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PALLADIUM-CATALYZED DESTRUCTION OF NITRO AROMATIC-CONTAMINATED GROUNDWATER

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AFIT/GEE/ENV/03-21

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PALLADIUM-CATALYZED DESTRUCTION OF NITRO AROMATIC-CONTAMINATED GROUNDWATER

THESIS

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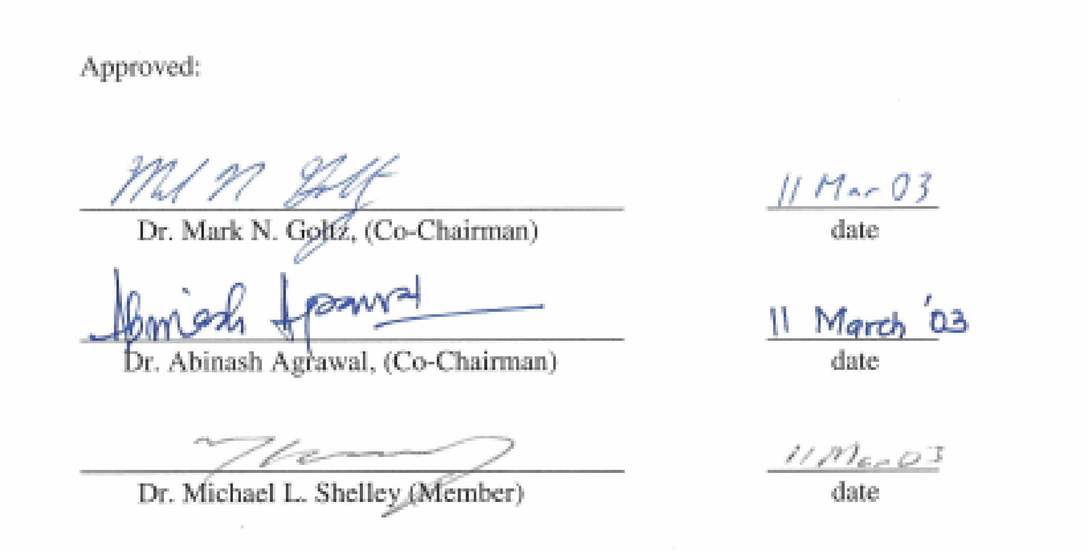

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D. Landon Phillips

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Abstract

Of the over 17,000 DoD sites that potentially require remediation, sites containing soil and groundwater contaminated by energetic compounds are prevalent (Larson et al., 2001). Production of energetics such as 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrasocine (HMX) for use in munitions has created a DoD-wide problem due to improper disposal techniques (Price et al., 2001). Nitro aromatic compounds (NACs) similar to those used in explosives can also be found in insecticides, herbicides, pharmaceuticals, dyes, plastics, and many other commonly used products. The natural breakdown of these contaminants creates byproducts such as amines, which are known neurotoxins and carcinogens.

The focus of this study was to determine the effectiveness of using a palladium (Pd) catalyst to reductively destroy NAC-contaminated groundwater under various conditions and to assess the feasibility of using a catalytic reactor in a horizontal flow treatment well (HFTW) system. Experimental results indicate reaction rates are dependent on both pH and reductant concentration in all experimental catalyst/reductant systems. Catalyst poisoning was seen at high contaminant concentrations in systems where molecular hydrogen was used as a reductant at low concentrations. However, no such effect was seen when using formate as a reductant and it was also observed that destruction rates were greater when formate, rather than hydrogen, was used as a reductant. Based on experimentally determined reaction rates and removal efficiencies, it appears there is promise for in-well use of Pd catalysis with a formate reductant as part of an HFTW system.

PALLADIUM-CATALYZED DESTRUCTION OF NITRO-AROMATIC CONTAMINATED GROUNDWATER

1.0 INTRODUCTION

1.1 Motivation

There are over 28,500 Department of Defense (DoD) sites that potentially will require environmental restoration. In FY01, the estimated cost to complete restoration of the remaining contaminated sites in the Air Force alone was $3.9 billion dollars (DoD, 2001). Of the 28,500 DoD sites, over 1,000 contain unexploded ordnance, discarded munitions, or munitions residue and this number is expected to grow when the total DoD inventory is completed and all sites characterized (DoD, 2001). It is estimated that as many as 87% of these munitions-contaminated sites have groundwater that is contaminated above permissible levels (Rodgers and Bunce, 2001). The main contributors to this groundwater contamination are the nitro aromatic compounds (NACs) such as 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrasocine (HMX). NACs, as well as the degradation byproducts of NACs, are of concern because of their toxicity and mutagenicity (Kaplan and Kaplan, 1982) and potential carcinogenicity.

The process currently being applied almost exclusively for management of NAC-contaminated groundwater is pump-and-treat using aboveground adsorption onto activated carbon as the treatment technology (Spain, 2000). The objective of pump-and-treat is containment of a contaminated plume and prevention of migration downgradient to susceptible human populations and environmental receptors. In this process, NAC-contaminated groundwater is pumped out of the subsurface and passed through a column packed with activated carbon. The carbon adsorbs the contaminants and the treated groundwater is disposed of, either by reinjection back into the subsurface or disposal to surface water. There are various disadvantages associated with this treatment method. The biggest problem with the use of adsorption on granular activated carbon (GAC) is that it is only a method of transferring a hazardous material from one medium to another. That is, it is a separation method rather than a means of contaminant destruction. Once the GAC's adsorption capacity has been exhausted, the GAC must be removed and replaced. The spent GAC must be treated and/or disposed of as a hazardous waste. Another problem with pump-and-treat is that the cost of pumping contaminated water to the surface for treatment, especially in deep aquifers, may be substantial. Also, bringing the contaminated water aboveground instead of treating it *in situ* (that is, in place, underground) results in health and safety risks, as well as imposition of additional regulatory constraints.

Natural attenuation is another possible strategy for management of NAC-contaminated groundwater. The Environmental Protection Agency (EPA) defines natural attenuation as "a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. These *in situ* processes include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants" (USGS, 2001). Lab studies have shown the potential for microorganisms to metabolize nitro aromatic compounds (NRC, 2000). However, field-scale studies have yet to determine the applicability of these results outside of the lab. Research is currently underway to determine the effects of aquifer soil and groundwater conditions on NAC fate and transport (Price et al., 2000), but the conditions needed for successful natural attenuation of NACs are not clearly understood (NRC, 2000) at this time.

Due to the above-noted limitations of currently available technologies, there is a need for development of new treatment technologies to more effectively treat NAC-contaminated groundwater. One innovative approach that has potential is to use a palladium (Pd) catalyst to chemically destroy the contaminants *in situ*. Due to the limited residence times and expense associated with *in situ* technologies, the need for sufficient mixing and fast reaction kinetics is imperative. An advantage of Pd catalysis is that it results in rapid and complete transformation of NACs into byproducts of little or no health concern. This is not necessarily the case with other catalysts (Niekamp, 2001). Noble metal catalysts such as nickel, ruthenium, and platinum have been studied, but these have exhibited slower kinetics than palladium. Some, such as Ni, are also highly susceptible to poisoning. Several zero-valent metals such as iron, tin, and zinc have also been used for the reduction of NACs, but these catalysts are less desirable because the reaction generally produces amines, which are an environmental concern as well (Niekamp, 2001).

Another advantage of using palladium catalysts is that due to the rapid rate of the catalytic reaction, a palladium catalyst has potential to be used in-well as a component of an *in situ* treatment system for degrading NACs. Horizontal flow treatment wells (HFTWs) could provide an ideal platform for the application of this technology. HFTWs combine the benefits of a traditional pump-and-treat system, such as active control of plume migration by pumping, with the added cost and safety benefits of being an *in situ* treatment method. HFTWs have been used in the past for *in situ* biotreatment of chlorinated solvents (McCarty et al., 1998). Currently, the effectiveness of using a HFTW system with an in-well Pd catalytic reactor to manage chlorinated solvent-contaminated groundwater is being evaluated (Munakata et al., 2002). In an HFTW system to remediate NAC-contaminated groundwater, contaminated groundwater would be amended with an electron-donor (perhaps hydrogen gas, formate, or some other donor) while passing through the HFTW treatment wells. The donor-amended water would then flow through an in-well palladium catalyst column where the NACs would be catalytically reduced to harmless byproducts (Boggs, 2000). As shown in Figure 1.1, the treatment wells in an HFTW system pump in opposite directions; some pumping upward and some pumping downward. This bi-directional flow creates a recirculating pattern for the water moving through the system. Overall removal efficiency (comparing NAC concentrations upgradient and downgradient of the HFTW system) is improved because the contaminants make multiple passes through the treatment system due to recirculation between the two treatment wells (Stoppel, 2001).

In order to determine the feasibility of the concept described above, the rate and extent of the catalytic destruction of NACs under various conditions, while groundwater is flowing through a Pd-catalyst reactor, must be quantified.

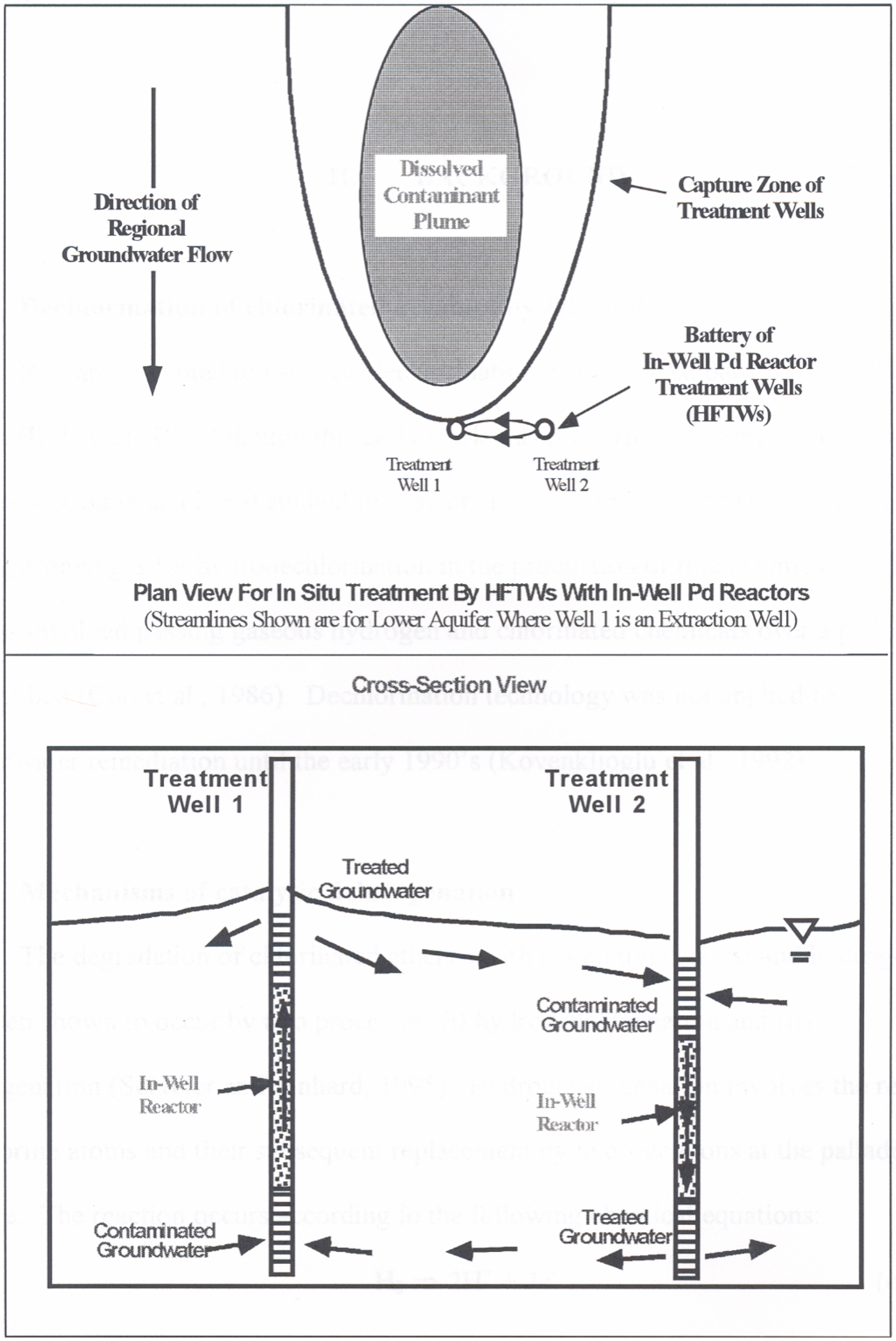

Figure 1.1 Horizontal Flow Treatment Well System (from Stoppel, 2001)

1.2 Research Objectives

The focus of this study will be to determine the effectiveness of using a Pd catalyst to remediate NAC-contaminated sites while preventing the production of byproducts which are hazardous and could cause potential health risks. Additionally, the study will investigate the feasibility of using a Pd reactor in-well as part of an HFTW system to safely and effectively remediate NAC-contaminated DoD sites.

This thesis will focus on answering the following questions:

1. How may we model the reaction kinetics of Pd-catalyzed transformation of NACs? What are the values of the kinetic parameters?
2. Are the reaction rates fast enough for Pd-catalyzed transformation of NACs to be used in an HFTW system? How does the catalyst perform under common HFTW conditions (e.g. flow rate, high NAC concentrations)?
3. What factors (e.g. reactant concentration, pH) influence the extent of NAC reduction and the distribution of transformation products?
4. How might Pd catalysis be used in-well to effect *in situ* destruction of NACs in groundwater?

1.3 Study Limitations

As there are laboratory safety issues associated with the use of NACs like TNT, HMX, and RDX, this study will use nitrotoluene as a model NAC. Nitrotoluene is similar to TNT, HMX, and RDX, but only has one nitro functional group making it safer for laboratory use. Under similar aquifer conditions, the transformation of nitrotoluene is thought to parallel that of TNT, HMX, and RDX. This study will also be focused only on groundwater contamination, not NAC-contaminated soil.

2.0 LITERATURE REVIEW

2.1 Groundwater Contamination by Nitro Aromatic Compounds (NACs)

The remediation of NACs is of interest because the nitro aromatic moiety is characteristic of many anthropogenic contaminants, being second in this regard only to organochlorine functional groups (Agrawal and Tratnyek, 1996). Production and unregulated disposal of NAC (also known as energetic) compounds such as 2,4,6-trinitrotoluene (TNT), hexahydro-1, 3,5-trinotro-1, 3,5-triazine (RDX), and octahydro-1, 3,5,7-tetranito-1, 3,5,7-tetrasocine (HMX) at munitions manufacturing, loading, and processing facilities has created a DoD-wide problem. An example of how DoD sites became contaminated by NACs can be seen by examining TNT production in the 80's. In the production process, wastewater used for purification, known as red water, which contained up to 30 NACs in addition to TNT (Rodgers and Bunce, 2001) was released into the environment untreated. Other common practices included disposal of solid wastes in unlined landfills or discharge of liquid wastes into waterways (Boopathy et al., 1999). Additionally, demilitarization and disposal of obsolete or unwanted weapons systems has further compounded the problem. During "washout operations" fuses were removed from munitions and jets of hot water were used to remove the explosive charge. All the untreated wastewater went straight to lagoons or sedimentation basins (Rodgers and Bunce, 2001). Open detonation and burning of explosives were also common at these sites.

After many years, NACs, which are readily soluble in water and which were disposed as described above, eventually leached from the soil into the groundwater.

Besides explosives, NACs can also be found in many other commonly used products such as insecticides, herbicides, pharmaceuticals, dyes, and plastics which create additional cleanup concerns outside of the DoD.

2.2 Health Effects of NACs

NACs in the environment are of concern because they have been shown to have various harmful or toxic effects on humans. Tests have confirmed that TNT is the most toxic energetic compound, suspected of causing pancytopenia as a result of bone marrow failure (Rodgers and Bunce, 2001). Kaplan and Kaplan (1982) showed that TNT was mutagenic, has toxicological effects on a number of organisms, and can cause liver damage and anemia in humans. TNT exposure led to deaths due to jaundice and aplastic anemia in some munitions workers during WWI and WWII (Rodgers and Bunce, 2001). The EPA has listed TNT as a priority pollutant. Nitrobenzene is listed as a hazardous air pollutant (HAP) in the 1990 Clean Air Act Amendment, section 112b by the EPA. According to the EPA, oral or inhalation of nitrobenzene can cause red blood cell damage as well as spleen swelling and engorgement and anemia. The toxicity of nitrobenzene to humans can potentially lead to death, especially in infants and children.

Like TNT, RDX and HMX have also been shown to cause adverse health effects in humans. RDX's main effects are on the central nervous system (CNS). Chronic exposure through inhalation by workers was shown to induce convulsions, headaches, nausea, vomiting, and unconsciousness. CNS toxicity effects, ranging from confusion to multiple seizures and amnesia were seen in soldiers burning composition C-4 explosives (containing 91% RDX) to heat food in the field (Faust, 1994). The EPA has listed RDX in weight-of-evidence Group C, possible human carcinogen, based on lab tests with mice and has placed RDX on the Drinking Water Contaminant Candidate List. There is limited information on adverse health effects of HMX exposure, but in laboratory studies on rats, mice, and rabbits, HMX has been shown to do damage to the liver and central nervous system. Due to the lack of information, the EPA has determined that HMX is not classifiable as to its human carcinogenicity (Abidin and Liccione, 1997).

The byproducts of the degradation of TNT and other NACs, such as anilines, hydroxylamines, and arylamines, have also been found to have these same or even more harmful toxic and mutagenic effects (Spain, 2001). These aromatic amines and hydroxylamines are carcinogenic due to the nitrenium ions created during enzymatic oxidation (Rodgers and Bunce, 2001). Unfortunately, one of the most important steps in the natural reduction of contaminants such as TNT and nitrobenzene is the transformation of the parent nitro compounds into their corresponding aromatic amines and intermediates. Due to the production of such potentially carcinogenic intermediates, any degradation reaction that is used as a treatment must be carried out beyond nitro reduction to assure the production of only harmless byproducts.

2.3 NAC Chemistry

As noted earlier, explosives and other NACs are environmental contaminants commonly found throughout the DoD (DERP, 2001). NACs that are used as explosives, such as 2,4,6-trinitrotoluene (TNT), hexahydro-1, 3,5-trinotro-1, 3,5-triazine (RDX), and octahydro-1, 3,5,7-tetranito-1, 3,5,7-tetrasocine (HMX) are relatively recalcitrant and can persist for many years in soil or groundwater. Characteristics such as stability, which makes the compounds desirable from an industrial use standpoint, also makes them long-lasting environmental hazards (Spain, 2000).

TNT is produced by the sequential three-step nitration of toluene. The first step in the process produces 2-nitrotoluene (2-NT) and 4-nitrotoluene (4-NT) (Figure 2.1) in equal amounts. 2-NT and 4-NT only contain one nitro functional group (NO_2), which makes them less toxic and easier to handle than the more nitrated compounds. For these reasons, mononitrotoluenes are safer for laboratory use than TNT, HMX, and RDX. Since the chemistry involved in the reduction of the nitro group to aniline ($ArNH_2$) (see Eq 3) is expected to be similar for all the nitrotoluenes, 2-NT and 4-NT can be used as model NACs with fewer health and safety concerns.

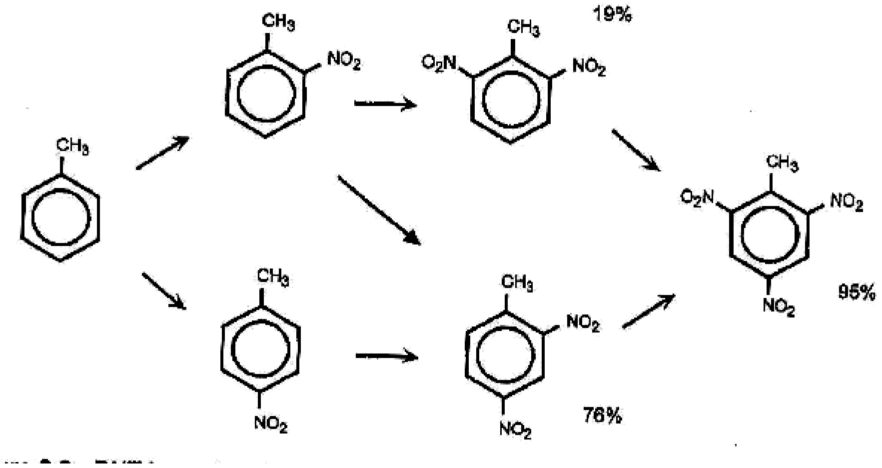

Figure 2.1 Nitration of Toluene (Spain, 2002)

The presence of the nitro group (see Figure 2.2) increases the polarity of the NAC, so that its solubility and mobility in subsurface water is greater than many other organic compounds (Spain, 2000). Additionally, the nitro group's electronegativity makes NACs resistant to chemical or biological oxidation and to hydrolysis. (Rodgers and Bunce, 2001). As the number of nitro groups around the aromatic ring increases, oxidative attack becomes more and more difficult. While NACs demonstrate a low affinity for oxidation, they are susceptible to reductive transformation by abiotic reactions. (Spain, 2000). The reduction of the nitro group is very important in NAC transformation and is key to its fate in the environment.

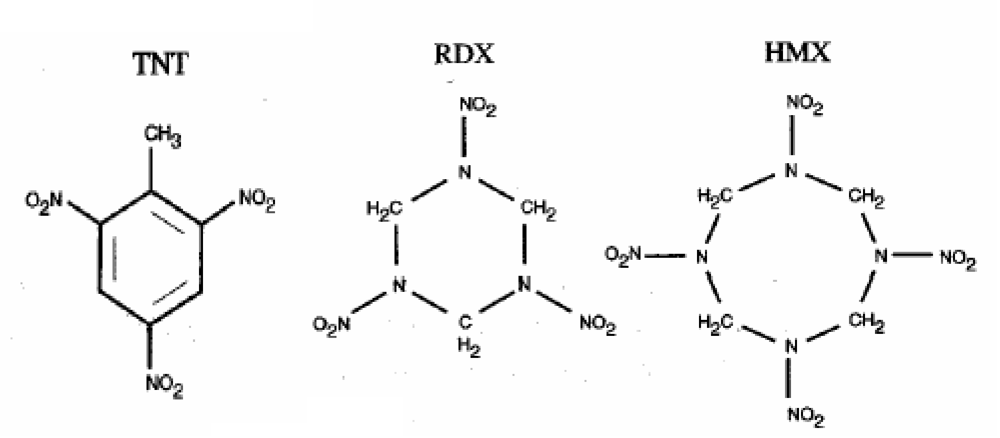

Figure 2.2 NAC Explosives (Spain, 2000)

Hydrogen (H_2) is commonly the sole electron donor (Eq. 1) in the reduction of NACs (Figueras, 2001). Among the processes contributing to the environmental fate of NACs, the most significant is the reduction of the nitro functional group. This process is of environmental importance because the transformation reaction generally produces corresponding aromatic amines and other byproducts, which can be just as harmful as the parent compound (Agrawal and Tratnyek, 1996). The catalytic reduction of nitrobenzene (NB), the simplest NAC, in the presence of molecular hydrogen follows two main steps: hydrogenolysis of an N-O bond producing nitrosobenzene (Eq. 2) and the hydrogenation of the nitrosobenzene to aniline (Eq 3), where Ar represents the aromatic ring (C_6H_5).

Arylhydroxylamine is formed as an intermediate during the hydrogenation reaction in aniline production (Eq. 3), but is generally not seen as a reaction product.

(1) H_2 (gas) = $2H^+ + 2e^-$

(2) $ArNO_2 + 2H^+ + 2e^- = ArNO + H_2O$

(3) $ArNO + 4H^+ + 4e^- = ArNH_2 + H_2O$

The nitrosobenzene is generally not observed either due to its adsorption on the catalyst surface or reaction with arylhydroxyamine to form azoxy intermediates, as shown in Figure 2.3 (Figueras, 2001). In the presence of a catalyst, these reactions are very rapid and often the only products seen are anilines.

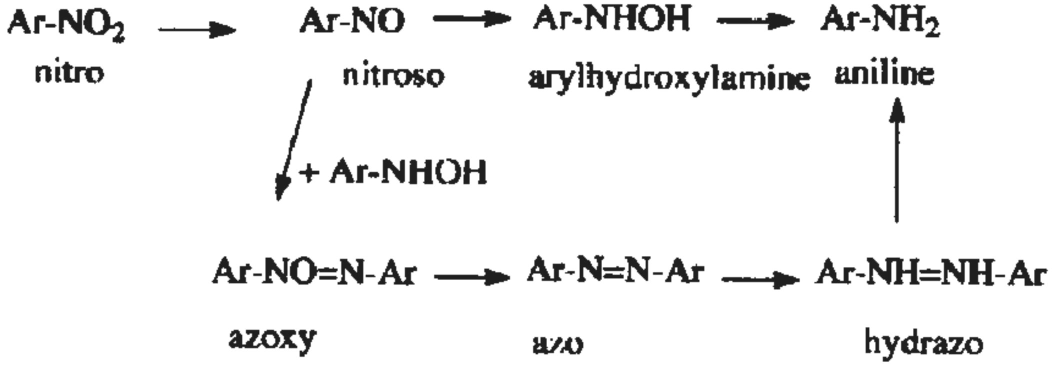

Figure 2.3 Reaction Network for Nitro Group Hydrogenation (Figueras, 2001)

The chemical properties of NACs outlined in this section, such as high solubility in the groundwater and their susceptibility to reductive transformation by abiotic reactions, make treatment of NAC contamination by catalysis a very plausible approach. In-well catalytic reactors have been used to control groundwater contaminated by chlorinated solvents *in situ* (McNab et al., 1999). However, as contaminated groundwater flows through treatment wells with residence times on the order of seconds or minutes, for in-well treatment to be effective, a catalyst must have a very rapid reaction rate for destruction of the contaminant of concern. Although in-well catalytic treatment of chlorinated contaminants appears practical (Lowry and Reinhard, 2000), it is unclear whether an in-well catalytic approach for dealing with NAC contamination is feasible. Several systems that use different catalysts, electron donors, and conditions are currently being studied.

2.4 Catalysts used for NAC Reduction

Reduction of NACs has been studied extensively, mainly by industry for the synthesis of amines. Reduction of NACs to treat NAC contamination has only been the subject of research in the past several years. Iron metal and bimetallic powders, such as Pd/Al, have recently proven to be very effective to completely and rapidly reduce many common organic pollutants (Boggs, 2000). Nitrobenzene reduction to aniline has been accomplished using zero-valent iron under anaerobic conditions (Agrawal and Tratnyek, 1996). The products of this reduction were observed to be aniline and trace amounts of nitrosobenzene with a potential third byproduct, most likely phenylhydroxylamine. Nitro and nitrosobenzene appeared to have similar first order reduction rates and results suggest that these rates were controlled by mass transfer of the NAC to the metal surface. The results also showed minimal effects of pH or ring substitution on nitro reduction rates. (Agrawal and Tratnyek, 1996). Heijman et al. (1995) also demonstrated that availability or regeneration of active sites, not electron transfer, was the rate-limiting process during iron reduction in a laboratory aquifer column.

Other metals have been used for the catalytic reduction of NACs as well. Ruthenium carbonyl catalysts, such as $Ru_3(CO)_{12}$ have been used for the reductive cabonylation of NACs (Tafesh and Beller, 1995). However, the reactivity of the catalyst was shown to decrease when exposed to dinitrotoluene due to catalyst decomposition. Additionally, Rhodium catalysts such as $Rh_6(CO)_{16}$ have been used in similar catalytic applications as ruthenium in the presence of nitrobenzene and aniline (Tafesh and Beller, 1995).

These noble metals, particularly palladium, have also been shown to rapidly destroy a wide range of pollutants including nitrate (Prusse et al., 2000), halogenated aromatics, chlorinated biphenyls, and halogenated organic compounds (Lowry and Reinhard, 1999). In addition many of these palladium-catalyzed reactions produce byproducts that are of little or no health concern. Therefore, palladium seems to be a good candidate for use in the catalytic reduction of NACs.

2.5 Pd Catalysis for NAC Reduction

Pd has been studied for catalytic reduction of many different contaminants such as PCE, TCE (Lowry and Reinhard, 2000), and nitrate (Prusse et al, 2000). While the contaminants are not NACs and the reaction pathways are different, it is useful to look at this previous work for insights on how Pd might be used to manage NAC contamination.

In a series of papers, Lowry and Reinhard (1999 - 2001) studied the Pd-Catalyzed dechlorination of halogenated organics, more specifically, TCE. They found that carbonate concentration and pH changes did not significantly affect transformation rates, but large $SO_4{}^{2-}$ and $SO_3{}^{2-}$ concentrations caused rapid catalyst deactivation. This deactivation was believed to be caused by the sorption affinity of the catalyst for $SO_4{}^{2-}$ and $SO_3{}^{2-}$. Additional studies by Lowry and Reinhard (2001) found that aqueous-phase H_2 concentration affected the transformation rate efficiency. When the concentration of H_2 dropped from 1000 μM to 100 μM, the TCE rate constant decreased by 55%. However, the effects of competing solutes and dissolved oxygen on transformation rate were seen to be negligible.

Several other interesting findings on improving Pd performance were discovered by Prusse et al. (2000) while working with Pd and nitrate. First, two new bi-metallic catalysts, Pd-Sn and Pd-In, were compared to the Pd-Cu catalysts that are currently used to reduce nitrate. In all cases, both new bi-metallics performed better, with Pd-Sn demonstrating the best results. The experiments also used a gel-like poly vinyl alcohol solution to encapsulate the catalyst, which proved to increase the mechanical stability and elasticity of the support media. This new support media improved diffusion by as much as four times over common oxide supports. One of the most important findings of this research was the observation that formic acid had a higher selectivity than hydrogen gas for the reduction of nitrate due to an *in situ* buffering effect (Prusse et al., 2000). When nitrate is reduced to nitrogen, hydroxide ions are formed as byproducts (Eq. 6). This causes the buildup of a pH gradient inside the catalyst particles, which in turn decreases both activity and selectivity of the catalyst (Prusse et al., 2000). To combat this phenomenon, formic acid was used to provide a buffering effect. Formic acid is decomposed at the metal catalyst sites and forms hydrogen and carbon dioxide as products (Eq. 5). As can be seen from Eq. 7, the carbon dioxide then serves as an *in situ* buffer and effectively neutralizes the inhibitor OH^-, preventing the inhibitory build-up of a pH gradient discussed above. The hydrogen, which is co-produced with the carbon dioxide, can then act as the reductant, uninhibited by increased pH (Eq. 6).

$$5HCOOH \xrightarrow{cat} 5H_2 + 5CO_2 \qquad (5)$$

$$2NO_3^- + 5H_2 \xrightarrow{cat} N_2 + 2OH^- + 4H_2O \qquad (6)$$

$$2CO_2 + 2OH^- \rightarrow 2HCO_3^- \qquad (7)$$

However, as opposed to hydrogen being the reductant, it is most likely that formic acid itself reduces adsorbed nitrate by transfer hydrogenation (Prusse et al., 2000).

These experiments, although not conducted using NACs, have shown some of the effects of environmental factors on Pd catalyst activity. Factors like pH, reductant type and concentration, effects of competing solutes, and catalyst support all impact Pd catalyst activity. While little work has been done investigating Pd catalyzed reduction of NACs, these previous studies provide a framework that can be used to guide such an application.

2.6 Pd/NAC Research

There has only been limited research in the area of reduction of nitrobenzene or other NACs using Pd catalysts. It is known that the reaction is very rapid, exothermic, and limited by diffusion on most metals (Figueras and Coq, 2001). Recent work by Figueras and Coq (2001) has shown that during the reaction with palladium and nitrobenzene, nitrosobenzene is initially formed, but only aniline is seen as an end product. As in other work with Pd, these experiments also showed that an increase in hydrogen pressure decreases selectivity for intermediate production. Since one of the products of hydrogenation of nitrobenzene is water, the hydrophobic nature of carbon makes it a good support media. Another important finding was the fact that formic acid can be used for the reduction of nitriles on Pd catalysts.

3.0 EXPERIMENTAL MATERIALS AND METHODS

3.1 Chemicals

High purity chemicals (> 99% pure) were obtained and used without further purification. As discussed in Section 2.2, the less toxic and safer to handle nitrotoulene (NT) was selected over TNT, HMX, or RDX as a model NAC. The three isomers of NT were both easier to obtain and safer for laboratory use than the more nitrated compounds. Certified ACS grade chemicals were obtained from Sigma-Aldrich Chemical Co., which included 2-nitrotoluene (2-NT), 3-nitrotoluene (3-NT), and 4-nitrotoluene (4-NT). Other chemicals used in this research included MES buffer (Hydrate, 99.5% / Hemisodium Salt, 98%, Sigma), formic acid (88%, Fischer Scientific), and sodium hydroxide (Fischer Scientific). High purity gasses were supplied by Air Products (Allentown, PA) and included zero grade (100%), 50%, and 20% hydrogen, as well as a 20% CO_2/80% H_2 mixture.

3.2 Pd Catalysts

Pd catalysts were supplied by Sigma-Aldrich in both pellet (0.5% on alumina, 3.2 mm diameter) and powder form (1% wt on alumina). Catalysts were supported on Al_2O_3, with the powder being used for batch experiments and the pellet form used in the flow-through column experiments. The catalyst obtained was already in a reduced form and did not require further treatment or analysis. The appropriate amounts of catalyst were added to each batch experiment (1 mg) or column (100g) without any special precautions to avoid exposure to air prior to experiments.

3.3 Batch Experiments

3.3.1 Effect of pH on NAC Destruction

Approximately 80 mL of Deionized (DI) water was added to a 100 mL glass serum bottle. 5 mL of an MES hydrate (99.5%, 200 mM) stock solution was added to the bottle to initially lower the pH. pH was measured with a Denver-instrument digital pH/mV meter (Model # AP10) and recorded. MES base (Hemisodium Salt) was added drop by drop to gradually increase the pH to desired levels (4.0, 4.5, 5.0, 5.5, and 6.0). After the desired pH was achieved, additional DI was added to bring the total reactor volume to 98 mL. 1 mg of the Pd-Al_2O_3 powder was then added to the serum bottle and the bottle was capped using a Teflon lined butyl rubber stopper (Wheaton, Milleville, NJ) and sealed with an aluminum crimp.

Before each experiment, reactor bottles were purged with hydrogen gas. This eliminated oxygen in the system and the hydrogen served as an electron donor for the reaction. After purging with hydrogen for approximately one hour, 2 mL of stock solution of contaminant at 400ppm or 500ppm was injected into the sample, bringing the total reactor volume to 100 mL. This resulted in an initial NAC concentration in the reactor of approximately 8-10 ppm. A complete listing of contaminants used and experimental conditions can be found in Table 3.1 . After vigorous hand mixing for one minute, the bottle was placed on a rotator (Glas-Col, Terre Haute, IN) for 15-20 minutes at approximately 40 RPM. Liquid samples were periodically drawn with a 1mL gas-tight syringe (Hamilton Co., Reno, NV) and then the bottle was placed back onto the rotator. Each sample was injected directly into a gas chromatograph (Hewlett Packard, HP6890 series GC System) or HPLC (Dynamax, Model #UV-1) for analysis to determine contaminant concentration in the reactor bottle. This process was continued for approximately 3-4 hours until the contaminant concentration had been reduced to at least 25% of its initial value. For each experiment, the reduction of contaminant concentration over time was plotted.

3.3.2 Effect of Hydrogen Concentration on NAC Destruction

In determining the effects of hydrogen concentration, all experiments were performed at pH = 4.0. The desired pH was achieved and preparation of reactor bottles was accomplished using the same methods outlined in 3.2.1. Before the injection of each contaminant, reactor bottles were purged at various hydrogen concentrations (20%, 50%, and 100%). After approximately one hour of purging at the appropriate hydrogen concentration, 2 mL of contaminant at various concentrations was injected into the reactor bottle with 98 mL DI and buffer solution, bringing the total reactor volume to 100 mL. A complete listing of contaminants and hydrogen concentrations used can also be found in Table 3.1. Sampling and analysis procedures were identical to those outlined in section 3.2.1.

3.4 Flow-through Column Experiments

A 316-gauge hollow steel tube (Mainline Supply, Dayton, OH) 16 cm in length and 4 cm in diameter, with an internal volume of 200 cm^3 was used to construct a column. The top and bottom of the column was packed with coarse sand. 100g of Pd/Al pellets were placed in between the two sand layers. The empty bed volume of the catalyst portion of the reactor was 100 mL, and the pore volume measured between the Pd/Al pellets was 32 mL. The two caps on the end of the column were lined with glass wool to prevent the media from infiltrating the tubing leading out of the column. The column was held in place vertically in such a manner that the influent entered the bottom of the column and the effluent exited the top for all experiments. At each end of the column, a sampling port was installed. The influent samples were taken using a 3-way valve (Cole-Parmer) and the effluent samples were taken from the tubing leading to the waste container. A diagram of the experimental setup can be seen in Figure 3.1.

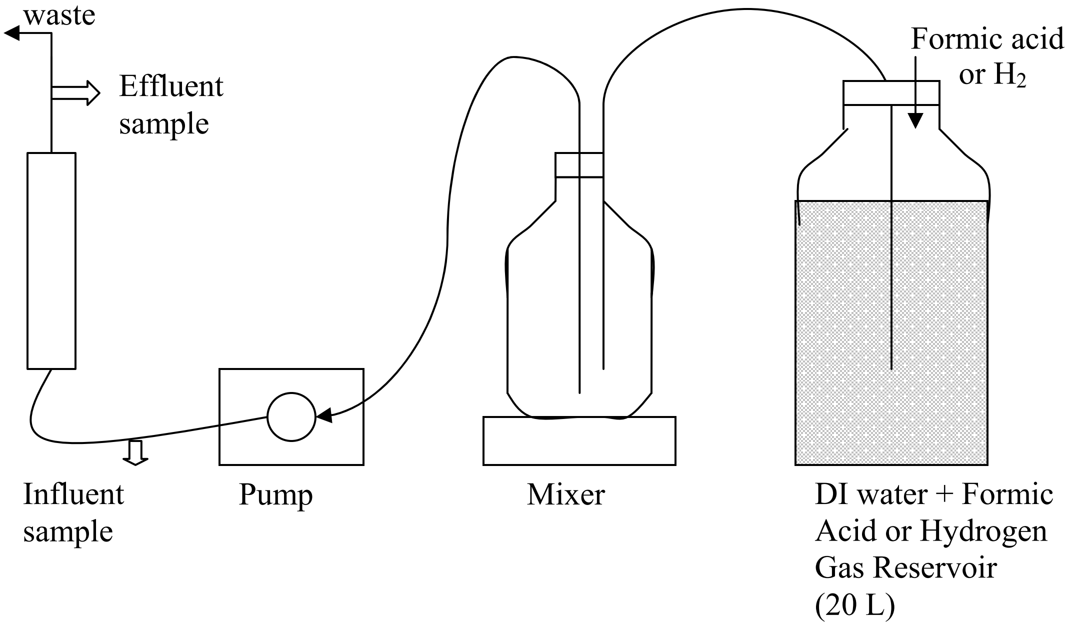

Figure 3.1 Column Reactor Setup

Various concentrations of formic acid or hydrogen gas were added to a 20 L glass vessel filled with DI water to supply electron donor for the Pd-catalyzed reduction reaction. Hydrogen was added to the 20 L vessel via continuous bubbling over the duration of each experiment. A diffuser was used for more even distribution of the gas. Formic acid was mixed in directly. After the formic acid or hydrogen was added and desired pH achieved, 4 L of this reservoir was transferred to a smaller vessel which was placed on a mixer. A known amount of nitroaromatic contaminant was added to this smaller reservoir, which was then capped with a rubber stopper. The stir plate was used to ensure sufficient mixing of the contaminant with the DI water/electron donor mixture. A peristaltic pump (Masterflex, model # 7090-42) pumped water from this 4 L vessel into and through the column containing the Pd/Al catalyst. Aqueous samples were then periodically withdrawn from both the influent and effluent sampling ports into 3-mL auto sampling vials. Samples were then withdrawn with a 1 mL gas-tight syringe (Hamilton Co, Reno, NV) from the vials and injected into the HPLC (Dynamax, Model # UV-1) for analysis. Calibration curves prepared from standards were used to determine concentrations of NAC in both effluent and influent samples.

3.4.1 Effects of Formate Concentration

The experimental setup to determine the effects of formate concentration on the degradation of NACs followed the procedures outlined in section 3.3. In this set of experiments, 2-NT was used at three different formate concentrations (15 ppm, 50 ppm, and 150 ppm). For each experiment, the appropriate amount of formate was added via injection of formic acid (88%, Fischer Scientific) into the DI water reservoir before pumping began. The formic acid was thoroughly mixed with the DI water and the initial pH was measured. Approximately 4 L of the 20 L reservoir was then transferred into the mixing chamber. After the solution was transferred, various amounts of pure 2-NT were added to the mixing chamber and allowed to fully dissolve before pumping started. . After pumping began, sampling and analysis procedures followed those outlined in section 3.3.

3.4.2 Effects of CO_2

The experimental setup to determine the effects CO_2 on the degradation of NACs followed the procedures outlined in section 3.3. The same contaminant (2-NT) that was used in the formate experiments was used, but for these experiments the DI water reservoir was purged with a 20% CO_2/80% H_2 mixture. A complete listing of these experiments can be found in Table 3.1. The DI reservoir was purged until the pH of the reservoir stabilized. The pH of the reservoir was then adjusted to desired levels using NaOH . Then, 4 L of reservoir water was transferred to the mixing chamber. Various concentrations of NAC were added to the mixing chamber before pumping began. Sampling and analysis procedures then followed those outlined in section 3.3.

3.4.3 Effects of Column Residence Time

The experimental setup to determine the effects of residence time in the Pd/Al reactor on the degradation of NACs followed the procedures outlined in section 3.3. Formic acid (50ppm) was used as the hydrogen donor in this set of experiments. After transferring 4L of the DI water/formic acid solution to the mixing chamber and spiking it with approximately 100 ppm of 2-NT, the NAC-contaminated water was pumped through the catalytic reactor column at flow rates of 38 and 75 mL/min. Residence time in the column is a function of flow rate. For the baseline experiments, 38 mL/min was chosen as the flow rate to provide a residence time equivalent to a realistic residence time in the field (~1 min). Flow rate was doubled to see if mass transfer to the catalyst surface limited the reaction. Dr. Jeffery Cunningham of Stanford University provided data on flow rates and residence time currently being used in a field scale HFTW system. This data was used to scale parameters to the experimental setup. Sampling and analysis was accomplished as previously described. Parameters to scale experiment:

Pd Column: 2% Pd on Al_2O_3, diameter = 5 inches, volume = 25L, porosity = 40%,
pore volume = (25 L/min)*(40%) = 10L
System pumping rate: Q = 10 L/min, retention time = (10 L)/ (10 L/min) = 1 min

3.5 Application of Michaelis-Menten Kinetics to Simulate NAC Degradation

A simple first order equation, $\frac{dC}{dt} = -k_1 C$ can be used to model degradation at low substrate (i.e. NAC) concentrations (C). This model assumes NAC concentrations decrease exponentially over time. This first-order model was used to describe degradation kinetics in the batch experiments. By measuring concentration with time, and then plotting ln (C/C_0) vs time (where C_0 is the NAC concentration at time = 0) the first-order model predicts that, using linear regression, the data can be fit with a line of slope k_1. An implicit assumption built into the first-order model is that there are no limiting factors, such as insufficient electron donor. However, as the concentration of the substrate increases, it has often been found that the degradation kinetics transition from a first-order to a zeroth-order process. Michaelis-Menten kinetics can be used to model this transition from first-order to zero-order kinetics with increasing substrate concentration using the following equation:

$$\frac{dC}{dt} = -\frac{(V_{\max})(C)}{(K_{1/2} + C)} \tag{8}$$

Where: dC/dt = reaction rate [mM T^{-1}]
V_{max} = maximum reaction rate [mM T^{-1}]
$K_{1/2}$ = half-velocity constant [mM]
C = substrate concentration [mM]

At low substrate concentrations, where $K_{1/2} >> C$, reaction kinetics are approximately first-order, with a first-order rate constant of $V_{max}/K_{1/2}$. As the substrate concentration is increased, the reaction rate (dC/dt) will eventually attain a maximum value, V_{max}. Once this rate is reached, the reaction rate no longer increases with increasing substrate concentration. This may be due to some factor that limits the reaction rate, such as insufficient reactive sites on the surface of the catalyst or insufficient electron donor available. When V_{max} is reached, the dC/dt vs C curve becomes horizontal (see Figure 3.2), signaling the transition to zeroth-order kinetics. $K_{1/2}$, also referred to as the affinity constant, represents the substrate concentration at which the reaction rate is 50% of V_{max}.

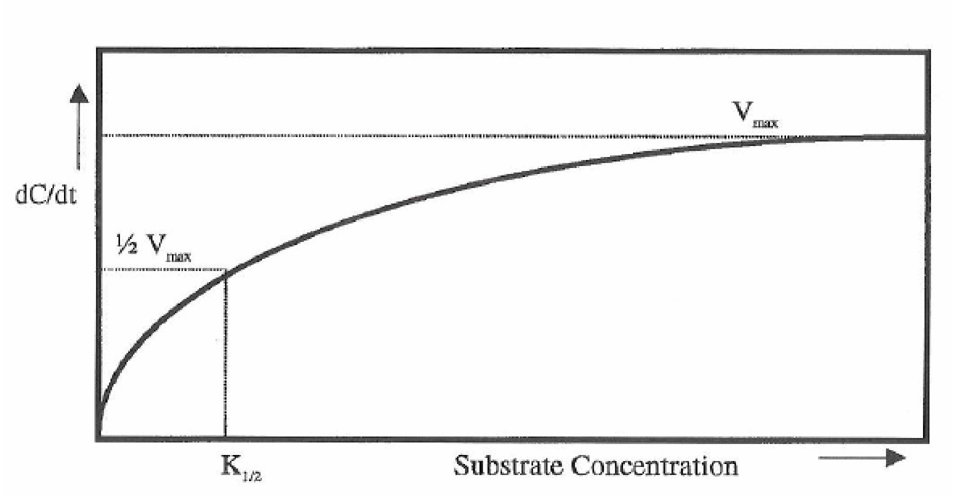

Figure 3.2 Typical Michaelis-Menton Curve (from Boggs, 2000)

The data collected from each batch experiment were plotted to depict the molar concentration of the NAC in the reactor bottle versus time elapsed since NAC injection. Least squares analysis was then used to fit the data to the integrated Michaelis-Menten equation as a function of time (Agrawal et al., 2002):

$$K_{1/2}/V_{max}\ln(C/\ C_0)+(1/V_{max})(C_0\text{-}C) = t \qquad (9)$$

where C_0 is the initial NAC concentration in the reactor bottle. Analysis was performed using a model developed by Christ (1997) that applies the Solver function in a Microsoft Excel 2000 spreadsheet to select values of V_{max} and $K_{1/2}$ that minimize the sum of the squared weighted differences between modeled (using Equation (9)) and measured values of ln (C/C_0) vs t . Since initial NAC concentrations were not sufficiently high, a unique solution for V_{max} and $K_{1/2}$ could not be determined. However, as noted earlier in this chapter, linear regression of the first-order portion of the curve could be used to determine a unique first-order reaction rate constant, k_1, which corresponds to $V_{max}/K_{1/2}$.

A plot of dC/dt versus C for the 2-NT column experiments was constructed using the method outlined by Logan and LaPoint (2001). In this method, concentration in the column (C) was approximated as the log-mean concentration, C_{lm}:

$$C_{lm} = \frac{C_{in} - C_{out}}{\ln(C_{in} / C_{out})} \tag{10}$$

where C_{in} and C_{out} are the influent and effluent 2-NT concentrations, respectively. The rate of 2-NT destruction was estimated as:

$$\frac{dC}{dt} = \frac{(C_{in} - C_{out})}{\theta} \tag{11}$$

where θ = hydraulic retention time in the column (min)

Note that in equation (11) we assume that the difference between C_{in} and C_{out} is relatively small. However, because of the high reaction rates of the palladium catalyst, at low concentrations of NAC or high formate concentrations, high removal percentages are expected and this assumption may not hold true. dC/dt vs. C_{lm} was graphed using Microsoft Excel 2000 spreadsheets and kinetic parameters (V_{max} and $K_{1/2}$) were estimated using a mathematical software package (Axum 7.0, Insightful Corporation, Seattle, WA). The package selected values of V_{max} and $K_{1/2}$ that minimized the sum of squares difference between measured and modeled values of dC/dt vs. C, where modeled values were determined using Equation (8). In addition, the ratio of $V_m/K_{1/2}$ was used to approximate the pseudo first-order reaction rate, k_1. As in the batch studies, in cases where the dC/dt vs. C_{lm} plots were linear, the slope of the regression line was used to approximate k_1 ($V_{max}/K_{1/2}$). A similar approach has been used to model reaction kinetics by Agrawal et al. (2002).

Batch Experiments

Chemical	Effect
2-NT	pH = 4.0
	pH = 4.5
	pH = 5.0
	pH = 5.5
3-NT	pH = 4.0
	pH = 4.5
	pH = 5.0
4-NT	pH = 4.0
	pH = 4.5
	pH = 5.0
2-NT	20% H2
	50% H2
	100% H2
3-NT	20% H2
	50% H2
	100% H2

Column Experiments

Chemical	Effect
2-NT	Formate (15 mg/L)
	Formate (50 mg/L)
	Formate (150 mg/L)
2-NT	H2 Conc (20%)
	H2 Conc (50%)
	H2 Conc (100%)
2-NT	20% CO_2/H_2 pH = 4.2
	20% CO_2/H_2 pH = 5.2
	20% CO_2/H_2 pH = 6.2
2-NT	100% H_2 pH = 4.0
	100% H_2 pH = 4.3
	100% H_2 pH = 4.6
	100% H_2 pH = 5.0
	100% H_2 pH = 5.5
2-NT	Flow Rate (5 mil/min)
	Flow Rate (20 mil/min)
	Flow Rate (50 mil/min)
2-NT	Conc (20 ppm)
	Conc (200 ppm)

Table 3.1 Experimental Schedule

4.0 RESULTS AND DISCUSSION

4.1 Batch Experiments

4.1.1 Effect of pH on NAC degradation

Experiments were carried out to determine how pH levels affected the rate of NAC degradation (See Sec 3.3). Experiments were conducted at pH levels of 4.0, 4.5, 5.0, 5.5, and 6.0 for 2-NT, 3-NT and 4-NT. Reduction in NAC concentration was tracked over time (Figure 4.1a, 4.1b, and 4.1c). In all cases, reaction rate was dependent on pH and rates were higher at lower pHs. This is to be expected because the hydrogen required for the catalytic reaction between the palladium and NAC is more plentiful at lower pHs. Because initial contaminant concentrations were not high enough to determine unique values of V_{max} and $K_{1/2}$, k_1 was determined from fitting the $\ln(C/C_0)$ versus time curve based on the linear regression

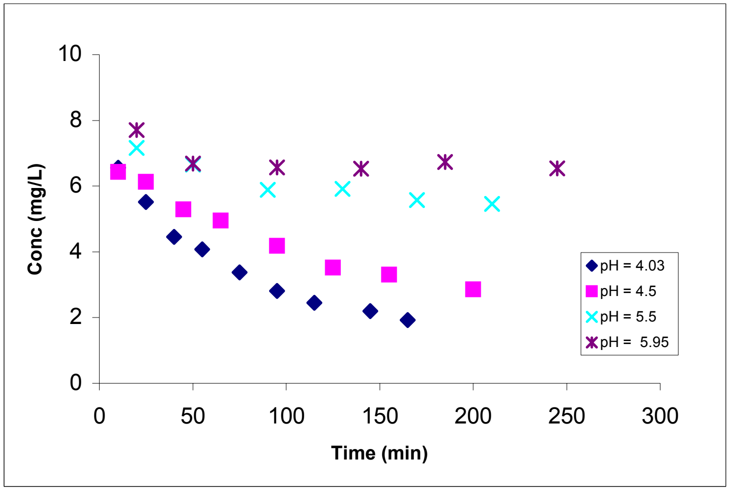

Figure 4.1a Batch Study of Effect of pH on 2-NT Degradation

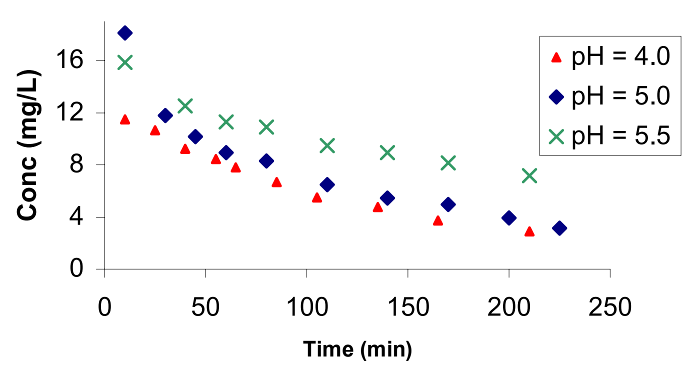

Figure 4.1b Batch Study of Effect of pH on 3-NT Degradation

method described in Sec 3.5. Modeled k_1 decreased as pH increased. Rates were fastest for 4-NT, followed by 3-NT, and then 2-NT. At pH of 5.0, the modeled k_1 for 4-NT, 3-NT, and 2-NT was 0.0154 min $^{-1}$, 0.00863 min^{-1}, and 0.00572 min $^{-1}$, respectively. This general trend was also seen for the three different NT isomers in the other batch pH experiments. This is expected because of the differences in distance between the methyl group and the nitro group for each isomer. Since 4-NT has the largest distance between the two groups, there are less electronic effects from the methyl group and therefore makes electron transfer in the reduction reaction easier than in 3-NT or 2-NT. The first-order rate constant for each experiment are shown in Table 4.1.

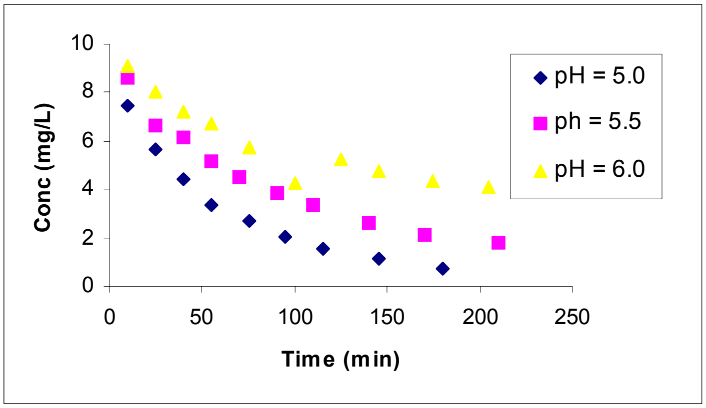

Figure 4.1c Batch Study of Effect of pH on 4-NT Degradation

These batch studies showed the potential to treat NACs with a palladium catalyst. For application in an HFTW, a catalyst must have a rapid reaction rate for effective treatment. In the batch studies, it was shown that even using a very small quantity of catalyst powder (1 mg), relatively rapid degradation (on the order of hours) was observed, thus justifying further studies.

. *Experimental contaminant*	*pH*	*Reductant*	*Buffer*	*Intial Conc (ppm)*	*Kinetic parameters* *(min^{-1})*
2-NT	4.03	100% H_2	MES	8	k_1 = .0088
					SSE = 2.18 E-5
	4.5	100% H_2	MES	8	k_1 = .00467
					SSE = 7.52 E-6
	5.0	100% H_2	MES	8	k_1 = .00573
					SSE = 5.85 E-5
	5.5	100% H_2	MES	8	k_1 = .00145
					SSE = 1.08 E-5
	5.95	100% H_2	MES	8	k_1 = .000542
					SSE = 3.13 E-5
	4.2	20% H_2	MES	10	k_1 = .0033
					SSE = 5.27 E-5
	4.2	50% H_2	MES	10	k_1 = .0127
					SSE = 7.63 E-6
3-NT	5.0	100% H_2	MES	12	k_1 = .00863
					SSE = 7.25 E-4
	5.5	100% H_2	MES	12	k_1 = .0040
					SSE = 1.42 E-4
	4.0	100% H_2	MES	12	k_1 = .00728
					SSE = 1.18 E-5
4-NT	6.0	100% H_2	MES	10	k_{1obs} = .0043
					SSE = 5.66 E-5
	5.5	100% H_2	MES	10	k_1 = .0088
					SSE = 3.82 E-5
	5.0	100% H_2	MES	10	k_1 = .0154
					SSE = 9.95 E-6

Table 4.1 Batch Experiment Results

4.1.2 H_2 Effects on NAC degradation

Experiments were carried out to determine how concentrations of hydrogen gas affected the rate of NAC degradation (See Sec 3.3). pH levels were set equal for each experiment while the batch reactors were purged with hydrogen gas at concentrations of 20%, 50%, or 100%. As can be seen from Figure 4.2, the rates are adversely affected by reduced concentrations of hydrogen. These experiments were carried out for 2-NT and

3-NT. However, the 3-NT experiment did not produce useable data and is not included in this section. First-order rate constants (k_1) at the different hydrogen concentrations are listed in Table 4.1.

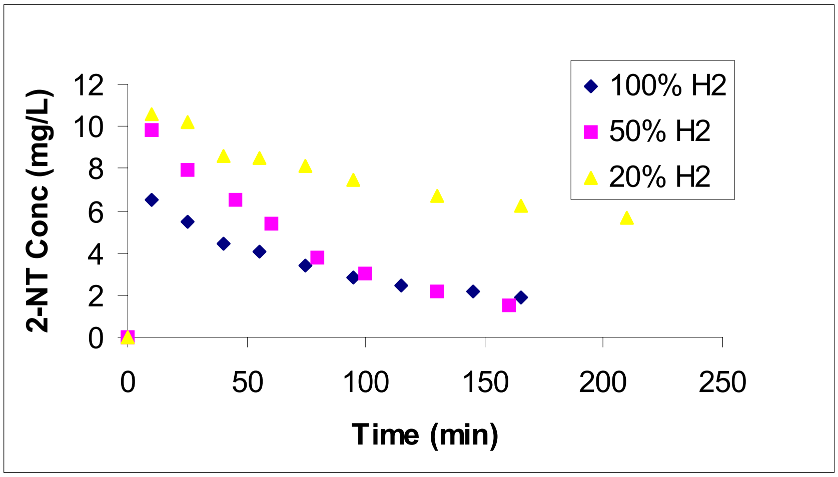

Figure 4.2 Effects of Hydrogen Concentration on 2-NT Degradation

This further illustrates the importance of available hydrogen to the catalyst system. For application in an HFTW system, there must be sufficient delivery and mixing of hydrogen to the contaminated groundwater. Insufficient levels of hydrogen gas may result in less than optimal reducing conditions. 100% hydrogen is expensive for field level applications and can be dangerous if not handled properly. However, a reduction in concentration might decrease reaction rates to an unacceptable level. The column experiments further investigated the optimal level of hydrogen, pH, and various other reaction conditions for a palladium catalyst system.

4.2 Column Experiments

4.2.1 pH Effects in a 100% H_2 System

Column experiments were carried out to determine the effects of pH on the palladium catalyst reactor. All experiments were run at the same flow rate (37 mL/min) while the influent reservoir was purged with 100% H_2 gas for the duration of the experiment. MES buffer was used to establish pH levels between 4.0 and 5.2. Figure 4.3 plots degradation rates for 2-NT over the range of log mean influent concentrations for three different pH levels. As discussed in Sec 3.5, Michaelis-Menten kinetics were used to approximate kinetic rate parameters V_{max} and $K_{1/2}$ using a mathematical software package. Correlations for the model results ranged from .97 - .996 for the various pHs. Visual inspection of Figure 4.3 shows, much like the pH batch studies, that as the pH levels increase, the reaction rates decline. The data appear to follow Michaelis-Menten type behavior. At low concentrations the degradation rates may be described by first-order kinetics. As concentrations increase, the curves gradually flatten out and appear to approach zero-order kinetics. Kinetic parameters fit to the data can be found in Table 4.2. As pH increased, V_{max} values declined as well. On the first-order portion of the curve, rates are approximately the same for each pH until a 2-NT concentration of .03 mM is reached. At that point, the degradation rates for the high pH systems begin to level off and approach V_{max}, while the rates for the lower pH systems continue to rise. V_{max} of the 5.0 pH experiment was determined to be 0.164 mM/min, while the V_{max} for the pH = 4.4 system was 0.173 mM/min. Results from the early experiments (LCE#1-3) were difficult to fit using Michaelis-Menten curves because the initial concentrations were insufficient to see the zero-order portion of the curve. In these cases, only k_1 ($V_{max}/K_{1/2}$) was determined with linear regression.

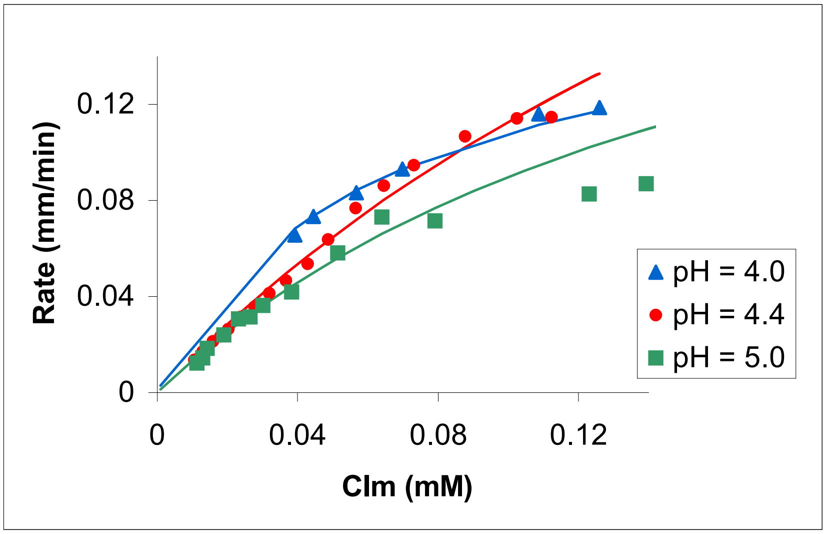

Figure 4.3 Effects of pH on 2-NT Degradation Rate in 100% H_2 System

The fraction of contaminant removed versus log mean contaminant concentration also produced results similar to those seen in the pH experiments—higher removal was seen at lower pH levels. As high as 75% removal was observed at a pH of 4.0 at low (<0.09 mM) log mean concentrations, while only 64% and 54% was removed at pHs of 4.4 and 5.0, respectively. Fraction contaminant removed vs influent concentration at various pH levels can be seen in Figure 4.4.

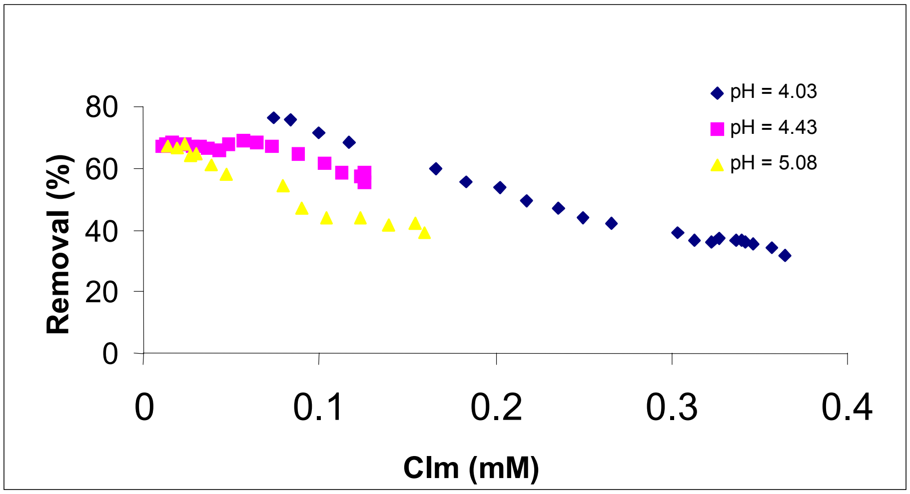

Figure 4.4 Fraction of 2-NT Removed in a 100% H_2 System

4.2.2 Effect of Hydrogen Concentration

Column experiments were carried out to study the effects of hydrogen concentration on the performance of the palladium catalyst. Three different hydrogen concentrations were selected (100%, 50%, and 20%) and used to purge the influent reservoir, as described in Section 3.4. All other parameters including pH and flow rate were held constant. Figure 4.5 shows that hydrogen concentration affects the rate of NAC destruction in the column reactor in a manner similar to what was observed in the batch studies. As concentrations of hydrogen gas decreased, so did reaction rates. Also, this set of column experiments highlighted another important phenomenon. At high contaminant concentrations, the reaction rates appear to drop below the V_{max} value. This is most likely caused by the formation of OH^- ions, a byproduct of the degradation reaction (see Sec 2.4), which creates a pH gradient. This buildup of a pH gradient inside the catalyst particles in turn decreases both activity and selectivity of the catalyst. At very high 2-NT concentrations, enough OH^- is formed to inhibit the reaction rate of the catalyst. Looking at Figure 4.5, we observe that for 2-NT concentrations exceeding about 0.035 mM in the 50% H_2 system and exceeding .02 mM in the 20% H_2 system, destruction rates decrease below their maximum values.   .

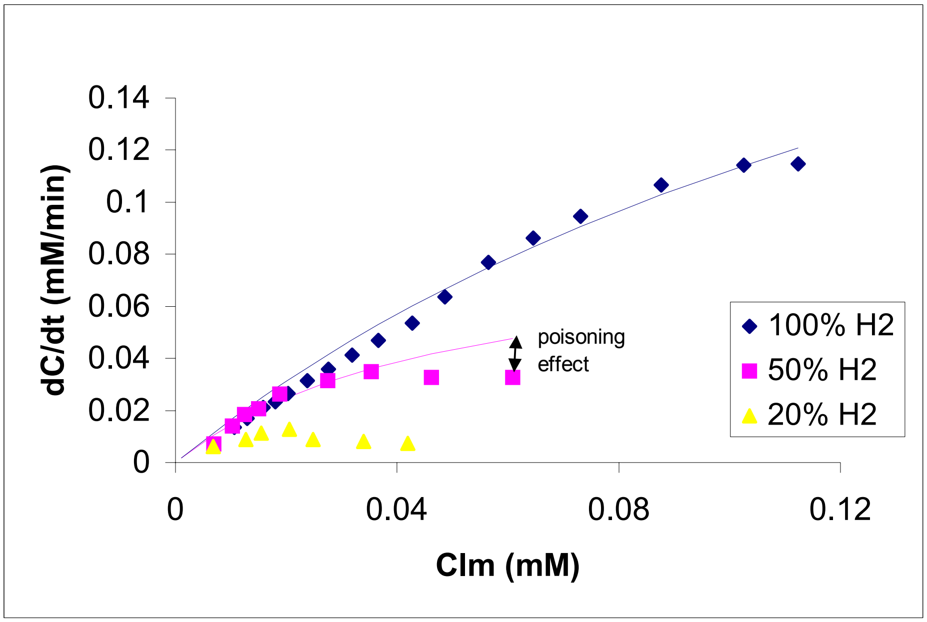

Figure 4.5 Hydrogen Concentration Effects on 2-NT Degradation Rates

These reductions in reaction rate at high influent concentrations (apparently due to catalyst poisoning by OH^-) were not included in our model. Fitted values for the kinetic parameters for the various column experiments can be found in Table 4.2.

This effect of OH^- on reaction rate illustrates the need for buffering the palladium catalyst system.   Since we have already noted that the reaction rate is highly dependent on the pH level, increase of pH should be avoided. Especially for an *in situ* technology application, such as an in-well reactor as part of an HFTW system, this emphasizes the importance of having not only the right type of reductant, but also having sufficient concentrations of both the reductant and pH buffer.

4.2.3 *pH effects for 20% CO_2 system*

Experiments were conducted to determine the effect of CO_2 on the column reactor at various levels of pH. The influent reservoir was purged with a 20% CO_2 / 80% H_2 mixture and experiments were done at pH 4.2, 5.2, and 6.2. In all of these experiments, and as illustrated in Figure 4.6, the same catalyst poisoning noted in the previous section was again seen. Figure 4.6 shows the 2-NT degradation rates at the three pH levels over the influent log mean concentration range. Rates were lower than rates observed at comparable pH levels in a 100% H_2 system. For example, V_{max} at pH = 4.2 is 0.154 mM/min in the CO_2 system and 0.164 mM/min in the 100% H_2 system. This is consistent over the entire range of pHs used for the two systems. Note from Figure 4.6 that the rates are approximately equal for all three pHs until a concentration of approximately 0.03 mM of 2-NT is reached. The rates continue to increase with log-mean concentration for pH = 4.2, while for higher pH the rates level off, and eventually decrease. V_{max} and $K_{1/2}$ for these experiments can be found in Table 4.2.

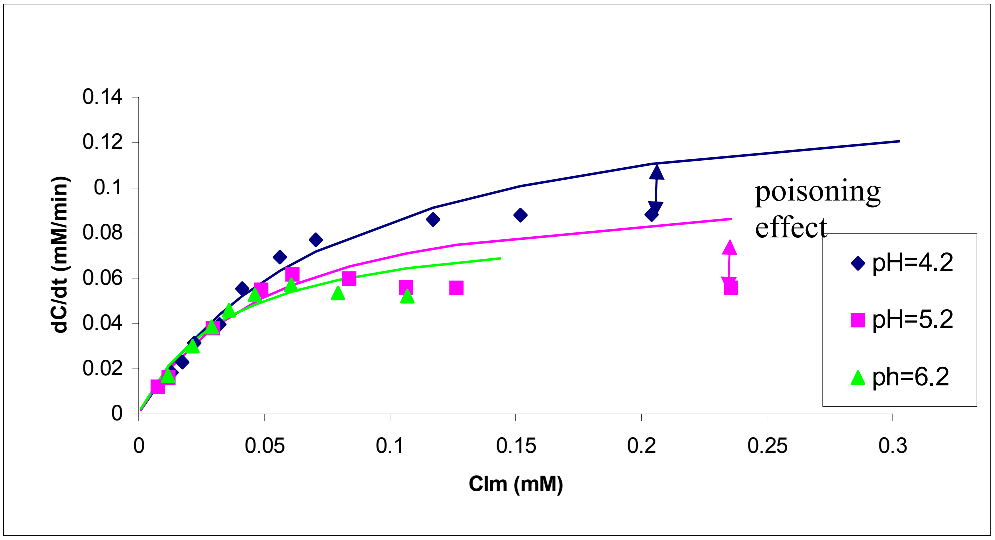

Figure 4.6 pH Effects on 2-NT Degradation Rates in a 20%CO_2/80% H_2 System

4.2.4 Formate Effects

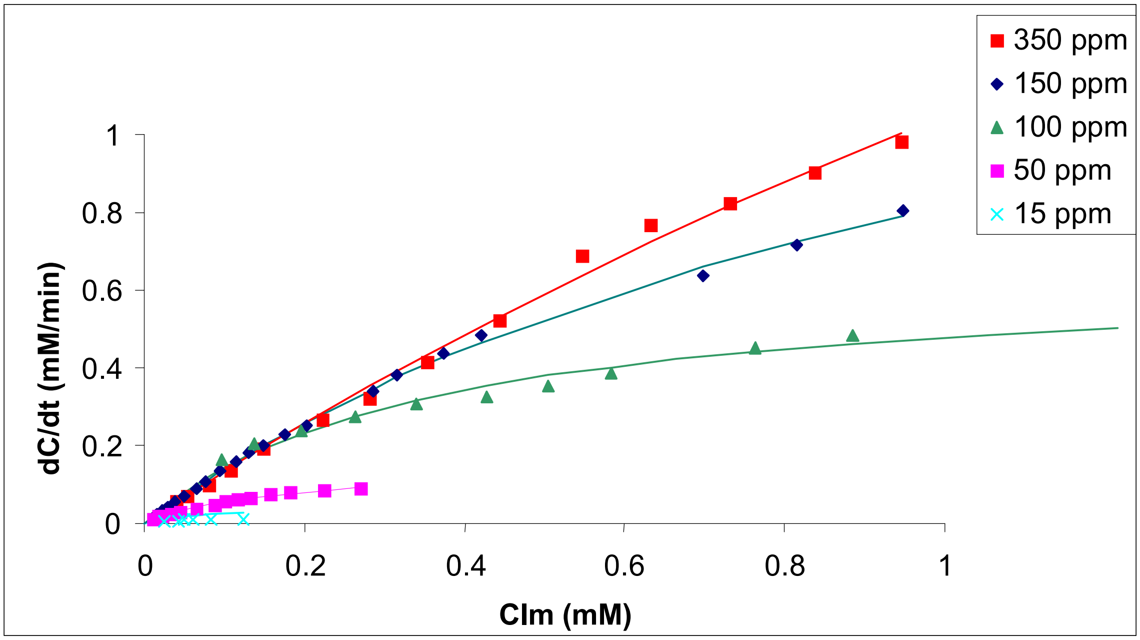

Figure 4.7 Effects of Formate Concentration on 2-NT Degradation Rate

Experiments were conducted in the column reactor to determine the effect of using formate as a reductant. Prusse et al (2000) found superior results in the reduction of nitrate by using formate as a reductant instead of hydrogen. The formate, delivered in the form of formic acid, creates a buffering effect to prevent a pH increase and catalyst poisoning due to OH^- inhibition as discussed above and in Sec 2.4. The effect of formate was tested at formate concentrations varying from 15 – 350 ppm with other experimental conditions remaining constant. Results are displayed in Figure 4.7. As can be seen, as formate concentrations increase, so does rate. No catalyst poisoning is observed, even at very low formate concentrations. Michaelis-Menten type kinetics are hard to fit to the data for high formate concentrations because the curves are almost linear. Figure 4.7 also illustrates that at high formate concentrations rates continue to rise even at very high 2-NT concentrations (> 250 ppm).

The parameters for formate concentrations greater than 150 ppm far exceed those determined from the 100% H_2 experiments. At a formate concentration of 50 ppm, the V_{max} of 0.1543 mM/min is comparable to that of a 100% H_2 system with a pH of 4.0 (0.173 mM/min). At a formate concentration of 100 ppm, the fitted V_{max} is four times that of the 100% H_2 system (0.650 mM/min and .173 mM/min, respectively). Reaction rates of the 150 ppm formate system were 10 times greater than those of the 100% H_2 system and that ratio steadily increases as the formate concentration increases.

As expected, since the 2-NT destruction rates increased when using formate as a reductant, the 2-NT removals also increased. At a formate concentration of 50 ppm, the fraction of 2-NT removed was comparable to removals observed in the 100% hydrogen system. As shown in Figure 4.8, at high concentrations of 2-NT (> 0.3 mM), the fraction of removal is small (20%). Removal fraction gradually increases to around 65% as concentrations of 2-NT decrease. This transition was not exhibited at concentrations of formate greater than 150 ppm. Even at very high 2-NT concentrations (>1.8 mM), the fraction of 2-NT removed was 72%. There did not seem to be a noticeable difference in fraction 2-NT removed for 150 ppm formate and 350 ppm. Both had a removal fraction of approximately 70% regardless of the contaminant concentration. However, at low

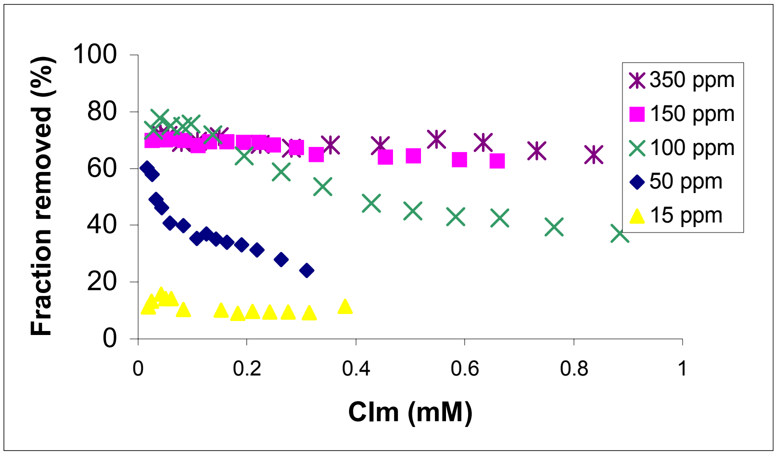

Figure 4.8 Effect of Formic Acid Concentration on 2-NT Fraction Removal

formate concentration (15 ppm), only approximately 10% of the contaminant was removed regardless of 2-NT concentration.

The rapid reaction rate and high removal efficiency observed when using formate appear to make it an ideal reductant for use in an HFTW system. The recirculation between the HFTW treatment wells result in multiple passes of NAC-contaminated water through the reactors. With 70% of the 2-NT removed in each successive pass through a reactor, an HFTW system with relatively short residence times could prove to be very successful to remediate groundwater with high NAC concentrations. However, in a pilot scale experiment with trichloroethylene, McCarty et al (1998) showed an 83 – 85% first pass removal with a HFTW system that promoted biodegradation via toluene and oxygen injection. For the palladium system to achieve such efficiencies, further optimization will be required.

4.2.5 Effects of Flow Rate

To determine the effects of flow rate on catalyst performance an experiment was conducted with identical parameters to the 50 ppm formate experiment, but the flow rate was doubled from 38 mL/min to 75 mL/min. This effectively halved the hydraulic retention time of the NAC in

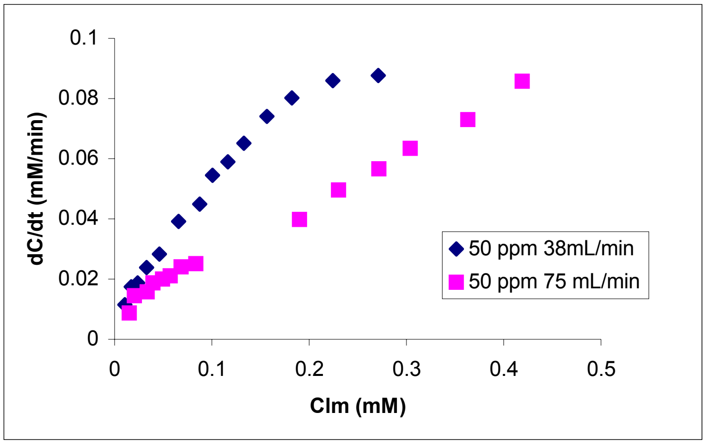

Figure 4.9 Flow Rate Effects on 2-NT Degradation Rate

the column and served as a test to see if the reaction was limited by mass transfer to the catalyst surface. Modeled V_{max} rates were very similar for the 38 mL/min flow and 75 mL/min flow systems and were 0.1524 mM/min and 0.1624 mM/min, respectively. There was a noticeable difference in the $K_{1/2}$ values as can be seen in Figure 4.9, but based on the modeled V_{max} values, the reaction rates were not assumed to be kinetically limited.

4.3 Comparison of Reductants

A graph was prepared to compare the three reductants used in the previously described studies. As noted in Sec 4.2.4, the formate rates of reduction were far greater than the rates obtained using 100% H_2 and 20% CO_2/H_2 mixture. This can readily be seen upon visual inspection of Figure 4.10. The 150 ppm formate, 100% H_2, and 20% CO_2/H_2 mixture had similar reduction rates until concentrations surpassed approximately .05 mM of 2-NT. The 150 ppm formate curve continues to increase linearly as 2-NT concentrations increased to as high as 0.3 mM, while rates using the other reductants leveled off at their respective V_{max} values at much lower concentrations. The 50 ppm formate system showed results similar to the 20% CO_2/H_2 mixture with fitted V_{max} values of 0.1524 and 0.1543 mM/min, respectively. All reductants outperformed the 50% H_2 system and not surprisingly, the fitted V_{max} value of the 50% system was the lowest (0.0088 mM/min) of all.

A rough comparison was accomplished to evaluate the cost of formic acid as compared to hydrogen gas as a reductant to treat 1000 gallons (3,785L) of NAC-contaminated water. The details of the calculation are included in Appendix B.

Based on those calculations, it is approximately four times cheaper to use formic acid than hydrogen gas to treat 1000 gallons of NAC-contaminated water. In addition, one 55 gallon drum of 88% formic acid could treat 967,000 gallons of contaminated water, while one tank of hydrogen could only treat approximately 107,000 gallons. There would also be additional costs, not factored into the comparison, for re-supplying hydrogen tanks and additional safety concerns with storing and transporting multiple tanks when using hydrogen gas instead of formic acid as a reductant.

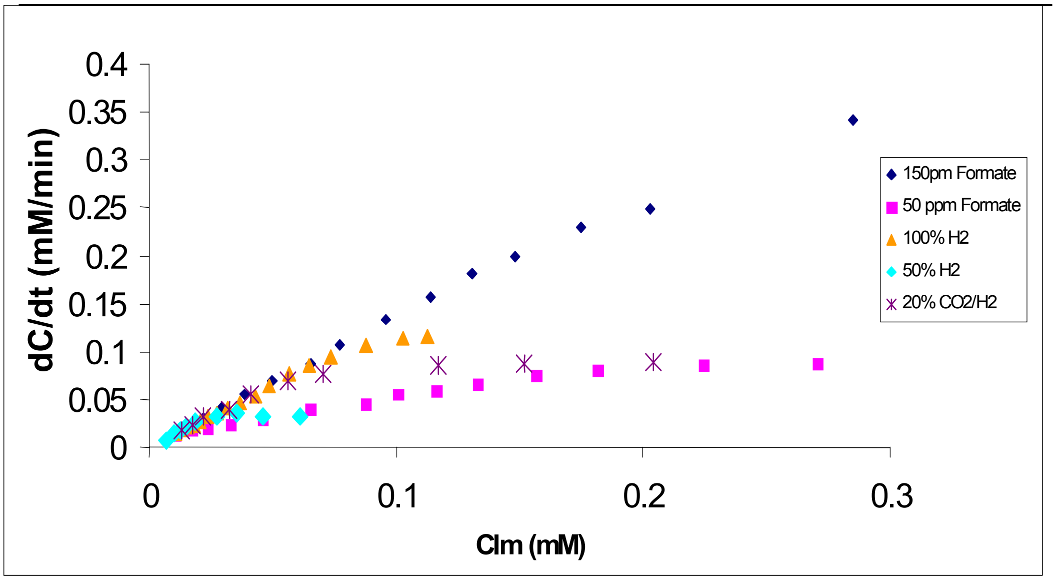

Figure 4.10 Comparison of the Effect of Reductant Type and Concentration on 2-NT Degradation Rates

Fraction of 2-NT removed for the three reductants was also plotted (see Figure 4.11). As can be seen, the fraction of 2-NT removal when 150 ppm formate is used as a reductant remains at a constant level and does not decrease with log-mean 2-NT concentration as the fraction removal does for the other three reductants.

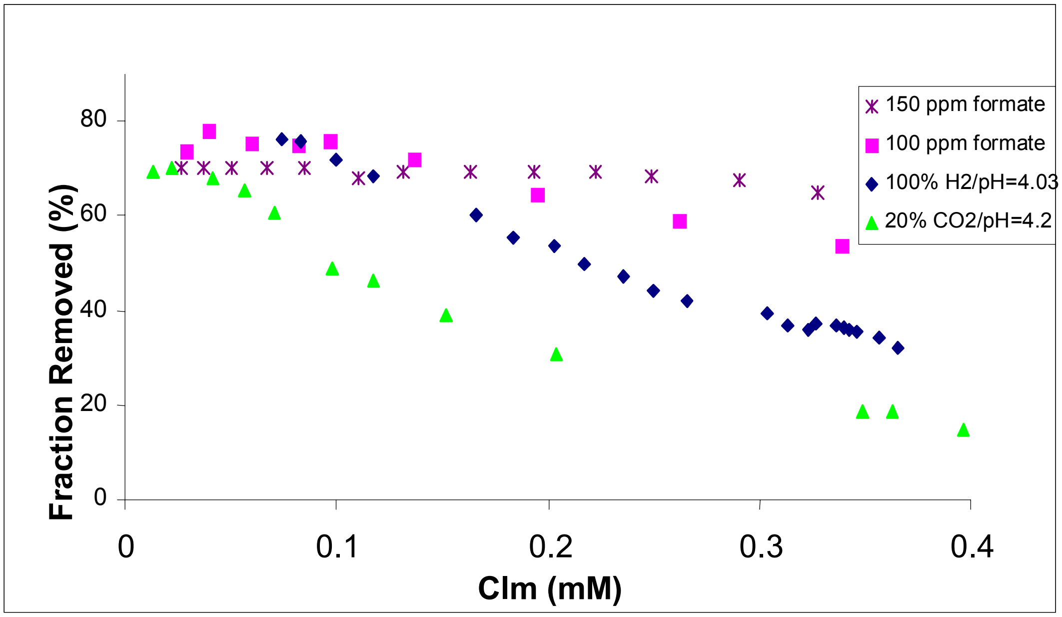

Figure 4.11 Comparison of the Effect of Reductant Type and Concentration on Fractional Removal of 2-NT

4.4 *Potential for In-Well Use of Pd-Catalysis*

Based on an experimentally determined first-order removal rate constant, and system parameters that have been used to implement an HFTW system in the field, a reactor size that would be adequate to achieve NAC-concentrations downgradient of an HFTW system that were 1% of upgradient concentrations was determined (Appendix C). 99% removal was specified as it appears, at least for HFTW application at a TCE-contaminated site, that an HFTW system that can achieve that magnitude removal is a viable treatment alternative (McCarty et al., 1998). Upgradient concentrations were assumed to be 1 ppm 2-NT and the rate parameter used in the calculations was based on adding 100 ppm formate. From Experiment LCE #16 (see Table 4.2) it was determined that at a NAC concentration of 1 ppm, destruction in the reactor could be modeled as a first-order process, with a rate constant, k_1, of 1.8 min^{-1}. Based on calculations with this rate constant, it was found that a residence time of 1.54 min was required to achieve the desired downgradient concentration level (<10 ppb). The possible reactor sizes determined were as follows:

L = 9.5 ft, dia = 10”
L = 14.8 ft, dia = 8 “
L = 26.3 ft, dia = 6 “

These dimensions are comparable to those of an HFTW in-well reactor that is currently being evaluated for use to treat TCE-contaminated groundwater (Munakata et al., 2002). The reactor has a length of 9 feet, a diameter of five inches, and a residence time of approximately 1 minute. The fact that a palladium-catalyst reactor can be sized for in-well use to remediate 2-NT, based on an experimentally determined degradation rate constant, shows potential for the reactor to be used as part of an HFTW system.

Experiment *(see Appendix A)*	*Reductant*	*Buffer*	*Intial (2-NT)*	*Influent pH*	*Effluent pH*	*Kinetic parameters Vm (mM/min)* $K_{1/2}$ *(mM)*
LCE #3	100% H_2	MES	30 ppm	4.6	5.43-5.08	Insufficient data
LCE #4	100% H_2	MES	50 ppm	5.08	5.29-5.34	Vm = .1639 $K_{1/2}$ = .1046
LCE #5	100% H_2	MES	50 ppm	4.35	4.82-4.64	Vm = .4312 $K_{1/2}$ = .2827
LCE #6	100% H_2	MES	150 ppm	4.03	4.59-4.52	Vm = .173 $K_{1/2}$ = .0599
LCE #7	100% H_2	MES	125 ppm	5.23	5.4-5.33	Vm = .1177 $K_{1/2}$ = .0329
LCE #7b	100% H_2	MES	125 ppm	5.2	5.4-5.26	
LCE #8	80% H_2 + 20%CO_2	none	100 ppm	4.22	4.57-4.31	Vm = .1543 0.0809
LCE #9	80% H_2 + 20%CO_2	NaOH	60 pm	6.2	6.73-6.10	Vm = .0858 $K_{1/2}$ = .0358
LCE #10	80% H_2 + 20%CO_2	NaOH	45 ppm	5.2	5.6-5.07	Vm = .1052 $K_{1/2}$ = .0515
LCE #11	50% H_2	MES	40 ppm	4.3	4.47-4.39	Vm = .00868 $K_{1/2}$ = .0497
LCE #12	20% H_2	MES	40 ppm	4.3	4.49-4.46	Insufficient data
LCE #13	50 ppm formate	none	45 ppm	3.43	3.98-3.66	Vm = .1524 $K_{1/2}$ = .181
LCE #14	150 ppm formate	none	50-200 ppm	3.17	3.51-3.29	Vm =1.772 $K_{1/2}$ = 1.175
LCE #15	15 ppm formate	none	100 ppm	3.64	4.66-4.17	Vm = .0652 $K_{1/2}$ = .1472
LCE #16	50 ppm formate	NaOH	100 ppm	3.5	4.01-3.76	Vm = .1624 $K_{1/2}$ = .4536
LCE #17	100 ppm formate	none	200 ppm	3.2	4.13-3.42	Vm = .650 $K_{1/2}$ = .360
LCE #18	350 ppm formate	NaOH	200 ppm	3.2	4.17-3.43	Vm =4.734 $K_{1/2}$ =3.507

Table 4.2 Column Experiment Results

5.0 CONCLUSIONS

5.1 Summary

In this thesis, the use of a palladium catalyst for the destruction of NACs was investigated. Both batch studies and a flow through column reactor were used to determine the reaction kinetic parameters (V_{max}, $K_{1/2}$, k_1). Nitrotoluene (NT) was selected as the model NAC to reduce lab safety and health concerns. Three different isomers (2-NT, 3-NT, and 4-NT) were tested at varying concentrations and reaction conditions. Reductant used, reductant concentration, pH, and flow rate were varied to find the optimum reaction conditions to promote the catalytic reduction of NT by palladium. Results were modeled using Michaelis-Menten kinetics with mathematical software packages to obtain kinetic parameters V_{max} and $K_{1/2.}$ For those experimental data that were unable to be fit using a Michaelis-Menten curve, simple linear regression was used to determine a first-order rate constant, k_{1obs}.

5.2 Conclusions

- **NAC degradation rates are dependent on the influent pH.** As pH levels increase the reaction rates slow down. This is to be expected because the hydrogen required for the catalytic reaction between the palladium and NAC is more plentiful at lower pHs. This pH dependence was seen in both batch and column experiments in 100% H_2 systems and in column work with a 20% CO_2 / 80% H_2 system. For application in an HFTW system, pH buffering must be achieved for optimal results.

- **NAC degradation rates are highly dependant on the concentration of the reductant used.** Degradation rates were reduced dramatically when H_2 concentration was decreased from 100% to 50% and 20%. This was noted in both batch and column studies. Column studies using formate as the reductant showed the same trend. Each increase in formate concentration produced increased reaction rates. For application in an HFTW, low hydrogen concentrations may result in insufficient reaction rates.
- **At low hydrogen concentrations, catalyst poisoning was caused by high 2-NT concentrations.** This poisoning caused a decrease in reduction rate as 2-NT concentrations increased. This phenomenon was seen in 20% and 50% H_2 systems and the 20% CO_2 / 80% H_2 system. This is most likely caused by the formation of OH^- ions, a byproduct of the degradation reaction, which creates a pH gradient. At very high 2-NT concentrations, enough OH^- is formed to inhibit the reaction rate by decreasing both the activity and selectivity of the catalyst. This poisoning effect, if not accounted for in an HFTW design, could result in insufficient treatment of highly contaminated groundwater. Use of 100% hydrogen as a reductant may prevent this poisoning. However, 100% hydrogen gas is expensive for field applications and can be dangerous if not handled properly.
- **In a palladium catalyst system, using formate as a reductant produced results far superior than when 100% H_2 gas was used.** At high contaminant concentrations, the formate system showed rates 4-10 times higher than observed in 100% H_2 systems. As formate concentration was increased, so were these ratios. At low pH levels, results at formate concentrations of 50 ppm were similar to those

observed when using 100% H_2 as a reductant. NAC removal fractions were also increased when formate was used as a reductant. Even at very high contaminant concentrations (>250 ppm), removal fraction was as high as 72% at a residence time of 1 minute. Removals when using hydrogen as a reductant were relatively low (30%) at high NAC concentrations and slowly increased as contaminant concentration decreased. This gradual increase with decreasing NAC concentration was not seen when formate at concentrations over 150 ppm was used as a reductant. Regardless of NAC concentration, removal efficiency was approximately 70%. Additionally, even at very low formate concentrations (15 ppm) no catalyst poisoning was observed.

- **Reaction rates and removal efficiencies of a palladium catalyst using formate as a reductant show potential for use in an HFTW.** The reaction rates and removal efficiencies for 2-NT achieved by formate show promise for in-well use as part of an HFTW system. More heavily nitrated compounds such as TNT and RDX are harder to degrade and have more byproducts, which must also be accounted for if the technology is to be used in the field. Up to 75% of the 2-NT was removed with a single-pass of contaminated water through a reactor with a residence time of only 1 minute, but other applications of HFTWs have required single-pass efficiencies as high as 85% to achieve required concentration goals downgradient of the HFTW system. However, additional recirculation of contaminated water between the wells may permit a properly designed HFTW system to successfully contain groundwater plumes with relatively high (> 25 ppm) NAC concentrations. Reactor sizing calculations based on experimentally determined rate parameters have shown that a

Pd/formate system could be installed in a reactor similar in size to those which are currently being evaluated in the field. Cost comparison data has also shown that formic acid is approximately four times cheaper than hydrogen gas as a reductant. In addition, formic acid does not have the safety concerns associated with storing, transporting, and injecting hydrogen gas.

5.3 Future Work

- **Extend studies to examine other NACs.** This thesis has investigated reduction of one of the simplest NACs to gain basic understanding. Future work should be done with more nitrated compounds such as DNT, HMX, RDX, and TNT. The effects of the additional nitro groups on the kinetics of this reaction should be compared to the NT kinetics observed in this study.
- **Continued investigation of formate as a reductant.** It has been demonstrated that formate has some properties that may make it superior to hydrogen as a reductant. Additional investigation into the effects of pH on reaction rate while using formate as a reductant on DNT, RDX, HMX, and TNT will help us to further understand how formate might be applied.
- **Conduct byproduct characterization.** Peak area data for byproducts was collected in both the batch studies and column experiments, but standards for preparing a calibration curve and identifying the byproducts were unavailable. This is a very important step in determining the feasibility of using palladium in HFTWs because for use, the byproducts of the catalytic reaction must be harmless.

- **Incorporate results into an existing HFTW model.** HFTW modeling for chlorinated ethene destruction by Pd catalysis has been accomplished by Stoppel (2001) and Ferland (2000). These models can perhaps be modified to model catalytic destruction of NACs in an HFTW system.
- **Investigate poisoning of palladium .** Understanding must be gained into the cause and effects of catalyst poisoning. What is the effective loss in reaction rate due to poisoning, how long does it last, and what is the best way to buffer the system to avoid this from happening are all questions that should be investigated.

APPENDIX A: ADDITIONAL COLUMN EXPERIMENT RESULTS

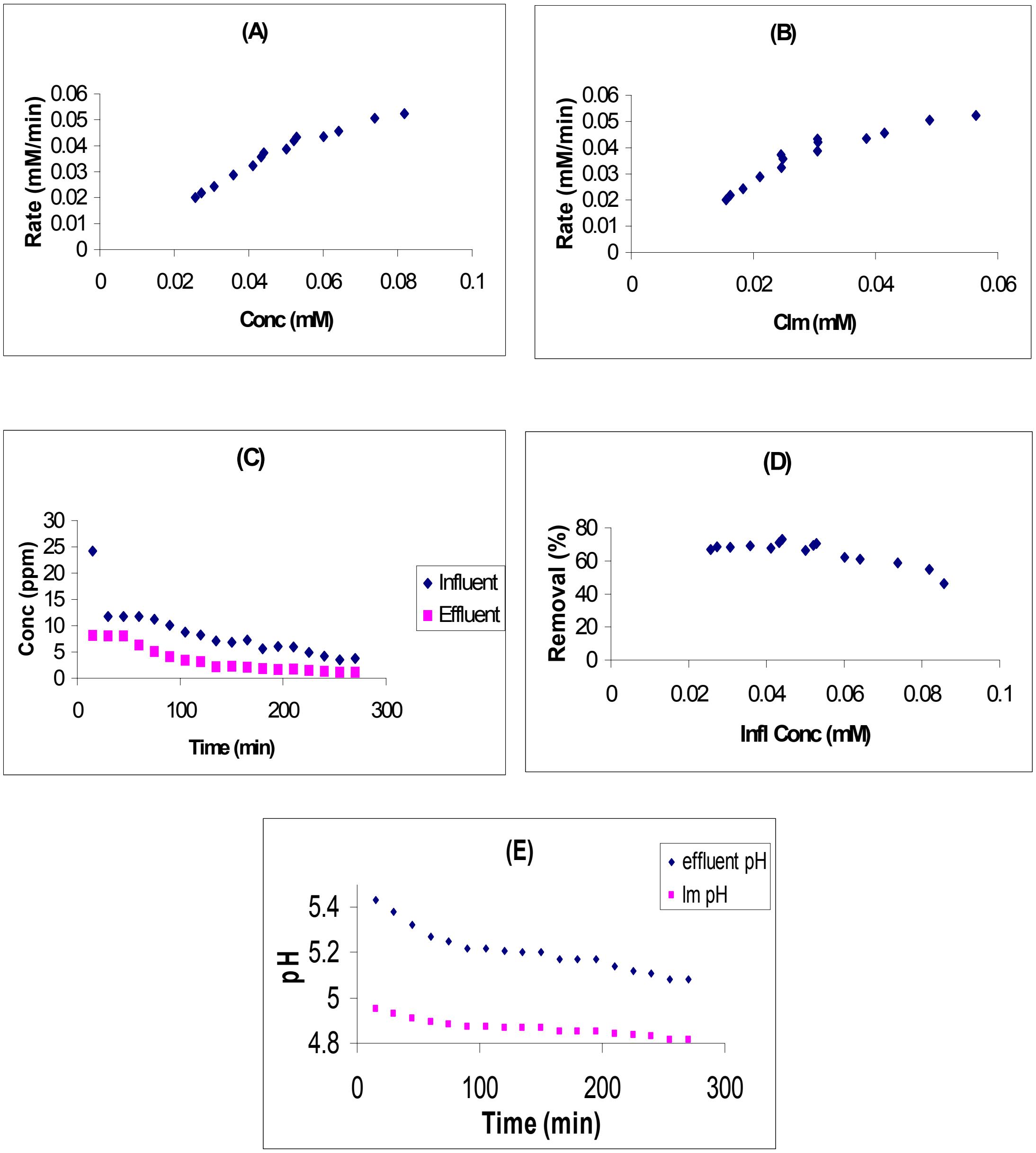

Figure A.1 LCE #3 – 100% H_2 pH = 4.60 (A) Degradation Rate vs. Measured Influent Concentration (B) Degradation Rate vs. Clm (C) Influent 2-NT Conc. vs, Effluent Conc. (D) Fraction of 2-NT Removed (E) Measured pH over time

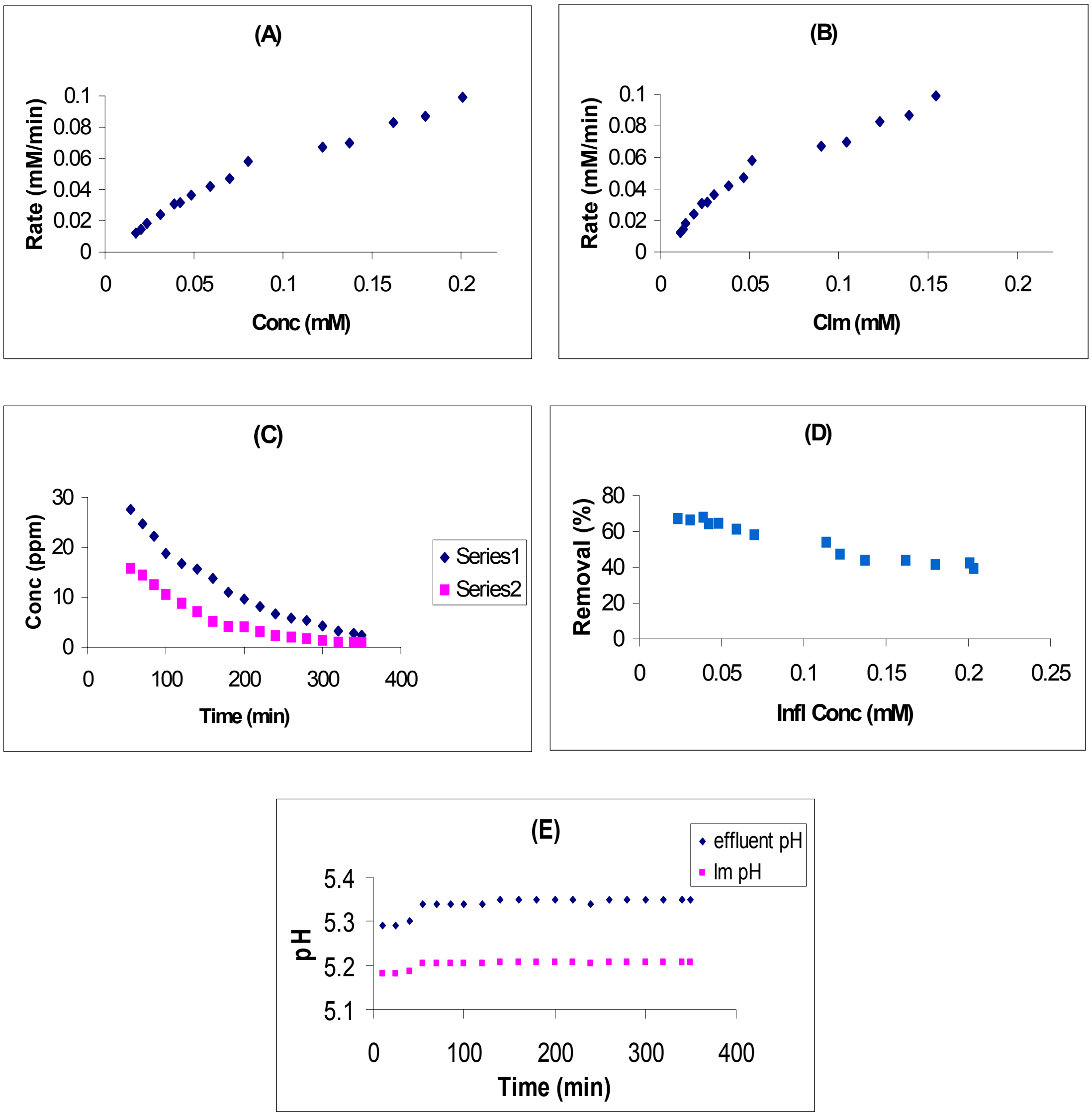

Figure A.2 LCE #4 – 100% H_2 pH = 5.08 (A) Degradation Rate vs. Measured Influent Concentration (B) Degradation Rate vs. Clm (C) Influent 2-NT Conc. vs, Effluent Conc. (D) Fraction of 2-NT Removed (E) Measured pH over time

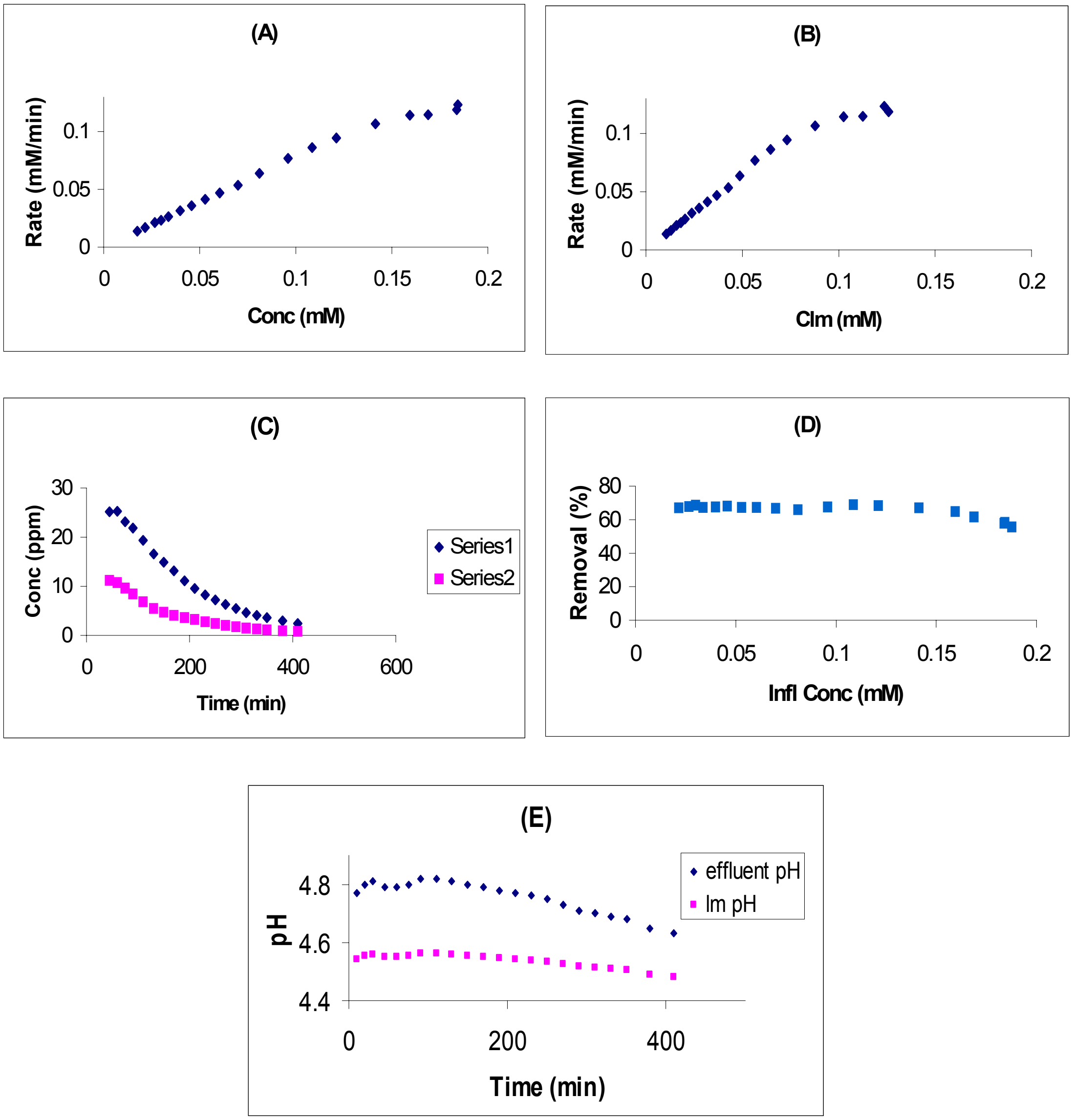

Figure A.3 LCE #5 – 100% H_2 pH = 4.35 (A) Degradation Rate vs. Measured Influent Concentration (B) Degradation Rate vs. Clm (C) Influent 2-NT Conc. vs, Effluent Conc. (D) Fraction of 2-NT Removed (E) Measured pH over time

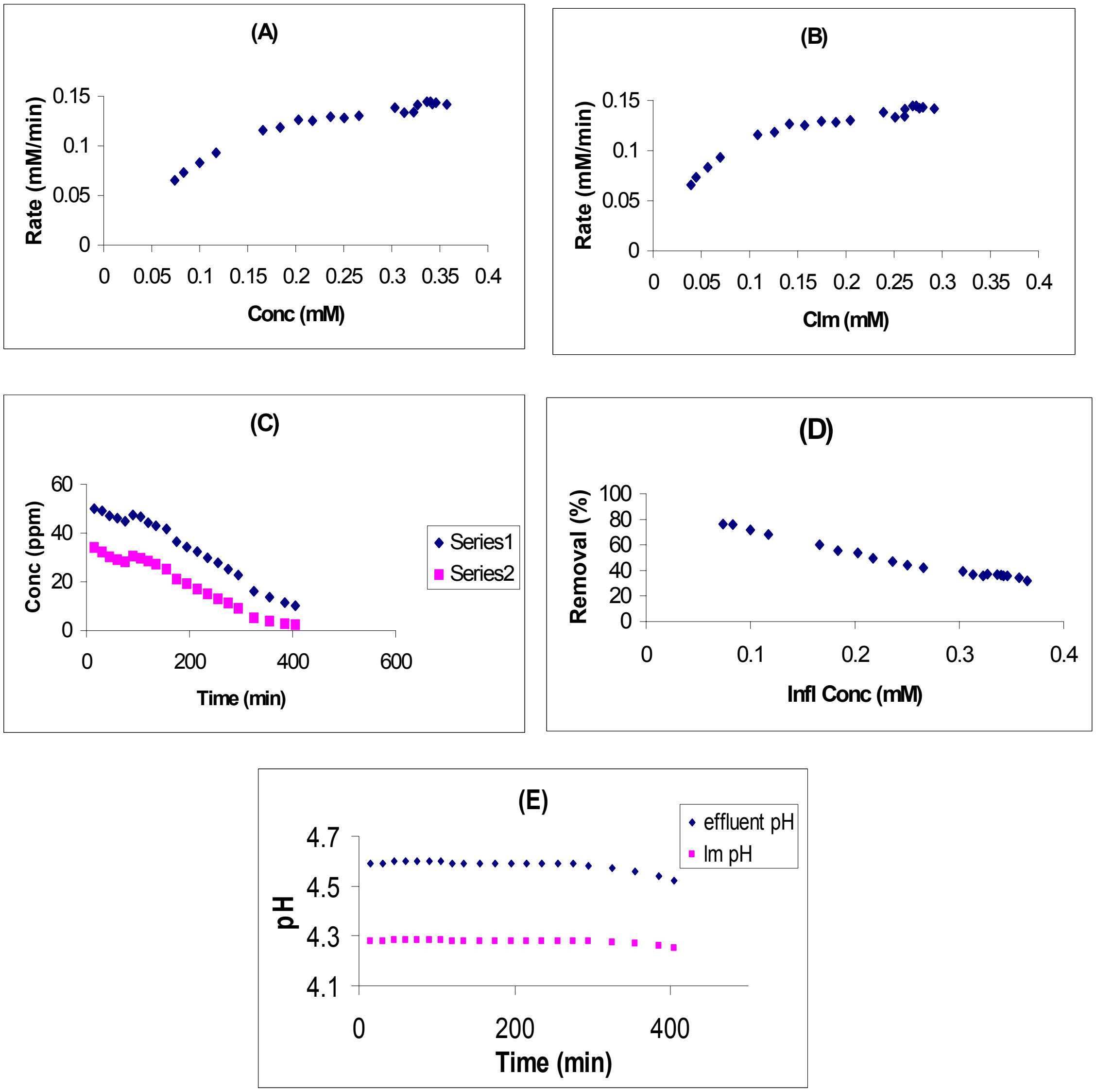

Figure A.4 LCE #6 – 100% H_2 pH = 4.0 (A) Degradation Rate vs. Measured Influent Concentration (B) Degradation Rate vs. Clm (C) Influent 2-NT Conc. vs, Effluent Conc. (D) Fraction of 2-NT Removed (E) Measured pH over time

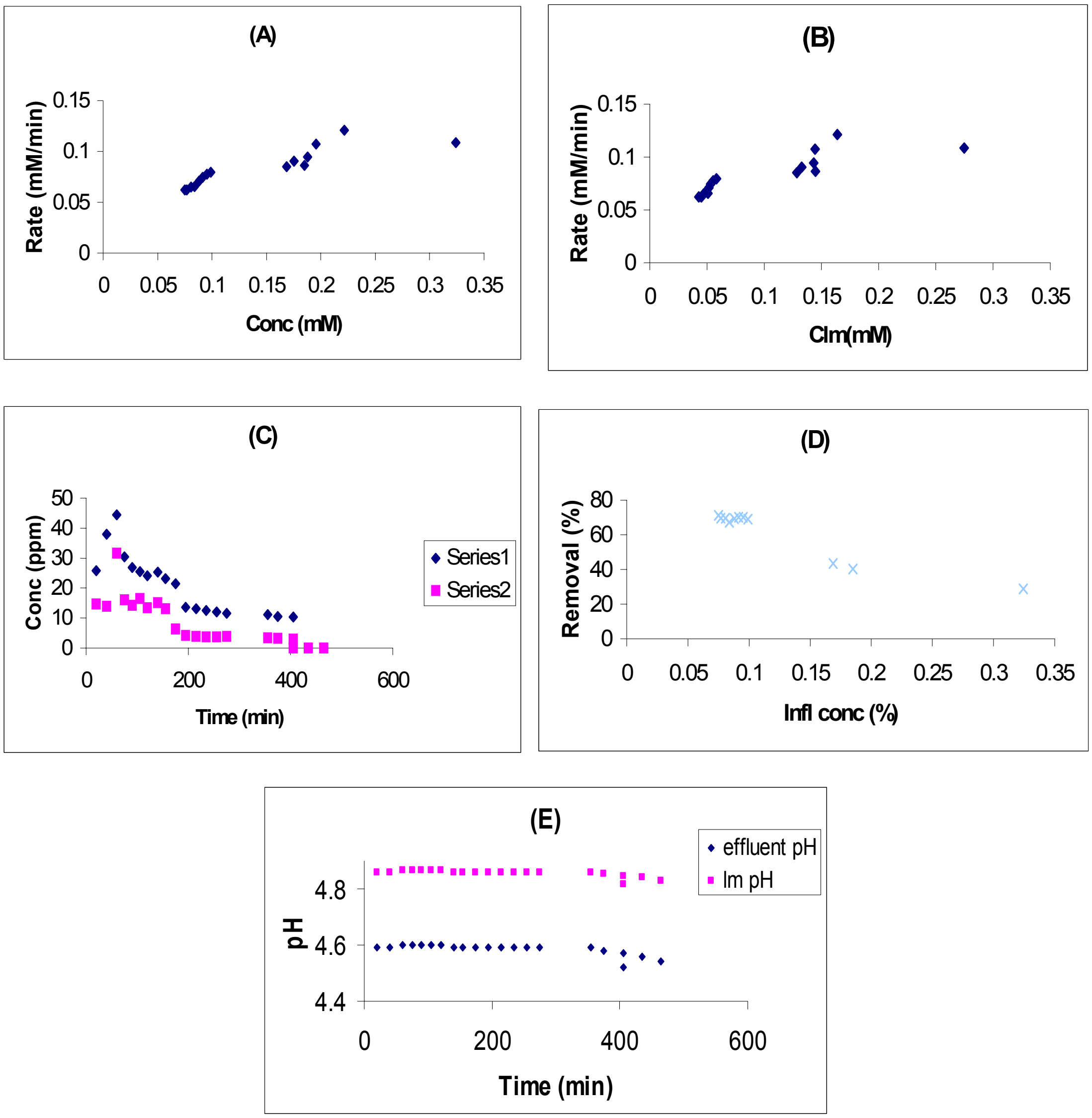

Figure A.5 LCE #7b – 100% H_2 pH = 5.2 (A) Degradation Rate vs. Measured Influent Concentration (B) Degradation Rate vs. Clm (C) Influent 2-NT Conc. vs, Effluent Conc. (D) Fraction of 2-NT Removed (E) Measured pH over time

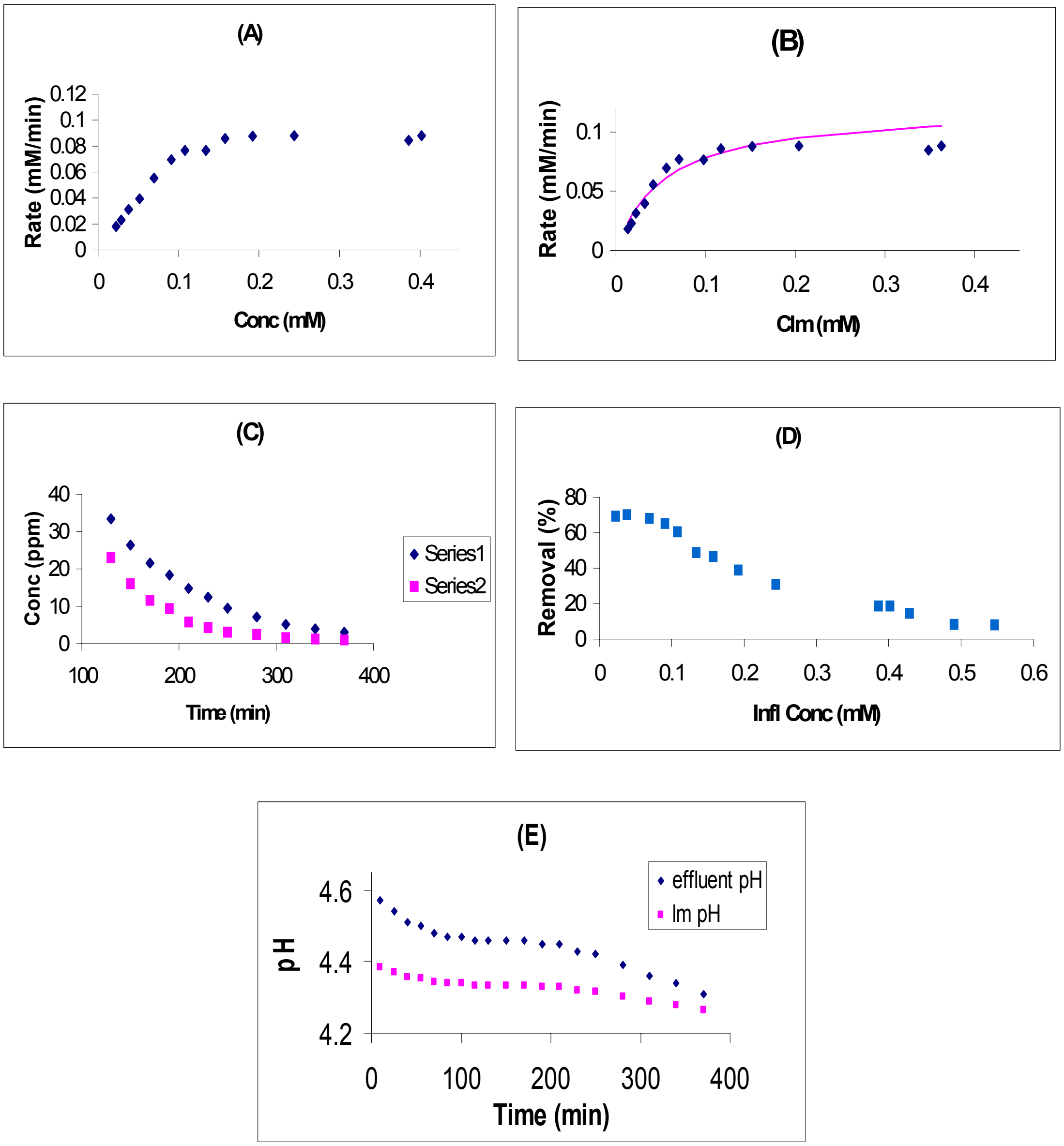

Figure A.6 LCE #8 – 80% H_2 + 20%CO_2 pH = 4.2 (A) Degradation Rate vs. Measured Influent Concentration (B) Degradation Rate vs. Clm (C) Influent 2-NT Conc. vs, Effluent Conc. (D) Fraction of 2-NT Removed (E) Measured pH over time

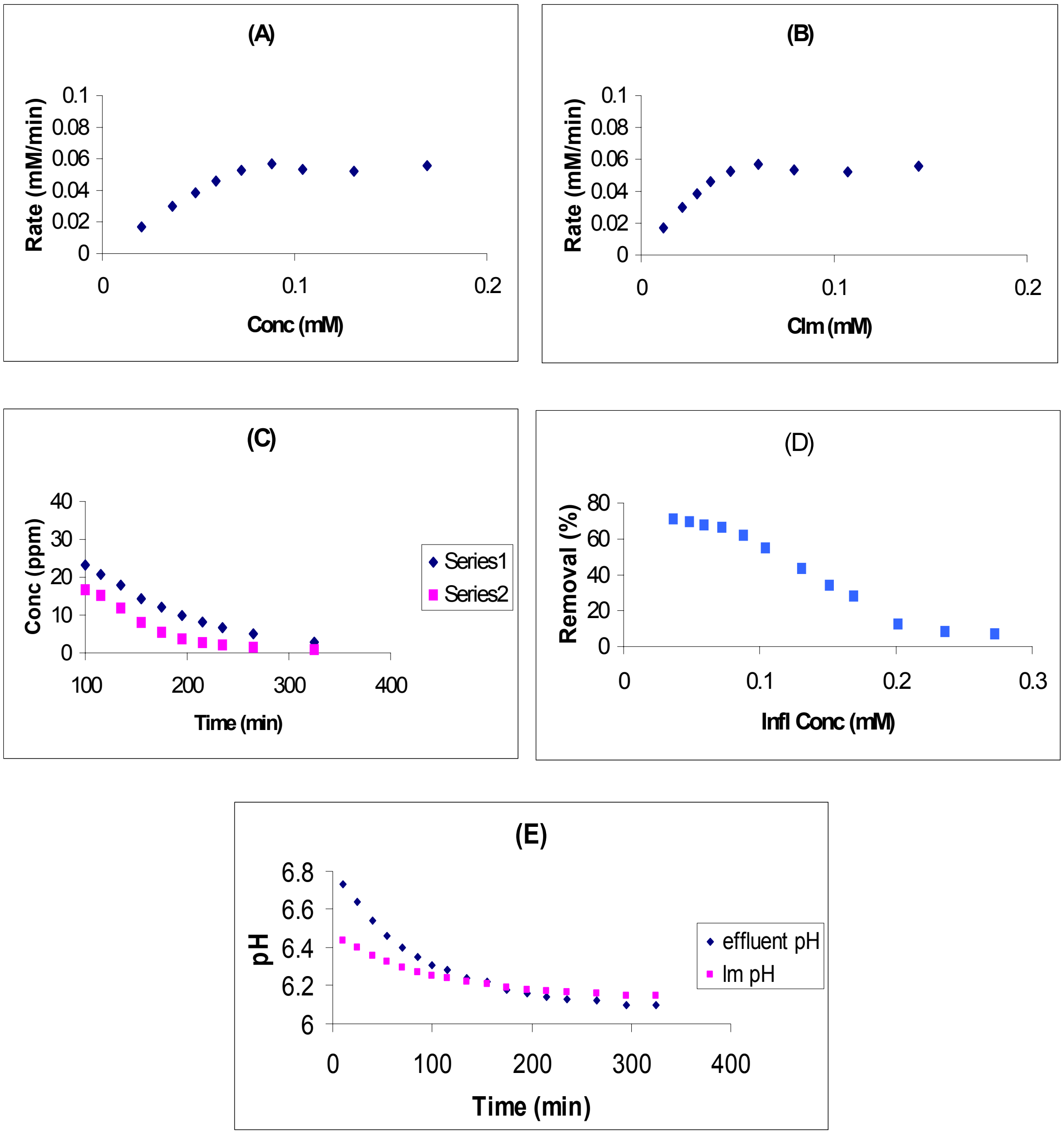

Figure A.7 LCE #9 – 80% H_2 + 20%CO_2 pH = 6.2 (A) Degradation Rate vs. Measured Influent Concentration (B) Degradation Rate vs. Clm (C) Influent 2-NT Conc. vs, Effluent Conc. (D) Fraction of 2-NT Removed (E) Measured pH over time

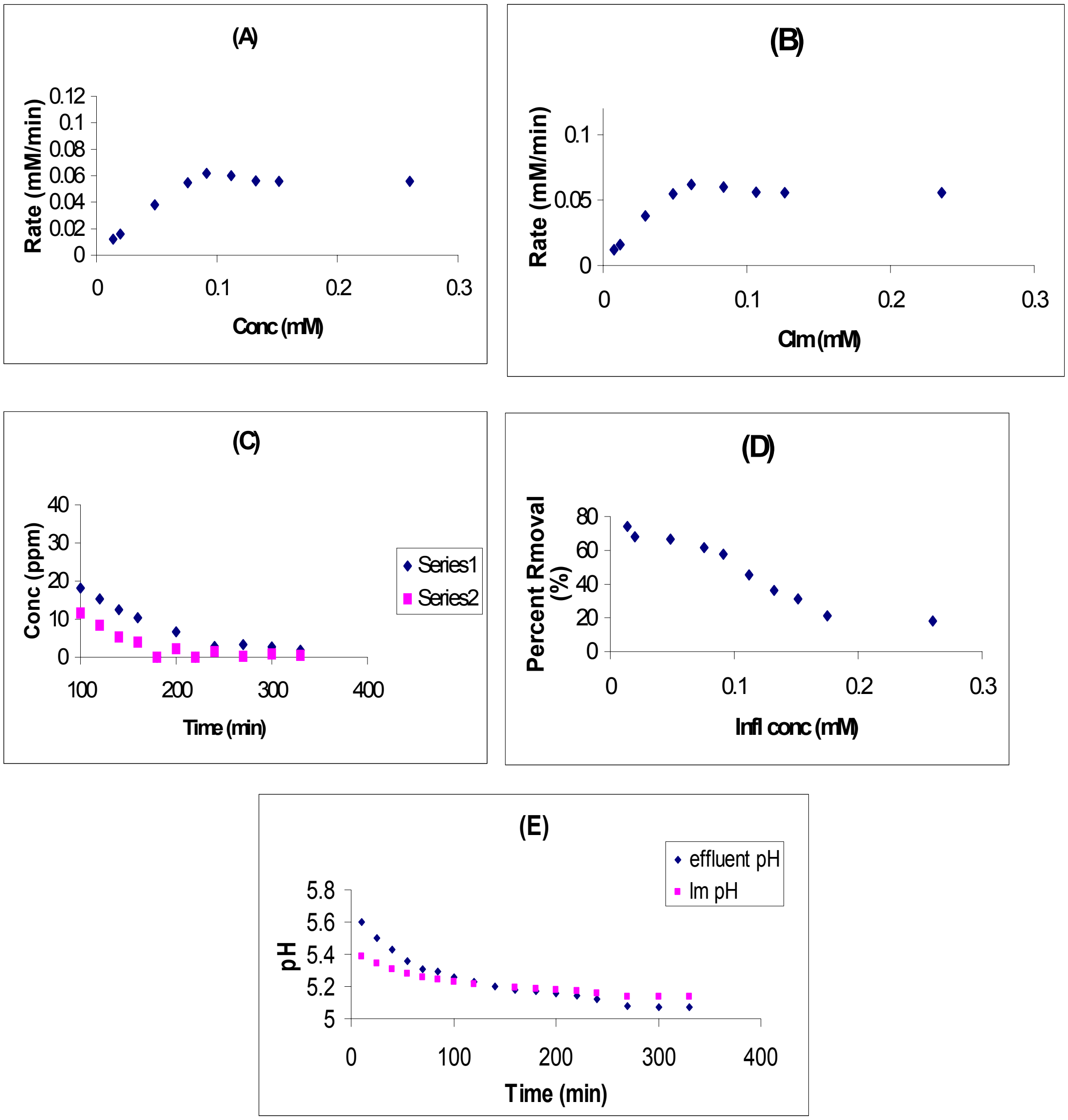

Figure A.8 LCE #10 – 80% H_2 + 20%CO_2 pH = 5.2 (A) Degradation Rate vs. Measured Influent Concentration (B) Degradation Rate vs. Clm (C) Influent 2-NT Conc. vs, Effluent Conc. (D) Fraction of 2-NT Removed (E) Measured pH over time

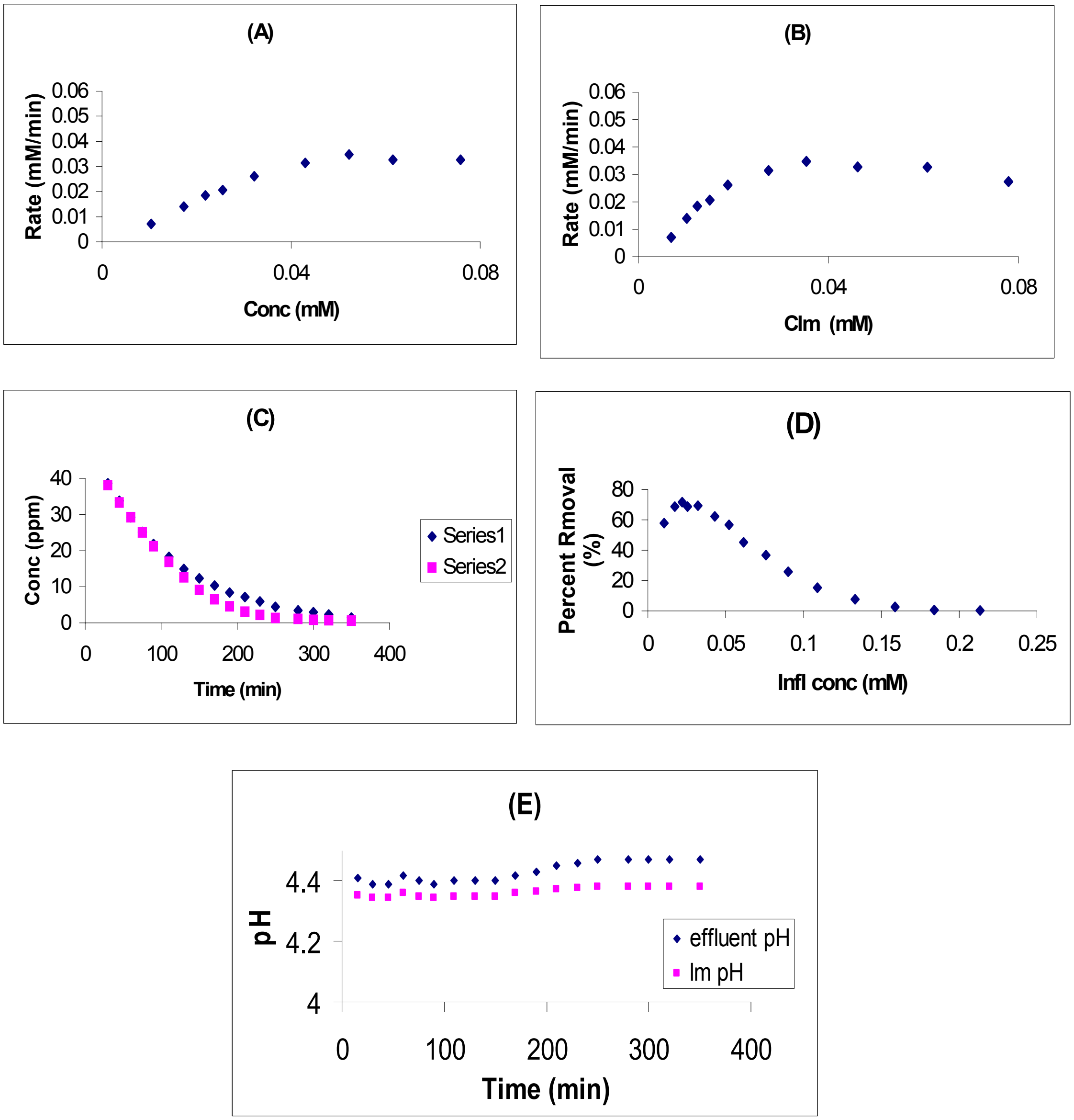

Figure A.9 LCE #11 – 50% H_2 (A) Degradation Rate vs. Measured Influent Concentration (B) Degradation Rate vs. Clm (C) Influent 2-NT Conc. vs, Effluent Conc. (D) Fraction of 2-NT Removed (E) Measured pH over time

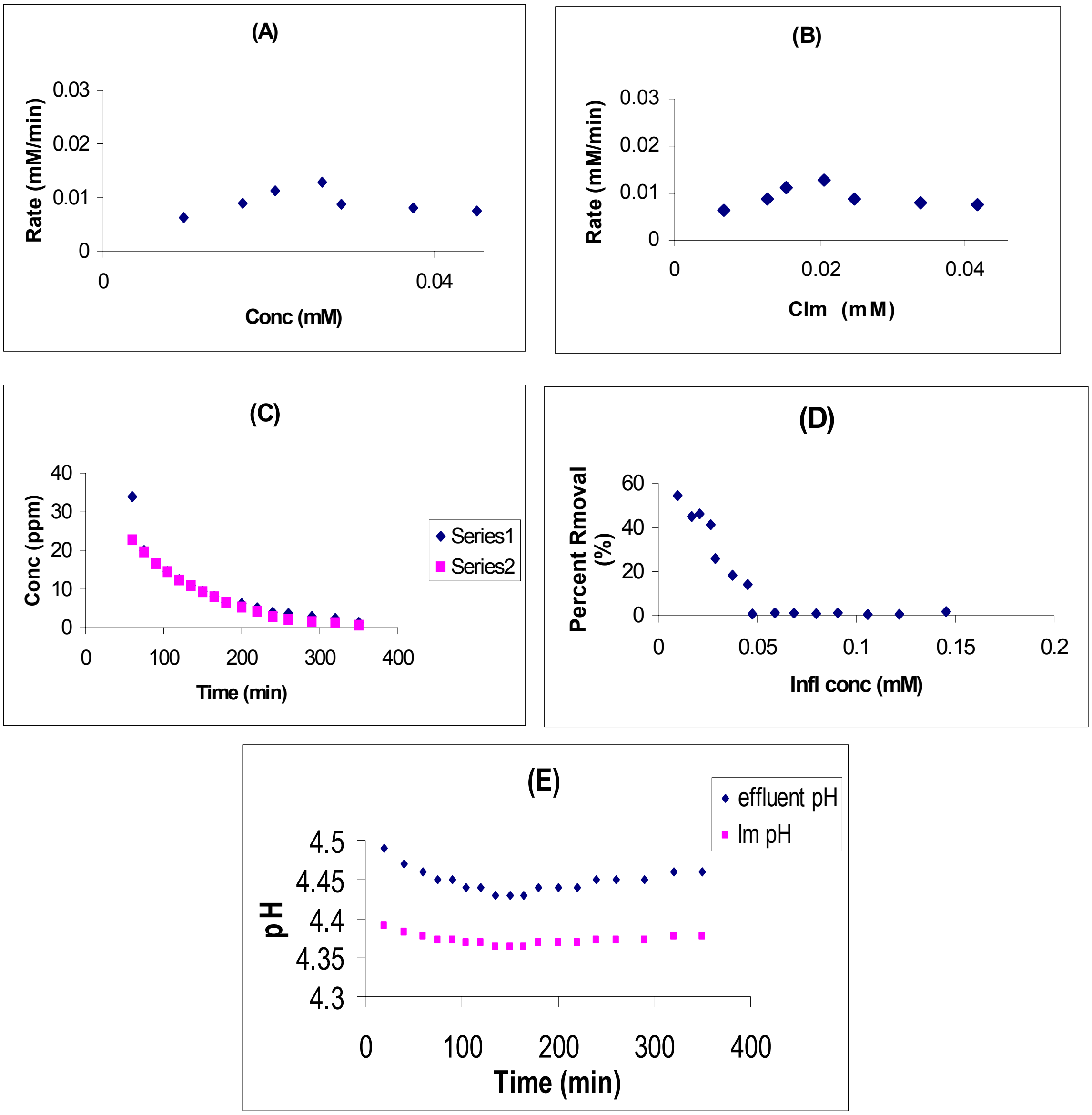

Figure A.10 LCE #12 – 20% H_2 (A) Degradation Rate vs. Measured Influent Concentration (B) Degradation Rate vs. Clm (C) Influent 2-NT Conc. vs, Effluent Conc. (D) Fraction of 2-NT Removed (E) Measured pH over time

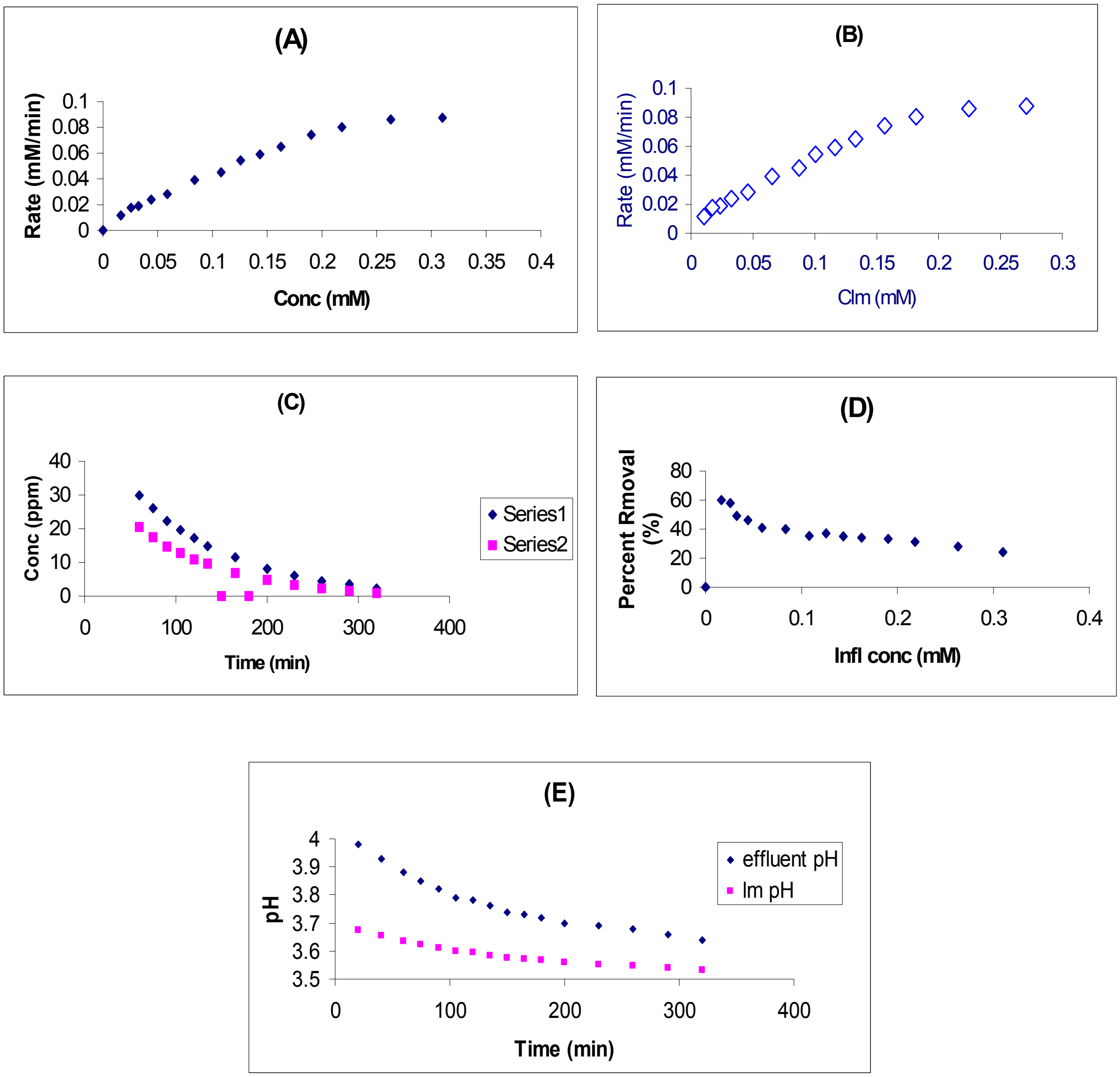

Figure A.11 LCE #13 – 50 ppm formate (A) Degradation Rate vs. Measured Influent Concentration (B) Degradation Rate vs. Clm (C) Influent 2-NT Conc. vs, Effluent Conc. (D) Fraction of 2-NT Removed (E) Measured pH over time

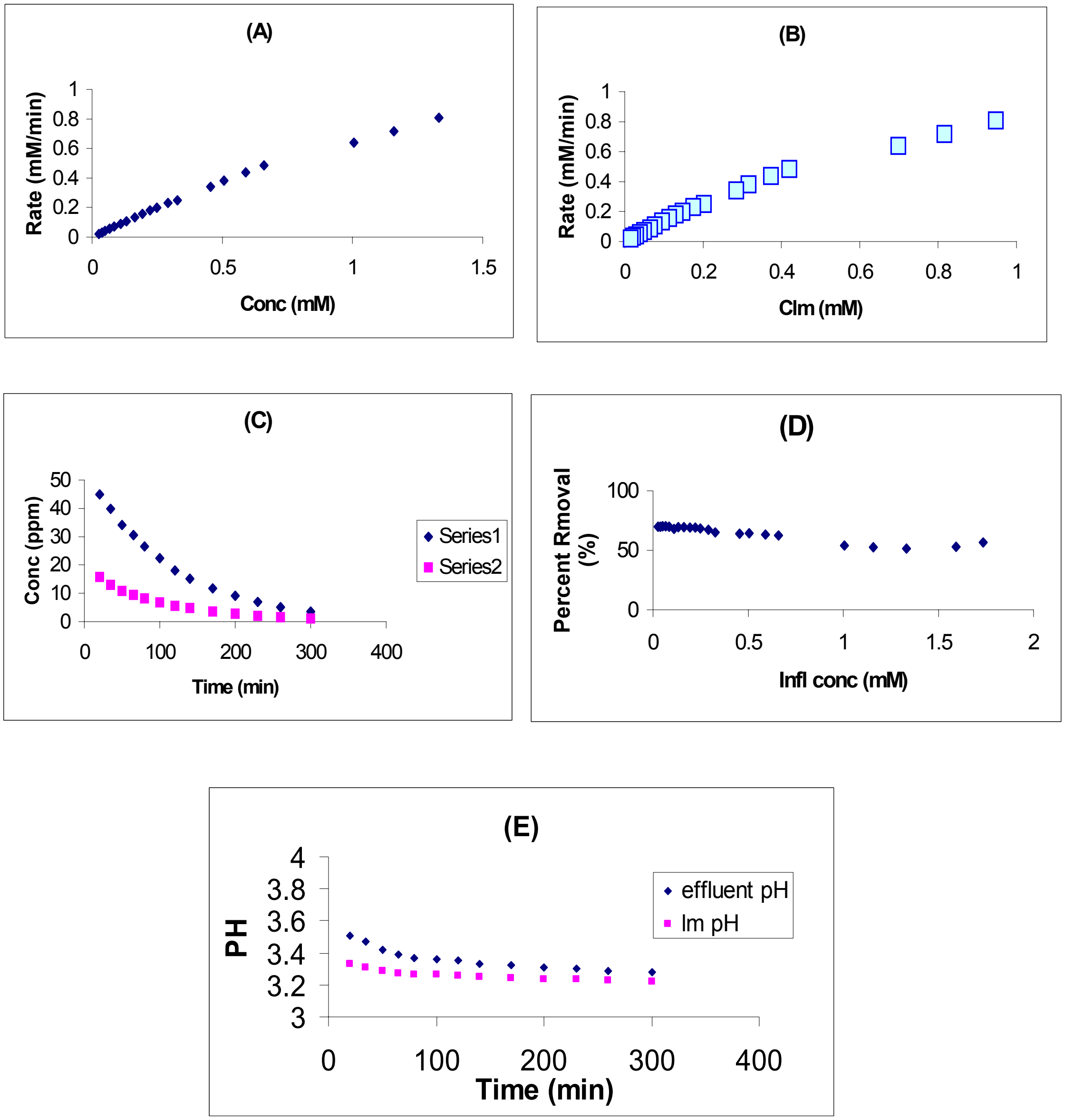

Figure A.12 LCE #14 – 150 ppm formate (A) Degradation Rate vs. Measured Influent Concentration (B) Degradation Rate vs. Clm (C) Influent 2-NT Conc. vs, Effluent Conc. (D) Fraction of 2-NT Removed (E) Measured pH over time

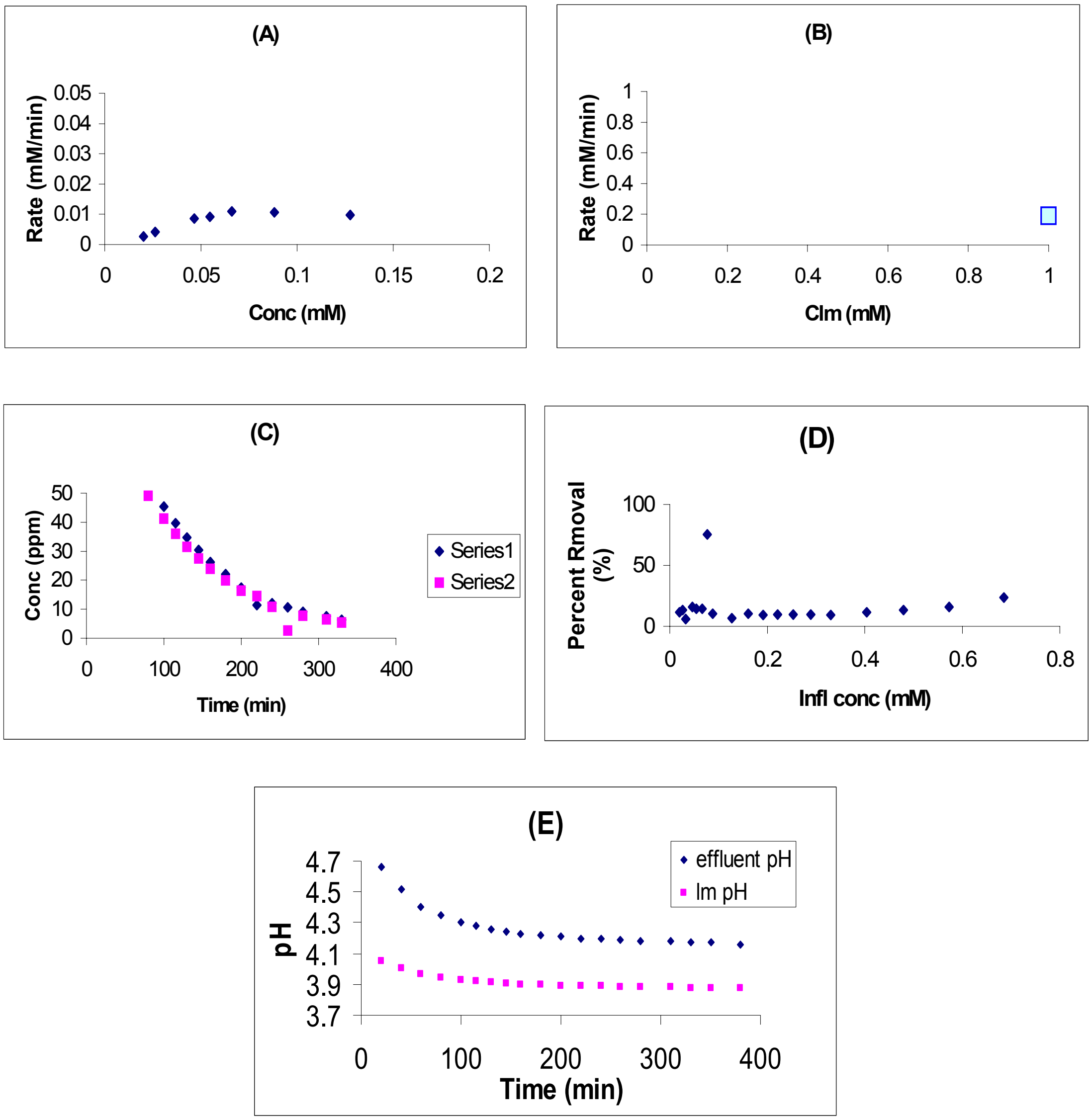

Figure A.13 LCE #15 - 15 ppm Formate (A) Degradation Rate vs. Measured Influent Concentration (B) Degradation Rate vs. Clm (C) Influent 2-NT Conc. vs, Effluent Conc. (D) Fraction of 2-NT Removed (E) Measured pH over time

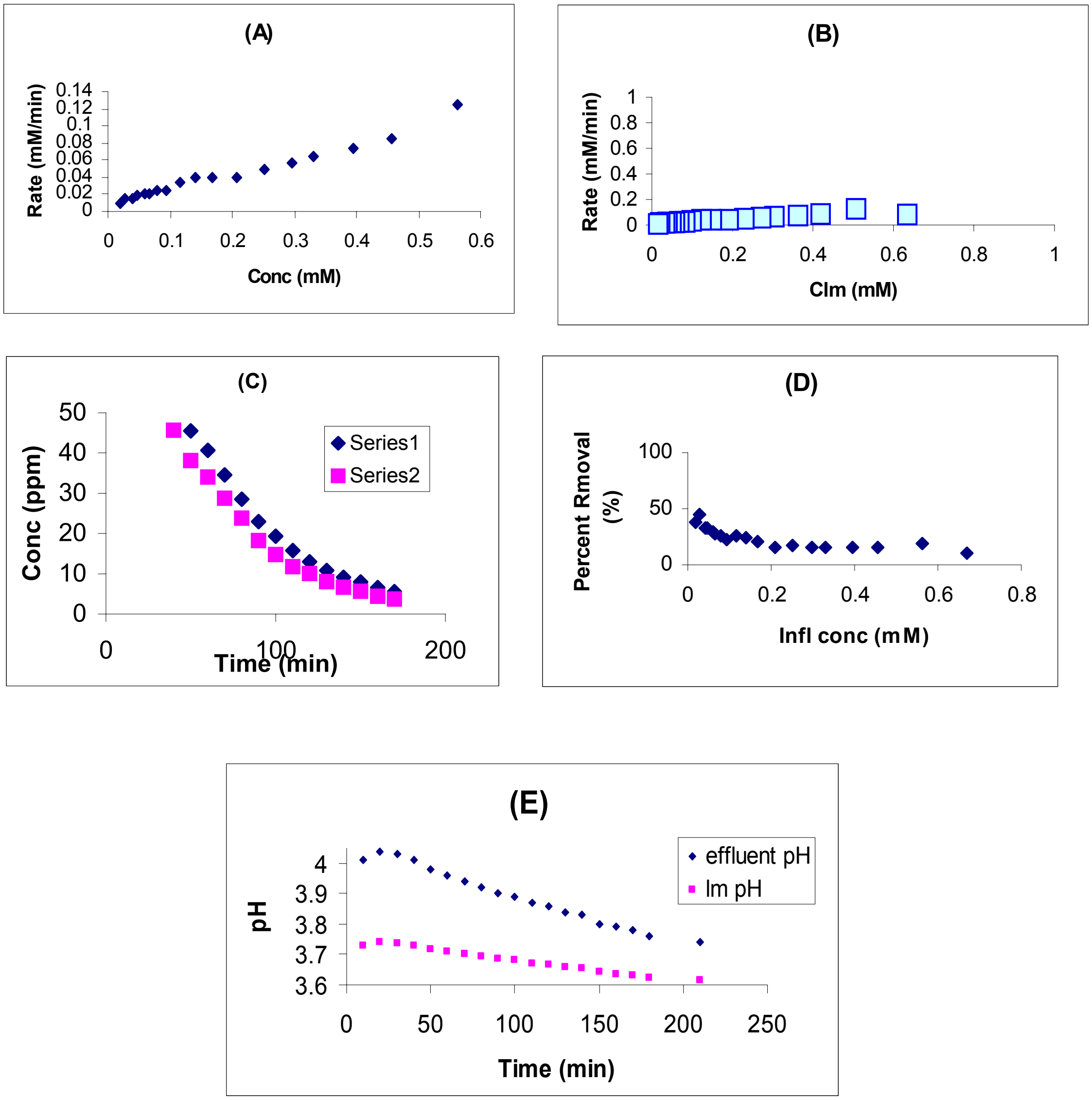

Figure A.14 LCE #16 - 50 ppm Formate 75 mL/min (A) Degradation Rate vs. Measured Influent Concentration (B) Degradation Rate vs. Clm (C) Influent 2-NT Conc. vs, Effluent Conc. (D) Fraction of 2-NT Removed (E) Measured pH over time

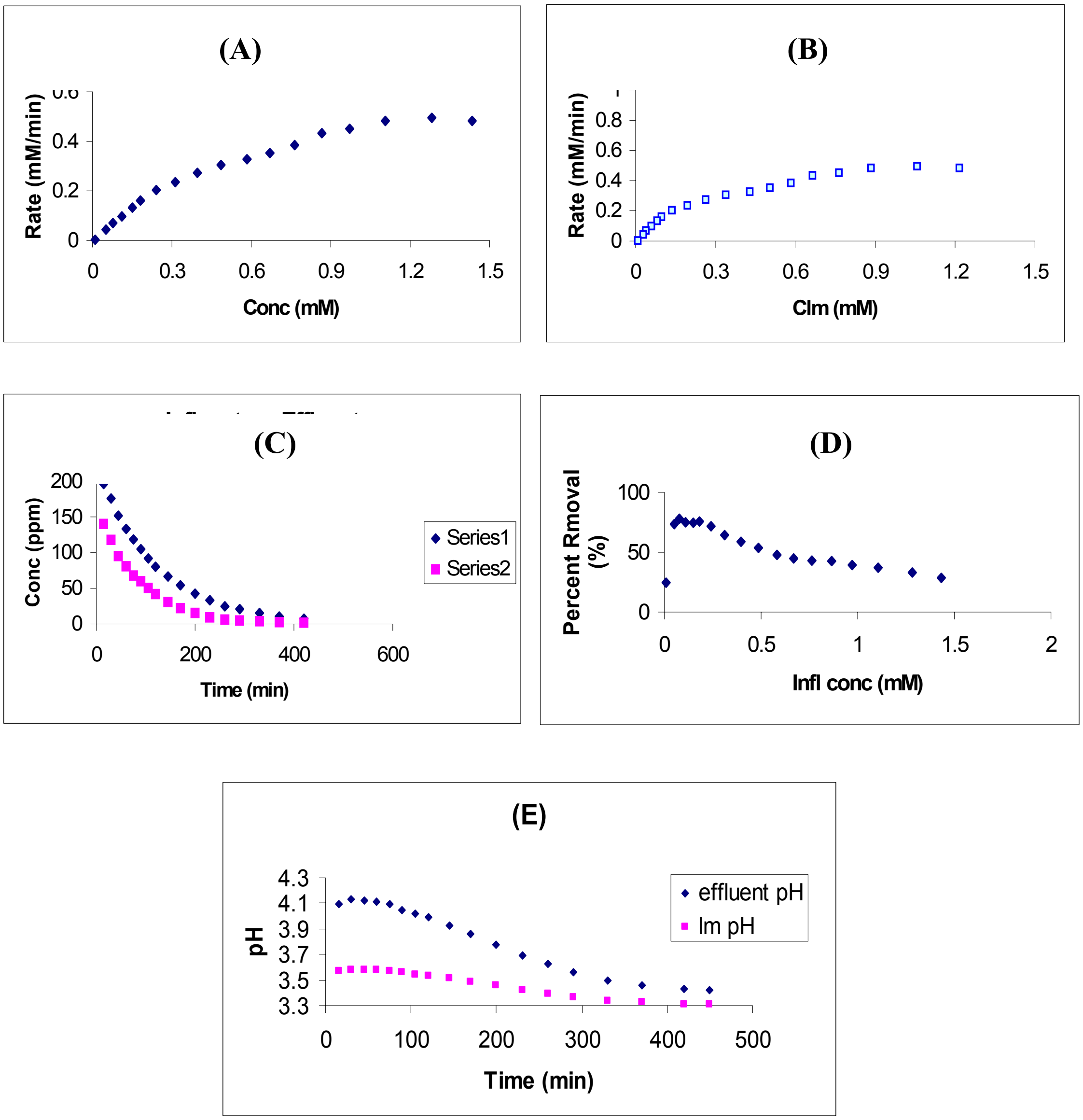

Figure A.15 LCE # 17 - 100 ppm formate (A) Degradation Rate vs. Measured Influent Concentration (B) Degradation Rate vs. Clm (C) Influent 2-NT Conc. vs, Effluent Conc. (D) Fraction of 2-NT Removed (E) Measured pH over time

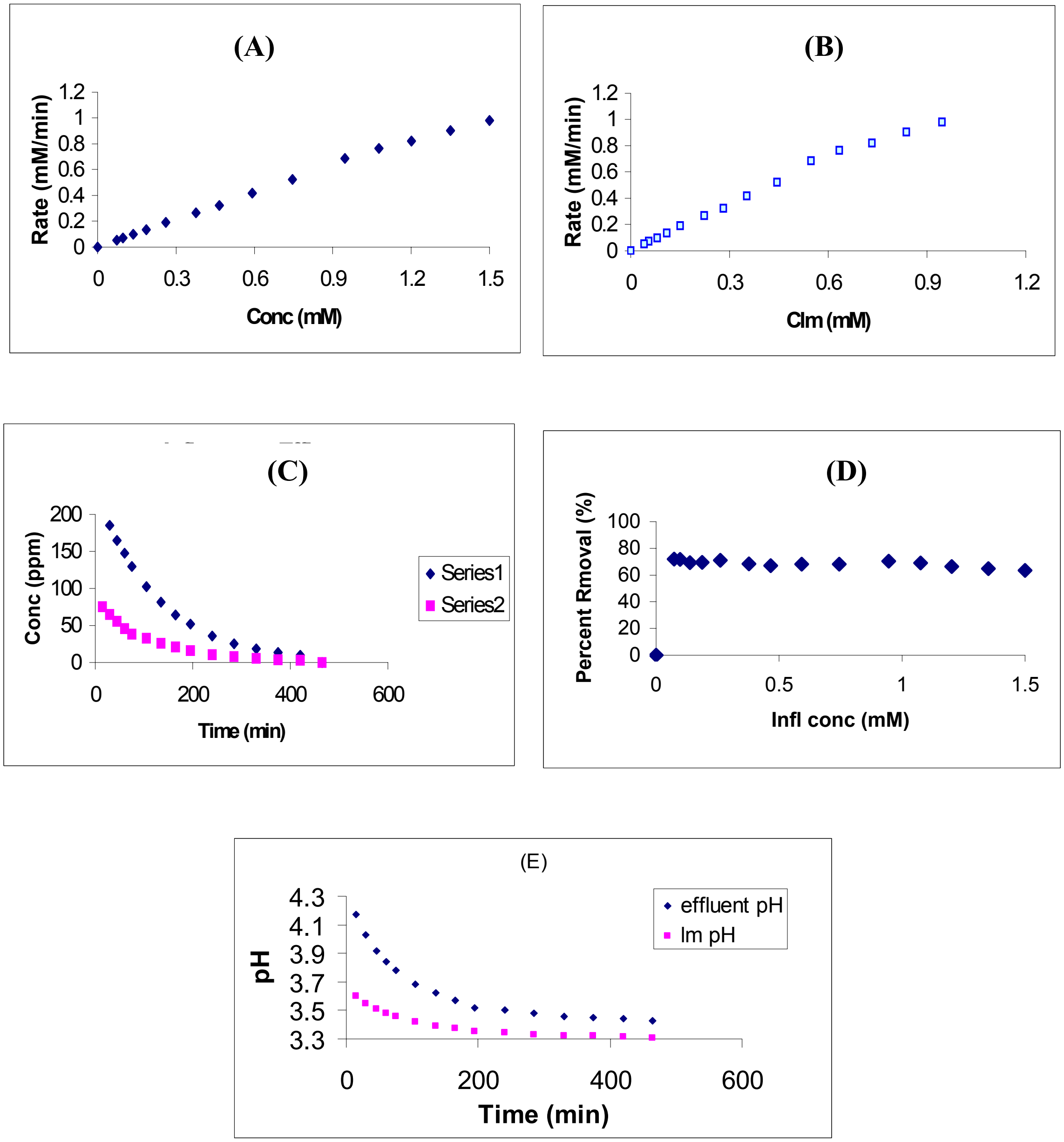

Figure A.16 LCE # 18 - 350 ppm formate (A) Degradation Rate vs. Measured Influent Concentration (B) Degradation Rate vs. Clm (C) Influent 2-NT Conc. vs, Effluent Conc. (D) Fraction of 2-NT Removed (E) Measured pH over time

APPENDIX B: FORMIC ACID VS. MOLECULAR HYDROGEN COST COMPARISON

Cost Comparison of Using 50 ppm Formic Acid vs. H_2 Gas at Solubility Limit to Treat 3,785 L of NAC-Contaminated Water

Formic Acid:

55 gallon (208 L) drum of (88%) formic acid ~ $400

$C_1V_1 = C_2V_2$

$(0.88)^* V_1 = (50\text{ppm})^*(3{,}785\text{L})$ where V_1 = volume of 88% formic acid needed to dose 3,785 L of water at 50 ppm

$V_1 = 0.215$ L

208 L per drum/0.215 L per 3,785 L water so 1 drum can treat 3.66×10^6 L and cost is $400/$3.66 \times 10^6$ L x 3,785 L/1000 gal = **$0.41/1000 gallon**

Hydrogen:

Hydrogen tank (51"L X 9"dia = 53L) @ 2300psig ~ $180

$$n = \frac{PV}{RT} \qquad \frac{(156 \text{ atm})\ (53 \text{ L})}{(.082 \text{ atm, L/ g-mole, deg K})(298 \text{ K})}$$

n = 338 moles H_2 per tank $180/338moles = $0.53/mole

solubility of hydrogen = .0214 vol/vol

1000 gal H_2O = 3,785 L*(.0214 vol/vol) = 75 L H_2 solubility limit

$$n = \frac{PV}{RT} \qquad \frac{(1 \text{ atm})\ (75 \text{ L})}{(.082 \text{ atm, L/ g-mole, deg K})\ (298 \text{ K})}$$

n ~ 3.1 moles 3.1 moles H_2/1000 gallon water*($0.53/mole) = **$1.65/1000 gallon**

APPENDIX C: REACTOR SIZING CALCULATIONS

In the Edwards AFB field evaluation of an HFTW system, two treatment wells located 10 m apart and pumping at approximately 38 L/min produced an interflow (I_{avg}) of ~ 85% (McCarty et al., 1998; Christ et al., 1999):

For 99% removal of 1 ppm 2-NT (to < 10 ppb):

$$\frac{C_{down}}{C_{up}} = 0.01 = \frac{(1-\eta_{sp})(1-I_{AVG})}{1-I_{AVG}(1-\eta_{sp})}$$

where C_{down} and C_{up} are 2-NT concentrations downgradient and upgradient of the HFTW system, respectively (Christ et al., 1999)

$$.01 = \frac{(1 - \eta_{sp})(1 - .85)}{1 - .85(1-\eta_{sp})}$$

so $\eta_{sp} = .937$

$k_1 = 1.8\ \text{min}^{-1}$ (from experiment LCE #16)

$C / C_o = (1-\eta_{sp}) = 0.063 = \exp(-kt_{res})$ where t_{res} is the residence time in the reactor

$0.063 = \exp(-1.8\ \text{min}^{-1} * t_{res})$ so $t_{res} = 1.54$ min

for 1.54 min residence time $= \dfrac{58.5\ \text{L pore volume}}{38\ \text{L/ min}}$

for porosity = 40%, necessary reactor volume = 58.5 L/.40 = 146L

cylindrical reactor dimensions: Vol = 146 L = 5.16 ft^3

Vol = 5.16 ft^3 = L $(\pi * r^2)$

Possible reactor sizes: L = 9.5 ft, dia = 10”

L = 14.8 ft, dia = 8 “

L = 26.3 ft, dia = 6 “

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14. ABSTRACT

Production of energetics such as 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrasocine (HMX) for use in munitions has created a DoD-wide problem due to improper disposal techniques. The natural breakdown of these contaminants creates byproducts such as amines, which are known neurotoxins and carcinogens. The focus of this study was to determine the effectiveness of using a palladium (Pd) catalyst to reductively destroy NAC-contaminated groundwater under various conditions and to assess the feasibility of using a catalytic reactor in a horizontal flow treatment well (HFTW) system. Experimental results indicate reaction rates are dependent on both pH and reductant concentration in all experimental catalyst/reductant systems. It was observed that destruction rates were greater when formate, rather than hydrogen, was sued as a reductant. Based on experimentally determined reaction rates and removal efficiencies, it appears there is promise for in-well use of Pd catalysis with a formate reductant as part of an HFTW system.

15. SUBJECT TERMS

Groundwater contamination, palladium catalyst, nitro aromatic compounds, Michaelis-Menton kinetics, formic acid

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