AVG</td><td>387</td></tr>
<tr><td colspan="2">STD</td><td>96</td></tr>
</table>

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Table A. 15. Biological Testing Condition 1 Results

	Days	[TNT], ppm	[TNB], ppm	[ADNT], ppm	Liquid [TNT], ppm	Liquid [TNB], ppm	Liquid [ADNT], ppm	pH	E_h
Duplicate Experiment I	0	26879	32.75	579.55	112.74	2.63	3.42	7.2	196
	5	24196	53.97	397.80	89.93	4.36	4.25	7.4	200
	8	27430	66.48	450.25	107.31	5.81	4.44	7.2	206
	13	26323	51.73	201.77	81.36	4.80	1.47	6.7	206
	17	28508	49.69	538.92	91.11	7.72	1.83	7.1	61
	21	26362	50.89	693.71	28.65	4.01	0.85	7.4	181
	26	24194	41.16	508.12	45.49	5.64	1.40	7.1	114
	29	28474	50.99	584.26	47.67	7.30	1.67	7.2	195
	34	25464	37.47	567.83	25.29	6.64	1.13	7.3	165
	40	27582	44.27	478.45	17.19	4.70	0.91	7.3	170
	43	24118	11.32	288.51	87.79	13.77	1.31	7.1	180
	58	37387	118.12	229.29	66.01	14.24	2.38	7	234
	71	30315	96.65	875.84	43.13	15.94	3.42	7.6	283
Duplicate Experiment II	0	31467	35.84	659.04	123.51	2.67	3.44	6.7	194
	5	33953	45.84	693.18	116.32	5.07	5.12	7.3	199
	8	35142	65.09	549.21	118.46	5.52	4.91	7	207
	13	35986	62.71	1164.88	91.98	5.26	1.71	7.6	200
	17	29996	44.80	577.60	95.27	8.21	1.97	8.1	108
	21	28060	40.89	517.95	38.12	4.72	1.37	7.1	174
	26	27084	48.43	502.46	61.53	6.94	13.67	7	119

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Table A. 15. Continue

	Days	[TNT], ppm	[TNB], ppm	[ADNT], ppm	Liquid [TNT], ppm	Liquid [TNB], ppm	Liquid [ADNT], ppm	pH	E_h
	29	27717	47.88	563.64	37.33	5.29	1.23	7.2	183
	34	28078	52.65	611.87	18.41	5.33	1.06	7.7	157
	40	30217	58.75	673.75	20.77	5.74	0.95	8	160
	43	31596	90.67	1515.33	68.2	10.95	3.16	7.9	177
	58	20308	9.44	1049.11	60.84	14.09	12.21	7.2	210
	71	27804	23.45	374.13	78.64	9.14	5.16	7.7	266
Average	Days	[TNT], ppm		[TNB], ppm		[ADNT], ppm		pH	
		Avg	Std	Avg	Std	Avg	Std	Avg	Std
	0	29173	3244	34.29	2.18	619.29	56.21	6.95	0.4
	5	29074	6899	49.90	5.75	545.49	208.87	7.35	0.1
	8	31286	5453	65.79	0.98	499.73	69.98	7.1	0.1
	13	31154	6833	57.22	7.76	683.32	681.02	7.15	0.6
	17	29252	1052	47.25	3.46	558.26	27.35	7.6	0.7
	21	27211	1201	45.89	7.07	605.83	124.28	7.25	0.2
	26	25640	2044	44.80	5.14	505.29	4.00	7.05	0.1
	29	28095	535	49.43	2.20	573.95	14.58	7.2	0.0
	34	27086	1848	45.06	10.73	589.85	31.14	7.5	0.3
	40	28899	1863	51.51	10.24	576.11	138.10	7.65	0.5
	43	27857	5288	50.99	56.11	613.41	867.49	7.5	0.6
	58	28847	12077	54.33	76.85	639.20	579.70	7.08	0.1
	71	29060	1776	60.05	51.76	624.98	354.76	7.65	0.1

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Table A. 15. Continue

	Days	Liquid [TNT], ppm		Liquid [TNB], ppm		Liquid [ADNT], ppm		E_h	
		Avg	Std	Avg	Std	Avg	Std	Avg	Std
Average	0	118.12	7.62	2.65	0.03	3.43	0.01	195	1
	5	103.12	18.66	4.71	0.50	4.68	0.62	199	1
	8	112.88	7.88	5.66	0.21	4.67	0.33	206	1
	13	86.67	7.51	5.03	0.33	1.59	0.17	203	4
	17	93.19	2.94	7.96	0.35	1.90	0.10	84.5	33
	21	33.38	6.70	4.36	0.50	1.11	0.37	177	5
	26	53.51	11.34	6.29	0.92	7.53	8.68	116	4
	29	42.50	7.31	6.30	1.42	1.5	0.31	189	8
	34	21.85	4.86	5.99	0.93	1.1	0.05	161	6
	40	18.98	2.53	5.22	0.74	0.93	0.03	165	7
	43	77.99	13.85	12.36	1.99	2.23	1.31	178	2
	58	63.42	3.66	14.16	0.11	7.30	6.95	222	17
	71	60.88	25.11	12.54	4.81	4.29	1.23	274	12

Condition:

Soil/Distilled Water

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Table A. 16. Biological Testing Condition 2 Results

	Days	[TNT], ppm	[TNB], ppm	[ADNT], ppm	Liquid [TNT], ppm	Liquid [TNB], ppm	Liquid [ADNT], ppm	pH	E_h
Duplicate Experiment I	0	36228	119.54	1057.66	41.07	2.61	14.99	7.3	137
	5	27664	122.17	953.08	37.43	5.46	16.49	7.7	135
	8	33023	145.90	951.68	48.81	11.27	23.72	8.3	130
	13	28028	137.98	778.42	45.28	18.09	14.8	8.2	124
	17	16612	94.63	284.95	43.68	24.53	20.23	8.3	-14
	21	17157	111.67	272.99	33.91	27.21	32.16	8.2	86
	26	14100	122.11	254.65	148.47	16.61	32.77	8.3	57
	29	11578	121.08	198.07	188	20.53	35.14	8.1	81
	34	11242	124.19	195.37	156.27	18.56	34.88	8.1	74
	40	9014	124.58	249.98	115.86	20.56	34.23	8.3	76
	43	6504	102.82	187.90	81.73	26.06	35.16	8	71
	58	7902	133.63	303.28	394.05	18.02	29.62	8.5	79
	71	7083	78.41	157.48	198.2	15.51	51.26	8.7	144
Duplicate Experiment II	0	47327	140.07	1393.30	51.33	4.99	19.94	7.5	106
	5	32275	121.98	1018.83	51.85	12.3	24.36	8	110
	8	28774	146.91	960.31	63.59	16.7	27.23	8.3	115
	13	23834	123.12	639.37	55.17	22.95	16.6	8.2	130
	17	36652	165.71	551.40	49.344	22.63	18.79	8.4	20
	21	16986	108.41	294.82	49.08	25.21	30.14	8.4	73
	26	17266	134.86	260.94	182.21	26.5	34.17	8.3	54

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Table A. 16. Continue

	Days	[TNT], ppm	[TNB], ppm	[ADNT], ppm	Liquid [TNT], ppm	Liquid [TNB], ppm	Liquid [ADNT], ppm	pH	E_h
	29	14794	140.04	237.46	138.94	23.07	23.98	8.1	74
	34	7742	146.48	164.55	103.32	10.42	29.16	8.1	61
	40	8778	154	99.35	147.9	13.08	28.27	8.4	69
	43	6927	139.35	248.51	276.36	33.18	31.52	8.1	61
	58	9069	130.32	156.16	157.3	54.59	42.59	8.6	66
	71	8724	161.84	93.91	165.51	64.56	46.48	8.7	139
Average	Days	[TNT], ppm		[TNB], ppm		[ADNT], ppm		pH	
		Avg	Std	Avg	Std	Avg	Std	Avg	Std
	0	41777	7848	129.80	14.52	1225.48	237.33	7.4	0.1
	5	29969	3260	122.35	0.13	985.96	46.49	7.85	0.2
	8	30898	3004	146.41	0.71	955.99	6.10	8.3	0.0
	13	25930	2966	130.55	10.51	708.89	98.32	8.2	0.0
	17	26632	14170	130.17	50.26	418.17	188.41	8.35	0.1
	21	17072	121	110.04	2.31	283.90	15.44	8.3	0.1
	26	15683	2239	128.49	9.02	257.80	4.45	8.3	0.0
	29	13186	2274	130.56	13.41	217.77	27.85	8.1	0.0
	34	9492	2475	135.39	15.76	179.96	21.79	8.1	0.0
	40	8896	167	139.29	20.80	174.67	106.51	8.35	0.1
	43	6715	299	121.08	25.83	218.21	42.86	8.05	0.1
	58	8485	825	131.97	2.34	229.72	104.03	8.53	0.1
	71	7904	1160	120.12	58.99	125.70	44.95	8.7	0.0

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Table A. 16. Continue

	Days	Liquid [TNT], ppm		Liquid [TNB], ppm		Liquid [ADNT], ppm		E_h	
		Avg	Std	Avg	Std	Avg	Std	Avg	Std
Average	0	46.20	7.25	3.8	1.68	17.46	3.50	121	22
	5	44.64	10.20	8.88	4.84	20.42	5.56	122	18
	8	56.20	10.45	13.98	3.84	25.47	2.48	122	11
	13	50.22	6.99	20.52	3.44	15.7	1.27	127	4
	17	46.51	4.01	23.58	1.34	19.51	1.02	3	24
	21	41.49	10.73	26.21	1.41	31.15	1.43	80	9
	26	165.34	23.86	21.55	6.99	33.47	0.99	56	2
	29	163.47	34.69	21.8	1.80	29.59	7.89	77	5
	34	129.79	37.44	14.49	5.76	32.02	4.04	67	9
	40	131.88	22.66	16.82	5.29	31.25	4.21	72	5
	43	179.04	137.62	29.62	5.03	33.34	2.57	66	7
	58	275.67	167.41	36.30	25.86	36.10	9.17	72	9
	71	181.85	23.12	40.03	34.68	48.87	3.38	141	4

Condition:

Na-acetate (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base

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Table A. 17. Biological Testing Condition 3 Results

	Days	[TNT], ppm	[TNB], ppm	[ADNT], ppm	Liquid [TNT], ppm	Liquid [TNB], ppm	Liquid [ADNT], ppm	pH	E_h
Duplicate Experiment I	0	43737	112.55	1531.45	64.03	2.97	36.75	7.6	88
	5	42739	111.68	1502.07	64.43	5.91	31.7	7.9	87
	8	35089	109.97	1293.29	88.11	11.85	44.13	8.3	86
	13	27030	87.36	1306.45	79.17	20.11	26.78	8.1	133
	17	23993	102.68	420.30	60.56	21.25	30.53	8.3	-9
	21	24657	118.52	397.94	46.88	22.12	36.75	8.4	66
	26	15674	99.54	277.57	171.38	24.64	39.74	8.3	45
	29	15962	137.43	239.84	261.28	30.14	47.02	8.1	67
	34	12250	158.33	172	149.31	13.52	35.83	8.1	54
	40	10868	85.26	97.46	211.12	26.44	56.33	8.3	61
	43	6885	109.21	93.67	51.66	67.15	54.12	8.5	32
	58	9417	31.86	291.86	423.66	136.74	71.15	8.55	53
	71	6772	167.86	347.08	253.45	150.18	62.45	8.7	129
Duplicate Experiment II	0	27353	137.57	1237.13	52.27	2.29	29.78	7.3	85
	5	38629	134.37	1513.06	54.4	4.85	24.35	7.9	86
	8	30352	142.88	1301.56	76.3	15.07	39.26	8.5	70
	13	25751	121.56	1279.72	72.33	17.86	25.65	8.2	127
	17	18282	79.55	315.30	70.46	18.43	31.57	8.3	17
	21	18459	106.55	364.39	63.59	22.46	35.58	8.3	64
	26	13255	119.21	257.34	204.43	24.97	43.51	8.3	51

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Table A. 17. Continue

	Days	[TNT], ppm	[TNB], ppm	[ADNT], ppm	Liquid [TNT], ppm	Liquid [TNB], ppm	Liquid [ADNT], ppm	pH	E_h
	29	16192	117.48	240.67	218.59	23.2	43.44	8	40
	34	8260	66.26	261.41	139.15	25.26	33.55	8	52
	40	9851	122.85	228.81	176.86	17.55	40.89	8.3	55
	43	6921	115.62	135.76	77.3	58.18	49.51	8.6	-12
	58	5599	162.50	501.20	225.97	155.68	64.59	8.27	56
	71	8062	2.65	246.43	204.15	167.51	59.81	8.8	119
Average	Days	[TNT], ppm		[TNB], ppm		[ADNT], ppm		pH	
		Avg	Std	Avg	Std	Avg	Std	Avg	Std
	0	35545	11585	125.06	17.69	1384.29	208.12	7.45	0.2
	5	40684	2906	123.03	16.04	1507.56	7.77	7.9	0.0
	8	32720	3350	126.42	23.27	1297.42	5.85	8.4	0.1
	13	26391	904	104.46	24.18	1293.08	18.90	8.15	0.1
	17	21137	4038	91.12	16.36	367.80	74.25	8.3	0.0
	21	21558	4383	112.53	8.46	381.16	23.72	8.35	0.1
	26	14465	1710	109.37	13.91	267.45	14.30	8.3	0.0
	29	16077	163	127.45	14.11	240.26	0.59	8.05	0.1
	34	10255	2821	112.29	65.10	216.70	63.22	8.05	0.1
	40	10360	719	104.06	26.58	163.14	92.88	8.3	0.0
	43	6903	25	112.42	4.53	114.71	29.76	8.55	0.1
	58	7508	2700	97.18	92.38	396.53	148.03	8.41	0.2
	71	7417	912	85.26	116.82	296.75	71.17	8.75	0.1

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Table A. 17. Continue

	Days	Liquid [TNT], ppm		Liquid [TNB], ppm		Liquid [ADNT], ppm		E_h	
		Avg	Std	Avg	Std	Avg	Std	Avg	Std
Average	0	58.15	8.32	2.63	0.48	33.26	4.93	86.5	2
	5	59.41	7.09	5.38	0.75	28.02	5.20	86.5	1
	8	82.20	8.35	13.45	2.28	41.69	3.44	78	11
	13	75.75	4.84	18.98	1.59	26.21	0.80	130	4
	17	65.51	7.00	19.84	1.99	31.05	0.74	4	18
	21	55.23	11.82	22.29	0.24	36.16	0.83	65	1
	26	187.89	23.37	24.80	0.23	41.62	2.67	48	4
	29	239.93	30.19	26.67	4.91	45.23	2.53	53.5	19
	34	144.23	7.18	19.39	8.30	34.69	1.61	53	1
	40	193.99	24.23	21.99	6.29	48.61	10.92	58	4
	43	64.48	18.13	62.66	6.34	51.81	3.26	10	31
	58	324.81	139.79	146.21	13.39	67.87	4.64	54.5	2
	71	228.8	34.86	158.84	12.25	61.13	1.87	124	7

Condition:

Na-acetate (2%)/Tween80 (1%)/N (50 ppm)/P (20 ppm); amended on a weekly base;

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Table A. 18. Biological Testing Condition 4 Results

	Days	[TNT], ppm	[TNB], ppm	[ADNT], ppm	Liquid [TNT], ppm	Liquid [TNB], ppm	Liquid [ADNT], ppm	pH	E_h
Duplicate Experiment I	0	39347	45.09	826.93	105.82	1.91	3.37	7.4	123
	5	25702	43.19	565.91	75.83	3.11	3.61	6.8	135
	8	27206	45.86	439.97	94.95	4.1	4.32	6.9	140
	13	24010	36.81	345.03	77.48	3.4	0.93	6.5	190
	17	21996	38.56	280.53	87.62	5.9	2.97	7	92
	21	19601	41.81	239.88	24.23	3.45	1.62	7	120
	26	19862	38.84	245.38	40.02	4.07	0.95	7	104
	29	15572	42.50	182.70	44.12	3.92	1.75	6.3	104
	34	13591	32.41	214.16	27.62	4.27	1.58	6.7	110
	40	15622	75.54	277.25	31.74	4.31	1.71	7	111
	43	18804	82.88	394.38	54.99	5.04	2.02	7	80
	58	12550	46.54	304.83	50.63	4.40	1.97	6.98	118
	71	8123	34.76	401.23	64.15	5.51	0.98	6.9	181
Duplicate Experiment II	0	34667	42.72	507.65	93.82	1.93	2.96	7.2	135
	5	35427	47.50	765.71	83.9	3	4.18	6.9	130
	8	31455	49.18	484.82	97.34	4.02	4.53	6.9	125
	13	24406	60.18	396.59	70.82	5.1	1.97	6.5	198
	17	19199	29.08	246.03	87.92	5.6	1.99	7	106
	21	16408	30.25	205.19	19.81	1.81	1.44	7	119
	26	19502	36.12	223.56	53.33	3.83	1.29	6.9	113

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Table A. 18. Continue

	Days	[TNT], ppm	[TNB], ppm	[ADNT], ppm	Liquid [TNT], ppm	Liquid [TNB], ppm	Liquid [ADNT], ppm	pH	E_h
	29	13830	34.91	205.49	51.26	3.99	2.39	6.1	115
	34	11776	51.23	262.96	32.85	3.64	1.74	6.5	117
	40	11400	72.10	264.87	27.93	3.61	1.59	6.9	119
	43	16710	43.80	358.84	44.58	2.86	1.64	7	100
	58	24405	84.99	306.62	56.55	3.51	2.02	6.9	131
	71	9491	29.52	128.66	45.56	6.95	2.64	6.6	180
Average	Days	[TNT], ppm		[TNB], ppm		[ADNT], ppm		pH	
		Avg	Std	Avg	Std	Avg	Std	Avg	Std
	0	37007	3309	43.91	1.68	667.30	225.77	7.3	0.1
	5	30564	6877	45.35	3.05	665.82	141.28	6.85	0.1
	8	29331	3004	47.52	2.35	462.40	31.71	6.9	0.0
	13	24208	280	48.50	16.53	370.81	36.46	6.5	0.0
	17	20598	1978	33.83	6.70	263.29	24.40	7	0.0
	21	18004	2258	36.03	8.17	222.54	24.53	7	0.0
	26	19682	255	37.48	1.92	234.48	15.43	6.95	0.1
	29	14701	1232	38.71	5.37	194.10	16.11	6.2	0.1
	34	12684	1283	41.82	13.31	238.56	34.51	6.6	0.1
	40	13511	2985	73.83	2.43	271.06	8.75	6.95	0.1
	43	17757	1481	63.35	27.63	376.61	25.13	7	0.0
	58	18478	8383	65.77	27.19	305.73	1.27	6.97	0.1
	71	8807	967	32.14	3.71	264.95	192.74	6.75	0.2

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Table A. 18. Continue

	Days	Liquid [TNT], ppm		Liquid [TNB], ppm		Liquid [ADNT], ppm		E_h	
		Avg	Std	Avg	Std	Avg	Std	Avg	Std
Average	0	99.82	8.49	1.92	0.01	3.16	0.29	129	8
	5	79.86	5.71	3.05	0.08	3.89	0.40	132	4
	8	96.14	1.69	4.06	0.06	4.42	0.15	132	11
	13	74.15	4.71	4.25	1.20	1.45	0.74	194	6
	17	87.77	0.21	5.75	0.21	2.48	0.69	99	10
	21	22.02	3.13	2.63	1.16	1.53	0.13	119	1
	26	46.67	9.41	3.95	0.17	1.12	0.24	108	6
	29	47.69	5.05	3.95	0.05	2.07	0.45	109	8
	34	30.23	3.70	3.95	0.45	1.66	0.11	113	5
	40	29.84	2.69	3.96	0.49	1.65	0.08	115	6
	43	49.78	7.36	3.95	1.54	1.83	0.27	90	14
	58	53.59	4.19	3.95	0.63	1.99	0.04	124	9
	71	54.85	13.15	6.23	1.02	1.81	1.17	180	1

Condition:

Potato starch (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base

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Table A. 19. Biological Testing Condition 5 Results

	Days	[TNT], ppm	[TNB], ppm	[ADNT], ppm	Liquid [TNT], ppm	Liquid [TNB], ppm	Liquid [ADNT], ppm	pH	E_h
Duplicate Experiment I	0	24673	34.28	606	54.96	0.8	9.36	6.7	161
	5	29347	51.58	719	47.44	0.41	10.89	6.6	152
	8	36234	34.63	785	62.92	1.68	11.48	7	140
	13	24475	37.58	642	46.13	1.13	5.27	6.7	179
	17	18513	26.29	339	80.66	1.52	8.17	7	98
	21	20894	30.35	289	30.20	1.6	0.95	6.9	123
	26	14919	26.44	207	45.06	3.19	2.47	6.8	103
	29	15329	39.98	271	52.53	3.42	4.85	6.2	112
	34	11621	26.82	206	26.81	3.59	1.97	6.8	105
	40	12881	10.33	83	40.41	4.31	2.58	7.1	111
	43	21838	33.98	207	26.14	0.77	2.08	6.5	25
	58	5933	19.43	159	25.26	0.81	3.80	6.7	28
	71	11520	29.39	172	37.56	1.05	3.34	7.2	176
Duplicate Experiment II	0	32849	36.08	1040	47.82	0.59	8.61	7	164
	5	35764	49.40	1079	47.75	2.31	6.97	6.8	149
	8	41188	44.51	1102	76.80	2.52	10.83	7.1	136
	13	28362	37.13	613	55.53	1.78	4.77	6.8	175
	17	20870	30.41	304	84.12	3.43	7.45	7.1	107
	21	21893	39.56	307	20.56	2.02	1.24	7	119
	26	17069	34.53	235	48.62	3.69	1.76	7	104

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Table A. 19. Continue

	Days	[TNT], ppm	[TNB], ppm	[ADNT], ppm	Liquid [TNT], ppm	Liquid [TNB], ppm	Liquid [ADNT], ppm	pH	E_h
	29	13790	46.96	227	47.84	3.82	3.93	6.9	112
	34	11939	46.45	279	24.69	3.86	1.81	6.7	105
	40	12829	43.32	241	22.23	3.58	1.77	7.1	113
	43	10017	58.22	188	21.97	0.83	1.57	6.4	44
	58	11661	43.63	223	15.85	0.83	1.26	6.89	80
	71	10079	46.58	67	35.34	0.99	1.34	7.2	166
Average	Days	[TNT], ppm		[TNB], ppm		[ADNT], ppm		pH	
		Avg	Std	Avg	Std	Avg	Std	Avg	Std
	0	28761	5781	35.18	1.27	823	306.88	6.85	0.2
	5	32556	4538	50.49	1.54	899	254.56	6.7	0.1
	8	38711	3503	39.57	6.99	943	224.15	7.05	0.1
	13	26418	2749	37.35	0.32	627	20.51	6.75	0.1
	17	19692	1667	28.35	2.91	322	24.75	7.05	0.1
	21	21393	706	34.95	6.51	298	12.73	6.95	0.1
	26	15994	1520	30.49	5.72	221	19.80	6.9	0.1
	29	14559	1088	43.47	4.94	249	31.11	6.55	0.5
	34	11780	225	36.63	13.88	243	51.62	6.75	0.1
	40	12855	37	26.82	23.33	162	111.72	7.1	0.0
	43	15927	8359	46.10	17.14	197	13.44	6.45	0.1
	58	8797	4050	31.53	17.11	191	45.25	6.81	0.1
	71	10800	1019	37.98	12.16	120	74.25	7.2	0.0

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Table A. 19. Continue

	Days	Liquid [TNT], ppm		Liquid [TNB], ppm		Liquid [ADNT], ppm		E_h	
		Avg	Std	Avg	Std	Avg	Std	Avg	Std
Average	0	51.39	5.05	070	0.15	8.98	0.53	162	2
	5	47.60	0.22	1.36	1.34	8.93	2.77	150	2
	8	69.86	9.81	2.1	0.59	11.15	0.46	138	3
	13	50.83	6.65	1.45	0.46	5.02	0.35	177	3
	17	82.39	2.45	2.475	1.35	7.81	0.51	102	6
	21	25.38	6.82	1.81	0.30	10.9	0.21	121	3
	26	46.84	2.52	3.44	0.35	2.11	0.50	103	1
	29	50.18	3.32	3.62	0.28	4.39	0.65	112	0
	34	25.75	1.50	3.72	0.19	1.89	0.11	105	0
	40	31.32	12.86	3.94	0.52	2.17	0.57	112	1
	43	24.05	2.95	0.80	0.04	1.82	0.36	34.5	13
	58	20.55	6.65	0.81	0.01	2.53	1.80	26	37
	71	36.45	1.57	1.02	0.04	2.34	1.41	171	7

Condition:

Molasses (2%)/N (50 ppm)/P (20 ppm); amended on a weekly base;

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Table A. 20. Bioslurry Experiments Initial Soil Characterization

		[TNT], ppm	[TNB], ppm	[ADNT], ppm
Control	Duplicate Reactor I	26879	32.75	579.55
	Duplicate Reactor II	31467	35.84	659.04
Na-acetate/N/P	Duplicate Reactor I	36228	119.54	1057.66
	Duplicate Reactor II	47327	140.07	1393.30
Na-acetate/Tween80/N/P	Duplicate Reactor I	43737	112.55	1531.45
	Duplicate Reactor II	27353	137.57	1237.13
Potato Starch/N/P	Duplicate Reactor I	39347	45.09	826.93
	Duplicate Reactor II	34667	42.72	507.65
Molasses/N/P	Duplicate Reactor I	24673	34.28	606
	Duplicate Reactor II	32849	36.08	1040
AVG		34452	73.65	943.87
STD		7408	47.08	363.22

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