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Destruction of Explosives in Groundwater and Process Water Using Photocatalytic and Biological Methods

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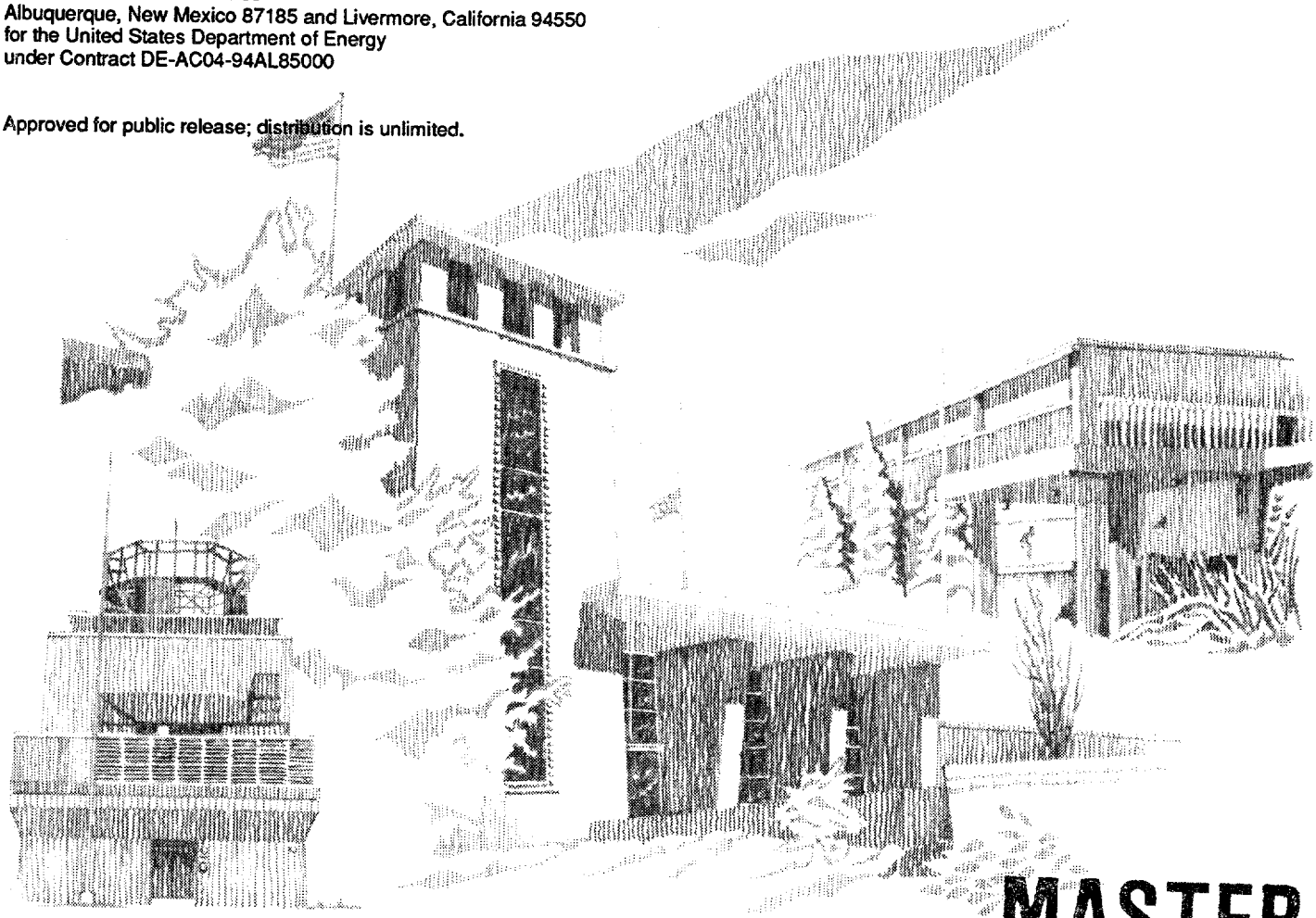

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Abstract

The environmentally safe destruction of pinkwater is a significant problem that requires a multidisciplinary approach to solve. We have investigated the application of advanced oxidation processes, including the use of both UV light sources and laser technologies. The reactions were run under both oxidizing and reducing atmospheres. Aerobic and anaerobic biotreatments were examined as both pre-and post-treatments to the oxidation processes. The toxicity of the wastewater at various stages of treatment was determined. Membrane preconcentration schemes were examined to determine their effectiveness as part of the total pinkwater treatment scheme.

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Foreword

The environmentally safe destruction of pinkwater is a significant problem, and requires a multidisciplinary approach to solve. The work described in this paper is the result of the combined efforts of several groups of researchers. In addition to many hours of fruitful discussions with people from across the country, we would like to specifically acknowledge the following contributors.

At the University of Arizona (Tucson, AZ), Raymond Sierka and Curtis Bryant, Chemical Engineering Department, along with their students, Sunil Kommineni and Pete Reko conducted numerous experiments to examine the effect of ozone and hydrogen peroxide on pinkwater photocatalysis. They also performed the membrane testing and toxicity measurements reported here. A summary of the work is included in this SAND report, but many details are not included. Rather, these details are reported in Sunil Kommineni's Master's thesis. This thesis is attached as Appendix B to this SAND report and thoroughly summarizes both the ozone and peroxide work.

We would also like to acknowledge Steve Flowers, Louisiana Army Ammunition Plant (LAAP), Shreveport, LA, for providing samples of pinkwater from their plant for "real-world" testing. In addition, he contributed to many useful discussions, and provided many of our contacts.

At Sandia National Laboratories, Michael Prairie and Bertha Stange of the Solar Thermal Technology Department performed the majority of the photocatalytic reactions described herein as well as the Total Organic Carbon(TOC) analyses. Cliff Renschler, Christine White, and Richard Buss, Properties of Organic Materials Department, were responsible for the laser studies. Pam Leslie and Phil Rodacy, Explosive Subsystems and Materials Department, prepared the test solutions, performed the bulk of the analytical work, coordinated the efforts of the various groups, and edited this final report.

General Introduction

Research over the last decade has demonstrated that ultraviolet (UV) light, in various combinations with photocatalysts and chemical oxidants, is very useful for destroying a variety of aqueous organic contaminants at low temperatures and pressures. For example, two different review articles [1,2] highlight the work summarized in

hundreds of publications demonstrating the effectiveness of semiconductor photocatalysis on hazardous waste. Likewise, the use of UV energy alone and with oxidants like H_2O_2 and O_3 has been documented.

As the understanding of these new advanced oxidation processes (AOPs) has been evolving, so has our awareness of the need for new methods to treat water contaminated with low concentrations of high explosives such as TNT, RDX, HMX, and PETN (Fig. 1). Consequently, the project described here was designed to determine the feasibility of photo-driven routes to remediate explosive-bearing waste.

Our specific objectives included determining the feasibility of using UV light alone and in various combination with (i) TiO_2 photocatalysts, (ii) H_2O_2, and (iii) O_3. We also investigated various combinations of (i)-(iii) with a variety of UV sources including broad-band Xe and Hg arc lamps and UV lasers. The use of membrane preconcentration was also studied, including the identification of a membrane that yields superior performance. Furthermore, we conducted tests with untreated and UV treated explosive waste samples to determine if the combination of UV treatment with traditional biological treatment shows merit.

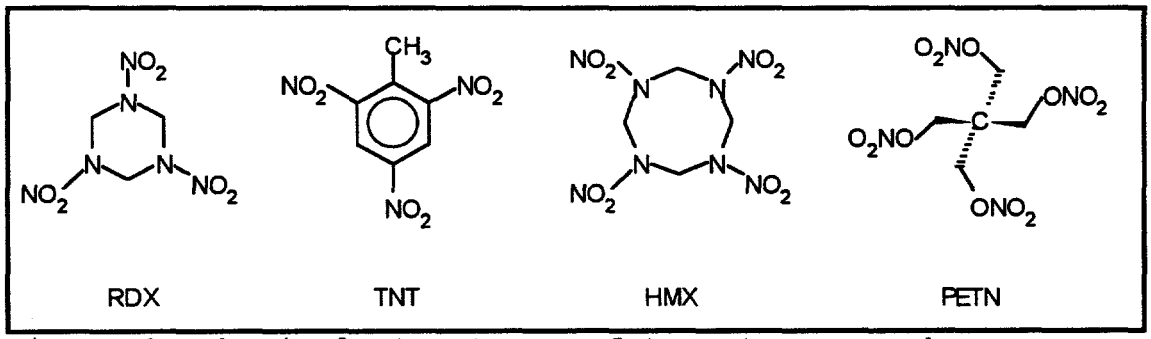


Figure 1 Chemical structures of target compounds.

The process described herein was used to treat both laboratory-prepared samples and samples of a munitions waste stream from the Louisiana Army Ammunitions Plant. We were able to totally destroy the explosives, the explosive byproducts. and intermediates in four days. The resulting material is a non-toxic effluent that could be discharged into a municipal sewage system. This report only includes the work done on TNT and RDX. HMX can be treated in the same manner as RDX, but because of its low solubility in water (approximately 4 ppm), the efficiency of the photocatalytic process is more difficult to monitor. We

briefly examined the treatment of PETN using the system described in this paper. Although no details will be included in this document, we found that the PETN was easily destroyed, and no intermediates were observed. The combined UV irradiation and biological process can be implemented at many DOE, DOD, and commercial plants with minimal modification of existing wastewater treatment facilities.

General Background

There has been a tremendous increase in the level of research and development on photocatalysis for environmental applications since the late 1980s. This is due to the increasing need for new waste treatment technologies coupled with the general optimism that semiconductor-based photocatalysis can be used cost effectively to mineralize organic contaminants and immobilize certain heavy metals. In addition, photocatalysis is the only low-temperature process that can utilize sunlight directly to drive detoxification chemistry. The most common photocatalyst is anatase titanium dioxide because of its relatively high activity, low cost, low toxicity, and high stability. Others have been tested (ZnO, CdS, SiC, $SrTiO_3$), but none has been as extensively applied as TiO_2.

Wastewaters generated in the military explosives and propellant industry contain a wide variety of harmful pollutants [3]. These wastes result from load, assembly, and pack (LAP) operations, munitions production, explosives machining operations, and demilitarization activities. Aqueous effluents resulting from trinitrotoluene (TNT) contact are termed pinkwaters. The characteristic pink color is due to the photolysis products of TNT. Another major water contaminant in the military explosives industry is hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). Strictly speaking, only the TNT streams should be called pinkwater, but any aqueous stream containing explosives of any type are often referred to as pinkwater. This common usage will be employed in this report.

In 1982, interim environmental criteria were identified for several munitions compounds [3]. For aquatic organisms, these criteria are 60μg/L and 200μg/L for TNT and RDX, respectively. Data were not available to calculate the criteria for human exposure to TNT; however, a value of 33.7 μg/L was established for RDX. In 1973 the Army Procurement

and Supply Agency published water quality standards for Army ammunition plant effluents [3]. These standards include a limitation on nitrobody concentration of 0.5 mg/L (500μg/L)

Currently, granulated active carbon (GAC) is used effectively to meet these discharge criteria. However, the common practice of using the carbon only once is expensive and pollutive because the spent carbon is destroyed by open burning [3-6]. Carbon regeneration via indirect firing is feasible for about four cycles, after which the carbon is destroyed by burning. During each regeneration, approximately 50% of the carbon can be reused; the remainder is too fine and restricts flow in the filtration units. In addition, the regenerated carbon often loses some of its activity and is thus not as efficient as virgin material. Consequently, GAC processes are expensive to operate and generate undesirable secondary gaseous waste streams. In addition, changing environmental regulations indicate that open burning and open detonation of these materials may be prohibited within a few years. Consequently, new, low-cost alternatives that do not produce secondary wastes are being sought for the treatment of aqueous munitions waste.

One other approach that has been tested is chemical neutralization followed by biological treatment (7). This approach has been successful for TNT removal at low concentrations, but not RDX. In addition, biological treatment of TNT can be difficult as high TNT concentrations typically kill the bacteria in many treatment plants.

To address the need for new treatment methods, we began a program to investigate heterogeneous photocatalysis. Photocatalysis shows tremendous promise for the safe, effective treatment of water contaminated with low concentrations of organic chemicals and certain heavy metals [8-10].

Photocatalysis, demonstrated schematically in Figure 2, occurs when light initiates the formation of electron/hole pairs in semiconductor particles that are suspended in contaminated water [11-14]. These electron/hole pairs can either recombine, producing thermal energy, or migrate to the particle surface where they interact with the external environment. The holes react with water to produce hydroxyl radicals which are capable of oxidizing dissolved organics into water, carbon dioxide, and dilute mineral acids. The electrons, in turn, react with dissolved oxygen to eventually form more hydroxyl radicals. Alternately, they

can react with other dissolved oxidants including organic chemicals (e.g. TNT, RDX, and other organic explosives), and certain metals (e.g. Hg, Cr). Titanium dioxide (TiO_2) is the most commonly used photocatalyst because of its effectiveness, stability, low cost, and because it is non-toxic. In addition, TiO_2 is activated with near UV light (390 nm or less); therefore, making it possible to power the process directly using the ultraviolet energy in sunlight.

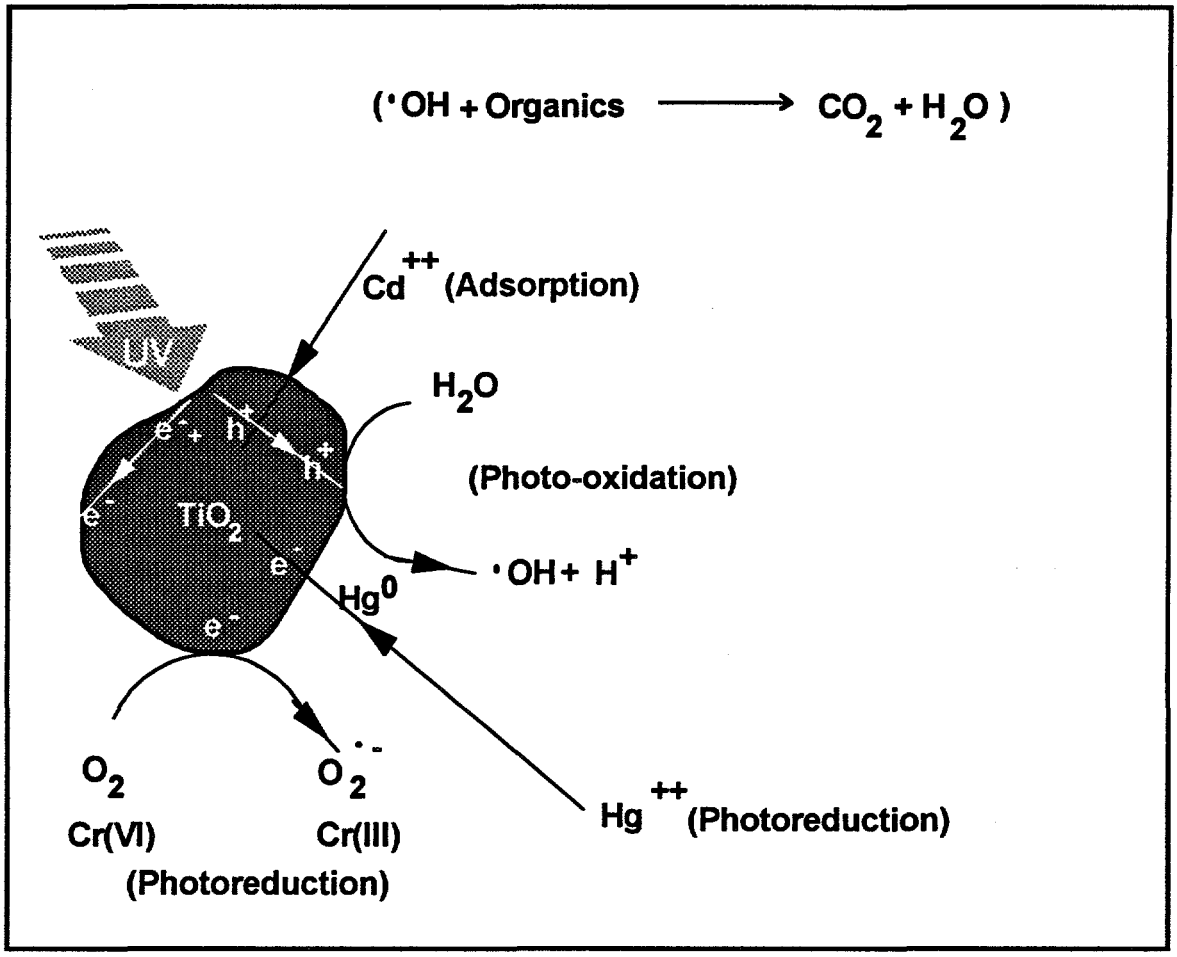


Figure 2. Photocatalytic reactions on a TiO_2 particle.

Although photocatalysis has been applied successfully to a wide variety of organic chemicals [15], little work has been done on its application to munitions waste. In one study [16], 800 ml of 50 ppm TNT in pure water was reportedly 90% mineralized with 2 hours exposure to UV light from a 450 Watt mercury lamp using TiO_2 as the photocatalyst. These authors concluded that photocatalysis may be highly effective for the treatment of TNT-contaminated waters. Our goal was to verify this effectiveness for TNT and to further investigate the applicability of photocatalysis to the degradation of RDX and actual waste streams containing these

contaminants [17]. Various analytical measurements including pH, total organic carbon (TOC), UV absorbance, toxicity, total suspended solids (TSS), oxygen uptake rates (OUR) and TNT / RDX concentration by high performance liquid chromatography (HPLC) were employed to quantify treatment efficiency.

Analytical equipment

Standards

TNT and RDX reference standards were prepared in-house from pure explosives and deionized water. The RDX powder used was > 99.99% pure. The TNT, also >99.99% purity, was 3x recrystallized to minimize the number of isomers and degradation products. The purity of these standards was verified by HPLC analysis using a photodiode array detector covering a wavelength range from 190 nm to 800 nm. A weighed amount of the appropriate explosive was placed in a volumetric flask and deionized water was added to the proper level. The high and low concentration TNT standards were approximately 90 ppm and 9 ppm; the RDX standards were approximately 40 ppm and 4 ppm. A Teflon-coated stir-bar was then added, and the solution stirred for approximately 24 hours to ensure complete dissolution. Since most polymeric materials are know to strongly absorb explosives, we verified that the Teflon-coated stir bar did not absorb enough explosive during the 24-hour stirring period to perturb the solution concentrations. While stirring, and before use, the flask was wrapped with aluminum foil to exclude light. Fresh standards were prepared for each set of samples analyzed.

Field Samples

Samples of pinkwater for this treatability study were obtained from the Louisiana Army Ammunition Plant (Shreveport, LA). Table 1 presents a characterization profile of this pinkwater that was done at the Louisiana Army Ammunition Plant. This table represents an average analysis of 10 samples taken over the course of one month. Exact concentrations vary somewhat due to the changing nature of the pinkwater waste stream. An analysis of the RDX and TNT concentrations was performed for each sample tested at Sandia; the other parameters listed (dissolved oxygen, suspended solids, iron, etc.) were not tested as

preliminary work indicated that they did not affect the experimental results.

Table 1.
Representative Analysis of Pinkwater from the Louisiana Army Ammunition Plant, Shreveport, LA

pH	7.8
TNT Concentration	176 mg/l
RDX Concentration	95 mg/l
Total Organic Carbon	137 mg/l
Dissolved Oxygen	3.6 mg/l
Total Suspended Solids	36 mg/l
Iron	0.5 mg/l
Hardness, as $CaCO_3$	14.5 mg/l

Laboratory-prepared Samples

The preliminary work was done using laboratory-prepared "synthetic" pinkwater. The only difference between the actual pinkwater and the laboratory-prepared pinkwater was the source; actual pinkwater originates from the processing of munitions, while the synthetic material was prepared at Sandia. In order to prepare synthetic samples, we first determined the saturated concentration of solutions of TNT, RDX, and HMX in Albuquerque tap water. Approximately one liter of tap water was placed in an amber-colored glass bottle. Excess explosives were added, and the solutions were stirred for a minimum of 24 hours. Aliquots of these solutions were filtered through a 0.2μm syringe filter into 1.0 ml autosampler vials for HPLC analysis. The saturation values of these solutions were determined to be 118 ppm, 43 ppm, and 4.5 ppm for TNT, RDX, and HMX, respectively. To prepare bulk samples for testing we added a weighed amount of explosive to 15 gallons of tap water in a polyethylene drum such that the final concentration would be approximately 10% less than the saturation values. The drums were agitated to ensure complete dissolution, and allowed to "age" in the presence of light for six months so that any naturally occurring decomposition products would form. The solution containing the TNT acquired the typical pink color associated with the decomposition products; the RDX and HMX solutions retained their colorless appearance. We chose to use tap water rather than distilled water because the minerals in the tap water would more closely represent the actual pinkwater. The composition of the tap water used to prepare these samples is shown in Table 2.

Most of the photocatalysis work was done using samples prepared in deionized water to minimize interferences. The treatability samples prepared in deionized water were prepared and treated as described in the above section.

Table 1.
Representative Analysis of Albuquerque Tap Water Used to Prepare Synthetic Pinkwater.

Visual Color	Colorless
Visual Appearance	Clear
pH	7.7
Iron	0.07 mg/l
Chloride	19.5 mg/l
Chemical Oxygen Demand	13 mg/l
Total Organic Carbon	2.5 mg/l
Total Dissolved Solids	270 mg/l
Total Suspended Solids	<5 mg/l
Alkalinity	172 mg/l
Turbidity	3 FTU

Sample Storage

Since the actual wastewaters at ammunition plants are exposed to ambient lighting under ambient temperatures, both the pinkwater from the Louisiana Army Ammunition Plant and the synthetic pinkwater were stored under ambient conditions while awaiting testing.

After testing (exposure to ultraviolet light, laser light, bioremediation, etc.) the aliquots selected for analysis were stored in the dark and under refrigeration until the analysis was begun. Early laboratory testing had indicated that refrigeration was necessary to preserve the integrity of the samples. Light was excluded to minimize the risk of additional decomposition due to naturally occurring UV radiation.

High Performance Liquid Chromatography (HPLC)

All samples analyzed by HPLC were pre-filtered using a 0.2µm syringe filter to remove the titanium dioxide and any other

suspended solids. The HPLC analytical conditions employed are listed in Table 3.

Table 3.
Equipment and Analytical Conditions Used for the HPLC Analyses

HPLC system	• Waters model 600E pumps (quaternary system) • Waters model 715 WISP autosampler with 96 position sample tray • Waters model 991M photodiode array detector (scanned 190 nm to 800 nm) • Waters temperature control module set at 23°C
Column	• Brownlee Spheri-5 RP-18, 250 x 3.9 mm ID, operated at ambient temperature (C_{18} reverse phase, 5 micron particles)
Mobile Phase	• Water/methanol gradient; 90/10 to 30/70 in 35 minutes
Flow Rate	• 1.0 ml/minute
Injection Volume	• 40 microliters (µl)
Instrument Control, detection, quantitation	• Waters Millenium™ software

Titanium Dioxide Reactor used at Sandia National Laboratories

All of the titanium dioxide reactions performed at Sandia utilized a 1500 ml Pyrex reactor containing 400 ml of solution. This system, shown schematically in Figure 3, had three sampling ports that were used to withdraw samples and allow the entrance and exit of sparge gases. This solution was stirred and thermostatted at 22 ° C under a 1000 W ozone-free Hg-Xe arc lamp or a 100 Watt spot lamp with Pyrex optics. These lamps were chosen due to their visible light output and their ability to mimic solar radiation. UV lamps

were not employed for these studies at Sandia, but were studied at the University of Arizona. The reaction solution was sparged with compressed air (or nitrogen, if an inert atmosphere was desired) to sweep out the headspace of the reactor unless otherwise specified. Titanium dioxide (Tioxide, 207 m^2/gm) was added as a loading of 0.1 wt.% in all reactions unless otherwise noted. Reactions were performed for 60 to 360 minutes, and samples were withdrawn at predetermined intervals; typically 0, 5, 10, 15, 30, 60, 120, 240, and 360 minutes. The aliquots were filtered through a 0.2 micron filter and then analyzed using UV-visible spectroscopy, total organic carbon analysis (TOC) analysis and high performance liquid chromatography (HPLC).

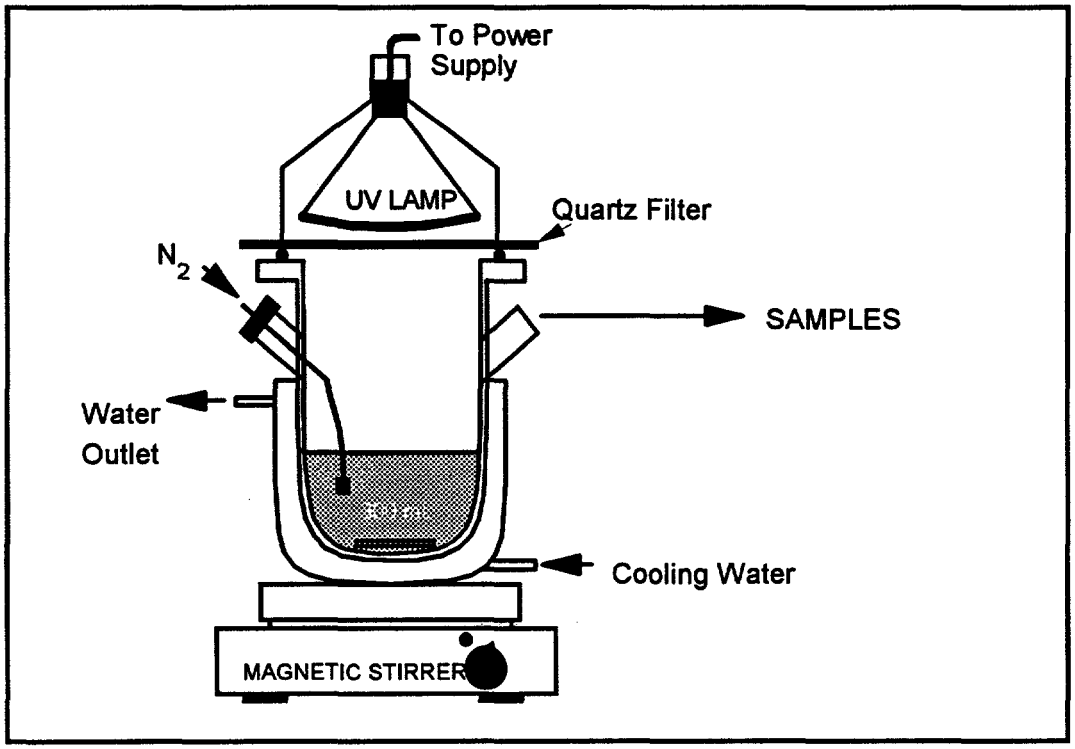


Figure 3. Sandia Titanium Dioxide Reactor

Preparation of Metallized Titanium Dioxide

Metallized TiO_2 was made using two different metals. The Ni-TiO_2 was prepared through incipient wetness methods by

adding the appropriate aqueous solution of nickel nitrate to the titanium dioxide, followed by calcination and reduction under H_2 gas at elevated temperature. This material was prepared at a loading level of 2.5% and 0.5%. The $Pt-TiO_2$ was prepared by mixing chloroplatininic acid of appropriate concentration with an aqueous slurry of Tioxide and an excess of methanol under the 100 W lamp. This was prepared at a loading level of 2.5%. After the reaction was complete, the catalyst was washed and dried before use.

University of Arizona Ultraviolet light reactor (UVR)

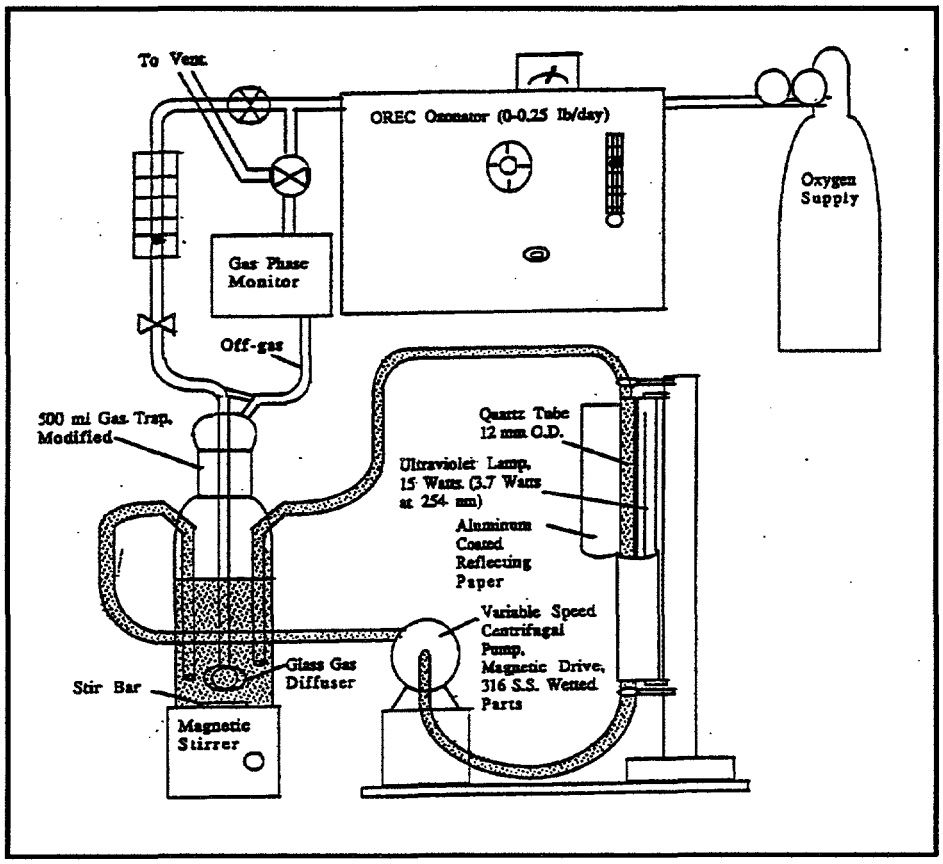


Figure 4. University of Arizona photoreactor.

The UVR setup shown in Figure 4 was used at the University of Arizona. It consisted of a gas washing bottle (used as a reservoir for mixing) connected to a centrifugal pump which recirculated the 800 ml of suspension through a quartz tube placed 3 millimeters (mm) away from and parallel to an ultraviolet lamp (Model #615T8, NIS Company, Japan).

Aluminum foil covered the lamp and quartz tube coupling to provide shielding from UV radiation. Glass inlet and outlet tubes were added into the sides of the 500-ml gas washing bottle and extended nearly to the bottom. The pump and these tubes, connected by Tygon tubing, recirculated the suspension through the lamp setup. Ozone was added to the gas washing bottle reactor through a porous glass diffuser. A 1.5 by 5.16 inch magnetic spinbar at the bottom of the reservoir rotated at 400 rpm for additional mixing. The one speed pump used for these experiments was manufactured by Teel (IP767A) and had a magnetic drive and polypropylene wetted parts. Its flowrate (without the dissolved ozone cell in-line) was measured as 2.99 ± 0.25 L/minute which translates to a Reynolds Number of approximately 79,000 for the solution in the quartz tube (12 mm O.D., 10 mm O.D.). The lamps required 15 Watts of power and were rated at 15 mW/cm^2 at 254nm) and 7.0 mW/cm^2 at 365nm. The lamp tubes were 16 inches long.

An Ozone Research and Equipment Corporation (OREC) ozonator (OREC #03V5-0) produced ozone by corona discharge using medical grade oxygen carrier at 2 L/min. flow into the generator. The rated output of the ozonator was 0 - 0.25 pounds per day. The generator pressure dial was set at 4.5 to 5 pounds per square inch gauge (psig). Oxygen and ozone gas flow through the glass diffuser was regulated by a rotameter at a constant flowrate of 2.0 L/min for all experiments. Unused gas from the ozonator was vented to the fume hood.

Membrane Separation

Membrane separation techniques are often used to purify materials or to preconcentrate waste streams prior to treatment. A waste stream (typically aqueous) is passed across a porous membrane, where diffusion of specific species can occur. In this manner, species of interest can be separated and concentrated. For example, as pinkwater flows across a membrane, water diffuses through the membrane, yielding two aqueous streams - pure water, and a more concentrated pinkwater. In this manner, we can reduce the volume of pinkwater that must be treated.

All membrane separation runs were carried out in a CEPA CELL apparatus manufactured by Osmonics, Inc. of Minnetonka, Minnesota. This apparatus is shown in Figure 5.

The test cell will accommodate any flat sheet membrane and has an effective area of 137 cm^2. After preliminary experiments, the BW 30 membrane was selected to concentrate the TNT and RDX from the laboratory prepared pinkwater. The BW 30 membrane, a low pressure reverse osmosis membrane, is produced by Film Tec Incorporated and is rated as having 98% rejection of 2,000 mg/L NaCl at 225 psig. The membrane is a composite with a polyamide barrier on a polysulfone support.

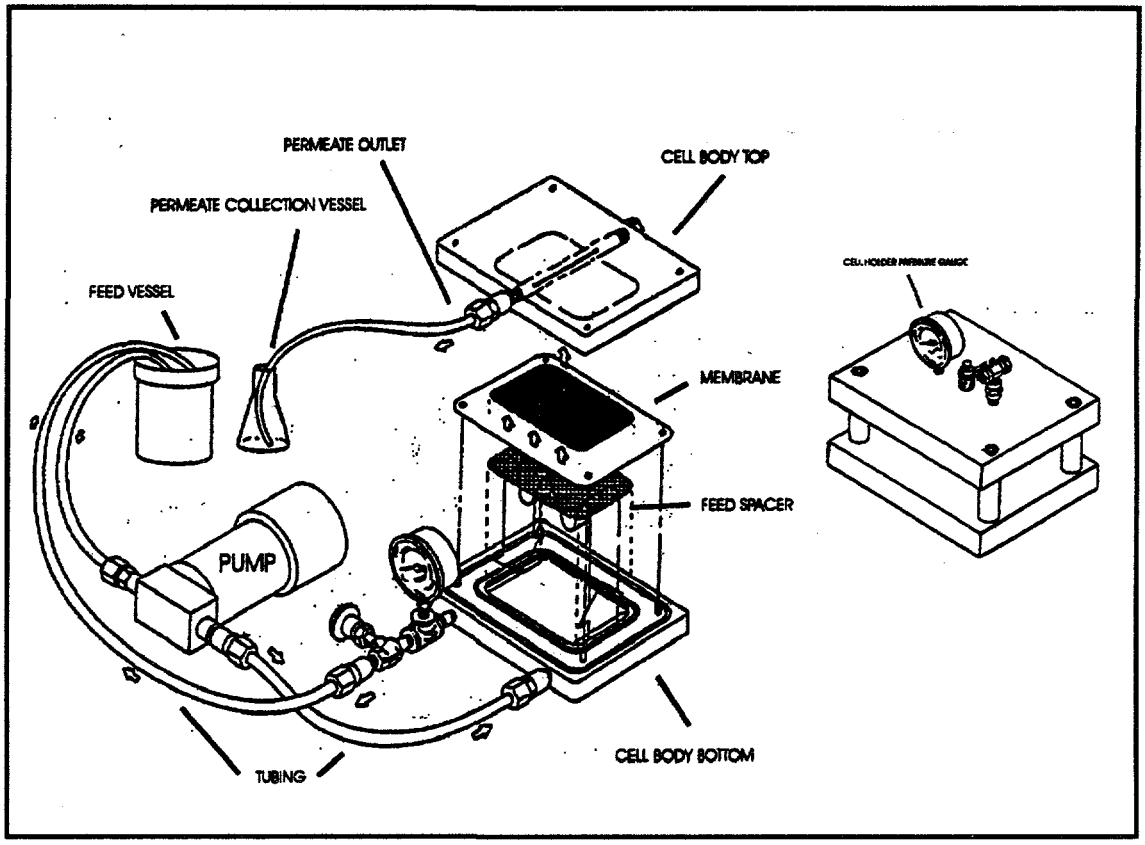


Figure 5. Membrane separation apparatus.

Excellent rejections of organics with molecular weights in excess of 200 are predicted by the manufacturer, based on laboratory tests with various classes of organic molecules.

Prior to munitions wastewater separations, the BW 30 membrane was flushed with 5 gallons of 18 Meg-ohm distilled water. Water flux rates were measured to ascertain the integrity of the membrane. Next, 4.0 liters of laboratory prepared pinkwater was recirculated for 30 minutes prior to commencement of permeate recovery. A total of 3,200 ml of permeate (80% recovery) and 800 ml of concentrate were produced.

Toxicity

MicroTox EC30 and EC50 measurements were made on the influents and the 7-day effluents from the aerobic biological treatment units. Microtoxicity measurements employ a fluorescent marine bacteria and a series of sample dilutions; the toxicity of the sample is reflected in the light output of the bacteria. A MicroTox Model 500 analyzer was used, and the basic test protocol as described in the MicroTox Handbook Volume II. Toxicity is defined as the effective concentration of sample that reduces the light output of marine fluorescent bacteria by 30% (EC 30). EC 30's were converted to Toxicity Units (TU's) from the following formula:

$$100/EC\ 30\ (\%) = TU's.$$

None of the samples were diluted prior to testing. During testing, sample concentrations of 45%, 22.5%, 11.25%, and 5.625% were analyzed. Effects were measured at exposure time increments of 5 minutes until a maximum impact was detected. In almost all cases the maximum impact was measured at an exposure of 30 minutes.

Ultraviolet/Visible Spectroscopy (UV/VIS)

Ultraviolet/visible light scans for the titanium dioxide catalyst reactions at Sandia were performed on a Hewlett Packard HP8452A Photo Diode Array Spectrophotometer. One centimeter quartz cuvettes were used, and the 190-820 nm range was examined. Samples were diluted with deionized water ½in order to get the absorbance within the linear range of 2.0 absorbance units.
Ultraviolet/visible light scans for untreated and membrane process wastewaters treated at the University of Arizona were made with a Shimadzu UV 160A variable length spectrophotometer in 1-cm cuvettes in the 200-600 range.

Total Organic Carbon (TOC)

At Sandia, the total organic carbon in solution was determined using 5 ml samples and a Shimadzu TOC-5000 total organic carbon analyzer. All samples were analyzed in triplicate for total carbon as well as inorganic carbon (CO_2). Detection was achieved through oxidation of the sample over a heated platinum catalyst and subsequent gas phase IR detection of CO_2 . The lower detection limit is approximately 1 ppm.

Organic concentration measurements in aqueous solutions and suspensions were made on a Dorhmann TOC analyzer, model 80. Dissolved CO_2 was removed by N_2 sparging of acidified samples (pH 2). Therefore, in contrast to the Sandia data, the TOC values reported do not include the inorganic carbon. All samples were analyzed in duplicate and the average reported as the result.

Ion Chromatography (IC)

Ion chromatography of individual samples was performed to determine the dissolved anions and cations in solution. Analysis was performed on a Dionex IC system with isocratic flow at ambient temperatures. Detection was through a Dionex conductivity cell. Anions were passed through a Dionex Ionpore AS4A 4mm (10-32) column with a solution of 1.8 mM Na_2CO_3 / 1.7 mM $NaHCO_3$ at 20 ml/min. Flow rate was 2.0 ml/minute. All analytes were detected within 10 minutes. Cations were passed through a Dionex Ionpore CS10 (10-32) column with an eluent of 40 mM methansulfonic acid at a rate of 1 ml/min. All cations were observed within 12 minutes.

Laser System

Depending on the wavelength desired, laser irradiation was done with either a Questek Series 2000 ArF excimer system, with output at 193 nm, or a Lambda Physik XeCl system with output at 308 nm.

Titanium Dioxide Reactions

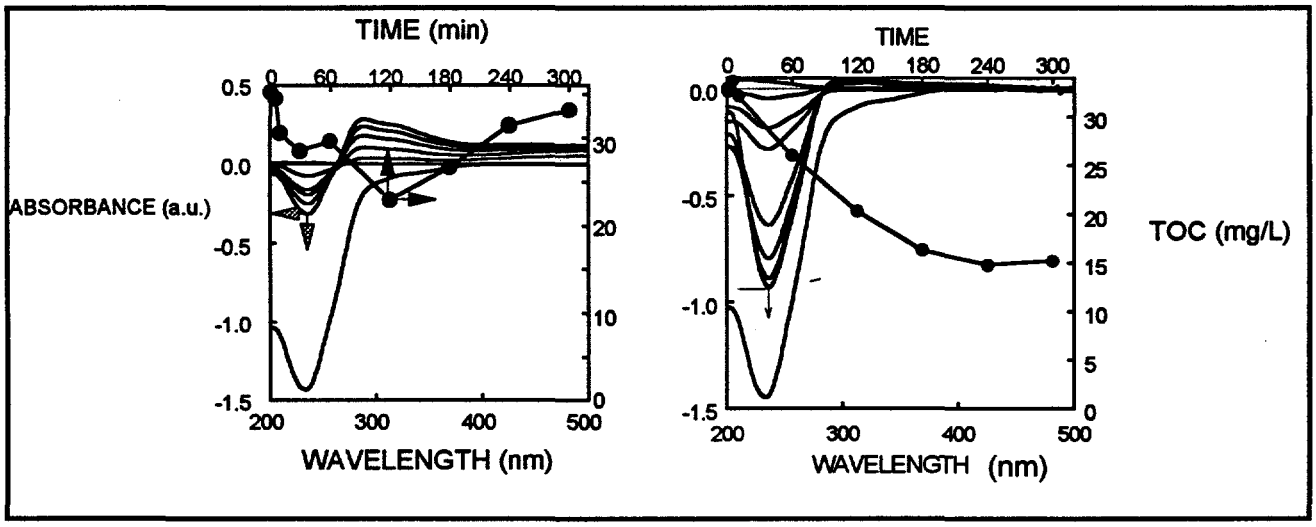


Figure 6. TNT Degradation with (left plot) and without (right plot) TiO_2

A series of experiments were performed at the beginning of this project in order to determine the best parameters for future study. Initially, tap water was used to simulate the water used to make up the experimental synthetic wastewater solutions. This complicated matters because of the dependence of the reaction on pH and dissolved inorganic carbon. These experiments showed that photocatalysis was able to degrade TNT, HMX and RDX in solution. Therefore, deionized water was used for the remainder of the experiments. The Oriel Hg-Xe 1000 W lamp was employed initially but after the initial series of pH experiments, a 100 W spot lamp was used.

Subsequent work has shown that the TNT reaction rate is 1^{st} order in light intensity. Thus experiments, performed with the two different lamps should only differ in reaction rate; the Oriel lamp, having 10 times the output of the spot lamp, should produce a reaction rate 10 times faster.

It is well known that TNT degrades in light. This is illustrated in Figure 6 for a solution of 90 ppm TNT that was illuminated in the absence of any photocatalyst. Twotypes of data are shown in the figure. The left ordinate with the bottom abscissa corresponds to UV/visible

difference spectra obtained by subtracting the initial spectrum (t=0) from the spectra taken at later times. The dashed spectrum shows what the difference spectrum would look like if all of the TNT initially present were destroyed, and the horizontal line at zero absorbance units is the difference spectrum for t=0. The spectra between these two extremes show the progress of the reaction.

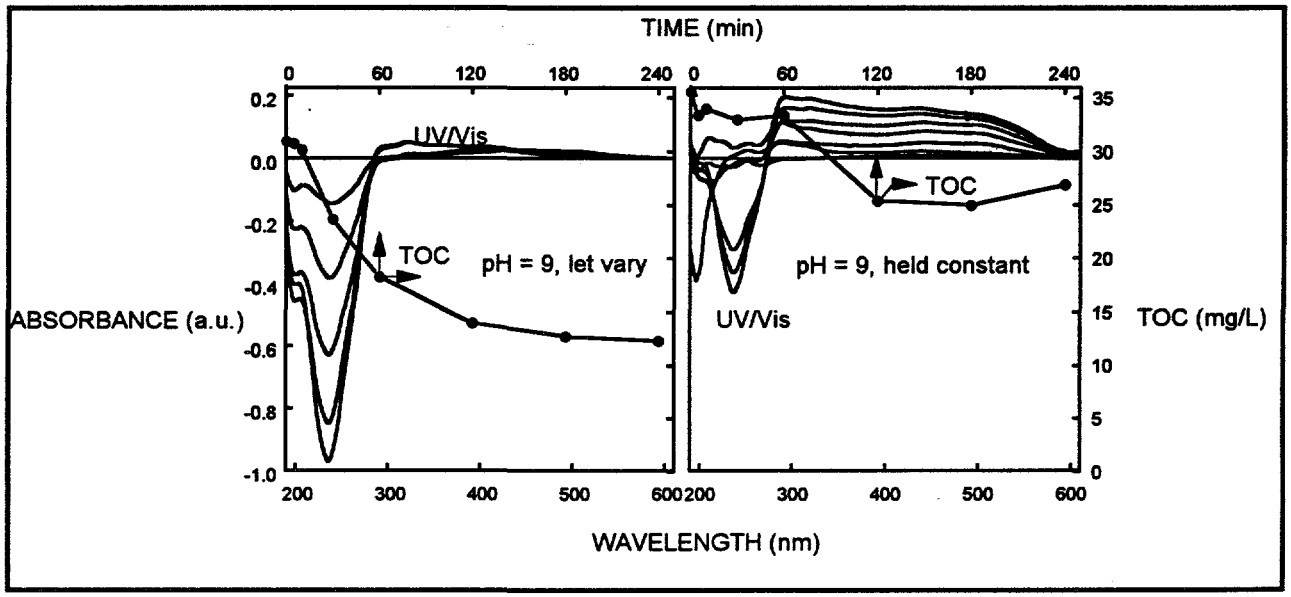


Figure 7. Difference in products for photolytic degradation when pH is allowed to "float" versus pH held constant.

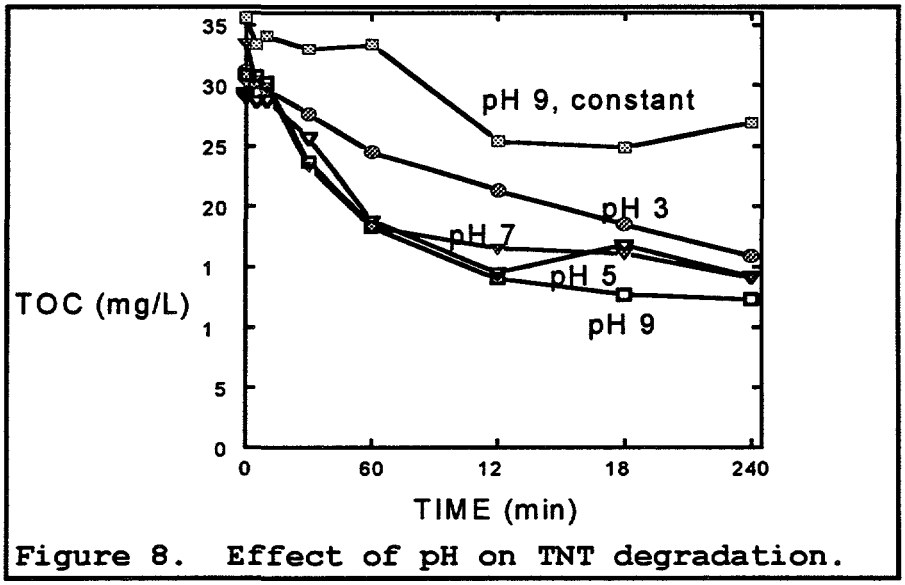


Figure 8. Effect of pH on TNT degradation.

Difference spectra were used because they highlight the formation of light-absorbing reaction intermediates. Any part of the spectrum that is greater than zero results from these intermediates. As shown in figure 6, the conversion of TNT is slow in the absence of catalyst and significant intermediates are formed. This result is confirmed by the TOC data which are plotted against the right ordinate and the top abscissa. The scatter in the data remains unexplained; however, it is evident that the extent of mineralization is very low even after five hours of light exposure.

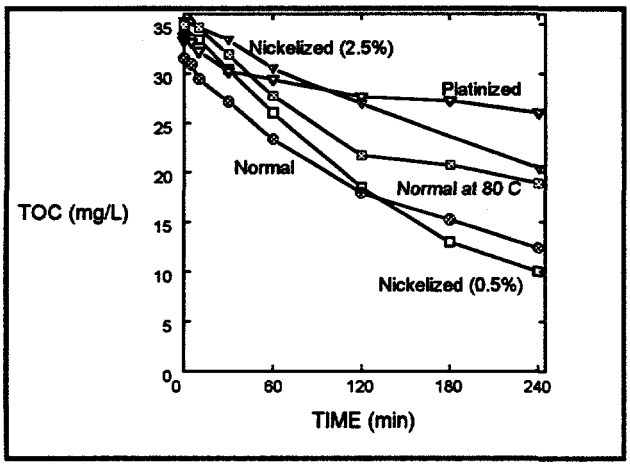


Figure 9. Reductive reaction of various metallized catalysts and variation of reaction temperature.

The pH of the solutions were measured at the beginning and end of the reactions. Typically, the solution would start at a pH of 4.0 and end at a pH of 3.0-3.5. When the solution is held at pH 9 throughout the reaction, it appears that photocatalysis shuts down almost completely (Figure 7). This can be shown by the growth of intermediates similar to that seen in Figure 6 for the no-catalyst trial. Therefore, the TNT is undergoing simple photolysis with the UV lamp. Attempts were made to adjust the pH with nitric acid and sodium hydroxide. As seen in Figure 8, the pH was adjusted to 3, 5, 7, and 9 at the beginning of the reaction and allowed to vary over the course of the reaction. It seems that there is a slight initial increase in rate when the pH is raised at the start of the reaction. If, however, the pH is held constant at pH 9 over the course of the reaction, then the reaction is, as shown previously, severely affected. This behavior may be related to the efficiency of the carbonate ion (CO_3^{-2}) for scavenging free radicals so that as the pH is raised, the inorganic carbon is unable to escape from solution as CO_2 and competes for hydroxyl radicals [18]. The benefit of having the pH high initially may have to do with creation of surface hydroxides on the surface of the TiO_2 that are then available as reactive intermediates for formation of hydroxyl radicals. More work needs to be performed to answer these questions.

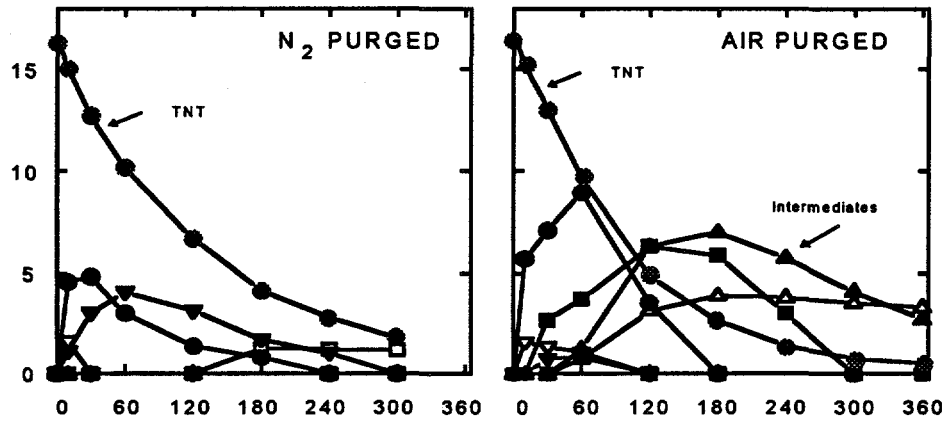


Figure 10. HPLC peak area versus time for anaerobic and aerobic TNT degradation.

The next variable to be investigated was the role of oxygen in the reaction. Figure 10 shows that the reaction under air is faster, but the reaction under nitrogen produces fewer intermediates as observed by HPLC. This smaller number/amount of intermediates could be beneficial from a toxicity standpoint. Although this process may take a little longer, fewer or no toxic intermediates are formed; this may be the most effective pathway for TNT destruction. However, until the identity and/or toxicity of the intermediates is determined, the preferred treatment method cannot be determined. When a hole scavenger (such as Na_2EDTA) is added to the solution under anaerobic conditions the rate of destruction of TNT increases greatly as seen in Figure 11. The circles again represent TNT which is effectively destroyed after 2 hours. Some intermediates are formed that are not destroyed by photocatalysis, however (as evidenced by the steady state after 30 minutes, of the inverted triangles). Attempts to raise the solution temperature during the reaction caused an inhibition of

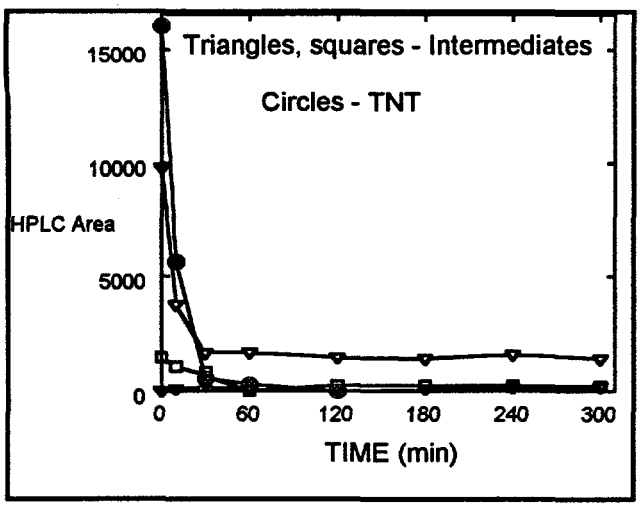


Figure 11. Reductive degradation of TNT in the presence of Na_2EDTA.

the catalyst activity.

The nature of the titanium dioxide catalyst itself can also be varied. Catalysts were prepared using either 2.5 wt% Ni and Pt, or 0.5 wt% Ni. Loading of nickel and platinum on the catalyst surface generally resulted in decreased activity, although a few experiments showed a slightly increased catalytic activity. One problem was with leaching of nickel from the catalyst surface that poisoned the biological degradation unit in later experiments.

RDX was tested under both aerobic and anaerobic conditions. The oxidation reaction is slow, but the reduction reaction is rapid. The graph (Figure 12) shows complete destruction of the RDX under aerobic conditions in about 2 hours. This is important because the biological degradation is ineffective on RDX. The addition of hole scavengers had little effect on RDX destruction; however the mixing of RDX with TNT accelerated the RDX destruction whereas the TNT degradation was unaffected. Therefore we can reduce the level of TNT and destroy all of

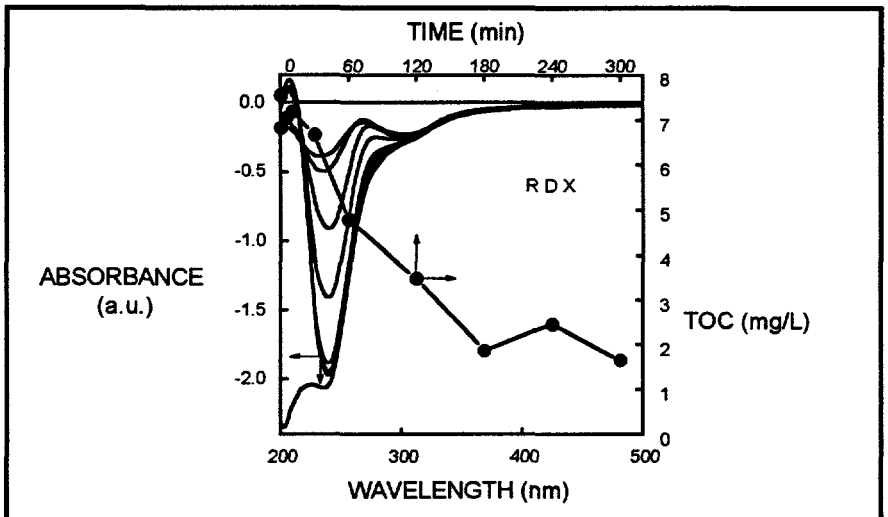


Figure 12. Anaerobic Destruction of RDX.

the RDX within 2 hours before feeding the wastewater to a biological remediation unit.

We also ran experiments on actual Louisiana Army Ammunition Plant (LAAP, Thiokol Corporation, Shreveport, LA) "pinkwater". The samples obtained contained 63 mg/L of TNT, 51.5 mg/L RDX and a number of photointermediates. No HMX was detected. Figure 13 shows that the degradation of RDX is very fast relative to TNT for this waste and that total mineralization is very slow. The latter is indicated by the high concentration of intermediates and TOC late in the reaction. The high level of intermediates may be a function of the high pH of this solution. The pinkwater was rather hard as received. (Table 1)

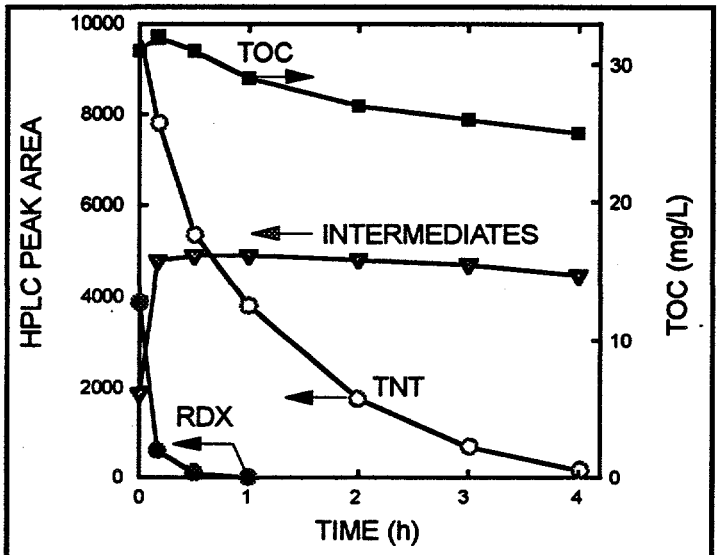


Figure 13. Photocatalytic degradation of LAAP pinkwater under anaerobic conditions.

Ion Chromatography

Ion chromatography was used to determine the absence or presence of nitrite, nitrate, and ammonium in the final reaction solutions. All percentages are based upon the final disposition of the nitrogen, versus the nitrogen available as explosive in the starting material. The balance of nitrogen is accounted for as unreacted explosive, intermediates, or precipitation of the catalyst surface. Aerobic TNT degradation produced significant amounts of ammonium (16% of the available nitrogen) and nitrate (12%) after 5 hours of reaction. Anaerobic TNT destruction generated the same amount of ammonium, but only 1% of the nitrogen was measured as nitrite and only 2% was measured as nitrite. The aerobic RDX reactions resulted in 48% nitrate, 1% nitrite, and 15% ammonium. The anaerobic RDX reaction produced <1% nitrate, <1% nitrite, and 4% ammonium products.

Table 4.
Ionic Compounds in Final Reaction Mixtures.

Reaction	Nitrate	Nitrite	Ammonium	Balance of N
TNT Aerobic	12%	<1%	16%	71%
TNT Anaerobic	<1%	2%	16%	81%
RDX Aerobic	48%	<1%	15%	64%
RDX Anaerobic	<1%	<1%	4%	94%
HMX Aerobic	20%	0%	23%	57%
HMX Anaerobic	<1%	0%	8%	91%

Our experiments indicate that oxidative conditions favor nitrate production, and reductive conditions favor ammonium production. This is in agreement with a mechanism where ammonia is produced first (through reductive elimination) and is then oxidized in solution to nitrite and then nitrate with molecular oxygen. The reaction of nitrite to nitrate is fast under aerobic conditions, and therefore nitrite does not build to appreciable levels. In the anaerobic cases, the ammonium is created, but not oxidized. Further ammonium production could be inhibited by this ammonium concentration. Ammonium production in TNT solutions does not seem to be affected by the presence or absence of oxygen. Therefore, the process by which ammonium is formed is oxygen-insensitive. This could be a function of the conjugated ring in TNT, whereas the other two compounds are aliphatic. Reductive elimination from a conjugated system is much more difficult than from an aliphatic system.

We believe that the nitro groups are being reduced to amines, but that the release of the amines from the cyclic ring is a slow step. Therefore, there is less chance for nitrate production because the rate of production of ammonium from TNT is not as fast as in the case of the aliphatic nitros. Recall that TNT reaction rates are very similar under nitrogen and oxygen, but that more intermediates are formed when aerobic conditions exist. We believe that future work will show these intermediates to be various phenyl amines. Mass balance calculations showed poor closure in some instances. In these cases, the remaining C, H, N, and O has been found to be deposited on the catalyst [19]. The possibility that this material will foul the catalyst is being investigated.

Excimer Laser Remediation Studies

Introduction to LASER work

Previous researchers have studied the photochemical destruction of explosives using conventional light sources, such as arc lamps. The unique characteristics of lasers indicate several reasons to consider their use as alternative sources. First, lasers often have very high peak intensity, i.e., mega or gigawatt. For this reason, the kinetics of non- linear and multi-step photochemistry may be enhanced over that of light sources with lower flux. In fact, saturation effects may even be observed, which are generally not possible with conventional sources.

Second, the highly directional nature of lasers minimizes efficiency losses due to stray light. Directing the entire output of the laser on the sample, without the need for complex optics, is easily accomplished.

Third, it is possible to take advantage of the fact that lasers emit over a very narrow band of wavelengths. Typically, photochemistry is only initiated by photons within the absorption band of the photoactive species. Conventional light sources tend to have very broad emission spectra, so that much of the energy produced is thermalized and therefore wasted.

Fourth, the quantum yield of photo-reactions might be expected to increase with higher energy photons, because excitation to a different electronic state might alter the chemical mechanism for dissociation.

Finally, the relative economics of photochemistry (expressed as cost per photon produced, or better still, the cost per waste molecule degraded), may be favorable relative to arc lamp and other sources. For each of these reasons, we undertook a brief study of the use of lasers as initiators for photochemical destruction of explosives.

Laser experimental

Laser irradiation was done with either a Questek Series 2000 ArF excimer system with output at 193 nm, or a Lambda Physik XeCl system with output at 308 nm. Solutions containing the appropriate concentrations of TNT, RDX, and pinkwater were placed in 1 cm quartz cuvettes with fluorocarbon caps for

light exposure. Solutions were not allowed to contact non-fluorinated polymeric surfaces, due to the strong adsorption of the explosives to such surfaces. A small fluorocarbon-coated stir bar was used in each cuvette to enhance mixing during exposure. However, we first verified that this small polymer surface area did not noticeably alter the explosive concentrations.

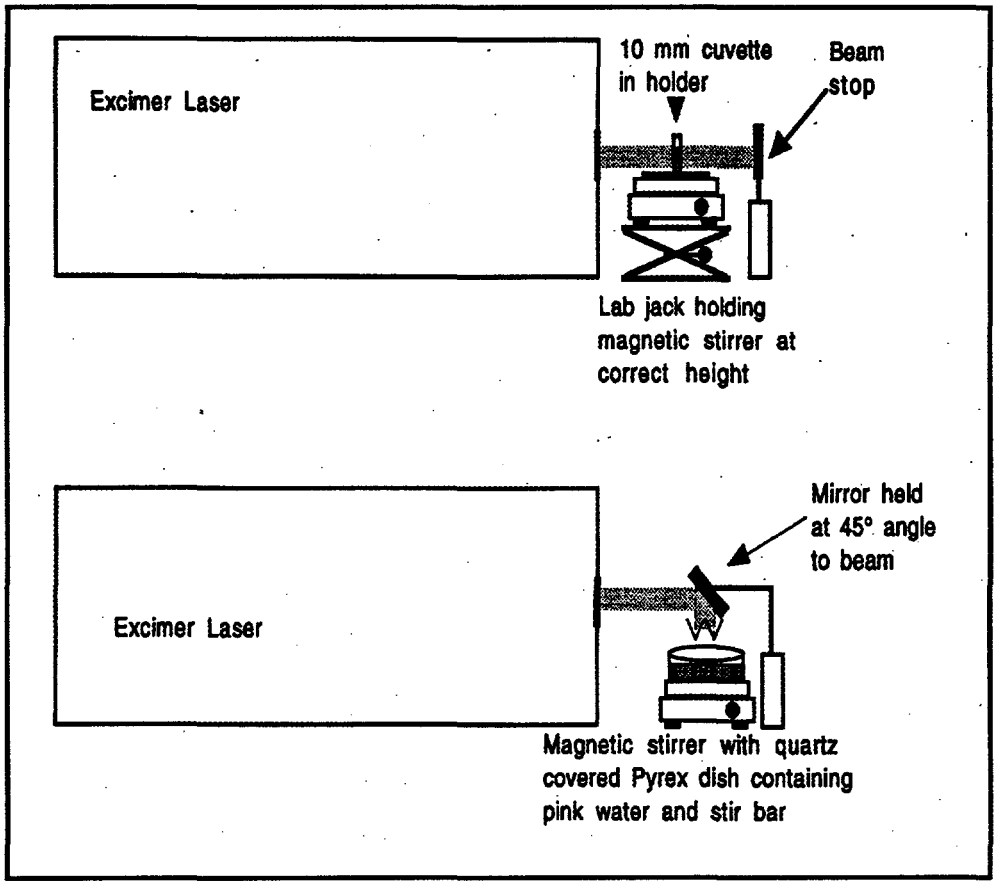


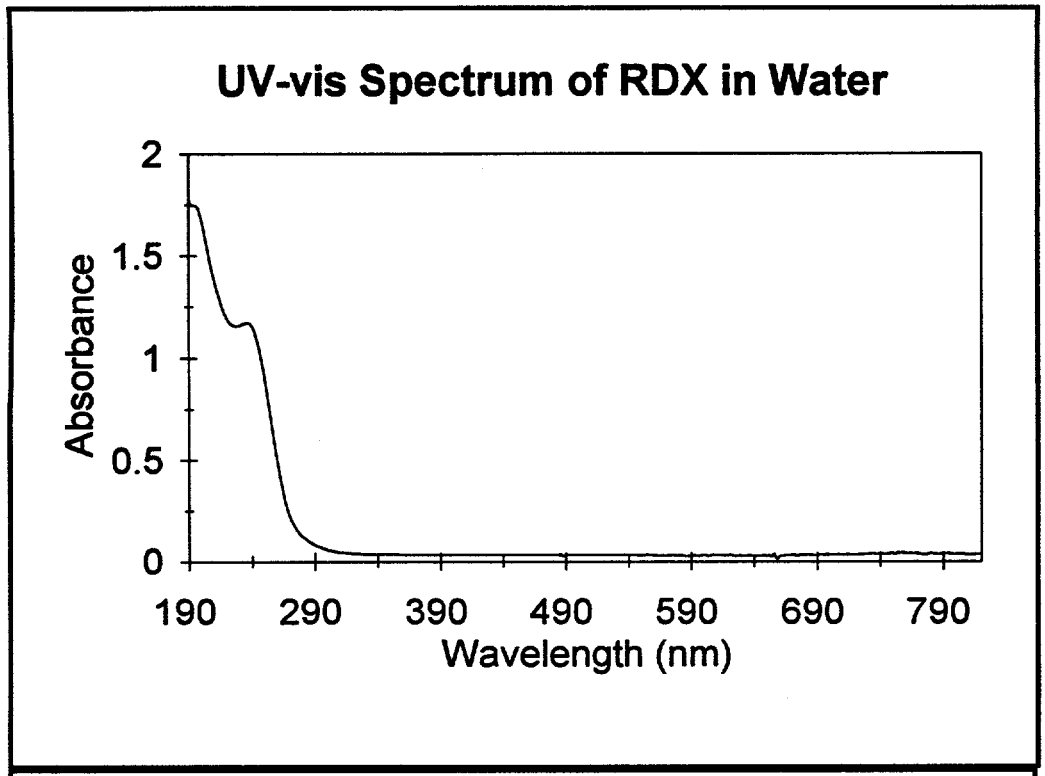
Figure 14. Laser irradiation of pinkwater samples.

Most exposures were done with 2 ml samples. The output from the excimer laser had a rectangular cross-section, approximately 1 cm high by 2.2 cm wide. With this geometry, half the sample height and full sample width was illuminated, but 54 per cent of the photons did not illuminate any part of the sample. The laser was typically run at 2 Hz and 200-230 mJ per pulse. Laser pulse rate was found not to influence the rate or extent of photo-destruction of explosive. Similarly, stirring rate was not important above a critical minimum; in the absence of stirring, the degradation efficiency was significantly reduced.

UV-visible absorption spectrophotometry was done on standard solutions, as well as all starting solutions prior to exposure, to determine molar absorptivities and initial concentrations. Explosive concentrations after light exposure were measured with high performance liquid chromatography (HPLC).

Laser Discussion

As the first step in selecting the best candidate exposure wavelengths for this study, we took electronic absorption spectra for both of the pure explosives, in addition to pinkwater. These data are shown in Figures 15a and 15b. Both TNT and RDX exhibit the strongest absorption at the shortest wavelengths measurable by our spectrophotometer. The apparent drop-off in absorbance below 190 nm is an instrumental artifact. TNT and RDX exhibit shoulders at approximately 232 and 237 nm, respectively, with corresponding molar absorptivities of 16700 and 7200 $M^{-1}cm^{-1}$. Unfortunately, absorption of light by photochemical byproducts made post-exposure quantitation of starting materials unreliable, thus necessitating the use of HPLC to track the degradation process. Addition of hydrogen peroxide to these solutions did not significantly alter quantitation of unexposed samples, since the molar absorptivity of hydrogen peroxide at these two wavelengths was in the 45-60 $M^{-1}cm^{-1}$ range.



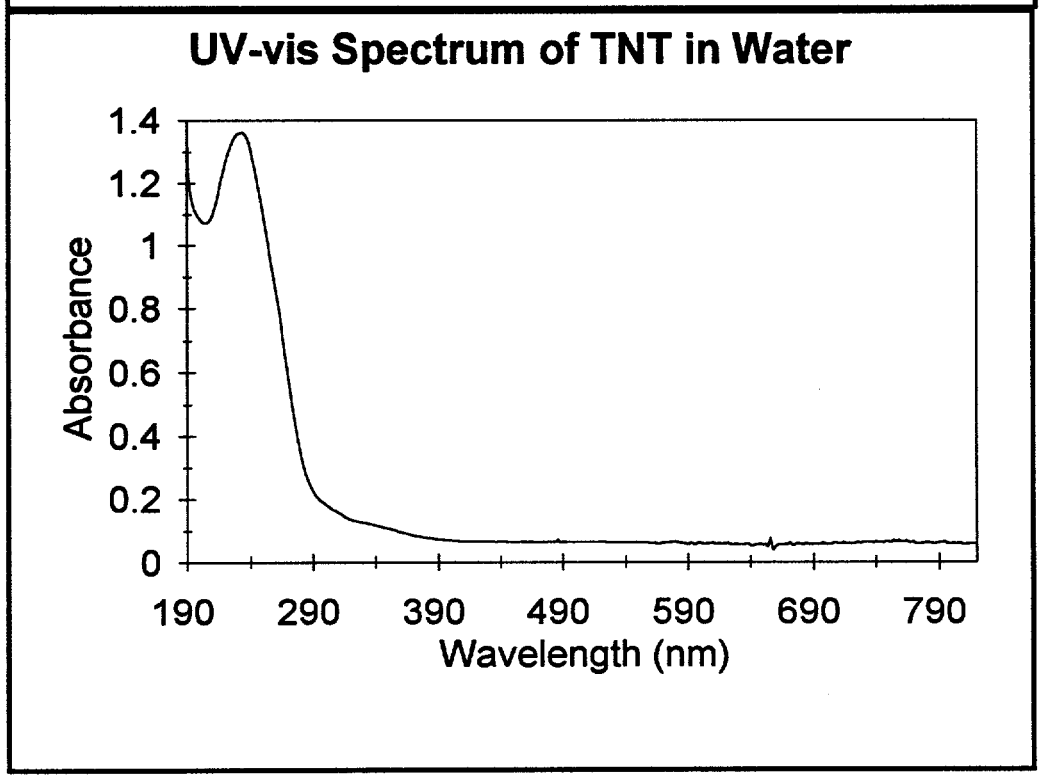


Figure 15a and 15b. Ultraviolet spectra of RDX and TNT.

Although the photochemistry of each of the explosives studied here was interesting in its own right, the scope of

the work did not allow a fundamental investigation of photochemical rates and pathways. Instead, we concentrated on the rate at which the most common waste product, pinkwater, could be remediated. Since pinkwater is a mixture of components, the study was necessarily phenomenological. However, as will be shown below, these data did allow a preliminary assessment of the efficacy of photochemical explosive remediation with a laser source relative to conventional arc sources.

For pure photochemical degradation, i.e., the case in which degradation is driven solely by the absorption of photons and not subsequent interactions with other species, the reaction rate is first order in excited state reactants. This has been treated for both optically dilute and optically concentrated cases [20]:

$$-dA/dt = k\{ 1- \exp[-A(\ln 10)]\} \quad (1)$$

where A is the total absorbance through the sample (along the photochemical exposure axis), k is a rate constant, and t is time (or energy, if total photo-exposure is proportional to exposure time). Solving for t yields

$$t = -A(\ln 10)/k - (1/k)\ln\{1- \exp[-A(\ln 10)]\} \quad (2)$$

For very small A, the first term of Eqn. 2 drops out, and the second term simplifies to the well-known exponential (first order) dependence of absorbance on time or exposure. For a system with a single absorber, Beer's Law allows a direct substitution of concentration for absorbance. Conversely, when A is large, the second term drops out, and the first term predicts a linear dependence of absorbance (or concentration) on exposure. This linear dependence, or constant rate of photodegradation, is the result of the sample absorbing effectively all the light, so that the number of excited states does not decrease as long as the sample remains optically concentrated.

The concentrations of TNT and RDX in the pinkwater used in this study (received from LAAP) were 176 and 95 ppm, respectively. Note that these values are higher than the saturated values determined in our laboratory. The difference is due to the matrix effects of various ions in the tapwater. The total absorbances in these sample cuvettes were 12.9 and 3.1, respectively. Figures 16 and 17 show the dependence of TNT and RDX concentration on total photo-exposure, as measured in joules of 193 nm light. The semi-log fits confirm an exponential exposure dependence, even though both explosives are clearly optically

concentrated. We should note that the single absorber assumption cited above is not satisfied. In addition, there may be a complex combination of reactions involving both explosives and their reaction products. Nevertheless, the exponential dependence was not expected.

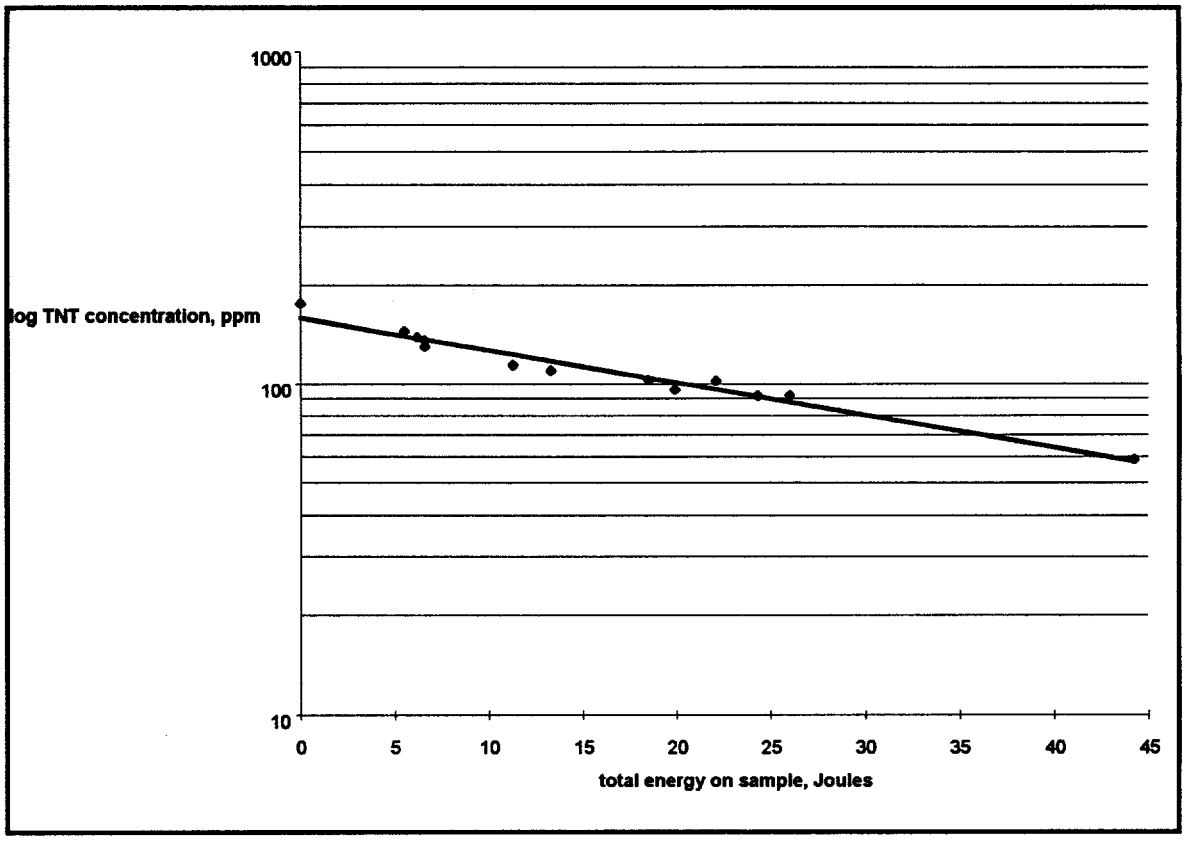


Figure 16. TNT degradation using 193nm laser light.

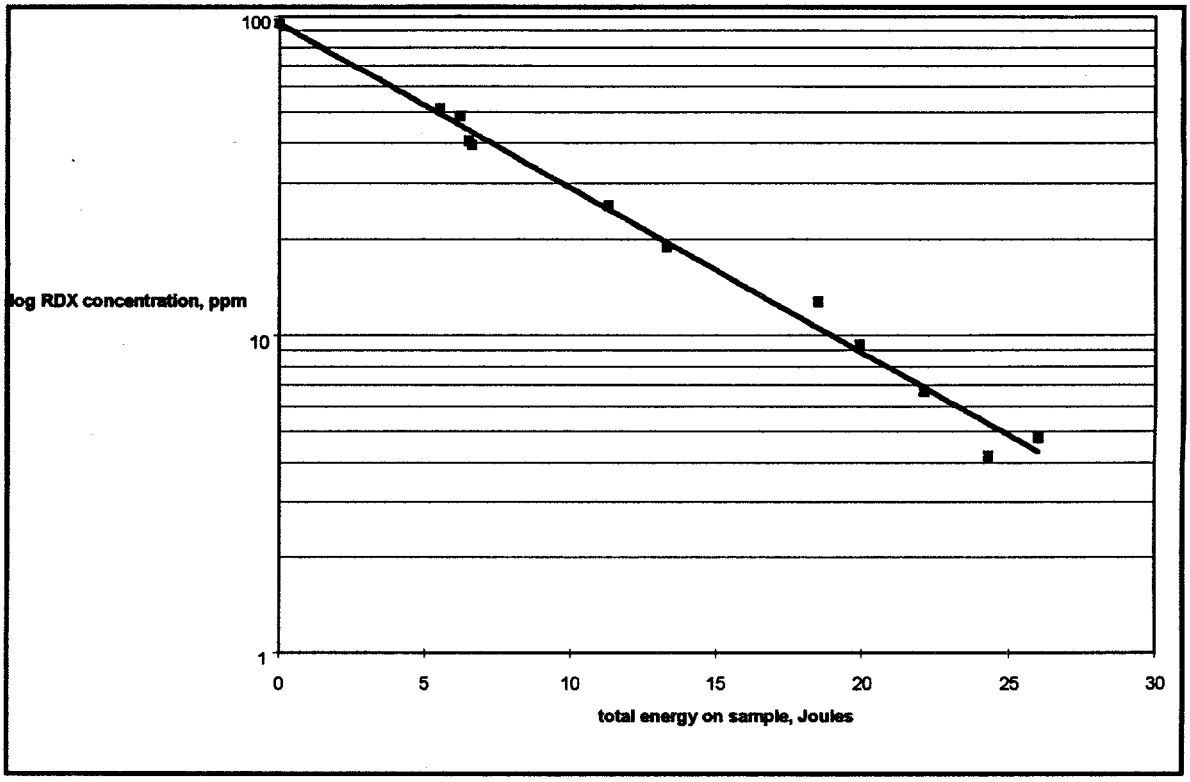


Figure 17. RDX degradation using 193nm laser light.

The slopes of the lines shown in Figures 16 and 17 are minus 0.023 and minus 0.12 J^{-1}, respectively, which give loss rates of approximately 2.3 per cent and 11 per cent per joule incident energy. Similar data taken with pure TNT, at a starting concentration of 45 ppm, also show an exponential concentration dependence, but with a slope of 0.1 J^{-1}. This higher slope results, at least in part, from the higher fraction of light absorbed by TNT in this case, since there is no RDX competing for those photons. Of course, the single absorber assumption was true, even in the pure TNT experiment, only at the beginning of the exposure, since TNT photoproducts also absorbed significantly at 193 nm.

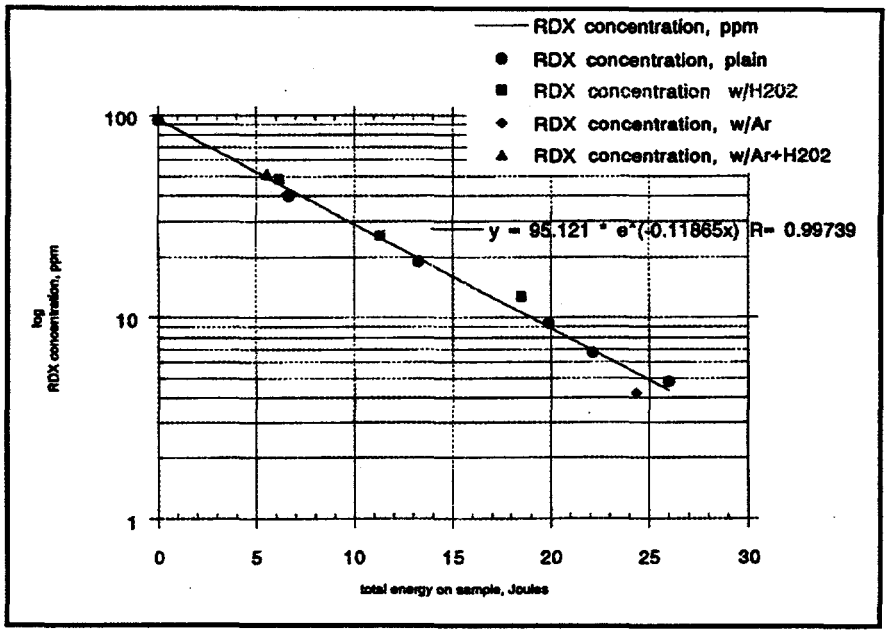


Figure 18. Decomposition of RDX under various reaction conditions.

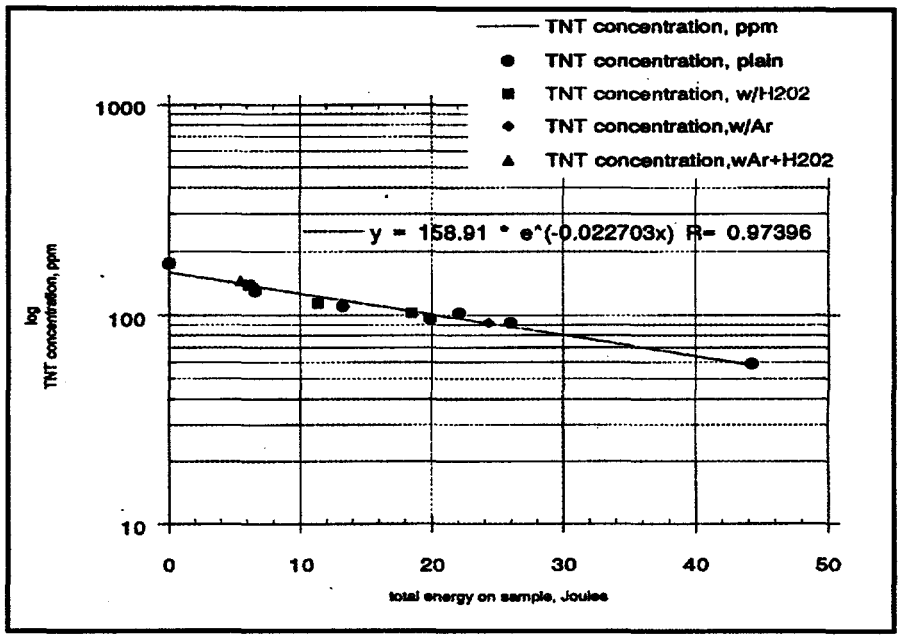


Figure 19. Decomposition of TNT under various reaction conditions.

There have been suggestions in the literature that the rate of photochemical destruction of explosives may be increased by the elimination of oxidative conditions by bubbling argon gas through the sample during exposure [16]. No significant effect on the rate of decomposition was observed with argon bubbling, for either component of pinkwater, as shown in Figures 18 and 19. However, the distribution of degradation byproducts varies significantly, with oxidative conditions producing considerably more products than reductive conditions, as was also seen with N_2.

The spectra shown in Figure 15 would lead one to suspect that the shortest wavelength exposure possible, e.g. 193 nm, would be most efficacious in inducing photochemistry. However, at least one other study [16] suggested that the longer wavelengths found in broadband sources contribute significantly to the initiation of the photochemistry of these materials. Therefore, we attempted to photodegrade both TNT and RDX using 308 nm light from a XeCl excimer laser. As shown in Figure 20, an exposure of 19 J on the 2 ml sample resulted in only a 10-15 per cent reduction in RDX concentration.

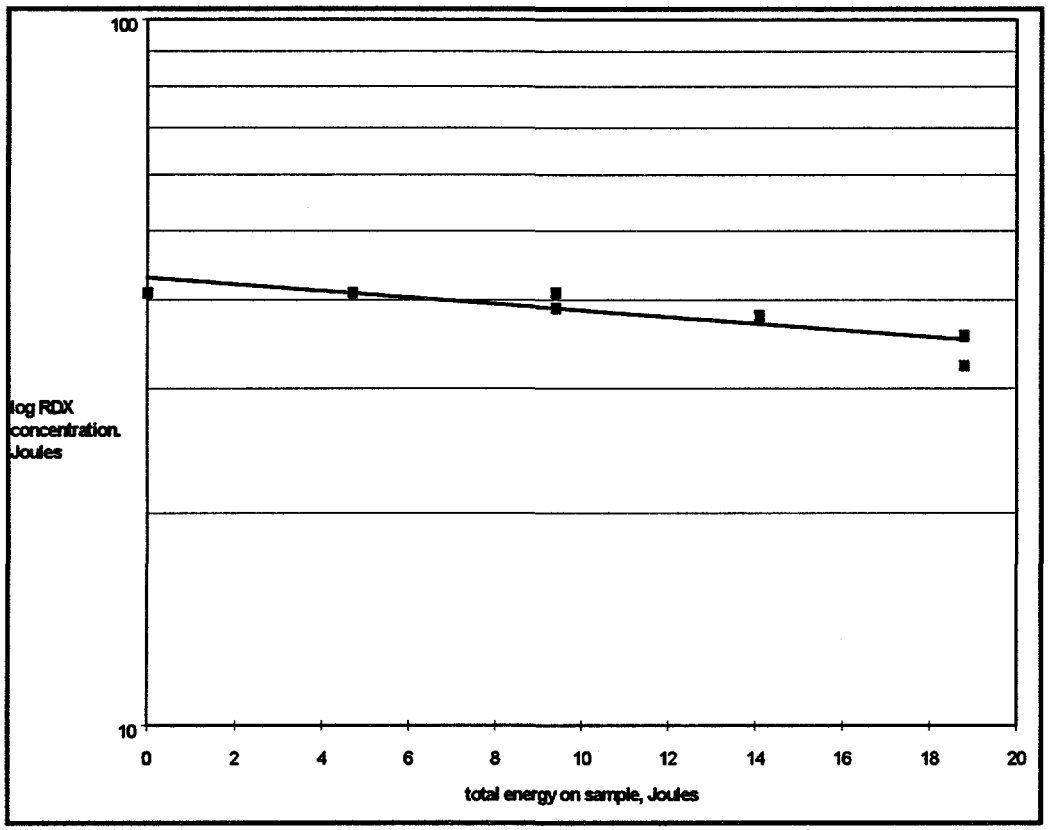


Figure 20. Decomposition of RDX using 308nm laser light

Exposure at 308 nm was similarly ineffective for TNT, as shown in Figure 21. In contrast to 193 nm exposure, however, there was a significant increase in the rates of photolysis of TNT when hydrogen peroxide was added to the solution.

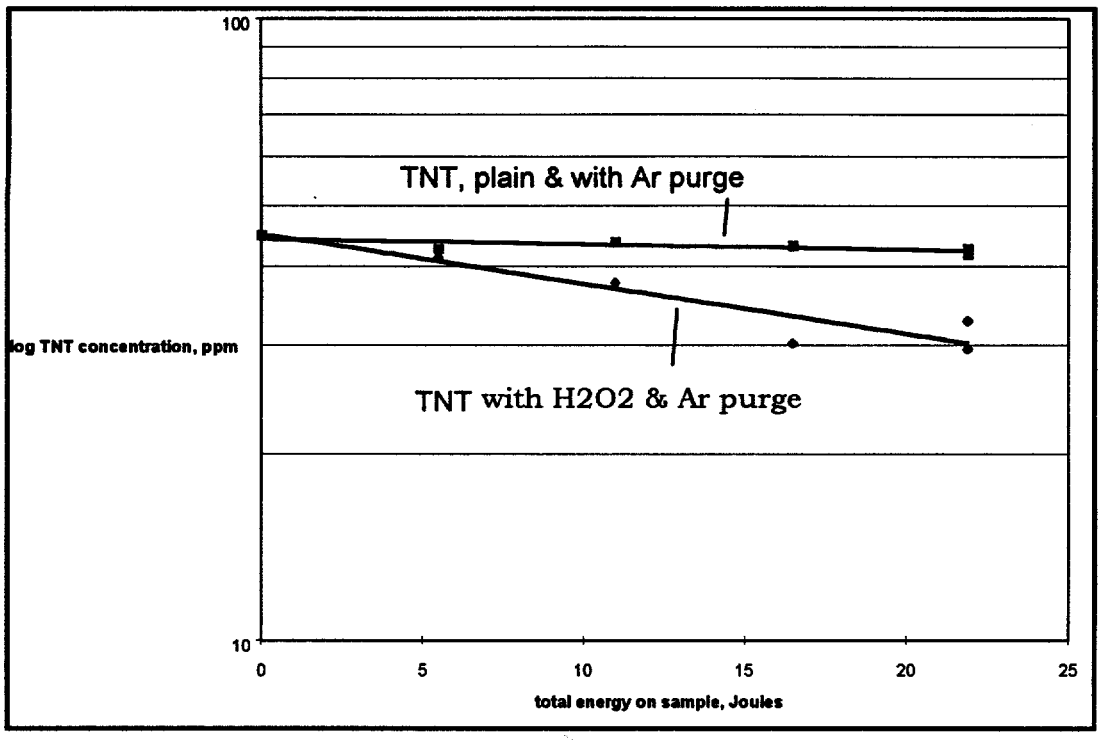


Figure 21. Degradation of TNT using 308nm laser light. Solution containing H_2O_2 showed significantly higher rate of photolysis.

In order to calculate achievable throughputs of remediated waste based on the above data, a few assumptions were made. For the analysis given below, we will assume that in a large scale remediation reactor, the condition of an effectively infinite explosive reservoir could be achieved, and that linear loss kinetics could be maintained throughout the exposure cycle. If this assumption is not justified, the linear loss rates of 0.07μm and 0.09μm per J for TNT and RDX will yield throughput estimates that are too high. In addition, we will assume that loss of TNT is the rate-determining step, since its initial loss rate is larger than that of RDX. However, pinkwaters and other explosive waste streams vary considerably in composition. Therefore, the throughputs given below could be underestimated for the case in which RDX was the predominate component.

Since the laser was operated at an average power level of 91 mW (measured as power incident on the sample), and with a

starting concentration of 176 ppm TNT, we calculate the throughput for remediated solution as 0.0046 ml/s. However, the average power level of this laser can be scaled up by a factor of 600. Scaling throughput to this power level and using 25 ppm starting concentration of TNT (as assumed in the pilot plant of ref. 20) yields a rate of 19.2 ml/s, or 0.3 gal/min. This compares to the 1-4 gpm flow rates demonstrated in ref. 20, in which a pilot system was developed using one hundred and twelve 65 watt UV lamps and ozonation of the waste stream.

The reason that the throughput of the laser-based system compares as favorably as it does to the conventional lamp system, even though no oxidizer was added, is due to a fifty-fold increase in quantum yield for photo-destruction of explosive at 193 nm compared to longer wavelengths. This quantum yield is reported to be approximately 10^{-3} at wavelength of 250 nm and longer [22], whereas we calculate the yield for TNT using 193 nm light to be 0.05.

Thus, the hoped for increase in efficiency of photo-degradation with shorter wavelength, higher energy photons was realized. A true engineering cost profile would require testing of the assumptions outlined above, as well as analysis of relative equipment costs for laser sources compared to arc lamps, which was beyond the scope of our initial study.

Biological remediation

It was noted throughout these experiments that although the TNT and RDX concentration decreased, it was usually not mineralized, i.e. converted to inorganics such as CO, CO_2, N_2, H_2O, and so forth. Rather, stable intermediates were formed. In keeping with the initial intent of the project to decompose explosives into "more environmentally acceptable products", it was necessary to evaluate the toxicity of the products that are produced to determine if they are indeed "more environmentally acceptable" or biodegradable than the parent explosive molecules. We did not propose to fully investigate biological materials to degrade either the explosives or the decomposition products. However, in order to obtain the biological and toxicity data, aerobic and anaerobic bacteria were trained to attack these materials. We thus obtained some preliminary data that will indicate whether or not biological treatments should be examined in greater detail.

Bacterial Acclimation

To acclimate bacteria for use in the treatment comparisons, both aerobic and anaerobic batch-fed reactors were operated for several weeks. The initial seed bacteria were taken from several sources, including municipal mixed liquor volatile suspended solids (MLVSS), papermill sludge, and lab-pure cultures (University of Arizona).

The measurement of activity in the acclimating cultures were oxygen uptake rate (OUR) and decrease in TNT concentration via Silas-Mason testing. Increasing the strength of pinkwater in the feed mixture yielded higher OURs and continued degradation of TNT. These were taken as indications of acclimation to the pinkwater.

Seed bacteria consisting of a mix of return-activated sludge from a domestic wastewater treatment plant and from a paper and pulp treatment facility was acclimated to pinkwater for aerobic and anaerobic processes. Acclimation was carried out over a span of five weeks by gradually increasing the content of pinkwater from 5% to 25% in increments of 5% each week. Primary effluent (PE) from domestic wastewater plant was added to facilitate gradual acclimation during the first few weeks and also to provide certain essential micronutrients required for bacterial growth during the later weeks. Additionally, 20 mg/l of ammonium phosphate ($NH_4H_2PO_4$) was added to ensure sufficient availability of free ammonium. Table 5 gives the schedule of acclimation process adopted for the entire period of acclimation.

Table 5. History of Operation and Acclimation of the Biological Reactor.

Week	Ingredient
First Week	5% pinkwater + 15% PE + 80% DI-water + 20 mg/l Ammonium phosphate
Second Week	10% pinkwater + 10% PE + 80% DI-water + 20 mg/l Ammonium phosphate
Third Week	15% pinkwater + 5% PE + 80% DI-water + 20 mg/l Ammonium phosphate
Fourth Week	20% pinkwater + 5% PE + 75% DI-water + 20 mg/l Ammonium phosphate
Fifth Week	25% pinkwater + 5% PE + 75% DI-water + 20 mg/l Ammonium phosphate

Aerobic bacterial acclimation was monitored by periodic measurement of oxygen uptake rate (OUR). An increase in oxygen uptake rate was observed with increase in percent of pinkwater, indicating good acclimation of seed bacteria. Table 6 gives the oxygen uptake rates recorded for the aerobic acclimating bacteria.

Table 6.
Oxygen Uptake Rates of the Aerobic Acclimation Reactors.

Ingredients	Week/Day	Oxygen Uptake Rate (mg/l-
15% pinkwater + 50% PE	3rd week/day = 0	0.047
15% pinkwater + 50% PE	3rd week/day = 5	0.049
15% pinkwater + 5% PE	3rd week/day = 7	0.061
20% pinkwater + 50% PE	4th week/day = 0	0.017
20% pinkwater + 50% PE	4th week/day = 7	0.095
25% pinkwater + 50% PE	5th week/day = 0	0.025
25% pinkwater + 50% PE	5th week/day = 7	0.165

An anaerobic culture was grown in a sealed anaerobic culture bottle kept on a shaker table maintained at 30°C. The culture bottle of anaerobic bacteria was flushed twice a week with nitrogen gas to maintain anaerobic conditions.

Toxicity Measurement

The MicroTox procedure was used as an indicator of the relative toxicity of wastewater samples. An initial experiment was conducted to select the test exposure at which a maximum response occurred. This maximum response time will vary as a function of the type of wastewater compounds. For samples of actual and synthetic pinkwater, MicroTox responses were measured at exposure times of 5, 15, and 30 minutes. As indicated by the data in Table 7, both types of pinkwater displayed a common response pattern of increasing response as a function of test exposure time. To identify the time of maximum response, additional testing of

the synthetic wastewater was conducted at exposure times of 45 and 60 minutes. A rather constant response was indicated at any exposure beyond 30 minutes, so a 30-minute exposure time was selected for all MicroTox measurements of pinkwater treatment.

Table 7.
Toxicity Measurement of Pinkwater (in Toxicity Units, TU)

Sample	5 min	15 min	30 min	45 min	60 min
LAAP pinkwater	13.7	20.96	32.36	50.51	47.4
Laboratory-prepared pinkwater	5.26	2.88	45.15	39.06	37.04

Co-Substrate Studies

Past research had reported a benefit in pinkwater biodegradation from the availability of alternate sources of organic carbon. For this research project, preliminary testing was used to screen several co-substrate sources, including municipal primary wastewater (composed of a range of relatively simple organic carbon compounds), glucose, and yeast extract (see Table 8). Extensive TNT biodegradation occurred in two days with the addition of 2500-5000 mg/l of yeast extract.

The benefits of yeast extract addition will be important in process design. If the benefit of cosubstrate addition is indirect (i.e. merely associated with supporting the rapid growth of a large bacterial population), then several treatment unit designs may be used that involve sludge contact. If, however, the cosubstrate effect is direct (i.e. associated with biomass growth in the presence of both pinkwater and soluble cosubstrate), the provisions for addition to the influent liquid must be emphasized in the biological process design. Further study would be focused on determining the direct or indirect aspect of cosubstrate benefit.

Table 8.
Effect of Co-Substrate Addition.

Sample Description	Absorbance at 525 nm	TNT (mg/l)
Day = 0; 50% LAAP + 50% MQ Water	0.287	45.6
Day = 0; 50% LAAP + 50% Primary Effluent	0.305	48.4
Day = 0; 50% LAAP + 250 mg/l Glucose + Nutrients	0.274	43.5
Day = 2; 50% LAAP + 50% MO Water	0.247	39.2
Day = 2; 50% LAAP + 50% Primary Effluent	0.258	41.0
Day = 2; 50% LAAP + 250 mg/l Glucose + Nutrients	0.199	31.6
Day = 4; 50% LAAP + 50% MQ Water	0.209	33.2
Day = 4; 50% LAAP + 50% Primary Effluent	0.165	26.2
Day = 0;100% LAAP + 250 mg/l Glucose + Nutrients	0.158	25.1
Day = 0;100% LAAP + 250 mg/l Yeast Extract + Nutrients	0.602	95.3
Day = 0; 100% LAAP + 2500 mg/l Yeast Extract + Nutrients	0.587	92.9
Day = 0;100% LAAP + 5000 mg/l Yeast Extract + Nutrients	0.572	90.6
Day = 2;100% LAAP + 250 mg/l Yeast Extract + Nutrients	0.471	74.6
Day = 2;100% LAAP + 2500 mg/l Yeast Extract + Nutrients	0.056	8.9
Day = 2;100% LAAP + 5000 mg/l Yeast Extract + Nutrients	0.048	7.6

Controls:
1. Dilution with MQ Water
2. Primary Effluent as Co-metabolite
3. Glucose as Co-metabolite
4. Yeast Extract at Different Concentrations

Notes:

- TNT concentrations were determined by HPLC analysis.
- All samples were filtered through 0.45 µm syringe filter to remove any solids.
- Absorbance at 525 nm was recorded according to the protocol for the Silas-Mason Test.
- LAAP = Louisiana Army Ammunition Plant pinkwater.

Aerobic Treatability

The photocatalytic pretreatment of pinkwater not only reduced the bioeffluent loading of TOC, but also improved the rate and extent of biodegradation of the residual pollutants. Nearly all aerobic degradation was complete after four days. Regardless of the method of pretreatment, (ozonation, hydrogen peroxide, photocatalysis, etc.) the effectiveness was essentially equal with respect to reduction of bioinfluent loading as well as rate and extent of biodegradation of the residual pollutants. Data is presented for TOC (Table 9), MicroTox (Table 10), Absorbance (Table 11), and total suspended solids (Table 12). The synthetic wastewater was more easily biodegraded than the actual pinkwater under comparable conditions. This may be due to the presence of different ions or other materials, but the exact reason for this difference was not determined.

Table 9.
Results of Aerobic Treatment of Synthetic and Actual Pinkwater. Test Parameter: Total Organic Carbon (TOC), mg/l

	Day 0	Day 2	Day 4	Day 7
LAAP Control	975.8	200.8	86.3	42.29
SPW Control	643.6	118.26	43.11	42.29
LAAP, ozone, 254nm, TiO_2 catalyst	988	141.32	80	63.75
LAAP, ozone, 254nm, no catalyst	722.2	125.72	47.67	43.73
LAAP, 365nm, TiO_2 catalyst	740.6	132.84	81	61.45
LAAP, N_2 purge, 365nm, TiO_2 catalyst	877.2	125.7	84.5	61.05
SPW, ozone, 254 nm	744.6	115.14	52.4	43.69
LAAP = pinkwater from Louisiana Army Ammunition Plant SPW = laboratory-prepared pinkwater				

Table 10.
Results of Aerobic Treatment of Synthetic and Actual Pinkwater. Test Parameter: MicroTox Toxicity (Toxicity Units)

	DAY					
	0	2	4	7	14	30
LAAP Control	77.52	2.64			1.3	
SPW Control	18.21	0.69			0.87	
LAAP, ozone, 254nm, TiO_2 catalyst	55.25	1.7			1.18	
LAAP, ozone, 254nm, no catalyst	Not detected	Not detected			Not detected	
LAAP, 365nm, TiO_2 catalyst	76.92	1.95			1.31	
LAAP, N_2 purge, 365nm, TiO_2 catalyst	29.85	2.05			1.25	
SPW, ozone, 254 nm	Not detected	Not detected			Not detected	

LAAP = pinkwater from Louisiana Army Ammunition Plant
SPW = laboratory-prepared pinkwater

Table 11.
Results of Aerobic Treatment of Synthetic and Actual Pinkwater.
Test Parameter: Absorbance of Area Under Scan 200-390nm

	DAY					
	0	2	4	7	14	30
LAAP Control	1414	1097	822	529	483	
SPW Control	1010	829	373	321	283	
LAAP, ozone, 254nm, TiO_2 catalyst	1231	1051	561	468	430	
LAAP, ozone, 254nm, no catalyst	951	764	527	478	448	
LAAP, 365nm, TiO_2 catalyst	1154	1076	539	446	365	
LAAP, N_2 purge, 365nm, TiO_2 catalyst	1275	964	552	459	384	
SPW, ozone, 254 nm	986	894	363	288	276	

LAAP = pinkwater from Louisiana Army Ammunition Plant
SPW = laboratory-prepared pinkwater

Table 12.
Results of Aerobic Treatment of Synthetic and Actual Pinkwater.
Test Parameter: Total Suspended Solids (TSS) mg/l

	DAY				
	Day 0	Day 2	Day 4	Day 7	Day 14
LAAP Control	180	236	246	208	146
SPW Control	160	274	310	206	194
LAAP, ozone, 254nm, TiO_2 catalyst	134	242	168	58	80
LAAP, ozone, 254nm, no catalyst	164	302	200	222	158
LAAP, 365nm, TiO_2 catalyst	154	248	242	238	206
LAAP, N_2 purge, 365nm, TiO_2 catalyst	108	312	180	154	84
SPW, ozone, 254 nm	162	248	130	164	116

LAAP = pinkwater from Louisiana Army Ammunition Plant
SPW = laboratory-prepared pinkwater

The added cosubstrate and nutrients supported significant bacterial growth in all test runs. The associated soluble TOC was removed and the total suspended solids (TSS) increased. Any toxicity of bioinfluents was almost completely removed in only two days of biotreatment, indicating that no biorecalcitrant, toxic intermediate was formed under any condition studied. The absorbance areas of all runs were quite similar after two days of biotreatment.

In control runs using pinkwaters without any preliminary physical or chemical treatment, TNT was degraded but RDX resisted biotreatment. At high TNT concentrations, bacteria can be adversely affected.

Several secondary points should be noted:

First, for any physical or chemical treatment considered prior to biotreatment, it would be desirable to obtain focused destruction of RDX and TNT. Thus, at any reduced level of physical or chemical treatment, the bioinfluent RDX would be minimized, and primarily biodegradable TNT would remain.

Second, the biodegradation of TNT and toxicity was more rapid in synthetic pinkwater than actual pinkwater. This effect indicates the significance of other background pollutants on the rate of destruction of measured target properties. It will be important to characterize these kinetic influences in each process wastewater, rather than design solely on the basis of initial TNT and RDX concentrations.

Third, the bioeffluent TNT concentration was never reduced below 10 mg/l via biodegradation under any condition. When the bioinfluent TNT was below 10 mg/l, no further reduction was measured during biotreatment. This threshold effect may reflect a mass transfer or adsorption-desorption phenomenon. Specific process engineering adjustments can be made to minimize or offset such an effect, and further testing can identify the bases of the effect.

Clearly, aerobic biotreatment can be used to remove any residual toxicity following physical or chemical treatment, could potentially reduce the TNT loading prior to physical or chemical treatment, but cannot be used for the direct destruction of RDX in pinkwater.

Anaerobic Treatability

Inclusion of a 14-day anaerobic treatment was examined as a possible alternative to the aerobic treatment.

If treated directly (without pretreatment), the synthetic wastewater control was more easily biodegraded than the actual pinkwater control, but following pretreatment, synthetic pinkwater was less biodegradable than the actual pinkwater cases. In both cases, the anaerobic treatment was considerable slower and less effective in treating the pinkwater than aerobic treatment. We therefore conclude that anaerobic treatment does not appear to be desirable as a method of handling the pinkwater. However, further work with anaerobic bacteria will be required to establish the method of treatment for byproduct biomass sludge.

Biotreatment Summary

Pretreatment of pinkwater in several variants has been shown to be an effective methodology for producing biodegradable intermediates. Anaerobic treatment exhibited no net benefit for biodegradation of any wastewater tested in this project. Since anaerobic conditions are more difficult to maintain in the types of treatment plants commonly available, we believe that aerobic treatment is preferable.

Although not discussed in detail in this report, the most effective pretreatment process examined consisted of illuminated (254nm) ozone. The reaction time, however, was very long (120 minutes). This combination produced a maximum amount of TNT and RDX destruction with minimal production of byproducts. All other treatments, with reaction times ranging from only 5 to 30 minutes, were essentially equal in terms of rate and extent of biodegradation and toxicity. These other treatments produced more byproducts, but since these products are easily treated biologically, the shorter reaction times could be beneficial in terms of processing large volumes of wastewater.

The viability of coupling physical or chemical pretreatment with aerobic biological processing to produce biodegradable intermediates is clearly indicated by these experiments.

Optimization of operating parameters should be the next research effort.

Heterogeneous Photocatalysis with External Oxidant Additions

Our results have shown that oxidation with O_3, or O_3 and H_2O_2, provided effluents with less toxicity than those which were produced with "O_2 only" as the oxidant. The absolute toxicity values were always higher for LAAP pinkwater than laboratory-prepared pinkwater treated in the identical manner. This would be expected since the TNT and RDX concentrations were higher in the corresponding LAAP materials.

In general, the largest removals of TNT and RDX were achieved when O_3 plus H_2O_2 was used with TiO_2 illuminated with 254nm light. The 365nm lamp did activate the TiO_2, but apparently was much less effective in decomposing O_3 and H_2O_2 to radicals, such as the hydroxyl radical.

In general, a number of observations concerning the addition of various oxidants to the reaction mixture can be made. Specifically:

- In the presence of either 254nm or 365nm illuminated TiO_2, O_3 or the combination of O_3 and H_2O_2 was superior to O_2 in treating either LAAP or synthetic pinkwater.
- UV 254nm was more efficient than 365nm as a photon source in activating TiO_2 and in decomposing O_3 and O_3 plus H_2O_2.
- The addition of the same mass of H_2O_2 or O_3 in a single or multiple doses did not affect treatment performance. However, ozone transfer was enhanced when H_2O_2 was present in the UVR, more so when the same mass was added in a single dose rather than in four equally spaced additions over the run.
- UV scans and HPLC chromatograms predict the presence of multiple partial oxidation products directly related to reaction conditions.

Nickel-Titanium Dioxide Heterogeneous Photocatalysis Experiments

In addition to examining the effect of different oxidizing conditions, we briefly tested the effect of different catalysts. A Nickel-Titanium Dioxide ($Ni-TiO_2$) catalyst produced at Sandia National Laboratories was tested to see if it would out-perform the standard anatase form of TiO_2 in the destruction of TNT and RDX. Experiments were conducted in oxidative (ozone) and reductive (nitrogen) atmospheres. One experiment without catalyst, but with ozone in the presence of 254nm illumination, was also carried out.

The best results in terms of TNT and RDX were obtained when no semi-conductor catalyst was present in the UVR. For this run, RDX was completely destroyed between 15 and 30 minutes of reaction time, while approximately 94% of the TNT was converted within 120 minutes.

Comparing the data from the nickel-titanium catalyst and standard titanium dioxide, it appears that equivalent results were obtained for TNT (72%) over 2.0 hours of reaction regardless of the types of gas atmosphere, oxidative or reductive, in the UVR. RDX was reduced by 98% in 120 minutes when ozone was present in the reactor but 100% removal occurred with nitrogen between 60 and 120 minutes.

In general, a number of observations concerning the two different catalysts can be made. Specifically:

- There appeared to be little difference in the destruction rates of TNT and RDX in the ultraviolet reactor under similar conditions.
- Oxidation rates of munitions components for similar amounts of ozone transferred are a function of reactant concentrations.
- The $Ni-TiO_2$ catalyst was as effective as the anatase form of TiO_2 in destroying TNT and RDX under similar reaction conditions. However, Ni appeared to dissolve from the TiO_2, imparting a greenish color to treated effluent. This suggests that a $Ni-TiO_2$ catalyst would lose its activity and that nickel concentrations in a treated wastewater would require further treatment.
- Simple catalytic photolysis, that is, UV-254nm in the presence of O_3 produced the best overall treated effluent in terms of toxicity and dissolved organic matter.

Membrane processing of synthetic pinkwater and heterogeneous photolysis of the concentrate stream

Most of the wastestreams treated in the experiments described here were fairly dilute, i.e. in the hundreds-of-parts-per-million range. To improve the efficiency of the process, we examined the feasibility of using a membrane to concentrate the feedwater prior to photocatalysis. A more concentrated feed would allow larger volumes of waste to be treated with a smaller photocatalysis system, would reduce the amount of catalyst needed, and perhaps increase the rate of treatment. A schematic of the membrane processing scheme is shown in Figure 22.

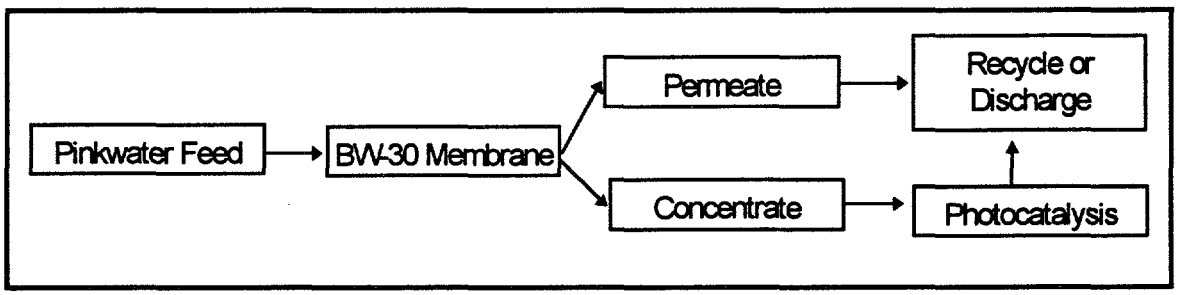


Figure 22. Schematic Diagram of Membrane Processing and Preconcentration.

The pinkwater feed stream flows across a semi-permeable membrane. Due to the porosity of the membrane surface, small molecules (such a water) can pass through the membrane, while larger molecules such as TNT and RDX cannot. As a result, the incoming feed becomes more concentrated with the larger molecules. This concentrated stream can then be photolytically treated or recycled to effect additional concentration. Table 13 lists the membrane processing conditions for these experiments, and Figure 5 shows the membrane processing system in detail.

Table 13.
Experimental Conditions for Membrane Processing of Synthetic Pinkwater and Heterogeneous Photocatalysis of the Concentrate Streams

Type	Film Tec BW-30
Initial Feed Volume	4.0 Liters
Pressure	150 psig
Recovery Membrane Permeate Concentrate	 80% of feed 20% of feed

Table 14.
Permeate and concentrate water quality as a function of recovery from pinkwater processed in a BW-30 membrane.

Permeate Recovery (%)	Conductivity Total Dissolved Solid (mg/L)	Permeate Flux (L/m^2*hr)	Total Organic Carbon (mg/L)	Toxicity (EC-50) (TU) [1]		RDX (mg/L) (HPLC)	TNT (mg/L) (HPLC)
0	360	39.24	22.62			0	--
0-10	4.0	37.64	4.10			0	2.3
10-20	3.5	34.92	3.15			0	2.3
20-30	4.8	34.10	3.19			0	2.2
30-40	4.8	28.10	2.39			0	1.9
40-50	5.3	28.10	4.35			0	2.1
50-60	6.0	25.42	2.35			0	2.3
60-70	8.0	25.20	3.10			0	2.5
70-80	10.0	24.15	3.16			0	2.9
Untreated lab-prepared pinkwater			22.62	2.22	45.0	16.9	33.8
Composite							
Permeate			3.37	39.47	2.53	0	2.3
Concentrate			106.60	4.37	82.6	76.9	110.6

Note: (1) TU = 100/EC-50(%)

Listed in Table 14 are the water quality data for permeates as a function of recovery level as well as information regarding cumulative permeate and concentrate wastewaters. The BW 30 membrane produced excellent rejection of inorganic matter as measured by conductivity. Over the course of permeate recovery to 80%, the rejection ranged from 99.1% to 97.3% with an average of 98.7%, which is well within the manufacturers rated performance.

The permeate flux rate for Milli-Q water was 60.4 L/m^2*hr. Laboratory-prepared pinkwater permeate flux rates after 30 minutes of re-circulating through the Cepa-Cell apparatus, that is recombining permeate and concentrate in the feed tank prior to initiation of permeate recovery, was 39.24 L/m^2*hr. Average flux rates were measured for each 10% recovery interval. These data show that foulants (i.e. inorganic colloids, organics) reduced the permeate flux by 38% to 24.15 L/m^2*hr. The pump pressure was maintained at 150 psig. The average fluid temperature was 32°C.

According to the manufacturer, the BW-30 rejection rates for methanol, ethanol, urea, and phenol are 25%, 40%, 70% and 90%, respectively. Based on molecular weight considerations, TNT (227.13 gm/mole) and RDX (222.26 gm/mole) are predicted to be highly rejected.

In the experiment with a BW-30 membrane and laboratory-prepared pinkwater as the feed, at 80% recovery the RDX in the concentrate stream was 76.9 mg/l (feed -16.9 mg/l). No RDX was found in the permeate. The TNT in the concentrate was 110.6 mg/l (feed - 33.8 mg/l). An average of 1.8 mg/l of TNT was found in the permeate. The Silas-Mason procedure yielded <0.6 mg/l of TNT. Performing a mass balance on the two munitions species yielded recoveries (permeate and concentrate) for 91 % RDX and 71 % for TNT. The lack of closure on the TNT balance may be due to experimental measurement protocols or adsorption to the membrane.

The TOC in the feed was 22.62 mg/l. At 80% recovery, the permeate contained 3.37 mg/l while the concentrate was 106.6 mg/l. A material balance indicated 106% recovery. The discrepancy is probably attributable to adsorption on the membrane and experimental measuring errors. Also, some low molecular weight compounds (< 100 gm/mole) are present in the untreated laboratory-prepared pinkwater and would permeate the membrane.

The toxicity of the untreated laboratory prepared pinkwater, and BW-30 permeate and concentrate were respectively, 45.0, 2.53 and 82.6 TUs. As expected, the toxicity of the permeate was greatly reduced by membrane processing.

Membrane concentration appears to be a viable method to pretreat the pinkwater feed stream. Specifically:

- The BW-30 membrane rejected 100% of the RDX, 98% of the TNT, approximately 98.7% of the inorganics, and 97% of the TOC in laboratory-prepared pinkwater.
- Toxicity reduction at 80% recovery by the BW-30 membrane were from 45.0 in the feed pinkwater to 2.53 in the permeate.
- The permeate from a BW-30 membrane processing pinkwater could be recycled as process water or discharged without negative environmental consequences.
- The concentrate can be treated photocatalytically.

Summary and Conclusions

The results of this work show that photocatalysis can effectively remove TNT, RDX and HMX from aqueous munitions waste. The catalyst itself is necessary to promote destruction of the parent compounds as well as the intermediates produced. RDX is easier to destroy photocatalytically than TNT. In both cases, the treatment times can be quite long depending on the operating conditions selected. The process is relatively insensitive to pH, although a constant high pH can increase the number and amount of undesirable intermediates. Temperature seems to have a slight negative effect and the rate increases linearly with the light intensity. Simple chemical accelerants such as peroxydisulfate and hydrogen peroxide do not seem to have a significant effect on the rate of oxidation of the explosives examined. There is a slight increase in activity of the titanium dioxide under reducing conditions when a small amount of nickel is added to the catalyst. Platinum seems to hinder the reaction under anaerobic conditions. Reducing conditions are more effective than oxidation for RDX destruction. TNT seems to accelerate the rate of anaerobic destruction of RDX while itself producing less intermediates under these conditions. RDX has no effect on TNT degradation. Hole scavengers can greatly accelerate the rate of reduction of TNT.

We have also shown that TNT and RDX can be removed via laser exposure without catalysts, but the economics of such a process has not been studied.

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APPENDIX A

Analysis of Sample Pinkwater "Pink 0602" taken from Louisiana Army Ammunitions Plant Thiokol Corporation, Shreveport, Louisiana:

pH	7.8
TNT	176 mg/l
RDX	95 mg/l
Total Organic Carbon	137 mg/l
Dissolved Oxygen	3.6 mg/l
Total Suspended Solids	36 mg/l
Iron	0.5 mg/l
Hardness, as $CaCO_3$	14.5 mg/l

Analysis of Albuquerque Tap Water:

Sodium	37 ppm
Potassium	3 ppm
Calcium	109 ppm
Nitrate	7.6 ppm
Sulfate	163 ppm
Chloride	57 ppm

APPENDIX B

Master of Science Thesis "Sequential Physical, Chemical and Biological Treatment of Munitions Wastewater" by Sunil Kommineni, University of Arizona, 1994

SEQUENTIAL PHYSICAL, CHEMICAL AND BIOLOGICAL TREATMENT OF MUNITIONS WASTEWATER

by

Sunil N. Kommineni

A Thesis Submitted to the Faculty of the

DEPARTMENT OF CIVIL ENGINEERING AND ENGINEERING MECHANICS

In Partial Fulfillment of the Requirements
For the Degree of

MASTER OF SCIENCE
WITH A MAJOR IN CIVIL ENGINEERING

In the Graduate College

THE UNIVERSITY OF ARIZONA

1994

STATEMENT BY AUTHOR

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APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

_____ _____

Dr. Curtis W. Bryant
Associate Professor
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Date

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CHAPTER 1

INTRODUCTION

TNT is manufactured by batch or continuous process (Patterson J. et al., 1976). Toluene is nitrated in a three-stage process by increasing temperatures and mixing with nitric and sulfuric acids to introduce nitro groups successively to form 2- and 4-mononitrotoluene (MNT), 2,4- and 2,6-dinitrotoluene (DNT) and 2,4,6-trinitrotoluene (TNT). Numerous other compounds are also formed, including partially nitrated toluenes, unsymmetrical isomers of TNT and oxidation products such as tetranitromethane, trinitrobenzoic acid and trinitrocresols. These undesired compounds are removed from the mixture by treatment with aqueous sodium sulfite solution (sellite), which reacts with most compounds, except the desired 2,4,6-isomer, to form water soluble sulfonate derivatives.

Two types of wastewaters are generated when munitions are manufactured. The first is a highly acidic "red water" that is the spent sellite waste solution formed during the TNT purification process. It is high in solids content and possesses intense red color. The red water contains TNT, its isomers, sodium carbonate, sodium sulfate and sodium sulfite. Many of the components of the red water are toxic and/or carcinogenic and it has been classified as a hazardous substance by the EPA (Ryon et al., 1984). Disposal of the waste generated during the sellite purification process has been a most serious concern for a long time. During the period between World War II and the Korean War, the red water wastes were released into streams as a means of disposal. Later, after the evaporative concentration of the red water at the Army Ammunitions Plant (AAP) facilities, the concentrates were either sold to the paper mills for incineration and recovery of the sodium sulfate needed for the pulping process or incinerated at the AAP. Transportation

of the concentrate is no longer feasible due to its hazardous classification and because the stricter pollution regulations have decreased the secondary market for the recoverable sodium sulfate. Incineration of the concentrate is not only expensive but also adds to the existing air and solid waste pollution problem. Current techniques are aimed at the recovery of the sulfur and the sodium present in the red water.

The second type of the munitions wastewater is the "pink water" that is generated during the TNT manufacture from the plant cleanup and scrubbing processes, LAP operations, and as a condensate from the evaporative concentration and incineration of the red water. Pink water comes from both the manufacturing plants and the loading, assembling, and packing (LAP) facilities. It contains varying amounts of TNT, its meta isomers, photo degradation products of TNT, DNT isomers, and trace quantities of nitrotoluenes and cyclotrimethyelenetrinitramine (RDX). Under the conditions of full production of TNT, it has been estimated that the amount of pink water generated could be as high as 100,000 gal/day/line and may contain 140 to 160 mg TNT per liter along with other contaminants and explosives (Forsten, 1980).

The two main munition components of the pink water are trinitrotoluene (TNT) and cyclotrimethylenetrinitramine (RDX). The treatment of the munitions' components in an aqueous solution can be accomplished either by physical-chemical methods like adsorption and oxidation or by biological processes. The proposed changes in the environmental regulations indicate that the current methods of treating the munitions wastewater might be inappropriate in the coming years. Currently under consideration are new environmental discharge regulations which will require the implementation of new treatment methods including catalyzed chemical oxidation, biological processes, membrane processing and coupled treatment systems.

CHAPTER 2

OBJECTIVE

2. 1 Research objective

The main objective of the research was to study the treatability of munitions wastewater (pink water) in sequences of physical/chemical and biological processes. The aim was to combine the best effects of both the physical/chemical and the biological processes and to arrive at an optimum and economical treatment scheme for treating the pink water. The effluent generated must be acceptable for discharge into the publicly owned wastewater treatment (POWT) plants. An array of experiments was designed and accomplished to fulfill the mission of the research.

The study investigated the pre-treatment of synthetic and actual pink waters by heterogeneous photocatalytic (O_3, UV, TiO_2), UV photocatalyzed-ozone (UV, O_3 or O_2) and nitrogen reduction procesess (N_2, UV, Na_2EDTA or TiO_2) operated in several configurations prior to the biological treatment. The variables of the various physical/chemical processes included the presence or absence of a catalyst (TiO_2 or Na_2EDTA), photon source (UV 254 nm or UV 365 nm lamp), reactor atmosphere (O_2, O_3, N_2) and reaction time.

The biotreatability of the pink water was studied under three schemes. The first scheme consisted of 30 days of aerobic treatment; the second scheme consisted of 14 days of anaerobic treatment followed by 16 days of aerobic treatment; the third sequence was 7-days of aerobic biotreatment prior to the physical/chemical treatment. Yeast extract and micro-nutrients were added to the pH-7.0-adjusted wastewaters prior to the biological treatment. Variously pretreated munitions wastewaters were contacted in semi-

continuous (constant liquid volume, continuous action) mixed reactors for the aerobic treatment. One-liter (Mason) jars were used as the anaerobic reactors.

The wastewater quality was quantified using various analytical measurements like pH, total suspended solids (TSS), total organic carbon (TOC), UV absorbance (200-390 nm), toxicity (EC50) and TNT-RDX species concentrations. Additionally, oxygen uptake rates (OUR) for aerobic processes and gas chromatograph (GC) analyses for the anaerobic processes were also performed.

2.2 Experimental plan

Table 2.1 gives the designations of the experimental runs that were carried out as part of this research. It also details the variables of heterogeneous photocatalysis that comprised the several sequence configurations prior to the biological treatment. Two types of pink waters (APW-2 and SPW) were tested. The variables of heterogeneous photocatalysis that were studied included the presence or absence of a catalyst (TiO_2 or Na_2EDTA), photon source (UV 254 nm or UV 365 nm lamp), reactor atmosphere (O_2, O_3, N_2) and reaction time.

Table 2.1 Experimental plan of physical/chemical treatment

Run#	Pink water type	Reaction Atmo-sphere	Oxidant	Photon Source (Lamp)	Catalyst	Reaction Time (min.)
BR-1	APW-2	O_2 - O_3	O_3	254 nm	TiO_2 (3 g/L)	5
BR-2	APW-2	O_2 - O_3	O_3	254 nm	None	120
BR-3	APW-2	O_2	None	365 nm	TiO_2 (3 g/L)	30
BR-4	APW-2	N_2	None	365 nm	TiO_2 (3 g/L)	30
BR-5	SPW	O_2-O_3	O_3	254 nm	TiO_2 (3 g/L)	5
BR-6	APW-2	N_2	None	Spectrum	Na_2EDTA (0.72 mM/L)+ TiO_2 (1 g/L)	10
BR-7	APW-2	N_2	None	Spectrum	Na_2EDTA (0.72 mM/L)+ TiO_2 (1 g/L)	30
BR-8	APW-2	O_2 - O_3	O_3	254 nm	None	5
BR-9	APW-2	O_2 - O_3	O_3	254 nm	None	30
BR-10	APW-2	O_2 - O_3	O_3	254 nm	None	60
BR-11	APW-2	O_2.O_3	O_3	254 nm half lamp	None	30

APW-2 = actual pink water, second batch
SPW = synthetic pink water

Table 2.2 gives the details of the biotreatment runs that followed the physical/ chemical treatment. Apart from the eleven runs mentioned in Table 2.2, there were controls using pink waters (APW-2 and SPW) without any physical/chemical treatment.

Table 2.2 Experimental plan of biological treatment

Run #	Biological Treatment	
BR-1	30 days aerobic	14 days anaerobic + 16 days aerobic
BR-2	30 days aerobic	14 days anaerobic + 16 days aerobic
BR-3	30 days aerobic	14 days anaerobic + 16 days aerobic
BR-4	30 days aerobic	14 days anaerobic + 16 days aerobic
BR-5	30 days aerobic	14 days anaerobic + 16 days aerobic
BR-6	7 days aerobic	
BR-7	7 days aerobic	
BR-8	7 days aerobic	
BR-9	7 days aerobic	
BR-10	7 days aerobic	
BR-11	7 days aerobic	

Table 2.3 gives the details of the one treatment run that tested biotreatment prior to the physical/chemical treatment.

Table 2.3 Experimental plan of bio- followed by P/C treatment

Run #	Bio-treatment	Physical/Chemical
BR-12	7 days aerobic	O_3, UV 254 nm, 120 min.

CHAPTER 3

LITERATURE REVIEW

3.1 Introduction

The removal of TNT and RDX in biological systems has been investigated by numerous researchers (Osmon and Klausmeier et al. 1972, Nay et al. 1972, Won et al. 1974, Hoffsommer et al. 1978, Carpenter et al. 1978 and Boopathy et al. 1993). The pollution of natural waters with waste from explosive production, loading, and disposal facilities has been known for some time. Various physical and chemical removal methods have practical limitations; biological treatment would have definite advantages. To date the literature concerning biodegradation of explosives has been contradictory and limited.

Fourteen methods to treat pink water were investigated by Tatyerek A. F. et al., 1976. Concentration methods included distillation, reverse osmosis, carbon adsorption and regeneration, polymeric adsorption and regeneration, liquid membrane separation, foam separation and solvent extraction. Destruction methods investigated included ozonolysis, ozone-UV treatment, gamma radiation, incineration, heterogeneous photocatalysis, and composting and soil disposal. Carbon adsorption and regeneration was found to be the best concentrating process.

The current method of choice for the pink water abatement is adsorption by activated carbon (Ryon et al., 1984). A study conducted at the Holston AAP indicated that while adsorption on the granular activated carbon is a viable treatment method for removal of TNT from de-ionized water when present alone, this would not be a method of choice for mixtures of munition compounds, since competition for adsorption sites and reduced overall efficiency have been demonstrated (Burrows, 1982). Other munitions are

progressively displaced in favor of the TNT adsorption. Patterson et al. (1976) reported that the activated carbon systems intended to remove RDX in addition to TNT from wastewaters must be optmized for RDX removal. This may result in over-design of the system relative to TNT control. Moreover, the activated carbon adsorption creates problems of regeneration and solid waste pollution.

3.2 Photodegradation of TNT

Exposure of TNT, both as a solid and in solution, to strong sunlight or ultraviolet radiation, results in the formation of decomposition products (Roth et al., 1979). TNT absorbs light in the region above 290 nm (Roth et al., 1979). The photochemical degradation of TNT was studied by numerous researchers across the world. An aqueous solution of TNT was fed into a continuous flow system, where it was irradiated with a mercury lamp fitted with a Pyrex filter so that only light above 280 nm passed into the TNT solution (Burlinson et al., 1973). This was similar to solar radiation because the earth's atmosphere absorbs 99% of the sun's radiation below 280 nm. Analysis of the solution after irradiation, at flow rates of 7 to 10 mL/minute, showed photolysis of 65% of TNT.

Andrews and Osman (1975) found that the photochemical degradation of TNT was dependent on exposure time and on the distance from the UV light source. It was also reported that the TNT concentration changed from 100 ppm at zero time to $\leq$ 1 ppm after 24 hours of exposure to UV radiation. The components formed by irradiation of an aqueous solution of TNT by UV light included both polar and non-polar single-ring compounds (Kaplan et al.,1975). On prolonged exposure to UV radiation, ring cleavage of TNT to form CO_2 and volatile organics has been shown (Andrews and Osman, 1976).

Several bench-scale models have undergone testing at the Holston AAP Industrial Liquid Waste Treatment Facility for their ability to degrade TNT in combination with other munition chemicals, like RDX, in aqueous solutions. These models include the Corona oxidation (Innova process), combined UV-ozone oxidation and UV radiation in the presence of hydrogen peroxide. Treatment of TNT and RDX in an aqueous solution by exposure of 1000 gallons/day to UV light in the presence of ozone resulted in a reduction of dissolved TNT and RDX to < 1.0 mg/L (Roth and Murphy, 1978). By converting the TNT rapidly to CO_2, HNO_3, and H_2O, no by-products requiring disposal were formed (Roth and Murphy, 1978).

3.3 Biodegradation of TNT

While attractive from the economic standpoint, biological treatment of pink water must be considered with caution (Patterson et al., 1976). Points of concern include: the need for large quantities of supplemental nutrient, pollutant biotransformations; and the nature and potential impact of treatment by-products on the receiving environment, or the need for application of supplemental polishing steps such as carbon treatment and resin adsorption (Patterson et al., 1976).

The objectives of most of the studies on the microbial degradation of TNT were to evaluate the effectiveness of microorganisms to degrade TNT contaminants in soils and in manufacturing wastewaters. Won et al. (1974) found three pseudomonads microorganisms that metabolically oxidize the TNT. The organisms were designated as isolate "Y" (nitrate reducer), "I" (indole former) and "II". "Y" degraded TNT most effectively while "II" was the least effective.

Osmon and Klausmeier et al. (1972) investigated the possible role of TNT as the sole nitrogen source and found that the degradation was more rapid in the presence of an additional inorganic nitrogen source (NH_4Cl, NH_4NO_3 or $NaNO_3$).

Klausimeier et al. (1979) studied the effect of TNT on various microorganisms including fungi, yeasts, actinomycetes and bacteria. No organism was found that could utilize the TNT as a sole source of carbon.

Degradation of TNT occurred most rapidly in bacterial cultures supplemented with 5 g/L yeast extract (Won et al., 1974). The addition of glucose or a nitrogenous compound also accelerated the TNT degradation. After relatively rapid depletion of TNT in 24 hours, the azoxy compounds degraded gradually, approaching complete disappearance after 96 hours (Won et al., 1974).

The results of batch experiments conducted by Hoffsommer et al. (1978) showed that TNT supplemented with glucose could be efficiently biotransformed by a mixed culture of microorganisms from a sewage disposal plant. The rates of TNT biotransformation by the mixed bacterial strains (activated sludge) was nearly the same as the rates for TNT biotransformation with pure pseudomonads-type organisms (isolate Y). According to Hoffsommer et al. (1978), TNT was adsorbed into the bacterial floc and was bioreduced to a mixture of amines, whereupon the bacteria died, encasing the amines. Next, the amines were slowly extracted into the water as this cell encasement ruptures or is degraded by other microrganisms.

In a 3-year pilot plant feasibilty study, Hoffsommer et al. (1978) studied the microbial degradation of TNT. Hoffsommer et al. (1978) showed that although TNT is itself toxic to the microorganisms, it undergoes biotransformation when supplemented with additional nutrient. When the concentration of TNT in water was 10 to 50 ppm, 97% of TNT was biotransformed by activated sludge microorganisms supplemented with

cornsteep water nutrient. Best results were obtained in the pH range 6 to 8 with a 50 : 1 nutrient-to-TNT ratio. Products formed included 4-A, 2-A, 2,4-DA, and 2,6-DA at a ratio of 1.0:0.12:0.10:0.013. The total amount of nitramines was 12% of the TNT feed concentration.

Carpenter et al. (1978) studied the metabolic fate of ^{14}C-labeled TNT in an activated sludge system. No [^{14}C]TNT was detected in the contents of an aerated reactor after 3 to 5 days of incubation. Only very low levels of $^{14}CO_2$ were produced, indicating that the aromatic ring was not cleaved. The radioactivity [^{14}C] was about equally divided between the floc and the supernatant.

Boopathy et al. (1993) studied the anaerobic removal of TNT under different electron-accepting conditions by a soil bacterial consortium. The results indicated that among the different electron acceptors studied (sulfate, nitrate and CO_2), significant TNT removal was observed under nitrate-reducing conditions. When there was no electron acceptor in the medium, TNT was not removed even after 60 days of incubation. Under nitrate-reducing conditions, 82% of TNT was removed from the original concentration of 100 ppm of TNT.

Nay et al. (1972) demonstrated that the color development in TNT waste occurs with an increase in pH and that the developed color has a derogatory affect on the subsequent waste treatment, both biological and physico-chemical. The intensity of the color produced in dilute solutions of TNT in natural water was found to be dependent on the concentration of TNT, the concentration of carbonate, or the alkaline constituents of the water which raised the pH, the temperature, and light conditions (Ruchhoft et al., 1945). The colored complex seemed more stable than the TNT, and the reaction was difficult to reverse once the colored complex was formed (Ruchhoft et al., 1945).

3.4 Photodegradation of RDX

Glover and Hoffsommer (1979) irradiated RDX in tap water by UV radiation. When ozone was present during the irradiation, the products formed included carbon dioxide, nitrate ion, ammonia, formic acid, cyanic acid and several organic nitro compounds. In the absence of ozone, exposure of RDX to UV produced nitrite ion, ammonia, formaldehyde, nitrous oxide, formamide and several organic nitrogen compounds. In all the cases, there was an additional major compound that was thought to be formic acid. The authors presented evidence from mass spectral data that RDX subjected to UV radiation undergoes stepwise elimination of three molecules of nitrous acid to form 1,3,5-triazine; 1,3,5-triazine and its precursors are cleaved to organic nitrogen compounds, such as formamidine and nitroformamidine, when further exposed to UV radiation and/or ozone. The combination of UV and ozone was much more effective than either agent alone.

3.5 Biodegradation of RDX

The decomposition of RDX in a biological system has been reported. Osmon and Klausimeier (1973) found that some RDX disappeared during soil enrichment studies, but evidence for RDX degradation by microorganisms was not obtained. The complete disappearance of RDX by mixed cultures of purple photosynthetic bacteria was reported by Soli (1973), who advanced the hypothesis that the strongly reducing conditions of the culture during photosynthesis were responsible for disruption of the RDX molecule. Hoffsommer et al. (1978) found no disappearance of RDX in an aerobic activated sludge system. Sikka et al. (1980) reported the disappearance of RDX, after a 20-day lag period,

from river water samples supplemented with river sediment. Biodegradation of RDX in the presence of TNT was monitored by Hoffsommer et al. (1978) in a three-year pilot plant study. The initial concentrations were 15.1 mg/L of TNT and 7.3 mg/L of RDX. With aerobic activated sludge microorganisms in a batch experiment, 99.6% of TNT was bioconverted. No bioconversion of RDX was observed.

Biodegradation of RDX was studied by McCormick et al., (1981). RDX at concentrations of 50 to 100 μg/mL disappeared within 4 days from nutrient broth cultures inoculated anaerobically. Analysis of anaerobic reaction mixtures revealed the presence of intermediates during incubation. According to a scheme proposed by McCormick et al. (1981) the RDX biodegradation proceeds via successive reduction of the nitro groups to a point where destabilization and fragmentation of the ring occurred. The noncyclic degradation products were formed through subsequent reduction and rearrangement reactions of the fragments. The scheme suggests the presence of several additional compounds that were not identified. Several of the products are mutagenic or carcinogenic or both.

3.6 Toxicity

TNT is acutely toxic. Absorption of TNT can cause a variety of clinical manifestations, including aplastic anemia, toxic jaundice, cyanosis, gastritis and dermatitis (Yinon J., 1990). It was found that anemia, caused by the destruction of red blood cells, is the most marked symptom of TNT poisoning. Reduction of the number of the red blood cells and of the hemoglobin are the most conspicuous signs of TNT anemia (Yinon J., 1990).

RDX is acutely toxic. Clinical manifestations and symptoms in humans poisoned by RDX include convulsions followed by loss of consciousness, muscular cramps, dizziness, headache, nausea and vomiting (Yinon J., 1990).

Pink waters were found to be toxic to fish. Degani (1943) found that the TNT wastewater killed fish (minnows and very young fry of the trout) when the dilution of an average sample was 600 times or less. Ruchhoft et al. (1945) stated that 5 mg/L of TNT was lethal to fish. Walsh et al. (1973) mentioned that 2.5 mg/L of TNT was toxic to fish. Bentley et al. (1977) evaluated the toxicity of RDX to aquatic organisms. Bioassays of RDX were conducted using three fresh water species: bluegill, channel catfish, and fathead minnow. It was found that RDX exerted an acute, toxic effect on all the freshwater fish species tested at concentrations ranging from 3.6 to 6.4 mg/L. Sullivan et al. (1979) determined water quality criteria for the protection of aquatic organisms. Studies conducted by the Office of The Surgeon General have recommended a 24-hour average maximum concentration of 0.30 mg of RDX per liter of wastewater to protect the aquatic life. It is beyond doubt that the discharge of untreated TNT/RDX wastewaters into streams and rivers constitutes a serious pollution hazard.

Won et al. (1974) and Patterson et al. (1976) reported that biological treatment might result in degradation compounds (azoxy and amino compounds) that are more toxic than TNT by itself. No well defined study has been conducted on the biodegradation by-products of TNT and RDX and their possible toxicity.

CHAPTER 4

MATERIALS AND METHODS

4.1 Wastewater acquisition and storage

Three types of pink waters were used in the research. These pink waters are identified henceforth in the report as:

1. Actual Pink Water-1 (APW-1)
2. Actual Pink Water-2 (APW-2) and
3. Synthetic Pink Water (SPW).

The synthetic pink water (SPW) was obtained from the Sandia National Labs, Albuquerque, New Mexico. The actual pink waters (APW-1 and APW-2) were obtained from the Louisiana Army Ammunitions Plant, Thiokol Corporation, Shreveport, Louisiana, via Sandia National Labs.

TNT and RDX were the major organic constituents in all the pink waters. Table 4.1 lists the concentrations of TNT and RDX in the three types of wastewaters. Table 4.2 lists the components of actual pink water-2 (APW-2) and synthetic pink water (SPW). The concentrations of TNT and RDX found in the actual pink water (APW-2) are 3.7 and 4.6 times more, respectively, than those found in the synthetic pink water (SPW).

The synthetic pink water (SPW) was prepared by dissolving known concentrations of TNT and RDX in the Albuquerque tap water. The laboratory-prepared synthetic pink water (SPW) was allowed to age approximately six months before testing so that the naturally occuring decomposition products could form. Table 4.3 lists the analytical results for the Albuquerque tap water used in the preparation of synthetic pink water (SPW).

The wastewaters were shipped by refrigerated air freight in sealed and opaque containers and subsequently refrigerated at 4 °C to inhibit biodegradation. The actual pink water-1 (APW-1) was received in a 1 L brown-bottle while the actual pink water-2 (APW-2) and the synthetic pink water (SPW) were received in 5 gallons and 15 gallons plastic containers. Previous researchers have shown that the pink water is photo sensitive. They also showed that the photochemical enhancement of the color effects the toxicity and biotreatability of the pink water (Nay et al., 1972). To minimize the exposure to light, the untreated actual pink waters (APW-1 & APW-2) and synthetic pink water (SPW) containers were placed in cardboard cartons prior to refrigeration.

The actual pink water-1 (APW-1) was only used for bacterial acclimation process. All the subsequent experiments of the research involved the actual pink water-2 (APW-2) and the synthetic pink water (SPW). Samples of the wastewater that were obtained in the course of the treatment experiments were sealed in 20-mL scintillation vials and stored at 4°C. Sampling and analytical methods are described in more detail in the subsequent sections of this chapter.

Table 4.1 Concentrations of TNT and RDX in pink waters

Pink Water	TNT (mg/L)	RDX (mg/L)
APW-1	58.5	31.9
APW-2	125.3	77.6
SPW	33.8	16.9

Table 4.2 Analytical results of untreated actual pink water (APW-2) and synthetic pink water (SPW)

Analytics	APW-2	SPW
pH	7.8	7.2
TNT	125.3 mg/L	33.8 mg/L
RDX	77.6 mg/L	16.9 mg/L
Total Organic Carbon (TOC)	64.0 mg/L	22.0 mg/L
Dissolved Oxygen (DO)	3.6 mg/L	N/A
Total Suspended Solids (TSS)	36.0 mg/L	N/A
EC50 Toxicity (% dilution)	3.1	2.2
TU50 Toxicity (toxicity units)	32.3	45.2
Iron	0.5 mg/L	N/A
Hardness as $CaCO_3$	14.5 mg/L	N/A

N/A - Not Available

Table 4.3 Analytical results of Abuquerque tap water used in the preparation of synthetic pink water (SPW)

Analytics	Concentrations
Sodium	37.0 ppm
Potassium	3.0 ppm
Calcium	109.0 ppm
Nitrate	7.6 ppm
Sulfate	163.0 ppm
Chloride	57.0 ppm

4.2 Seed bacteria

Aerobic and anaerobic seed bacteria were acclimated to the actual pink water (APW-1) in batch-fed reactors that were operated for several weeks. The initial seed bacteria were obtained from several sources including municipal mixed liquor volatile suspended solids (MLVSS) and papermill return activated sludge (RAS). The history of operation of acclimation and monitoring details is described in Appendix B.

4.3 Chemicals and reagents used

Table 4.4 lists the names, molecular formulae, formula weights and the manufacturers of the chemicals and reagents that were used in this research.

Table 4.4 Details of chemicals and reagents used

Name	Molecular Formula	Formula Weight	Vendor
Ammonium Chloride	NH_4Cl	53.49	Mallinckrodt AR. Co.
Sodium Chloride	NaCl	58.44	Mallinckrodt AR. Co.
Bacto-Yeast Extract	—	—	Difco Labs
Glucose	$C_6H_{12}O_6$	180.16	Sigma Chemicals
Magnesium Sulfate	$MgSO_4.\ 7H_2O$	246.48	Fisher Chemicals
Sodium Phosphate, Dibasic	Na_2HPO_4	141.96	Fisher Chemicals
Potassium Phosphate, Monobasic	KH_2PO_4	136.09	J. T. Baker Inc.
Titanium dioxide	TiO_2	79.88	Sigma Chemicals
Sodium Nitrate	$NaNO_3$	84.99	Sigma Chemicals
Sodium Acetate	$NaC_2H_3O_2.3H_2O$	136.08	Mallinckrodt AR. Co.
Sodium EDTA	$C_{10}H_{14}N_2Na_2O_8.2H_2O$	372.24	Sigma Chemicals
2-Diethylaminoethanol	$C_6H_{15}NO$	117.19	Fluka Chemicals

Bacto-Yeast Extract (B127) used in the research was the water soluble portion of the autolyzed yeast (Difco manual, 1964). The autolysis was carefully controlled to preserve the naturally occuring B-complex vitamins (Difco manual, 1964). Bacto-Yeast Extract is an excellent stimulator of bacterial growth and is an excellent source of B-complex vitamins according to the description in the Difco manual. In concentrations of 0.3 to 0.5 percent Bacto-Yeast Extract forms sparklingly clear solutions with a pH of 6.6 (Difco manual, 1964).

TiO_2 anatase is an n-type semiconductor which has an electron band gap energy of 3.0 eV. The UV adsorption spectrum of a typical anatase TiO_2 would show a sharp cut-off at about 400 nm, corresponding to the band gap energy.

4.4 Details of the reactors used

The following reactors were used in this research:

1. Ozone-Ultraviolet (UVR and UVR-Blue) reactors
2. Imhoff cones of one-liter capacity were used as the aerobic reactors and
3. Canning jars of one liter volume were used as the anaerobic reactors.

The details of various components of the reactors are described in the subsequent sections of this chapter.

4.4.1 Oxidation reactors

The Ozone-Ultraviolet Reactor (UVR) (Figure 4.1) consisted of a gas washing bottle, used as a reservoir for mixing, which was connected to a centrifugal pump that

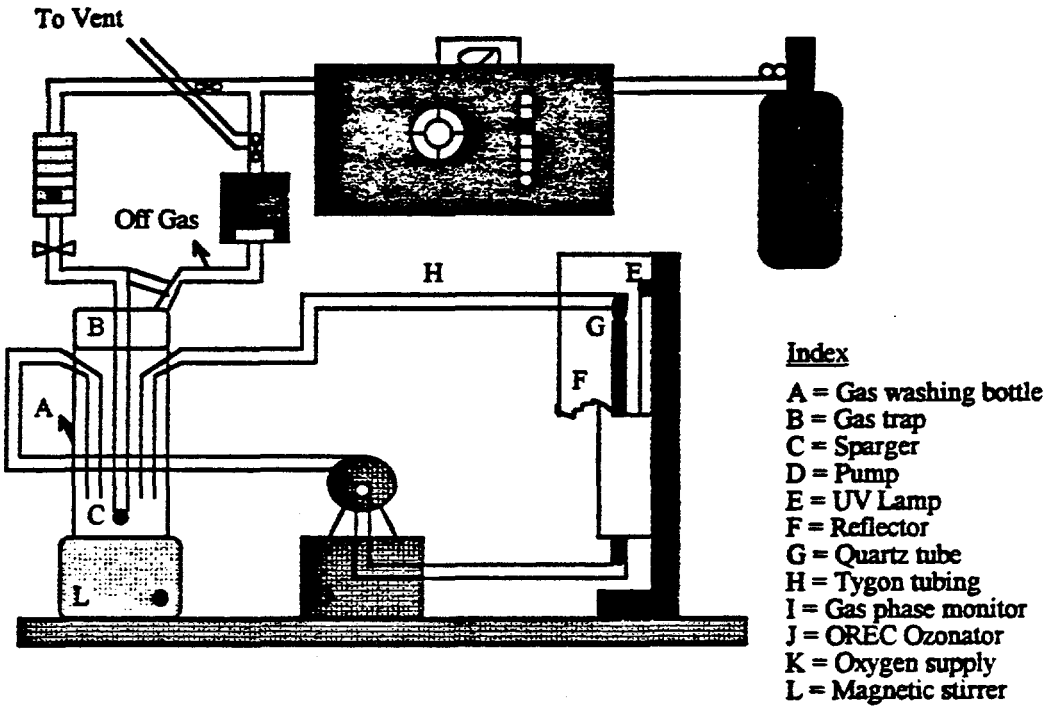


Figure 4.1 Oxidation Reactor (UVR/ UVR-Blue)

recirculated the 800 mL of suspension through a quartz tube placed 3 mm away from and parallel to an ultraviolet lamp (Model # 615T8, NIS Company, Japan). Aluminium reflecting paper covered the lamp and quartz tube coupling to prevent the UV radiation from escaping. Glass inlet and outlet tubes were added to the sides of the 500 mL gas washing bottle and extended nearly to the bottom. The pump and these tubes, connected by Tygon tubing, recirculated the suspension through the lamp setup. Ozone was added to the gas washing bottle reactor through a porous glass diffuser. A magentic stirrer rotated a 1.5 by 5/16 inch magnetic spinbar at the bottom of the reservoir at 400 rpm for additional mixing. The one speed pump used for the experiments was manufactured by Teel (IP767A) and had a magnetic drive and polypropylene wetted parts. Its flowrate (without the dissolved ozone cell in-line) was measured as 2.99 ± 0.25 L/minute which translates to a Reynolds Number of approximately 7,000 for the solution in the quartz tube. The quartz tube had 12 mm O.D., 10 mm I.D. and was 16 inches long. The 254 nm and 365 nm lamp output was measured by a UVP, Inc., Model UVX radiometer. The lamps required 15 Watts of power and were rated at 15 mW/cm^2 (254 nm) and 7.0 mW/cm^2 (365 nm). The lamp tubes were 16 inches long. A cross-section of quartz tubing, used in the ultraviolet, was placed over the sensor window to test for transmittance.

An Ozone Research and Equipment Corporation (OREC) ozonator (OREC # 03V5-0) produced ozone by corona discharge using medical grade oxygen carrier gas at 2 SL/minute (SL-standard liter) flow into the generator. The rated output of the ozonator was 0 - 0.25 pounds-O_3/day. The generator pressure dial was set at 4.5 to 5.0 pounds per square inch (psi). Ozone and oxygen gas flowrate through the glass diffuser was regulated by a rotameter at a constant flowrate of 2.0 SL/minute (SL-standard liter) for all

experiments. Unused gas from the ozonator was vented to the fumehood. The ozonator output and exit gases from the UVR were measured by an OREC Gas Phase Monitor (Model # O3DM-110). An identical reactor designated as the UVR-Blue was used for all the experiments which did not include TiO_2 catalyst.

Approximately 800 mL of pink water (actual or synthetic) were taken in the UVR or UVR-Blue reactor and treated for the period and atmospheric conditions as described in the experimental plan (Table 2.1). For the experimental runs of durations equal to or less than 30 minutes the intermediate samples were taken at 0, 1, 5, 10, 15 and 30 minutes. For the experimental runs of durations greater than or equal to 60 minutes the samples were collected at 0, 5, 10, 15, 30, 60, 90 and 120 minutes. All the samples were filtered through 0.45 μm Millipore filters prior to storage at 4°C for further analysis.

4.4.2 Aerobic bioreactors

Semi-continuous, completely mixed Imhoff Cone reactors were used as the aerobic reactors. According to Rich (1980), biodegradability studies can be performed effectively using aerated Imhoff Cones. The apparatus used is shown in Figure 4.2. Air stones (0.5" diameter and 1" long, Kordon Mist-Air 62503) made from bonded glass beads were used to provide consistent air bubbles. Six to seven systems were aerated simultaneously. Air supply was measured using a flowmeter. Bioreactor aeration was maintained between 2 to 3 SL/minute (SL-standard liters). The air was bubbled through a water trap prior to being contacted with the wastewater. This measure was undertaken to supply humid air rather than dry air to the biomass. Humid air minimizes evaporation losses. The cones were operated at the ambient room temperature that varied from 23°C to 26°C.

Approximately 750 mL of pink water, pretreated in different configurations as mentioned in the experimental plan, were added to each of the aerobic reactors. Three to four mL each of the acclimated biomass and the fresh MLVSS (Mixed Liquor Volatile Suspended Solids) were added to each reactor. The co-substrate (yeast extract at 0.25%) and micronutrients (Table 4.4) were added to the pH 7.0-adjusted wastewaters prior to the aerobic treatment. The bioreactors were covered by wet paper towels to lessen the evaporation losses. For the aerobic runs BR-1 through BR-5 samples were taken on day 0, 2, 4, 7, 14 and 30 while for the runs BR-6 through BR-10 samples were taken on day 0, 4 and 7. Approximately 50 mL of the sample was collected each time and filtered through 1 μm Borosilicate Microfiber filters for separating the biomass. All the samples were refrigerated at 4°C for TOC, toxicity and HPLC analysis.

Table 4.5 Aerobic micronutrients

(M-9 medium, Traxler R. W. et al., 1974)

Nutrient	Concentration added	
	g/L	mM/L
NaCl	5.0	85.6
KH_2PO_4	3.0	22.0
Na_2HPO_4	1.0	7.00
NH_4Cl	1.0	18.7
$MgSO_4 \cdot 7H_2O$	0.1	0.40

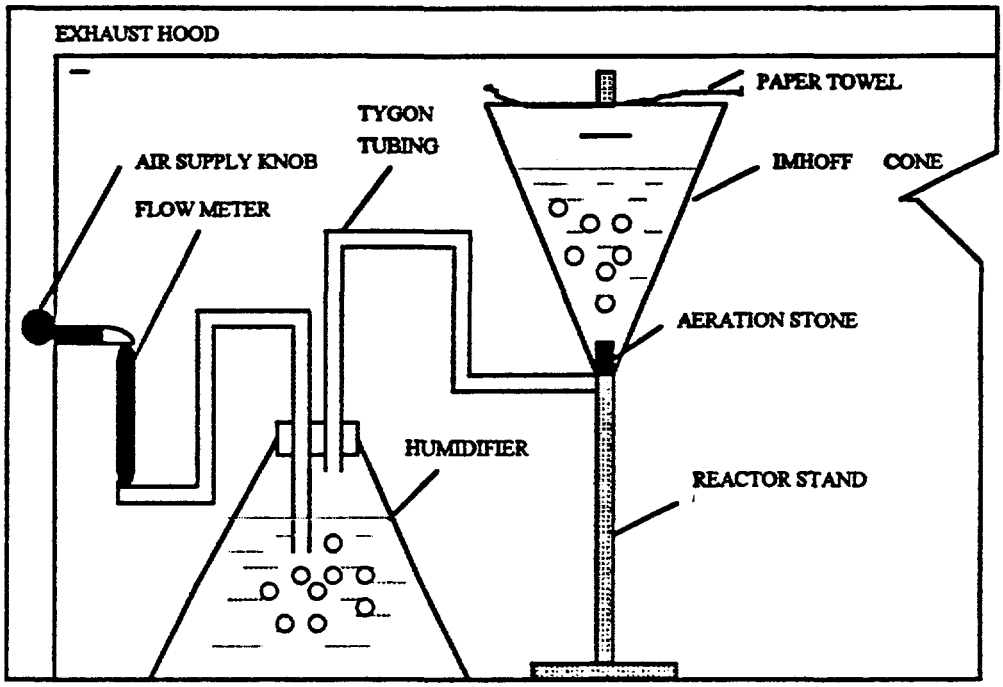


Figure 4.2 Imhoff Cone Aerobic Bioreactor

4.4.3 Anaerobic Bioreactors

Canning (Mason) jars of one liter capacity were used as the anaerobic reactors. These jars were sparged with N_2 gas prior to being sealed. The gases that were generated during the anaerobic processes were assumed to accumulate in the headspace provided. The anaerobic reactors were left on a shaker table in a water bath maintained at 30°C.

In the anaerobic reactors, approximately 500 mL of pink water samples, pretreated in different configurations as mentioned in the experimental plan, were added and sealed. Prior to sealing, the co-substrate (yeast extract at 0.25%) and micronutrients as listed in Table 4.6 were added to the pH 7.0 adjusted wastewaters. The threads of the reactors were wrapped with PTFE thread seal tape to ensure the maintenance of anaerobic conditions. Approximately 6 mL of acclimated biomass was added to each reactor. Since there was no provision for sampling, intermediate samples of the wastewaters were not obtained. The gases that were accumulated in the head space of each reactor were measured using inverted water-traps. Also, the gases from the anaerobic reactors were analyzed by the gas chromatograph for the presence of any low-molecular-weight-hydrocarbons including methane. Approximately 50 mL of the wastewater samples prior to and after the anaerobic treatment were collected in 20-mL scintillation vials and refrigerated at 4°C for TOC, toxicity, UV absorbance and HPLC analysis. Prior to refrigeration, wastewater samples were filtered by 1.0 μm Borosilicate Microfiber filters to measure the total suspended solids (TSS) and to filter out the biomass. The filtered anaerobic effluent wastewaters were then treated aerobically for 16 days, sampling days 0, 8 and 16. These wastewater samples were also tested for the parameters as listed earlier.

Table 4.6 Anaerobic micronutrients

(Boopathy R. et al., 1992)

Nutrient	Concentration added	
	g/L	mM/L
NaCl	5.0	85.6
KH_2PO_4	3.0	22.0
Na_2HPO_4	1.0	7.00
NH_4Cl	1.0	18.7
$MgSO_4.\ 7H_2O$	0.1	0.40
$NaNO_3$	1.7	20.0
$NaC_2H_3O_2.\ 3H_2O$	5.4	40.0

4.5 Analytics

The test parameters that were used to quantify the efficiency of treatment can be broadly classified into two categories, namely surrogate parameters and specific parameters. The surrogate parameters were affected by the presence of co-substrate (yeast extract) and its by-products. The following is the list of various surrogate parameters that were analyzed:

1. Total Suspended Solids (TSS)
2. Total Organic Carbon (TOC)
3. UV Absorbance Scan (200 nm - 390 nm)
4. Microtox toxicity
5. Oxygen Uptake Rate (OUR)
6. Silas-Mason TNT
7. Gas Chromatograph (GC) analysis

The specific parameters are the parameters that are not affected by the presence of the co-substrate. The actual parameters that were analyzed are:

8. High Precision Liquid Chromatograph (HPLC) analysis for TNT, RDX and their by-products.
9. pH

4.5.1 Total Suspended Solids (TSS)

All the wastewater samples were vaccum filtered through Borosilicate Microfiber filters (GC50 grade, 55 mm diameter, Micro Filtration Systems) of 1 μm effective pore-size and refrigerated at 4°C until analyzed. All the filters were placed in weighing boats, dried in a desiccator, and weighed prior to filtering for use in the total suspended solids (TSS) analysis. To ensure that the moisture was completely removed from the filters prior to use, the filters were weighed along with the weighing boats every 30 minutes and placed back in the desiccator until a constant weight was obtained. Prior to filtration of the wastewater, the filter elements were rinsed once with 100 mL of Milli Q water to remove any organics present in the filters. After the wastewater samples were filtered, the filters were returned to their respective weighing boats and placed in a 105°C oven to dry. After 2 hours of drying, the filters were removed from the oven, cooled in a desiccator, weighed, and placed back in the oven. This process was repeated until the combined weight of the used filter and the weighing boat was constant. TSS was determined by the following equation:

$$TSS = (W_f - W_i) / V_s \qquad (1)$$

where,

TSS = Total suspended solids (mg/L)

W_f = Final dry weight of used filter and weighing boat (mg)

W_i = Initial dry weight of filter and weighing boat (mg)

V_s = Volume of filter sample (L)

4.5.2 Total Organic Carbon (TOC)

The organic concentrations in aqueous solutions and suspensions were made using a Shimadzu 5000 TOC Analyzer. The measurement system is based on the combustion/non-dispersive infrared gas analysis method widely employed for TOC measurement. All the samples were acidified to pH 2.0 and the CO_2 produced was N_2 stripped. Hence the total organic carbon (TOC) represents only the non-volatile portion of the organic matter (NVDOC, non-volatile dissolved organic carbon). Samples were analyzed in duplicate and the results reported as average.

4.5.3 UV Absorbance Scans

A wavelength scan was run on all the wastewater samples using a Shimadzu UV-VIS Spectrophotometer UV-160A (P/N 204-04550), a micro-computer controlled double-beam recording spectrophotometer with variable wavelength and 2.0 nm band width. Absorbance measurements were recorded using 1 cm cuvettes in increments of 10 nm from 200 nm to 390 nm. The areas under the absorbance scans were then determined

using the trapezoidal method of integration on a spreadsheet program. It should be noted that the area under the absorbance scan can be an indirect measure of the organic matter in the wastewater since most of the organics show absorbances in the wavelengths between 200 nm to 390 nm.

4.5.4 Microtox Toxicity

The Microtox toxicity was used as an indicator of the relative toxicity of the wastewater samples. Toxicity was analyzed by the Microtox Toxicity Test System, using a Microtox Model 500 Analyzer, developed by the Microbics Corporation. The Basic Test Protocol, as described in the Microtox Manual (Volume II), was adopted for testing the toxicity of pink waters. Some of the wastewater samples that were highly toxic were diluted 1 : 10 or 1 : 100 prior to testing. During testing, sample dilutions of 45%, 22.5%, 11.25% and 5.625% were analyzed. The pH of the wastewater samples was adjusted to between 6.5 and 7.5 prior to testing.

An initial experiment (described in Appendix C) was conducted to select the exposure time for maximum toxicity. A 30-minute exposure was selected for all the toxicity measurements of pink water treatment on that basis.

Microtox is a system that detects and measures toxicity. It is a bioassay integrating living microorganisms with precision instrumentation. The reagent used in the microtox toxicity test consists of a suspension of luminescent microorganisms that are sensitive to a broad spectrum of toxic chemicals. The microorganisms emit light as a natural product of their metabolic processes. When toxic chemicals inhibit those processes, the light output drops in proportion to the toxicity of the sample. The light

loss measurements are taken by the Microtox Analyzer and automatically processed to generate detailed reports.

Appendix C gives more details on Microtox Toxicity Test and the Toxicity Protocol adopted for the pink waters (APW-2 and SPW). Appendix C also discusses some of the toxicity data reports obtained on pink waters.

4.5.5 Oxygen Uptake Rate (OUR)

Oxygen uptake rate (OUR) is calculated from the dissolved oxygen measurements. OUR is the slope of the line obtained by plotting the change in the dissolved oxygen as a function of time for a given aerobic wastewater sample. OUR measurements were taken only for aerobic processes. Dissolved oxygen measurements were made using an YSI Model 57, Oxygen-Meter. The wastewater samples were stirred with a magnetic stirrer to give consistent readings of dissolved oxygen. Appendix D shows a regression analysis of a specimen, performed to derive the oxygen uptake rates (OURs).

4.5.6 Silas-Mason TNT

The routine analytical procedure used for determining the TNT concentrations during the study was the Silas-Mason Test, developed by Mason and Hanger (1955). The Silas-Mason Test is a calorimetric procedure that complexes all the TNT isomers with diethylaminoethanol to a form with distinct color properties. After complexing, the absorbance of the test sample was compared with a blank sample (in which the tested sample was replaced with Milli Q water) at 525 nm using a Shimadzu UV-VIS Spectrophotometer. The measured absorbance was then converted to the corresponding

TNT concentration based on the calibration curve that was prepared using a stock solution of pure α-TNT (Kuo, 1982).

From previous studies (Nay et al., 1972 and Schulte et al., 1973), it was found that the reactable substances in the Silas-Mason test include TNT, dinitrotoluene (DNT) and some other nitroaromatic compounds. RDX was not a reactable substance in the Silas-Mason test.

As a quantitative method, the Silas-Mason procedure for TNT assay was subjected to a great deal of criticism. Variations of temperature and pH can cause significant variations in the test results (Osmon et al., 1972). Interferences in the color development can occur from the presence of other compounds in the wastewater. However, the method is quick and simple, and was considered satisfactory for detecting large changes in the concentration of TNT. More precise TNT assays were performed by liquid chromatography.

Appendix E describes the detailed procedure of the Silas-Mason Test and also shows the calibration curve used for TNT assay.

4.5.7 Gas Chromatograph (GC) analysis

Analyses of the gases that were generated and stored in the headspace of the anaerobic reactors were performed using Hewlett Packard 5790A Gas Chromatograph equiped with a flame ionization detector (FID). A 30m DB-624 megabore column with a 3 μm film was used under the following conditions: carrier flow (helium), 22 mL/min.; air flow, 178 mL/min.; and hydrogen flow, 38 mL/minute. Column temperature was set at 30°C isothermal. Injector temperature was 150°C and detector temperature was 200°C. Integration of the signal was carried out using an Hewlett Packard 3390A integrator.

Prior to testing a 2-point calibration was performed with standards of 1002 ppm and 1% methane in nitrogen (Aldrich Chemical Company). The retention time for methane peak was found to be approximately 0.62 minutes. All the test samples were run in duplicate and the values reported were averages.

4.5.8 High Precision Liquid Chromatograph (HPLC) analysis

The column used for HPLC analysis was a reverse phase carbon-18 column (Spheri-5) with silica support. The column was 25 cm long and 4.6 mm in diameter. The mobil phase started with 90% water and 10% methanol and ended with 30% water and 70% methanol over 40 minutes period with a linear gradient. The column was stabilized for 15 minutes with 90% water and 10% methanol prior to injections. The retention times for TNT and RDX were approximately 19.0±0.2 minutes and 29.0±0.2 minutes respectively. All the samples were tested in duplicate and values reported as averages. The concentrations of RDX and TNT were derived using the following expressions based upon HPLC response to RDX and TNT standards

$$\text{RDX (mg/L)} = 1.25 \times 10^{-5} \text{ (Area Counts recorded at 19.0±0.2 minutes)} - 0.65$$

$$\text{TNT (mg/L)} = 6.09 \times 10^{-6} \text{ (Area Counts recorded at 29.0±0.2 minutes)} + 1.48$$

4.5.9 pH

The pH measurements were made using an Orion Φ-32 pH/ millivolt meter equipped with a one combination pH electrode. Free-flowing silver-silver chloride acted as the reference elements. The Orion pH-meter was equipped with thermistor temperature sensors for automatic temperature compensation. The pH meter was calibrated daily using standard solutions. A two point calibration was used employing pH standards of 4 and 7 or 7 and 10. The samples were stirred during the pH measurement with a magnetic stirrer in order to expedite the attainment of stable pH.

4.5.10 Omission of BOD tests

Nay et al. (1974) reported that the static dilution bottle technique of BOD testing was unsuccessful as the results were small, erratic and not reproducible. It was also reported that the dilution factor, which is really the ratio of toxic material per unit of microbial solids has a strong effect on the BOD exerted. The microbial concentration in the dilution bottles was very small and hence the TNT : microorganism ratio in the dilution bottles was above the toxic levels. The only solution for this problem was to use the manometric BOD apparatus. In the manometric apparatus the TNT : microorganisms ratio was found to be below the toxic levels (Nay et al., 1974). The volumetric constraints prevented the use of manometric BOD apparatus.

4.5.11 Omission of COD tests

The initial attempts to measure the chemical oxygen demands (CODs) of the untreated SPW and APW-2 using the Hach COD apparatus proved to be futile. The CODs measured did not agree with the CODs computed from the concentrations of the organics present in the wastewaters. The measured CODs were approximately 50% lower than the CODs computed based on the known concentrations of TNT and RDX. Attempts were made to correct the CODs by prolonging the digestion time of the wastewater samples in the COD reactor from 2 hours to 4 hours. All the attempts to arrive at correct CODs for the untreated pink waters (APW-2 and SPW) proved to be unfruitful.

4.6 Results of co-substrate studies on actual pink water

Preliminary testing was used to screen several co-substrate sources, including municipal primary wastewater (composed of relatively simple organic compounds), glucose and yeast extract. Previous researchers (Won et al. 1974, Hoffsommer et al. 1978 and Klausimier et al. 1979) reported that the biodegradation of TNT occurred most rapidly in bacterial cultures supplemented with an alternate source of organic carbon. The preliminary tests showed that the presence of co-substrate (glucose/yeast extract/primary effluent) improved the biodegradation of TNT. As shown in Figure 4.3, extensive TNT degradation (> 90%) occurred in two days with the addition of 2.5 to 5.0 g/L of yeast extract. Hence the addition of yeast extract at 2.5 g/L (0.25%) was used for all the biological treatment experiments with pink waters (actual and synthetic).

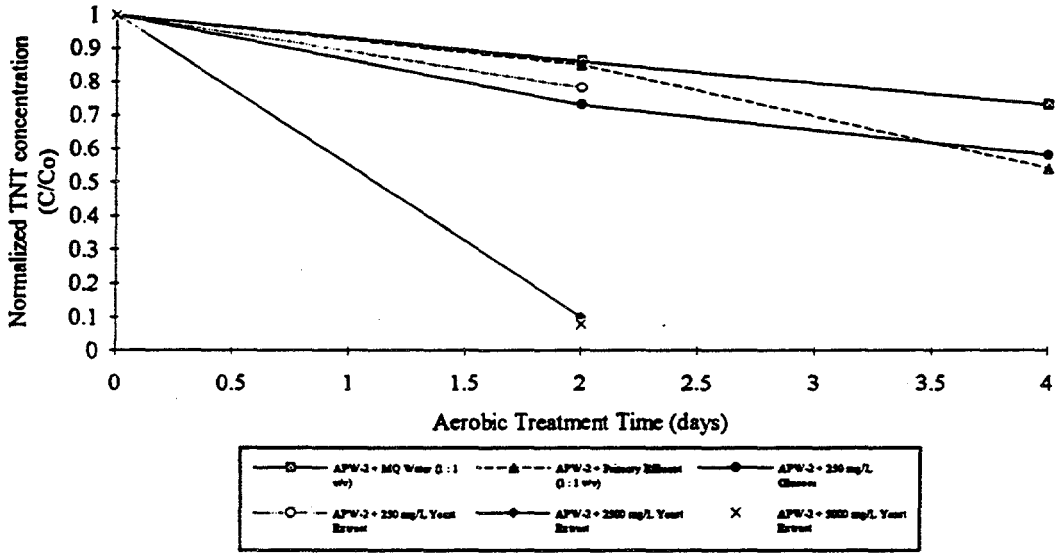


Figure 4.3 Effect of co-substrate addition on TNT biodegradation

CHAPTER 5

RESULTS

5.1 Physical and chemical treatment of pink waters for the first set of experiments (BR-1 through BR-5)

In the initial five experiments, the main objective was to study a wide range of physical/chemical treatments and to characterize the impact of pretreatment on biological treatment. The main goal of physical/chemical treatment was to break the TNT and RDX molecules to readily biodegradable by-products. Achieving partial oxidation (and not total oxidation) was the criterion of pretreatment. In other words, TOC degradation was not necessary in the physical/chemical pretreatment stage.

The experimental conditions and results of physical/chemical treatment for the initial set of experiments (BR-1 through BR-5) are listed in Table 5.1. The TOC reductions for the experimental runs with the actual pink water ranged from 29% to 65%. For the experimental runs involving ozone (BR-1, BR-2 and BR-5) the amount of organic destruction was directly related to the amount of ozone transferred. Greater TOC was removed under oxygen atmosphere (BR-3) than under nitrogen atmosphere (BR-4). In terms of the TOC removed per mass of ozone transferred, BR-1 (actual pink water) was more efficient than BR-5 (synthetic pink water), which reflects the type of organic molecules present in the actual and the synthetic pink waters.

TABLE 5. 1 EXPERIMENTAL CONDITIONS AND RESULTS OF P/C TREATMENT OF RUNS BR-1 THROUGH BR-5

EXPERIMENTAL DESIGNATION	RUN NUMBER				
	BR-1	BR-2	BR-3	BR-4	BR-5
PHYSICAL/CHEMICAL TREATMENT SCENARIO					
Type of Pink Water	APW-2	APW-2	APW-2	APW-2	SPW
Reaction Atmosphere	O_2-O_3	O_2-O_3	O_2	N_2	O_2-O_3
Oxidant	O_3	O_3	None	None	O_3
Photon Source	UV 254	UV 254	UV 365	UV 365	UV 254
Catalyst	TiO_2	None	TiO_2	TiO_2	TiO_2
Reaction Time (t = final) min.	5	120	30	30	5
TEST PARAMETER: OZONE TRANSFER					
Ozone Transfer	mg/.75L	27.6	278.3	–	–	17.7
	mg/L	36.8	371.1	–	–	23.6
TEST PARAMETER: TOC (mg/L)					
TOC mg/L	t = 0	64.0	64.0	64.0	64.0	24.0
	t = final	45.6	23.0	38.6	44.4	19.1
%TOC Removed		29.0%	65.0%	40.0%	31.0%	20.0%
TOC Removed/ O_3 Transfer		0.50	0.11	–	–	0.21
TEST PARAMETER: ABSORBANCE SCAN AREAS UNDER 200-390 nm						
Untreated Feed Water		1104.1	1104.1	1104.1	1104.1	432.0
After P/C Treatment		724.65	510.7	750.2	697.4	326.2
% Absorbance Area Removed		34.4	53.7	32.1	36.8	24.5
TEST PARAMETER: TNT (mg/L)						
TNT (mg/L)	t = 0	125.3	125.3	125.3	125.3	33.8
	t = final	71.2	4.7	62.5	55.3	33.8
%TNT Removed		43.2%	96.2%	50.1%	55.8%	0.0%
TNT Removed / O_3 Transfer		1.47	0.33	–	–	0.0
Silas-Mason TNT (mg/L)	t = 0	124.0	124.0	124.0	124.0	47.0
	t = final	62.3	17.1	47.3	56.8	26.9
TEST PARAMETER: RDX (mg/L)						
RDX (mg/L)	t = 0	77.6	77.6	77.6	77.6	16.9
	t = final	64.5	0.0	73.4	70.2	13.3
%RDX Removed		16.9%	100.0%	5.4%	9.5%	21.3%
RDX Removed / O_3 Transfer		0.36	0.21	–	–	0.15
TEST PARAMETER: MICROTOX TOXICITY (TU50) AND pH						
Toxicity (TU50)	t = 0	32.4	32.4	32.4	32.4	45.2
	t = final	151.5	61.7	104.2	138.9	62.9
pH	t = 0	7.13	7.30	7.20	7.20	8.32
	t = final	7.09	7.74	8.05	8.05	8.31

The Silas-Mason TNT test results agree to a certain extent with the results of TNT destruction obtained by the HPLC analysis. The data obtained from the HPLC analysis are deemed to be a better representation of the actual concentrations of TNT than those obtained by the Silas-Mason TNT assay, which is subject to interferences, especially color. Based on the HPLC data, the TNT destructions for the experiments listed in Table 5.1 ranged from 0% to 96%. Approximately 6% more TNT was destroyed under nitrogen atmosphere (BR-4) compared to the oxygen atmosphere (BR-3). On the basis of mass of TNT destroyed per mass of ozone transferred, BR-1 conditions are more efficient than the BR-2 conditions which reflects the type of by-products formed due to prolonged oxidation treatment. Under similar reactor conditions, the TNT removal for actual pink water (BR-1) was 43% greater than the TNT removal for synthetic pink water (BR-5).

The reductions in RDX for the actual pink water experiments (BR-1 through BR-4) ranged from 5% to 100%. Among the runs involving ozone, the RDX removed was directly proportional to the ozone transferred. Approximately 4% more RDX was removed under the reduction atmosphere (BR-4) compared to the oxygen atmosphere (BR-3). The RDX removal for synthetic pink water (BR-5) was approximately 4% more than the RDX removal for actual pink water (BR-1) for similar experimental conditions.

The toxicity of the munitions wastewaters increased drastically after each of the physical/chemical treatments. The experimental conditions of BR-1 produced the highest toxicity among the runs involving the actual pink water.

The changes in pH for all the five experiments (BR-1 through BR-5) were less than 1.0 unit. Depicted in Figures 5.1 and 5.2 are the absorbance scans of the effluent samples from the physical/chemical treatment. Among the actual pink water treatments, the most notable absorbance changes occurred in BR-2 treatment.

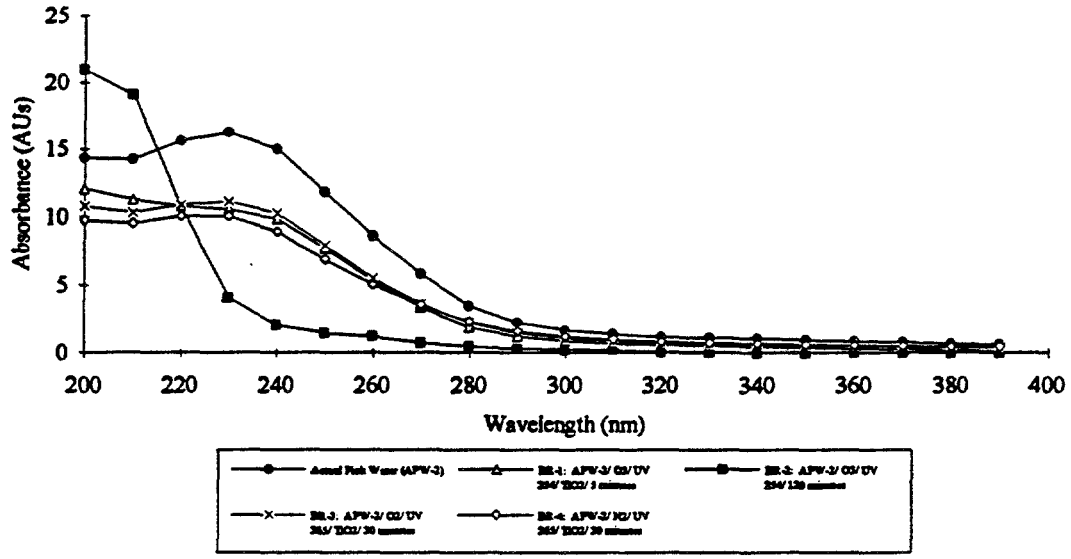


Figure 5.1 Absorbance scans from 200-390 nm of untreated and physical/chemical treated actual pink water

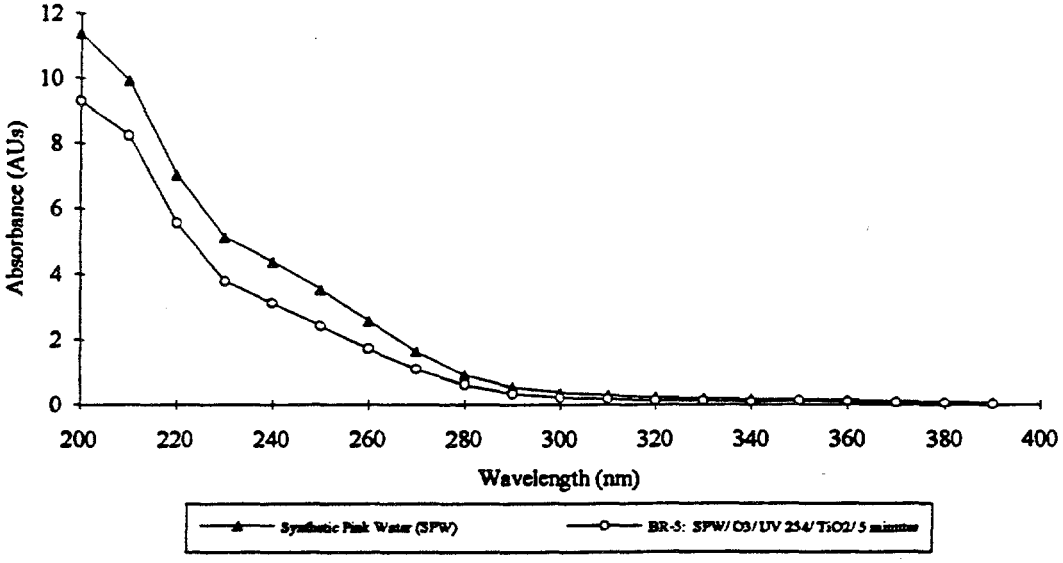


Figure 5.2 Absorbance scans from 200-390 nm of untreated and physical/chemical treated synthetic pink water

5.2 Aerobic treatment of pink waters for controls and the first set of pretreatments (BR-1 through BR-5)

The experimental conditions and results of aerobic treatment of actual and synthetic pink water controls and the first set of experiments (BR-1 through BR-5) are listed in Table 5.2. The high levels of TOC in the bioinfluents was due to the addition of yeast extract prior to the biotreatment.

Based on the TOC, TNT and absorbance scan area data, most of the biodegradation was completed in the first seven days of the aerobic treatment. From the results of Table 5.2 the aerobic degradation proceeded at a greater rate in the initial seven days. The associated soluble TOC was removed and the TSS increased significantly in the first seven days of biotreatment.

The synthetic pink water was more easily biodegraded than the actual pink water under comparable conditions. The bioeffluent from synthetic pink water reported lower TOC, TNT, RDX and absorbance scan areas than the bioeffluents from the actual pink water at any given time (except for BR-2).

Pretreatment of synthetic pink water (BR-5) had little impact on aerobic bioeffluent TOC, TNT, RDX and absorbance scan area, relative to the synthetic control. At any given time of biotreatment the bioeffluent TOC, TNT, RDX and absorbance scan area between the pretreated synthetic pink water (BR-5) and the synthetic control differed by less than 5%.

The toxicity of bioinfluents was almost completely removed in the first two days of biotreatment indicating that no biorecalcitrant, toxic intermediates were formed under any of the conditions studied. In all the experiments reported in Table 5.2 the toxicity of

TABLE 5.2 EXPERIMENTAL CONDITIONS AND RESULTS OF AEROBIC TREATMENT OF ACTUAL AND SYNTHETIC PINK WATERS OF CONTROLS AND RUNS BR-1 THROUGH BR-5

	RUN NUMBER						
	APW-2	SPW	BR-1	BR-2	BR-3	BR-4	BR-5
PRE-TREATMENT SCENARIO							
Pink Water	None	None	APW-2	APW-2	APW-2	APW-2	SPW
Reaction Atmosphere	None	None	O_2-O_3	O_2-O_3	O_2	N_2	O_2-O_3
Oxidant	None	None	O_3	O_3	None	None	O_3
Photon Source	None	None	UV 254	UV 254	UV 365	UV 365	UV 254
Catalyst	None	None	TiO_2	None	TiO_2	TiO_2	TiO_2
Time (min.)	None	None	5	120	30	30	5
TEST PARAMETER: TOTAL ORGANIC CARBON (TOC) mg/L							
Day 0	975.8	643.0	988.0	722.2	740.6	877.2	744.6
Day 2	200.8	118.3	141.3	125.7	132.8	125.7	115.1
Day 4	86.3	43.1	80.0	47.7	81.0	84.5	52.4
Day 7	72.3	42.3	63.8	43.7	72.5	69.1	43.7
Day 14	68.0	40.2	62.3	42.3	61.5	61.1	40.6
Day 30	55.6	36.5	47.8	32.1	43.6	54.9	39.7
TEST PARAMETER: TNT (mg/L)							
Day 0	125.3	33.8	71.2	0.0	62.5	55.3	33.8
Day 2	20.6	3.6	10.2	0.0	–	15.5	2.5
Day 4	15.6	4.1	9.8	0.0	10.0	14.8	–
Day 7	14.7	3.9	–	0.0	13.3	–	2.9
Day 14	3.9	3.7	5.1	0.0	5.4	–	3.1
Day 30	2.4	2.4	2.9	0.0	3.4	3.9	0.0
TEST PARAMETER: RDX (mg/L)							
Day 0	77.6	16.9	64.5	0.0	73.4	70.2	13.3
Day 2	59.2	13.5	50.2	0.0	–	57.0	10.2
Day 4	57.5	12.7	47.5	0.0	51.3	51.3	–
Day 7	58.7	11.7	45.2	0.0	50.0	–	9.2
Day 14	50.9	10.1	41.8	0.0	45.3	–	8.8
Day 30	33.2	9.0	29.8	0.0	31.1	36.9	8.4
TEST PARAMETER: MICROTOX TOXICITY (TU50)							
Day 0	32.4	45.2	151.5	61.7	104.2	138.9	62.9
Day 2	2.6	0.7	1.7	ND	1.95	2.1	ND
Day 4	–	–	–	–	–	–	–
Day 7	–	–	–	–	–	–	–
Day 14	1.3	0.9	1.2	ND	1.3	1.3	ND
Day 30	ND	0.5	1.1	ND	0.9	1.0	ND

(Table 5.2 continued)

	RUN NUMBER						
	APW-2	SPW	BR-1	BR-2	BR-3	BR-4	BR-5
TEST PARAMETER: ABSORBANCE SCAN AREAS UNDER 200-390 nm							
Day 0	1413.8	1009.7	1230.5	950.9	1154.3	1274.9	986.1
Day 2	1096.7	829.2	1051.4	763.9	1076.1	964.2	893.7
Day 4	822.1	373.0	561.5	527.1	539.5	551.7	362.9
Day 7	529.4	321.0	467.8	478.3	446.1	459.5	288.5
Day 14	483.5	283.2	429.8	447.8	364.7	384.1	276.5
TEST PARAMETER: pH							
Day 0	6.3	6.2	6.3	6.2	6.3	6.3	6.2
Day 2	7.0	7.0	7.1	6.9	7.0	7.1	6.9
Day 4	7.0	6.9	7.1	6.9	7.3	7.1	7.0
Day 7	7.2	6.9	7.1	6.9	7.1	7.1	7.0
Day 14	7.0	6.9	7.1	6.9	6.9	6.9	6.9
Day 30	6.6	6.5	6.7	6.7	6.8	6.9	6.6
TEST PARAMETER: TOTAL SUSPENDED SOLIDS (TSS) mg/L							
Day 0	180.0	160.0	134.0	164.0	154.0	108.0	162.0
Day 2	236.0	274.0	242.0	302.0	248.0	312.0	248.0
Day 4	246.0	310.0	168.0	200.0	242.0	180.0	130.0
Day 7	208.0	206.0	58.0	222.0	238.0	154.0	164.0
Day 14	146.0	194.0	80.0	158.0	206.0	84.0	116.0
Day 30	82.0	112.0	52.0	128.0	108.0	64.0	56.0

ND - Not detected.

the 30-day bioeffluents were less than the toxicities of 2-day bioeffluents indicating that the biotreatment by itself had not generated any increase of toxic intermediates or by-products.

No significant variation in pH was measured in the aerobic bioeffluents. The changes in pH for all the experiments were less than 1.0 unit. The pH of the physical/chemical effluents was buffered by the addition of phosphate buffers to the pH 7.0 adjusted waste waters prior to the biotreatment.

The removal of RDX by aerobic treatment was not as efficient as the removal of TNT. In the experiments reported in Table 5.2 the RDX removals ranged from 37% to 57% while the TNT removals ranged from 92% to 98%. The TNT concentrations in the 30 day bioeffluents were less than 4.0 mg/L in all the experiments reported in Table 5.2. In all the cases under consideration, the TNT concentrations reached levels of less than 5 mg/L after 14 days of aerobic treatment. The RDX concentrations in the 30-day bioeffluents from the actual pink water experiments were between 30 and 40 mg/L (except in the case of BR-2 which had no RDX in the bioinfluent). The RDX concentrations in the 30-day bioeffluents of synthetic pink water were between 8 and 9 mg/L. From the results for RDX and TNT, it can be seen that the rate of biodegradation of RDX was slower than the rate of biodegradation of TNT.

The pretreatment of BR-2 (O_3/ UV 254 nm/ 120 minutes) reduced the bioinfluent loading of TNT and RDX to non-detect (ND) levels. The UV-catalyzed ozone treatment of BR-2 not only reduced the bioinfluent loadings of TOC, TNT, RDX and absorbance scan area but also improved the rate and extent of biodegradation of the residual pollutants. The other pretreatments of actual pink water (BR-1, BR-3 and BR-4) were less effective than BR-2. The three cases were essentially equal with respect to the reduction of bioinfluent loading as well as rate and extent of degradation of residual pollutants.

The general trend of absorbance scans for all the runs was similar. The absorbances decreased gradually with increase in aerobic treatment time. As an example, the absorbance scans as a function of biotreatment time for actual pink water control are shown in Figure 5.3. From the scans of Figure 5.3 it can be seen that the absorbances decreased at a greater rate between 0-7 days compared to the 7-30 days of biotreatment.

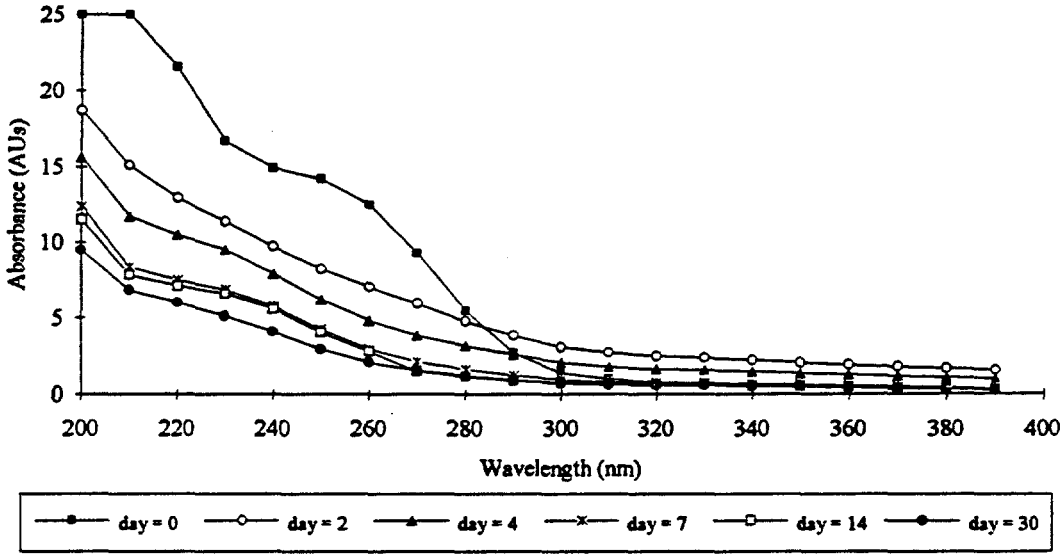


Figure 5.3 Absorbance scans as a function of aerobic biotreatment time for actual pink water control

5.3 Anaerobic/aerobic treatment of pink waters for controls and the first set of pretreatments (BR-1 through BR-5)

The experimental conditions and results of anaerobic/aerobic treatment of actual and synthetic pink water controls and the first set of pretreated pink waters (BR-1 through BR-5) are listed in Table 5.3. The high levels of TOC in the anaerobic and aerobic bioinfluents were due to the addition of yeast extract prior to the biotreatment.

The synthetic pink water was more easily biodegraded than the actual pink water under comparable conditions. The bioeffluents from the synthetic pink water reported lower TOC, TNT and RDX than the bioeffluents from the actual pink water in the aerobic phase following the anaerobic treatment.

Several benefits in the final effluent quality were achieved by the anaerobic/aerobic biotreatment sequence following certain physical/chemical treatments. The effluent concentration of TNT was essentially zero following the physical/chemical-anaerobic sequences, and even in the controls with no pretreatment the TNT levels reached zero in the anaerobic phase following the anaerobic treatment. These results would be of engineering significance only if very tight effluent limits were imposed.

The RDX concentrations dropped by 70 to 80% during the anaerobic biotreatment following the physical/chemical pretreatments with low-energy 365 nm lamps and under oxygen or nitrogen atmospheres. Such pretreatments would favor photolysis rather than the more normally preferred radical-accelerated photocatalysis. This surprising result indicates the ability to customize the physical/chemical-biotreatment sequence to the specific target compounds in the actual pink water matrix. Also, a very cost effective sequence is indicated. The RDX removals in the anaerobic/aerobic treatment were not as promising for the actual pink water runs that involved ozone. The RDX concentrations

Table 5.3 Experimental Conditions and Results of Anaerobic/Aerobic Treatment of Controls and runs BR-1 through BR-5

	RUN NUMBER						
	APW-2	SPW	BR-1	BR-2	BR-3	BR-4	BR-5
PRE-TREATMENT SCENARIO							
Pink Water	None	None	APW-2	APW-2	APW-2	APW-2	SPW
Reaction Atmosphere	None	None	O_2-O_3	O_2-O_3	O_2	N_2	O_2-O_3
Oxidant	None	None	O_3	O_3	None	None	O_3
Photon Source	None	None	UV 254	UV 254	UV 365	UV 365	UV 254
Catalyst	None	None	TiO_2	None	TiO_2	TiO_2	TiO_2
Time (min.)	None	None	5	120	30	30	5
TEST PARAMETER: VOLUME OF GAS BUILT-UP IN THE OVERHEAD AFTER ANAEROBIC TREATMENT							
Volume of gas measured in the overhead (mL)	535.0	655.0	535.0	650.0	639.0	610.0	646.0
Volume of gas/ Volume of sample treated	1.2	1.5	1.2	1.4	1.4	1.3	1.4
TEST PARAMETER: TOTAL ORGANIC CARBON (TOC) mg/L							
Day 0	1985.6	1920.8	2090.0	2078.0	1934.6	1851.6	1965.6
14	345.3	110.0	374.7	134.3	143.9	205.8	107.6
Day 0	2247.3	2010.5	2282.1	2025.7	2087.2	2021.7	2018.0
8	156.0	161.4	261.1	121.8	138.0	128.5	108.2
16	130.1	141.6	144.0	124.5	120.7	157.8	144.3
TEST PARAMETER: TNT (mg/L)							
Day 0	125.3	33.8	71.2	4.7	62.5	55.3	33.8
14	15.3	0.0	0.0	0.0	0.0	0.0	0.0
Day 0	15.3	0.0	0.0	0.0	0.0	0.0	0.0
8	0.0	0.0	0.0	0.0	0.0	0.0	0.0
16	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TEST PARAMETER: RDX (mg/L)							
Day 0	77.6	16.9	64.5	0.0	73.4	70.2	13.3
14	63.8	0.0	47.8	0.0	15.2	10.5	0.0
Day 0	63.8	0.0	47.8	0.0	15.2	10.5	0.0
8	38.2	0.0	38.2	0.0	13.8	10.4	0.0
16	38.9	0.0	38.6	0.0	13.8	7.7	0.0

(Table 5.3 continued)

		RUN NUMBER						
		APW-2	SPW	BR-1	BR-2	BR-3	BR-4	BR-5
TEST PARAMETER: MICROTOX TOXICITY (TU50)								
Day	0	32.4	45.2	151.5	61.7	104.2	138.9	62.9
	14	3.0	1.5	2.8	ND	1.95	ND	6.2
	0	--	--	--	--	--	--	--
	8	--	--	--	--	--	--	--
	16	ND	ND	ND	ND	ND	ND	ND
TEST PARAMETER: pH								
Day	0	6.29	6.24	6.26	6.20	6.31	6.27	6.18
	14	7.06	7.94	6.98	8.00	7.87	7.85	7.95
	0	--	--	--	--	--	--	--
	8	8.30	8.16	7.77	8.20	7.87	7.79	7.64
	16	7.49	7.40	8.04	7.60	7.44	7.56	6.69
TEST PARAMETER: TOTAL SUSPENDED SOLIDS (TSS) mg/L								
Day	0	148.0	116.0	208.0	136.0	168.0	148.0	202.0
	14	204.0	364.0	132.0	180.0	360.0	260.0	300.0
	0	--	--	--	--	--	--	--
	8	230.	277.0	136.5	251.0	196.0	200.0	125.6
	16	247.2	304.0	290.0	278.0	296.8	466.0	370.0

ND - Not detected.

dropped to non-detect levels for the synthetic pink waters after the anaerobic phase of the biotreatment.

The TOC reductions after 14-days of aerobic treatment ranged from 83% to 93%. The change in TOC includes the totally oxidized fractions of TNT, RDX and yeast extract. The bioeffluents from the anaerobic treatment are added with yeast extract at 0.25% thereby increasing the levels of TOC in the aerobic influents. After 16 days of aerobic treatment the TOCs in the bioeffluents in most of the cases were less than 150.0 mg/L.

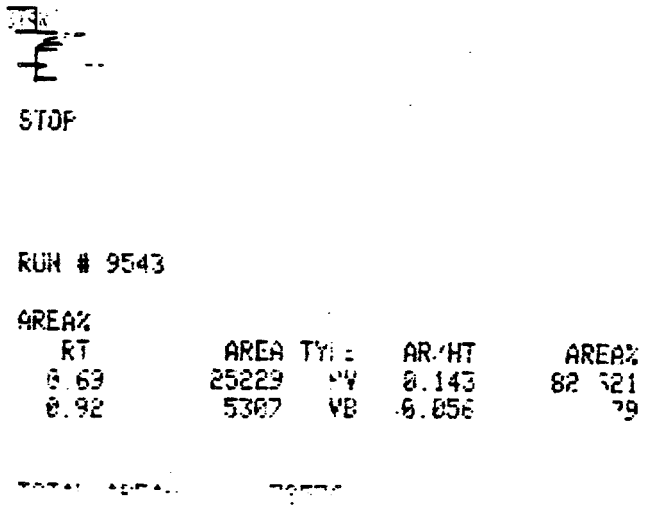
The volumes of gas generated after the anaerobic treatment varied from 535 to 655 mL for 450 mL of sample treated. The volume of overhead gas generated seems to

be more in the cases where greater RDX degradation was achieved. The GC chromatograms obtained from 20 μL injections of the headspace gases from various runs are shown in Figures 5.4 (a) - (i). Figures 5.4 (h) and (i) show the elution of the methane standard at 0.63 minute. For BR-2 (APW-2/O_3/UV-254 nm/120 minutes) pre-treatment, the peaks in the GC chromatogram were seen at 0.63 and 1.09 minutes corresponding to methane and nitrogen gases respectively. In all the other cases other-than BR-2, the GC peaks were observed at about 0.68 and 1.09 minutes corresponding to an undetermined low-molecular hydrocarbon and nitrogen gases respectively.

No significant variation in pH was seen in either the anaerobic or aerobic bioeffluents indicating that the buffers that were added to the bioinfluents were of sufficient capacity. The changes in pH for all the cases under consideration (Table 5. 3) were with-in 1.0 unit.

Figure 5.5 shows the absorbance scans for the bioinfluents and the bioeffluents from the anaerobic/aerobic biotreatment of the effluent from BR-2 pretreatment (O_3/ UV 254 nm/ 120 minutes). Figure 5.5 also shows the effect of yeast extract addition to the bioinfluents of both aerobic and anaerobic processes.

Toxicity of anaerobic effluents were generally low and reached negligible levels after the subsequent aerobic treatment.



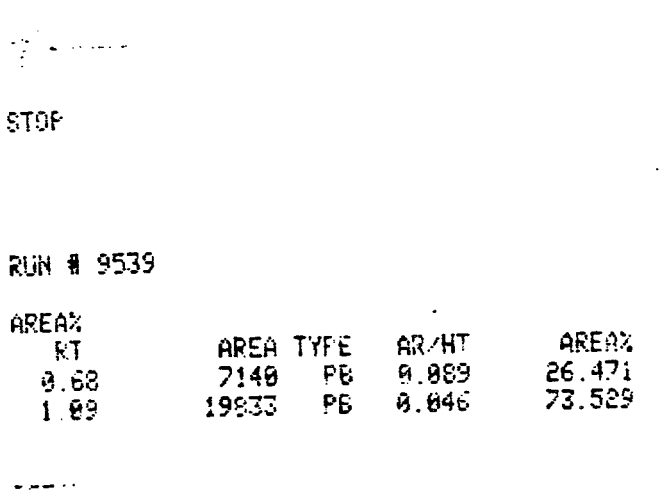
STOP

RUN # 9543

AREA%

RT	AREA	TYPE	AR/HT	AREA%
0.69	25229	PV	0.143	82.321
0.92	5387	VB	0.056	17.679

Figure 5.4 (a) GC chromatogram of the overhead gas from the 14 day anaerobically treated actual pink water control (injection volume = 20 µL)



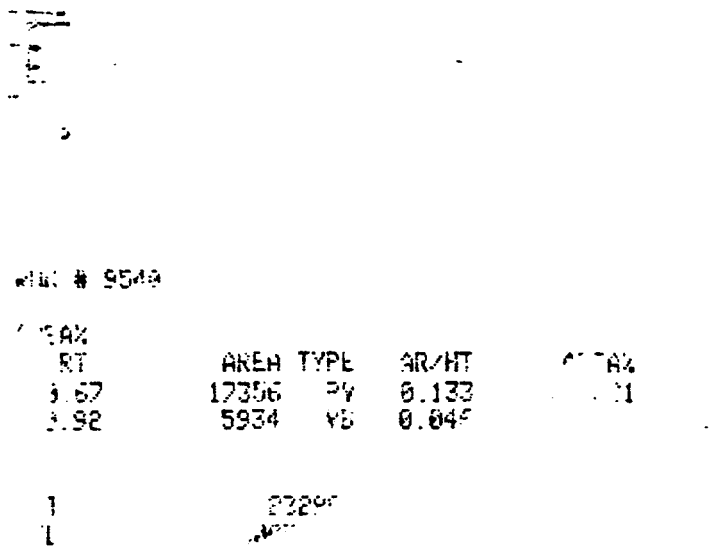
STOP

RUN # 9539

AREA%

RT	AREA	TYPE	AR/HT	AREA%
0.68	7140	PB	0.089	26.471
1.09	19833	PB	0.046	73.529

Figure 5.4 (b) GC chromatogram of the overhead gas from the 14 day anaerobically treated synthetic pink water control (injection volume = 20 µL)

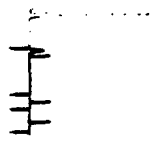


RUN # 9548

AREA%

RT	AREA	TYPE	AR/HT	AREA%
0.67	17356	BV	0.133	.91
1.92	5934	VB	0.04[illegible]	

Figure 5. 4 (c) GC chromatogram of the overhead gas from the 14 day anaerobically treated BR-1 (actual pink water pretreated with O_3, UV 254 nm and TiO_2 for 5 minutes) of injection volume = 20 μL



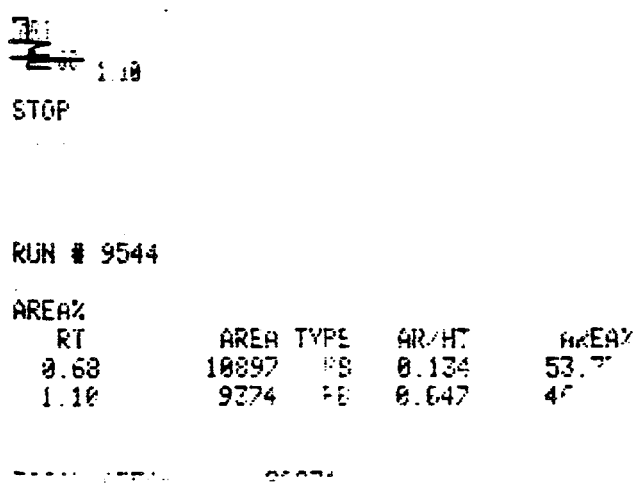
STOP

RUN # 9541

AREA%

RT	AREA	TYPE	AR/HT	AREA%
0.63	16221	BV	0.118	44.186
1.09	20488	VB	0.048	55.812

Figure 5. 4 (d) GC chromatogram of the overhead gas from the 14 day anaerobically treated BR-2 (actual pink water pretreated with O_3 and UV 254 nm for 120 minutes) of injection volume = 20 μL



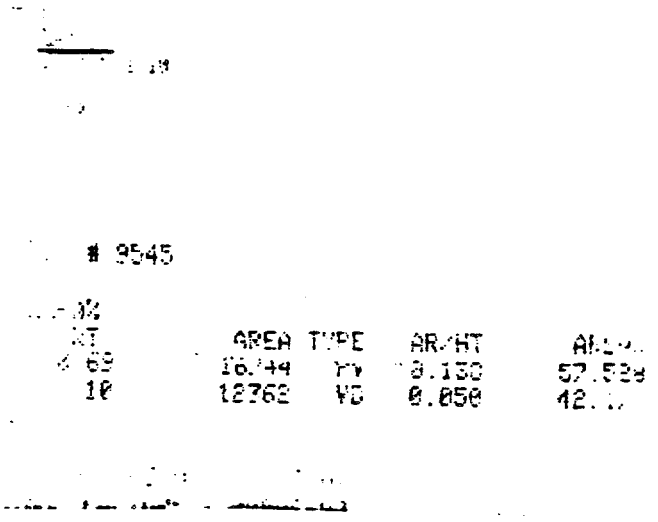
STOP

RUN # 9544

AREA%

RT	AREA	TYPE	AR/HT	AREA%
0.68	10897	PB	0.134	53.7
1.10	9374	PB	0.047	4[illegible]

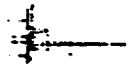
Figure 5. 4 (e) GC chromatogram of the overhead gas from the 14 day anaerobically treated BR-3 (actual pink water pretreated with O_2, UV 365 nm and TiO_2 for 30 minutes) of injection volume = 20 μL



9545

RT	AREA	TYPE	AR/HT	AREA%
0.69	16744	PV	0.130	57.53[illegible]
1[illegible]	12363	VB	0.050	42.[illegible]

Figure 5. 4 (f) GC chromatogram of the overhead gas from the 14 day anaerobically treated BR-4 (actual pink water pretreated with N_2, UV 365 nm and TiO_2 for 30 minutes) of injection volume = 20 μL



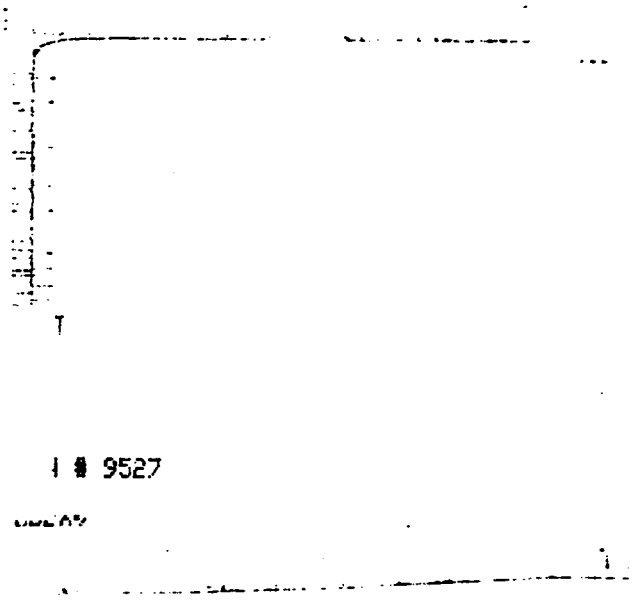
TOP

RUN # 9537

AREA%

RT	AREA	TYPE	AR/HT	AREA%
0.68	7630	FB	0.112	31.805
1.09	16360	BB	0.045	68.195

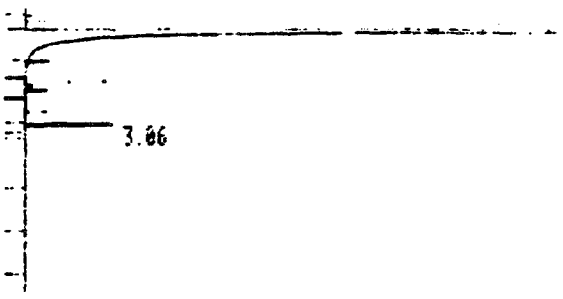
Figure 5. 4 (g) GC chromatogram of the overhead gas from the 14 day anaerobically treated BR-5 (synthetic pink water pretreated with O_3, UV 264 nm and TiO_2 for 5 minutes) of injection volume = 20 μL



T

9527

Figure 5. 4 (h) GC chromatogram of 1002 ppm methane standard (injection volume = 20 μL)



9530

AREA% RT	AREA	TYPE	AR/HT	AREA%
				99.351
				219
				430

Figure 5. 4 (i) GC chromatogram of 1% methane standard

(injection volume = 20 μL)

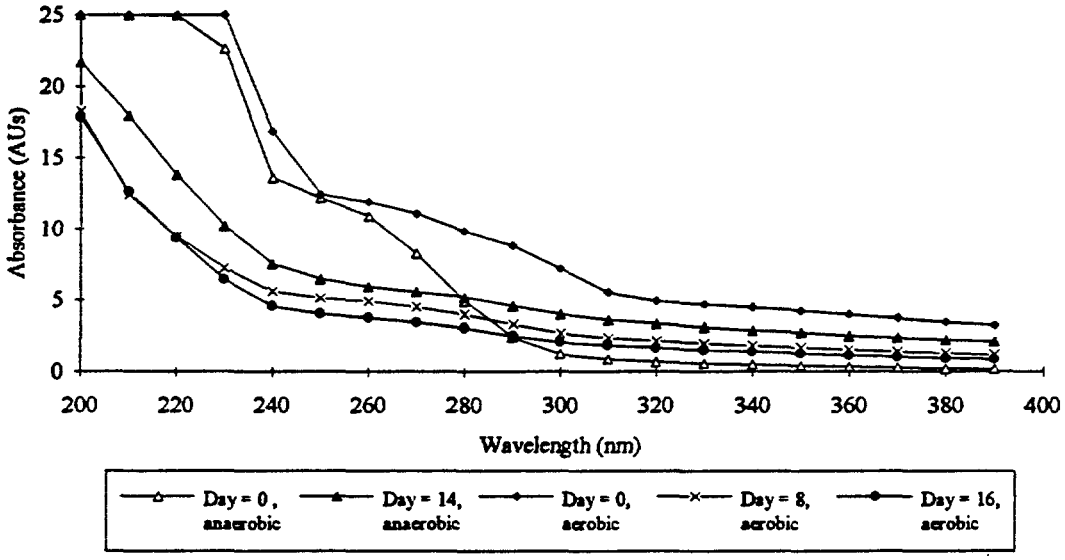


Figure 5.5 Absorbance scans as a function of anaerobic/aerobic biotreatment time for effluent from BR-2 (actual pink water treated for 120 minutes with O_3 and UV 254)

5.4 Physical and chemical treatment of actual pink water for the second set of experiments (BR-6 through BR-11)

Previous results (section 5.2) had shown that the aerobic degradation of RDX was not as fast as the aerobic degradation of TNT. Earlier pink water studies (section 5.1) had also shown that the destruction of RDX was achieved at a greater rate under UV-catalyzed ozone treatment (UV 254 nm/O_3) than under heterogeneous photocatalytic treatment (O_3/UV 254 nm/TiO_2). Considering the above mentioned factors, a series of experiments (BR-8 through BR-11) were conducted to quantify the degree of treatment in a UV 254 nm light-catalyzed ozone reactor and study the further degradation in an aerobic biological reactor.

Two samples of actual pink water were also treated at the Sandia National Laboratories with a combination of UV-spectrum light, N_2, Na_2EDTA and TiO_2. One of the objectives of this study was to determine the aerobic biotreatability of the actual pink water pretreated by the combination of UV-spectrum-N_2-Na_2EDTA-TiO_2.

The experimental conditions and results of physical/chemical treatment for the second set of experimental runs (BR-6 through BR-11) are listed in Table 5.4. All the runs were perfomed on actual pink water.

For the experimental runs involving ozone (BR-8, BR-9, BR-10 and BR-11) the TOC reductions ranged from 0% to 17%. The amount of organic destruction was directly related to the amount of ozone transferred and photon transfered. In terms of the TOC removed per mass of ozone transferred, BR-10 was more efficient than the rest, which reflects the type of by-products formed due to prolonged oxidation treatment. Not much difference was seen in the TOC removal between the runs involving the variation in the exposure to the UV-254

TABLE 5. 4 EXPERIMENTAL CONDITIONS AND RESULTS OF PHYSICAL/CHEMICAL TREATMENT RUNS BR-6 THROUGH BR-11

EXPERIMENTAL DESIGNATION	RUN NUMBER					
	BR-6	BR-7	BR-8	BR-9	BR-10	BR-11
PHYSICAL/CHEMICAL TREATMENT SCENARIO						
Type of Pink Water	APW-2	APW-2	APW-2	APW-2	APW-2	APW-2
Reaction Atmosphere	N_2	N_2	O_2-O_3	O_2-O_3	O_2-O_3	O_2-O_3
Oxidant	None	None	O_3	O_3	O_3	O_3
Photon Source	Spectrum	Spectrum	UV 254	UV 254	UV 254	UV 254 (1/2)
Catalyst	Na_2EDTA + TiO_2	Na_2EDTA + TiO_2	None	None	None	None
Reaction Time (t = final) minutes	10	30	5	30	60	30
TEST PARAMETER: OZONE TRANSFER						
Ozone	mg/.75L	–	–	13.1	82.7	156.4	86.4
Transfer	mg/L	–	–	17.4	110.3	208.5	115.2
TEST PARAMETER: TOTAL ORGANIC CARBON (TOC) mg/L							
TOC	t = 0	–	–	64.0	64.0	64.0	64.0
(mg/L)	t = final	153.5	151.2	64.0	60.3	52.7	60.0
%TOC Removed		–	–	0.0	5.8%	17.7%	6.3%
TOC Removed/ O_3 Transferred		–	–	0.0	0.03	0.05	0.03
TEST PARAMETER: ABSORBANCE SCAN AREAS UNDER 200-390 nm							
Untreated Feed Water		1104.1	1104.1	1104.1	1104.1	1104.1	1104.1
After P/C Treatment		988.0	987.7	749.5	631.3	558.1	566.6
% Absorbance Area Removed		10.5	10.5	32.1	42.8	49.5	48.7
TEST PARAMETER: TNT (mg/L)							
TNT	t = 0	125.3	125.3	125.3	125.3	125.3	125.3
(mg/L)	t = final	80.5	54.6	61.2	31.7	19.6	39.8
%TNT Removed		35.8%	56.4%	51.1%	74.7%	84.4%	68.2%
TNT Removed/ O_3 Transferred		–	–	3.70	0.85	0.51	0.74
TEST PARAMETER: RDX (mg/L)							
RDX	t = 0	77.6	77.6	77.6	77.6	77.6	77.6
(mg/L)	t = final	72.6	58.5	57.3	26.6	5.4	43.5
%RDX Removed		6.4%	24.6%	26.2%	65.7%	93.0%	43.9%
RDX Removed/ O_3 Transferred		–	–	1.17	0.46	0.35	0.30
TEST PARAMETER: MICROTOX TOXICITY (TU50)							
Toxicity	t = 0	32.4	32.4	32.4	32.4	32.4	32.4
(TU50)	t = final	122.0	58.0	65.0	118.0	28.0	86.0

lamp (BR-9 and BR-11). No significant difference was seen in the TOC removals between the runs that involved Na_2EDTA catalyst (see BR-6 and BR-7).

The TNT removals for the experiments listed in Table 5.4 ranged from 36% to 84%. On the basis of mass of TNT destroyed per mass of ozone transferred, BR-8 conditions are more efficient than the rest. It should be noted that the oxidation time is also a significant difference in the experimental conditions among the different runs. Approximately 6% more TNT was destroyed when full lamp (BR-9) was used compared to the half-lamp (BR-11). Between the runs involving the Na_2EDTA catalyst the amount of TNT destruction was proportional to the time of exposure to the UV-spectrum.

The reductions in RDX for the runs listed in Table 5.4 ranged from 6% to 93%. Among the runs involving ozone (BR-8, BR-9, BR-10 & BR-11) the RDX removal was directly proportional to the ozone transfer. Between the experiments involving the Na_2EDTA catalyst approximately 20% more RDX was removed under the conditions of BR-7 (30 minutes run) compared to the conditions of BR-6 (10 minutes run).

Depicted in Figure 5.6 are the absorbance scans of the effluent samples from the UV (254 nm)-catalyzed ozone treatments. The most notable absorbance changes occurred under the conditions of BR-10. Absorbance scans for UV-N_2-Na_2EDTA experiments (BR-6 and BR-7) are shown in Figure 5.7. The scans of Figure 5.7 also indicate the presence of dissolved EDTA.

The UV-N_2-Na_2EDTA-TiO_2 reductive reactions were not as effective as the UV 254 light-catalyzed ozone treatments in destroying TNT and RDX. The high levels of TOC in the reductive runs was due to the presence of EDTA in addition to the actual pink water. Apparently EDTA was not destroyed under the reductive reaction conditions.

An increase in toxicity was observed in all the physical/chemical effluents except for BR-10. The physical/chemical effluent from BR-6 (UV-spectrum/ N_2/ Na_2EDTA/ TiO_2/ 10 minutes) recorded the highest toxicity between the runs involving Na_2EDTA catalyst while the physical/chemical effluent from BR-9 (O_3/ UV 254 nm/ 30 minutes) recorded the highest toxicity among the runs involving ozone.

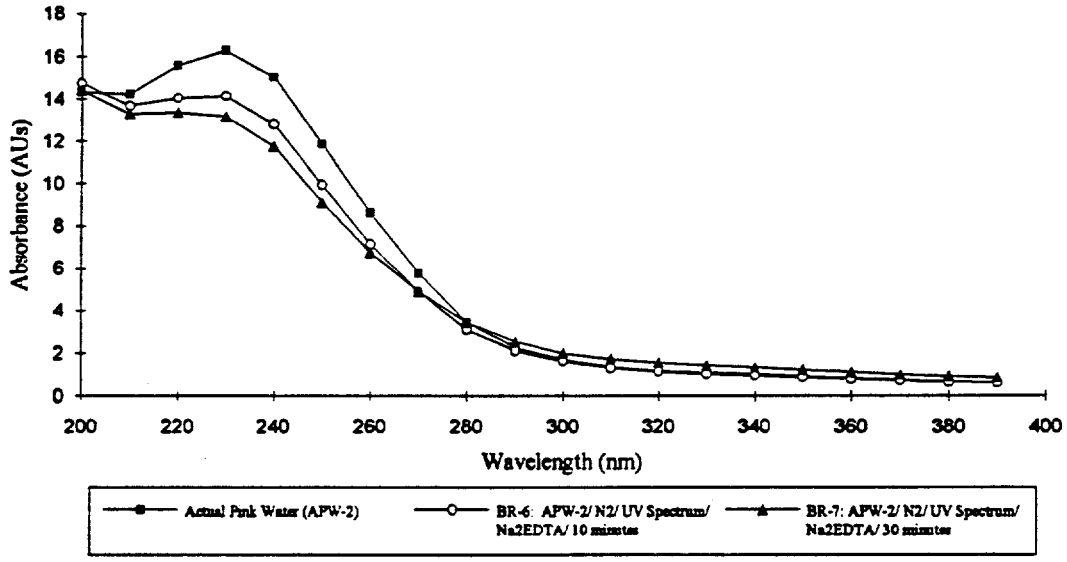


Figure 5.6 Absorbance scans from 200-390 nm of untreated and N_2/ UV Spectrum/ Na_2EDTA/ TiO_2 treated actual pink water

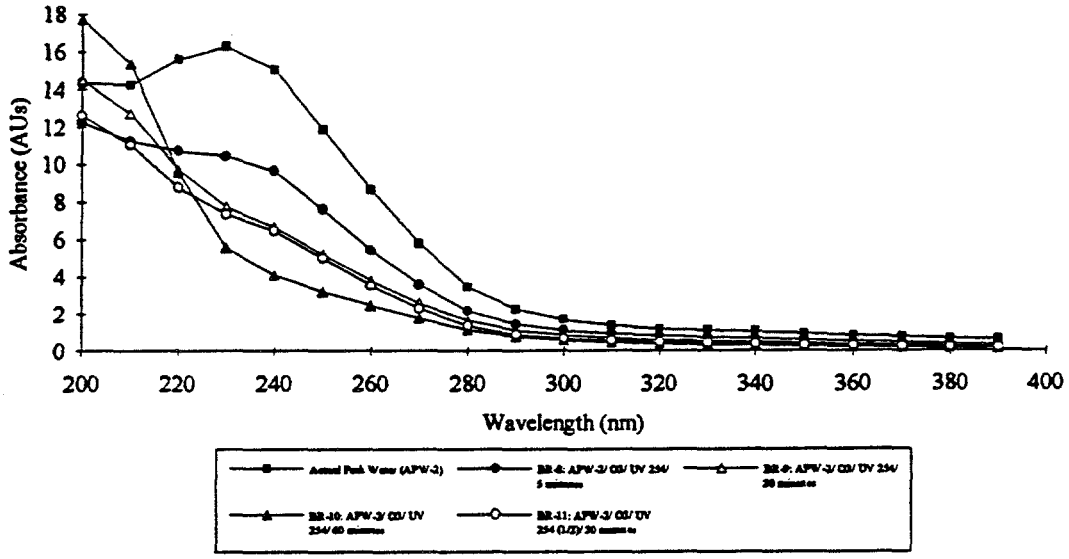


Figure 5.7 Absorbance scans from 200-390 nm of untreated and Ozone - UV 254 treated actual pink water

5.5 Results of aerobic treatment of actual pink water for the second set of experiments (BR-6 through BR-11)

Experimental conditions and results of 7-day aerobic degradation of the second set of treatments (BR-6 through BR-11) of actual pink water are listed in Table 5.5. As mentioned earlier the addition of yeast extract at 0.25% boosted the values of TOC's for the bioinfluents.

The aerobic treatment was conducted for only seven days because the earlier findings (section 5.2) indicated that most of the biodegradation was completed in the first seven days of treatment. As expected, the associated soluble TOC was removed and the TSS increased significantly during the first seven days of biotreatment.

The TOCs of the bioeffluents from the UV (254 nm)-catalyzed ozone pretreated runs were lower than the TOCs of the bioeffluents pretreated by N_2-Na_2EDTA-TiO_2-UV indicating that the dissolved EDTA in the latter runs was not biodegraded. The 7-day bioeffluent from the photocatalytic pretreated runs were about 60 mg/L in all the cases indicating that the nature of pretreatment had little or no impact on the TOC removal by aerobic treatment.

The TNT in the bioeffluents reached non-detect levels in all the cases reported in Table 5.5 after 7 days of aerobic treatment indicating that the TNT in the bioinfluents had insignificant effect on the TNT removal by biological treatment.

The RDX results reported in Table 5.5 show that the removal of RDX after 7 days of aerobic treatment is very minor (<10%). This finding confirms the earlier outcome of the section 5.2.

TABLE 5.5 EXPERIMENTAL CONDITIONS AND RESULTS OF AEROBIC TREATMENT OF RUNS BR-6 THROUGH BR-11

EXPERIMENTAL DESIGNATION	RUN NUMBER					
	BR-6	BR-7	BR-8	BR-9	BR-10	BR-11
PHYSICAL/CHEMICAL TREATMENT SCENARIO						
Type of Pink Water	APW-2	APW-2	APW-2	APW-2	APW-2	APW-2
Reaction Atmosphere	N_2	N_2	O_2-O_3	O_2-O_3	O_2-O_3	O_2-O_3
Oxidant	None	None	O_3	O_3	O_3	O_3
Photon Source	Spectrum	Spectrum	UV 254	UV 254	UV 254	UV 254 (1/2)
Catalyst	Na_2EDTA + TiO_2	Na_2EDTA + TiO_2	None	None	None	None
Oxidation Time (min.)	10	30	5	30	60	30
TEST PARAMETER: TOC (mg/L)						
Day 0	1100.0	1089.0	1005.0	959.5	927.8	919.3
Day 2	499.7	496.7	254.3	216.5	198.5	218.8
Day 4	235.3	234.6	75.4	69.2	67.6	66..3
Day 7	207.5	196.1	63.2	60.2	59.5	64.9
TEST PARAMETER: TNT (mg/L)						
Day 0	80.8	55.8	65.6	35.8	20.9	42.8
Day 2	3.8	4.2	5.6	4.0	4.3	5.1
Day 4	3.5	0.0	6.6	4.2	4.4	5.1
Day 7	0.0	0.0	0.0	0.0	0.0	0.0
TEST PARAMETER: RDX (mg/L)						
Day 0	71.8	58.4	58.8	26.8	5.4	42.9
Day 2	66.8	59.0	52.9	24.1	6.1	37.2
Day 4	61.1	52.9	46.5	20.7	4.4	34.5
Day 7	–	–	45.8	–	–	–
TEST PARAMETER: MICROTOX TOXICITY (TU50)						
Day 0	122.0	58.0	65.0	118.0	28.0	86.0
Day 2	–	–	–	–	–	–
Day 4	–	–	–	–	–	–
Day 7	4.2	2.1	1.7	ND	1.1	1.4

(Table 5.5 continued)

EXPERIMENTAL DESIGNATION		RUN NUMBER					
		BR-6	BR-7	BR-8	BR-9	BR-10	BR-11
TEST PARAMETER: TOTAL SUSPENDED SOLIDS (mg/L)							
Day	0	125.0	348.0	82.5	67.5	55.0	200.0
	2	230.0	240.5	332.5	339.9	452.0	309.9
	4	185.0	223.0	168.0	157.5	252.5	257.5
	7	100.0	156.0	94.0	98.0	166.0	140.0
TEST PARAMETER: pH							
Day	0	7.05	7.20	7.12	7.50	7.36	7.23
	2	6.83	6.92	7.07	7.00	7.01	7.09
	4	6.92	6.92	7.14	7.18	7.17	7.21
	7	7.03	7.56	7.19	7.20	7.20	7.23

ND - Not detected.

The toxicity of the bioinfluents was almost completely removed after 7 days of aerobic treatement indicating that no toxic intermediates were formed in course of biotreatment under any of the conditions that were studied.

No significant variations in pH were seen in the aerobic effluents. The changes in pH for all the cases under study were less than 0.5 unit.

Figures 5.8, 5.9 and 5.10 show the absorbance scans from 200 to 390 nm as a function of biotreatment time for variously pre-treated pink waters. Scans of the bioeffluents from the N_2-Na_2EDTA-TiO_2-UV (Figure 5.8) pre-treated pink waters differ drastically from the scans of UV (254 nm) catalyzed-ozone (Figure 5.9) pre-treated pink waters indicating the effect of pre-treatment on the by-products formed during biotreatment. Whereas the scans shown in Figures 5.9 and 5.10 appear alike indicating the likeness in the pre-treatment scenario (BR-9 used full lamp, while BR-11 used half lamp of UV 254 nm).

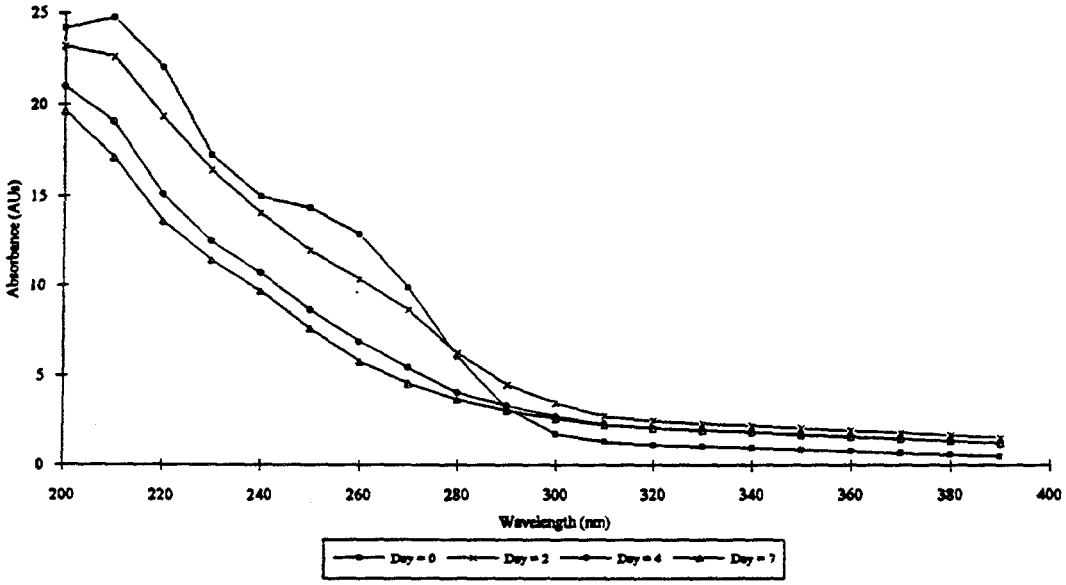


Figure 5.8 Absorbance scans as a function of aerobic treatment time for the effluent from BR-7 pretreatment (actual pink water treated for 30 minutes with N_2, Na_2EDTA, TiO_2 and UV-Spectrum)

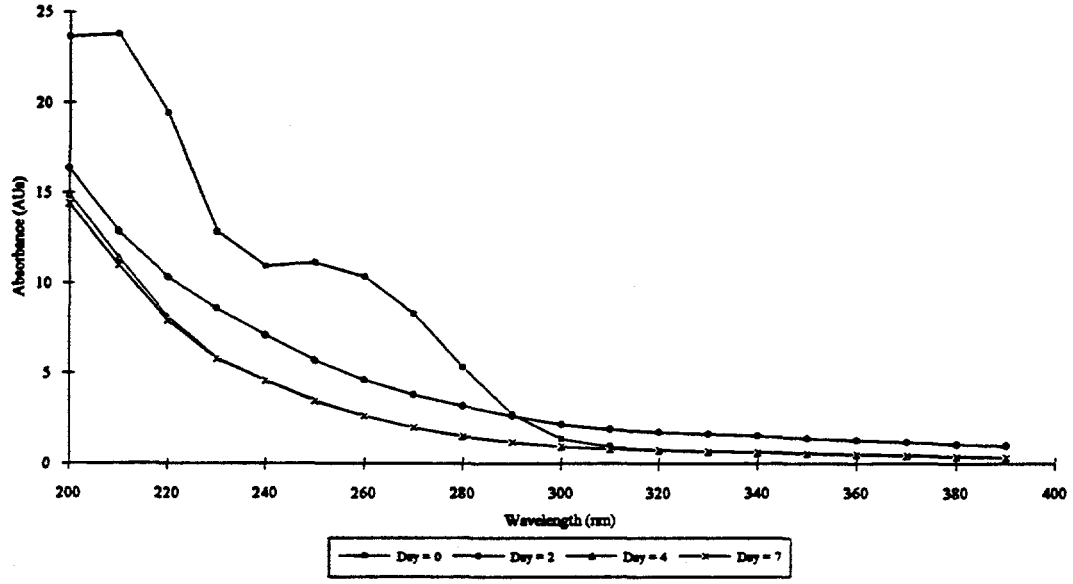


Figure 5.9 Absorbance scans as a function of aerobic treatment time for the effluent from BR-9 pretreatment (actual pink water treated for 30 minutes with O_3 and UV 254 nm lamp)

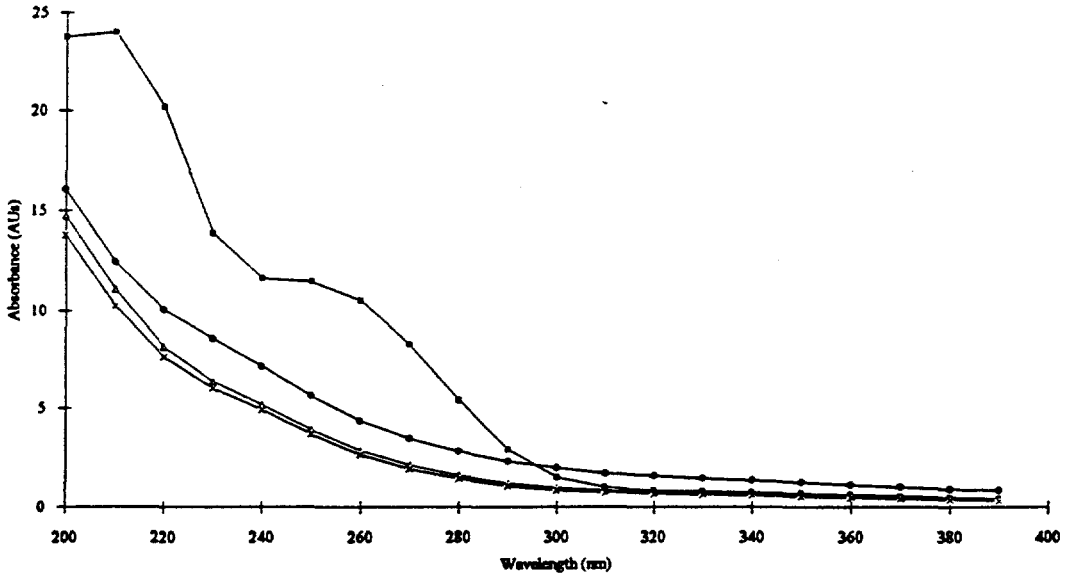


Figure 5.10 Absorbance scans as a function of aerobic treatment time for the effluent from BR-11 pretreatment (actual pink water treated for 30 minutes with O_3 and UV 254 nm half-lamp)

5.6 Physical/chemical (O_3/ UV 254 nm) treatment of actual pink water following 7-day aerobic treatment (BR-12)

One experiment was conducted with biotreatment prior to the UV (254 nm) catalyzed-ozone treatment. The idea behind this experiment was to reduce the loading of the munition components in physical/chemical influent and thereby reduce the oxidation time and hence reduce the cost and energy expended. The results of the test run are summarized in Table 5.6. From the results, it can be inferred that the 7-days of aerobic treatment resulted in 100% bioconversion of TNT while no bioconversion of RDX was observed. The reduction of RDX to non-detect levels by UV catalyzed-ozone treatment took approximately half the oxidation time and ozone transfer in case of the 7-day biotreated actual pink water compared to the untreated actual pink water for similar experimental conditions (O_3/ UV 254 nm, comparing the results of BR-12 and BR-10). No appreciable change in TOC was seen even after 2 hours of UV 254 nm/O_3 treatment indicating that the byproducts of biotreatment are recalcitrant to complete oxidation. Toxicity of the bio followed by physical/chemical treated effluent remained low indicating that the toxicity was not reintroduced by the P/C process.

TABLE 5.6 RESULTS OF PHYSICAL/CHEMICAL (O_3/ UV 254 nm) TREATMENT OF ACTUAL PINK WATER AFTER 7-DAYS OF AEROBIC TREATMENT

Oxidation Time (minutes)	Ozone Transferred (mg/L)	Total Organic Carbon (TOC) (mg/L)	TNT (mg/L)	RDX (mg/L)	Toxicity (TU50)
0.0	0.0	90.4	0.0	65.7	2.71
15.0	82.1	91.1	0.0	28.6	–
30.0	154.4	97.2	0.0	0.0	–
60.0	219.9	96.7	0.0	0.0	–
90.0	255.7	96.8	0.0	0.0	–
120.0	293.9	90.2	0.0	0.0	3.14

5.7 Sorption study conducted on TNT and RDX with yeast extract

To identify the possibility of sorption of munition components (TNT or RDX) to yeast extract, a known volume of actual pink water was added with yeast extract at 0.25% (2.5 g/L) and contacted for 24 hours. Samples were taken at 0, 2, 4, and 24 hours and filtered using 0.45 μm Millipore filter to separate out any suspended solids. The filtered samples were tested for TNT and RDX and the following figure (Figure 5.11) summarizes the results. The normalized concentrations were around 1.0 even after 24 hours of contact time indicating no appreciable sorption of TNT or RDX to yeast extract.

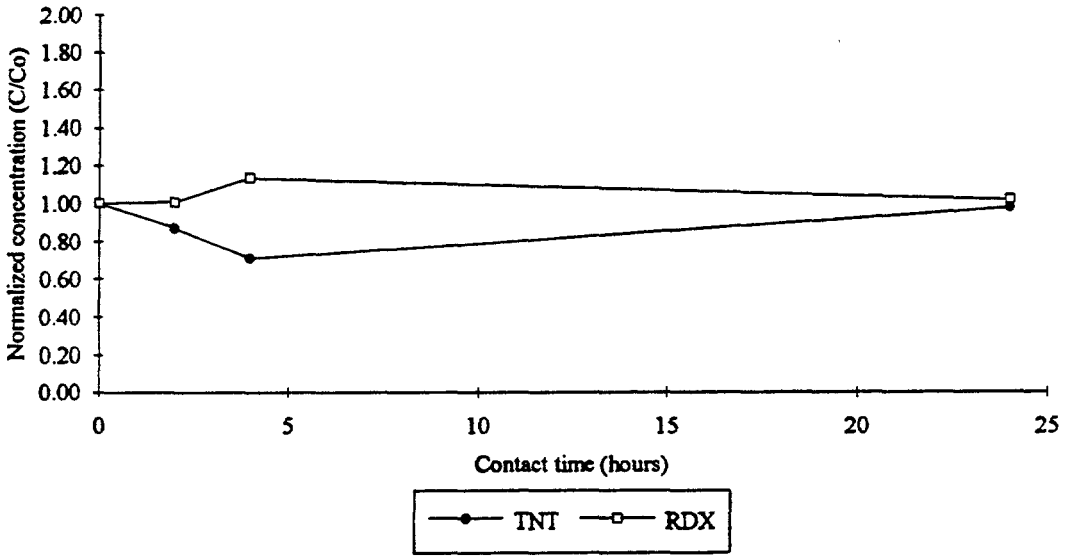


Figure 5.11 Results of sorption study for TNT and RDX on yeast extract

5.8 Aerobic degradation of RDX in the absence of external carbon or nitrogen source

Because of the poor performance of aerobic treatment on RDX degradation, an additional run was performed to improve the biodegradation of RDX by keeping it as the sole source of carbon and nitrogen for the seed bacteria. In this experiment, aerobic degradation of RDX in the absence of any external source of carbon or nitrogen was studied over a 10-day period. A known amount of crystalline RDX was added to ultra-pure (Milli Q) water and allowed to dissolve at room temperature. An appropriate amount of aerobic acclimated seed was added to this water and aerated in an Imhoff cone aerobic reactor. The results of the HPLC analysis are plotted in Figure 5.12. Over the 10-day period of aerobic treatment, the RDX concentration declined by approximately 30%. Note that the dissolved RDX in the synthetic feed water (used in this experiment) was approximately 12.5% of the dissolved RDX in the actual pink water and hence under similar experimental conditions the rate of RDX degradation at higher concentrations (of RDX) may not be the same as at the lower concentrations (of RDX).

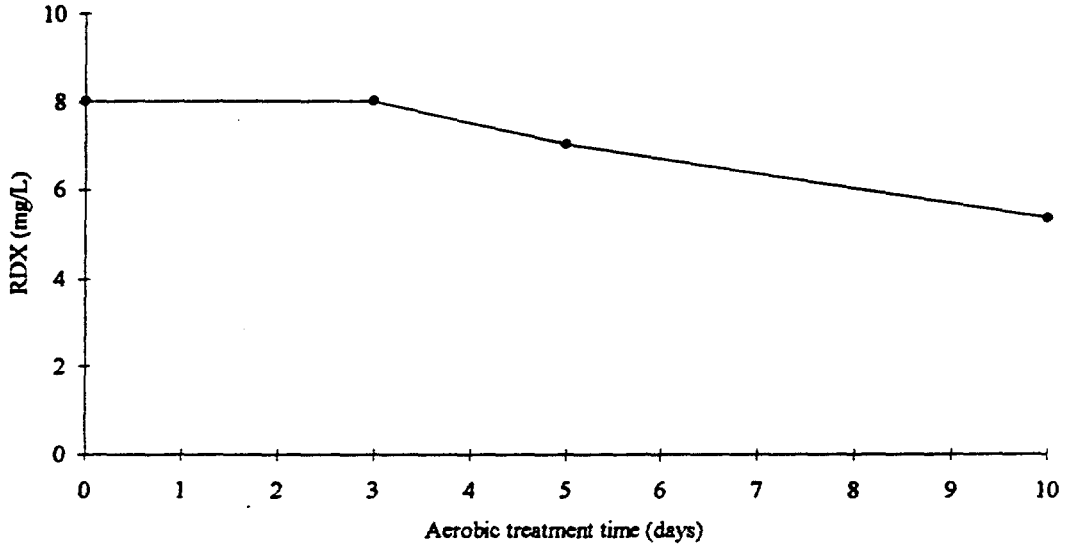


Figure 5.12 Results of aerobic biodegradation of RDX in the absence of any external carbon or nitrogen source

CHAPTER 6
DISCUSSION

6.1 Biodegradation of TNT

The significant differences between the earlier studies on biodegradation of TNT and the experiments carried out as part of this research include the use of acclimated seed and mixed substrates (TNT along with RDX, DNT and other by-products of physical/ chemical pretreatment). Most of the earlier studies (Osmon et al. 1972, Won et al. 1974 and Hoffsommer et al. 1978) on biodegradation of TNT were carried out using single substrate (TNT) and pure cultures or unacclimated-mixed cultures (activated sludge).

6.1.1 Effect of addition of supplemental carbon and nitrogen sources on TNT degradation

TNT degradation occurred very rapidly in biological treatment, both under aerobic and anaerobic conditions, in all the different cases of pink waters that were tested. One of the main reasons for the rapid biodegradation of TNT could have been due to the presence of supplemental carbon (yeast extract) and nitrogen (NH_4Cl) sources in the bioinfluents. This finding concurs with the earlier findings made by Won et al. (1974), Hoffsommer et al. (1978), Klausimier et al. (1979) and Boopathy et al. (1993). The results of this research strongly support the use of supplemental carbon and nitrogen source for biodegradation of TNT irrespective of the extent of oxidative pre-treatment and acclimation of bacteria.

Although microbes may preferentially utilize specific compounds, it is possible that different compounds may be oxidized simultaneously. Horvath (1972) defines co-metabolism as the process by which a microorganism oxidizes a substrate without being able to utilize the energy derived from this oxidation to support growth. Since a co-metabolite cannot serve as a sole source of carbon and energy, an additional source must be present. Dalton and Sterling (1982) defined co-metabolism as the transformation of a non-growth substrate in the obligate presence of growth substrate or another transformable compound. This non-growth substrate or co-metabolite will not support cell division.

The benefits of co-metabolite (yeast extract) addition will be important in the process design. Since the co-substrate effect is associated with the biomass growth in the presence of both pink water and soluble co-substrate, the provisions for addition of co-substrate to the influent liquid must be emphasized in the biological process design.

6.1.2 Effect of use of acclimated mixed cultures on the rate of biotransformation of TNT

Won et al. (1974) had isolated certain strains of P*seudomonads* that could degrade TNT. Hoffsommer et al. (1978) showed that the TNT supplemented with glucose was efficiently biotransformed by an unacclimated mixed culture of microorganisms. Depending on the loading of TNT (varying from 123.0 to 0.0 mg/L) in the bioinfluent, the levels of TNT were brought down to less than 5.0 mg/L within two weeks of aerobic or anaerobic treatment by the use of acclimated mixed bacterial culture. The results of this research confirm the fact that the rate of biotransformation of TNT with the acclimated mixed bacterial strains was nearly the same as the rate of biotransformation of TNT using

pure *Pseudomonads* organisms. The ability of a microbial community to degrade toxic chemicals like TNT seems to be enhanced by previous exposure of the community to the pollutant of interest.

6.1.3 Effect of bioinfluent color on TNT removal by biological processes

Nay et al. (1972) reported that the photochemically enhanced color in TNT wastes has a derogatory effect on the subsequent biological waste treatment. All the oxidative pretreatment experiments that were conducted as part of this research involved the exposure of the pink water to UV light (either 254 nm or 365 nm) resulting in the enhancement of color in the P/C effluents (or bioinfluents). Based on the results of biotreatment of TNT that were generated as part of this research, the enhanced color does not seem to hinder the biotreatability in any noticeable fashion.

Nay et al. (1972) also reported a significant increase in pH with increase in color for the TNT wastes on exposure to strong light. This leads us to believe that it is the change in pH that might be affecting the biotreatabilty of TNT wastes rather than the color enhancement. As mentioned earlier, phosphate buffers was added to the bioinfluents in all the experiments that were carried out as part of this research. Moreover, Nay et al. (1972) studied the effects of color enhancement on the biotreatability of TNT in the absence of a supplemental carbon source. Hence it can be concluded that the effects of color enhancement on biotreatability of TNT could be effectively regulated by controlling the pH and providing supplemental carbon and nitrogen sources.

6.1.4 Anaerobic vs. aerobic treatment of TNT

Boopathy et al. (1993) reported successful anaerobic removal (approximately 80%) of TNT under nitrate-reducing conditions. The results of anaerobic treatment studies of this research indicated 90 to 100% removal (in most of the cases) after 14-days of anaerobic treatment. The improvement could be credited to the availability of additional carbon source (yeast extract) in addition to the nitrate-reducing conditions. Moreover, the bacterial culture used in this research was acclimated over 2-3 months period.

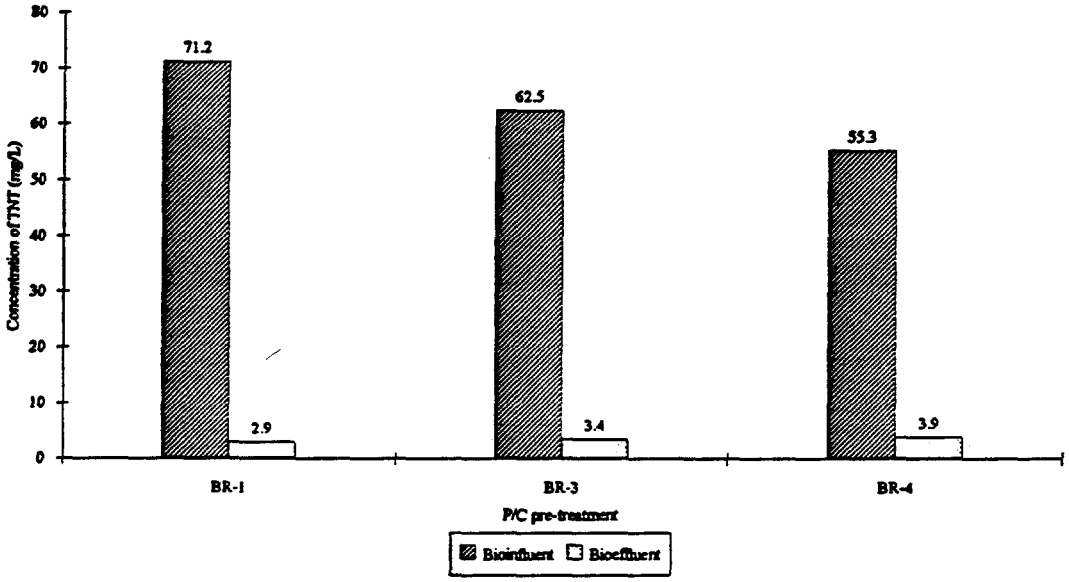
Since large volumes of gas were measured in the headspaces of the anaerobic reactors it seems that the complete degradation of TNT to carbon dioxide was achieved by the acclimated anaerobic bacterium. The GC analytics of the gases in the headspace did not show elutions at methane elution time, but, showed peaks corressponding to some undetermined low-molecular organic gases.

Since no intermediate samples were taken during the anaerobic treatment, no conclusions can be drawn with respect to the kinetics of the biodegradation of TNT. But the aerobic processes are generally faster than the anaerobic processes for most wastes. Moreover, anaerobic processes require strict maintenance and have other related problems. However, the idea behind conducting anaerobic treatment of pink water was to get a feeling for the end results and to compare the effluent quality of anaerobic treatment with the effluent quality of aerobic treatment.

The effluent concentration of TNT was essentially zero following the P/C-anaerobic sequences, and even in the controls (with no pretreatment) the TNT levels reached nearly zero after the anaerobic phase.

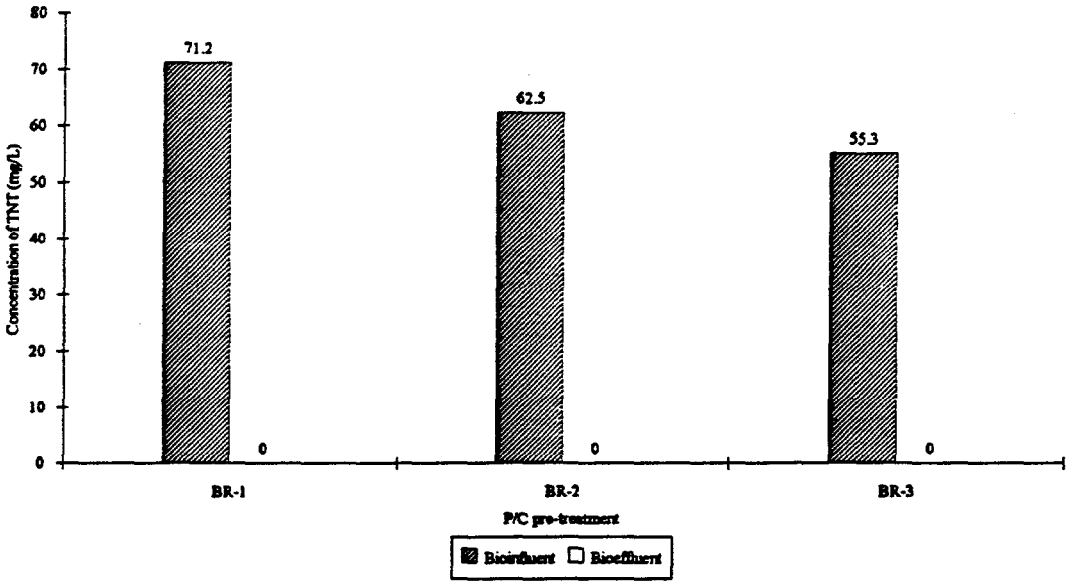
6.1.5 Effect of physical/chemical pretreatment on TNT biodegradation

The physical/chemical pretreatment of pink waters did not yield any appreciable improvement in the rate or degree of biodegradation of TNT. Irrespective of the influent TNT concentration, the effluent levels of TNT recorded low values after the biotreatment. Figures 6.1 and 6.2 show the TNT levels recorded in the bioinfluents and the bioeffluents of actual pink water pre-treated in different ways. For the three pre-treatment scenarios that were considered in Figures 6.1 and 6.2, the bioinfluent TNT levels ranged from 55 to 71 mg/L. After 30 days of aerobic treatment, the TNT levels that were recorded were less than 4 mg/L (Figure 6.1). After 14 days of anaerobic treatment the TNT levels reached non-detect in all the cases illustrated in Figure 6.2. The results summarized in Figures 6.1 and 6.2 indicate that the biodegradation of TNT in pink waters does not require any particular physical/chemical pretreatment.



BR-1: APW/ O_3/ UV 254 nm/ TiO_2/ 5 minutes BR-3: APW/ O_2/ UV 365 nm/ 30 minutes
BR-4: APW/ N_2/ UV 365 nm/ 30 minutes

Figure 6.1 Influent and effluent TNT concentrations after 30 days of aerobic treatment of actual pink water

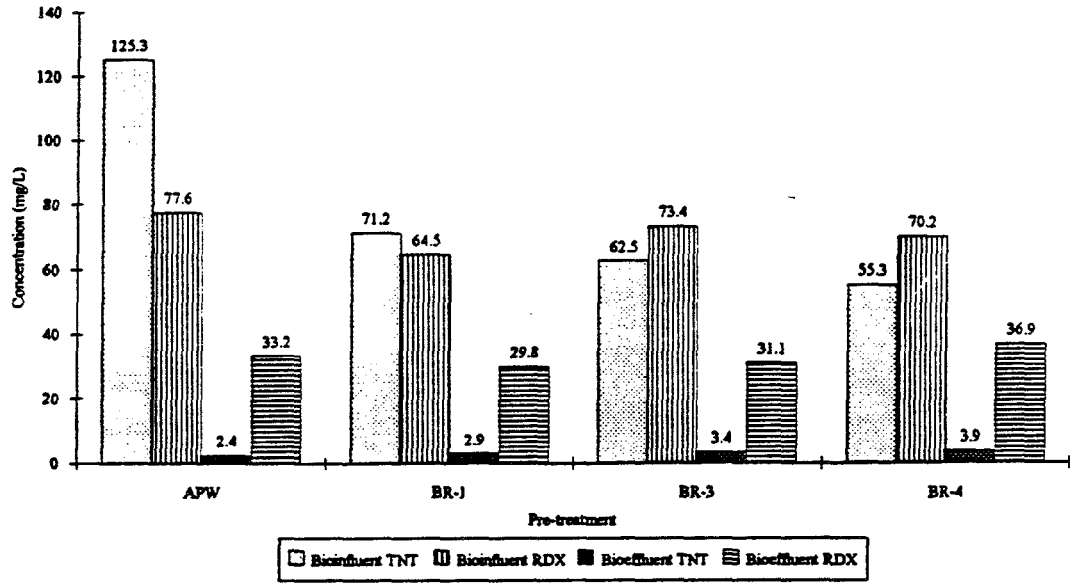


BR-1: APW/ O_3/ UV 254 nm/ TiO_2/ 5 minutes BR-3: APW/ O_2/ UV 365 nm/ 30 minutes
BR-4: APW/ N_2/ UV 365 nm/ 30 minutes

Figure 6.2 Influent and effluent TNT concentrations after 14 days of anaerobic treatment of actual pink water

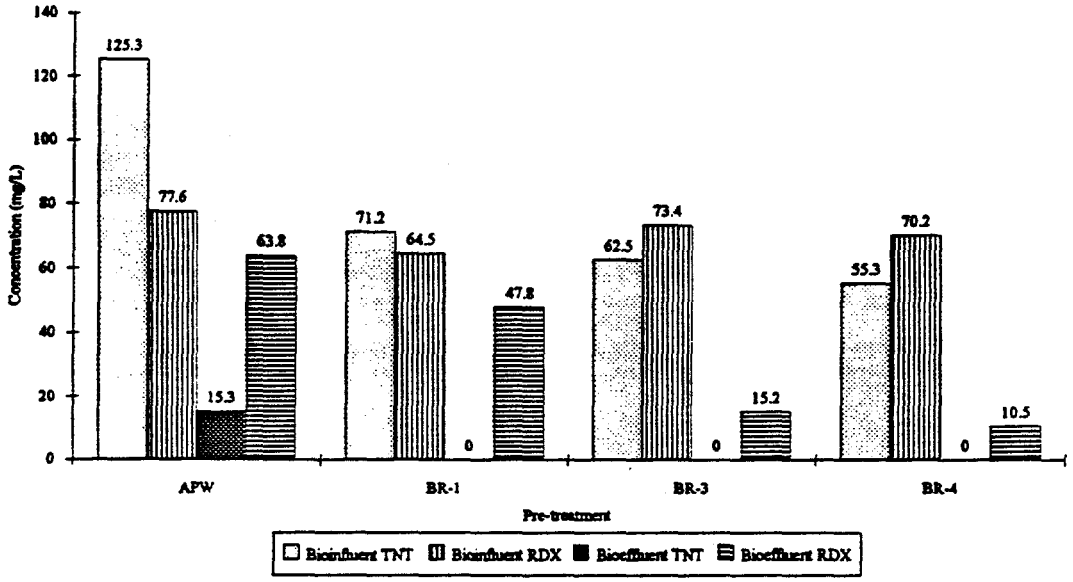
6.1.6 Effect of RDX concentration on TNT biodegradation

The treatment studies conducted as part of this research with actual and synthetic pink waters, pre-treated in different manners, had varying levels of TNT and RDX in the bioinfluents. A notable finding of this research was that the TNT biodegradation was not influenced in any contradictory manner by the presence of RDX, as shown by the Figures 6.3 and 6.4. In the case of anaerobic treatment of BR-3 and BR-4 the bioreduction in RDX did not hinder the biodegradation of TNT as shown in Figure 6.4. In other words, the RDX concentration in the pink waters did not influence the aerobic or anaerobic degradation of TNT in any noticeable manner.



APW: Actual pink water control
BR-1: APW/ O_3/ UV 254 nm/ TiO_2/ 5 minutes
BR-3: APW/ O_2/ UV 365 nm/ 30 minutes
BR-4: APW/ N_2/ UV 365 nm/ 30 minutes

Figure 6.3 Influent and effluent concentrations of TNT and RDX for 30-day aerobic treatment of actual pink water



APW: Actual pink water control
BR-1: APW/ O_3/ UV 254 nm/ TiO_2/ 5 minutes;
BR-3: APW/ O_2/ UV 365 nm/ 30 minutes
BR-4: APW/ N_2/ UV 365 nm/ 30 minutes

Figure 6.4 Influent and effluent concentrations of TNT and RDX for 14-day anaerobic treatment of actual pink water

6.2. Biodegradation of RDX

6.2.1 Aerobic bioconversion of RDX

No appreciable bioconversion of RDX was observed when the pink waters were treated aerobically with acclimated-mixed bacteriam. Physical/chemical pre-treatment also did not improve the aerobic conversion rate of residual RDX. In most of the cases, the RDX concentrations in the bioeffluents remained the same as the RDX concentrations in bioinfluents (Figure 6.5). This outcome agrees with the findings of earlier researchers (Hoffsommer et al., 1978). Sikka et al. (1980) reported the disappearance of RDX in an aerobic process after a long lag time. This would indicate that even a 30-day treatment

period did not provide the required lag time for the aerobic removal of RDX from the pink waters. Based on the earlier studies and the studies carried out in this research, it is safe to conclude that the aerobic conversion of RDX using acclimated-mixed bacterial cultures is not a viable option. This conclusion also leads to the idea of entailing a proper oxidative treatment unit that would target the removal of RDX if aerobic treatment is adopted for treating the pink waters.

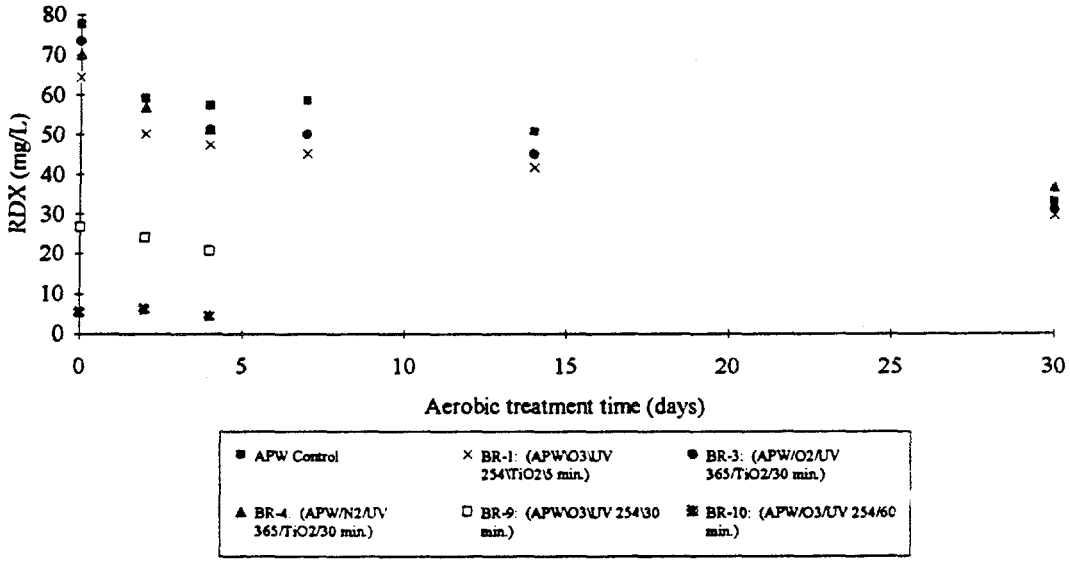


Figure 6.5 Aerobic degradation of RDX as a function of biotreatment time for actual pink water

6.2.2 Anaerobic bioconversion of RDX

The results of this research indicate that a certain amount of RDX bioconversion is possible by anaerobic treatment of pink waters which are pre-treated by p/c processes. The RDX concentration dropped by 70-80% during anaerobic biotreatment following the p/c pretreatments with low-energy 365 nm lamps and an oxygen or nitrogen atmosphere (without ozone) as shown in Figure 6.6. Such pretreatment conditions would favor photolysis rather than the normally preferred radical-accelerated photocatalysis. This surprising result indicates the ability to customize the p/c-biotreatment sequence to the specific target compounds in an actual pink water matrix. Also, a very cost effective sequence is indicated.

McCormick et al. (1981) reported on the anaerobic degradation of RDX. According to a scheme proposed by McCormick et al. (1981) the RDX biodegradation proceeds via successive reduction of nitro groups to a point where destabilization and fragmentation of the ring occurred. Hence the reported degradation of RDX that was observed in this research also concurs with the findings of McCormick et al. (1981). The findings of this research are significant because they dealt with the biodegradation of RDX in the presence TNT and other nitro-derivatives that are usually found in pink waters.

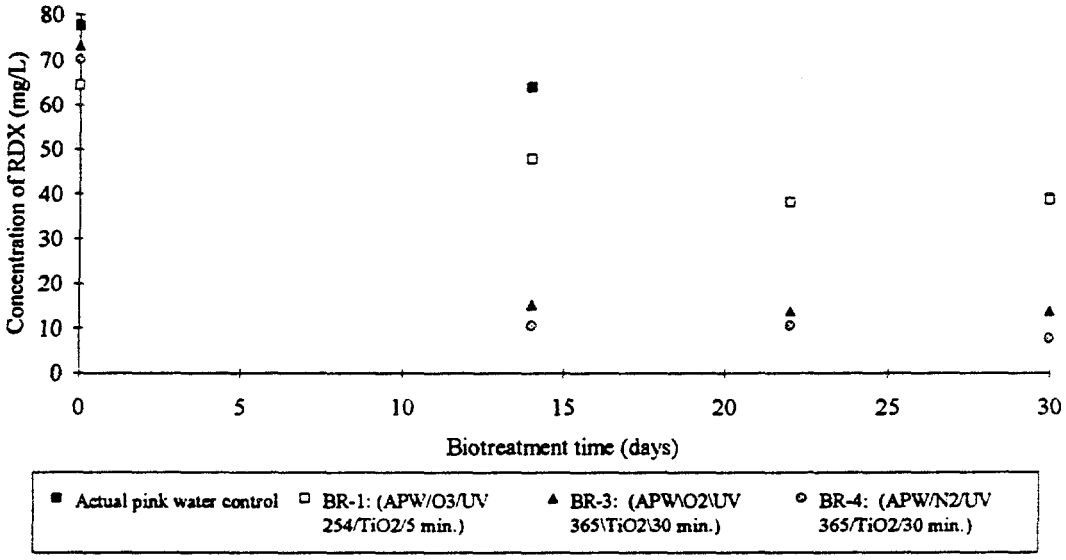
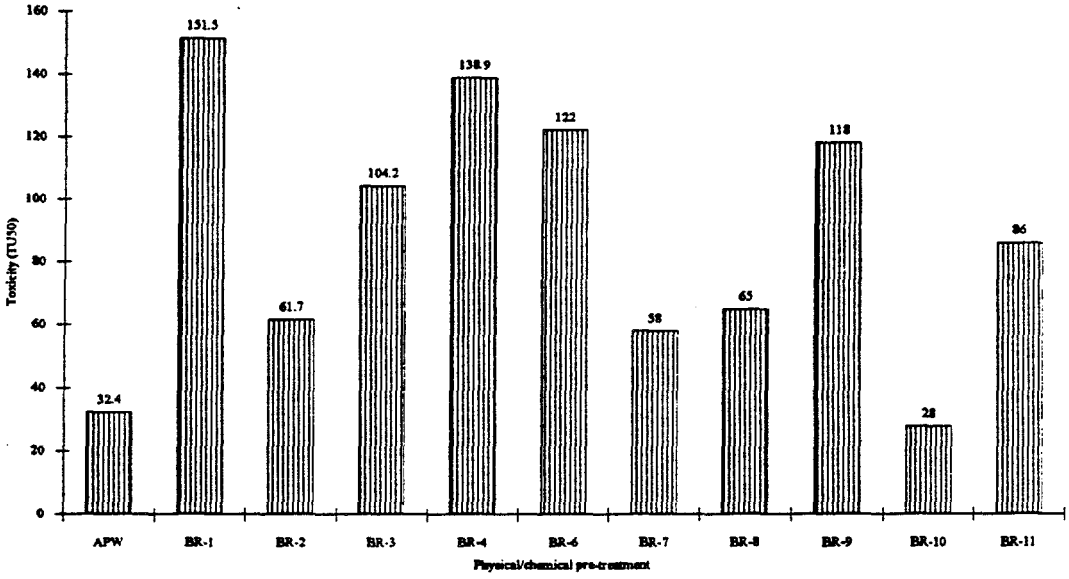


Figure 6.6 14-day anaerobic followed by 16-day aerobic biodegradation of RDX as a function of biotreatment time for actual pink water

6.3 Toxicity

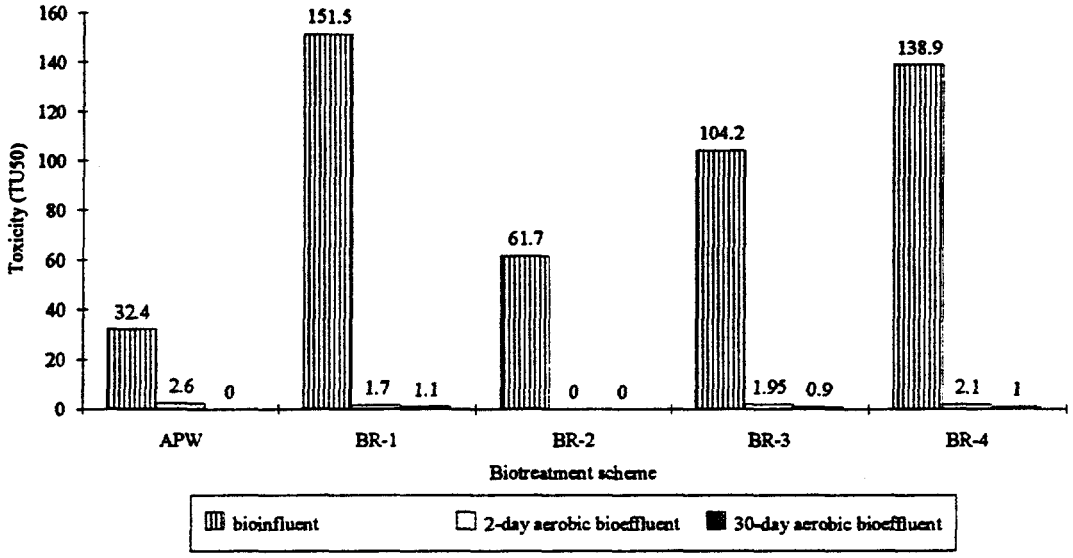
Won et al. (1974) reported the formation of intermediates like azoxy and amino compounds on biodegradation of TNT and also speculated that these intermediates were more toxic than TNT. No well defined study has been conducted on the biodegradation by-products and their possible toxicity when TNT and RDX are biodegraded.

Microtox toxicity data were collected on the influents and the effluents from all the treatment schemes. The toxicity measurements showed a sharp increase after physical/ chemical pre-treatment of pink waters indicating the formation of by-products that were more toxic than TNT and RDX (Figure 6.7). The toxicity of the bioinfluents was almost completely removed in the first two days of biotreatment indicating that no biorecalcitrant, toxic intermediates were formed under any of the conditions studied (Figures 6.8, 6.9 and 6.10). Also, the toxicities of bioeffluents did not show any increase even after prolonged biological treatment indicating that the biotreatment by itself had not generated any toxic intermediates or by-products (Figures 6.8, 6.9 and 6.10). This finding of the research refutes all the concerns of the earlier researchers (Patterson et al., 1976) who thought that biological treatment might result in degradation by-products that are more toxic than the TNT or RDX.



APW: actual pink water
BR-1: APW/ O_3/ TiO_2/ UV 254/ 5 min.
BR-2: APW/ O_3/ UV 254/ 120 min.
BR-3: APW/ O_2/ TiO_2/ UV 365/ 30 min.
BR-4: APW/ N_2/ TiO_2/ UV 365/ 30 min.
BR-6: APW/ N_2/ Na_2EDTA/ UV/ 10 min.
BR-7: APW/ N_2/ Na_2EDTA/ UV/ 30 min.
BR-8: APW/ O_3/ UV 254/ 5 min.
BR-9: APW/ O_3/ UV 254/ 30 min.
BR-10: APW/ O_3/ UV 254/ 60 min.
BR-11: APW/ O_3/ UV 254, half lamp/ 30 min.

Figure 6.7 Toxicity (TU50) of physical/chemical effluents of actual pink water



APW: actual pink water
BR-1: APW/ O_3/ TiO_2/ UV 254/ 5 min.
BR-2: APW/ O_3/ UV 254/ 120 min.
BR-3: APW/ O_2/ TiO_2/ UV 365/ 30 min.
BR-4: APW/ N_2/ TiO_2/ UV 365/ 30 min.

Figure 6.8 Toxicity (TU50) in the aerobic bioinfluents and bioeffluents of actual pink water

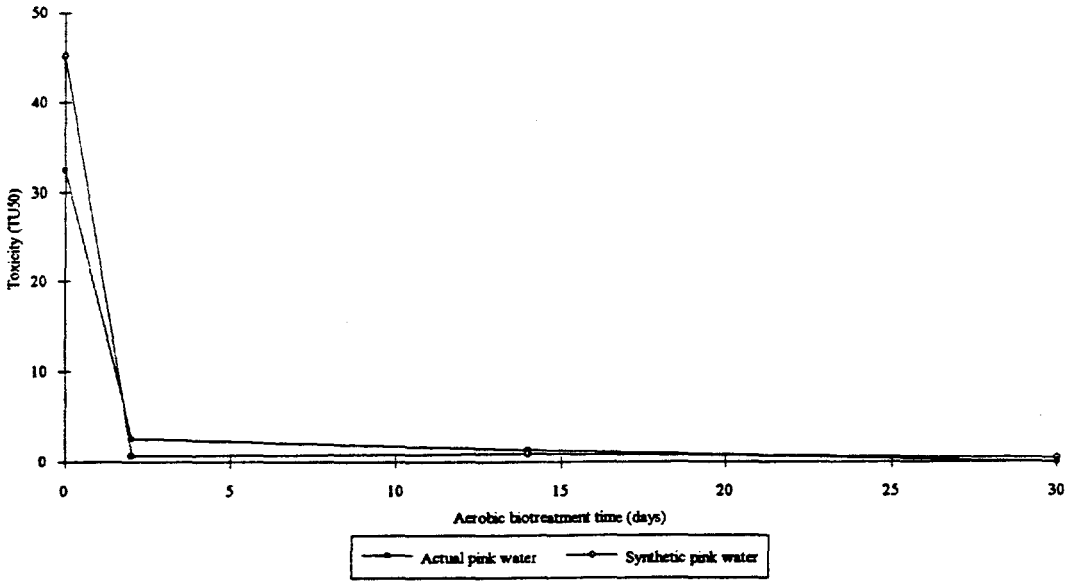
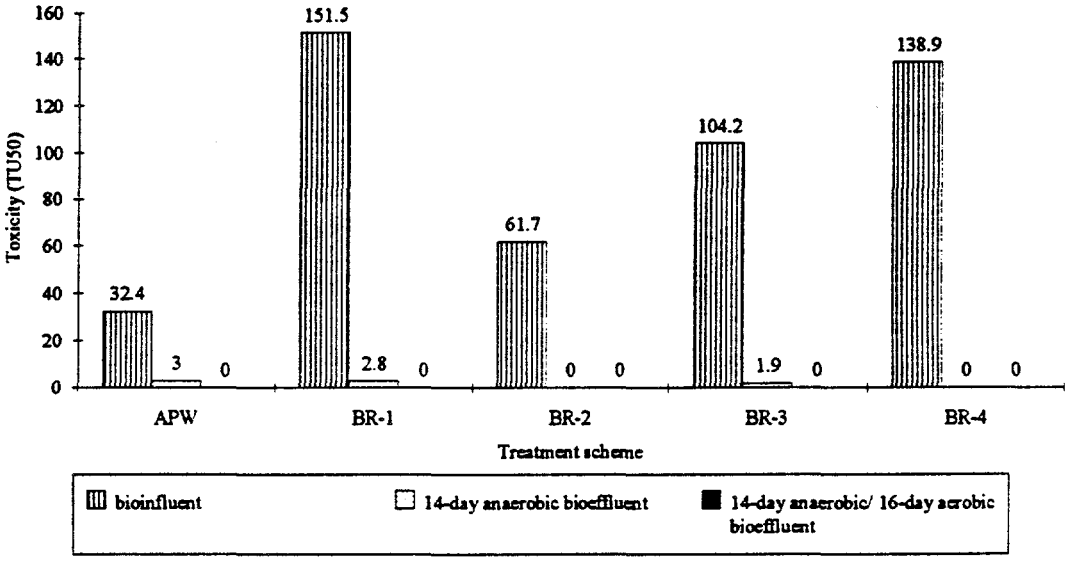


Figure 6.9 Toxicity (TU50) as a function of aerobic treatment time for actual and synthetic pink waters



APW: actual pink water
BR-1: APW/ O_3/ TiO_2/ UV 254/ 5 min.
BR-2: APW/ O_3/ UV 254/ 120 min.
BR-3: APW/ O_2/ TiO_2/ UV 365/ 30 min.
BR-4: APW/ N_2/ TiO_2/ UV 365/ 30 min.

Figure 6.10 Toxicity (TU50) as a function of anaerobic/ aerobic treatment time for actual pink waters

6.4 Physical/chemical treatment of pink waters

As mentioned earlier, the biodegradation of TNT does not require any physical/chemical pretreatment. However, aerobic biodegradation of RDX was not observed and anaerobic transformations occurred only after certain p/c pretreatments. Hence the applicability of a physical/chemical treatment (pre or post) is to be judged on the basis of its RDX removal potential rather than on the TNT or TOC removal. Obtaining partial oxidation, not total oxidation, was the goal of physical/chemical pre-treatments.

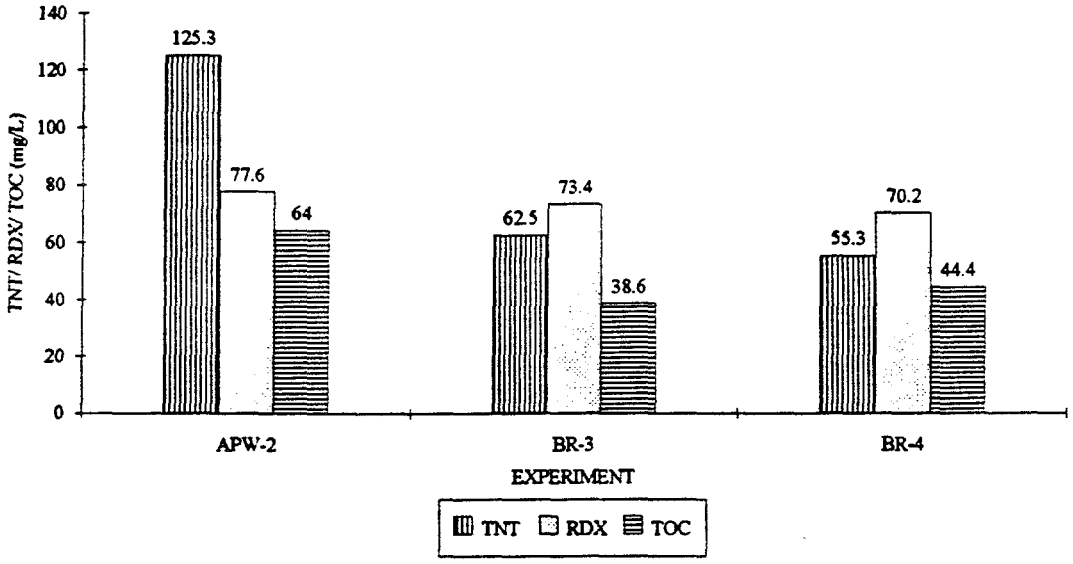
6.4.1 Effect of reaction atmosphere (O_2 vs. N_2) on the photocatalytic (UV 365 nm/TiO_2) pre-treatment of actual pink water

Two physical/chemical experiments that were carried out on actual pink water involved similar experimental conditions (UV 365 nm/ TiO_2/ 30 minutes) except for the reaction atmosphere (O_2 or N_2). Oxygen promotes radical generation by photolysis (UV and TiO_2). Nitrogen atmosphere does not promote radical generation but would help in maintaining proper mixing conditions apart from upholding the reducing conditions in the reactor.

Among the two runs, the experiment that was carried under the reduction atmosphere (N_2) resulted in slightly greater RDX and TNT removal than the experiment that was carried under oxidation atmosphere (O_2) (Figure 6.11). Greater break-up of TNT and RDX in reduction atmosphere also resulted in higher toxicity (TU50), indicating

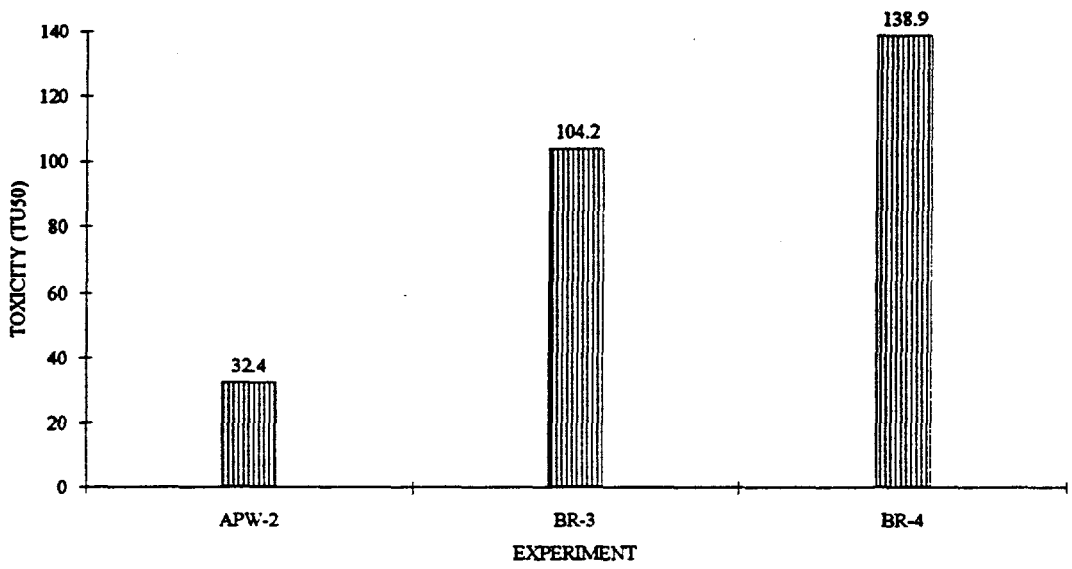
that a substantial part of toxicity in p/c effluents is caused by the partial oxidation products rather than by TNT or RDX (Figure 6.12). As expected, greater total oxidation (TOC removal) was achieved under oxidation atmosphere than under reduction atmosphere. Figure 6.13 gives the concentrations of TNT and RDX as a function of p/c treatment time for the oxygen and nitrogen atmosphere experiments.

Based on a pilot study, Patterson et al. (1976) reported that RDX was more sensitive to UV light than TNT. Generation of radicals would occur at a greater rate in oxygen atmosphere than in nitrogen atmosphere. Hence a greater degradation of TNT and RDX under nitrogen atmosphere implies the sensitivity of the munitions compounds to the UV light. This finding also substantiates the earlier findings (Patterson et al., 1976) that the RDX degradation occurs preferably by direct photolysis than by radical oxidation.



APW: untreated actual pink water
BR-3: APW/ O_2/ UV 365 nm/ TiO_2/ 30 min.
BR-4: APW/ N_2/ UV 365 nm/ TiO_2/ 30 min.

Figure 6.11 Comparison of performance of O_2 vs. N_2 atmospheres in photocatalytic (UV 365 nm/ TiO_2) treatment of actual pink water



APW: untreated actual pink water
BR-3: APW/ O_2/ UV 365 nm/ TiO_2/ 30 min.
BR-4: APW/ N_2/ UV 365 nm/ TiO_2/ 30 min.

Figure 6.12 Comparison of perfomance of O_2 vs. N_2 atmospheres with respect to toxicity (TU50) for actual pink water

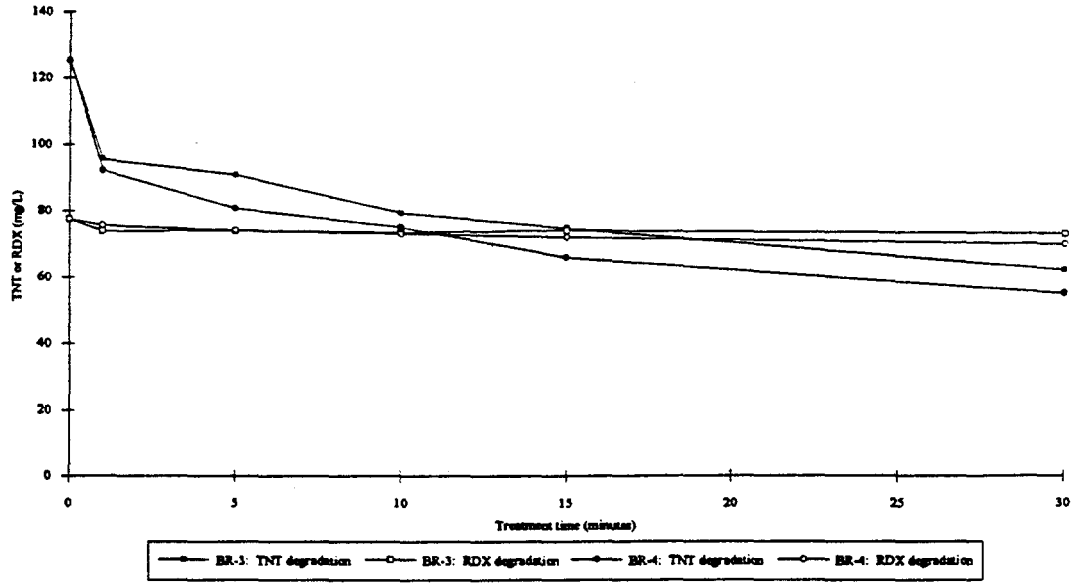
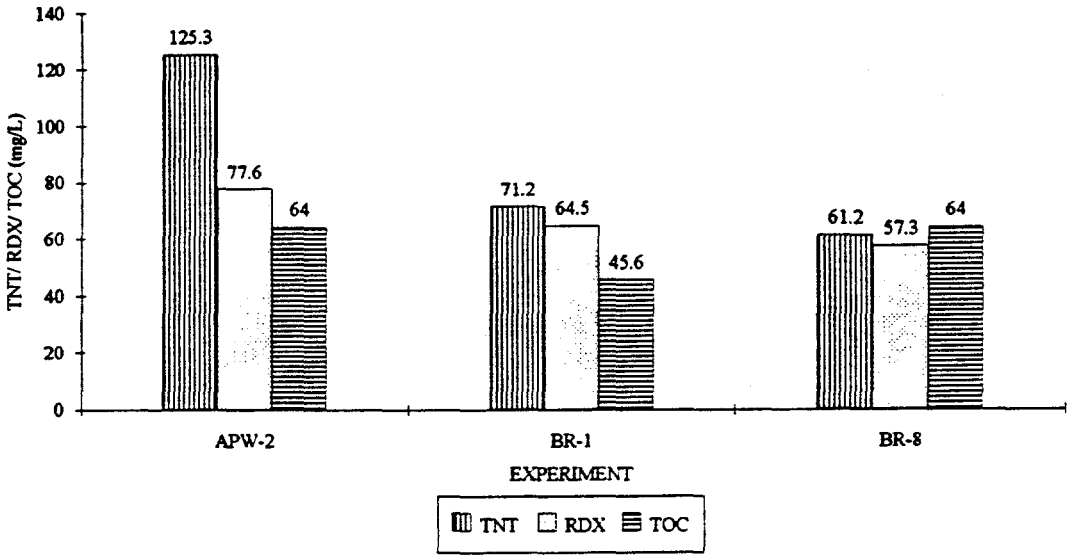


Figure 6.13 Comparison of perfomance of O_2 vs. N_2 atmospheres with respect to the kinetics of TNT and RDX degradation for actual pink water

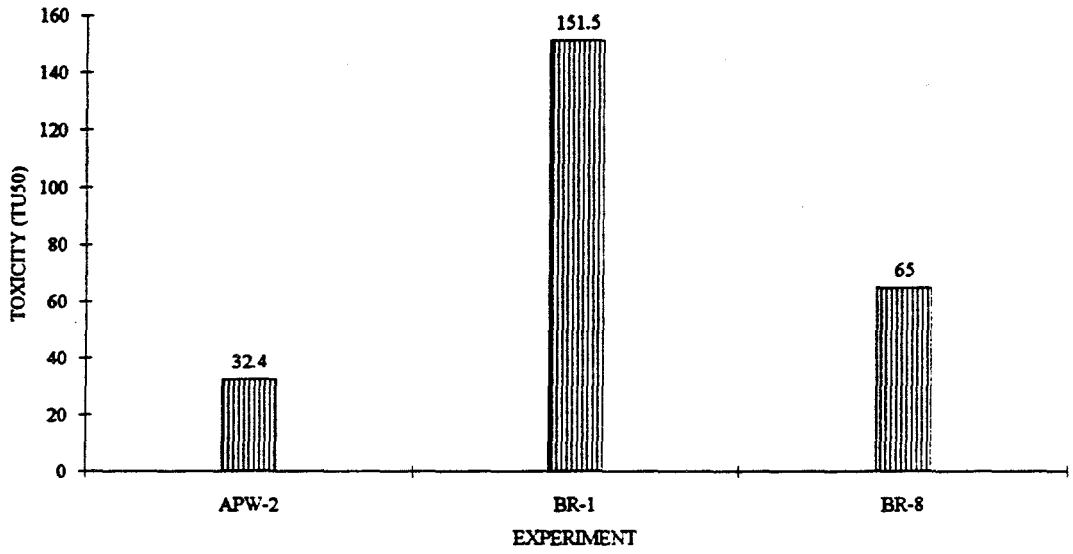
6.4.2 Comparison between the performance of UV 254 nm-catalyzed ozone vs. heterogeneous photocatalytic (UV 254 nm/ TiO_2/ O_3) pre-treatment of actual pink water

Under similar reactor conditions, greater RDX and TNT degradation was achieved by UV light-catalyzed (254 nm) ozone treatment compared to the heterogeneous photocatalytic (UV 254 nm, O_3, TiO_2) treatment (Figure 6.14). These results indicate that the additional radicals generated by the heterogeneous photocatalytic treatment are used in breaking down the partial oxidation products of TNT or RDX rather than TNT or RDX molecules. Hence greater total oxidation (TOC removal) was seen in heterogeneous photocatalytic treatment compared to the UV light-catalyzed ozone treatment (Figure 6.14). Moreover, lower toxicity values are observed under UV light- catalyzed ozone processes than under heterogeneous photocatalytic processes (Figure 6.15). From these results, it is advisible to adopt UV light-catalyzed ozone treatment compared to heterogeneous photocatalytic treatment for the pre or post treatment of pink waters.



APW: untreated actual pink water
BR-8: APW/ O_3/ UV 254 nm/ 5 min.
BR-1: APW/ O_3/ UV 254 nm/ TiO_2/ 5 min.

Figure 6.14 Comparison of TNT/ RDX/ TOC removals between UV 254 nm-catalyzed ozone and heterogeneous photocatalytic (UV 254 nm/ TiO_2/ O_3) pretreatments of actual pink water



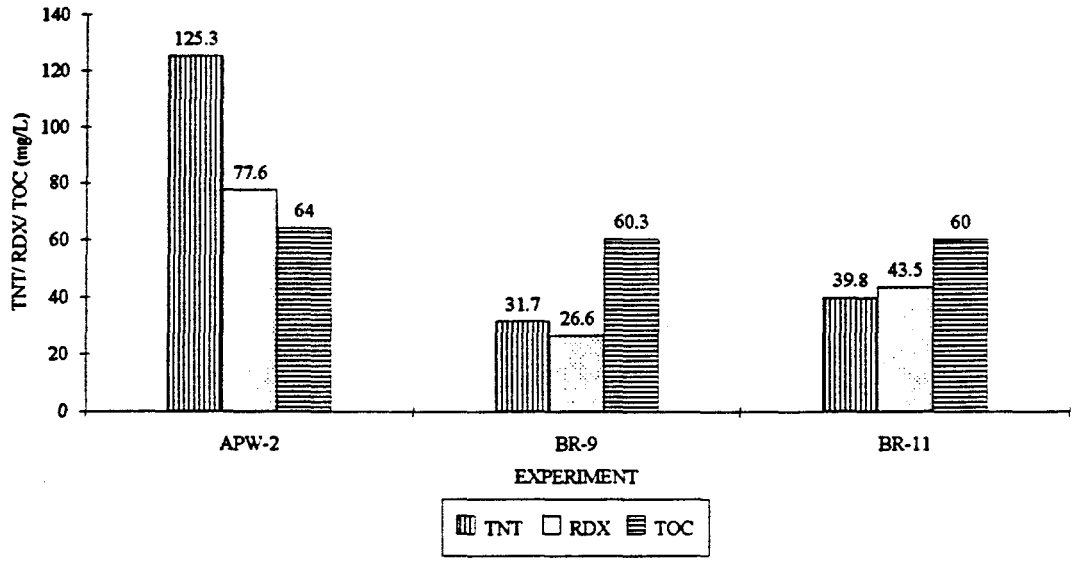
APW: untreated actual pink water
BR-1: APW/ O_3/ UV 254 nm/ TiO_2/ 5 min.
BR-8: APW/ O_3/ UV 254 nm/ 5 min.

Figure 6.15 Comparison of performance between UV 254 nm-catalyzed ozone and heterogeneous photocatalytic (UV 254 nm/ TiO_2/ O_3) pretreatments of actual pink water with respect to toxicity (TU50)

6.4.3 Effect of UV-254 lamp in UV light- catalyzed O_3 treatment of actual pink waters

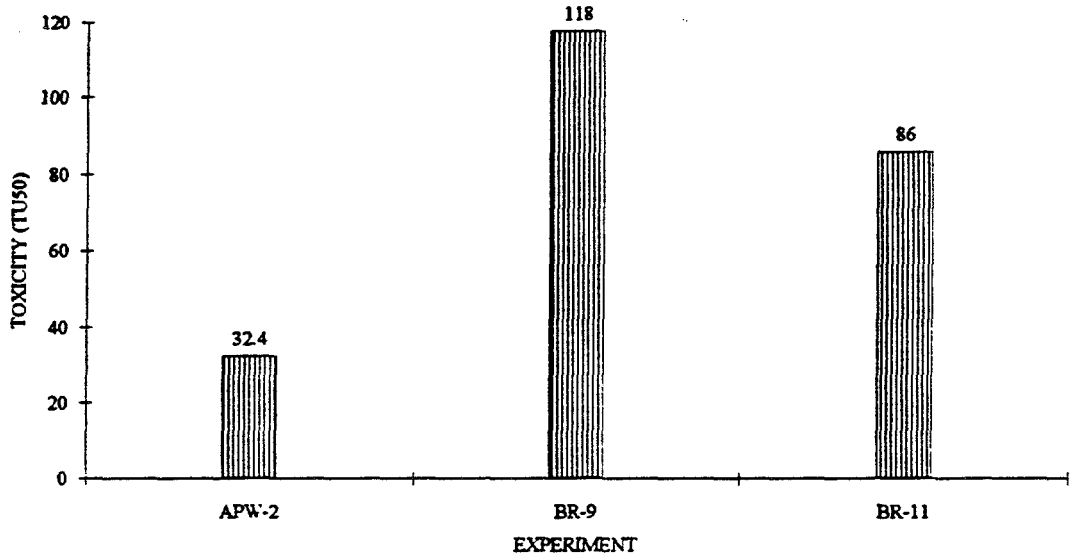
Two comparative runs were performed using similar experimental conditions except for the exposure to the UV 254 nm lamp. In one of the experiments (BR-11), approximately 50% of the UV 254 nm lamp was masked resulting in lower exposure time of the pink water to the UV light. Among the two experiments, greater TNT and RDX removals were seen in the experiment in which full UV lamp was used (Figure 6.16). Both the experiments resulted in similar TOC removal indicating that in UV light-catalyzed ozone treatments the TOC removal is not directly related to the exposure to the light (Figure 6.16). Greater toxicity was recorded in the full lamp experiment because greater partial-degradation of TNT and RDX occurred (Figure 6.17). As mentioned

earlier, an increase in the exposure time to the UV light led to a greater partial-degradation of TNT and RDX. All these results once again confirm the sensitivity of TNT and RDX to the UV light.



APW: untreated actual pink water BR-9: APW/ O_3/ UV 254 nm, full lamp/ 30 min.
BR-11: APW/ O_3/ UV 254 nm, half lamp/ 30 min.

Figure 6.16 Comparison of TNT/ RDX/ TOC removals for half and full lamps of UV 254 nm-catalyzed ozone pretreatments of actual pink water



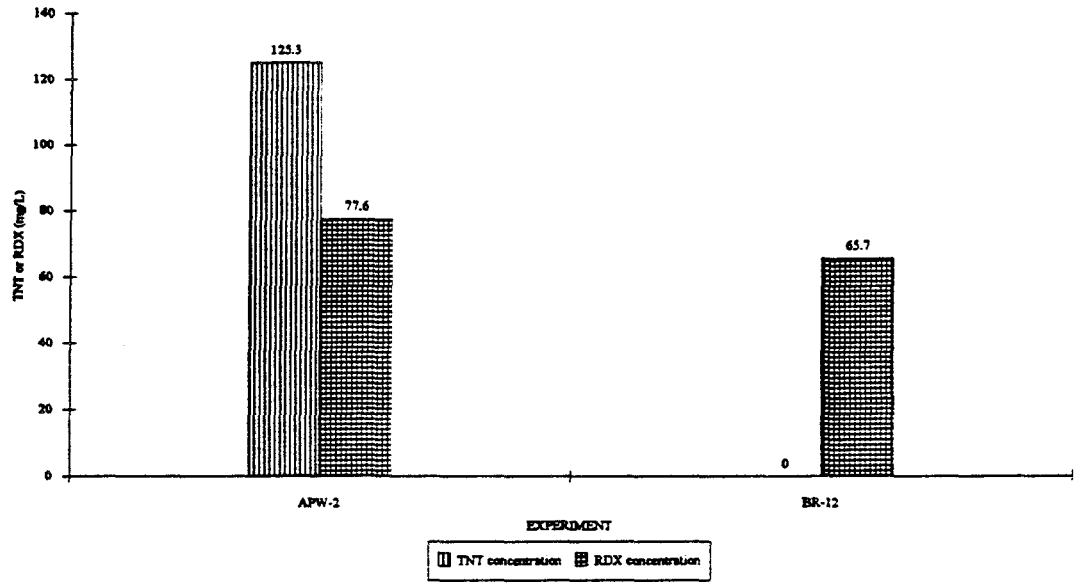
APW: untreated actual pink water BR-9: APW/ O_3/ UV 254 nm, full lamp/ 30 min.
BR-11: APW/ O_3/ UV 254 nm, half lamp/ 30 min.

Figure 6.17 Comparison of performance of half and full lamps for UV 254 nm-catalyzed ozone pretreatment of actual pink water with respect to toxicity (TU50)

6.4.4 Comparison of the performance of pre- and post- (physical/chemical) treatments to the biological treatment of actual pink water

As mentioned earlier, biodegradation of TNT does not seem to require any physical/chemical pre-treatment. Moreover, aerobic biodegradation of RDX does not seem to be a viable option from the various studies conducted as part of this research. My work shows that a proper oxidative treatment, either as a pre-treatment or as a post-treatment, was necessary for the removal of RDX from pink water. Also, between heterogeneous photocatalysis and UV light-catalyzed ozone treatments, the latter treatment was found to be a better option for RDX degradation.

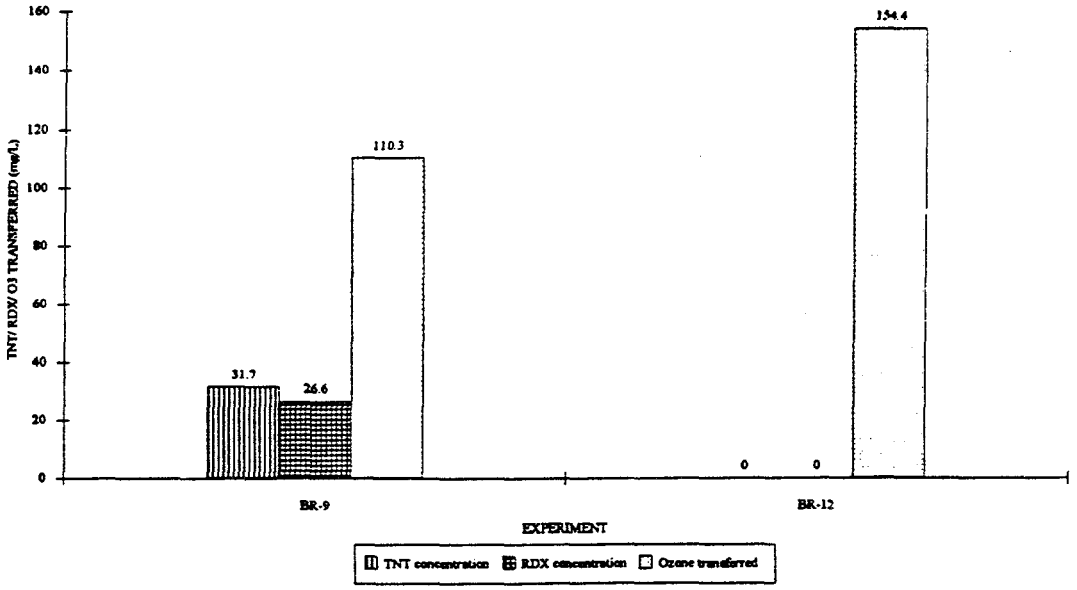
Based on all the factors discussed above, a single experiment was carried out in which the actual pink water was treated aerobically for 7-days prior to the UV light (254 nm)-catalyzed ozone treatment. The idea behind this experiment was to degrade the TNT by biotreatment and then break down the residual RDX in the bioeffluent by the subsequent physical/chemical treatment. Figures 6.18, 6.19 and 6.20 summarize the results of the UV-catalyzed ozone treatment of actual pink water (without any pre-treatment) and the actual pink water pre-treated by 7-day aerobic treatment. Figure 6.18 shows the P/C influent concentrations of TNT and RDX. As expected, the concentration of TNT in the 7-day aerobic treated bioeffluent reached non-detect level while the concentration of RDX is only slightly lower than that observed in the actual pink water (without any pretreatment) (Figure 6.18). After 30 minutes of oxidation, the RDX level in the case of the 7-day aerobic treated effluent reached non-detect (Figure 6.19) while the RDX concentration was still high (26.6 mg/L) in the case of the actual pink water (without any pretreatment) (Figure 6.19). The ozone transfer rate was also higher in the 7-day pretreated actual pink water. Even after 60 minutes of oxidation, trace amounts of RDX (5.4 mg/L) persisted in the P/C effluent from the actual pink water (without any pretreatment) (Figure 6.20). All the results discussed above suggest that there are definite benefits from adopting biotreatment prior to the P/C treatment of pink waters. In other words, pretreatment of pink waters by biotreatment reduces the ozone requirements and also the oxidation time of the P/C treatment.



APW-2: Untreated actual pink water

BR-12 : APW-2/ UV 254 nm/ O_3/ 120 minutes of 7-day aerobic bioeffluent

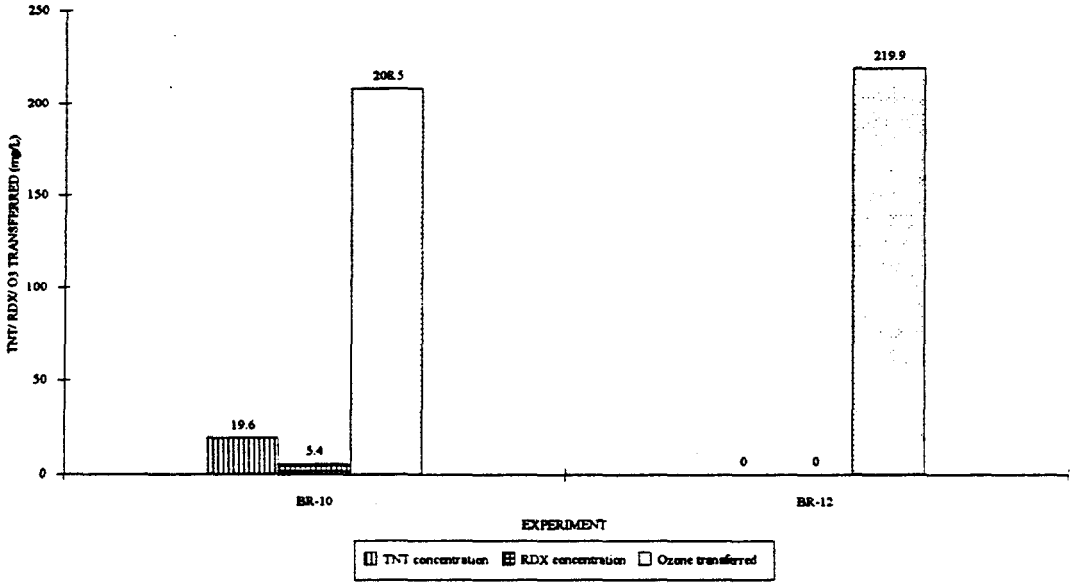
Figure 6.18 TNT and RDX concentrations in the actual pink water control and the bioeffluent from 7-day aerobic treatment



BR-9: APW-2/ UV 254 nm/ O_3/ 30 minutes

BR-12: APW-2/ UV 254 nm/ O_3/ 120 minutes of 7-day aerobic bioeffluent

Figure 6.19 TNT, RDX and ozone transfers for the 30-minute effluents from BR-12 and BR-9



BR-10: APW-2/ UV 254/ O_3/ 30 minutes

BR-12: APW-2/ UV 254/ O_3/ 120 minutes of 7-day aerobic bioeffluent

Figure 6.20 TNT, RDX and ozone transfers for the 60-minute effluents from BR-12 and BR-10

CHAPTER 7

CONCLUSIONS

The findings of this research can be summarized as follows

1. Biodegradation of TNT in pink waters achieved non-detect levels within 14 days aerobically and 14 days anaerobically.

2. TNT biodegradation was accelerated in the presence of supplemental carbon (yeast extract) and nitrogen (NH_4Cl) sources. Since the co-substrate (yeast extract) effect is associated with the biomass growth in the presence of both pink water and the soluble co-substrate, the provisions for addition of co-substrate to the bioinfluent liquid must be emphasized in the biological process design.

3. The rate of biotransformation of TNT with the acclimated, mixed bacterial seed was nearly the same as the rate of biotransformation of TNT using a pure *Pseudomonads* seed.

4. The photochemically enhanced color of pink water did not hinder the biotreatability of TNT in any noticeable fashion, if the pH was strictly controlled.

5. The effluent quality of anaerobic treatment was slightly better than the effluent quality of aerobic treatment with respect to TNT. This result would be of engineering significance only if very tight effluent limits were imposed.

6. The biodegradation of TNT in pink waters did not require any particular physical/chemical pre-treatment. The physical/chemical pre-treatment of pink waters did not yield any appreciable improvement in the rate or degree of biodegradation of TNT.

7. The presence of RDX in pink waters did not influence the aerobic or anaerobic degradation of TNT.

8. No appreciable bioconversion of RDX was observed with the pink waters that were treated aerobically. Physical/chemical pre-treatment also did not improve the aerobic conversion rate of RDX.

9. Substantial RDX bioconversion was possible by anaerobic treatment of pink waters following particular physical/chemical processes. The RDX concentrations dropped by 70-80% during anaerobic biotreatment following the P/C pre-treatments with low-energy 365 nm lamps and an oxygen or nitrogen atmosphere (without ozone).

10. The Microtox toxicity measurements showed a sharp increase after physical/chemical pre-treatment of pink waters, indicating the formation partial oxidation products that were more toxic than the TNT or RDX. The toxicity of the bioinfluents was almost completely removed in the first two days of biotreatment. Also, the toxicities of the bioeffluents did not show any increase even after prolonged biological treatment, indicating that no toxic by-products were generated biologically.

11. Toxicity of the bio-physical/chemical effluent remained low, indicating that the toxicity was not reintroduced by the P/C process.

12. RDX destruction was more sensitive to UV light than was TNT. From the results of P/C pre-treatment, the RDX degradation seems to occur preferably by direct photolysis rather than by the radical oxidation.

13. Greater TNT and RDX conversions were measured in UV-catalyzed ozone treatment than heterogeneous photocatalytic treatment of pink waters.

14. UV light was the most significant variable among the different variables of P/C pre-treatment that were tested, with respect to the TNT and RDX degradation.

15. Biotreatment prior to the physical/chemical treatment was found to have certain benefits, including a reduction in the oxidation treatment time and the ozone transfer requirement for a given level of removal.

Appendix A

Significance of TNT and RDX as Explosives

A.1 Introduction

Explosives have been classified in many ways according to different criteria. Explosives have been divided into high and low explosives according to the type and velocity of the reaction involved. High explosives are used as the detonating charges and low explosives are used as the propellants (Yinon J. et al., 1993).

Explosives have also been classified according to their chemical structure. The most important class includes organic compounds that contain the nitro group (NO_2). Explosives are subdivided according to the atom to which the NO_2 group is attached. Nitro compounds contain a C-NO_2 group, nitrate esters a C-O-NO_2 group and nitramines a C-N-NO_2 (Yinon J. et al., 1981). According to this classification TNT is a nitro compound while RDX is a nitramine.

A.2 TNT

2,4,6-Tinitrotoluene is the most widely used military explosive. Its main features include low melting point, stability, low sensitivity to impact, and high temperature and its relatively safe methods of manufacture (Yinon J. et al., 1993).

Isomers (Alm, A., et al., 1978) include:

2,4,6-TNT (α-TNT), m.p. 80.65 °C

2,3,4-TNT (β-TNT), m.p. 112 °C

2,4,5-TNT (γ-TNT), m.p. 104 °C

3,4,5-TNT (δ-TNT), m.p. 137.5 °C

2,3,5-TNT (ε-TNT), m.p. 97.2 °C

2,3,6-TNT (η-TNT), m.p. 111 °C.

When just TNT is mentioned, it is the 2,4,6-isomer.

The general chemical and physical properties of 2,4,6-trinitrotoluene are listed in Table A.1. Figure A.1 shows the structure of 2,4,6-TNT.

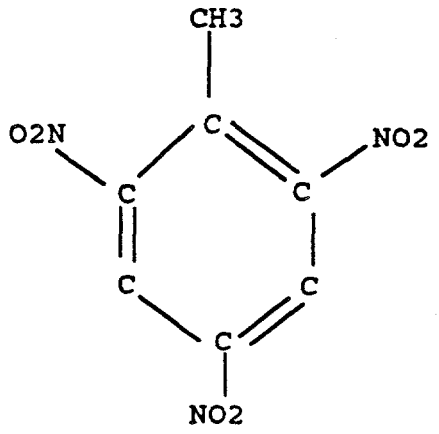


Figure A.1 Structure of 2,4,6-TNT

A.3 RDX

RDX is one of the most important military explosives used today. It has a chemical stability lower than that of the TNT, and an explosive power much greater than that of the TNT (Yinon et al., 1993). RDX is more susceptible than TNT to shock detonation.

RDX is manufactured mainly by two processes using hexamine as the starting material. In the Woolwich, or direct nitrolysis, process hexamine is reacted with nitric acid to produce RDX (Yinon et al., 1993). In the Bachmann process, hexamine is reacted at 75 °C with an ammonium nitrate-nitric acid mixture in the presence of acetic acid and acetic anhydride. Bachmann process has been found to be more adoptable to large-scale production than direct nitration (Yinon et al., 1993).

RDX is never handled pure and dry, because the danger of accidental explosion is too great. Following production, the RDX is immediately incorporated into formulations or desensitized with additives. When necessary the pure explosive is shipped water- or solvent-wet (Yinon et al., 1993).

RDX is used as a component in mixtures with other explosives such as TNT and as a plastic explosive. Mixtures of RDX and wax are used for booster charges in many military ammunitions including artillery shells (Yinon et al., 1993).

The general chemical and physical properties of RDX are listed in Table A.2. The following figure (Figure A.2) shows the structure of RDX.

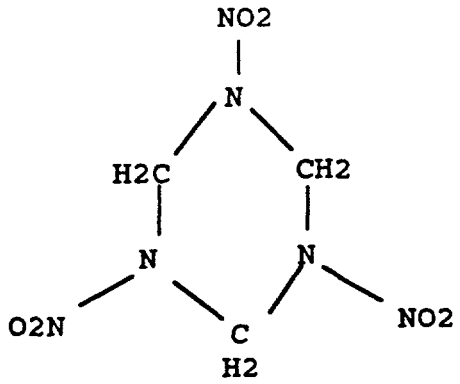


Figure A.2 Structure of RDX

Table A.1 General Chemical and Physical Properties of 2,4,6-Trinitrotoluene (TNT)

CAS number	118-96-7
Synonyms	TNT; α-trinitrotoluol; 1-methyl-2,4,6-trinitrobenzene; trotyl; tolite; triton; trilite; α-TNT
Molecular weight	227.13
Molecular formula	$C_7H_5N_3O_6$
Color	Yellow to white
Physical state	Monoclinic rhombohedral crystals
Specific gravity	1.654
Liquid density	1.465 g/cm^3
Vapor pressure	0.053 mm Hg (85 °C); 0.106 mm Hg (100 °C)
Solubility characteristics	
Water	0.013 g/100 g (20 °C)
Carbon tetrachloride	0.65 g/100 g (20 °C)
Toluene	55 g/100 g (20 °C)
Acetone	109 g/100 g (20 °C)
Melting point	80.1 to 81.6 °C
Boiling point	210 °C (10 mm Hg) to 212 °C (12 mm Hg)
Freezing point	80.75 ± 0.05 °C
Flash point	240 °C

Table A.2 General Chemical and Physical Properties of RDX

CAS number	121-82-4
Synonyms	RDX; Cyclonite; Hexogen; T_4; Cyclotrimethylenetrinitramine; Hexahydro-1,3,5-trinitro-1,3,5-trinitrazine *sym*-Trimethylenetrinitramine
Molecular weight	222.26
Molecular formula	$C_3H_6N_6O_6$
Physical state	White crystalline solid-orthorhombic crystal
Specific gravity	1.816 at 20 °C
Melting point	204.1 °C
Heat of combustion	2259.4 cal/g
Solubility characteristics	
Water	7.6 mg/L (at 25 °C) to 42.3 mg/L (at 20 °C)
Acetone	8.3% (w/w) at 25 °C
Nitrobenzene	1.5% (w/w) at 25 °C
Acetic anhydride	4.9% (w/v) at 30 °C
Conversion factor (air)	1 ppm = 9.09 mg/m^3

Adapted from Drinking Water Health Advisory: MUNITIONS, 1992.

Appendix B

Bacterial Acclimation

B.1 History of operation

To acclimate the bacteria for use in the biological treatment processes both aerobic and anerobic batch-fed reactors were operated for several weeks. The initial seed bacteria was taken from several sources including municipal mixed liquor volatile suspended solids (MLVSS) and papermill return activated sludge (RAS). The histories of operation of the acclimation reactors are listed in Table B.1.

The acclimation was carried out over a span of five weeks by gradually increasing the content of the actual pink water (APW-1) from 5% to 25% in increments of 5% every week. Primary effluent (PE) obtained from the domestic wastewater plant was added to facilitate gradual acclimation. The primary effluent (PE) would also provide the bacteria with the micronutrients that are required for growth. Additionally, 20 mg/L of ammonium phosphate ($NH_4H_2PO_4$) was added to the wastewater to ensure the sufficient availability of free ammonium and orthophosphate.

Table B. 1 History of Operation of the Acclimation Reactors

Week	Ingredient
First week	5% APW-1 + 15% PE + 80% MQ + 20 mg/L Ammonium phosphate
Second week	10% APW-1 + 10% PE + 80% MQ + 20 mg/L Ammonium phosphate
Third week	15% APW-1 + 5% PE + 80% MQ + 20 mg/L Ammonium phosphate
Fourth week	20% APW-1 + 5% PE + 75% MQ + 20 mg/L Ammonium phosphate
Fifth week	25% APW-1 + 5% PE + 75% MQ + 20 mg/L Ammonium phosphate

B.2 Aerobic and anaerobic acclimation

The aerobic bacterial acclimation was monitored periodically by the oxygen uptake rate (OUR). An increase in the OURs was observed with an increase in the pink water proportion indicating a good acclimation of the seed bacteria. Table B.2 gives the OURs recorded over the duration of the acclimation. The OUR is the slope of the line obtained by plotting the dissolved oxygen (DO) as a function of time. Appendix D shows specimen regression analysis performed to derive the oxygen uptake rates (OURs).

Table B.2 Oxygen Uptake Rates (OUR) of the Aerobic Acclimation Reactors

Week/ Day	Oxygen Uptake Rate (mg/L-min.)
3rd week/ day = 0	0.047
3rd week/ day = 5	0.049
3rd week/ day = 7	0.061
4th week/ day = 0	0.017
4th week/ day = 7	0.095
5th week/ day = 0	0.025
5th week/ day = 7	0.165

Anaerobic culture was acclimated and grown in a sealed anaerobic culture bottle kept on a shaker table maintained at 30 °C. The culture bottle of the anaerobic bacteria was flushed twice a week with the nitrogen gas to maintain strict anaerobic conditions.

Appendix C

Microtox Toxicity Test Protocol and Specimen Microtox Data Reports

C.1 Microtox Toxicity Test System

Toxicity was analyzed by Microtox Toxicity Test System developed by the Microbics Corporation. Microtox is a system that detects and measures toxicity. It is a bioassay integrating living microorganisms with precision instrumentation. The basic components of the Microtox Toxicity Test System include a Toxicity Analyzer, a Data Collection and Reduction System, Microtox Reagent and other associated supplies.

The reagent used in the microtox toxicity test consists of a suspension of luminescent microorganisms that are sensitive to a broad spectrum of toxic chemicals. The microorganisms emit light as a natural product of their metabolic processes. When toxic chemicals inhibit those processes the light output drops in proportion to the toxicity of the sample. The light loss measured by the Microtox system is a rate of biological activity, rather than the a count of organisms affected (quantal data). The light is a byproduct of the organism's respiration, and reflects change in respiration. The measurement of light integrates the response of about a million individual organisms per exposure to toxicant or control.

Light measurements taken by the Microtox Analyzer are automatically processed to generate detailed reports. The microorganims respond within minutes to the presence of toxicants. The Microtox Analyzer brings the reagent and the samples to standard temperatures, and measures the light output of the microorganisms under rigidly controlled test conditions.

C.2 Toxicity expressions

Since 1979, environmental toxicologists and ecologists in laboratories around the world have published numerous studies favorably comparing the Microtox results with those of the other bioassays (Applications in Industry - Microtox Toxicity Test Systems, 1992). The usual expression of sample toxicity measured by the Microtox sytem is the EC50 - the effective concentration that causes a 50% reduction in the light output of the Microtox test organisms. Toxicity can also be expressed interms of toxicty units (TU50) that is related to the EC50 (% dilution) by the following expression (Microtox Manual,1992):

$$\text{TU50 (toxicity units)} = 100 / \text{EC50 \% dilution} \qquad \text{...(Equation C.1)}$$

Various linear and polynomial relationships have been established between Microtox microrganisms and other species. The LC50 (LC-lethal concentration) of the fathead minnows was empirically related to the EC50 (% dilution) of Microtox toxicity for drilling fluids by the following expression (Curtis et al., 1982):

$$LC50 = 0.80(EC50) + 0.45 \qquad \text{...(Equation C. 2)}$$

Firth and Backman (1990) found an empirical relationship between the ChV (ChV-chronic value) of ceriodaphnia and the EC50 (% dilution) of Microtox toxicity for the paper-mill waste water as shown below :

$$ChV = 0.012(EC50)^2 - 0.047(EC50) + 8.659 \qquad \text{...(Equation C. 3)}$$

C.3 Toxicity protocol for pink waters

An initial experiment was conducted to select the test exposure time at which the maximum toxicity response occurred for the given pink waters. This maximum response time will vary as a function of the type of wastewater compounds. For samples of actual (APW-2) and synthetic (SPW) pink water, the Microtox responses were measured at exposure times of 5, 15, 30, 45 and 60 minutes. As indicated by the data in Table C.1 and Figure C.1, both the types of pink water (APW-2 and SPW) displayed a common response as a function of test exposure time. The Microtox toxicity responses increased with increase in the exposure time for about 30 minutes. Beyond 30 minutes, a constant response in the toxicity was indicated, hence a 30 minute exposure time was selected for all the Microtox measurements of pink water treatment.

Table C.1 Toxicity (TU50) responses as a function of exposure time for actual and synthetic pink waters

Untreated Pink Water	Time				
	5 min.	15 min.	30 min.	45 min.	60 min.
APW-2	13.70	20.96	32.36	50.51	47.4
SPW	5.26	22.88	45.15	39.06	37.04
APW-1	6.92	25.25	60.61	N/A	N/A

N/A -- Not available

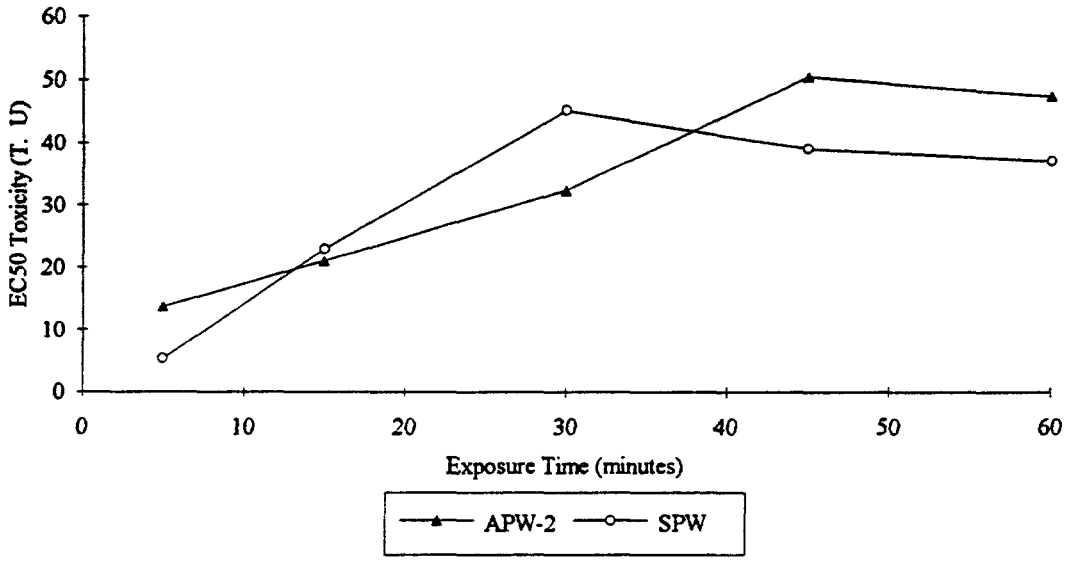


Figure C.1 Microtox toxicity (TU50) as a function of exposure time for untreated actual and synthetic pink waters

C.4 Specimen microtox data reports

Figures C.2 through C.6 show the specimen Microtox data reports obtained during different stages of treatment of actual pink water. Figure C.2 shows the microtox data report of the untreated actual pink water. Microtox data report of the effluent from physical/chemical treatment (BR-5: O_3, UV 254 nm, TiO_2, 5 minutes) of synthetic pink water is shown in Figure C.3. Since the physical/chemical effluents of pink water had reported high toxicities the sample of the data report shown in Figure C.3 had to be diluted (1 : 10) inorder to get a decent spread of the data points. Figure C.4 shows the

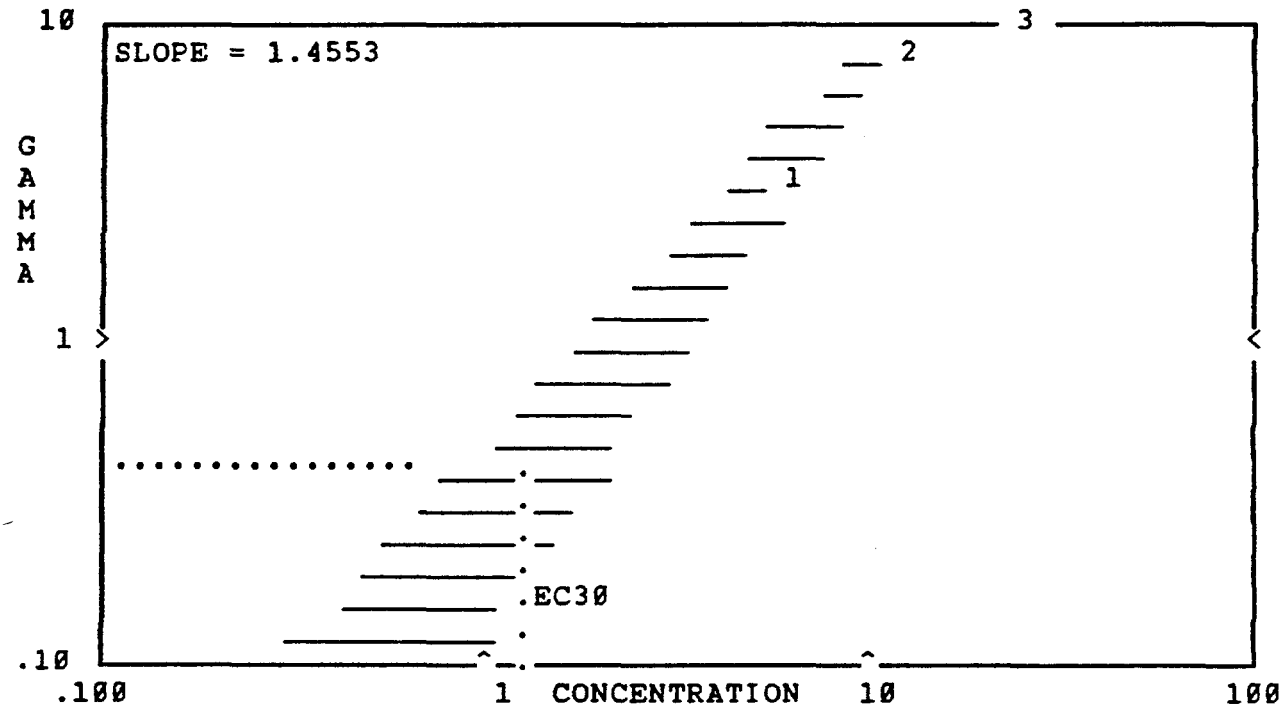
Microtox data report of the bioeffluent from the 7-day aerobic treated actual pink water. Since the bio treatment of pink waters brought the toxicity to low levels, at-times (as shown in Figure C.4) the Basic test was replaced with 80% Modified Basic test or with 100% test. In 100% test the highest concentration to which the flourescent bugs are exposed is 90% rather than 45% as in the Basic test. Increasing the concentrations of the very low toxic waters would improve the spread of the data points of the toxicity line. Figures C.5 and C.6 show the toxicity data reports of effluents after the anerobic treatment of pink waters pretreated under different schemes. In both the cases the reported toxcities are low.

Procedure: BASIC
Initial Concentration : 45 %
Test Time: 30 minutes

Osmotic Adjustment: moas
Dilution Factor : 2
Concentration Units: %

NUMBER	I0/IT	CONC.	GAMMA
1	60.71/ 8.86	5.6250	3.76280#
2	71.29/ 4.56	11.2500	9.86674#
3	88.08/ 2.09	22.5000	28.29318#
4	86.27/ 0.56	45.0000	106.07970*

CONTROL IT/I0 = 72.49/104.29 CORRECTION FACTOR = 0.6951



EC30 1.2790 (95% CONFIDENCE RANGE: 0.6156 TO 2.6574)

Used for calculations
* Invalid gammas

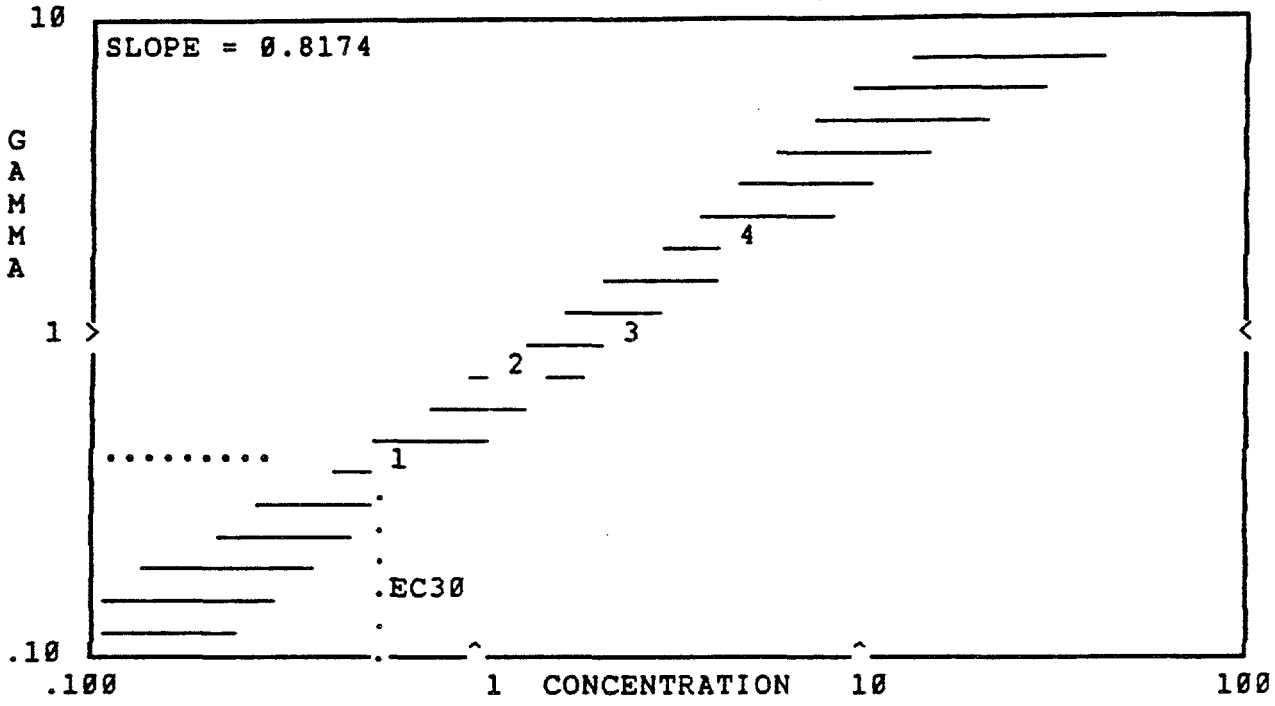
Figure C.2 Microtox data report of actual pink water (APW-2)

Procedure: BASIC
Initial Concentration : 4.5 %
Test Time: 30 minutes

Osmotic Adjustment: moas
Dilution Factor : 2
Concentration Units: %

NUMBER	I0/IT	CONC.	GAMMA
1	134.00/ 64.12	0.5625	0.40591#
2	116.58/ 42.65	1.1250	0.83888#
3	138.41/ 41.59	2.2500	1.23886#
4	124.42/ 24.94	4.5000	2.35615#

CONTROL IT/I0 = 64.98/ 96.59 CORRECTION FACTOR = 0.6727



EC30 0.5722 (95% CONFIDENCE RANGE: 0.3742 TO 0.8750)

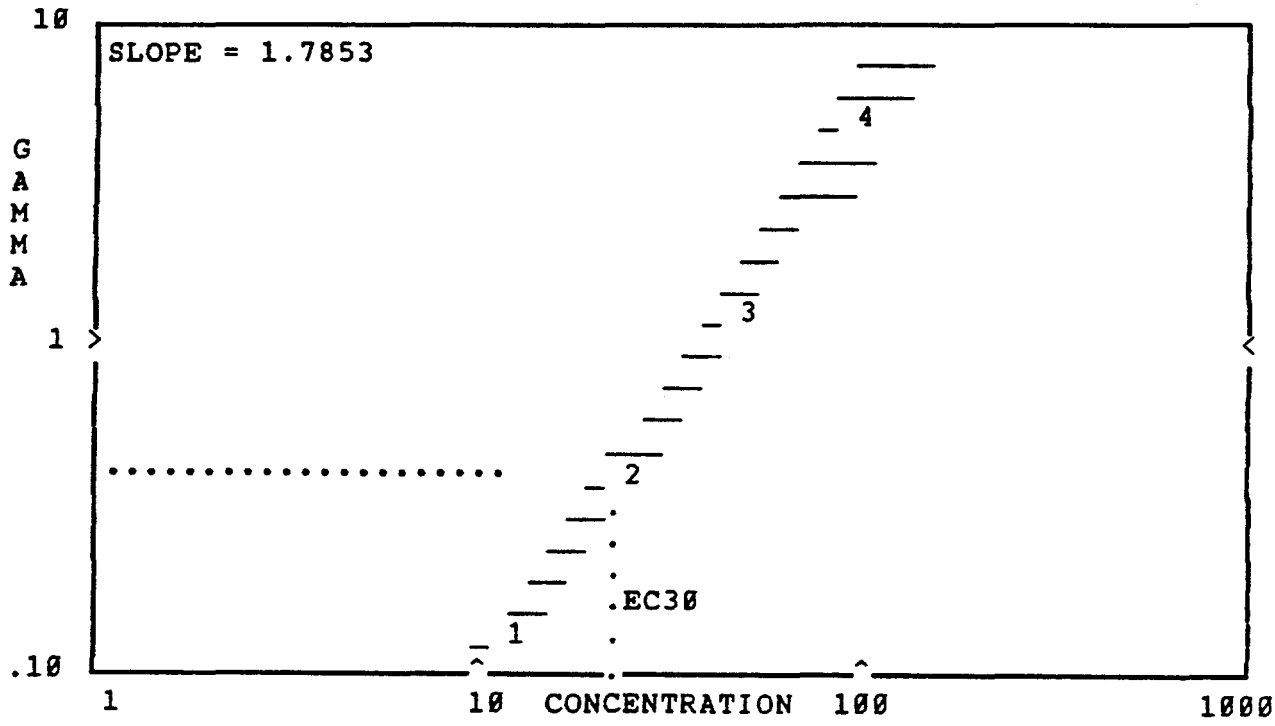
Figure C.3 Microtox data report of the effluent after heterogeneous photocatalysis (O_3, UV 254 nm, TiO_2 for 5 minutes) treatment of synthetic pink water (BR-5)

Procedure: 100%
Initial Concentration : 90 %
Test Time: 30 minutes

Osmotic Adjustment: MOAS
Dilution Factor : 2
Concentration Units: %

NUMBER	It	CONC.	GAMMA
1	76.76	11.2500	0.1136#
2	57.99	22.5000	0.4740#
3	37.42	45.0000	1.2843#
4	14.15	90.0000	5.0410#

CONTROL It's : 85.48



EC30 22.9759 (95% CONFIDENCE RANGE: 19.4228 TO 27.1791)

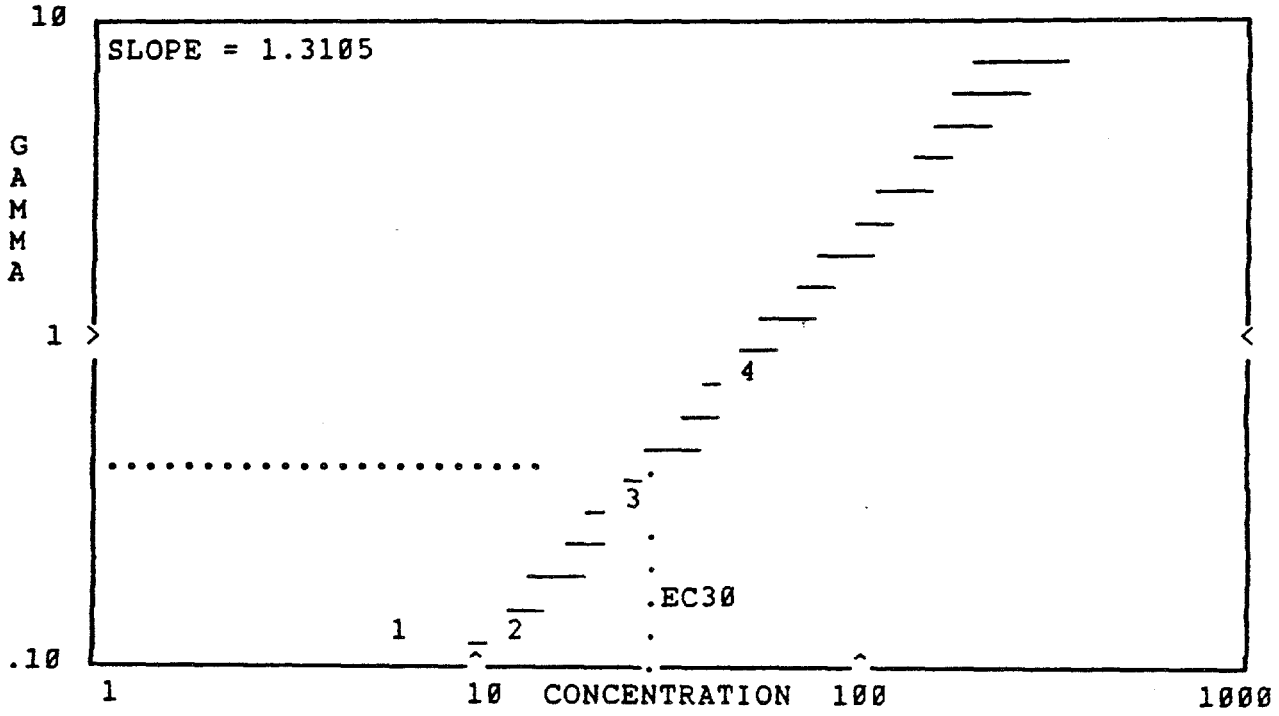
Figure C.4 Microtox data report of the bioeffluent after 7-day aerobic treatment of actual pink water

Procedure: BASIC
Initial Concentration : 45 %
Test Time: 30 minutes

Osmotic Adjustment: MOAS
Dilution Factor : 2
Concentration Units: %

NUMBER	I0/IT	CONC.	GAMMA
1	97.75/ 91.04	5.6250	0.05522#
2	77.13/ 66.91	11.2500	0.13290#
3	91.14/ 66.13	22.5000	0.35447#
4	81.94/ 44.19	45.0000	0.82234#

CONTROL IT/I0 = 92.48/ 94.10 CORRECTION FACTOR = 0.9828



EC30 26.9154 (95% CONFIDENCE RANGE: 24.8425 TO 29.1612)

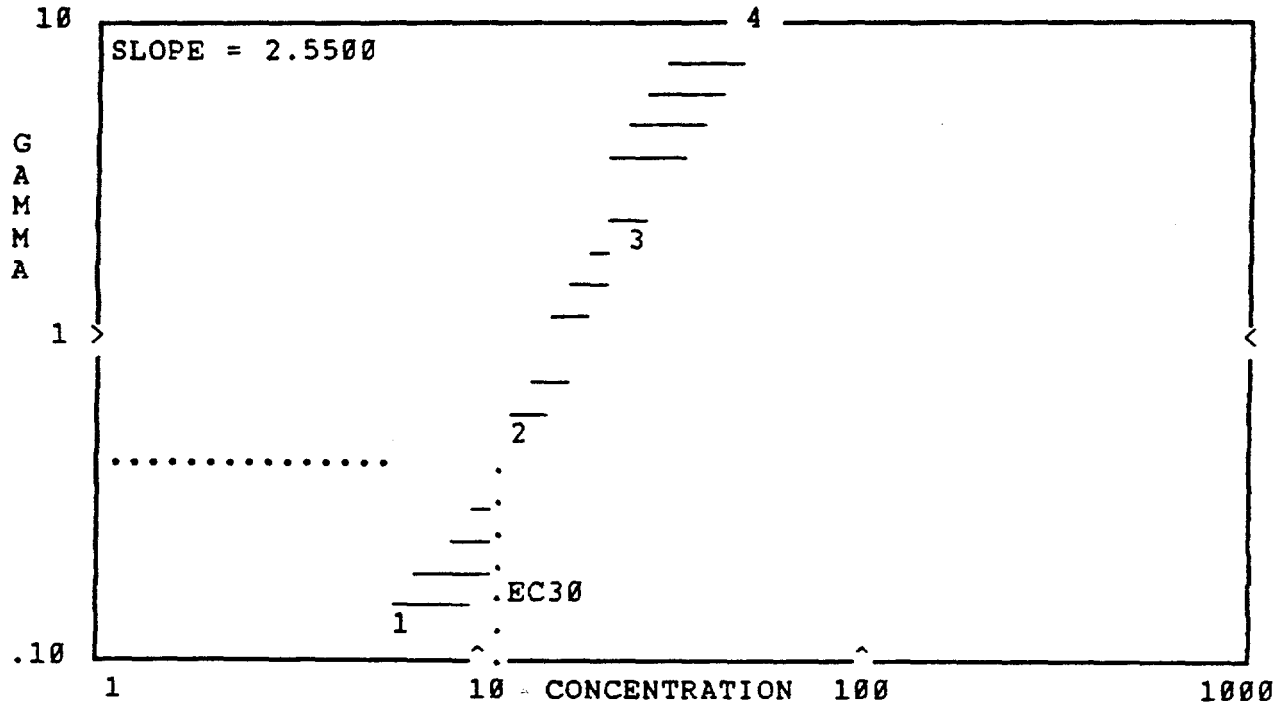
Figure C.5 Microtox data report of the bioeffluent after 14-day anaerobic treatment of BR-3 (actual pink water pretreated with O_2, UV 365 nm and TiO_2 for 30 minutes)

Procedure: BASIC
Initial Concentration : 45 %
Test Time: 30 minutes

Osmotic Adjustment: MOAS
Dilution Factor : 2
Concentration Units: %

NUMBER	I0/IT	CONC.	GAMMA
1	77.69/ 64.16	5.6250	0.05907#
2	72.17/ 41.45	11.2500	0.52285#
3	76.32/ 21.87	22.5000	2.05221#
4	78.39/ 4.71	45.0000	13.55677#

CONTROL IT/I0 = 77.16/ 88.22 CORRECTION FACTOR = 0.8746



EC30 11.6087 (95% CONFIDENCE RANGE: 9.3788 TO 14.3688)

Figure C.6 Microtox data report of the bioeffluent after 14-day anaerobic treatment of BR-5 (synthetic pink water pretreated with O_3, UV 254 nm and TiO_2 for 5 minutes)

Appendix D

Specimen Regression Analysis of Oxygen Uptake Rate (OUR)

D.1 Specimen regression analysis

Sample: 5th Week/ Day = 7, aerobic bacterial acclimation

Data:

Table D.1 Specimen measurements of dissolved oxygen as a function of time

Time (min.)	DO_2 Recorded	DO_2 Calculated*
0.00	8.5	8.43
2.50	8.0	8.01
5.00	7.5	7.60
8.50	7.0	7.02
12.0	6.5	6.44

Note: * DO_2 values calculated by linear regression analysis.

Regression Output

Constant	8.426
Standard error of Y-estimate	0.080
Coefficient of determination (R2)	0.992
Number of observations	5
Degrees of freedom	3
x-coefficient (*OUR*)	-0.165
Standard error of coefficient	0.008

D.2 Dissolved oxygen vs. time

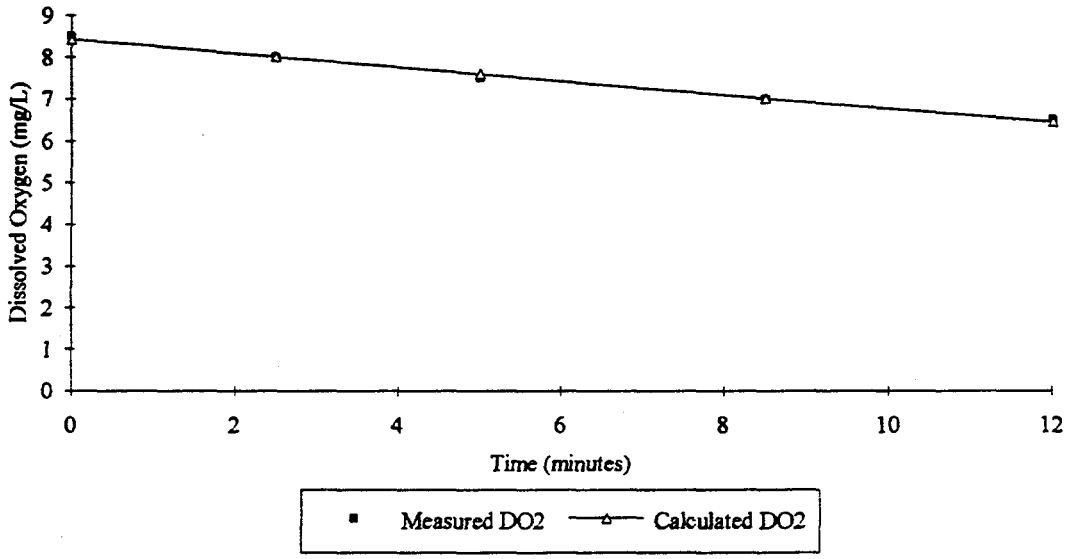


Figure D.1 Dissolved oxygen vs. time

Slope of the straight line in Figure D. 1 is -0.165.

Hence the oxygen uptake rate (OUR) for 5th week/ day 7 acclimation bacteria is 0.165.

Appendix E

Detailed Procedure of Silas-Mason TNT Test

E.1 Test procedure

1. 25 mL of wastewater sample was taken in a 125 mL flask
2. 5 mL of 100% diethylaminoethanol reagent was added to the sample.
3. The flask along with the solution was heated to 50°C on a water bath.
4. The mix was then cooled and diluted to 50 mL.
5. Milli Q water was taken instead of the sample and the steps 1 to 4 are repeated.
6. The blank cuvette was filled with the Milli Q sample and the reading cuvette was filled with the actual sample.
7. The absorbance at 525 nm (A525) was read using the Shimadzu UV 160A Spectrophotometer and 1 cm cuvettes.
8. The TNT concentration was then read from the calibration curve based on the A525 measured.

E.2 Calibration curve

Table E.1 shows the standards used in developing the calibration curve for TNT assay through Silas-Mason test (Kuo C. J., 1982). Figure E.1 shows the calibration curve plotting the A525 versus TNT concentration (Kuo C. J., 1982).

Table E.1 Standard values used in developing the Silas-Mason calibration curve

TNT (mg/L)	A525
0	0
10	0.061
20	0.124
30	0.192
50	0.314

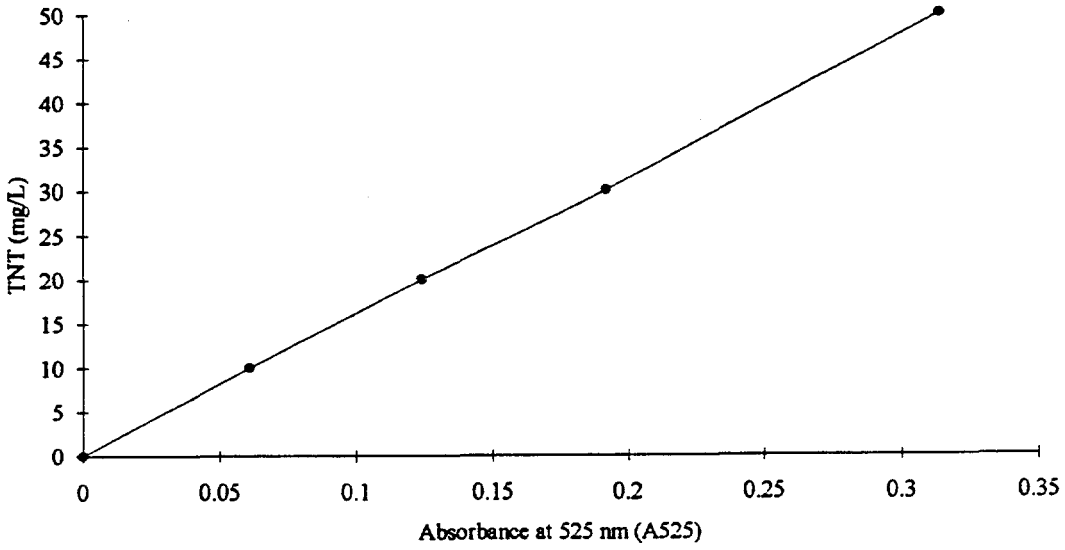


Figure E.1 Silas-Mason calibration curve

Equation for the calibration line for Silas-Mason test can be given as follows

$$TNT\ (mg/L) = 158.30 \times (A525)$$

Appendix F

Specimen Ozone Transfer Calculations

F.1 Ozone transfer calculations

The mass balance of ozone in the oxidation reactor system can be given as follows:

$$O_{3,\,applied} = O_{3,\,transferred} + O_{3,\,offgas} \quad ...(1)$$

$$O_{3,\,transferred} = O_{3,\,dissolved} + O_{3,\,decomposed} \quad ...(2)$$

$$O_{3,\,dissolved} = O_{3,\,direct\ oxidation} + O_{3,\,radical\ formation} \quad ...(3)$$

Ozone transferred can be calculated from equation (1) by measuring the ozone applied and ozone leaving the system as offgas. The rate of ozone decompostion can be neglected since the ozone applied and the offgas measurements are made at every fraction of a minute. The dissolved ozone goes into direct and indirect oxidation.

By monitoring the ozone applied and ozone offgas the ozone transfer for the UVR/UVR-Blue reactor set-up can be calculated as shown below:

Ozone applied in time of Δt (mg)

= Average ozone application rate (mg/SL) x Flow Rate (2 SL/min.) x Δt (min.)

Ozone exiting as offgas in time Δt (mg)

= Average ozone offgas rate (mg/SL) x Flow rate (2 SL/min.) x Δt (min.)

Ozone transferred in time Δt (mg)

= $\in$Ozone applied in Δt (mg) - $\in$ Ozone offgas in Δt (mg)

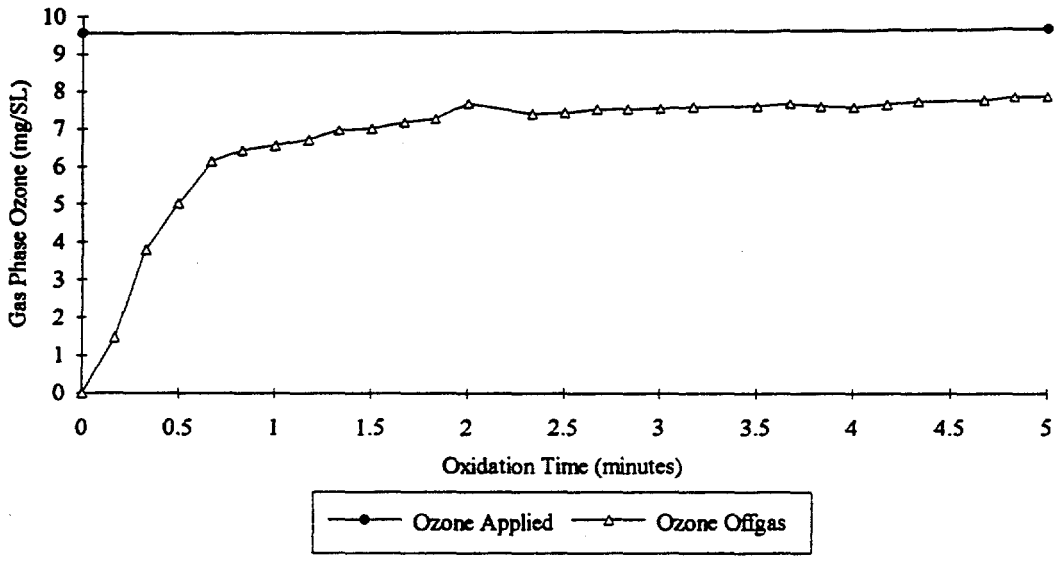
(* SL - standard liter)

Table F.1 shows a specimen spreadsheet used for calculating the ozone transfer for BR-1 (actual pink water treated for 5 minutes by O_3, UV-254, TiO_2). Figures F.1 through F.2 show the plots of ozone applied and ozone in the offgas used for calculating the ozone transfers. The area between the ozone applied line the ozone offgas curve for each of the gives the ozone transferred.

Table F.1 Specimen ozone offgas and applied measurements for BR-1 (Actual pink water, treated for 5 minutes by O_3/ UV 254/ TiO_2)

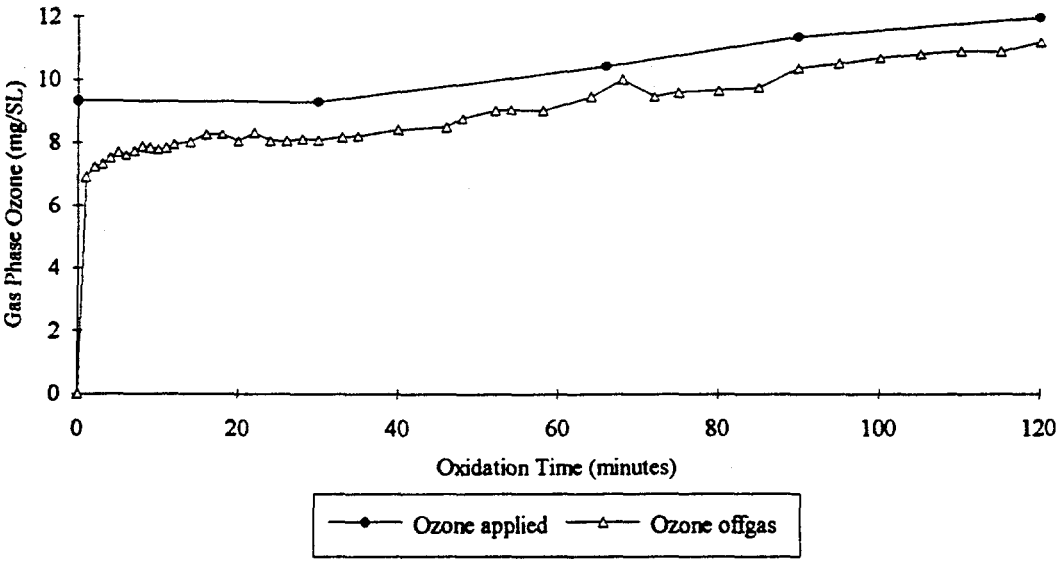
Time (minutes)	O_3 Applied (mg/SL)	O_3 Applied (mg)	O_3 Offgas (mg/SL)	O_3 Offgas (mg)
0.00	9.57			
5.00	9.72	96.45		
0.00			0.00	0.00
0.17			1.47	0.25
0.33			3.78	0.84
0.50			5.02	1.50
0.67			6.15	1.90
0.83			6.45	2.02
1.00			6.59	2.22
1.17			6.74	2.27
1.33			6.99	2.20
1.50			7.05	2.39
1.67			7.22	2.43
1.83			7.32	2.33
2.00			7.73	2.56
2.33			7.44	5.01
2.50			7.48	2.54
2.67			7.56	2.56
2.83			7.58	2.42
3.00			7.59	2.58
3.17			7.63	2.59
3.50			7.65	5.04
3.67			7.73	2.61
3.83			7.65	2.46
4.00			7.63	2.60
4.17			7.70	2.61
4.33			7.79	2.48
4.67			7.81	5.30
4.83			7.91	2.52
5.00			7.91	2.69
Summation		**96.45**		**68.87**

Net ozone transferred = 96.45 - 68.87 = 27.58 mg



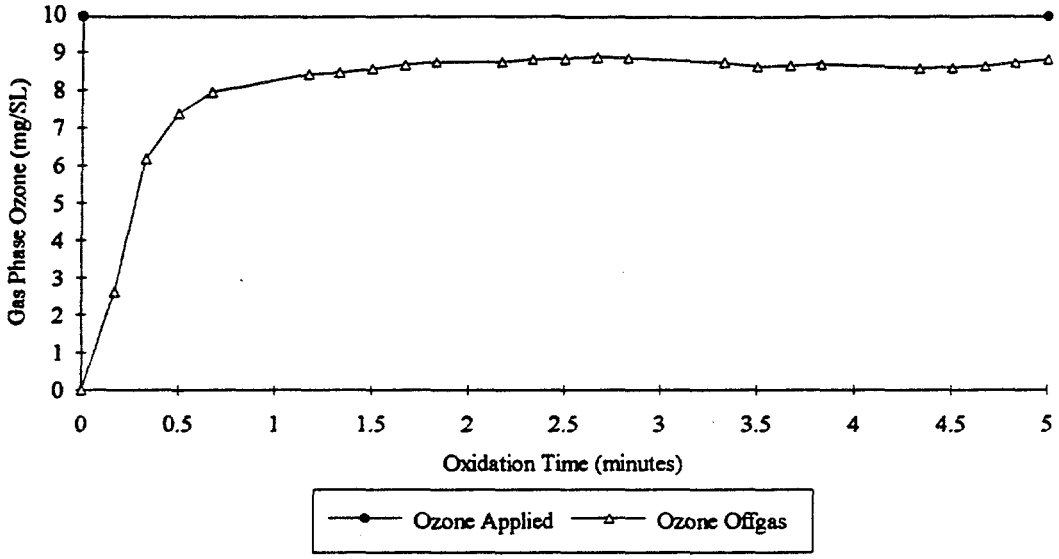
Net ozone transferred = 27.58 mg

Figure F. 1 Ozone Offgas and Applied measurements as a function of Oxidation Time for BR-1 (actual pink water treated for 5 minutes with O_3/ UV 254/ TiO_2)



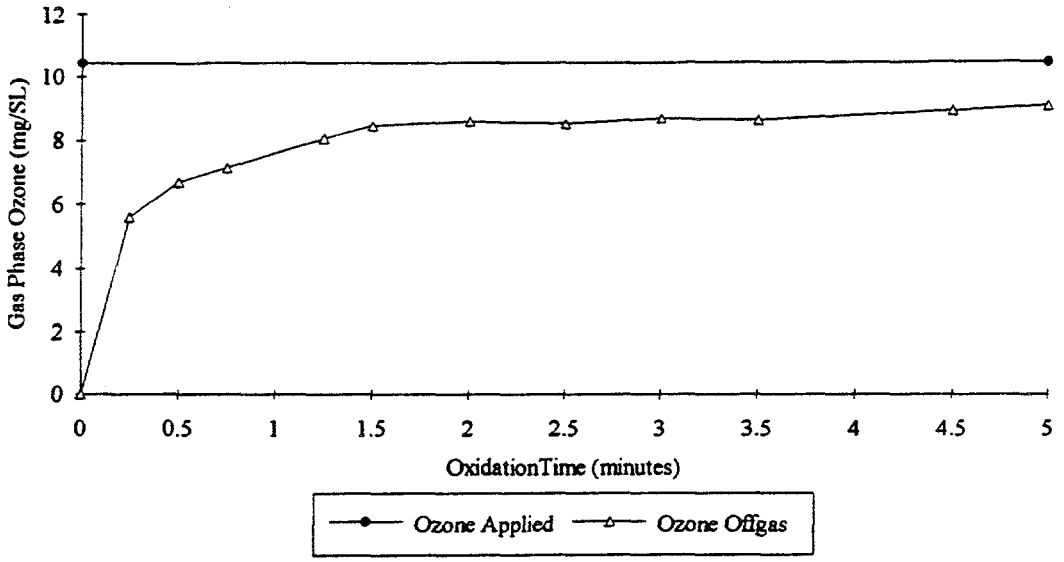
Net ozone transferred = 278.33 mg

Figure F. 2 Ozone Offgas and Applied measurements as a function of Oxidation Time for BR-2 (actual pink water treated for 120 minutes with O_3/ UV 254)



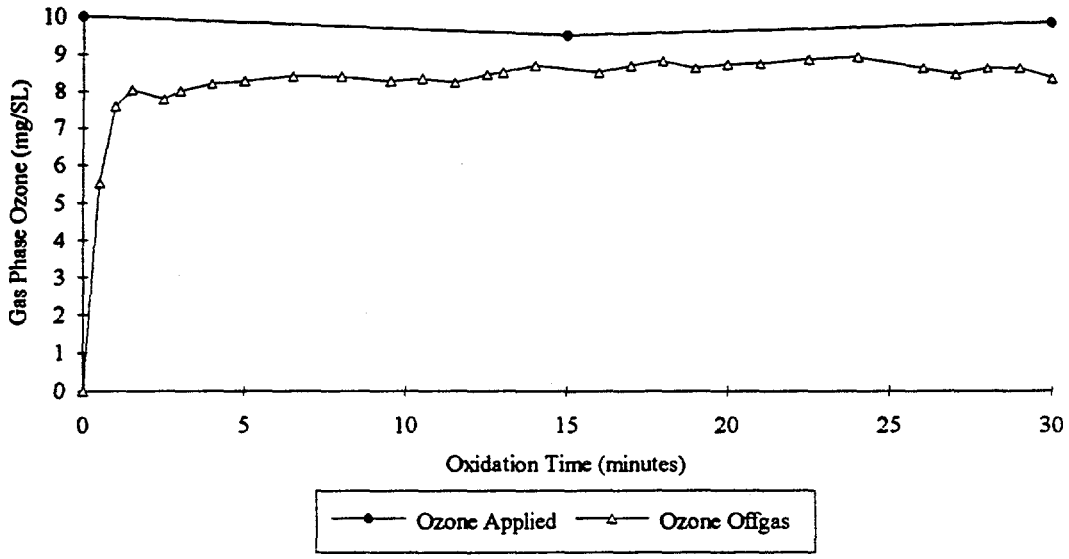
Net ozone transferred = 17.72 mg

Figure F. 3 Ozone Offgas and Applied measurements as a function of Oxidation Time for BR-5 (synthetic pink water treated for 5 minutes with O_3/ UV 254/ TiO_2)



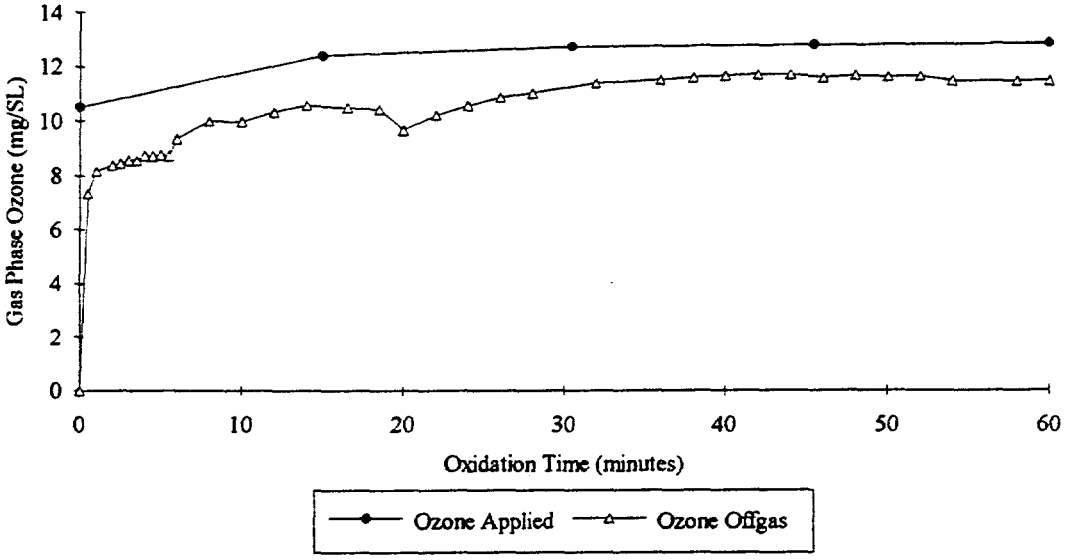
Net ozone transferred = 13.1 mg

Figure F. 4 Ozone Offgas and Applied measurements as a function of Oxidation Time for BR-8 (actual pink water treated for 5 minutes with O_3/ UV 254)



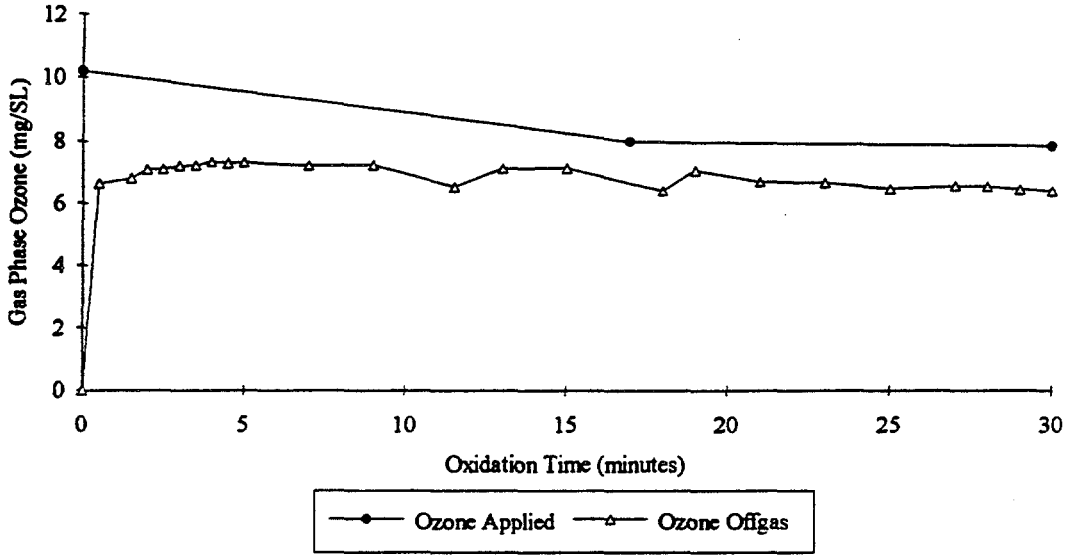
Net ozone transferred = 82.7 mg

Figure F. 5 Ozone Offgas and Applied measurements as a function of Oxidation Time for BR-9 (actual pink water treated for 30 minutes with O_3/ UV 254)



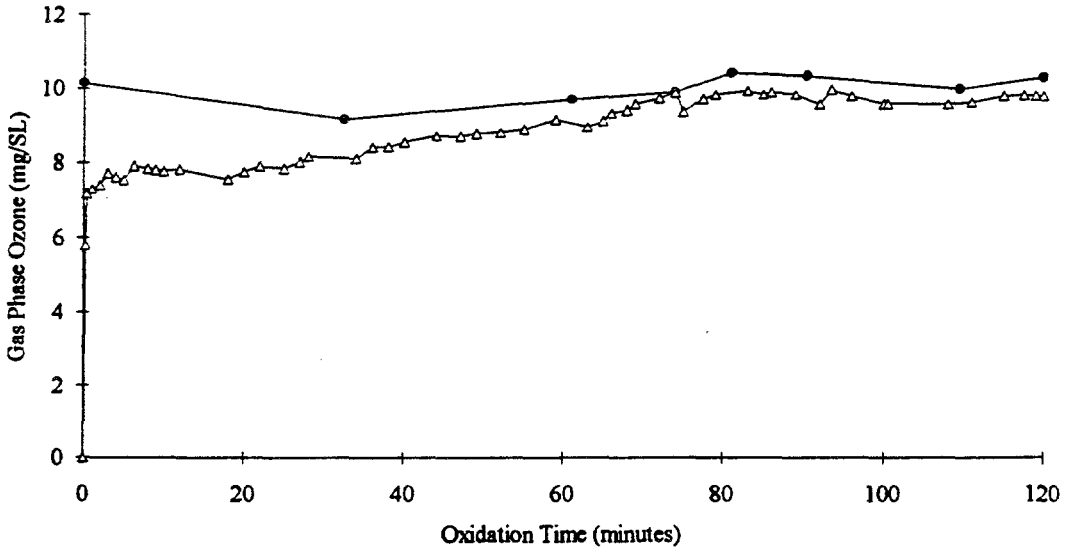
Net ozone transferred = 156.4 mg

Figure F. 6 Ozone Offgas and Applied measurements as a function of Oxidation Time for BR-10 (actual pink water treated for 60 minutes with O_3/ UV 254)



Net ozone transferred = 86.4 mg

Figure F. 7 Ozone Offgas and Applied measurements as a function of Oxidation Time for BR-11 (actual pink water treated for 30 minutes with O_3/ UV 254 half lamp)



Net ozone transferred = 220.4 mg

Figure F. 8 Ozone Offgas and Applied measurements as a function of Oxidation Time for BR-12 (O_3/ UV 254 treatment of 7 day aerobic biotreated actual pink water)

Appendix G

Specimen Calculations of Absorbance Scan Areas

UV absorbance measurements were recorded for all the wastewater samples in increments of 10 nm from 200 nm to 390 nm. The area under the absorbance scan gives an indirect measure of the cumulative organic content in the wastewater. Figure G.1 shows the absorbance scans of the untreated actual and synthetic pink waters. The Table G.1 illustrates the spreadsheet used in determining the areas under the absorbance scans for the actual pink water (APW-2).

Incremental area between 200 nm to 210 nm

= (Absorbance @ 200 nm + Absorbance @ 210 nm) ÷ 2.0 x (210 - 200)

Cumulative area between 200 nm to 390 nm

= Σ (Incremental areas from 200 nm to 390 nm)

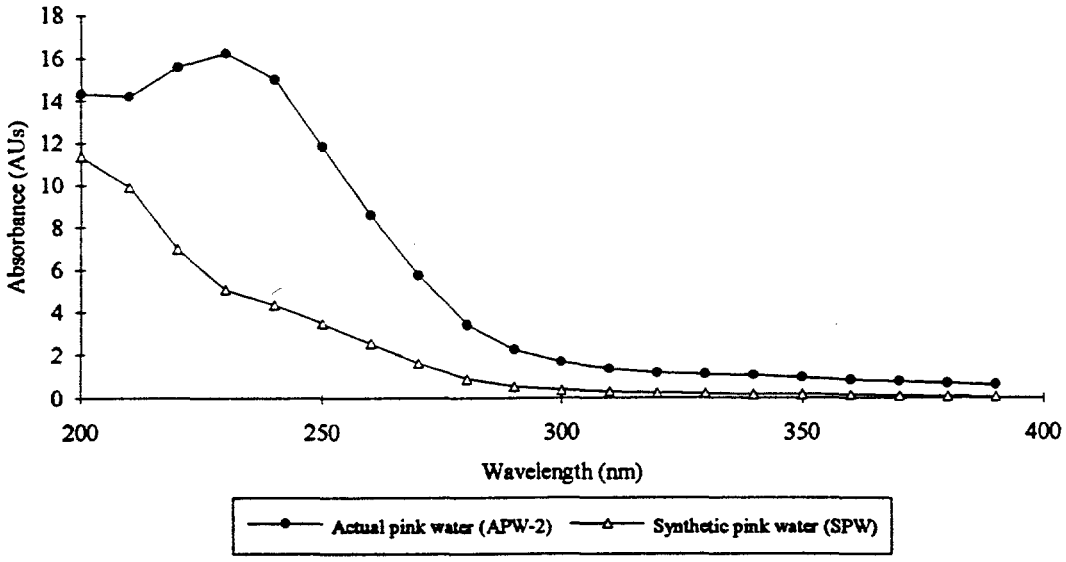


Figure G.1 Absorbance scans of untreated actual and synthetic pink waters

Table G.1 Spreadsheet illustrating the cumulative absorbance area calculations for untreated actual pink water

WAVELENGTH (nm)	ABSORBANCE (AUs)	ABSORBANCE AREA
200	14.34	142.8
210	14.21	149.0
220	15.59	159.3
230	16.27	156.5
240	15.02	134.4
250	11.86	102.4
260	8.62	72.0
270	5.78	46.1
280	3.44	28.5
290	2.25	19.7
300	1.69	15.3
310	1.37	12.7
320	1.17	11.4
330	1.10	10.8
340	1.05	9.9
350	0.94	8.9
360	0.83	7.9
370	0.76	7.2
380	0.67	6.5
390	0.62	3.1
Cumulative absorbance area		1104.1

Cumulative absorbance area under the scan from 200 nm to 390 nm for actual pink water is 1104.10.

Appendix H

Theoretical concepts behind the physical/chemical treatment schemes adopted for pink waters

H.1 Ozonolysis

Ozone is a triatomic molecule of oxygen which has been widely used in the removal of organic contaminants from the wastewaters since the turn of the century. Ozone is a powerful oxidant and also a good disinfectant.

The chemical oxidation potential of ozone is reported to be 2.07 V (W. H. Glaze, 1990). The oxidation potential is a thermodynamic value that indicates the power of an oxidant. The higher the oxidation potential, the faster is the rate of oxidation. In other words, oxidants having high potential require shorter contact times. In practical terms, the oxidation potential of ozone is approximately 1.5 times of the oxidation potential of chlorine indicating that ozone is 1.5 times stronger oxidant than chlorine.

Ozone is formed when molecular oxygen, $O_2(g)$ reacts with atomic oxygen, O(g). Once formed the ozone tends to decompose since the bond dissociation energy required to separate ozone is relatively low. The life time of ozone in aqueous solutions depends on several variables including pH, temperature, TOC level, and bicarbonate level (Staehelin et al., 1983).

Mass balance on ozone applied to a reactor yields the following equation (Dr. Sierka, 1993):

$$O_{3,t} = O_{3,u} + O_{3,e} + O_{3,d} + O_{3,a}$$

where,

$O_{3,t}$ = total ozone dose to the reactor

$O_{3,u}$ = actual ozone used in reaction

$O_{3,e}$ = dissolved ozone in the reacting liquid

$O_{3,d}$ = ozone in the reactor exit gas

$O_{3,a}$ = ozone consumed through autodecomposition.

According to Hoigne et al. (1983) the reaction of ozone in aqueous solutiuons proceeds by atleast two mechanisms:

1. a direct oxidation by molecular oxidation which is usually very selective
2. an indirect oxidation by entities resulting from decomposition of ozone in water.

Earlier studies (Glaze et al., 1987) on ozone decomposition showed that the ozonation of aqueous solutions below pH 7.0 favor direct oxidation while ozonation above pH 7.0 favors oxidation by *hydroxyl radicals*.

Glaze et al. (1987) proposed the following set of reactions for ozone decomposition in a pure aqueous solution:

$$O_3 + H_2O \quad \text{---->} \quad O_2 + 2OH\cdot \qquad \text{...(1)}$$

(*hydroxyl radical*)

$$O_3 + OH\cdot \quad \text{---->} \quad O_2 + HO_2\cdot \qquad \text{...(2)}$$

(*hydroperoxy radical*)

$$O_3 + HO_2\cdot \quad \text{---->} \quad 2O_2 + OH\cdot \qquad \text{...(3)}$$

$$OH\cdot + OH\cdot \quad \text{---->} \quad H_2O_2 \qquad \text{...(4)}$$

$$OH\cdot + HO_2\cdot \quad \text{---->} \quad H_2O + O_2 \qquad \text{...(5)}$$

$$OH\cdot + OH^- \quad \text{--->} \quad O^- + H_2O \qquad \text{...(6)}$$

(*oxide ion*)

$$HO\cdot + HO_2\cdot \quad \text{--->} \quad H_2O_2 + O_2 \qquad \text{...(7)}$$

$$O^- + O_2 \quad \text{--->} \quad O_3^- \qquad \text{...(8)}$$

(*ozonide ion*)

Equations (1) to (3) illustrate the three possible iniatiators to ozone decomposition in pure water. The chain reaction propogating radicals can be scavenged by several intermediates as shown in equations (4) to (7). Two mechanisms [equations (4) and (7)] are proposed for the formation of hydrogen peroxide. The *oxide ion* formed in equation (6) will react with dissolved oxygen to form ozonide ion.

Other agents that can initiate the decomposition of ozone in water include UV light, H_2O_2, ultrasound, metals and humics (Staehelin et al., 1983). Once initiated, the cyclic chain reactions produce several intermediates including *hydroxyl radicals*. The *hydroxyl radical* produced in the decomposition of ozone is one of the most powerful chemical agents known capable of reacting with almost any organic compound.

H.2 Photolysis

When light of a given frequency is adsorbed by a molecule, it may cause physical or chemical change. UV light has been used to provide the energy to produce the transition of electrons from one orbit to another. If this eleectron belongs to a chemical bond, the bond may be broken in the transition. Table H.1 lists the dissociation energies for some typical chemical bonds (Dr. Sierka, 1993).

Table H.1 Dissociation energies of some typical chemical bonds

Bond	Dissociation energy (kcal/gmol)	Maximum wavelength to break the bond, nm	If adsorbed will this light break the bond 253.7 nm	184.9 nm
C – C	82.60	346.1	Yes	Yes
C = C	145.8	196.1	No	Yes
C ≡ C	199.6	143.2	No	No
C – N	72.80	392.7	Yes	Yes
C = N	212.6	194.5	Yes	Yes
O – O	119.1	240.1	No	Yes
O – H	117.5	243.3	No	Yes

H.3 Photocatalysis or UV/TiO_2 system

TiO_2 anatase is an n-type semi-conductor powder which has electron band gap energy of 3.0 eV. The basic reaction mechanism of UV/TiO_2 system involves the formation of electron-hole pair on impingement with high energy photons (UV 254 nm light) at the TiO_2 surface. This electron-hole pairs migrate to the surface causing formation of hydroxyl radicals via the reactions given below (Dr. Sierka, 1993):

$$TiO_2 + hv \quad \longrightarrow \quad h_{vb+} + e_{cb^-}$$

$$OH^-(s) + h_{vb+} \quad \longrightarrow \quad OH\cdot + H^+$$

where

hv = UV energy in photons

h_{vb+} = valence band holes

e_{cb-} = conduction band electrons

Okamato et al. (1985) suggested that these radicals could also form via interaction through valence-band holes by the formation of H_2O_2 and superoxide ion ($O_2^{\cdot -}$). He also suggested that oxygen plays an important role in semi-conductor mediated reactions by trapping the conduction-band electrons as superoxide ion ($O_2^{\cdot -}$) and thus delaying the electron-hole recombination process:

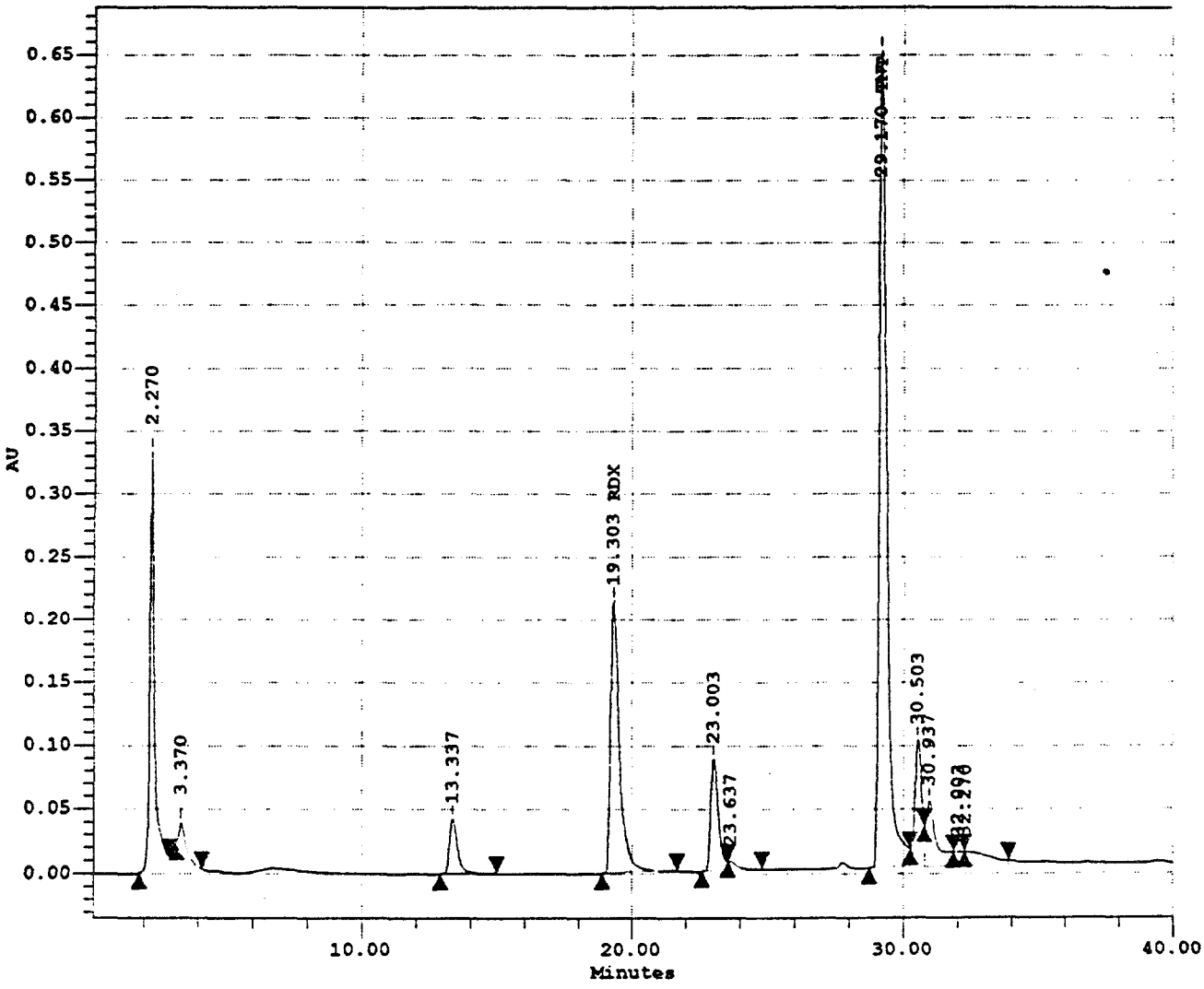
$$O_2 + e_{cb-} \quad \text{--->} \quad O_2^{\cdot -}$$

Appendix I

Specimen HPLC chromatographs of treated and untreated pinkwaters

Figures I.1 to I.10 show some typical HPLC chromatographs. Figures I.1 and I.2 show the HPLC chromatographs for the actual and synthetic pink waters. The presence of additional peaks in the actual pink water compared to the synthetic pink water indicates that the composition of actual pink water has more components than the synthetic pink water. Figure I.3 shows the HPLC chromatograph for yeast extract dissolved in ultra-pure (Milli Q) water at 0.25% (2.5 g/L). In Figure I.3 the size of the peaks are relatively small and no peaks were seen at the elution times corresponding to the RDX or TNT for the dissolved yeast extract. The HPLC chromatograph of BR-2 (APW-2/ O_3/ UV 254 nm/ 120 minutes) treated effluent appears relatively clean with a few minor peaks corresponding to the by-products of prolonged oxidation treatment of pink water (Figure I.4). Figures I.5 and I.6 show the HPLC chromatographs for the 14-day bioeffluents from the aerobic and anaerobic treatment respectively for BR-3 (APW-2/ O_2/ UV 365 nm/ 30 minutes) pretreated pink water. A comparison of HPLC chromatographs shown in the Figures I.5 and I.6 clearly indicate the significance of anaerobic treatment in RDX degradation. A number of small peaks, adjacent to the RDX peak, are seen in Figure I.6 probably corresponding to the by-products of RDX biodegradation. Figures I.7 and I.8 show the HPLC chromatographs for the 14-day bioeffluents from the BR-4 (APW-2/ N_2/ UV 365 nm/ 30 minutes) pretreated pink water. Figures I.9 and I.10 show the HPLC chromatographs for 7-day biotreated actual pink water prior to and after physical/chemical treatment with UV 254 nm catalyzed-ozone for a duration of 30 minutes. The degradation of RDX and other by-products of aerobic treatment occured after the

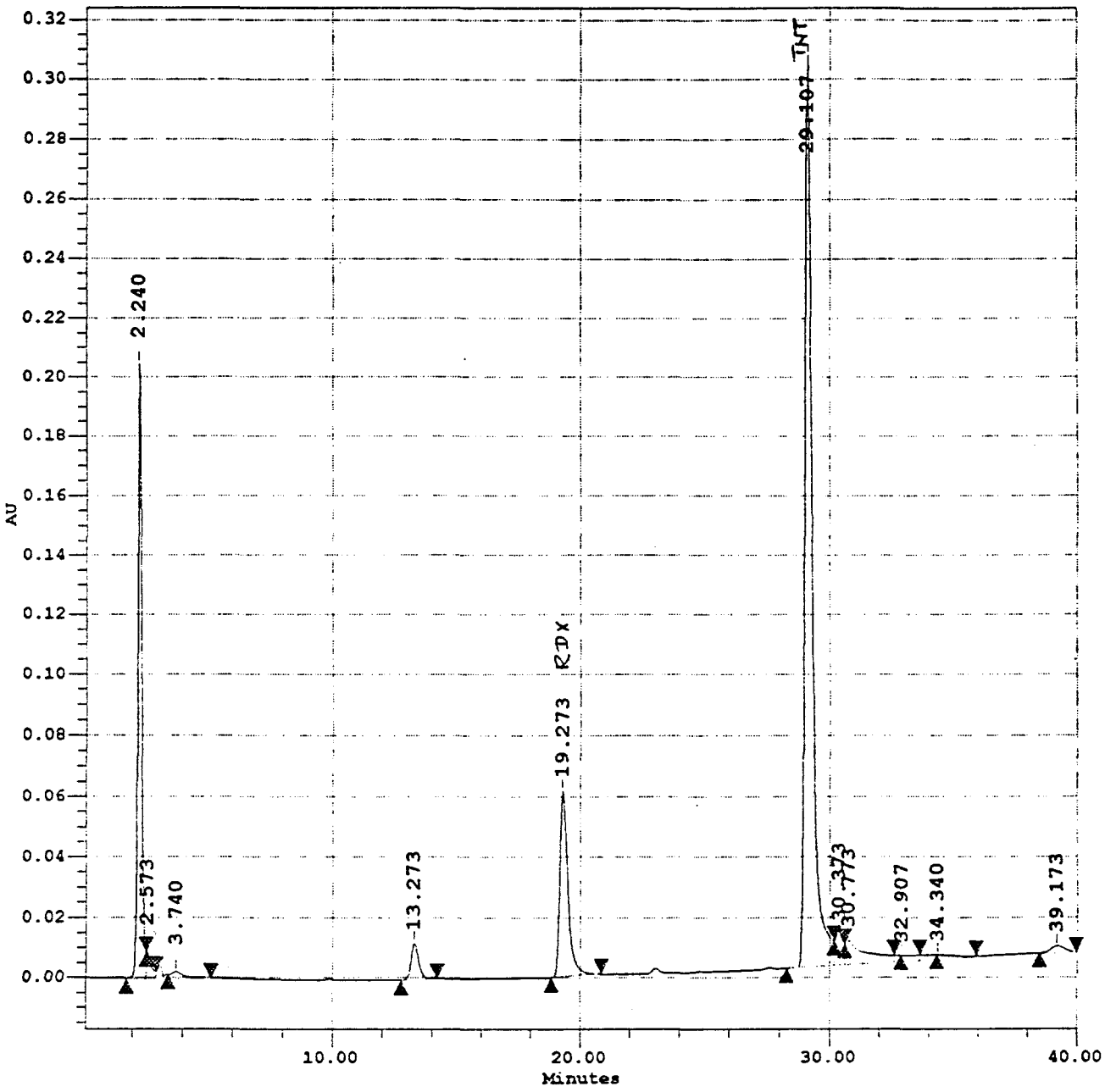
physical/chemical treatment leading to the disappearance of a number of small peaks in Figure I.10.



Peak Results

#	Name	Ret Time (min)	Area (uV*sec)	Height (uV)
1		2.270	3742053	328847
2		3.370	520361	28953
3		13.337	905098	42969
4	RDX	19.303	4978140	215344
5		23.003	1766520	88131
6		23.637	186208	7150
7	TNT	29.170	12655899	649328
8		30.503	1798865	99957
9		30.937	1450950	51866
10		32.003	274773	11487
11		32.270	778006	11361

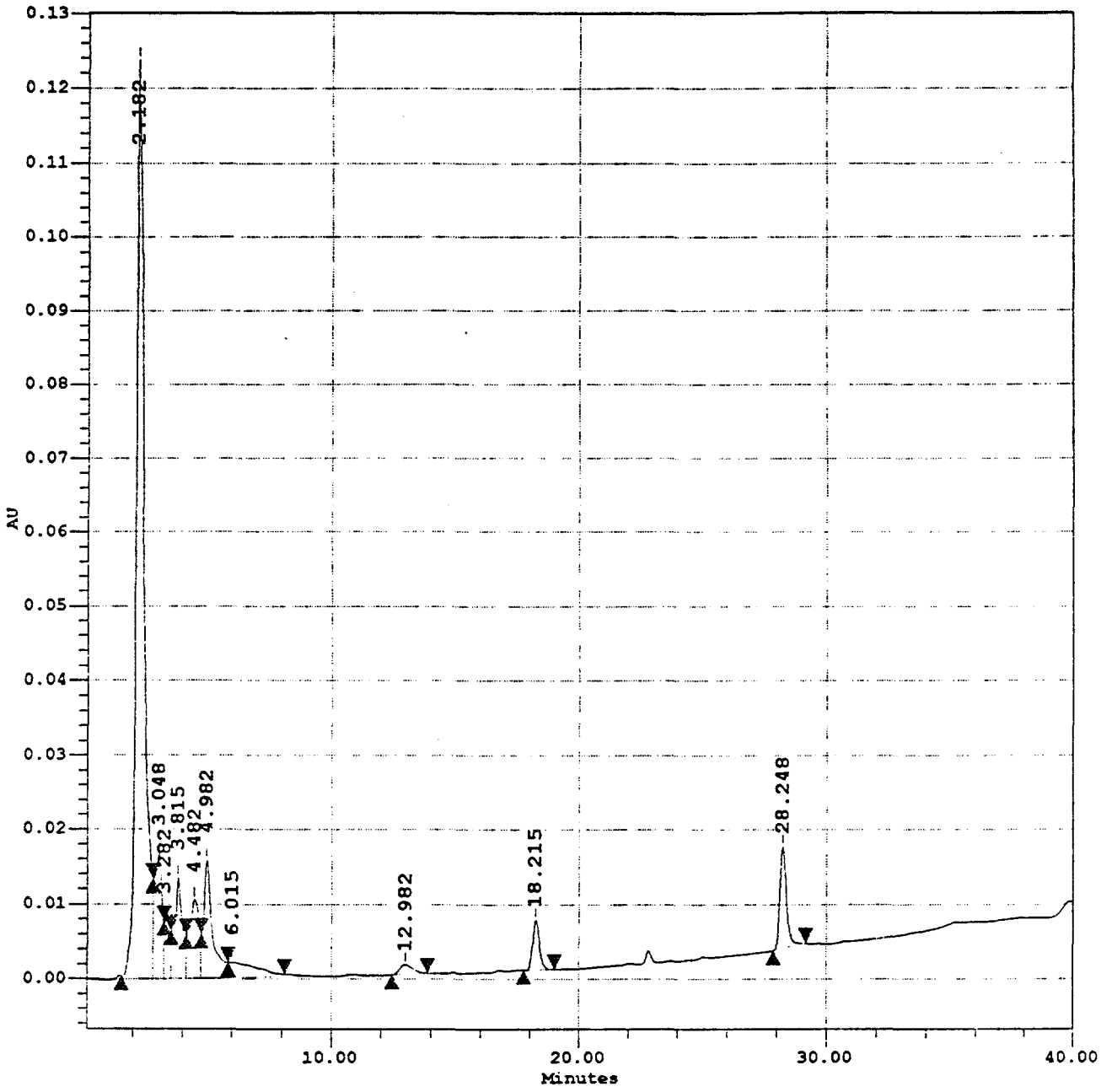
Figure I.1 HPLC chromatograph of actual pink water (APW-2)



Peak Results

#	Name	Ret Time (min)	Area (uV*sec)	Height (uV)	% Area
1		2.240	2135478	205259	18.73
2		2.573	120872	9438	1.06
3		3.740	93095	2463	0.82
4		13.273	267873	12311	2.35
5	RDX	19.273	1424061	61920	12.49
6	TNT	29.107	6303148	304643	55.29
7		30.373	232455	10223	2.04
8		30.773	493162	8059	4.33
9		32.907	96051	2155	0.84
10		34.340	115436	1888	1.01
11		39.173	117593	2619	1.03

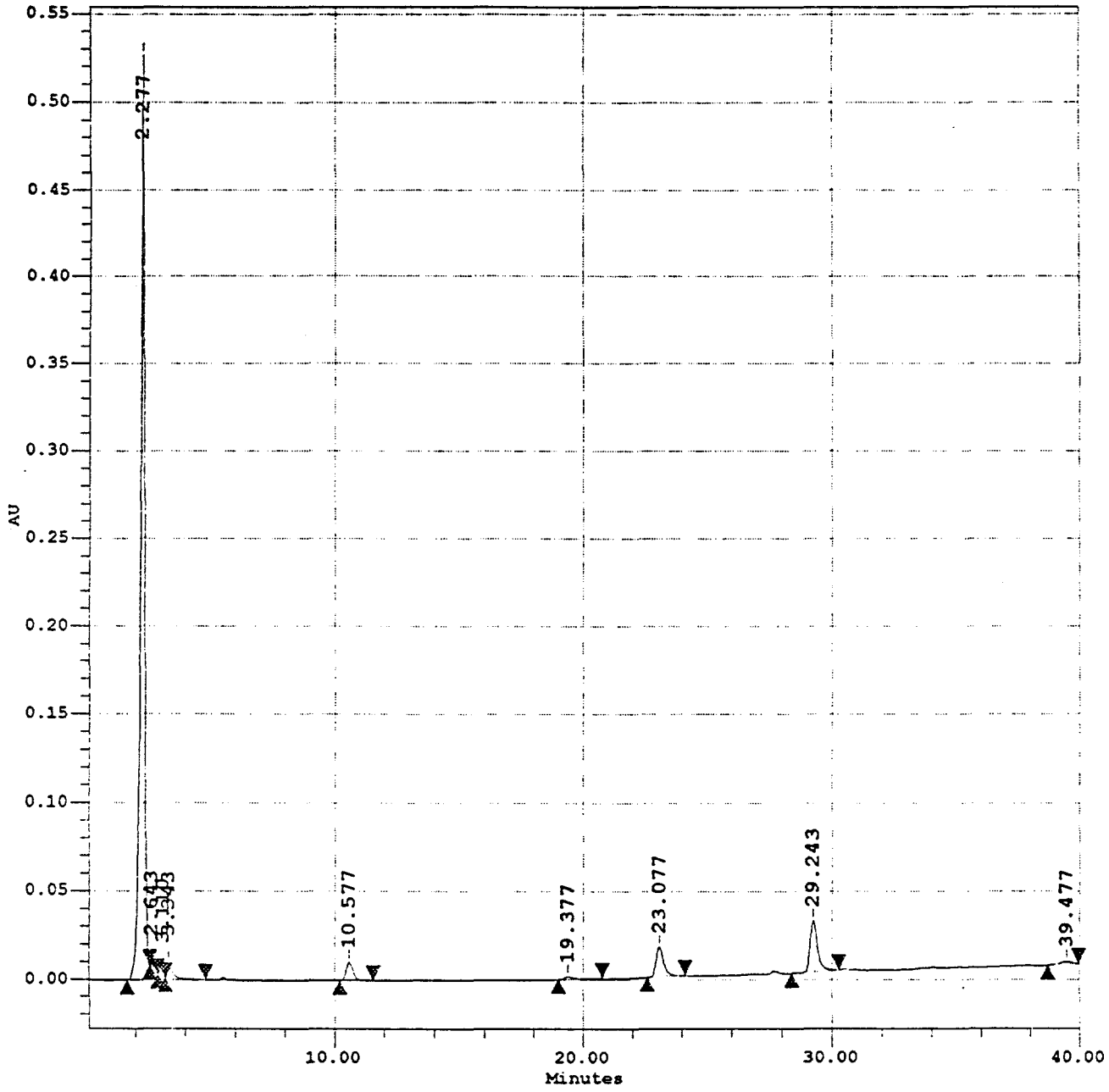
Figure I.2 HPLC chromatograph of synthetic pink water (SPW)



Peak Results

#	Name	Ret Time (min)	Area (uV*sec)	Height (uV)	% Area
1		2.182	2802789	124037	57.15
2		3.048	351043	16970	7.16
3		3.282	132499	7936	2.70
4		3.815	303694	13626	6.19
5		4.482	289854	10609	5.91
6		4.982	401652	15839	8.19
7		6.015	180368	2141	3.68
8		12.982	54241	1377	1.11
9		18.215	133035	6763	2.71
10		28.248	255474	13622	5.21

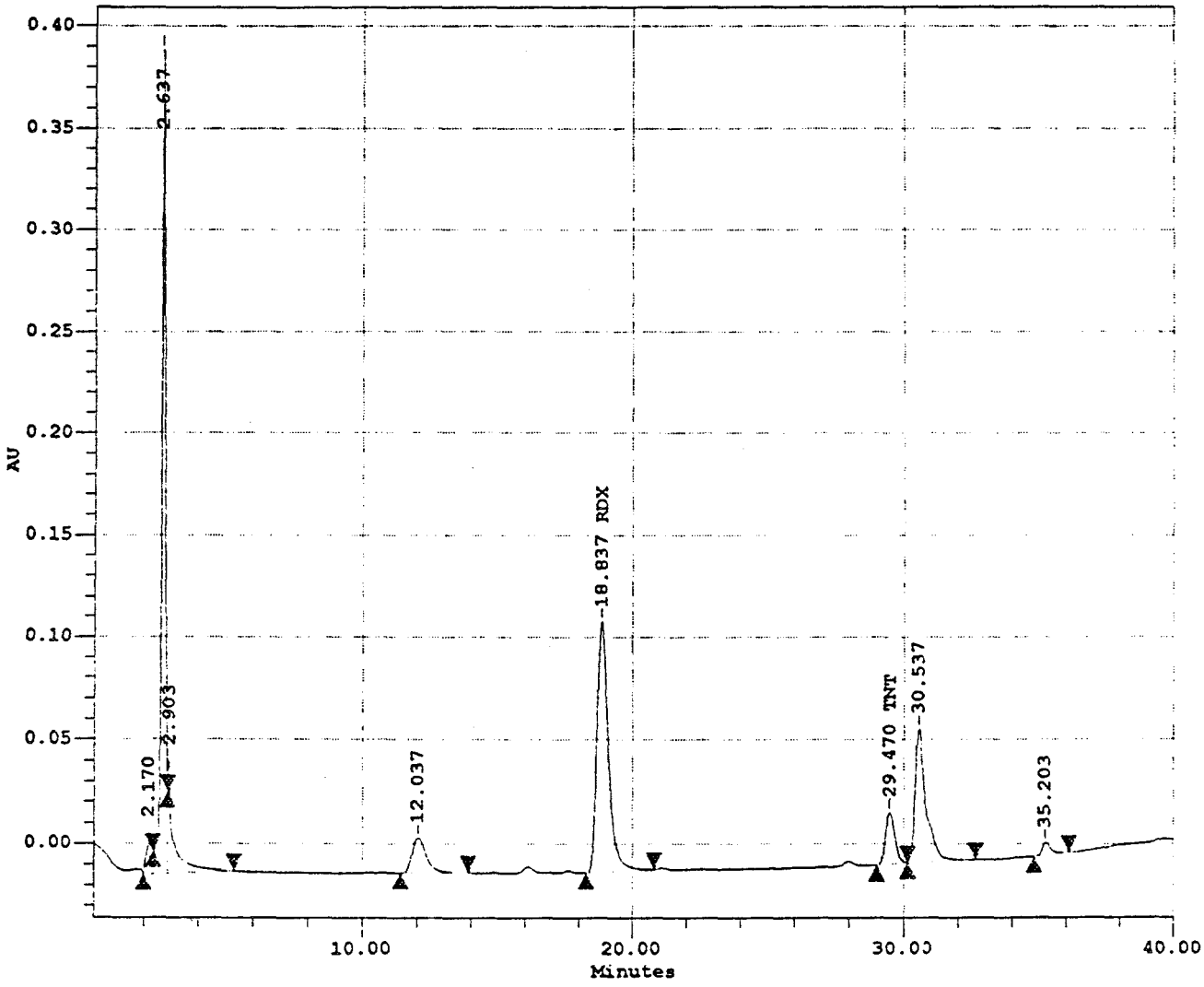
Figure I.3 HPLC chromatograph of Milli Q + 2.5 g/L yeast extract



Peak Results

#	Name	Ret Time (min)	Area (uV*sec)	Height (uV)	% Area
1		2.277	5742348	527703	76.33
2		2.643	135891	10108	1.81
3		3.110	72831	5826	0.97
4		3.343	204322	9658	2.72
5		10.577	221243	10880	2.94
6		19.377	50112	1754	0.67
7		23.077	388620	17014	5.17
8		29.243	641378	29522	8.53
9		39.477	65879	1832	0.88

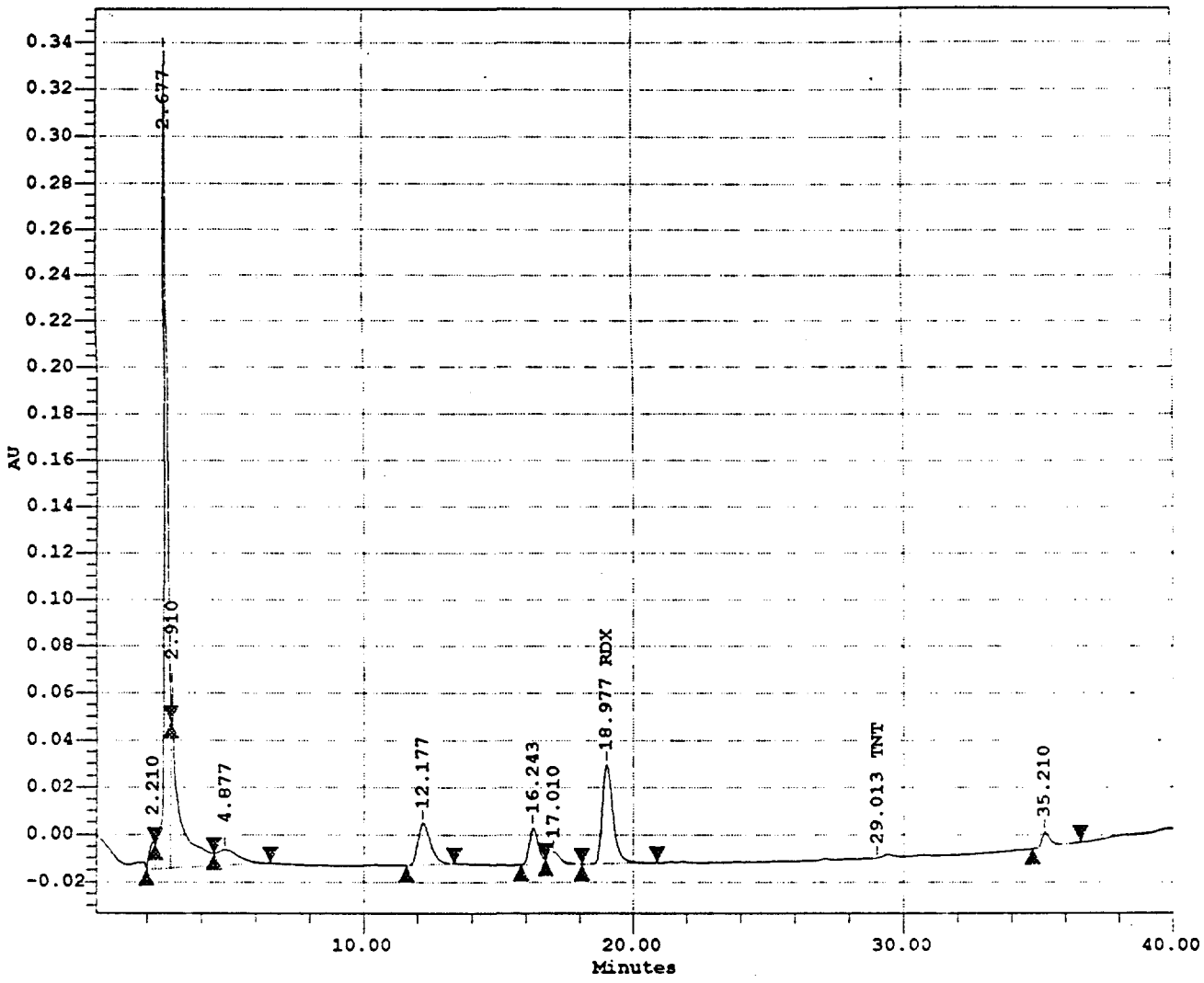
Figure I.4 HPLC chromatograph after BR-2 pretreatment (APW-2/ O_3/ UV 254 nm/ 120 minutes)



Peak Results

#	Name	Ret Time (min)	Area (uV*sec)	Height (uV)
1		2.170	237660	14555
2		2.637	3790307	403513
3		2.903	748734	48713
4		12.037	623539	17370
5	RDX	18.837	3628330	121895
6	TNT	29.470	612900	25933
7		30.537	1857665	65117
8		35.203	138790	6351

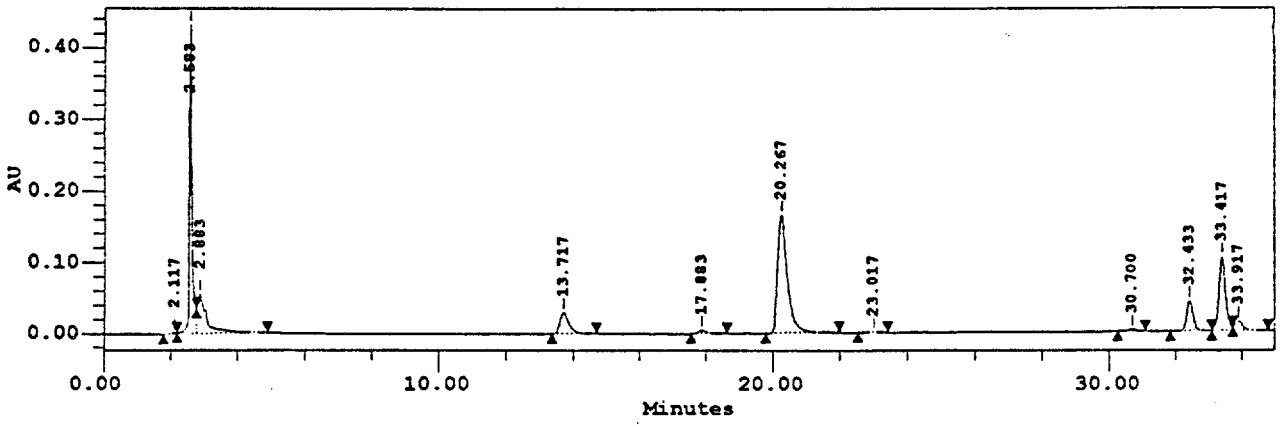
Figure I.5 HPLC chromatograph after 14 days of aerobic treatment of BR-3 (APW-2/ O_2/ UV 365 nm/ 30 minutes)

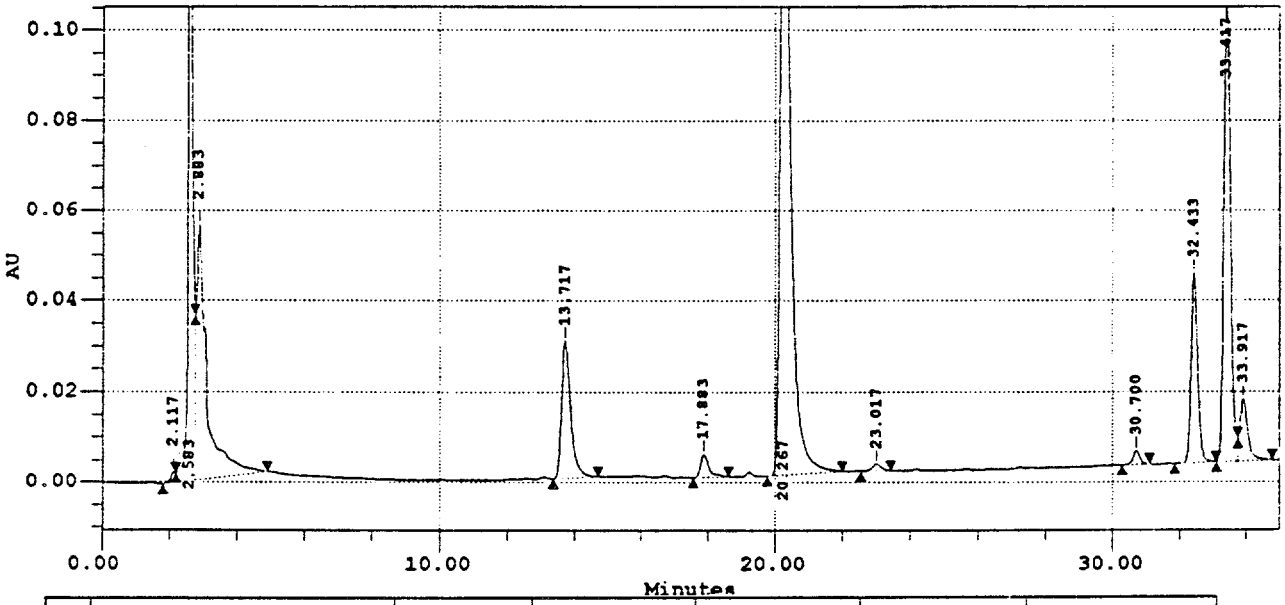


Peak Results

#	Name	Ret Time (min)	Area (uV*sec)	Height (uV)
1		2.210	171008	11557
2		2.677	3552080	351319
3		2.910	1537871	77499
4		4.877	398430	6815
5		12.177	590987	17883
6		16.243	382709	15895
7		17.010	170778	5466
8	RDX	18.977	1206482	42514
9	TNT	29.013		
10		35.210	150624	6724

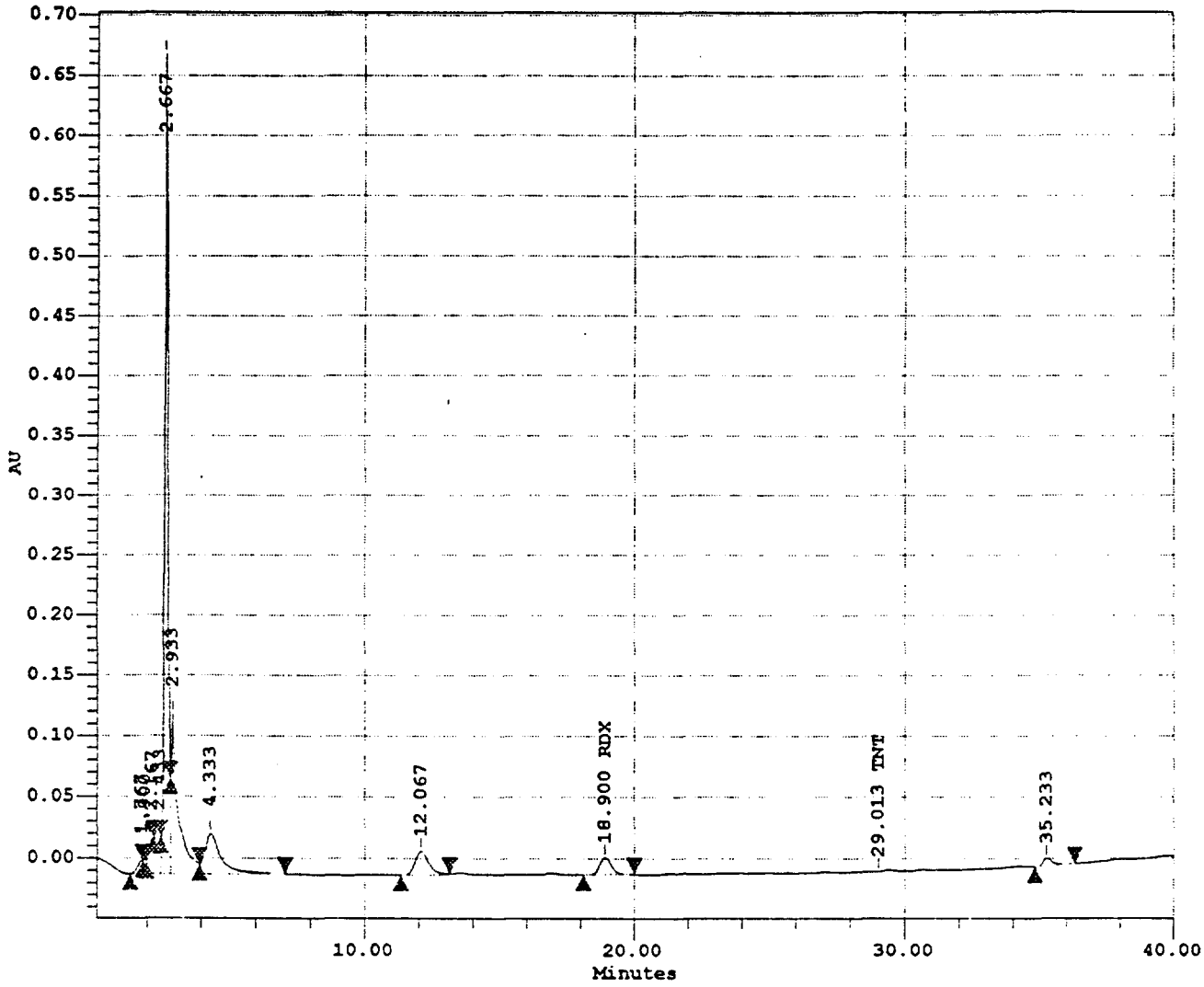
Figure I.6 HPLC chromatograph after 14 days of anaerobic treatment of BR-3 (APW-2/ O_2/ UV 365 nm/ 30 minutes)





#	Name	Ret Time (min)	Area (uV*sec)	Height (uV)	Amount	Int Type
1		2.117	27870	2619		BV
2		2.583	2309543	433142		VV
3		2.883	1212250	56397		VB
4		13.717	579301	30339		BB
5		17.883	90897	5159		BB
6	RDX	20.267	3386716	165231		BB
7		23.017	29284	1663		VB
8		30.700	44448	3046		VB
9		32.433	576201	41745		BV
10		33.417	1424128	102283		VV
11		33.917	226530	13695		VB

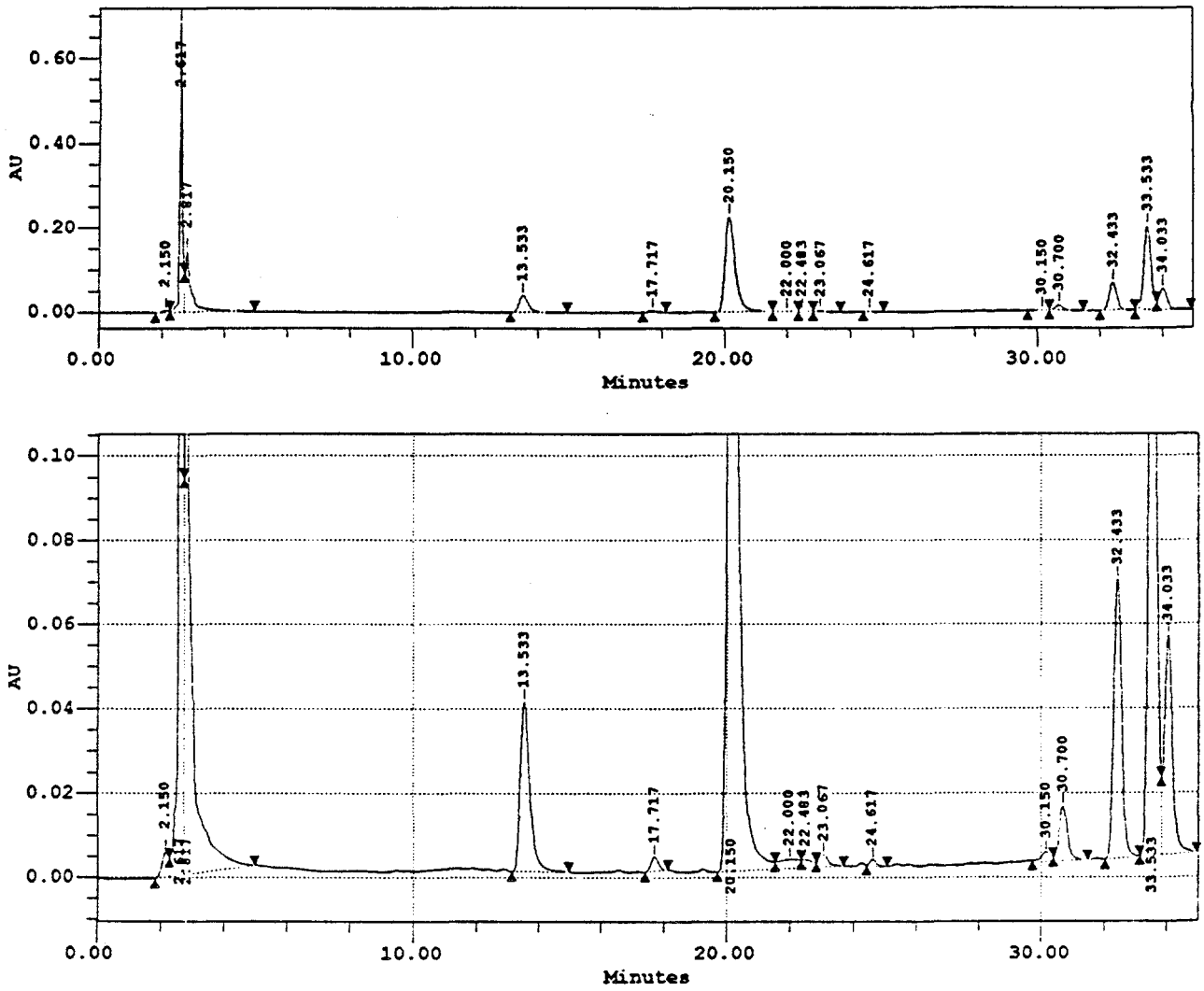
Figure I.7 HPLC chromatograph after 14 days of aerobic treatment of BR-4 (APW-2/ N_2/ UV 365 nm/ 30 minutes)



Peak Results

#	Name	Ret Time (min)	Area (uV*sec)	Height (uV)
1		1.767	153648	10840
2		1.900	84460	11024
3		2.167	377513	29075
4		2.433	481675	30671
5		2.667	6177576	681053
6		2.933	2254322	131246
7		4.333	1358965	32867
8		12.067	697014	19784
9	RDX	18.900	427678	14303
10	TNT	29.013		
11		35.233	141490	6385

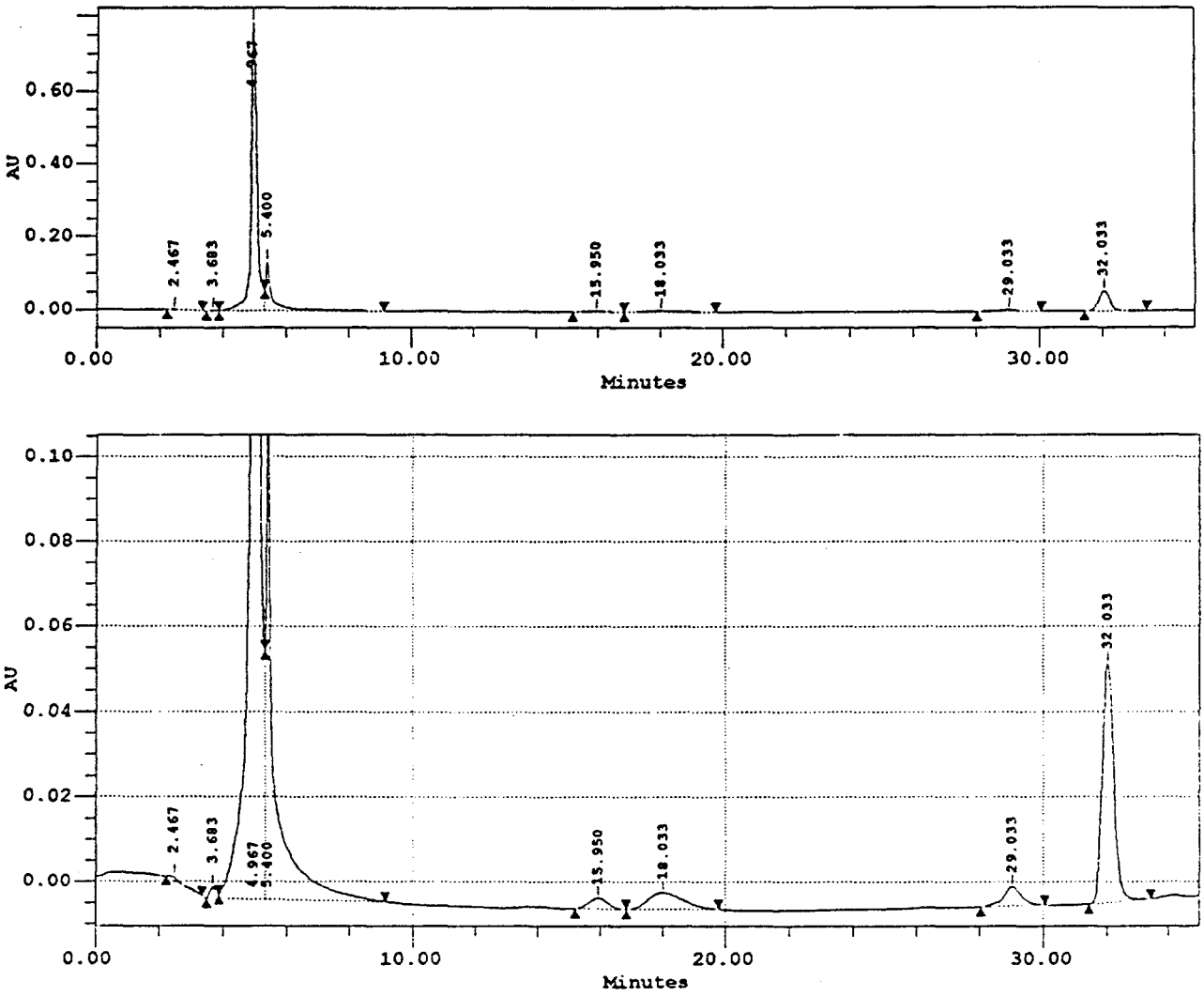
Figure I.8 HPLC chromatograph after 14 days of anaerobic treatment of BR-4 (APW-2/ N_2/ UV 365 nm/ 30 minutes)



Peak Results

#	Name	Ret Time (min)	Area (uV*sec)	Height (uV)	Amount	Int Type
1		2.150	86773	6053		BV
2		2.617	3766832	683918		VV
3		2.817	2239156	146667		VB
4		13.533	872359	40358		BB
5		17.717	57351	3457		BB
6	RDX	20.150	5225627	225819		BV
7		22.000	95289	2110		VV
8		22.483	45013	1913		VV
9		23.067	57444	2919		VB
10		24.617	23228	1633		VB
11		30.150	50127	2290		VV
12		30.700	242163	13062		VV
13		32.433	1160688	66222		BV
14		33.533	3229351	198688		VV
15		34.033	931766	51978		VB

Figure I.9 HPLC chromatograph after 7 days of aerobic treatment of actual pink water control



Peak Results

#	Name	Ret Time (min)	Area (uV*sec)	Height (uV)	Amount	Int Type
1		2.467	21180	805		BB
2		3.683	34995	2754		BV
3		4.967	10714082	787273		VV
4		5.400	2270093	134111		VB
5		15.950	107337	2529		BB
6		18.033	302326	3938		BB
7		29.033	180473	4600		BB
8		32.033	1477497	56346		BB

Figure I.10 HPLC chromatograph after 30 minutes of UV 254 -catalyzed treatment of 7 days aerobic treated actual pink water

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