DEVELOPMENT OF AN ELECTROCHEMICAL PRIMARY TREATMENT FOR

HEXAHYDRO-1,3,5-TRINITRO-1,3,5-TRIAZINE LADEN WASTEWATER

by

Jared Lynn Johnson

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HEXAHYDRO-1,3,5-TRINITRO-1,3,5-TRIAZINE LADEN WASTEWATER

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This thesis explores the development of direct electrochemical reduction as a means of providing primary treatment of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in a manufacturing process waste stream. An industrial process wastewater laden with RDX was successfully treated in small batch reactors. Reaction kinetics were used to design a proof of concept bench scale flow reactor that utilized parallel packed electrode plates. Following successful testing of this reactor, a pilot scale packed electrode flow reactor was built. The reactor performance as a function of residence time was fit by a first order decay equation. Greater than 97% reduction of RDX in a process wastewater was observed at a reactor residence time of 27 minutes. The work presented herein was successful in creating an electrochemical treatment system capable of removing RDX from an industrial process waste stream with no chemical addition, and without creating an additional hazardous waste stream.

DEDICATION

This research is dedicated to my wife, Karen, and my sons, Isaiah, Peter, and Gideon.

ACKNOWLEDGEMENTS

The author expresses his sincere gratitude for everyone who has assisted in the development and pursuit of this research. Dr. James Martin has shown exceeding patience in dealing with a non-traditional student with odd notions of research topic. The other committee members, Dr. Mark Bricka, Dr. Benjamin Magbanua, and Dr. William McAnally, also share this trait. None of this research would have gone forward without the sponsorship and mentoring of Dr. David Gent of the US Army Engineer Research and Development Center, who made available laboratory resources and guidance throughout.

TABLE OF CONTENTS

LIST OF TABLES

vii

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

The life cycle of military munitions constituents begins at Army Ammunition Plants (AAP), where the individual explosive constituents are produced and packaged. Explosive constituents are added to weapons system platforms at Load and Pack (LAP) plants. From that point, loaded munitions await use in storage. Munitions that are not fired during live training exercises and pass their useful life are demilitarized in specialized facilities. At each of the industrial operations in the munitions constituent life cycle, water may be used as part of the process or as part of area housekeeping. This creates a risk that water discharged from the operation may be contaminated with explosive constituents. Significant contamination is currently being treated at the former Nebraska Ordnance Plant (NOP) (Wani et al. 2007), the former Volunteer Army Ammunition Plant, and formerly used areas of Iowa Army Ammunition Plant. Continued production and processing of munitions constituents presents a continued risk of environmental exposure.

A major constituent in high explosive formulations is hexahydro-1,3,5-trintro-1,3,5-triazine (RDX). The United States Environmental Protection Agency (EPA) has determined RDX to be a possible carcinogen and set the lifetime drinking water health advisory at 2 µg/L (USEPA 2004). Some demonstrated options exist for treating RDX as

1

part of an industrial process waste stream. Granular activated carbon is in use at NOP (Wani et al. 2007) and Camp Edwards (Clausen et al. 2003) for cleanup of groundwater contamination. Anaerobic upflow bioreactors have been demonstrated to effectively remove explosives from the waste stream of McAlister AAP. This thesis will explore the development of a new technology, direct electrochemical reduction, as a means of providing primary treatment of RDX in a manufacturing process waste stream. The specific objectives will be to evaluate direct electrochemical reduction of RDX as a batch process to delineate the reaction kinetics as a function of reactive surface area and current density, and to develop a continuous flow treatment reactor capable of achieving 95% removal efficiency of RDX from a process manufacturing waste stream.

CHAPTER 2

LITERATURE REVIEW

RDX

Hexahydro-1,3,5-trinitro-1,3,5-triazine, also known as cyclotrimethylene-trinitramine, cyclonite, or RDX (Figure 1) is a powerful military explosive. The basic properties of RDX are given in Table 1. RDX was first synthesized and patented by Henning in 1899. A complete synthesis reaction was published by Hale (1925), and an alternative synthesis was discovered by Bachmann and Sheehan in 1941 and published later (1949). Since then it has been a major component of military munitions, including composition B and C-4.
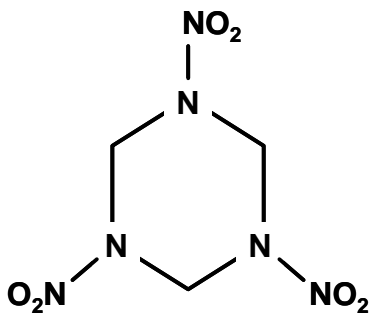
Figure 1   Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)

Table 1   Selected properties of RDX

CAS Number	121-82-4
Empirical Formula	$C_3H_6N_6O_6$
Molecular Weight	222.26 g/mol
Density	1.82 g/cm³
Melting Point	204.1°C
Aqueous Solubility	29 mg/L (10°C) 42 mg/L (20°C) 60 mg/L (25°C)

The United States Environmental Protection Agency (EPA) has determined RDX to be a possible carcinogen and set the lifetime drinking water health advisory at 2 µg/L (USEPA 2004). Contamination in the Cape Cod aquifer has forced a cessation of live fire training activities at Camps Edwards, MA (Clausen et al., 2003). Operating ammunition plants are also seeing increased regulatory interest (Hammack, 2008). In natural systems, RDX presents a greater risk for transport than 2,4,6-trinitrotoluene (TNT) partly because its soil partitioning coefficient has been observed to be an order of magnitude lower (Brannon and Pennington, 2002).

Treatment Options

Some demonstrated options exist for treating RDX as part of an industrial process waste stream. Granular activated carbon is in use at NOP (Wani et al., 2007) and Camp Edwards (Clausen et al., 2003) for cleanup of groundwater contamination. Where RDX mass loading onto GAC remains relatively low, this may work fine. Reports have indicated that explosive reactions may occur at loadings of ~10% (ORNL, 1988) and 8%

4

(Andern, 1975), though, indicating that the higher mass loadings corresponding to more concentrated waste streams may present a safety hazard. Army Environmental Command, along with EPA Region 10 and the Oregon Department of Environmental Quality, has used results that set the characteristic hazardous waste status of explosives laden soils at 12% (Noyes, 1996). Thermal regeneration of potentially explosive carbon is not recommended, though acetone (Fleming et al., 1996) and ethanol (Morley et al., 2005) have been studied as facilitators of RDX desorption from GAC. Solvent regeneration in this manner yields an RDX-laden solvent waste stream that must be treated, as well.

Alkaline hydrolysis of RDX has been reported since 1951 (Epstein and Winkler, 1951). Balakrishnan et al. (2003) proposed the mechanism of alkaline destruction of RDX detailed in Figure 2. Kinetic rates for this reaction have been reported in aqueous solutions (Heilmann et al., 1996, Hwang et al., 2006) and soil slurries (Brooks et al., 2003). The end products of alkaline hydrolysis at pH above 12 are primarily formate and nitrate (Davis et al., 2007). Alkaline hydrolysis is a relatively rapid and easy treatment for contaminated water and soil. It has been effectively demonstrated on active training ranges through the application of hydrated lime (Larson et al., 2008).

5
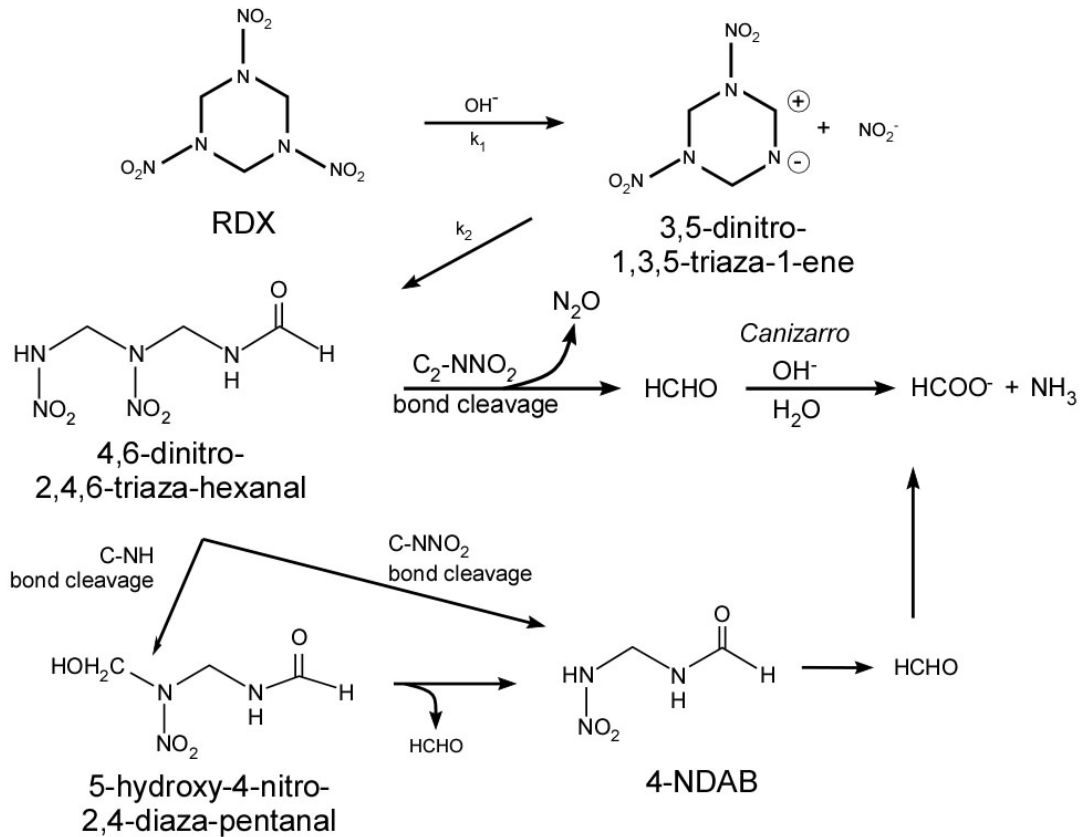
Figure 2   Mechanism of RDX destruction by alkaline hydrolysis proposed by
            Balakrishnan et al., 2003

RDX has proven susceptible to anaerobic biodegradation under a range of cultures and nutrient additions (Freedman and Sutherland, 1998, Wani and Davis, 2006, Beller, 2002, Binks et al., 1995). In situ biodegradation has been stimulated with the addition of both electron donors (Beller, 2002) and readily available carbon sources (Wani and Davis, 2006). Freedman and Sutherland (1998), with others, have reported that the presence of nitrates will inhibit the transformation of RDX. Bioremediation has been successfully demonstrated at the field scale as an in situ groundwater treatment

6

(Wani et al., 2007) and as a water treatment system in upflow fluidized bed reactors (Atikovic et al., 2008).

Iron and ferrous minerals have been demonstrated to degrade RDX in biologically active systems (Shrout et al., 2005, Oh et al., 2001, Wildman and Alvarez, 2001), as stand-alone mineral surfaces (Park et al., 2004, Hundal et al., 1997, Wanaratna et al., 2006), as nanoparticles (Naja et al., 2008), and as ions in solution (Kim and Strathmann, 2007). Investigations into the use of zero-valent iron have developed applications as permeable reactive barriers (Hundal et al., 1997), and as industrial wastewater treatment units (Oh et al., 2006).

Other unique technologies have been investigated for the destruction of RDX in environmental matrices. Various oxidative processes have been investigated for the degradation of RDX in water and soils (Bose, et al., 1998a-b, Adam et al., 2006, Fleming et al., 1997). These technologies make use of ultraviolet light either alone or in conjunction with chemical oxidants such as ozone or hydrogen peroxide. Advanced oxidation processes have been compared for treatment of RDX laden water ex situ (Fleming et al., 1997). Additional treatment technologies reported in the literature include nickel catalysts (Fuller et al., 2007), permanganate (Adam et al., 2004), plasma arc (Elmore and Lee, 1999), hydrogen sulfide (Kemper et al., 2008), mulch barriers (Ahmad et al., 2007), constructed wetlands (Low et al., 2007), and dithionite reduction (Boparai et al., 2008).

7

Electrochemical Cells

Electrochemistry may be broadly considered as the study of electron transfer, encompassing both oxidation and reduction. In practice, the term electrochemistry also infers an applied current or electric potential. The principles of electrochemistry have long been applied commercially in batteries, electroplating operations, and corrosion protection (Brown et al. 1997). In electrochemical engineering, it is helpful to think of an idealized electrochemical cell as the basis for defining electrochemical processes (Figure 3). Within the cell, electrons are transferred from a cathode to an anode through an electrolyte solution under the electric potential provided by a power supply. At the interface of cathode and electrolyte, electrons are transferred to chemical species creating reduced products. The reduced species and anions produced at the cathode migrate to the anode where complementary oxidation occurs at the anode/electrolyte interface.

8

DC Power Supply

`025`

e⁻

Anode

Cathode

cations →

← anions

mass transfer

R_{bulk} ——————→ R_{elec}

electron transfer

ne^-

mass transfer

P_{bulk} ←—————— P_{elec}

R_{bulk} : Reactant in bulk solution, R_{elec}: Reactant at electrode surface
P_{elec}: Product at electrode surface, P_{bulk}: Product in bulk solution
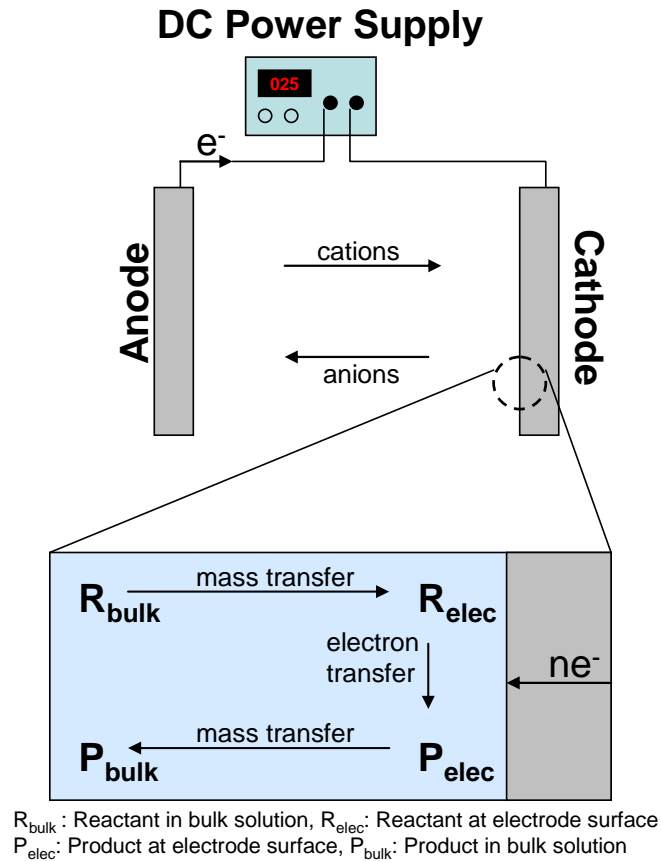
Figure 3   Idealized electrochemical cell.

Since direct reduction of reactants occurs at the surface of the electrode, the controlling processes in electrochemical reactions will be mass transport of reactants from the bulk fluid to the electrode surface, electron transfer to or from the reactants at the electrode surface, and mass transport of products from the electrode surface to the bulk fluid. In some electrochemical processes, it is desirable to prevent the complementary oxidation or reduction of reaction products. In these cases, a conductive membrane may be placed between the anode and cathode, creating separate anodic and cathodic compartments.

9

Electrochemical Treatment of Process Waste Streams

Electrochemistry has been effectively applied to pollution abatement processes in a wide variety of applications (Rajeshwar and Ibanez, 1997). Several broad mechanistic categories exist in environmental electrochemistry. Some applications use electrochemistry to generate reactive species that will degrade contaminants of concern (Alsheyab et al., 2009). In electrocoagulation and electroflotation processes, a sacrificial electrode is used to generate metal oxides that will complex with contaminants and facilitate separation from the waste stream (Emamjomeh and Sivakumar, 2009). Of relevance for this effort is the direct electrolytic oxidation/reduction of contaminants of concern at the surface of the electrodes (Wang et al., 2009, Fukunaga et al., 2008, Arevalo and Calmano, 2007).

Studies have investigated the effect of electrode composition (Malpass et al., 2008, Feng et al., 2009) and current density (Sarahney and Alshawabkeh, 2007) on reaction rates in electrochemical reactors. Peterson et al. (2007) noted the benefits of electrodes composed of expanded titanium meshes coated with sintered mixed metal oxides (MMO). These electrodes are available commercially for use as dimensionally stable anode materials, and compare favorably to other options in terms of cost and longevity in electrochemical treatment applications. In the cited paper, they report a reductive transformation of trichloroethene (TCE) using Ti/MMO cathodes. Gilbert et al. (2008) report that Ti/MMO electrodes last longer and perform as effectively as stainless steel or graphite electrodes in RDX treatment applications.

Others have focused on using unique configurations to increase the surface area available for reaction or improve the mass transport characteristics of the reactor. These

10

applications include particulate electrodes (Wu et al., 2008, Chalakov et al., 2009) and modified filter press cells (Andrade et al., 2008). Lipp and Pletcher (1997) note that expanded titanium meshes provide an effective means of building high surface area reactors without the unique challenges of other three dimensional electrode designs.

Electrochemical Reduction of RDX

Electrochemical reduction of RDX has been reported by several groups (Pehkonen et al. 1999, Bonin et al. 2004, Gilbert and Sale 2005, Wani et al. 2005). A proposed mechanism from Bonin et al. (2004) is detailed in Figure 4. The proposed mechanism exhibits a two step reduction. In an electrochemical application, this may be accomplished relatively quickly, so that the reduction occurs in essentially one step with MNX not being observed in the bulk fluid. Or, a buildup and subsequent reduction of MNX may be observed in batch experiments.
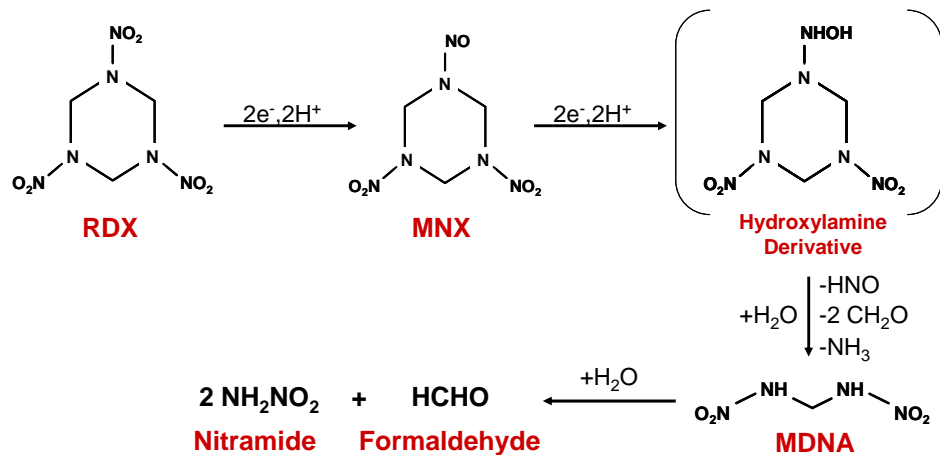
Figure 4   Mechanism for the direct electrochemical reduction of RDX as proposed by Bonin et al. (2004).

11

Electrochemical reduction has been investigated as a wastewater treatment technology (Doppalapudi et al. 2001) and an in situ treatment of contaminated groundwater (Wani et al., 2005, Gilbert and Sale, 2005, Gent, 2007). Doppalapudi et al. used a 2 L separated compartment electrochemical reactor with a vitreous carbon rod cathode. Gilbert and Sale determined that titanium mesh electrodes coated with a precious metal oxide layer (Ti/MMO) were effective and long lasting in groundwater applications. Gent observed direct reduction of RDX in a mixed compartment system using titanium mesh electrodes. In both all cases, the final products of RDX transformation were observed to be small compounds (formate, formaldehyde, nitrate) without buildup of the nitroso breakdown products.

Electrolysis Kinetics

The unbalanced reaction for the electrochemical destruction of RDX is

$$RDX + e^- + H^+ \xrightarrow{\text{k}} \text{End Products} \tag{1.1}$$
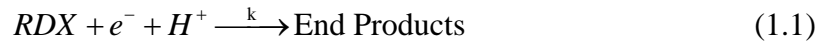
where the end products have been determined as formate, formaldehyde, and nitrate (Gent, 2007). This reaction is irreversible, so an appropriate rate law may be hypothesized as

$$\frac{dC}{dt} = k \left[RDX \right]^a \left[e^- \right]^b \left[H^+ \right]^c \tag{1.2}$$

where

        k   = reaction rate constant

        a, b, c = reaction order exponents

12

Near the cathode, electrons will be supplied across the electrode/fluid interface. Hydrogen is also present due to electrolysis of water, and if the system is operating in steady state [e$^-$] and [H$^+$] will be constant. It follows that the reaction kinetics for irreversible reduction of RDX may be assessed as a function of RDX concentration only.

Pletcher (1991) has observed that, whatever the magnitude of the rate constant, many batch electrochemical decay processes are likely to follow first order kinetics such that

$$\frac{dC}{dt} = -kC \tag{1.3}$$

where:

C = instantaneous concentration of reactant at time, t

t = reaction time

k = first order reaction kinetic rate constant

Alternatively, Walsh (1993) has equated the decay of reactant to electron transfer such that

$$\frac{dC}{dt} = -\frac{I}{nFV_R} \tag{1.4}$$

where:

I = instantaneous current in electrochemical cell at time t (A, or, C/sec)

n = number of electrons required for the complete reaction

F = Faraday's constant (Coulombs per electron)

V_R = volume of the reactor (L³)

13

If the reaction is under complete mass transfer control, then the rate limiting step is transport to and from the bulk fluid in the reactor. In this case, the current is a constant defined as

$$I_L = nFAk_mC \tag{1.5}$$

where:

I_L = the limiting current (A)

A = electrode surface area (L^2)

k_m = averaged mass transport coefficient of the reactor (L/T)

By combining (1.5) and (1.4), a mass transfer based first order kinetic decay expression may be developed as

$$\frac{dC}{dt} = -\frac{k_m A}{V_R}C \tag{1.6}$$

This expression is analogous to a basic first order kinetic rate expression. The difference is that the first order kinetic rate has been replaced by a mass transfer rate such that

$$k = k_m \frac{A}{V_R} \tag{1.7}$$

This provides a basis for scale-up of electrochemical reactors, since the observed first order kinetic rate constant may be adjusted to control for differences in electrode area and reactor volume. Trinidad and Walsh (1998) used this analysis, coupled with the standard design of a plug flow reactor. A plug flow reactor assumes no mixing along the direction of flow, making concentration at any point in the reactor a function of distance along the

14

reactor. In an electrochemical plug flow reactor, electrode surface are will also be a function of distance along the reactor such that

$$A = \int_0^L A'\, dx \tag{1.8}$$

where

A = total electrode surface area in the reactor (L²)

L = length of reactor (L)

A' = surface area as a function of distance along the reactor (L²/L)

Using first order kinetics and the mass transfer based kinetic rate constant, the rate law becomes

$$\frac{dC}{dx} = -k_m \frac{A'}{Q} C \tag{1.9}$$

where

x = distance along the flow path of the reactor (L)

A' = surface area as a function of distance along the reactor (L²/L)

Q = volumetric flow rate of the reactor (L³/T)

This rate law may be integrated to determine the effluent concentration of the reactor, C_{out}, as

$$C_{out} = C_0 e^{-k_m \frac{A}{Q}} \tag{1.10}$$

where

A = total reactive surface area of the reactor (L²)

15

This provides a method of analyzing results from a continuous flow reactor, assuming plug flow conditions. Since the flow term occurs in the denominator of the exponent, it can be seen that the effluent concentration for a plug flow reactor will exhibit first order kinetics with respect to the reactor residence time.

Summary

Given the nature of RDX contamination and its risk, including the shutdown of Army operations, an understandable amount of effort has been put into managing RDX waste streams. Several technologies exist and have been demonstrated that may treat process wastewaters laden with RDX. Each technology has its drawbacks. GAC creates a hazardous solid waste stream. Alkaline hydrolysis requires the addition of large amounts of chemicals. Demonstrated bioreactors require carbon source addition, and are not suited for process upsets since variations in flow rate or contaminant concentration require re-equilibration time for the degrading bacterial community. Each of these drawbacks may be overcome by adding electrochemical reduction as a treatment option, warranting further investigation of the topic. This thesis will carry forward the established electrochemical investigations of RDX reduction utilizing Ti/MMO electrodes to treat wastewater collected from an active processing plant. It will differ from previous work in that single compartment systems will be used to investigate a membrane free final system. Once the key reaction characteristics have been investigated on a small batch scale, this work will determine if a parallel plate arrangement of electrodes may serve as a unique high surface area electrochemical reactor design.

16

CHAPTER 3

BATCH ELECTROCHEMICAL EXPERIMENTS

Experimental Approach

The experimental approach followed to develop an electrochemical treatment system for RDX laden wastewater is laid out in Figure 5. Since the main objective of this thesis is the development of an effective electrochemical treatment reactor, two questions were asked during the initial batch reactor investigation. First, since direct reduction is an electrode surface mediated reaction, can a direct relationship between surface area and reaction rate be observed? Second, what is the relationship between current density and reaction rate, or, is there a current density that will maximize the effectiveness of a larger treatment system? After investigating those two questions, the approach calls for construction and testing of a continuous flow reactor, starting with a bench scale proof-of-concept.

17
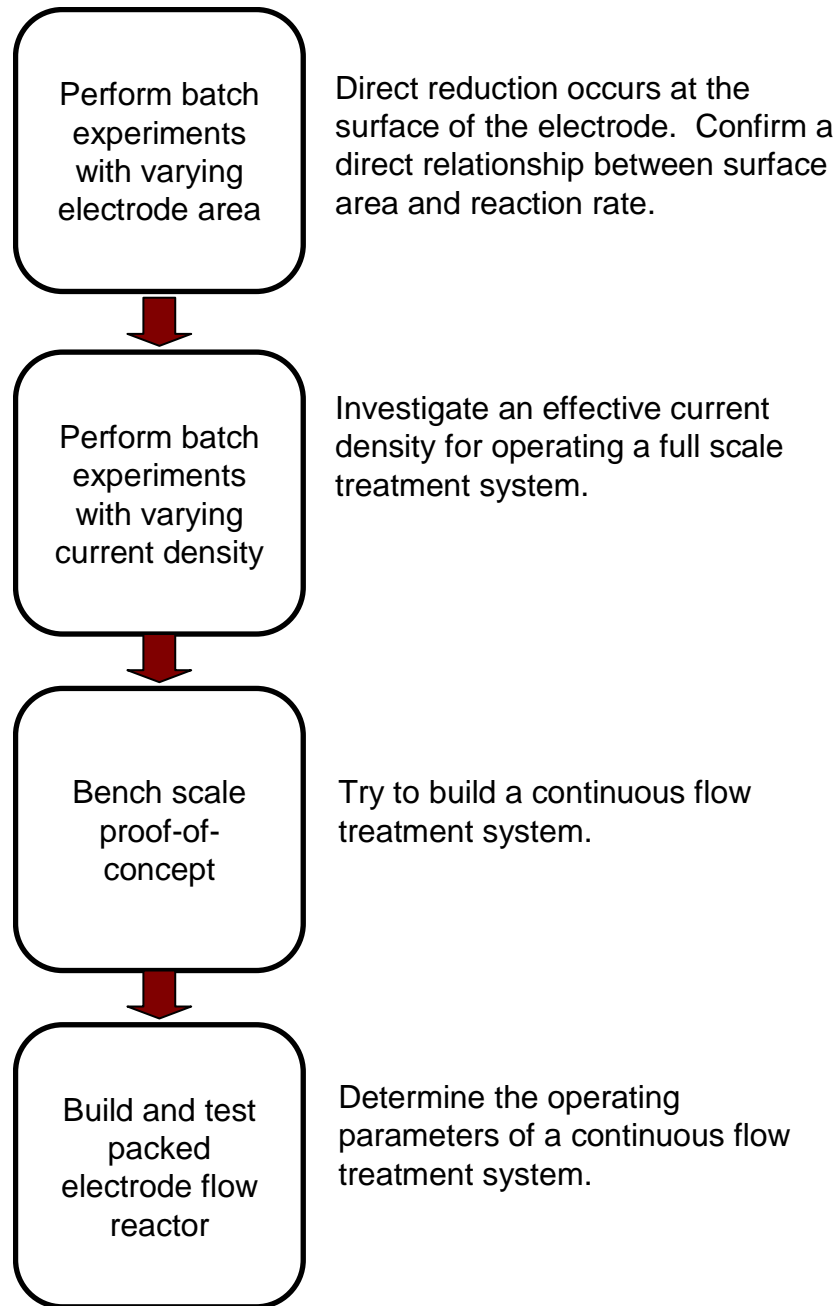
Figure 5   Experimental approach to the development of an electrochemical primary treatment for RDX laden wastewater.

Materials and Methods

Wastewater laden with RDX was collected from a processing waste stream for use in all laboratory batch studies of RDX degradation technologies. For the experimental trials in this thesis, wastewater from a single drum was used. The collected wastewater contained 10.03 mg/L of RDX at pH 7.3. The total alkalinity of the collected wastewater was determined by acid titration to be 18 mg/L as CO_3, and the total conductivity was 308 µS/cm. The water was analyzed by inductively coupled plasma spectroscopy (ICP) following USEPA method 200.7 (USEPA 2001) to determine the calcium and magnesium concentrations and hardness. The calcium and magnesium concentrations were 32.9 mg/L and 8.4 mg/L, respectively. The calcium, magnesium and total hardness from the sample was calculated to be 82.2, 34.6, and 116.8 mg/L, respectively, as $CaCO_3$.

The triplicate batch reaction system used for small batch scale evaluation of direct electrochemical reduction of RDX is shown in Figure 7 and Figure 7. Experiments were performed in triplicate using 500 mL polypropylene beakers as batch reactors. A threaded connection tapped in the bottom of each beaker held a barbed fitting, and was connected with clear thin walled Tygon® tubing through a two-way zero volume normally closed solenoid valve (Cole-Parmer®, 16 LPM, 12 VDC, C-01367-70) to 3.175 mm ID Tygon® tubing connected to an Eldex Universal Fraction Collector (UFC) base (#1243) unit with a UP-50 preparation rack containing 20 mL scintillation vials. A custom panel mounted timer/controller was assembled to operate three solenoid valves and to advance the fraction collectors to the next position by means of eight programmable digital timers (Atonics LE3S) and three 0.5-Amp SPST Reed Relays

(Radio Shack Model: 275-233, 12Vdc). The timer/controller system allowed for simultaneous gravity flow sampling in each reactor. Electrodes were held in the beakers at a submerged depth of 8.9 cm with inter-electrode spacing of 1.3 cm. Magnetic stir bars providing mixing at 300 rpm. Power was supplied to the electrodes with 500 mA/20 V direct current power supplies (Agilent Technologies, Santa Clara, CA).
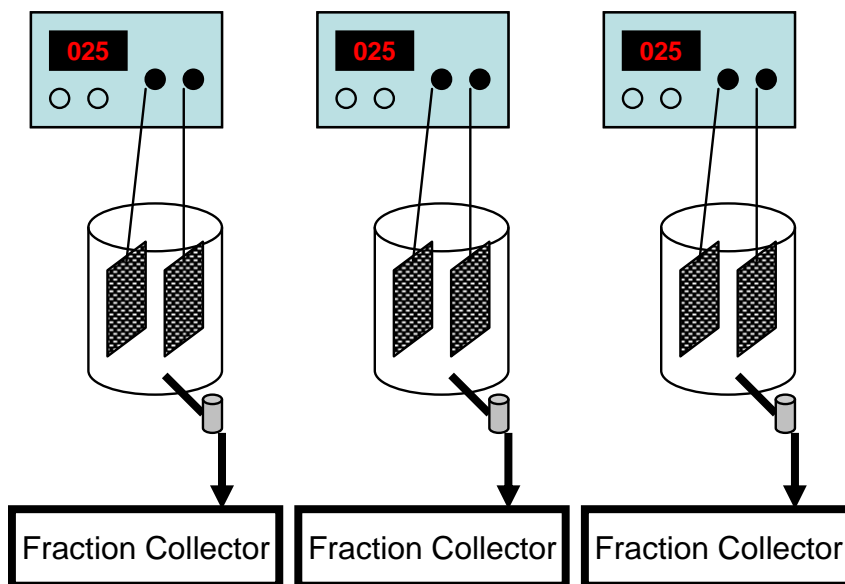
Figure 6   Basic schematic of batch reaction system for electrochemical reduction of RDX in triplicate.
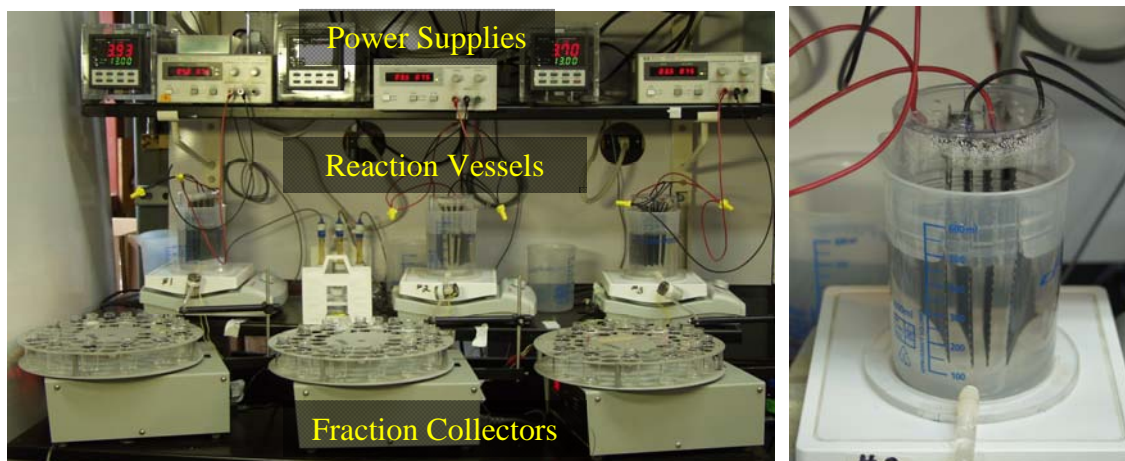
Figure 7   Batch reaction system used to perform electrochemical experiments in triplicate.

Direct electrochemical reduction of RDX was investigated in mixed compartment electrochemical cells using RDX processing wastewater as the sole electrolyte. Electrodes were constructed of an expanded titanium mesh substrate with a mixed precious metal oxide coating (Corrpro Companies, Medina, OH). This material has 2.46 m^2 of total surface area per square meter of electrode material. It was purchased in 16 cm by 122 cm sheets and cut to size in the laboratory. Electrical connections were made by physically crimping stranded copper wire to the electrode material and waterproofing the connection with epoxy resin putty. Three electrode setups were used during batch testing to investigate the relationship between reaction rate and electrode surface area. For the smallest electrode surface area, two electrodes 1.27 cm wide were used. A larger setup was also built using two electrodes, each 8 cm wide. The final setup used four electrodes (two anodes and two cathodes), each 8 cm wide. These three reactor setups resulted in cathode surface areas of 25, 150, and 300 cm^2.

21

Experiments were run concurrently in triplicate for each condition. No temperature control was implemented on the reaction system other than ambient laboratory conditions of 22°C. The initial pH of the wastewater used in the experiments was 7.3, and no change in pH was observed over the course of the reaction. Samples of 10-15 mL were removed during experiments at intervals of 5-240 minutes for explosives analysis. At lower current densities, the total reaction time was 24 hours. Reaction times of 6 hours were used at higher current densities. Samples were analyzed for RDX concentration on the same day.

Samples were analyzed for RDX and its associated breakdown products, hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3-dinitroso-nitro-1,3,5-triazine (DNX), and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX), using HPLC following a modified SW846 method 8330 (USEPA, 1994) on a Dionex Acclaim EC2 (cyano) column, utilizing a 1:1 v/v methanol-water mobile phase at 1 mL/min. Detection was made by monitoring absorbance at 254 nm on an electrode-diode array spectrophotometric detector. Analytes were identified by comparison to retention times of known standards and were quantified using a 7-point standard curve that was linear from 0.025 to 5 mg/L.

The analytical data from the batch titration results were modeled with a two parameter nonlinear exponential decay equation to determine apparent first order reaction rate coefficients with respect to RDX concentration. This model is an integrated form of equation (1.3) such that

$$C = C_0 e^{-kt} \tag{1.11}$$

22

where

C = instantaneous concentration of RDX in the reactor (mg/L)

C_0 = initial concentration of RDX in the treated wastewater

k = first order reaction rate constant (min^{-1})

t = reaction time (min)

A statistical software package, SigmaPlot$^{®}$, used the Marquardt-Levenberg algorithm to determine the parameters that minimize the sum of squares of differences between the RDX concentration values predicted by the equation model and the observed values. The dataset used to determine k was the complete time series of concentrations from the triplicate batch reaction system. Most reaction conditions were sampled ten times, so the dataset used toe estimate k would contain 30 values (n = 30). Values below 25 µg/L were not reported, leading to smaller values of n for some estimates.

Results and Discussion

Electrochemical batch experiments were carried out varying both electrode surface area and current density. A complete summary of the test conditions is given in Table 2. Summary results for RDX disappearance at varying electrode surface area are detailed in Figure 8. The first order reaction rates are shown with respect to electrode surface area in Figure 9. Across the range of surface areas studied, the reaction rate increased linearly with electrode surface area. This is consistent with the conceptual model of direct electrochemical reduction as a surface mediated reaction.

23

Table 2   Test conditions of batch electrochemical reduction of RDX.

Test #	Cathode Surface Area (cm²)	Current (mA)	Current Density (A/m²)	Test #	Cathode Surface Area (cm²)	Current (mA)	Current Density (A/m²)
1	25	20	8.0	8	300	125	4.2
2	150	105	7.0	9	300	150	5.0
3	300	210	7.0	10	300	150	5.0
4	300	25	0.8	11	300	200	6.7
5	300	50	1.7	12	300	250	8.3
6	300	75	2.5	13	300	300	10.0
7	300	100	3.3	14	300	350	11.7
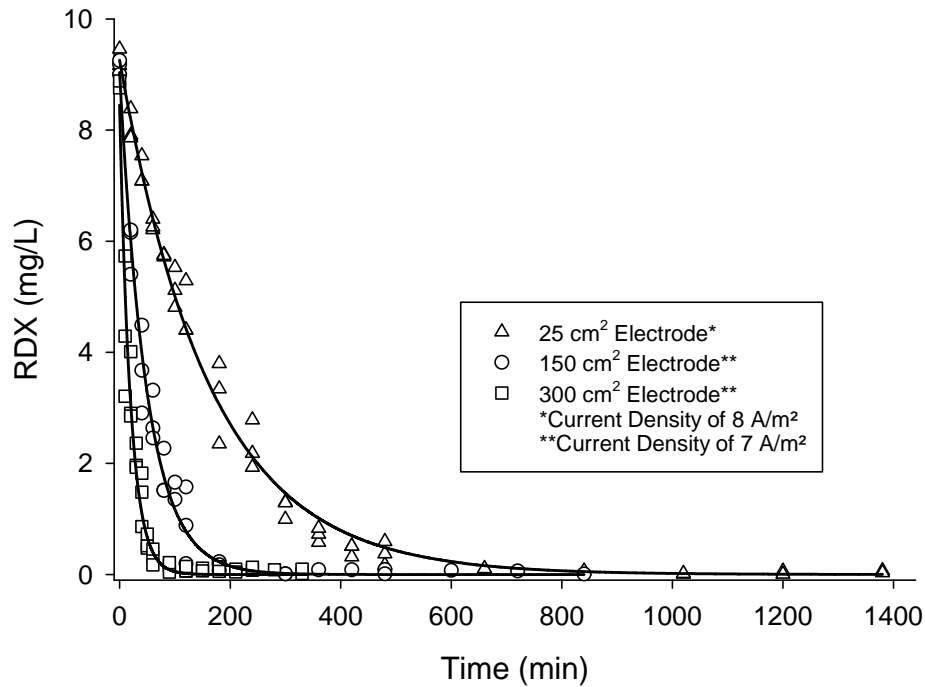
Figure 8   Disappearance of RDX over time in 500 mL batch electrochemical reactors at a current density of 7-8 A/m² and varying electrode surface area.
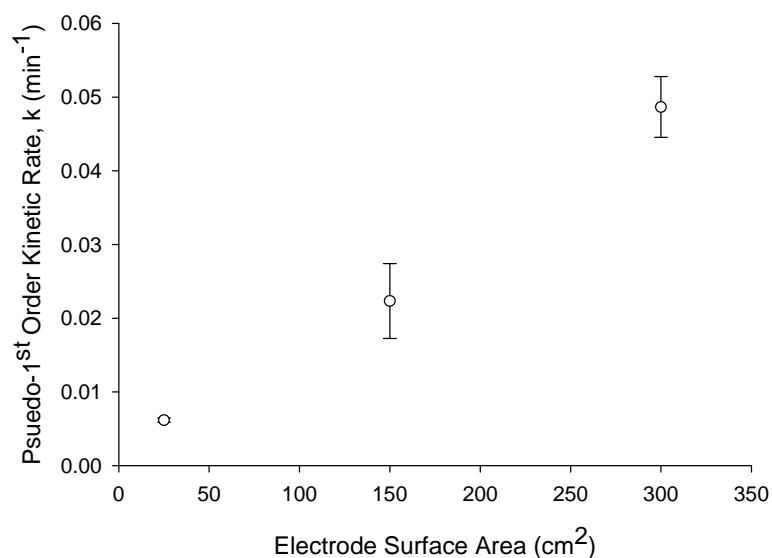
Figure 9   First order reaction rates for destruction of RDX on varied electrode
            surface areas in 500 mL electrochemical reactors with current densities of
            7-8 A/m² (95% confidence intervals).

First order reaction rates for RDX degradation in electrochemical batch experiments of varying current densities on 300 cm² of cathode surface area are detailed in Figure 10. Above a minimum current density of 2 A/m², the reaction rate increases effectively with current density.   Above 4 A/m², the reaction rate begins to show diminishing returns with increased current density.   Since the direct electrochemical reduction of RDX is a surface area mediated reaction, this point of diminishing returns likely indicates the point at which mass transfer from the bulk fluid to the electrode surface becomes important in the reaction. At higher current densities, it is expected that the reaction rate will reach a maximum value where the reaction becomes entirely mass transfer controlled.

25
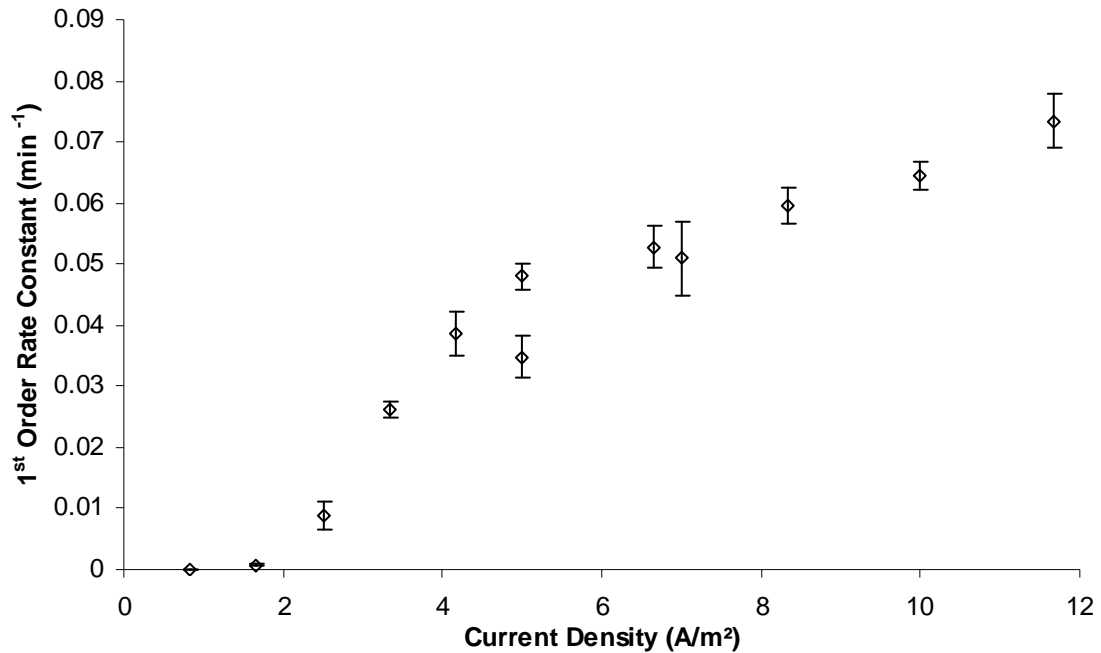
Figure 10   Apparent first order kinetic rate parameter for RDX disappearance in 500 mL electrochemical batch reactors with varying current density and 300 cm² of cathode surface area (95% confidence intervals).

Given the results of batch experiments, it is apparent that effective utilization of electrochemical reactors to destroy RDX in wastewater will depend on the total surface area available for reaction, the mass transfer characteristics of the reactor, and the current density of the electrochemical cell. To analyze reactor performance and provide a basis for reactor scale-up, a mass transfer based kinetic rate, k_m, may be used. This rate is defined as $k_m = k(V/A)$, where k is the first order rate constant, V is the reactor volume, and A is the active electrode surface area (Walsh 1993). The results from transforming the k values of two reactions with constant current density and differing surface areas are given in Table 3. Figure 10 is shown rescaled to k_m in Figure 11. Since the mass transfer based rate accounts for differences in total surface area and volume, reactor

26

configurations with similar mass transfer characteristics should have the same k_m value at any scale for a given current density. It is important to note that the observed batch reactions did not appear to be entirely mass transfer controlled. In this case, the assumption of mass transfer control is not strictly valid, but still provides a useful transformation to account for the effects of scale-up. Specifically, it allows scale-up design to account for differing ratios of electrode surface area to total reactor volume.

Table 3   Comparison of k and k_m values for electrochemical destruction of RDX in 500 mL reactors with differing reactive surface area

Electrode Surface Area (cm²)	Current Density (A/m²)	1st Order Reaction Coefficient, k (min⁻¹)	Mass Transfer Based Reaction Coefficient, k_m (m/min)
150	7.00	0.020 ± 0.001	0.0007 ± 0.0001
300	7.00	0.051 ± 0.003	0.0008 ± 0.0001
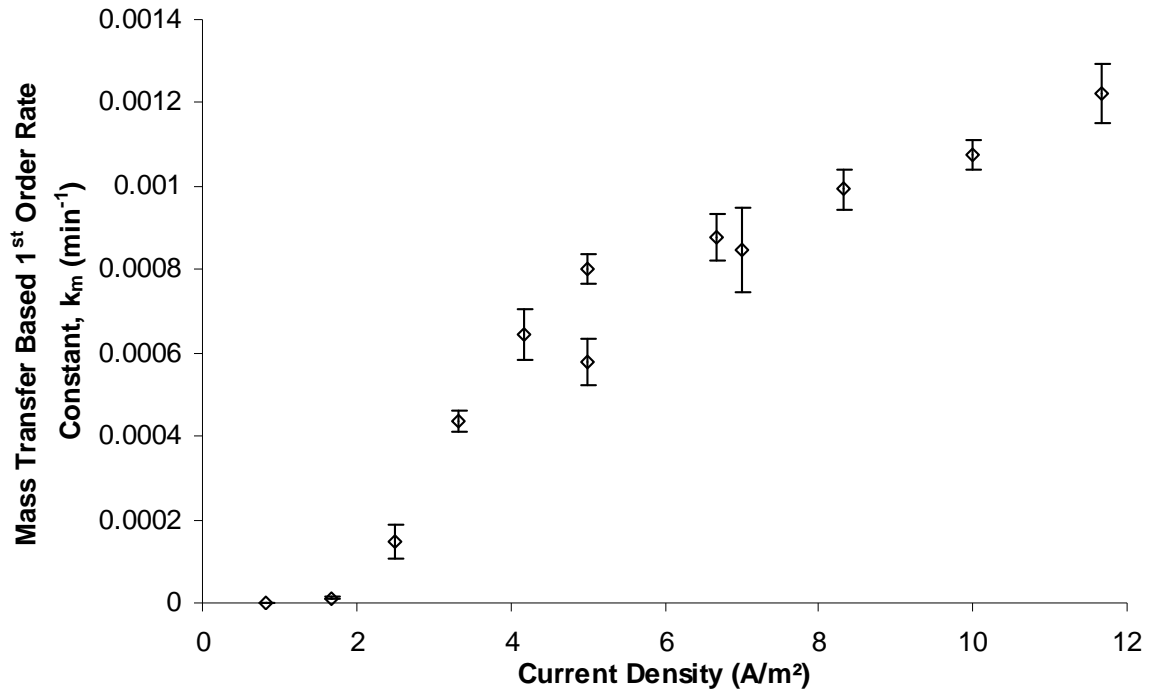
Figure 11   Observed mass transfer based first order rate constants, k_m, for the direct
electrochemical reduction of RDX.

Implementation of Current Reversal

During initial batch experiments it was observed that reaction kinetics appeared to
slow down over time. The apparent cause was a buildup of dissolved solids coating the
cathode surface. This reduced the efficiency of the electrodes, effectively reducing the
concentration of electrons and hydrogen ions available for reaction. Following from this
observation, current reversal was begun for each experiment. By reversing the electrode
polarity, scaling on the cathode was electrostatically removed, and electrode efficiency
was maintained. Electrode polarity was manually reversed every 20-30 minutes for the
duration of the batch experiments.

28

Suitability of Reaction Kinetic Model

Reaction kinetics were modeled for the batch experiments by fitting a first order reaction equation to the triplicate time series concentration data sets resulting from each reaction condition. As a measure of the suitability of the conceptual reaction kinetic model, the residuals of the model were analyzed as a group. A histogram of the model residuals (observed value minus predicted value) for each small batch observed value is given in Figure 12. The complete set of residuals has a mean of 0.042, a median value of 0.021, and a skewness of -0.26. Since the distribution of residuals appears to be about zero with little skew, the first order rate model is taken as valid in the range of concentrations studied.
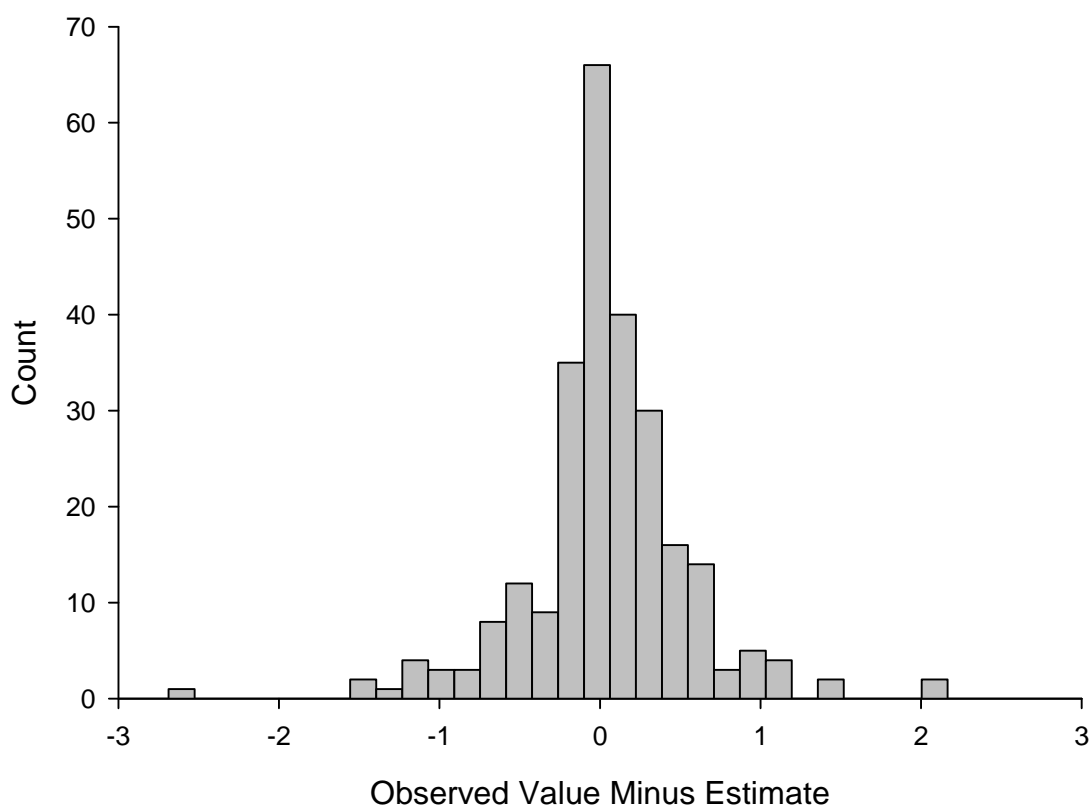
Figure 12   Histogram of the set of residuals resulting from first order reaction rate modeling of the direct electrochemical reduction of RDX in small batch reactors.

Comparison of Batch Electrochemistry with Published Results

The results of this batch reactor study were compared to results generated during previous efforts by Bonin et al. (2004), Pehkonen et al. (1999), and Doppalapudi et al. (2001). Two features of the current study stand out from previously published electrochemical treatment experiments. The first is the use of a mixed compartment reactor with no supporting electrolyte. The second is the use of mixed metal oxide/titanium mesh electrodes as both the cathode and anode. Even with the distinct reactor designs used in each study, the mass transfer based kinetic rates may be compared

30

as a point of reference (Table 4). The two modifications to reported experiments did not

result in a drop in kinetic rates when controlled for mass transfer effects.

Table 4   Observed reaction rates in different published studies of electrochemical destruction of RDX

Cathode Material	Observed	Bonin et al. (2004)	Pehkonen et al. (1999)	Doppalapudi et al. (2001)
	Mixed Metal Oxide / Ti Mesh	Reticulated Vitreous Carbon Foam	Glassy Carbon	Glassy Carbon
Compartment Type	Mixed	Separate	Separate	Separate
Reactor Volume (mL)	500	0.0039	2000	2000
Reactor Flow Regime	Batch	Plug Flow	Batch	Batch
Current Density (A/m²)	7.00	8.66	9.63	9.63
Mass Transfer Based Kinetic Rate, k_m x10^5 (m/min)	84.80	8.03	88.89	32.59

Summary

Direct electrochemical reduction of RDX has been demonstrated at the small

batch scale on Ti/mixed metal oxide electrodes. The observed rates compare well with

previously published results for electrochemical reduction of RDX. At this point, it was

decided to investigate the possible scale-up of electrochemical reduction to a full scale

treatment system. Specifically, since mass transfer and electrode surface area are the two

most important design characteristics, a reactor design that incorporates a high surface

area per unit volume with small travel distances was desired. To accomplish this, a

reactor configuration of packed electrode plates separated only by thin layers of

insulating material was investigated.

CHAPTER 4

BENCH PILOT UNIT

Materials and Methods

A continuous flow electrochemical reactor was constructed using a 2 L rectangular acrylic reactor. A photo detail is included in Figure 13, and the design is summarized in Figure 14. The reactor consisted of a 7.62 cm square flow channel 35 cm long. Inside this space 20 electrode plates 7.62 cm by 23 cm were placed parallel to the channel. Polypropylene mesh was placed between each electrode sheet to maintain electrical isolation in the absence of electrolyte. The final configuration contained 2,156 cm² of cathode surface area. Separate reservoirs were set up for the influent and effluent streams, and a peristaltic pump provided a constant volumetric flow rate through the reactor. Samples were taken at the reactor outlet. Wastewater from the same source as that used in the batch experiments was used for testing the proof-of-concept.
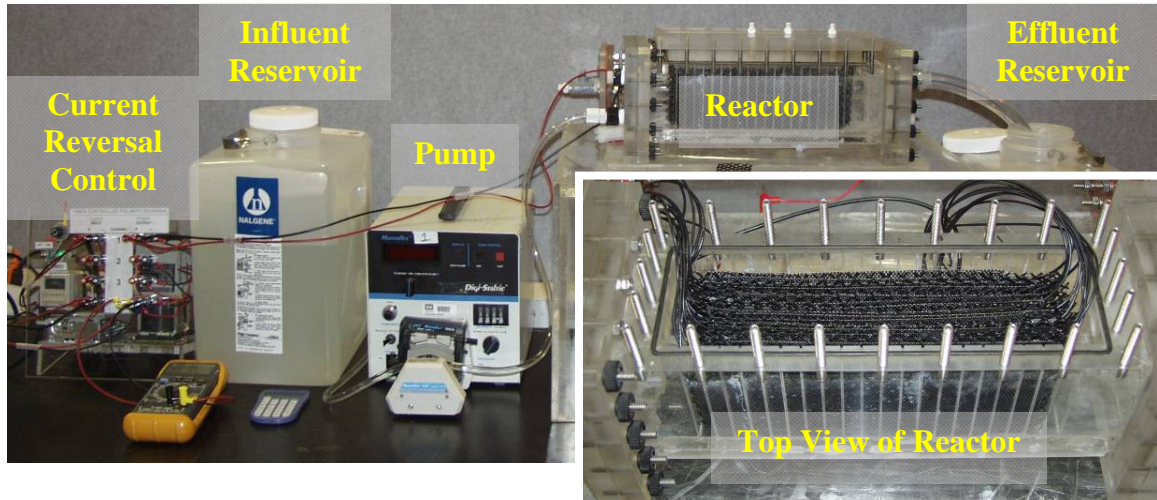
Figure 13   Benchtop packed electrode flow reactor for continuous destruction of RDX in a process wastewater
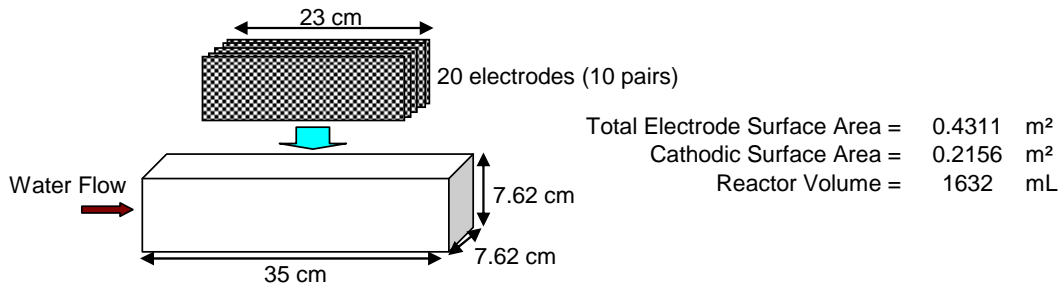
Figure 14   Basic design of packed electrode flow reactor for continuous destruction of RDX in a process wastewater

Power was supplied to each bench top reactor by a single 300V - 3A power supply (Sorensen Inc., San Diego, CA). During batch experiments it was observed that current switching would be necessary to prevent buildup of solids on the cathode surface. To that end, a current reversal system was also developed and used for ensuing bench top experiments.   The system utilized a timer/controller (Autonics Corp., Gyeoungnam,

33

South Korea) to switch mechanical relays (Square D, Palatine, IL) reversing the current polarity of the power source on 20 minute intervals.

Results and Discussion

Exit concentrations of RDX from the benchtop packed electrode flow reactor are detailed in Table 5. The mass transfer based kinetic reaction rate for the continuous flow reactor is similar to the rate observed in the small batch reactors, indicating similar mass transfer characteristics. Based on the observed reaction coefficients, treatment from 50 mg/L to less than 2 µg/L would be accomplished in this reactor at a flow rate of 16 mL/min. This corresponds to a power requirement of 0.03 kW-hr/gal.

Table 5   Observed RDX destruction results from bench-top packed electrode flow reactor

Current (A)	Voltage (V)	Current Density (A/m²)	Flow Rate (L/min)	k_m (m/min)	95% Confidence Interval (m/min)	% Destroyed
1.5	3	6.96	0.129	0.00074	0.00003	71.1%
1.75	3.3	8.12	0.129	0.00070	0.00004	69.4%
2	3.5	9.28	0.129	0.00061	0.00002	64.1%
2.5	3.7	11.60	0.129	0.00067	0.00007	67.4%

34

Summary

The bench-top unit was constructed from available materials as a proof-of-concept design. Since the benchtop pilot unit was able to continuously remove RDX from a process wastewater, it was determined that further investigation was warranted. The path forward was to build a pilot treatment unit that would incorporate the packed electrode flow reactor design into a completely sealed system that could replicate a demonstration unit.

CHAPTER 5

PILOT PACKED ELECTRODE FLOW REACTOR

Materials and Methods

The packed electrode continuous flow reactor cell was constructed of ½ inch (1.25 cm) clear acrylic. A photo detail is included in Figure 15. The basic unit was a rectangular channel 15 cm wide by 6.35 cm deep and 122 cm long with flanged end pieces. The end caps were also rectangular channels 15 cm wide by 8 cm deep by 25 cm long with ½ in nominal NPT fittings to facilitate connection to a pumping system. Electrodes were constructed of an expanded titanium mesh substrate with a mixed precious metal oxide coating (Corrpro Companies, Medina, OH). This material has 2.46 m² of total surface area per square meter of electrode material, and was purchased in 15 cm by 122 cm sheets. Electrical connections were made by physically crimping 14 AWG stranded copper wire to the electrode material and waterproofing the connection with epoxy resin putty. The reactor cell was loaded by layering electrodes with 15 cm by 124 cm polypropylene mesh material as insulators. A total of 18 electrode plates were packed into the reactor with alternating electrical leads protruding from the upper and lower ends of the rectangular channel. The electrical leads at each end of the reactor were bolted together with a common lead of 10 AWG stranded copper wire and waterproofed with epoxy resin putty to create two main electrical leads for the reactor cell. The two leads

36

for the reactor cell were brought out through the end caps using waterproof strain relief connections to create a watertight electrochemical reaction cell. The final reactor assembly was suspended vertically within a steel frame to provide access during the experimental runs.
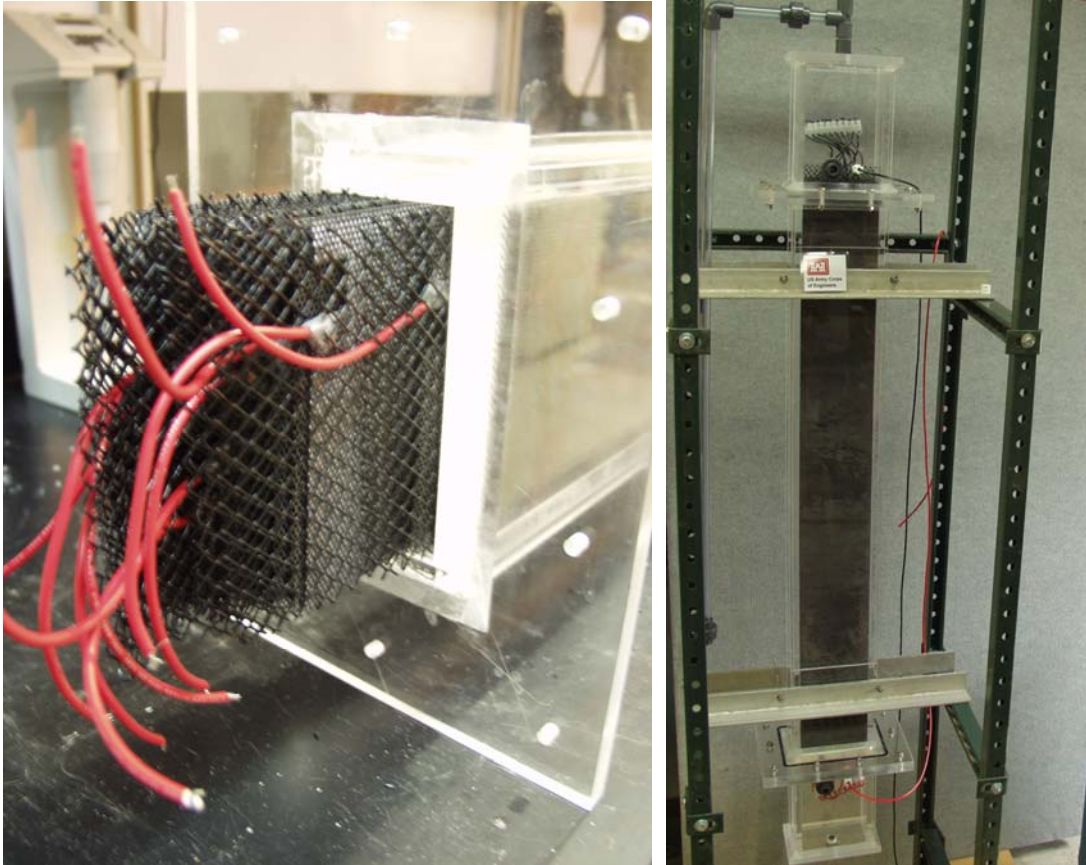
Figure 15: Photo detail of packed electrode flow reactor, including electrodes with insulator material and leads, and the reactor assembly.

The key functional characteristics of the reactor are summarized in Table 6. Current was supplied to the reactor cell through the constructed leads by a 30V–300A power supply (TDK Lambda Americas, Inc. San Diego, CA). Previous batch studies had determined the need for periodic current switching to keep the cathode clear of deposited

37

solids, so a current switching unit was constructed of DC power relays (Square D, Palatine, IL) controlled by a series of timer/controller switches (Autonics Corp., Gyeoungnam, South Korea).   A current switching interval of five minutes was maintained throughout all experiments with the flow reactor. Water was supplied to the reactor by means of a constant volume piston pump (Blue-White Industries, Huntington Beach, CA) so that the reactor would operate at a constant flow rate in upflow mode. Tests were carried out with flow rates ranging from 0.36 L/min to 3.7 L/min (corresponding to residence times of 3-27 minutes).

Table 6   Key functional characteristics of the packed electrode flow reactor for destruction of RDX in a process wastewater

L x W x H = 15 x 6.35 x 122 cm
Total Vol. = 11.62 L
Void Vol. = 9.61 L
Reactive Area = 4.05 m²

The small batch reaction was effectively modeled by

$$C = C_0 e^{-kt} \tag{1.12}$$

where

C = instantaneous concentration of RDX

C_0 = initial concentration of RDX

k = reaction rate constant

t = reaction time.

38

For a continuous flow reactor, reactor sizing is dependent on both the residence time in the reactor and the surface area of active electrode available for reaction. This makes it useful to use the mass transfer based kinetic rate, k_m,

$$k_m = k\frac{V}{A} \qquad (1.13)$$

where

V = reactor volume

A = reactive surface area of the electrode.

Using first order kinetics and the mass transfer based kinetic rate constant, the rate law becomes

$$\frac{dC}{dx} = -k_m\frac{A'}{Q} \qquad (1.14)$$

where

x = distance along the flow path of the reactor

A' = surface area as a function of distance along the reactor

Q = volumetric flow rate of the reactor.

This rate law may be solved to determine the effluent concentration of the reactor, C_{out}, as

$$C_{out} = C_0 e^{-k_m\frac{A}{Q}} \qquad (1.15)$$

where

A = total reactive surface area of the reactor

39

This was the basic design equation used to analyze results from the packed electrode flow reactor.

Results and Discussion

Experimental runs in the reactor varied both current density and flow rate (residence time). Results for the observed mass transfer based first order decay rates at a constant flow rate with varying current density are detailed alongside those observed during earlier trials in Figure 16. These values are estimated from trials conducted at a flow rate of 360 mL/min. Over the range of current densities studied, there was not a significant change in the observed k_m. This is consistent with a reactor operating under mass transfer controlled conditions. The reaction rates observed during testing are markedly lower than those observed during batch experiments and benchtop flow reactor testing.
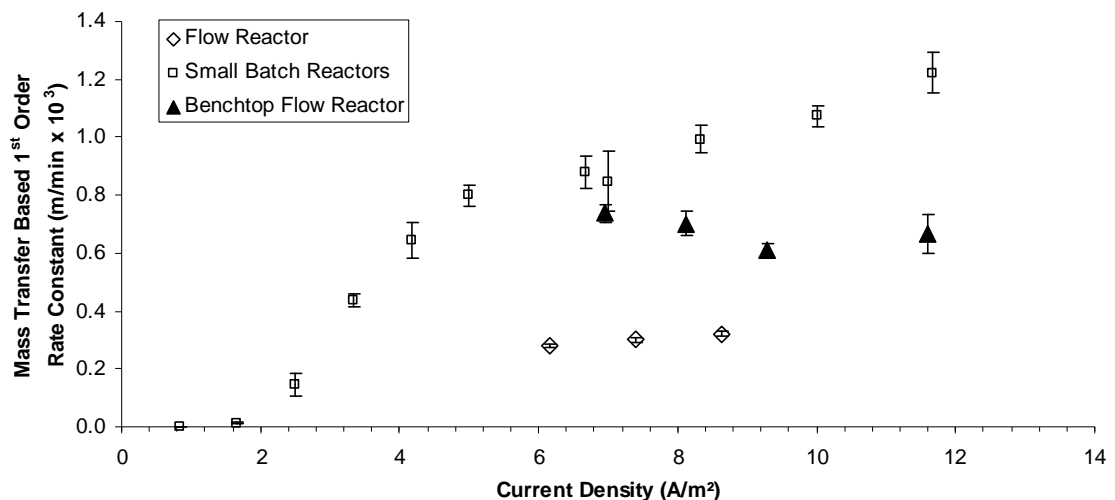
Figure 16   Comparison of observed mass transfer based first order decay constants from the packed electrode flow reactor with those observed in the small batch experiments.

40

The mass transfer based kinetic rates observed during testing of the packed electrode flow reactor are shown for several flow rates in Figure 17. There was a slight increase in the observed reaction rate at flow rates above 1 L/min. This increase did not continue as the flow rate was increased to 3.7 L/min.
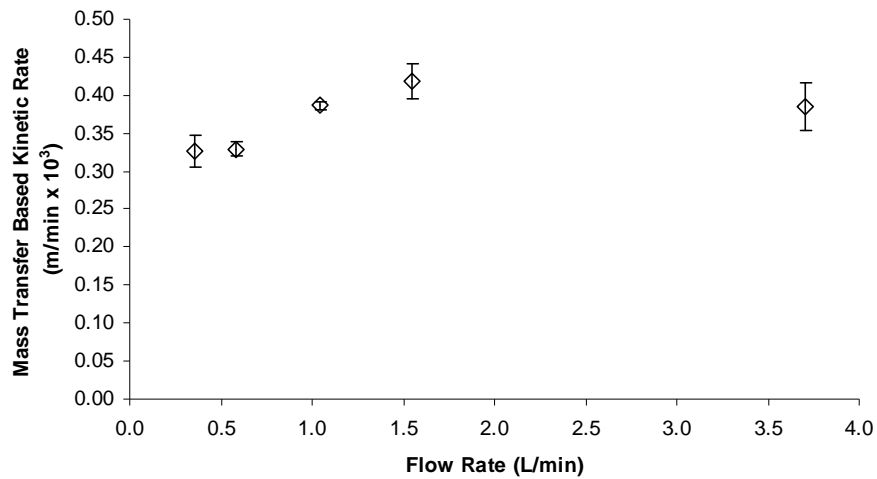
Figure 17   Observed mass transfer based first order decay constants from the packed electrode flow reactor at varying flow rates with a current density of 7.41 A/m².

Values of effluent concentration over influent concentration (C/C_0) are detailed as a function of retention time in the reactor in Figure 18. Flow rate trials were carried out at a current density of 7.4 A/m², corresponding to a total reactor current of 30 A. This current was accomplished at a potential of 6.3 V, so that treatment was accomplished with a power input of 0.19 kW, or 4.5 kW-hr/d. The total power input corresponding to 97.4% destruction of RDX was 8.8 kW-hr/m³. At 77.8% destruction the required power input for treatment was 3.0 kW-hr/m³. The mass transfer based kinetic rate across the

41

range of flow rates studied ranged from 3.3×10^{-4} to 4.2×10^{-4} m/min. With the large available surface area for reaction in the reactor, the residence time based half life for RDX destruction in the reactor was 4.23 min at a current density of 7.41 A/m², much less than the half lives observed during batch experiments.
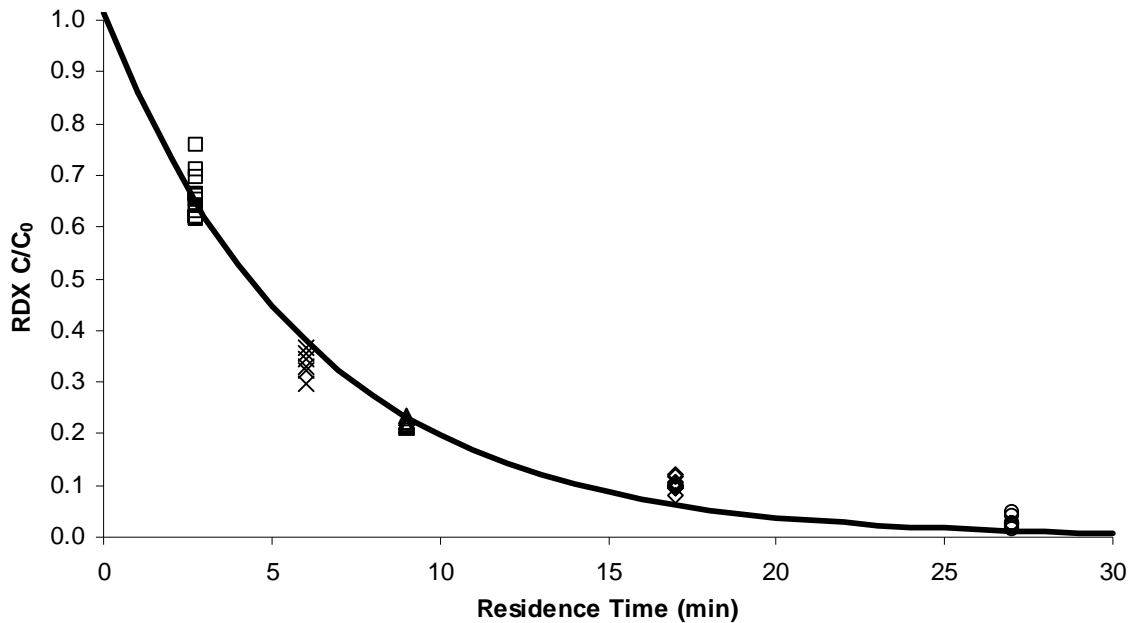
Figure 18   Observed reduction of RDX concentration across the packed electrode flow reactor as a function of residence time.

Summary

Scaling up from the small batch reactors and bench-top flow reactor resulted in a drop in mass transfer based kinetic rates. This indicates that the mass transfer characteristics of the packed electrode flow reactor are not necessarily comparable to the smaller reactors. The packed electrode flow reactor did accomplish 97% destruction of an RDX laden process waste stream. The reactor characteristics also matched those

42

expected of a plug flow reactor by exhibiting first order reaction kinetics as a function of residence time.

43

CHAPTER 6

SUMMARY AND CONCLUSIONS

This thesis explored the development of direct electrochemical reduction as a means of providing primary treatment of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in a manufacturing process waste stream. An industrial process wastewater laden with RDX was successfully treated in small batch reactors. The reaction kinetics exhibited a linear dependence on cathode surface area. Reaction kinetics also increased with a corresponding increase in current density, though this effect was reduced at higher current densities. Reaction kinetics were used to design a proof of concept bench scale flow reactor that utilized parallel packed electrode plates. Following successful testing of this reactor, a pilot scale packed electrode flow reactor was built. This reactor exhibited a lower mass transfer based reaction rate constant than that observed for the small batch reactors. The reactor performance as a function of residence time was fit by a first order decay equation. Greater than 97% reduction of RDX in a process wastewater was observed at a reactor residence time of 27 minutes.

The work presented herein was successful in creating an electrochemical treatment system capable of removing RDX from an industrial process waste stream with no chemical addition, and without creating an additional hazardous waste stream. Since the mass transfer characteristics of the pilot packed electrode flow reactor were lower

44

than those observed in the batch experiments and the bench top flow reactor, there may be improvements that can be made in future systems. Future work may focus on improving mass transfer by changing the flow or packing characteristics of the reactor. There are other questions that lay outside the scope of this thesis which may lead to more effective operation of an electrochemical system. Theses include investigating the effects of electrode material, sympathetic electrolytes, and the three dimensional arrangement of the electrode material.

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APPENDIX

SUPPORTING DATA FROM LABORATORY EXPERIMENTS

Supporting Data from Laboratory Batch Experiments

Figure A.1   Electrochemical reduction of RDX in a 500 mL reactor using 20 mA D.C. current on 25 cm² of cathode surface area

54

Figure A.2   Electrochemical reduction of RDX in a 500 mL reactor using 105 mA D.C. current on 150 cm² of cathode surface area

Figure A.3   Electrochemical reduction of RDX in a 500 mL reactor using 210 mA D.C. current on 300 cm² of cathode surface area

55

Figure A.4   Electrochemical reduction of RDX in a 500 mL reactor using 25 mA D.C. current on 300 cm² of cathode surface area

Figure A.5   Electrochemical reduction of RDX in a 500 mL reactor using 50 mA D.C. current on 300 cm² of cathode surface area

56

Figure A.6   Electrochemical reduction of RDX in a 500 mL reactor using 75 mA D.C. current on 300 cm² of cathode surface area

Figure A.7   Electrochemical reduction of RDX in a 500 mL reactor using 100 mA D.C. current on 300 cm² of cathode surface area

57

Figure A.8   Electrochemical reduction of RDX in a 500 mL reactor using 125 mA
             D.C. current on 300 cm² of cathode surface area
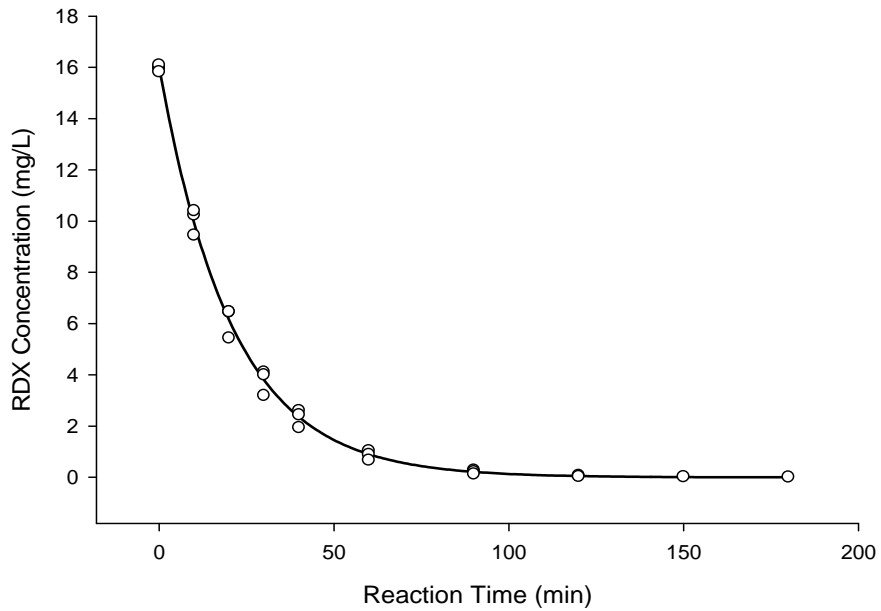
Figure A.9   Electrochemical reduction of RDX in a 500 mL reactor using 150 mA
             D.C. current on 300 cm² of cathode surface area

58
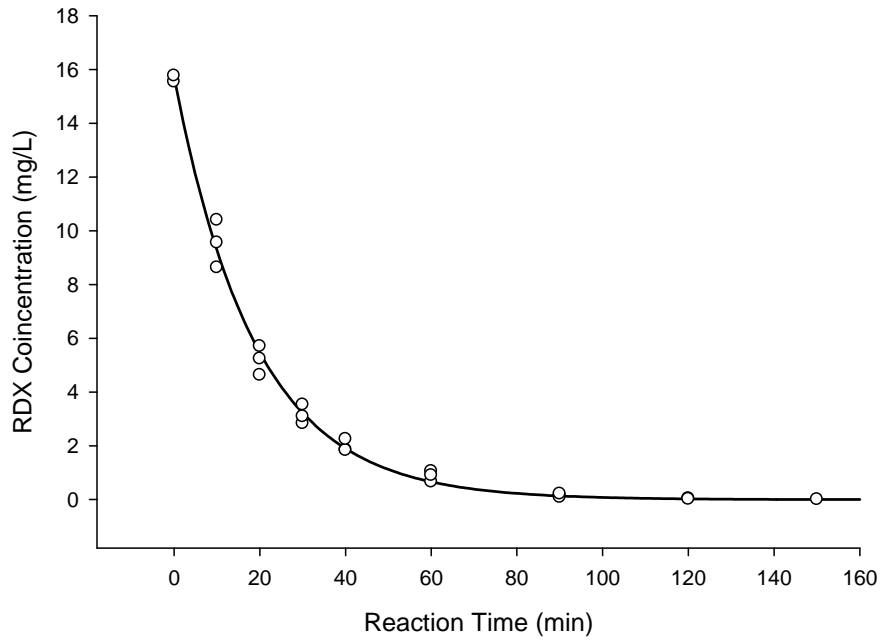
Figure A.10   Electrochemical reduction of RDX in a 500 mL reactor using 200 mA
D.C. current on 300 cm² of cathode surface area
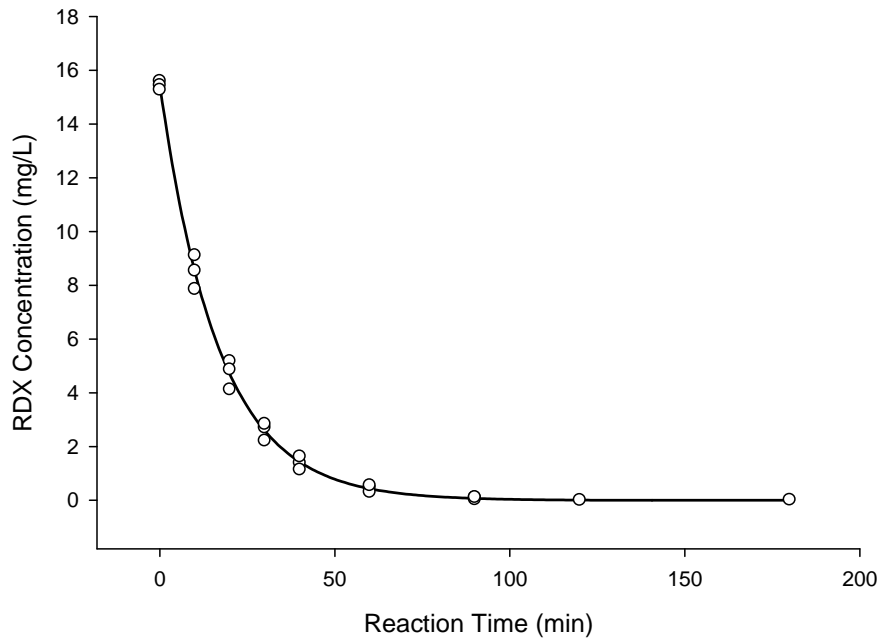
Figure A.11   Electrochemical reduction of RDX in a 500 mL reactor using 250 mA
D.C. current on 300 cm² of cathode surface area
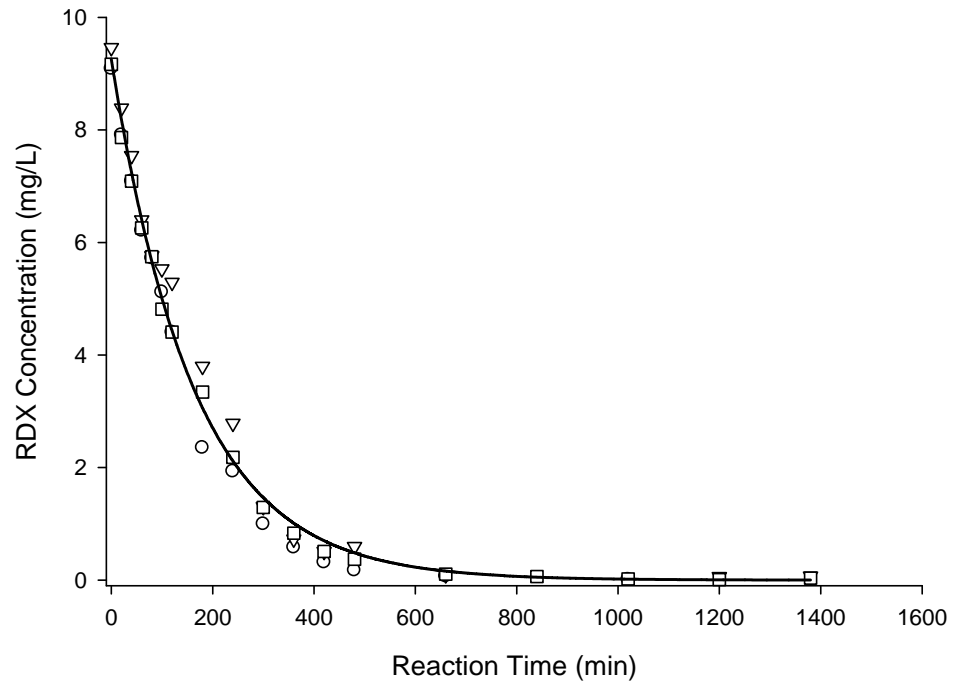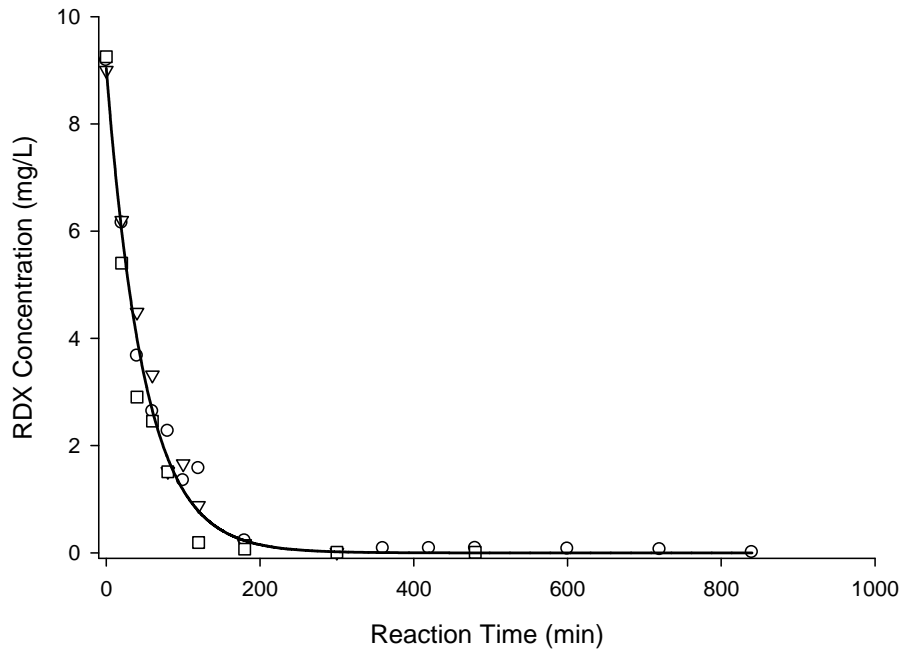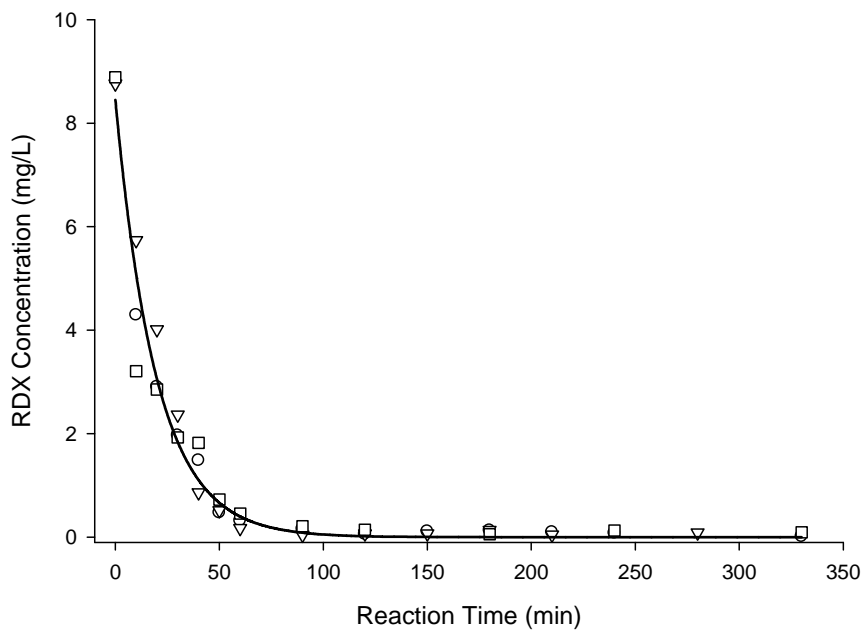
59
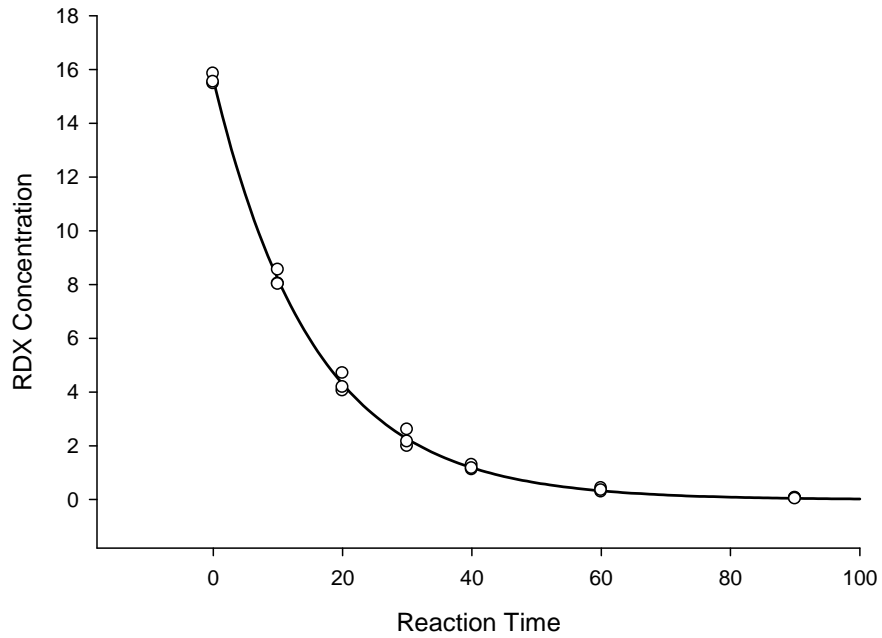
Figure A.12   Electrochemical reduction of RDX in a 500 mL reactor using 300 mA
                D.C. current on 300 cm² of cathode surface area
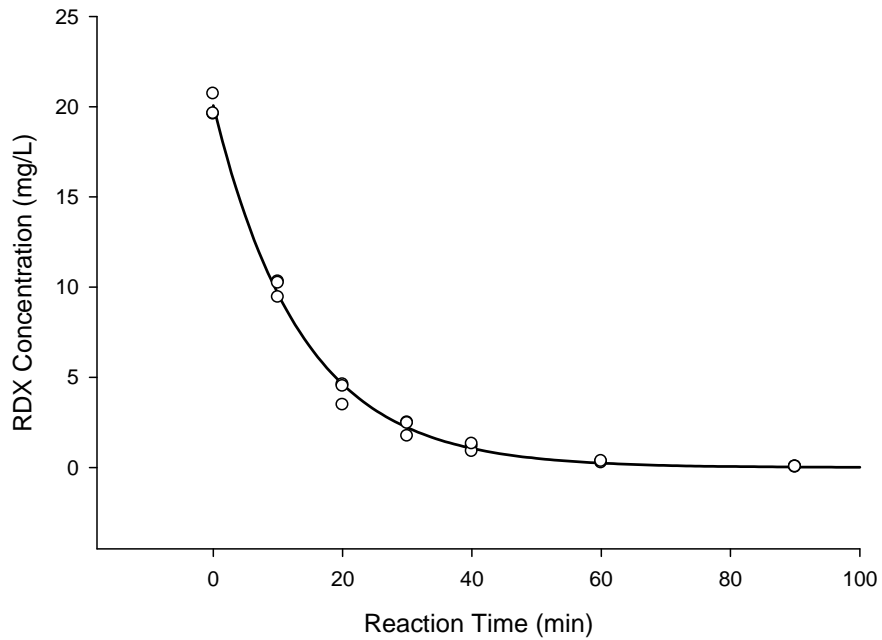
Figure A.13   Electrochemical reduction of RDX in a 500 mL reactor using 350 mA
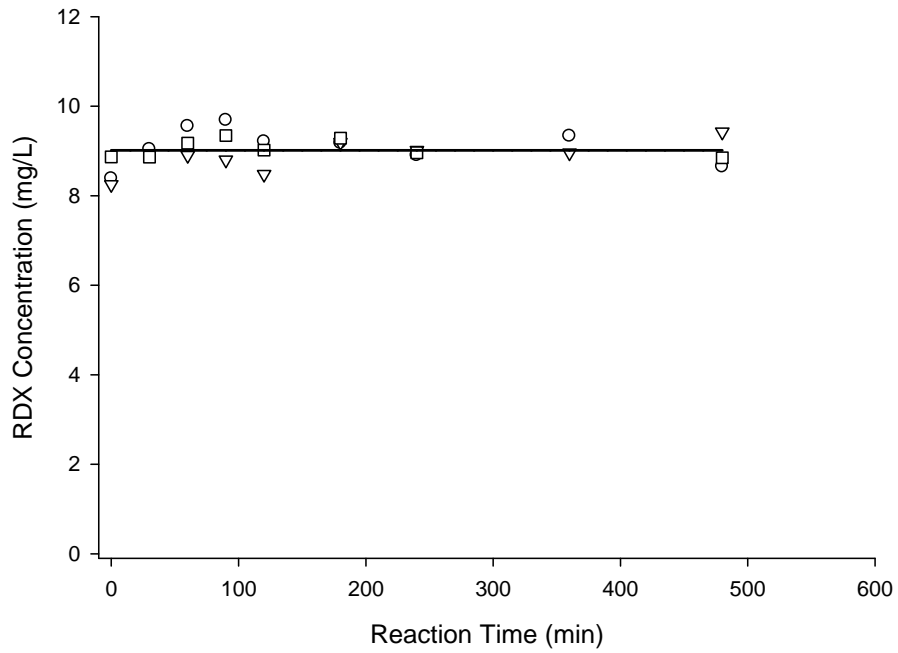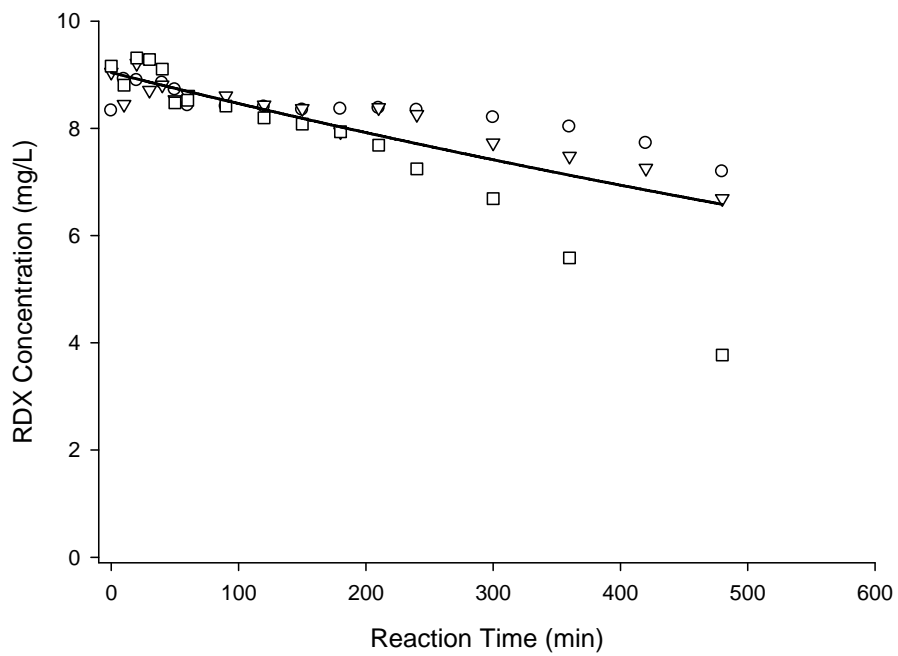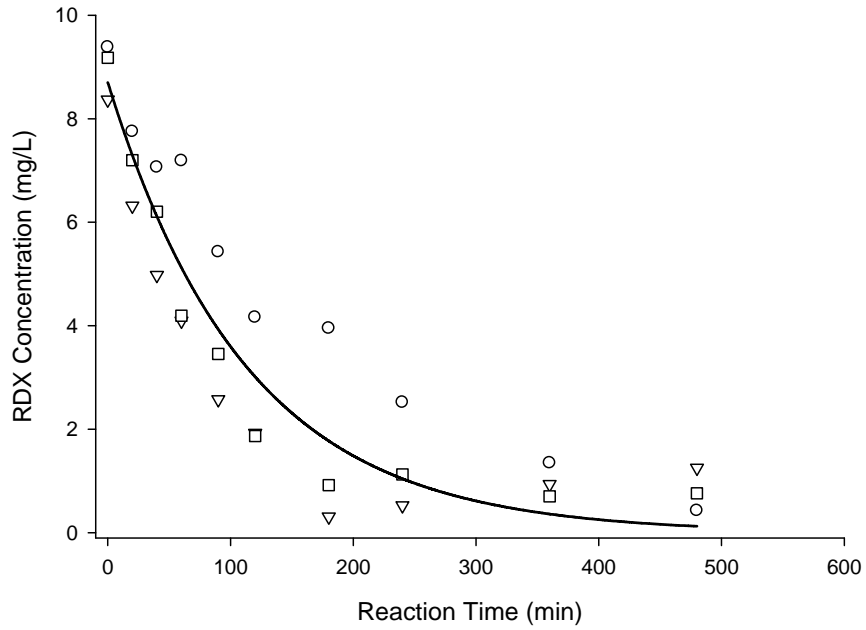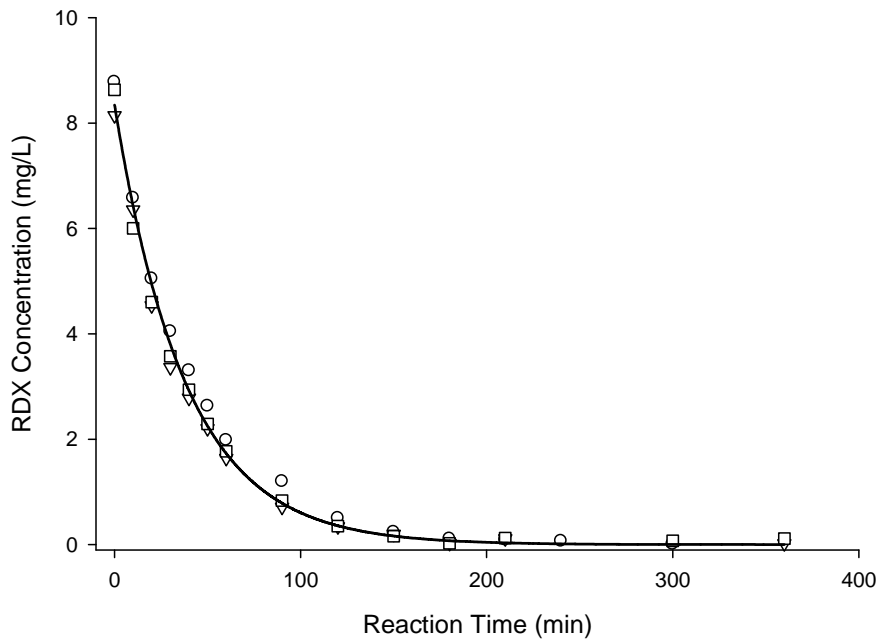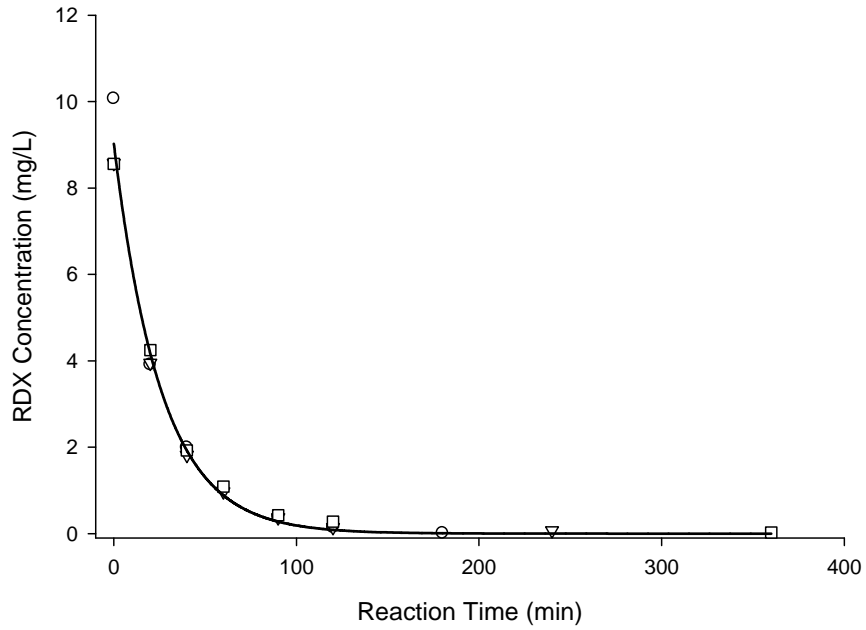   D.C. current on 300 cm² of cathode surface area

60

Supporting Laboratory Data from Bench Top Flow Reactor

Table A.1:   Reactor effluent data for experimental run #1 in the packed electrode flow
              reactor

Run #1 December 17, 2007						
C_0 (mg/L)	A (m²)	Q (L/min)	C (mg/L)	k_m (m/min)	Current (A)	Voltage (V)
9.059	0.2174	0.129	3.097	0.0006369	2	3.46
9.059	0.2174	0.129	2.752	0.0007070	2	3.46
9.059	0.2174	0.129	3.17	0.0006231	2	3.46
9.059	0.2174	0.129	3.194	0.0006186	2	3.46
9.059	0.2174	0.129	3.195	0.0006184	2	3.46
9.059	0.2174	0.129	3.149	0.0006270	2	3.46
9.059	0.2174	0.129	3.249	0.0006085	2	3.46
9.059	0.2174	0.129	3.226	0.0006127	2	3.46
9.059	0.2174	0.129	3.254	0.0006075	2	3.46
9.059	0.2174	0.129	3.298	0.0005996	2	3.46
9.059	0.2174	0.129	3.235	0.0006110	2	3.46
9.059	0.2174	0.129	3.296	0.0005999	2	3.46
9.059	0.2174	0.129	3.246	0.0006090	2	3.46
9.059	0.2174	0.129	3.274	0.0006039	2	3.46
9.059	0.2174	0.129	3.274	0.0006039	2	3.46
9.059	0.2174	0.129	3.334	0.0005931	2	3.46
9.059	0.2174	0.129	3.327	0.0005944	2	3.46
9.059	0.2174	0.129	3.002	0.0006554	2	3.46
9.059	0.2174	0.129	3.162	0.0006246	2.5	3.69
9.059	0.2174	0.129	2.882	0.0006796	2.5	3.69
9.059	0.2174	0.129	3.124	0.0006317	2.5	3.69
9.059	0.2174	0.129	2.92	0.0006718	2.5	3.69
9.059	0.2174	0.129	3.066	0.0006429	2.5	3.69
9.059	0.2174	0.129	2.864	0.0006833	2.5	3.69
9.059	0.2174	0.129	2.901	0.0006757	2.5	3.69
9.059	0.2174	0.129	2.792	0.0006984	2.5	3.69
9.059	0.2174	0.129	3.075	0.0006411	2.5	3.69
9.059	0.2174	0.129	2.789	0.0006990	2.5	3.69
9.059	0.2174	0.129	3.089	0.0006384	2.5	3.69

Table A.2: Reactor effluent data for experimental run #2 in the packed electrode flow reactor

C$_0$ (mg/L)	A (m²)	Q (L/min)	C (mg/L)	k$_m$ (m/min)	Current (A)	Voltage (V)
Run #2 December 18, 2007						
5.395	0.2174	0.129	1.685	0.0006905	1.5	3
5.395	0.2174	0.129	1.665	0.0006976	1.5	3
5.395	0.2174	0.129	1.706	0.0006832	1.5	3
5.395	0.2174	0.129	1.596	0.0007227	1.5	3
5.395	0.2174	0.129	1.661	0.0006990	1.5	3
5.395	0.2174	0.129	1.56	0.0007363	1.5	3
5.395	0.2174	0.129	1.57	0.0007325	1.5	3
5.395	0.2174	0.129	1.59	0.0007250	1.5	3
5.395	0.2174	0.129	1.598	0.0007220	1.5	3
5.395	0.2174	0.129	1.506	0.0007572	1.5	3
5.395	0.2174	0.129	1.594	0.0007235	1.5	3
5.395	0.2174	0.129	1.513	0.0007544	1.5	3
5.395	0.2174	0.129	1.548	0.0007408	1.5	3
5.395	0.2174	0.129	1.539	0.0007443	1.5	3
5.395	0.2174	0.129	1.57	0.0007325	1.5	3
4.384	0.2174	0.129	1.415	0.0006710	1.75	3.3
4.384	0.2174	0.129	1.339	0.0007038	1.75	3.3
4.384	0.2174	0.129	1.404	0.0006756	1.75	3.3
4.384	0.2174	0.129	1.336	0.0007051	1.75	3.3
4.384	0.2174	0.129	1.396	0.0006790	1.75	3.3
4.384	0.2174	0.129	1.381	0.0006854	1.75	3.3
4.384	0.2174	0.129	1.368	0.0006911	1.75	3.3
4.384	0.2174	0.129	1.254	0.0007427	1.75	3.3
4.384	0.2174	0.129	1.371	0.0006898	1.75	3.3
4.384	0.2174	0.129	1.352	0.0006980	1.75	3.3
4.384	0.2174	0.129	1.334	0.0007060	1.75	3.3
4.384	0.2174	0.129	1.341	0.0007029	1.75	3.3
4.384	0.2174	0.129	1.34	0.0007033	1.75	3.3
4.384	0.2174	0.129	1.299	0.0007218	1.75	3.3
4.384	0.2174	0.129	1.337	0.0007047	1.75	3.3

62

Supporting Laboratory Data from Pilot Packed Electrode Flow Reactor

Table A.3:   Laboratory pilot data for removal of RDX from a process waste stream by
a packed electrode flow reactor, flow condition #1

Q =   0.58   L/min
A =   4.05   m²
V =   11.62   L
V_{void} =   9.86   L

Run Time (min)	Influent RDX (mg/L)	Effluent RDX (mg/L)	Residence Time (min)	C/C_0	k (min^{-1})	k_m (m/min)
0	17.806					
20	20.628	1.637	17	0.0794	0.1490	0.0003627
40	20.787	2.242	17	0.1079	0.1310	0.0003188
60	20.741	2.061	17	0.0994	0.1358	0.0003305
80	20.648	1.971	17	0.0955	0.1382	0.0003363
100	20.735	1.975	17	0.0952	0.1383	0.0003366
120	20.187	1.939	17	0.0961	0.1378	0.0003354
140	19.769	1.941	17	0.0982	0.1365	0.0003322
160	19.92	1.953	17	0.0980	0.1366	0.0003325
180	19.948	1.977	17	0.0991	0.1360	0.0003309
240	18.565	1.921	17	0.1035	0.1334	0.0003247
300	12.941	1.533	17	0.1185	0.1255	0.0003054
360	8.06	0.973	17	0.1207	0.1244	0.0003027

Table A.4:   Laboratory pilot data for removal of RDX from a process waste stream by
a packed electrode flow reactor, flow condition #2

Q =   3.7 L/min
A =   4.05   m²
V =   11.62   L
V_{void} =   10.18   L

Run Time (min)	Influent RDX (mg/L)	Effluent RDX (mg/L)	Residence Time (min)	C/C_0	k (min^{-1})	k_m (m/min)
0	20.805					
10	19.39	1.178	2.75	0.0608		
20	1.85	1.136	2.75	0.6141	0.1773	0.0004453
30	1.684	1.118	2.75	0.6639	0.1490	0.0003741
40	1.55	1.025	2.75	0.6613	0.1504	0.0003777
50	1.43	0.917	2.75	0.6413	0.1616	0.0004058
60	1.27	0.802	2.75	0.6315	0.1672	0.0004198
80	1.111	0.689	2.75	0.6202	0.1737	0.0004363
100	0.888	0.619	2.75	0.6971	0.1312	0.0003295
120	0.729	0.451	2.75	0.6187	0.1746	0.0004385
150	0.594	0.387	2.75	0.6515	0.1558	0.0003913
180	0.51	0.337	2.75	0.6608	0.1507	0.0003784
210	0.396	0.281	2.75	0.7096	0.1247	0.0003133
240	0.294	0.223	2.75	0.7585	0.1005	0.0002524
280	0.22	0.135	2.75	0.6136	0.1776	0.0004460

63

Table A.5: Laboratory pilot data for removal of RDX from a process waste stream by a packed electrode flow reactor, flow condition #3

$Q =$ 4.9 L/min
$A =$ 4.05 m²
$V =$ 11.62 L
$V_{void} =$ 9.80 L

4.9 L/min

Run Time (min)	Influent RDX (mg/L)	Effluent RDX (mg/L)	Residence Time (min)	C/C_0	k (min^{-1})	k_m (m/min)
0	17.823					
5	5.477	3.967	2	0.7243	0.1613	0.0003901
10	5.911	2.433	2	0.4116	0.4438	0.0010736
15	5.708	3.362	2	0.5890	0.2647	0.0006402
20	5.131	3.202	2	0.6240	0.2358	0.0005703
25	5.196	2.978	2	0.5731	0.2783	0.0006732
45	4.25	2.445	2	0.5753	0.2764	0.0006686
60	3.723	2.177	2	0.5847	0.2683	0.0006489
75	2.884	1.841	2	0.6383	0.2244	0.0005429
90	2.662	1.635	2	0.6142	0.2437	0.0005895
105	2.427	1.36	2	0.5604	0.2896	0.0007004
120	2.192	1.235	2	0.5634	0.2869	0.0006939

Table A.6: Laboratory pilot data for removal of RDX from a process waste stream by a packed electrode flow reactor, flow condition #4

$Q =$ 1.55 L/min
$A =$ 4.05 m²
$V =$ 11.62 L
$V_{void} =$ 9.30 L

Run Time (min)	Influent RDX (mg/L)	Effluent RDX (mg/L)	Residence Time (min)	C/C_0	k (min^{-1})	k_m (m/min)
	30.554					
20	35.358	10.548	6	0.29832004	0.2016	0.0004627
40	32.619	10.713	6	0.32842822	0.1856	0.0004260
60	29.912	9.605	6	0.32110859	0.1893	0.0004346
80	26.785	9.249	6	0.34530521	0.1772	0.0004068
100	23.037	8.218	6	0.35673048	0.1718	0.0003943
120	18.939	6.957	6	0.36733724	0.1669	0.0003831

64

Table A.7: Laboratory pilot data for removal of RDX from a process waste stream by a packed electrode flow reactor, flow condition #5

Q = 1.04 L/min
A = 4.05 m²
V = 11.62 L
V_{void} = 9.36 L

Run Time (min)	Influent RDX (mg/L)	Effluent RDX	Residence Time (min)	C/C_0	k (min^{-1})	k_m (m/min)
	17.059					
10	17.187	3.642	9	0.211904	0.1724	0.0003983
20	17.163	3.793	9	0.220999	0.1677	0.0003875
30	17.1	3.811	9	0.222865	0.1668	0.0003853
40	17.498	3.77	9	0.215453	0.1706	0.0003940
50	17.259	3.723	9	0.215714	0.1704	0.0003937
60	16.891	3.744	9	0.221657	0.1674	0.0003867
80	16.299	3.645	9	0.223633	0.1664	0.0003845
100	14.016	3.308	9	0.236016	0.1604	0.0003706
120	12.444	2.864	9	0.230151	0.1632	0.0003771

Table A.8: Laboratory pilot data for removal of RDX from a process waste stream by a packed electrode flow reactor, flow condition #6

Q = 0.355 L/min
A = 4.05 m²
V = 11.62 L
V_{void} = 9.59 L

Run Time (min)	Influent RDX (mg/L)	Effluent RDX (mg/L)	Residence Time (min)	C/C_0	k (min^{-1})	k_m (m/min)
	9.509					
40	9.798	0.396	27	0.040416	0.1188	0.0002811
50	9.755	0.17	27	0.017427	0.1500	0.0003548
60	9.379	0.233	27	0.024843	0.1369	0.0003238
80	9.358	0.182	27	0.019449	0.1459	0.0003452
100	8.719	0.223	27	0.025576	0.1358	0.0003212
120	9.124	0.224	27	0.024551	0.1373	0.0003248
180	8.609	0.419	27	0.04867	0.1120	0.0002648
240	9.463	0.127	27	0.013421	0.1597	0.0003777
300	9.172	0.187	27	0.020388	0.1442	0.0003411
360	9.373	0.234	27	0.024965	0.1367	0.0003233

65

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Table A.9: Laboratory pilot data for removal of RDX from a process waste stream by a packed electrode flow reactor, flow condition #7

Current = 25 A
Q = 0.352 L/min
A = 4.05 m²
V = 11.62 L
V_{void} = 9.50 L

Run Time (min)	Influent RDX (mg/L)	Effluent RDX (mg/L)	Residence Time (min)	C/C_0	k (min^{-1})	k_m (m/min)
	32.022	1.178	27	0.036787	0.1223	0.0002869
	34.467	1.399	27	0.04059	0.1187	0.0002784
	33.977	1.381	27	0.040645	0.1186	0.0002783

Table A.10: Laboratory pilot data for removal of RDX from a process waste stream by a packed electrode flow reactor, flow condition #8

Current = 35 A
Q = 0.352 L/min
A = 4.05 m²
V = 11.62 L
V_{void} = 9.50 L

Run Time (min)	Influent RDX (mg/L)	Effluent RDX (mg/L)	Residence Time (min)	C/C_0	k (min^{-1})	k_m (m/min)
	33.354	0.936	27	0.028063	0.1323	0.0003104
	36.162	0.854	27	0.023616	0.1387	0.0003254
	36.721	0.808	27	0.022004	0.1414	0.0003316
	28.69	0.726	27	0.025305	0.1362	0.0003194

66