

TREATMENT TRAIN WITH TIRE CRUMB RUBBER AND *CYPERUS HASPAN*: A NEW APPROACH FOR REMEDIATION OF EXPLOSIVES-CONTAINING WATER

by

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ABSTRACT

The objective of this work was to study the adsorption capacity of TNT and DNT by the use of tire crumb rubber (TCR) and the phytoremediation capacity of a native plant known as dwarf papyrus. Several batch and continuous-flow experiments were performed in order to study the treatment capacity of the tire crumb rubber and dwarf papyrus, individually and in combinations. Results showed that the TCR was capable of reducing the TNT and DNT concentrations in the water. For example, TNT was decreased in 24 hours from 7.6 to 0.18 ppm by adsorption to 15 g TCR. Smaller TCR sizes (mesh 30) decreased more explosives than bigger sizes (mesh 14–20). TCR adsorption of explosives was greater at a higher temperature (10 vs. 40 °C). However, pH did not play an important role in explosives adsorption to TCR. The explosives adsorption to TCR was slightly lower than that to granular activated carbon (GAC) in the early period of adsorption, but they were comparable at a longer adsorption time with a higher amount of adsorbents. For instance, after 24 hours, 25 g of GAC removed greater than 98% of TNT and DNT, whereas 25 g TCR removed 86.5% TNT and 89% DNT. But after 48 hours, 50 g GAC removed >99% of both explosives and 50 g TCR achieved 91 and 96% adsorption of TNT and DNT, respectively. Dwarf papyrus was able to reduce the explosives concentration without suffering adverse damage in its growth and development. For example, the TNT concentration decreased in a week by 53–97% depending on the initial TNT concentration at 0.5–10 ppm. TNT was mostly found in the roots, followed by the stems and the flowers. An in-series continuous-flow treatment train of TCR adsorption followed by dwarf papyrus phytoremediation was able to reduce TNT and DNT concentrations by approximately 52 and 50%, respectively. These results are expected to promote beneficiation of a solid waste TCR in environmental remediation in combination with green phytoremediation with dwarf papyrus.

RESUMEN

El objetivo de este trabajo fue estudiar la capacidad de adsorción de TNT y DNT mediante el uso de neumáticos triturados y la capacidad fitorremediativa de una planta nativa conocida como papiro enano. Diversos experimentos de lote y flujo continuo fueron realizados con el fin de estudiar la capacidad de tratamiento de los neumáticos triturados y el papiro enano, individualmente y en combinación. Los resultados mostraron que los neumáticos triturados son capaces de reducir las concentraciones de TNT y DNT en el agua. Por ejemplo, TNT se redujo en 24 horas de 7.6 a 0.18 ppm por la adsorción de 15 g de neumáticos triturados. Neumáticos triturados de menor tamaño (malla 30) redujeron más explosivos que los tamaños mayores (malla 14–20). La adsorción de explosivos por parte de los neumáticos triturados fue mayor a mayores temperaturas (10 vs. 40 °C). Sin embargo, el pH no fue un factor determinante en la adsorción de explosivos por los neumáticos triturados. La adsorción de explosivos por los neumáticos triturados fue ligeramente inferior que el carbón activado granulado temprano en el periodo de adsorción, pero eran comparables a tiempos de adsorción mayores y con mayor cantidad de adsorbente. Por ejemplo, después de 24 horas, 25 g de carbón activado granulado removió más de 98% de TNT y DNT, en cambio 25g de neumáticos triturados removieron 86.5% de TNT y 89% de DNT. Pero después de 48 horas, 50 g de carbón activado granulado removió >99% de ambos explosivos y 50 g de neumáticos triturados alcanzaron 91% y 96% de adsorción de TNT y DNT, respectivamente. El papiro enano fue capaz de reducir la concentración de los explosivos sin sufrir daños adversos a su crecimiento y desarrollo. Por ejemplo, la concentración del TNT disminuyó en una semana por 53–97% dependiendo de la concentración inicial del TNT a 0.5–10 ppm. TNT se encontró mayormente en las raíces, seguido por los tallos y flores. Un tren de tratamiento en serie de flujo continuo de adsorción por

neumático triturado seguido por la fitorremediación del papiro enano fue capaz de reducir las concentraciones de TNT y DNT por aproximadamente 52 y 50%, respectivamente. Estos resultados se esperan promuevan el beneficio de un desperdicio sólido como lo son los neumáticos triturados en la remediación ambiental en combinación con la eco-amigable fitorremediación del papiro enano.

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LIST OF ABBREVIATIONS

ACN	Acetonitrile
ACS	American Chemical Society
AOPs	Advance Oxidation Processes
ASCE	American Society of Civil Engineering
BOD ₅	Biological Oxygen Demand (5-day)
COD	Chemical Oxygen Demand
CR	Crumb Rubber
DEGDN	Diethylene Glycol Dinitrate
DI	Deionized Water
DNB	Dinitrobenzene
DNT	Dinitrotoluene
DoD	Department of Defense
ECW	Explosives Containing Water
EEL	Environmental Engineering Laboratory
EPA	Environmental Protection Agency
GAC	Granular Activated Carbon
g/L	Grams Per Liter
HMX	High Melting Explosive
HPLC	High Performance Liquid Chromatography
M	Molar (concentration)
MCL	Maximum Contaminant Level
MeOH	Methanol
mg	Milligrams

mg/L	Milligrams Per Liter
Mm	Millimeters
Nm	Nanometers
NO _x	Nitrogen Oxides
NPL	National Priorities List
PETN	Pentaerythrite Tetranitrate
ppm	Parts Per Million
RDX	Royal Demolition Explosive
REMA	Rubber Recycling and Manufacturing, Inc.
RMA	Rubber Manufacturers Association
rpm	Revolutions Per Minute
TCR	Tire Crumb Rubber
TDF	Tire Derived Fuels
TNT	Trinitrotoluene
TT	Treatment Train
UPRM	University Puerto Rico - Mayagüez Campus
UXO	Unexploded Ordnance
μL	Micro Liter
μm	Micro Meter
μS/cm	Micro Siemens Per Centimeter

1 INTRODUCTION

Military practices and munitions development have led to an increase in the use of explosives or explosives derived materials. Although explosives such as TNT and DNT are not currently used in these activities, sites where they were used in the past impose a potential hazard to humans and the environment. To humans, at higher concentrations and/or prolonged exposure periods, the explosives can lead to severe health problems. Environmental problems at sites identified as polluted by these explosives are directly associated to high concentration of explosives found in soil and water (Rodgers & Bunce, 2001).

1.1 Justification

There is a worldwide concern for the loss of our natural resources due to the environmental pollution caused by human activities and the direct implications it may have on the humans who have been exposed to the pollutants. Resources such as water, air, and soil have been the most affected by different types of pollutants which include heavy metals, volatile organic compounds, pesticides, radioactive materials, and explosives. Most of them have been classified as hazardous compounds due to their adverse effect on the human health and ecosystems (Lima et al., 2011).

As mentioned earlier, explosives are one of the materials classified as hazardous compounds due to their associated hazard. Explosives have been present in human history for many centuries, however, in the past 100 years their use and study have increased. One of the main characteristics of the explosives is the nitro groups that many of them contain as part of their chemical structure. Among the explosives with nitro groups in their chemical structures are

the following ones: trinitrotoluene (2,4,6–TNT), dinitrotoluene (2,4–DNT and 2,6–DNT) and dinitrobenzene (DNB). Particularly, TNT for many decades was the one most commonly used by the explosives industry. Its production, testing, and use have been the major factors for their prominence in the environment. Furthermore, facilities designated to the creation and production of explosives, artillery ranges, military open field practices, ordnance disposal sites, and demilitarization activities are among the most common and known sources of explosives that could lead to environmental pollution. The contamination with TNT and other explosives as a consequence of the aforementioned activities has been found in environmental resources such as soil, surface water and groundwater. The Department of Defense (DoD) has identified many sites contaminated with explosives around the United States as well as on other territories. They have identified and recorded the presence of explosives in the groundwater, sediments, soil and the surface water at the different sites investigated. The distribution percentages of explosives found in the groundwater, sediments, soils and surface water are 5.41, 3.37, 4.98 and 5.44%, respectively (EPA, 2004).

There are several risks associated with the exposure to sites contaminated with explosives. Among them is the toxicity of the nitro aromatic explosives and the byproducts to which they are transformed when exposed to the environment. One of the major concerns arisen by the exposure to the environment is that they decompose or degrade to substances such as hydroxilamines and aromatic amines that are proven to be carcinogens (Rodgers & Bunce, 2001). Based on this, the Environmental Protection Agency (EPA) has DNT in their Priority Pollutants List, which is a list that contains about 126 pollutants considered hazardous to

humans. The two forms of DNT, 2,4-DNT and 2,6-DNT are included in this list at the numbers 35 and 36, respectively (EPA, 2010a).

Over the time, several technologies have been developed for the removal and/or treatment of sites contaminated with explosives. One of the technologies that have been used for the removal of explosives is incineration of the contaminated soils. This technique, although it removes the pollutant from the soil, has the disadvantages that also produces harmful gases as a result of the incineration process and leaves the treated soil deteriorated and barren.

Another commonly used technology is the adsorption of explosives, a technique that involves the use of a material that enables the separation of a pollutant from the contaminated site. For the removal of explosives in water and soil, activated carbon has been the most common material used in the application of adsorption technique.

Explosives have also been removed by a technology known as advanced oxidation processes (AOPs). This technology consists of the addition of an agent that oxidizes and decompose the contaminant of interest into less harmful substances.

Last but not least, ecological technologies have also been used to remove and/or treat explosives. In this technology, living organisms are used for the removal of explosives from the soil and water. For example, bacteria and microorganisms are added to the contaminated site to degrade the contaminants or promote the activity of other bacteria or microorganisms capable of degrading the contaminants in a technique called bioremediation. Moreover, the phytoremediation technique involves the use of plants to either accumulate, transform the

pollutant in various parts (flowers, stems, leaves and roots) or promote bacterial activity in the root zone (Rodgers & Bunce, 2001).

Nevertheless, a combination of the technologies mentioned above promises to be a cost effective alternative for remediation of the sites contaminated with explosives. Therefore, we decided to combine the adsorption and phytoremediation technologies. For the adsorption technology, tire crumb rubber (TCR) took the place of the activated carbon as an absorbent media. And for the phytoremediation technology, the plant selected was the dwarf papyrus (*Cyperus haspan*).

The selection of the TCR was based primarily on factors such as the abundance of waste tires in the solid waste stream, their biodegradation rate and the main components of the tires. By 2003, in the United States an estimated 290 millions of scrap tires were generated and only about a 9.3% (27 millions) ended in the landfills. Fortunately, 85% of the scrap tires were either reused or recycled (EPA, 2010b). The estimated biodegradation time for a tire after it is dumped in a landfill is for 500 to 3,000 years. Due to this slow process, the scrap tires represent two major concerns; pests and fires. The curved shape of the tires allows rainwater to be collected in their interior, creating an ideal habitat for pests (rodents and mosquitoes). The tires stockpiles are prone to retain heat which can ignite and create fires that liberate unhealthy smoke and toxic oils (EPA, 2010b). Regarding the tire's components, carbon black is one of the major components (RMA, 2011). Carbon black is pure elemental carbon (97%) in the form of colloidal particles that are produced by incomplete combustion or thermal decomposition of gaseous or liquid hydrocarbons under controlled conditions (International Carbon Black Association, 2006). This is the main reason why TCR is expected to readily adsorb contaminants such as explosives.

On the other hand, for many years different plants have been studied and used by the field of phytoremediation to remediate explosives contaminated sites. Furthermore, in order to remove, degrade or promote bacterial activity in the root zone; phytoextraction, phytodegradation or phytostabilization are used. Plants such as the kidney bean (*Phaseolus vulgaris*), parrot feather (*Myriophyllum aquaticum*), and alfalfa (*Medicago sativa*) have been previously used for the removal of explosives in both soil and water. Also, for the removal of heavy metals and other contaminants present in water, water lettuce (*Pistia stratiotes*), a type of floating aquatic plant, has been used in constructed wetlands (Gerhart et al., 2009). To the best of our knowledge, there are no reports in the literature suggesting the use of dwarf papyrus (*Cyperus haspan*) for the remediation of sites contaminated with explosives.

Both, the tire crumb rubber and the dwarf papyrus, showed characteristics and properties that make them excellent candidates in a treatment train (TT) for the removal of explosives in water. It will depend on the success of the experiments and the results obtained in order to recommend this combination and TT for removal of explosives and other contaminants in the water. For waste tires, this would represent a new reutilization approach of solid waste management in the environmental remediation field and, for the dwarf papyrus, it will expand the utilization of the *Cyperus* genus in the green remediation of pollutants. At the same time, this effort would help to preserve our resources and the environment as well.

1.2 Scope

Over the past decades, different technologies for remediation of sites contaminated with explosives have been studied and proved. But still there is a need for the development of new technologies and also the implementation of new materials in the task of remediating

contaminated sites. A wide range of discarded materials can be reused to remediate current and future environmental issues. But research is essential in order to prove the feasibility of the materials and associated methods in the remediation of contaminated sites.

The main goal of this research was to study the feasibility to reutilize scrap tires in the form of tire crumb rubber and to also use plants, such as dwarf papyrus, for remediation of water contaminated with explosives, specifically, TNT and DNT. The advantages and disadvantages of combining the adsorption capacity of the tire crumb rubber and the phytoremediation ability of the dwarf papyrus were evaluated in relation to their impact on the environmental quality of a contaminated site.

1.3 Objectives

To meet the aforementioned goal, a series of experiments were conducted to:

- Determine the explosives adsorption capacity by the TCR under different conditions or parameters;
- Compare the adsorption capacity of tire crumb rubber with granular activated carbon, the most common and effective material for water treatment by adsorption;
- Determine the extent of explosives remediation that can be achieved by the dwarf papyrus; and
- Analyze different configurations and combinations of the TT with TCR and dwarf papyrus in order to achieve the greatest remediation efficiency of explosives and, at the same time, to maximize waste reutilization rate.

2 LITERATURE REVIEW

In the following section, several researches and efforts previously done related to the remediation of explosives containing water (ECW) are described. Different topics and basic concepts are discussed in detail, with respect to explosives, adsorption, tire crumb rubber, bioremediation and remediation of explosives containing water.

2.1 Explosives

An explosive can be defined as a chemical material that, under the influence of mechanical or thermal shock, decomposes rapidly with the evolution of large amounts of heat and gas. Explosives can be classified as either low or high explosive, based on their explosion velocity. Low explosives are characterized by lower combustion rates and large production of controllable gases, while high explosives decompose almost instantaneously after a blast or shock (EPA, 2005). Throughout human history different types of explosives have been developed and used.

The earliest known explosive mixture is black powder, which is a mixture of potassium nitrate, sulfur and powdered charcoal. It was usually used as an explosive itself and as propellant. Later, Alfred Nobel prepared nitroglycerine and used it as an explosive in 1864, but due to its instability, safe to handle and detonating, a new material was required to be developed. By mixing the nitroglycerine with an absorbent and the use of a mercury fulminate detonator, the dynamite was developed (EPA, 2005).

But it was during the World War I and II when 2,4,6-TNT was developed, manufactured and used. It was used at the greatest scale during World War II. Furthermore, during these wars

and the time between them, other explosives were also developed. The list includes: Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) also known as Royal Demolition eXplosive, pentaerythrite tetranitrate (PETN), Diethylene glycol dinitrate (DEGDN), lead styphnate, lead azide, pentolite, diazodinitrophenol, Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) also known as High Melting eXplosive, tetrytol, picratol, cycotols, tritonal, torpex and minol. Most of these explosives are mixtures of different explosives or a combination of them at different ratios. Although, many explosives were developed, due to their performance and manufacture costs, TNT, RDX and HMX were the explosives mainly used (EPA, 2005).

Explosives have been used in wars, military activities and munitions development. Water and soils of the sites where they were used, may be polluted or may be classified as contaminated sites. The contamination sources could be low-order detonations, deterioration of the Unexploded Ordnance (UXO) containers, leaching of munitions constituents, residual propellants and open burning and detonation, which disperse the material through the soil (EPA, 2005).

Explosives in the soil usually move by dispersion from zones at which they are at higher concentrations to zones at lower concentrations. When the contaminants are in the soils they are usually washed out by precipitation, percolation and surface runoff. These events, move contaminants either to other nearby unpolluted soils, surface water and groundwater, or if the site is already polluted, the concentration of the pollutants in the site may increase. The environmental fate of the explosives can be attributed mainly to three chemical properties such as: molecular structure, water solubility and adsorption to soil particles (Thiboutot et al., 2002). Also, chemical fixation can affect the availability of explosives in the soil, where they are subject

to metabolic transformations, catalytic degradation, and biodegradation processes (Lima et al., 2011). For example, TNT tends to degrade by photolysis, while RDX and HMX do not, also TNT is adsorbed better to soils such as clay than other explosives; the results depend on the solubility of explosives (Thiboutot et al., 2002). Contaminated sites (soil and water) represent a thread to the environment and humans as well.

Explosives, as mentioned earlier may have impacts on both the ecology and the human health. When explosives are present in the ecosystem they may cause disturbances to the habitat and may also promote the development of health and behavioral problems in the exposed receptors. Their effects depend on the concentration of the explosives and the pathways by which the receptors became exposed. Some of the effects and toxicity on the ecology for some of the major explosives are described in Table 1 (EPA, 2005).

Table 1 Toxicity and Effects on the Ecology for the Major Explosives

Explosive	Ecological Toxicity/Effect
TNT	Can be taken up by a variety of plants (terrestrial, aquatic, wetland, trees). In animals serious effects in reproductive systems, ataxia, tremors, mild convulsions.
RDX	It is not bioaccumulated in crops or cattle. Can be up taken by plants and therefore be of potential exposure to herbivorous wildlife.
HMX	It has not been determined if it is present in tissues of humans, animals or plants living in or near areas contaminated with this explosive.
DNT (2,4–Dinitrotoluene)	Transferred to plants by roots uptake. Animals showed lower number of sperm count and reduction in fertility, also reduction in red blood cells, nervous system disorders, liver cancer and, liver and kidney damage.
DNT (2,6–Dinitrotoluene)	Shows the same effects as 2,4–Dinitrotoluene on biota.

To humans, the exposition to explosives may lead to different effects. As for the ecosystem, the effects on humans will depend on the concentration, pathways of exposure and also exposition time. Moreover, depending on the explosives present, the effects on humans varies. Table 2 depicts the main explosives used and found in contaminated sites and their potential toxicity and effects on humans (EPA, 2005).

Table 2 Toxicity and Effects of the Major Explosives on Human Health

Explosive	Human Toxicity/Effect
TNT	Human carcinogen (possible), targets liver, skin irritations, cataracts.
RDX	Human carcinogen (possible), prostate and/or nervous system problems, nausea, vomiting. Potential organ damage (laboratory exposure to animals).
HMX	Potential liver and central nervous system damage (laboratory exposure to animals).
DNT (2, 4–Dinitrotoluene)	Exposure can cause methemoglobinemia, anemia, leukopenia, liver necrosis, vertigo, fatigue, dizziness, weakness, nausea, vomiting, dyspnea, arthralgia, insomnia, tremor, paralysis, unconsciousness, chest pain, shortness of breath, palpitations, anorexia, and loss of weight.
DNT (2,6–Dinitrotoluene)	Exposure can cause methemoglobinemia, anemia, leukopenia, and liver necrosis.

The explosives themselves when managed and discarded appropriately does not represent a risk to either the environment neither the humans. Hazardous environments are present when the concentration or the presence of the contaminants in a site is higher than what nature can handle by itself, therefore the ecology and the humans are directly or indirectly exposed to them. Different techniques or approaches have been developed and studied for the treatment and/or removal of contaminants such as explosives in the environment. Some of them are described in the following sections.

2.2 Adsorption

Adsorption is a process in which substances in an aqueous solution are removed by their deposition or attachment on another surface. A process which should not be mistaken with absorption, since it is a physical treatment where the adsorbate (substance of interest) moves from the solution in which it is present to the adsorbent (material where the substance of interest gets attached to its surface). Figure 1 exemplifies the adsorption process of an adsorbate in a substance (shown in red) in a solution by an adsorbent (shown in gray).

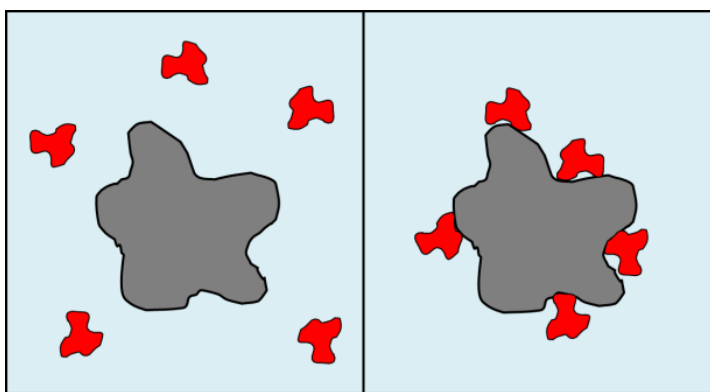


Figure 1 Adsorption Process Schematic

There are several important characteristics which an adsorbent should have in order to make its use more efficient, these characteristics are: size, amount, surface area, shape, porosity and polarity, among others. The first three characteristics are related since in a defined volume, a smaller size adsorbent will require more material to fill the space, therefore more surface area will be exposed to the adsorbate. The opposite will occur if, for the same volume, a bigger size adsorbent is used.

Regarding the shape of the adsorbent, regular shape adsorbents will tend to accommodate or arrange in a way that gaps may be present between the adsorbents, therefore decreasing the amount of surface area available for contact with the adsorbate. On the other hand, irregular

shape adsorbents will be clustered in a way that the gaps between them will decreased and more adsorbents will have more surface area exposed.

The porosity that an adsorbent shows will also have an effect on its ability to adsorb the adsorbate of concern. An increase in porosity will increase the chances on an adsorbate to be adsorbed. The pores present will allow more adsorbate to accumulate in and between them.

Regarding the polarity, adsorbents and adsorbates with similar polarities, either polar or nonpolar, will tend to interact better with each other due to their intermolecular forces and affinity than the ones with opposite polarities.

Almost any material can be used as an adsorbent, but there are several materials which are frequently used as adsorbents: activated carbon, polymers, and synthetic polymers and silica-based, among others (Tchobanoglous et al., 2003). Among them, the activated carbon is the most commonly used adsorbent material and it is typically made from hard woods, coconut shells, fruit stones, coals or synthetic macromolecular systems, among others. In order to transform the material into activated carbon, the material is processed in order to increase its porosity by either thermal (gasification of carbon atoms) or chemical activation (usually using phosphoric acid) (Marsh & Rodriquez-Reinoso, 2006). The increase in the material porosity allows substances to get deposited or attached onto the surface or between pores of the material no matter if the substances are in continuous movement or stagnant (Tchobanoglous et al., 2003).

A wide variety of materials have been used and studied as adsorbents for the removal of different adsorbates mostly present in water and gases. In aqueous solutions, phenolic compounds have been treated by the use of activated carbon as the adsorbent material

(Dabrowski et al., 2005). Activated carbon has also been studied as an adsorbent material for the treatment of nitrates from wastewater (Nunell et al., 2012). Kaolinite, a very common mineral had being used as a adsorbent material for the removal of Rhodamine B dye from aqueous solutions (Khan et al., 2012). Additionally, wastewater adsorbents such as lignite, peat, pith, lignite char, wood, alumina and silica have been used for the removal of different pollutants in (McKay, 1995). In the air, gases such as nitrogen (N₂), methane (CH₄), carbon monoxide (CO) and carbon dioxide (CO₂) have been treated with carbon nanotubes (Lithoxoos et al., 2010).

2.3 Tire Crumb Rubber

Worldwide, millions of tires are used daily in all human activities and as a result, millions of tires are discarded yearly. In the United States approximately 290 million of tires were discarded and stockpiled in 2003 (EPA, 2010c). Efforts have been made to reduce the number of stockpiled tires and by the end of 2007, about 128 millions of tires remained stockpiled, a reduction of approximately 56.0% (RMA, 2009). Nowadays, approximately over 75.0% of the scrap tires are either reused or recycled in the United States (EPA, 2012a). In Puerto Rico, it is estimated that 4.7 millions tires are discarded annually (approximately, 18,000 daily) (LexJuris, 2011). Since the average weight of a scrap tire is about 22.5 lbs (RMA, 2011), the amount of weight discarded in Puerto Rico is estimated to be 528,750 tons representing 14.7% of the annual measured weight discarded in Puerto Rico landfills (ADS, 2011a). Only 13.0% (800,000 scrap tires) of the scrap tires discarded are recycled or reused (LexJuris, 2012). Although, there is an evident trend in the reduction of tire stockpiles, still the numbers represent an environmental hazard due to the characteristics of the tires themselves and the implications tire stockpiles bring.

Tires are made of a mixture of different materials. A typical tire consists of the following materials: synthetic and natural rubber, sulfur and sulfur compounds, silica, oils, phenolic resins, fabrics, petroleum waxes, pigments, fatty acids, carbon black, steel wires and other inert materials (RMA, 2011). In the materials section, these components are presented with their respective typical percentages of composition by tire (Table 4).

Due to the amount of materials and their complex composition, the estimated biodegradation time for scrap tires in the environment (landfills) ranges from 500 to 3,000 years (EPA, 2010b). The slow biodegradation time of the tires raises health and environmental concerns, such as possible pests and fires. Pests, like mosquitoes and rodents may live in tire stock piles. The stagnant water collected inside the tires mainly due to rainfall events serves as a breeding place for mosquitoes which may carry diseases such as dengue, yellow fever, West Nile virus, malaria and encephalitis (EPA, 2010c). In the case of fires, the ones generated by burning tires are hard to extinguish, usually burn for long periods and release a thick black smoke and an oily residue to the environment (EPA, 2010b). The effects tend to increase when water is applied to the burning tires since soil, surface water and groundwater can be potentially contaminated with toxic emissions from tires, such as sulfuric acid and gaseous nitric acid (EPA, 2010c). Beside the concerns that tire stock piles raise, new techniques, methods and processes are being developed in order to decrease the presence of tires in the environment, which leads to the development of a scrap tires market.

There is a market for the scrap tires in the United States and other parts of the World. The tires market uses the scrap tires in a variety of productive and environmentally friendly applications. There are different divisions in which the tires market concentrates their efforts for

the reuse of scrap tires. These divisions are: the fuels derived from the tires (TDF), the ones specialized in civil engineering applications and the ones that used ground or crumb rubber for the development of products and applications (EPA, 2010d). Scrap tires are used as fuel derivatives due to their high heating value. The TDFs present the following advantages: same production of energy as oil and 25% higher than coal, residues contain less heavy metals than some coals and the emissions of NO_x (nitrogen oxides) are lower than some coals (EPA, 2010e). In the practice, there are being used by industries such as in the cement kilns (26.9%), paper and pulp industry (42.9%), electric utilities (13.8%), and boilers and tire-to-energy facilities (16.3%).

In the civil engineering field, the scrap tires are used mostly for the replacement or complementation of typical construction materials. Civil engineering applications such as landfill construction and operational applications (cap closures, gas venting systems, alternative daily cover, leachate collection systems and operational layers), drainage for septic systems, subgrade fill and embankments, backfill for walls and bridge abutments, subgrade insulation for roads, vibration dampening layers and baled tires, among others, have used scrap tires in many ways (EPA, 2010f). The industry of crumb or ground rubbers uses the scrap tires to either create new products or surfaces as well as to improve the properties of surfaces. In the United States the most common applications for the ground rubbers are the automotive industry (9%), molded, extruded products (37%), sports surfacing (27%), play grounds, mulch, animal bedding (9%), asphalt (9%) and exportation (9%) (EPA, 2010d).

As mentioned above, there are different industries and diverse applications for the scrap tires. The scrap tires industry still has space for the implementation of new applications for the scrap tires that are discarded in landfills as shown below in Figure 2, this shows the distribution

of the scrap tire used by the industry and the percentage of scrap tires that ended in the landfills in the United States in 2003 (EPA, 2010b).

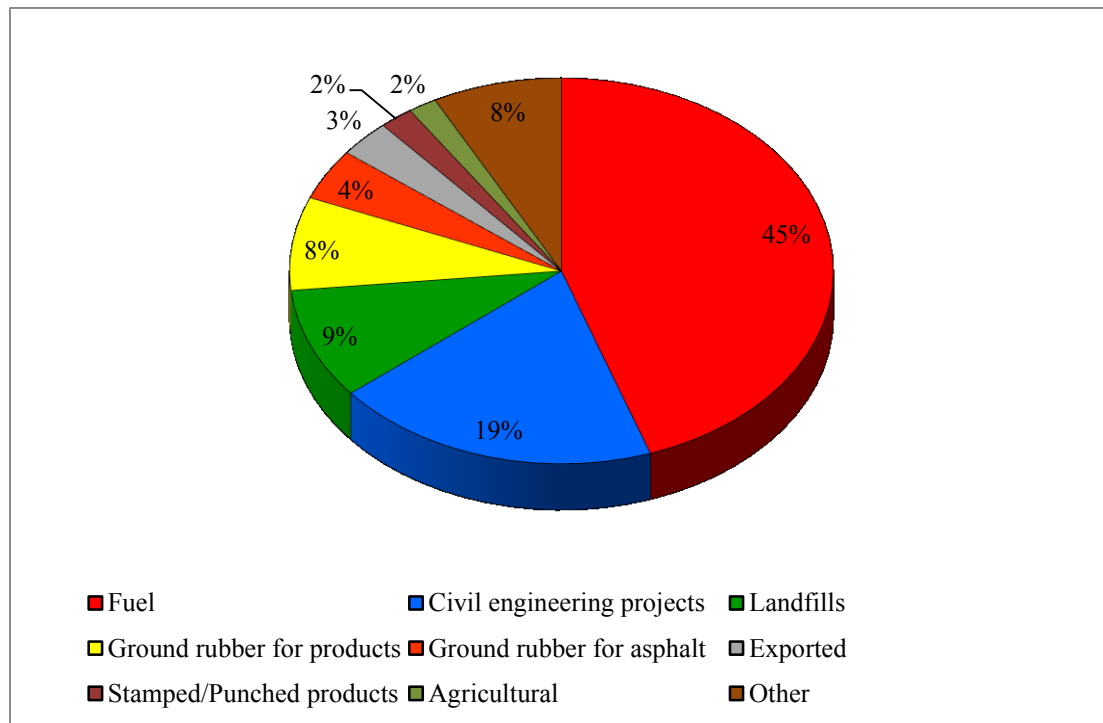


Figure 2 Scrap Tire Uses and Distribution in the US

In Puerto Rico, there are industries and individuals dedicated to the reuse and the recycling of scrap tires. Playgrounds floor mats, recreational and sport facilities have used the recycled scrap tire produced in Puerto Rico. In schools such as Escuela Agustín Arroyo in Jayuya, they have used scrap tires as flowers pots and as protection from lawn mowers. Also in a farm in Jayuya, Finca Armonía, the scrap tires were used in the construction of dirt roads and retention walls (piles of soil filled tires stacked all together) (ADS, 2011b). As safety and sound barriers, the scrap tires have been used in the El Tuque racing track facility in Ponce and alongside Expreso De Diego and Expreso Luis A. Ferré, respectively (ADS, 2011b).

Some of the uses and applications of the scrap tires need processing of the tires. The processing of the scrap tires is the same regardless of the type of final products. The process starts with the positioning of the tires in machine for the removal of the steel bracing and later for its shredding. Further shredding and sieving will depend upon the requirements of the materials to be made with the scrap tires. The classification of the scrap tires used is based on their size. Tire shreds are sized between 50 and 300mm, usually with a rectangular or square shape. Tire chips are sized between 12 and 50 mm with the same shape as the shreds. Ground and crumb rubber are sized from 19 to 0.15 mm and from 4.75 to 0.075 mm with an irregular shape (Moo-Young et al., 2003).

Figure 3 represents scrap tires the processing, to prepare them for a new product or application. The diagram also shows some of the materials and final applications where either the tires as a whole unit or shredded (shred, chips, ground or crumb) are used.

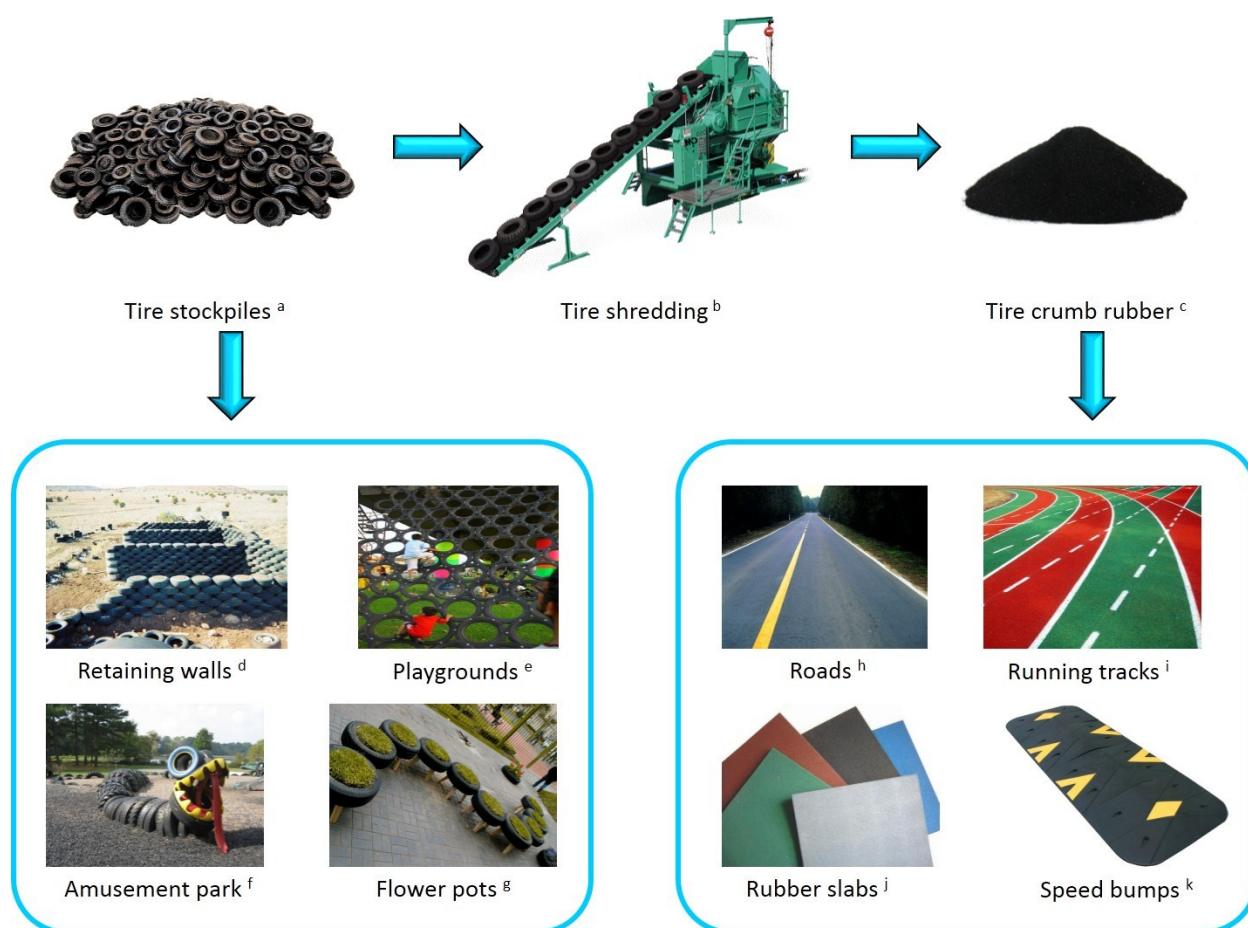


Figure 3 Schematic of the Scrap Tires Processing and Final Products

a, b, c, d, e, f, g, h, i, j, k The following pictures were taken from the following websites: sceneryunlimited.net, cmtirerecyclingequipment.com, tradekeyindia.com, squidoo.com, lisastown.com, www.menv.com, architecture-view.com, tireshare.biz, my.qoop.com, recycling-tires.com, materialflow.com, respectively.

One new application for which the scrap tires are being used is the treatment of water, usually contaminated water, or to improve the water quality prior to advanced treatment processes. Different experiments have been conducted in order to understand the effects of shredded tires in the water quality. When tires were placed below the water table in a four year field study some water quality parameters increased whereas others decreased. The concentration of metals such as iron, manganese, zinc and chromium in water increased, but the concentration of metals such as arsenic, barium, cadmium, copper, silver, aluminum and sodium

either remained constant or decreased when exposed to crumb tire (Humphrey & Katz, 2001). Also tire shreds appeared to release volatile organic compounds such as dichloroethene, benzene, dichloroethane, 4-methyl-2-pentanone, acetone, 1,1,1-trichloroethane, 1,1-dichloroethene, xylenes, toluene, trichloroethene, 2-butanone, and chloroethane but most of their concentrations were below the drinking water standards. Tire shreds also appeared to release trace amounts of semi volatile organics such as aniline, phenol, benzoic acid, and N-nitrosodiphenylamine (Humphrey & Katz, 2001).

The same group of researchers conducted another field experiment with the tire shreds being placed above the water table. The experiment ran for 5 years and water quality parameters of pH, total and dissolved solids, chemical oxygen demand (COD), biological oxygen demand (BOD₅), metals and organic compounds were measured. Values for pH remained constant ranging from 6 to 8, dissolved and total solids had values no higher than 3,000 ppm and COD and BOD₅ reported values that ranged from 0 to 600 ppm and 0 to 3 ppm, respectively (Humphrey & Katz, 2000). In case of the metals a clear reduction was seen in the concentration of iron. And for organic compounds and volatile organic compounds, all the values appeared below the detection limit (Humphrey & Katz, 2000). These studies suggest that tire shreds have no relevant effect on the water quality and that the removal of some metals is possible due to the presence of the tire shreds.

Particular contaminants which are of concern in water have been studied for their removal. Petroleum derivatives such as toluene and xylene were analyzed when present in water and exposed to crumb rubber. The removal of both components from the water was associated with two different sorption mechanisms: one was most likely to be exhibited by carbonaceous

sorbents (carbon black) and the other showed a linear pattern (styrene-butadiene polymer) (Alamo et al., 2011). In their research they found that, for aqueous solutions of toluene and xylene at an initial concentration of 50 ppm, in 30 minutes of exposure the removal percentage was 60 and 81%, respectively. They also measured heavy metals concentrations and they were either not present or if present, their values were below the EPA's maximum contaminant levels (MCL) (Alamo et al., 2011).

In another research made by the same group of researches, the tire crumb rubber removal capacity was analyzed for copper (Cu-II) in aqueous solutions. Their experiments confirmed that adsorption depended on pH, contact time and initial concentration. The best copper removal was achieved at pH 6 and with increasing the contact time, the percentage of removal increased until 72 hours when the system seemed to achieve equilibrium (Calisir et al., 2009). The variation in the initial concentrations showed that at lower initial concentrations the percentage of removal at 72 hours was higher, for example at 1 and 50 ppm the percentage of removal obtained were 99.8 and 33.0%, respectively (Calisir et al., 2009).

The use of crumb rubber as a filtration media was analyzed by Tang et al. (2006). In their research they evaluated the use of crumb rubber for the filtration of ballast water. Variables such as turbidity, particle number, phytoplankton and zooplankton were investigated and the results showed that crumb rubber was able to remove each of them. The highest percentages of removal achieved for turbidity and particle number were 42 and 46%, respectively. For phytoplankton and zooplankton the average removal were 58 and 50%, respectively (Tang et al., 2006). Variables like media size, filter depth and filtration rate were also analyzed, but only the

media size had a significant impact on the removal of the parameters mentioned before. A better removal was achieved with a smaller size media (Tang et al., 2009).

For either filtration or removal of contaminants in water and for improvement of water quality, TCR has proven to work well. The fact that no harmful materials are added to water when exposed to TCR and that added materials are below the EPAs MCL makes the TCR more feasible for water treatment. Finding that TCR was able to remove toluene from water opens the possibility of reduction of TNT and DNT due to the presence of toluene in their chemical structures.

2.4 Bioremediation

Bioremediation can be defined as an in-situ or ex-situ treatment method, where a biological organism is applied for the remediation of pollutants. The most common organisms used in bioremediation treatments are bacteria, fungi and plants. The technique relies on the natural processes and behavior of the organism to achieve the desired goal. Due to the nature of the processes, the techniques although slow when compared to engineering techniques it is typically less expensive than other engineering treatment methods (Rodgers & Bunce, 2001; Dillewijn et al., 2007; Rylott & Bruce, 2008).

For every remediation project, the first step is the site characterization. The site characterization consists primarily of the site survey, evaluation of components, and status of contamination. Based on the information gathered, all the possible treatment technologies are proposed and if a bioremediation treatment is selected, all the biological information available is used in order to remediate the site. Among the common biological information collected at the site are the bacteria, fungi, and plants that lived, continue living and developing in soil or water

at the contaminated site. If there are none of them present due to the contaminants, then addition of microorganisms could be considered. Most of the time, the first microorganisms used are those that are known to be at the site since they have been acclimated to the pollutants levels. Addition of new microorganisms to a site requires extensive research on the site characteristics and also research on other microorganisms known to treat the contaminants of concern.

The main reasons for the addition of microorganisms into polluted sites are: the conversion of pollutants in less harmful substances, direct removal of pollutants, promotion of the mobility of the pollutants and also enhancement of the properties and characteristics of the in situ microorganisms (Rylott & Bruce, 2008; Glick, 2003).

As mentioned earlier, plants are one of the organisms used by the bioremediation field. When plants are used for the treatment of contaminants the treatment is known as phytoremediation. This treatment relies on the plants natural growth process for the remediation of pollutants. The contaminants are remediated in different ways when a phytoremediation technique is applied. Contaminants are either fixed to the soil or uptaken by the plant. When the contaminants are fixed to the soil they are either immobilized (therefore not more fate and transport of the contaminant could be possible) or the contaminants are directly attenuated in the soil.

If the contaminants are uptaken by the plant, their concentration in the soil will decrease and the contaminant will be located within the plants tissues. The most common locations for the up taken contaminants are the roots, stems, and leaves; the flowers, seeds and fruits are not the preferred locations for the contaminants. What happens with the pollutants once they enter the plant will depend on the mechanism of action. The most common mechanisms with a brief

description and way of clean up are summarized in Table 3 and mechanisms and their target tissues in the principal parts of a plant are depicted in Figure 4.

Table 3 Phytoremediation Mechanisms, Description and Clean Up Method

Phytoremediation Mechanisms	Description	Clean Up Method
Phytosequestration Phytostabilization	Relies on the abilities of plants to immobilized contaminants present in the soil into the rhizosphere by the exudation phytochemicals and/or on the roots by transport proteins and cellular processes.	Remediation by Inhibition
Rhizodegradation Rhizofiltration	Relies on the phytochemicals exudates from the roots to enhance the microbial activity in the rhizosphere and/or the direct removal of contaminants from soil or water due to direct exposition and contact between the contaminant and the roots.	Remediation by Destruction (Root)
Phytohydraulics	Relies on the plants water absorption capacity and its subsequent evaporation which restrains the pollutant transport.	Remediation by Inhibition due to Hydrologic Control
Phytoextraction	Relies on the nutrients, metals and contaminants plants uptake ability and their subsequent translocation and storage in the plants tissue by transpiration.	Remediation by Plant Up take
Phytodegradation	Relies on the plant contaminant breakdown ability by enzymes, photosynthetic processes and reduction.	Remediation by Destruction (Plant)
Phytovolatilization	Relies on the absorption and liberation capacity of plants by which contaminants are exudated from the plant by natural transpiration. The contaminants do not suffer any changes while it moves from soil or water to the air.	Remediation through Plants Tissue

Sources: (Raskin & Ensley, 2000; Kvesitadze et al., 2006; EPA, 2012b)

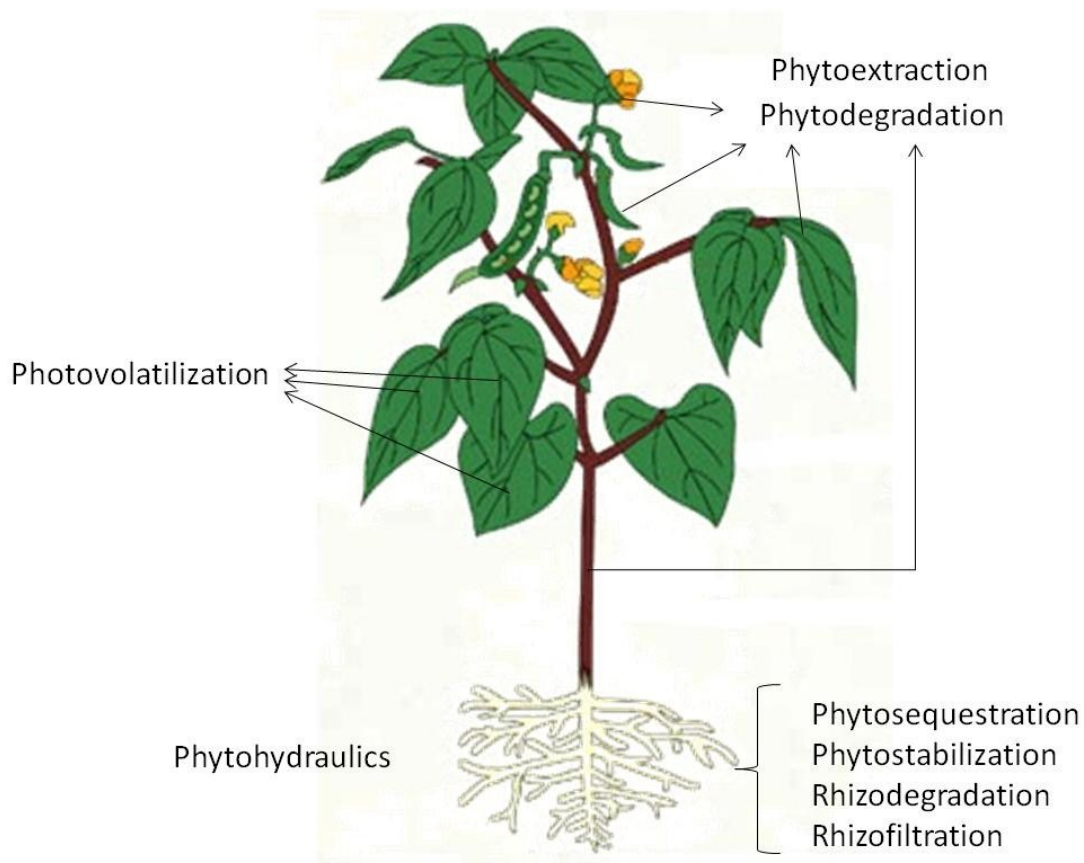


Figure 4 Phytoremediation Mechanisms and Target Plant Parts
Source: (infovisual.info)

The mechanisms mentioned before are not better than the others. Their implementation and effectiveness depend on many factors but mainly on what the contaminants are and how they are present in either soil or water. The other important parameter is the cleanup goal required or to be achieved by the application of a phytoremediation process. When phytoremediation techniques are applied most of these mechanisms are combined since these are naturally occurring processes in the plants. There are several factors which have effects on the phytoremediation of contaminants: contaminant availability, toxicity and solubility. Regarding to its availability, if the contaminant is located too deep in the soil, phytoremediation may not be

possible since it relies on the number and length of the roots as well as their extraction capacity. One of the most common trees used in phytoremediation treatments of contaminants located deep in the soil are the poplar trees (*Populus sp.*) whose roots are long enough to reach contaminants present deep in the soil (Kvesitadze et al., 2006). Higher toxicity levels present a threat to this technique since it may kill the plants or simply stop their development, therefore, eliminating the remediation possibility. Contaminants' water solubility is also important because less soluble compounds will prefer to stay in the soil than to travel along with the water, and also because highly water soluble compounds will travel faster. Contaminated water can be also treated by some of the phytoremediation mechanisms mentioned in Table 3.

Most of the phytoremediation mechanisms, when applied to the remediation of contaminated water, are implemented through the development of constructed wetlands. Constructed wetlands can be defined as a manmade artificial wetland that consists of shallow ponds or channels planted with wetland, aquatic plants or submerged aquatic plants. The treatment relies on the natural microbial, biological, physical and chemical plant processes (EPA, 2000). These wetlands are engineered designed structures for the control of flow and retention time of the treated water. Other important parameters in the design and construction of the wetlands are materials such retaining walls, liners, beddings and media. The placement of media in the constructed wetlands is optional since it is mostly used for plant root support. Contact time increases with water flow and level control. The media should not react with contaminants present in the water since the treatment is due to the presence of the plants and not by direct adsorption to the media. An example of the most common components in a constructed wetland is shown in Figure 5 (United States Environmental Protection Agency, 2000).

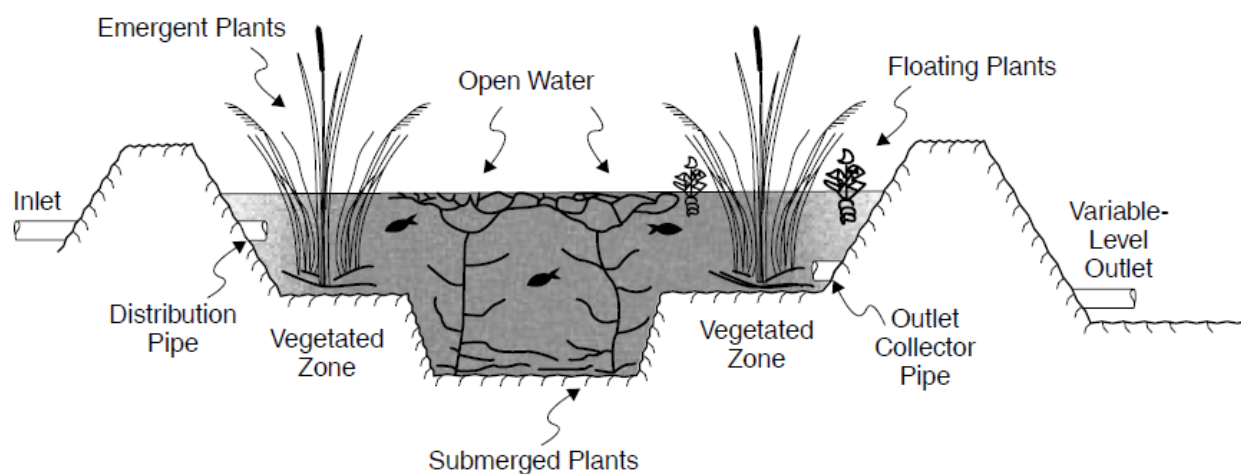


Figure 5 Example of a Typical Constructed Wetland

2.5 Remediation of Explosives Containing Water

In the Iowa Army Ammunition Plant, the Corps of Engineers performed a screening of the aquatic and wetland plants appropriate for the remediation of the explosives contaminated groundwater. The submerged plants analyzed were American pondweed (*Potamogeton nodosus*) and Coontail (*Ceratophyllum demersum*). The group of emergent plants studied were Water-plantain (*Alisma subcordatum*), Common arrowhead (*Sagittaria latifolia*), Fox sedge (*Carex vulpinoidea*), Wool-grass (*Scripus cyperinus*), Blunt spikerush (*Eleocharis obtuse*), Reed canary grass (*Phalaris arundinacea*), narrowleaf cat-tail (*Typha angustifolia*) and Parrot feather (*Myriophyllum aquaticum*). The concentration of TNT in the water was found to be 680 ± 70 $\mu\text{g/L}$.

Experimental results showed that most of the plants were able to achieve complete removal of the TNT in 10 days at 25°C . The percentage removal values obtained in the plants studied were as follows: American pondweed 100%, Coontail 100%, Water-plantain 99%,

Common arrowhead 100%, Fox sedge 100%, Wool-grass 98%, Blunt spikerush 95%, Reed canary grass 100%, narrowleaf cat-tail 95%, and Parrot feather 94% (Best, et al., 1997).

3 MATERIALS AND METHODOLOGY

The materials and methods used for the remediation of ECW are discussed in this section. The materials sections are divided into six sub-sections; the first two sub-sections explain the explosives used, followed by the tire crumb rubber sub-section, two sub-sections for the adsorption and bioremediation of explosives, and the remaining sub-section for the analytical instrumentation. In the methodology section, four divisions were made: adsorption mechanism, bioremediation mechanism, treatment train (combination of both mechanisms) and samples analysis.

3.1 Materials

In this section are presented the materials used throughout the experiments. The explosives used are described in the first sub-section followed by sub-section of the tire crumb rubber used as the sorption material. The adsorption sub-section describes all the materials used in the experiments under the different configurations. As part of the bioremediation sub-section, the plants tested and the one employed for the remediation of explosives are described. Lastly, the materials used in the collection and analysis of samples are described. Among the materials used for the experiments are general laboratory equipment, tools and glassware and American Chemical Society (ACS) grade chemicals. Special equipment and materials used in the sections mentioned above are described in each of the following sub-sections.

3.1.1 Explosives

During the course of the experiments the ECW solution was prepared by dissolving different explosives in water. The explosives used for the ECW were TNT and DNT. The

mixture of explosives crystals were bought from Chem Service and they came in 1.0 g vials. Figure 6 shows a picture of the mixed explosives crystals used for the preparation of the ECW.



Figure 6 Picture of the Explosives Crystals Used

3.1.1.1 Explosive: TNT

One of the main explosives used on the experiments was 2,4,6-TNT. Its molecular formula and weight are $C_7H_5N_3O_6$ and 227.13 g/mol, respectively. The TNT chemical and 3 dimensional structure are shown in Figure 7. They are yellow monoclinic rhombohedra form alcohol crystals needles. Its specific gravity is 1.654 g/cm³. It has a melting point of 80.1 °C and burns at 295 °C when not confined. TNT boils at 240 °C and it is produced by the nitration of toluene with mixed acid ($HNO_3 + H_2SO_4$) in three steps or by continuous flow (O'Neill, et al., 2001). It has solubility in water of 115 mg/L at 23 °C (Phelan & Barnett, 2001). The octanol-water partition coefficient (K_{ow}) is 1.6 (Agency for Toxic Substances and Disease Registry, 1995). Prolonged exposure to TNT produces health problems in the organs such as eyes, skin, respiratory system, blood, liver, cardiovascular system, central nervous system and the kidneys (NIOSH, 2011).

The TNT standards used for the calibration curve and the chemical analyses were bought from AccuStandards. It came in a 1 mL vial at a concentration of 1000 µg/mL in methanol (MeOH) and acetonitrile (ACN).

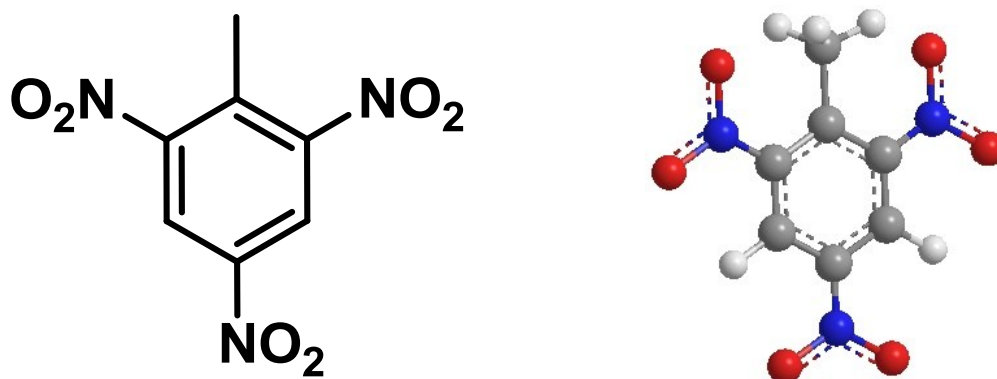


Figure 7 TNT Chemical Structure and Corresponding 3D Model

3.1.1.2 Explosive: DNT

The other explosive used on the experiments was 2,4–DNT. The molecular formula and weight of this explosive is $C_7H_6N_2O_4$ and 182.14 g/mol, respectively. The DNT chemical and 3 dimensional structure is shown below in Figure 8. They are yellow needles or monoclinic prisms. Its specific gravity is 1.3208 g/cm³. It has a melting point of 70.5 °C and boils at 300 °C (Lide, 2005). DNT can be synthesized by the utilization of nitric acid and solid state catalysts such as Molybdenum Trioxide and Silicon Dioxide ($MoO_3 + SiO_2$) or Phosphoric Acid, Molybdenum Trioxide and Silicon Dioxide ($H_3PO_4 + MoO_3 + SiO_2$) (Adamiak & Skupinky, 2010). It has solubility in water of 188 mg/L at 22 °C (Phelan & Barnett, 2001). The octanol-water partition coefficient (K_{ow}) is 1.98 (Agency for Toxic Substances and Disease Registry,

1998). Similar to TNT, the prolonged exposure to DNT produces health problems in the organs such as blood, liver, cardiovascular system and reproductive system (NIOSH, 2011).

The DNT standards used for the calibration curve and the chemical analyses were bought from AccuStandards. It came in a 1 mL vial at a concentration of 1000 µg/mL in MeOH.

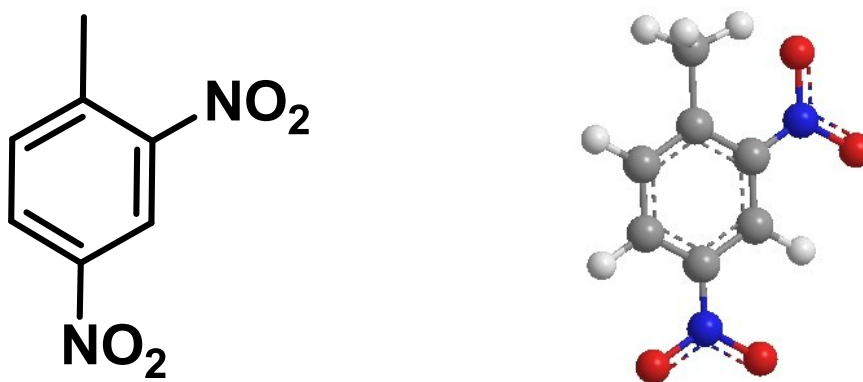


Figure 8 DNT Chemical Structure and Corresponding 3D Model

3.1.2 Tire Crumb Rubber

One of the main materials for treatment of ECW in this experiment was the TCR which was obtained from Rubber Recycling and Manufacturing, Inc. (REMA) Puerto Rico. REMA, located in Caguas, Puerto Rico, is a company dedicated to the recycling of tire and the manufacture of tire derived materials. In the scrap tires processing market, the tires are shredded and the steel bracings are removed. The tires are shredded into different sizes depending on what they will be used for (REMA, 2010). The classification of the shredded tires depends on their sizes, for example shred (50 to 300 mm), ground (19 to 0.15 mm) and crumb (4.75 to 0.075

mm) (Moo-Young et al., 2003). The typical components of a tire and their composition by weight for a passenger and a truck tire are shown in Table 4 (RMA, 2011).

Table 4 Typical Tire Components and Composition for Typical Passenger and Truck Tires

Component	Passenger Tire Composition by weight (%)	Truck Tire Composition by weight (%)
Synthetic rubber	27	14
Natural rubber	14	27
Carbon black	28	28
Steel wire	14 -15	14 -15
Sulfur and sulfur compounds	16 -17	16 -17
Silica		
Phenolic resin		
Oil: aromatic, naphthenic, paraffinic		
Fabric: polyester, nylon		
Pigments: zinc oxide, titanium dioxide		
Fatty acids		
Inert materials		

The samples of the shredded tires were obtained from UPRM professors Felix Roman and Felipe Acosta for the experiment. The sizes of the tires collected from Prof. Roman had the following sieve sizes 1.40 to 0.853 mm (mesh 14 – 20) and sieve size 0.599 mm (mesh 30). The collected shredded tires from Prof. Acosta were sieved into the following sieve sizes 1.68 to 1.00 mm (mesh 10 – 16) and sieve sizes 1.00 to 0.500 mm (mesh 16 – 35). Prior to use, the TCR was rinsed with deionized (DI) water and air-dried at room temperature (25 °C). Figure 9 shows a picture, as an example, of the TCR used for the experiments.



Figure 9 Sample TCR Material Used for the Experiments

3.1.3 Adsorption

Although the main material used for the adsorption of explosives was the crumb rubber, additional materials were used. Among the additional materials used in the experiments were the following: different sizes and diameters of Kontes Flex Columns, Cole Palmer peristaltic pump with a speed of 1 – 100 rpm with its controller, and a Barnstead Thermolyne LABQUAKE Shaker Rotisserie.

For comparison purposes, granular activated carbon (GAC) was also used for the adsorption of explosives in water. Activated carbon is typically made from hard woods, coconut shell, fruit stones, coals, and synthetic macromolecular systems, among others. These materials are processed in order to increase their porosity either by thermal (gasification of carbon atoms) or chemical activation (usually using phosphoric acid). Activated carbon is commonly produced and used for water and air filtration as well as separation of gas mixtures (Marsh & Rodriguez-Reinoso, 2006). Their porosity, size and surface area depends on the purpose and for the

application it will be used. In this research we worked with a GAC available in the EEL that was sieved to match the same size as the TCR used, sieve sizes 1.68 to 1.00 mm (mesh 10 - 16) and sieve sizes 1.00 to 0.500 mm (mesh 16 - 35).

3.1.4 Bioremediation

As mentioned earlier, bioremediation is a biological technology which uses living microorganisms in order to treat contaminated sites. Under the bioremediation category we can find the phytoremediation technology that relies on the natural growing process and development of plants for the treatment of pollutants.

Different plants were first tested for the treatment of the ECW. The selection of the plants was based mostly on their characteristics such as: location, growth rate, propagation, root abundance and extension, water susceptibility and consumption and their previous use for the remediation of contaminants in water. These characteristics are mostly found in wet soil plants such as wetland, pond plants or aquatic plants.

Two of the most commonly used plants in the treatment of water are the water lettuce (*Pistia stratiotes*) and water hyacinth (*Eichhornia crassipes*). These two plants were subject to different toxicity experiments and were able to survive at explosives concentrations in water below the 5 ppm. Although they were able to grow under such concentrations, they started to show signs of deterioration or discoloration known as chlorosis (Hannink et al., 2002). An example of the discoloration exhibited by the water lettuce is shown below in Figure 10. Another concern with these plants was the difficulty they presented when we were trying to grow them indoor and under hydroponic conditions. Although we provided them all the required plant

care, plants did not behave as expected. In most of the researches where these plants had been used, the experiments were conducted outdoors or in greenhouses (Mishra & Tripathi, 2008).

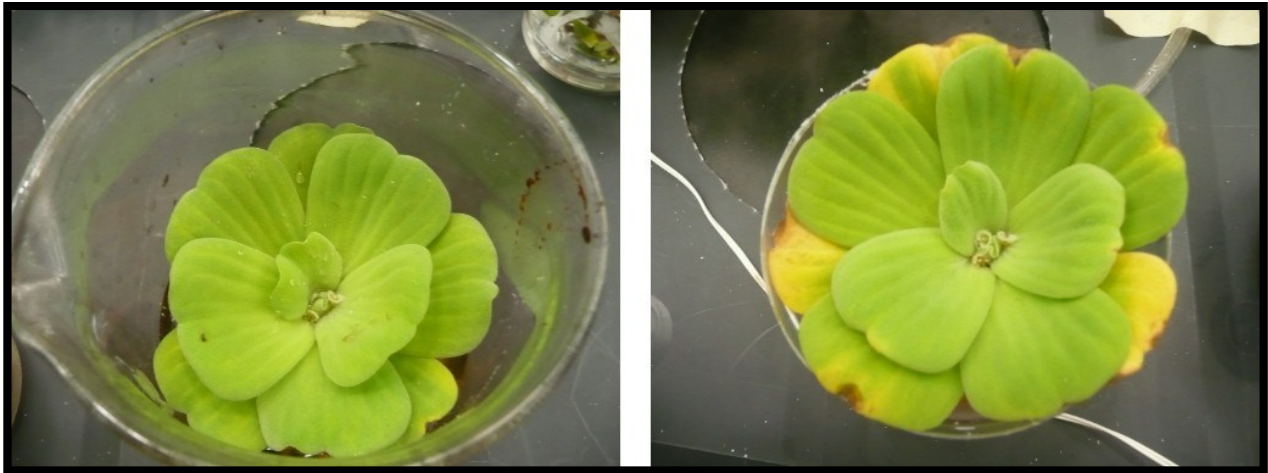


Figure 10 Chlorosis on Water Lettuce

The third and final plant selected for our experiments was the dwarf papyrus (*Cyperus haspan*). This plant is native in Puerto Rico, found in wet saturated sandy soils near roadsides, pastures, grasslands, pond borders, marshy areas and waste places (Acevedo-Rodriguez & Strong, 2005). It belongs to the genus *Cyperus*, the same the genus of the papyrus, the plants used by the ancient Egyptians for the development of paper. The *Cyperus haspan* is a perennial plant that grows approximately up to 180 cm tall. It is about 4–6 mm thick, leaves are described as bladeless sheaths, and flowers are umbel-like corymb with ascending rays with diameters between 4–15 cm (Acevedo–Rodríguez & Strong, 2005). A picture of the dwarf papyrus plant used throughout the experiments is shown in Figure 11.



Figure 11 Dwarf Papyrus

Other important characteristics of the dwarf papyrus are its classification as perennial, moderate growth rate, long lifespan, high salinity tolerance, medium tolerance to anaerobic conditions, low drought tolerance, and intolerant to shade. It grows in zones where pH is ranges from 4.5–7.5, propagates by sprigs and blooms in late spring (NRCS, 2010). In several investigations the papyrus had been used for the removal of pollutants in water and soil (Kyambadde et al., 2004; Perbangkhem & Polprasert, 2010).

Despite the fact that there are no references about the use of dwarf papyrus for the removal of contaminants, their similarities with the papyrus post it as an appropriate candidate for it. After exposing the dwarf papyrus to different concentrations of explosives containing water they showed that they were able to handle concentrations up to 10 ppm without vitally affecting their growth rate, appearance and health inside the laboratory.

All the plants mentioned above were collected at two local nursery farms located in San German, PR. These nurseries were the Caribbean Nursery Farm and the Bokeana Corporation. In the nurseries, these plants are maintained only by the addition of a small amount of pond nutrients and the presence of fishes in the ponds where they grow. In this regard, in order to maintain the health of the plants indoor and under the desired conditions a hydroponic nutrient solution was used. The nutrient solution used was Flora Nova Grow from General Hydroponics, a solution that only requires a simple mixture of the solution with water. Its main nutrient components are as follows: total nitrogen – 7.0%, available phosphate – 4.0%, soluble potash – 10.0%, calcium – 4.0%, magnesium – 1.5%, sulfur – 2.0% and chelated iron – 0.1%. The concentration of the nutrients was determined based on conductivity measurements by the Oakton Acorn CON 6 Conductivity Meter. Since the experiments were conducted inside the laboratory, no sunlight was readily available. Therefore, artificial lighting was provided with Phillips Plants & Aquarium T12 1,600 lumens fluorescent light attached to an automatic timer for the on and off setups.

3.1.5 Analytical Instrumentation

In order to determine the explosives concentrations in the water in the various experiments, a High Performance Liquid Chromatogram (HPLC) was used. It was a Perkin Elmer Series 200, comprised mainly of a hundred vials auto sampler, UV/VIS detector, and a pump. All of them were connected and controlled by TotalChrom Workstation computer software. The HPLC basically works by taking a sample, injects it to a mobile phase (water and methanol) and pass it through a column that serves as the stationary phase. In the column all the sample components are separated and analyzed through a UV detector. As a result from this

procedure the instrument gives an absorbance vs. time graph on which all the components are shown. By calculating the area below the curves produced, the concentration of the components of interest are determined with calibration curves made from standard solutions. A detailed explanation on the analyses applied during all the experiments is provided in the Methodology section presented below.

3.2 Methodology

This section describes the methodology used for all the experiments for the assessment of the TT remediation process. The methodology was comprised of four sections: adsorption, bioremediation, treatment train and the samples analyses.

As a brief introduction, the adsorption section discusses the use of TCR as sorption material employed in batch and continuous reactors operated under different physicochemical operating conditions. The bioremediation section explains how the different plants were used in batch reactors experiments in order to determine their interaction and behavior when subjected to ECW. The main experiments were conducted with papyrus since it resulted in the best candidate among the plants studied. The combination of the TCR and the papyrus are discussed in the TT section where two experiments two-in-one and in-series, were performed to compare different configurations and are highlighted for their respective advantages and disadvantages in the treatment of ECW. And the sample analyses sections describe the procedure followed for the collection and the analysis of the ECW and plants previously mentioned.

3.2.1 TCR Adsorption

The TCR adsorption was evaluated through different experiments in order to study its behavior under different conditions and parameters: amount and size of TCR, temperature, pH,

contact time and the TCR adsorption kinetics. Batch experiments as well as continuous flow column experiments were conducted to address the aforementioned parameters and conditions. All of these conditions and parameters studied are discussed in detail in the sections below.

3.2.1.1 TCR Amount

A batch reactor experiment was set to analyze the effect that the amount of TCR had on the TNT concentration in water. In four 40 mL glass vials, TCR was placed as follows: one with 5 g, two with 10 g and the last one with 15 g. One of the 10 g reactors served as the control, the remaining three served as the treatments. TCR in mesh size 14–20 (sieve sizes 1.40 to 0.853 mm) was used for this experiment. The volume of water and ECW in each reactor was 24 mL. The initial TNT concentration in the water was approximately 7.5 mg/L. All the reactors were covered with aluminum foil in order to prevent photolysis of the explosives.

One milliliter samples were taken from each reactor at the following hours after the experiment started: 1, 2, 4, 8, 24 and 48. Each reactor was replenished with the same volume of water or ECW that was sampled in order to maintain a constant reaction volume throughout the experiment. Samples collected were stored in a refrigerator and analyzed within 24 hours following the procedure described in the chemical analyses section. A schematic of this experiment is shown in Figure 12.

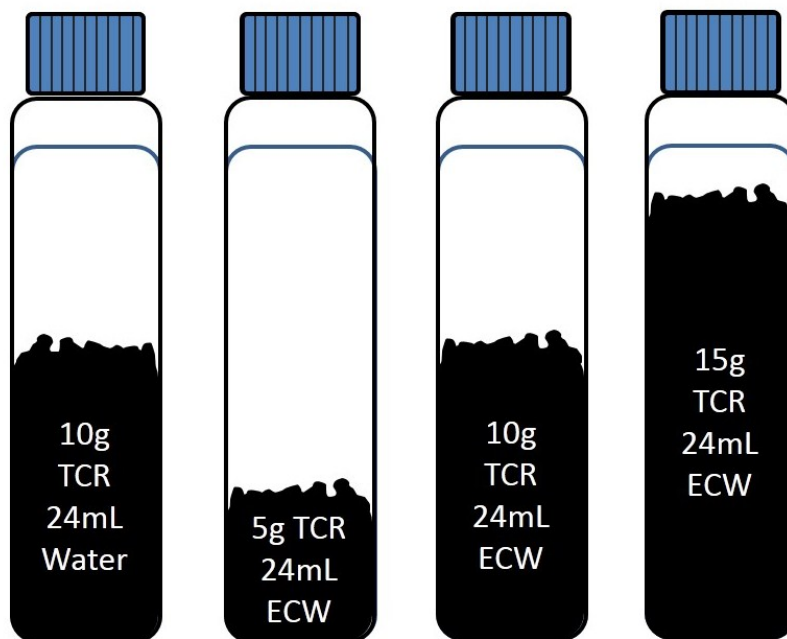


Figure 12 Schematic for the TCR amount and ECW experiment

3.2.1.2 TCR Size and Pore Volume

A continuous-flow column experiment was performed to compare the adsorption capacity of different size TCR in a similar volume. Since the volumes were similar it allowed to determine the effect of pore volume of the different sizes of TCR on explosives adsorption. The TCR sizes used were mesh size 14 – 20 (sieve sizes 1.400 to 0.853 mm) and mesh size 30 (sieve size 0.599 mm). The experiment were set in columns filled with the respective mesh size TCR. The amount of TCR used in each column was weighed in order to determine the pore volume per each TCR mesh size inside the columns. The most relevant details and characteristics of each column are summarized in Table 5.

Table 5 TCR Size and Pore Volume Experiment Columns Characteristics

Characteristic	Mesh 14 - 20	Mesh 30
Length (in)	9.00	9.00
Diameter (in)	1.00	1.00
Volume (measured by water) (cm ³)	114.00	115.00
Column Weight (g)	69.00	68.90
Column Weight + Cotton Round (g)	69.20	73.90
Column Weight + Shredded Tire (g)	127.90	125.70
Shredded Tire (g)	58.70	51.80
Column Weight + Shredded Tire + Water (g)	182.60	185.20
Amount of water	54.70	59.50
Density (g/cm ³)	0.514	0.450

An ECW was prepared at an initial TNT concentration of 12 ppm. It should also be noted that the solution also contained DNT and its concentration varied greatly among the prepared solutions. The ECW solutions were stored in amber bottles to prevent photodegradation. The ECW were pumped into the columns filled with TCR with a peristaltic pump at a rate of 2.7 mL/min and samples were taken every 30 minutes. A schematic configuration of this experiment is shown in Figure 13.

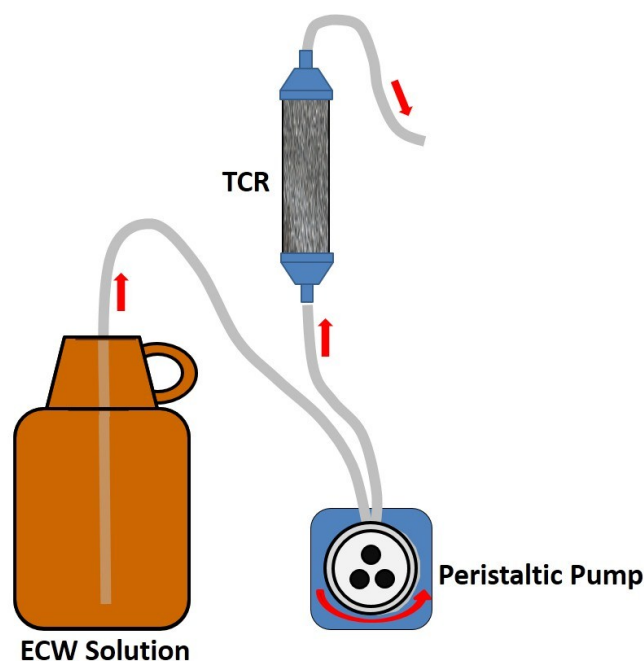


Figure 13 Schematic for the TCR Size and Pore Volume Experiment

3.2.1.3 Temperature

This batch experiment was done to evaluate the impact of temperatures on the treatment of ECW with TCR. All the samples were made in duplicate. The experiment was performed in two different stages. First, the samples were subjected to a temperature of 10 °C and second to a temperature of 40 °C. Each experiment consisted of 6 reactors (250 mL Erlenmeyer flask). Two were the control reactors only filled with 200 mL of the ECW at a TNT concentration of 10 mg/L. For the remaining four reactors, two were filled with 25 g TCR and others two with 50 g of TCR. All reactors contained the same volume and concentration of the ECW. In order to maintain the reactors at a constant temperature, the reactors were placed inside a Styrofoam box, filled with water that recirculated through a temperature-controlled bath system, as depicted in Figure 14. Samples with a volume of 1.5 mL were taken at regular intervals at 0.5, 1, 2, 4, 8, 12,

24, 48, and 168 hours. The volume inside the reactors was kept constant by adding 1.5 mL of ECW to each reactor after the samples were taken.

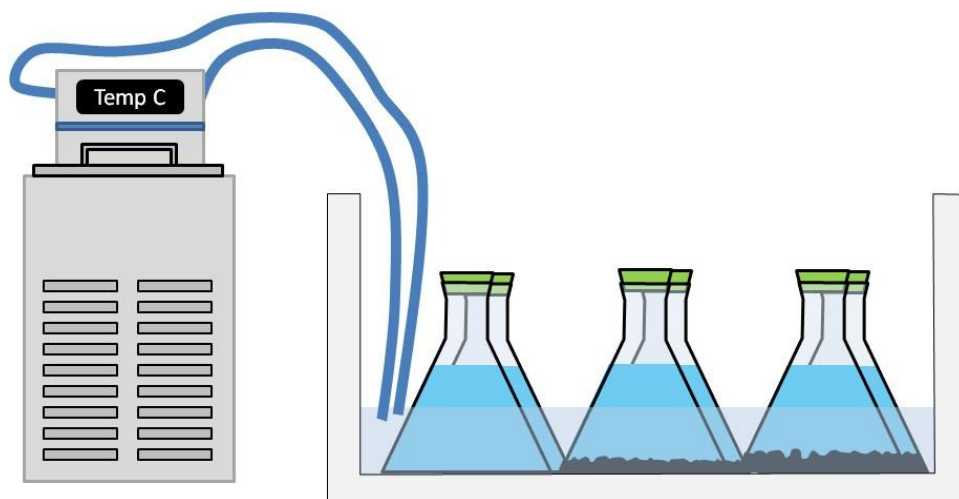


Figure 14 Schematic of the Configuration for the Temperature Experiments

3.2.1.4 pH

In order to verify if acid or alkaline solutions have an effect on the ECW adsorption capacity by the TCR, this experiment was developed. The experiment consisted of sixteen 500 mL Erlenmeyer flasks, filled with 200 mL of either water or ECW (8 with water and 8 with ECW). Five grams of TCR were added to half of the flasks containing either water or ECW were filled with 5 g of TCR, 10 g of TCR in sieve size of 1.68 to 1.00 mm (mesh 10 – 16) were added to the remaining flasks. The initial TNT concentration in the ECW was approximately 10 mg/L. Their pH was adjusted to 3, 5, 7 and 9 with 0.1 M hydrochloric acid (HCl) or 0.1 M sodium hydroxide (NaOH). The flasks were closed, covered with aluminum foil and kept at room temperature.

Samples were analyzed daily for explosives concentrations and pH. A sample of 1.0 mL was taken and each reactor was refilled the same volume of the stock solution at their

corresponding pH in order to maintain a constant volume. The experiment was run for 7 days.

Figure 15 shows a schematic representation of the experiment.

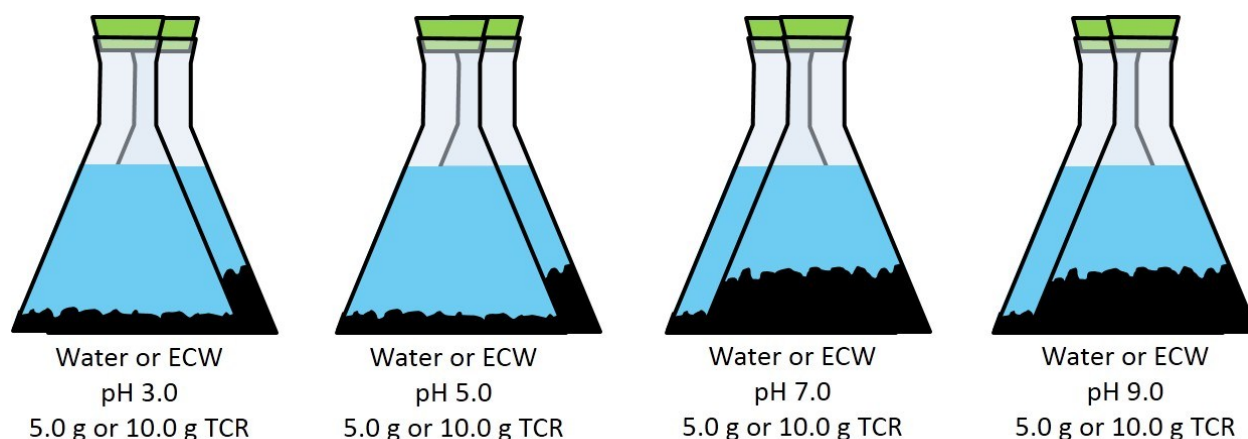


Figure 15 Schematic of the pH Experiment

3.2.1.5 Activated Carbon vs. Tire Crumb Rubber

It is known that activated carbon could remove explosives in water (Rodgers & Bunce, 2001; Tomaszewski et al., 2003). In this research GAC was used to compare the adsorption capacity between the GAC and TCR for explosives. The setup for this experiment consisted of five 250 mL Erlenmeyer flasks filled with a volume of 200 mL ECW at a TNT concentration of 50 mg/L. The control flask was filled with the ECW solution only; to the remaining four flasks 25 and 50 g of TCR or GAC, respectively were added. Both materials were sieved previously and the sieve size used for this experiment was 1.0 to 0.50 mm (mesh 16 – 35). All the flasks were covered with aluminum foil to prevent photodegradation and kept at room temperature.

1 mL samples were taken for chemical analyses at the following time intervals: 0.5, 1, 2, 4, 8, 24, 48 and 72 hours. After samples were collected all the flasks were refilled with their

respective initial ECW solution in order to maintain a constant volume throughout the experiment. Figure 16 depicts a schematic configuration used for this experiment.

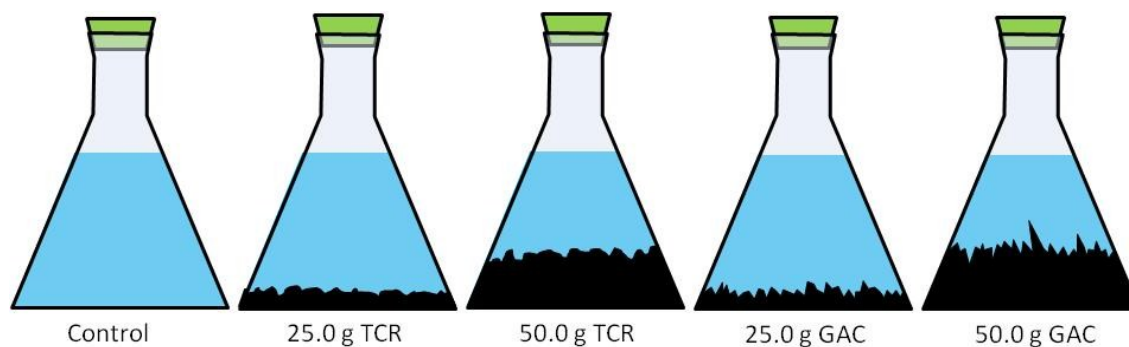


Figure 16 Configuration for the Granular Activated Carbon and Tire Crumb Rubber Experiment

3.2.2 Bioremediation

The *Cyperus haspan* specimens (dwarf papyrus) were bought from a local nursery farm, Caribbean Nursery Farm at Hormigueros, Puerto Rico. The plants were grown in pots filled with top and potting soil. After the plants were transported to the Environmental Engineering Laboratory, they were maintained in the outdoors under shade and were irrigated daily automatically. Prior to the experiments, the plants were removed from their respective pots and they were washed to remove soil from their roots by submerging them in water while gently shaking them. Secondly, the remaining soil attached to the roots was removed by applying water directly to the roots while manually removing it. The plants were then left in fresh water for 24 hours and then changed to water enriched with nutrients.

The water enriched with nutrients was prepared with the Flora Nova Grow nutrient solution. The conductivity of the prepared enriched water ranged between 600 to 1,300 $\mu\text{S}/\text{cm}$

as specified by the manufacturer for plants in their early growing stage and development. After allowing the plants to be exposed to the nutrients, plants were ready to switch to ECW.

The bioremediation experimental setup consisted of the exposure of the dwarf papyrus to different explosives concentrations and the analysis of the explosives concentrations at regular intervals. Plants were exposed to TNT concentrations as follows: control (no explosives) and approximately 1, 5, and 10 mg/L. The ECW also contained nutrients and all the glass containers were wrapped with aluminum foil to prevent photo degradation of the explosives. Since the experiments were conducted indoor, artificial lighting was provided with a Phillips Plants & Aquarium light, turned on automatically for 18 hours and turned off 6 hours daily. Figure 17 depicts the experimental setup.

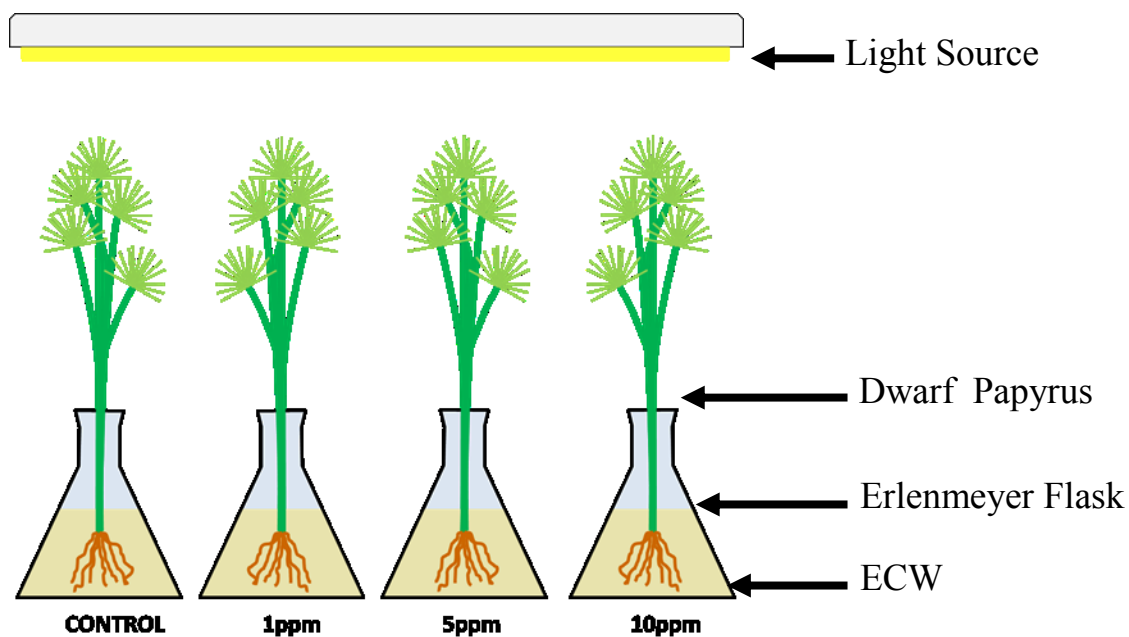


Figure 17 Schematic of the Bioremediation Experiment

There were two important stages in this experiment: the first consisted of taking samples and solution replenishment, while the second stage consisted of the evaluation and measurement

of the plants characteristics. One milliliter of ECW samples were taken twice a week from each reactor and in order to maintain the volume a 1 mL of fresh solution was added to each reactor. Water characteristics of pH, conductivity and temperature were measured twice a week. Once a week the volume of the solution was measured and then the ECW solution was added to each reactor until the initial volume of 350 mL was reached. Weekly, plants were weighed and characteristics such as stem and root lengths and the number of stems and flowers were measured. After a month, the experiment was stopped and the plants were sacrificed for explosives analyses in the roots, stems and flowers.

3.2.3 Treatment Train

Treatment Train (TT) is the name given to the combination of different technologies for the treatment of pollutants. In our case the TT consisted of the application of the adsorption by the TCR and phytoremediation with dwarf papyrus as a combined unit process. By combining the TCR adsorption with the dwarf papyrus bioremediation, the concentration of explosives in water was expected to decrease to a greater extent than by the application of them alone as a single treatment.

Among several experimental setups that could be designed for the application of the TT, two were selected. The selection was made based on their ease of construction and material management, as well as their applicability and expected behavior. One of the selected setups consisted of the treatment of the ECW in an in-series configuration (Figure 18).

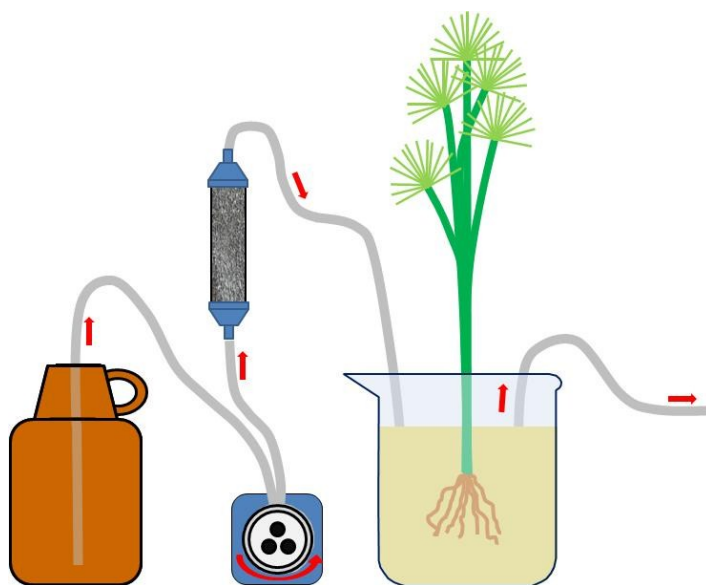


Figure 18 Treatment Train In-Series Configuration Setup

First, the ECW entered an adsorption column filled with TCR and then entered a 500 mL reactor that contained the dwarf papyrus as the polishing treatment. The column was filled with a 50/50% mixture of the TCR sizes available (mesh 10–16 and mesh 16–35). The ECW was pumped to and out of the system using a peristaltic pump at a rate of 2.5 mL/min. Thereby, the TT had a hydraulic retention time of 3.5 hours in the phytoremediation basin. ECW samples were taken every 30 minutes from the sampling ports located before and after the TCR column and also at the exit of the papyrus reactor.

The second TT setup consisted of a two-in-one combination of treatments (Figure 19). The TCR could be placed in the reactor as a loose material or a confined material inside a porous membrane. Loose TCR addition would provide better treatment but at the same time would require special equipment at the time of collection and replacement of material, while the TCR addition as confined material would require the removal of the porous media that contained the

TCR. The latter would be more practical and efficient. Although previous batch experiments showed that loose TCR worked better at early stage of the treatment and that lower concentrations of ECW were achieved faster than with the confined material, the latter was selected based on the ease of management and replacement of the TCR. At last, the setup consisted of a 500 mL reactor filled with the dwarf papyrus and the TCR inside porous nylon mesh.

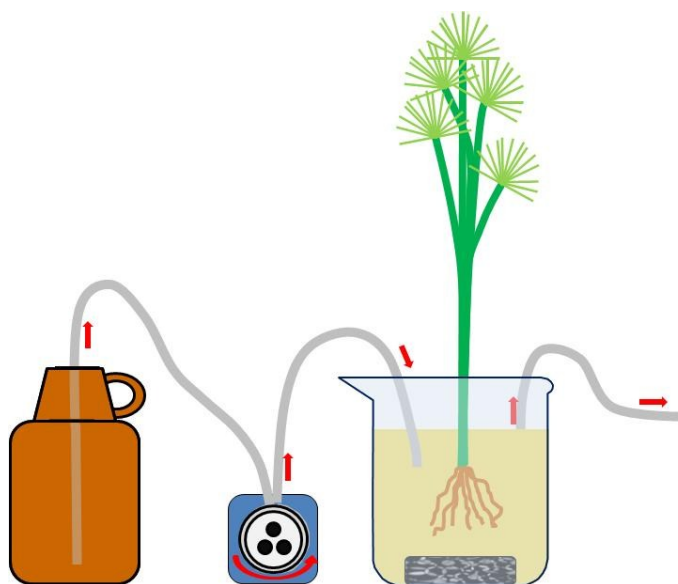


Figure 19 Treatment Train Two-in-One Configuration Setup

In order to be able to compare and contrast both TT configurations, the parameters such as ECW concentration, nutrients, flow rate, volume, sampling rate, running time, type and amount of TCR remained constant or equal. The initial concentration of explosives (TNT) in water was set at 10 mg/L. The nutrients conductivity in phytoremediation reactor was set at 600 $\mu\text{S}/\text{cm}$. As mentioned earlier, ECW was pumped at a rate of 2.5 mL/min. The TCR used was a mixture 50/50% of mesh sizes 10–16 and 16–35. The amount of TCR was pre-determined by

the small column experiments. The amount of TCR inside the nylon mesh was set to be equal to the one packed inside the adsorption columns. The replacement of TCR was done when the effluent explosives concentration reached the initial value.

During the phytoremediation experiments, the dwarf papyrus were weekly weighed and characteristics such as stem and root length, and the number of stems and flowers were measured. After a month, the experiment was stopped and the plants were sacrificed for explosives analyses.

3.2.4 Samples Analyses

As mentioned earlier, the equipment used for the determination of explosives concentrations in the ECW was a Perkin Elmer Series 200 HPLC. The mobile phase consisted of a mixture of deionized water (DI) and methanol (MeOH) at a ratio of 30 to 70%, respectively. Supelco® Ascentis™ C18 column (250.0 mm long and 4.6 mm in diameter) with a non-polar packing consisting of silica beds was used. Inside the column the silica beds works as the stationary phase while the DI and MeOH ratio works as the mobile phase. The separation of the components in a sample inside the column relies on their polarity. Non-polar components in the sample travel slower through the column while as the components increase in their polarity, they travel faster along with the mobile phase, and therefore low polarity components are retained for a longer time. Samples were set at a temperature of 10 °C in the auto sampler. For each sample, the HPLC was set to inject 1 µL at a flow rate of 1.0 mL/min. The wavelength used in the UV detector was set as 254 nm.

The retention times for the explosives TNT and DNT were approximately 5.65 min and 6.70 min, respectively. In order to determine the concentration of ECW in the samples,

calibration curves were made. The calibration curve was developed for each explosive. Various known concentrations of explosives ranging from 0 mg/L (DI water) to 50 mg/L were injected for the development of the calibration curve (Figure 20).

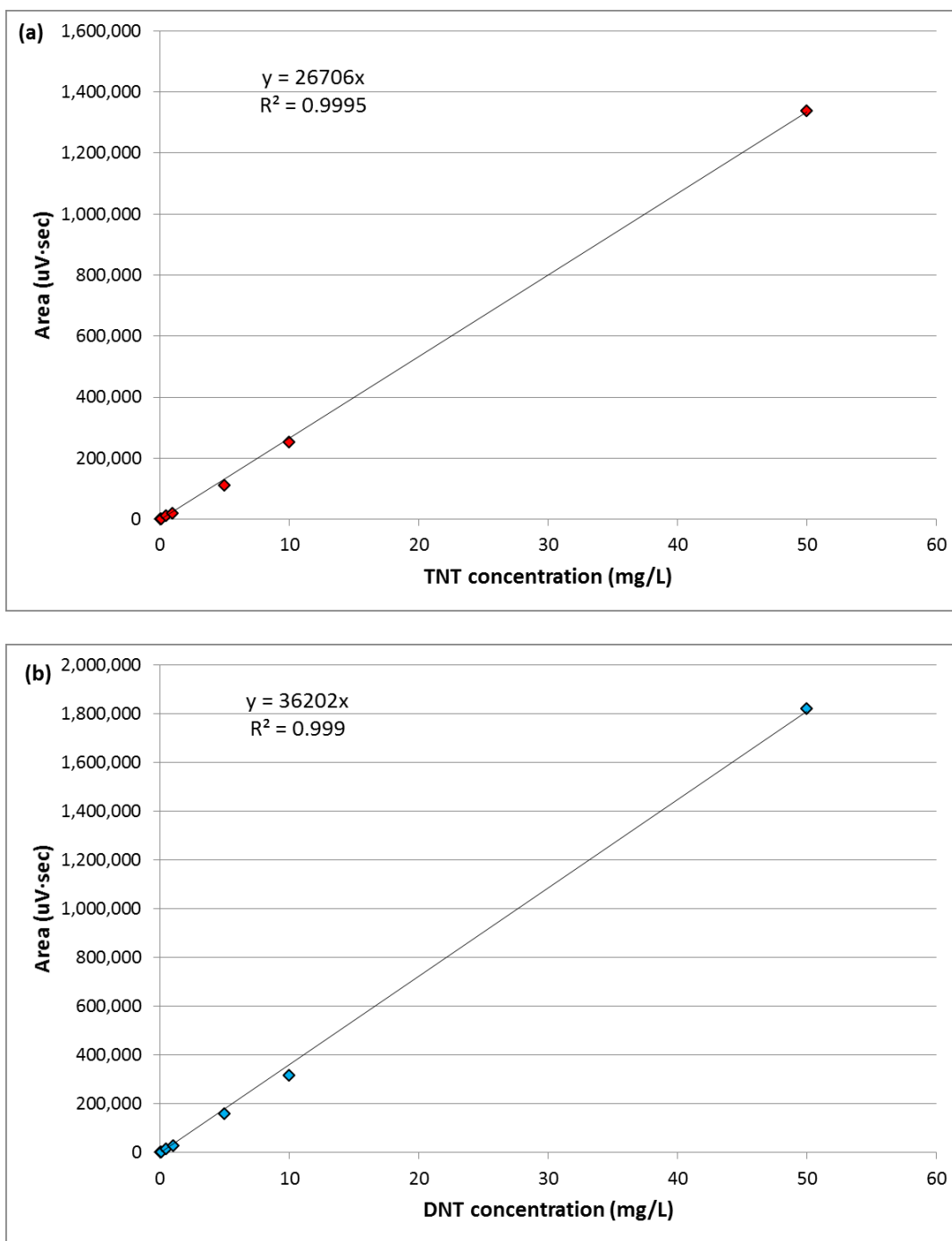


Figure 20 Examples of the Calibration Curve for TNT (a) and DNT (b).

In order to analyze the concentration of explosives in the plants, the EPA Method 8330 – Nitroaromatics and Nitramines by High Performance Liquid Chromatography was used. This

method is used for the evaluation of explosives materials in water, soil and sediment matrix. The method specifies how and under what conditions the samples must be taken and also mentions the processing and management of the samples, the solutions, reagents, general laboratory materials and equipment required for the sampling and analysis of the samples. Finally the method suggests the parameters for the samples analysis by the HPLC (EPA, 1994). Although EPA Method 8330 does not specify a methodology for the analysis of explosives in plants, it was construed that the Method was still valid for the plant material with some minor changes in the sample preparation.

After the experiments with plants were finished, all the plants were left undisturbed without water and air dried in the shade for 4 hours in order to remove ECW from the roots. After air drying, plants were cut and divided into plants, stems and roots and then they were chopped into small pieces smaller than 1 cm. The chopped plant parts were air dried in the shade for 48 hours until the pieces had a constant weight. For the samples extraction, 2 g of each part were placed in a vial filled with 10 mL of ACN, and then closed and placed in a vortex swirl for 1 minute. All the samples were then placed in an ultrasonic bath for 18 hours at a constant temperature of 25 °C. Samples were then set to rest for 30 minutes and later 5 mL of the supernatant were removed from each vial and placed in new vial that contained 5 mL of calcium chloride solution at 5 g/L. Samples were shaken and were settled for 15 minutes. In order to make the samples ready for their analysis on the HPLC, 5 mL were taken and filtered through a 0.45 µm filter. The analyses of the samples in the HPLC were made as described previously.

4 RESULTS AND DISCUSSION

This chapter focuses on the presentation and discussion of the results obtained from the experiments of the ECW treatment, by either TCR adsorption or dwarf papyrus phytoremediation, and both. It is divided into three major sections: Adsorption by TCR, Phytoremediation by Dwarf Papyrus and Removal by Treatment Train.

4.1 Explosives Adsorption by Tire Crumb Rubber

Several experiments were conducted to test the adsorption capacity of the TCR when exposed to ECW under different operating conditions. The results obtained from each experiment performed were as follows.

4.1.1 TCR Amount

This experiment showed an inversely proportional relationship between the amount TCR in a fixed volume and the explosives concentration in the ECW. In other words, as the amount of TCR increased in a fixed volume, the TNT concentration decreased. In this experiment 24 mL of ECW were treated with 5, 10 and 15 g of TCR in the same sizes (mesh 14–20). Results showed that the TNT concentration in the ECW decreased more in the reactor where the amount of TCR was 15 g, followed by 10 g and lastly by 5 g as depicted in Figure 21. Noticeable differences in the TNT concentration were observed during the first hour of the experiment where the TNT concentration in the ECW were 0.46, 1.67 and 3.80 ppm for the reactors contained 15, 10 and 5 g TCR, respectively.

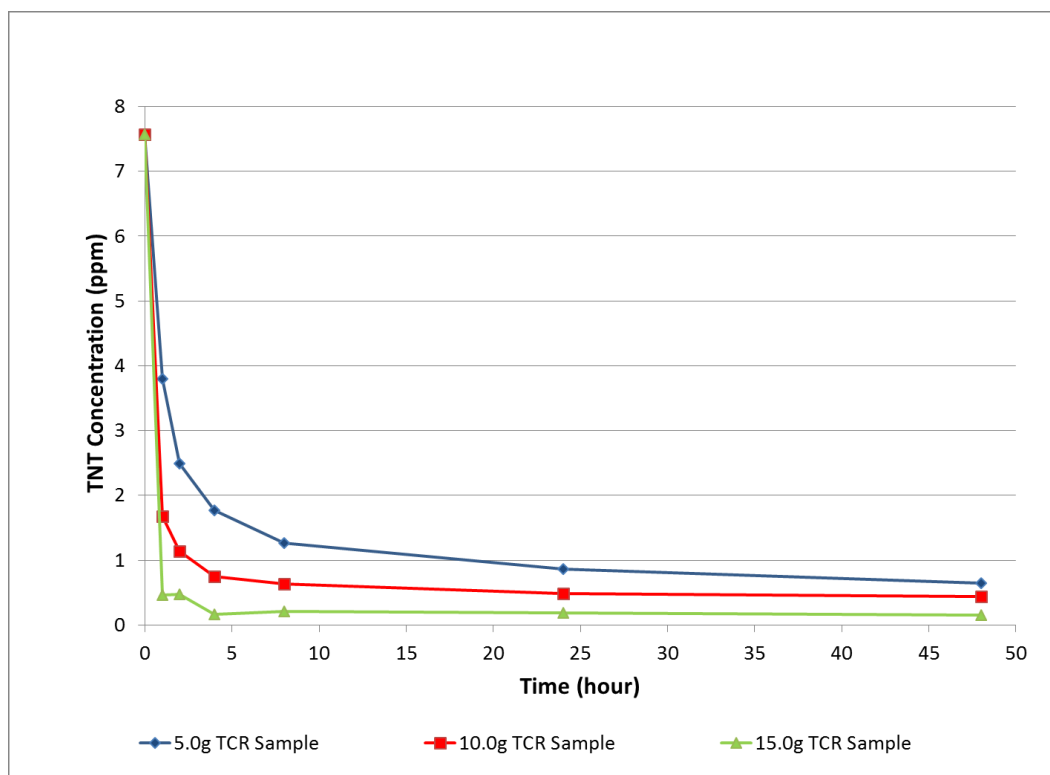


Figure 21 TCR Amount and Explosives Concentration Experiment. In a Control Experiment without TCR, the Initial and Final TNT (after 48 Hours) Concentrations were 13.56 and 13.24 ppm, respectively.

Although there was a significant difference in the TNT concentrations at the early stage of adsorption, all systems reached the TNT concentrations below 1 ppm after 24 hours. For example, the reactors with 15, 10 and 5 g of TCR had TNT concentrations of 0.18, 0.48 and 0.86 ppm, respectively. By the end of the experiment after 48 hours, the TNT concentrations in the reactors were at: 0.15, 0.43 and 0.64 ppm in the reactors filled with 15, 10 and 5.0 g of TCR, respectively.

TNT removal achieved by the TCR adsorption was above the 90% or greater. The highest removal percentage was achieved from the reactor with 15 g TCR at 97.9%, followed by the one with 10 g at 94.2% and the other with 5.0 g at 91.5%.

The results obtained from this experiment were expected since the amount of TCR present in a reactor was directly proportional to the surface area available for TNT adsorption. It was evident that more surface area was available in the reactor with 15 g, followed by the ones with 10 g and 5 g TCR in the same particle size (mesh 14–20). Therefore higher percentages of TNT removal were achieved in the same order as mentioned earlier.

4.1.2 TCR Size and Explosives Concentration per Pore Volume Treated

Two different TCR sizes were used during this experiment, mesh 14–20 (sieve sizes 1.400 to 0.853 mm) and mesh 30 (sieve size 0.599 mm) inside the columns of the same dimensions. Results showed that the smaller size TCR produced a lower explosives concentration than the bigger size TCR. Figure 22 illustrates the TNT and DNT concentrations in the different reactors over the pore volume treated.

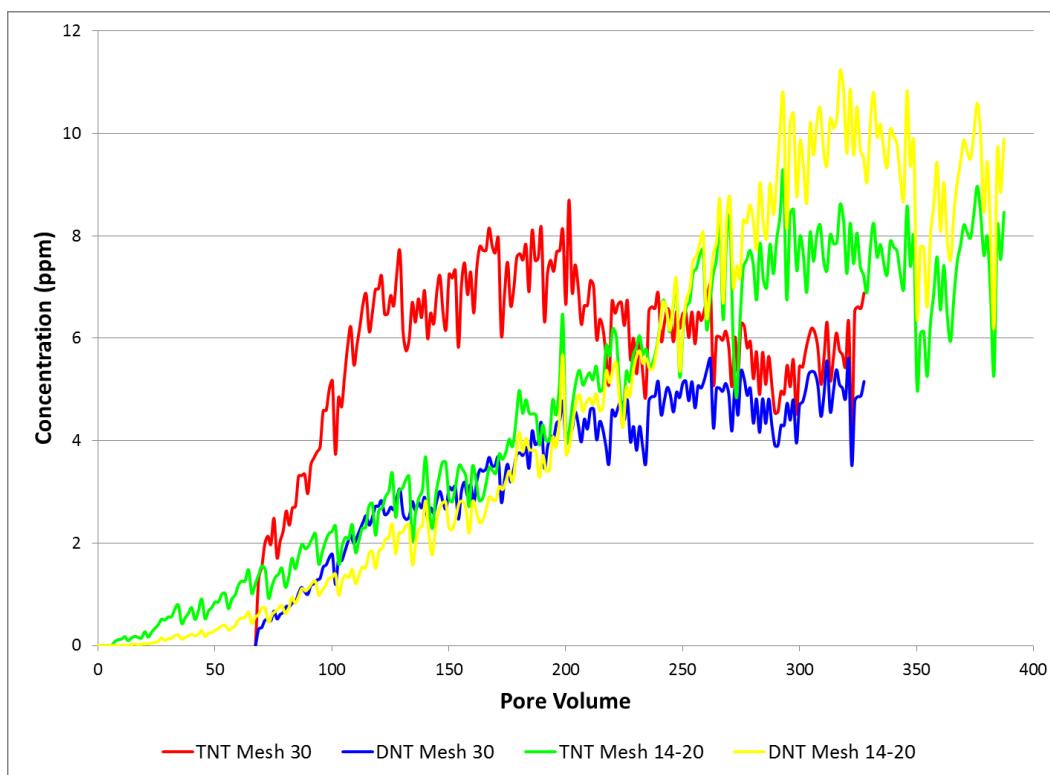


Figure 22 Explosives Concentration per Pore Volume

In Figure 22, the concentration of the explosives are clearly exhibited. The first noticeable difference between two TCR sizes was that the explosives concentrations were not detected until approximately 68 pore volume treated (4 L) for the smaller size TCR. In comparison, for the Mesh 14–20 explosives concentrations were measured from the beginning of the adsorption experiment.

The results from this experiment showed that the relationship between the TCR size and explosives concentration was inversely proportional. Additionally, this experiment showed that a smaller size TCR provided more surface area and more volume of ECW could be treated, compared to a bigger size TCR. By far, the best combination to treat ECW was with a smaller size and more amount TCR in a fixed volume. Adsorption of different alcohols using carbon

nanotubes also showed that the size of the adsorbent material was inversely proportional to the concentration of the adsorbates in the solution. Approximately 40% more adsorbate was removed when the size of the adsorbent was decreased by 5 times (Furmaniak et al., 2010). Pore volume has also been studied for the adsorption of vapor phase compounds by Sasaki et al., (2008). They showed that as the pore volume increased, more vapor phase compounds were adsorbed by the activated carbon.

4.1.3 Temperature

The purpose of this experiment was to test if different temperatures affected the explosives adsorption to TCR. Typically, temperature changes tend to impact the characteristics and properties of the materials. In order to compare if there was an effect on the TCR adsorption capacity of explosives with changes in temperature, batch adsorption experiments were set at a lower temperature (10 °C) and a higher temperature (40 °C).

For the experiment at a lower temperature, the explosives concentration followed the same decreasing pattern regardless of the amount of TCR present in the reactors as expressed in the previous section of the results from the TCR amount. Neither TNT nor DNT concentration was changed significantly in control reactors. After the first 12 hours of the experiment the TNT concentration decreased by 80.1 and 84.5% for the reactors with 25 and 50 g of TCR, respectively (Figure 23). The TNT concentration in the ECW continued decreasing as the experiment progressed. For the 25 g TCR reactor, the TNT concentrations decreased on average by 82.0, 87.4 and 91.8% after 24, 48 and 168 hours, respectively. With the 50 g TCR, the TNT concentrations decreased by 86.8, 89.5 and 92.7%, respectively, after the same reaction times aforementioned.

The DNT concentrations in the ECW were also decreased. The DNT concentrations in the 25 g reactor were 84.3, 85.5, 89.3 and 91.9% after the 12, 24, 48 and 168 hours of the experiment, respectively. The DNT reduction percentage in the 50 g TCR reactor increased when compared to the values obtained from the 25 g TCR reactor. The DNT reduction percentages in 50 g TCR reactors were 88.0, 89.5, 91.2 and 93.3% after the 12, 24, 48 and 168 hours, respectively.

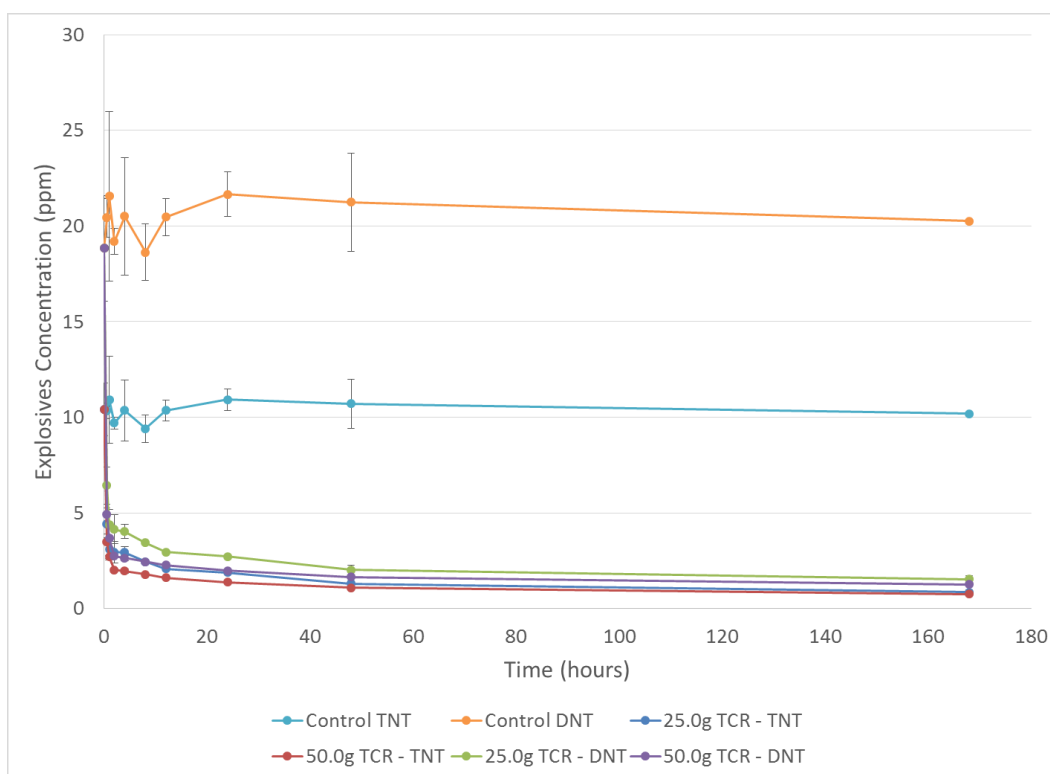


Figure 23 Explosives Concentration in Low Temperature ECW

At a higher temperature, the explosives concentrations in the reactors followed the same pattern as found in the reactors run at a lower temperature. Similar to the case at lower temperatures neither TNT nor DNT concentration changed significantly in the control reactor. During the first 12 hours, the TNT concentration in the ECW decreased by, on average, 84.3 and

87.8% in the 25 and 50 g TCR reactors, respectively. The TNT concentration in the ECW continued to decrease as the experiment progressed and in the 25 g reactor the TNT concentrations decreased on average by 89.0, 87.2 and 90.0% after 24, 48 and 168 hours, respectively. In the 50 g TCR reactor, the TNT concentrations decreased by 90.9, 89.2 and 91.7%, respectively, after the same reaction times aforementioned.

The DNT concentrations in the ECW were also decreased and the DNT concentrations in the 25 g reactor were 90.7, 88.9 and 91.0% after 24, 48 and 168 hours of the experiment, respectively. The DNT reduction percentage in the 50 g TCR reactor increased when compared to the values obtained from the 25 g TCR reactor. The DNT reduction percentage in this reactor were 92.7, 91.3 and 93.0% after 24, 48 and 168 hours, respectively. Figure 24 shows the concentrations of TNT and DNT in the 25 g and 50 g reactors run at a higher temperature ECW.

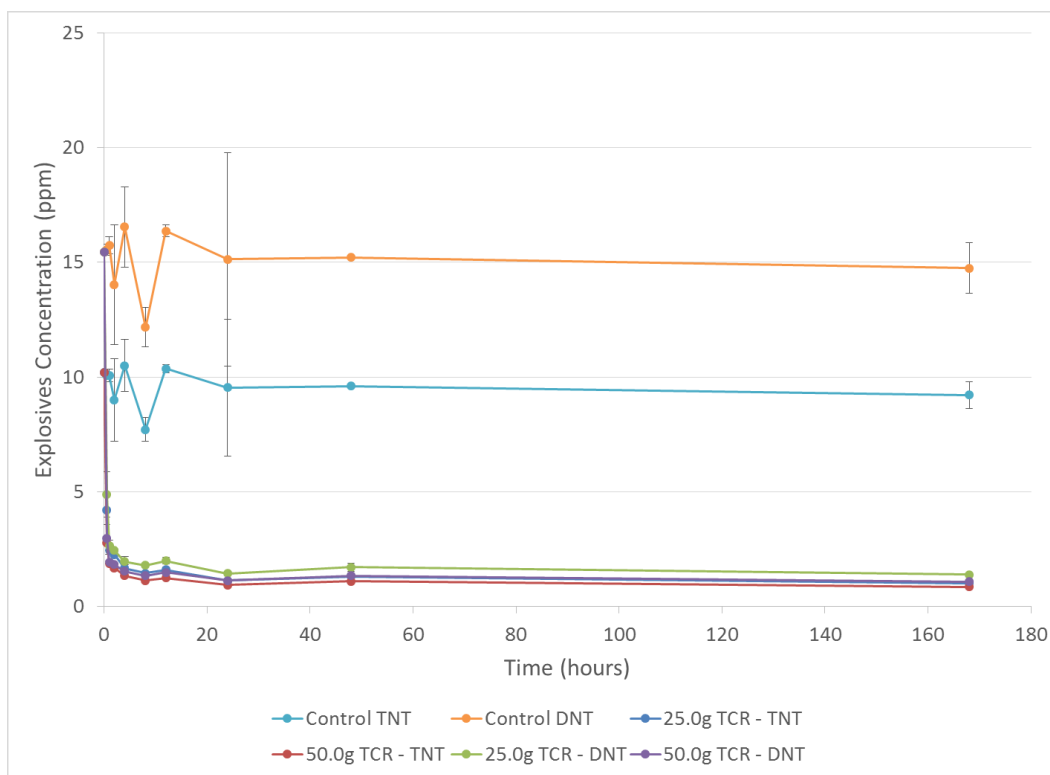


Figure 24 Explosives Concentration in High Temperature ECW

Results showed that temperature did not have substantial effect on the adsorption of TNT by the TCR, but it did have a noticeable effect on the adsorption of DNT. Figure 25 and Figure 26 show normalized TNT and DNT concentrations for the lower and higher temperature experiments, respectively, for comparison purposes.

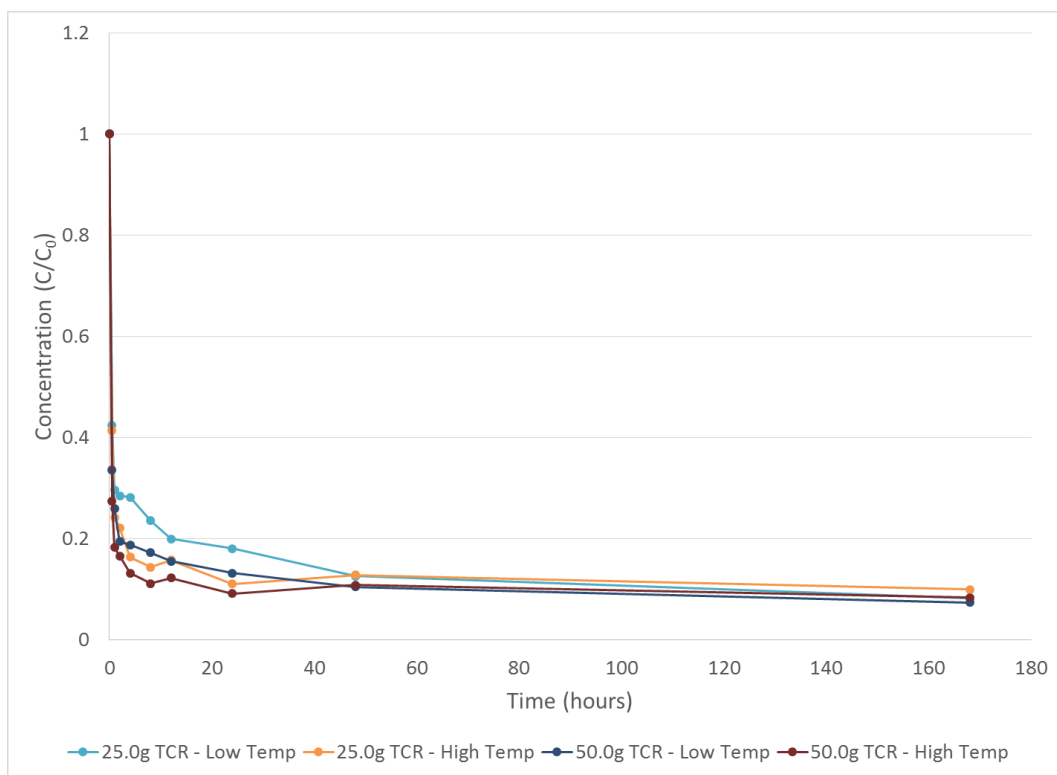


Figure 25 TNT Concentration Comparison

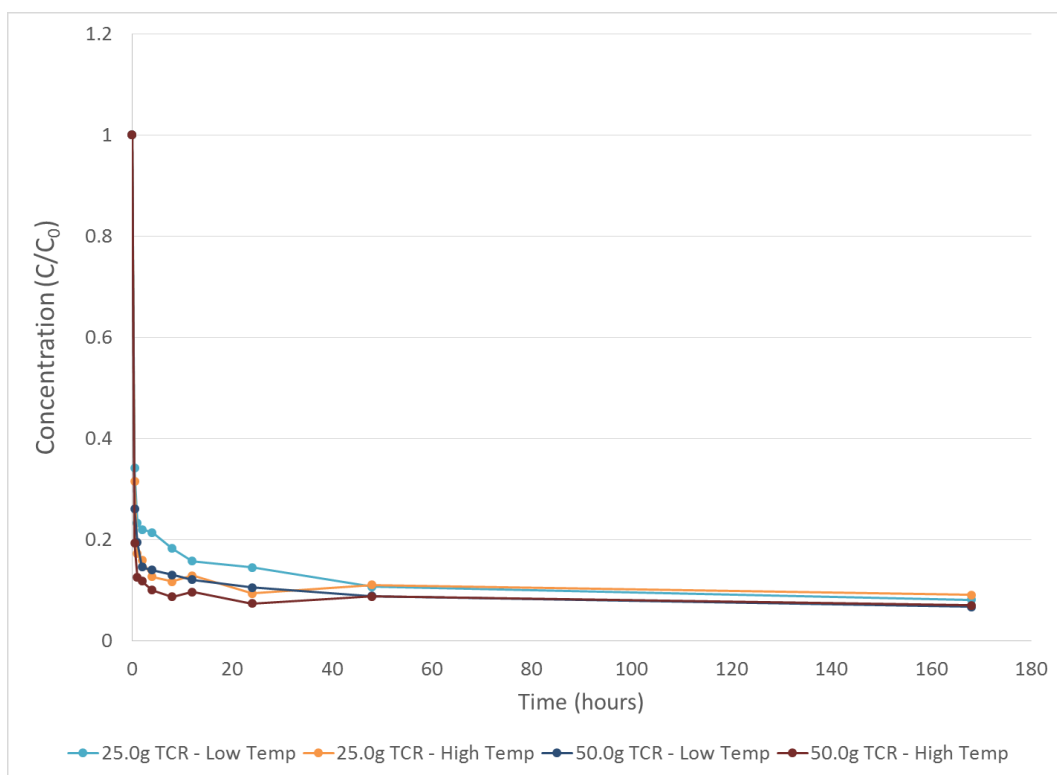


Figure 26 DNT Concentration Comparison

The results from this experiment once again showed that the explosives adsorption was affected by the TCR amount present in the reactor. Also these results showed that adsorption pattern and capacity of the TCR was not affected by changes in temperature. But, in the case of DNT, although the adsorption pattern was the same, the adsorption capacity was affected by changes in adsorption temperature. As shown in Figure 25 and Figure 26, the explosives adsorption by the TCR seemed to be better at the higher the temperature in the first 48 hours of the experiment. But only a significant difference was found in the DNT adsorption by the TCR. Studies showed that temperature has an effect in the adsorption capacity of the adsorbates, but not in the consistent pattern. Depending on the adsorbates and adsorbents, the effect of temperature in the adsorption capacity of an adsorbate changes. Experiments performed by Chen et al. (2011) showed that adsorption of methane by coal was inversely proportional, to the increase of temperature. Chiang et al. (2001) also reported the adsorption of volatile organic compounds by activated carbon was decreased with increase in adsorption temperature.

4.1.4 pH

The purpose of this experiment was to evaluate if pH played a role in the explosives adsorption by the TCR. Also, this experiment served to evaluate if the TCR had an effect on the pH along the experiment period. First, discussed are how the pH values changed over time when exposed to TCR and how explosives concentration varied in the adsorption experiment run with acidic and alkaline ECW are discussed.

Results showed that the presence of TCR in acidic and alkaline environment tended to change the pH value to a neutral value, approximately 7.0. Only samples where the pH value was 3.0 were not affected by the presence of the TCR. Neither the amount of TCR nor the

presence of explosives in the samples was a factor on the effect, since all samples exhibited the same behavior. By the second day of the experiment, the pH values of the systems at 5.0, 7.0 and 9.0 changed to approximately 7.0. Figure 27 and Figure 28 show the pH response during the explosives adsorption by 5 and 10 g of TCR, respectively.

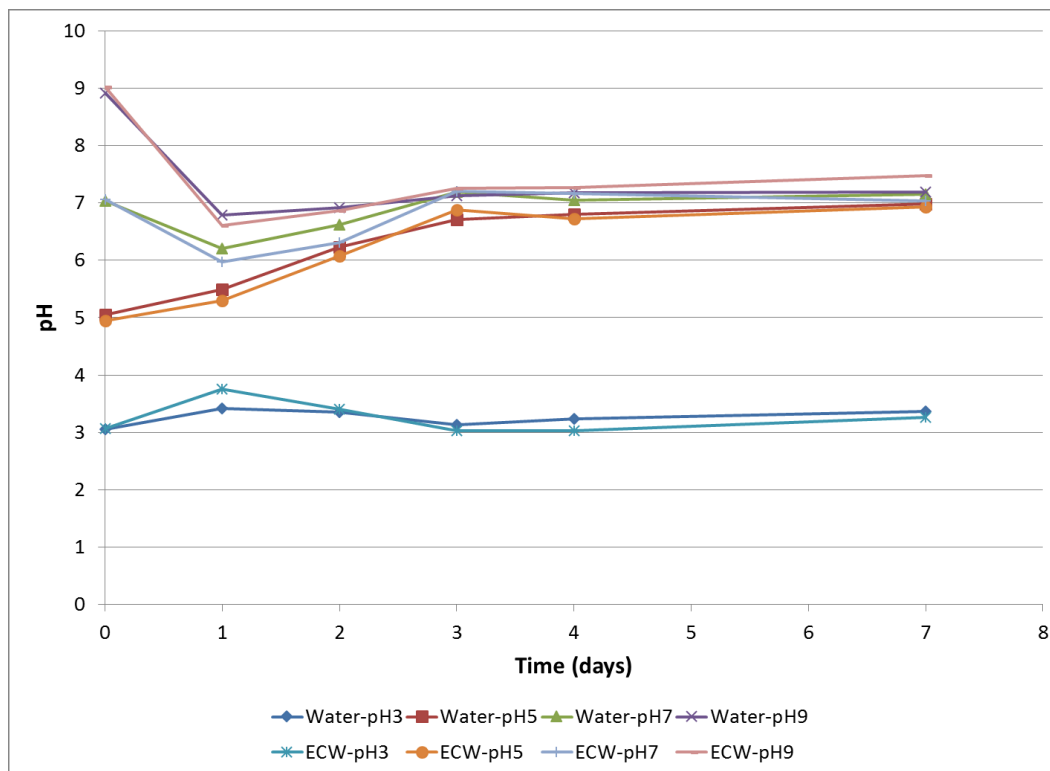


Figure 27 pH Change with 5 g of TCR

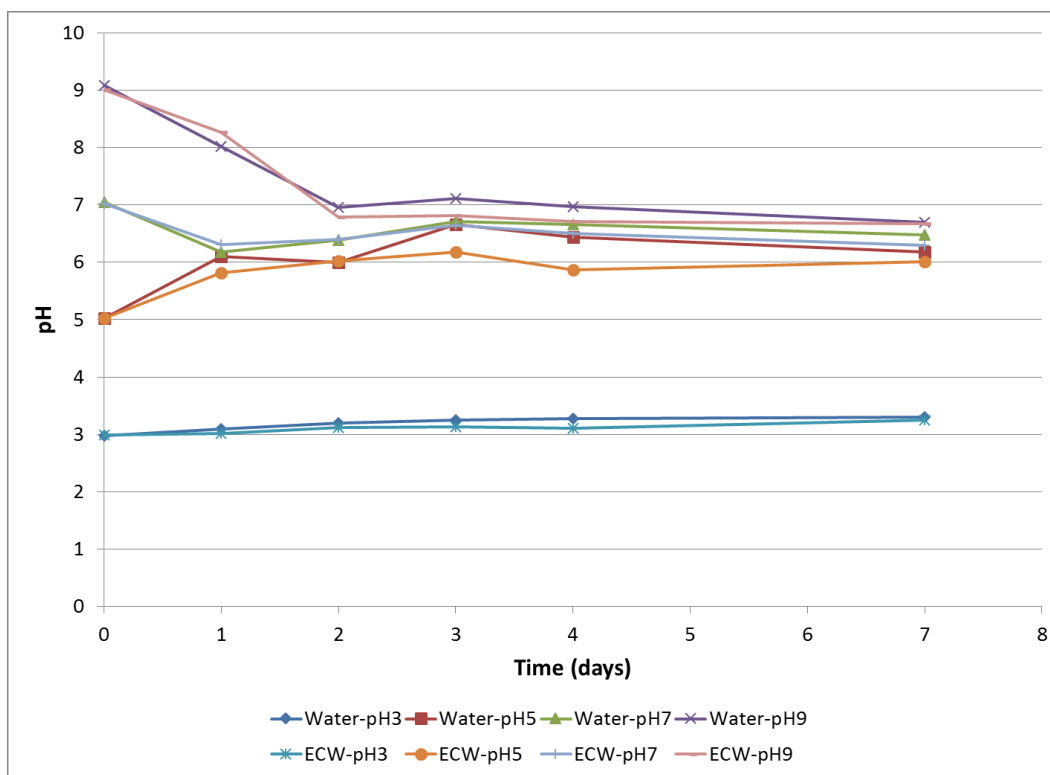


Figure 28 pH Change with 10 g of TCR

The explosives concentration after TCR adsorption in the acidic or alkaline environment was affected for neither TNT nor DNT. The concentration of both explosives decreased significantly over the first 72 hours of the experiment and then they stabilized until the last day of the experiment. For the samples with 5 and 10 g of TCR, the percentage of explosives reduction at pH reduction at pH values of 3.0, 5.0, 7.0 and 9.0 is shown in

Table 6.

Table 6 Explosives Reduction Percentage at Different pH

Sample	Time (days)	5.0 g TCR		10.0 g TCR	
		TNT Reduction (%)	DNT Reduction (%)	TNT Reduction (%)	DNT Reduction (%)
pH 3.0	1	28	40	64	71
	2	60	67	74	78
	3	61	67	78	80
	4	63	68	77	79
	7	66	69	80	80
pH 5.0	1	27	39	50	59
	2	57	64	73	76
	3	58	64	82	82
	4	65	69	81	81
	7	66	68	83	83
pH 7.0	1	23	35	50	60
	2	49	58	73	78
	3	59	64	78	80
	4	62	65	77	79
	7	64	65	81	81
pH 9.0	1	34	46	58	67
	2	63	69	73	78
	3	65	70	78	81
	4	66	69	79	81
	7	69	71	81	82

The noticeable differences in the explosives reduction by the end of the experiment were found between the 5 and 10 g TCR adsorptions. This was in line with the results discussed before that the explosives removal was proportional to the TCR amount in the adsorption system. Figure 29 and Figure 30 depict the concentration of TNT and DNT from adsorption reactors that contained 5 g TCR and run at the different pHs.

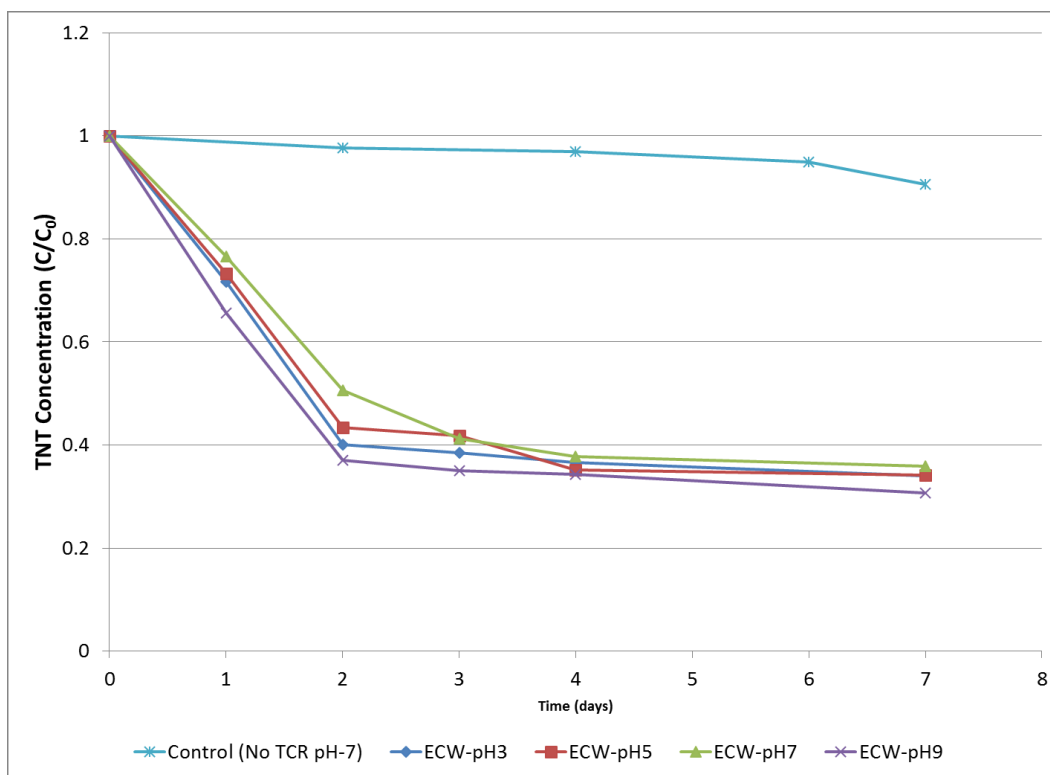


Figure 29 TNT Concentration at Different pH Samples

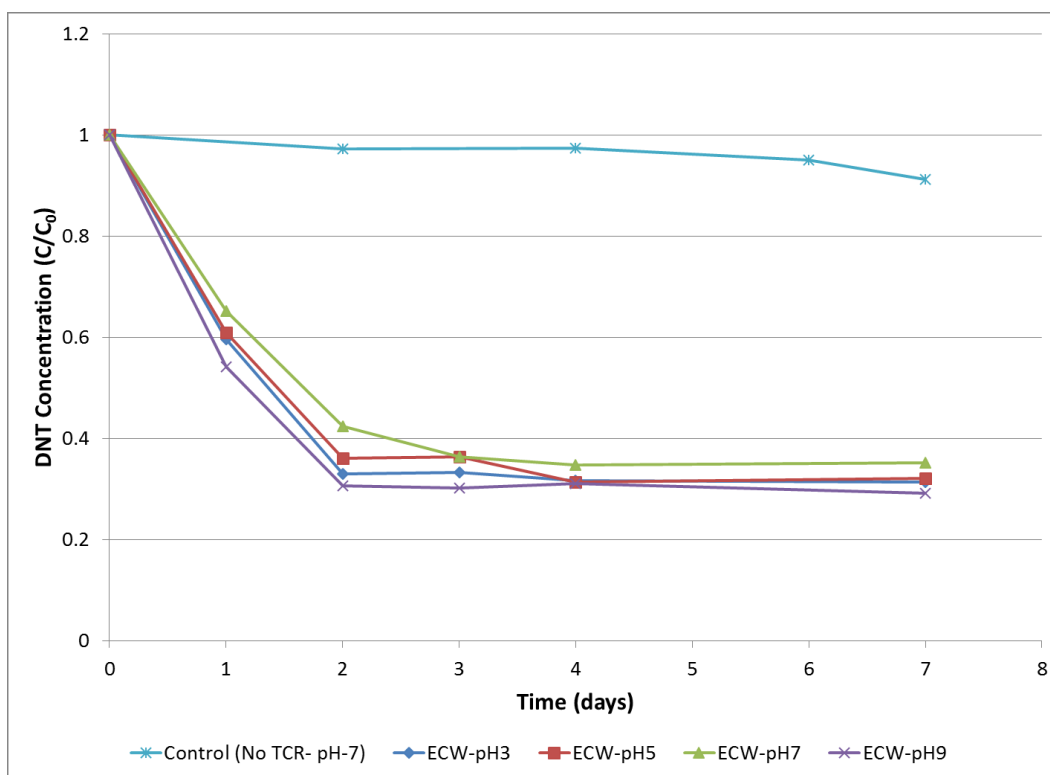


Figure 30 DNT Concentration at Different pH Samples

As aforementioned, when the adsorption was conducted at the pHs ranging 5 to 9, the system pH changed to ~7. In comparison, when the system run at pH 3, the pH value did not change but maintained ~3. In addition, explosives adsorption by TCR was not affected by the pHs. It was, therefore, confirmed that explosives adsorption by TCR was pH-independent and that TCR possessed a pH buffering capacity to some extent by adsorbing the hydrogen and hydroxyl ions that determine the pHs.

Studies executed by other scientists showed that the presence of TCR had an effect on acidity and alkalinity as exhibited in the current experiments. In an experiment performed by Zhao et al. (2011), the presence of the TCR had an effect on the pH value of the soil and the soil alkalinity was reduced by TCR. Calisir et al. (2009) studied the effect of the pH in the copper ion adsorption by TCR and found that copper ion was better adsorbed to TCR as the pH values in the solution increased but the adsorption pattern was not affected.

4.1.5 Activated Carbon vs. Tire Crumb Rubber

This experiment was performed to compare the explosives adsorption efficiency by GAC and TCR. GAC is the most commonly used adsorbent and is known for its effectiveness and utilized in the treatment of pollutants in water, including TNT (Vasilyeva et al., 2002). Under similar conditions and parameters, GAC was expected to outperform TCR.

As expected, the results from this experiment showed that GAC was more effective in explosives adsorption than TCR under the same conditions. The explosives concentration in the ECW decreased faster in the GAC than in the TCR reactor in the first 24 hours. From 24 hours to the end of the experiment (72 hours), the explosives concentrations were, however, similar in both reactors.

The concentrations of TNT and DNT in the reactor with 25 g GAC as adsorbent decreased in the first 24 hours by 98.0 and 98.4%, respectively. In the reactors with 50 g GAC, the concentrations decreased by 98.9 and 99.1%, respectively. The TCR achieved reductions in the concentrations of TNT and DNT in the reactor with 25 g TCR were 86.5 and 89.0%, respectively. When the amount of TCR were increased to 50 g, the concentrations decreased by 93.5 and 94.7%, respectively. By the end of the experiment, the explosives concentrations in the reactor with either 25 or 50 g GAC decreased by 99.9% for both TNT and DNT. The concentrations of TNT and DNT decreased by 90.1 and 91.1% and by 95.3 and 95.9%, respectively, for the reactors with 25 and 50 g TCR. Figure 31 and Figure 32 show the concentration of the explosives when exposed to both the GAC and the TCR.

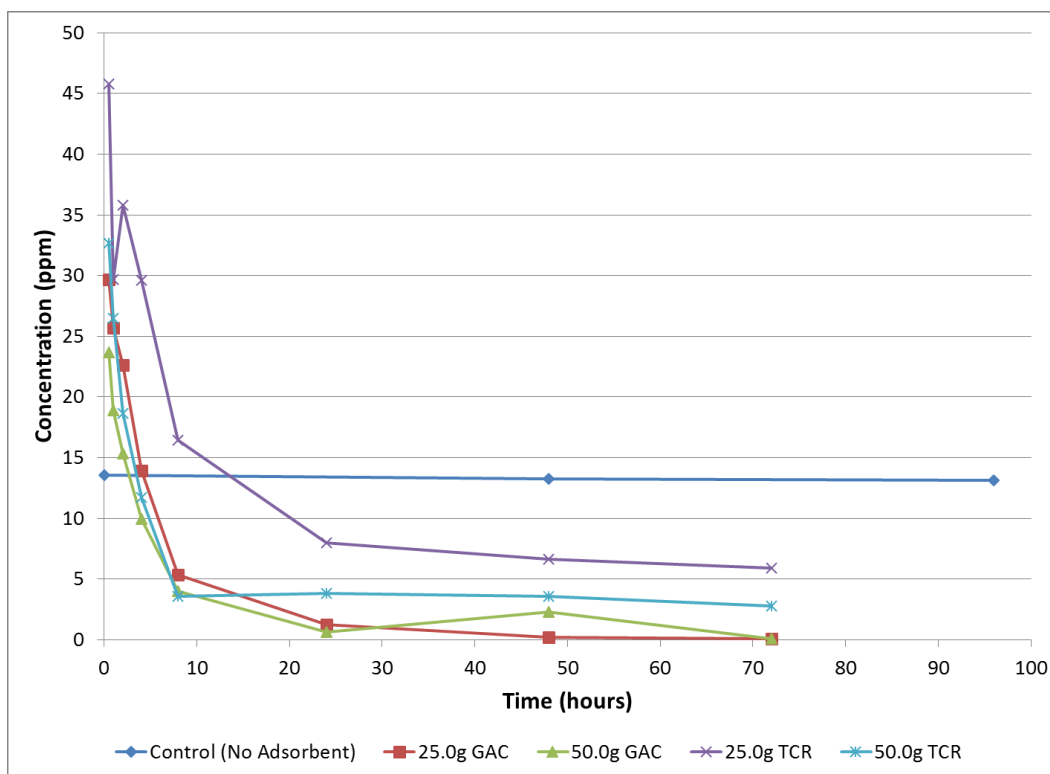


Figure 31 TNT Concentration with GAC and TCR as Adsorbent

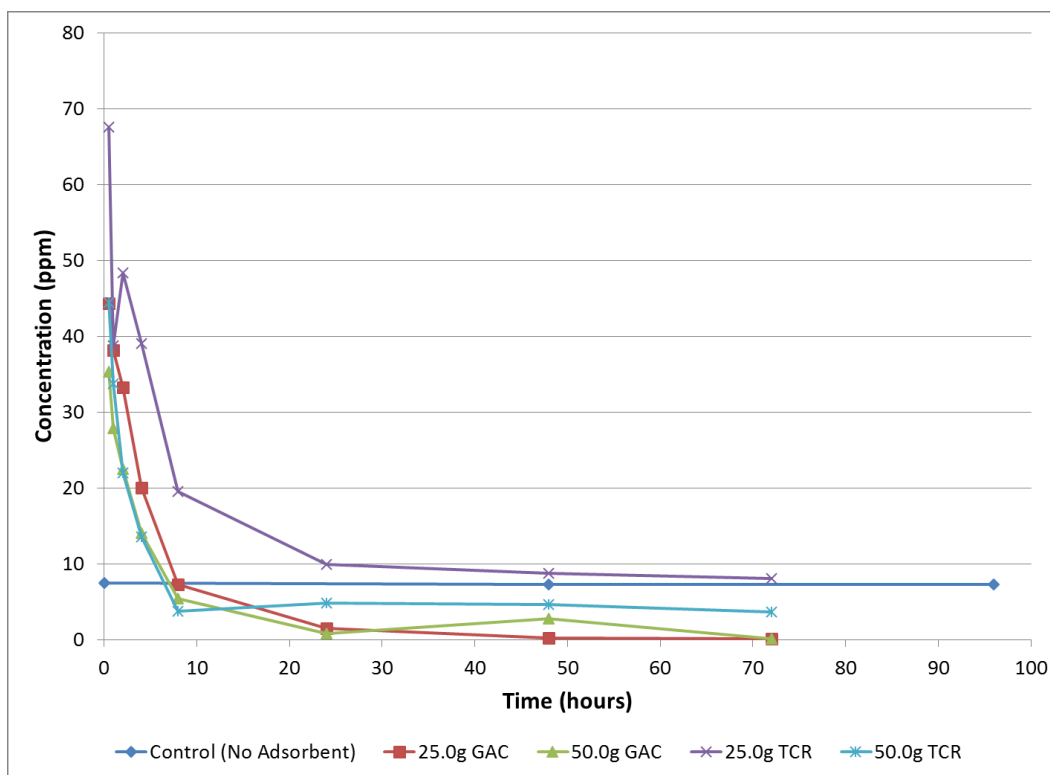


Figure 32 DNT Concentration with GAC and TCR as Adsorbent

Experimental results showed that GAC was a better adsorbent than TCR. These results were expected since GAC is the most commonly used adsorbent for the treatment of polluted water due to its effectiveness. Although there was a noticeable outperformance of GAC in the beginning of the adsorption period, difference was minimized at the end of the experiment. Impressively, after 72 hours the adsorption with 25 g of TCR exhibited a difference by ~10% for TNT and DNT, compared to the counterpart of GAC. Similarly, the adsorption efficiency was different by ~4% between the GAC and TCR systems at the end of the experiment when 50 g of adsorbent was used. Therefore, it is construed that the use of TCR as an adsorbent for the treatment of ECW is not only technically feasible but also cost-effective due to the fact that TCR is produced by shredding waste tire stockpiles.

4.2 Explosives Containing Water Phytoremediation by Dwarf Papyrus

Several experiments were performed in order to determine which plant was better to bioremediate ECW. Among the plants of water lettuce, water hyacinth and dwarf papyrus, only the dwarf papyrus was successfully grown inside the laboratory. The dwarf papyrus was exposed to ECW in order to see if it survived harsh conditions due to explosives concentration in the ECW by phytoremediation.

The results of the phytoremediation experiment performed are discussed below. The conductivity, pH and temperature were measured in the ECW in order to understand if any of these parameters changed due to the presence of the dwarf papyrus. The growth (mass) of the dwarf papyrus was recorded for 3 weeks in order to assess if the explosives concentration in the ECW had an effect on the growth and development of the papyrus. The initial conditions in each reactor are shown in Table 7.

Table 7 Initial Conditions for the Dwarf Papyrus and ECW Experiment

Sample	Conductivity ($\mu\text{S}/\text{cm}$)	pH	Temperature ($^{\circ}\text{C}$)	Papyrus Weight (g)
Control	615	6.13	21.5	19.3
Papyrus and 0.5 TNT ECW	605	6.27	21.7	10.0
Papyrus and 1.0 TNT ECW	599	6.33	21.6	13.3
Papyrus and 2.5 TNT ECW	603	6.77	21.7	10.8
Papyrus and 5.0 TNT ECW	597	6.21	21.4	10.3
Papyrus and 10.0 TNT ECW	593	6.42	21.7	19.0

While the experiment progressed, the conductivity in all the reactors increased but not in a clear pattern. This may be due to the presence of the dwarf papyrus and the interaction between the roots and the solutions in each reactor. The pH values in the reactors were fluctuating but steady around the initial conditions values. The same trend occurred with the temperatures in the reactors. None of these parameters seemed to be affected by either the dwarf papyrus and/or the ambient conditions. The final values at the end of the experiment (3 weeks after) are shown in Table 8.

Table 8 Final Conditions for the Dwarf Papyrus and ECW Experiment

Sample	Conductivity (uS/cm)	pH	Temperature (°C)	Weight (g)
Control	1340	6.94	20.8	32.0
Papyrus and 0.5 TNT ECW	1305	5.80	21.3	21.2
Papyrus and 1.0 TNT ECW	959	6.05	21.3	25.8
Papyrus and 2.5 TNT ECW	1431	5.75	21.2	25.6
Papyrus and 5.0 TNT ECW	941	6.47	21.6	21.4
Papyrus and 10.0 TNT ECW	1082	6.54	21.7	26.6

The results from this experiment showed that the dwarf papyrus continued to grow when exposed to explosives at different concentrations in the ECW. The dwarf papyrus in the control reactor exposed only to nutrient solution showed the second poorest growth percentage of 65.8% among the systems. The poorest growth (37.2%) percentage was achieved by the reactor with 10 ppm TNT. The growth percentages for the remaining reactors were between 94.0 and 137.0% by the end of the experiment. Therefore it is construed, that TNT concentrations in ECW up to 5

ppm could enhance the growth of dwarf papyrus probably by serving as a growth substrate. The growth behavior of the plants along the experiment is depicted in Figure 33.

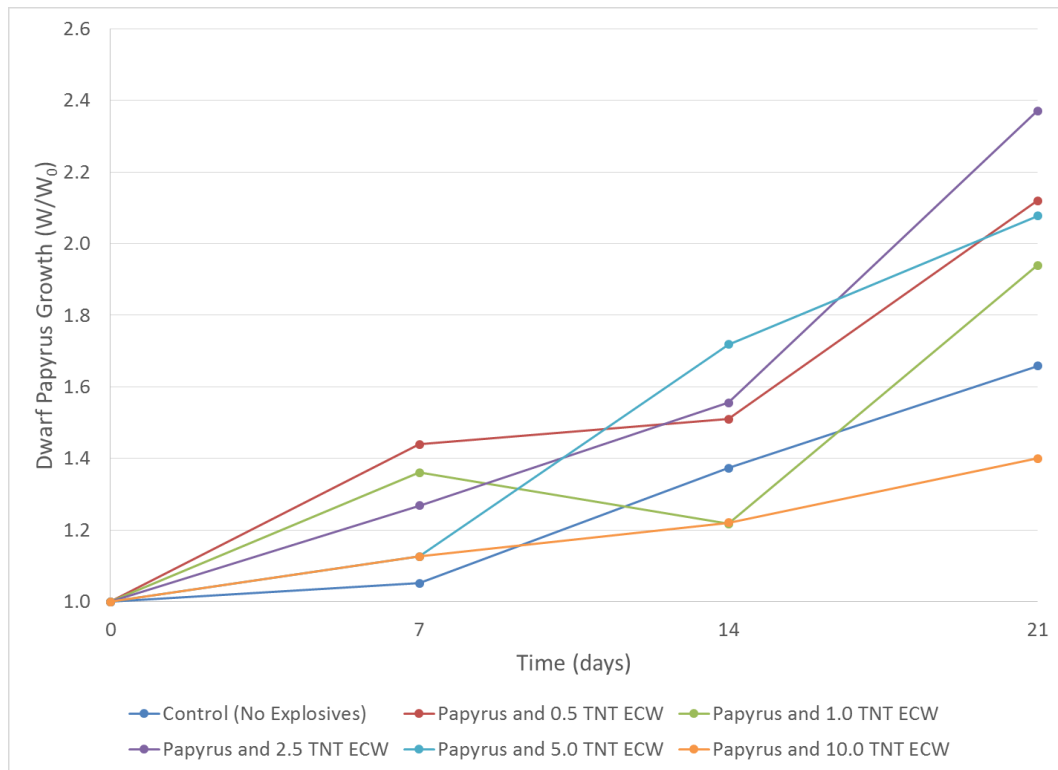


Figure 33 Dwarf Papyrus Growth at Different Concentration ECW

The explosives concentrations in the ECW were measured in each reactor and the results showed that the concentration of TNT and DNT decreased, as shown in

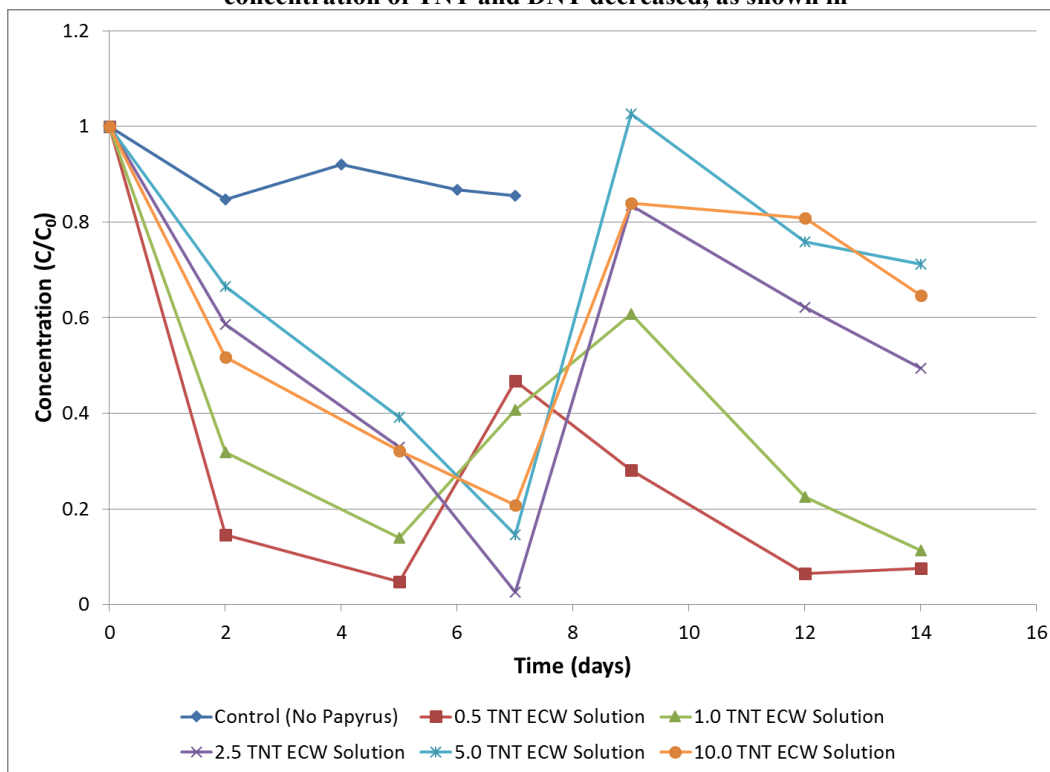


Figure 34 and Figure 35. Significant decreases in the explosives concentration were observed in the first week of the experiment. After the first week of the experiment the TNT concentration in the reactors decreased by 53.3, 59.4, 97.3, 85.5 and 79.2%, for the reactors with the initial TNT concentrations of 0.5, 1.0, 2.5, 5.0 and 10.0 ppm, respectively. For the same sequence of reactors, the DNT concentrations decreased by 88.8, 46.2, 77.6, 62.8 and 27.2%, respectively.

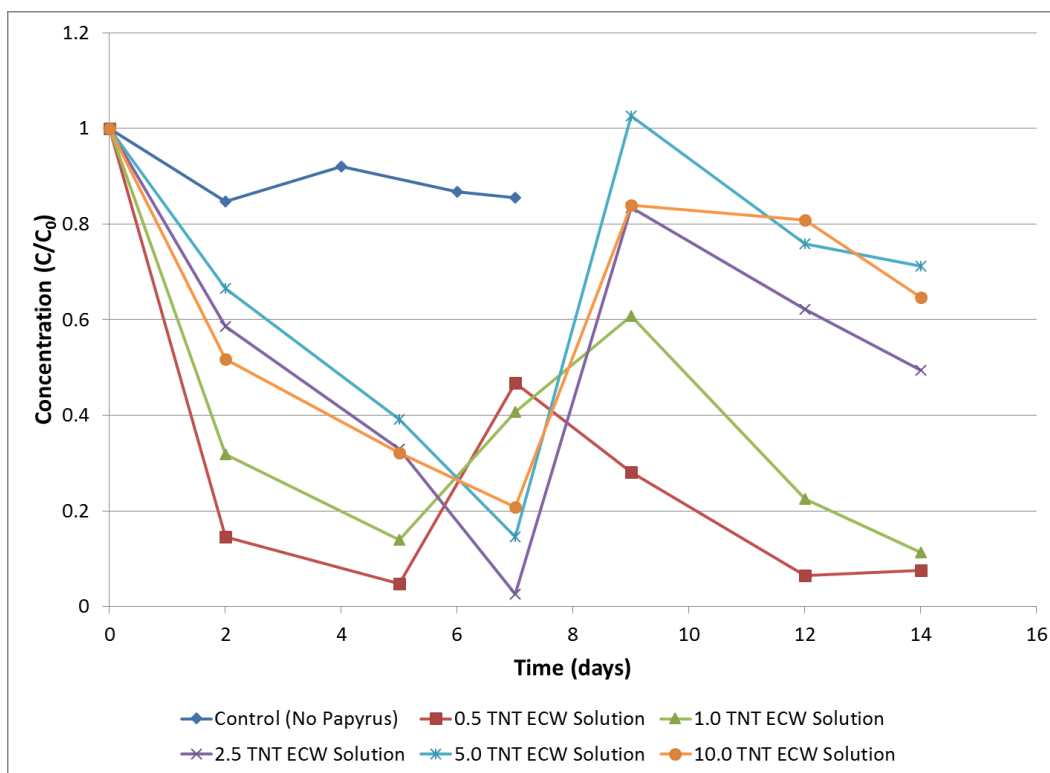


Figure 34 TNT Concentration Phytoremediated by Dwarf Papyrus

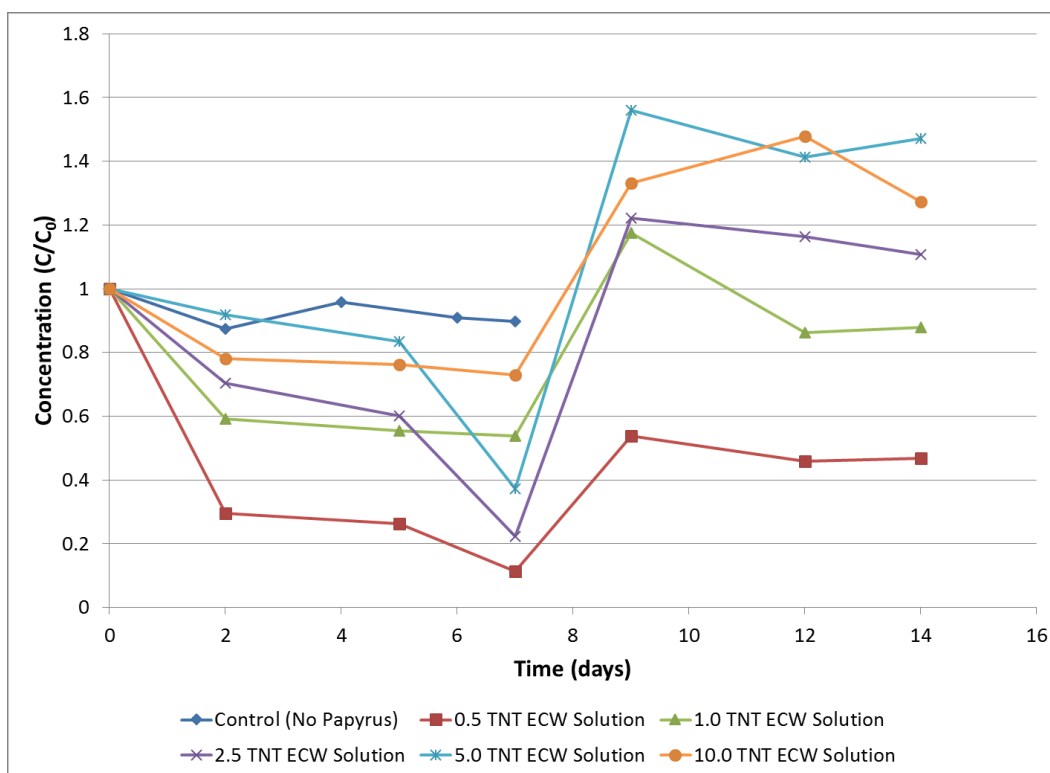


Figure 35 DNT Concentration Phytoremediated by Dwarf Papyrus

Since the volumes of the ECW in each reactor decreased considerably after a week, the reactors were refilled to their initial volumes with their corresponding initial ECW concentrations. Due to the reactors refilling, the concentrations abruptly increased. However, TNT concentrations kept decreasing as the experiment proceeded, whereas DNT concentrations stayed fairly the same during the second week of the experiment.

After the second week of the experiment the TNT concentration in the reactors decreased by 92.4, 88.7, 50.7, 28.9 and 35.3% for the reactors with the initial TNT concentrations of 0.5, 1.0, 2.5, 5.0 and 10.0 ppm, respectively. For the same sequence of reactors, the DNT concentrations decreased by 53.2, 12.1, 10.8, 47.3 and 27.4%, respectively. Similar results were achieved by Best et al. (1997) who performed experiments to screen the aquatic and wetland plants for the phytoremediation of explosives. Both the submersed and emergent plants tried were able to achieve TNT removal percentages between 94 to 100% in 10 days.

At the end of the experiment, all the plants in the experiment were sacrificed in order to evaluate the concentration of TNT and DNT inside the different parts of the plants. The flowers, stems and roots of each plant were analyzed for explosives concentrations. The results showed that TNT was mostly present in the roots of the plants, followed by the stem and lastly the flower. TNT concentrations were only shown in the reactors exposed to concentration higher than 2.5 ppm and increasing as the initial concentration in the reactors increased. The fact that higher concentrations were found in the roots did not mean that plant allocated the TNT in this zone, but this might be due to direct contact between explosives and roots. In the stems, TNT concentrations were also found, but not in a clear pattern. Flowers did not show TNT concentrations. The TNT concentrations were 0.0059 and 0.0320 mg/g at the initial TNT

concentration of 2.5 ppm, 0.0102 and 0.0924 mg/g at 5 ppm, and 0.0027 and 0.4746 mg/g at 10.0 ppm in the stems and roots, respectively. The DNT concentrations in the plants were inconclusive instrumental errors in quality control for this specific case. Figure 36 and Figure 37 show the concentration of both explosives found in the flowers, stems and roots of each plant.

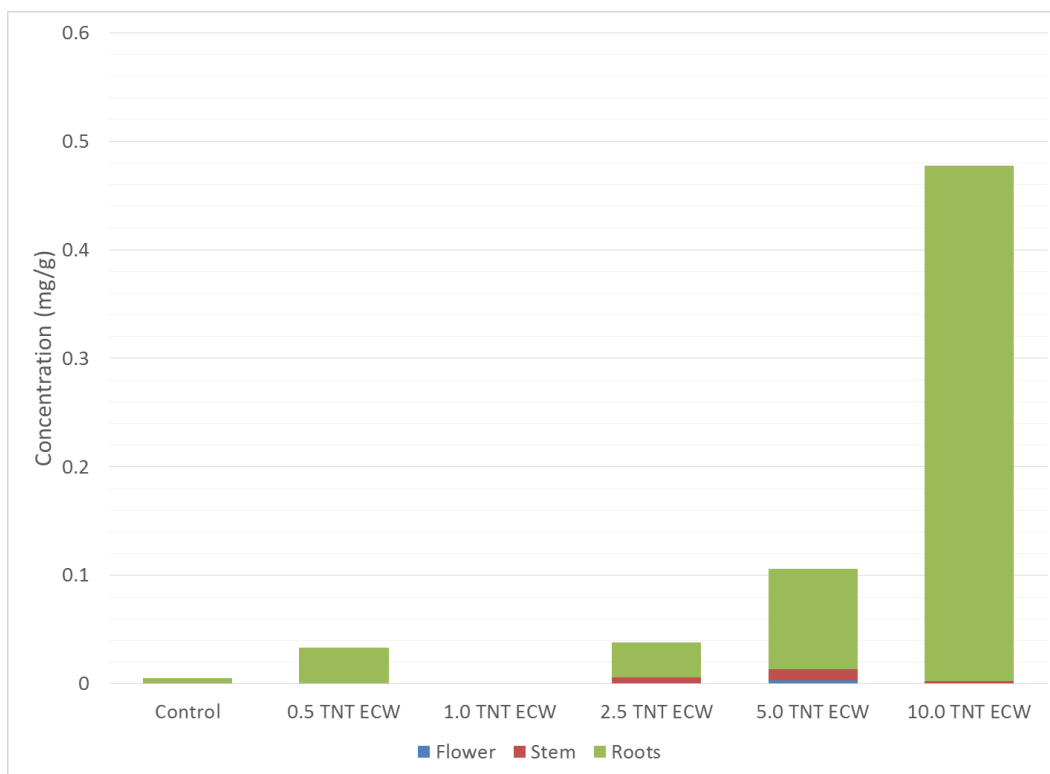


Figure 36 TNT Concentration in the Flower, Stem and Roots

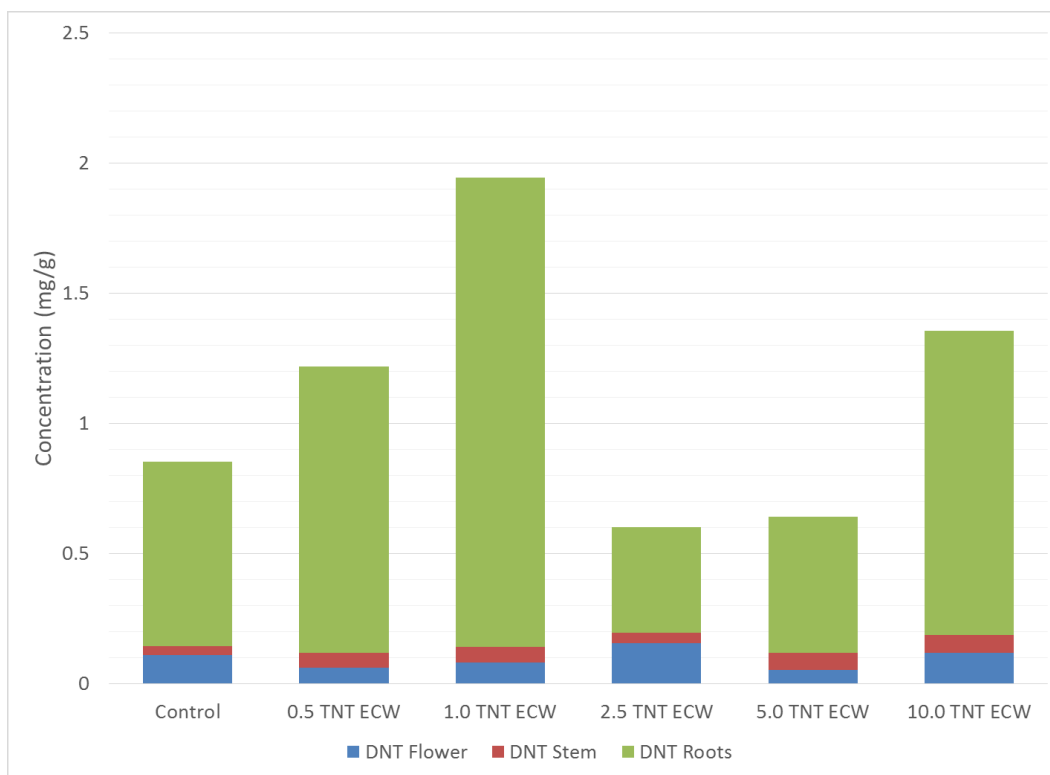


Figure 37 DNT Concentration in the Flower, Stem and Roots

This experiment showed that the dwarf papyrus had the capability to grow in harsh environments such as the ones polluted with explosives. Due to this characteristic exhibited by the dwarf papyrus, the treatment of ECW by phytoremediation is feasible. Clearly, ECW with a high explosives concentration affected the growth and development of plants but at concentration below 5 ppm the dwarf papyrus survived and stayed healthy. The phytoremediation seemed to work better for the treatment of TNT than DNT. Experiments showed that TNT concentrations decreased faster than DNT concentrations.

TNT concentrations were reported higher in the roots than in any other part of the dwarf papyrus but that could be attributed to the fact that the roots were in direct contact with the explosives and it be adhered to the surface of the roots. The TNT concentrations found in the

stems suggest that the papyrus translocated the explosive to the stems. In case of DNT, its concentration decreased in the ECW but experiments were inconclusive on where the plants located it. Panz & Miksch (2012) reported the phytoremediation of explosives by both wild-type and transgenic plants. Their results showed that TNT specifically transformed into other byproducts in the roots and most of the plants were able to uptake between 0.08 to 1.03 mg/g of TNT.

4.3 Explosives Containing Water Remediation by Treatment Train

Two TT experiments were performed: the two-in-one TT where TCR was added to the dwarf papyrus reactor and the TT in-series where the TCR adsorption was followed by the dwarf papyrus phytoremediation. These experiments were performed to determine which TT configuration achieved a better treatment of the explosives present in the ECW.

4.3.1 Two-in-One Treatment Train

This TT had both the TCR and the dwarf papyrus in a system for the treatment of the explosives present in the ECW. The TCR used was comprised of two 50/50% mixture of mesh sizes. The system did not contain ECW but had only water and nutrient at the beginning.

Figure 38 shows the influent and effluent explosives concentration throughout the experiment. On average, the effluent TNT concentration was ~8 ppm achieving ~21% reduction in concentration. In the case of DNT, the concentration was on average ~11 ppm which meant 23% reduction. Concentration of explosives in the ECW decreased noticeably when the TT was at rest. Experiment results showed that when this TT configuration was on hold over the night so as to work as a batch reactor, the TNT concentrations decreased by a minimum, maximum and average of 15.2, 45.6 and 33.5%, respectively. The DNT concentrations decreased during the

same on-hold times by a minimum, a maximum and average of 13.4, 42.8 and 30.2%, respectively. Even though this TT configuration did not achieve significant reductions in explosives concentration, it is believed that increasing the amount of dwarf papyrus and TCR in the TT as well as a longer contact time would increase the capacity of explosives treatment of this TT configuration.

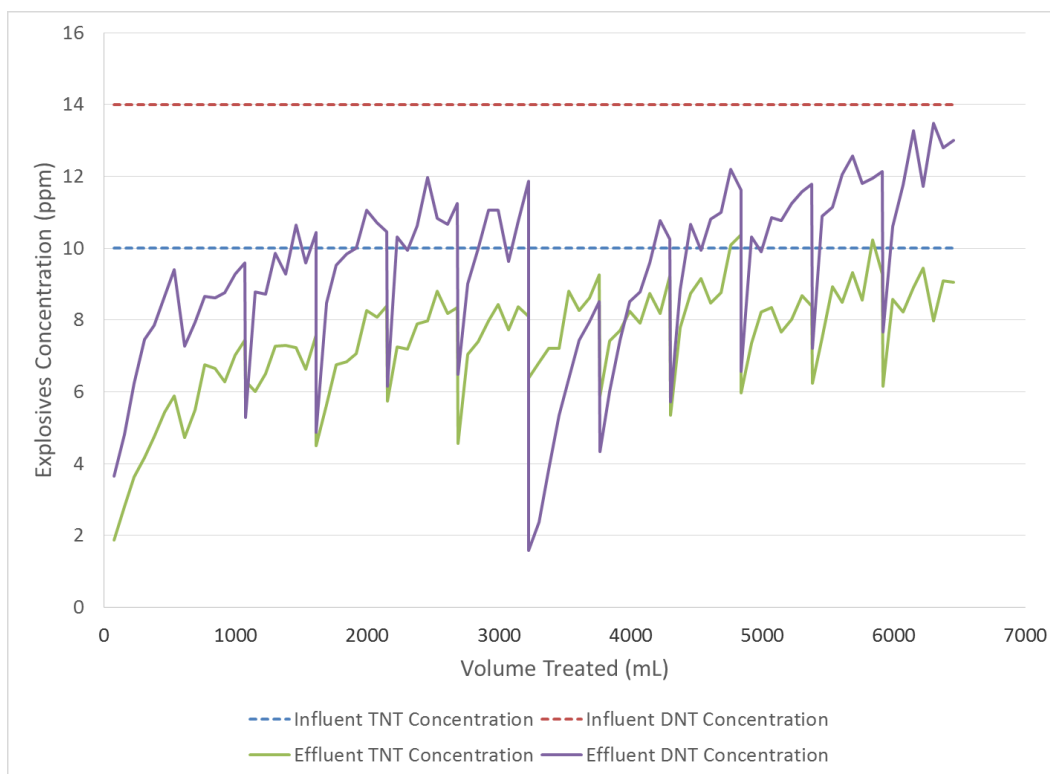


Figure 38 Two-in-One Treatment Train ECW Concentrations

4.3.2 In Series Treatment Train

The in-series TT configuration contained TCR adsorption followed by dwarf papyrus phytoremediation. The TCR mesh size used in this configuration was the same as the one used in the two-in-one TT configuration. Two sample ports were used in this TT configuration. The

first sampling port was placed just after the TCR column and the second port was placed after the phytoremediation with the dwarf papyrus.

Figure 39 shows the explosives concentration at the first sampling port (after the treatment with TCR). Explosives concentrations after the TCR adsorption column were equal or lower than the concentrations achieved in the two-in-one TT configuration. As aforementioned, the explosives concentration increased in the TT when the system was running and decreased while it was on hold.

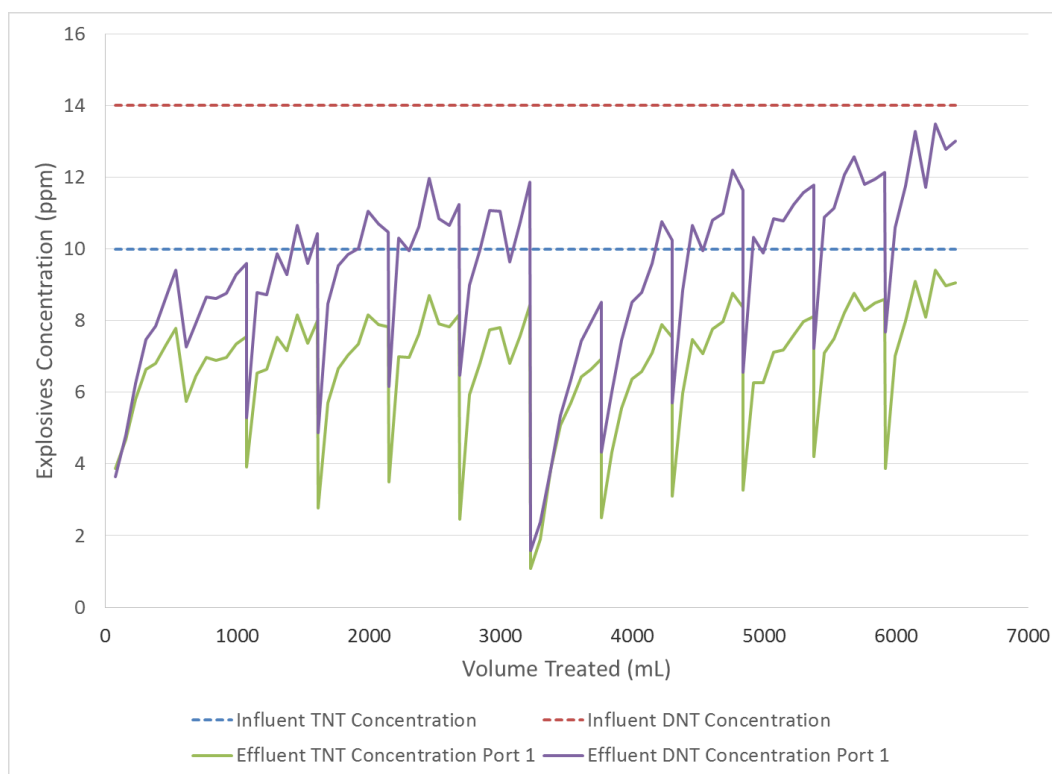


Figure 39 In-Series Treatment Train Port 1 ECW Concentrations

For this TT configuration, the TNT concentration in the treated ECW was on average ~6.7 ppm that was 33.0% lower than its initial concentration. Judged by the trend the effluent

TNT concentration, TCR adsorption was not saturated with TNT and it produced a steady-level TNT concentration. In the case of DNT, the concentration was on average ~9.3 ppm that was 33.5% lower than its initial concentration. However, an increasing trend of the effluent DNT concentration was observed over the experiment period. It is not certain whether the increase of DNT concentration was due to TCR column saturation with DNT or due to TNT transformation to DNT during the on-hold mode.

Experimental results showed that when the system was on-hold mode, the TNT concentrations decreased by a minimum, maximum and average of 48.1, 87.1 and 61.3%, respectively. The DNT concentrations decreased during the on-hold mode by a minimum, a maximum and average of 36.8, 86.7 and 48.1%, respectively.

As shown in Figure 40, TNT was further decreased to an average concentration of 4.8 ppm in the effluent from the phytoremediation basin. This was lower by 52% than the TNT concentration in the untreated ECW. Considering the effluent TNT concentration in the effluent from TCR column, TNT was additionally reduced by 24.8% from 6.7 to 4.8 ppm, on average. During the period of on hold, the TNT concentrations decreased by a minimum, maximum and average of 30.9, 60.3 and 49.0%, respectively.

Similar to the results from the TCR column, the effluent DNT concentration kept increasing and reaching the initial concentration in the untreated ECW (14 ppm). However, the on-hold mode significantly decreased DNT concentrations by a minimum, a maximum and average of 22.8, 44.5 and 35.8%, respectively.

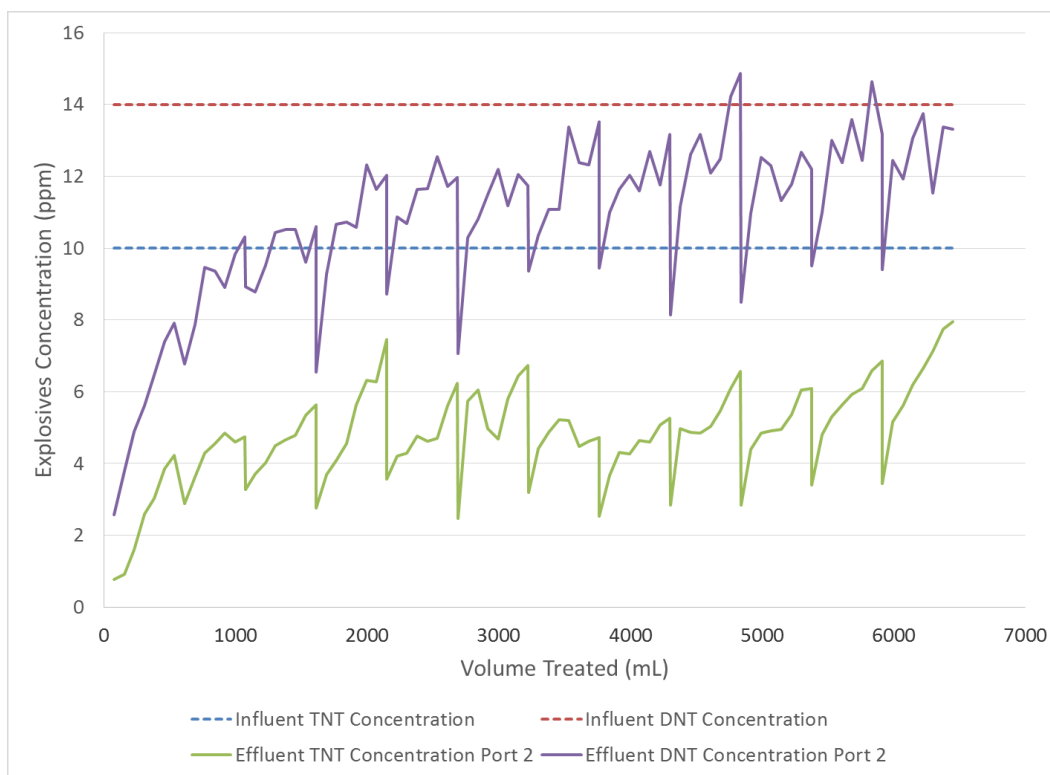


Figure 40 In-Series Treatment Train Port 2 ECW Concentration

The explosives concentrations in both configurations of TTs are shown in Figure 41 and Figure 43 for the purpose of comparison. As shown, the in-series TT was better in remediation of ECW than the two-in-one TT. The in-series TT utilized the individual remediation capacity of the TCR and the dwarf papyrus in sequential unit processes. The sole treatment performance achieved by separate systems in series, led to greater reductions in the explosives concentrations in the ECW, therefore resulting in a more efficient treatment. In order to improve the results obtained with the in series TT a few adjustments could be made: adjustments such as decrease in the TCR size, increase in the TCR amount, increase in the contact time in the column as well as in the reactor, and the addition of another TCR column after phytoremediation by the dwarf papyrus.

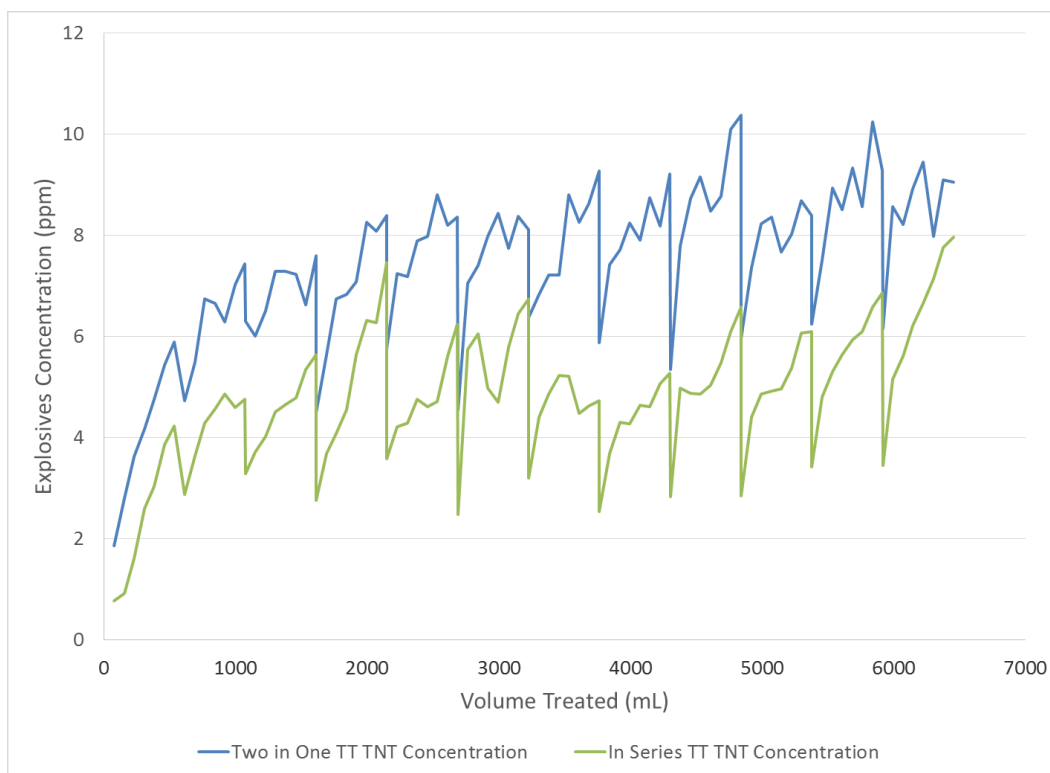


Figure 41 Effluent TNT Concentration from Two Different TT (Influent TNT Concentration=10ppm)

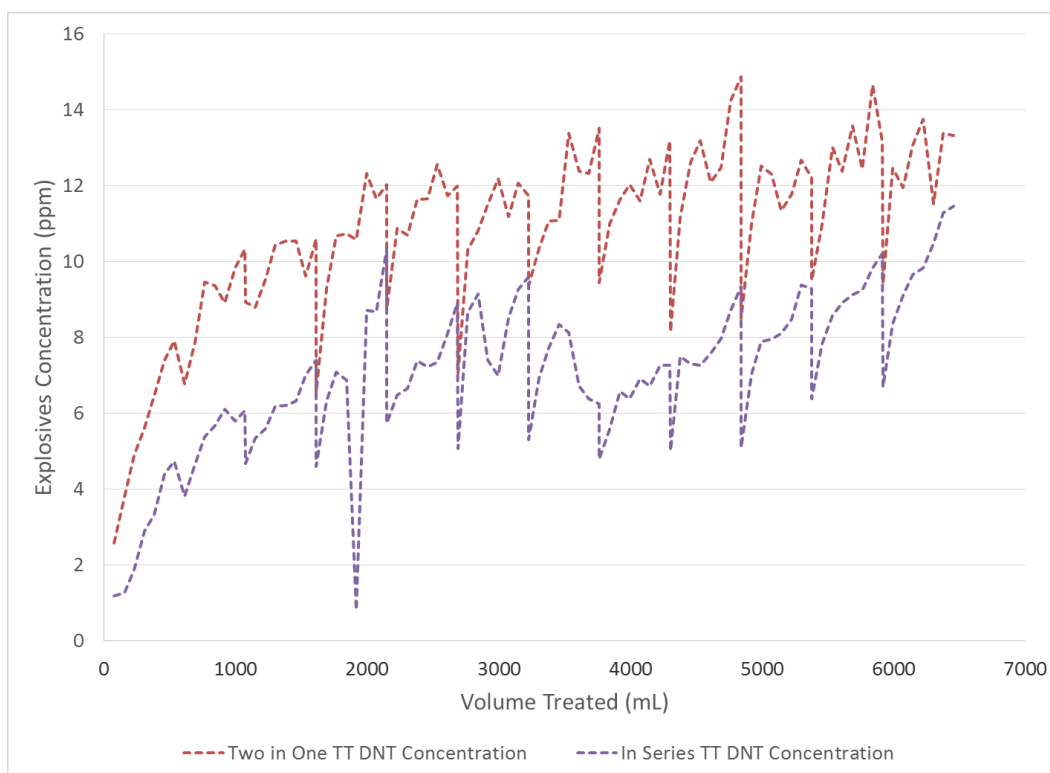


Figure 42 Effluent DNT Concentration from Two Different TT (Influent DNT Concentration=14ppm)

4.3.3 Dwarf Papyrus Analysis After Treatment Train

The explosives concentrations inside the dwarf papyrus used in each TT configuration were analyzed. As shown in Figure 43, explosives were not found in the flower, but the stems and roots contained explosives. For both the two in one and in series TT configurations, explosives concentrations were found to be higher in the roots and in the stems. Similar results were achieved in the previously discussed batch experiment with the dwarf papyrus. The dwarf papyrus in the two-in-one TT contained ~ 0.008 and ~ 0.038 mg/g of TNT and ~ 0.016 and ~ 0.086 mg/g of DNT in the stems and roots, respectively. Almost similar explosives concentrations were found in the dwarf papyrus used for the in-series TT. ~ 0.006 and ~ 0.029 mg/g of TNT and ~ 0.025 and ~ 0.069 mg/g of DNT in the stems and roots, respectively.

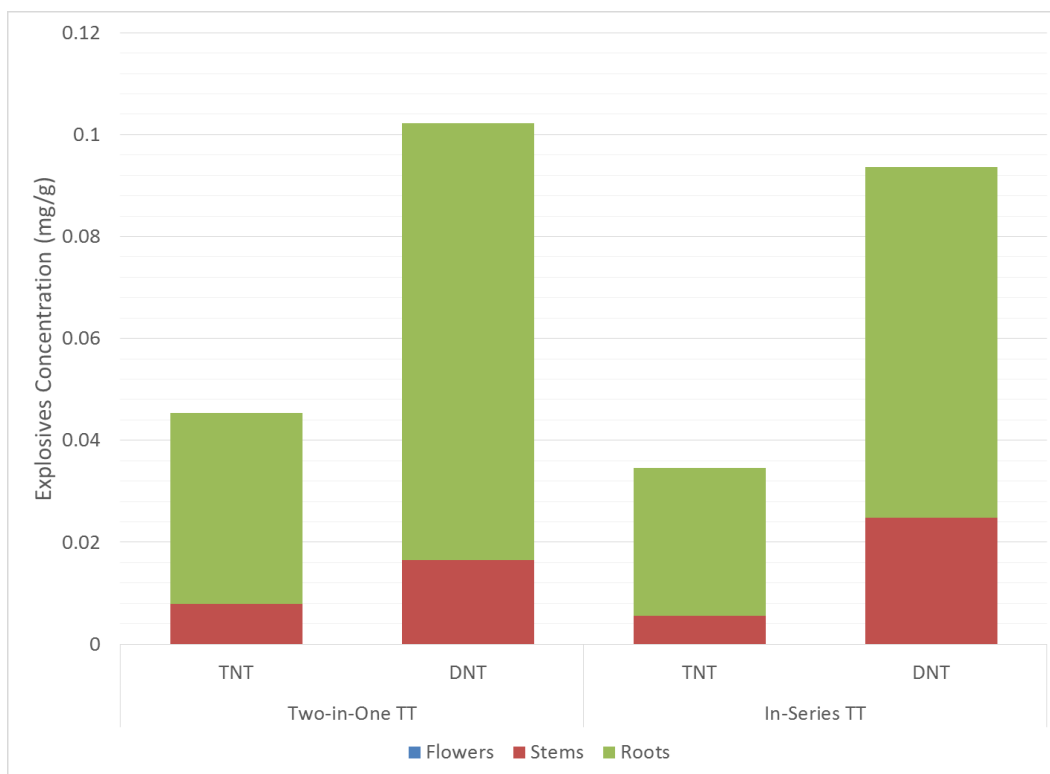


Figure 43 Explosives Concentration in the Dwarf Papyrus

The explosives concentrations found in the dwarf papyrus were congruent with the experimental setups, higher explosives concentrations were found in the plants in the two-in-one TT. This was probably due the fact that in the two-in-one TT the dwarf papyrus was subject to higher explosives concentrations in the ECW. Although experimental results showed that the in-series TT was a better configuration for the treatment of explosives than the two-in-one TT, modifications to this configuration can be made in order to improve the treatment of ECW and get lower explosives concentrations. For example, Trichloroethylene (TCE) in aquifers was treated with 3-stage treatment train system. The treatment train was applied on an in series pattern allowing TCE removal percentages after each stage of 87.6, 10.7 and 1.7% for a complete removal of TCE (Tsaia et al., 2008).

5 CONCLUSIONS

Based on the experimental results obtained from the current study, the following conclusions can be made:

- TCR adsorption was effective in reducing explosives concentrations. For example, the initial TNT at 7.6 ppm was decreased after 24 hours to 0.18, 0.48 and 0.86 ppm by batch adsorption with 15, 10 and 5 g of TCR. After a 48-hour adsorption, TNT removal by TCR adsorption was greater than 90% for all cases.
- In a continuous-flow adsorption, smaller TCR sizes (mesh 30) decreased more explosives than bigger sizes (mesh 14-20) due to the increase of the surface area available for explosives adsorption. Also explosives concentration (initial TNT at 12 ppm) was not detected from TCR adsorber packed with smaller sizes until 68 pore volumes.
- TCR adsorption was temperature-dependent but only at the early adsorption phase. For example 82 and 89% of TNT was adsorbed after 24 hours at the temperatures of 10 and 40 °C, respectively, with 25 g TCR and at the initial TNT at ~20 ppm.
- TNT and DNT adsorption to TCR was not affected by the different adsorption pHs ranging 3-9.
- TCR showed a slightly lower explosives adsorption than granular activated carbon (GAC) in 24 hours. 25 g of GAC removed >98% of TNT and DNT in 24 hours, whereas 25 g TCR adsorbed 86.5% TNT and 89% DNT. However, they were comparable at a longer adsorption time with a higher amount of adsorbents. 50 g GAC removed >99% of both explosives and 50 g TCR achieved 91 and 96% adsorption of TNT and DNT, respectively after 72 hours.

- In a two-in-one TT, the presence of TCR did not exert any effects on the growth and/or development of the plants.
- Dwarf papyrus was able to treat ECW without suffering adverse damage in its growth and development when the initial TNT concentration was below 10 ppm. Above 10 ppm, dwarf papyrus showed interference in growth and development, such as chlorosis.
- TNT concentration decreased in a week by 53-97% with dwarf papyrus, depending on the initial TNT concentration at 0.5–10 ppm. TNT was mostly found in the roots, followed by the stems and the flowers.
- An in-series continuous-flow treatment train of TCR adsorption followed by dwarf papyrus phytoremediation was able to reduce TNT and DNT concentrations by approximately 52 and 50%, respectively.

Therefore, the results confirmed that either adsorption with TCR or phytoremediation with dwarf papyrus was capable of treating the explosives TNT and DNT, but the combination of TCR and dwarf papyrus in a TT proved to be a better treatment. These results are expected to promote beneficiation of a solid waste TCR in environmental remediation in combination with green phytoremediation with dwarf papyrus.

6 RECOMMENDATIONS

Additional studies are recommended for the following topics:

- Other Puerto Rico native plants for the treatment of sites contaminated with explosives;
- Bioaugmentation known with bacteria capable of the treatment of explosives to the reactors filled with TCR;
- Incorporate toxicological studies to understand whether the ECW treated by TCR is toxic or not;
- Regenerate the TCR by the addition of substances capable of degrading or desorbing the explosives from the TCR spent with explosives;
- Implement experiments with the dwarf papyrus and TNT and DNT radioactive isotopes in order to clearly establish the phytoremediation mechanism, location and pathways achieved by the dwarf papyrus;
- Perform a field TT experiment under environmental circumstances (sun, rain and plants pests); and
- Improve the in series TT configuration by modifying the parameters, conditions and parameters studied in the aforementioned experiments. Modifications such as the increase of the amount of TCR and/or dwarf papyrus and the addition of a post TCR adsorber. A schematic of such a recommended setup is shown in Figure 44 below.

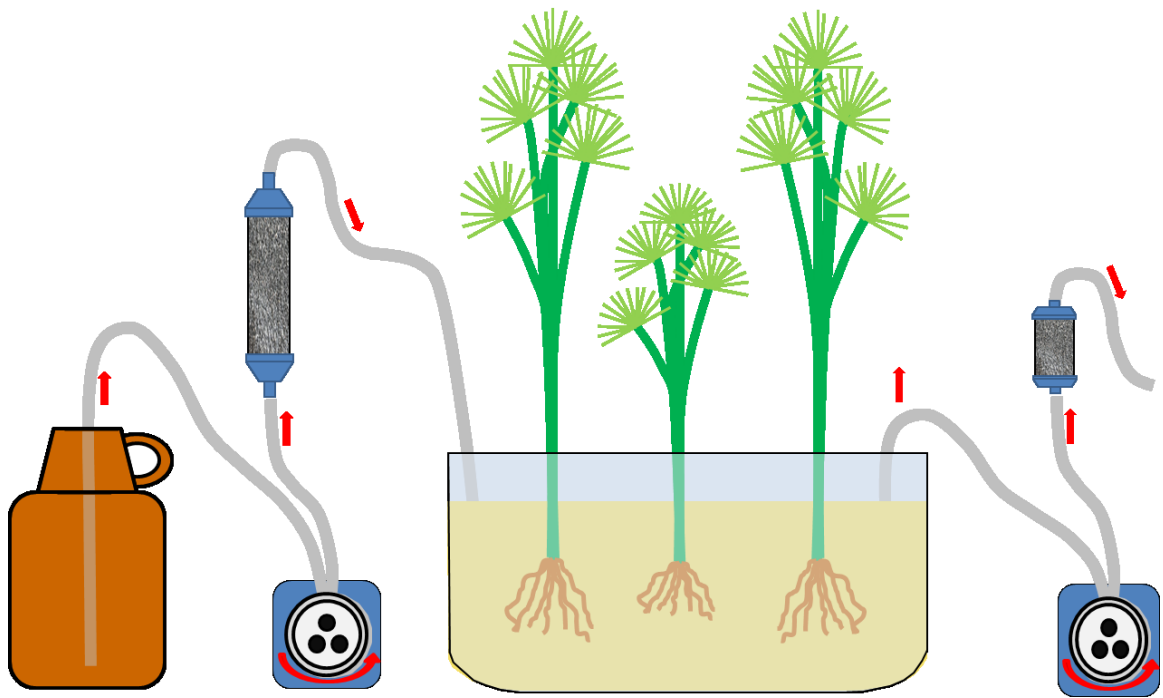


Figure 44 Recommended In-Series TT Configuration

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