

# **REMEDIATION OF EXPLOSIVES-CONTAINING WATER USING ADVANCED OXIDATION AND SORPTION PROCESSES**

by

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A project submitted in partial fulfillment of the requirements for the degree of

MASTER OF ENGINEERING

in

CIVIL ENGINEERING

(Environmental Engineering)

UNIVERSITY OF PUERTO RICO

MAYAGÜEZ CAMPUS

2009

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## ABSTRACT

The main objective of this work is to develop a procedure to degrade and remove explosives contained in water (ECW). Specifically, this investigation assessed the degradation and removal of TNT and DNT using advanced oxidation and sorption processes. The initial concentrations used for the experiments were 0.4–1.0 mg/L. For the advanced oxidation process it was used a batch reactor with an ultra violet light and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) concentrations of 50, 100 and 300 mg/L. The contact time with the  $\text{H}_2\text{O}_2$  was 2 hours. This process reduced the initial concentration of the explosive in 44, 52 and 60%, respectively. The sorption process experiments used coal ash aggregate (CAA). In these experiments, the CAA was placed in small batch reactors in contact with the ECW for 2 hours. The amount of explosives that the aggregate can sorb was calculated to be 0.0254 mg TNT/g CAA according to the Freundlich constant.

## RESUMEN

El principal objetivo de este trabajo es proveer un procedimiento para degradar y remover explosivos disueltos en agua. Específicamente, esta investigación evaluó la degradación y remoción de TNT y DNT usando oxidación avanzada y sorpción. Las concentraciones iniciales de los explosivos fueron 0.4–1.0 mg/L. Para el proceso de oxidación avanzada se utilizó una cámara con una lámpara de luz ultravioleta y concentraciones de Peróxido de Hidrógeno ( $H_2O_2$ ) de 50, 100 y 300 mg/L. El tiempo de contacto con el  $H_2O_2$  fue de 2 horas. Se logró reducir la concentración inicial del explosivo en 44, 52 y 60%, respectivamente. El proceso de sorpción se hizo utilizando agregado de cenizas de carbón. En estos experimentos, se colocó el agregado en pequeñas cámaras en contacto con explosivos disueltos en agua durante 2 horas. Se pudo calcular la cantidad de explosivo que puede sorber el agregado, en 0.0254 mg TNT/g CAA según la constante de Freundlich.

*To my parents, Iris Ramos and Victor Hernandez for supporting me and guiding me through this journey.*

*To my beloved wife Maria Labayen for believing in me and encouraging me to work harder every day.*

*To God for letting all this happen and letting me be part of this great family.*

## ACKNOWLEDGEMENTS

First I will thank God for giving me the opportunity to pursue this degree.

Thanks to my mother for her unconditional support throughout my life and my career.

Thanks to my father who gave me the advices when I needed them.

Thanks to Dr. Sangchul Hwang for giving me the opportunity to participate in the Environmental Laboratory Research Team and make my project. Also thanks, for giving me the guidance necessary to complete all the research activities during this project.

Thanks to Dr. Ingrid Padilla for her support on the Environmental Laboratory activities.

Also Thanks to Dr. Jorge Rivera for sharing some of his knowledge through these years of research.

I would like to thanks to the Environmental Laboratory Research Team for all the help provided in the day to day laboratory activities, for their guidance using the laboratory equipment and the correct use of the experimental methods.

# TABLE OF CONTENT

ABSTRACT .....	ii
LIST OF ABBREVIATIONS .....	x
1 Introduction .....	1
1.1 Justification .....	1
1.2 Objectives.....	2
2 Literature Review .....	4
2.1 Explosives .....	4
2.2 Fate and Transport of Explosives .....	5
2.3 Remediation of Explosives .....	6
2.4 Sorption.....	7
2.5 Coal Combustion by-Product Ash Aggregates .....	8
2.5.1 Fly Ash.....	8
2.5.2 Bottom Ash.....	9
2.5.3 Manufactured Aggregate.....	9
2.6 Advanced Oxidation Process .....	10
2.7 Effect of pH Exerted by CAA on Explosives Sorption .....	12
3 Materials and Methods .....	14
3.1 Materials.....	14
3.1.1 Explosive: TNT .....	14
3.1.2 Explosive: DNT .....	15
3.1.3 Advanced Oxidation Process.....	15
3.1.4 Sorption .....	17
3.1.5 Effect of pH on Sorption .....	19
3.1.6 Analytical Instrumentation .....	19
3.2 Methods.....	20
3.2.1 Advanced Oxidation Process.....	20
3.2.2 Sorption .....	23
3.2.3 Desorption .....	27
3.2.4 pH Profile in the Presence of CAA.....	28
3.2.5 Chemical Analysis .....	29
3.2.6 Analysis of Data.....	31
4 Results and Discussion .....	33
4.1 Advanced Oxidation Process .....	33
4.1.1 Control Experiment: UV Only .....	34
4.1.2 Experiment 2: UV/ H <sub>2</sub> O <sub>2</sub> – 50 mg/L.....	35
4.1.3 Experiment 3: UV/ H <sub>2</sub> O <sub>2</sub> – 100 mg/L.....	37
4.1.4 Experiment 4: UV/ H <sub>2</sub> O <sub>2</sub> – 300 mg/L.....	38
4.1.5 Experiment 5: UV/ H <sub>2</sub> O <sub>2</sub> – 300 mg/L turning the UV ON/OFF at Different Intervals .....	39
4.1.6 Experiment 6: UV/ H <sub>2</sub> O <sub>2</sub> – 300 mg/L; [TNT] <sub>0</sub> = 1.0 mg/L .....	40
4.1.7 Summary of AOP Results .....	41
4.1.8 Statistical Analysis for AOP.....	49
4.1.9 Energy Requirements.....	52
4.2 Sorption.....	53

4.2.1	Effect of pH on Sorption .....	54
4.2.2	Sorption Kinetics .....	56
4.2.3	Sorption Isotherm.....	57
4.2.4	Sequential Batch Reactor .....	60
4.2.5	Small-Size Particles .....	62
4.2.6	Desorption .....	68
4.2.7	Application to Actual ECW Produced .....	69
5	Summary, Conclusions, and Recommendations .....	76
5.1	AOP .....	76
5.2	Sorption Kinetics .....	77
5.3	Sorption Isotherm .....	77
5.4	Sequential Batch Reactor System.....	78
5.5	AOP Followed by Sorption Process .....	78
5.6	Desorption .....	79
5.7	Application to Actual ECW Produced.....	79
5.8	Recommendations for Combined Treatment Processes .....	79
5.9	Further Studies .....	80
6	References .....	82
7	Appendix.....	85

## LIST OF FIGURES

Figure 1. Schematic drawing of AOP system.....	21
Figure 2. Schematic drawing of sorption kinetic experiment.....	24
Figure 3. Slow speed shaking device for vials .....	24
Figure 4. Schematic drawing of sorption isotherm experiment.....	25
Figure 5. Sequential batch reactor schematic procedure.....	27
Figure 6. pH verification procedure schematic without return (left) with return flow (right) .....	29
Figure 7. Calibration curve for Sorption experiments .....	30
Figure 8. Control experiment plot: UV only with $TNT_o = 0.4$ mg/L.....	34
Figure 9. Experiment 2 plot: UV/ $H_2O_2 = 50$ mg/L & $TNT_o = 0.4$ mg/L .....	36
Figure 10. Zoom view of the experiment 2 plot. ....	36
Figure 11. Experiment 3 plot: UV/ $H_2O_2 = 100$ mg/L & $TNT_o = 0.4$ mg/L .....	37
Figure 12. Experiment 4 plot: UV/ $H_2O_2 = 300$ mg/L & $TNT_o = 0.4$ mg/L .....	38
Figure 13. Experiment 5 plot: UV - on-off / $H_2O_2 = 300$ mg/L & $TNT_o = 0.4$ mg/L .....	39
Figure 14. Experiment 6 plot: UV/ $H_2O_2 = 300$ mg/L & $TNT_o = 1.0$ mg/L .....	40
Figure 15. Normalized TNT degradation plot for all of the experiments. ....	42
Figure 16. $H_2O_2$ degradation plot for all of the experiments.....	43
Figure 17. Zoom view of the $H_2O_2$ degradation plot for all of the experiments .....	44
Figure 18. Maximum TNT degradation vs. $H_2O_2$ concentration.....	45
Figure 19. $H_2O_2$ concentration versus time for diffusion verification. ....	48
Figure 20. Histogram for the Control experiment (n=30). ....	50
Figure 21. Picture of the Manufactured Aggregate (MA) (left) and the Bottom Ash (BA) (right). .....	54
Figure 22. Coal Ash dilution. ....	55
Figure 23. Sorption kinetic plot .....	56
Figure 24. TNT sorption using CAA; $[TNT]_o = 1.0$ mg/L.....	57
Figure 25. Repeat of TNT sorption using smaller increments of CAA mass; $[TNT]_o = 1.0$ mg/L .....	58
Figure 26. Freundlich adsorption model plot .....	59
Figure 27. Langmuir adsorption model plot.....	60
Figure 28. Sequential batch reactor plot CAA = 2.5 g & $TNT_o = 1.0$ mg/L .....	61
Figure 29. Head space on both experiment setups; Sequential .....	62
Figure 30. Comparison of small (left) and coarse (right) particle aggregate. ....	63
Figure 31. TNT sorption using CAA particle size <0.0394 inches .....	64
Figure 32. Post-sorption filtration assembly.....	65
Figure 33. Comparison of turbid (left) and filtered water (right). ....	66
Figure 34. Sorption Isotherm Chart using low pH value. ....	67
Figure 35. TNT desorption plot, $[TNT]_o=1.0$ mg/L.....	68
Figure 36. First batch of TNT and DNT remediation of ECW with UV/ $H_2O_2$ 300 mg/L.....	71
Figure 37. Second Batch of TNT and DNT remediation of ECW using AOP.....	72
Figure 38. Remediation of ECW previously treated with second batch AOP now using Sorption proces .....	74
Figure 39. Remediation of ECW using only sorption process .....	75
Figure 40. Recommendation of the process flow of the degradation and sorption of TNT and DNT.....	81



## LIST OF TABLES

Table 1. Standard electrode potential (V) for selected substances (Source: Metcalf and Eddy, 2003) .....	11
Table 2. Summary of the different TNT and H <sub>2</sub> O <sub>2</sub> combinations assessed. ....	22
Table 3. Statistical comparison between the data trends of the different experiments using a 90% confidence level. ....	42
Table 4. Summary of degradation constant for all the experiments .....	45
Table 5. Results of the normality test.....	50
Table 6. Student's t-test result summary.....	51
Table 7. Electrical energy consumption required for oxidation .....	52
Table 8. Summary of difference between initial and final concentrations of explosives. ....	73
Table 9. Electric Energy consumed by the treatment of ECW from other research.....	73

## LIST OF ABBREVIATIONS

AOP	Advanced Oxidation Process
CAA	Coal Combustion By-Product Ash Aggregate
DI	Deionized Water.
DNT	Dinitrotoluene
ECW	Explosives Containing Water
HPLC	High Performance Liquid Chromatogram
H <sub>2</sub> O <sub>2</sub>	Hydrogen Peroxide
K <sub>f</sub>	Freundlich coefficient
MeOH	Methanol
mg/L	Milligrams per Liter
mL	Milliliters
min <sup>-1</sup>	Minutes <sup>-1</sup>
nm	Nanometers (10 <sup>-9</sup> m)
NPDES	National Pollution Discharge Elimination System
RDX	Royal Demolition eXplosive
SBR	Sequential Batch Reactor
TiSO <sub>4</sub>	Titanium Sulfate
TNT	Trinitrotoluene
UPRM	University of Puerto Rico – Mayagüez Campus
UV	Ultra Violet

# **1 Introduction**

Due to the increasing military activity in the past years, the utilization of explosives has also increased. These explosives represent a potential threat to the environment and the people living near where the explosives are. Some areas of military training activity are of special importance due to the continuous use of the explosives on a limited area. The problem with these explosives is that high concentrations can lead to health problems on humans and the environment [Karjalainen, 1999; Singh, et al. 2003; US EPA, 1993].

## **1.1 Justification**

The University of Puerto Rico – Mayagüez Campus (UPRM) has been involved in various projects dealing with the fate, transport, and detection of explosives. Some of these projects have been conducted in the Environmental Engineering Laboratory in the Civil Engineering Department, which produces waters and soils contaminated with explosives related compounds. The waters and soils used in the experiments need to be remediated to a condition where it represents no harm to the environment or to the people that manage it.

In order to comply with local and federal water quality laws, the water that comes out of the experiments is stored in a safe container at satellite area until it is picked up by a hazardous waste management company which treats the water to an acceptable quality at a predetermined charge rate. Although most of the expenses for the explosives experiments are currently covered by the funding agencies, the cost of treating the contaminated water is currently covered by the UPRM. In order to reduce the cost of doing experiments and to become a more sustainable campus, a need exists to remediate the explosives-containing water (ECW) at the point of origin instead of giving it to a third party to remediate it.

A low-cost process known as advanced oxidation process (AOP) was utilized for this study. AOPs are known to be very effective to remediate recalcitrant organic contaminants [Guzzella et al. 2002; Momani et al. 2007; Peternel et al. 2006]. In the experiments performed for this project, an ultraviolet light (UV) in conjunction to hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) oxidation (UV/ $\text{H}_2\text{O}_2$ ) was tested to meet the objectives.

A second process assessed was the sorption mechanism that was utilized to complement the AOP. In order to obtain maximum benefit of this project, the materials for the sorption studies to remediate the ECW were low-cost Coal Combustion By-product Ash Aggregates (CAA), which is currently being produced by a local coal combustion power plant in Guayama, Puerto Rico. Since this material is a by-product of their daily process, they produce large amounts of it and it is free of charge to use. The CAA has sorption properties, thus it can be used as a sorption material [Lin and Yang, 2002; Pathan et al., 2003].

## **1.2 Objectives**

The main goal of this project was to develop an on site process to remediate the ECW that was being produced in the Environmental Engineering Laboratory in Civil Engineering Department. This goal was achieved by the use of AOP and Sorption as the two main mechanisms to remediate the ECW.

A specific objective of the AOP experiments was to find the optimum concentration of oxidant as a combination of UV and  $\text{H}_2\text{O}_2$  concentration that needs to be applied to the ECW in order to achieve maximum degradation possible with the least amount of time and materials. A specific objective of the sorption process experiments was to find the sorption capacity as the

mass of explosive absorbed by mass of sorbent. To do this, the behavior of the low-cost CAA was assessed with various sorption isotherm and kinetic studies.

## 2 Literature Review

This section is divided into several sub-sections that introduce some previous work related to remediation of ECW. Basic concepts on explosives, fate and transport of explosives, and remediation of explosives, are also discussed.

### 2.1 Explosives

An explosive can be defined as a substance or mixture of substances, which is capable, by chemical reaction, of producing gas at such a temperature, pressure and rate as to be capable of causing damage to the surroundings [US EPA, 2005]. The earliest known explosive mixture discovered was what is now commonly referred to as black powder. For over 1,200 years, black powder was the universal explosive and was used as a propellant for guns [US EPA, 2005]. Later in the 1840s, nitroglycerine was first prepared and its explosive properties were described. It was first used as an explosive by Alfred Nobel in 1864 [US EPA, 2005]. For the World War I and II, the development of 2, 4, 6-trinitrotoluene (TNT) had advanced and it was being produced at a really fast rate and in more manageable ways, so it was a preferred explosive to black powder. Since 1945, military researchers have recognized that, based on both performance and cost, RDX<sup>1</sup>, TNT, and HMX<sup>2</sup> are not likely to be replaced as explosives of choice for military applications [US EPA, 2005].

One of the main problems of exposure to explosives is the possibility of causing diseases on humans. Some of the diseases that can be caused by TNT are: non-malignant diseases and abnormalities of red and white blood cells like anemia, disease of the eye due to chemical corruptions like cataract, toxic liver disease, and also cancer [Karjalainen, 1999; ATSDR, 1995a].

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<sup>1</sup> Royal Demolition eXplosive

<sup>2</sup> High Melting eXplosive

Some of the diseases that can be caused by DNT are: heart disease, anemia, cyanosis, and hepatitis. Other effects reported by people exposed to DNT are headache, dizziness, and insomnia [ATSDR, 1998]. Some of the diseases that can be caused by RDX are asthma, chronic bronchitis, pneumonia and pulmonary congestion. Some studies suggest that at acute high doses of oral ingestion it can even cause death [ATSDR, 1995b]. Acute and intermediate oral exposure to HMX can be lethal and mild hematological effects may occur following exposure to large doses of HMX [ATSDR, 1997].

## **2.2 Fate and Transport of Explosives**

Fate and transport of some munitions constituents in the environment have not yet received the level of focus of some more commonly found chemicals associated with other military operations (such as petroleum hydrocarbons in groundwater from jet fuels) [US EPA, 2005]. Several experiments have been undertaken to test the mobility of TNT in several porous media [Torres, 2008; Anaya, 2009]. The results of these experiments conclude that explosives like TNT and RDX that were put in contact with soils were sorbed to the soil matrices and are difficult to desorb from the soil [Falone et al, 2006]. Robertson et al. [2007] made analysis to soil samples on an explosives factory in Australia and demonstrated that the TNT plume propagated very slowly along the flow path within the aquitard.

Hwang et al. [2005a] demonstrated that after  $\text{H}_2\text{O}_2$  application, the values of Freundlich coefficient  $K_f$  were increased by ~160% for average and high pH soils and by ~120% for an iron-rich soil, showing that the soils became more favorable for TNT sorption after  $\text{H}_2\text{O}_2$  application. On the other hand, when TNT in the presence of methanol is passed through soil columns

(bentonite/sand), almost complete recovery of the injected amount is recovered at the exit of the column with limited retardation [Selim et al., 1995].

These experiments show that explosives like TNT (if they are discharged) will move through the soil at a slow rate because the soil will sorb them. This means that instead of having a sudden increase in concentration at a certain point due to a spill or other way of explosive intake, there will be a slow release of the explosive for a very long time. Also several environmental conditions such as amount of rain (water flow), solar radiation, or the presence of other chemicals can increase or reduce the rate of movement and path of the explosive [Anaya, 2009].

### **2.3 Remediation of Explosives**

There are several types of remediation that can be used to remediate ECW, including: bioremediation, oxidation, sorption, and chemical reduction [Rodgers and Bunce, 2001]. Each remediation process has its own advantages and disadvantages. The type of remediation to use on all situations is very site specific. A combination of safety, logistical, throughput, and cost issues often determines the practicality of treatment technologies [US EPA, 2005].

Plants can be used to uptake explosives from soils into leafs or other harvestable zones (phytoextraction) or volatilize them (phytovolatilization), but high concentrations of explosives in the soils can be toxic to some plants [Rodgers and Bunce, 2001]. Although bacteria that are able to utilize the explosives molecules as carbon or nitrogen source are not abundant, some environmental conditions can be modified (like injection of nutrients for bacterial growth) in order to achieve biological degradation of pollutants [US EPA, 2005].



Oxidation processes are efficient but depend on several factors (e.g., pH, suspended materials, and other constituents) [Metcalf and Eddy, 2003]. Selected reactive compounds may be introduced into the soil to chemically transform or degrade contaminants through oxidative or reductive processes. For aqueous media, hydrogen peroxide, oxygen release compounds (e.g., magnesium peroxide), ozone, or microorganisms are added to the water to degrade reactive and/or ignitable materials more rapidly. Depending on the depth of the contaminants, spray irrigation may be used, or for deeper contamination, injection wells may be used. The primary advantage of in-situ remediation is that soils do not need to be excavated or screened prior to treatment, thus resulting in cost savings. In addition, soils and groundwater can be treated simultaneously [US EPA, 2005].

Sorption processes introduce the method of “separating” the explosives from the solid or aqueous phase to another medium for further treatment or for landfill disposal, but do not modify them to non-hazardous materials [Rodgers and Bunce, 2001]. This technology has been proved to treat contaminated water and can serve well for ECW.

## **2.4 Sorption**

Sorption is a process by which a dissolved substance is transferred to and becomes associated with solid material. It includes both the accumulation of dissolved substances on the surface of solids (adsorption) and in the interpenetration or intermingling of substances with solids (absorption). The substance that is sorbed is called the sorbate and the solid is called the sorbent [Chapra, 1997].

Several media can be used to sorb the explosives with different results. Naturally occurring materials, like seed shells [Amuda et al., 2007; Badmus, et al., 2007], as well as

manmade polymers or modified activated carbon can be used to sorb toxic organic compounds with good results [US EPA, 1980]. Some advantages of the natural materials are that they are typically cheap and easy to find although most properties are uncontrollable. Manmade or man-altered materials typically have properties that are more favorable. The performance of a granular activated carbon (GAC) bed depends on the type of carbon, particle size, pore size, hydraulic loading, and operating temperature [Rodgers and Bunce, 2001].

## **2.5 Coal Combustion by-Product Ash Aggregates**

This material has many potential environmental applications in the field [Pando and Hwang, 2006]. Two properties of interest for the current study are the high pH which can produce alkaline hydrolysis and its high surface area that can act as a sorption material. The high void ratio content of the coarse aggregate was found to be related to a structure of an agglomerate of particles. These large particles are actually agglomeration of finer particles that were found to be susceptible to abrasion and breakdown [Pando and Hwang, 2006].

The two main by-products that come out of the combustion process are fly ash (FA) and bottom ash (BA). At the coal combustion power plant, the two ashes are collected and then combined with water to produce a third by-product called manufactured aggregate (MA). Generally the FA is the fine particles that go “flying” up the chimney of the furnace and the BA is the (heavier) ash that falls down to the bottom of the furnace.

### **2.5.1 Fly Ash**

Pando and Hwang [2006] stated that fly ash is the finely divided mineral that results from the combustion of pulverized coal produced during the steam generation process in the power

plant. The FA particles solidify while suspended in the exhaust gases and are collected by electrostatic precipitations. It consists primarily of silica, aluminum, iron, and calcium oxides. Other elements, such as magnesium, potassium, sodium, titanium and sulfur, are also present to a lesser degree. Typically, FA consists of spherical silt-sized particles finer than Portland cement and lime, i.e., particle sizes ranging between 10 and 100 microns [Pando and Hwang, 2006]. Fly ash is usually dark gray in color, but this depends on its chemical composition and mineral constituents [Pando and Hwang, 2006].

### **2.5.2 Bottom Ash**

Bottom ash is a CAA consisting of coarse grained particles that fall to the bottom of the furnace as a result of the coal combustion procedures. It is usually the smaller portion of the total ash produced during the coal combustion process. The chemical composition of BA is similar to FA. However, BA is more inert than FA, and as a result, BA particles have a greater tendency to fuse together. The physical properties of BA are similar to those of natural sand, with particle sizes ranging from gravel to fine sand with low percentages of silt and clay-sized particles. Bottom ash is typically grey to black in color and has a large particle size, angular shape and high porous surface resulting in a higher water requirement and lower compressive strength [Pando and Hwang, 2006].

### **2.5.3 Manufactured Aggregate**

Manufactured aggregate (MA) is an agglomerate of fly and bottom ash particles. This material gains strength with time due to cementitious reactions [Pando and Hwang, 2006]. The chemical and physical properties of MA fall within the average of the properties of the individual

FA and BA. Since the ashes have cement-like properties, the individual particles tend to agglomerate and form big clusters of particles. Because of this, the particle size of MA is actually bigger than FA and BA individual size before they were mixed together. Since each individual ash is fine in size before they are mixed into MA and form bigger clusters, there is a possibility of having small pore size with really high surface area that can be used as a sorption material for ECW.

## 2.6 Advanced Oxidation Process

This technique has been implemented on a variety of applications such as treatment of drinking water and wastewater [Hwang, 2006; Metcalf and Eddy, 2003]. Several different methods can be used to achieve the high oxidation potential needed for the particular job. Some of these methods use ozone ( $O_3$ ) alone or in presence of UV light,  $H_2O_2$  in the presence of UV, and others to produce hydroxyl radicals ( $OH^\bullet$ ). When in contact with the aromatic rings,  $OH^\bullet$  initiate ring opening and ultimate mineralization to carbon dioxide ( $CO_2$ ) and water [Rodgers and Bunce, 2001]. For example, when the  $H_2O_2$  molecules are irradiated with UV light they separate and form an even stronger oxidizer known as  $OH^\bullet$ . In the UV/ $H_2O_2$  process, the O–O bond in hydrogen peroxide is cleaved by UV irradiation to generate  $OH^\bullet$  [Zang and Farnood, 2004]. The general reaction is as follows:



The idea of the AOP is to oxidize a hazardous material into more noble non-hazardous materials. To oxidize means to lose an electron. The counterpart of oxidation is reduction, process by which the molecule gains electrons. The combination of both processes is called redox (reduction-oxidation) because they occur simultaneously. Many materials have the ability

of being oxidizers and they are ranked by the oxidizing power they have. The power of an oxidant or a reductant is measured by the electrode potential of the substance [AWWA, 1999]. The electrode potential of some chemicals used in typical treatment processes, are shown in Table 1.

**Table 1. Standard electrode potential (V) for selected substances (Source: Metcalf and Eddy, 2003)**

<b>Oxidant</b>	<b>Standard electrode potential (V)</b>
Chlorine	1.36
Hydrogen Peroxide	1.78
Ozone	2.08
Hydroxyl Radical	2.80
Fluorine	3.06

Although the  $\text{OH}^\bullet$  is a great candidate to be used to remediate contaminated water due to its high electrode potential, it is not widely used because the half-life is short, in the order of microseconds, so it is not feasible to sustain high concentrations [Metcalf and Eddy, 2003]. For example,  $\text{OH}^\bullet$  reacts with ozone,  $\text{H}_2\text{O}_2$ , hydroperoxyl ion ( $\text{HO}_2^-$ ), and hydroperoxyl radical ( $\text{HO}_2^\bullet$ ) very fast at  $1.1 \times 10^8$ ,  $2.7 \times 10^7$ ,  $7.5 \times 10^9$ , and  $1.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ , respectively [Bose et al., 1998]. The latter two compounds are intermediates of the reaction that produce  $\text{H}_2\text{O}_2$  back in an AOP [Bose et al., 1998; Zang et al. 2005].

Depending on the amount and type of materials present on the water, the oxidation potential to the target material can be reduced due to the presence of other materials that can be oxidized at a higher rate than the target compound. For example, photon efficiency is compromised by turbidity, by the presence of other light absorbers, and by metal oxides and grease, which foul the quartz sleeves through which UV radiation must pass [Rodgers and Bunce, 2001].

Advanced oxidation processes are used to oxidize complex organic constituents that are difficult to degrade into simpler end products, by other means [Metcalf and Eddy, 2003]. The  $\text{OH}^\bullet$  reacts with the dissolved constituents, initiating a series of oxidation reactions until the constituents are completely mineralized [Metcalf and Eddy, 2003]. Being nonselective in their mode of attack and able to operate at normal temperature and pressures,  $\text{OH}^\bullet$  are capable of oxidizing almost all reduced materials present in the solution [Metcalf and Eddy, 2003]. The main advantage of AOP compared to other treatment processes is that wastewater compounds are degraded rather than concentrated or transferred to other phase [Metcalf and Eddy, 2003].

## **2.7 Effect of pH Exerted by CAA on Explosives Sorption**

Alkaline, or basic, solutions are ones that have pH values above 7, where the pH of a neutral solution (i.e., one which is neither acidic nor alkaline) is 7. A pH value provides a measure of the hydrogen ion concentration of a solution [Columbia, 2009a]. Hydrolysis is chemical reaction of a compound with water, usually resulting in the formation of one or more new compounds [Columbia, 2009b]. Therefore, the combinations of both would be to produce a chemical reaction with water in environmental conditions of pH levels above 7. Alkaline hydrolysis has been used in the past to degrade explosives as RDX and HMX where they are transformed into organic and inorganic salts, soluble organic compounds, benign nitrogen gases and ammonia. These reactions have been seen to be very dependant to pH level. In general, higher levels of pH (11-12) yielded lower levels of residual explosives concentrations on batch reactors [Hwang 2006a].

The CAA produced a high pH environment when in contact with water [Pando and Hwang, 2006]. This high pH environment could be used to produce an alkaline hydrolysis of

explosives [Hwang, 2005b]. For these reasons the CAA could potentially be a material that can be used for an alkaline hydrolysis of explosives.

### 3 Materials and Methods

The materials that were used on the explosives remediation experiments and the methods that were followed throughout the experiments are discussed in this section. The Method section is divided in four sections; two main remediation processes, AOP and the sorption mechanism, one for effect of pH on sorption, and a section for the analysis of the samples taken during the experiments.

#### 3.1 Materials

This section presents the materials used on the experiments. First, a description of the explosives used is presented. The AOP section describes the oxidation system and the principal materials that were used:  $\text{H}_2\text{O}_2$  and the UV lamp. The sorption section describes the principle materials used, BA and MA. Then the materials used for the assessment on the effect of pH on sorption are described. Finally, the materials used for the sample analysis are described.

##### 3.1.1 Explosive: TNT

The main explosive used on the experiments was TNT. The molecular formula of this explosive is  $\text{C}_7\text{H}_5\text{N}_3\text{O}_6$ . Its molecular weight is 227.15 g/mol and it exists in crystal form as colorless orthorhombic crystals or as yellow monoclinic needles [Yinon, 1990]. Its melting point is  $80.65^\circ\text{C}$  and the specific gravity is  $1.654 \text{ g/cm}^3$ . It is typically manufactured from the treatment of liquid toluene with nitric and sulfuric acid followed by removal of undesired isomers and residual dinitrated toluene. [Yinon, 1990]. The boiling point is  $240^\circ\text{C}$  where it explodes [ATSDR 1995]. The TNT used for this investigation was purchased from Restek, Corp, which came in TNT Standard composed of 99.9% Acetonitrile and 0.1% TNT. The



MSDS [2008] indicates that this standard solution is highly flammable and toxic, so precautions are needed when handling this material. In this form the specific gravity of the standard is 0.7857 g/cm<sup>3</sup> at 20°C. It can affect the kidneys, liver, central nervous system, and the respiratory system if absorbed by skin, through inhalation or ingestion [Restek, 2008].

### **3.1.2 Explosive: DNT**

The second explosive used for the experiments was DNT. The molecular formula of this explosive is C<sub>7</sub>H<sub>6</sub>N<sub>2</sub>O<sub>4</sub>. Its molecular weight is 182.14 g/mol. Its melting point is 71°C and the density is 1.3208 g/cm<sup>3</sup>. It is manufactured as a mixture of 2,4- and 2,6-DNT by the nitration of toluene with concentrated sulfuric and nitric acid [ATSDR, 1998]. The DNT used for this investigation was purchased from Restek, Corp, which came in DNT Standard composed of 99.9% Acetonitrile and 0.1% DNT. The MSDS [2008] indicates that this standard solution is highly flammable and toxic, so precautions are needed when handling this material. In this form the specific gravity of the standard is 0.7857 g/cm<sup>3</sup> at 20°C. It can affect the kidneys, liver, central nervous system, and the respiratory system if absorbed by skin, through inhalation or ingestion [Restek, 2008].

### **3.1.3 Advanced Oxidation Process**

The AOP process involved the use of H<sub>2</sub>O<sub>2</sub> solutions, a low pressure UV lamp, a batch reactor, a stirrer, and pipettes for taking samples. A diagram of the experimental setup is presented later in the Method section. In order to ensure that the procedures that took place were as controlled as possible, several vials of known standard concentration of the explosives were acquired. For this particular project, the explosives tested were TNT and dinitrotoluene (DNT).

The idea of using  $\text{H}_2\text{O}_2$  and UV light for the AOP is that the  $\text{H}_2\text{O}_2$  is easily transformed into one of the strongest oxidants known (i.e.  $\text{OH}^\bullet$ ), when exposed to UV light [Metcalf and Eddy, 2003].

The  $\text{OH}^\bullet$  then oxidizes the TNT and DNT to mineralization.

### **3.1.3.1 Hydrogen Peroxide**

The  $\text{H}_2\text{O}_2$  at a concentration of 30% was purchased from Fisher Scientific [2007]. This high concentration gives the opportunity of using a range of different concentrations from high (30% maximum) to the minimum desired. This chemical is also known as hydrogen dioxide and hydroperoxide.

According to the Material Safety and Data Sheet provided by the manufacturer [Fisher Scientific, 2007],  $\text{H}_2\text{O}_2$  is a strong oxidizer so that contact with other material may cause fire. It is corrosive and will cause burns to skin, eyes, and respiratory tract. It is harmful if swallowed or inhaled. Some of its physical and chemical properties are as follows: It is a clear colorless liquid at ambient temperature. It has a slight acrid odor. It is infinitely soluble in water, has a density of 1.11, and a boiling point of  $108^\circ\text{C}$ . Normally, it is stable if uncontaminated, but slowly decomposes to release oxygen. It is unstable with heat, may result in dangerous pressures. It is a strong oxidizer, reacts violently upon contact with many organic substances. It decomposes to water and oxygen with rapid heat release. The solution can decompose violently upon heating [Fisher Scientific, 2007].

### **3.1.3.2 UV Lamp**

The UV lamp that was used for the experiments was a low pressure, 3.15 Watts, mercury arc immersion lamp, with a principle wavelength of 254 nanometers (manufactured by Canrad-Hanovia). The lamp power consumption (including power supply) is 12 watts, operating on 120 volts, 60 cycles AC. The dimensions are 27 cm long and a diameter of 1.5 cm. The lamp was placed in the center of a reaction chamber with a diameter of 8 cm and 30 cm long which can hold up to 1000 mL. This gives a UV intensity of 0.0063 Watts/L (assuming each batch consisted of 500 mL of ECW). All of these materials were purchased from Ace Glass.

This configuration should give a very good UV intensity because the distance between the UV lamp and the ECW is very short (average of 3.25 cm). Based on the Beer–Lambert law, the average light intensity in the solution decreases with increasing path length of UV light and peroxide concentration [Zang and Farnood, 2005]. For this reason, the UV lamp was kept closest possible to the ECW.

### **3.1.4 Sorption**

The materials used were the CAA from the Guayama power plant, a pH probe to measure its pH, several sieves to collect specified particle sizes, an analytical weighing scale and different vial sizes to accommodate the small scale experiments. For the experiments, only the BA and the MA were used. For this reason, only the description of these two materials is made. Diagrams showing the experiment setup are shown in the method section.

#### **3.1.4.1 Bottom Ash**

Pando and Hwang [2006] used a chemical analysis carried out by SGS North America Inc. to publish that the main components of the BA are silica + alumina + ferric oxide ( $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ ), lime ( $\text{CaO}$ ), and sulfur trioxide ( $\text{SO}_3$ ), representing 47%, 36%, and 12.8% by weight, respectively [Pando and Hwang, 2006]. In the same analysis the specific gravity for the BA was determined to be 2.78 using procedures in accordance to the ASTM standards [Pando and Hwang, 2006]. Gradation results indicate that the BA has a gradation similar to a fine to medium sand [Pando and Hwang, 2006].

The BA was used as received for all of the experiments. The particle size being like sand makes it easy to handle for the experiments. It was expected that the pH of this material to be high because of the relatively high lime content. Due to this property, the main assessment on this material was the pH measurements for potential alkaline hydrolysis of explosives [Hwang et al. 2005].

#### **3.1.4.2 Manufactured Aggregate**

Based on the same chemical analysis carried out by SGS North America Inc. Pando and Hwang [2006] published that the main components of the MA are silica + alumina + ferric oxide ( $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ ), lime ( $\text{CaO}$ ), and sulfur trioxide ( $\text{SO}_3$ ), representing 51%, 30%, and 14.7% by weight, respectively. In the same analysis it was reported that the average specific gravity for the coarse fraction was found to be about 1.16, while the fine fraction had a specific gravity of about 2.69. The low specific gravity of the coarse aggregate is due to the high void content of this fraction. Manufactured aggregate has a similar gradation as natural gravel, with

particle sizes ranging from gravel to fine sand with very low percentages of silt and clay-sized particles [Pando and Hwang, 2006].

Since the particle sizes available to the experiment were in a wide range, they were smashed and sieved so that a particle size convenient for the experiment was utilized. The criteria for choosing the particle size were the manageability, packaging, and available sieves sizes. However, this will limit the different possibilities that several variables can contribute, like different MA particle size interacting with the ECW at the same time. Amuda et al. (2007) demonstrated that particle size can affect the amount of material that can be sorbed. The property of clustering together will be more favorable for increasing the pore quantity thus having a higher surface area to sorb the explosives. As CaO quantity being somewhat lower than the BA, it was expected to have a lower pH value than Bottom Ash.

### **3.1.5 Effect of pH on Sorption**

Similar to the sorption experiments, the materials used were the CAA from the Guayama power plant, a pH probe to measure its pH, several sieves to use specified particle sizes, an analytical weighing scale, a column to place the CAA and pass water through it, and pumps to move the water through the columns. Diagrams showing the experimental setup are shown in the Method section.

### **3.1.6 Analytical Instrumentation**

During the experiments, analyses of samples were performed. In order to do this several equipments were used as follows: high performance liquid chromatogram (HPLC) to measure the concentrations of the explosives in the samples, and an UV spectrometer to measure the concentration of the  $\text{H}_2\text{O}_2$  in the samples during the AOP experiments. The HPLC uses

methanol (MeOH) and deionized (DI) water. The UV spectrometer uses titanium sulfate. A detailed explanation on the analysis is provided in the Method section.

## **3.2 Methods**

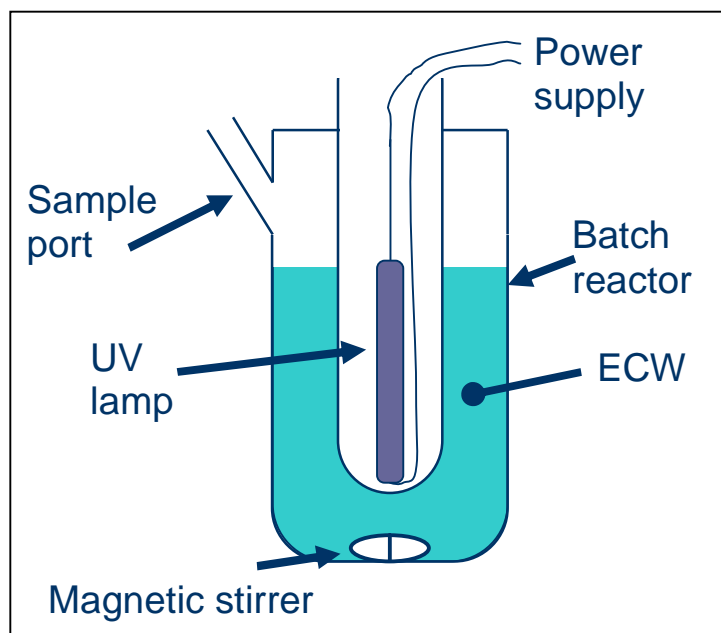
This section describes the methods that were used for the assessments of the remediation processes. It is composed of four sections which describe the methods used in the AOP, sorption, and effect of pH on sorption experiments, and the methods used for the analysis of the samples. Briefly, the AOP process had the ECW in a batch reactor with the UV lamp in the center, the  $\text{H}_2\text{O}_2$  was injected to the system and temporal samples were taken for analysis. The sorption experiments had several vials with the CAA in contact with the ECW and were stirred to enhance contact. The effect of pH on sorption experiments had the CAA inside the column and a pump providing water to flow through it.

### **3.2.1 Advanced Oxidation Process**

The reactor setup (Figure 1) was kept simple by using a batch reactor type. In this way the experiment is more controllable and fewer variables (like flow, residence time, mixture and others) need to be addressed. The reactor had a removable cap which was used as a sampling port.  $\text{H}_2\text{O}_2$  was introduced through the sampling port using a pipette and the samples were taken using a syringe.

The UV lamp was placed in the center of the reactor, so it irradiated to the whole reactor at the same time with the same intensity. The lamp was placed inside a double wall transparent glass serving two purposes: to protect the lamp from getting wet during the experiments, and to pass cooling water through the double wall so the temperature can remain constant during the experiments. First, water with the explosives was introduced in the batch reactor, and then the

lamp with the double wall protector was placed in the middle. Once the lamp was in place and connected, the  $\text{H}_2\text{O}_2$  was introduced at the same time that the magnetic stirrer was turned on. Once the  $\text{H}_2\text{O}_2$  was introduced to the system, the UV lamp was turned ON and the start time was noted.



**Figure 1. Schematic drawing of AOP system**

The time of irradiation was determined by doing a kinetic experiment so the most remediation possible can be done using the least amount of time. This was achieved by taking samples of the ECW at different time intervals (i.e. 0, 2.5, 5, 10, 15, 30, 45, 60, 90, and 120 mins) after the  $\text{H}_2\text{O}_2$  was injected and the UV lamp is turned on. In order to save energy, a sequential on/off method was also tested to see to what extent the UV irradiation is needed to remediate explosives but using less energy. The total energy consumption of the experiment was calculated by multiplying the power consumption of the UV lamp with the time intervals during which the lamp was on.

In order to see the effect of the  $\text{H}_2\text{O}_2$  concentration on the remediation of explosives, different concentrations of  $\text{H}_2\text{O}_2$  were used for the experiment at 50, 100, and 300 mg/L while

leaving a TNT concentration of 0.4 mg/L constant. Concentrations as high as 544 mg/L [Bose et al. 1998] has been used for degradation of explosives. Concentrations as low as 60 mg/L [Zang and Farnood, 2004] has been used for degradation of other chemicals. Also Hwang et al. (2004) used dosages of 10 – 300 mg/L of H<sub>2</sub>O<sub>2</sub> to treat decolorization of TNT effluents with good results. To start with a round number, 100 mg/L of H<sub>2</sub>O<sub>2</sub> was chosen. After the results of the first experiment were analyzed, the second experiment was chosen to have half of the original concentration and look for differences. After the results were analyzed a decision was made to triple the first concentration and look for differences. After those experiments were finished and analyzed, the concentration of H<sub>2</sub>O<sub>2</sub> that best made the degradation effect was used on another experiment with TNT concentration of 1.0 mg/L. Table 2 summarizes the different TNT and H<sub>2</sub>O<sub>2</sub> combinations used in this project.

**Table 2. Summary of the different TNT and H<sub>2</sub>O<sub>2</sub> combinations assessed.**

Experiment name	H <sub>2</sub> O <sub>2</sub> (mg/L)	[TNT] <sub>o</sub> (mg/L)	UV
Experiment 1	0	0.4	Constant
Experiment 2	50	0.4	Constant
Experiment 3	100	0.4	Constant
Experiment 4	300	0.4	Constant
Experiment 5	300	0.4	ON/OFF
Experiment 6	300	1.0	Constant

In order to save energy on the process of degradation another experiment was made, having the same conditions as the other experiments except for the amount of energy consumed. In this experiment setup the UV light was ON during part of the time and but was turned off at the following intervals 2.5-5, 10-15, 30-45, 60-90 minutes. With this, the intent was to start the TNT degradation process going on and then turning the UV lamp off (to save energy) for some



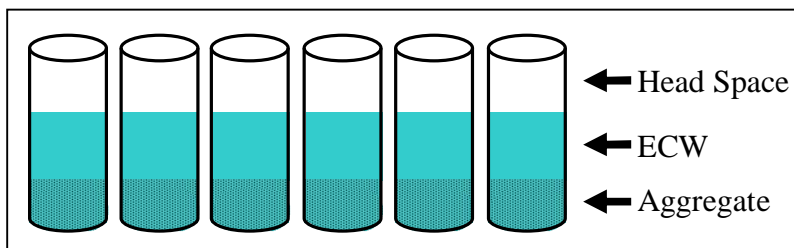
time and then turning the lamp on again to continue with the process. This was repeated for several intervals until the 120 minutes mark.

The TNT concentration was measured using the samples taken at the different time intervals with the HPLC. Also the  $\text{H}_2\text{O}_2$  concentration was measured with a portion of the samples taken using the UV spectrometer. It was expected that greater concentrations of  $\text{H}_2\text{O}_2$  would yield more effective remediation or that it would take less time to achieve the same remediation effect.

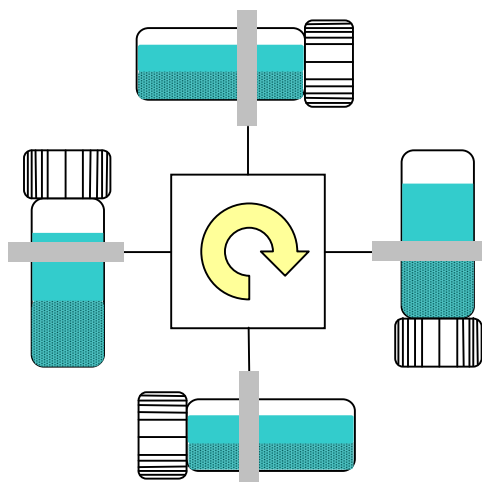
### **3.2.2 Sorption**

The reactors for this experiment were in a batch setting (Figure 2). They were agitated using a slow speed shaking device (Figure 3) in order to provide enhanced contact between the CAA and the ECW. The first experiment was a sorption kinetic study in order to assess an equilibrium time for the explosives to be sorbed to the CAA. In this experiment, the same amounts of the CAA mass (2.5 grams) were placed in several batch reactors and the same amount of volume (12 mL) and TNT concentration (1.0 mg/L) was added to them. The batches were continuously shaken for the length of the experiment. They started at the same time and each batch was “sacrificed” at a different time while the rest of the batch reactors continued with their process. This was done to represent the different contact time that can be used to achieve complete sorption of ECW to CAA. The content of each batch was filtered with an MF-Millipore Membrane (mixed cellulose esters, hydrophilic, 0.45  $\mu\text{m}$ ) filter to eliminate any particles that might interfere with the analysis. The TNT concentration was measured using the samples taken at the different time intervals with the HPLC. This gave an idea of how much time was required for the sorption to be in equilibrium. Making a plot with the experimental data

having the TNT concentration against treatment time, the sorption rate was calculated. It was done first so the rest of the experiments could follow the same sorption contact time determined from this experiment.



**Figure 2. Schematic drawing of sorption kinetic experiment**



**Figure 3. Slow speed shaking device for vials**

The sorption isotherm study was performed using a similar procedure as the kinetic study. Each batch was prepared using different amount of mass of the CAA with the same volume and concentration of ECW (see Figure 4). The initial TNT concentration was 1.0 mg/L, the volume of the ECW was 12 mL (mass of TNT is =  $1.0 \text{ mg/L} * 12 \text{ mL} * 10^{-3} \text{ L/mL} = 0.012 \text{ mg TNT}$ ), and the amount of aggregate added were in the range of 1 g to 3.5 g with 0.5 increments. The experiment was conducted at room temperature (i.e.  $23 \pm 1^\circ\text{C}$ ).

As in the kinetic study, the batches were continuously shaken for the sorption equilibrium time obtained from the previous kinetic experiment. Each batch was then filtered and a sample taken to be analyzed for concentration of explosives on the HPLC. The sorbed concentration is estimated from a mass balance analysis, in which it is assumed that the amount of mass removed from the solution (initial concentration – final concentration) is sorbed on the solid. This is given by the following equation:

$$V = \frac{(\text{initial concentration} - \text{final concentration}) * \text{Volume}}{\text{mass of aggregate}} \quad \text{Equation 2}$$

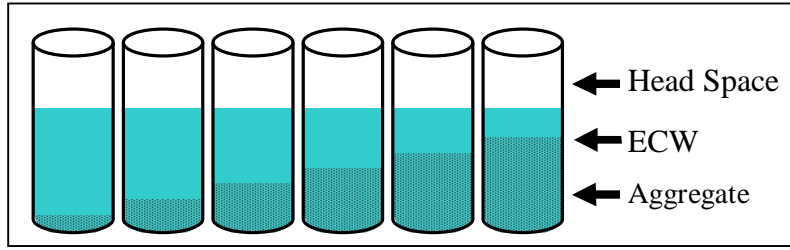


Figure 4. Schematic drawing of sorption isotherm experiment

The concentration of contaminant on the solids was plotted versus the equilibrium dissolved concentration to verify the relationship between them. This plot is called an isotherm. From the graph, the information of the maximum amount of contaminant sorbed into the aggregate can be obtained. Several models have been proposed to mathematically represent the isotherm. Among the most popular are the Langmuir and Freundlich isotherms [Chapra, 1997].

Langmuir isotherm	$v = \frac{v_m b c_d}{1 + b c_d}$	Equation 3
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Freundlich isotherm	$v = K_f c_d^{1/n}$	Equation 4
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Where:

$v$  is the concentration of the contaminant on the solids,

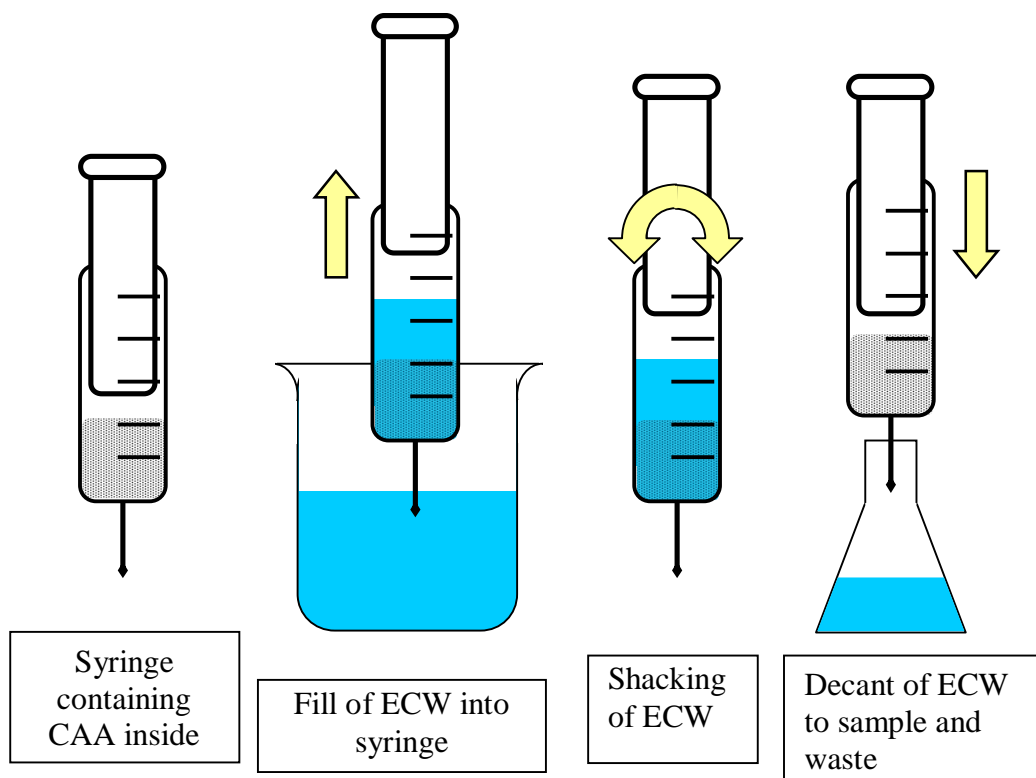
$c_d$  is the contaminant dissolved concentration,

$v_m$  is the maximum concentration on the solid, and

$b$ ,  $K_f$ , and  $n$  are coefficients used to calibrate the curves to the data

When the experiments were finished and the data was collected, the above equations were used to fit the data. The information obtained from the data of the experiments is the contaminant dissolved concentration. The mass of CAA for each data point is the other information needed; the rest of the information is obtained from the graph that will be presented in the results and discussion section. Using the axis intercepts and the slope of the curves the rest of the variables ( $v_m$ ,  $b$ ,  $K_f$ , and  $n$ ) can be obtained.

A sequential batch reactor (SBR) was developed where 12 mL of ECW at TNT concentration of 1.0 mg/L were introduced in a syringe which had 2.5 g of CAA. The SBR was closed and put to shake for an hour. After one hour, the ECW was emptied from the syringe for TNT analysis and another 12 mL of ECW were introduced to the syringe (with the same 2.5 g of CAA still there) and the system was shaken for another hour. This process was repeated for six consecutive hours totaling 72 mL of ECW in contact with the initial 2.5 g of CAA in a sequential manner. Figure 5 shows a schematic view of the process. It is important to mention that, at the moment of designing this experiment setup (i.e. 1 hour contact time), the results of the analysis of the kinetic study were not done yet due to problems with the HPLC.



**Figure 5. Sequential batch reactor schematic procedure**

Here the processed water was poured into the holding cup where the filter membrane (MF-Millipore Membrane Filter: 47 mm diameter, pore size 0.45  $\mu\text{m}$ , of mixed cellulose esters) was placed. When the vacuum pump was turned on, the suction created forces the water to pass through the filter, leaving the solid particles on the top. Under the filter was the clear water.

### **3.2.3 Desorption**

Two desorption experiments were done: desorption kinetic, and desorption isotherm. They consisted on two parts, the first was the same as the sorption kinetic and sorption isotherm, and the second was done as described below. The desorption kinetic experiment consisted of using the vials that were used for the sorption kinetic and taking all the ECW out of them and replace it with pure water. Again, the same volume was used for all the vials (12 mL) which had the same mass (2.5 grams) each. The pure water was added to the vials and started to shake at

the same time, then each one was “sacrificed” at a different time for sampling. The desorption isotherm experiment was done using the vials that were used for the sorption isotherm. Here, the ECW was completely taken out of the vials and replaced the same volume (12 mL) of pure water. All of them had a contact time of 2 hours.

#### **3.2.4 pH Profile in the Presence of CAA**

The values of pH were measured to assess if the CAA was able to produce alkaline environment which could induce an alkaline hydrolysis. The pH of the CAA's was verified using a flow-through reactor with a flow rate at 0.03 L/min for both MA and BA. In order to have a higher pH, a return flow of 0.08 L/min (meaning that the water was recirculated through the CAA ~2.6 times before exiting the system) was introduced to the system so as to enhance the contact between the ash/aggregate particles and the water. This was done because Hwang et al. (2005b) demonstrated that at high pH levels greater than 11.0 some TNT degradation can be achieved via an alkaline hydrolysis. Figure 6 shows a schematic view of the experimental setup.

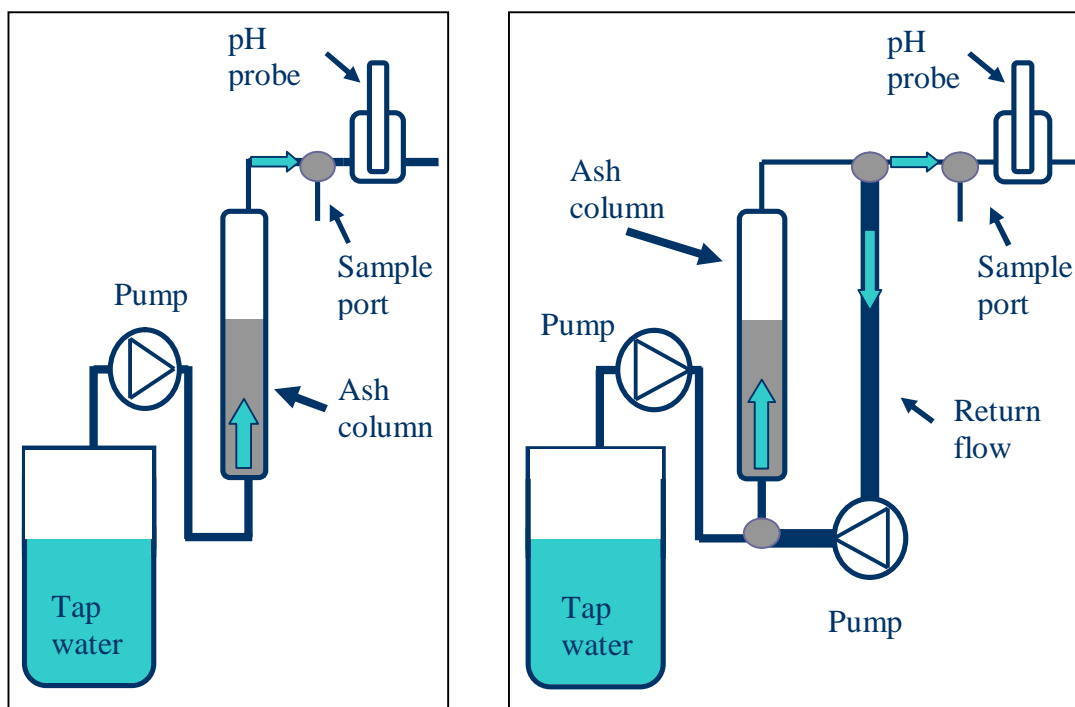


Figure 6. pH verification procedure schematic without return (left) with return flow (right)

### 3.2.5 Chemical Analysis

The equipment used to determine the concentrations of the explosives was a Perkin Elmer Series 200 HPLC. This equipment takes the sample and injects it to a moving phase where it is passed through a column that separates the different materials and then takes it through a UV detector where it is analyzed. The result that the instrument gives is a time-absorbance curve that when processed, the area under the curve can be translated to the amount or concentration of the explosive in the sample in reference to a calibration.

The mobile phase mentioned above was a mixture of methanol (MeOH) and deionized (DI) water at a ratio of 70% MeOH to 30% DI water. A Supelco® Ascentis™ C18 column (static phase, 25 cm long, 4.6 mm in diameter) had a long, non polar packaging consisting of silica beads. The method of having a hydrophobic (non-polar) packaging used in conjunction with a polar mobile phase is called Reversed Phase Chromatography [Dean, 1995]. The molecules that are high in polarity (or polar strength) will not be attracted by the packaging

material and will pass relatively fast. Molecules that have low polarity are retained for a relatively longer time in the column. In this way the different molecules in the sample are separated. The flow used for the analysis was 1 mL/min. The UV lamp in the HPLC was set to wavelength amplitude at 254 nm. The sample injection was made at 1  $\mu$ L.

All the samples of the experiment were placed in the vial auto sampler to be analyzed by the instrument and the results were interpreted from the calibration curve. A calibration curve (Figure 7) was made using different, but known, concentrations of the explosive ranging from the highest concentration possibly expected to the least concentration expected. Five steps were used ranging from 0 mg/L as in pure water, to a maximum of 2 mg/L of the explosive. Using the results of this analysis, a calibration curve was constructed where any other values obtained from the experiments were interpolated using the calibration curve. The appendix B shows the calibration curves (and raw data) used for the two different experiments (i.e. AOP and Sorption). Two calibration curves were constructed since two different vials of the stock explosives were used.

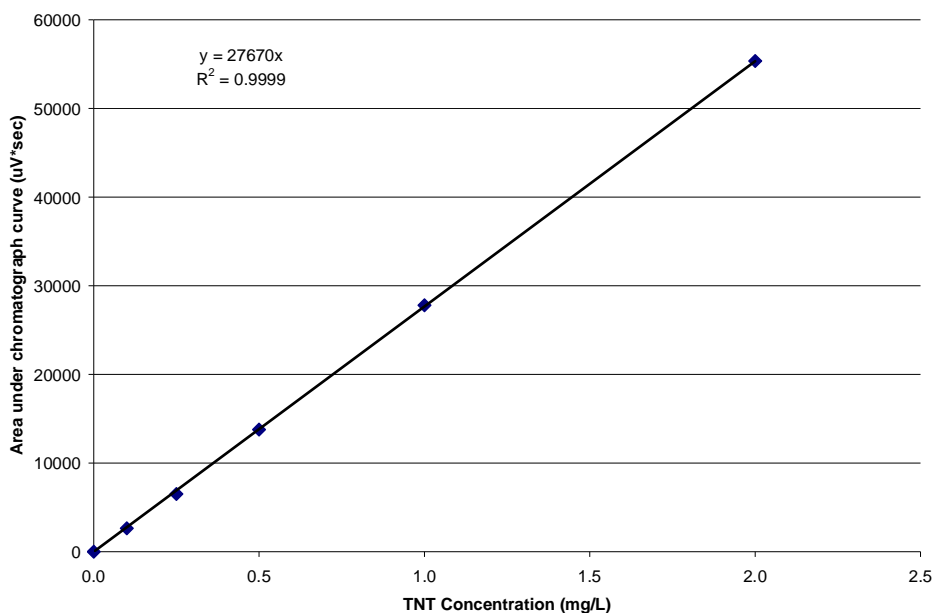


Figure 7. Calibration curve for Sorption experiments



For the AOP experiments, one of the materials used was  $\text{H}_2\text{O}_2$  and its concentration can be determined using a Perkin Elmer UV/VIS Spectrometer Lambda 20. This equipment takes a sample in a batch mode and exposes it to a visible light at 407 nm (in a closed compartment). The intensity of the incoming light to the sample and the intensity of the light that passed through the sample are measured. The two values are then compared. The difference in intensity is the light that was absorbed by the sample. As in the previous equipment a calibration curve was constructed. Since the  $\text{H}_2\text{O}_2$  is colorless, a color developing chemical needs to be used. This chemical is titanium sulfate ( $\text{TiSO}_4$ ) that develops a yellow-like color (in contact with  $\text{H}_2\text{O}_2$ ). The amount of  $\text{TiSO}_4$  used for the experiments was 100  $\mu\text{L}$  for mixed with 900  $\mu\text{L}$  of sample. The information from the instrument is the intensity of the light absorbed at 407 nm by the sample, where less intense color means less concentration of  $\text{H}_2\text{O}_2$  in the sample.

### **3.2.6 Analysis of Data**

The oxidation and sorption rate and extent was determined by using the results of the analysis made by the HPLC and UV spectrometer. For the oxidation experiments, the TNT concentration was plotted against the treatment time to determine the degradation rate (or half life). Linear and exponential lines were verified to determine the best regression curve fitting the data points. The maximum TNT degradation achieved by each  $\text{H}_2\text{O}_2$  concentration assessed was plotted against the  $\text{H}_2\text{O}_2$  concentration used.

The sorption rate was determined from plots of treatment time vs. TNT concentration. The sorption extent was determined by plotting equilibrium water vs. sorbed concentrations. The data was modeled using the two sorption isotherm models mentioned earlier and comparing them to see which model correlates better to the data points.

A statistical analysis called Student's t-test was used to analyze the data sets. This test can be used to statistically compare sample group between different experimental settings. If the means of the TNT concentration in the untreated ECW are proven to be statistically different (lower) from the means of the TNT concentration in the treated ECW, it can be said that the treatment successfully or significantly achieved the degradation of the explosives.

## 4 Results and Discussion

For the results of the experiments involving the degradation of explosives containing water, the analysis will be divided in four sections: Advanced Oxidation Process, Sorption, Desorption, and Effect of pH on Sorption.

### 4.1 Advanced Oxidation Process

Several experiments were made in order to maximize the degradation of the ECW using the minimum materials possible, thus finding the optimum arrangement of the procedure. All of the experiments followed the same procedure using the same volume of ECW (500 mL) at the same initial explosive concentration (0.4 mg/L) for the same treatment time (120 minutes total), and varying only the initial concentration of the  $\text{H}_2\text{O}_2$ . The ECW was exposed to UV radiation for the determined amount of time with the different  $\text{H}_2\text{O}_2$  concentrations. The experiments were conducted using the following combination of  $\text{H}_2\text{O}_2$  and TNT concentrations as follow:

- Control Experiment: UV Only,  $[\text{TNT}]_0 = 0.4 \text{ mg/L}$
- UV/  $\text{H}_2\text{O}_2 - 50 \text{ mg/L}$ ,  $[\text{TNT}]_0 = 0.4 \text{ mg/L}$
- UV/  $\text{H}_2\text{O}_2 - 100 \text{ mg/L}$ ,  $[\text{TNT}]_0 = 0.4 \text{ mg/L}$
- UV/  $\text{H}_2\text{O}_2 - 300 \text{ mg/L}$ ,  $[\text{TNT}]_0 = 0.4 \text{ mg/L}$
- UV/  $\text{H}_2\text{O}_2 - 300 \text{ mg/L}$  turning UV ON/OFF at some intervals,  $[\text{TNT}]_0 = 0.4 \text{ mg/L}$
- UV/  $\text{H}_2\text{O}_2 - 300 \text{ mg/L}$ ,  $[\text{TNT}]_0 = 1.0 \text{ mg/L}$

The results are presented below.

#### 4.1.1 Control Experiment: UV Only

In the plot below (Figure 8) it is shown the concentration ratio with respect to treatment time. It showed the average values and standard deviation of the data of the three experiments. For this case, the ECW was irradiated with UV light for 120 minutes in a batch reactor. Neither the exponential nor the linear regression curves fit the data points well. Also it can be seen that the data points are above and below the initial concentration (which is 0.4 mg/L) with no apparent degradation. Due to the difference in the values (above and below the initial concentration) this experiment was repeated two additional times to see if it was an error on the analysis, but it turned out that the repetitions yielded almost the same results (i.e. the data points were above and below the initial concentration). This means that the analysis of the data was correct and that the TNT did not undergo degradation.

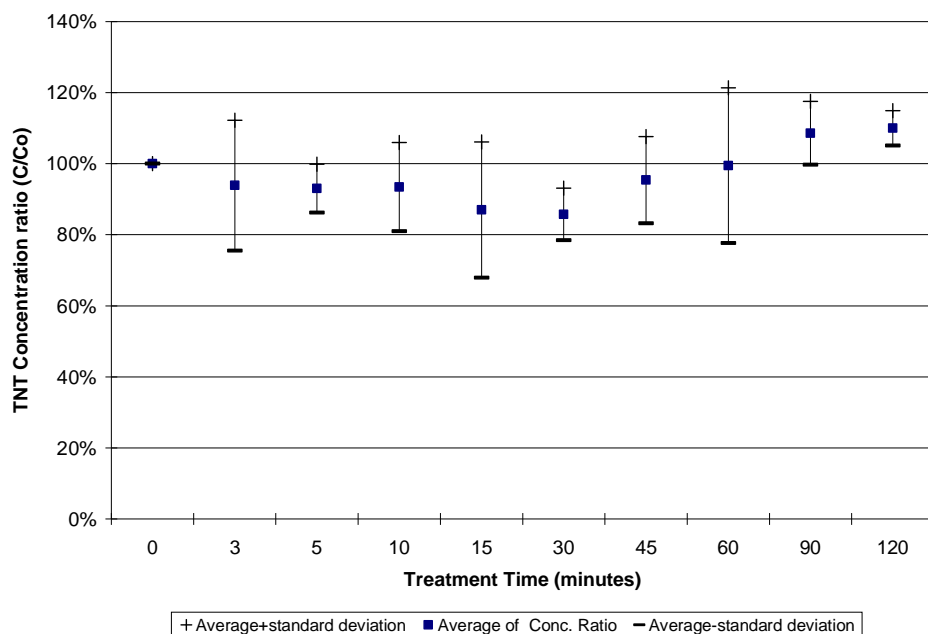


Figure 8. Control experiment plot: UV only with  $TNT_0 = 0.4 \text{ mg/L}$

#### 4.1.2 Experiment 2: UV/ H<sub>2</sub>O<sub>2</sub> – 50 mg/L

In Figure 9 the normalized concentration values of TNT and H<sub>2</sub>O<sub>2</sub> are plotted against the treatment time. TNT degradation was best fitted with the exponential regression for TNT degradation, implying a first-order reaction. At two hours of treatment the TNT concentration was about 0.2 mg/L. This means that the maximum degradation of TNT was a 43.9% reduction in two hours of treatment under the experimental conditions. Compared to the control experiment with no H<sub>2</sub>O<sub>2</sub> added, this treatment method shows a considerable better performance.

Figure 9 also shows that there was no significant degradation of H<sub>2</sub>O<sub>2</sub> during the experiment. However there was an initial degradation of H<sub>2</sub>O<sub>2</sub> at the beginning of the experiments, as shown in Figure 10, which is magnified for the first 30 minutes of the experiment. Then the H<sub>2</sub>O<sub>2</sub> concentration goes up again during the experiment. This behavior can probably be explained by the initial consumption of H<sub>2</sub>O<sub>2</sub> producing OH<sup>•</sup>.



It is not clear on how the H<sub>2</sub>O<sub>2</sub> concentration resumed to the original concentration in the later period of the treatment time. This might be attributed to a recombination of OH<sup>•</sup> to H<sub>2</sub>O<sub>2</sub> [Peralta et al., 2006, Metcalf and Eddy, 2003].



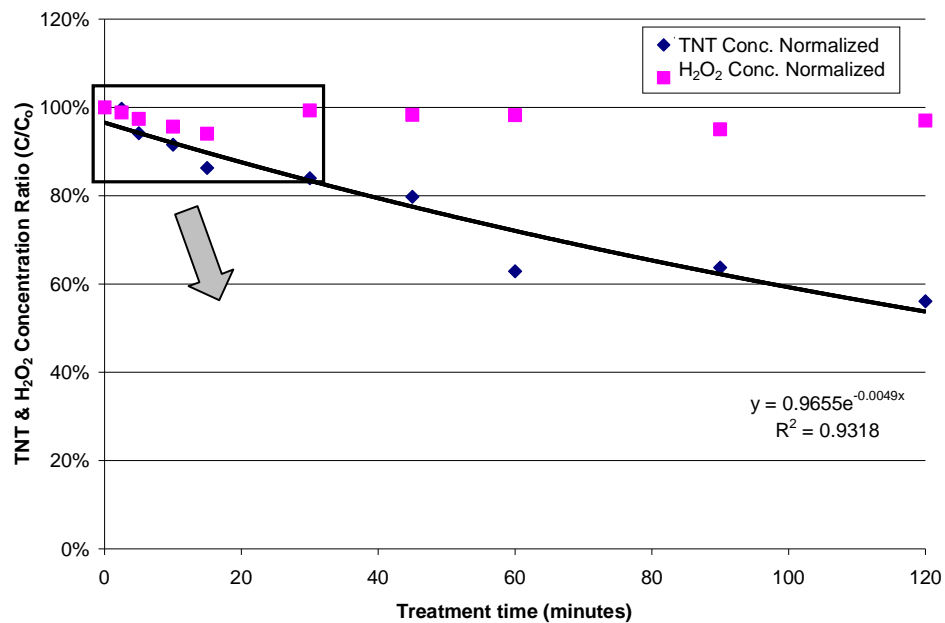


Figure 9. Experiment 2 plot: UV/H<sub>2</sub>O<sub>2</sub> = 50 mg/L & TNT<sub>0</sub> = 0.4 mg/L

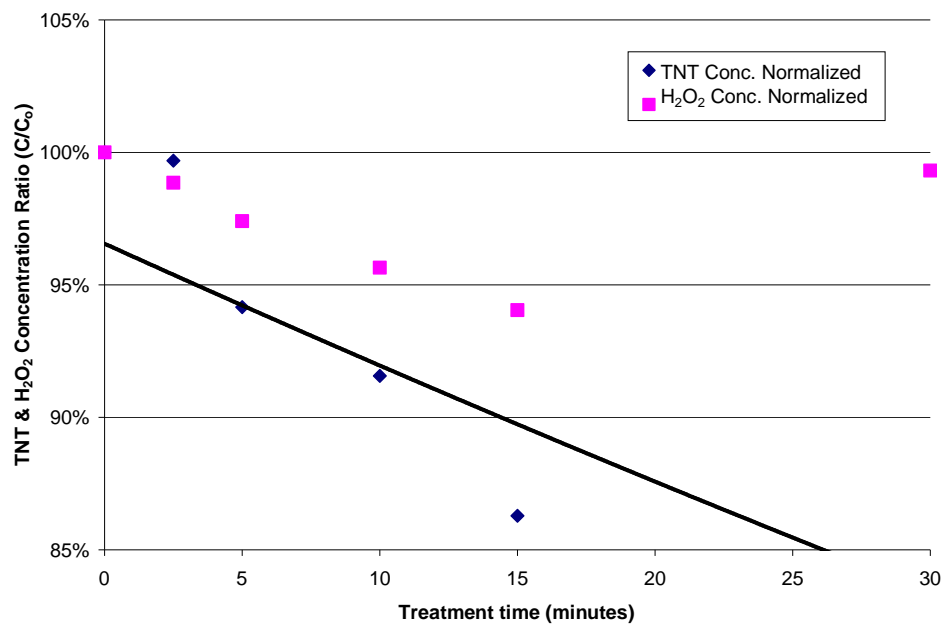


Figure 10. Zoom view of the experiment 2 plot.

### 4.1.3 Experiment 3: UV/ H<sub>2</sub>O<sub>2</sub> – 100 mg/L

The concentration at 120 minutes of treatment, as seen in Figure 11, achieved by this treatment method yielded a value (0.17 mg/L) that was slightly lower than the treatment method of 50 mg/L of H<sub>2</sub>O<sub>2</sub> and UV light for the same treatment time. This treatment achieved a degradation of 52% of the original concentration. The increase in the concentration of H<sub>2</sub>O<sub>2</sub> did not cause the same proportional degradation of ECW. Doubling the concentration of H<sub>2</sub>O<sub>2</sub> (everything else the same) caused an increase in degradation of 8.1% (when compared to the 43.9% of the previous experiment). Again, the concentration of the H<sub>2</sub>O<sub>2</sub> was not lowered during the experiment. The first two data points of the H<sub>2</sub>O<sub>2</sub> plot were lost due to equipment malfunction (momentary power shortage). That is why they are not presented in the plot.

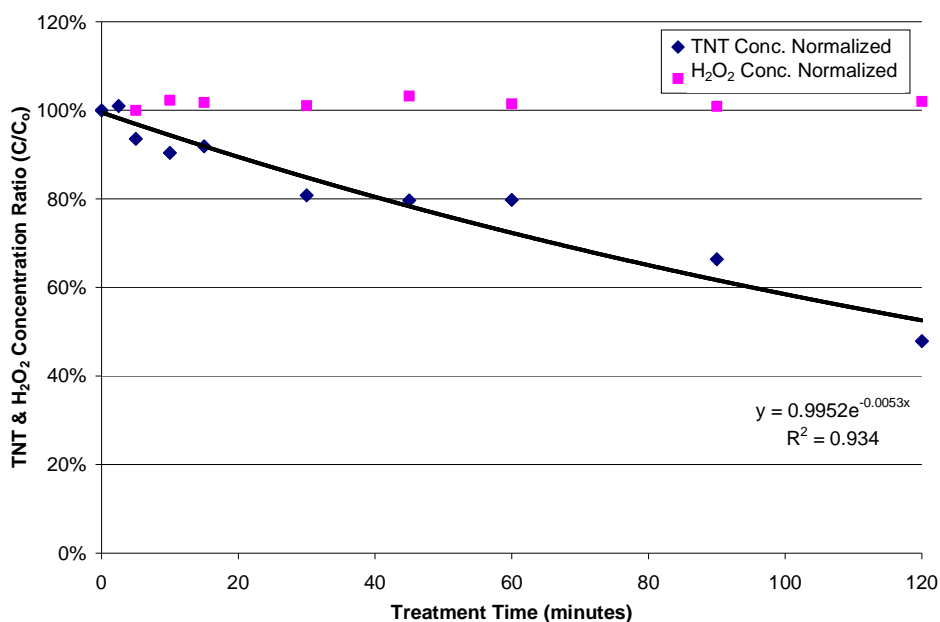


Figure 11. Experiment 3 plot: UV/H<sub>2</sub>O<sub>2</sub> = 100 mg/L & TNT<sub>0</sub> = 0.4 mg/L

#### 4.1.4 Experiment 4: UV/ H<sub>2</sub>O<sub>2</sub> – 300 mg/L

The TNT concentration for this treatment method was 0.134 mg/L at 120 minutes of treatment which is slightly lower than that of the previous experiment (100 mg/L of H<sub>2</sub>O<sub>2</sub> and UV light). The final concentration ratio after 120 minutes of treatment was 40% of the original amount, meaning that 60% was degraded. Compared to Experiment 2 (50 mg/L of H<sub>2</sub>O<sub>2</sub> and UV light) the concentration of H<sub>2</sub>O<sub>2</sub> is six times higher and it achieved a degradation of 16.1% more. This means that, although more H<sub>2</sub>O<sub>2</sub> in the system yielded more TNT degradation, the concentration of H<sub>2</sub>O<sub>2</sub> does not have a 1:1 relationship with the extent of TNT degradation. For the H<sub>2</sub>O<sub>2</sub> data points the concentration lowered the first few minutes and then remained relatively constant through the rest of the experiment.

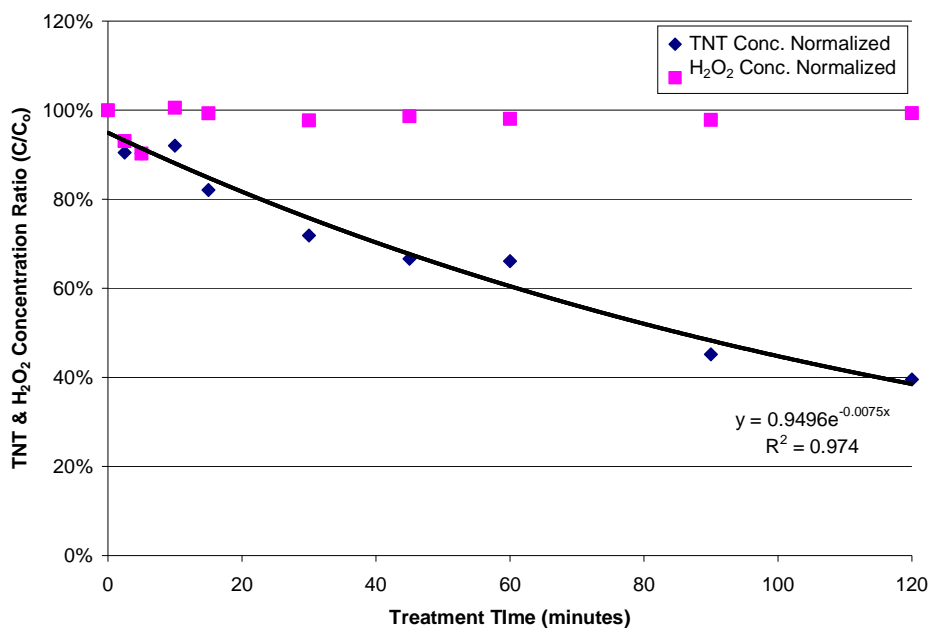


Figure 12. Experiment 4 plot: UV/H<sub>2</sub>O<sub>2</sub> = 300 mg/L & TNT<sub>0</sub> = 0.4 mg/L



#### 4.1.5 Experiment 5: UV/ H<sub>2</sub>O<sub>2</sub> – 300 mg/L turning the UV ON/OFF at Different Intervals

In order to save energy on the experiments, the UV light was turned off at some intervals as discussed in the Methods section. As it can be seen from Figure 13, the regression produced a poor fit of the TNT data ( $R^2=0.343$ ). There was “not much” TNT degradation, resembling the control experiment where there was no H<sub>2</sub>O<sub>2</sub> in the system. In this experiment the H<sub>2</sub>O<sub>2</sub> concentration lowered for the first minutes of the experiment but, as the other experiments, it returned to the original concentration.

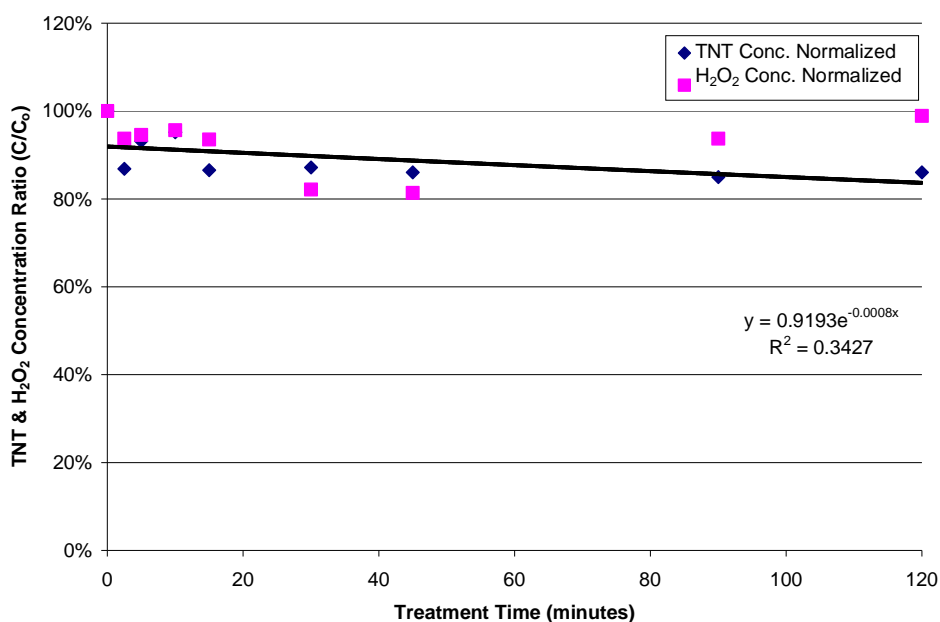


Figure 13. Experiment 5 plot: UV - on-off /H<sub>2</sub>O<sub>2</sub> = 300 mg/L & TNT<sub>0</sub> = 0.4 mg/L

#### 4.1.6 Experiment 6: UV/ H<sub>2</sub>O<sub>2</sub> – 300 mg/L; [TNT]<sub>0</sub> = 1.0 mg/L

The initial TNT concentration of the experiment was increased to 1.0 mg/L to see the effect of higher initial TNT concentration on the degradation process. As shown in Figure 14, the trend of the degradation was the same as the other degradation process (i.e. pseudo-first order) and had similar results as the H<sub>2</sub>O<sub>2</sub> of 100 mg/L when [TNT]<sub>0</sub> was 0.4 mg/L (degradation constant rate of .0053t<sup>-1</sup>). This data suggest that a higher [TNT]<sub>0</sub> requires more H<sub>2</sub>O<sub>2</sub> to achieve the same degradation level or that it takes more time to degrade the higher [TNT]<sub>0</sub> with the same H<sub>2</sub>O<sub>2</sub> concentration.

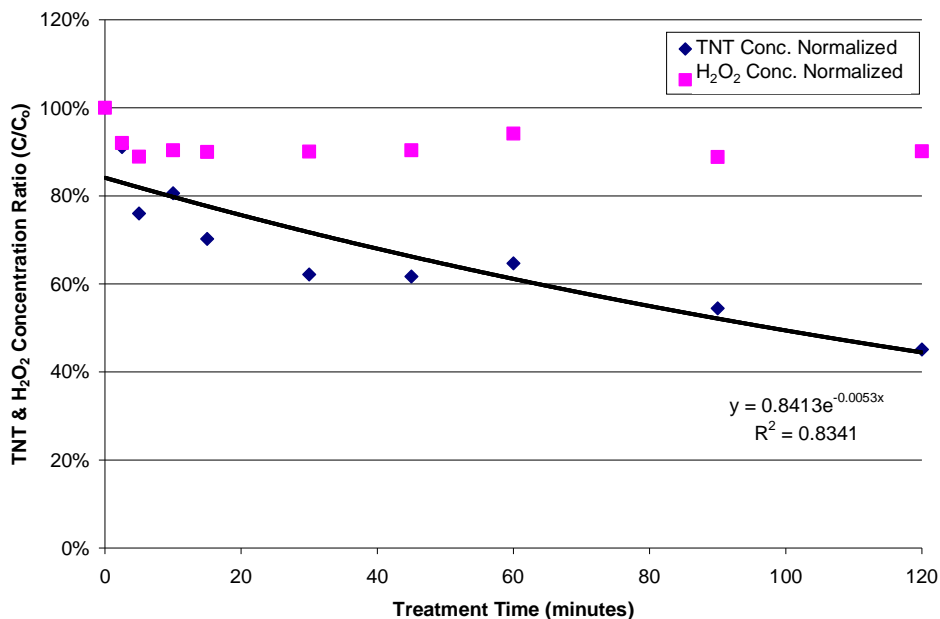


Figure 14. Experiment 6 plot: UV/H<sub>2</sub>O<sub>2</sub> = 300 mg/L & TNT<sub>0</sub> = 1.0 mg/L

#### 4.1.7 Summary of AOP Results

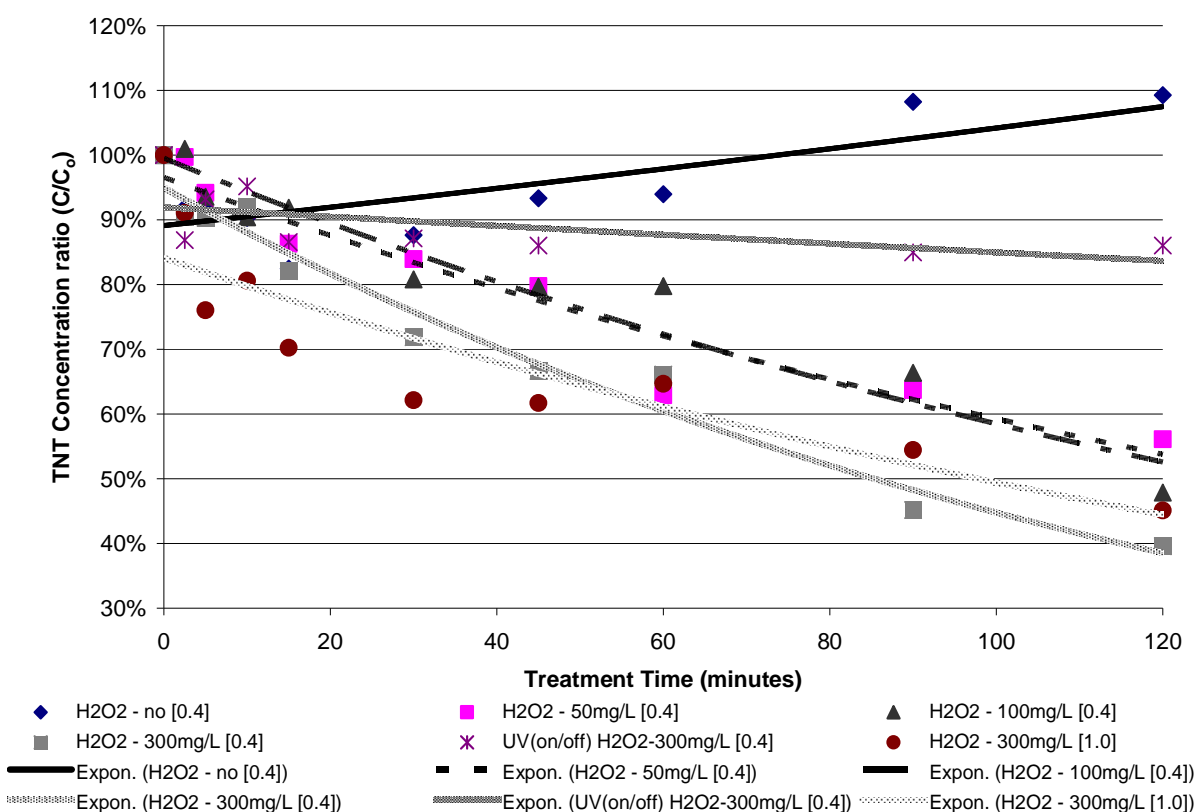
In order to visualize and compare the different TNT degradation trends, all the treatment scenarios were normalized with respect to the different initial  $\text{H}_2\text{O}_2$  and TNT concentrations (Figures 15 and 16). It can be noticed that the experiments which had UV only and UV ON/OFF had almost no degradation and the data did not fit the first order model accurately. There was no degradation at all without  $\text{H}_2\text{O}_2$  and almost no degradation in the UV ON/OFF system. The configuration which resulted in the best TNT degradation was using the 300 mg/L of  $\text{H}_2\text{O}_2$  in the presence of continuous UV light radiation. Therefore, in general it can be said that the more  $\text{H}_2\text{O}_2$  used, more degradation was achieved.

Taking into account the slopes of the regression lines of the data gathered from the different experimental setups, there is statistical difference between the control experiment (no  $\text{H}_2\text{O}_2$  in the system) and each of the other experiments. Also the slope of the curve that fits the data of the experiment with the UV ON/OFF is statistically different from all the other slopes. The experimental setup of  $\text{H}_2\text{O}_2$  concentration of 50 mg/L is not different from the experimental setups of 100 mg/L and 300 mg/L. The experimental setup of 100 mg/L is not different from the experimental setup of 300 mg/L of  $\text{H}_2\text{O}_2$  and the  $[\text{TNT}]_0$  was 0.4 mg/L and 300 mg/L of  $\text{H}_2\text{O}_2$  and the  $[\text{TNT}]_0$  was 1.0 mg/L. The experimental setup of 300 mg/L of  $\text{H}_2\text{O}_2$  and the  $[\text{TNT}]_0$  was 0.4 mg/L was not different from the 300 mg/L of  $\text{H}_2\text{O}_2$  and the  $[\text{TNT}]_0$  was 1.0 mg/L. This analysis was done taking into account the correlation between the trends of the data of all the experimental setups using a 90% of confidence. Below, a table is shown summarizing this information.

**Table 3. Statistical comparison between the data trends of the different experiments using a 90% confidence level.**

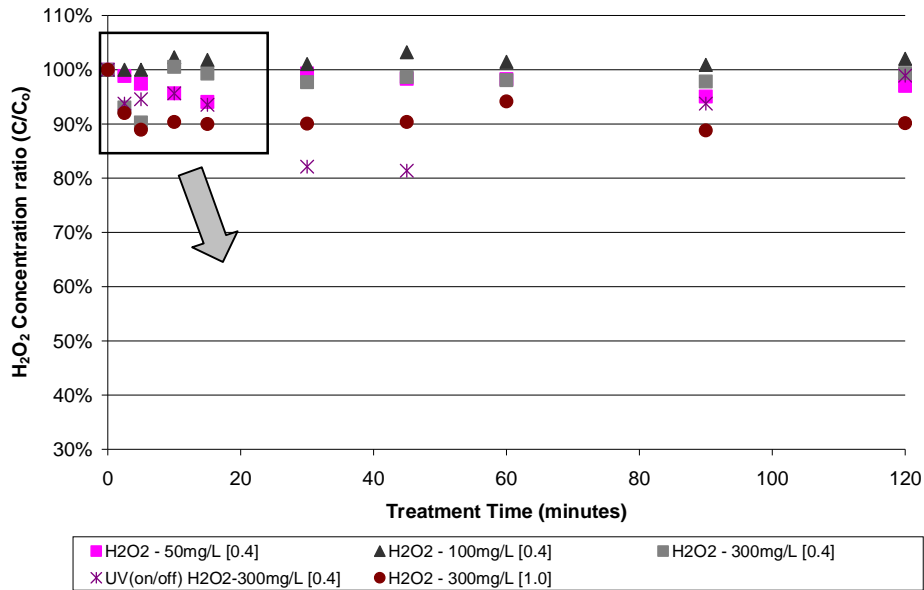
[H <sub>2</sub> O <sub>2</sub> ]	Control	50 mg/L	100 mg/L	300 mg/L	300 mg/L on/off
Control	--	--	--	--	--
50 mg/L	different	--	--	--	--
100 mg/L	different	not different	--	--	--
300 mg/L	different	not different	not different	--	--
300 mg/L on/off	different	different	different	different	--
300 mg/L TNT1.0	different	different	not different	not different	different

Figure 15 has the normalized concentration of TNT for all the experiments assessed with different H<sub>2</sub>O<sub>2</sub> concentrations, starting with no H<sub>2</sub>O<sub>2</sub> addition to the system (i.e. H<sub>2</sub>O<sub>2</sub> – no) to the maximum 300 mg/L. The values in the bracket are the TNT initial concentrations for each experiment.



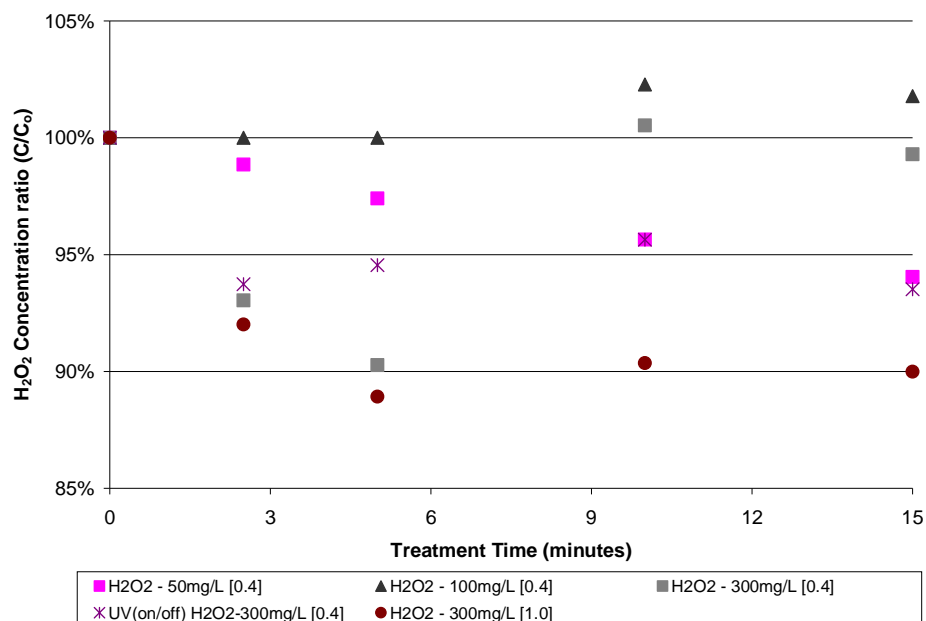
**Figure 15. Normalized TNT degradation plot for all of the experiments.**

Figure 16 shows the analysis results of the  $\text{H}_2\text{O}_2$  concentration. The  $\text{H}_2\text{O}_2$  concentration was also normalized using the concentration ratio ( $C/C_0$ ) against the treatment time. It can be seen that the concentration did not decrease during the entire experiment. It can be noticed that, at the beginning of the experiment, there was some degradation but then the  $\text{H}_2\text{O}_2$  concentration bounced back to almost 100% for all of the experiment setups (except for the 100 mg/L).



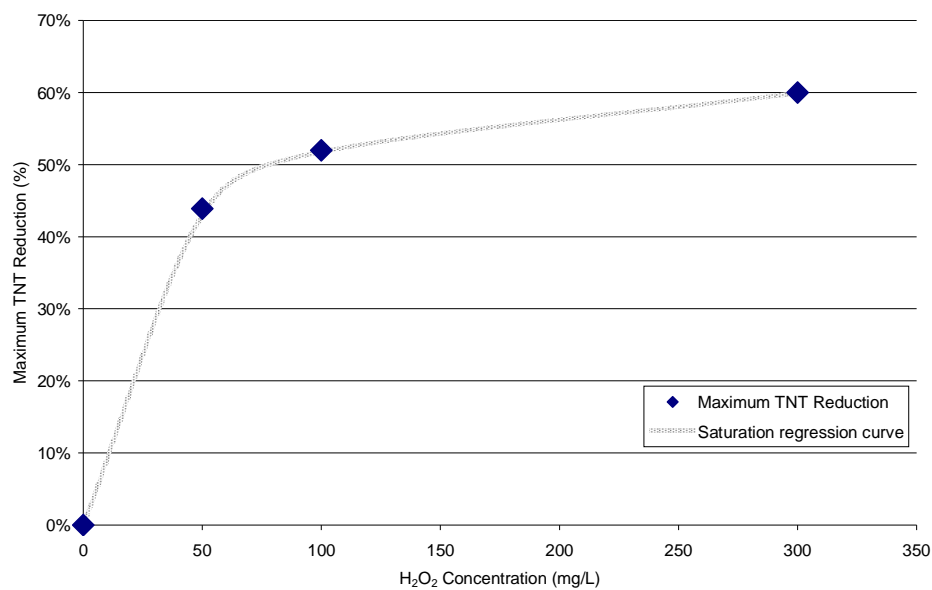
**Figure 16.  $\text{H}_2\text{O}_2$  degradation plot for all of the experiments**

The first 15 minutes of the  $\text{H}_2\text{O}_2$  concentration ratio trend was zoomed and shown in Figure 17. It can be seen that all (except for the 100 mg/L) of the data points had a tendency to reduce in the first few minutes of the experiment. The first two data points are not shown in the plot since they were lost due to a momentary power shortage. Most of the experiments made an almost full recovery of the  $\text{H}_2\text{O}_2$  concentration during the experiments.



**Figure 17. Zoom view of the  $H_2O_2$  degradation plot for all of the experiments**

The values of maximum reduction in TNT concentration was compiled and shown in Figure 18. This was calculated subtracting the concentration ratio at the 120 minutes of treatment from the initial concentration ratio for each experiment. It can be easily seen that the maximum reduction in concentration was not proportional to the increase in the  $H_2O_2$  concentration. This plot suggests that as the concentration of  $H_2O_2$  increased, the maximum reduction in TNT concentration also increased. But, the maximum reduction reached a plateau despite the increased  $H_2O_2$  concentration. This curve resembles a typical saturation curve.



**Figure 18. Maximum TNT degradation vs. H<sub>2</sub>O<sub>2</sub> concentration**

In order to be able to analyze and predict the behavior of next experiments or actual application of this treatment, a saturation curve model was used to fit the data points.

Table 4 shows the summarized results of the TNT degradation constants calculated from the regression curves. The target initial TNT concentration in the water was 0.4 mg/L, except for the Experiment 6 where the theoretical initial concentration was 1.0 mg/L.

**Table 4. Summary of degradation constant for all the experiments**

Experiment Name	UV	[H <sub>2</sub> O <sub>2</sub> ] mg/L	TNT Degradation Constant (min <sup>-1</sup> )	Calculated Initial TNT Concentration (mg/L)	R <sup>2</sup>
Control	Const.	0	0.0016	0.3808	0.521
50 mg/L	Const.	50	-0.0049	0.3312	0.932
100 mg/L	Const.	100	-0.0053	0.3477	0.934
300 mg/L	Const.	300	-0.0075	0.3210	0.974
300 mg/L on/off	ON/OFF	300	-0.0008	0.3102	0.343
300 mg/L TNT1.0	Const.	300	-0.0053	0.8413	0.834

Using the  $R^2$  as a reference it can be said that the data from the Control experiment and the UV ON/OFF experiment does not properly fit the first order models. The linear model is not a good fit for the experimental data for the two experiments mentioned above. In general they both produce little TNT degradation. From the other experiments, it can be said that there is a maximum amount of concentration of  $H_2O_2$  that causes the best degradation possible. Adding more  $H_2O_2$ , thus increasing the concentration to the system, will not cause a substantial increase in degradation from a point on. So in order to maximize the resources available the concentration of  $H_2O_2$  shall not be in excess of the maximum calculated, otherwise the  $H_2O_2$  will be wasted. The saturation curve model used to fit the data points can be seen below in Equation 7. Using this equation to fit the data points, it was found that the maximum degradation that can be achieved by the  $H_2O_2$ /UV system is 65%.

$$\begin{aligned} -TNTreduction &= \frac{k_{\max} * [C]_{H_2O_2}}{k_s + [C]_{H_2O_2}} \\ -TNTreduction &= \frac{65 * [C]_{H_2O_2}}{25.5 + [C]_{H_2O_2}} \end{aligned}$$

**Equation 7.**

where,

$k_{\max}$  = Maximum achievable TNT reduction (%),

$k_s$  = Half-saturation [ $H_2O_2$ ] (mg/L), and

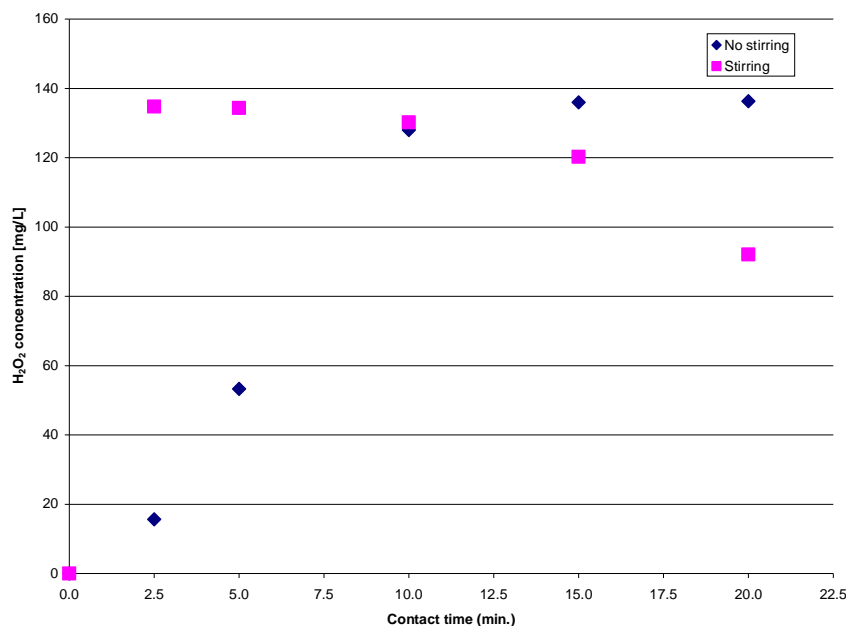
$[C]_{H_2O_2}$  = Concentration of  $H_2O_2$

The  $H_2O_2$  concentration of 300 mg/L yielded 60% degradation and the maximum achievable TNT reduction was projected to be 65%. In general, it can be said that the more  $H_2O_2$  used, the more degradation will be achieved. However, the addition of  $H_2O_2$  in the system beyond the 300 mg/L will increase TNT degradation only by 5% in accordance to the model shown above.



The apparent degradation of  $\text{H}_2\text{O}_2$  during the first few minutes of all of the experiments can be explained by two different ways. The first is that due to diffusive effects, the  $\text{H}_2\text{O}_2$  was not completely mixed at the time and location where the samples were taken, but as the time elapsed, the batch actually reached a complete mixing. Since the samples were taken at the same location but different times, the batch was probably not completely mixed and different concentrations of  $\text{H}_2\text{O}_2$  existed at different locations at the same time in the batch until it was completely mixed. The other explanation is that the UV light produced  $\text{OH}^\bullet$  at a very rapid rate, thus lowering the concentration of  $\text{H}_2\text{O}_2$  at the beginning and then the  $\text{OH}^\bullet$  recombined themselves to form  $\text{H}_2\text{O}_2$  again [Peralta et al., 2006; Metcalf and Eddy, 2003].

To demonstrate which phenomenon most likely explains the situation, a simple experiment was made. A flask was filled up with 500 mL of water and the  $\text{H}_2\text{O}_2$  was injected as in the other experiments. The samples were taken at the same intervals as in the other AOP experiments. The special characteristic of this procedure is that there was no mixing or agitation during the experiment. The  $\text{H}_2\text{O}_2$  was injected from the top of the batch and the samples were taken from the bottom as in the previous experiments. For this setup it took about ten minutes to the  $\text{H}_2\text{O}_2$  to reach maximum steady concentration level. The second flask had the same design of experiment except that there was a magnetic stirrer on the inside of the batch just like in all previous AOP experiments. For this design the  $\text{H}_2\text{O}_2$  reached a maximum concentration on the first sample taken (i.e. 2.5 minutes).



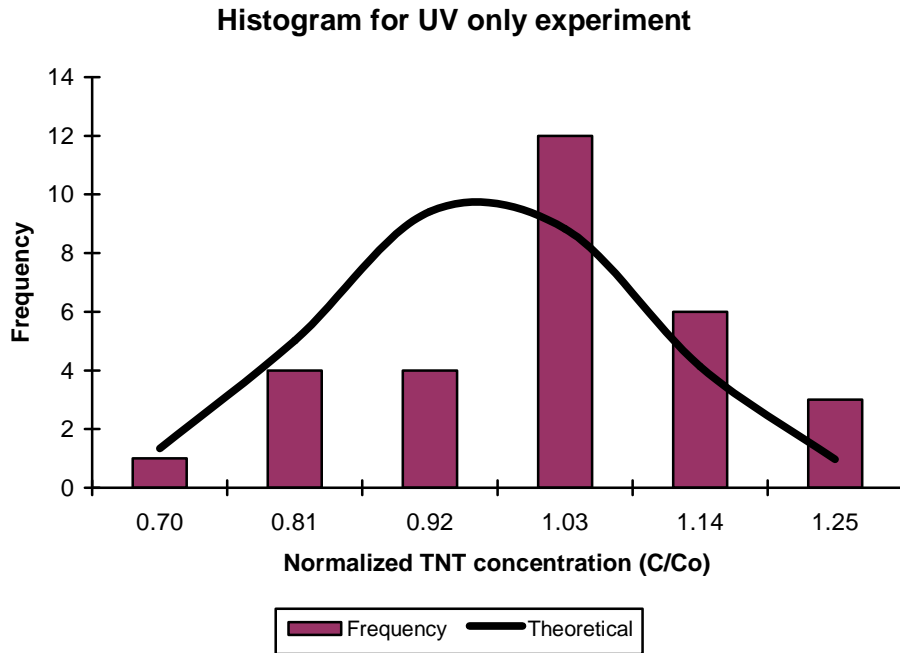
**Figure 19. H<sub>2</sub>O<sub>2</sub> concentration versus time for diffusion verification.**

This means that if the diffusion of H<sub>2</sub>O<sub>2</sub> was not a limiting factor on the experiments, then the apparent initial reduction in H<sub>2</sub>O<sub>2</sub> concentration was most probable due to the rapid conversion of H<sub>2</sub>O<sub>2</sub> to OH<sup>•</sup> to start degrading TNT. Then the recovery of the H<sub>2</sub>O<sub>2</sub> through the rest of the experiment must be the reversible reaction taking place forming H<sub>2</sub>O<sub>2</sub> out of OH<sup>•</sup> and water with the UV radiation. This behavior can also explain the phenomenon that there was a faster TNT degradation in the beginning of the experiment and there was a slower TNT degradation as the time went by. When the H<sub>2</sub>O<sub>2</sub> was injected to the batch (containing the TNT water at specified concentration) in 30% concentration (300,000 ppm), there was a large localized generation of OH<sup>•</sup> because of the UV radiation. The OH<sup>•</sup> in turn reacted with the TNT, degrading it. As the time went by and the localized concentration of H<sub>2</sub>O<sub>2</sub> was lower (completely mixed batch of 50 – 300 mg/L), the generation of OH<sup>•</sup> had a slower rate thus less TNT degradation per time.

#### 4.1.8 Statistical Analysis for AOP

For the analysis of the results of the data produced by the AOP experiments, the Student's t-test was used. The data were analyzed to verify if the mean were statistically different. The samples were compared against the Control experiment (no-H<sub>2</sub>O<sub>2</sub>) with all the other settings and each setting compared to each other. Since the TNT degradation follows a pseudo-first order behavior, the first few data points are essentially the same ( $C/C_0 \approx 100\%$ ). For the first minutes of all experiments, the concentration ratio reduced to different values depending on the treatment used. In the last minutes of each experiment, the concentration ratio of all the experiments (except the Control experiment) reached the lowest points of each experiment. In order to actually compare the effect of the H<sub>2</sub>O<sub>2</sub> concentration on TNT degradation, the t-test was applied to the last half of the experiment's data points.

Since the t-test assumes normal distribution [Mendenhall and Sincich, 1988; Meyer, 1975] the experimental data points need to be compared to a normal distribution to see if they follow the same trend. To verify if the experimental data follows a normal distribution indeed, one of the experiments was repeated 3 times in order to get enough data points to make a normality test. The experiment that was repeated was the Control experiment. Figure 20 shows the histogram with the data of the 3 experiments (n=30). Also the Shapiro-Wilks normality test was used in order to determine if the experimental data repetitions follow a normal trend. The result of the test is shown in Table 5. The test result of  $p=0.5934$  ( $p>0.05$ ) means that the normality distribution of the data can be accepted.



**Figure 20. Histogram for the Control experiment (n=30).**

**Table 5. Results of the normality test.**

Shapiro-Wilks (modified) - Normal test					
Variable	n	Median	St. Dev.	W*	p(one tail)
Control Experiment	30	0.97	0.13	0.96	0.5934

Table 6 shows the t-test results at a confidence level of 95% ( $\alpha = 0.05$ ). In the table, the first column and the first line presents the different experiment arrangements. In the other cells, the results of the t-test intersection of the different experiment arrangements are shown (i.e. the comparison between the experiments). Table 2 in the Methods section summarizes the different setup of the experiments.

**Table 6. Student's t-test result summary**

Experiment name	Control	50 mg/L	100 mg/L	300 mg/L	300 mg/L on/off
Control	--	--	--	--	--
50 mg/L	different	--	--	--	--
100 mg/L	different	not different	--	--	--
300 mg/L	different	not different	not different	--	--
300 mg/L on/off	different	different	not different	different	--
300 mg/L [TNT]1.0	different	not different	not different	not different	different

One of the most important pieces of information that the table gives is that the experiments that had H<sub>2</sub>O<sub>2</sub> in the system resulted in a statistical difference from the control experiment which did not have H<sub>2</sub>O<sub>2</sub> in the system. See Appendix C for the p values used for these conclusions. The t-test shows that the result from 50 mg/L of H<sub>2</sub>O<sub>2</sub> system was not statistically different from that from the 100 mg/L of H<sub>2</sub>O<sub>2</sub> system, the 300mg/L of H<sub>2</sub>O<sub>2</sub> system neither from the system which had TNT concentration of 1.0 mg/L. It was statistically different from the system where the UV light was turned off at some intervals. Also it shows that there was no statistical difference between the 100 mg/L and: 300 mg/L, 300 mg/L on/off or 300 mg/L of H<sub>2</sub>O<sub>2</sub> with TNT concentration of 1.0 mg/L systems.

This analysis shows that adding H<sub>2</sub>O<sub>2</sub> to the system (with the presence of UV radiation) lowered the concentration of TNT. Using the absolute value of TNT degradation of each treatment, it can be seen that higher concentration of H<sub>2</sub>O<sub>2</sub> produced more TNT degradation. With the t-test it was demonstrated that TNT degradation was achieved when it was exposed to H<sub>2</sub>O<sub>2</sub> in the presence of UV environment and not with UV radiation only. Also it is shown that there was no statistical difference between adding concentrations of 50, 100, or 300 mg/L of H<sub>2</sub>O<sub>2</sub> in the system as long as the UV radiation was constant. Statistically, the lowest concentration needed to achieve TNT reduction in concentration was with only 50 mg/L of H<sub>2</sub>O<sub>2</sub> with constant UV radiation.

#### 4.1.9 Energy Requirements

The electrical energy required for oxidation can be expressed in EE/O units, defined as the electrical energy input per unit volume per log order of reduction [Metcalf and Eddy, 2003]. The values are presented in the Table 7. All the experiments had the same EE<sub>i</sub> value (0.024 kWh) except for the Experiment 5, where the UV light was turned off at several intervals to save energy (0.0135 kWh).

$$EE/O = \frac{EE_i}{V[\log(C_i/C_f)]} \quad \text{Equation 8.}$$

Where:

EE/O is the electrical energy input per log reduction in kWh/m<sup>3</sup>•log order of reduction,

EE is electrical energy input in kWh,

V is the volume of the solution treated in m<sup>3</sup>,

C<sub>i</sub> is the initial concentration of the explosive in the solution in mg/L, and

C<sub>f</sub> is the final concentration of the explosive in the solution in mg/L.

**Table 7. Electrical energy consumption required for oxidation**

Experiment name	H <sub>2</sub> O <sub>2</sub> (mg/L)	[TNT] <sub>o</sub> (mg/L)	UV	C <sub>i</sub> mg/L	C <sub>f</sub> mg/L	log(C <sub>i</sub> /C <sub>f</sub> )	EE/O (kWh/m <sup>3</sup> •log)
Control	0	0.4	Constant	0.415	0.454	--	--
50 mg/L	50	0.4	Constant	0.343	0.192	0.251	191.12
100 mg/L	100	0.4	Constant	0.349	0.167	0.320	150.04
300 mg/L	300	0.4	Constant	0.338	0.134	0.403	119.15
300 mg/L on/off	300	0.4	ON/OFF	0.337	0.290	0.065	413.44
300 mg/L [TNT]1.0	300	1.0	Constant	1.161	0.524	0.346	138.80

$$EE_{\text{constant}} = 12\text{W} * 2\text{hr} = 0.024\text{kWh}$$

$$EE_{\text{ON/OFF}} = 12\text{W} * ((2.5+5+15+15+30\text{min})/60) \text{ hr} = 0.0135 \text{ kWh}$$

$$V = 500 \text{ mL} = 0.0005\text{m}^3$$

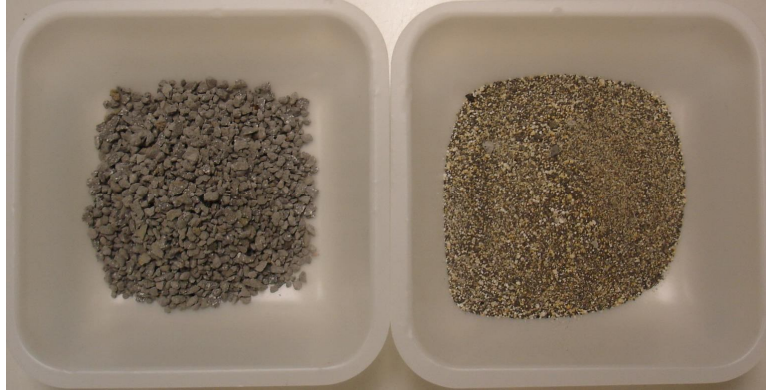
When comparing the energy consumption of all the experiments it can be seen that it required less energy when the  $\text{H}_2\text{O}_2$  concentration was increased. Ignoring the result of the Control experiment where the final concentration ended being more than the initial (i.e. no degradation at all), it can be seen that when more  $\text{H}_2\text{O}_2$  was added to the system (50, 100, and 300 mg/L), less electrical energy was required to make one log order of TNT reduction. In the experiment where the UV light was turned off at several intervals in order to save energy, it resulted in more energy consumption (per log of [TNT] degradation) because there was little TNT degradation in the experiment.

## **4.2 Sorption**

For this remediation process, several different experiments were made in order to assess the sorption capacity of the CAA for the explosives containing water. These experiments were:

- Effect of pH on sorption
- Sorption Kinetics
- Sequential Batch Reactor
- Sorption Isotherm
- Desorption

In order to have experiments as controlled as possible, the MA particles were sieved and one particle size was used. The particle size used was the ones that passed the mesh of the sieve size number 10 (opening size of 0.0787”) and that remained on the mesh of the sieve size number 18 (opening size of 0.0394”). This corresponds to a particle size of 0.0557 inches. The BA was used as was received. Figure 21 shows the final products of the MA used for the sorption experiment and the BA for the effect of pH on sorption experiment.



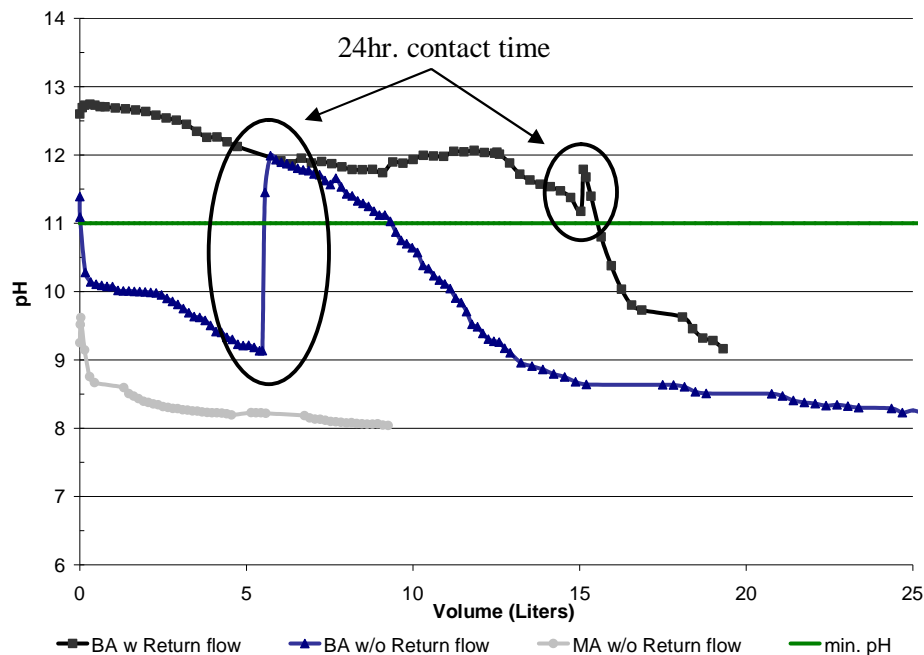
**Figure 21. Picture of the Manufactured Aggregate (MA) (left) and the Bottom Ash (BA) (right).**

#### **4.2.1 Effect of pH on Sorption**

This section explains the results of the experiments made in order to test if the environmental conditions in the presence of the CAA in solution with water produced a pH value high enough for alkaline hydrolysis to be produced. Hwang et al. [2006a] demonstrated that TNT water can be remediated using alkaline hydrolysis as the main driver. Although no direct measurements of alkaline hydrolysis were taken, the environmental condition produced by the CAA was measured using the parameter of pH level in this experiment.

Figure 22 shows the values of pH measured in the system against the volume of water flushed and it appears that the values of pH were not developed high enough to exert an alkaline hydrolysis in the current experimental settings. The decreasing trend of pH values was attributed to continuous dilution of the influent water that had a pH of ~7.0. The two “jumps” seen in the graph were due to an arbitral contact time of water to the CAA in the system which was left without a flow overnight and run next morning.





**Figure 22. Coal Ash dilution.**

Since the pH of the MA was far lower than 11.0 it was not tested with a return flow. The average pH was  $8.34 \pm 0.33$  throughout the entire experiment so that the experiment was discontinued with 9.25 liters of water. The average pH of the BA throughout the entire experiment was  $9.88 \pm 1.13$  without a return flow and was increased to  $11.72 \pm 0.94$  with a return flow. The flow rate going into the system was 0.03 L/min and the return flow was 0.08 L/min. The ratio of the return flow to the inflow rate was 2.67 so the water passed through the ash column several times before exiting the system thus enhancing the contact.

#### 4.2.2 Sorption Kinetics

Figure 23 shows the data points from the kinetic experiment. It can be seen that the treatment time of two hours was enough for the CAA to almost completely sorb all the TNT from the ECW. The initial concentration of this ECW is 1.0mg/L and after two hours of contact time, the concentration was decreased to 0.02mg/L. At 60 minutes of treatment time the TNT went down to 0.07mg/L so it took 1 hour to sorb the first ~90% and 1 more hour to sorb the ~10% remaining. The data show a pseudo-first order sorption behavior with an  $R^2=0.9009$ . The two data points that appear at the top were from the blank sample. The blank system did not contain any aggregate, but only TNT and water. It can be seen that there was almost no TNT reduction in the blank system during the two-hour experiment.

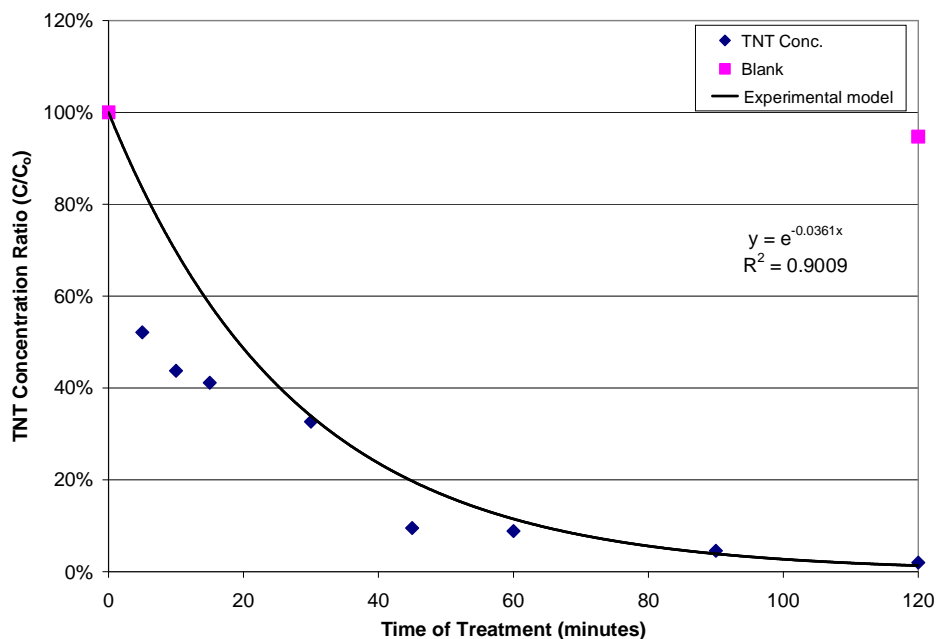


Figure 23. Sorption kinetic plot

### 4.2.3 Sorption Isotherm

A sorption isotherm study where different mass of CAA were added to same volumes of ECW was conducted to see how much CAA was needed to treat a known amount of explosive. As shown in Figure 24, it can be noted that 1.5 grams of CAA were needed to completely sorb 1.0 mg/L of TNT in 12 mL solution (preliminary CAA sorption capacity =  $0.012 \text{ mg TNT} / 1.5 \text{ g CAA} = 0.008 \text{ mg TNT/g CAA}$ ). Using this preliminary result, another experiment was done, but this time the maximum mass of aggregate was set to 1.6 g and an increase of 0.2 g was used to increase resolution (Figure 25).

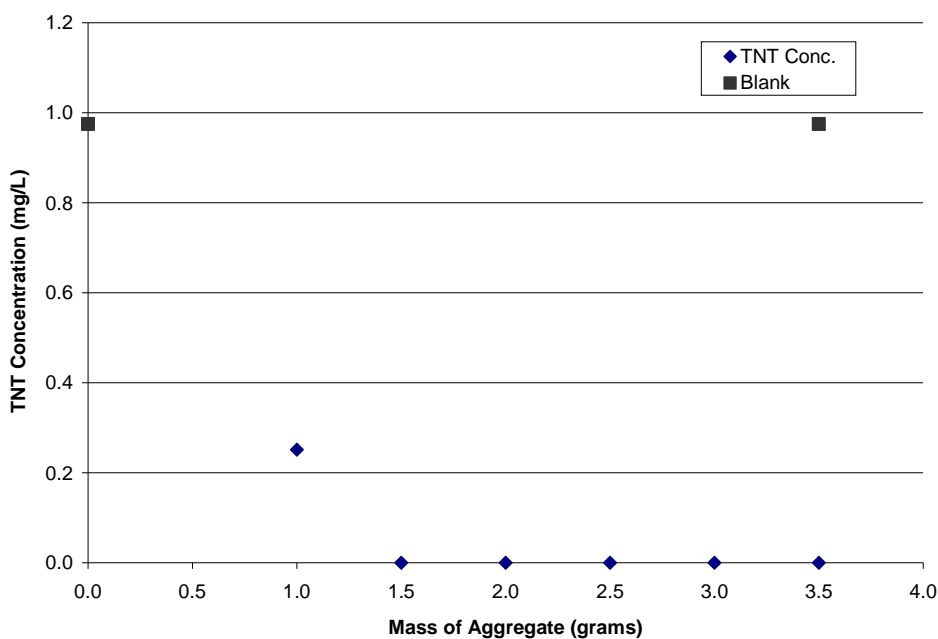
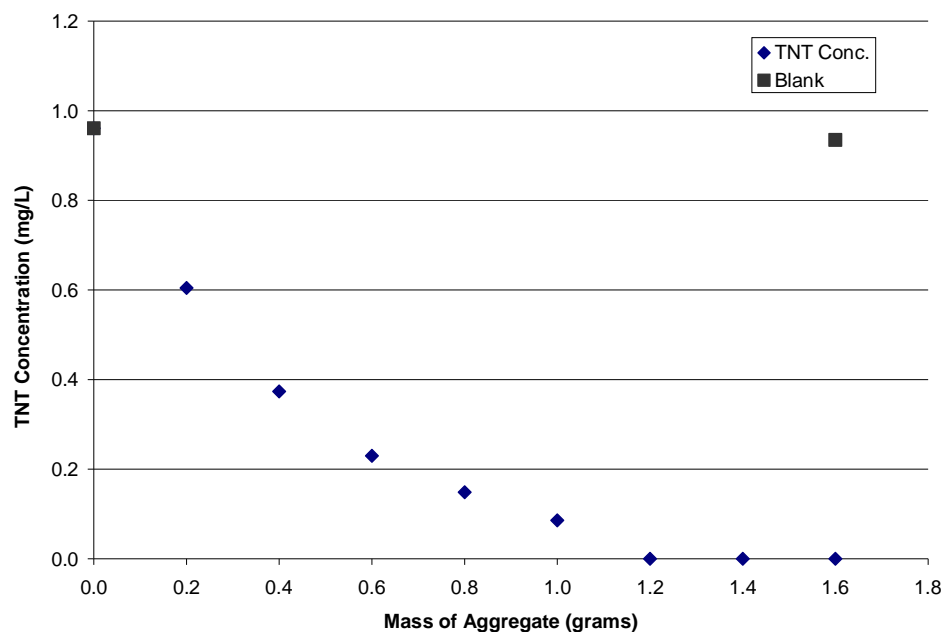


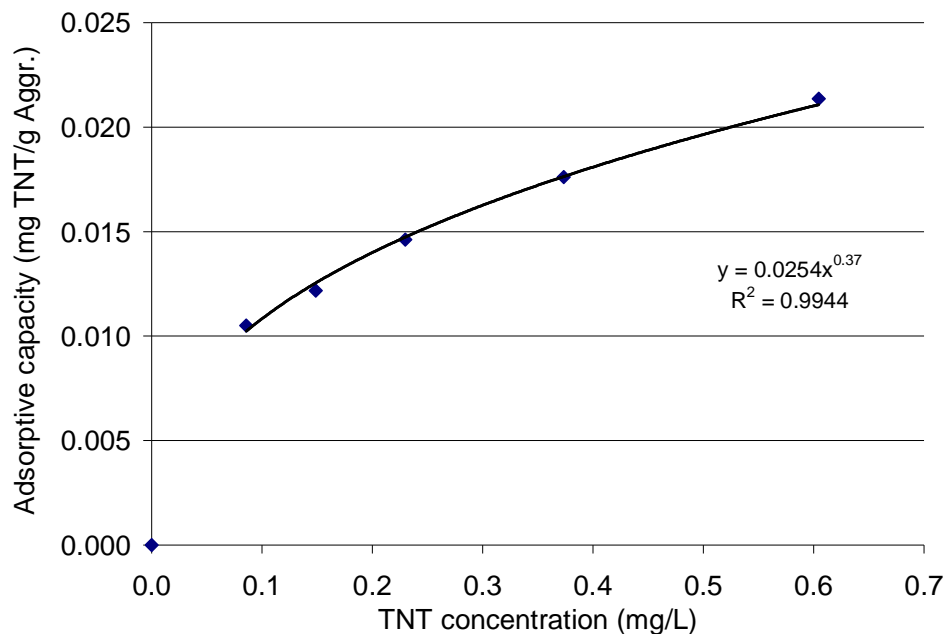
Figure 24. TNT sorption using CAA;  $[\text{TNT}]_0 = 1.0 \text{ mg/L}$

The maximum amount of CAA needed to sorb all of the TNT in 12 mL of ECW at 1.0 mg/L (i.e. 0.012 mg of TNT) was actually less than 1.5 g, in this case about 1.2 g (second preliminary CAA sorption capacity =  $0.012 \text{ mg TNT} / 1.2 \text{ g CAA} = 0.010 \text{ mg TNT/g CAA}$ ). This gives us an idea of how much aggregate is needed to sorb a known mass of TNT in ECW.



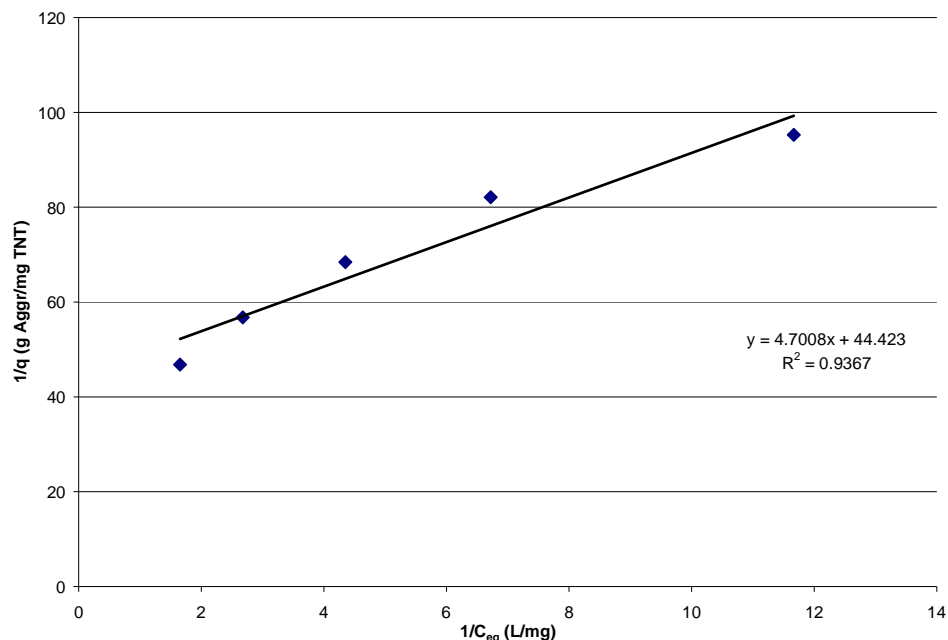
**Figure 25. Repeat of TNT sorption using smaller increments of CAA mass;  $[TNT]_0 = 1.0$  mg/L**

Using the data of this experiment the Freundlich and Langmuir constants were calculated. As shown in Figure 26, the Freundlich adsorption model fit very accurately ( $R^2=0.9944$ ) with the data obtained from the TNT sorption isotherm experiment. The Freundlich constant  $K_F$  was 0.0254 mg TNT/g CAA. with  $1/n = 0.37$ .



**Figure 26. Freundlich adsorption model plot**

The Langmuir model also fit very well to the data ( $R^2=0.9367$ ) from the isotherm experiment (Figure 27) but with less accuracy than the Freundlich model did. In this case the maximum adsorption capacity of the CAA for TNT was 0.0225 mg TNT/g CAA, which was very close to the calculated maximum adsorption capacity of the CAA mentioned.

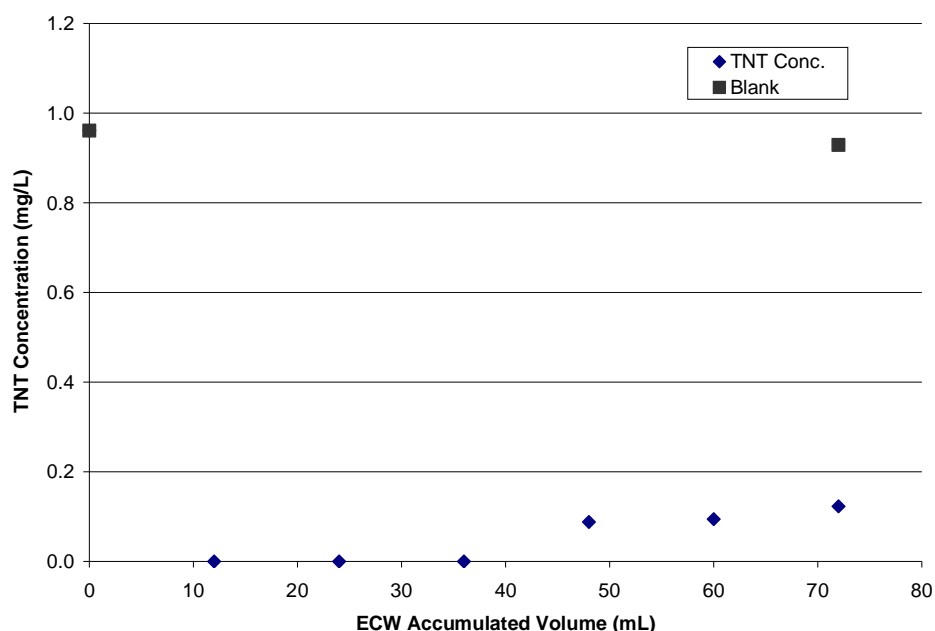


**Figure 27. Langmuir adsorption model plot**

Based on the experimental results the CAA was able to completely sorb a specified amount of TNT. The first experiment (sorption kinetic) demonstrated that the rate of TNT sorption to the CAA was  $0.0361 \text{ min}^{-1}$  (see Figure 24) which is much higher than any of the AOP assessed (maximum of  $0.0075 \text{ min}^{-1}$ ). This rate is about 4 times faster than that from the AOP, which means that less time was required to “process” the same amount of ECW. Also, the amount of TNT that could be sorbed to the MA was calculated to be  $0.0254 \text{ mg TNT/g CAA}$ . If enough MA was used, it completely sorbed all the TNT that was in the water.

#### **4.2.4 Sequential Batch Reactor**

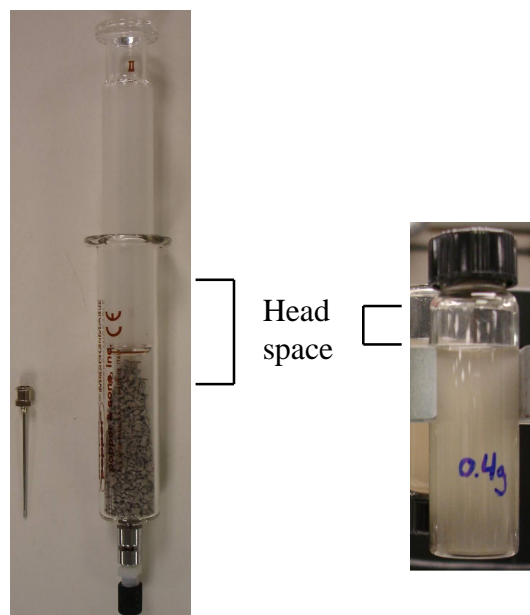
Figure 28 shows the results of the SBR experiment. It can be seen that the first three batches sorbed all the TNT from the water and the next consequential batches resulted in higher TNT concentration in the solution. More mass of TNT than the MA can sorb will lead to a residual TNT concentration in the water.



**Figure 28. Sequential batch reactor plot CAA = 2.5 g & TNT<sub>0</sub> = 1.0 mg/L**

The result of this system was that 2.5 grams of CAA could completely sorb all the TNT that was in the first 3 batches. This was a total of 36 mL of TNT at a concentration of 1.0 mg/L (meaning 36  $\mu$ g of TNT in the 2.5 grams of CAA). The last three batches had final concentration that was successively higher, implying that the CAA reached a maximum sorption capacity for TNT.

Although there was a discrepancy in contact time between the sorption kinetic experiment (more than two hours needed to completely sorb the ECW) and the sequential batch reactor (only one hour needed), they both yielded the same sorption result (see appendix A: experiment results for details). This discrepancy can be explained by the physical configuration of the experiments. As it can be seen in Figure 29, the dimensions of the reactors were different. The sequential batch reactor was bigger in diameter but the same volume of ECW and aggregate was used which resulted in more head space. So in the SBR there was room for mixing and in the sorption kinetic there was not too much room for mixing.



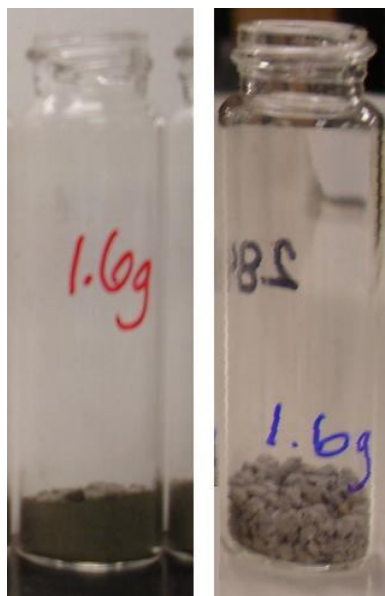
**Figure 29. Head space on both experiment setups; Sequential batch reactor (left) and sorption kinetic (right).**

#### **4.2.5 Small-Size Particles**

All of the above experiments were made using the particle size of 0.0557 inches. Another experiment was done to verify the effect of the CAA particle size on TNT sorption. The particles used in this experiment were those smaller than 0.0394 inches that passed through the mesh number 18. Figure 30, shows a comparison of the small size with the coarse size CAA.

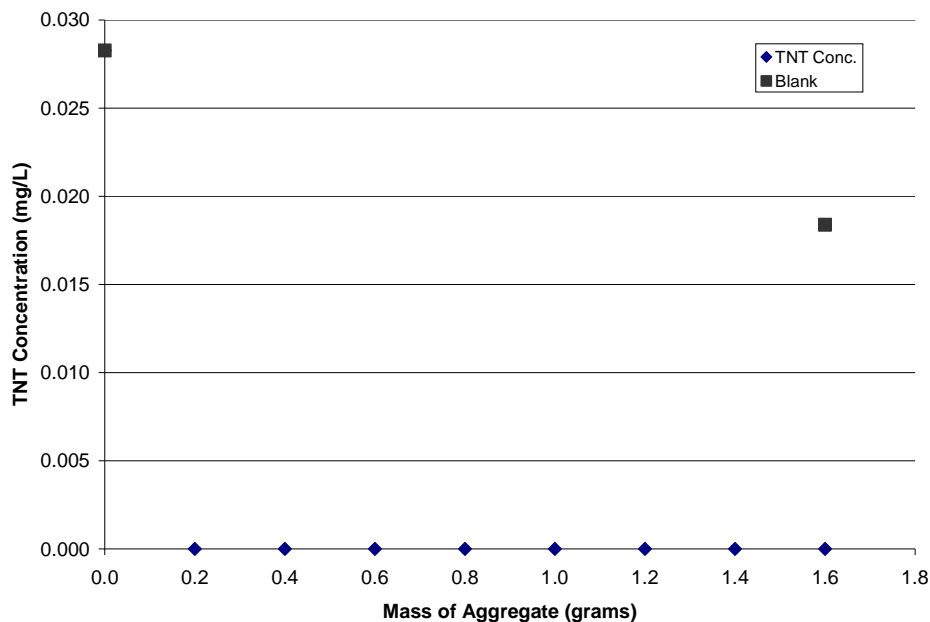
For this experiment it was used the same method as in sorption isotherm study except for the size of the particles. Each batch was prepared using different amount of mass of the CAA with the same volume and concentration of ECW (see Figure 4). Each batch was then filtered and a sample taken to be analyzed for concentration of explosives on the HPLC.





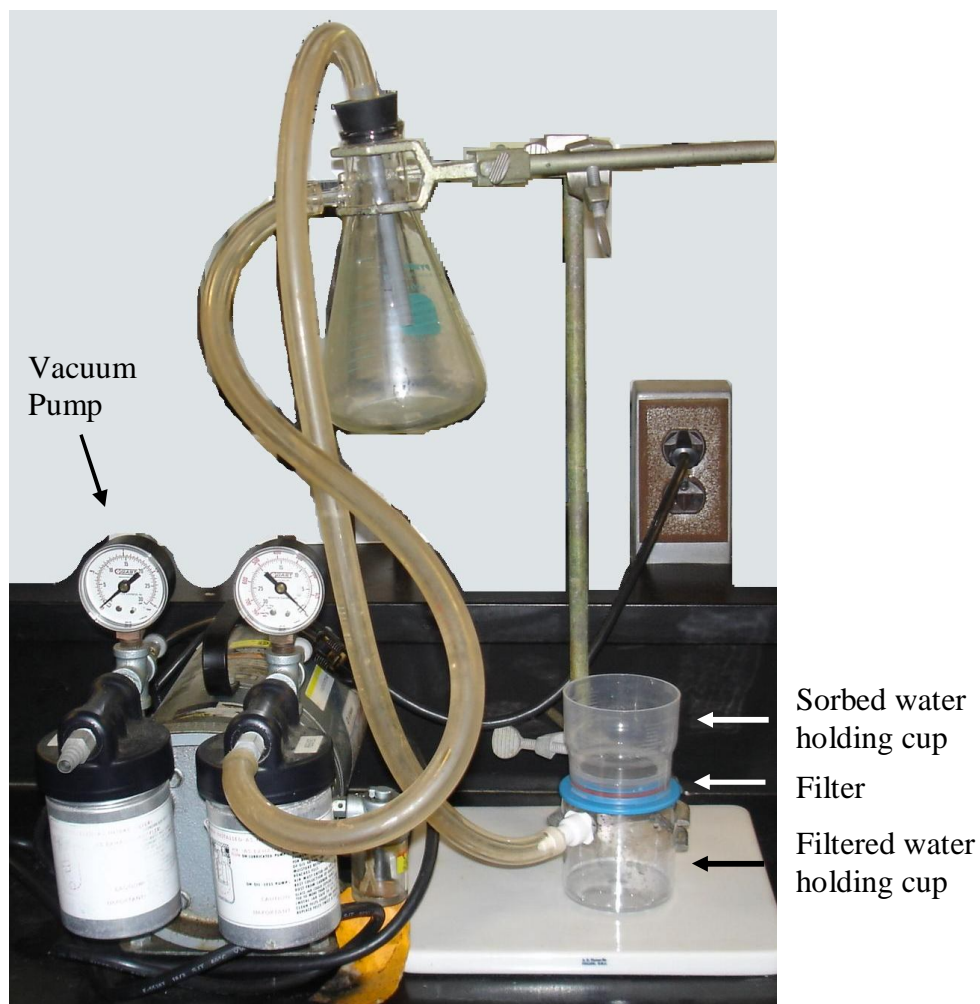
**Figure 30. Comparison of small (left) and coarse (right) particle aggregate.**

Figure 31 shows the results from the sorption experiment with the smaller size particles. It can be seen that all of the TNT concentration left in the solution were below the detection limit of the HPLC. Although the initial concentration of the TNT was substantially lower than that used for the previous sorption experiments, it is clearly shown that the particle size did affect the sorption phenomena. In this case the smaller particles completely sorbed the explosives with a small amount (0.2 grams) of CAA. This did not leave any room for additional sorption isotherm study to calculate the sorption coefficient since all of the results, except the blank, were zero.



**Figure 31. TNT sorption using CAA particle size <0.0394 inches**

A special situation that resulted from the small size particle sorption experiments was that small size CAA particles were suspended in the water making it turbid. Since turbidity is controlled through national pollution discharge elimination system (NPDES) permits, it must be controlled before it is discharged. The particles that caused the turbidity were believed to be the particles that most likely had TNT molecules sorbed to them. If this water is not cleared the small size CAAs that caused water to be turbid and had TNT sorbed to them would end up in the sewer system. For this reason an extra step was required in order to be able to get rid of the already processed water on a safe manner. A post-filtration was used to be able to dispose of the processed water. This was done using a membrane filter where the water was forced through it using a vacuum pump (see Figure 32).



**Figure 32. Post-sorption filtration assembly**

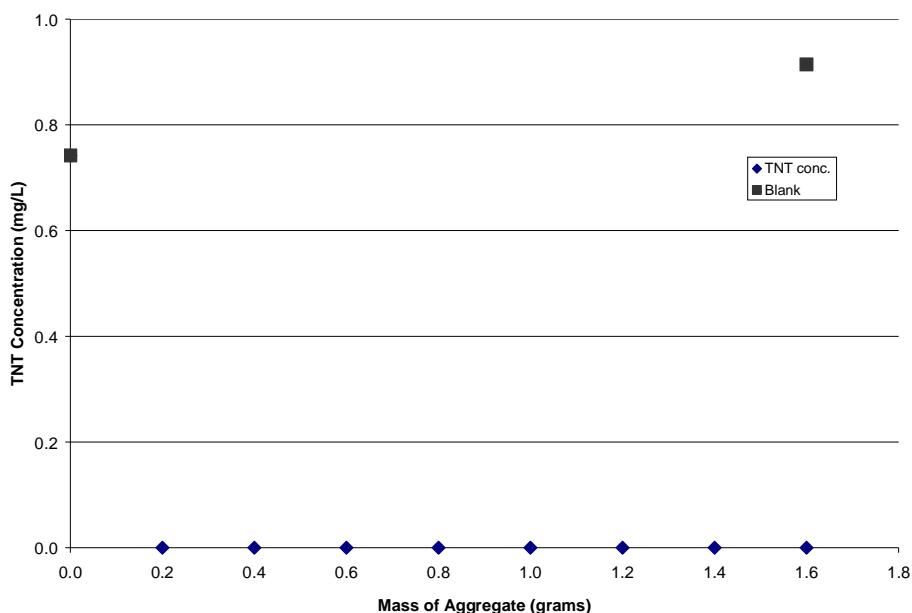
In Figure 33 it can be seen the difference in turbidity before and after the filtration. On the left bottle is the sorbed water with the large size CAA on the bottom and the small size particles suspended on the water. On the right bottle is presented the filtered water.



**Figure 33. Comparison of turbid (left) and filtered water (right).**

Hwang et al. (2006a) used alkaline hydrolysis to degrade explosives with good results. During the experiments a  $\text{pH} > 11.0$  had the best results for degradation. Based on literature review of explosive degradation using alkaline hydrolysis and the environmental conditions created by the CAA (i.e. high value of pH) there might be a possibility that the TNT degradation using CAA was due to alkaline hydrolysis effects. Although the value of pH was not developed higher than 11.0 there might have been an alkaline hydrolysis which would affect the TNT concentration during the sorption experiment. To verify if the alkaline pH developed by the CAA was a significant factor in TNT sorption, an additional experiment was conducted. The idea was to prove or eliminate the possibility that the high pH was not the most significant factor on TNT reduction in aqueous phase during the sorption experiment, but that the sorption was the most important mechanism for the TNT reduction. The experiment consisted of lowering the pH of the water in the batch with an addition of sulfuric acid. The average pH value of the low pH experiment was  $3.28 \pm 0.95$ , whereas the average pH value of the high pH experiments was  $9.50 \pm 0.25$ .

The low pH (~3.28) experiment proved to achieve even better sorption capacity. Figure 34 shows that all of the TNT concentration on the experiment was below detectable limit (see Figure 34) even using 0.2 grams of aggregate (smallest of the mass assessed). The blank sample which had no CAA but had sulfuric acid, the TNT concentration remained constant through the sorption experiment and did not achieved any degradation. This means that the pH did not affect sorption via an alkaline hydrolysis, but the sorption mechanism was responsible for TNT reduction in the aqueous phase.



**Figure 34. Sorption Isotherm Chart using low pH value.**

#### 4.2.6 Desorption

In Figure 35 it can be seen the TNT had almost no desorption at all from the aggregate. It passed through 2 hours of agitation with the clean water but the TNT did not desorb from the CAA. The first data point shows the concentration from the blank batch reactor which had 12 mL of TNT in solution with water (at a concentration of 1.0 mg/L) and no CAA. The other data points show the TNT concentration of the other batches with the different masses of CAA. What Figure 35 is showing is that the CAA that contained the TNT did not desorb virtually any of the TNT that was previously sorbed. Only the batch with 0.6 grams of CAA shows some small trace of TNT in the solution. The rest of the batches did not desorb TNT enough to be detected by the HPLC. The desorption kinetic experiment had the same results where all the vials showed concentrations below the detectable limit of the HPLC.

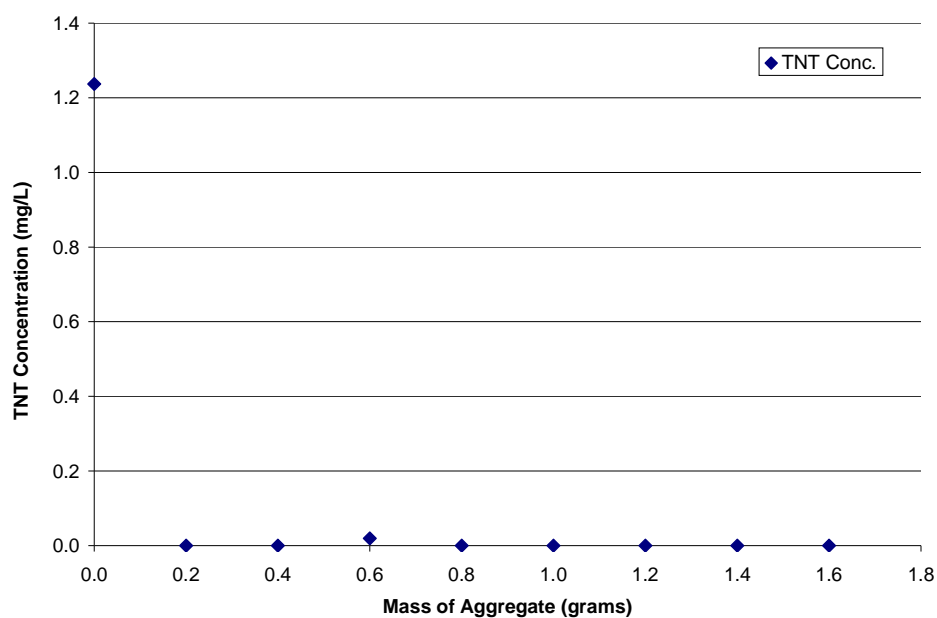


Figure 35. TNT desorption plot,  $[TNT]_0 = 1.0$  mg/L

There was an insignificant small amount of TNT that was desorbed from the CAA in the experiment time frame (2 hours of contact time). This suggest that the desorption process is much more rate limited than the sorption process. This information alone is not enough to say that the process was reversible. To confirm or reject that the sorption is reversible it would require more experiments (longer contact time; use a solvent instead of water, or other).

The idea of assessing the desorption characteristic of the CAA with TNT was to develop a process that would increase the degradation effect. The process would be to combine the effect of the AOP to degrade as much TNT possible, with the sorption effect of the CAA to take out the remaining TNT from the water. The two steps would be done in series. The AOP would be used to reduce the TNT in the water form a “high” concentration to “low” concentration. The CAA would be used to sorb the remaining TNT amount (out of the water) from the AOP effluent. Once the CAA does not have more capacity to sorb more TNT, the desorption process would be used to take the TNT out of the CAA. Once the TNT is out of the CAA the effluent of that process could be injected back to the beginning of the process so the TNT is degraded again in the AOP making a small loop of TNT degradation. The proposed process would be similar to the water filtration using sand filter were the filtration process stops in order to make backwash to “clean” the sand filter.

#### **4.2.7 Application to Actual ECW Produced**

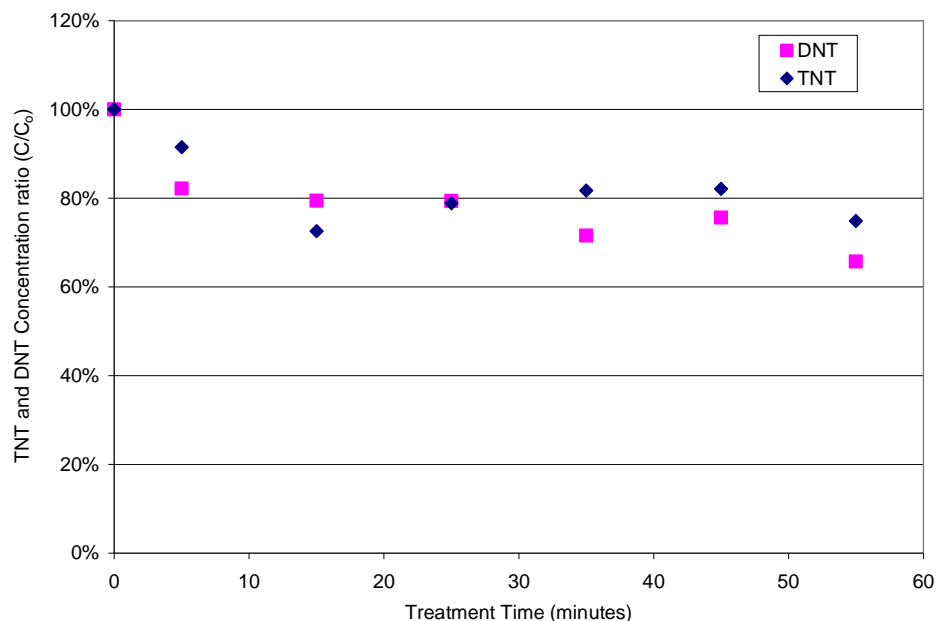
After the technical data and information acquired from the experiments was done, where TNT was used as the single solute in the pure water, real ECW produced from various explosives research experiments in the laboratory were treated. In this way the treatment process that was

assessed could be tested on a “larger” scale. By doing this experiment the remediation process could be exposed to a closer to real life application.

#### **4.2.7.1 AOP**

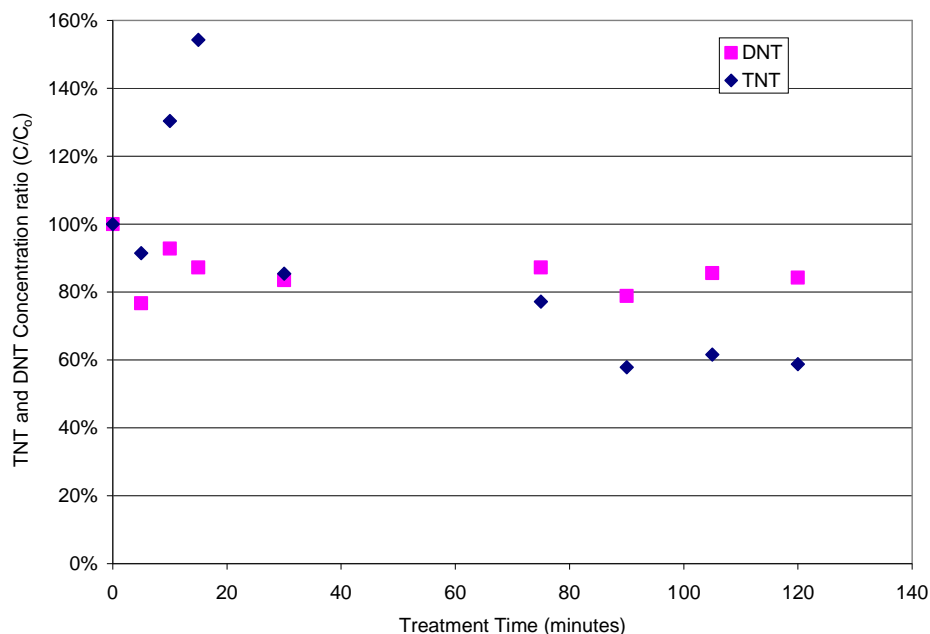
The explosives-containing water from various experiments were mixed so that there was enough volume of water to remediate. Combining the ECW from one experiment which had a volume of about 50 liters with a concentration of 0.017 mg/L of TNT with the water from other experiments that contained TNT and DNT with higher concentration resulted in a final concentration of 0.045 mg/L of TNT and 0.065 mg/L of DNT. With this new “higher” concentration, the remediation processes were made following the same procedures used as the previous experiments. Figure 36 shows the degradation trends of the TNT and the DNT, where they were degraded by 25% and 33%, respectively using the AOP method of UV/H<sub>2</sub>O<sub>2</sub> 300 mg/L. The difference between the initial and final concentrations for TNT and DNT for this batch was 0.010 mg/L and 0.018 mg/L respectively.





**Figure 36. First batch of TNT and DNT remediation of ECW with UV/H<sub>2</sub>O<sub>2</sub> 300 mg/L**

The reaction time was augmented up to 2 hours to verify if the ECW could be completely remediated with a longer reaction time. The concentration of the explosives at the end of the 120 minutes of treatment was lowered by 41% for the TNT and 26% for the DNT (Figure 37). The difference between the initial and final concentrations for TNT and DNT for this batch was 0.015 mg/L and 0.008 mg/L respectively.



**Figure 37. Second Batch of TNT and DNT remediation of ECW using AOP**

Although the TNT and DNT concentration reduction was about the same as in the previous experiments (~40% reduction), the difference between the initial and the final concentrations was very small. The difference between the initial and the final concentration of TNT and DNT was less than 0.018 mg/L in all cases. In Table 8 below there is a summary of the initial–final TNT (and DNT) concentration of the first experiments and the two batch of the remediation application (using AOP treatment only). Here it can be seen that the difference between the initial and final TNT concentration of the last two experiments (remediation of ECW from other experiments) are much alike the Experiment 5 which had the least degradation effect.

**Table 8. Summary of difference between initial and final concentrations of explosives.**

Experiment name	Difference between initial and final TNT concentration	Difference between initial and final DNT concentration
UV/ H <sub>2</sub> O <sub>2</sub> - 50mg/L	0.151	N/A
UV/ H <sub>2</sub> O <sub>2</sub> - 100mg/L	0.182	N/A
UV/ H <sub>2</sub> O <sub>2</sub> - 300mg/L	0.204	N/A
UV/ H <sub>2</sub> O <sub>2</sub> - 300mg/L - UV ON/OFF	0.047	N/A
UV/ H <sub>2</sub> O <sub>2</sub> - 300mg/L - [TNT] <sub>o</sub> = 1.0 mg/L	0.640	N/A
ECW from other experiments – batch 1	0.010	0.018
ECW from other experiments – batch 2	0.015	0.008

N/A; not available because no experiments were done

This small reduction in concentration taking place in two hours of treatment was not too effective in terms of materials, energy, and time used, as shown in Table 9. The electrical energy required to lower one log order of magnitude of TNT is comparable to the energy required with Experiment 2 which had 50 mg/L of H<sub>2</sub>O<sub>2</sub> (and an EE/O value of 191.12). Therefore starting with a smaller TNT concentration does not improve (reduces) the energy consumption. It can be said that the energy consumption increases if compared with the same H<sub>2</sub>O<sub>2</sub> concentration of the previous experiments.

**Table 9. Electric Energy consumed by the treatment of ECW from other research**

	EEi (kWh)	Volume (m <sup>3</sup> )	C <sub>i</sub> mg/L	C <sub>f</sub> mg/L	log(C <sub>i</sub> /C <sub>f</sub> )	EE/O (kWh/m <sup>3</sup> •log)
First batch	0.012	0.0005	0.040	0.030	0.126	191.05
Second batch	0.024	0.0005	0.037	0.022	0.231	207.56

The water that was treated with 2 hours AOP was then placed on a batch sorption reactor which contained 100 grams of CAA. The reactor was agitated for 3 hours in order to ensure a complete sorption of all the TNT that was left over from the AOP. Samples were taken after 1.5 and 3.0 hours, considering the results that sorption equilibrium time was achieved after 2 hours. Figure 38 presents the concentration of TNT after the sorption process. It can be seen that 0.02

mg/L of TNT and 0.041 mg/L of TNT which were left over from the AOP was completely sorbed to the CAA.

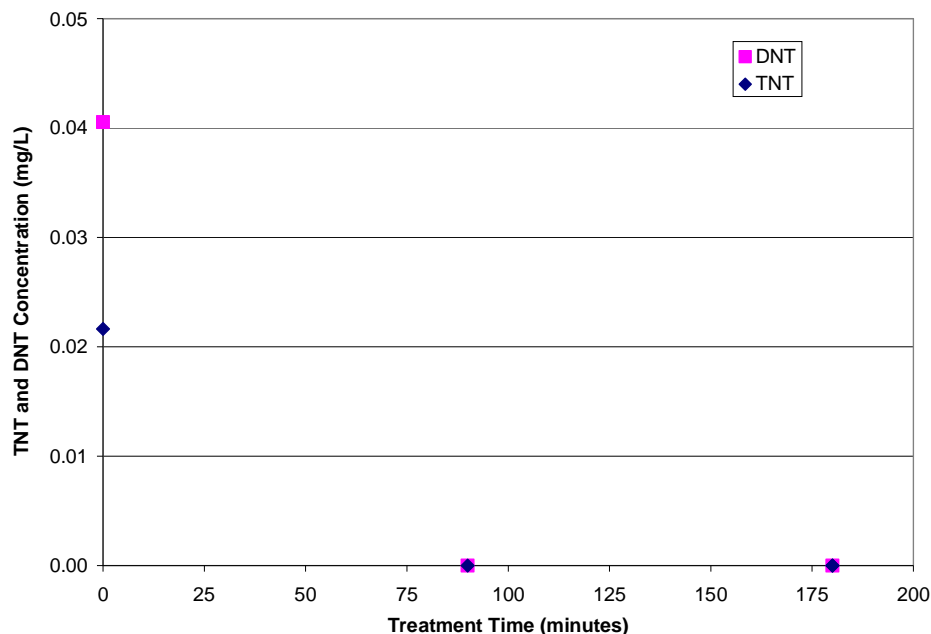
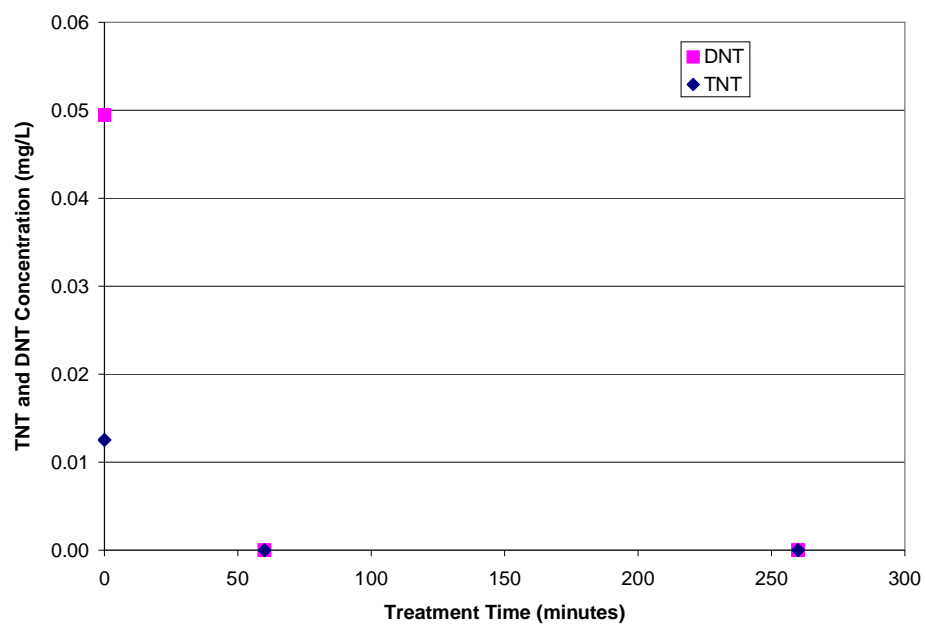


Figure 38. Remediation of ECW previously treated with second batch AOP now using Sorption proces

#### 4.2.7.2 Sorption Alone

Although the AOP showed explosives degradation in both pure water system and real ECW produced in the laboratory, it was not able to achieve a complete degradation, resulting in residual explosives concentrations in the water. Sorption process showed however a complete reduction of explosives even with very small initial concentration. This suggests that AOP process can be a better remediation process for higher explosive concentrations, whereas sorption can be better for lower concentrations. After several more batches treated with the same procedure and having the same trend of results, it was decided to use only sorption since it seemed more effective for the “low” concentration of the explosives, which was true for the wastewater produced by other experiments. As shown in Figure 39, the TNT and DNT

concentrations went below the detectable limit from the first sample taken after 1 hour of contact time.



**Figure 39. Remediation of ECW using only sorption process**

## 5 Summary, Conclusions, and Recommendations

This section summarizes the findings of the different UV/H<sub>2</sub>O<sub>2</sub> and sorption experiments and states the advantages and disadvantages of each method assessed. Then, recommendations are made for the actual application of the processes and further investigation.

### 5.1 AOP

The AOP batch mode system effectively lowered the explosives concentration in the provided treatment time (i.e. 120 minutes). The highest concentration of H<sub>2</sub>O<sub>2</sub> assessed was 300 mg/L which resulted in the best degradation achieved. This concentration of H<sub>2</sub>O<sub>2</sub> was capable of lowering the TNT concentration by 60% when the initial TNT concentration was 0.4 mg/L and 55% when the initial concentration was 1.0 mg/L. The higher concentration of 300 mg/L of H<sub>2</sub>O<sub>2</sub> proved to be near the top of the saturation curve for TNT remediation. Theoretically, the maximum achievable degradation of TNT by the UV/H<sub>2</sub>O<sub>2</sub> system was projected to be 65% of the initial concentration.

It was not possible to completely remediate all the TNT that was in the system within a reasonable time (less than 120 minutes). When the initial TNT concentration to be treated was at 0.04 mg/L or less, the AOP was not able to lower the TNT concentration further more. Also, when DNT concentration was low, the AOP system was not able to further lower the DNT concentration.

Statistically, there was a significant difference between the means of the TNT concentrations from UV/H<sub>2</sub>O<sub>2</sub> systems and those from the control experiment which had no H<sub>2</sub>O<sub>2</sub> in the system, but UV radiation only. Although the systems that had concentrations of 50, 100, and 300 mg/L of H<sub>2</sub>O<sub>2</sub> yielded different concentrations at the end of the treatment, there

was no statistical difference in the means of their data. Hence, the use of the t-test proved that the system that had 50 mg/L of  $\text{H}_2\text{O}_2$  in the presence of a constant UV radiation was the best combination among the tested systems for remediating TNT; using less materials to achieve TNT degradation.

The analysis made to the energy requirements showed that the use of more  $\text{H}_2\text{O}_2$  in the system had the effect of lowering the amount of electrical energy required to lower the same amount of TNT concentration. So higher  $\text{H}_2\text{O}_2$  concentration, with the same TNT initial concentration, lowered the amount of electrical energy used (via UV lamp) for the same result. So it can be said that there is an amount of energy that needs to be input to the system in order to achieve the degradation of TNT and that energy can either come from chemicals (i.e.  $\text{H}_2\text{O}_2$ ) or from electrical energy (i.e. UV lamp).

## **5.2 Sorption Kinetics**

The experiments performed showed that the treatment time of two hours was enough for the CAA to almost completely sorb all the TNT from the ECW. The first hour of the experiment time, the TNT concentration went down by ~90% and in the second hour the remaining ~10% concentration was lowered. So in order to optimize the process a one hour of treatment time was considered to be the required time to treat the ECW at the conditions of the experiments.

## **5.3 Sorption Isotherm**

From the sorption isotherm results, it can be said that the CAA was capable of completely sorb a specified amount of TNT. The Freundlich sorption constant was found to be 0.0254 mg TNT/g CAA.

When the concentration of TNT was high (1.0 mg/L) the amount of CAA that was needed to completely sorb all the TNT in the system was high, but when the concentration of TNT was low ( $<0.04$  mg/L) the amount of CAA needed to completely sorb all the TNT in the system was low. With a small amount of CAA it was possible to treat large amounts of ECW at low concentrations.

Although CAA, when in contact with water, produced a relatively high pH ( $\sim 9.5$ ), it was not enough to achieve the conditions for an alkaline hydrolysis. Actually the low pH ( $\sim 3.28$ ) sorption experiments resulted in a lower TNT residual concentration in the treated water.

#### **5.4 Sequential Batch Reactor System**

The SBR experiment proved that small quantities of TNT could be completely sorbed into the MA, but when the volume of ECW increased, the MA was not capable of completely sorbing all the TNT that was in the system. As the mass of TNT increases in the system with a constant mass of MA, there was some TNT residual in the solution. More TNT in the system required more MA to completely sorb it.

#### **5.5 AOP Followed by Sorption Process**

For the treatment of large quantities of ECW a combination of processes in series will work better since they complement each other. The AOP worked better for high concentration of explosives and did not perform well with low concentrations. The sorption process proved to lower the TNT and DNT concentration to levels below the detectable limit of the HPLC when in contact with low explosives concentrations. So, the best approach to use these processes together is to have them placed in series. The first process should be the AOP system, using 300



mg/L of H<sub>2</sub>O<sub>2</sub>, to lower the ECW concentration to a level that is more manageable to the next system. Then the sorption system could be used as a polishing treatment to completely sorb all the explosives remaining.

## **5.6 Desorption**

The desorption of the TNT from the CAA was not measurable during this investigation. Probably the rate of TNT desorption was too slow to be measured (desorption is rate limited) or the TNT will actually not desorb from the CAA at all. More investigation should be done in this topic to better understand the TNT desorption behavior from the CAA. One way would be to use a solvent (i.e. Acetonitrile, Methanol, or other) to desorb the TNT from the CAA.

## **5.7 Application to Actual ECW Produced**

In the case of the application of the treatment to the ECW from other experiments, the initial TNT and DNT concentrations were very low compared to the previous experiments performed. This scenario seems more realistic for large volumes of water that have been contaminated with explosives. The large volume of water might dilute the explosive concentration thus looking more like the application to actual ECW assessed in this project. In this case the AOP system did not give good results but the CAA system was able to completely sorb the explosives in the water.

## **5.8 Recommendations for Combined Treatment Processes**

Using the result from these experiments a schematic diagram showing the recommended order of treatment is shown in Figure 40. First, the TNT and DNT containing water should be

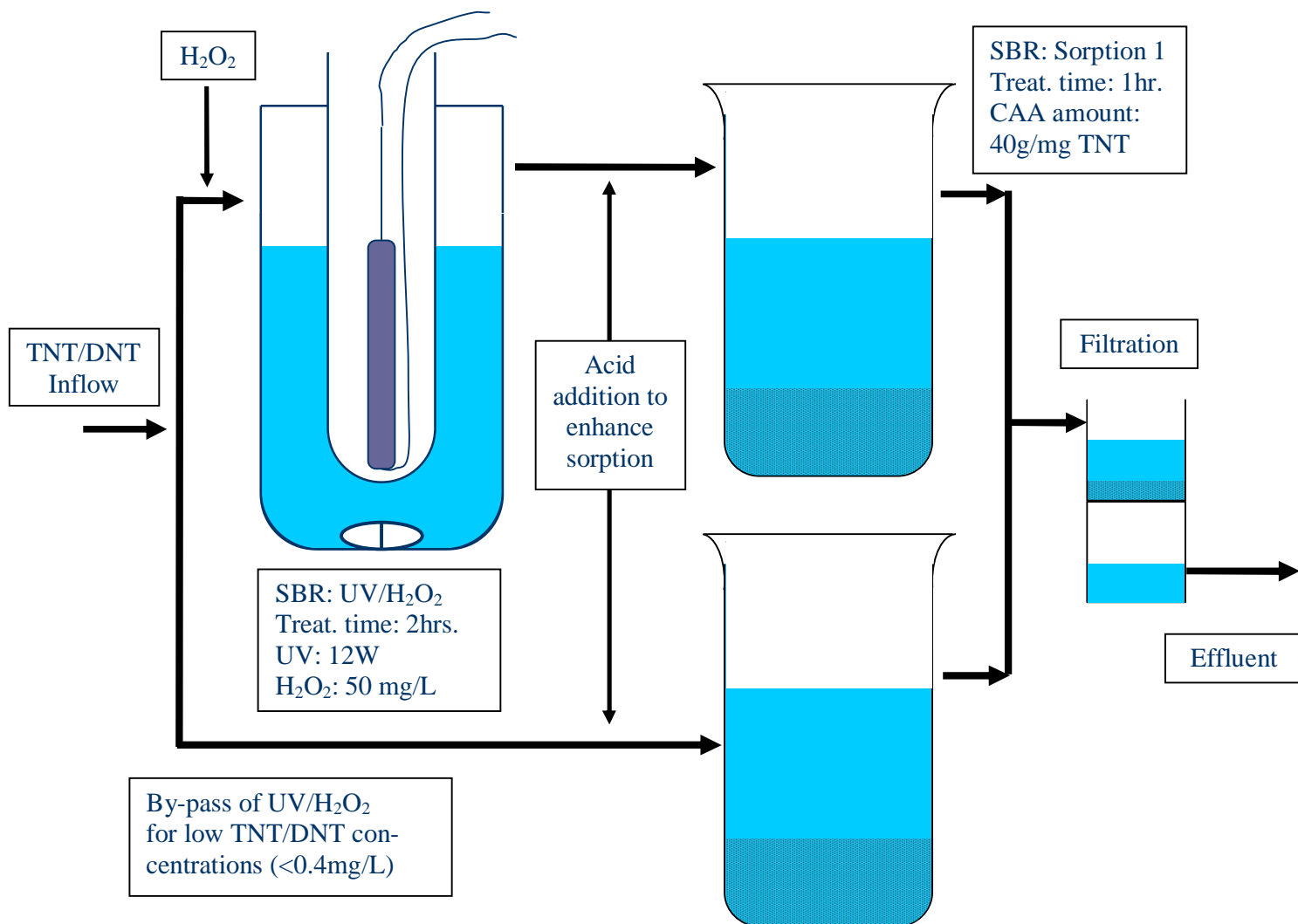
treated with UV/H<sub>2</sub>O<sub>2</sub> using a concentration of H<sub>2</sub>O<sub>2</sub> of 50 mg/L for 2 hours using a UV lamp of 12 Watts. After the two hours of the AOP treatment, the ECW (already treated with AOP) should be transferred to the sorption treatment using 40 grams of CAA per mg of TNT in solution. This treatment should be used for TNT and DNT concentrations of more than 0.4 mg/L. In the case that the TNT and DNT concentration is low (for these experiments was less than 0.4 mg/L) the UV/H<sub>2</sub>O<sub>2</sub> treatment should not be used and instead only the sorption treatment should be used.

## **5.9 Further Studies**

It is recommended that more investigation be done on several topics in order to strengthen the data found in this project. Several recommendations are made for further studies as follows:

For the AOP experiments, only a batch reactor was used to determine the TNT and DNT remediation behavior. In order to further understand the AOP applied for explosives remediation, other types of reactors should be evaluated (e.g., plug flow and/or complete-mix reactor) with a wider range of H<sub>2</sub>O<sub>2</sub> and explosives concentrations.

For sorption experiments, the particle size of CAA showed to have an effect on the sorption capacity but the experiments were done using only two particle sizes. More experiments should be done to determine the effect of the particle size on sorption capacity using CAA. During the sorption experiments only two pH values were assessed. In order to determine the impact of the pH in the sorption capacity, varying pH values should be used for the sorption experiments. Also, more investigation should be done for desorption of TNT to better understand the TNT desorption behavior from the CAA.



**Figure 40. Recommendation of the process flow of the degradation and sorption of TNT and DNT.**

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## 7 Appendix

### A. Data of the experiments:

#### Control Experiment: UV only

Using Average of the original Experiment and the Repetitions

Treatment time		TNT peaks		Concentration mg/L	Concentration ratio (C/C <sub>0</sub> )
		Time (min)	Area (uV*sec)		
0.0	min	6.203	12,934.87	0.415	100%
2.5	min	6.088	11,881.20	0.382	92%
5.0	min	6.036	11,851.49	0.381	92%
10.0	min	6.181	11,680.74	0.375	90%
15.0	min	6.064	10,668.23	0.343	82%
30.0	min	6.449	14,336.86	0.461	111%
45.0	min	6.005	12,074.37	0.388	93%
60.0	min	5.878	12,153.56	0.390	94%
90.0	min	5.873	14,001.60	0.450	108%
120.0	min	5.882	14,133.93	0.454	109%
Average		6.066	12,571.685	0.404	
Std. Dev.		0.180	1,227.805	0.039	

#### Experiment 2: UV/ H<sub>2</sub>O<sub>2</sub> - 50mg/L

Treatment time		TNT peaks		Concentration mg/L	Concentration ratio (C/C <sub>0</sub> )
		time (min)	Area (uV*sec)		
0	min	5.689	10,679.50	0.343	100.0%
2.5	min	5.674	10,646.20	0.342	99.7%
5	min	5.725	10,056.13	0.323	94.2%
10	min	5.665	9,778.36	0.314	91.6%
15	min	5.667	9,214.72	0.296	86.3%
30	min	5.674	8,965.07	0.288	83.9%
45	min	5.657	8,517.72	0.274	79.8%
60	min	5.665	6,717.49	0.216	62.9%
90	min	5.667	6,803.42	0.219	63.7%
120	min	5.677	5,989.70	0.192	56.1%
Average		5.676	8,736.831	0.281	
Std. Dev.		0.019	1,697.580	0.055	
			initial – final	0.151	

**Experiment 3: UV/ H<sub>2</sub>O<sub>2</sub> - 100mg/L**

Treatment time	TNT peaks		Concentration mg/L	Concentration ratio (C/C <sub>0</sub> )
	time (min)	Area (uV*sec)		
0 min	5.593	10,876.68	0.349	100%
2.5 min	5.663	10,980.45	0.353	101%
5 min	5.653	10,177.01	0.327	94%
10 min	5.686	9,832.82	0.316	90%
15 min	5.676	9,991.95	0.321	92%
30 min	5.681	8,789.88	0.282	81%
45 min	5.666	8,664.79	0.278	80%
60 min	5.659	8,674.64	0.279	80%
90 min	5.667	7,218.53	0.232	66%
120 min	5.669	5,206.82	0.167	48%
Average	5.661	9,041.357	0.290	
Std. Dev.	0.026	1,773.701	0.057	
		initial – final	0.182	

**Experiment 4: UV/ H<sub>2</sub>O<sub>2</sub> - 300mg/L**

Treatment time	TNT peaks		Concentration mg/L	Concentration ratio (C/C <sub>0</sub> )
	time (min)	Area (uV*sec)		
0 min	5.66	10,522.89	0.338	100%
2.5 min	5.674	9,520.13	0.306	90%
5 min	5.647	9,504.56	0.305	90%
10 min	5.654	9,686.12	0.311	92%
15 min	5.687	8,635.72	0.277	82%
30 min	5.662	7,560.97	0.243	72%
45 min	5.653	7,013.75	0.225	67%
60 min	5.663	6,956.47	0.223	66%
90 min	5.633	4,754.09	0.153	45%
120 min	5.676	4,161.89	0.134	40%
Average	5.661	7,831.659	0.252	
Std. Dev.	0.016	2,145.399	0.069	
		initial – final	0.204	



### Experiment 5: UV/ H<sub>2</sub>O<sub>2</sub> - 300mg/L turning the UV ON/OFF at different intervals

ON/OFF	Treatment time	TNT peaks		Concentration mg/L	Concentration ratio (C/C <sub>0</sub> )
		time (min)	Area (uV*sec)		
ON	0 min	5.647	10,503.46	0.337	100%
OFF	2.5 min	5.661	9,122.77	0.293	86.9%
ON	5 min	5.657	9,784.06	0.314	93.2%
OFF	10 min	5.675	9,997.38	0.321	95.2%
ON	15 min	5.666	9,091.37	0.292	86.6%
OFF	30 min	5.660	9,153.26	0.294	87.1%
ON	45 min	5.686	9,036.10	0.290	86.0%
OFF	60 min	Damaged			
ON	90 min	5.665	8,924.11	0.287	85.0%
	120 min	5.68	9,037.06	0.290	86.0%
Average		5.666	9,405.508	0.302	
Std. Dev.		0.012	552.870	0.018	
			initial – final	0.047	

### Experiment 6: UV/ H<sub>2</sub>O<sub>2</sub> - 300mg/L [TNT]<sub>0</sub> = 1.0 mg/L

Treatment time	TNT peaks		Concentration mg/L	Concentration ratio (C/C <sub>0</sub> )
	time (min)	Area (counts)		
0 min	6.708	2,791,527	1.161	100%
2.5 min	6.708	2,660,991	1.058	91%
5 min	6.707	2,408,890	0.883	76%
10 min	6.706	2,490,239	0.936	81%
15 min	6.715	2,298,245	0.816	70%
30 min	6.724	2,127,334	0.722	62%
45 min	6.723	2,117,390	0.716	62%
60 min	6.719	2,182,884	0.751	65%
80 min	6.725	1,942,763	0.632	54%
120 min	6.728	1,680,082	0.524	45%
Average		6.716	2,270,034.500	0.820
Std. Dev.		0.009	333,296.279	0.194
			initial – final	0.640

### Maximum Degradation achieved on each experiment

Experiment Name	UV	[H <sub>2</sub> O <sub>2</sub> ] mg/L	Maximum Reduction
Control	Const.	0	0%
Experiment 2	Const.	50	44%
Experiment 3	Const.	100	52%
Experiment 4	Const.	300	60%
Experiment 5	ON/OFF	300	14%
Experiment 6	Const.	300	55%

## Sorption Kinetic

[TNT]:	1.0mg/L		Time to peak	Area (uV*sec.)	Concentration (mg/L)	Concentration ratio (C/C <sub>o</sub> )	Sorbed
	Treatment time						amount (C-C <sub>o</sub> )
Blank initial	0	min	5.774	21,411.30	0.77	100.0%	0.0%
	5	min	5.764	11,159.89	0.40	52.1%	47.9%
	10	min	5.763	9,363.51	0.34	43.7%	56.3%
	15	min	5.768	8,807.55	0.32	41.1%	58.9%
	30	min	5.752	6,993.30	0.25	32.7%	67.3%
	45	min	5.763	2,033.16	0.07	9.5%	90.5%
	60	min	5.758	1,893.47	0.07	8.8%	91.2%
	90	min	5.769	977.17	0.04	4.6%	95.4%
	120	min	5.770	420.46	0.02	2.0%	98.0%
Blank final	120	min	5.761	20,277.79	0.73	94.7%	5.3%

## Sequential Batch Reactor

Title			Conc. (mg/L)	Concentration ratio (C/C <sub>0</sub> )
Blank initial	0	ml	0.961	100%
Accumulated	12	ml	0.000	0%
Volume of	24	ml	0.000	0%
ECW	36	ml	0.000	0%
Contact time	48	ml	0.088	9%
(1 hour	60	ml	0.094	10%
each)	72	ml	0.123	13%
Blank final	0	ml	0.929	--

## Sorption Isotherm

Title			Conc. (mg/L)	Concentration ratio (C/C <sub>0</sub> )
Blank initial	0.0	g	0.975	100%
	1.0	g	0.251	26%
	1.5	g	0.000	0%
	2.0	g	0.000	0%
	2.5	g	0.000	0%
	3.0	g	0.000	0%
	3.5	g	0.000	0%
Mass of Agregate				

### Sorption Isotherm (high resolution)

Title			Conc. (mg/L)	Concentration ratio (C/C <sub>0</sub> )	pH
Blank initial	0.0	g	0.961	99%	9.00
	0.2	g	0.605	62%	
	0.4	g	0.373	38%	
	0.6	g	0.230	24%	
	0.8	g	0.149	15%	
	1.0	g	0.086	9%	
	1.2	g	0.000	0%	
	1.4	g	0.000	0%	
	1.6	g	0.000	0%	
Blank final			0.935	96%	8.70

### Sorption Isotherm (low pH)

	Title		Time to peak	Area (uV*sec.)	Conc. (mg/L)	Concentration ratio (C/C <sub>0</sub> )	pH
Blank initial	0.0	g	5.811	20535.23	0.742	100%	1.90
	0.2	g	N/A	0	0.000	0%	
	0.4	g	N/A	0	0.000	0%	
	0.6	g	N/A	0	0.000	0%	
	0.8	g	N/A	0	0.000	0%	
	1.0	g	N/A	0	0.000	0%	
	1.2	g	N/A	0	0.000	0%	
	1.4	g	N/A	0	0.000	0%	
	1.6	g	N/A	0	0.000	0%	
Blank final		0.0	5.791	25295.90	0.914	123%	1.50

### Freundlich Isotherm

Freundlich Isotherm Sorption				
(m)	C <sub>eq</sub>	Volume	sorbed mass (x)	adsorptive capacity (x/m)
Mass Aggr.	TNT (mg/L)	TNT (L)	TNT (mg)	TNT (mgTNT/gAggr.)
0.0 g	0.961	0.012	0.00000	-
0.2 g	0.605	0.012	0.00427	0.02136
0.4 g	0.373	0.012	0.00705	0.01761
0.6 g	0.230	0.012	0.00877	0.01461
0.8 g	0.149	0.012	0.00974	0.01218
1.0 g	0.086	0.012	0.01050	0.01050
1.2 g	0.000	0.012	0.01153	0.00961
1.4 g	0.000	0.012	0.01153	0.00823
1.6 g	0.000	0.012	0.01153	0.00720

## Langmuir Isotherm

Langmuir Isotherm Sorption						
Mass Aggr.	(C <sub>eq</sub> )	Volume	Sorbed mass (x)	(q=x/m)	1/q	1/C
	TNT (mg/L)		TNT (mg)	TNT (mgTNT/gAggr.)		
0.0 g	0.961	0.012	0.00000	0.00000	--	--
0.2 g	0.605	0.012	0.00427	0.02136	46.81	1.65
0.4 g	0.373	0.012	0.00705	0.01761	56.78	2.68
0.6 g	0.230	0.012	0.00877	0.01461	68.42	4.35
0.8 g	0.149	0.012	0.00974	0.01218	82.12	6.72
1.0 g	0.086	0.012	0.01050	0.01050	95.25	11.67
1.2 g	0.000	0.012	0.01153	0.00961	104.10	--
1.4 g	0.000	0.012	0.01153	0.00823	121.45	--
1.6 g	0.000	0.012	0.01153	0.00720	138.80	--

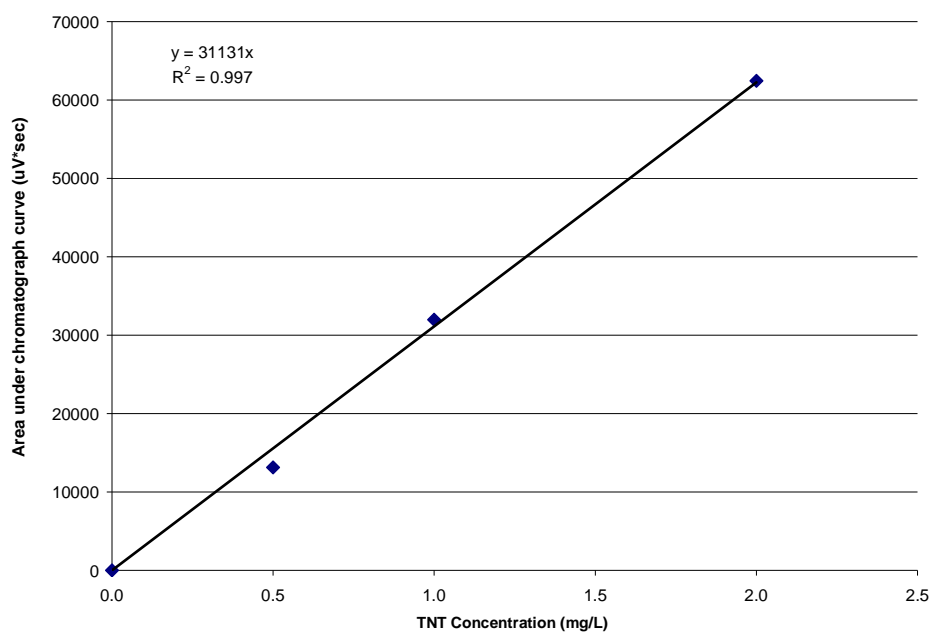
## Alkaline and Acid measurements

Aggregate only - Alkaline			Aggregate and sulfuric acid
	Mass (g)	pH	pH
Blank initial	0.0	8.70	1.50
	0.2	9.00	1.90
	0.4	9.50	2.04
Mass of Aggregate (grams)	0.6	9.67	2.63
	0.8	9.67	3.48
	1.0	9.70	3.76
	1.2	9.30	4.06
	1.4	9.72	4.20
	1.6	9.45	4.15
Blank final	0.0	8.70	1.50
Average		9.5013	3.2775

## B. Calibration Curves for the experiments

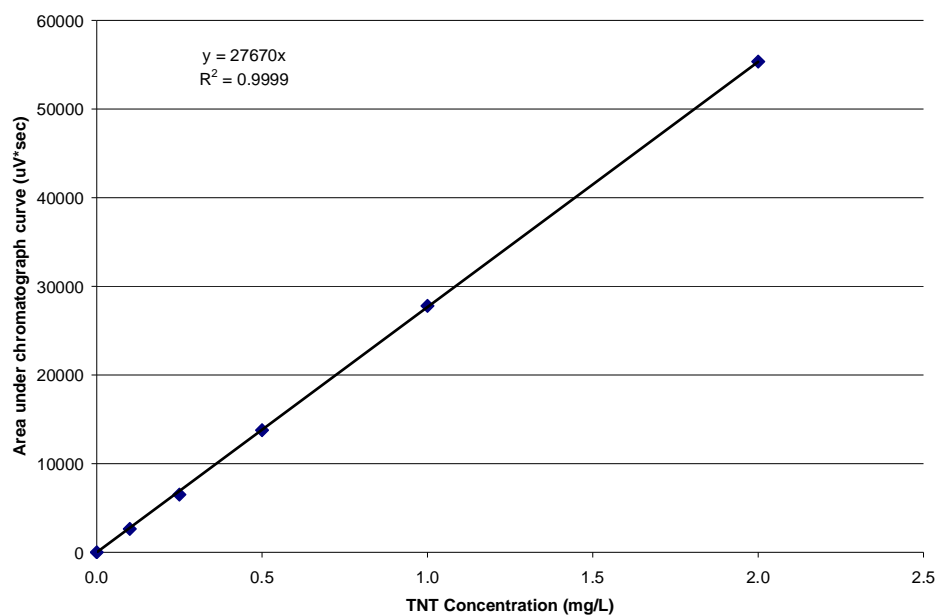
### TNT calibration curve for the AOP experiments

Calibration curve (AOP)			
Concentration		TNT peaks	
		time (min)	Area (uV*sec)
0.00	mg/L	--	0.00
0.05	mg/L	--	--
0.10	mg/L	--	--
0.50	mg/L	5.523	13139.03
1.00	mg/L	5.545	31971.86
2.00	mg/L	5.532	62447.45



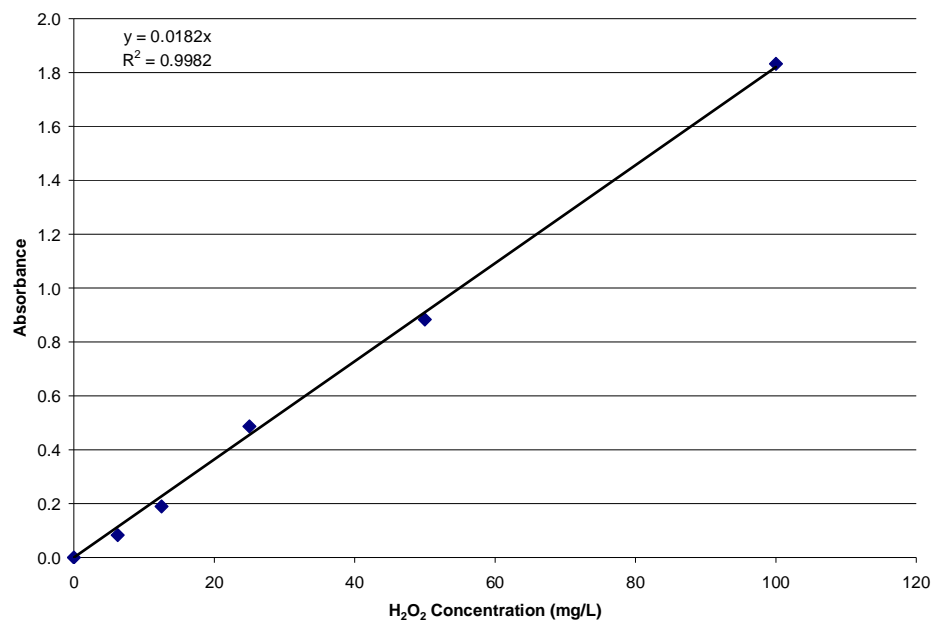
### TNT calibration curve for the Sorption experiments

Calibration curve (sorption)			
Concentration		Time peak	Area
0.00	mg/L	0.000	-
0.10	mg/L	5.643	2,631.78
0.25	mg/L	5.617	6,515.59
0.50	mg/L	5.643	13,766.67
1.00	mg/L	5.650	27,795.25
2.00	mg/L	5.664	55,351.92



### H<sub>2</sub>O<sub>2</sub> calibration curve for the AOP experiments

UV/VIS Spectrometer		
wavelength: 407 nm		
Perking Elmer Lambda 20		
Calibration curve		
Sample ID	Conc. (mg/L)	Value
1.A01	100	1.8326
2.A02	50	0.8835
3.A03	25	0.4864
4.A04	12.5	0.1893
5.A05	6.25	0.0834
4.A06	0.00	0.00



### C. Statistical Analysis: t-test results and correlation

	<i>Control</i>	<i>50ppm</i>
Mean	0.98494	0.69279
Variance	0.00940	0.01427
Observations	5	5
Hypothesized Mean Difference	0	
df	8	
t Stat	4.24626	
P(T<=t) one-tail	0.00141	
t Critical one-tail	1.85955	
P(T<=t) two-tail	0.00281	
t Critical two-tail	2.30600	

	<i>Control</i>	<i>100ppm</i>
Mean	0.98494	0.70894
Variance	0.00940	0.02011
Observations	5	5
Hypothesized Mean Difference	0	
df	7	
t Stat	3.59268	
P(T<=t) one-tail	0.00441	
t Critical one-tail	1.89458	
P(T<=t) two-tail	0.00883	
t Critical two-tail	2.36462	

	<i>Control</i>	<i>300ppm</i>
Mean	0.98494	0.57868
Variance	0.00940	0.02093
Observations	5	5
Hypothesized Mean Difference	0	
df	7	
t Stat	5.21624	
P(T<=t) one-tail	0.00062	
t Critical one-tail	1.89458	
P(T<=t) two-tail	0.00123	
t Critical two-tail	2.36462	

	<i>Control</i>	<i>300ppm on/off</i>
Mean	0.98494	0.86044
Variance	0.00940	0.00008
Observations	5	4
Hypothesized Mean Difference	0	
df	4	
t Stat	2.85636	
P(T<=t) one-tail	0.02305	
t Critical one-tail	2.13185	
P(T<=t) two-tail	0.04610	
t Critical two-tail	2.77645	



	<i>Control</i>	<i>300ppm 1.0</i>
Mean	0.98494	0.57606
Variance	0.00940	0.00633
Observations	5	5
Hypothesized Mean Difference	0	
df	8	
t Stat	7.28884	
P(T<=t) one-tail	0.00004	
t Critical one-tail	1.85955	
P(T<=t) two-tail	0.00008	
t Critical two-tail	2.30600	

	<i>50ppm</i>	<i>100ppm</i>
Mean	0.69279	0.70894
Variance	0.01427	0.02011
Observations	5	5
Hypothesized Mean Difference	0	
df	8	
t Stat	-0.19476	
P(T<=t) one-tail	0.42522	
t Critical one-tail	1.85955	
P(T<=t) two-tail	0.85044	
t Critical two-tail	2.30600	

	<i>50ppm</i>	<i>300ppm</i>
Mean	0.69279	0.57868
Variance	0.01427	0.02093
Observations	5	5
Hypothesized Mean Difference	0	
df	8	
t Stat	1.36002	
P(T<=t) one-tail	0.10545	
t Critical one-tail	1.85955	
P(T<=t) two-tail	0.21091	
t Critical two-tail	2.30600	

	<i>50ppm</i>	<i>300ppm on/off</i>
Mean	0.69279	0.86044
Variance	0.01427	0.00008
Observations	5	4
Hypothesized Mean Difference	0	
df	4	
t Stat	-3.12749	
P(T<=t) one-tail	0.01764	
t Critical one-tail	2.13185	
P(T<=t) two-tail	0.03527	
t Critical two-tail	2.77645	

	<i>50ppm</i>	<i>300ppm 1.0</i>
Mean	0.69279	0.57606
Variance	0.01427	0.00633
Observations	5	5
Hypothesized Mean Difference	0	
df	7	
t Stat	1.81843	
P(T<=t) one-tail	0.05591	
t Critical one-tail	1.89458	
P(T<=t) two-tail	0.11183	
t Critical two-tail	2.36462	

	<i>100ppm</i>	<i>300ppm</i>
Mean	0.70894	0.57868
Variance	0.02011	0.02093
Observations	5	5
Hypothesized Mean Difference	0	
df	8	
t Stat	1.43778	
P(T<=t) one-tail	0.09422	
t Critical one-tail	1.85955	
P(T<=t) two-tail	0.18844	
t Critical two-tail	2.30600	

	<i>100ppm</i>	<i>300ppm on/off</i>
Mean	0.70894	0.86044
Variance	0.02011	0.00008
Observations	5	4
Hypothesized Mean Difference	0	
df	4	
t Stat	-2.38308	
P(T<=t) one-tail	0.03787	
t Critical one-tail	2.13185	
P(T<=t) two-tail	0.07573	
t Critical two-tail	2.77645	

	<i>100ppm</i>	<i>300ppm 1.0</i>
Mean	0.70894	0.57606
Variance	0.02011	0.00633
Observations	5	5
Hypothesized Mean Difference	0	
df	6	
t Stat	1.82717	
P(T<=t) one-tail	0.05872	
t Critical one-tail	1.94318	
P(T<=t) two-tail	0.11745	
t Critical two-tail	2.44691	

	300ppm	300ppm on/off
Mean	0.57868	0.86044
Variance	0.02093	0.00008
Observations	5	4
Hypothesized Mean Difference	0	
Df	4	
t Stat	-4.34468	
P(T<=t) one-tail	0.00610	
t Critical one-tail	2.13185	
P(T<=t) two-tail	0.01221	
t Critical two-tail	2.77645	

	300ppm	300ppm 1.0
Mean	0.57868	0.57606
Variance	0.02093	0.00633
Observations	5	5
Hypothesized Mean Difference	0	
df	6	
t Stat	0.03548	
P(T<=t) one-tail	0.48642	
t Critical one-tail	1.94318	
P(T<=t) two-tail	0.97284	
t Critical two-tail	2.44691	

	300ppm on/off	300ppm 1.0
Mean	0.86044	0.57606
Variance	0.00008	0.00633
Observations	4	5
Hypothesized Mean Difference	0	
Df	4	
t Stat	7.92780	
P(T<=t) one-tail	0.00069	
t Critical one-tail	2.13185	
P(T<=t) two-tail	0.00137	
t Critical two-tail	2.77645	

Correlation between the data trends

[H2O2]	Control	50mg/L	100mg/L	300mg/L	300mg/L on/off	300mg/L TNT1.0
Control	100%					
50mg/L	-58%	100%				
100mg/L	-67%	92%	100%			
300mg/L	-64%	94%	96%	100%		
300mg/L on/off	-7%	63%	55%	72%	100%	
300mg/L TNT1.0	-37%	89%	91%	93%	74%	100%

**D. Data for remediation to ECW produced in other experiments:**

Treatment time		TNT peaks	Concentration mg/L	Concentration ratio (C/C <sub>o</sub> )	DNT peaks	Concentration mg/L	Concentration ratio (C/C <sub>o</sub> )
		Area (uV*sec)			Area (uV*sec)		
0.0	min	1,244.00	0.040	100%	1,592.96	0.051	100%
5.0	min	1,137.98	0.037	91%	1,308.62	0.042	82%
15.0	min	902.88	0.029	73%	1,265.22	0.041	79%
25.0	min	981.17	0.032	79%	1,264.32	0.041	79%
35.0	min	1,016.49	0.033	82%	1,140.28	0.037	72%
45.0	min	1,021.49	0.033	82%	1,205.03	0.039	76%
55.0	min	931.54	0.030	75%	1,047.02	0.034	66%
Average			0.033		Average	0.040	
Std. Dev.			0.004		Std. Dev.	0.006	
initial – final			0.010		initial – final	0.017	

Treatment time		TNT peaks	Concentration mg/L	Concentration ratio (C/C <sub>o</sub> )	DNT peaks	Concentration mg/L	Concentration ratio (C/C <sub>o</sub> )
		Area (uV*sec)			Area (uV*sec)		
0.0	min	1,147.32	0.037	100%	1,498.18	0.048	100%
5.0	min	1,049.71	0.034	91%	1,148.88	0.037	77%
10.0	min	1,495.92	0.048	130%	1,390.12	0.045	93%
15.0	min	1,770.35	0.057	154%	1,306.55	0.042	87%
30.0	min	979.69	0.031	85%	1,251.04	0.040	84%
75.0	min	885.06	0.028	77%	1,306.85	0.042	87%
90.0	min	663.17	0.021	58%	1,180.77	0.038	79%
105.0	min	706.22	0.023	62%	1,282.34	0.041	86%
120.0	min	673.64	0.022	59%	1,262.17	0.041	84%
Average			0.033		Average	0.041	
Std. Dev.			0.012		Std. Dev.	0.003	
initial – final			0.015		initial – final	0.007	