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Pilot-Scale Reactor for Electrochemical Reduction of Nitroaromatics in Water

Simulated Wastewater Testing

Rajesh Doppalapudi, Dinesh Palaniswamy,
George Sorial, and Stephen W. Maloney

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Foreword

This study was conducted for Headquarters, U.S. Army Corps of Engineers (HQUSACE) under Project 4A162720D048, "Industrial Operations Pollution Technology"; Work Unit CNE-U041, "Reductive Electrochemical Treatment Processes." The technical reviewer was Chris Vercauten, Operations Support Command.

The Environmental Processes Branch (CN-E) of the Installations Division (CN), Construction Engineering Research Laboratory (CERL) performed the work. The study was performed in part by the University of Cincinnati, Cincinnati, Ohio, under contract to CN-E. The CERL principal investigator was Dr. Stephen W. Maloney. Dr. Ilker R. Adiguzel is Chief, CN-E; and Dr. John T. Bandy is Chief, CN. The technical editor was Linda L. Wheatley, Information Technology Laboratory — Champaign. The Director of CERL is Dr. Alan W. Moore.

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1 Introduction

Background

The large-scale manufacture and use of nitroaromatic compounds such as 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) has led to significant production of munitions wastewater. Apart from TNT, DNT, and RDX, Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraazocine (HMX) was also found in the munitions wastewater. Wastewater containing TNT, RDX, and HMX is commonly referred to as pinkwater. TNT constitutes a significant component of a widespread munition contamination problem. The United States ceased production of TNT in the mid-1980s, but TNT-contaminated wastewater generation still exists as a result of demilitarization. The U.S. Department of Defense (DoD) has identified more than 1,000 sites with explosives contamination. More than 95 percent of these sites were contaminated with TNT and 87 percent exceeded permissible ground water contaminant levels (Walsh et al. 1993). Most of the sites have been found to contain significant amounts of explosives in soil and water samples, the major contaminant being pinkwater generated by demilitarization operations that were conducted in the 1970s.

Contamination of water by TNT and RDX occurs during munitions loading and demilitarization, whereas DNT enters waste streams during propellant production. Production-grade RDX contains several percent HMX, which is also a military explosive, so its presence in RDX is not detrimental. HMX enters wastewater mainly during manufacturing and cleaning operations. Both TNT and DNT are listed as priority pollutants by the U.S. Environmental Protection Agency (USEPA) because of their toxicology hazards.

DNT is prepared by the nitration of toluene and nitrotoluene in the presence of nitric and sulfuric acids. DNT is commercially used as an intermediate in the manufacture of toluene diisocyanate, which is then used in the production of polyurethane foams. For military purposes, DNT is primarily used as a plasticizer and burn rate modifier in single-base propellants.

TNT is prepared by the nitration of toluene with a mixture of nitric acid and sulfuric acid. TNT is the most commonly used explosive because of its low melting point (80.1 °C), stability, low sensitivity to impact, and relatively safe methods of manufacture compared with other explosives. TNT is the most widely used explosive for both military and commercial purposes. TNT is used in bombs and explosives in a binary mixture, with a primary explosive to trigger the detonation. It enters waste streams during manufacturing, loading, and packing operations.

RDX is an explosive extensively used in military operations as an explosive in artillery shells and projectiles. It acts as a good explosive because of its higher density, lower flame temperatures, and release of higher energy. It is also used as a primary explosive in grenades. The manufacture, handling, and disposal of munitions generate wastewater with significant amounts of RDX.

HMX is an acronym for high melting explosive. HMX is used for nuclear detonations, plastic-bonded explosives, solid fuel rocket propellants, and other specialty explosives (McLellan, Hartley, and Brower 1988). HMX is found in wastewater streams mainly from manufacturing and cleaning operations.

Objectives

A previous study (Doppalapudi et al. 2000) evaluated a pilot-scale reactor for electrochemical reduction of energetically contaminated wastewater. The main goal of the study reported here was to modify the existing pilot-scale reactor from the previous study and evaluate the performance of the modified reactor for electrochemical reduction of simulated munitions wastewater. The specific objectives of this study were to: (1) develop kinetics of electrochemical reduction of RDX, HMX, and Tritanol (munitions wastewater with suspected aluminum and iron metal ions); (2) modify the pilot-scale reactor to account for mass transfer limitations; and (3) evaluate the performance of the modified pilot reactor in the reduction of propellant wastewater (100 mg/L of DNT and 300 mg/L of ethanol) and pinkwater (70 mg/L of TNT and 10 mg/L of RDX).

Approach

Kinetic rate determination of RDX, HMX, and Tritanol reduction was studied at the bench-scale in an electrochemical batch reactor. The rate of electrochemical reduction was measured under various experimental conditions including current density, stir rates, and presence and absence of dissolved oxygen. The pilot-scale reactor was modified from the previous study and electrochemical experiments were conducted on the modified reactor to study the reduction of propellant wastewater and pinkwater. The by-products of electrochemical reduction of DNT were identified by gas chromatography (GC), and those of TNT were identified by high performance low chromatography (HPLC). For the continuous flow experiments, a mass balance for the products was obtained both in the aqueous phase and the solid phase. The reduction behavior was then assessed in light of the experimental results obtained, and conclusions were drawn from the data in order to address the objectives of the research.

Scope

The techniques described in this report apply to Army industrial activities. The agencies responsible for development and treatment of Army-specific explosives and other aqueous waste streams will benefit from the information presented herein. The goals of developing and understanding new treatment technology potentially applicable to nitrated explosives are addressed.

Mode of Technology Transfer

If the results of this research effort prove promising, the portable bench scale reactor will be tested on site with actual Army wastewaters.

This report will be accessible through the World Wide Web (WWW) at URL: http://www.cecer.army.mil.

2 Literature Review

Biological Pathways

A number of studies have been done on the biological degradation (biodegradation) of various nitroaromatics. These studies could be broadly classified into aerobic or anaerobic degradation. In both of these categories, effective removal of chemicals have been reported. The most common mechanism is reduction, which converts nitroaromatic compound to aryl amines.

Bioremediation usually employs aerobic conditions in order to achieve the two-fold purpose of complete mineralization to carbon dioxide (CO_2) and water (H_2O) and also to realize higher throughput than that achieved by anaerobic systems (Rodgers and Bunce 2001a). The *Pseudomonas* species is shown to degrade both DNT and TNT aerobically with supplemental glucose as a carbon source (Parrish 1997). Haidour and Ramos (1996) showed that pseudomonas species perform two types of reduction processes with TNT. One involves the removal of a nitro group and utilizing it as a nitrogen source, while the other leads to unproductive compounds.

Under anaerobic conditions, the sulfate-reducing bacteria *Desulfovibrio* transformed TNT into many reduction products (Boopathy and Kulpa 1992; Boopathy, Wilson, and Kulpa 1993; Preuss, Fimpel, and Diekert 1993; Preuss and Rieger 1995). Lenkey at al. (1998) used an anaerobic sludge reactor to treat a mixture of 2,4-DNT and TNT with sucrose as co-substrate. The reduced products 2-hydroxylamino-4, 6-dinitrotoluene, 4-hydroxylamino-2, 6-dinitrotoluene, 2,4,6-triaminotoluene, and azoxy compounds were bound irreversibly to the sludge. Mineralization occurred aerobically after dewatering with an overall removal efficiency of more than 99 percent and no evidence of residual toxicity.

Berchtold et al. (1995) designed a fluidized-bed anaerobic granular-activated carbon reactor, which effectively transformed DNT to DAT. They also showed that conversion of DNT is unaffected by influent ethanol concentration, though 200 mg/L of ethanol was determined to be the minimum concentration of ethanol needed to affect the reduction of DNT to DAT. The DAT formed was then successfully degraded below detection levels using a second stage activated sludge reactor. Bradley, Chapelle, and Landmeyer (1997) carried out a laboratory study of 2,4-DNT using aerobic microorganisms. It was noted that 22 percent of the substrate was reduced to 4-amino-2-nitrotoluene, 6 percent was reduced to 2-amino-4-nitrotoluene, 28 percent was mineralized, and 20 percent remained unchanged. McCormick, Peltonen, and Kaplan (1985) studied 2,4-DNT in continuous culture in a nutrient-rich medium under both aerobic and anaerobic conditions. A variety of intermediates, including 4-amino-2-nitrotoluene, 2-amino-4-nitrotoluene, and 4-acetamide-2-nitrotoluene, were found in the aerobic system along with a variety of unidentified intermediates.

RDX and a related N-acetylated derivative (AcRDX) were studied in aqueous systems and found to be biologically transformed by mixed populations of microorganisms under aerobic conditions when supplemental carbon was provided. Intermediates in this pathway included mono-, di-, and tri-nitroso compounds formed during the sequential reduction of the nitro groups on the parent compound (Sikka et al. 1980; McCormick, Cornell, and Kaplan 1981; McCormick, Cornell, and Kaplan 1985a, 1985b). Young et al. (1996) observed biotransformation of RDX in liquid culture by a consortium of five types of bacteria found in horse manure. The most abundant of the five types was *Serratia marcesens*. Observation of molar balance indicated the conversion of RDX to mono-, di-, and tri-nitroso RDX, respectively.

HMX was found to be biodegradable under anaerobic conditions at 50 mg/L, although rates were slower than for RDX (McCormick, Cornell, and Kaplan 1985b). Biotransformation was incomplete and mono and dinitroso intermediates were identified. HMX degraded at a slower rate in continuous culture under anaerobic denitrification conditions than it did in the batch studies, and none of the intermediates were detected. Jackson, Green, and Hash (1976) reported that anaerobic degradation of HMX in aqueous solutions and in wastewater from a nitro amine manufacturing facility. In follow-on studies with wastewater derived from nitro amine manufacture, complete removal of HMX was reported under anaerobic biological treatment systems with supplemental carbon in the form of hydroxyethyl cellulose (Jackson et al. 1978). Burrows, Paulson, and Carnahan (1989) reported that HMX was not significantly reduced in biological wastewater treatment of effluents from an ammunition plant.

Chemical Pathways

Many commonly used chemical remediation technologies for the removal of nitroaromatics are separation processes rather than destruction processes. They include resin adsorption, surfactant complexing, liquid-liquid extraction, ultrafiltration, and reverse osmosis, all of which concentrate the nitroaromatic explosives for further treatment (Rodgers and Bunce 2001a). Granular activated carbon (GAC) is a nonspecific absorbent that can treat both contaminated ground water and wastes at explosives manufacturing plants. Since the bed has high affinity for organics but a finite capacity, GAC is most effective as a polishing technique. The spent GAC is classified as a K045 hazardous waste and must be further treated (Levsen et al. 1993). Options include disposal in a hazardous waste landfill, incineration, or regeneration by partial oxidation of the GAC. Anaerobic fluidized bed GAC (AFBGAC) was also shown to be effective in the transformation of DNT to DAT. Reduction of DNT was unaffected by influent ethanol concentration, and the majority of the products remained as DAT (Berchtold et al. 1995).

Advanced oxidation processes (AOPs) use reactive oxidizing agents such as hydrogen peroxide or ozone, with or without the addition of catalysts or photolysis, in the degradation of nitroaromatics (Bolton and Cater 1993). In most of these AOPs, hydroxyl radicals are generated, which initiates ring opening of the nitroaromatics and ultimately mineralizes them to CO_2 and H_2O. Ho (1986) used ultraviolet (UV) oxidation with hydrogen peroxide (H_2O_2) to remediate nitroaromatic explosives. Schmelling, Gray, and Kamat (1998) have separately resolved reduction and oxidation of TNT by aqueous electrons (e^-_{aq}) and $OH\cdot$. TNT was shown to have a significantly higher rate of reaction with e^-_{aq} in comparison to $OH\cdot$. Li, Shea, and Comfort (1998) used Fenton's reagent ($H_2O_2 + Fe^{2+}$) alone and in combination with UV (254nm), for remediating aqueous wastes that contained nitroaromatics. The reaction rate depended on the number and position of the nitro groups on the aromatic ring. Titanium dioxide (TiO_2) photocatalysis using near-UV radiation has been demonstrated to be highly effective in the remediation of TNT contaminated wastes (Schmelling and Gray 1995). Trinitrobenzoic acid, trinitrobenzene, and trinitrophenol were observed as oxidative intermediates and 3,5-dinitroaniline was identified as a reductive product.

Hydrothermal technologies, which include wet air oxidation and supercritical water oxidation, are the AOPs that involve mineralization of organics by oxygen or H_2O_2 at high temperatures and pressures. Treatment by wet air oxidation was shown to be a function primarily of temperature and to a lesser extent the partial pressure of oxygen (Hao et al. 1993). The aromatic nitro-group was also catalytically hydrogenated to amines in acidic solution (Rodgers and Bunce 2001a). Hydrogenation alone is not a complete remediation method because the anilines are toxic and must be further treated. Rajashekharam, Jagannathan, and Chaudhari (1998) successfully hydrogenated DNT on 5 percent paladium/aluminum oxide (Pd/Al_2O_3), using a trickle bed reactor.

Electrochemical Pathways

Electrochemistry, with its unique ability to oxidize or reduce compounds at a well-controlled electrode potential by just adding or withdrawing electrons, offers many interesting possibilities in environmental engineering (Simonsson 1997). Electrochemical methods of dechlorinating aromatic compounds were shown to offer promise because of their high energy efficiency and the relative simplicity of the equipment (Bunce, Merica, and Lipkowski 1997). Hintze and Wagner (1992) reduced nitroaromatic explosives to amines in the cathode compartment of an electrochemical cell. Rodgers and Bunce (2001b) reduced TNT and DNT isomers to aminotoluenes with high current efficiencies at a variety of cathodes. They further suggested subsequent electrochemical oxidation to polymerize the aminotoluenes to insoluble byproducts. Jolas, Pehkonen, and Maloney (2000) conducted experiments for the electrochemical reduction of DNT with graphite and titanium mesh cathodes under open and deoxygenated conditions. Mass transfer limitations were observed to effect the reduction of DNT with graphite rod, whereas reduction using titanium mesh cathode showed almost no effect of mass transfer limitations. The intermediates formed during the reduction of DNT were identified as 2,4-diaminotoluene (DAT), 4-amino-2-nitrotoluene, and one of the dinitro-azoxytoluene dimers.

3 Materials and Methods

Bench Scale Batch Experiments

Batch experiments were carried out in a 2.5 L glass reactor. The experimental set up originally developed by Jolas, Pehkonen, and Maloney (2000) is shown in Figure 1.

A Nafion membrane (#117 from Solution Technology/C.G Processing, Rockland, DE) was used to separate the transfer of anode compartment and the cathode rod, which allowed the transfer of ions only and prevented the transfer of any of the organic compounds being degraded or being formed.

A Universal Digital Controller (UDC) 3000 (Honeywell, Morristown, NJ) was the source of current. A Thermix Stirrer (Fisher Scientific, Pittsburgh, PA), along with 2-in. Teflon-coated bars, were used for all experiments.

The cathode was a glassy carbon (Sigradur G) rod, 7 mm in diameter and 150 mm in length from SGL Carbon Corporation (St. Mary's, PA). Table 1 lists the various properties of the glassy carbon cathode. A 6-in.-long platinum wire (Fisher Scientific) was used as the anode.

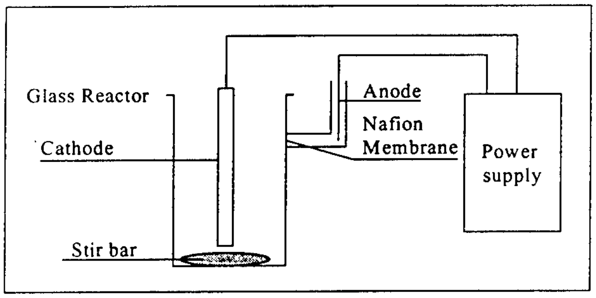

Figure 1. Experimental setup for batch experiments.

Table 1. Physical properties of the glassy carbon cathode.

Property	Metric units
Apparent density	1.42 g/cm^3
Total Porosity	0 %
Electrical Resistivity	4.4 x 10^3 μ ohm-cm
Ash	0 %

Chemicals used to simulate the feed were RDX, HMX, and Tritanol water. All were obtained from the Army and used as received. Sodium sulfate dibasic anhydrous (Fisher Scientific) was added to the reactor for constant ionic strength. Sodium phosphate (Fisher Scientific) was used as buffer to maintain the desired pH level.

Previous reports (Pehkonen et al. 1999) identified the various intermediates during the electrochemical degradation of DNT, TNT, and RDX. For the quantification of these intermediates, the following chemicals were purchased:

Analytical standards for TNT, RDX, and TNT intermediates:
- 2,4,6-trinitrotoluene – 1,000 mg/L, Solvent: Acetonitrile (Cerelliant Inc., Austin, TX)
- 4-amino-2,6-dinitrotoluene – 1,000 mg/L, Solvent: Acetonitrile (Cerelliant Inc.)
- 2-amino-4,6-dinitrotoluene – 1,000 mg/L, Solvent: Acetonitrile (Cerelliant Inc.
- 2,4-diamino-6-nitrotoluene, obtained at a concentration of 0.1 mg/mL in acetonitrile (Accustandard, Inc., New Haven, CT)
- 2,6-diamino-4-nitrotoluene, obtained at a concentration of 0.1 mg/mL in acetonitrile (Accustandard, Inc.)
- 2,2',6,6'-tetranitro-4,4'-azoxytoluene, obtained at a concentration of 0.1 mg/mL in acetonitrile: methanol (1:1) (Accustandard, Inc.)
- 4,4',6,6'-tetranitro-2,2'-azoxytoluene, obtained at a concentration of 0.1 mg/mL in acetonitrile: methanol (1:1) (Accustandard, Inc.)

Experiments were conducted in a 2.5-L glass reactor as shown in Figure 1. The length of the experiments was always less than 12 hours. For experiments involving RDX or HMX, 20 mg of RDX or HMX was first dissolved in 20 mL acetonitrile because of their low solubility in water and then added to 1,930 mL of water. On the day of an experiment, before the experiment began, 50 mL of sodium phosphate buffer (0.02M) and 71 mg of sodium sulfate salt were added to the RDX or HMX mixture and the pH was adjusted to 8. For tritanol (TNT + metals [mainly iron and aluminum]) experiments, the wastewater sample received from the Army had a TNT concentration of 143.8 mg/L and an RDX concentration of 1.09 mg/L. A 200 mL sample of well-mixed Tritanol wastewater was added to 1,750 mL water. As with the RDX/HMX experiments, 50 mL of sodium phosphate buffer (0.02M) and 71 mg of sodium sulfate salt were then added before the experiment began, and the pH was adjusted to 8. Six to eight samples were taken for each experimental run. The pH level of the solution was regularly monitored and kept at 8. For TNT, RDX, and HMX analysis, a 1050 HPLC system using an LC 18 column (for TNT) and RP 18 column (for RDX and

HMX) was used (Supelco, Bellefonte, PA). The method for analyzing TNT had the LC 18 column eluted with 50:50 acetonitrile:buffered water (2.5 millimoles sodium phosphate dibasic anhydrous) with a flow rate of 0.700 mL/min and the method for RDX. HMX had the RP 18 column eluted with 60:40 methanol:HPLC-grade water at a flow rate of 1.00 mL/min. The sampling event consisted of filtering a 2 to 4 mL sample through a 0.10-μm filter paper, and then injecting it into the HPLC system.

Although the other intermediates for TNT had been purchased from the requisite sellers, TAT was not commercially available. The intermediates of RDX (mono-, di-, and tri-nitroso RDX) were not commercially available as were the supposed intermediates of HMX (mono-, di-, and tri-nitroso HMX).

Pilot-Scale Continuous Flow Reactor

Experimental Setup

Continuous flow experiments conducted on the pilot-scale reactor showed only about 20 percent reduction of DNT (Doppalapudi et al. 2000). It is speculated that the low efficiency of the reactor could be due to the effect of mass transfer limitations coupled with low salt concentrations in the influent solution. To overcome these drawbacks, the pilot-scale reactor was modified. The basic reactor setup was kept the same, but the Nafion membrane that was originally in a sheet attached to a perforated Teflon tube was completely replaced by a Nafion tube of larger diameter that had more exposed surface. Figure 2 shows the experimental setup for the modified pilot-scale flow-through reactor. The main reactor consisted of two concentric cylinders. The outer cylinder — the cathode compartment of the reactor — was graphite carbon with surface impregnation of vitreous carbon (glassy carbon). This carbon cylinder (fabricated by M.G.P., Inc., Robesonia, PA), had an internal diameter of 12 cm (4.72 in.) and a height of 60 cm (23.62 in.). The inner cylinder was a Nafion membrane supported by Teflon flanges at both ends. The diameter of the membrane was 8.3185 cm (3.275 in.); whereas the previous set up was 5.715 cm (2.25 in.). In the previous set up (Doppalapudi et al. 2000), only about half the total area of the inner cylinder was exposed because of the Teflon tube. In the new setup the membrane by itself acts as a cylinder, so the total area of the membrane is the net contact area. A 24-in. platinum wire (Fisher Scientific), spans the length of the inner cylinder and acts as the anode. The two feed tanks are made of stainless steel and have a capacity of 75 L. The effluent and salt tanks are 7-gal polyethylene tanks obtained from Fisher Scientific. Three pumps, with a pumping capacity of 6 to 20 L/day, are used in the experimental setup. All three pumps are positive displacement pumps HD-MA type 01-10 (Barnant Co., Barrington, IL) with a maximum capacity of 1 L/hour. The maximum number of strokes is 100/min and the pump has a maximum pressure of 142 psig, with a suction height of 1.5 m. A Honeywell UDC 3000 was used as a constant source of current. Two 500-mL stainless steel holding tanks were used for pH adjustment. One is used for adjusting the pH in the recycle stream and the other for the salt solution stream. These tanks have secure lids with two ports each. One port is used for the pH probe and the other port is fitted with a septum for injection of acid for pH adjustment. High power magnetic stirrers (Thermix Stirrer Models from Fisher Scientific) were used for mixing the feed solution. All piping connections are made of either Teflon or stainless steel.

The feed solution containing 100 mg/L of DNT and 300 mg/L of ethanol or 70 mg/L of TNT is prepared in the two large feed tanks, each of 60-L volume. The feed tank was first filled with deionized (DI) water and the required amount of sodium phosphate buffer (0.02M) added. The pH level was adjusted to 8, and the water was left overnight to be purged by nitrogen gas. The next day the required amounts of nitroaromatic compound and electrolyte were added to the water and the tank was closed and sealed with clamps under a head pressure of nitrogen gas. The feed solution was mixed for 2 days before any experimental run. After mixing, the feed solution was pumped into the reactor using one of the positive displacement pumps at the desired flow rate.

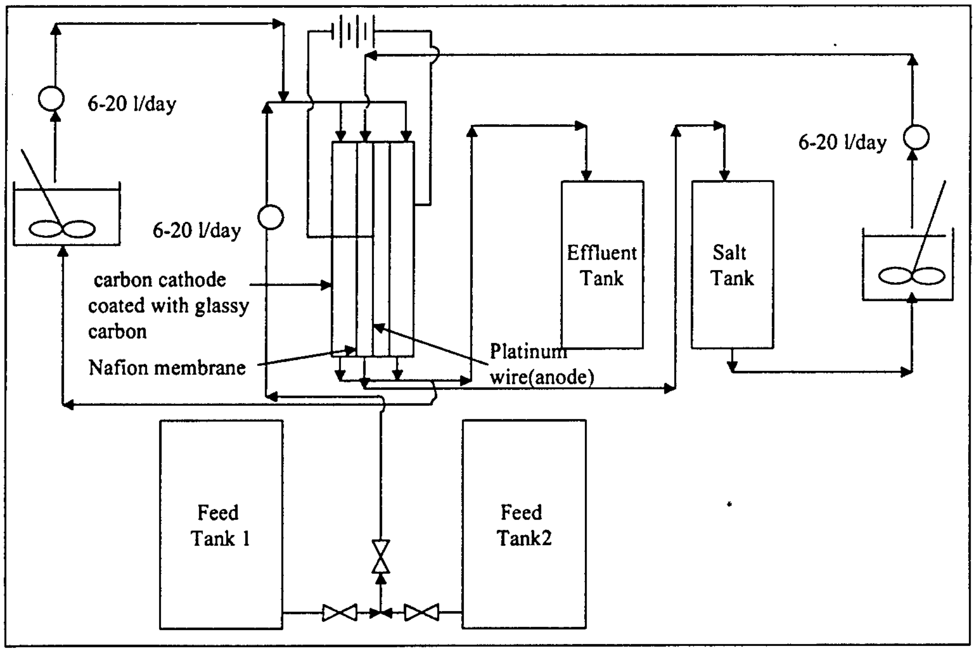

Figure 2. Schematic for electrochemical flow-through reactor.

A 0.25M sodium sulfate solution was used as the electrolyte solution in the anode compartment of the reactor. The salt solution was pumped through the Nafion membrane in the reactor in a closed loop fashion and was changed every 2 weeks when the conductivity of the solution dropped to 30 m mho/cm. The rate of salt solution pumping was maintained at a constant 20 L/day. The third pump was used to recycle part of the effluent into the reactor.

DNT was obtained from Aldrich Chemical Co. (Milwaukee, WI) at 97 percent purity and was used as received. For quantification of the various intermediates formed during the experiment, the following compounds were obtained: 2,4-DAT was obtained from Aldrich and used as received; 2-amino-4-nitrotoluene and 4-amino-2-nitrotoluene (also obtained from Aldrich and used as received). Previous studies also reported the formation of nitrosotoluenes and dimers during the reduction of DNT (Jolas, Pehkonen, and Maloney 2000). Since these intermediates were not available commercially, they were synthesized in the laboratory using the synthesis methods reported by (Pehkonen et al. 1999).

DNT and its intermediates were analyzed by GC, an HP 5890 Series II with an FID detector, 30 m x 0.32 mm i.d. fused silica capillary column and 0.25 mm film thickness (J & W Scientific, DB-1), and a carrier gas of nitrogen (80 psi). A 2.5-mL sample of the solution was withdrawn from the reactor into a 10-mL glass vial and 0.5 mL of dichloromethane containing an internal standard quinoline (25 ppm) is added to it. The vial is then shaken for a period of 2 min and 1 μL of the extract from the dichloromethane layer is injected in the GC system.

Initial Continuous Flow Experiments for Reduction of DNT

Continuous flow experiments were initially conducted on the pilot-scale reactor. These experiments were conducted by continuously pumping the feed solution through the reactor at the desired flow rate. Samples were taken once every day to observe the reduction of DNT. The pH of solution, conductivity of salt solution, and dissolved oxygen of influent and effluent were monitored at least three times a day.

The results obtained from these initial continuous flow experiments yielded low reduction of DNT. To further study the effects of various parameters such as current density, salt concentration of influent, and dissolved oxygen on the reduction of DNT, batch simulation experiments were conducted.

Batch Simulation Experiments With DNT

To simulate batch conditions on the pilot-scale reactor, the reactor was filled with feed solution and the feed pump was turned off. The experiment was then conducted with full recycle to ensure mixing. The anodic solution was allowed to continuously flow through the anode compartment. Samples were collected at regular intervals to monitor the reduction of DNT. At the end of each experiment, the reactor was emptied and the collected solution filtered. The solids retained on the filter paper were analyzed for the various intermediates.

Continuous Flow Experiments With DNT

Based on the results obtained from the batch simulation experiments, continuous flow experiments were conducted on the pilot-scale reactor using the optimized values of the parameters for DNT reduction. Samples were taken once every day to observe DNT reduction. The pH of solution, conductivity of salt solution, and dissolved oxygen of influent and effluent were monitored at least three times a day.

Batch Simulation Experiments for Reduction of TNT

Batch simulation experiments are presently being conducted on the pilot-scale reactor to determine the optimum conditions for future flow-through runs for the reduction of TNT.

4 Results and Discussion

Batch Experiments for RDX, HMX, and Tritanol

The experimental conditions for the batch reactor are shown in Table 2.

Table 2. Experimental parameters for batch experiments.

Parameters	Values
Total volume of simulated wastewater in the batch reactor	2000 mL
Salt concentration	35.5 g/L
pH	8.0
Applied current	23mA-65mA
Stir rate	630, 2040 rpm
Electrodes	Glassy carbon
Surface area	67.5 cm^2
Porosity	0
Dissolved oxygen	< 1.0 mg/L (Deoxygenated condition) 8.34mg/L (Open system)

The RDX or HMX wastewater was simulated as a concentration of 10 mg/L by dissolving 20 mg of RDX or HMX in 20 mL of acetonitrile and then adding the solution to 1930 mL of water with 50 mL of a sodium phosphate buffer (0.02M) and salt (anhydrous sodium sulfate - 71 mg to give a concentration of 35.5 mg/L). The solution was then mixed for 48 hours. Ten experiments were conducted for each compound. For each compound, experiments were conducted at five different current rates of 23, 34, 45, 53, and 65 mA and two different stir rates of 630 and 2040 rpm. These stir rates correspond to calibration points 4 and 5 on the stirrer. All the experiments for RDX and HMX were conducted under open-system conditions.

The Army provided 2 L of Tritanol water to study the influence of metal ions on the degradation characteristics of the nitroaromatic. The Tritanol water contained aluminum and ferrous ions. The wastewater sample was analyzed first and was found to have 143.8 mg/L of TNT and 1.09 mg/L of RDX. A 200-mL sample of Tritanol wastewater was mixed with 1750 mL of water and 50 mL of buffered water (sodium phosphate 0.02M) and salt (anhydrous sodium sulfate - 71 mg to give a concentration of 35.5 mg/L). Experiments for Tritanol were conducted under both open and deoxygenated conditions. The deoxygenated conditions were obtained by purging the DI water with nitrogen gas until the DO level read below 1 mg/L. The Tritanol, buffer, and salt were then added to the nitrogen-purged water and the reactor sealed under a nitrogen headspace. The contents were mixed for 48 hours. The pH level was adjusted to 8 before commencing the experiment. Experiments were conducted at five different current rates 23, 34, 45, 53, and 65 mA, a stir rate of 2040 rpm, and under open and deoxygenated conditions.

For all experiments, samples were collected at different intervals. The concentrations determined from the samples were then used to obtain the pseudo first order rate constants for the reduction of the respective contaminants through regression analysis.

Electrochemical Reduction of RDX

Batch experiments were conducted to study the electrochemical reduction of the RDX simulated wastewater. Table 3 shows the rate constants determined. Two sets of experiments were conducted by using two different glassy carbon cathodes referred to as Cathode-1 and Cathode-2. Cathode-1 was the cathode used in the past experiments (Doppalapudi et al. 2000) involving DNT, TNT, and RDX (both open system and deoxygenated). Cathode-2 is a new set of glassy carbon electrodes obtained from the manufacturer of Cathode-1 (SGL Carbon Corporation).

Table 3. Rate constants for the reduction of RDX in the batch reactor.

Current (mA)	Stir rate (rpm)	pH	Rate (min^{-1}) for Cathode-1	Rate (min^{-1}) for Cathode-2	Rate (min^{-1}) from Pehkonen et al. (1999)
25	630	8	0.0003	0.0003	0.001
34	630	8	0.0003	0.0006	0.0018
45	630	8	0.0006	0.0005	0.002
53	630	8	0.0004	0.0007	0.0018
65	630	8	0.0008	0.0009	0.0017
25	2040	8	0.0004	0.0005	0.0012
34	2040	8	0.0005	0.0008	0.002
45	2040	8	0.0006	0.0005	0.0026
53	2040	8	0.0006	0.0010	0.003
65	2040	8	0.0005	0.0011	0.003

Experiments for Reduction of RDX With Cathode-1

The rate constants obtained in the present study compared with the results obtained by Pehkonen et al. (1999) show significantly lower rate constants. It is speculated that the cathode electrode was malfunctioning. Figure 3 shows the plot of the current versus the rate constant for Cathode-1. From Figure 3, it is observed that the rate constant varies between 0.0008 and 0.0003 min^{-1}. The maximum reduction of RDX obtained was less than 30 percent.

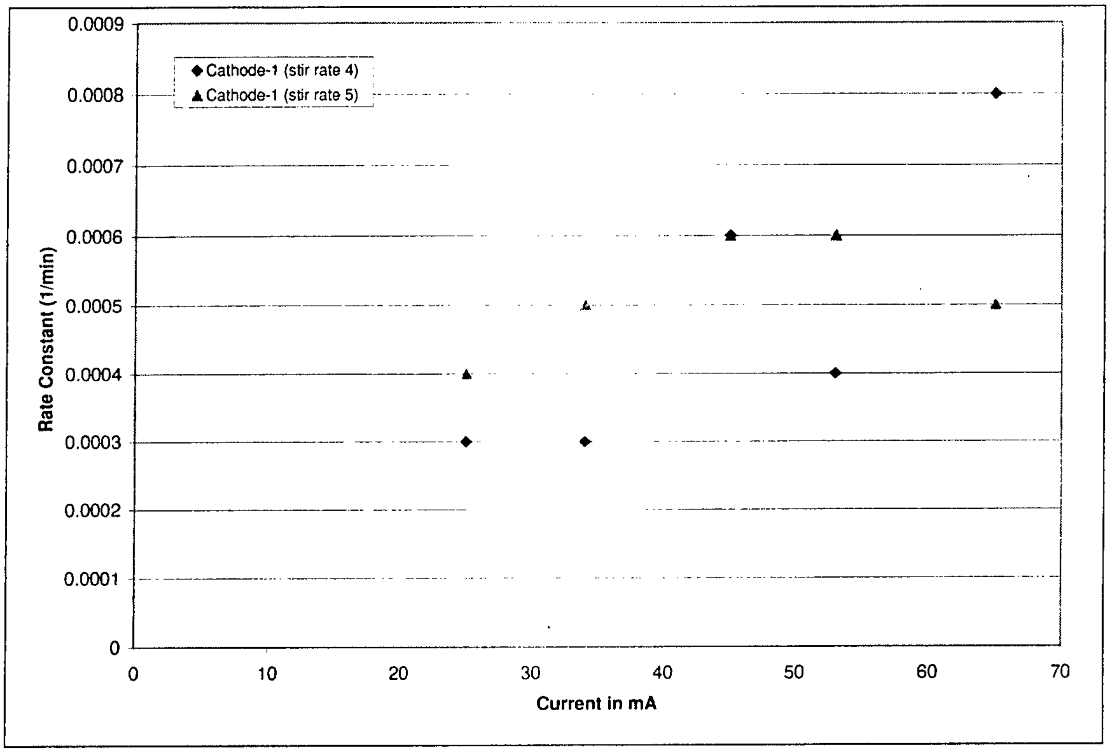

Figure 3. Current versus rate constant (Cathode-1).

Experiments for Reduction of RDX With Cathode-2

Table 3 also shows the rate constants obtained for experiments conducted by using Cathode-2. Figure 4 shows a plot of current versus rate constant for the two stir rates. It is observed that the rate constants varied between 0.0003 and 0.0011 min^{-1}. The maximum reduction of RDX obtained was less than 30 percent.

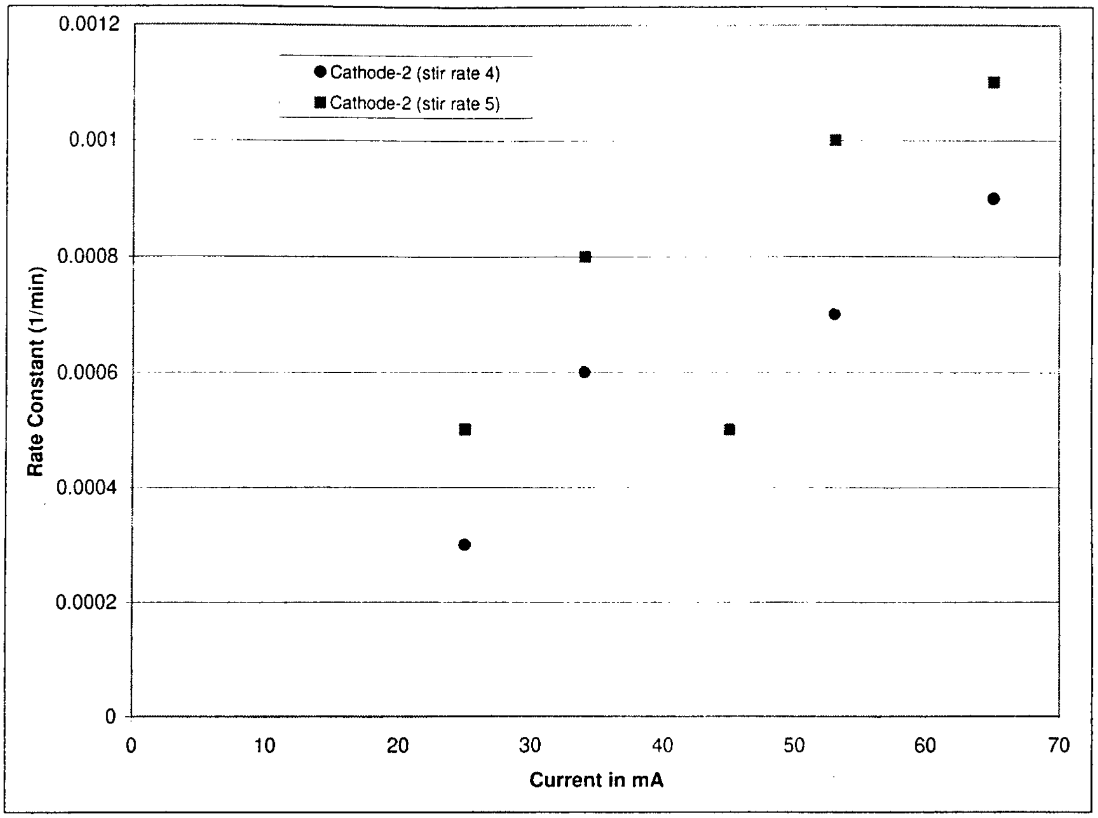

Figure 4. Current versus rate constant for RDX (Cathode-2).

Using the results shown in Table 3 to compare the rates obtained for Cathode-1 and Cathode-2, it is observed that there is a substantial increase in the rate, especially at the higher current values – the increase was over 120 percent for the 65 mA at 2040 rpm. A comparison of these two rates, however, with the ones obtained by Pehkonen et al. (1999), shown in Table 3, indicate that the rates were still comparatively low.

It is worthwhile to note that a significant concentration (20 to 30 percent of the total concentration of RDX) of HMX was observed in the analysis of RDX prior to experimental runs. It is speculated that this contamination might have hindered the electrochemical reaction for reduction of RDX. During the course of the experiments with Cathode-2, remedial measures were taken to remove any contaminant polymer film on the cathode, which may have been hindering the reaction. For example, the cathode was allowed to soak in a dichloromethane solvent overnight before starting the experiment. No improvement in rate constants could be achieved throughout the experimental runs, however.

The reduction rates were less than 30 percent of the initial mass, so no intermediates could be detected in the analysis of the liquid samples.

Electrochemical Reduction of HMX

Batch experiments were conducted for HMX at currents ranging from 25 mA to 65 mA. For every current, two stir rates of 640 and 2040 rpm were used. These experiments were conducted by using the same Cathode-2 that was used for the RDX experiments. Table 4 shows the rate constants.

Table 4. Rate constants for reduction of HMX.

Current in mA	Stir rate in rpm	pH	Rate Constant (min^{-1})
25	630	8	0.0006
34	630	8	0.0009
45	630	8	0.0007
53	630	8	0.0007
65	630	8	0.001
25	2040	8	0.0003
34	2040	8	0.0009
45	2040	8	0.0008
53	2040	8	0.0015
65	2040	8	0.0016

From Figure 5 it is observed that the rate constants for HMX varied between 0.0003 to 0.0016 min^{-1}. A maximum HMX reduction of only 48 percent could be achieved during the course of the experiments. It is speculated that, as a highly recalcitrant compound, HMX polymerizes and forms a coating on the cathode, thus hindering the electrochemical reduction reaction from taking place. Remedial measures were taken to remove any such recalcitrant film on the cathode. The cathode, for example, was allowed to soak in dichloromethane solvent overnight prior to experimental runs, but no significant improvement in cathode performance could be achieved.

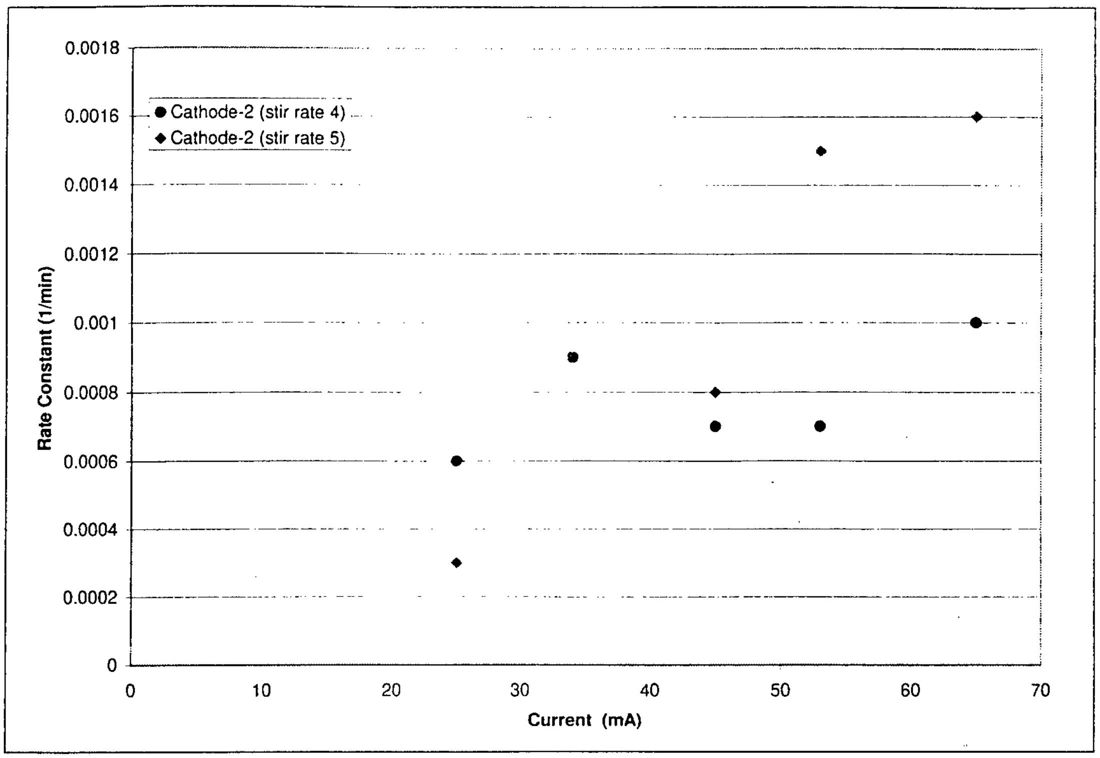

Figure 5. Current versus rate constant for HMX (Cathode-2).

Electrochemical Reduction of Tritanol Wastewater

Batch experiments were conducted for Tritanol wastewater at currents ranging from 25 mA to 65m A. A stir rate of 2040 rpm was used for every current. Ten experiments were conducted; five under open and five under deoxygenated conditions. These experiments were conducted with the Cathode-2. Table 5 shows the rate constants observed for these experiments.

Table 5. Rate constants for reduction of TNT in tritanol water.

Experimental Condition	Current (mA)	Stir rate (rpm)	PH	Rate Constants For TNT (min^{-1})
Open system	25	2040	8	0.0005
Open system	34	2040	8	0.0007
Open system	45	2040	8	0.0007
Open system	53	2040	8	0.0010
Open system	65	2040	8	0.0011
Deoxygenated	25	2040	8	0.0008
Deoxygenated	34	2040	8	0.0008
Deoxygenated	45	2040	8	0.0014
Deoxygenated	53	2040	8	0.0017
Deoxygenated	65	2040	8	0.0010

From Figure 6, it is observed that the rate constants varied between 0.0017 to 0.0005 min^{-1}. A maximum TNT reduction of only 40 percent could be achieved throughout the experimental runs. The analysis of the liquid samples yielded no intermediates, as the reduction rates were low. It is speculated that the low reduction results are attributed to a malfunctioning cathode.

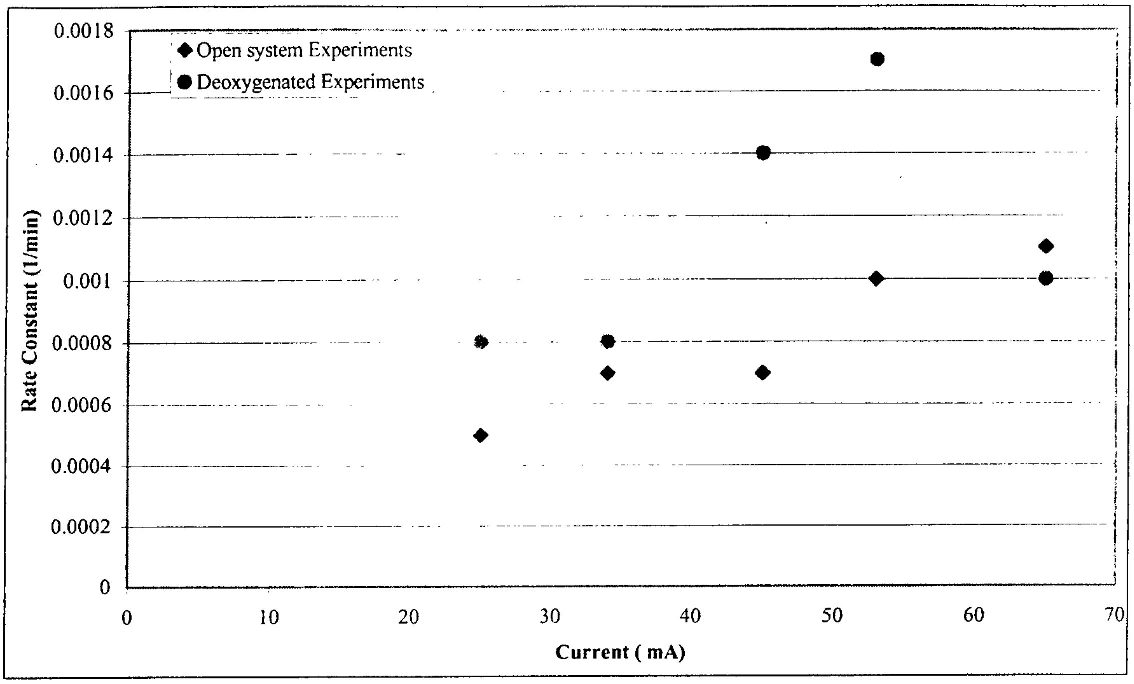

Figure 6. Current versus rate constant for tritanol wastewater (Cathode-2).

Pilot-Scale Continuous Flow Experiments for DNT

Initial Continuous Flow Experiments

Experiments were conducted on the modified pilot-scale reactor to study the reduction of DNT in the presence of ethanol. Experiments were conducted at 53 mA current for 14 days. No electrolyte was added to the feed solution. The feed and recycle flow rates were varied to observe any effect in the reduction of DNT. For the first 5 days the flow rate of feed was maintained at 6 L/day with a recycle of 20 times the flow rate. From day 5 to day 9 the flow rate was increased to 14 L/day and the recycle was reduced to 4.5 times the flow rate. For the last 5 days the flow rate was maintained at 14L/day, but the recycle was increased to 9 times the flow rate.

Figure 7 shows the plot of effluent concentration normalized to the influent concentration and the percent efficiency versus time. It can be observed that only about 15 percent DNT reduction was attained, and no significant difference is noted for the various feed and recycle flow rates used. The low DNT reduction could be due to mass transfer limitations and low conductivity of the influent solution.

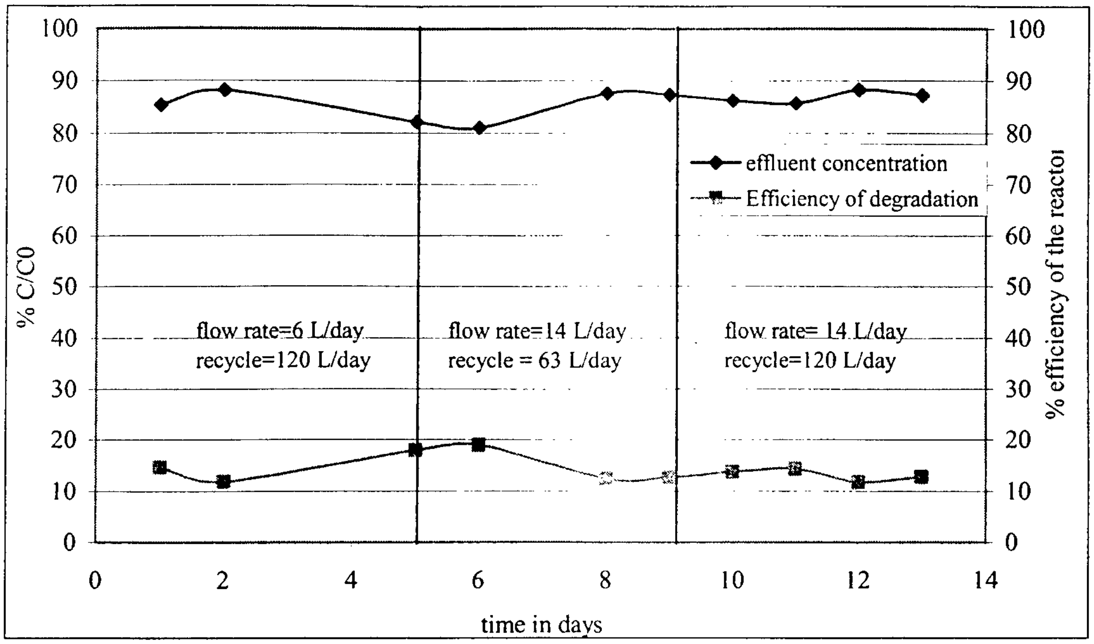

Figure 7. Degradation of DNT with time.

Batch Simulation Experiments for DNT

The continuous flow experiments reported in the previous section showed very low DNT reduction. To determine the impact of the various parameters on DNT reduction, batch simulation experiments were conducted on the pilot-scale reactor. Experiments simulating batch conditions were conducted for studying the impact of applied current (53 mA-200 mA), ionic strength of feed (0-0.027M), type of electrolyte (NaCl and Na_2SO_4), and the effective length of the reactor (1.9 L = 1/2 full, 3.8 L = completely full). To simulate batch conditions, the feed solution was pumped into the reactor until it was either full or half full depending on the condition of the experimental run and whether the feed pump was turned off. The recycle pump was then turned on at full speed and the experiment conducted with complete recycle to ensure mixing. Samples were taken from the reactor at regular intervals. At the end of each experimental run the reactor was emptied, the collected solution filtered, and the solid phase analyzed for intermediate reduction products. The dissolved oxygen in all the experimental runs was maintained at 1.2 – 1.4 ppm.

The concentrations of DNT collected for the various experiments were used to determine the first order rate constants. Table 6 shows the determined first order rate constants.

Table 6 shows that, for current densities above 100 mA, no significant difference is noticed between using NaCl or Na_2SO_4 as an electrolyte. Furthermore, a current density of 150 mA and 200 mA provided better reduction rate constants than lower current densities. The rate constants obtained for the reduction of DNT on a bench-scale batch reactor for 53 mA current were 0.0061 and 0.0063 min^{-1} for stir rates 630 and 2040 rpm respectively (Doppalapudi et al. 2000). Comparing these results with the rate constants shown in Table 6, it can be observed that the reduction of DNT is very low in the pilot-scale reactor. The low reduction could be due to low ionic strength (I = 0.78 M for batch experiments compared to 0.027M in the pilot-scale reactor) and/or mass transfer limitations due to inefficient mixing in the pilot-scale reactor. Figure 8 shows a plot of rate constant versus current for the two electrolytes and ionic strength of 0.027M for the reactor completely full. From Figure 8 it is observed that the rate constant reaches a plateau at a current above 150 mA.

Table 6. Observed first order rate constants for the reduction of DNT.

Current (mA)	Volume of Reactor (L)	Electrolyte	Ionic strength of feed (M)	Rate constant (min^{-1})
53	1.9	NaCl	0	0.0005
53	1.9	NaCl	0.009	0.0007
53	1.9	NaCl	0.018	0.0016
53	1.9	NaCl	0.027	0.0028
53	1.9	Na_2SO_4	0.027	0.004
100	3.8	NaCl	0.027	0.0036
100	3.8	Na_2SO_4	0.027	0.0032
100	1.9	NaCl	0.027	0.0038
100	1.9	Na_2SO_4	0.027	0.0045
150	3.8	NaCl	0.027	0.0042
150	3.8	Na_2SO_4	0.027	0.0047
200	3.8	NaCl	0.027	0.0043
200	3.8	Na_2SO_4	0.027	0.0047

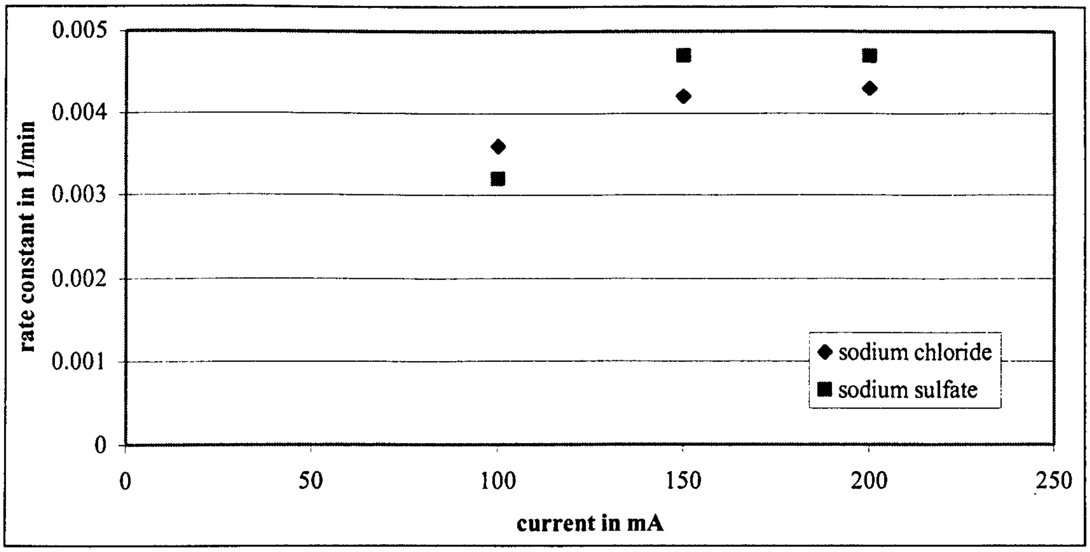

Figure 8. Rate constants for reduction of DNT in batch simulation experiments.

Furthermore, performing an electron balance in the system for 90 percent reduction of DNT to DAT over a certain fixed time, one can obtain the minimum current to be applied. For a specific time and applied current, the number of electrons released into the system can be calculated as:

Number of electrons = It/F moles of electrons.

Where:

I = current applied

t = time for which current is applied

F = Faraday's constant (96500)

For the reduction of one nitro group to an amino group, six electrons are consumed. Since there are two amino groups on DNT, for reduction of each molecule of DNT to DAT, 12 electrons are required.

Concentration of DNT = 100 mg/L

Volume of cathode compartment = 3.8 L

Mass of DNT in the reactor = 380 mg

Number of moles of DNT = $380 * 10^{-3}/182 = 2.09 * 10^{-3}$ moles

For 90 percent reduction,

Number of moles of DNT to be reduced = $0.9 * 2.09 * 10^{-3} = 1.88 * 10^{-3}$ moles

Total number of electrons required = $12 * 1.88 * 10^{-3} = 22.54 * 10^{-3}$ moles.

Hence,

$It/F = 22.54 * 10^{-3}$

Here, t = 11 hr (retention time of the reactor)

Hence $I = 22.54 * 10^{-3} * 96500 / (11 * 3600) = 54.93$ mA

The above calculations show that, theoretically, supplying a current of 55 mA will be enough to obtain a 90 percent reduction of DNT to DAT. The above calculations are based, however, on the assumption that electron usage is 100 percent efficient for the reduction of DNT. In reality the electrons released at the cathode not only reduce DNT but also form hydrogen gas. The experimental results shown here demonstrate that the efficiency of the usage of electrons for reduction of DNT is very low at ~30 percent.

At the end of each batch simulation experiment, the reactor was emptied and the collected solution filtered to quantify the various end products formed. Table 7 shows the percent molar conversion of DNT to various compounds obtained for some of the experiments. Table 7 shows that about 60 to 80 percent mass balance was attained. About 70 to 80 percent of the intermediates were in the solid phase. 2,2',4,4'-Tetranitro-6,6'-azoxytoluene (dimer 1) was the major intermediate in the solid phase, whereas 2,4-diaminotoluene was the only intermediate observed in the liquid phase. Aminonitrotoluenes formed during the experiment were only in the form of solids.

These experiments showed no significant difference in the reduction of DNT for the two different electrolytes used in the pilot-scale reactor. The rate constants were also observed to increase with increased current but stabilize at higher currents (150 mA and higher).

Table 7. Mass balance of DNT for batch simulation experiments.

Current (mA)	Volume of Reactor (l)	Electrolyte	Ionic Strength (M)	Compound	% molar conversion of DNT (solid phase)	% molar conversion of DNT (aqueous phase)
53	1.9	NaCl	0	DNT	--	53.78
				DAT	--	4.56
				4-A-2-NT	0.47	--
				2-A-4-NT	0.41	--
				Dimer 1	9.17	--
53	1.9	NaCl	0.009	DNT	--	39.9
				DAT	--	4.84
				4-A-2-NT	1.163	--
				2-A-4-NT	0.964	--
				Dimer 1	12.42	--
100	1.9	NaCl	0.027	DNT	--	3.1
				DAT	--	8.47
				4-A-2-NT	6.33	--
				2-A-4-NT	4.62	--
				Dimer 1	40.56	--
100	3.8	NaCl	0.027	DNT	--	11.16
				DAT	--	9.8
				4-A-2-NT	3.37	--
				2-A-4-NT	2.49	--
				Dimer 1	24.67	--
100	1.9	Na_2SO_4	0.027	DNT	--	2.28
				DAT	--	8.87
				4-A-2-NT	4.36	--
				2-A-4-NT	3.85	--
				Dimer 1	38.7	--
200	3.8	Na_2SO_4	0.027	DNT	--	2.49
				DAT	--	7.76
				4-A-2-NT	3.49	--
				2-A-4-NT	3.21	--
				Dimer 1	38.02	--

4-A-2-NT : 4-Amino-2-nitrotoluene

2-A-4-NT : 2-Amino-4-nitrotoluene

Dimer 1 : 2,2',4,4'-Tetranitro-6,6'-azoxytoluene

Continuous Flow Experiments for DNT

The results obtained from the batch simulation experiments showed that the rate of reduction of DNT leveled off at higher currents (150 and 200 mA). Continuous flow experiments were then conducted on the pilot-scale reactor to determine the reduction of DNT in the reactor. Experiments were conducted for three different currents (150 mA, 200 mA, and 300 mA). The ionic strength of the feed solution was maintained at 0.027M using Na_2SO_4. The DO level of the feed solution is maintained at 1.3-1.5 mg/L. The flow rate of the feed into the reactor was maintained at 8.5±0.5 L/day with a recycle of 20 times the flow rate. The pH level of the solution in the reactor was maintained at 8. Salt solution was pumped through the anode compartment in the closed-loop fashion described in Chapter 3 on materials and methods. The salt solution was changed when its conductivity was below 30 m mho/cm, and this usually occurred every 2 weeks of operation. Samples were collected every hour for the first 3 hours and thereafter every day.

Figure 9 shows the performance of the reactor for the experiments conducted on the pilot-scale reactor. For the first 15 days the current was maintained at 200 mA. The efficiency of the reactor during this period was 80.5±1.93 percent. It was noted that the performance of the reactor started to drop after 2 weeks of operation, so the experiment was terminated and the reactor was emptied. The collected solution was filtered and analyzed to quantify the various end products formed during the experimental run. Prior to any further experiments, the reactor was flushed first with DI water to remove easily detachable solids from the surface of the membrane and the cathode. DI water was then pumped through the reactor continuously with a recycle of 160 L/day to flush out any remaining solids.

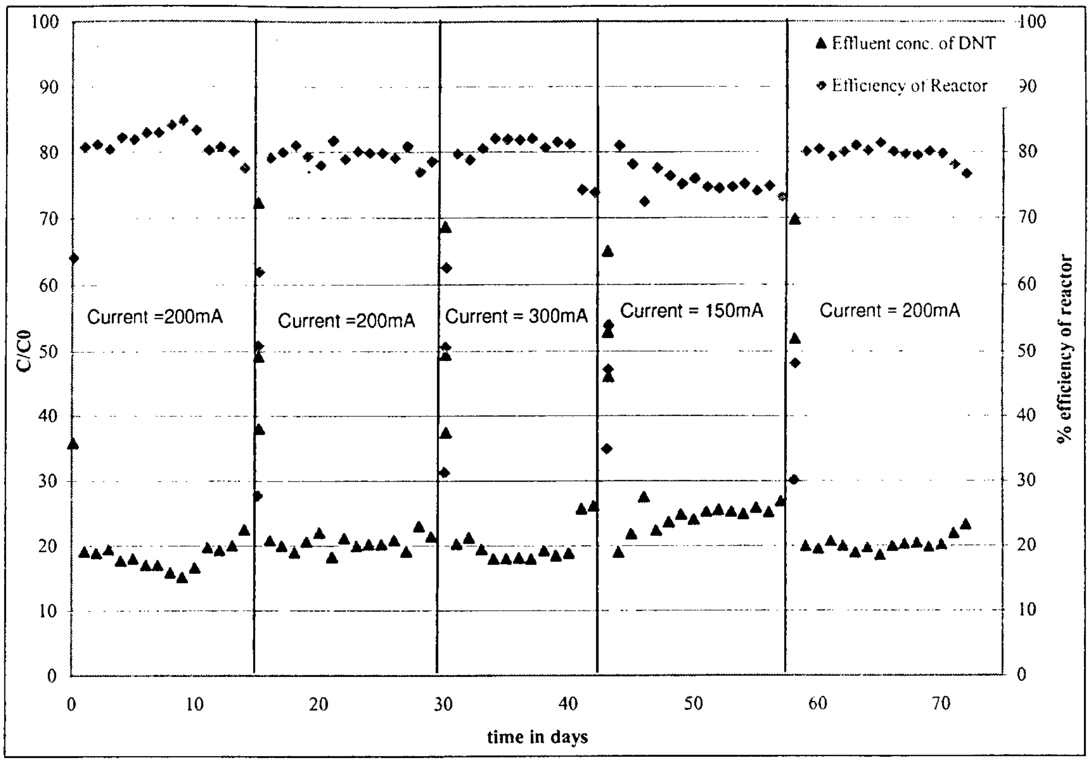

Figure 9. Performance of reactor.

After cleaning the reactor, experiments were conducted at 200 mA current to determine the reproducibility of the results. Days 15 to 30 in Figure 9 show the results obtained for this experiment. The efficiency of the reactor during this period was 80.1±1.04 percent, which is in good agreement with the results obtained in the previous batch experiments (Pehkonen et al. 1999). The performance of the reactor was again observed to drop after a period of 15 days and the reactor was emptied and cleaned as for the previous experiment. Following the cleaning of the reactor, an experimental run was conducted at 300 mA. Days 30 to 42 in Figure 9 represent the results obtained for this experiment. The efficiency of the reactor was observed to be 81.5±1.31 percent. The experiment was run for only 13 days because of the drop in efficiency of the reactor. The next experimental run was conducted for 150 mA. Days 43 to 57 in Figure 9 show the results obtained during this experimental run. The efficiency of the reactor was 75.55±2.2 percent during this period. The experiment was terminated after 15 days. From the above results, it can be said that no significant increase in efficiency occurred as the current was increased from 200 mA to 300 mA. When the current was reduced to 150 mA, however, efficiency dropped about 5 percent. The current at which optimum efficiency could be obtained, therefore, was 200 mA. A final experiment was conducted using 200 mA current to observe whether the previous results obtained could be reproduced. Days 58 through 72 in Figure 9 show the results obtained during this period. The efficiency for the reactor was observed to be 80.2±1.17 percent, which compares well with the results obtained for the first two experiments (80.5 and 80.1 percent).

Figures 10, 11, 12, and 13 show the variation of the various experimental parameters with time for all the experiments. Figure 10 shows the flow rate of the feed solution into the reactor. On an average the flow rate was 8.2±0.67 L/day for all the experiments. Figure 11 shows the pH of the solution in the cathode compartment. It can be observed from the plot that the pH level was maintained at 7.91±0.03 for all the experiments. Figure 12 shows the variation of salt solution conductivity during the experiments. The graph shows that the conductivity gradually decreased with time. The conductivity of the salt solution was never allowed to drop below 30 m mho/cm. Figure 13 shows the variation of voltage across the electrodes for the experiments. The voltage was observed to be 2.92±0.12 V for 150 mA, 3.18±0.22 V for 200 mA, and 3.48±0.07 V for 300 mA.

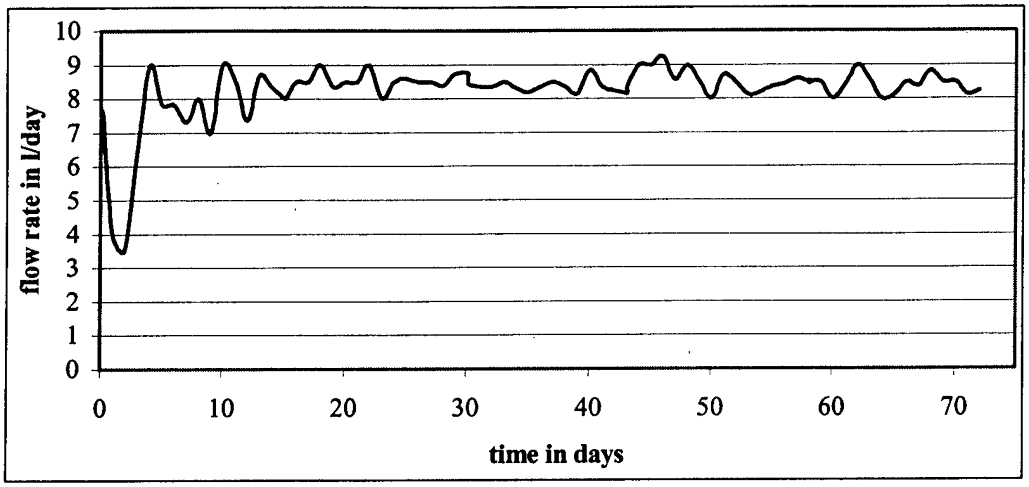

Figure 10. Flow rate of the feed solution.

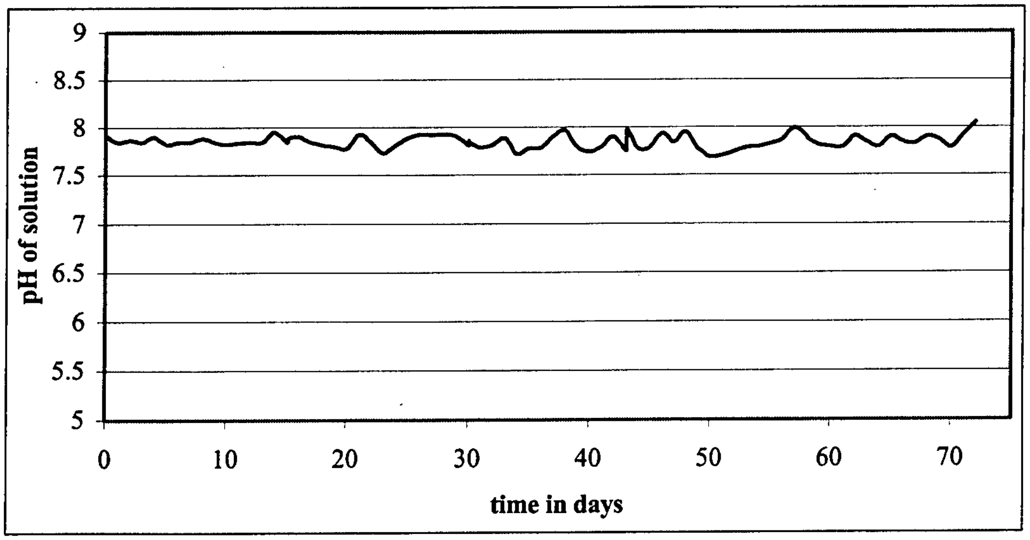

Figure 11. The pH of the feed solution.

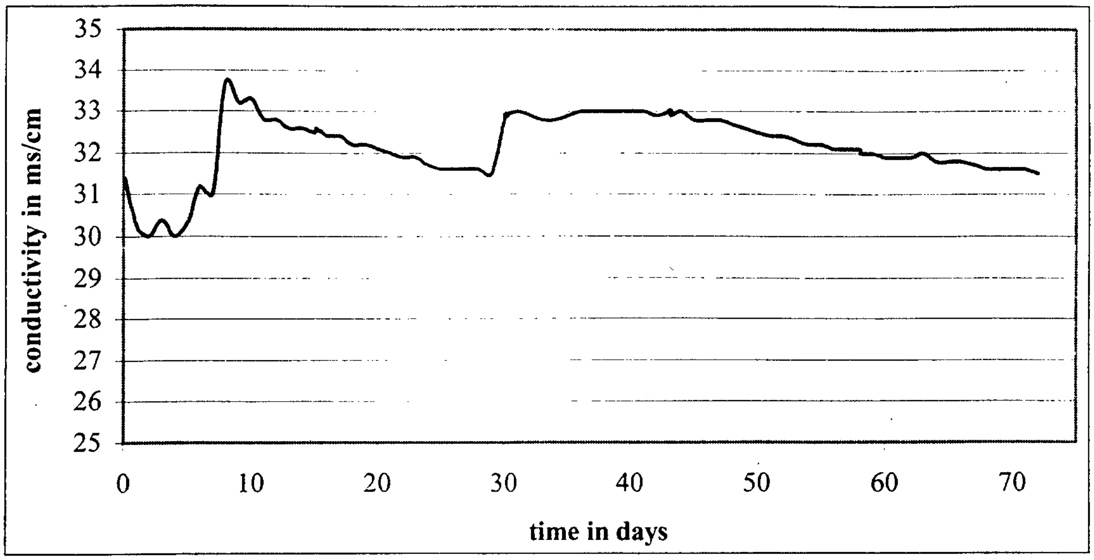

Figure 12. Salt solution conductivity.

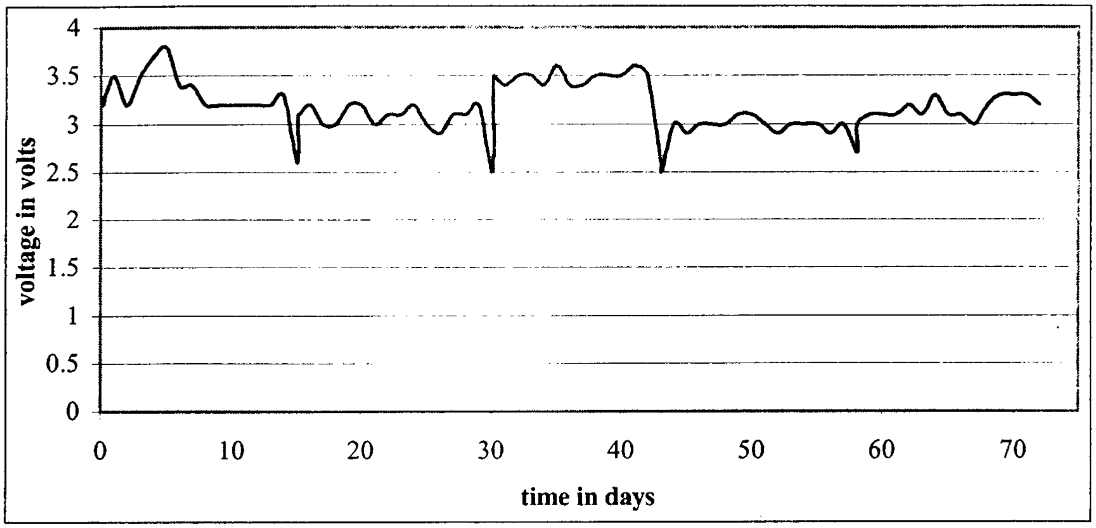

Figure 13. Voltage across the electrodes.

At the end of each experiment, effluent samples were collected to analyze for the intermediates formed during the experiment. Table 8 shows the various intermediates obtained. A mass balance closure could be attained for all the experiments within a 5 to 10 percent error. About 80 percent of the intermediates are in the solid phase, consisting only of the two dimers. In the liquid phase, DAT is about 15 percent and the aminonitrotoluenes consist of about 5 percent of the intermediates.

Table 8. Mass balance of DNT for continuous flow experiments.

Experiment	Current	Compound	% molar conversion of DNT (solid phase)	% molar conversion of DNT (aqueous phase)
Exp 1	200 mA	DAT	--	10.67
		4-A-2-NT	--	2.97
		2-A-4NT	--	2.84
		Dimer 1	34.6	--
		Dimer 2	29.5	--
Exp 2	200 mA	DAT	--	7.16
		4-A-2-NT	--	2.8
		2-A-4NT	--	2.72
		Dimer 1	27.24	--
		Dimer 2	34.06	--
Exp 3	150 mA	DAT	--	9.43
		4-A-2-NT	--	3.24
		2-A-4NT	--	3.13
		Dimer 1	36.46	--
		Dimer 2	32.06	--
Exp 5	200 mA	DAT	--	12.54
		4-A-2-NT	--	3.16
		2-A-4NT	--	2.98
		Dimer 1	35.4	--
		Dimer 2	31.11	--

DAT : 2,4-Diaminotoluene

Dimer 1 : 2,2',6,6'- Tetranitro-6,6'-azoxytoluene

Dimer 2 : 4,4',6,6'-Tetranitro-2,2'-azoxytoluene

4-A-2-NT : 4-Amino-2-nitrotoluene

2-A-4-NT : 2-Amino-4-nitrotoluene

Effectiveness of Reactor Cleaning

To determine the effectiveness of the cleaning procedure, DI water was pumped into the reactor in a continuous fashion with a recycle flow rate of 160 L/day. To measure the concentration of solids, 500 mL samples were collected over time and filtered. Figure 14 shows the concentration of solids obtained over time for two experiments. Approximately 95 percent of the solids could be removed after about 18 hours.

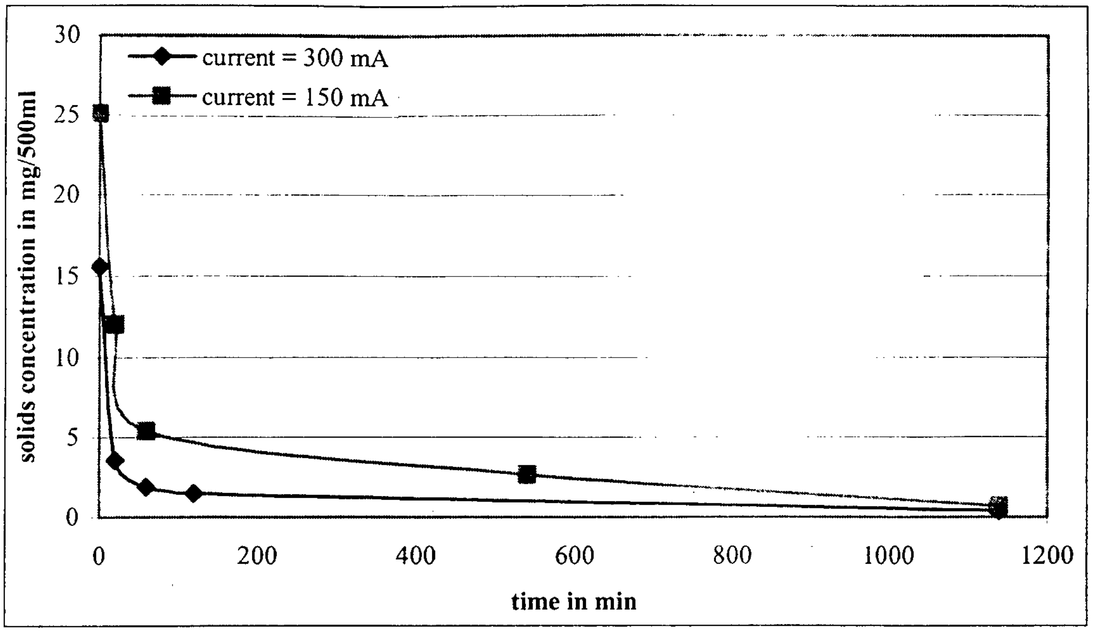

Figure 14. Concentration of solids during the cleaning of the reactor.

Continuous Versus Batch Simulation

To compare the reduction of DNT in the continuous flow experiments to the reduction in the batch simulation experiments, the following calculations were performed. Figure 15 shows the variation of concentration of DNT over time.

The following are the specifications of the continuous flow reactor:

Flow- rate = 8.2 ±0.67 L/day

Volume of reactor = 3.8 L

Retention time = 3.8/8.2 = 0.476 days = 684.88 min

Since about 80 percent reduction of DNT was observed in the continuous flow reactor for 200 mA, the rate of reduction of DNT can be calculated as:

Rate of reduction = $(C_0 - C_{eff})$/retention time = (100 − 20)/684.88 = 0.117 mg/L-min

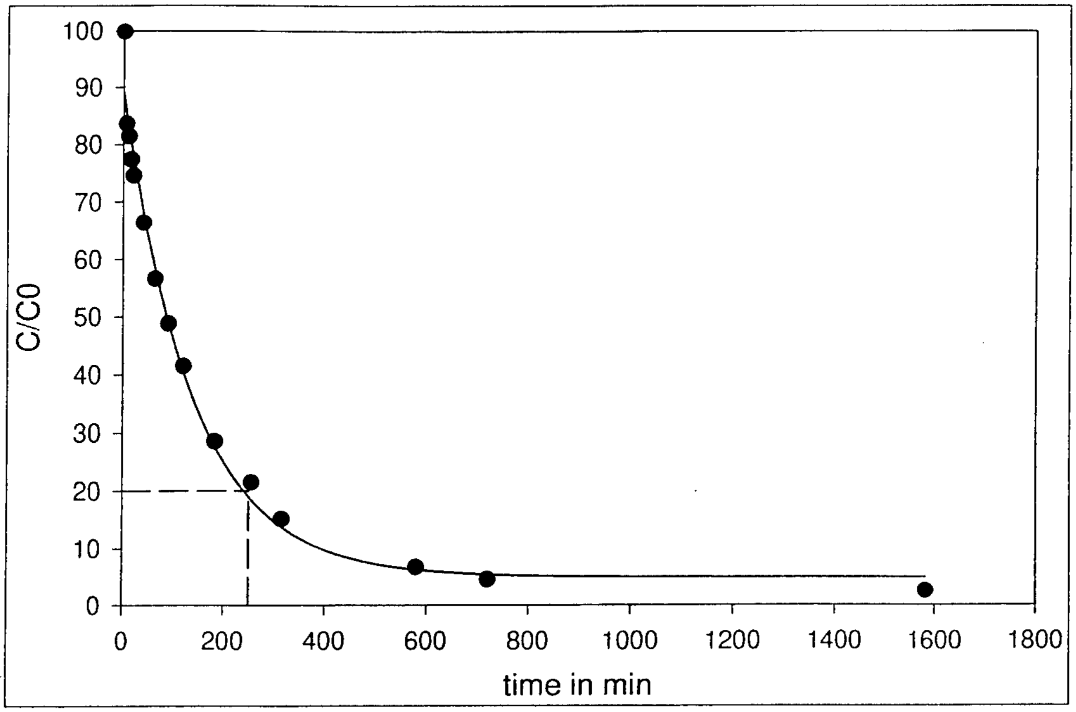

Figure 15. Batch simulation experiment: DNT conc. = 100 mg/L, current = 200 mA, I = 0.027 M using sodium sulfate.

From the batch simulation experiment conducted for the same conditions (shown in Figure 15), the rate was determined from the tangent at the point the dashed line intersects on the curve. This point represents the time at which 80 percent reduction of DNT was observed in the batch simulation experiment. The rate was determined to be:

Rate of reduction = 43/480 = 0.09 mg/L-min.

This result shows that the continuous flow reactor rate is closely predicted by the batch simulation experiments.

Batch Simulation Experiments for TNT

Batch simulation experiments were conducted on the pilot-scale reactor using the simulated munitions wastewater (70 mg/L). The experiments were conducted for an ionic strength of 0.018M in the feed using anhydrous sodium sulfate as the electrolyte, and currents ranging from 75 mA to 250 mA.

The analytical sampling procedure is as described on Section 3.1 of this report. Each experiment was conducted for 24 hours. Samples were collected at the following time intervals: 15, 30, 60, 90, 120, 180, 240, 270, and 300 minutes. Later samples were collected at staggered intervals within a 24-hour period. The experiment was terminated after 24 hours, and the effluent was filtered and analyzed for solids.

The TNT concentration collected during various experiments were used to determine the first order rate constants. The determined rate constants are shown in Table 9.

Table 9. Rate constants for batch simulation experiments for TNT.

Current (mA)	Ionic Strength	pH	Rate Constant (1/min)	DO (mg/L)
75	0.018	8	0.0033	0.75
100	0.018	8	0.0041	0.75
150	0.018	8	0.0045	0.75
200	0.018	8	0.0052	0.75
250	0.018	8	0.0053	0.75

From Figure 16 it is seen that the rate constants range from 0.0033 min^{-1} to 0.0053 min^{-1}. It can also be observed that rate constant increases with increased current and flattens out at higher current values. Mass transfer limitations are speculated to be the reason for the relative decrease in rate constants for a steady increase in current beyond 200 mA.

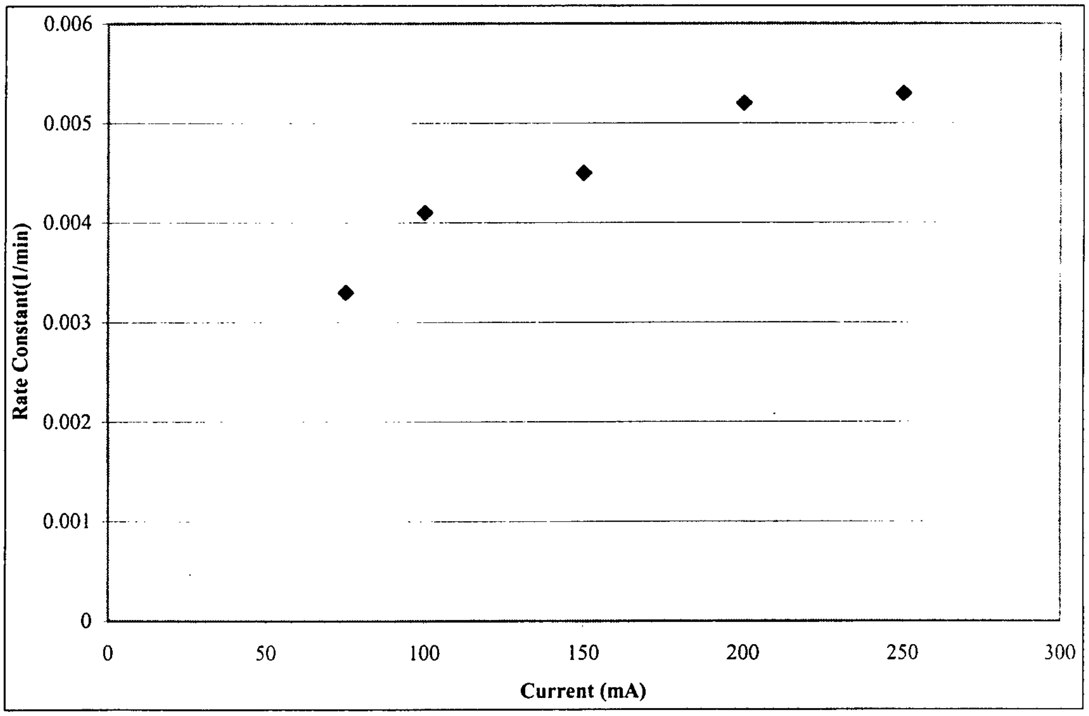

Figure 16. Current versus rate constant for batch simulation of TNT treatment (Ionic strength = 0.018M).

5 Conclusions and Future Work

Electrochemical bench-scale experiments conducted for RDX, HMX, and Tritanol yielded low rate constants. It is speculated that the obtained low rate constants could be due to malfunctioning of the electrode, which may be attributed to film coating on the electrode that hinders the electrochemical reaction.

The pilot-scale reactor used in this study was modified to account for the mass transfer limitations observed in the previous report. Continuous flow experiments conducted on the modified reactor showed very low reduction of DNT. To get a better understanding of the various parameters effecting the reduction of DNT, therefore, experiments simulating batch conditions were conducted on the pilot-scale reactor. From the batch simulation experiments, it was concluded that optimum reduction could be attained when 200 mA current was applied and 1.23 g/L of Na_2SO_4 was used as the electrolyte. End product studies conducted for the batch simulation experiments showed a mass balance of 60 to 90 percent and most of the intermediates were observed in the solid phase. Based on these results, continuous flow experiments were conducted on the pilot-scale reactor using the above parameters. A DNT reduction of about 80 percent could be attained for these experiments. End product studies conducted on the continuous flow experiments showed a mass balance of about 100 percent, with 80 percent of the intermediates observed in the solid phase.

To improve the performance of the pilot-scale reactor so that reductions above 80 percent are attained, a series of tubular reactors could be used. It is expected that, for example, using two tubular reactors with partial recycle of effluent, each being half the size of the reactor used in this study, the overall performance of the system will be higher than was the system reported here. This improvement is expected because the behavior of the system will approach the plug flow regime as the number of reactors is increased.

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14. ABSTRACT

The large-scale manufacture and use of nitroaromatic compounds such as TNT, DNT, and RDX has led to significant production of munitions wastewater. Wastewater containing these compounds is commonly referred to as pinkwater. The United States ceased production of TNT in the mid-1980s, but TNT-contaminated wastewater generation still exists as a result of demilitarization. Both TNT and DNT are listed as priority pollutants by the U.S. Environmental Protection Agency because of their toxicology hazards.

This study used an existing pilot-scale reactor, which was modified to account for mass transfer limitations observed in a previous study, to evaluate the performance of the modified reactor for electrochemical reduction of simulated munitions wastewater and pinkwater. Kinetic rate determination of RDX, HMX (a military explosive), and Tritanol (munitions wastewater with suspected aluminum and iron metal ions) reduction was studied at the bench-scale in an electrochemical batch reactor. These experiments yielded low rate constants.

Continuous flow experiments conducted on the modified reactor showed very low DNT reduction. End product studies for batch simulation experiments conducted on the pilot-scale reactor showed a mass balance of 60 to 90 percent, and most of the intermediates were observed in the solid phase. Based on these results, continuous flow experiments were conducted on the pilot-scale reactor. A DNT reduction of about 80 percent could be attained for these experiments. End product studies conducted on the continuous flow experiments showed a mass balance of about 100 percent, with 80 percent of the intermediates observed in the solid phase.

15. SUBJECT TERMS
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