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**Zero Valent Iron and Ultrasound as Potential Remediators of
Certain Pollutants in Water**

by

Marcin Pawlak, B.Sc.

**A Thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of**

Master of Science

Department of Chemistry

**Carleton University
Ottawa, Ontario
May 04, 1999
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Chair, Department of Chemistry

Thesis Supervisor

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Abstract

The effects of iron particles and ultrasound both separately and together on aqueous solutions of 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), aniline, chlorobenzene, toluene, and nitrosodimethyl amine (NDMA) were investigated. In addition the combined effects of ferrous chloride and ultrasound on aniline alone were studied. Degradation rate constants for all analytes were determined from batch studies conducted at two standard pHs; 4 and 6. Sonications of samples were performed at 20 and 900 kHz, at power levels of 32.5 and 17.2 W/cm² respectively.

Comparative analysis of rate constants demonstrated that: i) ultrasound in water causes degradation of most of the compounds, ii) the dinitrotoluenes rapidly disappear on treatment with iron, iii) variations in ultrasonic frequency produced noticeable differences and iv) there seem to be no synergisms between iron and ultrasound.

This thesis is dedicated to my mother,
my father and my future companion
Jennifer Vethamuthu

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1.0 Introduction

1.1 Elimination of Toxic Compounds from Water by Conventional Methods

In the United States alone there are over 14900 contaminated land and groundwater sites.¹ As a result, groundwater contamination by various pollutants has become a subject of increasing concern due to the persistence of and toxic effects associated with certain organic compounds. Consequently the development of innovative and efficient methods for reducing groundwater pollutant concentrations to legally acceptable levels has emerged as an area of extensive research.

Since the late 70's one of the most popular remediation technologies has been the pump and treat method, which is a two stage clean up procedure comprising of an extraction and an *ex-situ* treatment process. It has been routinely applied by various industries primarily due to its ease of installation, operation and most importantly acceptance by regulatory authorities. However, over the years studies have shown that its effectiveness at extracting pollutants from subsurface environments is rather poor, especially from soils with low permeability characteristics, and in zones containing dense non-aqueous phase liquids (DNAPLs).^{1, 2, 3} DNAPLs are a class of chlorinated solvents, which not only have densities higher than water, but also exhibit strong hydrophobic properties.² Therefore even after excessively long and aggressive pumping periods, contaminant concentrations in freshly remediated zones have been known to return to nearly original levels after only a brief interruption in pumping.

To remedy this drawback, a recently developed extraction technique termed air sparging has shown to have large scale remediation potential.^{2, 4} It operates by injecting air or oxygen bubbles one meter below the deepest point of contamination. Since many

of the DNAPL contaminants are highly volatile, the upward passage of bubbles results in them being “stripped” from the groundwater and carried upward into designated unsaturated zones. Once there, a soil vapor extraction system draws the contaminant-laden vapors to the surface where they are treated using various *ex-situ* techniques. Compared to the conventional extraction technique, air sparging has several advantages. Most importantly, it does not require contaminated water to be pumped to the surface. Existing monitoring wells or even pump and treat facilities can be converted into gas injection tubes, making costs of start-up and maintenance significantly lower. However, as with most techniques there are some drawbacks: i) it is inefficient at extracting contaminants which have low volatilization rates e.g., nitro-aromatics, ii) the minimum depth of a contaminated plume must be greater than five feet and iii) it is ineffective in soils that have low permeability.³

Apart from methodologies which continuously require energy for extracting contaminants to above surface treatment plants, other technologies, namely *in-situ* type remediation have recently been explored. *In-situ*, unlike extraction remediation involves treatment of contaminants in their home environment. For example, a permanent subsurface chemical barrier requires strategic placement of immobile solid materials into subsurface environments in order to trap or degrade groundwater contaminants on contact.^{5,6} Bioremediation, another *in-situ* method uses naturally occurring organisms found in soil and groundwater for contaminant biodegradation. Usually the limiting factor in the biodegradation process is the lack of oxygen. Thus, air or oxygen is pumped through the soil and groundwater. Furthermore, depending on the type of contamination and soil characteristics, nutrients may also be required to keep sufficient colonies of

organisms alive. This approach has been particularly successful in remediating hydrocarbon-laden soils and groundwater.² Bioremediation has proven to be one of the most economical and least invasive methods of direct groundwater treatment. However like all applications it will most likely not be suitable for degrading contaminants which form complexes with the soil matrix.^{2,3}

Apart from extraction and *in-situ* remediation methods there is also a growing number of *ex-situ* technologies. For example, bioremediation has also been employed in various types of bioslurry reactors, fixed-film or fluidized-bed reactors, several of which are commercially available.^{2,7,8} However, in either condition, bioremediation type technologies were found to have several limitations. First, they are ineffective for compounds that are resistant to biodegradation. Second, under certain conditions the contaminants are toxic to the bacteria, killing off entire colonies.³

Gasification, another *ex-situ* process proceeds by thermally degrading organic substances. It involves the sorption of contaminants onto a macroporous char matrix followed by treatment with substoichiometric amounts of an oxidizing or reducing gas. The products of the gasification process are combustible gases, condensable water vapor, and a non-reactive carbon and mineral solid. Although highly effective, the main disadvantages of this process are the costs of operation and maintenance.^{9,10}

Recently, a new family of *ex-situ* remediative technologies, namely advanced oxidative processes (AOPs) has evolved. In general, AOPs are found to be more effective at remediating groundwater contaminated with certain undesirable chemical compounds. Furthermore, unlike any of the other remediative technologies, AOPs involve the production of hydroxyl radicals (OH*), a species known as a powerful

oxidizing agent. Examples of AOPs include; ozonolysis ¹¹, UV-oxidation ^{12, 13} and ultrasonic irradiation.^{3, 14, 15, 16, 17, 18, 19}

One of the most powerful *ex-situ* remediating processes is UV-oxidation. It is a highly destructive process, which combines ultraviolet light with chemical oxidants, such as ozone (O₃) or hydrogen peroxide (H₂O₂). Remediation of pollutant proceeds by oxidation, usually resulting in the production of water and carbon dioxide. Hydroxyl radicals are the dominant oxidizing agent and are generated from the reaction of ultraviolet irradiation with H₂O₂.^{20, 21, 22} The hydroxyl radical attacks organics by initiating a series of chain reactions. One of the predominant routes of attack is hydrogen atom abstraction usually resulting in contaminant destruction via various radical reactions. In order for this technique to be effective the contaminated groundwater must allow for transmission of UV light. However, if the aqueous sample has high turbidity due to a high concentration of suspended solid particles the effectiveness is significantly diminished. Furthermore aqueous streams consisting of 10 mg/L of heavy metal ions, or water containing insoluble oil or grease, may foul the quartz windows that admit the UV radiation.^{3, 23}

More recently ultrasonic irradiation has received much attention. It has been considered to be quite a special technique since it was found to be highly effective at decreasing contaminant concentration in aqueous samples.²⁴ It will be discussed in the following section.

1.2 **Elimination of Toxic Compounds from Water by Ultrasonic Methods**

The application of ultrasonic irradiation has numerous advantages over other AOPs. First, addition of oxidants is not necessary since radicals are spontaneously produced *in-situ*. Two, pyrolysis type conditions are generated within the aqueous medium similar to those encountered in gasification. Both of these unusual phenomena originate from the cyclical growth and in some cases violent collapse of cavities generated by passage of ultrasonic sound waves through an aqueous medium. Suslick has reported that localized pressures as high as 1000 atm and temperatures on the order of 5000 K can be generated during the collapse phase of ultrasound induced cavities.²⁵

Hoffmann et al. have investigated the degradation of various contaminants by ultrasonic irradiation at frequencies of 20 and 500 kHz. They reported that chemical contaminants such as chlorinated hydrocarbons, pesticides, phenols, explosives as well as esters can easily be transformed into short chain organic acids, CO₂ and inorganic ions following irradiation times ranging from minutes to hours.¹⁶

Hua et al. investigated the effects of ultrasonic irradiation at 20 kHz on the degradation of aqueous carbon tetrachloride solutions. They reported that chloride ions had formed as the final product, with hypochlorous acid and dichlorocarbene as the intermediate species.¹⁷

In contrast to UV-oxidation, ultrasonic remediation processes can be applied directly to the groundwater since the passage of sound, unlike light is not affected by the opacity or non-aqueous content of the medium.

Furthermore, in terms of efficiencies when compared to photochemical processes, sonochemistry has shown to be far superior, as presented in table 1.2.1. As shown, homogenous sonochemistry is typically more efficient than photochemistry, and heterogenous sonochemistry is several orders of magnitude better.²⁵

	Photochemistry	Homogeneous Sonochemistry	Heterogeneous Sonochemistry
Source	250-W quartz-Halogen	200-W cell disrupter at 60 % power	200-W cleaning bath
Approximate Cost (1987)	\$1800	\$1900	\$700
Typical rates $\mu\text{mol min}^{-1}$	7	10	500
Electrical Efficiency $(\text{mmol}(\text{kWh})^{-1})$	2	5	200

Table 1.2.1: Comparison of sonochemical and photochemical apparatus ²⁵

1.3 Elimination of Toxic Compounds from Groundwater by Metals

Historically the application of metals for dehalogenation purposes traces back to 1874 at which point zero valent zinc was first used for the vicinal dehalogenation of dibromides.²⁶ Other metals such as zero valent titanium were also employed for the reduction of fluorotrichloromethane to chlorofluorocarbene.²⁷ In the late 1980's studies were conducted to examine the corrosive effects of water contaminated with chlorinated solvents on polyvinylchloride and polytetrafluoroethylene pipes. These pipes, in conjunction with aluminum and galvanized steel pipes served to transport water in and out of groundwater monitoring wells. Throughout the study, little attention was paid to the reductive dehalogenation of the chlorinated solvents following passage through the metal pipes. Thus, at the time of publication, the decrease of the original contaminant concentration was noted, but regarded as experimental error.²⁸ It wasn't until 1992 that the same authors, Gillham and O'Hannesin, reported on the reductive dechlorination of halogenated methanes and ethenes by metals in batch or column studies.^{29, 30} Since this fundamental paper, the current use of zero valent metals to degrade contaminants represents an active area of research.^{10, 32-47}

For example zero valent zinc has been reported to reductively dechlorinate hexachlorobenzene to pentachlorobenzene, carbon tetrachloride to chloroform and dichloromethane to chloromethane. In the same study, when zinc was replaced with copper, no reducing effect was encountered.³⁵ However, an independent study conducted by Hagenmaier et al. reported that copper can dechlorinate polychlorinated dibenzodioxins and polychlorinated dibenzofurans.⁴⁶

Manganese has been reported to be effective for the destruction of trichloroethane, dichloroethylene and tetrachloroethylene. In comparison to zero-valent iron, manganese was found to have a slightly better ability at dechlorinating contaminants in laboratory made solutions. However, when leachate samples were taken from two municipal landfills, manganese did not react with tetrachloroethylene or dichloroethylene, whereas the same compounds were partially degraded by zero valent iron.³⁹ In each study both metals stopped functioning after a one month period possibly due to a build up of oxides on the surface of the metal, a topic which will be discussed in section 1.6.2.

Over the last several years, new *in-* and *ex-situ* remediation technologies involving mostly zero valent iron particles have been researched. In comparison to other metals the use of granular iron has shown to have several advantages. First, it is inexpensive and readily available. Second, it is environmentally innocuous and most importantly, it can easily be applied in field tests following batch or column type studies in the laboratory. Because of these advantages, zero valent iron filings are being used to fill large scale subsurface walls, better known as chemical barriers.³ A schematic representation of a subsurface treatment wall is presented in figure 1.3.1. The idea of using permeable iron walls was initially developed by R.W. Gillham at the University of Waterloo, Ontario. The first large scale application of this new technology was employed at a former semiconductor manufacturing plant, which was plagued for more than a decade with contaminated groundwater. Following its implementation the permeable wall, composed of sand and two hundred and twenty tons of iron fillings, was found to break down contaminants such as trichloroethene to below EPA standards.⁴⁷

The degradative effects of zero valent iron particles on numerous organic compounds have recently been reported. Some of the more outstanding publications, or those which investigated analytes with functional groups similar to our studies are discussed in the section 1.6.1.

Figure 1.3.1: Top-down schematic representation of remediative wall design.

1.4 Purpose and Plan of Research

The purpose of this research was to investigate the effects of zero valent iron particles and ultrasound both separately and together on aqueous solutions of certain aromatic pollutants: 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), aniline, chlorobenzene, toluene and N-nitrosodimethylamine (NDMA) with the following objectives:

- (i) to acquire enough data in order to make some general conclusions regarding the effects of: pre-treated vs. un-treated zero valent iron particles, ultrasonic frequency and initial pH of the solution on the degradation rate of various compounds.
- (ii) to extend the list of compounds/functionalities that were reactive to either method
- (iii) to determine if ultrasound would enhance the degradation rates of compounds that had already been known to have modest degradation rates with zero valent iron particles alone
- (iv) to postulate on the degradation pathways of various compounds following ultrasonic irradiation or stirring with zero valent iron particles
- (v) to determine if additives, such as ferrous chloride would enhance the degradation rate of aniline during ultrasonic irradiation at 20 kHz

1.5 Ultrasound

1.5.1 Historical Background and Modern Day Applications

Ultrasound can be characterized as sound waves propagated at high frequencies beyond the audible range to humans. The upper frequency limit of human hearing differs from one person to another, but in general ultrasound can be classified as ranging from 20 kHz up to 1GHz.

Historically the study of ultrasound is parallel with that of general acoustics, but due to several important differences it has been classified into a separate domain. The generation of ultrasonic sound waves is accomplished by employing the piezoelectric effect of a thin crystal, whereas acoustic sound generation into the audible range is delivered through a loudspeaker.²⁵

The first study of ultrasonic sound waves was performed by Galton in 1833.⁴⁸ In studying the acoustic limits perceived by humans Galton utilized a special whistle. Historically, it can be regarded as one of the first man-made ultrasonic transducers. However, presently it is better known as a dog whistle. At the turn of the 19th century two very important discoveries took place, each having crucial importance for the development of ultrasonic technology. They were, the discovery and first exploration of magnetostriction by J.P. Joule and the study of the piezoelectric effect by the brothers of J. P. Curie.²⁵

The study of underwater acoustics or more precisely the development of ultrasonic technology for the detection of submerged objects emerged during

World War I due to the development of high speed submarines. Langevin, a French scientist at the time, investigated the use of quartz transducers for transmission and reception of ultrasonic waves, of relatively low frequencies in water.²⁵

Following the war, the rapid development of electronics allowed Pierce to use nickel and quartz transducers for generating ultrasonic frequencies extending into the Mega-Hertz range.²⁵ In 1927, Richards and Loomis published the first account of the chemical effects of ultrasound.^{49, 50} In their paper they reported on two types of processes occurring during sonication. First, the acceleration of conventional reactions and second, reduction-oxidation reactions in aqueous solutions. Furthermore, they explained some of the effects, which typically occur following the passage of ultrasound waves through various media, such as the heating of solid and liquid materials and the formation of emulsions and aerosols from liquids. Their observations and experimental techniques opened new frontiers for scientists and engineers of diverse interests resulting in the application of ultrasound in synthetic organic chemistry⁵¹ and in various industrial^{25, 48, 52} as well as medicinal applications.²⁵

Ultrasonic applications are classified as being of either low or high intensity. For example, by using a Scanning Acoustic Microscope⁵³, low intensity ultrasound is used for investigating the properties of materials. In medicine, ultrasound is routinely used for the diagnostics of renal abnormalities as well as pre-natal sonographic imaging of the fetus. In most cases it is important that the specimen does not suffer any permanent changes in its structural and chemical properties. Therefore, many medical applications employ low-intensity, very high frequency ultrasound, typically in the Mega-Hertz range.

The acoustic powers delivered under these conditions may range from a few microwatts to several tens of milliwatts.²⁵

At high intensities, ultrasound is generally used for changing the properties of the material through which it is passed. High intensity applications are nearly always made at low frequencies, often just above the audible limit. Acoustic powers used in these instances may extend from a few milliwatts into the kilowatt region.^{25, 53, 54}

Typically the advantages of using ultrasound are faster reaction rates and higher yields. More importantly, since the passage of high intensity sound waves through liquids generates localized high temperatures and pressures, experiments which would have normally been conducted at high temperatures can be carried under ambient conditions.^{51, 53}

For industrial purposes large scale ultrasonic units are employed, which can process liquids at 200 L min^{-1} . These type of devices are used for the degassing of liquids, dispersion of solids into liquids and emulsification of immiscible liquids.²⁵

1.5.2 Cavitation

The term “cavitation” was first used by Sir John Thornycraft following his observations of propeller inefficiencies of torpedo boat destroyers.⁵⁵ Soon after, cavitation became a topic of scientific research primarily due the development of high-powered, high rpm steam turbines. In the early 1900’s the British Admiralty appointed Lord Rayleigh to investigate the phenomenon of rapid blade corrosion. He concluded that as a result of poor propeller design, the blades slipped creating large cavities. He

postulated that the collapse of these cavities created large variations in pressure, liberated large amounts of heat and inevitably led to blade destruction.⁵⁶

Ultrasonically induced cavitation refers to the spontaneous formation of bubbles in liquid media. It occurs in localized areas where the pressure drops sufficiently lower than the vapor pressure of the liquid. Once formed, cavities have a limited life span governed by the properties of the medium surrounding them. In general, following formation a cavity will quickly disintegrate into smaller cavities, or completely disappear, sometimes resulting in quite dramatic effects on the surrounding medium.^{16, 25, 57}

Cavitation can occur in water, organic solvents, molten metals, liquid helium and in biological fluids. The formation of cavities has been known to occur from a variety of causes: hydrodynamic effects, boiling of water, acoustic irradiation, laser heating, and electrical discharge.²⁵

Due to the extreme conditions which result from cavitation implosion (see the following two sections), scientists have been developing and testing new methods in order to prevent the formation of cavities in various industrial applications. More recently, research has focused on the effects of low intensity and high frequency ultrasonic waves through biological materials. It has been reported that under biological circumstances cavity formation is very difficult to detect, however it does occur and may result in damage to the surrounding tissue.^{25, 58}

1.5.3 Acoustic Cavitation

The mechanism of acoustic cavitation can be divided into three separate phases; nucleation, growth, and eventually collapse of bubbles. As already mentioned in section 1.2, ultrasound induced cavitation is initiated by the passage of high intensity sound waves through a medium. During the positive half cycle of the wave, the liquid in this region is compressed, conversely during the negative half cycle the liquid expands. When the acoustic pressure amplitude is greater than the hydrostatic pressure, the molecules of the liquid are ripped apart at sites where the tensile strength of the liquid is dramatically lowered, termed “weak spots”. Following liquid separation a void is created which expands during the negative part of the pressure cycle. It is typically followed by an instantaneous collapse accompanied by a highly localized release of energy resulting in the propagation of a shockwave.^{25, 53, 57} An example of such an occurrence has been captured by high speed camera at 20.8 million frames per second, as seen in figure 1.5.1.⁵⁷ Referring to this figure, it is evident that only one shock wave is present, commencing at the end of the second row. In the third row, its growth can be followed from left to right.

Figure 1.5.1: Laser induced cavity in water. Picture taken at 20.8 million frames per second, shock wave growth can be followed in third, row from left to right.

Cavity formation under these circumstances is termed “hard”, “true” or “vapor” cavitation. It has acquired the name “true” cavitation since the void is primarily composed of vapor from the surrounding liquid. This type of cavity formation is typical of homogenous liquids since they are generally free from particulate matter. The collapse of this cavity is audibly characterized by a sharp audible popping sound.⁵³

For water the theoretically calculated negative tensional pressure necessary to achieve “true” cavitation is on the order of 1000 bar. However, threshold studies in “normal” and even ultrapure water have shown that tensile strengths of only 1-2 bar and 300 bar respectively were necessary to achieve cavitation.²⁵ Such significant discrepancies between ultrapure and the theoretically predicted negative tensional pressures can most likely be attributed to “weak spots” found even in ultrapure liquids. For example, Apfel estimated that ultrapure water can contain 100,000 microscopic particles per cm^3 which remain in suspension as a result of Brownian motion.⁵⁸

The cavitation threshold can also be affected by the dissolution of gas resulting in the production of microscopic bubbles. These bubbles can also act as cavitation nuclei and disrupt the cohesive forces of the liquid resulting in the lowering of the cavitation threshold. However because of the “Laplace Pressure” i.e., an internal pressure caused by surface tension and equal to $2\sigma/R$, where R is the bubble radius these bubbles gradually dissolve as gas is forced out of their interior into the liquid. It is important to realize that ordinary liquids contain pockets of gas (nuclei) that can be easily activated. However, nuclei are not free gas bubbles, and require a mechanism for their stabilization.

Numerous theories relating to nuclei stabilization have been proposed; e.g., the organic skins theory⁵⁹ or the hydrophobic ion theory.⁶⁰ The most generally accepted theory has been the crevice model, which assumes that gas pockets are stabilized at the bottom of cracks or on conical crevices found on hydrophobic contaminants present in the liquid. In order for nucleation to occur, the balance between the stabilized gas pocket and the outside pressure must be disturbed. Under ultrasonic conditions the passage of the negative half cycle of the sound wave results in the bowing outwards of the contents of the gas/vapor filled crevice. At sufficiently low negative half cycles, contents of the crevice are released into solution creating a microbubble.^{61, 62}

Once formed, a microbubble depending on its size can either re-dissolve into the liquid or float away and burst at the surface. However, if an optimal microbubble radius is obtained, i.e., one which permits for the bubble to interact with the passing sound waves, then the microbubble will grow by drawing energy from the alternating pressure cycles in a process called rectified diffusion.²⁵

The process of rectified diffusion allows microbubbles to replenish themselves with gas to varying degrees depending on the amplitude of the sound wave. At certain sound amplitudes the effect of rectified diffusion will compensate for the loss of gas due to the combined effects of the hydrostatic pressure and internal pressure caused by the surface tension. At higher amplitudes more gas will diffuse into the bubble during the negative half cycle than is forced out of the bubble during the positive half cycle resulting in bubble growth. Once the bubble is large enough and it can no longer sustain itself, the surrounding liquid rushes in resulting in cavity implosion, and the creation of a local “hot spot”.^{25, 51, 53}

1.5.4 External Factors Affecting Acoustical Cavitation

The threshold of cavity formation as well as the intensity of collapse is governed by the following external parameters: temperature of the aqueous medium, dissolved gases, properties of the medium itself and the intensity as well as the frequency of the ultrasound. The threshold of cavity formation can be defined as the value of the acoustic pressure amplitude necessary for rendering the nucleus of the microbubble unstable resulting in its growth.^{25, 53} These parameters will be discussed in brief in the following sections.

1.5.4.1 Temperature

Temperature is one of the more important cavitation parameters since the solvent's vapor pressure is directly related to it, i.e., at higher solvent temperatures the intensity of a cavitation collapse is significantly decreased. This is primarily due to a higher vapor pressure of solvent residing within the cavity contributing a cushioning effect during implosion. As a result, the temperature generated is insufficient to completely attain the maximum thermal activation energy during the cavitation event. This consequently results in decreased amounts of hydroxyl radicals, which in turn significantly diminishes secondary reactions. In general the cavitation threshold varies inversely with temperature, i.e., the decrease in threshold with increasing temperature is roughly linear except for liquids near the boiling point.²⁵

1.5.4.2 Characteristics of Ambient Gas

Dissolved gases increase the heterogeneity of the liquid medium by increasing the concentration of microscopic bubbles. Consequently, the amount and nature of dissolved gases governs the amount of heat liberated at the time of collapse.

Thermal conductivity as well as the polytropic ratio (C_p/C_v) of a gas are two of the most important parameters governing the intensity of sonochemical reactions. The thermal conductivity of a gas affects the amount of energy allowed to dissipate into the surrounding liquid medium at the time of collapse. The polytropic ratio defines the amount of heat released during the adiabatic collapse.^{25, 63} A recent study conducted by Hua et al. has demonstrated the effects of various saturating gases on the rate of hydrogen peroxide production. The physical properties of saturating gases are presented in table 1.5.1, and the results obtained from their studies are presented in figure 1.5.2.²⁴

Gas	Polytropic Index (K)	Thermal Conductivity (mW/m-K)	Water Solubility (m^3/m^3)
Kr	1.66	17.41	5.94×10^{-2}
Ar	1.66	30.8	3.37×10^{-2}
He	1.63	0.0252	8.60×10^{-4}
O ₂	1.41	48.1	3.05×10^{-4}

Table 1.5.1: Physical properties of saturating gases

Figure 1.5.2: Production of H_2O_2 at 20 kHz in Kr, Ar, O_2 or He saturated solutions at pH 7 and 25°C ²⁴

A gas with a higher conductivity allows more energy to dissipate into the surrounding medium during cavity collapse. Thus it is evident from table 1.5.1 and figure 1.5.2, that the maximum sonochemical reactivity is obtained from gases which have a high solubility, high polytropic ratio, and low thermal conductivity. For example, Kr is the least heat conducting and most soluble of the gases. Consequently its presence yields the highest temperatures of collapse and the highest production of H_2O_2 .

1.5.4.3 Properties of the Sonicated Medium

Apart from the hetero- or homogeneity of the liquid medium, the liquid's vapor pressure has a substantial effect on cavitation. In general, liquids with high vapor pressures endure less intense cavitational collapse, due to the cushioning effect.

High viscosity has also been known to affect cavitation by diminishing the overall cavitational expansion and increasing the acoustic pressure during the negative half cycle of the sound wave, as seen in table 1.5.2.⁵⁴

Liquid	Viscosity N s m⁻² (25°C)	Pressure (atm)
Castor oil	0.630	3.90
Olive oil	0.084	3.61
Corn oil	0.063	3.05
Linseed oil	0.038	2.36
CCl ₄	0.001	1.75

Table 1.5.2: Effect of liquid viscosity on acoustic pressure during cavitation implosion⁵⁴

1.5.4.4 Acoustic Frequency and Intensity

Ultrasonic frequency affects the reaction environment by determining the resonant bubble radius. The radius of a bubble resonating in an applied acoustic field can be calculated by

$$R=(3\gamma p/\rho\omega^2)^{1/2} \quad \text{eqn 1.5.1}$$

Where γ is the heat capacity ratio of specific heats of the gas in the bubble, γ is also known as the polytropic ratio C_p/C_v , which is correlated to the heat released upon compression of a gas. Pressure is represented by p , ρ is the density of liquid and ω is the radial frequency of the ultrasound. Entezari and Kruus studied the effects of frequency on sonochemical reaction on the oxidation of iodine at 20 and 900 kHz. They estimated that in water at 300K the radii at 20 kHz and 900kHz were 164 μm and 3.6 μm respectively.⁶³ Since the

overall surface area of a bubble dictates the rate of heat transport out of a bubble, it is evident that at 20 kHz, bubbles would lose energy at a greater rate. However, the rate at which the temperature decreases during cavitational collapse depends on the surface to volume ratio, which varies as a reciprocal of bubble radius implying that the 900kHz bubble should cool at a greater rate.

Besides controlling the resonant size radii of bubbles, acoustic frequency has a significant effect on the net amount of cavitational events. This can be explained by the fact that at higher frequencies rectified diffusion occurs more readily due to the greater number of acoustic cycles per unit time and results in greater number of nuclei at resonance, thereby producing a greater amount of sonochemical reactions.

The resonant radius has also a contributing effect to the length and intensity of collapse since it is inversely proportional to the surface tension imposed on a collapsing bubble. For a bubble in the absence of an acoustic field, the pressure varies as

$$P = P_h + (2\sigma/R) \quad \text{eqn 1.5.2}$$

where P is the pressure that the bubble must maintain to avoid dissolution, P_h is the hydrostatic pressure, σ is the surface tension, and R is the bubble radius. Thus at a given acoustic pressure, i.e., sound intensity, the total implosive force on a bubble at the resonant radius may be larger at higher frequencies, resulting in a more complete collapse and more extreme temperatures. It should be noted that the frequency dictates the size of bubble radii, whereas the acoustic intensity determines the strength of cavitational implosion.²⁴

1.5.5 The Sonochemical Reaction Site

Over the last seventy years, two theories were proposed for the mechanism of sonochemical reactions. In the late 1930's Harvey and Frenkel proposed the "electrical discharge theory". However, following numerous re-investigations their proposal was dismissed since it was found to be inconsistent with observed sonochemical reactivities and sonoluminescent behavior.²⁵

In the 1950's, Griffing proposed that adiabatic heating resulting from bubble implosion produced local "hot spots". He suggested that the contents of these local "hot spots" were heated to several thousand degrees with pressure variations of several thousands of atmospheres. Over the years various predictions for maximum temperature and pressure variations were made. In most cases the proposals were based on hydrodynamic models which were very rudimentary in design, since they failed to incorporate the effect of heat transport and internal cavity vapor. As a result, maximum temperatures of 10,000 K and pressures of 10,000 atmospheres were predicted.²⁵

More recently Suslick and coworkers studied the implosion process in order to determine whether the sonochemical reactions occurred within the gaseous phase or in the liquid phase adjacent to the cavitation boundary.⁶⁴ They employed volatile metal carbonyls as chemical dosimeters and measured the first-order rate coefficients of ligand substitution as a function of metal carbonyl vapor pressure. They determined that the reaction zone, which can be interpreted as an intermediate layer between the gaseous phase and the surrounding liquid, extends up to 200 nm from the bubble's surface. It was estimated that it has a lifetime of approximately 2 μ s. In addition, they estimated that the

temperature of the gaseous phase is $5200 \pm 650\text{K}$ whereas the liquid immediately surrounding the bubble is approximately 1900K . The results of their studies are presented in figure 1.5.3.

Figure 1.5.3: Reaction rates of ligand substitution of volatile metal carbonyls calculated as a function of time and distance from bubble surface assuming only conductive heat transport from a sphere with radius 150 μm at 5200K.²⁵

1.5.6 Effect of Ultrasound on Aqueous Solutions

Historically, the production of hydrogen peroxide originating from the sonolysis of water was first reported by Schmitt et al. in 1929.²⁵ Later on in 1936 Schultes and Gohr discovered that by subjecting water to an ambient atmosphere of N₂ gas, nitric acid as well as nitrous acid were formed.⁶⁵ In a more diversified application, Miyagawa in 1942 reported on the use of ultrasound to increase the rates of acetate hydrolysis and fat saponification, as well as the rates of aging whiskey, sake and soy sauce.⁶⁶

To date, the physical phenomenon leading to the sonochemical effects in aqueous solutions are not fully understood. However, locations where molecules are brought to an excited state and undergo various types of chemical reactions have been proposed. By considering the nature of the cavitation event two separate regions have been determined: (i) interior of the cavity i.e., the gas phase and (ii) the thin liquid shell surrounding the collapsing cavity i.e., the liquid phase or solvent layer. The gas phase is an area filled with solvent as well as analyte vapor whereas the liquid phase is believed to be independent of vapor pressure. In the solvent layer surrounding the hot bubble, both combustion and free-radical reaction are possible.^{24, 25, 67, 68, 69}

In cases where water has been saturated with air, the initial step was postulated as cleavage of a water and oxygen molecule as presented in reactions 1.5.1 and 1.5.2 respectively.¹⁸ It should be noted that “*” denotes radical species.

The recombination of a certain percentage of these highly reactive species is believed to occur at the interfacial region by reaction pathways presented in reactions 1.5.3 to 1.5.9.

However a certain amount of radicals as well as hydrogen peroxide tends to escape the interfacial boundary and react with other species in the bulk of the solution.

In addition radicals can interact with other gases present within the cavity. For example, Kruus et al. have reported that under ambient conditions nitrate and nitrite spontaneously formed following ultrasonic irradiation.⁷⁰ Their proposed reactions are presented in reactions 1.5.10 and 1.5.11

Furthermore, hydroxyl and hydroperoxyl radicals in the bulk as well as within the cavity can interact with organic molecules generally resulting in the formation of highly oxidized products. In addition, organic molecules can undergo pyrolysis type reactions as demonstrated in reaction 1.5.12.²⁵

More recently, studies of the cavitation bubble liquid interface have revealed several important characteristics. Kotronarou et al. following various studies of pH effects on the degradation rate of *p*-nitrophenol proposed that variations in pH altered the concentration of analyte in the high-temperature zone of the bubble liquid interface. In addition, it was suggested that the cavitation bubbles are hydrophobic in nature and that hydrophobic compounds can accumulate in the hot surroundings of the interfacial region where they undergo high temperature reactions.⁷¹ In an independent study, Henglein et al. examined the trapping of OH[•] as a function of added organic compound. They discovered that it was the hydrophobicity of a compound which affected its ability to scavenge OH[•] radicals. Aniline, being one of their analytes of interest was found to be quite hydrophobic, i.e., slightly below ethyl lactate but above acetone and ethanol.²⁵

It should be emphasized that in order for a direct comparison to be made between independent studies at two different ultrasonic frequencies several conditions must be

kept the same. These conditions include: solution concentration, initial temperature prior to and during sonication, intensity of sonication, power delivered, and the configuration of the reaction cell.

1.5.7 Effect of Ultrasound on Metal Surfaces

Ultrasound can be successfully employed for removing surface inhibitors such as dust, grease films and oxide films from various forms of metals normally used in chemical reactions i.e., powders, dispersions, chips, and wires. The effectiveness of ultrasonic cleaning is strongly affected by the frequencies used. For example, low frequency ultrasound generally produces transient cavitation that generate powerful shock waves upon collapse, whereas high frequency sonication generally produces bubbles which experience small vibrations and give rise to small pressure pulses.

Under most applications transient cavitation bubbles are primarily responsible for the cleaning action, usually accomplished by three mechanisms: jet cleaning, peeling and emulsification. Jet cleaning occurs as a pulsating cavitation bubble moves over the contaminated film clearing paths that trace its journey. This cleaning action is a result of the impact of liquid jets that are generated during the division of large unstable bubbles into smaller ones on the surface. An example of a jet projection onto a solid surface was captured by Lauterborn, as seen in figure 1.5.4.⁵⁷

Figure 1.5.4. Bubble implosion near a flat solid boundary taken at 75000 frames per second

Figure 1.5.4, starting in the top left hand corner and proceeding left to right, shows a high-speed photographic series of bubble growth and collapse in water near a flat solid wall. A flat solid surface nearby causes the bubble to involute from the top (surface below the bubble) and to develop a high-speed liquid jet towards this solid surface. Once the jet hits the opposite bubble wall from the inside it pushes the bubble wall ahead causing a funnel shaped protrusion with the jet inside.⁵⁷

Peeling occurs when cavitation bubbles adhere to the interface of surface and film and, through their pulsating motion, separate them.

Surface cleaning by high frequency ultrasound occurs through acoustic streaming. This mechanism differs from jet cleaning because it rapidly exchanges the solvent at the surface, reducing the thickness of the boundary layer.

1.5.8 Reactive Pathways

The recent work of Petrier et al. will be used as an example of possible reactive pathways occurring during the sonication process. Exposure of air equilibrated aqueous solutions of phenol [A] (5×10^{-4} M) to ultrasonic irradiation at 20 and 500 kHz has shown a higher rate of analyte loss at the higher frequency. It was proposed that the increased rate at higher frequencies was attributed to a higher release of hydroxyl radicals in the solution. In both cases, catechol [B], hydroquinone [C], and benzoquinone [D] were detected as primary intermediates for the degradation process. Products other than these were not detected, however when the reactor was closed, analysis of the atmosphere showed CO_2 as the only final gaseous product.²⁴ The following degradation scheme was proposed.

Figure 1.5.5: Products detected during degradation of phenol in aerated aqueous solutions

1.6 Zero Valent Iron (Fe^0)

1.6.1 Applications of Zero Valent Iron

Over the years research into various remediative applications of zero valent iron has resulted in numerous publications. Some of the outstanding ones, in terms of similarities of compound and functional groups to those used in this study are presented in this section.

Reductive dehalogenation reactions are generally divided into two categories, each being accompanied by a net transfer of electrons: hydrogenolysis (replacement of a halogen by a hydrogen) and reductive elimination in which halide ions are released.

Roberts et al. applied zero valent iron to reductively eliminate *cis* and *trans* dichloroethylene. The iron used was Fisher 40 mesh pretreated in a solution of Ar sparged 1 N HCl. The authors reported that both isomers of dichloroethylene were dechlorinated primarily to acetylene and ethylene with trace amounts of methane, propane, propene, butane and 1-butene.³⁷

Agrawal et al. demonstrated first order rate constants for the reduction of nitrobenzene to aniline by using Fluka 18-20 mesh iron filings. The authors investigated the effect of increased carbonate concentration on the rate of denitration. At higher carbonate concentrations the authors noticed the formation of a gray precipitate on the iron's surface as well as a decrease in the rate of nitro reduction. It was later determined that the precipitate consisted mainly of non-reactive carbonate aggregates capable of

inhibiting mass-transfer of reactants and products to and/or from the reactive sites on the metal surface.³³

An example of rate reduction due to carbonate aggregates is presented in figure

1.6.1. Scanning electron micrographs of a pre-treated iron sample and the same iron sample following 18 hours of exposure to bicarbonate buffer are provided in figure

1.6.2.⁷² It should be noted that the loss of texture in picture B) is due to the formation of carbonate aggregates.

Figure 1.6.1: Effect of iron incubation time in a bicarbonate buffer on the degradation rate constant of nitrobenzene

(A)

(B)

Figure 1.6.2: Scanning Electro Micrograph pictures
(A) Iron following HCl (10%) pre-treatment
(B) Same iron sample as in (A) following 18 hrs of exposure to bicarbonate buffer

Zero valent iron has also been employed as a catalyst in conjunction with the ChemChar thermal waste gasification process. It was reported that the destruction removal efficiency of chlorobenzene increased from 99.75 % when only char was used to >99.99 % when char treated with iron was used. Char is a highly macroporous compound with a surface area of 600 m²/g. It is a laboratory prepared compound that is initially formed by grinding subbituminous coal to an appropriate mesh size. In the case of iron treated char, the ground coal is mixed in a solution of iron (III) nitrate solution, followed by overnight drying. In both cases the ground coal is then loaded into a steel pipe, and the pipe is heated to incandescence at the top, while from the bottom oxygen flow is initiated. This combination results in the formation of a thermochemical gasification zone, which travels downwards until it reaches the bottom of the pipe at which point the oxygen flow is stopped.¹⁰

Weber investigated the reductive reaction mechanism of various nitro aromatic compounds via zero valent iron particles. He concluded that the reaction pathway involved reductive transformation at the surface of the metal, and that the rate of degradation increased following iron pre-treatment, further supporting the proposed surface mediated mechanism.⁷³

Cheung et al. reported that the use of zero valent iron promoted the hydrodechlorination of polychlorinated biphenyls in the absence of solvent in a high temperature environment. The major product formed following 10 min at 400 °C was biphenyl.³⁶

Siantar et al. extended their work with zero valent iron to include its effects on nitrate and 1,2-dibromo-3-chloropropane (DBCP). The authors reported that DBCP

followed a pseudo-first order rate of reduction that was proportional to the iron content in the batch system. Furthermore, when nitrate was added to the iron DBCP solution, the rate onset was delayed in proportion to the nitrate concentration suggesting a competitive process between nitrate and DBCP transformation. Further research revealed that nitrate was reduced to nitrite with a half-life of 3.3 min. Nitrite alone was also tested and it was found that a concentration of 4.3 g/L decreased the rate of reduction by 15%.⁴⁰

1.6.2 Effect of Iron Surface Oxidation

In aqueous solutions spiked with chlorinated or nitrated compounds, four possible oxidants are available to drive the oxidation of zero valent iron to ferrous iron (Fe^{2+}): i) water (reaction 1.6.1), ii) dissolved oxygen (reaction 1.6.2), iii) chlorinated compounds (reaction 1.6.3), and nitroaromatic compounds (reaction 1.6.4). In addition, if a substantially strong oxidant is present the ferrous iron will undergo further oxidation to ferric iron (Fe^{3+}).

Various authors have reported that the reduction of certain toxic compounds using zero valent iron is a surface mediated reaction dependent on the concentration of reactive surface area.^{32, 33, 36, 43, 74} Agrawal et al. have proposed that the reduction mechanism involves adsorption of the nitroaromatic analyte onto the iron surface leading to the formation of a donor-acceptor complex, the precursor to electron transfer. The order of electron transfers, proton transfers and dehydration reactions has been a subject of many detailed electrochemical studies from which a conclusive theory has not evolved. However, the fact that electron transfer is the initiating and rate limiting step has been concluded by Schwarzenbach et al.⁷⁵ Therefore, since nitro reduction is strongly governed by the mass transport of analyte to the iron surface, which also influences the distribution of detectable reduction products, it is not surprising that reduction increases linearly with reactive iron surface area.

Tratnyek et al. have reported that the pre-treatment process enhances degradation rates by removing crystalline oxides from the metal's surface, leaving behind a fresh amorphous elemental iron that is more reactive, as seen in figure 1.6.3.⁷⁴

In an independent study Johnson et al. have confirmed this trend and in addition have noticed that acid pre-treatment does indeed increase the reactive surface, but to varying degrees.³²

Figure 1.6.3: Effect on degradation rate of CCl_4 following various pre-treatments of zero valent iron (Fe^0) particles

1.7 Fenton Chemistry

As mentioned in section 1.2, research has shifted to the investigation and application of various advanced oxidative processes (AOPs) for the purposes of groundwater remediation. However besides studies of various degradative technologies such as ozonolysis,⁷⁶ and UV-oxidation^{12, 13}, much research has also been devoted to Fenton-type AOPs since they produce highly reactive hydroxyl radicals (OH*[•]).⁷⁷

Fenton type chemistry requires the presence of hydrogen peroxide and ferrous iron at low pH. In aqueous solutions the following process takes place.⁷⁸

Since the *in-situ* generated hydroxyl radical is known to be a powerful oxidizing agent, it is not surprising that Fenton-type AOPs have been applied on a large scale for treatment of wastewaters and polluted groundwater.⁶ In aqueous solutions, Fe³⁺ formed from reaction 1.7.2 can be reduced back to Fe²⁺ in the presence of hydrogen peroxide (reaction 1.7.2). It can also be reduced by processes involving hydroperoxyl radicals (reaction 1.7.3) and/or by interaction with organic intermediate radicals (reaction 1.7.4).⁷⁹

Under most applications of Fenton-type AOPs, hydrogen peroxide must be supplied to the reaction vessel, however under ultrasonic irradiation conditions, hydrogen peroxide, hydroxyl radicals as well as hydroperoxyl radicals are generated *in situ*. Thus the addition of ferrous iron prior to sonication would result in a net increase of hydroxyl radical according to reaction 1.7.1. To date, publications pertaining to the combination of ferrous iron and ultrasound have not been reported. However, the combination of ferrous iron with hydrogen peroxide under electrochemical ⁷⁸ as well as UV ⁷⁹ conditions has been reported to increase the rate of aniline degradation over that of studies in the absence of ferrous iron.

2.0 Equipment and Methods

2.1 Ultrasound

2.1.1 Sonication with the 20 kHz Probe

The 20 kHz ultrasound generator was a Vibra-Cell VC375 Ultrasonic Processor. It was coupled to a titanium steel probe having a tip size of 1.1 cm². To maintain reproducibility, solutions were sonicated in a custom fabricated reaction vessel. The bottom of the vessel was concave in order to redirect the ultrasound in an upward direction back into the sample. The reaction vessel was equipped with a sampling port capable of being sealed with a disposable PTFE/rubber septum. The upper part of the vessel had a very precisely sized port so as to accept the probe with minimal clearance. The maximum loading capacity with probe submerged into the vessel was 70 mL. A picture of the 20 kHz sonication cell is provided in figure 2.1.1.

Figure 2.1.1: Custom fabricated 20 kHz sonication cell,
sampling port on right hand side of cell

Since throughout sonication, heat is dissipated into the solution, the reaction cell was immersed up to the opening of the sampling port in a cooling bath. The temperature of the cooling bath was maintained at 2°C using an immersed coil and a GCA Precision Scientific thermostated circulating system #245. Temperature inside the reaction vessel during sonication was thus maintained between 5-7°C. During sonication the titanium tip was located ~3 cm from the bottom of the flask. A gasket of teflon-paper bridging the cell's upper port and the probe completed the sealing of the cell to prevent loss of any material due to volatility.

2.1.2 Power Calibration for Direct Sonication

One of the most common methods available to estimate the amount of ultrasonic power delivered into a sonochemical reaction under direct sonication conditions is calorimetry. This method requires the measurement of the initial rate of temperature rise produced when a system is irradiated by ultrasound.

For the 20 kHz apparatus the power calibration was very easily done by immersing the ultrasonic probe into a Dewar flask, containing a known amount of water. The temperature (T) was recorded against time (t) for about 6 min using a thermocouple placed in the Dewar flask. The total ultrasonic power actually delivered into the system per unit time was calculated by substituting the value of dT/dt at $t=0$ min into the following equation

$$\text{Power} = (dT/dt) \cdot C_p \cdot m \qquad \text{eqn 2.1.1}$$

where C_p is the heat capacity of the water (4.2 J/g K) and m is the mass of the water used in grams. If a power in Watts is introduced into the system from a probe tip of known area, then the intensity of the power delivered in (W/cm^2) can be calculated. For the 20 kHz apparatus the calculated power was $32.5 \text{ W}/\text{cm}^2$ on average. See figure 2.1.2 for power calibration.

Figure 2.1.2: Thermal calibration of power for the 20 kHz apparatus

2.1.3 Sonication with 900 kHz Cup-Horn Apparatus

The ultrasound delivery unit was a custom fabricated cup-horn apparatus. The apparatus was designed during the doctoral work of M.H. Entezari and is further described in a recent publication.⁸⁰ A simple schematic of the apparatus is shown in figure 2.1.3.

Unlike the 20 kHz sonication apparatus, ultrasound in the 900 kHz apparatus was delivered indirectly into the reaction cell. This was done in order to eliminate any interaction between the organic compounds in solution and the RTV resin used to seal the transducer in place. The apparatus delivered 900 kHz ultrasound through a flat transducer located at the bottom of the “cup”. The power to the transducer was delivered by a generator, which was manufactured by Meinhardt Ultrasonics, Liepzig, Germany. The sides of the cup-horn consisted of a hollow double walled cylindrical glass chamber (dia. 6.5 cm * 10 cm deep) that was cooled to 1-2 °C with a Lauda K-2R water circulating system. The cup-horn cell was filled with water (100 ml) which acted as the coupling medium as well as a coolant for the reaction cell. It was important to maintain the same amount of coupling medium for each experiment otherwise changes in the amount of power delivered to the cell occurred.

Figure 2.1.3: Schematic of 900 kHz Cup-Horn Sonicator

- A** = support frame
- B** = cooling liquid wall
- C** = coupling medium (100 mL)
- D** = RTV resin
- E** = transducer

The sonication cell was a custom fabricated round bottomed Erlenmeyer flask. The flask opening was sealed with a screw-cap housing a disposable PTFE/rubber septum. This opening allowed for the cell to be filled and also functioned as the sampling port. The maximum loading capacity of the sonication vessel was 150 mL. Pictures of the 900 kHz sonication cell as well as of the entire 900 kHz apparatus are provided in figure 2.1.4 and 2.1.5 respectively. In order to maintain reproducible results, the reaction flask was precisely positioned 1 cm from the bottom of the cup-horn and totally immersed in the coupling medium.

Figure 2.1.4: Custom fabricated 900 kHz sonication cell with sampling port on top

**Figure 2.1.5: Entire 900 kHz cup-horn sonication apparatus
including sonication cell**

2.1.4 Power Calibration for Indirect Sonication

The determination of power delivered to a reaction flask by indirect sonication can be very easily calculated by using a chemical dosimeter. A common chemical dosimeter method involves calculating, via spectroscopic standards, the amount of triiodide ion liberated from the irradiation of potassium iodide, better known as the Weissler reaction.⁵⁴ The measured amount of triiodide ion following an adequate time of sonication can be regarded as a relative measure of the power of ultrasound.

Recalling from section 1.5.6, the sonication of water produces OH* radicals, which can easily interact with iodine present in solution, presented in rxn 2.1.2, resulting in the formation of a spectroscopically visible product the triiodide ion, I₃⁻:

Thus, prior to the determination of power, a calibration curve composed of various concentration of KI was measured on a Beckman DU-7 spectrophotometer at 355 nm. A new solution of 0.2 mol/L KI, was poured into the reaction vessel for each point of the study. Aliquots of the KI stock following sonication were immediately analyzed and compared with the calibration curve. Experiments involving the calibration of this exact apparatus under identical conditions involving calorimetric as well as chemical dosimeter studies had recently been reported by Entezari et al.⁸⁰ It was reported that under calorimetric studies, 2.35 μmol of I₃⁻ was obtained when 50 mL of iodide stock solution (0.2M) was directly sonicated for 3 min at 25 °C.⁵⁴ This amount of I₃⁻ corresponded to 29

W of power. In addition the authors reported that under indirect sonication and with 100 ml of coupling medium 1.63 μmol of I_3^- had formed corresponding to a power delivery of about 20 W. In our studies 2.78 μmol of I_3^- was formed following 6 min of indirect sonication, which was calculated to deliver on average 17.2 W with an intensity of 5.8 W/cm^2 .

2.2 Solid Phase Microextraction

2.2.1 Introduction

Solid Phase Microextraction (SPME) is a patented technique, which was initially developed for the extraction of benzene and its derivatives from aqueous samples. It was only later applied to semi-volatile organic compounds, such as phenols, polynuclear aromatic hydrocarbons, and polychlorinated biphenyls.⁸¹ It is a fast, simple, and sensitive technique, which does not require the use of solvents as in the case of liquid-liquid extraction. The method involves two steps: i) partitioning of analytes between the sample and the fused-silica fiber coated with a suitable stationary phase and ii) desorption of concentrated analytes into the injector of a gas chromatograph. The length of the fused-silica fiber is usually 1 cm, and the thickness of the stationary phase can be from 7 to 100 μm . A schematic diagram of an SPME holder assembly is presented in figure 2.2.6.

SPME fibers utilize various types of selective coatings with different thicknesses. Highly crosslinked polymers e.g. divinylbenzene polymers, template resins or porous

carbons can be chosen alone or in combination with standard coatings. For example, for low molecular weight or volatile compounds such as toluene, the 100 μm

Polydimethylsiloxane (PDMS) fiber is recommended. However for chlorobenzene, also a volatile compound, the 85 μm Carbowax fiber was recommended. For larger molecular weight or semivolatile compounds a 7 μm PDMS fiber was suggested and for very polar analytes, the 85 μm polyacrylate. For amines, and for nitro containing compounds the polydimethylsiloxane/divinylbenzene (PDMS/DVB) coated fiber was designed. (ref supelco catalog)

Prior to use each fiber was properly conditioned by thermally desorbing contaminants at the specified injector temperature and for the required period of time. In most cases the conditioning procedure was repeated several times.

The initial step in the development of a reproducible SPME method is the measurement of an absorption time profile from which the correct equilibration time for each analyte can be obtained. The equilibration time can be quite different depending on the distribution constant of the analyte and the volume of stationary phase. Usually the more volatile the analyte, the lower the distribution constant, and as a result a thicker coating is required for adequate sensitivity.

Figure 2.2.6: Schematic representation of SPME fiber assembly

2.2.2 SPME Sampling Procedure with Vibrational Apparatus

A special apparatus was built to facilitate SPME sampling by decreasing analyte equilibration time to one tenth of its conventional time. The significant decrease in equilibration time can be attributed to faster mass transfer due to fiber vibration during sampling. The results are presented in figure 2.2.7.

The SPME device was constructed out of a discarded Braun razor. The razor shaving foils were replaced by a thin metal strip ($\sim 0.05 \times 0.5 \times 10$ cm). The metal strip had a small hole drilled at the opposite end over which a pre-drilled rubber septum was glued. The purpose of the septum was two fold. First, to act as a cushion between the septum-piercing needle, which housed the fiber, and the metal strip. Second, to act as a guide, by directing the needle into the sample vial, which was nested in a rubber mount directly below. Once the tip of the septum-piercing needle entered the headspace of the sample vial, the fiber was only then extended into the aqueous solution. Immediately, the apparatus and the pre-set count-down timer were simultaneously turned on. While operating the metal strip displaced the fiber from its resting position a total of 0.2 cm to the left and 0.2 cm to the right at a frequency of 30 Hz. Since the septum piercing needle passes through the sampling vial's septum, its movement at this point was restricted, thus creating a node. As a result the extracted fiber experiences lateral displacements of ~ 0.3 cm from its resting position generating a small vortex. Such vibrations greatly decreased the time required to saturate the fiber with analyte. Following equilibration the fiber was withdrawn and inserted into the GC where the compound(s) were thermally desorbed and

analyzed. A photograph of the entire vibrational apparatus including the SPME fiber inserted into a sampling vial is provided in figure 2.2.8.

Figure 2.2.7: Effect of vibration on chlorobenzene adsorption onto an 85 μ m Carbowax SPME fiber

Figure 2.2.8: Picture of entire vibrational apparatus including SPME and sampling vial

2.3 Chromatographic Analyses

2.3.1 Gas Chromatography with Flame Ionization Detection (GC/FID)

The analytes, including some of their breakdown products, were extracted from the aqueous phase via various SPME fibers. Analyses of all compounds were performed using a Varian 3300 Gas Chromatograph equipped with a Flame Ionization Detector (FID), excluding NDMA and aniline which were analyzed by HPLC/UV-VIS. Separation of analytes was achieved by using a DB-5, 15 m Megabore (0.53 mm internal diameter), 0.25 μm film thickness polymethyl (5% phenyl) siloxane column. Helium was employed as the carrier gas at a flow rate of 8.5 ml/min. Retention times were recorded in minutes. A standard column temperature program was used for the analysis of all analytes: 60 °C, hold 2 min, ramp to 300 °C at 20 °C/min with a final hold of 2 min. The injector was maintained at 265 °C and the FID at 280 °C. Air and H₂ flows to the FID were 300 ml/min and 30ml/min respectively. N₂ makeup gas flow was 30 ml/min.

2.3.2 Gas Chromatography with Mass Spectroscopy (GC/MS)

Confirmation of the identities of breakdown products as well as standards were performed with a Varian Saturn GC/MS system using SPME or liquid injections (1 μl). Separation of analytes was achieved on a DB-5 column (30m, 0.25 mm ID, 0.25 film thickness) with a helium flow rate of 3.5 ml/min. The standard column temperature program was: 50 °C, ramp to 170 °C at 8 °C/min, then ramp to 270 °C at 26 °C/min.

2.3.3 Reverse Phase-High Performance Liquid Chromatography (RP-HPLC)

As mentioned NDMA was analyzed by using RP-HPLC by direct injection of aqueous samples (10 μ l). The setup consisted of a Varian 9010 solvent delivery system, a Varian 9095 Autosampler, and a Varian 9050 variable wavelength UV-VIS detector set at 227 nm. The analytical column was a Zorbax 250 mm x 2.5 mm x 5 μ m C₁₈ column. A guard column of the same material was also used. The eluent consisted of 100% distilled water at T = 0 min, followed by a gradual increase in methanol to 30% at T = 10 min and terminated by 100 % methanol at T = 15 min. The retention time for NDMA under these conditions was approximately 6.58 min at a flow rate of 1.5mL/min.

Aniline analyses were obtained by direct injection of aqueous sample (10 μ l) using a home built RP-HPLC system comprising of a Bio-Rad UV-monitor (model 1035 A) set at 230 nm and an Perkin Elmer 250 LC pump. The column used was a μ -Bondpack 250 mm x 2.5 mm x 5 μ m C₁₈ with a flow rate of 1.5 mL/min. The mobile phase was isocratic 90 % H₂O (deionized), 10 % Acetonitrile (Optima grade) adjusted to pH ~ 7 with NaOH.

2.3.4 Ion Chromatography (IC)

Nitrite, nitrate, formate, glycolate and acetate analyses were performed by direct injection of filtered aqueous samples (50 μ L) using a Dionex Series 4000I Ion Chromatograph equipped with a conductivity detector. The column used was an Ion Pac

Dionex AS4A (150 x 4 mm). The anion eluent was 1.7 mM NaHCO₃ (60%) and Deionized Milli-Q Water (40%) at a flow rate of 2.0 mL/min.

2.4 Experimental Procedures

2.4.1 Materials

The representative pollutants were commercially available and used as received: 2,4-dinitrotoluene (Aldrich, 97% Purity), 2,6-dinitrotoluene (Aldrich, 98 % Purity), Monochlorobenzene (Fisher, 99% Purity), Toluene (Sigma-Aldrich, 99.8 % Purity) HPLC grade and Aniline (Aldrich, 99.5 % Purity), NDMA was obtained from Dr. Parker, Carleton University Engineering Dept.

The representative breakdown products were commercially available and used as received: 2-methyl-3-nitroaniline (Aldrich, 97% Purity), 2-methyl-3-nitroaniline (Aldrich, 97% Purity), 2,6-diaminotoluene (Aldrich, 97% Purity), 1,3-dinitrobenzene (Aldrich, 97% Purity), 2,4- diaminotoluene (Aldrich, 98% Purity), 4-methyl-3-nitroaniline (Aldrich, 97% Purity), 2-methyl-5-nitroaniline (Aldrich, 99% Purity), Quinone (Aldrich, 99% Purity), Hydroquinone (Aldrich, 97% Purity), Nitrobenzene (Aldrich, 99% Purity), o-nitrophenol (Aldrich, 99% Purity), acrylic acid (Aldrich, 95% Purity).

Various types of iron were used since it was discovered that there was a large discrepancy in their reactivity following identical pre-treatment. They were: 20 mesh, (99.2% metal basis) (Alfa Aesar), iron metal filings, ~40 mesh (Fisher), iron powder, finer than 100 mesh (electrolytic 99 + % total iron) (Fisher).

The water used for all experiments was distilled. For HPLC/UV-VIS reverse phase, a combination of distilled water and Optima Grade methanol as well as acetonitrile were used. For Ion Chromatography experiments only deionized Milli-Q water was used.

2.4.2 Iron preparation and Storage

Iron directly out of the bottle was placed in a 15 % HCl solution at a ratio of 1g to 10ml. The mixture was sonicated at 50 kHz in a 2210 Branson sonifier for a period of approximately 15 min. Following sonication the mixture was washed with a saturated solution of sodium bicarbonate (3 times) in order to neutralize the acid, followed by several washes with distilled water. (If the water washing step was omitted, the solution pH was unacceptably raised following iron addition). The Erlenmeyer containing the treated iron was sparged with a continuous flow of Ar , while heating with a heat gun. The activated iron was used immediately or in some cases stored under vacuum inside a dessicator for a maximum period of 3-4 hours.

2.4.3 Stock Solution Preparation and Storage

Stock solutions of 20 ppm were prepared by adding 20 mg (2,4-DNT, 2,6-DNT) or 20 μ L (toluene, chlorobenzene, aniline and NDMA) of the respective analyte into 1 L of distilled water. The stock solutions were stirred overnight in air tight teflon sealed 1L erlenmeyer flasks maintaining minimal headspace. Certain analytes such as 2,4-DNT and 2,6-DNT required a longer stirring period, due to their slow solubilitizations, while

others such as NDMA dissolved within minutes. Solutions were stored in a refrigerator to minimize volatilization.

2.4.4 SPME Fiber-Analyte Equilibration Time Study

Following the preparation of a stock solution, 1.2 ml aliquots were placed in 1.5 ml Varian auto-sampler vials. The vials were allowed to equilibrate to room temperature. Fibers were inserted for pre-specified times. Extraction times began at 1 min and were increased by ~ 2 minute increments for each new sample vial. Following each extraction the fiber was immediately desorbed into the GC. The optimum equilibration time for each analyte was determined from a plot of peak area vs. time. It was noticed that the fiber-analyte equilibration times were different for each compound being tested and these are presented in table 2.4.1.

Analyte	Fiber Used for extraction	Equilibration Period (min)
2,4-Dinitrotoulene	65 μ m Polydimethylsiloxane/divinylbenzene	1
2,6-Dinitrotoluene	65 μ m Polydimethylsiloxane/divinylbenzene	14
Aniline	65 μ m Polydimethylsiloxane/divinylbenzene	13
Chlorobenzene	85 μ m Carbowax	5
Toluene	100 μ m Polydimethylsiloxane	11

Table 2.4.1 Fiber-analyte equilibration times

2.4.5 Standard Sonolytical Protocol

Following the preparation of a stock solution, a calibration curve, an SPME fiber-analyte equilibration period and a volatility test were done on the each analyte. It was important to establish all of these parameters prior to any experimental work in order to be certain of the rates of degradation. For example, toluene as well as chlorobenzene were found to be quite volatile at room temperature even when dissolved in water.

For the six analytes to be studied, various experimental conditions were applied. They were: **a)** stirring with Fe⁰ powder only, **b)** sonication with 20 kHz ultrasound only, **c)** sonication with 900 kHz only, **d)** combination of a) and b), **e)** combination of a) and c). Furthermore for each of these five conditions two different pHs were investigated, i.e. ~ pH 5.8 (this was the pH of laboratory distilled and deionized water) and pH 4.0 (adjusted with dilute HCl prior to experiment).

Aliquots of each sample were taken at appropriately timed intervals out of each reaction vessel through a septum sealed sampling port. Aliquots were contained in 1.5 ml auto-sampler vials and refrigerated at 4°C until analysis, which was performed within 24 hours of sampling.

Each experiment was repeated three times or until a discrepancy of less than 15 % existed in the rate of degradation.

2.4.6 Experiments with Zero Valent Iron Particles

A special reaction vessel was designed for stirring with iron at room temperature (for experiments not involving ultrasound). The vessel was built using an Erlenmeyer flask to which had been added a single screw-cap opening capable of being sealed with a disposable PTFE/rubber septum as seen in figure 2.4.1. This allowed for easy sampling without the loss of analyte due to volatilization. The reaction flask also had a larger opening (glass stoppered) at the top which permitted the vessel to be filled or emptied. During experimental conditions, in order to ensure no loss of analyte due to volatilization, teflon tape was used around the glass stopper.

Prior to beginning experimentation, 50 mL of stock solution was allowed to equilibrate to room temperature after which 1 g of iron was added. A glass coated magnetic stirrer was set at a constant RPM for each experiment. Samples were taken at 15 min intervals over a period of 60 min. During sampling a strong magnet was used to contain the fine iron particles away from the sampling port, so as to avoid plugging the syringe.

Figure 2.4.1: Bench-top reaction vessel for stirring at room temperature

2.4.7 Experiments at 20 and 900 kHz

In a typical experiment 50 mL of the stock solution contained in a volumetric flask was placed in a cooling bath reservoir and allowed to equilibrate for approximately 15 min to 3–4 °C. The stock solution was then transferred into the reaction vessel (see Figure 2.1.1 for the 20 kHz vessel and see Figure 2.1.4 for the 900 kHz vessel). For the 20 kHz apparatus the vessel was firmly attached by an adapter to the probe in such a way that the position of the cell relative to the probe was reproducible. For the 900 kHz apparatus the vessel was first attached to a holder and then lowered into the coupling medium so that the bottom of the reaction vessel rested 1 cm from the transducer.

In sonication experiments which called for the presence of iron, 1 g of iron particles were placed in the reaction vessel just prior to the attachment of the probe or insertion into the coupling medium. Samples were taken every 15 min over a 60 min period. In certain experiments at 20 kHz samples were taken only every 2 h over a period of 12 h.

2.4.8 Detection of Intermediates and Final Products

Under most experimental conditions, i.e., sonication, iron stirring or a combination of both, new peaks were detected on the chromatogram. It was important to identify the compounds, which appeared and subsequently disappeared throughout the course of the experiment. Therefore peak identification was initially obtained by comparing peak retention times and their shapes against known standards under identical column program conditions on the GC/FID and later reconfirmed by GC/MS. For

example, in the case of 2,4-DNT we found that before the complete disappearance of the initial analyte, intermediates such as: 2-nitro-4-aminotoluene, 2-amino-4-nitrotoluene and final products such as 2,4-diaminotoluene had formed. For detection of small organic acids as well as ions, ion chromatography was used.

2.4.9 Data Treatment

Assuming first order kinetics of reaction of the starting compound, A, we have

$$\frac{d[A]}{dt} = -k[A_0] \quad \text{eqn: 2.4.1}$$

where k is the first order rate constant. Integrating, using an initial value $[A_0]$ at $t=0$,

$$\ln \frac{[A]}{[A_0]} = -kt \quad \text{eqn: 2.4.2}$$

Thus, plots of $\ln [A]/[A_0]$ vs time yielded the value of k. Peak areas were used in place of actual solution concentrations.

2.4.10 Regression Calculation

Linear regression for all degradation rates were obtained using SigmaPlot (ver 1.04), however due to software limitations all regression lines drawn on each figure were drawn manually based on program calculations.

SigmaPlot calculated the regression by using least squares to fit a set of data points (x_i, y_i) $i = 1, \dots, n$ to a polynomial of order p where

$$y = \beta_0 + \beta_1 x + \beta_2 x^2 + \dots \beta_p x^p$$

In vector-matrix notation this problem is formulated as

$$Y = X\beta + \varepsilon$$

where the $n \times 1$ vector containing the y_i data is

$$Y = [y_1 \ y_2 \dots y_n]$$

and the $n \times (p + 1)$ design matrix is

$$X = \begin{bmatrix} 1 & x_1 & x_1^2 & \dots & x_1^p \\ 1 & x_2 & x_2^2 & \dots & x_2^p \\ \dots & \dots & \dots & \dots & \dots \\ 1 & x_n & x_n^2 & \dots & x_n^p \end{bmatrix}$$

β is a $(p + 1) \times 1$ vector of parameters to be estimated

$$\beta = [\beta_0 \ \beta_1 \ \beta_2 \dots \beta_p]$$

ε is an $n \times 1$ vector of residuals.

The solution for the least squares estimates of the parameters β is

$$B = (X^T X)^{-1} X^T Y$$

SigmaPlot uses the Cholesky decomposition to invert the $X^T X$ matrix. This produces the regression curve

$$\gamma_o = b_o + b_1x_o + b_2x_o^2 + \dots b_px_o^p \quad \text{eqn: 2.4.3}$$

Calculations of error from triplicate experiments was done by calculating the standard deviation by

$$S = (\sum_i (x_i - x_{ave})^2 / n - 1)^{1/2} \quad \text{eqn: 2.4.4}$$

3.0 Results and Discussion

3.0 Results and Discussion

3.1 Fiber-Analyte Equilibration Studies

SPME fiber-analyte equilibrium periods for all analytes, with the exception of 2,4-DNT and NDMA, are presented in figure 3.1.1. As described in section 2.4.4, three different fibers were used, i.e., a 65 μm polydimethylsiloxane/divinyl benzene fiber for 2,6-DNT and aniline, a 85 μm carbowax fiber for chlorobenzene and a 100 μm polydimethylsiloxane fiber for toluene.

Referring to figure 3.1.1, several observations were noted. First, determination of the equilibration period prior to any quantitative analysis is essential. For example, if the vibrational time of chlorobenzene during the initial two minutes varied by even 20-30 seconds, a significant difference in area counts was obtained. Second, it is not only the concentration of a particular analyte in solution which determines the amount extracted, but also its affinity for a particular fiber. For example, at the point of equilibration different amounts, represented by area counts were noted for 2,6-DNT and aniline.

2,4-DNT was not included in figure 3.1.1, since all work performed on this analyte preceded the design of the vibrational apparatus. However, consistent static immersion periods of a 65 μm polydimethylsiloxane/divinyl benzene fiber in a stock solution provided reproducible results for 2,4-DNT. The analysis of NDMA was performed by RP-HPLC since it could not be successfully extracted out of solution by SPME.

Referring to figure 3.1.1 the minimum equilibration time was taken as the point at which the plot of peak area versus time leveled off. These times, which are summarized in table 3.1.1, were actually used throughout all analyses.

Analyte	Minimum Equilibration Period (min)
Aniline	13
2,6-DNT	14
Toluene	11
Chlorobenzene	5

Table 3.1.1. SPME fiber-analyte equilibration times

Figure 3.1.1. SPME fiber-analyte equilibration time study

- ◆ Aniline
- 2,6-DNT
- ▲ Toluene
- Chlorobenzene

3.2 Zero Valent Iron (Fe^0)

3.2.1 Various Zero Valent Iron Pre-treatment Methods and Their Effects on Degradation Rate Constants of 2,4-DNT

Measurements and calculations of degradation rate constants were performed as described in section 2.4.8. 2,4-DNT was chosen as the reference analyte for studying the degradative effects of zero valent iron particles. It was selected over chlorobenzene and toluene since due to its higher vapor pressure it was less likely to volatilize from solution, and so any decrease in 2,4-DNT concentrations could be taken as a measure of its degradation.

Iron, pre-treated as described in section 2.4.3, was employed in comparative rate studies against ultrasonically pre-treated iron at 900 kHz, untreated iron at pH 6 and untreated iron at pH 4. Degradation rate constants of all studies, which are presented in table 3.2.1, are representative of first order degradation rates. Plots of $\ln A/A_0$ versus time are provided from studies at pH 6 and pH 4 in figures 3.2.1 and 3.2.2 respectively. In addition, the effect of stirring in the absence of iron or ultrasound on 2,4-DNT degradation is presented on each figure for comparison purposes.

Iron Pre-treatment Conditions		Degradation rate constant (k) min ⁻¹
pH 6	Ultrasound pre-treated	0.06 ± 0.01
	At 900 kHz	
	Untreated	0.18 ± 0.01
	Pre-treated	0.42 ± 0.02
pH 4	Untreated	0.27 ± 0.01
	Pre-treated	1.15 ± 0.21

Table 3.2.1. Degradation rates of 2,4-DNT following stirring in the presence of iron pre-treated under various conditions

The obtained degradation rate constants produced several interesting results. At pH 6, the order of increasing degradation rate is; ultrasonically pre-treated iron at 900 kHz followed by untreated iron and then pre-treated iron. At pH 4, the fastest degradation rate was observed with pre-treated iron.

As can be seen in table 3.2.1, zero valent iron particle pre-treatment involving acid washing significantly increased the degradation rate at both values of pH. This difference in reactivities following pre-treatment can be explained by the conclusions of Tratnyek et al.⁷⁴, who have reported that acid-wash pre-treatment processes enhance degradation rates by removing crystalline oxides from the metal's surface, leaving behind a fresh amorphous elemental iron that is more reactive.⁷⁴ In an independent study Johnson et al.^{32, 33} also reported that the acid-wash pre-treatment is effective at increasing the reactive surface area, but to varying degrees.

Figure 3.2.1: Effect of various iron pre-treatment methods on 2,4-DNT degradation rate constant at pH 6

- ▼ **Stirring without iron, $(k) = -0.0002 \pm 0.0001 \text{ min}^{-1}$**
- ▲ **Ultrasound pre-treated iron (900 kHz), $(k) = 0.062 \pm 0.009 \text{ min}^{-1}$**
- **Untreated iron, $(k) = 0.180 \pm 0.006 \text{ min}^{-1}$**
- **Treated iron, $(k) = 0.42 \pm 0.02 \text{ min}^{-1}$**

Figure 3.2.2: Effect of various iron pre-treatment methods on 2,4-DNT degradation rate constant at pH 4

- ▲ **Stirring without iron at pH 6, (k) = $-0.0002 \pm 0.0001 \text{ min}^{-1}$**
- **Untreated iron, (k) = $0.27 \pm 0.01 \text{ min}^{-1}$**
- **Treated iron, (k) = $1.15 \pm 0.21 \text{ min}^{-1}$**

The higher degradation rate at pH 4 can be explained by reaction 1.6.4 from which it is evident that the increased hydronium ion concentration shifts the equilibrium to the right, and at the same time it increases the reduction rate of analyte and dissolution of iron.

The use of iron pre-treated by ultrasound at 900 kHz resulted in a three fold rate decrease in comparison to untreated iron. Recalling from section 1.5.7, ultrasound can be used for cleaning metal surfaces, but in order for this process to be effective, lower frequencies which predominately produce transient cavitation are required. At 900 kHz stable cavitation processes predominate suggesting that cavitation induced cleaning and erosion of surface oxides would be very limited. In addition, it was noticed that the iron particles rested on the bottom of the reaction vessel thereby blocking or perhaps reflecting the ultrasonic sound waves, which were emitted from below. An explanation of the decreased reactivity of iron particles following sonication requires a detailed study of the metal surface before and after treatment.

3.2.2 Variation of Degradation Rate Constants of 2,4-DNT with Iron Mesh Size and Supplier

Three different irons were chosen; Fisher 40 and 100 mesh and Alfa Aesar 20 mesh. Mesh is a measurement of particle size where the mesh number is inversely proportional to the size of the particles, i.e., 100 mesh has a smaller grain size than 20 mesh. Experimental factors such as pH, pre-treatment, and even the rate of stirring were kept consistent for each analysis since it has been reported that they play a significant role in the rate of degradation.³²

The results, which are presented in figure 3.2.3 and table 3.2.2, show first-order degradation rates of 2,4-DNT. In addition, figure 3.2.3 includes for purposes of comparison, the degradation rate of 2,4-DNT obtained from stirring in the absence of iron.

Iron Mesh Size and Supplier	Degradation Rate Constant (k) min^{-1}
2,4-DNT stirring without iron	-0.0002 ± 0.0001
20 Mesh (Alfa Aesar)	0.12 ± 0.01
100 Mesh (Fisher)	0.137 ± 0.001
40 Mesh (Fisher)	0.42 ± 0.02

Table 3.2.2. Effect of iron mesh size and supplier on degradation rate of 2,4-DNT

Note: All iron samples were pre-treated and employed under identical conditions

The degradation rate constants using Fisher 40, 100 and Alfa Aesar 20 mesh iron were found to be $0.42 \pm 0.02 \text{ min}^{-1}$, $0.13 \pm 0.01 \text{ min}^{-1}$ and $0.12 \pm 0.01 \text{ min}^{-1}$ respectively. Since these results show very little correlation between mesh size and degradation rate, other factors such as *physical* surface area, particle porosity and *reactive* surface area must have contributing effects.

Physical surface area is the surface area per unit mass of metal as determined by measuring the amount of N_2 gas absorbed onto the surface of the metal. This measurement was not performed in our studies. *Reactive* surface area is the amount of reactive sites which contributes directly to contaminant degradation.³²

As mentioned previously the concentration of reactive sites on the surface of the metal is a contributing factor to the overall degradation rate of a particular analyte.³² Therefore, since table 3.2.2 and figure 3.2.3 demonstrate that Fisher 40 mesh iron particles are most efficient at degrading 2,4-DNT in aqueous solutions, it is possible that following pretreatment they have the highest concentration of reactive sites. The similarities in reactivities of Fisher 100 mesh and Alfa-Aesar 20 mesh suggest that both samples have similar concentrations of reactive sites. However, if this is the case then the Alfa-Aesar 20 mesh particles, which are 5 times in size must have a high concentration of reactive sites, possibly due to a more porous structure.

Figure 3.2.3: 2,4-DNT degradation rate as a factor of mesh size and various suppliers

- ▲ **Stirring without iron, (k) = $-0.0002 \pm 0.0001 \text{ min}^{-1}$**
- ▼ **40 Mesh (Fisher), (k) = $0.42 \pm 0.02 \text{ min}^{-1}$**
- **100 Mesh (Fisher), (k) = $0.137 \pm 0.001 \text{ min}^{-1}$**
- **20 Mesh (Alfa Aesar), (k) = $0.12 \pm 0.01 \text{ min}^{-1}$**

3.2.3 Summary of Results

The highest degradation rate of 2,4-DNT was obtained at pH 4 with acid-washed pre-treated Fisher 40 mesh zero valent iron particles.

3.3 Results of Experiments on 2,4-DNT

3.3.1 Effect of Stirring Aqueous Solutions in the Absence of Zero Valent Iron Particles and Ultrasound

The effect of stirring a stock solution of 2,4-DNT at pH 6, in the absence of zero valent iron particles and ultrasonic irradiation was important to determine since the results provided a baseline for all subsequent experimental conditions. Furthermore, by conducting the experiment in an open bench-top reaction vessel, possible loss of analyte due to volatilization could be determined. The results of this study have already been presented, in figures 3.2.1, 3.2.2 and 3.2.3, however other important characteristics pertaining to the behavior of 2,4-DNT in aqueous solution require further discussion. First, the degradation rate of $(k) = -0.0002 \pm 0.0001 \text{ min}^{-1}$ suggests that simple stirring has virtually no degradative effect. This is reinforced by the fact that no new peaks were observed on the chromatogram. Second, analyte concentration in solution remains constant suggesting that there is no volatilization under these conditions. Third, the degradation rate has a negative value, but is so small as to be insignificant.

3.3.2 Effect of pH and Ultrasonic Frequency

Results of 2,4-DNT degradation rate constants were grouped into two categories, effect of pH, presented in figures 3.3.1 to 3.3.5 and effect of ultrasonic frequency, presented in figures 3.3.6 to 3.3.9. Most of the points shown on all figures represent an average of several determinations. In addition, each figure contains for purposes of rate comparison the results of stirring a stock solution of 2,4-DNT in the absence of iron or ultrasound.

Higher degradation rates were obtained at lower pH. For example, referring to figure 3.3.1, an approximate three fold rate increase was obtained at pH 4 over that at pH 6. An explanation pertaining to the effects of a higher hydronium ion concentration in the presence of zero valent iron particles, on the degradation rate of nitro aromatic compound has already been addressed in section 3.2.1.

Experiments involving only ultrasound at 20 and 900 kHz, presented in figures 3.3.2 and 3.3.3 respectively, also resulted in faster degradation rates at lower pH. It should be emphasized that there have been very few publications addressing the effects of pH on degradation rates of various analytes in aqueous solutions, and from the recent reports it is evident that a unified theory has not evolved. For example, certain literature reports involving ultrasonic degradation of phenolated aromatics¹⁸ and chlorinated aliphatics¹⁶, both in aqueous solutions have stated that variations in pH do not affect degradation rate. However, Hua et al.²⁴ have shown that under ultrasonic irradiation conditions, the rate of hydrolysis of *p*-nitrophenol acetate in aqueous solutions was increased by two orders of magnitude by lowering the pH from 8 to 3. Based on these

reports as well as our findings it is possible that the degradation rate of a particular analyte depends on the nature of analyte and on the variation of solution pH.

Degradation rate results from studies involving the coupling of ultrasound at 20 and 900 kHz with zero valent iron particles at a lower pH are presented in figures 3.3.4 and 3.3.5 respectively. As with previous studies of pH effects, it is evident from both figures that the degradation rate increases at a higher hydronium ion concentration. By comparing figures 3.3.2 and 3.3.3, it is important to notice that ultrasound provides a very small contribution, if any, towards the degradation rate and that it is the presence of zero valent iron particles which drives the degradation rate forward. This is not surprising, since the presence of zero valent iron particles provides an abundant source of electrons necessary for initiating the reduction of the nitro group.

It is important to note that degradation rates from studies which used only zero valent iron particles were generally higher than those from combined iron and ultrasound studies. A satisfactory explanation of this effect is not available since it is not known how ultrasound affects the mass transport of analyte to the metal's surface, or if ultrasound generated ions such as nitrate and nitrite would compete with the analyte for reactive sites. Therefore, a detailed explanation of the effects of pH under ultrasonic conditions in the presence of zero valent iron particles and nitro aromatic compounds requires further research.

Table 3.3.1 is presented which provides a summary of all degradation rates from studies on 2,4-DNT.

Experimental Conditions	Degradation rate constant (k) min⁻¹ at pH 4	Degradation rate constant (k) min⁻¹ at pH 6
Stirring in the absence of zero valent iron particles or ultrasound	_____	-0.0002 ± 0.0001
Stirring in the presence of Zero valent iron particles	1.2 ± 0.2	0.42 ± 0.02
20 kHz Ultrasound only	0.0055 ± 0.0006	0.0022 ± 0.0009
20 kHz Ultrasound in the presence of zero valent iron particles	0.85 ± 0.03	0.44 ± 0.03
900 kHz Ultrasound only	0.0041 ± 0.0007	0.00056 ± 0.00009
900 kHz Ultrasound in the presence of zero valent iron particles	0.055 ± 0.003	0.035 ± 0.002

Table 3.3.1: Summary of degradation rates of 2,4-DNT

Figure 3.3.1: Effect of pH on 2,4-DNT degradation rate constant in the presence of zero valent iron particles

- pH = 4, (k) = $1.15 \pm 0.21 \text{ min}^{-1}$
- pH = 6, (k) = $0.42 \pm 0.02 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, (k) = $-0.0002 \pm 0.0001 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

Figure 3.3.2: Effect of pH on 2,4-DNT degradation rate constants at 20 kHz in the absence of zero valent iron particles

- pH = 6, (k) = $0.0022 \pm 0.0009 \text{ min}^{-1}$
- pH = 4, (k) = $0.0055 \pm 0.0006 \text{ min}^{-1}$
- ▲ Stirring, no iron or ultrasound,
(k) = $-0.0002 \pm 0.0001 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

Figure 3.3.3: Effect of pH on 2,4-DNT degradation rate constants at 900 kHz in the absence of zero valent iron particles

- pH = 4, (k) = $0.0041 \pm 0.0007 \text{ min}^{-1}$
- pH = 6, (k) = $0.00056 \pm 0.00009 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, (k) = $-0.0002 \pm 0.0001 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

Figure: 3.3.4: Effect of pH on 2,4-DNT degradation rate constants at 20 kHz in the presence of zero valent iron particles

- pH = 4, $(k) = 0.85 \pm 0.03 \text{ min}^{-1}$
- pH = 6, $(k) = 0.44 \pm 0.03 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, $(k) = -0.0002 \pm 0.0001 \text{ min}^{-1}$

Note: error bars represent standard deviation from duplicate experiments

Figure: 3.3.5: Effect of pH on 2,4-DNT degradation rate constants at 900 kHz in the presence of zero valent iron particles

- pH = 6, $(k) = 0.035 \pm 0.002 \text{ min}^{-1}$
- pH = 4, $(k) = 0.055 \pm 0.003 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, $(k) = -0.0002 \pm 0.0001 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

The effects of frequency are presented in figures 3.3.6 to 3.3.9. It was mentioned in the introduction that frequency is predominately responsible for the size of resonant bubbles. Consequently the resonant bubble size is a determining factor for the temperature and pressure created during cavity implosion. Furthermore it also controls the type of cavitation implosion, during which a corresponding amount of reactive species are released into the surrounding liquid.

The effects of frequency at pH 4 and 6, in the absence of zero valent iron, are presented in figures 3.3.6 and 3.3.7 respectively. Both these figures show that by starting at a similar pH, the degradation rates obtained under different ultrasonic frequencies are comparable. For example, at pH 4 the degradation rate at 900 kHz is $0.0041 \pm 0.0007 \text{ min}^{-1}$ whereas at 20 kHz the rate is $0.0055 \pm 0.0006 \text{ min}^{-1}$. At pH 6 the variation is more pronounced, $0.0006 \pm 0.0001 \text{ min}^{-1}$ at 900 kHz and $0.002 \pm 0.001 \text{ min}^{-1}$ at 20 kHz.

Prior to proposing explanations for differences in degradation rates of studies that employed only sonication, the nature of cavities generated under each frequency has to be considered. As mentioned in the introduction, Entezari and Kruus have proposed that the 900 kHz sonication apparatus produces stable cavitation whereas the 20 kHz probe produces transient type cavities.⁸⁰ It is important to consider differences in the time and temperature of cavitation collapse and the amount of chemical species released into the surrounding medium. For example, the collapse time of a bubble occurring at 20 kHz has been calculated to be $4.5 \mu\text{s}$ and at 900 kHz it is $0.19 \mu\text{s}$.⁸⁰ In terms of chemical species, Petrier et al. have suggested that because the collapse time at higher frequencies is shorter, more hydroxyl radicals are ejected out of the bubble before they can recombine in the gas phase.¹⁸ However, if this is the case, then at 20 kHz there would be

substantially less hydroxyl radicals, which does not provide an explanation for a degradation rate comparable to that at 900 kHz. In a recent paper by Hoffman et al. it was proposed that, besides hydroxyl radical attack, a separate mechanism involving denitration via pyrolytic cleavage of the C-N bond could occur.¹⁶ In addition, because the interface of the bubble has been proposed to be hydrophobic, a higher concentration of 2,4-DNT could be present at the high temperature interface.⁷¹ At 900 kHz the estimated temperature of bubble collapse has been proposed to be on the order of 1800 K, whereas at 20 kHz the collapse temperature has been predicted at 5000 K.⁴⁶ Thus based on temperatures of cavitation collapse it is speculated that at 20 kHz pyrolytic cleavage is predominately responsible for degrading 2,4-DNT, whereas as at 900 kHz it is proposed that the degradation mechanism involves hydroxyl radical attack.

Effects of frequency on the degradation rate from combined ultrasound and zero valent iron particle studies at pH 4 and 6 are presented in Figures 3.3.8 and 3.3.9 respectively. Referring to both of these figures it is apparent that greater degradation rates were obtained at 20 kHz.

Johnson et al. have reported that the rate of stirring of iron particles can have a significant effect on the degradation rate of oxidizing analytes in aqueous solutions.³² Based on visual observations, at 900 kHz, zero valent iron particles simply rest on the bottom of the reaction flask. However at 20 kHz the iron particles are vigorously circulated through out the cell suggesting that at low frequency the degradation rate constant enhanced by mixing.

Figure 3.3.6: Effect of frequency on 2,4-DNT degradation rate constants at pH 4 without zero valent iron particles

- 20 kHz, $(k) = 0.0055 \pm 0.0006 \text{ min}^{-1}$
- 900 kHz, $(k) = 0.0041 \pm 0.0007 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, $(k) = -0.0002 \pm 0.0001 \text{ min}^{-1}$

Note: replot of data from Figures 3.3.2. and 3.3.3

Figure 3.3.7: Effect of frequency on 2,4-DNT degradation rate constants at pH 6 without zero valent iron particles

- 20 kHz, (k) = $0.002 \pm 0.001 \text{ min}^{-1}$
- 900 kHz, (k) = $0.0006 \pm 0.0001 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, (k) = $-0.0002 \pm 0.0001 \text{ min}^{-1}$

Note: replot of data from Figures 3.3.2 and 3.3.3

Figure 3.3.8: Effect of frequency on 2,4-DNT degradation rate constants at pH 4 with zero valent iron particles

- 20 kHz, $(k) = 0.85 \pm 0.03 \text{ min}^{-1}$
- 900 kHz, $(k) = 0.055 \pm 0.003 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, $(k) = -0.0002 \pm 0.0001 \text{ min}^{-1}$

Note: replot of data from Figures 3.3.4 and 3.3.5

Figure 3.3.9: Effect of frequency on 2,4-DNT degradation rate constants at pH 6 with zero valent iron particles

- 20 kHz, $(k) = 0.44 \pm 0.03 \text{ min}^{-1}$
- 900 kHz, $(k) = 0.035 \pm 0.002 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, $(k) = -0.0002 \pm 0.0001 \text{ min}^{-1}$

Note: replot of data from Figures 3.3.4 and 3.3.5

3.3.3 Degradation Products of 2,4-DNT

Initial degradation products of 2,4-DNT were identified as 2-nitro-4-aminotoluene, 2-amino-4-nitrotoluene, 2,4-diaminotoluene, and 1,3-dinitrobenzene. Their identification was based on GC retention times and mass spectral analysis. The amounts of these initial decomposition products detected was only a small percentage of the amount of disappearing parent analyte suggesting that their formation was either a result of several degradation pathways, or that they themselves were rapidly destroyed. The possibility of their volatilization from solution was eliminated with negative volatility tests.

The degradation of 2,4-DNT under reducing conditions, i.e. in the presence of only zero valent iron, has been speculated by Hoffman et al. to proceed via sequential nitro reduction to 2,4-diaminotoluene through initial intermediates involving $\text{NO}_2 \rightarrow$ nitroso (NO) $\rightarrow$ hydroxylamine (NHOH) $\rightarrow$ amine (NH_2).²² Neither of these compounds were observed as intermediates prior to the detection of 2-amino-4-nitro- and 2-nitro-4-aminotoluene suggesting that they could have formed for only brief periods of time or that they did not desorb from the surface of the iron. Formally, the overall reaction

occurs in six steps, each involving a two-electron reduction, with Fe^0 as the ultimate electron donor. A possible mechanism based on the reduction of nitrobenzene proposed by Agrawal et al. is presented in figure 3.3.10.³³

Figure 3.3.10: Possible degradation pathway of 2,4-DNT in the presence of zero valent iron particles.

Under oxidizing conditions, i.e., in the presence of ultrasound a different mechanism is believed to be responsible for the degradation of 2,4-DNT. For example, at 20 kHz, Hoffman et al. have reported that 2,4,6-trinitrotoluene (TNT) undergoes denitration via pyrolytic cleavage of the C-N bond to release NO₂ to solution.¹⁶ Kotronarou et al. have reported that the degradation of *p*-nitrophenol is linked to thermal decomposition in the vicinity of the hot collapsing gas cavities resulting in the cleavage of the C-NO₂ bond.⁷² In our studies none of products emanating from the above mentioned degradative pathways were isolated, but the presence of 1,3-dinitrotoluene was noted. A possible degradative pathway under similar conditions for the degradation of TNT has been proposed¹⁶, however since only 1,3-dinitrotoluene was isolated, the proposition of a degradation mechanism reflecting our studies requires further research.

3.3.4 Summary of Results

Referring to table 3.3.1., it is evident that greater degradation rates were obtained at pH 4 than at pH 6. Furthermore, the most effective method for remediating 2,4-DNT contaminated groundwater, would involve stirring with pre-treated zero valent iron particles. It should be emphasized that the pre-treatment of iron prior to use is essential for an effective degradation. The effects of various iron pre-treatments on the degradation rate of 2,4-DNT at pH 6 were $0.06 \pm 0.01 \text{ min}^{-1}$ for ultrasound (900 kHz) pre-treated iron, $0.18 \pm 0.01 \text{ min}^{-1}$ for untreated iron and $0.42 \pm 0.02 \text{ min}^{-1}$ for pretreated iron. While those at pH 4 were $0.27 \pm 0.01 \text{ min}^{-1}$ for untreated iron and $1.15 \pm 0.21 \text{ min}^{-1}$ for pre-treated iron.

The irradiation of 2,4-DNT stock solutions at either ultrasonic frequency without zero valent iron resulted in the lowest degradation rates. The combination of iron and ultrasound at either frequency, resulted in significant degradation rate increases at 20 kHz, but only moderate increases at 900 kHz above the rates seen with ultrasound alone. However these rates were lower than those determined using zero valent iron alone. Increases in degradation rates at either frequency resulted from the addition of iron, but the differences in degradation rates between ultrasonic frequencies were largely due to different efficiencies of mixing the iron particles in solution.

3.4 Results of Experiments on 2,6-DNT

3.4.1 Effect of Stirring Aqueous Solutions in the Absence of Zero Valent Iron Particles and Ultrasound

Prior to degradation rate studies, a baseline of comparison was obtained as described in section 2.4.8. It is evident from the results, which are presented in figure 3.4.1, that 2,6-DNT did not degrade nor did it volatilize under the effect of stirring in an open reaction flask.

Figure 3.4.1: Effect of stirring an aqueous solution 2,6-DNT in the absence of zero valent iron particles

● Stirring at pH 6, (k) = $-0.0003 \pm 0.0002 \text{ min}^{-1}$

3.4.2 Effect of pH and Ultrasonic Frequency

Degradation rates obtained from various experimental conditions have been grouped into two sections; effects of pH and of frequency. As in 2,4-DNT studies, most of the points shown in all figures represent an average of several determinations. In addition, each figure includes, for purposes of rate comparison, the effect of stirring a 2,6-DNT solution in the absence of iron or ultrasound.

It should be noted that similar trends in degradation rates were obtained in comparison to studies of 2,4-DNT. Because of the similarities in structure of 2,4- and 2,6-DNT, explanations pertaining to certain results will not be provided in this section, in turn locations where a similar topic was discussed will be given.

The effects of pH on the degradation rate of 2,6-DNT are presented from figures 3.4.2 to 3.4.6. The results of frequency studies are provided from figures 3.4.7 to 3.4.10. In addition table 3.4.1 is presented which provides a summary of all degradation rates.

Experimental Conditions	Degradation rate constant (<i>k</i>) min⁻¹ at pH 4	Degradation rate constant (<i>k</i>) min⁻¹ at pH 6
Stirring in the absence of zero valent iron particles or ultrasound	—————	-0.0003 ± 0.0002
Stirring in the presence of Zero valent iron particles	0.13 ± 0.05	0.026 ± 0.006
20 kHz Ultrasound only	0.0041 ± 0.002	0.00075 ± 0.0007
20 kHz Ultrasound in the presence of zero valent iron particles	0.14 ± 0.01	0.068 ± 0.004
900 kHz Ultrasound only	0.0015 ± 0.0006	0.00069 ± 0.00004
900 kHz Ultrasound in the presence of zero valent iron particles	0.0051 ± 0.0009	0.0065 ± 0.009

Table 3.4.1: Summary of degradation rates of 2,6-DNT

Figure: 3.4.2: Effect of pH on 2,6-DNT degradation rate constants in the presence of zero valent iron particles

- pH = 4, (k) = $0.13 \pm 0.05 \text{ min}^{-1}$
- pH = 6, (k) = $0.026 \pm 0.006 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, (k) = $-0.0003 \pm 0.0002 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

Figure 3.4.3: Effect of pH on 2,6-DNT degradation rate constants at 20 kHz in the absence of zero valent iron particles

- pH = 6, $(k) = 0.00075 \pm 0.00007 \text{ min}^{-1}$
- pH = 4, $(k) = 0.0041 \pm 0.0002 \text{ min}^{-1}$
- ▲ **Stirring at pH 6, no iron or ultrasound,**
 $(k) = -0.0003 \pm 0.0002 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

Figure 3.4.4: Effect of pH on 2,6-DNT degradation rate constants at 900 kHz in the absence of zero valent iron particles

- pH = 6, (k) = $0.00069 \pm 0.00004 \text{ min}^{-1}$
- pH = 4, (k) = $0.0015 \pm 0.0006 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, (k) = $-0.0003 \pm 0.0002 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

Figure 3.4.5: Effect of pH on 2,6-DNT degradation rate constants at 20 kHz in the presence of zero valent iron particles

- pH = 4, (k) = $0.14 \pm 0.01 \text{ min}^{-1}$
- pH = 6, (k) = $0.068 \pm 0.004 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, (k) = $-0.0003 \pm 0.0002 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

Figure 3.4.6: Effect of pH on 2,6-DNT degradation rate constants at 900 kHz in the presence of zero valent iron particles

- pH = 4, $(k) = 0.00511 \pm 0.00001 \text{ min}^{-1}$
- pH = 6, $(k) = 0.0065 \pm 0.0001 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, $(k) = -0.0003 \pm 0.0002 \text{ min}^{-1}$

Note: error bars represent standard deviation from duplicate experiments

Figure 3.4.7: Effect of frequency on 2,6-DNT degradation rate constants at pH 4 without zero valent iron particles

- 900 kHz, $(k) = 0.001507 \pm 0.0006 \text{ min}^{-1}$
- 20 kHz, $(k) = 0.0041 \pm 0.0002 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, $(k) = -0.0003 \pm 0.0002 \text{ min}^{-1}$

Note: replot of data from Figures 3.4.3 and 3.4.4

Figure 3.4.8: Effect of frequency on 2,6-DNT degradation rate constants at pH 6 without zero valent iron particles

- 20 kHz, $(k) = 0.00075 \pm 0.00007 \text{ min}^{-1}$
- 900 kHz, $(k) = 0.000697 \pm 0.00004 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, $(k) = -0.0003 \pm 0.0002 \text{ min}^{-1}$

Note: replot of data from Figures 3.4.3 and 3.4.4

Figure 3.4.9: Effect of frequency on 2,6-DNT degradation rate constants at pH 4 with zero valent iron particles

- 20 kHz, $(k) = 0.14 \pm 0.01 \text{ min}^{-1}$
- 900 kHz, $(k) = 0.0065 \pm 0.0001 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, $(k) = -0.0003 \pm 0.0002 \text{ min}^{-1}$

Note: replot of data from Figures 3.4.5 and 3.4.6

Figure 3.4.10: Effect of frequency on 2,6-DNT degradation rate constants at pH 6 with zero valent iron particles

- 20 kHz, $(k) = 0.068 \pm 0.004 \text{ min}^{-1}$
- 900 kHz, $(k) = 0.0065 \pm 0.0001 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, $(k) = -0.0003 \pm 0.0002 \text{ min}^{-1}$

Note: replot of data from Figures 3.4.5 and 3.4.6

3.4.3 Summary of Results

The most effective methods of remediating water contaminated with 2,6-DNT involve stirring with pre-treated zero valent iron particles or the combination of pre-treated zero valent iron particles with ultrasound at 20 kHz. Both of these methods would be most effective at a pH of 4.

3.5 Results of Experiments on Aniline

3.5.1 Effect of Stirring Aqueous Solutions in the Absence of Zero Valent Iron Particles and Ultrasound

The degradation rate constant of aniline obtained from simply stirring a stock solution in an open bench-top reaction flask is $-1.6 * 10^{-3} \pm 8.0 * 10^{-4} \text{ min}^{-1}$. The results of this study are presented in figure 3.5.1 from which it is apparent that aniline is unaffected by stirring, nor does it volatilize.

Figure 3.5.1: Effects of stirring an aqueous solution of aniline in an open bench-top reaction vessel without zero valent iron particles or ultrasound

● Stirring at pH 6, $(k) = -0.0016 \pm 0.0008 \text{ min}^{-1}$

3.5.2 Effect of pH and Ultrasonic Frequency

Degradation rate constants of aniline, which are summarized in table 3.5.1, produced several interesting results. First, higher degradation rates always occurred at a lower pH. Second, the application of zero valent iron particles is speculated to have no effect. Third, the combination of zero valent iron particles and ultrasound did not enhance the degradation rate, and fourth, high frequency ultrasound when used alone was most effective.

In general, most points shown in all figures represent an average of several determinations. In addition each figure includes, for purposes of rate comparison, the effect of stirring a stock solution of aniline in the absence of zero valent iron particles or ultrasound.

Figures 3.5.2 to 3.5.6 represent the effects of pH. It can be seen from figure 3.5.2 that the presence of zero valent iron particles caused a very small decrease in concentration of parent analyte. However, since no new peaks were noted on the chromatogram and aniline was not capable of volatilization, an explanation of its slow disappearance from solution requires further research. Recently Agrawal et al. reported that aniline, the end product of nitrobenzene reduction by iron metal would not undergo further reduction, however, it continued to slowly disappear from solution.³³ Based on its corrosion inhibition and adsorption properties, the authors proposed that the presence of aniline hindered the mass transport of nitrobenzene to the metal surface through a competition by adsorption at reactive sites. In our studies, it is speculated that the

degradation rate constants from studies with zero valent iron particles are a result of an adsorption process to the surface of the metal .

Referring to table 3.5.1, it can be seen that regardless of experimental conditions higher degradation rate constants were obtained at a lower pH. It is not know if at a lower pH the protonated form of aniline (pK_a 4.6) would be more reactive and/or more hydrophobic. However, based on the propositions presented in section 1.5.6 by Kotronarou an increased hydrophobicity would occur at the cavitation interface at a lower pH. Since aniline is naturally hydrophobic it would tend to accumulate in the interfacial region, however it is possible that once protonated it would likely reside in the bulk of the liquid.

Experimental Conditions	Degradation rate (<i>k</i>) min⁻¹ at pH 4	Degradation rate (<i>k</i>) min⁻¹ at pH 6
Stirring without zero valent iron or ultrasound	_____	-0.0016 ± 0.0008
Stirring in the presence of Zero valent iron particles	0.00022 ± 0.00001	0.00013 ± 0.00003
20 kHz Ultrasound only	0.0039 ± 0.0005	0.0018 ± 0.0003
20 kHz Ultrasound in the presence of zero valent iron particles	0.0019 ± 0.0007	0.0015 ± 0.0005
900 kHz Ultrasound only	0.023 ± 0.004	0.014 ± 0.007
900 kHz Ultrasound in the presence of zero valent iron particles	0.0086 ± 0.0007	0.0023 ± 0.0007

Table 3.5.1: Summary of degradation rate constants of aniline

Figure 3.5.2: Effect of pH on aniline degradation rate constants in the presence of zero valent iron particles

- pH = 4, (k) = $0.00022 \pm 0.00009 \text{ min}^{-1}$
- pH = 6, (k) = $0.00013 \pm 0.00003 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, (k) = $-0.0016 \pm 0.0008 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

Figure 3.5.3: Effect of pH on aniline degradation rate constants at 20 kHz in the absence of zero valent iron particles

- pH = 4, $(k) = 0.0039 \pm 0.0005 \text{ min}^{-1}$
- pH = 6, $(k) = 0.0018 \pm 0.0003 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, $(k) = -0.0016 \pm 0.0008 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

Figure 3.5.4: Effect of pH on aniline degradation rate constants at 900 kHz in the absence of zero valent iron particles

- pH = 6, (k) = $0.014 \pm 0.007 \text{ min}^{-1}$
- pH = 4, (k) = $0.023 \pm 0.004 \text{ min}^{-1}$
- ▲ **Stirring at pH 6, no iron or ultrasound,**
(k) = $-0.0016 \pm 0.0008 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

Figure 3.5.5: Effect of pH on aniline degradation rate constants at 20 kHz in the presence of zero valent iron particles

- pH = 4, $(k) = 0.0019 \pm 0.0007 \text{ min}^{-1}$
- pH = 6, $(k) = 0.0015 \pm 0.0005 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, $(k) = -0.0016 \pm 0.0008 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

Figure 3.5.6: Effect of pH on aniline degradation rate constants at 900 kHz in the presence of zero valent iron particles

- pH = 4, (k) = $0.0086 \pm 0.0007 \text{ min}^{-1}$
- pH = 6, (k) = $0.0023 \pm 0.0007 \text{ min}^{-1}$
- ▲ **Stirring at pH 6, no iron or ultrasound,**
(k) = $-0.0016 \pm 0.0008 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

Referring to table 3.5.1, a common trend is observed by comparing the degradation rate constants from ultrasound studies with those from combined ultrasound and zero valent iron particle experiments. For example, at 900 kHz the addition of zero valent iron particles significantly decreases the degradation rate constant. From visual observations, it is apparent that the bulk of zero valent iron particles resides on the bottom of the reaction flask and hinders the passage of ultrasound into the reaction mixture. At 20 kHz, because of the lowered degradation rate constant, it was speculated that the zero valent iron particles lowered the cavitation threshold, consequently decreasing the temperature of implosion as well as the production rate of radicals. Therefore, based on these findings, it is proposed that the presence of zero valent iron particles act as a source of interference.

Variation in ultrasonic frequency has a significant effect on the degradation rate constants of aniline. Figures 3.5.6 and 3.5.7 present these effects in the absence of zero valent iron particles. It is apparent that the degradation rate constants following sonication at 900 kHz in comparison to 20 kHz is six times greater at pH 4 (i.e. 0.023 ± 0.004 and 0.0039 ± 0.0005 respectively) and eight times greater at pH 6 (i.e. 0.014 ± 0.007 and 0.0018 ± 0.0003 respectively). With respect to the reaction mechanism, it has already been proposed that the initial step of degradation involves hydrogen atom abstraction.^{82, 83, 87, 88} Nonetheless a satisfactory explanation cannot be proposed for the increased degradation rate at lower pH since it is not known why the protonated form of aniline would be more susceptible to either hydrogen atom abstraction in the bulk of the liquid or in the interfacial region.

As discussed in section 3.3.2, ultrasonic frequency affects numerous aspects of cavitation implosion. At higher frequencies, the resonant bubble radius decreases causing an increase of the surface to volume ratio. The surface to volume ratio also plays an important role in cavitation dynamics since it has a direct relationship with the rate of radical production and the rate at which temperature decreases. Therefore, it is proposed that the rate of aniline degradation is directly related to the concentration of radical species in the interfacial region, a quantity which is controlled by the frequency of sonication.

Results pertaining to combined ultrasound and zero valent iron particle studies at pH 4 and 6 are presented in figures 3.5.8 and 3.5.9 respectively. The most significant rate decrease is apparent at 900 kHz. As mentioned previously, it is most likely attributed to the obstruction of the ultrasound into the reaction vessel. At 20 kHz the effect of iron particles is less pronounced, however it is possible that their presence causes a reduction in ultrasonic intensity by lowering the cavitation threshold.

Figure 3.5.7: Effect of frequency on aniline degradation rate constants at pH 4 without zero valent iron particles

- 20 kHz, $(k) = 0.0039 \pm 0.0005 \text{ min}^{-1}$
- 900 kHz, $(k) = 0.023 \pm 0.004 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, $(k) = -0.0016 \pm 0.0008 \text{ min}^{-1}$

Note: replot of data from Figures 3.5.3 and 3.5.4

Figure 3.5.8: Effect of frequency on aniline degradation rate constants at pH 6 without zero valent iron particles

- 20 kHz, (k) = $0.0018 \pm 0.0003 \text{ min}^{-1}$
- 900 kHz, (k) = $0.014 \pm 0.007 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, (k) = $-0.0016 \pm 0.0008 \text{ min}^{-1}$

Note: replot of data from Figures 3.5.3 and 3.5.4

Figure 3.5.9: Effect of frequency on aniline degradation rate constants at pH 4 with zero valent iron particles

- 20 kHz, $(k) = 0.0019 \pm 0.0007 \text{ min}^{-1}$
- 900 kHz, $(k) = 0.0086 \pm 0.0007 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, $(k) = -0.0016 \pm 0.0008 \text{ min}^{-1}$

Note: replot of data from Figures 3.5.5 and 3.5.6

Figure 3.5.10: Effect of frequency on aniline degradation rate constants at pH 6 with zero valent iron particles

- 20 kHz, (k) = 0.0015 +/- 0.0005 min⁻¹
- 900 kHz, (k) = 0.0023 +/- 0.0007 min⁻¹
- ▲ Stirring at pH 6, no iron or ultrasound, (k) = -0.0016 +/- 0.0008 min⁻¹

Note: replot of data from Figures 3.5.5 and 3.5.6

3.5.3 Degradation Products of Aniline

It should be emphasized that to date there have been very few publications addressing the issue of aniline degradation in aqueous solutions. Of these reports the conditions involved photocatalytic or electrochemical processes.^{82, 83, 84} In our studies we have shown that aniline in water can also be degraded using ultrasound, of possible use for ground water remediation; and that some of the breakdown products correspond to intermediates observed by other processes.

Ultrasonic irradiation at 20 kHz was chosen as the standard condition from which degradation products were studied, since on a remediative scale, a 20 kHz reactor would be commercially feasible.

Under all previous experimental conditions, degradation rate studies were conducted over a time scale of only sixty minutes. Such a short time period was sufficient for the determination of a degradation rate constant, but inadequate for a complete study of breakdown products. As a result, the reaction time was extended to a period of twelve hours during which the formation and disappearance of some breakdown products was observed. We attempted to characterize these breakdown products of aniline using RP-HPLC, SPME-GC/MS and IC.

Ultrasonic irradiation of air-equilibrated aqueous solutions has been reported to spontaneously produce nitrite and nitrate ions.⁷⁰ Coincidentally, under identical conditions, Hoffman et al. have proposed that the amino group of aniline can undergo oxidation, and/or even cleavage also resulting in the formation of nitrite and nitrate ions.¹⁶ Thus, to correctly account for the fate of nitrogen during aniline degradation,

sonication and analysis of only deionized water was performed. These solutions were used as blanks in the determination of nitrite and nitrate in experiments involving aniline.

Ultrasonic irradiation of 20 ppm aniline solutions at pH 6 resulted in the identification of the following organic breakdown products: quinone, hydroquinone, *o*-nitrophenol and a trace amount of nitrobenzene. In addition, several ions were detected: formate and/or glycolate, acetate, nitrite and nitrate. In order to present a comprehensive picture encompassing all breakdown products, the results from a single analysis were divided into two figures. Figure 3.5.11 presents the degradation of aniline in terms of carbon concentration (ppm) over time, while figure 3.5.12 represents degradation in terms of nitrogen concentration (ppm) over time. In addition each figure includes a plot of either total carbon or nitrogen. Figure 3.5.13 as proposed by Brillas et al. presents a possible pathway for the degradation of aniline, but which also fits with the species which we identified. In this figure, species which were identified are colored red.

Figure 3.5.11: Degradation products of aniline following ultrasonic irradiation at 20 kHz (ppm C)

- ◆— Acetate ppm C
- Formate + Glycolate ppm C
- ▲— Aniline ppm C
- ×— Hydroquinone ppm C
- *— o-Nitrophenol ppm C
- Quinone ppm C
- Total Carbon
- Nitrobenzene ppm C

Figure 3.5.12: Degradation products of aniline following ultrasonic irradiation at 20 kHz

◆ Aniline ppm N

■ Nitrite ppm N

○ Nitrobenzene ppm N

× o-Nitrophenol ppm N

* Total Nitrogen

Figure 3.5.13: Proposed degradation pathways of aniline following ultrasonic irradiation at 20 kHz

Note: species marked red were found in this study

It is obvious from figure 3.5.11 that the initial and most abundant breakdown products of aniline is quinone. At approximately seven hours of sonication the quinone concentration reaches a maximum, followed by a rapid decrease which coincides with the disappearance of aniline. In section 3.5.2, it was proposed that the initial step of aniline [1] degradation could be initiated by hydrogen atom abstraction.^{82, 83, 84}, perhaps by ultrasonically generated hydroxyl, hydroperoxyl radicals, resulting in the production of a highly reactive imino radical [2].^{83, 84} Since the hydroperoxyl radical has a much weaker oxidizing power than a hydroxyl radical, Brillas et al. proposed that its attack on the imino radical would result in a termination reaction resulting in the formation of nitrobenzene [4].^{88, 90} Referring to figure 3.5.12, it is evident that the production of nitrobenzene is very small, implying that its formation is either a secondary type of reaction or that it is very short lived.

Apart from radical attack it is also important to consider pyrolytic cleavage of the C-NH₂ bond, resulting in the production of an aromatic and amino radical. The aromatic radical could undergo termination reactions by reacting with another aromatic radical, or it could be quenched by a hydroxyl radical resulting in the formation of phenol [3].²² Phenol was not detected in our studies.

The electron donating effect of an aromatic amine functional group tends to activate the *ortho* and *para* positions, thus it is possible that hydroxyl radical attack would occur at these two positions producing an o-phenolimine [5] and a quinonimine [6] respectively. Neither of these compounds were identified in our studies, however the presence of the corresponding oxygenated species was confirmed by RP-HPLC and by mass spectral analysis. Based on electrochemical degradation studies Brillas et al.

proposed that quinonimine [6] would result in the formation of quinone, whereas oxidation of o-phenolimine [5] could possibly result in the formation of o-nitrophenol [7] as seen in figure 3.5.13. Referring to figure 3.5.12, it is evident that detection of o-nitrophenol [7] does not occur until half way through the reaction, possibly suggesting that hydroxyl radical attack is less favored at the *ortho* position.

It was important to determine the fate of quinone and its breakdown products thus ultrasonic irradiation of 20 ppm quinone solutions was investigated. The results which are presented in figure 3.5.14, suggest that prior to formate and glycolate formation, quinone was reduced to hydroquinone [9].

The drop in total carbon probably represents ultimate formation, and loss, of CO₂.

Figure 3.5.14: Degradation products from quinone following ultrasonic irradiation at 20 kHz

- ◆— Quinone ppm C
- Hydroquinone ppm C
- ▲— Formate + Glycolate ppm C
- total Carbon

In order to further understand the breakdown of quinone's degradation products, a complementary study involving the sonication of 20 ppm hydroquinone was performed. It was apparent from the results, which are presented in figure 3.5.15, that even at time zero, at least 50% of hydroquinone had been oxidized to quinone, in the presence of water and air. The results of these studies provided further insight not only into the ultrasonic degradation of aniline, but also into the effects of ultrasonic irradiation on aqueous solutions of quinone and hydroquinone.

It is evident from figure 3.5.11 that formate, glycolate and acetate are formed following the appearance of quinone. Further evidence of their presence has been presented in figures 3.5.14 and 3.5.15. Since these ions are observed during the sonication of hydroquinone and quinone, it is speculated that their formation must originate from further oxidation of their parent analytes, [8] and [9].

Brillas et al. reported that electrochemical degradation of quinone results in the formation of maleic [10] and fumaric acid [11].⁹⁰ Neither of these compounds have been detected under our conditions. However, it does not imply that they can be ruled out as intermediates, especially since further oxidation of these compounds would lead to the formation of glycolate [12], formate [13] and acetate [14]. Due to the limited separation ability of the ion exchange column used, it could not be determined if it was glycolate, formate or both ions that were formed.

It should be noted that on both figures 3.5.14 and 3.5.15, the total carbon line decreases with increasing sonication time. This suggests that following the formation of formate and/or glycolate and acetate, these ions are further degraded into carbon dioxide.

Figure 3.5.15: Degradation products from hydroquinone following ultrasonic irradiation at 20 kHz (ppm C)

- Quinone ppm C
- ▲— Hydroquinone ppm C
- Formate + Glycolate ppm C
- ◆ Total Carbon
- *— Acetate ppm C

Referring to figure 3.5.11 it is apparent that the total carbon line gradually decreases throughout the reaction, however following the complete transformation of aniline into other products, at least half of the original carbon remains in solution. It is evident that the concentration of *o*-nitrophenol is increasing however its formation is not understood and requires further research.

Referring to figure 3.5.12, it is evident that the final total nitrogen concentration is only slightly below the starting amount. It should be recalled that during the sonication of air-saturated aqueous solutions, the production of nitrite as well as nitrate occur. Both of these ions had been accounted for prior to experimentation and incorporated into this figure. As in figure 3.5.11, *o*-nitrophenol formation increases with time, contributing to the total nitrogen content, this occurrence is not understood and also requires further investigation.

3.5.4 Effect of Ferrous Chloride Coupled With Ultrasound on the Degradation Rate Constant of Aniline

The combination of ferrous iron with hydrogen peroxide is known to result in the production of hydroxyl radicals thorough the classical Fenton's reaction, shown in rxn

3.5.1.²⁶

Since ultrasonic irradiation of aqueous solutions spontaneously produces hydroxyl, hydroperoxyl radicals and hydrogen peroxide,²⁵ we proposed that the presence of ferrous iron in solution would form an *insitu* Fenton's reagent, resulting in an enhanced production of hydroxyl radicals and thus an increased degradation rate constant. Similar studies using other AOPs have already reported that the combination of hydrogen peroxide with ferrous iron produces increased concentrations of hydroxyl radicals.^{82, 87}

Results representing concentrations of carbon and nitrogen over time are presented in figures 3.5.16 and 3.5.17 respectively. By comparing figures 3.5.16 and 3.5.11 it is apparent that the presence of ferrous iron increases the initial degradation rate of aniline. This trend is consistent with recent results from Sanchez et al. in which it was proposed that within the first several hours the rapid degradation rate is a result of an increased hydroxyl radical concentration. However, following this rapid hydrogen peroxide depletion period, the degradation rate decreases during which H_2O_2 builds up to a steady-state concentration resulting in a slower degradation rate of aniline.⁸⁵

In comparing the degradation products from studies with and without ferrous ion, it can be seen that they are the same, but their concentrations in solution are different. For example, in studies with ferrous ion, formate/glycolate and *o*-nitrophenol production rates as well as final concentrations are higher. Quinone on the other hand exhibits a delayed formation, a short-lived existence followed by a rapid disappearance, whereas in the absence of ferrous iron, quinone's formation and disappearance follows aniline's degradation profile. The presence of hydroquinone is very small as seen in figure 3.5.11, however under ferrous ion conditions its time of formation coincides with the decreasing concentration of quinone.

Based on the results obtained from ferrous ion studies, it is speculated that there exists another degradative pathway in addition to the ones mentioned in figure 3.5.12. This then suggests that the initial high concentration of hydroxyl radicals results in a very rapid degradation of aniline towards formate and/or glycolate. It is only later in the experiment that other degradation products are formed.

By comparing figures 3.5.12 and 3.5.17, it is evident that in the presence of ferrous iron the production of nitrite is lower than that obtained from ultrasonic irradiation of pure water. Since under these conditions highly reactive species are spontaneously formed, it is possible that a large portion of nitrite ions could be converted into radical species capable of interaction with other degradation products.

Figure 3.5.16: Degradation products of aniline following ultrasonic irradiation at 20 kHz in the presence of ferrous chloride

- Acetate ppm C
- ▲— For+Gly ppm C
- X— Aniline ppm C
- *— Quinone ppm C
- Hydro-Q ppm C
- +— Nitrobenzene ppm C
- o-nitrophenol ppm C
- Carbon Total

Figure 3.5.17: Degradation products of aniline following ultrasonic irradiation at 20 kHz in the presence of ferrous chloride (ppm N)

- ◆— Aniline ppm N
- ▲— o-nitrophenol ppm N
- Nitrobenzene ppm N

3.5.5 Summary of Results

The presence of zero valent iron particles in solution alone or during ultrasonic irradiation at either frequency decreased the degradation rate constant of aniline. In comparing the effects of sonication frequencies, highest degradation rates were obtained at 900 kHz. It was proposed that the higher degradation rates were a result of an increased concentration of hydroxyl radicals in solution.

Studies exploring the formation of an *in-situ* Fenton's reagent following the addition of FeCl_2 at 20 kHz resulted in an increased degradation rate constant in comparison to that obtained from sonication alone. Degradation products, i.e., *o*-nitrophenol, quinone, benzoquinone, nitrobenzene, formate/glycolate, acetate, nitrite and nitrate were obtained from both studies, however the formation of certain intermediate degradation products was delayed in FeCl_2 studies. It was proposed based on the conclusions of Brillas et al.⁸² that due to the increased initial concentration of hydroxyl radicals resulting from the formation of an *in-situ* Fenton's reagent, the degradation proceeded very quickly, not allowing for intermediate products to be detected. Only later in the reaction when the initial concentration of oxidizing species decreased to a steady state production were degradation products detected. Therefore, increased degradation rates of aniline in the presence of FeCl_2 can most likely attributed to a higher concentration of hydroxyl radicals as a result of an *in-situ* Fenton's reagent. Table 3.5.2 is provided from which provides a comparison of degradation rates of aniline at 20 kHz with and without FeCl_2 , it should be noted that these studies were done over a 12 hour period.

Sonication at 20 kHz, pH 6	Degradation rate constant (<i>k</i>) of aniline (min ⁻¹)
without FeCl ₂	0.238 ± 0.034
with FeCl ₂	0.449 ± 0.051

Table 3.5.2: Effect of FeCl₂ on the degradation rate of aniline at 20 kHz, pH 6 over a 12 hour period

3.6 Results of experiments on Chlorobenzene

3.6.1 Effect of Stirring Aqueous Solutions in the Absence of Zero Valent Iron Particles and Ultrasound

Stirring aqueous solutions of chlorobenzene in an open bench-top reaction vessel resulted in a significant loss of analyte from solution. The possibility of analyte degradation was eliminated since new peaks were not noted on corresponding chromatograms. Therefore, the combination of analyte disappearance and absence of new compounds suggested that chlorobenzene volatilized from solution. In order to eliminate any ambiguous degradation rates from subsequent experiments, volatility studies were conducted in the standard sealed bench-top reaction vessel, the 20 and 900 kHz sonication vessels, without the application of ultrasound. Results obtained from these studies are presented in figure 3.6.1. It should be noted that a new parameter, volatility rate (k_v) has been introduced in order to distinguish between analyte volatility and degradation rate constant (k). It is evident from figure 3.6.1 that the 20 kHz sonication vessel had the highest volatility rate, however when compared to the open bench-top reaction vessel, it was essentially zero. Therefore any disappearance during sonication in a closed reaction vessel could be ascribed to chemical degradation in the solution.

Figure 3.6.1: Effect of stirring chlorobenzene in the absence of zero valent iron particles or ultrasound

Reaction vessels used:

- open bench-top, $(k_v) = 0.053 \pm 0.006 \text{ min}^{-1}$
- ▲ closed bench-top, $(k_v) = (-1.3 \pm 0.7) \times 10^{-3} \text{ min}^{-1}$
- closed 900 kHz, $(k_v) = (1.5 \pm 1.0) \times 10^{-4} \text{ min}^{-1}$
- ▼ closed 20 kHz, $(k_v) = (8.4 \pm 5.3) \times 10^{-4} \text{ min}^{-1}$

3.6.2. Effect of pH and Ultrasonic Frequency

Degradation rate constants of chlorobenzene are summarized in table 3.6.1.

Several generalities were obtained from these results. First, a relationship was not established between solution pH and degradation rate constants. Second, presence of zero valent iron particles had no effect on the degradation rate and when combined with ultrasound at either frequency resulted in degradation rates below those obtained using ultrasonic irradiation only. Third, high frequency ultrasound at pH 6 resulted in highest degradation rate constants.

In general, most points shown in all figures represent an average of several determinations. In addition each figure includes, for purposes of rate comparison, the results of stirring only a stock solution of chlorobenzene in a closed bench-top reaction vessel.

To date numerous studies have reported the effectiveness of zero valent iron particles on chlorinated C1, C2 and C3 compounds,^{32, 37, 40, 45, 72} however very few have studied the effects of iron particles on mono and polychlorinated aromatics.^{36, 38.}

Degradation rate constants from sonication studies at 20 and 900 kHz, presented in figures 3.6.7 and 3.6.8 respectively, demonstrated on average a ten fold increase over those obtained from stirring with zero valent iron particles, as seen in figure 3.6.2. In addition, because a decrease in rate was noted from combined iron and ultrasound studies, it is proposed that the iron particles not only act as a source of interference, but also in general have very little degradative effect.

Variations in initial solution pH produced varied effects. For example, studies at 20 kHz with and without zero valent particles, as presented in figures 3.6.3 and 3.6.5 respectively, resulted in practically identical rate constants. However, identical studies conducted at 900 kHz, as seen in figures 3.6.4 and 3.6.6, resulted in increased degradation rates at pH 6. A satisfactory explanation for these results is not known. It is possible that the spontaneous formation of nitrite and nitrate ions would have an effect on the degradation rate by altering solution pH,⁷⁰ however this is only speculation and requires further research.

Experimental Conditions	Degradation rate constant (k) min⁻¹ at pH 4	Degradation rate constant (k) min⁻¹ at pH 6
Closed bench-top reaction vessel, no zero valent iron particles or ultrasound	_____	- 0.0013 ± 0.0007
Stirring in the presence of Zero valent iron particles	0.0039 ± 0.0007	0.0019 ± 0.0009
20 kHz Ultrasound only	0.026 ± 0.003	0.029 ± 0.0003
20 kHz Ultrasound in the presence of zero valent iron particles	0.021 ± 0.002	0.021 ± 0.007
900 kHz Ultrasound only	0.0072 ± 0.0004	0.044 ± 0.002
900 kHz Ultrasound in the presence of zero valent iron particles	0.0021 ± 0.0006	0.0067 ± 0.0009

Table 3.6.1: Summary of degradation rate constants of chlorobenzene

Figure 3.6.2: Effect of pH on chlorobenzene degradation rate constants in the presence of zero valent iron particles

- pH = 4, (k) = $0.0039 \pm 0.0007 \text{ min}^{-1}$
- pH = 6, (k) = $0.0019 \pm 0.0009 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, (k_v) = $-0.0013 \pm 0.0007 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

Figure 3.6.3: Effect of pH on chlorobenzene degradation rate constants at 20 kHz in the absence of zero valent iron particles

- pH = 4, (k) = $0.026 \pm 0.003 \text{ min}^{-1}$
- pH = 6, (k) = $0.029 \pm 0.003 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, (k_v) = $-0.0013 \pm 0.0007 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

Figure 3.6.4: Effect of pH on chlorobenzene degradation rate constants at 900 kHz in the absence of zero valent iron particles

- pH = 4, (k) = $0.0072 \pm 0.0004 \text{ min}^{-1}$
- pH = 6, (k) = $0.044 \pm 0.002 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, (k_v) = $-0.0013 \pm 0.0007 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

Figure 3.6.5: Effect of pH on chlorobenzene degradation rate constants at 20 kHz in the presence of zero valent iron particles

- pH = 4, (k) = 0.021 $\pm$ 0.002 min⁻¹
- pH = 6, (k) = 0.021 $\pm$ 0.007 min⁻¹
- ▲ Stirring at pH 6, no iron or ultrasound, (k_v) = -0.0013 $\pm$ 0.0007 min⁻¹

Note: error bars represent standard deviation from triplicate experiments

Figure 3.6.6: Effect of pH on chlorobenzene degradation rate constant at 900 kHz in the presence of zero valent iron particles

- pH = 4, (k) = $0.0021 \pm 0.0006 \text{ min}^{-1}$
- pH = 6, (k) = $0.0067 \pm 0.0009 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, (k_v) = $-0.0013 \pm 0.0007 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

Effects of ultrasonic frequency are presented from figures 3.6.7 to 3.6.9.

Referring to table 3.6.1, it is evident that sonication at 900 kHz at pH 6 resulted in the highest degradation rate. An explanation pertaining to the effects of frequency on aqueous solutions has already been addressed in section 3.4.2, however it will be recalled that at higher frequencies there are more cavitation events per unit area resulting in an increased degradation rate. The results presented here are consistent with the findings of Kruus et al.,⁷⁰ not only because the same trend was observed in their studies, but also because the degradation rate constant was 1.5 - 2 times greater than with 900 kHz.

By comparing figures 3.6.7 with 3.6.9 as well as 3.6.8 with 3.6.10 it is obvious that the presence of zero valent iron particles decreases the degradation rate. At 20 kHz their presence lowers the cavitation threshold thereby diminishing the strength of cavitation collapse. At 900 kHz, the particles rest at the bottom of the reaction vessel and block the passage of ultrasound into the bulk of the liquid. Such an occurrence following the addition of zero valent iron particles has already been observed in studies of aniline as discussed in section 3.4.2.

Figure 3.6.7: Effect of frequency on chlorobenzene degradation rate constant at pH 4 without zero valent iron particles

- 20 kHz, $(k) = 0.026 \pm 0.003 \text{ min}^{-1}$
- 900 kHz, $(k) = 0.0072 \pm 0.0004 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, $(k_v) = -0.0013 \pm 0.0007 \text{ min}^{-1}$

Note: replot of data from Figures 3.6.3 and 3.6.4

Figure 3.6.8: Effect of frequency on chlorobenzene degradation rate constant at pH 6 without zero valent iron particles

- 20 kHz, $(k) = 0.029 \pm 0.003 \text{ min}^{-1}$
- 900 kHz, $(k) = 0.044 \pm 0.002 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, $(k_v) = -0.0013 \pm 0.0007 \text{ min}^{-1}$

Note: replot of data from Figures 3.6.3 and 3.6.4

Figure 3.6.9: Effect of frequency on chlorobenzene degradation rate constants at pH 4 with zero valent iron particles

- 20 kHz, $(k) = 0.021 \pm 0.002 \text{ min}^{-1}$
- 900 kHz, $(k) = 0.0021 \pm 0.0006 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, $(k_v) = -0.0013 \pm 0.0007 \text{ min}^{-1}$

Note: replot of data from Figures 3.6.5 and 3.6.6

Figure 3.6.10: Effect of frequency on chlorobenzene degradation rate constants at pH 6 with zero valent iron particles

- 20 kHz, (k) = $0.021 \pm 0.007 \text{ min}^{-1}$
- 900 kHz, (k) = $0.0067 \pm 0.0009 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, (k_v) = $-0.0013 \pm 0.0007 \text{ min}^{-1}$

Note: replot of data from Figures 3.6.5 and 3.6.6

3.6.3 Degradation products of chlorobenzene

Chlorobenzene degradation can proceed via either a unimolecular or bimolecular mechanism.¹⁰ Unimolecular decomposition involves a simple rupture of the weakest bond within the molecule. Morlando et al. have suggested that this is a rather unlikely pathway since the lowest bond dissociation energy (C-Cl) in Cl-C₆H₅ is 95 kcal/mol. They also suggested that destruction would proceed through bimolecular processes involving addition or abstraction of functional groups by free radical species, such as hydroxyl or hydrogen radicals.¹⁰ Kruus et al.⁷⁰ recently reported that the major degradation products following ultrasonic irradiation of aqueous chlorobenzene solutions were chloride ions, chlorophenols, chloronaphthalenes, biphenyls, mono and dichlorobiphenyls and naphtho or dibenzo furans.

Since the main purpose of our studies involved determining degradation rate constants from different experimental conditions, studies of breakdown products were a secondary priority. Nonetheless, two analytes namely, *ortho* and *para* chlorophenol were identified based on GC retention times and mass spectral analysis. Therefore based on our results as well as those reported by Kruus et al., it is proposed that analyte disappearance proceeded via the bimolecular mechanism. A possible location for both reactions was proposed by Kruus et al. to occur in the solvent layer surrounding the cavitation bubble and in the bulk solution phase.⁷⁰ As mentioned previously these locations are not only synonymous with high temperatures, but also with high concentrations of radical species.

3.7 Results of experiments on Toluene

3.7.1 Effect of Stirring Aqueous Solutions in the Absence of Zero Valent Iron Particles and Ultrasound

Preliminary testing involving stirring a stock solution of toluene in an open bench-top reaction vessel showed that a significant amount of analyte had disappeared over a one hour period. As in the case of chlorobenzene, it was evident from corresponding chromatograms, due to the absence of new peaks, that toluene had not degraded, but rather volatilized from solution. Under identical conditions, a closed bench-top reaction vessel was employed to test the effects of stirring. It was found that the concentration of toluene remained constant over a period of one hour. The volatility rate (k_v) from the open bench-top cell was 0.048 min^{-1} , and for the closed system it was $-6.7 * 10^{-4} \text{ min}^{-1}$. It was thus evident that subsequent experimental studies on toluene had to be performed in closed systems so as to minimize errors in degradation rates due to volatility.

Volatility tests were also done in the 900 and 20 kHz sonication cells, without the application of ultrasound. The obtained volatility rate constants were quite small, $3.46 * 10^{-3} \text{ min}^{-1}$ from the 900 kHz sonication cell and $1.1 * 10^{-3} \text{ min}^{-1}$ from the 20 kHz sonication cell. All of the results obtained from these studies are presented in figure 3.7.1.

Figure 3.7.1: Effect of stirring a 20 ppm solution of toluene at pH 6 in the absence of zero valent iron particles or ultrasound

Reaction vessels used:

- open bench-top, $(k_v) = 0.048 \pm 0.004 \text{ min}^{-1}$
- closed bench-top, $(k_v) = (-6.7 \pm 4.0) \times 10^{-4} \text{ min}^{-1}$
- ▲ closed 900 kHz, $(k_v) = (3.5 \pm 4.6) \times 10^{-3} \text{ min}^{-1}$
- ▼ closed 20 kHz, $(k_v) = (1.1 \pm 0.6) \times 10^{-3} \text{ min}^{-1}$

3.7.2 Effect of pH and Ultrasonic Frequency

The following generalities were observed from degradation studies of toluene. First, variation of initial solution pH did not produce an increased overall degradation rate at one particular pH for all experimental conditions. Second, as with chlorobenzene, use of zero valent iron particles had no degradative effect. Third, combined zero valent iron particles and ultrasound at either frequency decreased the rate constant below that obtained using ultrasound only. Fourth, low frequency ultrasonic irradiation was most effective.

In general, most of the points shown in all figures represent an average of several determinations. In addition each figure includes, for purposes of rate comparison, the effect of stirring only a stock solution of toluene in a closed bench top reaction vessel.

The effects of pH on degradation rate of aniline are presented in figures 3.7.2 to 3.7.6. In addition table 3.7.1 is provided which summarizes degradation rates. As already mentioned, it is evident from table 3.7.1, that the effects of pH are quite varied. For example, lower values of pH were found to increase the degradation rate under ultrasonic conditions only, whereas the opposite was noted from all studies in which zero valent iron particles were used. A reasonable explanation of these events is not known and thus requires further research. However, it is evident from table 3.7.1, that stirring aqueous solutions with pre-treated zero valent iron particles at either pH had no degradative effect. In fact, the rate constant was comparable to that obtained from stirring a stock solution in a closed bench-top reaction vessel in the absence of zero valent iron particles. Therefore, it can be assumed by comparing figures 3.7.3 with 3.7.5

and 3.7.4 with 3.7.6, that under ultrasonic conditions the iron particles acted as a source of interference.

Experimental Conditions	Degradation rate constant (k) min ⁻¹ at pH 4	Degradation rate constant (k) min ⁻¹ at pH 6
Stirring in the absence of zero valent iron particles and ultrasound	_____	-0.0007 ± 0.0004
Stirring in the presence of zero valent iron particles	0.000036 ± 0.00006	0.00027 ± 0.00003
20 kHz ultrasound only	0.037 ± 0.003	0.0337 ± 0.0001
20 kHz ultrasound in the presence of zero valent iron particles	0.022 ± 0.002	0.027 ± 0.002
900 kHz ultrasound only	0.0074 ± 0.0003	0.0027 ± 0.0003
900 kHz ultrasound in the presence of zero valent iron particles	0.0008 ± 0.0001	0.0033 ± 0.0005

Table 3.7.1: Summary of degradation rate constants of toluene

Figure 3.7.2: Effect of pH on toluene degradation rate constants in the presence of zero valent iron particles

- pH = 4, (k) = $0.000036 \pm 0.00006 \text{ min}^{-1}$
- pH = 6, (k) = $0.00027 \pm 0.00003 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, (k_v) = $-0.0007 \pm 0.0004 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

Figure 3.7.3: Effect of pH on toluene degradation rate constant at 20 kHz in the absence of zero valent iron particles

- pH = 4, $(k) = 0.037 \pm 0.003 \text{ min}^{-1}$
- pH = 6, $(k) = 0.0337 \pm 0.0001 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, $(k_v) = -0.0007 \pm 0.0004 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

Figure 3.7.4: Effect of pH on toluene degradation rate constant at 900 kHz in the absence of zero valent iron particles

● pH = 4, $(k) = 0.0074 \pm 0.0003 \text{ min}^{-1}$

■ pH = 6, $(k) = 0.0027 \pm 0.0003 \text{ min}^{-1}$

▲ Stirring, no iron or ultrasound, $(k) = -0.007 \text{ min}^{-1}$
 $(k_v) = -0.0007 \pm 0.0004 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

Figure 3.7.5: Effect of pH on toluene degradation rate constants at 20 kHz in the presence of zero valent iron particles

- pH = 4, (k) = $0.022 \pm 0.002 \text{ min}^{-1}$
- pH = 6, (k) = $0.027 \pm 0.002 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, (k_v) = $-0.0007 \pm 0.0004 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

Figure 3.7.6: Effect of pH on toluene degradation rate constant at 900 kHz in the presence of zero valent iron particles

- pH = 4, (k) = $0.0008 \pm 0.0001 \text{ min}^{-1}$
- pH = 6, (k) = $0.0033 \pm 0.0005 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, (k_v) = $-0.0007 \pm 0.0004 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

The effects of ultrasonic frequency are most noticeable on the degradation rates of toluene. The results of these studies are presented in figures 3.7.6 to 3.7.9. Referring to figures 3.7.6 and 3.7.7, it is evident that at either value of initial pH, a higher degradation rate was obtained at lower frequency.

Based on a recent publication by Hali et al., who have proposed that toluene, following hydroxide radical attack at the *ortho*, *meta*, or *para* position would produce various phenolated derivatives.⁸⁵ We suspect that the increased degradation rate of toluene at 20 kHz is a result of a high concentration of hydroxyl radicals in solution. The attack of hydroxyl radicals on toluene would result in various phenolated compounds which in our studies were not detected.

Figure 3.7.7: Effect of frequency on toluene degradation rate constants at pH 4 without zero valent iron particles

- 20 kHz, (k) = $0.037 \pm 0.003 \text{ min}^{-1}$
- 900 kHz, (k) = $0.0074 \pm 0.0003 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, (k_v) = $-0.0007 \pm 0.0004 \text{ min}^{-1}$

Note: replot of data from Figures 3.7.3 and 3.7.4

Figure 3.7.8: Effect of frequency on toluene degradation rate constant at pH 6 without zero valent iron particles

- 20 kHz, $(k) = 0.0337 \pm 0.0001 \text{ min}^{-1}$
- 900 kHz, $(k) = 0.0027 \pm 0.0003 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, $(k_v) = -0.0007 \pm 0.0004 \text{ min}^{-1}$

Note: replot of data from Figures 3.7.3 and 3.7.4

Figure 3.7.9: Effect of frequency on toluene degradation rate constant at pH 4 with zero valent iron particles

- 20 kHz, (k) = $0.022 \pm 0.002 \text{ min}^{-1}$
- 900 kHz, (k) = $0.0008 \pm 0.0001 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound,
(k_v) = $-0.0007 \pm 0.0004 \text{ min}^{-1}$

Note: replot of data from Figures 3.7.5 and 3.7.6

Figure 3.7.10: Effect of frequency on toluene degradation rate constant at pH 6 with zero valent iron particles

- 20 kHz, $(k) = 0.027 \pm 0.002$
- 900 kHz, $(k) = 0.0033 \pm 0.0005$
- ▲ Stirring at pH 6, no iron or ultrasound,
 $(k_v) = -0.0007 \pm 0.0004 \text{ min}^{-1}$

Note: replot of data from Figures 3.7.5 and 3.7.6

It has already been discussed in section 3.3.2, that one the most significant differences between the two ultrasonic frequencies is the temperature of cavitation collapse. In order for true cleavage of a $\text{CH}_3\text{-C}_6\text{H}_5$ bond to occur, high temperatures, well above 700 K must be present.²⁵ Recalling that temperatures well above 700 K are possible in the interfacial regions during cavitation collapse at 20 kHz suggests that besides hydroxyl radical attack, analyte degradation would proceed via pyrolytic cleavage.

Referring to table 3.7.1, it is evident that the combination of zero valent iron particles with ultrasonic irradiation resulted in decreased degradation rates below those obtained using ultrasound only. A similar occurrence has already been encountered in the studies of aniline and chlorobenzene, thus an explanation of these effects has been provided in section 3.5.2 and 3.6.2 respectively.

3.7.3 Summary of Results

The most effective method for remediating groundwater contaminated with toluene involves low frequency ultrasonic irradiation at pH 4.

3.8 Results from Various Studies on NDMA

3.8.1 Effect of Stirring Aqueous Solutions in the Absence of Zero Valent Iron and Ultrasound

Results obtained from stirring aqueous solutions of NDMA in an open bench-top reaction vessel had no degradative effect. The results are presented in figure 3.8.1.

Figure 3.8.1: Effect of stirring an aqueous solution of NDMA in an open bench-top reaction vessel without zero valent iron particles or ultrasound

● Stirring at pH 6, (k) = - 0.0003 +/- 0.0002 min⁻¹

3.8.2 Effect of pH and Ultrasonic Frequency

Variations in pH and frequency had little remediative effect on aqueous solutions of NDMA. Nonetheless, subtle differences between experimental results as well as general trends were noted and will be discussed here. First, studies at pH 4 yielded slightly faster degradation rates. Second, experiments involving ultrasonic irradiation in the absence of zero valent iron particles at either frequency resulted in lowest degradation rates. Third, zero valent iron particles alone, and in combination with ultrasonic irradiation at low frequency proved to be most effective.

In general, all figures presented in this section represent an average of several determinations. In addition each figure includes, for purposes of rate comparison, the effect of stirring an aqueous solution of NDMA in the absence of iron particles or ultrasound.

Effects of pH on the degradation rate of NDMA are presented in figures 3.8.2 to 3.8.5, from which it can be seen that a lower pH marginally enhanced degradation rates. The most significant rate enhancements at pH 4 were noted by stirring with zero valent iron particles, as seen in figure 3.8.2. In combined zero valent iron particle and low frequency ultrasound studies, as presented in figure 3.8.5, a synergism was noted, but a similar 10 fold rate enhancement was not observed.

It section 3.3.2 it was suggested that if low frequency ultrasound had a very low degradative effect on a particular analyte, but the coupling of zero valent iron particles with ultrasound resulted in an increased degradation rate, then the presence of ultrasound acted merely as a source of mixing.

Since this was the case with NDMA, it is hypothesized that the presence as well as the rate of zero valent iron particle mixing was a controlling factor of NDMA degradation. In support of this, it is known that reduction of nitroso compounds to their corresponding amines can occur in the presence of zinc and HCl.²⁵ Thus, it is possible that zero valent iron in combination with HCl at pH 4 is responsible for the reduction of the nitroso group. A possible reaction sequence is provided in rxn 3.8.1. It should be emphasized that this is only a speculation of the possible degradation mechanism of NDMA.

The effects of frequency are presented in figures 3.8.7 to 3.8.10. It has already been mentioned that ultrasonic irradiation alone has minimal effect on the degradation of NDMA. In comparing figures 3.8.5 and 3.8.6, it is evident that faster degradation rates occurred at 20 kHz.

Based on the concentrations of radical species and temperatures of cavity implosion as already discussed in section 3.3.2, it is possible that NDMA degradation favors high temperature pyrolytic conditions over high concentrations of hydroxide radical species. However since no breakdown products were noted on the chromatogram, a more extensive analysis of reaction samples is required.

In addition table 3.8.1 is presented which provides a summary of these results.

Experimental Conditions	Degradation rate constant (k) min⁻¹ at pH 4	Degradation rate constant (k) min⁻¹ at pH 6
Stirring without zero valent iron particles and ultrasound	_____	-0.0003 ± 0.0002
Stirring in the presence of Zero valent iron particles	0.0021 ± 0.0007	0.00023 ± 0.00008
20 kHz Ultrasound only	0.00092 ± 0.00007	0.0006 ± 0.0002
20 kHz Ultrasound in the presence of zero valent iron particles	0.0029 ± 0.0002	0.0030 ± 0.0005
900 kHz Ultrasound only	0.00041 ± 0.00003	0.00034 ± 0.00004
900 kHz Ultrasound in the presence of zero valent iron particles	0.00034 ± 0.00005	0.00022 ± 0.00008

Table 3.8.1: Summary of degradation rate constants of NDMA

Figure 3.8.2: Effect of pH on NDMA degradation rate constants in the presence of zero valent iron particles

- pH = 4, (k) = $0.0021 \pm 0.0007 \text{ min}^{-1}$
- pH = 6, (k) = $0.00023 \pm 0.00008 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, (k) = $-0.0003 \pm 0.0002 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

Figure 3.8.3: Effect of pH on NDMA degradation rate constants at 20 kHz in the absence of zero valent iron particles

- **pH = 4, (k) = 0.00092 +/- 0.00007 min⁻¹**
- **pH = 6, (k) = 0.0006 +/- 0.0002 min⁻¹**
- ▲ **Stirring at pH 6, no iron or ultrasound, (k) = -0.0003 +/- 0.0002 min⁻¹**

Note: error bars represent standard deviation from triplicate experiments

Figure 3.8.4: Effect of pH on NDMA degradation rate constants at 900 kHz in the absence of zero valent iron particles

- pH=4, (k) = $0.00041 \pm 0.00008 \text{ min}^{-1}$
- pH = 6, (k) = $0.00034 \pm 0.00004 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, (k) = $-0.0003 \pm 0.0002 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

Figure 3.8.5: Effect of pH on NDMA degradation rate constants at 20 kHz in the presence of zero valent iron particles

- pH = 4, $(k) = 0.0029 \pm 0.0002 \text{ min}^{-1}$
- pH = 6, $(k) = 0.0030 \pm 0.0005 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, $(k) = -0.0003 \pm 0.0002 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

Figure 3.8.6: Effect of pH on NDMA degradation rate constants at 900 kHz with zero valent iron particles

- pH = 4, (k) = $0.00034 \pm 0.00005 \text{ min}^{-1}$
- pH = 6, (k) = $0.00022 \pm 0.00008 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, (k) = $-0.0003 \pm 0.0002 \text{ min}^{-1}$

Note: error bars represent standard deviation from triplicate experiments

Figure 3.8.7: Effect of frequency on NDMA degradation rate constants at pH 4 without zero valent iron particles

- 20 kHz, $(k) = 0.00092 \pm 0.00007 \text{ min}^{-1}$
- 900 kHz, $(k) = 0.00041 \pm 0.00008 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, $(k) = -0.0003 \pm 0.0002 \text{ min}^{-1}$

Note: replot of data from Figures 3.8.3 and 3.8.4

Figure 3.8.8: Effect of frequency on NDMA degradation rate constants at pH 6 without zero valent iron particles

- 20 kHz, (k) = $0.0006 \pm 0.0002 \text{ min}^{-1}$
- 300 kHz, (k) = $0.00034 \pm 0.00004 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, (k) = $-0.0003 \pm 0.0002 \text{ min}^{-1}$

Note: replot of data from Figures 3.8.3 and 3.8.4

Figure 3.8.9: Effect of frequency on NDMA degradation rate constant at pH 4 with zero valent iron particles

- 20 kHz, $(k) = 0.0029 \pm 0.0002 \text{ min}^{-1}$
- 900 kHz, $(k) = 0.00034 \pm 0.00005 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, $(k) = -0.0003 \pm 0.0002 \text{ min}^{-1}$

Note: replot of data from Figures 3.8.5 and 3.8.6

Figure 3.8.10: Effect of frequency on NDMA degradation rate constants at pH 6 with zero valent iron particles

- 20 kHz, $(k) = 0.0030 \pm 0.0005 \text{ min}^{-1}$
- 900 kHz, $(k) = 0.00022 \pm 0.00008 \text{ min}^{-1}$
- ▲ Stirring at pH 6, no iron or ultrasound, $(k) = -0.0003 \pm 0.0002 \text{ min}^{-1}$

Note: replot of data from Figures 3.8.5 and 3.8.6

3.9.3 Summary of Results for NDMA

Results obtained from these studies suggest that the remediation of groundwater contaminated with NDMA would proceed at a very slow rate based on the low degradation rate constants obtained from all studies.

The most effectively method for degrading NDMA requires low intensity ultrasound coupled with zero valent iron (Fe^0) particles. A comparable remediation method would involve simply stirring contaminated solutions with zero valent iron particles. Both of these methods would be most effective at pH 4.

4.0 Overall Summary

The rate constants of our survey of the effects of zero valent iron and ultrasound both separately and together on aqueous solution of 2,4-DNT, 2,6-DNT, aniline, chlorobenzene, toluene and NDMA, are summarized in table 4.0.1.

From these studies some general observations can be made. First, ultrasound in water causes degradation of most of the compounds, this is quite encouraging since this is a first report aniline and toluene. Second, both dinitrotoluenes rapidly disappear on treatment with pre-treated zero valent iron particles. This was expected as it has been reported that the nitro group can be reduced readily to amino with passive zero valent iron treatment.³³ Third, there are some effects of ultrasound frequency as seen in practically all studies conducted. Fourth, there seem to be no significant synergisms by combining zero valent iron particles with ultrasound. For example, ultrasound does not enhance the reactivity of the dinitrotoluenes when combined with zero valent iron particles. Furthermore, zero valent iron does not affect the reactivity of chlorobenzene or toluene with ultrasound. Fifth, aniline degradation when subject to combination of FeCl_2 with ultrasonic irradiation at 20 kHz resulted in two fold rate increases when compared to rates from sonication alone.

	pH	2,4-DNT	2,6-DNT	Aniline	Chlorobenzene	Toluene	NDMA
A	4	1.2 ± 0.2	0.13 ± 0.05	0.00022 ± 0.00001	0.0039 ± 0.0007	0.0000036 ± 0.00006	0.0021 ± 0.0007
	6	0.42 ± 0.02	0.026 ± 0.006	0.00013 ± 0.00003	0.0019 ± 0.0009	0.00027 ± 0.00003	0.00023 ± 0.00008
B	4	0.0055 ± 0.0006	0.0041 ± 0.002	0.0039 ± 0.0005	0.026 ± 0.003	0.037 ± 0.003	0.00092 ± 0.00007
	6	0.0022 ± 0.0009	0.00075 ± 0.00007	0.0018 ± 0.0003	0.029 ± 0.0003	0.0337 ± 0.0001	0.0006 ± 0.0002
C	4	0.85 ± 0.03	0.14 ± 0.01	0.0019 ± 0.0007	0.021 ± 0.002	0.022 ± 0.002	0.0029 ± 0.0002
	6	0.44 ± 0.03	0.068 ± 0.004	0.0015 ± 0.0005	0.021 ± 0.007	0.027 ± 0.002	0.0030 ± 0.0005
D	4	0.0041 ± 0.0007	0.0015 ± 0.0006	0.023 ± 0.004	0.0072 ± 0.0004	0.0074 ± 0.0003	0.00041 ± 0.00003
	6	0.00056 ± 0.00009	0.00069 ± 0.00004	0.014 ± 0.007	0.044 ± 0.002	0.0027 ± 0.0003	0.00034 ± 0.00004
E	4	0.055 ± 0.003	0.0051 ± 0.0009	0.0086 ± 0.0007	0.0021 ± 0.0006	0.0008 ± 0.0001	0.00034 ± 0.00005
	6	0.035 ± 0.002	0.0065 ± 0.009	0.0023 ± 0.0007	0.0067 ± 0.0009	0.0033 ± 0.0005	0.00022 ± 0.00008

- A: Stirring with zero valent iron particles
 B: Sonication at 20 kHz
 C: Sonication at 20 kHz with zero valent iron particles
 D: Sonication at 900 kHz
 E: Sonication at 900 kHz with zero valent iron particles

Table 4.0.1: Degradation rate constants (min⁻¹) of pollutants under various conditions

Publications and Presentations

1. "Zero-Valent Iron (Fe⁰) and Ultrasound as Potential Remediators of Certain Pollutants in Groundwater", paper presented at *EnviroAnalysis'98*, (May, 1998) with P. Kruus, R.H. Wightman and R.C. Burk.
2. "Use of Fe(0) and Ultrasound for Remediation of Pollutants in Water" poster presented at the 11th annual ESTAC day, Mississauga, ON (Nov 17, 1997). with R.H. Wightman, P. Kruus and R.C. Burk.
3. "Remediation of Organic Pollutants in Water Using Fe(0) and Ultrasound" paper presented at the 80th CSC Conference, Windsor, ON, Canada (June 1-4, 1997) with R.H. Wightman, P. Kruus, and R.C. Burk.
4. "Remediation of Organic Pollutants in Water Using Fe(0) and Ultrasound" paper presented at the 5th Chemical Congress of North America (Environmental Section), Cancun, Mexico, (Nov 11-15, 1997) with R.H. Wightman, P. Kruus and R.C. Burk.
5. "Remediation of Organic Pollutants in Water Using Fe(0) and Ultrasound" poster presented at Ottawa-Carleton Chemistry Institute poster competition. (March 1997), with R.H. Wightman, P. Kruus and R.C. Burk.

6.0 **References**

-
- 1 Mackay, D.M. and Cherry, J.A., "Groundwater Contamination; Pump and Treat Remediation", *Environ. Sci. Technol.*, **23** (6), 630-636, (1989)
 - 2 Maimone, M., "Coping With Groundwater Contamination", *Chem. Eng.*, **10**, 195-201, (1997)
 - 3 Roote, D.S., Miller, R.R., Sacre, J.A. and Merski, A.T., "Groundwater Clean-up Options", *Chem. Eng.*, **5**, 104-111, (1997)
 - 4 Bloes, M.B., Rathfelder, K.M. and Mackay, D.M., "Laboratory Studies of Vapor Extraction for Remediation of Contaminated Soil", *Subsurface Contamination of Immiscible Fluids*, Weyer (ed.), 255-262, (1992)
 - 5 Tratnyek, P.G., "Putting Corrosion To Use: Remediating Contaminated Groundwater with Zero-valent Metals", *Chem. & Indust.*, **13** (7), 499-503, (1996)
 - 6 Appleton, E.L., "A Nickel-iron Wall Against Contaminated Groundwater", *Environ. Sci. Technol.*, **30** (12), 536A-539A, (1996)
 - 7 Dahab, M. and Kalagiri, J., "Nitrate Removal From Water Using Cyclically Operated Fixed Film Bio-denitrification reactors", *Wat. Sci. Tech.*, **34** (1-2), 331-338, (1996)
 - 8 Klecka, G.M., McDaniel, S.G., Wilson, P.S., Carpenter, C.L. and Clark, J.E., "Field Evaluation of a Granular Activated Carbon Fluid-bed Bioreactor for Treatment of Chlorobenzene in Groundwater", *Environ. Prog.*, **15** (2), 93-107, (1996)
 - 9 Medcalf, B.D. and Manahan, S.E., "Fate of Nitrogen In Nitrogen-Containing Compounds During Cocurrent Flow Gasification (Chem Char Process)", *Environ. Sci. Technol.*, **31** (1), 194-197, (1997)
 - 10 Morlando, R., Manahan, S.E. and Larsen, D.W., "Iron-Catalyzed Cocurrent Flow Destruction of Chlorobenzene During Gasification", *Environ. Sci. Technol.*, **31** (2), 409-415, (1997)
 - 11 Lelacheur, R.M. Glaze, W.W.H., *Environ. Sci. Technol.*, **30**, 1072-1080, (1996)
Reference cited from No16

-
- 12 Preis, S., Krichevskaya, M. and Kharchenko, A., "Photocatalytic Oxidation of Aromatic Aminocompounds in Aqueous Solutions and Groundwater From Abandoned Military Bases", *IAWQ*, Elsevier Science Ltd, 266-273, (1997)
 - 13 Calza, P., Minero, C. and Pelizzetti, E., " Photocatalytically Assisted Hydrolysis of Chlorinated Methanes Under Anaerobic Conditions", *Environ. Sci. Technol.* **31** (8), 2198-2203, (1997)
 - 14 Phull, S.S., Newman, A.P., Lorimer, J.P., Poller, B. and Mason, T.J., "The Development and Evaluation of Ultrasound in the Biocidal Treatment of Water" *Ultrasonics Sonochemistry*, **4**, 157-164, (1997)
 - 15 Newman, A.P., Lorimer, J.P., Mason, T.J. and Hutt, K.R., " An Investigation Into the Ultrasonic Treatment of Polluted Solids" *Ultrasonics Sonochemistry*, **4**, 153-156, (1997)
 - 16 Hoffmann, M.R., Hua, I. and Hochemer, R., "Application of Ultrasonic Irradiation for the Degradation of Chemical Contaminants in Water" *Ultrasonics Sonochemistry*, **3**, S163-S172, (1996)
 - 17 Hua, I., and Hoffmann, M.R., "Kinetics and Mechanism of the Sonolytic Degradation of CCl_4 Intermediates and Byproducts", *Environ. Sci. Technol.*, **30** (3), 864-871, (1996)
 - 18 Petrier, C., Marie-Francoise, L., Francony, A., Benancene, A., David, B., Renaudin, V. and Gondrexon, N., "Sonochemical Degradation of Phenol in Dilute Aqueous Solutions: Comparison of the Reaction Rates at 20 kHz, and 487 kHz", *J. Phys. Chem.*, **98**, 10514-10520, (1994)
 - 19 Pugin, B., "Qualitative Characterization of Ultrasound Reactors for Heterogenous Sonochemistry", *Ultrasonics Sonochemistry*, **25**, 49-55, (1987)
 - 20 Plant, L. and Jeff, M., "Hydrogen Peroxide: a Potent Force to Destroy Organics in Wastewater", *Chem. Eng.*, **9**, E16-E20, (1994)
 - 21 Huck, P.M., Andrews, S.A., Anderson, W.A., Peldszus, S. and Moralejo, C., "Investigation of Intermediate Products Formed During the UV/Oxidation of Organic Contaminants", personal communication at the 11th annual ESTAC day, Mississauga, **11**, (1997)
 - 22 Stevens, S. and Bertrand, W.D., "Destroy Organics on the Spot", *Chem. Eng.*, **10**, 223, (1997)

-
- 23 Chin, K., Fouhy, Ken. and Kamiya, T., "Advanced Oxidation Mission: Search and Destroy", *Chem. Eng.*, **7**, 39-43, (1997)
 - 24 Hua, I., and Hoffmann, M.R., "Optimization of Ultrasonic Irradiation as an Advanced Oxidation Technology", *Environ. Sci. Technol.*, **31** (8), 2237-2243, (1997)
 - 25 Suslick, K.S., "Ultrasound; its Chemical, Physical and Biological Effects", New York, 339, (1988)
 - 26 March, J., "Advanced Organic chemistry", Third edition, Wiley & Sons; New York, (1985)
 - 27 Dolbier, W.R.Jr. and Burkholder, C.R., "Chlorofluorocarbene From Reaction of Fluorotrichloromethane with Reduced Titanium, Synthesis of 1-chloro-1-fluorocyclopropanes", *J. Org. Chem.*, **55**, 589-594, (1990)
 - 28 Reynolds, G.W., Heff, J.T. and Gillham, R.W., "Sampling Bias Caused by Materials Used to Monitor Halocarbons in Groundwater", *Envir. Sci. Technol.*, **24** (1), 135-142, (1990)
 - 29 O'Hannesin S.F. and Gillham, R.W., "Metal Enhanced Degradation of Halogenated Organic Compounds", Environmental Research and Technology. Final Program and Conference Proceedings, Toronto, Ontario, Canada, (1992) Referenced from reference number 31
 - 30 Assaf-Anid, N. and Nies, L., "Reductive Dechlorination of Carbon Tetrachloride and Hexachlorobenzene By Zero-Valent Metals", Anaheim, Preprinted Extended Abstracts, Division of Environmental Chemistry, **April 2-7**, 809-811, (1995)
 - 31 Powell, R.M. and Puls, R.W., "Proton Generation by Dissolution of Intrinsic or Augmented Aluminosilicate Minerals for in Situ Contaminant Remediation by Zero-Valence-State Iron", *Environ. Sci. Technol.*, **31** (8), 2244-2251, (1997)
 - 32 Johnson, T.L., Scherer, M.M. and Tratnyek, P.G., "Kinetics of Halogenated Organic Compound Degradation by Iron Metal", *Environ. Sci. Technol.*, **30** (8), 2634-2640, (1996)
 - 33 Agrawal, A. and Tratnyek, P.G., "Reduction of Nitro Aromatic Compounds by Zero-Valent Iron Metal", *Environ. Sci. Technol.*, **30** (8), 153-160, (1996)
 - 34 Ravary, C. and Lipczynska-Kochany, E., "Abiotic Aspects of Zero-Valent Iron Induced Degradation of Aqueous Pentachlorophenol", Anaheim, Preprinted Extended Abstracts, Division of Environmental Chemistry, **April 2-7**, 738-741, (1995)

-
- 35 Roberts, A.L., Totten, L.A., Arnold, W.A., Burris, D.R. and Campbell, T.J. "Reductive Elimination of Chlorinated Ethylenes by Zero-Valent Metals", *Environ. Sci. Technol.*, **30** (8), 2654-2659, (1996)
- 36 Chuang, F., Larson, R.A. and Wessman, M.S. "Zero-Valent Iron-Promoted Dechlorination of Polychlorinated Biphenyls", *Environ. Sci. Technol.*, **29** (8), 2460-2463, (1995)
- 37 Orth, W.S. and Gillham, R.W. "Dechlorination of Trichloroethene in Aqueous Solution Using Fe(0)", *Environ. Sci. Technol.*, **30** (1), 66-71, (1996)
- 38 Fendorf, S.E. and Li, G. "Kinetics of Chromate Reduction by Ferrous Iron", *Environ. Sci. Technol.*, **30** (5), 1614-1617, (1996)
- 39 Schreirer, C.G. and Reinhard, M. "Transformation of Chlorinated Organic Compounds by Iron and Manganese Powders in Buffered Water and in Landfill Leachate", *Chemosphere*, **29** (8), 1743-1753, (1994)
- 40 Siantar, D.P., Schreier, C.G. and Reinhard, M. "Transformation of the Pesticide 1,2-dibromo-3-chloropropane (DBCP) and Nitrate by Iron Powder and by $H_2/Pd/Al_2O_3$ ", Anaheim, Preprinted Extended Abstracts, Division of Environmental Chemistry, **April 2-7**, (1997)
- 41 Weber, J.E. "Iron-Mediated Reductive Transformations: Investigations of Reaction Mechanisms", Anaheim, Preprinted Extended Abstracts, Division of Environmental Chemistry, **April 2-7**, (1995)
- 42 Klausen, J., Trober, S.P., Haderlein, S.B., and Schwarzenbach, R.P. "Reduction of Substituted by Fe(II) in Aqueous Mineral Suspensions", *Environ. Sci. Technol.*, **29** (6), 2396-2404, (1995)
- 43 Gillham, R.W. and O'Hannesin, S.F. "Enhanced Degradation of Halogenated Aliphatics by Zero-Valent Iron", *Environ. Sci. Technol.*, **32** (4), 958-967, (1994)
- 44 Agrawal, A., Tratnyek, P.G., Stoffyn-Egli, P. and Liang, L. "Processes Affecting Nitro Reduction By Iron Metal: Mineralogical Consequences of Precipitation in Aqueous Carbonate Environments", Anaheim, Preprinted Extended Abstracts, Division of Environmental Chemistry, **April 2-7**, (1995)
- 45 Afiouni, G.F., Clausen, C.L., Geiger, C.L. Reinhart, D., and Ruiz, N.E. "The Use of Zero-Valent Iron and Ultrasonic Energy For In-Situ Groundwater Remediation", Division of Environmental Chemistry Preprints of Extended Abstracts, **36** (2), 42-44, (1996)

-
- 46 Hagenmaier, H., Brunner, H., Haag, R. and Kraft, M. *Environ. Sci. Technol.*, **21**, 1085, (1987)
- 47 Wilson, W.K. "Zero-Valent Metals Provide Possible Solution to Groundwater Problems", *C&EN*, **7**, 19-22, (1995)
- 48 El'piner I.E., "Ultrasound, Physical, Chemical, and Biological Effects", Consultants Bureau Inc, New York, (1964)
- 49 Henglein, A., "Sonochemistry: Historical Developments and Modern Aspects", *Ultrasonics*, **25** (1), 5-16, (1987)
- 50 Richards, W.T. and Loomis, A.L., *J. Am. Chem.*, **95**, 3086, (1927) referenced from number 51
- 51 Einhorn, C., Einhorn, J. and Luche, J. "Sonochemistry-The Use of Ultrasonic Waves in Synthetic Organic Chemistry", *Synthesis*, **11**, 787-812, (1987)
- 52 Kruus, P. "Production of Zinc Dust Using Ultrasound", *Ultrasonics*, **26** (7), 216-218, (1988)
- 53 Kuttruff, H., "Ultrasonics, Fundamentals & Applications", Elsevier Applied Science, New York, (1991)
- 54 Entezari, H.M., "The Effect of Frequency on Sonochemical Reactions", Doctoral Thesis, Carleton University, (1994)
- 55 Thornycroft, J. and Barnaby, S.W., *Inst. Civ. Eng.*, **122**, 51, (1895) referenced from 54
- 56 Rayleigh, L. *Phil. Mag.*, **34**, 94, (1917) referenced from number 54
- 57 Lauterborn, W., and Ohl, C., "Cavitation Bubble Dynamics", *Ultrasonics Sonochemistry*, **4**, 65-75, (1997)
- 58 Apfel, R.J., "Ultrasonics", Edmonds, P.Ed., Academic Press, New York, **19** (7), 355-441, (1981)
- 59 Fox, F. and Herzfeld, K.J., *Acoustic. Soc. Am.*, **26**, 843, (1954) referenced from 25
- 60 Akulichev, V., *Sov. Phys. Acoust.*, **12**, 144, (1966) referenced from 25
- 61 Apfel, R.J., *Acoust. Soc. Am.*, **48**, 1179, (1970) referenced from 25
- 62 Winterton, R.J., *J.Phys. Appl. Phys.*, **10**, 2041, (1977) referenced from 25

-
- 63 Entezari, M.H. and Kruus, P. "Effect of Frequency on Sonochemical Reactions. I: Oxidation of Iodide", *Ultrasonics Sonochemistry*, **1**, S75-S79, (1994)
- 64 Suslick, K.S. and Hammerton, D.A. *IEEE Trans. Ultrason. Ferroelec., Freq. Cont.* **33**, 143, (1986) Referenced from 25
- 65 Schultes, H. and Gohr, H. *Agnew. Chem.* **49**, 420, (1936) Referenced from 25
- 66 Miyagawa, I. *J. Soc. Org. Syn. Chem.* **7**, 167, (1942) Referenced from 25
- 67 Hart, E. J. and Henglein, A., "Sonochemistry of Aqueous Solutions: H_2O_2 Combustion in Cavitation Bubbles", *J. Phys. Chem.*, **91**, 3654-3656, (1987)
- 68 Makino, K., Mossoba, M. and Riesz, P., "Chemical Effects of Ultrasound on Aqueous Solutions. Formation of Hydroxyl Radical", *J. Phys. Chem.*, **87**, 1369-1377, (1983)
- 69 Fisher, C-H, Hart, E.J. and Henglein, A., "Ultrasonic Irradiation of Water in the Presence of $^{18}\text{O}_2$: Isotope Exchange and Isotopic Distribution of H_2O_2 ", *J. Phys. Chem.*, **90**, 1954-1956, (1986)
- 70 Kruus, P., Burk, R.C., Entezari M.H., and Otson, R., "Sonication of Aqueous Sonication of Chlorobenzene", *Ultrasonics Sonochemistry*, **4**, 229-233, (1997)
- 71 Kotronarou, A.G. and Hoffmann, M.R., "Ultrasonic Irradiation of *p*-Nitrophenol in Aqueous Solution", *J. Phys. Chem.*, **95**, 3630-3638, (1991)
- 72 Agrawal, A., Tratnyek, P.G., Stoffyn-Egli, P, and Liang, Liyuan., "Processes Affecting Nitro Reduction by Iron Metal: Mineralogical Consequences of Precipitation in Aqueous Carbonate Environments. Personal communication, Preprint Extended Abstract, Presented before the I&EC Special Symposium, ACS, Atlanta, Sept. 17-20, (1995)
- 73 Weber, E.J. "Iron-Mediated Reductive Transformations: Investigations of Reaction Mechanisms", ACS, Anaheim, Ca, (1995)
- 74 Tratnyek, P.G., Johnson, J. and Schattauer. A., "Interfacial Phenomena Affecting Contaminant Remediation with Zero-valent Iron Metal. Personal communication, Preprint Extended Abstract, Presented before the I&EC Special Symposium, ACS, Atlanta, Sept. 17-20, (1995)
- 75 Schwarzenbach, R. P., Stireli, R., Lanz, K. and Zeyer, J., *J. Environ. Sci. Technol.*, **24**, 1566-1574, (1990) referenced from 33
- 76 Lelacheur, R.M. Glaze, W.W.H. *Environ. Sci. Technol.*, **30**, 1072-1080, (1996)

-
- 77 Chen, R. and Pignatello, J.J. "Role of Quinone Intermediates as Electron Shuttles in Fenton and Photoassisted Fenton Oxidants of Aromatic Compunds", *Environ. Sci. Technol.*, **31** (6), 2399-2406, (1997)
- 78 Brillas E., Sauleda, R. and Casado J., "Peroxi-coagulation of Aniline in Acidic Medium Using an Oxygen Diffusion Cathode", *J. Electrochem. Soc.*, **144** (7), 2374-2379, (1997)
- 79 Brillas, E., Mur, E. and Casado, J., "Iron(II) Catalysis of the Mineralization of Aniline Using Carbon -PTFE O₂-fed cathode", *J. Electrochem. Soc.*, **143** (3), L49-L52, (1997)
- 80 Entezari, M.H., Kruus, P. and Otson, R. "The Effect of Frequency on Sonochemical Reactions III: Dissociation of Carbon Disulfide", *Ultrasonics Sonochemistry*, **4**, 49-54, (1997)
- 81 Potter, D.W.; Pawliszyn, J. *Environ Sci. Technol.*, **28**, 298, (1994)
- 82 Brillas, E., Sauleda, R. and Casado, J., "Peroxi-coagulation of Aniline in Acidic Medium Using an Oxygen Diffusion Cathode", *J. Electrochem. Soc.*, **144** (7), 2374-2379, (1997)
- 83 Sanchez. L., Peral, J. and Domenech, X., "Photocatalyzed destruction of aniline in UV-illuminated aqueous TiO₂ suspensions", *Electrochimica Acta.*, **12**, 1877-1882, (1997)
- 84 Brillas, E., Bastida, R.M., Llosa, E. and Casado, J., "Electrochemical destruction of aniline and 4-chloroaniline for wastewater treatment using a carbon-PTFE O₂-fed cathode" *J. Electrochem. Soc.*, **142**, 6, 1733-1741, (1995)
- 85 Forstner, H. J. L., Flagan, R.C. and Seinfeld, J. H., "Secondary Organic Aerosol from the Photooxidation of Aromatic Hydrocarbons: Molecular Composition", *Environ. Sci. Technol.* **31**, 1345-1358, (1997)