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I, Dinesh Kumar Palaniswamy ,
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Approved by:

Dr.George Sorial

Dr.Dionysios Dionysiou

Dr.Makram Suidan

ELECTROCHEMICAL REDUCTION OF 2,4,6 -TRINITROTOLUENE

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Dinesh Kumar Palaniswamy

B.E., Civil Engineering, P.S.G College of Technology, Coimbatore, 1998

Committee Chair: **Dr. George Sorial**

ABSTRACT

2,4,6-trinitrotoluene (TNT) is a major constituent of munitions contaminated wastewater. This research aims at studying the efficiency of electrochemical processes in reducing TNT. A laboratory scale reactor was designed and developed to electrochemically reduce TNT in simulated munition wastewater. Experiments simulating batch conditions were first conducted on the laboratory scale reactor to study the effect of various parameters including applied current, type of electrolyte and the molar concentration of the electrolyte in the feed solution on the reduction kinetics of TNT. The results showed that the reduction rates of TNT increased with an increase in applied current and molar concentration of electrolyte in feed. The rates of reduction leveled off at higher currents (250 & 300 mA). Mass transfer limitations were speculated for this flattening of rate constants at higher currents. Experimental studies were conducted with two types of electrolyte in the feed- sodium sulfate (Na_2SO_4) and lithium sulfate (Li_2SO_4), and the results indicated that there was no significant difference in the reduction rates for TNT. Based on the batch simulation experimental results, continuous flow experiments were conducted on the laboratory scale reactor using three different currents (150, 200, and 250 mA) and for two different concentrations of the electrolyte (6 and 9 mM). Sodium sulfite was used as electrolyte in the feed to maintain strict anoxic conditions in the reactor, thereby preventing the formation of solid dimers. An average TNT reduction efficiency between 82.5-85% was achieved for the three currents studied. A mole balance closure of 85-92% was achieved. 2,4,6-triaminotoluene (TAT) was observed as the only liquid phase intermediate. A 3-stage reactor in series was simulated and experimental

studies were conducted to ascertain the combined reduction efficiency for TNT. The results showed that an overall reduction efficiency of over 99 % was achieved.

Keywords: 2,4,6-trinitrotoluene (TNT), electrochemical reduction, munitions wastewater, laboratory scale reactor, 2,4,6-triaminotoluene (TAT), water treatment.

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1. INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

Environmental contamination of soil, surface water and ground water by hazardous and toxic chemicals has a detrimental effect on human health and the natural ecosystem. Energetic compounds are substances containing molecules that undergo exothermic reactions at a very high rate and are primarily associated with munitions manufacturing and processing industry.

Organic energetic compounds are found as contaminants in soils, sub surface and surface water at sites where these compounds were processed and produced. 2,4,6-trinitrotoluene (TNT) is a major constituent of organic energetic compounds that are found in munitions production wastewater. The United States Department of Defense (DOD) has identified more than 1000 sites with explosive contamination of which more than 95 % were contaminated with TNT and 87% exceeded permissible ground water levels (Walsh et al. 1993).

TNT has three structural isomers: 2,3,5-TNT, 2,4,6-TNT and 2,4,5-TNT. The symmetrical isomer 2,4,6-TNT is the most commonly found form of the three. In this thesis, the acronym TNT refers to 2,4,6-Trinitrotoluene. TNT finds wide use as a high explosive because of its low melting point (80.1° C) stability and low sensitivity. It is produced by nitration of toluene to nitrotoluene, dinitrotoluene (DNT) and finally to TNT using a mixture of nitric and sulfuric acids (Palmer et al. 1996). TNT is used in bombs and explosives, in a binary mixture with a primary explosive to trigger the detonation.

TNT is reported to be toxic to both humans and animals. TNT may be absorbed through the skin and mutation data had been reported. The orl-rat LD 50 value for TNT is 795 mg/kg (Sax and Lewis 1989). The United States Environmental Protection Agency

(USEPA) has set a drinking water limit of 20 µg/L as the life time exposure limit for TNT (EPA 1989).

Munitions wastewater is mainly of two types: red water and pink water. The process water resulting from purifying operation of the crude TNT is called “Red Water” and is a major environmental problem associated with TNT manufacturing processes. Another type of wastewater stream results from the various production stages of TNT and is called “Pink water”. It is the wastewater stream resulting from the load, assemble and packing operations where the munitions casings are filled with explosive formulations. (Palmer et al. 1996). Also, continual leaching from TNT contaminated soil has resulted in the contamination of ground water.

The current practice to treat munition-contaminated waste is through incineration. Incineration is the currently used treatment practice and is used to treat an assortment of munition-related wastes at Army installations (Stratta et al. 1998), but is costly and produces unusable ash and has poor public acceptance due to safety concerns regarding air emissions such as cyanide and NO_x (Zoh and Stenstrom 2001). Another treatment practice is adsorption using granular activated carbon but the problem with this practice is that of the spent carbon which is a hazardous waste and needs to be disposed safely.

1.2 Literature Review

1.2.1 Biological Treatment Processes

The use of microorganisms to transform or mineralize toxic and hazardous chemicals is called bioremediation. When the target chemical is converted to end products such as carbon dioxide, water, methane and nitrogen, the process is termed as Mineralization. Biotransformation is the modification of the target chemical, such as change in its

functional groups but not necessarily mineralization. The biodegradation pathways identified for most of the organic energetic compounds require cometabolites (Kaplan 1989), which implies that the microorganism needs an alternate energy source as substrate other than the target chemical to sustain itself. This implies that the biodegradation of the target chemical is due to secondary effects and not due to direct utilization of the microorganism as substrate.

Biological transformations may be of two types – oxidative and reductive. Oxidation occurs when oxygen is the reactant and oxygenase or peroxidase enzymes mediate the nitroaromatic ring cleavage. Reduction takes place when the nitroaromatic compound is reduced to arylamines by a mechanism of hydrolytic deamination, acetylation, reductive deamination and cyclization. In the case of the nitramines and nitroaromatics, three moles of hydrogen are required for the reduction of each nitro group to the corresponding amino group in the reductive pathways (Kaplan 1989).

Pseudomonas sp clone A was able to use TNT, 2,4-dinitrotoluene (24DNT), and 2,6-dinitrotoluene (26DNT) as N-source after the enzymatic removal of nitro groups from the aromatic ring (Haidour and Ramos 1996). The authors had identified 2-hydroxylamino-4,6-dinitrotoluene (2HA46DNT), 4-hydroxylamino-2,6-dinitrotoluene (4HA26DNT), 4-amino-2,6-dinitrotoluene (4A26DNT), 2-amino-4,6-dinitrotoluene (2A46DNT) and 2,4-diamino-6-nitrotoluene (24D6NT) as transformation intermediates. About 25% (wt/wt) of the initial TNT load was recovered as azoxy toluenes. The biotransformation of 175 μM of TNT by *Phanerochaete chrysosporium* with molasses and citric acid at pH of 4.5 was studied and it was reported that complete removal of TNT occurred in 2 weeks but less than 1% was mineralized (Hawari et al. 1999). A time study by the authors revealed the

presence of several intermediates marked by the initial formation of two monohydroxylaminodinitrotoluenes (2- and 4- HADNT) followed by their successive transformation to several other products including monoaminodinitrotoluenes (ADNT). Furthermore, the authors have reported that a fraction of HADNTs was transformed to their corresponding phenolamines while another group dimerized to azo compounds and eventually to their corresponding hydrazo derivatives.

A sulfate-reducing bacterium using TNT as the sole nitrogen source and isolated with pyruvate and sulfate as the energy sources was able to reduce TNT to TAT in growing cultures and cell suspensions and further transformed TAT to unknown end products (Preuss et al. 1993). 220 μ M of TNT were biotransformed by using anaerobic sludge (10%, vol/vol) supplemented with 3.3 g/L of molasses (Hawari et al. 1998). The authors reported two distinctive cycles in the degradation of TNT. One cycle was responsible for the stepwise reduction of TNT to eventually produce TAT while the other cycle involved TAT and was responsible for the production of azo derivatives, e.g., 2,2'-4,4'-tetraamino-6,6'-azotoluene and 2,2'-6,6'-tetraamino-4,4'-azotoluene at a pH of 7.2. TNT was reductively transformed by *Clostridium bifermentans* to TAT and phenolic products of TAT hydrolysis (Lewis et al. 1996).

Pink water with varying influent concentrations of TNT was biodegraded in Granular Activated Carbon filled Fluidized Bed Reactor (GAC-FBR) by an anaerobic bacterial consortium (Maloney et al. 2002). The authors had observed 2A46DNT, 4A26DNT, 24DA6NT, 26DA4NT and TAT as transformation intermediates. Boopathy et al. (1993) studied the anaerobic removal of 100-mg/L TNT under different electron accepting conditions by a soil bacterial consortium. The authors have reported that, under nitrate

reducing conditions about 82% of TNT was removed and under sulfate reducing conditions about 30% of TNT was removed. It was observed that when carbon dioxide (CO₂) was used as the electron acceptor and hydrogen (H₂) was used as the electron donor, a 35% TNT removal could be achieved. TNT was rapidly degraded by a nitroreductase enzyme obtained from *Pseudomonas aeruginosa* (Oh et al. 2000). The authors reported that the nitroreductase, biocatalyzed reduction of TNT to 4HA26DNT and 4A26DNT.

1.2.2 Physical/Chemical Processes

Some of the physical/chemical processes used for the treatment of nitroaromatic compounds include activated carbon adsorption, photocatalysis, advanced oxidation processes (AOP's) and electrochemical processes. Activated carbon can remove TNT from aqueous solution and act as catalyst for TNT oxidation (Vasilyeva et al. 2002). The authors reported that activated carbon in the presence of 3 mM CaCl₂ catalyzed the oxidation of TNT to 2,4,6-trinitrobenzyl alcohol, which was readily oxidized to 2,4,6-trinitrobenzaldehyde and 2,4,6-trinitrobenzene in the absence of activated carbon under dark conditions.

The photocatalytic degradation of TNT and the nitrated benzenes, dinitro and trinitro benzenes using titanium dioxide (TiO₂) as catalyst followed reductive and oxidative pathways (Nahen et al. 1997). The authors observed that the oxidative derivatization of TNT in these compounds leads to trinitrobenzene, which is degraded mainly by reduction to amino-nitro compounds. It was also observed that reduction reaction is enhanced in the presence of alcohols such as methanol. Wang and Kutal (1995) studied the photocatalytic destruction of TNT in aqueous suspensions of TiO₂.

The authors observed that under aerobic conditions, irradiation with the pyrex-filtered output of a 200-W high-pressure mercury-arc lamp resulted in complete ($95\pm 5\%$) mineralization of 50 mg/L of TNT within few hours. An analysis of the photodegradation of TNT in a TiO_2 slurry reactor was studied and it was reported that photocatalytic transformation of TNT involves both oxidative and reductive steps (Schmelling and Gray 1995). Trinitrobenzoic acid, trinitrobenzene and trinitrophenol were observed as oxidative intermediate species and 3,5-dinitroaniline was identified as a reduction intermediate.

Some of the advanced oxidation processes include wet-air oxidation (WAO) and oxidation using Fenton's reagent. Hao et al. (1993) conducted batch WAO experiments using diluted red water and showed that the WAO removal efficiency was primarily a function of temperature and to a lesser extent the oxygen pressure. At 320°C and Po_2 of 1.31 Mpa, a Chemical Oxygen Demand (COD) of 8 mg/L and Total Organic Carbon (TOC) of 30 mg/L remained after 1-hour of reaction. Hawthorne et al. (2000) used subcritical water to treat two soils from former defense sites, which were contaminated with explosives. Their studies demonstrated that significant degradation of TNT began at 125°C . Hundal et al. (1997) studied the potential of zero valent iron to promote remediation of water and soil contaminated with TNT. The authors reported that the sequential treatment of a TNT-contaminated solution (70 mg/L TNT spiked with ^{14}C -TNT) with Fe^0 (5% w/v) followed by H_2O_2 (1% v/v) completely destroyed TNT and removed about 94 % of the ^{14}C from solution, 48% of which was mineralized to $^{14}\text{CO}_2$ within 8 hours.

1.2.3 Electrochemical Treatment Processes

Electrochemical remediation of recalcitrant wastes is a treatment option that offers the possibility of efficient energy use and relatively simple equipment. Electrochemistry with its unique ability to oxidize or reduce compounds at well-combined electrode potentials by just adding or withdrawing electrons offers many interesting possibilities in environmental engineering (Simonsson 1997).

Electrochemical processes are mainly of two types: electrochemical oxidation and reduction. Polcaro and Palmas (1997) studied the electrochemical oxidation of 2-chlorophenol and 2,6-dichlorophenol from aqueous solutions using porous carbon anodes with current input, ratio between electrode and solution volume and influent concentration as operating variables and 2-chloro-benzoquinone was observed as a transformation by product. The study reported maleic and oxalic acids as final end products along with CO₂ gas. An electrohydraulic discharge (EHD) process for the treatment of hazardous chemical wastes in water has been developed by Willberg et al. (1996). The authors reported that combined EHD/ozone treatment of a 160 μ M TNT solution resulted in the complete degradation of TNT and a 34% reduction of TOC. 200 μ M of TNT in an aqueous solution with 100 mM KCl as the electrolyte was observed to readily undergo reductive transformation by a platinum electrode at -0.40 V vs. Normal Hydrogen Electrode (NHE) and aminodinitrotoluenes were detected as early reduction products (Schmelling et al. 1996).

Electrochemical degradation of 2,4-dinitrotoluene (2,4-DNT) in a bench scale reactor was studied by and the effect of a number of parameters including dissolved oxygen, current, voltage, and electrode shape and material on the reduction kinetics of

DNT was investigated (Jolas et al. 2000). Pseudo-first order kinetics was reported for electrochemical reduction of DNT. The study identified diaminotoluene (DAT) and azoxy dimers as end products. It was observed that azoxy dimers were formed as end products in experiments with the presence of dissolved oxygen.

A bench scale batch reactor study for the electrochemical reduction of DNT and a mixture of TNT and RDX with glassy carbon as cathode and platinum wire as anode was conducted (Doppalapudi et al. 2002b). The authors investigated the effect of various parameters including applied current, stir rate and the presence and absence of oxygen on the reduction of nitro aromatics. The study identified 2,2'-4,4'-tetranitro-6,6'-azoxytoluene and 4,2'-6,6'-tetraamino-2,4'-azotoluene as solid phase end products and 2-amino-4,6-dinitrotoluene as the liquid phase end product for TNT experiments conducted under the presence of oxygen. Under anoxic conditions, unknown solid phase end products were observed along with 2,6-diamino-4-nitrotoluene and 2,4-diamino-6-nitrotoluene as liquid phase end products.

The electrolytic reduction of nitrotoluene congeners was studied using a 3-electrode system with either platinum foil or IrO_2/Ti (10cm^2) as anode and solid Pb, Ni-plated nickel wire (0.5mm diameter), raney nickel, Pt or reticulated carbon (10 cm^2) as cathode at potentials of -0.5 to -1 vs. Standard Calomel Electrode (Rodgers and Bunce 2001). It was reported that DNT reduces to form 2-amino-4,6-nitrotoluene and 4-amino-2,6-nitrotoluene as early reaction intermediates followed by the formation of 2,4-DAT. The study also reported that TAT was only a minor intermediate in the reduction of TNT.

An electrochemical laboratory scale reactor with a graphite carbon cylinder (impregnated with glassy carbon) as cathode and a platinum wire as anode was used to

treat DNT under anoxic conditions (Doppalapudi et al. 2002a). In the batch mode study the effect of various parameters like applied current, concentration of electrolyte in feed and type of electrolyte on the reduction kinetics of DNT was studied. The results of the batch mode study showed that the reduction rates of DNT increased with increase in applied current and electrolyte concentration. In the continuous flow study, for a 200 mA applied current and 0.027 M ionic strength of sodium sulfate as electrolyte of feed, a reduction efficiency of 80% was achieved for DNT for a period of 14 days after which reactor cleaning was necessary for removal of suspended solids that were formed within the reactor. 2,2'-dinitro-4,4'-azoxytoluene and 4,4'-dinitro-2,2'-azoxytoluene accounted for 80% of the end products and were observed in the solid phase.

1.3 Objectives

The main objectives of this research are (1) to study the electrochemical reduction kinetics of TNT in simulated munitions waste water using a laboratory scale reactor; (2) to investigate the impact of various parameters such as type of electrolyte, concentration of electrolyte and applied current on the reduction kinetics of TNT; (3) to evaluate the performance efficiency of the laboratory scale reactor under a continuous flow mode for reducing simulated munitions waste water containing TNT without the need for periodic reactor cleaning; and (4) to identify the various intermediates and end products formed during the reduction of TNT.

The following tasks were performed to achieve the above-mentioned objectives:

1. Batch simulation experiments were conducted to study the electrochemical reduction kinetics of TNT and to investigate the effect of applied current (100, 150, 200, 250 & 300 mA), concentration of electrolyte (0, 1.77, 3.53, 6 & 9 mM) in the feed and type of electrolyte (Na_2SO_4 & Li_2SO_4) on the reduction kinetics of TNT. All the experiments were conducted at a dissolved oxygen (DO) concentration of 1.0 ± 0.5 mg/L.
2. Continuous flow experiments were conducted on the laboratory scale reactor to study the reduction kinetics of TNT based on the results obtained from the batch simulation experiments. Sodium sulfite was used as the electrolyte in the feed to maintain strict anoxic conditions in the reactor. The reactor was operated under three applied currents (150, 200 and 250 mA) and for two electrolyte concentrations (6 and 9 mM) of sodium sulfite. All the experiments were conducted with DO levels between 0-0.2 mg/L.

3. A three-stage reactor in series system was simulated and was studied to determine the combined average efficiency of the reactor for the electrochemical reduction of TNT.

During all experimental runs, samples were collected and analyzed to determine the various transformation intermediates and end products.

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2. ELECTROCHEMICAL REDUCTION OF 2,4,6-TRINITROTOLUENE - KINETIC STUDY¹

¹Paper Submitted for Publication in *Water Research*

2.1 Abstract

A laboratory scale reactor was used to study the electrochemical reduction of 2,4,6-trinitrotoluene (TNT) in simulated munitions wastewater. A graphite cylinder impregnated with glassy carbon (zero porosity) was used as the cathode and a platinum wire was used as the anode. Initially, experiments simulating batch conditions were conducted to evaluate the effect of electrolyte type, molar concentration of the electrolyte, and the applied current on the reduction kinetics of TNT. All experiments were conducted under anoxic conditions (dissolved oxygen concentration of 1 ± 0.5 mg/L). The results from the TNT reduction experiments showed that the reduction kinetics is pseudo-first order. For the various currents studied, no significant changes in rate constants were observed for experiments conducted with sodium sulfate or lithium sulfate as electrolyte in the feed. Results showed that the rate of TNT reduction increased with an increase in molar concentration of the electrolyte and the applied current.

Keywords: munition wastewater, electrochemical reduction, 2,4,6-trinitrotoluene (TNT), reduction kinetics, water treatment.

2.2 Introduction

Environmental contamination by munitions wastewater is a problem, which is primarily associated with the explosives industry. 2,4,6-trinitrotoluene (TNT) constitutes a significant component of a wide spread munitions contamination problem which exists at many current and former U.S. Department of Defense (DOD) and U.S Department of Energy (DOE) facilities (Schmelling and Gray 1995). TNT is a suspected carcinogen and is toxic to humans and aquatic life. The orl-rat LD 50 value for TNT is 795 mg/kg. TNT may be absorbed through skin and mutation data has been reported (Sax and Lewis 1989). Waters containing TNT have been classified as a RCRA regulated waste (K047) based on its reactivity (Hao et al. 1993). In the U.S., explosives contaminated ground water is treated almost exclusively by pump and treat with carbon adsorption (Spain 2000). The spent carbon after adsorption is usually incinerated. Energy intensive treatment processes like incineration may be too expensive at low concentrations or may cause other environmental problems such as NO_x gas emissions (Rodgers and Bunce 2001a). This prompted research into alternate technologies like biodegradation, physical/chemical processes and electrochemical reduction. Biodegradation and physical/chemical processes are discussed in Chapter 3.

2.2.1 Electrochemical Reduction

Nitroaromatic compounds are more susceptible to electrochemical reduction, because of the electron withdrawing nature of the nitrogroups. Electrochemical reduction of 2,4-dinitrotoluene (2,4-DNT) in a bench scale reactor was studied and the effects of a number of parameters including dissolved oxygen, current, voltage, and electrode shape and material on the reduction kinetics of DNT were investigated (Jolas et al. 2000)

Products of reduction were identified as 2,4-diaminotoluene and azoxy dimers. Doppalapudi et al (2002b) studied the electrochemical reduction of DNT, TNT and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in a bench scale batch reactor. Electrochemical reduction of nitroaromatics was shown to be readily taking place under oxic and anoxic conditions and the rate constants were observed to be increasing with current and stir rate, but at higher currents mass-transfer limitations govern the rates. The reduction rates for the nitroaromatics were higher under anoxic conditions than those obtained from the oxic conditions. Azoxy dimers and amino substitutes of nitrogroups were identified as intermediates.

Rodgers and Bunce (2001) carried out studies on the electrolysis of nitrotoluene congeners. Reduction of aminotoluenes was carried out at high current efficiencies for a variety of cathodes at potentials -0.5 to -1 V Standard Calomel Electrode (SCE). The authors also studied the oxidation of the reaction intermediates.

An electrochemical laboratory scale reactor was used to treat DNT by Doppalapudi et al (2002a). Batch simulation experimental studies were conducted using a graphite carbon cylinder impregnated with glassy carbon as the cathode and a platinum wire as the anode to investigate the effect of various parameters such as applied current, electrolyte concentration and type of electrolyte on the reduction kinetics of DNT. The authors reported that the rates of reduction of DNT increased with increase in current or electrolyte concentration. In their continuous flow experimental studies the authors have observed that a current of 200 mA provided a stable reduction of DNT at the 80% level for a period of 14 days. Azoxy dimers and 2,4-diaminotoluene were identified as intermediates. The authors had also observed that stable performance of the reactor could

be maintained for a period of 14 days after which reactor cleaning was necessary for the removal of solid dimers adhering to the membrane surface or the glassy carbon surface. On average, the authors reported that 80% of the intermediates were observed in the solid phase and were identified as dimers.

2.2.2 Objectives

This research study has been divided into two parts. In the first part of this study, simulated batch experiments were conducted to (1) determine the electrochemical reduction kinetics of TNT and (2) investigate the impact of type of electrolyte, molar concentration of electrolyte, and applied current on the reduction kinetics of TNT. In the second part of the study the performance efficiency of the reactor to effectively reduce TNT was evaluated under continuous flow mode and the transformation intermediates were identified (see Chapter 3).

2.3 Materials and Methods

2.3.1 Experimental Setup

Figure 2.1 shows the experimental setup for the laboratory scale reactor. The reactor consisted of two concentric cylinders. The cathode compartment was the outer cylinder, which was made of graphite carbon with surface impregnation of vitreous carbon (glassy carbon with zero porosity). It had an internal diameter of 12 cm and a height of 60 cm. The carbon cylinder was fabricated by M.G.P, Inc (Robeson, PA). The inner cylinder constituted the anode compartment of the reactor. The anode compartment was made of 8.32 cm diameter Nafion Membrane tube N424 (C.G Processing, Rockland, DE). The ends of the tube were supported by TeflonTM flanges. A platinum wire (Fisher Scientific, Pittsburgh, PA) spanned through the entire length of the inner cylinder and acted as the anode. The effluent and salt tanks were 7-gallon polyethylene tanks (Fisher Scientific, Pittsburgh, PA). Three pumps were used in the reactor. The first pump with a capacity of 6-20 L/day was used to pump the feed solution into the reactor. The second pump with a maximum capacity of 160 L/day was used for recirculating the effluent back into the recycle loop of the reactor. The third pump with a capacity of 6-20 L/day was used for pumping the salt solution/anodic solution from the salt tank into the anode compartment of the reactor. All the three pumps were positive displacement pumps (Barnant Company, Barrington, IL). Two 500 mL holding tanks were used. One was used in the salt solution loop and the other in the recycle loop of the reactor. These holding tanks were made of stainless steel and were covered with a sealed lid that had two ports. One port was used for pH measurement and the other port was fitted with a rubber

septum for manual injection of acid for pH adjustment (this port was also used as a sampling port in the recycle loop holding tank). Two AP50 pH/ATC combination electrodes with silver/silver chloride reference (Fisher Scientific, Pittsburgh, PA) were used as pH probes. Two 75 L stainless steel tanks were used for the feed solution. The mixing of the feed solution was done by using two high power magnetic stirrers (Thermix Stirrer Models), obtained from Fisher Scientific (Pittsburgh, PA). A Honeywell UDC 3000 Universal Digital Controller (Honeywell, Philadelphia, PA) was used as a constant source of current supply, and was connected directly to the electrodes. All the piping connections were made of either TeflonTM or stainless steel.

2.3.2 Chemicals

TNT was obtained from the US Army and was used as received. Sodium phosphate dibasic obtained from Fisher Scientific (Pittsburgh, PA), was used as the buffer. Anhydrous sodium sulfate (Fisher Scientific, Pittsburgh, PA), or lithium sulfate (Sigma-Aldrich, Milwaukee, WI) were used as electrolytes. TNT standards were obtained from Radian International, Austin, Texas. For quantification of various intermediates formed during the reduction of TNT, the following compounds were obtained. 4-amino-2,6-dinitrotoluene (4A26DNT) and 2-amino-4,6-dinitrotoluene (2A46DNT) were obtained from Radian International, Austin, Texas. 2,4,6 Triaminotoluene trihydrochloride (TAT.3HCl), 2,4-diamino-6-nitrotoluene (24DA6NT), 2,6-diamino-4-nitrotoluene (26DA4NT), 2,2'-6,6'-tetranitro-4,4'-azoxytoluene and 4,4'-6,6'-tetranitro-2,2'-azoxytoluene were obtained from Accustandard Inc, New Haven, CT.

2.3.3 Experimental Methods

The feed tanks were initially filled with 61 L of deionized (DI) water plus 0.02 M of sodium phosphate dibasic buffer. The pH was then adjusted to 8.0 ± 0.2 by adding 1N sulfuric acid and the water was purged with nitrogen for 12 hours in order to remove the dissolved oxygen (DO). In order to simulate a munitions TNT wastewater, which has an average concentration of 70 mg/L, 4.270 g of TNT was added to the purged water. Together with TNT the particular electrolyte (either Na_2SO_4 , or Li_2SO_4) was added to achieve the required molar concentration of the electrolyte. The feed tank was immediately closed with the lid securely tightened and the tank was kept under a head pressure of nitrogen gas and left to mix for 4 days. The simulated feed was then pumped into the reactor using the feed pump. A 0.25 M sodium sulfate solution (anodic solution) was used as the electrolyte solution in the anode compartment of the reactor. The anodic solution in the salt tank was continuously pumped inside the Nafion membrane tube in the reactor in a closed loop. The salt solution was changed when the conductivity of the solution dropped below 30 mS/cm. The pumping rate for the anodic solution was maintained at 20 ± 1 L/day.

Experiments simulating batch conditions were conducted to study the impact of applied current (75, 100, 150, 200, 250 and 300 mA) or current density (0.033 mA/cm^2 - 0.133 mA/cm^2), molar concentration of the electrolyte in the feed (0.0, 1.77, 3.53, 6 and 9 mM) and the type of electrolyte (Na_2SO_4 or Li_2SO_4) on the reduction kinetics of TNT. To simulate batch conditions, the feed solution was pumped into the reactor until the reactor was completely full. The feed pump was then turned off and the recycle pump was turned on and kept at its maximum speed of 160 L/day to ensure mixing. The effluent valve was

kept closed throughout the experimental run. The anodic solution was allowed to flow continuously through the anode compartment in a closed loop. Samples were collected from the holding tank in the recycle stream at time intervals of 0, 5, 15, 30, 60, 90, 120, 180, 240, 300, 360 and 720 minutes for monitoring the reduction of TNT. At the end of each experiment the effluent solution was collected from the reactor and filtered to measure the concentration of solids in the effluent.

2.3.4 Monitored Parameters

An Accumet AP63 Handheld pH meter (Fisher Scientific, Pittsburgh, P.A) was used to measure the pH. The pH of the solution in the reactor was monitored and maintained at 8.0 ± 0.2 by adding 1N H_2SO_4 . A Corning Model 311 portable conductivity meter (Fisher Scientific, Pittsburgh, P.A) was used to measure the conductivity. A Hanna HI 9143 portable waterproof dissolved oxygen meter (Fisher Scientific, Pittsburgh, PA) was used to measure the dissolved oxygen content. The DO in all the experimental runs was maintained at 1.0 ± 0.5 mg/L. For the batch simulation experiments, the DO and conductivity of the feed solution, anodic solution, and the effluent were measured at the start and the end of the experiments respectively. The voltage in the display window of the constant current supplier was also noted down.

2.3.5 Analytical Procedure

2-mL samples were taken from the feed tank and from the holding tank in the recycle loop of the reactor to measure the influent and effluent concentration of TNT, respectively, and to evaluate the performance of the reactor on a daily basis. The samples were filtered using a $0.1\mu\text{m}$ nylon membrane filter (Fisher Scientific, Pittsburgh, PA) before they were injected into the High Performance Liquid Chromatograph (HPLC). An Agilent 1100 series HPLC (Agilent technologies, Waldbronn, Germany) with a Diode

Array Detector was used for the analysis of TNT and its transformation products. A 15 cm x 4.6 mm inner diameter SUPELCOSIL[™] LC-18-DB 5 μ M column (Supelco, Bellefonte, PA) was used as the stationary phase. The mobile phase used was HPLC grade acetonitrile and HPLC grade water in a 50:50 ratio with a flow rate of 0.700 mL/min. The column compartment was maintained at a temperature of 40° C. A wavelength of 205 nm was used to identify and analyze the samples. The retention time of TNT and TAT were 6.5 and 1.45 minutes, respectively. The retention time of 2A46DNT and 4A26DNT were 5.23 and 5.30 minutes, respectively. The retention time of 26DA4NT and 24DA6NT were 3.03 and 3.01 minutes, respectively. The retention time of the dimers 2,2'-6,6'-tetrinitro-4,4'-azoxytoluene and 4,4'-6,6'-tetrinitro-2,2'-azoxytoluene were 30.60 and 30.04 minutes, respectively.

2.4 Results and Discussion

2.4.1 Reactions Mechanism

At the anode surface, the oxidation half reaction given by equation 1 takes place.

The hydrogen protons formed at the surface of the anode pass through the Nafion membrane towards the cathode surface because of electrolytic attraction from the negatively charged cathode. A reduction half reaction as shown below occurs at the cathode

The hydrogen radicals formed at the surface of the cathode then participate in the reduction of TNT as shown by the equations 3-5

The above reactions show the reduction of one nitro group to amino group. In a similar fashion the remaining nitro groups are reduced to amino groups to yield eventually TAT.

2.4.2 Batch Simulation Experiments

The TNT concentrations obtained at the aforementioned time intervals for the various batch simulation runs were plotted on a semi logarithmic scale of $\ln(C/C_0)$ versus

time, where C represents the concentration of TNT at a specific time when the sample was taken and C_0 represents the initial concentration of TNT. Linear regression analysis was conducted to obtain the pseudo first order rate constants. Figure 2.2 shows the regression lines for experiments conducted using 3.53 mM concentration of sodium sulfate as electrolyte. The five regression lines correspond to 5 currents, namely, 75, 100, 150, 200 and 250 mA. The rate constants were obtained from the slope of the lines. Figure 2.3 shows the regression lines for experiments conducted using 3.53 mM concentration of lithium sulfate as electrolyte. All the regression lines had a R^2 value of above 0.99 indicating a very good linear fit.

A comparison of the rate constants, obtained for Na_2SO_4 & Li_2SO_4 at a molar concentration of 3.53 mM is shown in Figure 2.4. By choosing a cation smaller than the Na^+ , a competition between the cation and H^+ might occur which would eventually lead to a reduced rate of reaction. However the results, shown in Figure 2.4 indicate that no competition between Li^+ and H^+ occurred since the TNT reduction rate was not impacted by using Li_2SO_4 instead of Na_2SO_4 .

Figures 5-8 show the regression lines for experiments conducted with 0, 1.77, 6 & 9 mM sodium sulfate electrolyte concentration in the feed. The regression lines correspond to the respective applied currents for the experiment. The linear regressions yielded an R^2 value of more than 0.99, further proving that the reduction kinetics is of pseudo-first order.

A summary for the various currents studied (100, 150, 200, 250 & 300 mA) under the various molar concentrations of sodium sulfate electrolyte (0.0, 1.77, 3.53, 6 & 9 mM) is shown in the Figure 2.9. It is seen from Figure 2.9 that the rate constant

increases with an increase in molar concentration of the electrolyte and the applied current. The rate constant increased by 20.8% for 200mA applied current when the molar concentration of electrolyte was increased from 0 mM (0 g/L) to 9 mM (1.27 g/L). An increase of 21.82% for a 9mM electrolyte concentration was observed when the current was increased from 100 mA (0.110 mA/cm²) to 250 mA (0.044 mA/cm²). This clearly indicates that the rate constants increased with increase in electrolyte concentration and applied current. It is also observed from Figure 2.9 that the rate constants for 250 & 300 mA applied current were almost the same, which indicates that mass transfer limitations occur at higher currents. In an electrochemical system, two factors that can have a major impact on the reaction rate constants are the molar concentration of the electrolyte and the applied current. The impact of the first parameter could be explained through Ohms Law, which is represented as

$$V = iR \quad (6)$$

Where V is the potential difference, *i* is the current and R is the resistance.

The resistance offered by a conductor to the flow of current is directly proportional to its length (*l*) and inversely proportional to the area of cross section of the conductor (*a*).

$$\therefore R \propto l / a \quad (7)$$

$$\therefore R = \rho \cdot l / a \quad (8)$$

Where ρ is the specific resistance of the conductor. The reciprocal of specific resistance is the specific conductance (κ)

$$\therefore \kappa = 1 / \rho = \frac{1}{R} \cdot \frac{l}{a} \quad (9)$$

For a given cell (in this case, the electrochemical reactor) the distance between the two electrodes (l) and area of cross section (a) are constant and hence (l/a) is a constant. It is known as cell constant which has the unit meter⁻¹.

$$\therefore R = \text{cell constant} / \kappa \quad (10)$$

Substituting this in Ohms law we get,

$$V = i \times (\text{cell constant} / \kappa) \quad (11)$$

By increasing the specific conductance of the conducting media, the potential difference V decreases, hence the rate of transfer of ions increases. One way to increase specific conductance is to increase the ionic strength of electrolyte in the solution. Molar concentration is a good measure of the ionic strength of electrolyte.

$$I = \frac{1}{2} \sum_i m_i Z_i^2 \quad (12)$$

Where I – the ionic strength

m_i -Concentration of species i (mol/kg)

Z_i - Charge for species i .

Therefore, by increasing the molar concentration of the electrolyte, the conductivity increases which in turn leads to a decrease in the potential difference of the electrolyte. By increasing conductivity, the rate at which the protons reach the surface of the cathode would increase. This would result in a faster rate of formation of hydrogen radicals, which would lead to a faster reduction of TNT at the cathode surface. The effect of molar concentration of the electrolyte on the rate constant is clearly shown for the experimental runs conducted in the absence of electrolyte. The rate constant versus current for 0 mM electrolyte concentration in Figure 2.9 clearly indicates that there is no increase in rate constants for increase in the applied current. The number of electrons in

the system is increased with increase in current but since the conductivity of the solution is low due to an electrolyte concentration of zero (water is a poor conductor in itself), the rate at which the protons are transferred to the cathode is severely limited. Due to the slow mobility of hydrogen ions (H^+) towards the cathode surface, the rate of hydrogen radical formation would not increase. This would result in the same reduction rates for TNT, irrespective of the increase in applied current.

Another significant parameter that would affect the rate constant is the applied current. By increasing the applied current, more rapid release of electrons occurs and hence a more rapid conversion of hydrogen protons to hydrogen radicals results. A steeper concentration gradient of protons from the bulk phase to the cathode surface would result. This would lead to a lower concentration of protons in the diffusion layer surrounding the cathode, which would help in higher transfer rates of TNT molecules, and, therefore, higher reduction rates are observed at higher currents. But at higher currents (250mA & 300 mA) there is a rapid formation of hydrogen radicals at the surface and the nitroaromatic cannot diffuse through this layer to the cathode surface at

the same rate as hydrogen radicals are produced. The reduction efficiency would decrease, as these hydrogen radicals would combine to form hydrogen gas instead (see equation 13).

2.4.3 Intermediates and End Products

The aqueous phase samples collected during the aforementioned experiments were analyzed for the possible formation of the following intermediate products: 4-amino-2,6-dinitrotoluene, 2-amino-4,6-dinitrotoluene, 2,4,6-triaminotoluene

trihydrochloride, 2,4-diamino-6-nitrotoluene, 2,6-diamino-4-nitrotoluene, 2,2'-6,6'-tetranitro-4,4'-azoxytoluene, and 4,4'-6,6'-tetranitro-2,2'-azoxytoluene. None of these intermediates were detected.

At the end of each batch simulation experiment, the reactor was emptied and the collected effluent was filtered. An average solid concentration in the range of 13.24 mg/L to 36.20 mg/L was observed in the effluent for the batch simulation experiments. These solids were found to be insoluble in mobile phase solvent (acetonitrile). Therefore, the intermediates formed could not be identified.

2.5 Conclusions

The reduction kinetics of TNT in simulated munitions wastewater was studied by conducting batch simulation experiments in the laboratory scale reactor. The results showed that the electrochemical reduction kinetics for TNT is of pseudo-first order. The effects of applied current, molar concentration of electrolyte and the type of electrolyte on the reduction kinetics of TNT were studied in batch simulation experiments. A comparative study conducted between the two electrolytes sodium sulfate and lithium sulfate at a molar concentration of 3.53 mM for the electrolytes showed no significant change in rate constants. The rate constant was observed to increase with increase in molar concentration of the electrolyte and the applied current. For an applied current of 200 mA (0.088 mA/cm^2) a 20.8% increase in rate constant was observed for 9 mM (1.27 g/L) when compared with 0 mM (0 g/L) concentration of sodium sulfate electrolyte. For a 9 mM concentration of sodium sulfate electrolyte the rate constant increased by 21.82% at 250 mA (0.110 mA/cm^2) as compared to 100 mA (0.044 mA/cm^2).

2.6 References

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Fig. 2.1. Setup of the laboratory scale electrochemical reactor

Figure 2.2. TNT reduction using 3.53 mM Na_2SO_4 as the electrolyte in the feed in batch simulation experiments. Lines show linear regressions for each applied current. Initial target concentration of TNT was 70 mg/L. C = concentration of TNT over time; C_0 = initial concentration of TNT at time $t = 0$.

Figure 2.3. TNT reduction using 3.53 mM Li_2SO_4 as the electrolyte in the feed in batch simulation experiments. Lines show linear regressions for each applied current. Initial target concentration of TNT was 70 mg/L. C = concentration of TNT over time; C_0 = initial concentration of TNT at time $t = 0$.

Figure 2.4. Comparison of TNT reduction rate constants versus applied current for 3.53 mM Li₂SO₄ and Na₂SO₄ as electrolytes in the feed in batch simulation experiments

Figure 2.5. TNT reduction in the absence of electrolyte in the feed in batch simulation experiments. Lines show linear regressions for each applied current. Initial target concentration of TNT was 70 mg/L. C = concentration of TNT over time; C_0 = initial concentration of TNT at time $t = 0$.

Figure 2.6. TNT reduction using 1.77 mM Na_2SO_4 as the electrolyte in the feed in batch simulation experiments. Lines show linear regressions for each applied current. Initial target concentration of TNT was 70 mg/L. C = concentration of TNT over time; C_0 = initial concentration of TNT at time $t = 0$.

Figure 2.7. TNT reduction using 6 mM Na_2SO_4 as the electrolyte in the feed in batch simulation experiments. Lines show linear regressions for each applied current. Initial target concentration of TNT was 70 mg/L. C = concentration of TNT over time; C_0 = initial concentration of TNT at time $t = 0$.

Figure 2.8. TNT reduction using 9 mM Na_2SO_4 as the electrolyte in the feed in batch simulation experiments. Lines show linear regressions for each applied current. Initial target concentration of TNT was 70 mg/L. C = concentration of TNT over time; C_0 = initial concentration of TNT at time $t = 0$.

Figure 2.9. Variation of TNT reduction rate constant with applied current for different molar concentrations of Na_2SO_4 as electrolyte in the feed in batch simulation experiments. Lines indicate parabolic curve fit.

3. ELECTROCHEMICAL REDUCTION OF 2,4,6- TRINITROTOLUENE - CONTINUOUS FLOW STUDY²

²Submitted for Publication in *Water Research*

3.1 Abstract

Continuous flow experiments were conducted to evaluate the performance of the laboratory scale electrochemical reactor to effectively reduce 2,4,6- trinitrotoluene in simulated munition wastewater. The reactor comprises of a glassy carbon (zero porosity) impregnated graphite cylinder as cathode and a platinum wire as the anode. Experiments were conducted with three different currents: 150, 200 & 250 mA and for two electrolyte concentrations in the feed: 6 mM and 9 mM sodium sulfite. Sodium sulfite was used as the electrolyte in the feed to maintain strict anoxic conditions, thereby preventing the formation of solid dimers that could foul the nafion membrane separating the anodic and cathodic compartments. Under undetectable dissolved oxygen concentration levels in the system, the reactor operated continuously at a stable performance for the total experimental period conducted (105 days). On average, TNT reduction efficiency in the mid 80% level was achieved for the three currents studied. The only intermediate observed in the aqueous phase was 2,4,6-triaminotoluene (TAT). A mole balance closure of 85-92% was achieved. A combined overall TNT reduction efficiency over 99% was achieved by using three reactors in series.

Keywords: electrochemical reduction, 2,4,6-trinitrotoluene (TNT), munition wastewater, 2,4,6-triaminotoluene (TAT), water treatment.

3.2 Introduction

Environmental contamination of water and soils occur by the wastes generated from the munitions and defense industries. 2,4,6-trinitrotoluene (TNT) is commonly found as the main contaminant of soils and ground water originating from facilities for manufacturing, processing and disposal of explosives (Spain 1995). TNT finds wide use as a high explosive because of its stability and low sensitivity. It is produced by the nitration of toluene to nitrotoluene, dinitrotoluene (DNT) and finally to TNT using a mixture of nitric and sulfuric acids (Palmer et al. 1996). In the U.S., cleanup of soils heavily contaminated with explosives is being conducted primarily by excavation followed by composting or incineration and explosives contaminated ground water is treated almost exclusively by pump and treat with carbon adsorption (Spain 2000). The spent carbon after adsorption is usually incinerated. Incineration is currently the most common method for treating munition contaminated soils and waste water but is costly and produces unusable ash and has poor public acceptance due to safety concerns regarding air emissions such as cyanide and NO_x (Zoh and Stenstrom 2001). This has prompted research into other environmentally friendly technologies

3.2.1 Biological Treatment Processes

A laboratory scale anaerobic fluidized bed reactor containing granular activated carbon (GAC) as a microbial support media was tested and the results showed effective transformation of TNT. 2,4,6-triaminotoluene (TAT) was observed as a transformation product along with 2-amino-4,6-dinitrotoluene (2A46DNT), 4-amino-2,6-dinitrotoluene (4A26DNT), 2,4-diamino-6-nitrotoluene (24DA6NT) and 2,6-diamino-4-nitrotoluene (26DA4NT) (Maloney et al. 2002). Biotransformation of TNT by using an anaerobic

sludge supplemented with molasses was studied by Hawari et al (1998). The authors observed two distinctive cycles in the degradation of TNT. One cycle was responsible for the stepwise reduction of TNT to eventually produce TAT. The other cycle involved TAT and was responsible for the production of azo derivatives, e.g., 2,2',4,4'-tetraamino-6,6'-azotoluene and 2,2',6,6'-tetraamino-4,4'-azotoluene.

Pseudomonas sp. clone A was able to use TNT, 2,4-dinitrotoluene (DNT) and 2,6-dinitrotoluene (DNT) as a N-source after the enzymatic removal of nitro groups from the aromatic ring (Haidour and Ramos 1996). 2-hydroxylamino-4,6-dinitrotoluene (2HA46DNT), 4-hydroxylamino-2,6-dinitrotoluene (4HA26DNT), 4A26DNT, 2A46DNT and 2,4DA6NT were observed as intermediates. The authors also observed that spontaneous condensation of partially reduced TNT leads to production of azoxy toluenes.

3.2.2 Physical/ Chemical Treatment Processes

Vasilyeva et al (2002) studied the removal of TNT by activated carbon in the presence of 3 mM CaCl_2 . The authors had observed that the activated carbon, in the presence of CaCl_2 catalyzes the oxidation of TNT to 2,4,6-trinitrobenzylalcohol, which was readily oxidized to 2,4,6-trinitrobenzaldehyde and trinitrobenzene in the absence of activated carbon under dark conditions. An analysis of the photodegradation of TNT in a TiO_2 slurry reactor was presented by Schmelling and Gray (Schmelling and Gray 1995). The authors had compared the rates and extent of TNT mineralization and transformation for photocatalytic and direct photolytic reactions under conditions of varying light energies and also in the presence and absence of oxygen. It was observed by the authors that TNT degradation was faster and more complete with TiO_2 photocatalysis. Wet air

oxidation studies on red water (water resulting from TNT purification process) were conducted (Hao et al. 1993). The authors had demonstrated the efficiency of the process using diluted red water (1:100) and had concluded that the efficiency of the process was primarily a function of temperature and, to a lesser extent, the oxygen pressure.

3.2.3 Electrochemical Treatment Processes

Most of the physical processes commonly used are separation techniques, which only concentrate the waste for further treatment. Incineration is a preferred second-generation treatment option but it has many disadvantages such as air pollutant emissions, safety and regulatory requirements. The usage of a GAC bioreactor by Vanderloop et al (1999) for DNT waste offered considerable scope as a pilot scale treatment option. Biological processes previously discussed require that the biomass be maintained even when there is no nitroaromatic in the waste stream, as often happens at industrial production facilities. This proves to be less cost effective and hence has prompted research into numerous alternate technologies. Electrochemical reduction is one such technology.

Doppalapudi et al. (2002b) studied the electrochemical reduction of DNT, TNT and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in a bench scale batch reactor. Electrochemical reduction of nitroaromatics was shown to be readily taking place under oxic and anoxic conditions and the rate constants were observed to be increasing with current and stir rate but at higher currents, mass-transfer limitations govern the rates. The reduction rate constants for anoxic experiments were observed to be higher than those obtained from the oxic experiments. Azoxy dimers and amino substitutes of nitrogroups were identified as intermediates. 200 μM of TNT in an aqueous solution with 100 mM

KCl as the electrolyte was observed to readily undergo reductive transformation by a platinum electrode at -0.40 V vs. Normal Hydrogen Electrode (NHE) and aminodinitrotoluenes were detected as early reduction products (Schmelling et al. 1996). Rodgers and Bunce (2001) carried out studies on the electrolysis of nitrotoluene congeners. Reduction of aminotoluenes was carried out at high current efficiencies for a variety of cathodes at potentials -0.5 to -1 V Standard Calomel Electrode (SCE). The authors also studied the oxidation of the reaction intermediates.

Doppalapudi et al (2002a) treated DNT in a previous study by using the same electrochemical laboratory scale reactor shown in Figure 2.1. Continuous flow-through experiments were conducted at 3 different currents (150 mA, 200 mA & 250 mA) and at one electrolyte concentration (0.027 M ionic strength of sodium sulfate). It was reported that 80% reduction of DNT was achieved for a 200 mA applied current over a period of 14 days. The authors reported that 80% of the intermediates were observed in the solid phase and were identified as dimers. It was observed that these solid dimers adhered to the nafion membrane surface and to the glassy carbon surface, resulting in a decrease in the performance efficiency of the reactor after a period of 14 days. The reason for the formation of the solid dimers was attributed to the presence of dissolved oxygen (DO) in the feed. The authors reported that reactor cleaning was conducted for every 14 days to remove these solid dimers adhering to the membrane surface or the glassy carbon surface. Though the normal performance (80% DNT reduction) of the reactor was regained after reactor cleaning was performed, the periodic reactor cleaning disrupted the continuous performance of the reactor as the reactor needs to be stopped during the time period when

the reactor cleaning was done. This problem could be solved by maintaining strict anoxic conditions in the feed so that no solid dimers are formed.

3.2.4 Objectives

In the first part of this research study (see Chapter 2) the impact of parameters such as electrolyte type, concentration of electrolyte in feed and applied current on the reduction kinetics of TNT was investigated. The main objectives for the second part of this research study were: (1) to test the performance of the reactor for reduction of TNT under a continuous flow mode without the need for periodic reactor cleaning; and (2) to determine the transformation products formed during the electrochemical reduction of TNT under continuous flow mode.

3.3 Materials and Methods

Details of the laboratory scale reactor and experimental procedure for simulating munition wastewater, chemicals procured and the analytical procedure were given in Section 2.3. The feed solution consisted of 70 mg/L TNT, 0.02 M sodium phosphate dibasic buffer and 6 or 9 mM molar concentration of electrolyte (Na_2SO_3). Sodium sulfite (Fisher Scientific, Pittsburgh, PA) was used as the electrolyte in the feed instead of sodium sulfate in order to reduce the DO of the feed to undetectable levels. This was done to avoid the formation of solid dimers as intermediates, which would cause membrane-fouling problems necessitating periodic reactor cleaning (Doppalapudi et al. 2002a). The anodic solution was allowed to flow continuously through the anode compartment in a closed loop. The feed was allowed to continuously flow-through the reactor for about 30 minutes and then the recycle pump was started for recycling part of the effluent into the reactor at a recycle ratio of 20:1. The flow rate of the feed was maintained at 10.3 ± 1.45 L/day. The current supply was then turned on after flow stability was attained. Effluent samples were taken at a time interval of 60, 360 minutes and then once every day for determining the performance of the reactor with respect to TNT reduction. 2 L of effluent was collected from the effluent valve periodically, filtered and monitored for the solids concentration. An Accumet AP63 Handheld pH meter (Fisher Scientific, Pittsburgh, P.A) was used to measure the pH. The pH of the solution was maintained at 8.0 ± 0.2 by adding 3N H_2SO_4 . A Corning Model 311 portable conductivity meter (Fisher Scientific, Pittsburgh, P.A) was used to measure the conductivity. A Hanna HI 9143 portable waterproof dissolved oxygen meter (Fisher Scientific, Pittsburgh, PA) was used to measure the dissolved oxygen content. The

reactor was monitored daily for feed flow rate, recycle flow, and the flow rate of the salt solution. The pH and conductivity of the solution in the reactor and the conductivity of the anodic solution were monitored at least 3 times a day. The DO of the feed and the effluent were measured once every day. The voltage display in the current supplier was also recorded 3 times per day.

3.4 Results and Discussion

3.4.1 Performance of Reactor

The reaction mechanisms are provided in Section 2.4.1. If one performs an electron balance in a system, say for 100% reduction of TNT to TAT over a certain period of time, the minimum applied current could be determined using the Faraday's Law. According to this law, the mass of substance liberated at the electrodes during electrolysis is directly proportional to the quantity of electricity that is passed through the electrolyte.

$$\text{Number of moles of electrons released} = \frac{It}{F} \quad (1)$$

Where I = applied current in amperes

t = time for which current is applied in seconds

F = Faraday's constant = 96,500 Coulombs/mol

A total of 6 hydrogen radicals are needed to convert one nitro group to amino group (Section 2.4.1, equations 3-5). There are a total of 3 nitro groups in TNT. Therefore for reduction of all the nitro groups a total of 18 electrons are required. For 70 mg/L of TNT and 4.8 L volume of the reactor, the mass of the TNT within the reactor is 336 mg (1.48×10^{-3} moles). For 100% reduction, the number of moles of TNT reduced is 1.48×10^{-3} . The number of electrons that are required will be 26.64×10^{-3} moles. If a flow rate of 10 L/day is used, then the retention time is 11.52 hour. Using equation (1) the amount of current required for 100% reduction of TNT is calculated as 62 mA. The above calculations are based on the assumption that all the electrons are utilized for TNT reduction. But it has been reported in electrochemical processes ((Jolas et al. 2000), (Doppalapudi et al. 2002a)) that hydrogen gas is also produced at the cathode. Therefore

in a real case not all the hydrogen radicals are used to reduce TNT, there might be loss of radicals that would result in hydrogen gas formation. This is the reason for using higher currents than that is needed (62mA).

The batch simulation analysis conducted in part I of this study (chapter 2) have shown that the rate of reduction increased with molar concentration of electrolyte and applied current. The results also revealed that the rate of reduction leveled off for currents above 200 mA. Continuous flow experiments were conducted on the reactor to determine the performance of the reactor for reducing TNT. Figure 3.1 shows the performance of reactor with time. Initially, the reactor was started by applying a current of 200 mA (0.088 mA/cm^2) and using a 6 mM molar concentration of sodium sulfite. Samples collected after 24 hours showed a 72.39% reduction of TNT. Under the above operating conditions the performance of the reactor was observed for a period of 12 days. The average reduction of TNT obtained during this period (Day 1-Day 12) was $78 \pm 1.5\%$. On Day 13, the molar concentration of the electrolyte for the feed was increased to 9 mM while maintaining the applied current at 200 mA. Samples collected after 24 hours showed a TNT reduction of 77.78%. Under the above operating conditions the reactor performance was observed for a period of 54 days. The average reduction of TNT obtained during this period (Day 13-Day 67) was $82.76 \pm 2\%$.

On Day 68, the applied current was increased to 250 mA (0.110 mA/cm^2) while maintaining a molar concentration of 9 mM for the electrolyte of the feed. Samples collected after 24 hours showed a TNT reduction of 83.49%. The above operating conditions were maintained for a period of 19 days and the performance of the reactor was observed. The average reduction of TNT observed during this period (Day 68- Day

87) was $84.68 \pm 2.3\%$. On Day 88, the applied current was reduced to 150 mA (0.066 mA/cm^2) while maintaining a molar concentration of 9 mM for the electrolyte. Samples collected after 24 hours showed 84.23% reduction for TNT. The above operating conditions were maintained for a period of 17 days and the reactor performance was monitored. The average reduction of TNT achieved during this period (Day 88- Day 105) was $84.68 \pm 1.7\%$. It is seen from Figure 3.1 that the average reduction efficiency for various currents (150, 200 and 250 mA) was between 82.5-85%. A 5% increase in reduction was observed when the molar concentration was increased from 6 mM to 9 mM.

3.4.2 Continuous Versus Batch Simulation

A plot of the variation of TNT concentration with time for 200 mA applied current and for a concentration of 9 mM sodium sulfate electrolyte in feed as determined from the batch simulation experiment (Chapter 2) is shown in Figure 3.2. In order to compare the reduction of TNT in the continuous flow experiment to the reduction in the batch simulation experiment (Chapter 2), the following calculations were made. The continuous flow experiments were conducted for a flow rate of $10.3 \pm 1.45 \text{ L/day}$ in a reactor volume of 4.8 L, which gives a retention time, (τ) of 671 minutes. Since an average reduction of 82.76% was observed for the above-mentioned operating conditions, the rate of reduction in the continuous flow mode can then be determined.

$$\text{Rate of reduction} = (C_o - C_{\text{eff}})/\tau = (70 - 12.07)/671 = 0.0863 \text{ mg/L min}^{-1}.$$

For the batch simulation experiment, reduction rate of TNT is determined by the slope of the tangent (shown by the inclined solid line in Figure 3.2) to the curve at 82.76 % reduction of TNT for $C/C_o = 0.1724$. The rate determined is $0.0615 \text{ mg/L min}^{-1}$. A

28.73% decrease was observed for the rate constants of the batch simulation experiment when compared to the continuous flow experiment and is speculated to be because of the different transformation pathways of TNT reduction in batch simulation and continuous flow experiments.

3.4.3 Electrochemical Reactors in Series

Results from the batch simulation experiments (Section 2.4.2) indicated that the kinetics for TNT reduction is of pseudo-first order. Since first order kinetics is independent of the initial concentration, using more than one reactor in series would eventually provide a better overall reduction. The following experimental runs were conducted as part of a study to determine how many electrochemical reactors with the same specification as specified in this study would be needed in series to achieve an overall reduction efficiency of over 99% for TNT. The performance of the first stage reactor was observed by applying a current of 200 mA (0.088 mA/cm^2) and using 9 mM sodium sulfite electrolyte. Samples collected after 24 hours showed 80.61% reduction for TNT. The performance of the reactor was monitored with the above operating conditions for a 5-day period. The average reduction of TNT achieved during this period was $82.58 \pm 1.22\%$. The second stage performance of the reactor was observed under the same operating conditions as the first stage but the effluent collected from the first stage was used as the feed for the second stage. The combined average reduction efficiency for the two stages was $97.71 \pm 0.39\%$ for a 5-day period. The third stage performance of the reactor was observed under the same operating conditions with the effluent collected from the second stage used as the feed for the third stage. The combined average

reduction efficiency for the three stages was observed as $99.52 \pm 0.03\%$ for a 5-day period. The performance of the three reactors operated in series is shown in Figure 3.3.

3.4.4 Intermediates and End Products

The measured average solids concentration during the experiments was determined to be 1.56 ± 0.48 mg/L, which is about 5 – 11.8% of the solids determined in the batch simulation experiments (Section 2.4.3). The only intermediate observed was TAT. It was observed as a liquid phase intermediate. A mole balance closure of 85-92% was achieved. No hydroxyl amino toluenes and amino toluenes were observed in the liquid phase sample analysis. Table 3.1 shows the mole balance closure for transformation products of TNT obtained during the continuous flow experiments.

3.4.5 General Discussion

Doppalapudi et al (2002a) operated the laboratory scale electrochemical reactor in an earlier study to treat 2,4-dinitrotoluene (DNT). The authors had observed that a current of 200 mA (current density of 0.088 mA/cm^2) provided a stable reduction of DNT at the 80% level for a period of 14 days after which reactor cleaning was necessary for the removal of suspended solids that were formed within the reactor. In our study the reactor was run continuously for the whole duration of 105 days without any deterioration of performance. This stable performance could be attributed to the absence of solid dimers, which could attach to the membrane surface and reduce its capacity.

Figure 3.4 shows a possible mechanism for the transformation of TNT to TAT (Hawari et al. 1998) and to azoxy dimers (Kaplan 1996). The following chemical reaction explains the pathway for dimer formation.

The above reaction shows the pathway wherein the hydroxyl-amino-dinitro-toluenes undergoes a transformation to tetra-nitro-azoxy-toluene dimers in the presence of dissolved oxygen. This pathway could be eliminated by avoiding the presence of dissolved oxygen in the feed. The use of sodium sulfite as the electrolyte instead of sodium sulfate, which was used in the batch simulation runs (refer Chapter 2) was based upon the idea where the sulfite could utilize the dissolved oxygen left in the system after the 12-hour N₂ purging period and be oxidized to sulfate. This helped in maintaining strict anoxic conditions where the measured DO was below detectable limits. The chemical analysis of the samples collected during the reactor performance confirmed the absence of dimers.

The major contaminant that will be left in the effluent aqueous stream is TAT. TAT is an electron rich compound and should be readily oxidized when treated aerobically (Knackmuss 1996). Preuss et al (1993) conducted a study on the anaerobic transformation of TNT using a sulfate reducing bacterium. The authors observed that the organism was able to reduce TNT to TAT in growing cultures and cell suspensions and further transform TAT to unknown products. The study also observed that TAT was anaerobically converted to unknown products by a bacterial isolate under sulfate reducing and by a pseudomonas strain under denitrifying conditions. TAT conversion was also catalyzed in the absence of cells under aerobic conditions by trace elements especially by Mn²⁺ accompanied by the elimination of ammonia in a stoichiometry of one mole of NH₃ released per TAT transformed (Preuss et al. 1993). There is no conclusive evidence yet as whether biodegradation would lead to mineralization. Hawari et al. (1998) had studied

the transformation products of TAT under anoxic conditions. The authors reported an abiotic transformation of TAT to phenolic end products. The authors also reported the formation of azo polymers under biotic conditions. Further research needs to be conducted for exploring the possible mechanisms for mineralizing TAT.

3.5 Conclusions

Continuous flow experiments were conducted in the electrochemical reactor for three different currents (150, 200 & 250 mA) with current densities 0.066 mA/cm^2 to 0.11 mA/cm^2 using 6 and 9 mM concentration of sodium sulfite as the electrolyte. Sodium sulfite was used instead of sodium sulfate to maintain a DO level below detectable limits. The absence of DO prevented the formation of solid dimers. The solid concentration measured during batch simulation experiments (Section 2.4.3) was in the range of 13.24 – 36.20 mg/L and during flow-through experiments was $1.56 \pm 0.5 \text{ mg/L}$ (a drop of 88 - 95%). This drop in solid concentration enabled continuous operation of reactor for the whole experimental period (105 days) without any deterioration in performance. The results showed that for 150, 200, and 250 mA and for a 9 mM sodium sulfite, the observed average reduction percentages for TNT were 84.68, 82.76 and 84.68, respectively. A comparison of the reduction rates obtained from the flow-through experiment to the batch simulation experiment conducted (Chapter 2) with 200mA applied current and 9 mM electrolyte concentration showed that the reduction rate for the batch simulation experiment decreased by 28.73% as compared to the flow-through experiment and this decrease is speculated to the different transformation pathways for TNT reduction in continuous and batch simulation experiments. The simulated three-stage reactor study showed that more than 99% reduction efficiency could be achieved for TNT. The only intermediate observed with the continuous flow experiment was TAT and was observed in the liquid phase. A mole balance closure of 85-92% was achieved.

3.6 References

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Table 3.1. Mole Balance of TNT for Continuous Flow Experiments

S.No	Current (mA)	Molar Concentration (mM)	Compound	Solid Phase (% Molar Conversion of TNT to)	Liquid Phase (% Molar Conversion of TNT to)
1	200	6	TNT TAT 2A46DNT 4A26DNT 26DA4NT 24DA6NT Dimer1 Dimer 2	-- -- -- -- -- -- -- --	19.12 66.27 -- -- -- -- -- --
2	200	9	TNT TAT 2A46DNT 4A26DNT 26DA4NT 24DA6NT Dimer1 Dimer	-- -- -- -- -- -- -- --	15.17 77.07 -- -- -- -- -- --
3	250	9	TNT TAT 2A46DNT 4A26DNT 26DA4NT 24DA6NT Dimer1 Dimer	-- -- -- -- -- -- -- --	13.75 75.14 -- -- -- -- -- --
4	150	9	TNT TAT 2A46DNT 4A26DNt 26DA4NT 24DA6NT Dimer1 Dimer	-- -- -- -- -- -- -- --	14.04 75.43 -- -- -- -- -- --

Figure 3.1. Reactor performance with time in continuous flow mode. Vertical lines represent days at which the operating conditions (applied current / molar concentration of Na_2SO_3 electrolyte in the feed) were changed.

Figure 3.2. Variation of TNT Concentration with time for 200 mA applied current and for 9 mM Na_2SO_4 electrolyte in the feed as determined from the batch simulation experiment (refer Chapter 2). An exponential curve fit is shown. Inclined solid line indicates tangent drawn to the curve fit at $C/C_0 = 0.1724$ (82.76% TNT reduction). C = concentration of TNT over time; C_0 = Concentration of TNT at time $t = 0$.

Figure 3.3. Three stage electrochemical reactor performance for TNT reduction

Figure 3.4. Proposed Mechanism for Reduction of TNT

4. RECOMMENDATIONS

4.1 Recommendations

In the previous chapters, a research study on the use of electrochemical reduction to treat munition wastewater contaminated with TNT was presented. The first part of this research investigated the impact of various parameters like type of electrolyte, concentration of electrolyte in feed and applied current on the electrochemical reduction kinetics of TNT by conducting batch simulation experiments in the laboratory scale reactor. In the second part, the performance efficiency of the laboratory scale reactor to effectively reduce TNT was evaluated under continuous flow mode. Some recommendations that would give an outline for future studies are suggested below:

The simulated 3-stage reactor study (refer figure 3.3) proved conclusively that such a system operated in series would be ideal as TNT removal efficiencies greater than 99% were achieved. The use of sodium sulfite as electrolyte (apart from purging the water with nitrogen) helped maintain strict anoxic conditions in the reactor. This stopped the formation of solid dimers, thus enabling continuous operation of reactor for 105 days without any stoppages for reactor cleaning.

The major contaminant that will be left in the effluent aqueous stream is TAT. TAT is an electron rich compound and should be readily oxidized when treated aerobically (Knackmuss 1996). Preuss et al. (1993) conducted a study on the anaerobic transformation of TNT using a sulfate reducing bacterium. The authors observed that the organism was able to reduce TNT to TAT in growing cultures and cell suspensions and further transform TAT to unknown products. The study also observed that TAT was anaerobically converted to unknown products by a bacterial isolate under sulfate reducing and by a pseudomonas strain under denitrifying conditions. TAT conversion was also

catalyzed in the absence of cells under aerobic conditions by trace elements especially by Mn^{2+} accompanied by the elimination of ammonia in a stoichiometry of one mole of NH_3 released per TAT transformed. There is no conclusive evidence yet as to whether biodegradation would lead to mineralization. Hawari et al. (1998) had studied the transformation products of TAT under anoxic conditions. He reported an abiotic transformation of TAT to phenolic end products. He also reported the formation of azo polymers under biotic conditions. A major problem is the tendency of TAT to form solid dimers in the presence of oxygen and also its capacity to react with itself and polymerize (Hawari et al. 1998), (Knackmuss 1996). Further studies need to be done to study the scope of biological, chemical and electrochemical processes to effectively mineralize the TNT transformation product TAT. Rodgers and Bunce (2001) suggested the coupling of anodic oxidation of aminotoluenes with the cathodic reduction of nitro toluenes but a major concern would be the formation of dimers resulting in anode fouling. Biological and chemical processes need to be explored for the mineralization of TAT. A 3-stage electrochemical reactor that would effectively reduce more than 99% TNT to TAT coupled with a system (biological/chemical) that would mineralize TAT would be an ideal system that would fulfill the set research objectives.

All the experiments were conducted using simulated munitions wastewater, which was prepared by adding the required amounts of chemicals to de-ionized water. Experiments may be conducted using the munitions process wastewater. The other organic and inorganic compounds present in the munitions wastewater could have a significant effect on the reduction of TNT and its transformation pathways.

4.2 References

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APPENDIX

Batch Simulation Experiments for Reduction of TNT

Co = 70 mg/L; Current = 100 mA; DO = 1.17 mg/L

Electrolyte = Na₂SO₄; Electrolyte Concentration = 0.0 mM.

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.47	-----	52.66
5	7.50	2.1	46.66
20	7.54	2.2	45.00
30	7.55	2.2	45.83
60	7.62	2.3	39.40
90	7.77	2.3	37.13
120	7.75	2.3	32.74
180	7.92	2.4	25.53
240	7.58	2.5	21.10
310	7.72	2.6	15.80
360	7.83	2.6	13.47

Co = 70 mg/L; Current = 150 mA; DO = 0.72 mg/L

Electrolyte = Na₂SO₄; Electrolyte Concentration = 0.0 mM.

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.93	-----	60.30
15	7.93	2.6	53.03
30	7.94	3.0	49.10
60	7.96	3.1	43.70
90	7.97	3.1	39.33
120	7.94	3.1	36.03
180	7.98	3.1	30.17
245	7.97	3.1	22.90
300	7.91	3.1	19.23
345	7.95	3.1	16.64

Co = 70 mg/L; Current = 200 mA; DO = 0.85 mg/L

Electrolyte = Na₂SO₄; Electrolyte Concentration = 0.0 mM.

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.96	-----	61.87
15	7.98	2.8	48.40
30	7.93	3.2	47.97
72	7.98	3.2	40.90
102	7.98	3.2	33.27
135	7.99	3.2	31.80
180	7.90	3.3	27.00
263	7.90	3.3	19.63
305	7.93	3.3	16.33
360	8.00	3.1	12.98

Co = 70 mg/L; Current = 250 mA; DO = 0.60 mg/L

Electrolyte = Na₂SO₄; Electrolyte Concentration = 0.0 mM.

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.99	-----	61.30
15	8.01	3.3	50.00
30	7.98	3.3	46.83
60	7.95	3.2	41.60
120	7.98	3.2	33.80
180	7.95	3.2	27.67
250	7.98	3.2	20.95
310	7.90	3.2	16.06
363	7.89	3.2	13.16

Co = 70 mg/L; Current = 100 mA; DO = 0.72 mg/L

Electrolyte = Na₂SO₄; Electrolyte Concentration = 1.77 mM.

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.93	-----	63.63
5	7.93	3.1	55.30
15	7.93	3.2	53.27
30	7.98	3.3	50.83
60	7.92	3.4	44.33
120	7.98	3.4	37.00
200	7.95	3.5	27.44
250	7.89	3.6	22.59
300	7.95	3.7	19.30
385	7.85	3.9	14.11

Co = 70 mg/L; Current = 150 mA; DO = 1.17 mg/L

Electrolyte = Na₂SO₄; Electrolyte Concentration = 1.77 mM.

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.82	-----	64.70
5	7.86	2.5	58.77
15	7.86	2.6	55.07
30	7.87	2.7	51.67
60	7.94	3.1	45.67
90	7.93	3.0	39.63
123	8.00	3.0	37.33
205	7.93	3.0	27.10
240	7.89	3.0	24.03
305	7.80	3.0	19.00
370	7.96	3.0	15.20

Co = 70 mg/L; Current = 200 mA; DO = 1.09 mg/L

Electrolyte = Na₂SO₄; Electrolyte Concentration = 1.77 mM.

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.95	----	65.43
5	7.95	2.9	55.93
15	7.95	3.0	52.70
30	8.00	3.2	49.30
60	7.99	3.1	43.53
120	7.95	3.1	37.37
180	8.00	3.1	28.27
240	7.86	3.1	22.84
300	7.97	3.0	17.77
360	7.90	3.0	14.88

Co = 70 mg/L; Current = 250 mA; DO = 0.70 mg/L

Electrolyte = Na₂SO₄; Electrolyte Concentration = 1.77 mM.

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.93	-----	69.33
5	7.93	3.7	56.30
15	7.93	4.1	53.10
35	7.94	4.2	48.90
65	7.93	4.1	42.40
95	7.96	4.1	37.67
170	7.90	4.1	28.11
200	7.95	4.0	24.40
250	7.85	4.0	20.68
300	7.80	4.1	16.30
360	7.95	4.0	13.04

Co = 70 mg/L; Current = 75 mA; DO = 1.20 mg/L

Electrolyte = Na₂SO₄; Electrolyte Concentration = 3.53 mM

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.87	-----	65.30
5	7.89	2.1	54.00
15	7.90	2.2	53.00
30	7.89	2.3	49.80
60	7.88	2.3	44.67
120	7.85	2.4	35.37
182	7.83	2.4	27.84
242	7.80	2.4	22.56
315	7.78	2.5	17.05
360	7.76	2.6	13.87

Co = 70 mg/L; Current = 100 mA; DO = 0.80 mg/L

Electrolyte = Na₂SO₄; Electrolyte Concentration = 3.53 mM

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	8.01	-----	71.33
5	7.82	2.2	55.60
15	7.96	2.3	54.32
30	7.99	2.4	50.80
60	7.90	2.5	46.20
120	7.90	2.6	35.83
190	7.90	2.7	27.43
260	7.97	2.9	20.07
300	7.84	3.0	18.41
360	7.98	3.1	13.17

Co = 70 mg/L; Current = 150 mA; DO = 1.10 mg/L

Electrolyte = Na₂SO₄; Electrolyte Concentration = 3.53 mM

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.83	-----	63.73
5	7.82	2.4	51.17
15	7.81	2.6	50.67
30	7.81	2.8	46.23
60	7.84	3.2	42.50
120	7.83	3.3	32.20
200	7.96	3.3	23.00
240	7.89	3.3	19.29
300	7.85	3.4	14.65
360	7.80	3.4	11.29

Co = 70 mg/L; Current = 200 mA; DO = 1.16 mg/L

Electrolyte = Na₂SO₄; Electrolyte Concentration = 3.53 mM

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.93	-----	63.33
5	7.95	2.5	53.60
15	7.95	2.8	51.73
30	7.98	3.2	48.67
60	7.90	3.4	42.33
120	7.83	3.4	33.22
205	7.94	3.4	21.73
250	7.92	3.4	17.56
300	7.91	3.4	13.60
360	7.95	3.4	10.05

Co = 70 mg/L; Current = 250 mA; DO = 1.0 mg/L

Electrolyte = Na₂SO₄; Electrolyte Concentration = 3.53 mM

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.6	-----	62.33
5	7.64	2.6	50.37
15	7.68	2.9	48.17
30	7.72	3.0	45.97
60	7.88	3.2	38.23
95	8.12	3.2	32.97
120	7.35	3.2	29.50
180	7.55	3.2	20.77
240	7.92	3.3	15.59
300	7.64	3.3	12.30
360	7.93	3.4	9.03

Co = 70 mg/L; Current = 100 mA; DO = 1.15 mg/L

Electrolyte = Na₂SO₄; Electrolyte Concentration = 6 mM

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.89	-----	46.40
16	7.90	2.4	40.43
30	7.91	2.4	38.90
70	7.98	2.5	32.03
90	7.94	2.5	30.33
120	7.95	2.6	25.89
180	7.80	2.8	19.22
240	7.99	2.9	16.51
315	7.97	2.9	12.48

Co = 70 mg/L; Current = 150 mA; DO = 1.00 mg/L

Electrolyte = Na₂SO₄; Electrolyte Concentration = 6 mM

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.89	-----	48.67
21	7.89	2.8	37.20
42	7.61	3.0	35.31
60	7.61	3.1	33.01
90	7.70	3.2	29.11
120	7.75	3.2	24.79
190	7.72	3.2	17.30
250	7.85	3.2	13.36
300	7.57	3.3	10.03

Co = 70 mg/L; Current = 200 mA; DO = 0.90 mg/L

Electrolyte = Na₂SO₄; Electrolyte Concentration = 6 mM

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.54	-----	46.73
15	7.54	2.8	39.60
30	7.54	3.1	36.47
60	7.58	3.1	30.95
145	7.86	3.1	20.27
201	7.87	3.2	15.37
270	7.89	3.2	10.73
330	7.50	3.3	7.79

Co = 70 mg/L; Current = 250 mA; DO = 1.38 mg/L

Electrolyte = Na₂SO₄; Electrolyte Concentration = 6 mM

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.30	-----	56.70
6	7.34	2.6	51.50
16	7.35	2.7	47.49
33	7.39	2.9	45.03
60	7.41	3.1	40.23
95	7.46	3.1	34.82
120	7.50	3.1	28.60
186	7.60	3.1	20.64
240	7.69	3.1	15.73
300	7.82	3.2	12.14
360	8.00	3.2	8.86

Co = 70 mg/L; Current = 300 mA; DO = 0.50 mg/L

Electrolyte = Na₂SO₄; Electrolyte Concentration = 6 mM

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.53	-----	64.80
5	7.54	2.7	50.54
15	7.54	3.1	47.55
30	7.58	3.2	43.33
60	7.60	3.3	37.43
90	7.76	3.3	32.07
120	7.94	3.3	27.18
190	7.78	3.3	18.85
250	7.62	3.3	14.00
300	7.86	3.3	10.57
360	7.76	3.3	7.89

Co = 70 mg/L; Current = 100 mA; DO = 0.72 mg/L

Electrolyte = Na₂SO₄; Electrolyte Concentration = 9 mM

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.83	-----	51.00
5	7.83	2.1	48.30
15	7.85	2.3	46.17
30	7.87	2.4	40.07
60	7.92	2.5	30.35
120	7.88	2.7	30.27
180	7.92	3.0	23.89
255	7.96	3.1	16.80
320	7.90	3.1	12.20
360	7.91	3.1	14.30

Co = 70 mg/L; Current = 150 mA; DO = 0.86 mg/L

Electrolyte = Na₂SO₄; Electrolyte Concentration = 9 mM

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.63	-----	63.53
5	7.63	2.3	49.37
15	7.64	2.5	45.90
30	7.64	2.6	44.53
60	7.64	2.9	38.97
120	7.67	3.2	29.56
180	7.73	3.2	22.09
260	7.82	3.2	15.42
310	7.89	3.2	12.43
360	7.97	3.2	8.77

Co = 70 mg/L; Current = 200 mA; DO = 0.72 mg/L

Electrolyte = Na₂SO₄; Electrolyte Concentration = 9 mM.

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.72	-----	61.83
10	7.73	2.8	49.97
20	7.73	2.8	46.83
35	7.73	3.3	44.33
60	7.74	3.3	40.33
90	7.80	3.3	35.53
120	7.85	3.3	29.13
180	7.89	3.4	20.19
240	7.97	3.8	15.18
310	7.92	3.7	9.55
360	7.91	3.6	8.90

Co = 70 mg/L; Current = 250 mA; DO = 0.580 mg/L

Electrolyte = Na₂SO₄; Electrolyte Concentration = 9 mM.

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.50	-----	68.13
5	7.50	2.6	52.80
15	7.50	2.7	48.93
33	7.52	3.1	44.33
60	7.57	3.2	38.10
90	7.63	3.3	33.10
123	7.70	3.3	28.29
180	7.86	3.3	20.54
242	7.52	3.3	15.47
300	7.61	3.3	11.11
360	7.87	3.3	6.90

Co = 70 mg/L; Current = 300 mA; DO = 0.750 mg/L

Electrolyte = Na₂SO₄; Electrolyte Concentration = 9 mM

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.51	-----	68.50
6	7.51	3.1	52.47
16	7.52	3.3	49.60
30	7.54	3.4	46.17
60	7.65	3.4	39.23
90	7.83	3.4	33.12
123	7.97	3.4	28.14
185	7.50	3.4	19.14
240	7.64	3.4	14.35
300	7.88	3.4	9.95
360	7.70	3.4	7.06

Co = 70 mg/L; Current = 75 mA; DO = 1.20 mg/L

Electrolyte = Li₂SO₄; Electrolyte Concentration = 3.53 mM

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.97	-----	57.00
5	7.98	2.2	49.87
15	7.99	2.2	48.23
30	7.90	2.3	45.77
60	7.93	2.3	41.40
90	7.83	2.4	37.43
120	7.80	2.4	32.39
190	7.88	2.5	25.20
240	7.97	2.6	20.83
360	7.98	2.9	11.97

Co = 70 mg/L; Current = 100 mA; DO = 1.30 mg/L

Electrolyte = Li₂SO₄; Electrolyte Concentration = 3.53 mM

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.96	-----	59.70
5	7.98	2.2	51.13
15	7.98	2.4	49.10
30	7.88	2.4	47.13
60	7.96	2.6	38.90
120	7.91	2.7	32.20
196	7.90	3.0	23.05
260	7.90	3.1	18.41
300	7.94	3.1	14.86
360	7.95	3.2	11.83

Co = 70 mg/L; Current = 150 mA; DO = 1.25 mg/L

Electrolyte = Li₂SO₄; Electrolyte Concentration = 3.53 mM

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.85	-----	59.17
5	7.85	2.4	49.60
15	7.85	2.6	47.47
30	7.85	2.8	43.83
60	7.88	3.2	39.27
128	8.04	3.3	29.20
180	7.97	3.3	24.96
260	7.85	3.3	16.81
300	7.95	3.3	14.23
360	7.90	3.3	10.56

Co = 70 mg/L; Current = 200 mA; DO = 1.25 mg/L

Electrolyte = Li_2SO_4 ; Electrolyte Concentration = 3.53 mM

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.87	-----	61.47
5	7.87	2.6	51.13
15	7.88	2.8	48.80
30	7.91	3.3	45.90
60	7.76	3.3	40.70
120	7.81	3.4	31.07
180	7.78	3.3	23.32
240	8.07	3.3	17.09
300	7.81	3.3	12.92
360	7.75	3.4	9.62

Co = 70 mg/L; Current = 250 mA; DO = 1.05 mg/L

Electrolyte = Li_2SO_4 ; Electrolyte Concentration = 3.53 mM

Time (min)	pH	Voltage (V)	Concentration (mg/L)
0	7.87	-----	59.47
5	7.88	2.8	50.57
15	7.89	3.4	47.83
30	7.92	3.5	44.13
60	7.80	3.6	39.07
135	7.90	3.6	25.53
180	7.85	3.6	19.13
245	7.87	3.6	14.22
300	7.92	3.6	10.48
360	7.90	3.6	8.99

Continuous Flow Experiments with TNT

Co = 70 mg/L; Current = 200 mA;

Electrolyte: Na₂SO₃; Electrolyte Concentration = 6 mM

Time (days)	pH of Feed	DO of Feed (mg/L)	Salt Solution Conductivity mS/cm	Voltage (V)	Influent Concentration (mg/L)	Effluent Concentration (mg/L)
1	7.93	0.150	33.2	3.3	71.74	19.81
2	7.77	0.150	33.2	3.2	72.24	17.33
3	7.50	0.150	33.3	3.3	71.74	16.84
4	7.50	0.150	33.2	3.3	71.14	15.20
5	8.20	0.270	33.0	3.3	71.84	16.04
6	7.96	0.120	33.1	3.3	71.82	16.85
7	7.77	0.120	32.8	3.3	73.11	16.98
8	7.62	0.130	32.7	3.3	68.21	15.05
9	7.78	0.130	32.4	3.3	70.22	13.43
10	7.75	0.130	32.3	3.4	69.21	14.60
11	7.36	0.080	32.0	3.2	58.38	12.82
12	7.70	0.080	32.0	3.3	56.12	11.35
13	7.55	0.080	31.8	3.3	68.41	15.20

Co = 70 mg/L; Current = 200 mA;

Electrolyte: Na₂SO₃; Electrolyte Concentration = 9 mM

Time (days)	pH of Feed	DO of Feed (mg/L)	Salt Solution Conductivity mS/cm	Voltage (V)	Influent Concentration (mg/L)	Effluent Concentration (mg/L)
14	7.46	0.100	31.60	3.2	64.88	13.89
15	7.79	0.100	31.50	3.3	69.65	12.70
16	7.86	0.300	31.00	3.3	72.04	14.03
17	7.92	0.300	31.10	3.3	71.75	13.19
18	7.82	0.200	31.10	3.3	65.64	11.47
19	8.10	0.200	30.90	3.3	61.88	10.19
20	7.94	0.200	30.70	3.3	77.15	12.28
21	7.89	0.270	30.40	3.3	76.27	12.62
22	8.12	0.270	30.20	3.4	73.34	10.10
23	7.72	0.100	30.20	3.4	77.59	11.43
24	7.71	0.100	30.10	3.3	75.02	11.45
25	7.50	0.100	31.80	3.2	69.26	11.76
26	7.83	0.100	31.80	3.2	65.23	11.38
27	7.72	0.100	31.70	3.3	63.69	11.22
28	7.50	0.000	32.00	3.4	58.02	9.67
29	7.53	0.000	31.60	3.3	60.87	9.08
30	7.98	0.000	31.70	3.4	70.65	11.07
31	7.90	0.000	31.50	3.4	68.50	13.55

Time (days)	pH of Feed	DO of Feed (mg/L)	Salt Solution Conductivity mS/cm	Voltage (V)	Influent Concentration (mg/L)	Effluent Concentration (mg/L)
32	8.00	0.000	31.3	3.3	67.88	11.87
33	8.15	0.000	31.4	3.4	64.72	12.93
34	7.61	0.000	31.0	3.3	74.26	10.22
35	7.52	0.000	31.0	3.4	68.67	10.68
36	8.07	0.000	31.2	3.3	66.15	12.42
37	8.00	0.000	30.9	3.3	69.80	13.27
38	8.25	0.000	30.9	3.2	58.93	11.44
39	7.61	0.200	30.7	3.2	61.80	10.33
41	8.04	0.200	30.2	3.1	77.82	13.68
42	7.88	0.200	30.3	3.2	74.95	14.42
43	7.50	0.200	30.3	3.3	70.95	13.39
44	7.98	0.000	30.1	3.5	77.25	13.39
45	8.04	0.000	32.5	3.5	72.67	12.01
47	7.80	0.000	32.2	3.3	75.53	14.76
48	7.78	0.000	32.4	3.3	64.08	12.19
49	7.57	0.000	32.0	3.2	68.09	10.04
50	8.02	0.300	32.0	3.3	70.83	10.80
51	8.04	0.300	32.2	3.1	69.82	10.64
52	7.71	0.300	32.1	3.1	69.28	11.79

Time (days)	pH of Feed	DO of Feed (mg/L)	Salt Solution Conductivity mS/cm	Voltage (V)	Influent Concentration (mg/L)	Effluent Concentration (mg/L)
53	7.70	0.300	32.0	3.1	64.67	11.18
54	8.18	0.300	33.0	3.2	51.50	9.03
55	7.95	0.000	31.8	3.1	68.08	13.15
56	7.50	0.000	31.5	3.2	70.57	11.43
57	7.87	0.000	31.4	3.1	64.67	11.18
58	7.60	0.000	31.0	3.1	69.07	11.07
59	8.30	0.000	30.6	3.2	72.62	10.07
60	7.69	0.000	30.8	3.1	73.25	10.55
61	7.56	0.000	30.6	3.3	72.67	14.71
63	7.83	0.000	30.4	3.4	71.41	13.85
64	7.77	0.000	30.3	3.4	65.80	11.45
65	7.70	0.000	29.8	3.7	61.80	10.30
66	7.48	0.000	32.0	3.4	58.93	9.54
67	7.70	0.000	31.7	3.4	66.38	11.56

Co = 70 mg/L; Current = 250 mA;

Electrolyte: Na₂SO₃; Electrolyte Concentration = 9 mM

Time (days)	pH of Feed	DO of Feed (mg/L)	Salt Solution Conductivity mS/cm	Voltage (V)	Influent Concentration (mg/L)	Effluent Concentration (mg/L)
68	7.60	0.000	32.3	3.3	64.75	10.69
69	7.76	0.000	32.3	3.4	72.43	10.83
70	7.61	0.000	32.2	3.4	64.10	9.94
71	8.40	0.000	32.2	3.4	69.87	9.48
73	8.34	0.000	32.0	3.5	77.13	13.91
74	7.50	0.000	32.2	3.3	78.47	11.02
75	7.98	0.000	32.1	3.5	54.88	9.92
76	7.92	0.000	31.8	3.4	72.43	11.53
77	7.70	0.000	31.7	3.4	73.09	12.83
78	7.74	0.000	31.5	3.3	67.32	11.53
80	7.80	0.000	31.4	3.6	71.80	9.87
81	7.54	0.000	31.4	3.5	64.10	8.66
82	7.56	0.000	31.3	3.4	72.45	8.85
83	7.86	0.000	31.0	3.4	69.87	13.14
85	7.92	0.000	30.7	3.5	55.58	10.39
86	7.80	0.000	30.7	3.4	53.21	8.02
87	7.71	0.000	30.5	3.4	62.57	8.40

Co = 70 mg/L; Current = 150 mA;

Electrolyte: Na₂SO₃; Electrolyte Concentration = 9 mM

Time (days)	pH of Feed	DO of Feed (mg/L)	Salt Solution Conductivity mS/cm	Voltage (V)	Influent Concentration (mg/L)	Effluent Concentration (mg/L)
89	7.28	0.000	30.5	2.9	79.05	12.46
90	7.34	0.000	30.1	3.0	78.98	13.28
91	7.52	0.000	32.4	2.9	80.95	13.47
92	7.45	0.000	32.6	2.9	67.02	12.20
93	7.84	0.000	32.3	3.1	68.29	9.80
94	8.15	0.000	32.3	3.2	78.08	13.18
95	9.34	0.000	31.6	3.2	73.98	12.01
96	7.88	0.000	31.7	3.1	72.09	12.39
97	7.77	0.000	31.4	3.1	68.92	10.88
98	8.08	0.000	31.8	3.0	78.40	11.14
99	7.85	0.000	31.8	3.1	75.24	11.14
101	7.96	0.000	31.5	3.3	73.67	11.14
102	7.76	0.000	31.0	3.1	60.80	8.89
103	7.85	0.000	31.3	3.0	54.07	6.79
104	7.60	0.000	31.1	3.1	50.27	6.39
105	8.02	0.000	31.2	3.1	60.19	7.90

III-Stage Reactor Study for Reduction of TNT

Stage I; Co = 70 mg/L; Current = 200 mA;

Electrolyte: Na₂SO₃; Electrolyte Concentration = 9 mM

Time (days)	pH of Feed	DO of Feed (mg/L)	Salt Solution Conductivity mS/cm	Voltage (V)	Influent Concentration (mg/L)	Effluent Concentration (mg/L)
1	7.83	0.000	30.4	3.4	71.41	13.85
2	7.77	0.000	30.3	3.4	65.80	11.45
3	7.70	0.000	29.8	3.7	61.80	10.30
4	7.48	0.000	32.0	3.4	58.93	9.54
5	7.50	0.000	31.7	3.4	66.38	11.56

Stage II; Co = 12.25 mg/L; Current = 200 mA;

Electrolyte: Na₂SO₃; Electrolyte Concentration = 9 mM

Time (days)	pH of Feed	DO of Feed (mg/L)	Salt Solution Conductivity mS/cm	Voltage (V)	Influent Concentration (mg/L)	Effluent Concentration (mg/L)
6	7.67	0.000	31.0	3.2	10.07	1.34
7	7.90	0.000	30.8	3.2	12.38	1.29
8	7.45	0.000	30.5	3.1	8.97	1.43
9	7.61	0.000	30.6	3.3	5.81	0.75

Stage III; Co = 1.25 mg/L; Current = 200 mA;

Electrolyte: Na₂SO₃; Electrolyte Concentration = 9 mM

Time (days)	pH of Feed	DO of Feed (mg/L)	Salt Solution Conductivity mS/cm	Voltage (V)	Influent Concentration (mg/L)	Effluent Concentration (mg/L)
10	8.10	0.000	30.5	3.1	0.86	0.17
11	7.78	0.000	30.3	3.1	0.72	0.16
12	7.62	0.000	30.1	3.1	0.73	0.14
13	7.67	0.000	30.0	3.1	0.74	0.15