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ELECTROCHEMICAL DEGRADATION OF 2,4,6 – TRINITROTOLUENE; 2,4-DINITROTOLUENE and HEXAHYDRO- 1,3,5-TRINITRO- 1,3,5- TRIAZINE

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ABSTRACT

The electrochemical reduction of nitro-aromatic compounds 2,4,6- trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT – in water-ethanol mixture) and hexahydro-1,3,5– trinitro- 1,3,5 -triazine (RDX) was studied to optimize the degradation conditions and to propose the design of a plug flow reactor based on those conditions. Controlled experiments based on single solute nitroaromatics were carried out initially to ascertain the degradation of these chemicals by electrochemical means and to establish the effect of various experimental factors such as the applied current, the stir rate of the reactant solution, pH and the surface area of the electrode. Glassy Carbon rod was used as the cathode.

The degradation rates increased with the initial increase in the current, but flattened out at higher currents, pointing out to the fact that mass-transfer was limiting at higher current values. Experiments carried out with improved hydrodynamics so as to enhance the mass transfer did not show this flattening-out behavior. The degradation rates were higher at larger stir rates and at lower pH. The studies extended to mixtures, which are more representative of army industrial waste streams, indicated that the degradation kinetics of the nitroaromatics are mutually independent.

The degradation of 2,4,6-TNT yielded the following intermediates and products: 4amino-2,6-dinitrotoluene, 2-amino,4,6-dinitrotoluene; 2,2',6,6'-trinitro,4,4'azoxytoluene, 4,4',6,6'-trinitro,2,2'-azoxytoluene and 4,2',6,6'-trinitro,2,4'azoxytoluene.

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SECTION 1

INTRODUCTION

Nitro-aromatics: 2,4,6- trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT) and hexahydro-1,3,5- trinitro- triazine (RDX) are the major constituents of munitions production wastewaters discharged from explosive manufacturing units and munitions load, assembly and pack operations. The explosive TNT constitutes a significant component of a widespread munitions contamination problem which exists at many current and former U.S. Department of Defense (DOD) and U.S. Department of Energy (DOE) facilities. There are over 1200 sites with explosive contamination (Tri-service panel, 1992). At many of these sites, an explosive contamination problem has been found in the ground water. TNT is the most common contaminant found in both the soil and water samples (Jenkins and Walsh, 1993). Most process water found at the contaminated sites is pinkwater that was generated by demilitarization operations that were conducted in the 1970s. 2,4-dinitrotoluene and 2,6-dinitrotoluene are the products of incomplete nitration of toluene during the synthesis of TNT and hence find their way to the munitions wastewaters. DNT has also been frequently found at munitions contaminated sites. Both TNT and DNT are listed as priority pollutants by the USEPA because of their toxicological hazards. Redwater is classified by the USEPA as a RCRA regulated hazardous waste because of its reactivity. The LD₅₀ value of DNT in rats is 268 mg/kg (Sax and Lewis, 1989). From a toxicological standpoint, the identification of the products from the transformation of DNT and for that matter for any nitroaromatic compound is essential as the products may turn out to be more hazardous.

Besides TNT and DNT, the wastewaters and contaminated sites also contain DNT sulfonated compounds because sodium sulfite is added to react with unsymmetric TNTs. These compounds are generally responsible for the characteristic red color of the munition wastewaters. RDX is also commonly found in the waters and contaminated sites, because TNT is often used in binary mixtures with RDX.

Trinitrotoluene can have three structural isomers: 2,3,5 TNT, 2,4,6 TNT and 2,4,5 TNT. The symmetrical 2,4,6 Trinitrotoluene is the most commonly found form of the three and henceforth in this report the acronym TNT will be used to refer to 2,4,6 - trinitrotoluene only. TNT is still the most widely used military explosive because of its low melting point (80.1° C), stability, low sensitivity to impact, and relatively safe methods of manufacture. TNT has been classified as a high explosive (Kline, 1990) and used as a military explosive in bombs and grenades, generally in binary mixtures with a primary explosive to trigger the main explosion. It is also used as an industrial explosive for deep water and underwater blasting. TNT is prepared by the nitration of toluene with a mixture of nitric acid and sulfuric acid (Fisher and Taylor, 1983). It is released into the waste stream during manufacturing, loading, assembling and packing operations.

Dinitrotoluene (DNT) has six isomers. The 2,4- and 2,6- isomers are the most important because they are the greatest quantities produced anthropogenically (Beard et al., 1981).

DNT is prepared by the nitration of toluene and nitrotoluene in the presence of nitric and sulfuric acids. It is also the major impurity in the production of trinitrotoluene (TNT), due to a partial nitration of the nitrotoluenes. DNT is an important impurity since it comprises nearly one percent of the total TNT produced (Ryon et al., 1984). One of the major uses of DNT is as an intermediate in the manufacture of toluene diisocyanate, which is then used in the production of polyurethane foams. Another major use of DNT is as an ingredient in military and commercial explosives; the purified form of 2,4-DNT is used in smokeless powders (Bausum et al., 1992).

Hexahydro- 1,3,5- trinitro- 1,3,5- triazine (RDX), or Cyclonite as it is commonly referred to, is an explosive used extensively as a propellant for propelling artillery shells and in projectiles. It is so used because it offers higher energy, higher density and lower flame temperatures. It is often used in binary mixtures with TNT. It finds its way into the munition wastewaters during manufacturing and blending operations.

SECTION 2

OBJECTIVES

The objective of this research is to study the degradation kinetics of nitroaromatics: TNT, DNT and RDX in a batch reactor and to evaluate the effect of various physical and chemical parameters on the electrochemical reduction of these compounds. The final goal is to optimize the degradation conditions, find the major intermediates and products and propose an efficient electrochemical system for the treatment of these nitroaromatics in munition redwaters. For this, the following tasks have been performed:

Evaluation of the effect of applied current, stir rate (which in turn varies the fluid velocity inside the reactor), dissolved oxygen, and the pH of the solution using glassy carbon rod as the cathode.

Identification of the products and stable intermediates to elucidate the reaction pathways involved in the degradation of TNT.

Proposal of a theoretical explanation of the observed kinetic results and identification of the mass transfer limitations encountered in the system. Also, the explanation of the reasons for the observed effects because of the variations in different operational parameters.

An attempt to overcome the mass transfer limitations by changing the hydrodynamics and design of an electrochemical reactor to carry out the degradation of nitroaromatics.

4

SECTION 3

BACKGROUND AND LITERATURE REVIEW

3.1 SIGNIFICANCE OF THE RESEARCH

As per the OSHA assessment of LD₅₀, both TNT and DNT have been classified as "Slightly Toxic" to humans. TNT has been investigated to be toxic to a number of organisms and aquatic life (Burrows, 1989; Ney, 1974). TNT has been established to be mutagenic to humans (Kaplan, 1982). Additionally, TNT can be adsorbed through skin and can cause severe cardiovascular/ liver injuries. Both TNT and DNT have been listed as priority pollutant by the USEPA (Keither and Telliard, 1979). Moreover, TNT and DNT containing redwaters have been classified as a RCRA regulated hazardous waste (K047) based on the reactivity. RDX has been shown to be acutely and chronically toxic to fish (Burton, 1992). Chronic toxicity of RDX has also been observed in some species of invertebrates (Peters, 1991). RDX has also been shown to be toxic to some species of Algae (Burton, 1993). The USEPA has set a final acute value of 5.18 mg/L for RDX.

As can be seen from the previous discussion, it is important to degrade these nitroaromatics and also make sure that the end products are not hazardous. At present these nitroaromatics are treated by incineration or by granular activated carbon (GAC) adsorption. However, these techniques are not the most efficient ones and also pose environmental problems. Hence, active research is being carried out in finding out

efficient biological or advanced chemical methods of degradation. It has been recently shown that electrochemically activated biofilms are more effective in denitrification (Sakakibara et al., 1994) and dechlorination (Norton et al.,1996) than more traditional techniques. In the denitrification experiment, hydrogen gas is formed on the electrode, which subsequently diffuses into the biofilm and helps in the denitrification process in the biofilm by acting as an electron donor. These compounds have been found to react vigorously with reducing agents. DNT can be reduced to DAT by catalytic hydrogenation (Janssen et.al , 1990) and electrochemical reduction of DNT has been found to be an effective means of synthesizing DAT (Lessard et.al, 1990). Hence, it is worth investigating this new technique of reducing the aforementioned nitroaromatics.

3.2 USE OF ELECTROCHEMICAL METHODS

Although electrochemistry is a well-developed science for applications like metal-plating and synthetic chemistry, its use in water/wastewater industry has been almost nonexistent. Significant interest has been generated recently in researching this method as a part of advanced reduction/oxidation technologies for application in degradation industry. It is believed that electrochemical methods can be used in this context for any of the following reasons:

- to modify chemical structure of a hazardous compound to make it more biodegradable.
- to partially destroy a hazardous compound to decrease the overall toxicity.
- to completely oxidize/reduce the hazardous compound.

Electrochemical methods do offer certain advantages as compared to other conventional technologies in the following ways:

- They are more efficient than traditional biological methods in terms of the degradation kinetics. The degradation by electrochemical methods is much faster.
- The system is more resistant to sudden shocks, such as a sudden change in concentration or temperature in the inlet stream. These shocks might kill the microorganisms in a biological system. Selecting electrochemical systems can also aid in excluding pretreatment which is usually required in biological systems.
- The electrochemical system is typically much more compact and easier to control and monitor.

7

3.3 DEGRADATION PATHWAYS

3.3.1 Biological Pathways

There can be two main biological transformations - oxidation and reduction. Oxidation occurs when oxygen is the reactant and oxygenase or peroxidase enzymes mediate the cleavage of the aromatic ring. Reduction is the more common mechanism and takes place when the nitroaromatic compound is reduced to arylamines by a mechanism of hydrolytic deamination, acetylation, reductive deamination and cyclization.

It was found (Schackmann, 1991; Parrish, 1997) that a *Pseudomonas* species degraded both DNT and TNT aerobically with supplemental glucose as a carbon source. Reduction of the nitro groups took place only at the para positions and proceeded through the hydroxylamino-nitrotoluene to the amino-nitrotoluene. McCormick et al. (1978) identified the biotransformation products during the conversion of DNT to 2,4diaminotoluene (DAT). Haidour et al. (1996) observed 2-hydroxylamino-4,6dinitrotoluene, 4-hydroxylamino-2,6-dinitrotoluene, 4-amino-2,6-dinitrotoluene, 2amino-4,6-dinitrotoluene, and 2,4-diamino-nitrotoluene as the products of degradation of TNT with *Pseudomonas* sp. Boopathy et al. (1993) reported the anaerobic degradation of TNT under different electron accepting conditions by soil bacterial consortium. McGrath (1995) proposed the pathway shown in Figure 3.1 for the in-situ degradation of TNT. Hughes et al. (1998) demonstrated the ability of *Clostridium acetobutylicum* to reduce TNT to 2,4-dihydroxylamino-6-nitrotoluene and then to phenolic products via the Bamberger rearrangement. The transformation pathway is shown in Figure 3.2. The white rot fungus *Phanerochaete chrysosporium* was found to degrade ring labeled ¹⁴ C - 2,4,6-trinitrotoluene sorbed to soils (Fernando, 1990).



Fig. 3.1: In situ degradation pathways of TNT (McGrath, 1995; Kaplan, 1983)



Fig. 3.2: Pathway of TNT transformation observed in *C. acetobutylicum* crude cell extracts. (Hughes et. al, 1998)

A fungi *Mucrosporium* aerobically degraded DNT (McCormick et al., 1978). The transformation pathway is shown in Figure 3.3. The products in parenthesis are the hypothetical intermediates: nitroso-nitrotoluene and hydroxylamino-nitrotoluene. Liu et al. (1984) successfully identified the nitroso compounds. Spanggord et al. (1991) showed the ability to completely mineralize DNT by an oxidative pathway with Pseudomonas species using the DNT as the sole carbon source. Dioxygenase was responsible for the nitro group reduction and its subsequent release as nitrite.



Fig. 3.3 Reaction Pathway for the Biotransformation of DNT to DAT (McCormick et al., 1978)

Valli et al. (1992) was able to degrade DNT by the lignin-degrading fungus *Phanerochaete chrysosporium*. This fungus contained two peroxidases which are responsible for the complete mineralization of DNT to CO_2 in nitrogen-limiting cultures. The treatment of DNT using a two stage system has also been shown to completely mineralize DNT (Berchtold et al., 1995). The first stage was a fluidized bed anaerobic granular activated carbon reactor. The granulated activated carbon provided a good surface for the biomass to grow, while the anaerobic environment was conducive for the conversion of DNT to DAT. The formed DAT was subsequently degraded in the second stage, the aerobic activated sludge reactor, to undetectable levels.

Biotransformation of RDX has been observed by a number of researchers. Soli (1973) reported the complete disappearance of RDX in a mixed culture of photosynthetic bacteria. McCormick et al. (1981) observed the complete degradation of RDX by anaerobic sewage sludge. Young et al. (1997) also found a bacterial consortium in horse manure capable of degrading RDX at the rate of 0.032 L/gram cells per hour. Most of the research in the biological degradation of RDX has been carried out under anaerobic conditions. However, Binks et al. (1995) reported that *Stenotrophomonas maltophilia* degraded RDX aerobically.

Kitts et al. (1994) isolated three different genera of bacteria, which were able to degrade RDX. The most effective degrader of these three isolates was identified as *Morganella morganii*. One pathway for the biotransformation of RDX is a stepwise reduction of each

of RDX's three nitro groups to form nitroso groups (McCormick et al., 1981; Kitts et al., 1994) as shown in Figure 3.4.



Products of Ring Cleavage



(McCormick et al., 1981; Kitts et al. 1994).

McCormick et al. (1981) observed formaldehyde as a final product of the complete cleavage of the ring. Hydroxylamines were believed to be intermediates, but were not detected by any of the researchers.

3.3.2 Chemical Pathways

The most common present method of transformation of the nitroaromatics is incineration. However, while incineration has been demonstrated as an effective technology, issues such as safety concerns, noise, air emissions, costs, regulatory requirements, etc., has motivated research in alternative treatment technologies. The adsorption of TNT and DNT (Ho and Daw., 1988l; Wujcik et al., 1992) on activated carbon was one of the most common treatment technologies used by the military ammunition plants. This technology is effective at removing a wide variety of explosive contaminants from water, but is nondestructive and expensive to operate (Tri-service panel, 1992; Sisk, 1993). Moreover, after the carbon is exhausted, it has to be disposed off into hazardous waste disposal sites or incinerated. The disposal of the used carbon is a very costly proposition.

There has been extensive research on the photochemical degradation TNT. It has been considered both as a primary treatment technology and as a pretreatment to bioremediation. TNT strongly absorbs UV radiation between 200 and 280 nm. Exposure of TNT to sunlight or near UV radiation results in the rapid conversion of TNT into a variety of aromatic photolysis products including the nitroamines and azoxy dimers,

which are also found in biodegradation (Burlinson et al, 1973; Kaplan et al., 1975; Andrews and Osmon, 1975; Spanggord et al., 1983).

It was demonstrated by Schmelling and Gray (1995) that TiO_2 photocatalysis using near UV radiation may be highly effective in the remediation of TNT contaminated waters. Photocatalytic transformation of TNT was shown to include both oxidative and reductive steps. Trinitrobenzoic acid, trinitrobenzene, and trinitrophenol were observed as oxidative intermediate species and 3,5-dinitroaniline was identified as a stable reduction product. These two pathways are shown in Figures 3.5 and 3.6.



Fig. 3.5: Reaction pathway for the initial oxidative transformation of TNT under photocatalytic conditions (Schmelling and Gray, 1995)



Fig. 3.6: Photochemical transformation observed during the reductive degradation of TNT (Schmelling, Gray, and Kamat, 1996).

Other technologies which have been investigated in application to TNT remediation are: clay/resin adsorption, ionizing radiation, supercritical oxidation, UV- ozone and wet-air oxidation. Wet air oxidation was demonstrated to be successful in degrading nitroaromatics in red waters (Hao et al., 1993).

The other major chemical method, which is widely reported in the scientific literature, is the catalytic hydrogenation of DNT over a Pd/C catalyst (Dovell et al., 1970; Bird and Thompson, 1980; Kut et al., 1987; Janssen et al., 1990a, b; Benedetti et al., 1991; Suh et al.,1992; Neri et al., 1994). Janssen et al.(1990) proposed two parallel reaction pathways for the formation of DAT from DNT. The reaction mechanism is shown in Figure 3.7a. The reaction was carried out between 300-370 K and a pressure of 4-6 MPa. There were three stable intermediates that were formed: 4-hydroxylamino-2-nitrotoluene, 4-amino-2nitrotoluene and 2-amino-4-nitrotoluene. Very low concentrations of 4-hydroxylamino-2nitrotoluene ware detected, suggesting that the nitro group in the ortho position was almost entirely converted to the amino group. Neri et al. (1995) carried out the catalytic hydrogenation of DNT over Pd/C in the temperature range between 278 and 323 K and at a pressure of 0.1 MPa. The 4-hydroxyamino-2-nitrotoluene (4HA2NT) was found to be the main reaction intermediate. The amino-nitro compounds: 4-amino-2-nitrotoluene (4A2NT), and 2-amino-4-nitrotoluene (2A4NT) were the other compounds formed during the hydrogenation of DNT. Neri et al. (1995) have proposed three different mechanisms for the formation of DAT, these are shown in Figures 3.7a, 3.7b, and 3.7c.



Fig. 3.7 (a) A possible mechanism for the catalytic hydrogenation of DNT to DAT (Neri et al., 1995)



Fig. 3.7 (b) A possible Mechanism for the catalytic hydrogenation of DNT to DAT (Neri et al.,1995)



Fig. 3.7 (c) A possible mechanism for the catalytic hydrogenation of DNT to DAT (Neri et al.,1995)

3.3.3 ELECTROCHEMICAL PATHWAYS

The relative recalcitrance of these nitroaromatics to complete degradation by biological methods has promulgated active research in the advanced oxidation/reduction techniques. Electrochemical methods due to aforementioned reasons have attracted a great deal of attention in recent years. Although the degradation by electrochemical methods, of many different toxic chemicals like chlorophenols and chloroanilines has been investigated, there has been no reported work on the electrochemical degradation of the nitroaromatics.

Electrochemical reduction has been reported to be used for the synthesis of DAT from DNT. Experiments were carried out under conditions that maximized the yield of DAT. The electrochemical reduction of dinitrotoluene has been carried out in protic media under acidic, neutral and basic conditions using a silver electrode (Fine et al., 1983). The process was also carried out by indirect electrolysis in strongly acidic medium on a lead cathode using the Ti³⁺/Ti⁴⁺ redox couple as a mediating system (Udupa, 1988). Lessard et al. (1990) carried out the synthesis of DAT by the electroreduction of DNT in a basic solution of pH 13. The initial concentration of DNT was 0.01 M which was made possible by using a methanolic solution with a methanol:water ratio of 93:7 (by weight). Electrodes consisted of particles of Devarda copper or Raney nickel embedded in a nickel matrix.

The possible mechanism proposed by Lessard et al. (1990) is the reduction of the nitro group to the hydroxylamino group by a combination of electronation-protonation (EP) and electrocatalytic hydrogenation (ECH). This is followed by the reduction of the hydroxylamino group to the amino group, an ECH mechanism.

Thus the overall conversion of DNT to DAT may occur by an ECH mechanism summarized by equations (3.1-3.4) where M is the surface of the electrode, M(H) represents chemisorbed hydrogen generated at the surface of the electrode by the reduction of water, and M(DNT) and M(DAT) are the adsorbed starting material and product, respectively.

$$M + H_2O + e^- \rightarrow M(H) + OH^-$$
(3.1)

$$M + DNT \rightarrow M(DNT)$$
(3.2)

$$M(DNT) + 12 M(H) \rightarrow M(DAT) + 4H_2O$$
(3.3)

$$M(DAT) \rightarrow M + DAT \tag{3.4}$$

Electrochemical reduction of nitrobenzene is an extensively studied process and the resulting mechanistic pathways may be regarded typical for nitroaromatic compounds. The first reduction stage is the formation of nitrosobenzene, followed by β -phenylhydroxylamine (Haber, 1898), and finally aniline (Elbs, 1891).

$C_6H_5 \text{ NO}_2 + 2H \rightarrow C_6H_5 \text{ NO} + 2H \rightarrow C_6H_5 \text{ NHOH} + 2H \rightarrow C_6H_5 \text{NH}_2$

Since the nitrosobenzene is a good depolarizer, it is rapidly reduced to β -phenylhydroxylamine, in fact the process is a reversible one (Conant, 1923), and the hydroxylamine derivative is then either further reduced to aniline or it undergoes coupling reactions to form dimers.
SECTION 4

MATERIALS AND METHODS

4.1 MATERIALS

2,4,6-trinitrotoluene (TNT) was obtained from Chem Service (West Chester, PA) containing 30 weight % water and was used as such by making appropriate adjustments while weighing the TNT to be added into the reactor. Dinitrotoluene (DNT) was obtained from Aldrich Chemical Co. (Milwaukee, WI) at 97% purity and was used as received. RDX was obtained from Rock Island Arsenal, Rock Island, Champaign, IL, at 99% purity and was used as received. Sodium phosphate from Aldrich Chemical Co. was used as the buffer to maintain the desired pH. Anhydrous sodium sulfate from Fisher (Pittsburgh, PA) was added to the reactor for maintaining a constant ionic strength.

A Nafion membrane #117 from Solution Technology/C.G.Processing (Rockland, DE) was used to separate the anode and the cathode and allow the transfer of ions only and to prevent the transfer of any of the organic compounds being degraded or being formed. The cathode used was a glassy carbon (Sigradur[®] G) rod with a diameter of 7 mm and a height of 150 mm from SGL Carbon Corporation (St. Marys, PA). The properties of the glassy carbon electrode are shown in Table 4.1. A six-inch long 18G platinum wire (Fisher Scientific) was used as the anode. A Honeywell UDC 3000 Universal Digital

Controller was used as a constant current source. A Fisher Scientific Thermix® Stirrer Model 120S was used for all experiments along with a two-inch Teflon-coated stir bar. For the recycle flow experiments a ND 300 TT 18 type pump supplied by KNF FLODQS was used with an output rating of 18W, and a frequency of 60Hz. All experiments were carried out in a two-liter solution of the reaction mixture. For all experiments, 18 MW-cm resistivity water was used (distilled and deionized).

For the identification and quantification of the products and intermediates following chemicals were purchased:

2,4-diaminotoluene (DAT) was purchased from Aldrich (Milwaukee, WI) and was used as such. DAT and DNT were further used for the synthesis of other products and intermediates for the DNT experiments.

For the identification of TNT products and intermediates following chemicals were purchased from AccuStandard Inc. (New Haven, CT).

2,4-Diamino-6-nitrotoluene, obtained at concentration of 0.1mg/ml in Acetonitrile.

2,6-Diamino-4-nitrotoluene, obtained at concentration of 0.1mg/ml in Acetonitrile.

2,2',6,6'-tetranitro,4,4'-azoxytoluene, obtained at concentration of 0.1mg/ml in Acetonitrile: Methanol (1:1).

4,4',6,6'-tetranitro,2,2'-azoxytoluene, obtained at concentration of 0.1mg/ml in Acetonitrile: Methanol (1:1).

4-amino-2,6-dinitrotoluene, obtained at 1mg/ml in Acetonitrile: Methanol (1:1).2-amino,4,6-dinitrotoluene, obtained at 1mg/ml in Acetonitrile: Methanol (1:1).

Table 4.1

Physical Properties of the Glassy Carbon Cathode

| Property | Metric Units |
|------------------------|------------------------------------|
| Maximum Grain Size | - |
| Apparent Density | 1.42 g/cm^3 |
| Total Porosity | 0 % |
| Electrical Resistivity | $4.4 \times 10^3 \mu$ ohm-cm |
| Flexural Strength | $2.6 \times 10^5 \text{ kg/ cm}^2$ |
| Compressive Strength | $4.8 \times 10^5 \text{ kg/ cm}^2$ |
| Tensile Strength | - |
| Modules of Elasticity | 35000 kg/ mm ² |
| Ash | 0 % |

4.2 ELECTROCHEMICAL DEGRADATION EXPERIMENTS

All experiments were conducted at room temperature and carried out in a 2.5liter glass reactor. The nitroaromatic was added in the desired amount to 1liter water and was stirred continuously overnight to ensure complete dissolution. 900ml water was added at the start of the experiment along with 100ml of 0.4M sodium phosphate (dibasic) solution. Sodium phosphate was used as a buffer to maintain the desired pH. Furthermore, anhydrous sodium sulfate was added at 36 g/L to increase the ionic strength and hence conductivity. The pH was monitored throughout the experiments and a few drops of a 0.1M sulfuric acid solution were added regularly to maintain the solution at the desired pH. An Oakton[®] WD-35615-Series pH/mV/Temperature meter was used as the pH probe. A summary of reactor conditions is shown in Table 4.2. The reactor and other glassware were thoroughly washed - first with soap water and then rinsed with distilled and deionized water- prior to the beginning of each experiment.

2,4,6-Trinitrotoluene (TNT) was added to the reactor to yield an initial concentration of 50 ppm. Hexahydro-1,3,5– trinitro- 1,3,5 -triazine (RDX) was added to yield an initial concentration of 25ppm. The same individual concentrations were maintained in experiments involving the combination of the above two compounds. The initial concentration of 2,4-dinitrotoluene (DNT) used was 50mg/l. Ethanol content varying from 150ppm to 450ppm was used, with most experiments carried out at ethanol concentration of 300ppm.

A diagram of the reactor is shown in Figure 4.1.

Table 4.2

A Summary of Experimental Conditions

| Serial | Parameters | Values |
|--------|-------------------------------------|---------------------------------------|
| .10 | | |
| 1 | Reactor Volume | 2000 ml |
| 2 | Salt Concentration | 36 g/l |
| 3 | Initial Nitroaromatic Concentration | 25 - 50ppm |
| 4 | PH | 7.0-9.0 |
| 5 | Applied Current | 23mA - 72mA |
| 6 | Stir rate | 630, 2040 rpm |
| 7 | Electrodes | Glassy Carbon |
| | | (Sigradur [®] G) |
| 8 | Surface area | 67.5 cm ² (Glassy Carbon). |
| 9 | Porosity | 0 |
| 10 | Dissolved Oxygen | 0.2 mg/l (Deoxygenated) |
| | | 8.4 mg/l (Open System) |

4.2.1 Oxygenated experiments with Glassy-Carbon as the Cathode - The effect of the variation in current

Experiments were carried out at five different current settings, namely 23, 34, 45, 53 and 65mA. The Honeywell UDC is capable of providing a constant current input to the electrodes. The voltage may change with a change in the ionic strength of the reaction mixture in the cathode compartment. The resistance of the aqueous solution for a current higher than 65mA was too high so we decided on 65mA is the upper limit for the current range in most of the experiments. The experimental setup was as shown in Figure 4.1.

4.2.2 Oxygenated experiments with Glassy-Carbon as the Cathode - The effect of stirring rate

Experiments were carried out at two different speed settings of the stirrer for a given applied current. The stir rate in turn effects the velocity, the diffusion layer thickness and the mixing rate in the reactor. Stir rates of 630 rpm and 2040 rpm were used. These stir rates correspond to calibration points 3 and 6 labeled on the stirrer. The rotations per minute were calculated by recording the rotation of the stir bar with a video camera (Sony TR-81, Sony Corp.) and then by replaying the video in slow motion and counting the rotation in each frame. The plot of rotational speeds v/s the stirrer settings is shown in Figure 4.2.



Figure 4.1. Setup for oxygenated semi-batch reactor experiments using glassy carbon cathode.



Figure 4.2. Calibration Curve for stir-rate settings.

4.2.3 Oxygenated experiments with Glassy-Carbon as the Cathode - The effect of pH of the cathode solution.

pH was expected to be a sensitive parameter in the overall degradation mechanism since the availability of protons and hence the concentration of the reactive hydrogen radicals will be determined by the pH of the solution. The pH was varied by adding to the buffered solution - either sulfuric acid or sodium hydroxide as required. Experiments were done with pH settings between 7.0 & 9.0.

4.2.4 De-oxygenated experiments with Glassy-Carbon as the Cathode

These experiments had glassy carbon as the cathode, and the reactor was closed to the atmosphere throughout the experiments. The reactor was degassed by spurging with nitrogen gas for twelve hours. These experiments were carried out not for kinetic purposes, but to identify the products and intermediates formed. Experiments were carried out using only TNT as the nitroaromatic. The initial TNT concentration was kept at 50mg/l, using a pH of 8.0 and with the same salt concentration of 36g/l. The experimental setup is shown in Figure 4.3.

4.2.5 Oxygenated experiments with Glassy-Carbon Cathode - using recycle flow.

Recycle flow experiments were carried out to overcome the mass transfer limitations encountered in the system. The cathode solution was withdrawn from the bottom of the reactor with a pump and allowed to trickle down over the cathode surface, so as to disturb the diffusion layer. Only TNT was used and the rest of the parameters were kept same. The recycle flow setup is shown in Figure 4.4.

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Figure 4.3. Experimental setup for deoxygenated experiments



Figure 4.4. Experimental setup for recycled flow experiments

4.3 ANALYTICAL TECHNIQUES

The length of time for one experiment varied between 6 to 12 hours. Six to eight samples were taken at regular intervals in each experiment. When the samples were taken, the pH and voltage were also monitored. TNT & DNT were analyzed by gas chromatography. Samples for the gas chromatography (GC) were withdrawn from the reactor with a 2.5mL pipette. The samples were then extracted into 0.5mL of dichloromethane with vigorous shaking for about 2 minutes. An internal standard of Quinoline (25ppm) was used for analysis precision. The GC instrument used in the analysis is 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 (80psi).

RDX was analyzed by a Shimadzu UV-1201 spectrophotometer. 10ml samples of the solution in the cathode compartment were withdrawn at the predetermined intervals and measured by UV - absorption using the spectrophotometer at a wavelength of 240nm. Minimal UV absorption by other components of the solution at this wavelength has been ascertained.

The pseudo first order rate constants were obtained by plotting the natural log of the nitroaromatic concentration in ppm versus time in minutes. Only the kinetic data with an R^2 value more than 0.95 are reported.

In batch reactor the rate equation can be written as:

rate of reaction = k [C] [H^+]ⁿ

where,

k, is the reaction rate constant,

[C], is the concentration of the contaminant,

[H⁺], is the concentration of protons, causing the reduction of the compound,

and n depends on the number of steps of reduction in the multi-step reduction reactions.

For semi-batch reactor, pH is maintained at constant value throughout the process , or $[H^+]$ is constant ,

thus,

rate =
$$K [C]$$
;

where,

$$K = k[H^+]^n$$

This makes it a pseudo first-order reaction,

Or,

$$[C] = C_0 e^{-Kt}$$

or

$$\ln [C] = \ln [C_0] - Kt$$

The ln[C] is plotted v/s time and the slope of the curve (K) gives the degradation rate constant. The slope attained would be the same if the area-ratio as obtained from the GC results is plotted instead of the concentration, [c]. A sample graph is shown in Figure 4.5. All experiments were performed under semi-batch conditions.



Figure 4.5. Sample graph for Electrochemical degradation of TNT. Current: 34mA; Stir rate: Fast (2040rpm); pH: 8.0

The GC analysis allowed the monitoring of the degradation of DNT and the formation of intermediates and products. The GC-MS analysis allowed the identification of stable intermediates and final products. The GC-MS instrument is an HP 5890 GC and MS 5970, a selective mass ion detector, 30 m x 0.25 mm i.d. fused silica capillary column and 0.25 mm film thickness (J & W Scientific, DB-5), and a carrier gas of helium (50psi).

The intermediates and end products of degradation of TNT were found to be thermally unstable. Hence no distinct peaks are observed in either the GC or the GC-MS for these products. To identify and quantify these intermediates and products, HPLC with the following specifications was used: A HP 1050 system using a C-18 column, with a Quaternary pump and a UV Diode Array Detector (DAD). The method used was the EPA 8330 method. The HPLC-18 column was eluted with 5.4:4.6 acetonitrile/ water at a flow rate of 1.5 mL/min. An internal library is constructed by analyzing pure compounds. Thereafter, the compounds in the reactor solution were identified by matching their UV absorbance-spectra and the retention time with those of the pure compounds. The pure intermediates and products were either purchased, if available commercially, or otherwise synthesized.

4.4 IDENTIFICATION OF THE INTERMEDIATES AND PRODUCTS AND MASS BALANCE STUDIES

Identification of products and intermediates helps in the determination of reaction pathway. Identification of the nature of the products can also help to assess if they are harmful to the environment and if they pose bigger hazard than the starting compounds. The quantification of the products brought out by the mass balance approach can help to identify the exact nature of the effluent and this can help in selecting further treatment methodologies. Moreover, such an approach can always help in maintaining greater control over the performance of the system and is also very useful while mathematically modeling the system.

Most of the DNT intermediates and products were identified and quantified using the GC-MS for identification and GC for quantification. The specifications of the instruments are mentioned in the previous section. Samples were taken both from the supernatant solution as well as from the settled solids.

The supernatant solution samples for gas chromatography-mass spectrometry (GC-MS) for product identification were withdrawn from the reactor once or twice: a larger 50mL sample was taken and extracted into benzene, dichloromethane or diethyl ether. At the end of each experiment, 250mL volume was saved for further extraction to identify the final products. All samples were kept at 40° C until analyzed.

The residue was collected after turning off the system at the required predetermined time and then filtering off using a HA type 0.45μ m filter paper. The residue was dissolved in acetone or acetonitrile and then analyzed over GC, GC-MS or HPLC.

Previous researchers involved in this project (Devakumaran, 1998, and Jolas, 1996) had carried out complete identification and quantification of the products and intermediates, while studying the electrochemical reduction of DNT. Consequently, for experiments involving reduction of DNT (with ethanol) in this work, only the identification of the products and intermediates were carried out. Mass balance was not worked out for DNT degradation. Many of the products and intermediates were synthesized as explained in section 4.4.1.

For TNT experiments complete identification as well as quantification (mass balance) was carried out. Again the supernatant and residue was analyzed. Since almost all of the products and intermediates of TNT were found to be thermally unstable - all work was carried out on HPLC with the previously mentioned specifications. The mass balance was worked out on molar basis. Many of the intermediates and products of TNT were commercially available (AccuStandard Inc., CT). An effort was made to synthesize the compounds that were not available commercially. The details of the synthesis are given in section 4.4.2.

4.4.1 Synthesis of products and intermediates of 2,4-dinitrotoluene

The synthesis of the different possible products and intermediates of DNT are detailed below:

Synthesis of 4,4'-dinitro-2,2'-azoxytoluene (McCormick et al., 1978):

- 1.52 g (10 mmol) of 2-amino-4-nitrotoluene (Aldrich Chem. Co.) was added to 75 ml of dichloromethane.
- 4.1 g (20 mmol) of *m*-chloroperoxybenzoic acid (Aldrich Chem. Co.) was added to the above solution and allowed to stand overnight.
- The precipitate of chlorobenzoic acid was removed by filtration and the filtrate extracted with 5% aqueous sodium bicarbonate solution.
- The dichloromethane was allowed to evaporate and the resulting precipitate was recrystallized with 95% ethanol.
- A slightly yellow solid of the dimer was collected

The above procedure is repeated with 4-amino-2-nitrotoluene as the starting compound to produce the other possible isomer.

Synthesis of Caroís acid:

- 145 g (0.64 moles) of ammonium persulfate was added to 54 ml of cold, concentrated H_2SO_4
- The mixture was allowed to stand for about an hour and poured into 355 g of crushed ice.

Synthesis of 2-nitro, 4-nitroso Toluene:

• A cold suspension of 3.5 g (0.23 mole) of 2-nitro,4-amino Toluene in 6 ml of sulfuric acid and 1 ml of water is mixed in an ice bath for 1 hour.

Caroís acid is added to the above and stirred for 17 hours. The yellow precipitate was recrystallized with acetone.

4.4.2 Synthesis of products and intermediates of 2,4,6 -trinitrotoluene

Synthesis of 2,2',6,6'-tetranitro,4,4'-azoxytoluene (Sandler and Karo, 1971):

- A vigorously stirred solution of 0.062 mole of 2,4,6-trinitrotoluene was prepared in 75ml of acetic acid and 10ml of acetic anhydride.
- The temperature was maintained throughout between 30°C and 35°C, by adjusting the addition rate of zinc dust and doing the heating or cooling as needed.
- 12.0gm of zinc dust is added over a 1.5 hr. period.
- The pasty reaction mixture is then diluted with 1liter of ice water and solid is separated by filtration.
- The solid product is then treated for 15 min. with 300ml of a 10% aqueous sodium carbonate solution at 40°C.
- It is filtered and pressed dry. The solid is then dissolved in warm ethanol.

A solid crystallizes out on drying. However, when the solid was analyzed on GC-MS no prominent peak was observed.

Other chemicals: 4-amino-2,6-dinitrotoluene; 2-amino,4,6-dinitrotoluene; 2,2',6,6'trinitro,4,4'-azoxytoluene, and 4,4',6,6'-trinitro,2,2'-azoxytoluene, were obtained from AccuStandard Inc. (New Haven, CT).

4.5 ADSORPTION STUDIES ON GLASSY CARBON CATHODE

Adsorption studies were conducted on glassy carbon cathode as a part of control experiment to confirm the electrochemical degradation of the nitroaromatics. Experiments were performed with an initial TNT concentration of 50ppm. The experiment was setup as an oxygenated experiment, except that no current was passed through the electrodes. The salt concentration was 36g/l.

Samples were taken at regular intervals, in the same manner as taken for the other experiments and analyzed on GC for the TNT concentration.

SECTION 5

RESULTS AND DISCUSSION

5.1 GENERAL

To study the kinetics of electrochemical degradation, the first order rate constants were studied. Three kinetic parameters - the current, stirring rate and the pH - were studied in order to find the most optimum conditions on which to operate the electrochemical reactor to be designed in the next stage. The role of stirring rate, current, and pH were investigated for the three nitroaromatics separately, and then in combination with each other to simulate the pinkwater more closely and to find out if there is any inhibitory effect on degradation rates due to the combination. Also the degradation rates under different conditions were studied with an aim of better understand the dynamics in the reactor.

Experiments that gave R^2 value less than 0.95 were discarded and repeated. Some of the experiments with similar settings were carried out in replicate to find the variance in the data. Variation in excess of 10% was not observed between two similar experiments.

5.2 PRELIMINARY AND CONTROL EXPERIMENTS

Initial experiments were carried out to

- Ascertain the degradation of the nitroaromatics by electrochemical means
- Establish credible control for the later experiments, and
- Identify the operational parameters that change during the degradation process.

In the first set of experiments, the viability of using electrochemical methods for the reduction of nitroaromatics was investigated. TNT was put in the electrochemical reactor and reduced under fully-batch conditions. The TNT concentration was seen to decrease from 50ppm to about 10ppm in about 6hrs. The reactor was operated at 65mA current at a pH of 8.0. The TNT concentration as a function of time is shown in Figure 5.1.

Next a control experiment was carried out keeping everything in the reactor as the same, but with no current applied to the electrodes. No decrease in the TNT concentration was observed, confirming the role of electrically produced electrons in the degradation process. The TNT concentration as a function of time observed in the control experiment is shown in Figure 5.2.

In another experiment the change in the pH of the cathode solution and the applied voltage was monitored for a reactor operated under fully-batch conditions. Unlike the other subsequent experiments, no sulfuric acid was added during the course of the experiment. While the pH of the cathode solution was monitored regularly, the pH of the anode



Figure 5.1. Disappearance of TNT as a function of time under batch conditions.

Figure 5.2. Adsorption experiment on glassy carbon cathode with TNT



solution could only be monitored at the end of the experiment. The starting pH at both the cathode and anode was 8.0. At the end of the experiment (at about 6hrs.) the pH stabilized at around 9.7 at the cathode and at 1.2 at the anode.

The increase in pH of the cathode solution confirmed that the "reduction" of the nitroaromatic species was going on. The following reactions could be inferred to be going on at the cathode and the anode.

Based on these preliminary results, the following reactions could be expected at cathode:

$$2\mathbf{H}^+ + 2\mathbf{e} \rightarrow 2\mathbf{H} \tag{1}$$

$$C_7H_5N_2O_4.NO_2 + 2H \rightarrow C_7H_5N_2O_4.NO + H_2O$$
 (2)

$$C_7H_5N_2O_4.NO + 2H \rightarrow C_7H_5N_2O_4.NHOH$$
 (3)

$$C_7H_5N_2O_4.NHOH + 2H \rightarrow C_7H_5N_2O_4.NH_2 + H_2O$$
(4)

$$2H \rightarrow H_2$$
 (5)

These reactions were later confirmed by the presence of above-mentioned compounds as intermediates and products in the TNT experiments. The consumption of Hydrogen radicals during the reduction of the nitroaromatic drives the reaction (1) towards the right side, causing a increase in the pH. The reaction (5), which entailed combination of two hydrogen radicals to produce hydrogen gas, was a side reaction causing a decrease in the efficiency of conversion.



Figure 5.3. Variation of pH of cathode solution v/s time in batch experiments.

Figure 5.4. Variation of the Voltage as a function of time in batch experiments.



The following reaction can be speculated at the anode:

$$2H_2O \rightarrow 4H^+ + 4e + O_2 \tag{6}$$

The production of the protons at the anode, caused a drop in pH in the anode solution. The oxygen bubbles can also be observed to be rising from the anode solution.

Furthermore, making an electron balance (or Hydrogen radical balance) in the system over a certain fixed time can give us an idea of the efficiency of the reduction process at cathode. The electron released at the cathode, is absorbed by the proton to form the hydrogen radical (reaction 1). The hydrogen radical can undergo reduction reactions (2,3,4) or combine with each other to form hydrogen gas. The ratio of the number of hydrogen radicals combining with the nitroaromatic to the number of those combining with each other can give the efficiency of the process.

A reactor operated at 65mA current for six hours produces

2

 $65 \times 10^{-3} \times 6 \times 3600 / 96500 = 0.014$ moles of electrons

If we assume all the nitro-groups in TNT undergo reduction to form amines, and also that all the TNT initially added (50ppm) gets completely reduced, then the number of electrons required would be

$$50 \times 10^{-5} \times 2 / 227 = .176 \times 6 \times 3 = 0.006$$
 moles e

Thus clearly the efficiency of the nitroaromatic reduction is very low, and the most dominant reaction is that involving the production of hydrogen gas (reaction 6).

5.3 ELECTROCHEMICAL DEGRADATION OF NITROAROMATICS

5.3.1 Electrochemical reduction of 2,4,6 - trinitrotoluene (TNT)

The rate constants for the reduction of TNT with glassy carbon cathode are shown in Table 5.1. The current was varied between 23 to 72mA. pH varied between 7.5 - 9.0. Two stir rate settings (630, and 2040rpm) were used. Initial TNT concentration in all the experiments was 50ppm.

The rate constants varied between 0.0026 to 0.0080 min⁻¹ (half-lives of 266 minutes to 87 minutes). The rate constants for different stir rates and pH are plotted as a function the current in Figure 5.5. As can be seen from the figure, the degradation rates increase with the initial increase in current, and flatten out at higher current values. This clearly shows that at higher current values, it is the mass-transfer limitations that are governing the degradation kinetics. The nitroaromatic at such high currents is not able to reach the cathode surface at the same rate as the production of electrons. As a result the efficiency of the nitroaromatic reduction would decrease and more hydrogen gas would be evolved instead. The mass-transfer rate at high currents thus effectively becomes the overall degradation rate. At lower currents, it is the intrinsic chemical reduction rate along with the mass-transfer that is governing the reaction process. A more elaborate explanation based on the diffusion layer theory is provided in section 5.4.

Table 5.1

Experimental Data for Glassy Carbon Cathode:

Degradation of TNT

| Current | Stir Rate | pH | Rate Constant |
|---------|-----------|-----|---------------|
| (mA) | (rpm) | | (\min^{-1}) |
| 23 | 630 | 8.0 | 0.0026 |
| 23 | 2040 | " | 0.0033 |
| 34 | 630 | | 0.0032 |
| 34 | 2040 | " | 0.0060 |
| 45 | 630 | " | 0.0047 |
| 45 | 2040 | " | 0.0059 |
| 53 | 630 | " | 0.0053 |
| 65 | 630 | | 0.0061 |
| 65 | 2040 | " | 0.0057 |
| 72 | 2040 | " | 0.0053 |
| 23 | 630 | 7.5 | 0.0040 |
| 34 | 630 | | 0.0045 |
| 45 | 630 | " | 0.0055 |
| 53 | 630 | " | 0.0059 |
| 65 | 630 | " | 0.0052 |
| 65 | 2040 | 9.0 | 0.0078 |
| 53 | 2040 | " | 0.008 |
| 23 | 2040 | " | 0.0035 |



Figure 5.5. Degradation rate constant v/s current for reduction of TNT

The degradation rate is seen to increase with the increase in stirring rate. The higher stirring tends to produce greater agitation or turbulence near the cathode surface. This in turn causes a decrease in the diffusion layer thickness (explained in section 5.4), allowing more rapid movement of the nitroaromatic towards the cathode surface. This caused an increase in the degradation rate.

pH was found to be a sensitive parameter in the overall degradation process. The degradation rates increased both, with the decrease in pH as well as with an increase in pH. Lower pH, increases the concentration of protons and hence can easily account for the higher rate constants, since the measured rate constants (K) are directly proportional to the concentration of protons (section 4.3)

 $K = k[H^+]^n$,which was done to obtain the pseudo-first order rate constants.

But the rates do not see an appreciable jump at the lower pH, as could be predicted by the above expression. This could be attributed to the further decrease in the efficiency. Higher concentration of protons also increases the bi-molecular conversion of protons to produce hydrogen gas. This leads to decrease in efficiency. At higher pH, the rate of this bi-molecular conversion would decrease, hence increasing the efficiency of the nitroaromatic reduction. This can account for the observed increase in rate constants at higher pH.

Table 5.2

Experimental Data for Glassy Carbon Cathode:

Degradation of RDX

| Current | Stir Rate | pН | Rate Constant |
|---------|-----------|-----|---------------|
| (mA) | (rpm) | | (\min^{-1}) |
| 23 | 630 | 8.0 | 0.0010 |
| 23 | 2040 | " | 0.0012 |
| 34 | 630 | " | 0.0018 |
| 34 | 2040 | " | 0.0020 |
| 45 | 630 | " | 0.0020 |
| 45 | 2040 | " | 0.0026 |
| 53 | 630 | " | 0.0018 |
| 53 | 2040 | " | 0.0030 |
| 65 | 630 | " | 0.0017 |
| 65 | 2040 | " | 0.0030 |

5.3.2 Electrochemical reduction of RDX

The degradation rate constants for the electrochemical reduction of hexahydro-1,3,5-trinitro-1,3

The degradation rates are plotted as a function of current in Figure 5.6. As for TNT, the rate constants increase initially with the increase in current, but flatten out at higher current values. The degradation rates were also larger at higher stir-rate settings.

5.3.3 Electrochemical reduction of 2,4-dinitroltoluene (DNT) with ethanol

Earlier researchers (Devakumaran, 1998, and Jolas, 1996), have done considerable work on the electrochemical reduction of 2,4-DNT. In the present work, the electrochemical degradation of DNT was investigated in the presence of ethanol. Ethanol is often present in typical DNT wastewater discharges from army munitions units. For the most of the experiments, ethanol was kept at 300mg/l, which is the typical concentration in the wastewater. The initial DNT concentration was 50ppm, and most experiments were performed at a pH of 8.0. The rate constants for the electrochemical reduction of DNT in the presence of ethanol are listed in Table 5.3.



Figure 5.6. Degradation rate constants for RDX as a function of current.

Table 5.3

Experimental Data for Glassy Carbon Cathode:

Degradation of DNT (with ethanol)

| Current | Stir Rate | pН | Ethanol | Rate Constant |
|---------|-----------|-----|---------|---------------|
| (mA) | (rpm) | | (mg/l) | (\min^{-1}) |
| 23 | 630 | 8.0 | 300 | 0.0026 |
| 34 | 630 | " | " | 0.0036 |
| 45 | 630 | " | " | 0.0050 |
| 45 | 2040 | " | " | 0.0052 |
| 53 | 630 | " | " | 0.0056 |
| 53 | 2040 | " | " | 0.0056 |
| 65 | 630 | " | " | 0.0060 |
| 65 | 2040 | " | " | 0.0061 |
| 65 | 630 | " | 450 | 0.0068 |
| 65 | 630 | " | 150 | 0.0060 |
| 65 | 630 | 7.0 | 300 | 0.0076 |

The degradation rate constants are plotted as a function of current in Figure 5.7. The presence of ethanol did not alter the rate constants significantly. The rate constants observed for the "DNT and ethanol" experiments were similar to those reported by Devakumaran and Jolas for "DNT alone" experiments. Again the degradation rates increased with the initial increase in current and flattened out at higher values. The degradation was faster for more vigorous mixing. The change in the ethanol content (varied between 150 to 450mg/l) did not have much effect on the degradation kinetics. However, the rate constants were higher at lower pH (7.0). This can be explained following the same reasoning as presented in the TNT sub-section. The rate constant varied between 0.0026 to 0.0076 min⁻¹ (half-lives varying between 267 minutes to 91 minutes).

5.3.4 Electrochemical reduction of TNT in a combined mixture of TNT and RDX

The pink-water discharged from the munitions manufacturing facilities has a combination of TNT and RDX in different proportions. Hence experiments were carried out by mixing both TNT and RDX in the reactor in order to simulate the pink waters more closely. 50ppm of TNT and 25ppm of RDX was added to the reactor. Currents were varied between 23mA to 65mA and two stir-rates were used. The pH for all the experiments was kept at 8.0. The degradation rate constants for TNT in the combined TNT and RDX experiments are shown in Table 5.4.



Figure 5.7. Degradation rate constants for DNT (with ethanol), plotted as a function of current.
Table 5.4

Experimental Data for Glassy Carbon Cathode:

Degradation of TNT in a combined mixture of TNT & RDX

| Current | Stir Rate | рН | Rate Constant (min^{-1}) |
|---------|-----------|-----|----------------------------|
| (IIIA) | (TpIII) | | |
| 23 | 630 | 8.0 | 0.0036 |
| 23 | 2040 | " | 0.0045 |
| 34 | 630 | " | 0.0043 |
| 34 | 2040 | " | 0.0058 |
| 45 | 630 | " | 0.0049 |
| 45 | 2040 | " | 0.0054 |
| 53 | 630 | " | 0.0059 |
| 53 | 2040 | " | 0.0065 |
| 65 | 630 | " | 0.0062 |
| 65 | 2040 | " | 0.0061 |

The samples were analyzed for the concentration of TNT. RDX analysis was not possible because TNT interfered at the absorbing wavelength of RDX in spectrophotometer experiments. The degradation rate constants varied between 0.0036 to 0.0065min⁻¹ (half-lives varied between 193 minutes to 107 minutes).

5.3.5 Electrochemical reduction of TNT in recycled flow experiment

As mentioned previously, the results of the various degradation experiments showed that the mass transfer limitations were governing at higher current values. Thus an effort was made to overcome these limitations by improving the hydrodynamics. One such way was to recycle the fluid in the reactor and make it fall over the cathode surface in order to disturb the diffusion layer. The experiment was carried at one of the higher current values (65mA), where the mass-transfer limitations were encountered. TNT was used with an initial concentration of 50ppm and a pH of 8.0 was maintained throughout the experiment. The resulting degradation and its comparison with degradation under similar conditions, except for the recycle, are shown in Figure 5.8.

The rate constant under recycle-flow conditions was 0.0101 min⁻¹, as compared to a rate constant of 0.0062 min⁻¹ under semi-batch conditions. This clearly showed that the mass-transfer was limiting the degradation at higher currents, which can be overcome by using the recycle flow.



Figure 5.8. Comparison of degradation rates for batch and recycled flow reactor.

5.4 THE DIFFUSION LAYER THEORY

Formation of diffusion layer near the surface of the electrode (between the solid-fluid surface) is widely accepted fact in the electrochemical reaction engineering. This concept of diffusion layer can successfully explain many of the results observed in the present work. Thus, an effort is made here to correlate the effect of the variation of the operational parameters (current, stir-rate, etc.) with the observed results, citing the diffusion layer theory.

There are three distinct chemical rates (phases) that determine the reaction kinetics for a nitroaromatic molecule. First is the bulk movement of the nitroaromatic in the solution towards the electrode surface. Because the nitroaromatic is dissolved and well mixed, this can be safely assumed to be extremely fast. The reactor solution is completely mixed in the bulk. On the other hand, at the cathode surface because of the solid – liquid interface convective mixing does not take place. Hence the protons from the bulk move to the cathode surface (to undergo reaction 1) by diffusing from the bulk to the surface. This mechanism is extremely slow and hence is the rate-governing step in the mass transfer limited reactions. The opposite exists for the Hydrogen radicals. The hydrogen radicals are extremely reactive and hence besides undergoing the reactions 2,3, and 4 that result in the degradation of the nitroaromatic, they readily combine with each other to form hydrogen gas (reaction 5). Thus the nitroaromatic has to move through the diffusion layer formed by the protons and hydrogen radicals to undergo the reduction reaction. The third

phase is the intrinsic chemical reaction between the nitroaromatic and the hydrogen radical.

Without any mixing (or stirring) the cathode region would get depleted of protons (because of conversion to hydrogen radicals - reaction 1), and the anode region would get richer in protons (because of the production of protons - by reaction 6). Thus the proton concentration profile would look something like the dotted line in Figure 5.9 (qualitatively). The stirring causes good mixing in the middle of the solution so that the proton concentration evens out in the middle (the solid line in figure 5.9 - qualitative). The cathode region is magnified in Figure 5.10, and the effect of the variation of stir rates and current on the diffusion layer thickness is explained with reference to this figure. The stirring in the solution (or agitation by other means) would determine the mixing in the bulk in the vicinity of the cathode. This in turn would determine the diffusion layer thickness. Higher stirring (or agitation), results in a smaller diffusion layer thickness (dashed line v/s the other two lines in Figure 5.10). Thus, the smaller the diffusion layer, faster would be the movement of nitroaromatic towards the electrode and hence higher would be the degradation rate. This explains the higher rate constants observed at high stir-rate settings in all the experiments performed with the nitroaromatics.

Similar reasoning can be applied to the current density. An increase in current causes more rapid release of electrons (or a more rapid conversion of H^+ to H), and hence a steeper concentration gradient of protons from the bulk to the electrode surface (solid line v/s dash-solid line). This would in turn lead to a lower proton concentration in the diffusion layer, which would again yield higher transfer rates of nitroaromatics and hence higher degradation rates are observed at higher currents.

66



Figure 5.9. Variation of proton concentration (qualitative)



Cathode Surface

Bulk Fluid



5.5 INTERMEDIATES AND PRODUCT IDENTIFICATION AND MASS BALANCE

Intermediates and end-products were identified for the degradation of TNT. All TNT products and intermediates were identified and quantified on HPLC. Two of the dimers, two mono-amino isomers and two di-amino isomers were purchased from AccuStandard Inc. (New Haven, CT). A calibration curve of these compounds were prepared on HPLC and then the products identified by matching the retention time and absorbance-spectra of the peaks of compounds from reactor solution with the peaks of pure compounds. Synthesis was tried for one of the dimers, but the synthesized product yielded no peak.

An approximate 90% mass balance (on molar basis) was achieved for experiments conducted with TNT. An important finding from this study is that most of the products in the experiment are present in the solid precipitate which is formed during the degradation of TNT and which settles down in the reactor. In contrast, the diaminotoluene (i.e., DAT) and 2-nitroso,4-nitrotoluene are found in the aqueous phase in the DNT experiments.

The solid phase of TNT consists primarily of three types of dimers - D-1 (i.e., 2,2',6,6'trinitro,4,4'-azoxytoluene), D-2 (i.e., 4,4',6,6'-trinitro,2,2'-azoxytoluene) and D-3 (i.e., 4,2',6,6'-trinitro,2,4'-azoxytoluene), with a minor contribution from the 2-amino-4,6dinitrotoluene and 4-amino-2,6 dinitrotoluene. The HPLC spectra gave three closely spaced peaks around a retention time of 13 minutes. Two of the peaks were identified to be dimers with a 99% match obtained on the HPLC. The third peak gave a 98% match on the spectra, and was thus assumed to be of the third dimer which could not be obtained commercially or synthesized in the laboratory. Much smaller peaks were observed for the 2-amino-4,6-dinitrotoluene and 4-amino-2,6 dinitrotoluene. No peaks were observed for the di-amino-nitrotoluenes. Also, the supernatant solution did not give any peaks. All peaks were observed from the residue, dissolved in acetonitrile. It is known that some of the degradation products, such as the dimers mentioned above, are much less soluble in water compared to TNT and thus precipitate out of the water once their concentration increases and super-saturation occurs. Table 5.5 lists the various products and intermediates formed along with their quantities. In Figure 5.11, the time profiles of the product are shown. The experiments were stopped at the designated times, the solution filtered, and the residue dissolved in acetonitrile. This solution was then analyzed on HPLC.

Based on the product studies and the mass balance shown in Figure 5.11 and in Table 5.5, we can assess the importance of the relative pathways in the mechanistic scheme of 2,4,6 -TNT degradation shown in Figure 5.12. Two of the intermediates nitroso-dinitrotoluene and hydroxylamino-dinitrotoluene, were not detected. But based on the reported existence of these two products in all nitroaromatic reductions (but hardly detected due to their high instability), these two are included in the mechanistic scheme. Also the reduction of nitrotoluene directly to aminotoluene, without undergoing the partial reduction to the nitroso and hydroxylamino substitutes is highly unlikely.

Table 5.5

Mass Balance of TNT with the Glassy Carbon Cathode, at 2040 rpm, Oxygenated

pH:8.0

| Current (mA) | Compounds | Solid Phase (% | Aqueous Phase (% Molar |
|--------------|-------------|------------------|------------------------|
| | | Molar Conversion | Conversion of TNT to) |
| | | of TNT to) | |
| 65 | D-1 | 30.3 | - |
| | D-2 | 22.7 | - |
| | D-3 | 19.6 | - |
| | 4-A-2,6-DNT | 2.7 | - |
| | 2-A-4,6-DNT | 2.1 | - |
| | TNT | - | 12.1 |
| | Total | 77.4 | 12.1 |

Total Mass Balance (% Molar Conversion of TNT to identified Products) = 89.5 %

Total Mass Balance (% Molar conversion of TNT to identified products) = 115 %

PRODUCT ABBREVIATIONS USED IN TABLES 5.5:

4-A-2,6-DNT = 4-amino-2,6-dinitrotoluene; 2-A-4,6-DNT = 2-amino,4,6-

dinitrotoluene; D-1 = 2,2',6,6'-trinitro,4,4'-azoxytoluene, D-2 = 4,4',6,6'-trinitro,2,2'-

azoxytoluene and D-3 = 4,2',6,6'-trinitro,2,4'-azoxytoluene.



Figure 5.11. Time profile of products and intermediates in TNT experiments



Figure 5.12. Proposed reduction pathway for 2,4,6 trinitrotoluene (TNT)

RDX was expected to give mono, di, and tri-nitroso substitutes of nitro groups in RDX – commonly called MNX, DNX and TNX, respectively. An effort was made to commercially obtain these compounds, but no commercial manufacturer was found. Also no published method of synthesis could be obtained.

The intermediates and products of 2,4-dinitrotoluene were found to be present in both the supernatant solution, as well as in the residue. DNT reduction on the glassy carbon cathode yielded 2,4-diaminotoluene and the azoxy-dimers. This was similar to what was found by Devakumaran. These compounds were only identified and no quantification was carried out.

SECTION 6

REACTOR DESIGN

An electrochemical treatment assembly is proposed based on the trends and information obtained from the studies conducted on the batch reactor. Following is a summary of points that were observed and heeded to, while proposing the design of the electrochemical reactor:

- 1. Current density and the agitation are the two most effective parameters to optimize the degradation rates. The degradation rates do show sensitivity towards the pH of the solution, but the effect is smaller as compared to the above two. Moreover changing the pH of the influent through chemical addition will tremendously increase the operational cost. Hence the influent pH of the waste stream will be maintained throughout the process and in the design.
- 2. The mass transfer limitations govern the degradation rates at higher currents. Hence to increase the efficiency of the process, improvement in hydrodynamics, so as to disturb the diffusion layer is proposed. This is accomplished by two ways. First by rotating the electrodes a shear is created between the liquid and solid interface, which will decrease the diffusion layer thickness. Secondly by making the water flow over the electrodes the diffusion layer can be disturbed. The flow is to be maintained in the turbulent regime.

- 3. The degradation rates are shown to increase by the increase in current density (until the mass transfer limitations creep in). Hence flow is tried to be exposed to the maximum possible surface area of the cathode. Therefore the cathode is chosen as the outer cylinder with water flowing in between.
- 4. Both the anode and cathode reactions produce gases: oxygen and hydrogen respectively. The evolution of these gases will cause a convection current in the opposite direction and thus will lead to a decrease in the degradation efficiency. Thus arrangement (in the form of circulation) is made so that these gases may easily escape out of the reactor solution.
- 5. The electro-neutrality between the anode and cathode solution is maintained through the transfer of electrons - a process called electron hopping which is essentially accomplished through diffusion caused by a concentration gradient. Thus the surface area of the Nafion membrane comes out to be a critical factor. Thus the membrane is also provided in the form of a cylinder (wrapped over a wire mesh) which spans the length of the reactor.
- 6. The resistance of the solution and hence the voltage required to generate a fixed current is dependent on the length of the solution between the anode and the cathode. The product of the current and the voltage would determine the power consumed and

hence the cost. Thus effort is made to keep the diameter of the cylinder small and increase the length instead.

7. The products of the degradation of TNT and DNT with the glassy carbon cathode have been found to be highly insoluble in water and hence tend to settle down. Thus a sedimentation basin can be used after the reactor to separate these solids. At the same time these product may also tend to settle down over the nafion membrane or on the electrode surface. To avoid this a minimum flow velocity should always be maintained in the reactor to avoid the scaling of the cathode and the membrane.

A schematic of the electrochemical reactor is shown in Figure 6.1.



Figure 6.1. Schematic for the proposed Electrochemical Reactor

To complete the design of the reactors the following design variables will need to be determined:

- The diameter of the reactor, D,
- Anode chamber diameter, d,
- The influent flow, Q_o is provided to be varying between 6-20 l/day,
- Length of the reactor, L,
- Volume of the stir tank, V_T,
- Circulation flow rate of the anode and cathode fluids,
- Rotation frequency, *w*,
- The influent concentration of the nitroaromatic has been taken to be 70ppm for TNT, 25ppm for RDX and 100ppm for DNT.
- The effluent concentration desired is taken to be 5ppm for all the nitroaromatics.
- The recycle ratio, α , is varied between 0 to 4.0, with an increment of 0.25.

Following assumptions are made in the design of the reactor:

- Ideal plug-flow conditions are assumed, entailing no axial-mixing.
- Mass-transfer is assumed to be not the limiting factor in the degradation kinetics.
- Parallel pathways of degradation for the three nitroaromatics are assumed.
- First order reaction kinetics is assumed, so that the rate of reaction, $r_A = -kC$



 $\alpha Q, C_A$

Making a material balance around point 1 gives:

$$QC_{Ai} + \alpha QC_{Ae} = (Q + \alpha Q)C_{Ai}^*$$

$$C_{Ai}^* = \frac{C_{Ai} + \alpha C_A}{(1+\alpha)}$$

Considering a first order reaction:

$$\frac{V}{Q+\alpha Q} = \int_{C_{Ai}}^{A} \frac{-dC}{kC_{A}}$$
$$\frac{C_{A}}{C_{Ai}^{*}} = e^{-k\theta}H$$

Where θ^*_{H} is given by:

$$\theta_{\rm H}^* = \frac{V}{Q(1+\alpha)} = \frac{\theta_{\rm H}}{(1+\alpha)}$$

where, θ_H is the residence time given by V/Q.

Therefore, V the volume required for the reactor can be calculated as

$$\mathbf{V} = \boldsymbol{\theta}_{\mathrm{H}}^{*} \mathbf{Q} (1+\alpha)$$

The length to diameter ratio can be taken to be 5:1. As discussed previously smaller diameter would be beneficia from voltage point of view. At the same time smaller diameter will save on the space and make it portable.

The diameter of the anode chamber should again be as small as possible and should be fixed from practical and construction considerations. A diameter of about 2cm should work well.

Thus L = 5D,

And,
$$V = (\pi/4) (D^2 - d^2) L = (5\pi/4) (D^2 - d^2) D$$

Design can be carried out by varying α (the recycle ratio) between 0.25 to 4.0, giving an increment value of 0.25. The flow rate Q = 20 L/day would be the governing for each design and will be used in all the expressions. A safety factor of 20%, will be by multiplying the volume obtained by 1.2. The safety factor can take into account the non-ideality of the reactor. The lower safety factor is appropriate, since the next phase will involve pilot-scale testing and not actual application.

For TNT,
$$C_{Ai} = 70$$
 ppm, and $C_A = 5$ ppm,

Taking the value of k to be 0.01 min⁻¹ for TNT (at higher current values - assuming mass transfer limitations are overcome).

The results are obtained and tabulated in Table 6.1.

For RDX, $C_{Ai} = 25$ ppm, and

$$C_A = 5ppm$$
,

Taking the value of k to be 0.003 min^{-1} for RDX (at higher current values).

The results are tabulated in Table 6.2.

| α | C _{Ai} *(mg/l) | $\theta_{\rm H}^{*}$ (mins.) | V(L) |
|------|-------------------------|------------------------------|------|
| 0.25 | 57 | 243.3 | 3.9 |
| 0.5 | 48.3 | 226.8 | 4.4 |
| 0.75 | 42.1 | 213.1 | 4.8 |
| 1 | 37.5 | 201.4 | 5.2 |
| 1.25 | 33.9 | 191.3 | 5.5 |
| 1.5 | 31 | 182.4 | 5.9 |
| 1.75 | 28.6 | 174.5 | 6.2 |
| 2 | 26.6 | 167.3 | 6.5 |
| 2.25 | 25 | 160.9 | 6.7 |
| 2.5 | 23.5 | 155.0 | 7.0 |
| 2.75 | 22.3 | 149.6 | 7.2 |
| 3 | 21.25 | 144.7 | 7.5 |
| 3.25 | 20.2 | 140.1 | 7.7 |
| 3.5 | 19.4 | 135.8 | 7.9 |
| 3.75 | 18.6 | 131.8 | 8.1 |
| 4 | 18 | 128.1 | 8.3 |

 Table 6.1. Design parameters for the reactor designed for the degradation of TNT.

| α | C _{Ai} [*] (mg/l) | $\theta_{\rm H}^{*}$ (mins.) | V(L) |
|------|-------------------------------------|------------------------------|------|
| 0.25 | 9 | 195.9 | 3.2 |
| 0.5 | 8.3 | 170.2 | 3.3 |
| 0.75 | 7.8 | 150.6 | 3.4 |
| 1 | 7.5 | 135.1 | 3.5 |
| 1.25 | 7.2 | 122.5 | 3.5 |
| 1.5 | 7 | 112.1 | 3.6 |
| 1.75 | 6.8 | 103.3 | 3.6 |
| 2 | 6.6 | 95.8 | 3.7 |
| 2.25 | 6.5 | 89.4 | 3.7 |
| 2.5 | 6.4 | 83.7 | 3.8 |
| 2.75 | 6.3 | 78.7 | 3.8 |
| 3 | 6.2 | 74.3 | 3.8 |
| 3.25 | 6.1 | 70.4 | 3.8 |
| 3.5 | 6.1 | 66.8 | 3.9 |
| 3.75 | 6.0 | 63.6 | 3.9 |
| 4 | 6 | 60.7 | 3.9 |

Table 6.2. Design parameters for the reactor designed for the degradation of RDX.

For DNT, $C_{Ai} = 100$ ppm, and

$$C_A = 5ppm$$
,

Taking the value of k to be 0.01 min^{-1} for DNT (at higher current values - again assuming mass-transfer limitations have been overcome).

The results are tabulated in Table 6.3.

On comparison of the results for the three nitroaromatics, TNT, DNT and RDX, tabulated in Tables 6.1, 6.2 and 6.3 respectively, it can be observed that the volume required for DNT degradation is the largest of the three nitroaromatics. Thus further calculations in terms of the diameter and the length required is done for the DNT case only. A factor of safety of 1.2 is inculcated in the volume. The results for the diameter and length calculations are listed in table 6.4.

| α | C _{Ai} [*] (mg/l) | $\theta_{\rm H}^{*}$ (mins.) | V(L) |
|------|-------------------------------------|------------------------------|------|
| 0.25 | 81 | 278.5 | 4.5 |
| 0.5 | 68.3 | 261.4 | 5.1 |
| 0.75 | 59.2 | 247.2 | 5.6 |
| 1 | 52.5 | 235.1 | 6.1 |
| 1.25 | 47.2 | 224.5 | 6.5 |
| 1.5 | 43 | 215.1 | 6.9 |
| 1.75 | 39.5 | 206.8 | 7.3 |
| 2 | 36.6 | 199.2 | 7.7 |
| 2.25 | 34.2 | 192.3 | 8.1 |
| 2.5 | 32.1 | 186.0 | 8.4 |
| 2.75 | 30.3 | 180.2 | 8.7 |
| 3 | 28.7 | 174.9 | 9.0 |
| 3.25 | 27.3 | 169.9 | 9.3 |
| 3.5 | 26.1 | 165.2 | 9.6 |
| 3.75 | 25 | 160.9 | 9.9 |
| 4 | 24 | 156.8 | 10.1 |

Table 6.3. Design parameters for the reactor designed for the degradation of DNT.

| α | Vx1.2(L) | D(cm) | L(cm) |
|------|----------|-------|-------|
| 0.25 | 5.4 | 11.26 | 56.3 |
| 0.5 | 6.1 | 11.71 | 58.55 |
| 0.75 | 6.7 | 12.1 | 60.5 |
| 1 | 7.3 | 12.43 | 62.15 |
| 1.25 | 7.8 | 12.72 | 63.6 |
| 1.5 | 8.3 | 12.98 | 64.9 |
| 1.75 | 8.8 | 13.15 | 65.75 |
| 2 | 9.3 | 13.44 | 67.2 |
| 2.25 | 9.7 | 13.64 | 68.2 |
| 2.5 | 10.1 | 13.83 | 69.15 |
| 2.75 | 10.5 | 14 | 70 |
| 3 | 10.9 | 14.16 | 70.8 |
| 3.25 | 11.2 | 14.3 | 71.5 |
| 3.5 | 11.6 | 14.45 | 72.25 |
| 3.75 | 11.9 | 14.58 | 72.9 |
| 4 | 12.2 | 14.7 | 73.5 |

Table 6.4. Design geometric parameters for the final reactor design.

The α value of 1.0, can be considered a good approximation, giving

V/Q = 235.1 minutes At Q = 20 l/day, this yields V = 6.1 liter,

Based on this consideration the diameter D = 12.43 cm and the length will be

$$L = 62.2 \text{ cm}.$$

The rotation speed, w, can be varied between 2 - 10 rpm and optimized after experimentation. Different flow rates of the recycle can also be tried and optimized. The volume of the tank V_T should be such that it gives a retention time of about 5 - 10 minutes.

SECTION 7

CONCLUSIONS

The research shows that electrochemical reduction of all the three nitroaromatics 2,4,6-TNT, 2,4-DNT and RDX is taking place readily in the reactor. The rates of degradation observed for TNT and DNT are almost similar, while the degradation rates of RDX are much slower under the applied conditions. The degradation rates of DNT, with added ethanol are almost similar to the rates observed with DNT alone. In the combined experiments carried out with both RDX and TNT added to the solution, the degradation rates of TNT were unaffected by the presence of RDX. For TNT and DNT degradation rates upto 0.008 min⁻¹ and 0.0076 min⁻¹ respectively were obtained. RDX rates were obtained upto 0.0030 min⁻¹.

The products of electrochemical reduction of TNT were three kinds of dimers and various amino-substitutes of the nitro groups. The products of the electrochemical degradation of DNT are primarily 2,4-DAT and a mixture dominated with the azoxy dimers. In oxygenated systems, a large fraction of the products is present in the form of precipitate rather than in the aqueous phase.

The two factors that have the most significant effect on the degradation rates among the various parameters analyzed are – stirring rate and current density. Change in the pH

does alter the degradation kinetics but the effect is not as prominent as the above two factors. Moreover, alteration of the effluent stream pH by addition of chemicals may not be a good option since it may increase the operational cost significantly. The available surface area of the cathode has a linear effect on the rate of degradation of 2,4-DNT. The effect of surface area will be included if we work on current density (rather than current alone) as the parameter.

Among the two aforementioned controlling factors, the stirring rate determines the mass transfer rate and the current density determines both – the intrinsic chemical rate as well as the mass transfer.

The mass-transfer rates were found to be limiting at the higher current values. Improvement in the hydrodynamics, so as to decrease the diffusion layer thickness, was able to overcome the mass-transfer limitations. Degradation rates upto 0.01 min⁻¹ were obtained with such improved hydrodynamics.

Design of a plug-flow electrochemical reactor was carried out, assuming ideal conditions. DNT degradation was found to be governing in the design. The diameter required was calculated to be around 13cm and a length of approximately 65cm would be required.

SECTION 8

FUTURE WORK

The electrochemical reduction of the nitroaromatics can be used to degrade them effectively. The studies carried so far involved synthetically manufactured waters, containing single (or in some cases - double) nitroaromatics dissolved in deionized, distilled waters. The pink waters may contain multiple nitroaromatics along with other chemicals. The follow up studies should now start investigating the degradation kinetics of pink waters directly. The waters may be synthesized in the laboratory, simulating the exact composition as found in the pink waters, or they may be obtained directly from the discharge of a munitions-handling unit.

Some of the parameters specified above will need to be optimized by running the plugflow reactor as shown in the schematic (Figure 6.1). Various factors like the recycle ratio (α), and the rotation speed (ω), may need to be fixed by running at various vales and optimizing them subsequently. The operational currents in the actual treatment assembly may also be predicted by running the experiments on the plug-flow reactor.

The products of TNT are quantified and have been found to be primarily in the precipitated solid phase. Therefore any scale-up process would investigate the settling characteristics of these solids and subsequently design the sedimentation basin. Studies

can also be carried out to use other means (such as biological treatment) to completely mineralize these solids. For example, DAT, a product of DNT degradation is not desirable from toxicity point of view. However, DAT is easily biologically degraded in an activated sludge reactor (Berchtold et al., 1995). Toxicity studies need to be carried out for the TNT products in order to determine their hazard-level as compared to the original compounds.

Experiments carried out so far involved addition of salt (sodium sulfate - 36g/l), to improve the conductivity of the solution. Experiments with a lower salt concentration, which is more representative of army munitions wastewater should also be carried out.

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