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Toktam Moghbeli

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Effect of plant-based filtration and bio-treatment on toxicity of bio-oil process water

By

Toktam Moghbeli

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Effect of plant-based filtration and bio-treatment on toxicity of bio-oil process water

By

Toktam Moghbeli

Approved:

Susan V. Diehl Professor of Forest Products Director of Thesis	Paul David Jones Assistant Extension Professor of Forest Products Committee Member
R. Dan Seale Professor of Forest Products Committee Member	Tor P. Schultz Professor of Forest Products Graduate Coordinator
George M. Hopper Dean, College of Forest Resources	

Name: Toktam Moghbeli

Date of Degree: May 10, 2013

Institution: Mississippi State University

Major Field: Forest Products

Major Professor: Dr. Susan Diehl

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Candidate for Degree of Master of Science

This study evaluated physical and biological treatments of bio-oil process water to decrease organic contaminants. A three-sequential-column filtration system compared four treatments: three columns filled with kenaf only; three columns filled with wood shavings only; first column filled with wood shavings and two with kenaf; and first column filled with kenaf and two with wood shavings. The kenaf and wood shavings were composted after filtration. The filtrate water underwent further bio-treatment by adding aeration and selected bacteria. After filtration and bio-treatment, oil and grease concentrations were reduced over 80% and toxicity reduced over 90%. There were no significant differences among filtration treatments. Most of the oil and grease was removed by the first column. Aeration significantly decreased the concentration of oil and grease and toxicity in the filtrate water. Composting of the bio-filtration matrices significantly reduced the oil and grease concentrations at day 45 by 80%.

DEDICATION

I lovingly dedicate this thesis to my wonderful husband, who supported me each step of the way. Also, this thesis is dedicated to my beloved parents who have been a great source of motivation and inspiration.

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CHAPTER I

INTRODUCTION

Development of new alternative energy sources is receiving considerable worldwide attention. This is due primarily to high energy prices which are forcing governments and industries to look for ways to reduce dependency on fossil fuel. There is a growing tendency toward using modern technologies to utilize wood or other plant based materials to produce biofuels, which could be cost-effective when compared to fossil fuels (Demirbas, 2007).

Biomass has the potential to become a major source of energy for humans. It has been estimated that biomass generates 10-14% of the world's energy (McKendry, 2002). It is predicted that from 2008 to 2035, United States energy utilization will accelerate by 14%, while the national energy production will increase by 22%. Biofuels are predicted to have the highest growth in national utilization sectors rising from 3.5% to over 11% compared to liquid fuels (U. S. Department of Energy, 2012). As biofuel technology matures, more attention should be given to the waste by-products generated during biofuel production (Arthur et al., 2005; Fakhru'l-Razi et al., 2009).

Large amounts of wastewater containing organic and inorganic matter are generated during the production of bio-oil. This must be properly disposed, because of its negative effect on the environment (Arthur et al., 2005; Fakhru'l-Razi et al., 2009). Development of widely applicable, efficient low cost methods for treatment of this type of wastewater is a high priority and needs to be examined, since several bio-oil refineries will start operating throughout the USA in the next few years (Arthur et al., 2005; Daifullah et al., 2003).

Treatment of wastewater is commonly carried out using several techniques, such as physical (filtration using activated carbon), chemical, and biological processes. Nevertheless, the costs of filtration by activated carbon and chemical methods are relatively expensive. On the other hand, biological treatments and use of bio-based filtration matrices could offer an effective treatment method for this type wastewater due to its low cost and friendliness to the environment (Fakhru'l-Razi et al., 2009).

Today, biological remediation methods have been broadly applied to treat water contaminated by organic materials. Biological treatment utilizes microorganisms which are mainly bacteria, fungi, and yeast (Borazjani et al., 2007). Identified biological treatment techniques include: (i) free-cell bioreactors that support a high population of acclimated microorganisms suspended in wastewater and; and (ii) a biological fixed film connected to a support that is in contact with the wastewater. The primary assessment of this type of wastewater is by the Biochemical Oxygen Demand (BOD) test (Li et al., 2005; Otani et al., 1984).

An alternative and inexpensive method for removing contamination from process water is called bio-filtration. In this method, different types of bio-based materials are used such as wood shavings, rice straw, sugar cane fibers, and kenaf. Kenaf, *Hibiscus cannabinus*, is a tropical plant that has been grown for 4000 years in its native Africa (Florence et al., 2011). Moreover, kenaf is an environmentally friendly crop and can be substituted for wood in paper production (Abe and Ozaki, 2007). Kenaf-based filtration has been effective in decontamination of polluted waters under aerobic as well as anaerobic conditions and is comparatively a low cost method of disposal (Borazjani et al., 2007).

Kenaf contains distinct fibers that are a mixture of mainly cellulose, lignin and hemicelluloses. Crystalline cellulose is the major supporting component, whereas lignin and hemicelluloses provide the matrix (Florence et al., 2011). The kenaf fibers provide surface to enhance microbial colonization as well as providing high adsorption of water and oil compounds (Borazjani et al., 2005; Borazjani et al., 2007). In addition, kenaf fibers are low-density, have high mechanical characteristics, and are simple to recycle (Florence et al., 2011). At the end of the process, spent kenaf can be composted and used as a soil amendment (Borazjani et al., 2005; Borazjani et al., 2007). Wood shavings have also been shown to remove oil from soil and water. Pine shavings when spread over sea water contaminated with Saudi Arabian sweet crude oil removed more than 80% of oil from water and contaminated sands (Seale et al., 2012).

The objectives of this research are to: 1) Evaluate the effectiveness of kenaf and wood shavings alone and together as filter matrices in a multi-stage filtration system for treatment of bio-oil process waters, 2) Use biological treatment to break down leftover organic pollutants in process waters after filtration, and 3) Compost spent kenaf and wood shavings with chicken litter to biodegrade the adsorbed pollutants.

CHAPTER II

LITERATURE REVIEW

Energy Sources

Sources of energy are extremely important for the world's future. Energy sources are classified into three categories: fossil fuels, renewable and nuclear. Fossil fuels include coal, petroleum and natural gas accounting for three quarters of the world's main energy utilization. Petroleum is responsible for 33%, coal 24% and natural gas 19%. Alternative sources of energy which are responsible for the other quarter of the world's energy consumption include nuclear power 5%, hydropower 6%, and biomass 13% (Demirbas, 2001; Stöcker, 2008). The nuclear sources are fission and fusion. The renewable energy sources include: solar, wind, hydroelectric, biomass and geothermal power (Demirbas, 2001). Approximately 25% of the consumption of biomass for energy is in industrialized countries where environmental protection laws require a tremendous level of investment (Parikka, 2004).

Biomass

Biomass is one of the ancient sources of energy for mankind, and it is considered a clean and renewable energy source (Bridgwater, 2003; Demirbas, 2001). Biomass is utilized for different intentions, including producing energy, heating homes, fueling vehicles and producing heat for industrial facilities (Demirbas, 2001). Biomass is defined as any organic matter composed of carbon, hydrogen, oxygen and nitrogen. Also, some kinds of biomass contain inorganic materials such as potassium, sodium, phosphorus, calcium, and magnesium (Mohan et al., 2006; Yaman, 2004).

Sources of biomass for energy can come from trade and industry, forestry, and agriculture (Stöcker, 2008). Biomass resources consist of different natural and derived matters, such as woody and herbaceous species, wood waste, bagasse, agricultural and industrial residues, waste paper, municipal solid waste, sawdust, biosolids, grass, waste from food processing, animal waste, aquatic plants and algae (Yaman, 2004). All wood waste and bark can be used for the production of energy. Some examples of wood waste include: bark, coarse residues, cores, sawdust, planner shavings, sander dust, urban wood wastes, and particleboard dust (Parikka, 2004).

Generally, biomass energy is divided into modern biomass energy and traditional biomass energy. Modern biomass energy has a wide variety of applications and is intended to be a replacement for conventional energy sources. However, traditional biomass energy has a narrow range of applications and is restricted to developing countries. Traditional energy includes charcoal and fuel wood for domestic purposes, rice husks and other plant remains and animal wastes (Demirbas, 2001).

It has been estimated the overall world biomass energy potential is about 92 quads per year, which accounts for 19% of total global energy consumption. In 2003, biomass provided approximately 2.9 quads of energy to the United States. Biomass accounted for 47% of the total renewable energy utilization and is the largest renewable source of energy. It is estimated that woody biomass has the capacity to support the United States with about five quads of the total energy by the year 2050 (Mohan et al., 2006; Pimentel et al., 2009).

Advantages and Disadvantages of Biomass Energy

Biomass energy is a renewable source of energy. It is used for producing different forms of energy and energy-intensive products such as solid, liquid, and gaseous fuels. Biomass can potentially be used to provide about 3-5% of the electric energy in the United States. Derivative products from biomass can be used as replacements for metallic or plastic materials that need considerable amounts of energy to be produced (Hughes, 2000; Jefferson et al., 2005). Generated fuels from biomass are efficient and burn clean. One advantage of biomass energy is the creation of less greenhouse gases compared to the fossil fuels conversion process (Stöcker, 2008). Biomass tends to have friendly environmental effects, particularly carbon recycling in the biological processes, with less emission of carbon dioxide and a low concentration of sulfur (Cadenas and Cabezudo, 1998). Also, emission of NOx from bio-oil fuels production is 50% lower than diesel oil production (Mohan et al., 2006).

The disadvantages of biomass energy include costly conversion of biomass to fuel since it is a new technology, and it also has costly capital construction. The process of transformation of biomass requires energy to produce renewable energy such as using heat in the pyrolysis process. There are limited sources of crops because the plants that are utilized are not grown all year and some plants, such as corn has alternative uses. It does cause some air pollution due to incineration of biomass that releases carbon dioxide into the environment (Thornton et al., 2004).

Components of Biomass

Biomass consists of three components, cellulose, hemicellulose, and lignin. Biofuels are produced from depolymerization of these three components of biomass (Czernik and Bridgwater, 2004). Cellulose is a crystalline compound that contains between 2000 and 14000 sugar residues. Cellulose is a glucose polymer that has a high molecular weight and is composed of β-D-glucopyranose elements in the C1 conformation. Cellulose gives biomass its strength and accounts for 40-50% of dry wood weight. Hemicellulose is a semi-crystalline compound and contains a combination of different polysaccharides such as glucose, mannose, galactose, xylose, arabinose, and 4-O-methyl glucuronic acid. Hemicellulose has a lower molecular weight than cellulose. It is the second most abundant component of wood and accounts for 25-35 % of dry wood weight. The third component, lignin, is considered an amorphous and high molecular weight compound that has a three-dimensional structure with numerous branches. The building blocks of lignin are polymers of 4-propenylphenol (p-coumaryl alcohol), 4-propenyl-2-methoxy phenol (guaicyl alcohol), and 4-propenyl-2,5-dimethoxy phenol (syringyl alcohol). Lignin makes up 23-33 % of softwood weight and 16-25 % of hardwood weight (Bridgwater and Boocock, 1997; McKendry, 2002; Mohan et al., 2006).

Conversion of Biomass to Biofuel

Biomass is converted to biofuel by two main pathways: biological digestion and chemical decomposition. The conversion processes can be further divided into three fundamental classifications: biochemical processes, direct combustion, and thermochemical processes (Demirbas, 2001).

Biochemical processes include anaerobic digestion and alcoholic fermentation. In anaerobic digestion, degradation of biomass is carried out by bacterial action in the absence of oxygen. This is a fermentation process that generates a combination of methane and carbon dioxide. In alcoholic fermentation, the production of ethanol is achieved from specific biomass materials containing sugars, starch, or cellulose. Extracted sugar from the biomass is mixed with water and yeast and the mixture is maintained in a fermenter tank. To eliminate the water and other contaminations from the diluted alcohol, a distillation process is accomplished. Then, the concentrated ethanol is compressed to a liquid form (Demirbas, 2001).

Generally, direct combustion is the most commonly used form of biomass conversion and is the most ancient kind of biomass conversion for humans. Combustion is simply burning biomass to convert it to heat, mechanical power, or electricity. The end products include carbon dioxide and water as well as energy (Brown, 2011; Goyal et al., 2008; Klass, 1998). The advantage of combustion is that it is a way for disposal of waste, as well as energy recovery (Klass, 1998). However, there are some disadvantages of combustion such as the required drying, chopping, and grinding of biomass materials before processing (Goyal et al., 2008).

Thermochemical process involves high temperature around or above 1000°C in the presence or absence of catalysts. Thermochemical conversion can be separated into three different categories including gasification, direct liquefaction, and pyrolysis to convert biomass to a more beneficial energy (Basu, 2010; Bridgwater, 2003). In the gasification process, fractional oxidation of biomass at a high temperature of 800-900°C is performed to convert biomass into combustible gas combinations such as carbon monoxide, hydrogen, methane, nitrogen, and carbon dioxide. The heating of biomass is performed in the absence of air, and methane and hydrogen are generated by thermal splitting of organic material (Brown, 2011; Goyal et al., 2008). In the liquefaction process, conversion of biomass to oily liquid is obtained by the interaction of biomass with water at high temperatures in the range of 300-350°C with elevated pressure of 12-20 MPa for a specified time applying a catalyst and hydrogen. This method is costly and produces a tarry fragment (Basu, 2010; Goyal et al., 2008).

Pyrolysis is a thermal degradation of biomass or other feedstock in the absence of air or oxygen at a specified temperature known as the pyrolysis temperature, and maintaining it in that temperature for a particular time (Basu, 2010). The focus of this study is process water from pyrolysis; therefore this system will be discussed in detail. Pyrolysis converts biomass into solid, liquid, and gaseous substances without oxygen (Goyal et al., 2008). Pyrolysis is a suitable thermal process to convert biomass to liquid fuel. In this process, degradation of biomass occurs in the absence of air or oxygen at a temperature range of 350-550°C although it may increase up to 700°C. This process results in the production of beneficial liquid oil, gases and solids. The property of the end products depends on the pyrolysis temperature and heating rate (Basu, 2010; Goyal et al., 2008).

The products of pyrolysis include gas (CO_2, H_2O, CO, C_2H_2, C_2H_4, C_2H_6, C_6H_6), solids (mainly char or carbon), and liquid (tars, heavier hydrocarbons, organic acid, carbonyl fractions of high molecular weight phenols, aromatic compounds, aliphatic alcohols, acetic acid, and water) (Khiari et al., 2004; Manara and Zabaniotou, 2012). The produced gas consists of a high amount of hydrocarbons and directly provides energy in the biomass plant. Condensable gases (vapors) and noncondensable gases (primary gas) are produced from primary decomposition of biomass. The condensable gases are composed of heavier molecules and they are condensed by cooling. The noncondensable gases have lower molecular weight and include carbon dioxide, carbon monoxide, methane, ethane, and ethylene that do not condense by cooling. The solid production of pyrolysis is char that can be utilized as a fuel or briquettes, activated carbon, char oil or charcoal water slurries. Char is mainly 85% carbon and the rest is oxygen and hydrogen. The pyrolysis liquid part is a black tarry liquid known as tar, bio-oil, or bio-crude that can carry up to 20% water. Furthermore, the liquid products can be upgraded to refined fuels or may be combined with petroleum refinery feed stocks. Pyrolysis liquid products are easy to store and transport thus does not need to be utilized at or close to the plant (Basu, 2010; Karaosmanoglu et al., 1999).

Pyrolysis occurs by two different processes based on the heating rate, called slow pyrolysis and fast pyrolysis. These two processes vary in terms of chemistry, total production and quality of yields. Slow pyrolysis converts biomass into effective and suitable forms of energy. In slow pyrolysis, the residence time of vapor occurs in minutes or longer using a lower temperature around 400°C for a long time to increase the production of char. This process leads to char production through carbonization (Basu, 2010; Karaosmanoglu et al., 1999).

In fast pyrolysis, biomass is quickly heated at an elevated temperature of 450-600°C in the absence of oxygen to generate organic vapors, gases, and char. It is fast due to the short vapor residence time that lasts for seconds or milliseconds. The temperature of produced vapor is reduced to room temperature to attain the liquid yield, generally called bio-oil which is the major goal of fast pyrolysis. The main difference between slow pyrolysis and fast pyrolysis is that slow pyrolysis is at lower temperatures with longer vapor residence times leading to generation of charcoal, while fast pyrolysis is performed at high temperatures with short residence times resulting in liquid production (Bridgwater, 2012; Hassan et al., 2009).

The principals of fast pyrolysis to generate liquids includes 1) the biomass supply needs to be finely milled, less than 3 mm in diameter, and heated at high heating rates and elevated temperature transfer rates due to poor thermal conductivity of the biomass; 2) the run temperature is around 500°C to increase the liquid production; 3) a short residence time of 2 s to lessen other reactions; 4) fast elimination of char to diminish cracking of vapors; and 5) cooling the vapor to yield the bio-oil (Bridgwater, 2012).

The feed is basically dried to less than 10% water at 120~130℃ temperature, so that the water is reduced in the liquid oil yield. In order to obtain the small sizes of the feed particles the grinding of the feed is performed to maintain rapid reaction, fast pyrolysis, fast and sufficient separation of char, and rapid quenching and collection of liquid yield which is known as bio-oil. The main section in fast pyrolysis is the reactor. The impact of reactor in fast pyrolysis involves very high heat and heat transfer rate, medium controlled temperature, and fast cooling of pyrolysis vapors. A cyclone is used for physical removal of tar. The char is removed by a hot vapor filter; otherwise some fragments of the char will remain in the cyclones. Therefore, removal of char can be carried out by cartridge or rotary filters. The continuation of high temperatures results in the vapor cracking, so the higher the temperature the more significant cracking. The importance of a few hundred milliseconds of vapor residence time is to attain the optimal chemical yields. However, reduction of organic products from cracking processes requires long residence times. There are some issues with collecting the liquid product due to the character of liquid which is aerosol rather than a true vapor. So, electrostatic precipitation accommodates the recovery of the aerosol (Basu, 2010; Bridgwater and Peacocke, 2000). Figure 1 shows the process of fast pyrolysis.

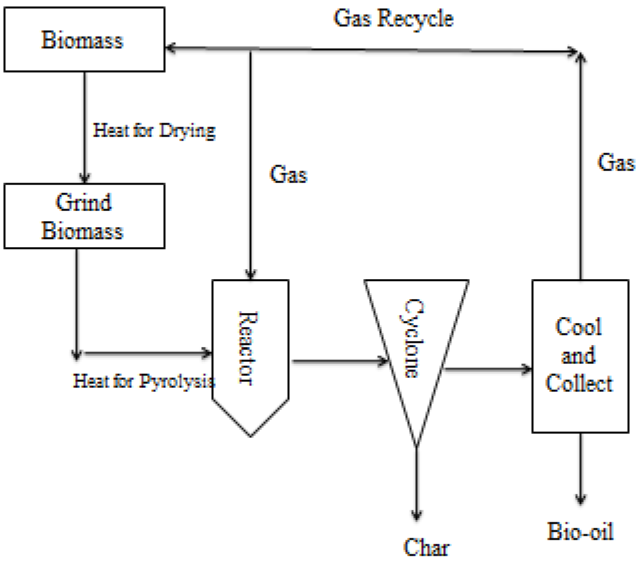

Figure 1 Schematic process of fast pyrolysis (Bridgwater and Peacocke, 2000)

Torrefaction is a mild pyrolysis which is a thermal process with a lower temperature range of 225-300°C in the absence of oxygen. In torrefaction, the biomass is dried and devolatilized leading to a mass reduction of biomass while maintaining the energy content. The torrefaction method eliminates water and CO_2 from biomass. This process changes the chemical structure of wood and generates carbon dioxide, carbon monoxide, water, acetic acid, and methanol (Basu, 2010; Prins et al., 2006).

There are other kinds of pyrolysis including flash pyrolysis and ultra-rapid pyrolysis (Basu, 2010). In flash pyrolysis, rapid heating of biomass in the absence of oxygen is performed at a temperature of 450 to 600°C. The yield is condensable and noncondensable gases which remain in the pyrolysis system for a short residence time of 30 to 1500 ms (Bridgwater, 1999). Cooling the condensable gas results in the condensation of the vapor into the liquid fuel identified as bio-oil. This process enhances the liquid production and diminishes the char yield. Ultra-rapid pyrolysis includes extremely fast combination of biomass with a heat-carrier solid that leads to high heat-transfer and heating rate. The primary yield of pyrolysis is rapidly quenched. The hot heat-carrier solids are separated from noncondensable gases and primary vapors by a gas-solid separator. Noncondensable gases and primary vapors are heated in another combustor. An important feature of ultra-rapid pyrolysis is short residence time, and the temperature is around 1000 to 650°C (Basu, 2010).

Production of Wastewater from Pyrolysis

The removal of tar in fast pyrolysis generates wastewaters that contain a high concentration of organic compounds that make the treatment of wastewater challenging. The contaminants are organic, inorganic acids, NH_3, and metals. Accumulation of tar is considered a hazardous waste if it is produced at high temperatures. Different technologies are available to treat these pollutants before ultimate disposal (Basu, 2010). Hasler et al. (1997) introduced some treatment technologies including extraction with organic solvent, distillation, adsorption on activated carbon, wet oxidation, oxidation with hydrogen peroxide, oxidation with ozone, incineration, and biological treatment.

Clean Water Act

The Clean Water Act was legislated to preserve surface water from point and nonpoint contaminants. According to this act, release of all pollutants to the aquatic environment is regulated and requires a permit based on the National Pollutant Discharge Elimination System (NPDES) which is issued by the Environmental Protection Agency (EPA) or the state. The Clean Water Act established two kinds of standards including categorical standards and water quality standards. Categorical standards are used for different categories of industrial discharges. Water quality standards are not issued but are announced and revised sporadically (Elliott, 1992). Water quality standards are defined as laws or regulations that contain 1) specified use or uses of a water body, 2) the water quality principles that are required to protect the use or uses, and 3) an antidegradation statement (Ryan and Association, 2003).

Wastewater Treatment

There are different ways to evaluate the quality of water before release into the environment, such as total organic carbon (TOC), biochemical oxygen demand (BOD), and chemical oxygen demand (COD). These measurements determine the amount of organic compounds present in the wastewater. In addition, oil and grease (O&G) and total petroleum hydrocarbons (TPH) tests can estimate the presence of oil, grease, and other hydrocarbons. Physical properties of wastewater can also be assessed before discharge by measuring total suspended solids (TSS), pH, temperature, color, and odor (Bagajewicz, 2000).

Treatment of wastewater occurs by chemical (coagulation and flocculation, advanced oxidation, chemical oxidation), physical (sedimentation, aeration, filtration, floatation and skimming), and biological processes (aerobic, anaerobic) to remove different levels of contaminants (Khiari et al., 2004; Manara and Zabaniotou, 2012).

In the chemical process, coagulation and flocculation are performed to combine colloidal particles and very fine suspended solids into larger agglomerates that can be separated by sedimentation and filtration. The process is done by adding some chemical coagulants to the wastewater to destabilize colloid dispersion and agglomeration from colloidal particles. The most popular coagulants for wastewater treatment are aluminum salts (alum), ferric and ferrous salts, lime, cationic polymers, and anionic and non-ionic polymers (Armenante, 2012).

Oxidation technologies, which are forms of chemical treatment, include advanced oxidation (cavitation, photocatalytic oxidation, and Feton chemistry), chemical oxidation (utilizing ozone and hydrogen peroxide), and electrochemical process that can be applied for highly concentrated wastewaters (Gogate and Pandit, 2004) .

Advanced oxidation processes generate high volumes of hydroxyl radicals which are able to oxidize complex compounds, organic and inorganic, in the wastewater. Advanced oxidation processes include cavitation, photocatalytic oxidation, and Fenton chemistry. Cavitation functions by using ultrasonic irradiation or constrictions such as valves and orifices within the hydraulic machines. There are four types of cavitation in terms of generation of the ultrasonic irradiation including acoustic, hydrodynamic, optic, and particle, however only acoustic and hydrodynamic cavitation are useful for chemical modifications. Additionally, photocatalytic oxidation operates by utilizing ultraviolet radiation and sun light with semiconductor catalyst. Fenton chemistry oxidation is based on the Fenton's reagent which is hydrogen peroxide in the presence of ferrous salt. This reaction treats both organic and inorganic pollutants. Based on this process, reactive oxidizing species are formed and able to destroy the contaminants in the wastewater (Gogate and Pandit, 2004).

Chemical oxidation uses oxidizing factors such as ozone and hydrogen peroxide, although degradation of pollutants is less than in the advanced oxidation processes that generate free radicals. Mixtures of ozone with hydrogen peroxide or the action of ozone or hydrogen peroxide by energy scattering elements such as UV/sun light or ultrasound results in the generation of free radicals and these combined methods of treatment are superior to any of the single methods. Nevertheless, most of the oxidation methods are not able to fully destroy the chemical compounds (Gogate and Pandit, 2004).

Electrochemical technology is another oxidation treatment for industrial wastewaters that contain phenolic compounds and generated by oil refineries, coal conversion plants, petrochemicals, polymeric resins, coal tar distillation, and pharmaceuticals. Phenolic compounds influence biological treatment by inhibiting microbial function. Therefore, biological procedures are not able to remove high concentrations of phenolic compounds in industrial wastewaters. Electrons are used as a reagent for electrochemical treatment. In this treatment, direct or indirect oxidation is applied to remove contaminants. Direct oxidation involves absorption of pollutants on the anode surface and afterwards they are degraded by an anodic electron transfer reaction, while in indirect oxidation resilient oxidants such as hypochlorite/chlorine, ozone, and hydrogen peroxide are produced electrochemically (Rajkumar and Palanivelu, 2004).

Physical treatment of wastewater is accomplished with no chemical changes in the structure of target materials (Sincero and Sincero, 2002). Physical procedures typically take out suspended matters rather than dissolved contaminants. Sedimentation is a physical treatment that removes solid substances that are heavier than the liquid. In this process, wastewater is kept in a tank under inactive conditions for a short period of time to settle the solid particles and separate solids from clarified effluent. Aeration is the addition of air to supply oxygen to the wastewater. The wastewater passes through a filter to remove solids. Different types of filters are used such as reverse osmosis, nanofiltration, and ultrafiltration. These filtrations have thin layers of very porous polymer or plastic to separate solids (Sperling, 2007). Two major floatation processes are 1) dispersed or induced air floatation (IAF) which is the introduction of air bubbles into the wastewater applying high speed impellers, and 2) dissolved air floatation (DAF) which is suspension of air in the wastewater using pressure, and air leaves solution when pressure is released (Wang, 2010).

Filtration is a physical treatment in which pollutants bind to solid media. Common filter media include activated carbon and wood-based materials. Activated carbon adsorption has been identified as a primary treatment of industrial wastewaters that contain non-biodegradable toxic compounds and contaminants. Activated carbon comes from natural materials such as coal, lignite, wood, and coconut shells that are activated by steam at a temperature range of 800 to 1000°C. There are two types of activated carbon reactors including Powder Activated Carbon (PAC) which mainly removes non-degradable compounds from biological treatment, so PAC is basically combined with biological treatment, and Granular Activated Carbon (GAC) which is used for industrial wastewaters. Granular activated carbon has larger particles than powder activated carbon and less surface area. The presence of a large surface area is important in the adsorption of high amounts of contaminants. Therefore, each kind of activated carbon has a different adsorption capacity. The adsorption process occurs by either physical or chemical bonds including Van Der Waals, covalent, London dispersion force, and hydrogen bonds. Surfaces of activated carbon are both hydrophobic (repelled by water) and oleophilic (attracted to oil). Therefore, dissolved compounds in the water bind to the surface of carbon and form a thin layer while water passes through activated carbon. However, activated carbon is not able to adsorb all compounds such as acids and bases, glycols, alcohols, and many inorganics (lead, iron, arsenic, sodium, lithium) (Cecen and Aktas, 2011). The performance of activated carbon also depends on different factors including molecular weight, pH, flow rate, and temperature. The higher molecular weight provides more effective adsorption of contaminants due to the solubility of the molecules in water. A lower pH leads to easy adsorption and less solubility of most organics. Therefore, as pH increases, removal of pollutants is reduced. Low flow rate allows contaminants to diffuse into pores for a longer time so more adsorption occurs. Higher temperature diminishes viscosity of the solution and interrupts the adsorptive bonds therefore adsorption decreases (DeSilva, 2000).

Some studies have investigated the capability of wood-based matter to decontaminate different kinds of wastewater such as ground water, water high in nitrate, water contaminated by infected systems, aquaculture, other highly contaminated waters, and subsurface drainage water (Ruane et al., 2011).

Woodchips are cost-effective, easily obtainable, minimum maintenance, and a renewable material (Ruane et al., 2011; Ruane et al., 2012). Wood-based materials in the form of its natural or chemically altered shape have been introduced as a method to eliminate contamination from water. The inherent chemical structure of the wood provides for the adsorption of different chemicals (Eberhardt et al., 2006).

Borazjani et al. (2012) showed that a substantial amount of oil from contaminated seawater and sand could be adsorbed by wood shavings. This study showed the reduction of total petroleum hydrocarbon (TPH) to less than 100 mg/L, chemical oxygen demand (COD) to 603 mg/L, total organic carbon (TOC) to 7.5 mg/L, and total Kjeldahl nitrogen (TKN) to 0.14 mg/L. They demonstrated that this technique offers an advantageous and speedy removal of oil from contaminated water. Saliling et al. (2007) found that wood chips could remove as much as 99% of nitrate from aquaculture wastewater of 200 mg NO_3–N/L influent concentration. Blowes et al. (1994) reported that wood shavings provide an effective treatment of runoff and irrigation water as a biofilter media. Based on this study the wastewater from runoff containing NO_3-N concentrations of 3–6 mg/L was treated in reactors (NO_3-N < 0.02 mg/L) at a rate of 10–60 L/day over one year period. Vinten et al. (2006) found that filtration of dairy soiled water (DSW) using wood shavings diminished the bacterial contamination and dissolved organic carbon in the water 5 to 10 fold. Ruane et al. (2011) studied a laboratory-scale filtration with wood shavings to treat the diary soiled water (DSW). The wood shaving filtration was able to remove 99% of suspended solids (SS), 97% of chemical oxygen demand (COD), and 89% of total nitrogen (TN). Therefore, this study suggested the effectiveness of wood chip filtration for treatment of DSW.

Wood fibers can also be modified to enhance absorption of certain compounds. Pretreatment of wood fibers provides a successful adsorption of chemicals by either better exposing or retaining functional groups of wood to contaminants in wastewater.

For instance, treatment of wood shavings by base is able to split esters bonds so more carboxylate groups are available (Eberhardt et al., 2006). Eberhardt et al. (2006) indicated that pretreating wood fibers by an aqueous solution of a non-toxic anionic polymer, carboxymethyl cellulose (CMC), could increase the removal of phosphate from the storm water runoff.

Kenaf is also suitable for physical filtration due to its light density, inertness, insolubility, cost-effectiveness, and homogeneity. The kenaf plant consists of an internal core accounting for 60-75% of the structure and outer bast fibers accounting for 25-40% of the plant. The kenaf core media has been used for filtration and demonstrated considerable absorption of contaminants (Lee and Eiteman, 2001). Furthermore, kenaf fibers resist water clogging and they have effective durability for heavy loads of contaminants. Kenaf adsorption capacity is based on its sugar content, lignin substances, and extractive compounds. Reduction of lignin and cellulose leads to a lower density of kenaf. This enhances the adsorptive capacity of kenaf and consequently ions can easily bind to the reactive sites on the kenaf surface (Han, 1999).

One study compared the adsorption capacity of kenaf core, raw peanut hulls, kenaf stalk, peat moss, and crushed peanut hulls for removal of the organic contaminants trinitrotoluene (TNT) and 2,4-dichlorophenol (2,4-DCP). The adsorption of 2,4-DCP was evaluated between 60 and 180 minutes and between 60 and 120 for TNT. Eighty percent removal of these contaminants happened during the first 30 minutes of contact, showing that adsorption is a quick process. However, the adsorption capability of the selected materials illustrated a much lower adsorption than granular activated carbon (GAC) due to low surface area (Subramani, 2002). Zappi et al. (2001) found that crushed whole kenaf provided less effective adsorption of dichlorophenol (CDP) than activated carbon. Nevertheless, the adsorption of 2, 4, 6 trinitrotoluene (TNT) by kenaf was similar to activated carbon.

Kenaf has also been tested for removal of microorganism from water. In a comparison of diatomaceous earth (DE) versus kenaf, kenaf removed 40% of bacteria while the DE only removed 10% from bacterial solution (Lee and Eiteman, 2001). A laboratory study by Borazjani et al. (2007) investigated the removal of total petroleum hydrocarbon (TPH) from polluted water using hay and different forms of kenaf such as Kengro Delta Dry, Kengro Kenaf Fiber, Kengro Brand X, Kengro Aqua Kenaf, and Kengro Bio-Sorb. Based on this study, the effectiveness of TPH removal was 98.45% for hay, 99.55% for Delta Dry, 98.85% for Kengro Fiber, 99.76% for Brand X, 98.48% for Aqua Kenaf, and 96.93% for Bio-Sorb. Varghese and Cleveland (1998) used kenaf media to filter oil from oil-in-water emulsions. They applied continuous flow, constant pressure, and surfactant stabilized emulsions for the filtration of oil contaminated water. The range of oil and grease removal ranged from 70% to 95% for 500 mg/L oil-in-water emulsion stabilized by surfactants. The higher removal of oil occurred for larger oil drops, finer kenaf particles, higher filtration pressure, lower pH, cationic surfactant, and deeper media.

The bioremediation process uses natural or genetically engineered microorganisms including fungi, yeast, and bacteria to convert toxic materials to non-toxic or less toxic compounds. Microorganisms degrade organic compounds to attain carbon, energy, and food for survival. The degradation of organics is carried out by the enzymes from natural metabolic functions of microorganisms (Csuros and Csuros, 1999).

Bioremediation has received substantial attention due to its cost-effective approach to removing contaminants. Bioremediation of contaminated waters has been proven in many different systems such as in situ, above ground, and bioreactors. During in situ bioremediation, pollutants in water are subjected to in-place microbial degradation. Nevertheless, circulation of oxygen and nutrients is essential and may be accomplished by water pumping or vacuum aeration (Gabriel, 1991).

Biological treatment includes anaerobic and aerobic systems. The focus of this study is on the aerobic treatment. Anaerobic processes occur in the absence of molecular/free oxygen by the anaerobes that do not need oxygen to digest contaminants. The final products of this process include methane, carbon dioxide, and biomass. On the other hand, aerobic treatment is performed by using microbes and molecular/free oxygen to degrade organic contaminants and potentially convert them into carbon dioxide, water, and biomass. There are different types of aerobic biological treatments including conventional activated sludge process (ASP) system, cyclic activated sludge system (CASS), integrated fixed film activated sludge (IFAS) system, and membrane bioreactor (MBR) (Mittal, 2011; Schultz, 2005).

Conventional activated sludge process is the oldest and most common type of bio-treatment used for industrial wastewater. After removal of suspended contaminants the wastewater is treated in an activated sludge system consisting of an aeration tank followed by a secondary clarifier. In the aeration tank is where a certain concentration of mixed liquor suspended solids (MLSS) or mixed liquor volatile suspended solids (MLVSS) is retained with adequate concentration of dissolved oxygen (DO) to enhance biodegradation of organic pollutants. Fine bubbles are distributed into the aeration tank to provide sufficient oxygen to the biomass. The aerated mixed liquor in the aeration tank runs over to the secondary clarifier to remove the biomass and then the water flows to a filtration system for further removal of suspended solids. The isolated biomass is transferred to the aeration tank by return activated sludge (RAS) pump. Then, the biomass is disposed to the sludge handling and dewatering system (Mittal, 2011).

Cyclic activated sludge system (CASS) is used for treatment of municipal wastewater and industrial wastewater including refineries. This process has advantages over the conventional activated sludge process. All processes that are applied to the conventional activated sludge process are also performed for cyclic activated sludge system by utilizing a single variable volume basin. The Cyclic Activated Sludge System provides cost and space effective process as well as simple, flexible, and reliable operation which are not applicable for conventional activated sludge system. Also, the exclusive design of CASS is very effective for controlling the filamentous sludge that is an issue with conventional processes and the other activated sludge systems. The main characteristics of the CASS include the plug-flow initial reaction and complete-mix reactor basin. The basin consists of three zones, selector (Zone 1), secondary aeration (Zone 2), and main aeration (Zone 3). The removal of degradable soluble materials is taking place by recycling the sludge biomass from Zone 3 to the Zone 1in which develops the flock-forming microorganisms (Mittal, 2011).

Integrated fixed film activated sludge is also referred to as a hybrid treatment, in which fixed film is combined with conventional activated sludge. In integrated fixed film activated sludge, fixed or free floating media is added to the activated sludge tank to enhance the generation of biomass and treatment. The fixed film provides a surface area for the attachment and development of biomass. The enhancement of biomass growth on the media depends on dissolved oxygen concentration, temperature, mixing energy, suspended phase biomass concentration, and solids retention time (Mittal, 2011).

Membrane bioreactor (MBR) is the newest technique for bioremediation of soluble organic pollutants. It is similar to the conventional activated sludge in which mixed liquor solids are suspended in an aeration tank. However, the separation of bio-solids varies between the two processes. In the MBR process, the isolation of bio-solids is performed by using polymeric membrane such as microfiltration and ultrafiltration, while in conventional activated sludge the separation of sludge is achieved by gravity settling process in the secondary clarifier (Mittal, 2011).

CHAPTER III

MATERIALS AND METHODS

Wastewater

The wastewater used in this study was provided by KIOR Company from the Houston, Texas plant. The chemical composition of this wastewater is listed in Table 1. The wastewater was stored in a stainless steel barrel at room temperature until used for filtration. The wastewater was tested for pH, oil and grease concentration, and toxicity determination with appropriate statistical analysis.

Table 1 Chemical composition of wastewater used in this study

Oxygena	Wt.%	Hydrocarbons:	Wt.%
Furans	0.01	Cyclohexanes	0
Aldehydes	3.37	Cyclopentanes	0
Ketones	0.67	BTEX	0
Carboxylic Acids	0.76	Other PAHs	0
Phenols	0.54	Other Benzenes/ Toluene's	0
Indenols	0.01	Alkanes	0
Diols	0.68	Indenes	0
Indanols	0	Indanes	0
Naphthols	0	Tetralins/Decalins	0
Anhydrosugars	0	Naphthalenes	0
		Dicyclohexanes	0

Phase I Filtration

Filtration with Flow Rate of 1 Liter/90 Seconds

Southern yellow pine wood shavings and Delta Dry kenaf were provided by Sunbelt Shavings Company in Macon, MS and KenGro Corporation in Charleston, MS, respectively, for the filtration process. The multi-stage filtration system consisted of a large 40 liter reservoir to store the wastewater which was connected to three PVC columns that were filled with kenaf and/or wood shavings. Each column was 14 inches (35 cm) long and 2 inches (5 cm) in diameter with a volume of 47.1 inches^3 (771.8 cm^3) (Figure 2). Inside each column there was a 13 inch (32.5 cm) stainless steel rod attached to a round screen with a mesh size of No. 200 with a 2 inch diameter to allow for the unobstructed flow of wastewater through each column. Each column was filled with 65 grams kenaf and/or 40 grams wood shavings.

In this study, there were four different treatments for filtration with three replications per treatment. The treatments were as follows:

1. Treatment 1 (T1): All three columns filled with kenaf (K) only
2. Treatment 2 (T2): All three columns filled with wood shavings (WS) only
3. Treatment 3 (T3): First column filled with wood shavings and the other two columns filled with kenaf
4. Treatment 4 (T4): First column filled with kenaf and the other two columns filled with wood shavings

In the first treatment, all three columns were filled with 65 grams of kenaf per column. The wastewater from the reservoir passed through the first column and three samples were collected one after another from the first column by opening the valve. The first column valve was closed to let the wastewater accumulate in both the first and second columns. After filling both columns with wastewater, the second valve was opened to collect the three samples from the second column. The same process was repeated to collect three samples from column three. The flow rate for this phase was adjusted to 1 liter/90 seconds and was gravity fed. All 9 samples were collected in one liter amber bottles. Collected samples were stored in the cold room to prevent any reaction by heat and light.

In treatment two, all three columns were filled with 40 grams of wood shavings. The whole process was repeated as in the first treatment. Three replications for each column and 9 total bottles of samples were collected.

In treatment three, the first column was filled with 40 grams of wood shavings and the other two columns were filled with 65 grams of kenaf. The process was again repeated with three replications collected from each column.

In treatment four, the first column was loaded with 65 grams kenaf and the other two columns were filled with 40 grams wood shavings. Three replications were collected from each column.

After filtration, all collected samples were analyzed for pH, oil and grease, and microtox toxicity test which are discussed below.

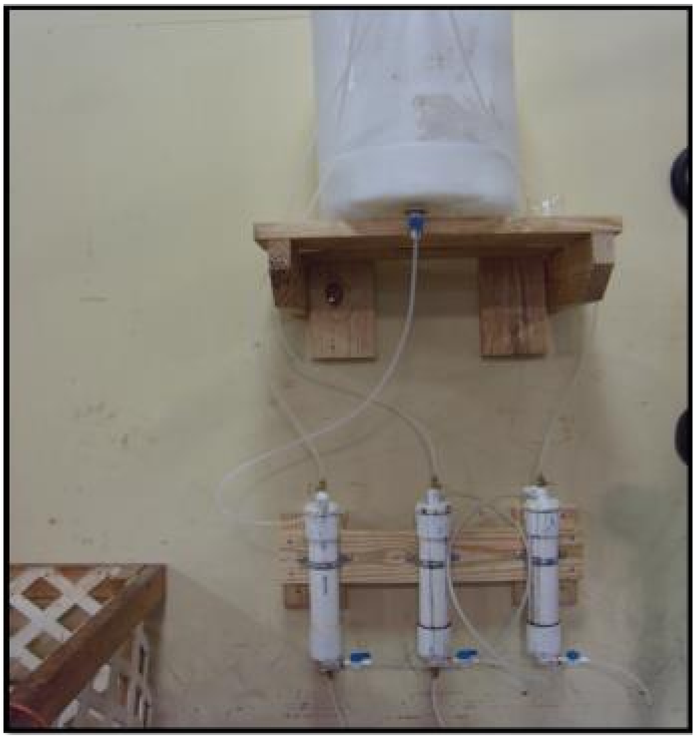

Figure 2 Multi-stage filtration unit with a reservoir connected to three columns

Bio-treatment of Filtrates

Filtrate from the treatment which showed the highest removal of contaminants was used for bioremediation. For this bioremediation study, 3 liters of filtrate was collected from the third column of the selected treatment. Before doing bio-treatment the pH of the wastewater was adjusted to 6-7 to provide a neutral environment for growth of the bacteria since the samples were still acidic after filtration. For adjusting the pH, sodium hydroxide (10 N) was used. The color of samples turned to black after increasing the pH.

The bio-treatment reactor consisted of an aquarium air pump with tubes connected and 9 one liter rectangular glass canning jars (Figure 3). There were three jars for controls, three jars for air treatment, and three jars for air and bacteria treatment. Each jar received an air tube except for controls (wastewater only).

For this study, three different treatments with three replications per treatment were as follows:

1. Wastewater only (control)-no added air
2. Wastewater with air
3. Wastewater with air and bacteria

Each jar was filled with 500 ml of the wastewater. The wastewater with air treatment consisted of just air that was pumped by an aquarium air pump. The wastewater with air and bacteria treatment involved the wastewater mixed with air and a consortium of three kinds of bacteria from a PCP-contaminated groundwater source. The air was sparged into 6 of the jars that were receiving the air treatments. The bio-reactor was run for 7 days. Over this period of time, the glass jars were monitored to maintain the volume by adding deionized water every day. After bio-treatment, all samples from the bio-treatment were analyzed for oil and grease content and toxicity test that are described below.

Figure 3 Bio-treatment units (glass canning jars) with sparged air distribution system

Composting Kenaf and Wood Shavings

Composting of the used filter media was done to evaluate the effectiveness of degrading the toxic substances adsorbed to the kenaf and wood shavings. Therefore, the contaminated kenaf and wood shavings from phase one filtration from all three columns were removed and stored in the cold room until needed.

The spent kenaf weighed 710 grams and the spent wood shavings weighed 520 grams. The spent kenaf and wood shavings were composted with 10% chicken litter for three months. Therefore, the kenaf was mixed with 20 grams of chicken litter and the spent wood shavings were mixed with 16 grams of chicken litter. Two aluminum pans were weighed and then the kenaf/chicken litter mixture was placed in one pan and the wood shavings/chicken litter mixture was placed in another pan (Figure 4). They were kept outside for 90 days. The moisture content was monitored and adjusted weekly by adding 200 ml deionized water as needed. Also, the composts were mixed by hand after watering to aerate the samples for microbial activity.

Samples from day 0, 45, and 90 were analyzed for pH, oil and grease content, microtox toxicity test, moisture content, and compost maturity test as discussed below.

Figure 4 Kenaf and wood shavings mixed with 10% chicken litter

Analytical Tests

pH Test

For measurement of the pH of each of the water replicates, 5 ml of samples were taken from each column of four treatments (one replicate from each column). A Mettler Toledo Seven Go Portable pH meter unit was used to determine the pH of each sample. The unit was calibrated with a buffer of pH 7 before testing.

In addition, the pH of compost materials was measured. One gram of each compost sample was mixed with 9 ml sterile deionized water in the test tubes. The test tubes were sonicated in a water bath (Ultrasonic Cleaner Branson 2200) unit for ten minutes to fully separate compost material from the aqueous phase. The samples were kept in the refrigerator for 12 hours. Then, the test tubes were centrifuged for 20 minutes at 50,000 rpm to mix to separate the solid phase from the aqueous phase. A Mettler Toledo Seven Go Portable pH meter unit was again used to determine the pH of the water from each compost sample (one replicate from each treatment).

Liquid-liquid Extraction of Phase One Filtrates and Bio-treated Samples

Water samples from the phase one filtration and the bio-treated samples were extracted to determine the concentration of oil and grease using EPA method 3510C (U. S. Environmental Protection Agency, 1992). For this procedure, 500 ml of the wastewater was transferred to a 1 liter separatory funnel. The sample was acidified to pH 2 by adding 0.5 ml sulfuric acid, H_2SO_4. Then 200 ml of methylene chloride was added to the separatory funnel. The separatory funnel was sealed and mixed vigorously for 1-2 minutes with intermittent releasing of the extra pressure that had accumulated. This process was repeated 2-3 times until there was no pressure after shaking the funnel. The clear layer of methylene chloride containing the organic compounds formed at the bottom and water layer formed the top.

Sodium sulfate anhydrous, Na_2SO_4 was added to remove water from the collected sample. To do this, a paper filter was placed on the glass funnel and 5 grams of sodium sulfate was added to the paper filter. The methylene chloride portion of each sample was filtered gradually through the sodium sulfate until all of the methylene chloride was filtered. The samples were collected into 300 ml Erlenmeyer flasks which contained boiling chips. The remaining waste after extraction was properly disposed. The flasks with boiling chips were weighed before sample collection. The flasks with samples were boiled at approximately $70^{\circ}C$ under a fume hood to evaporate the methylene chloride. The leftover materials after evaporation of the methylene chloride in each flask were considered to be the remaining oil and grease from samples. The flasks were cooled before weighing. The difference between initial weight and final weight was calculated as the amount of oil and grease.

Methylene Chloride Extraction of Compost Samples

The kenaf and wood shavings were extracted by Soxhlet extraction SW-846 modified version of USEPA method 3540A (Brilis and Marsden, 1990). The extraction was accomplished for composts from day 0, 45, and 90. For this test, 5 grams of each sample were placed into 30mm x77mm extraction thimbles. Each sample was extracted with 250 ml of methylene chloride for eighteen hours (Figure 5).

Sodium sulfate anhydrous, Na_2SO_4 was used to remove water from collected sample. The paper filter was placed on the glass funnel and 5 grams of sodium sulfate was added on the paper filter. The flasks with boiling chips were weighed before sample collection. The soxhlet extracts were filtered through the sodium sulfate filter, and then were boiled under a fume hood to evaporate the methylene chloride. The leftover material was considered to be the remaining oil and grease from the sample. The difference between initial weight and final weight was used to calculate the amount of oil and grease.

Figure 5 Soxhlet extraction of kenaf and wood shavings compost

Toxicity Test

Microtox model 500 toxicity auto analyzer (Microbics Corporation, Carlsbad, California) was used to determine the wastewater toxicity after filtration and bio-treatment (Figure 6). The toxicity analyzer measured the concentration of toxic materials needed to decrease the light output of a luminescent bacteria, *Photobacterium phosphoreum*, by 50% (effective concentration, EC50).

For the toxicity test, the pH of all replications was first adjusted to between 6-8 using either 0.1 M sodium hydroxide or hydrochloric acid. One ml of sample and 9 ml of sterile deionized water were placed in a test tube. The dilution process was performed four times resulting in a 10000 fold dilution.

Two hundred and fifty µl of Microtox Osmotic Adjusted Solution (OSA) (SDIX, Newark, Delaware) was mixed with 2.5 ml of the diluted extracted samples in Microtox cuvettes and placed in Microtox cooling wells to reach a target temperature of 15^{o}C. The bacteria solution was prepared by mixing one ml Microtox Reconstitution Solution (SDIX, Newark, Delaware) to the freeze dried bacterium vial. Microtox Acute Reagent (SDIX, Newark, Delaware) was cooled before use. The Microtox Basic Test was used for these samples which had a high toxicity. In the Basic Test Method, 1.5 ml of the extracted sample was added to the OSA solution, then three consecutive two fold dilutions were made into 1.5 ml of Microtox diluent (SDIX, Newark, Delaware). Ten µl of bacterial solution was added to 10 cuvettes prior to addition of the sample. The concentration of luminescent bacteria was measured before adding the extracted sample, and also 5 and 10 minutes after addition of 500 µl of the sample.

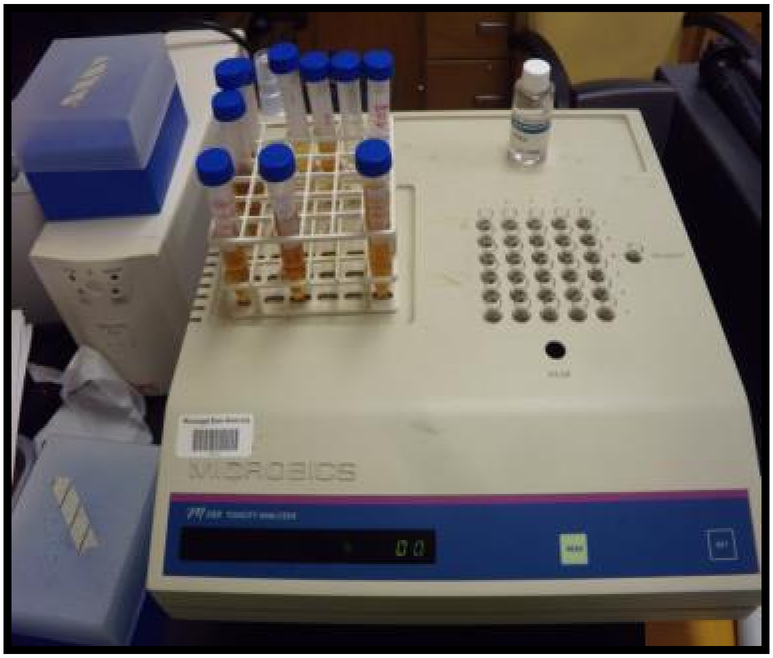

Figure 6 Microtox analyzer unit

Moisture Content of Compost Samples

Determination of the moisture content of the compost material was done by the oven-dry method. Each compost, kenaf and wood shavings, were tested in three replications. Two grams of wet composted materials were weighed in the small pre-weighed aluminum pans. The samples were kept in the oven over night for at least 16 hours at 100°C in order to dry the samples. The dried samples were removed from the oven and weighed. The weight of the pan was subtracted from the total weight. The dried weights of samples were subtracted from the wet weight of composts to determine the percent moisture content.

Compost Maturity Test

The plant germination test was performed on the compost in order to determine the maturity of the composted products. This test was based on the Florida's Online

Composting Center (2012) using radish seed (http://sarasota.ifas.ufl.edu/compost-info). The test was applied to all kenaf and wood shavings compost samples taken from day 0, 45, and 90. Six radish seeds (Cherry belle radish, Ferry Mors Seed Company) were planted into the compost in disposable cups. Three replicates were used for each day 0, 45, and 90. The cups were exposed to the sun and irrigated regularly with deionized water as needed for one week. After one week, the numbers of germinated seeds were recorded in each cup and germination rate was calculated for each replicate. A control soil was selected in order to compare the results of the composts to normal potting soil, so three replicates of potting soil from the greenhouse in the Plant and Soil Science Department at Mississippi State University was used as control.

Statistical Analysis

The toxicological and analytical results of the experiment were statistically analyzed by applying a completely random design with three replications for each treatment. Tukey's multiple comparisons was utilized to compare treatment mean differences at p=0.05. The data were processed by SPSS (Statistical Package for the Social Science) statistics software.

Phase II Filtration

Filtration with Flow Rate of 1 Liter/60 Seconds

Phase II filtration was performed in order to determine if the filtration rates could be increased. The same four treatments as in phase I were run with three replications per treatment. The only difference between phase I and II was the flow rate. The flow rate for phase II was adjusted to 1 Liter/60 seconds. In addition, the bio-treatment of the filtrate was not done, nor was the spent kenaf and wood shavings composted. Tests that were run on the phase II filtrates were determination of oil and grease concentration and toxicity test. The same statistical analysis was used.

CHAPTER IV

RESULTS AND DISCUSSION

Phase I Filtration Results

pH Results of Filtrates

Table 2 presents the results of pH measurements for the water collected from each column for the phase I filtrations. The pH of all water samples were acidic for all columns of each treatment and ranged from a low of 2.39 to a high of 2.51. There were no noticeable increases in the pH of the water after treatment. There were also no distinguishable differences in the pH of the water filtered through kenaf versus wood shavings. One explanation for these results could be attributed to the acidic functional groups found in the kenaf and wood shavings.

Table 2 pH measurements for all columns of each treatment after filtration

Treatments	pH
No Treatment	2.44
T1-K1	2.4
T1-K2	2.43
T1-K3	2.41
T2-WS1	2.4
T2-WS2	2.4
T2-WS3	2.4
T3-WS1	2.39
T3-K2	2.51
T3-K3	2.47
T4-K1	2.39
T4-WS2	2.39
T4-WS3	2.4

Oil and Grease Concentrations of Filtrates

The results of oil and grease concentrations from the water for phase I filtration are shown in Figures 7 through 12. Figure 7 compares the concentrations of oil and grease in the water after the first column of each treatment. All four treatments significantly removed oil and grease when compared to the unfiltered control. Even though there were no statistically significant differences among the four treatments, the kenaf columns (Treatments 1 and 4) removed more oil and grease compared to the wood shavings columns (Treatments 2 and 3). These differences are shown in Figure 8. The two kenaf columns removed just below 40% of the oil and grease from the water, while the wood shavings removed about 35.5%.

Figure 9 compares the concentrations of oil and grease in the water after the second column of each treatment. All four treatments significantly removed oil and grease when compared to the unfiltered control. There was no significant difference among the four treatments; however, in this case the columns containing wood shavings removed slightly more oil and grease than the kenaf columns. This is shown in Figure 10 in which the wood shavings columns (Treatments 2 and 4) removed 34-38% of the oil and grease compared to 28-31% removed by the kenaf columns.

Figure 11 compares the oil and grease concentrations in the water after passing through the third column of each treatment. Once again all four treatments were significantly less than the unfiltered control, however, there were also some differences among treatments. Figure 12 demonstrates that the wood shavings column of treatments 2 and 4 as well as the kenaf column of treatment 3 removed significantly more oil and grease when compared to the kenaf column of treatment 1. The percent removal of oil and grease ranged from 26% in treatment 1 to 39% in the treatment 2 column.

Figures 13 and 14 compare all three columns of each treatment. All three columns of each treatment significantly removed oil and grease when compared to the unfiltered control. There were also some significant differences among the columns in each treatment as well as among the treatments. However, overall the second and third columns of all four treatments did not remove noticeable amounts of oil and grease.

Note: one of the replications in T1column 3 was removed, but it was replaced with the average of the other two replications; also the same action was done for T2 column 3.

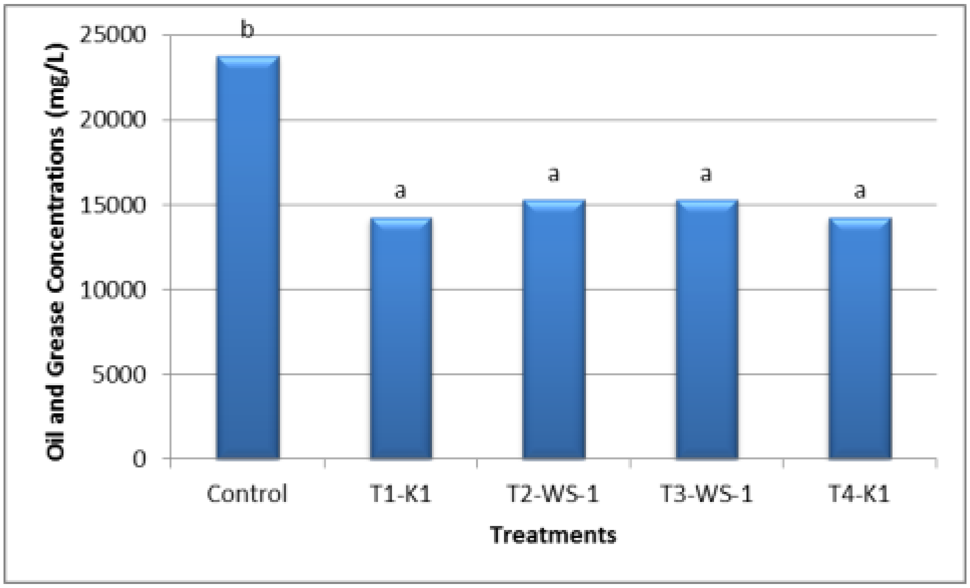

Figure 7 Oil and grease concentrations (mg/L) after filtration for first column in each treatment.

Different letters indicate significant difference in oil and grease concentrations at the P=0.05 level of significance for a given treatment.

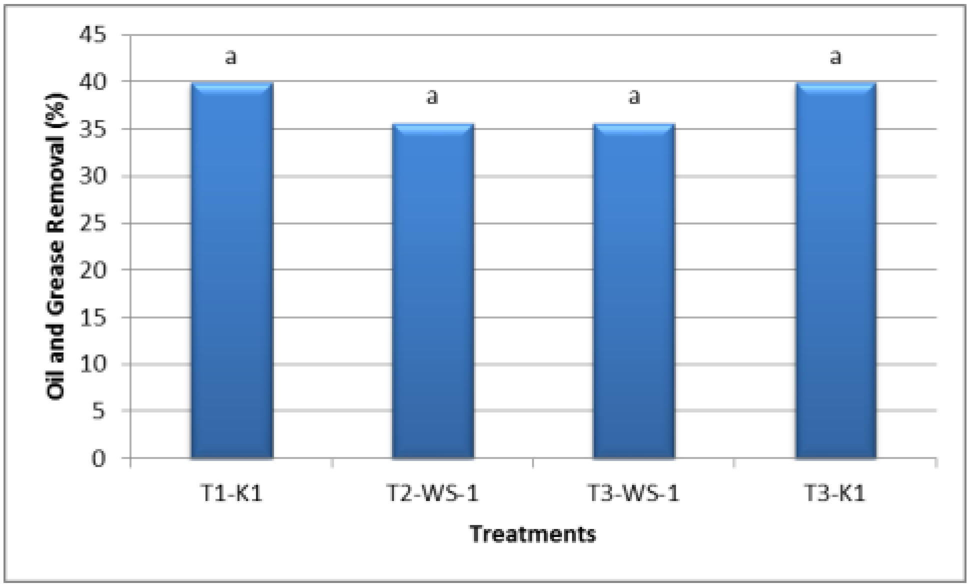

Figure 8 Percent oil and grease reduction rate after filtration for first column in each treatment.

Different letters indicate significant difference in percent oil and grease reduction rate at the P=0.05 level of significance for a given treatment.

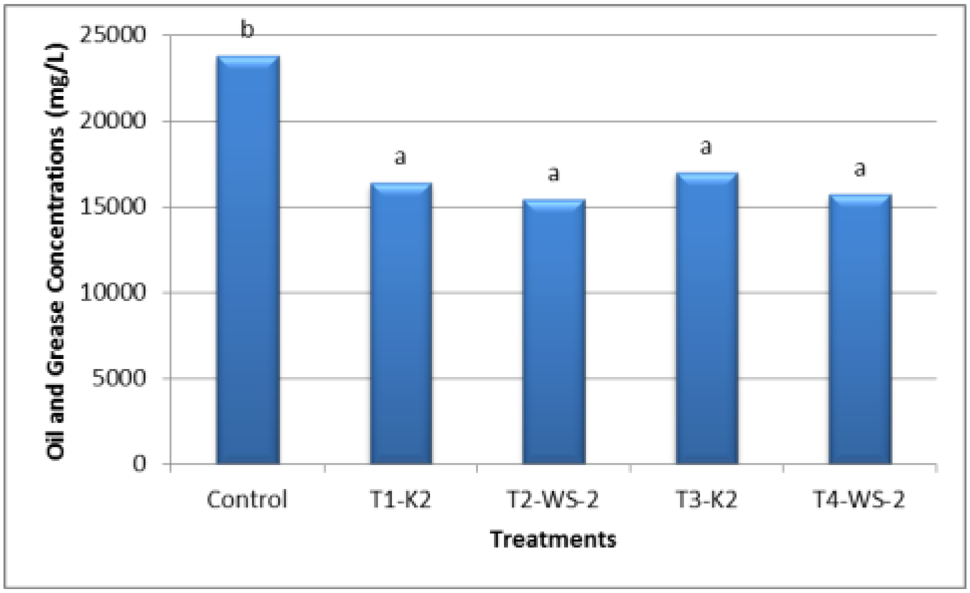

Figure 9	Oil and grease concentrations (mg/L) after filtration for second column in each treatment.

Different letters indicate significant difference in oil and grease concentrations at the P=0.05 level of significance for a given treatment.

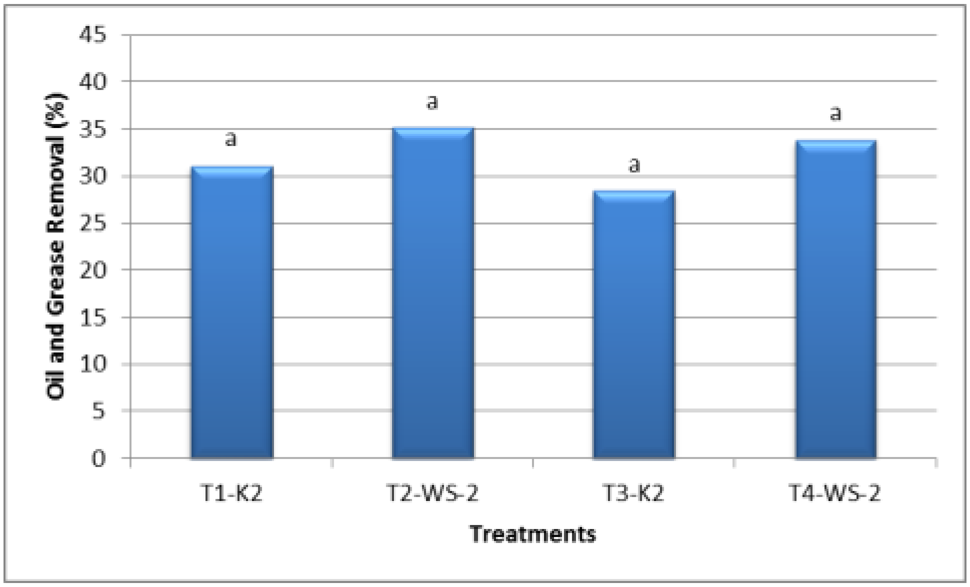

Figure 10	Percent oil and grease reduction rate after filtration for second column in each treatment.

Different letters indicate significant difference in percent oil and grease reduction rate at the P=0.05 level of significance for a given treatment.

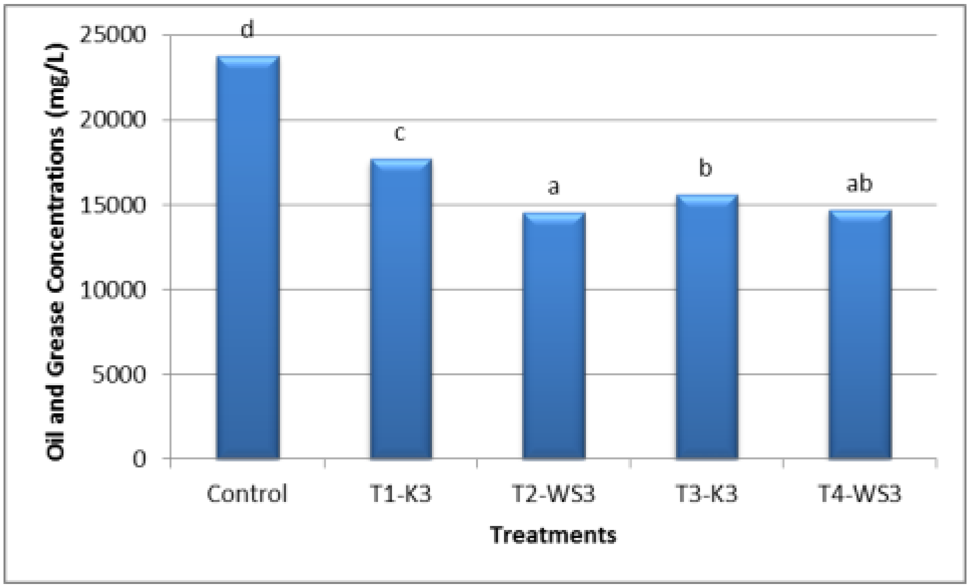

Figure 11 Oil and grease concentrations (mg/L) after filtration for third column in each treatment.

Different letters indicate significant difference in oil and grease concentrations at the P=0.05 level of significance for a given treatment.

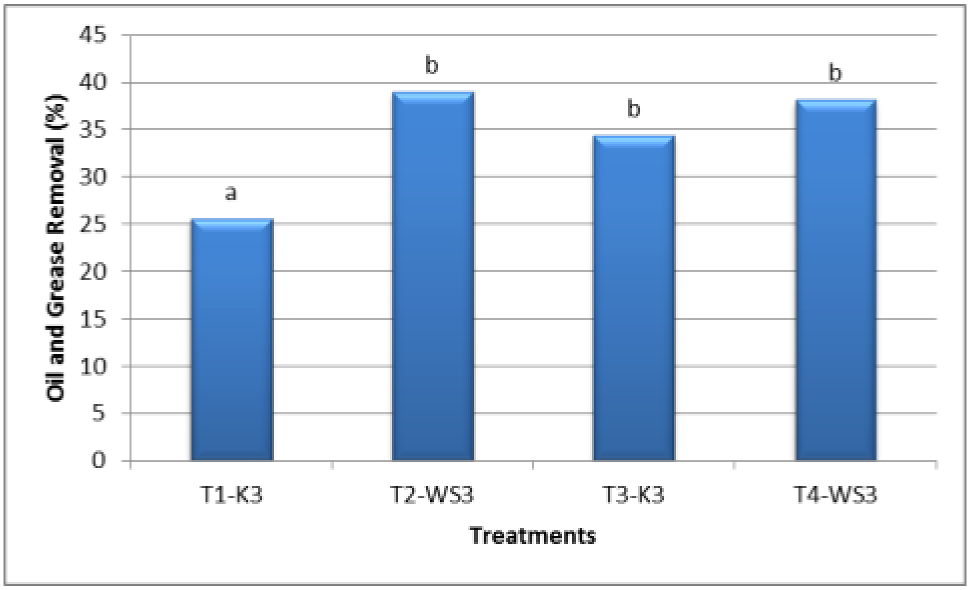

Figure 12 Percent oil and grease reduction rate after filtration for third column in each treatment.

Different letters indicate significant difference in percent oil and grease reduction rate at the P=0.05 level of significance for a given treatment.

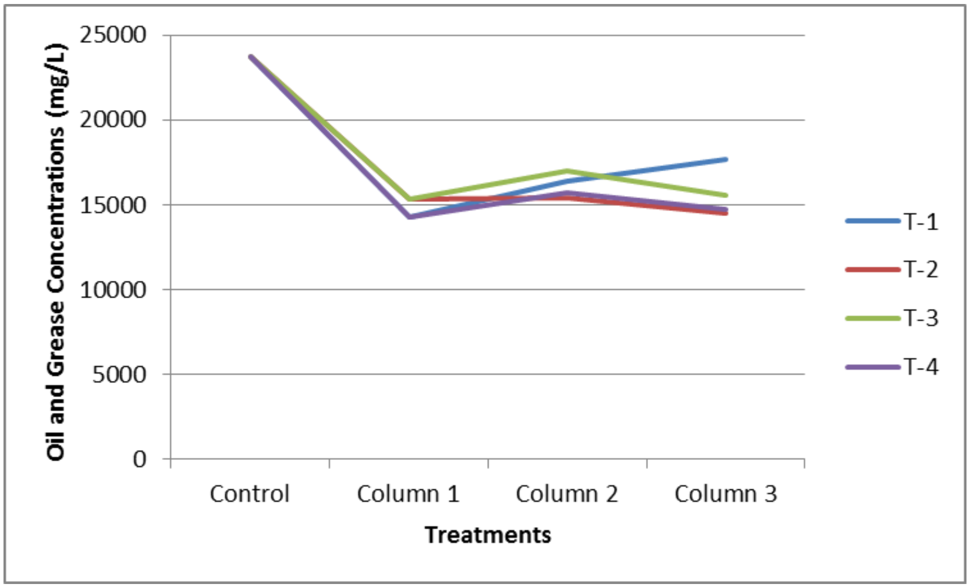

Figure 13 Comparison of oil and grease concentrations of three columns of each treatment

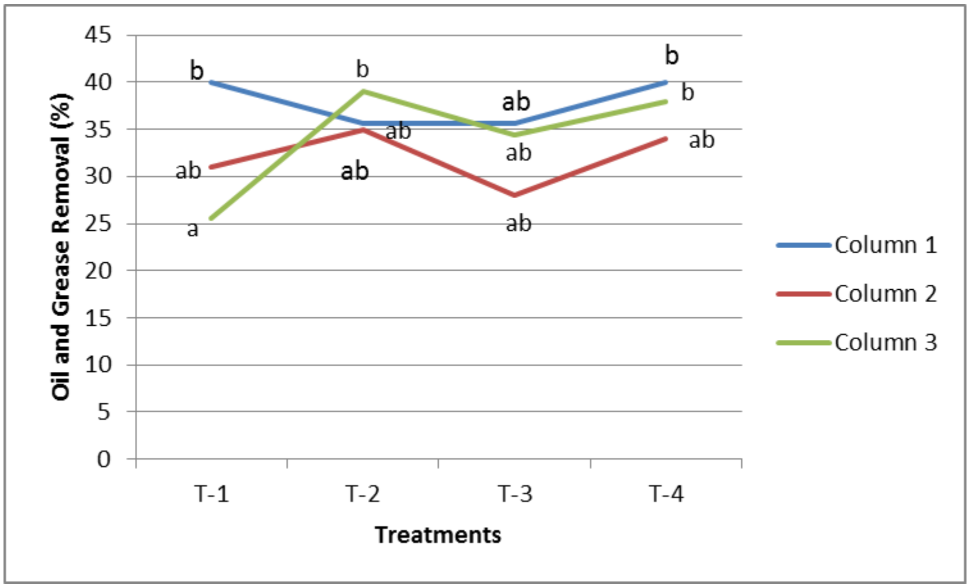

Figure 14 Comparison of percent oil and grease reduction rate of three columns of each treatment.

Different letters indicate significant difference in percent oil and grease reduction rate at the P=0.05 level of significance for a given treatment.

Toxicity Results of Filtrates

Filtration resulted in a decrease in the overall toxicity of all treatments (Figure 15 through 21). Figure 15 compares the toxicity of the water after the first column of each treatment. All treatments significantly decreased the toxicity of the water when compared to the unfiltered control. Even though statistical analysis showed that there were no significant differences among the four treatments; the kenaf column in treatment 4 and the wood shavings in treatment 3 decreased the toxicity more when compared to the kenaf in treatment 1 and wood shavings in treatment 2.

Figure 16 compares the toxicity of the water after the second column of each treatment. All treatments significantly decreased the toxicity of the water when compared to the unfiltered control. Although statistically there were no significant differences among the treatments; the wood shavings in treatment 4 decreased the toxicity compared to the other three treatments.

Figure 17 compares the toxicity of the water after the third column of each treatment. Once again all treatments significantly decreased the toxicity of the water when compared to the unfiltered control. However, there were significant differences among treatments. The toxicity levels in the water from the wood shavings in treatment 2 and in treatment 4 was significantly less than the kenaf in treatment 1.

Figures 18 through 21 show the toxicity differences among three columns of each of the four treatments. Statistical analysis showed that there were no significant differences among the three columns of treatments 1, 2, and 3. However, Figure 21 shows that there were significant differences among the three columns of treatment 4 in which columns 1 and 2 decreased the toxicity compared to the third column.

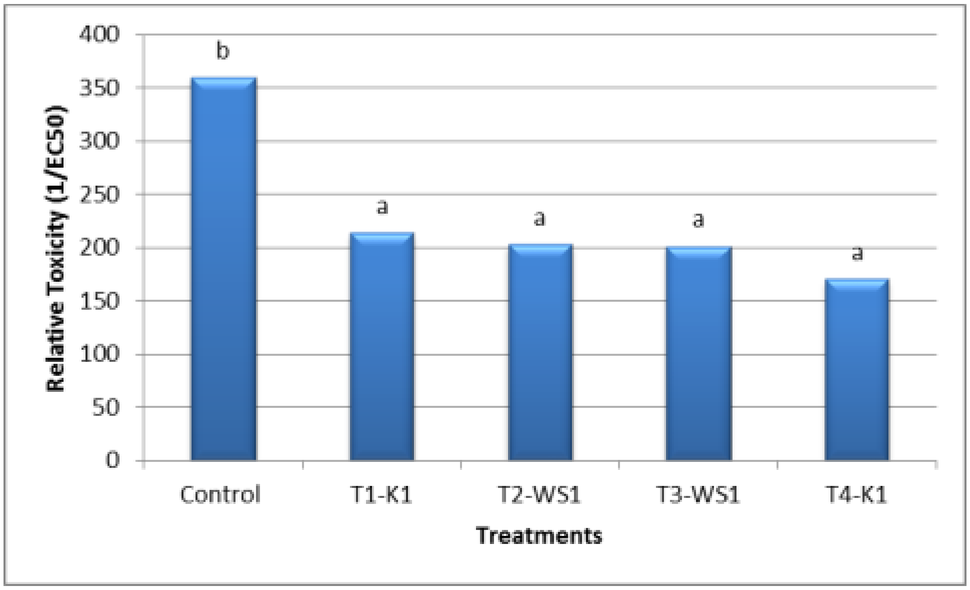

Figure 15 Toxicity differences in column one for four treatments.

Different letters indicate significant difference in toxicity at the P=0.05 level of significance for a given treatment.

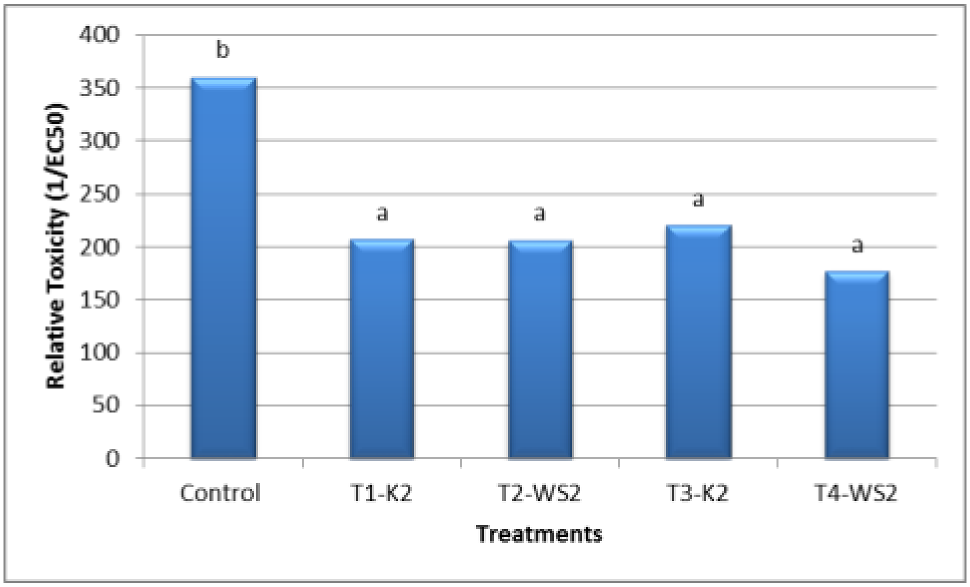

Figure 16 Toxicity differences in column two for four treatments.

Different letters indicate significant difference in toxicity at the P=0.05 level of significance for a given treatment.

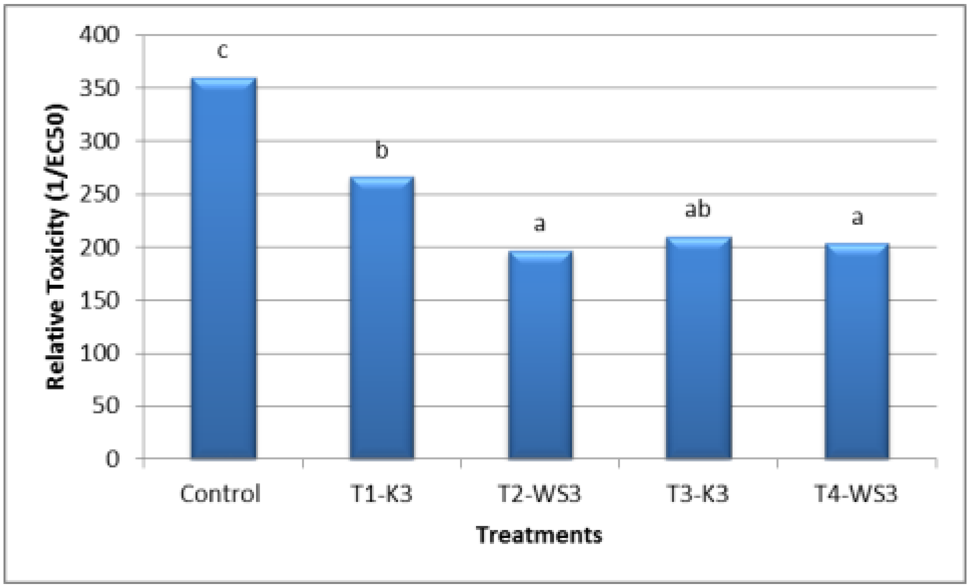

Figure 17 Toxicity differences in column three for four treatments.

Different letters indicate significant difference in toxicity at the P=0.05 level of significance for a given treatment.

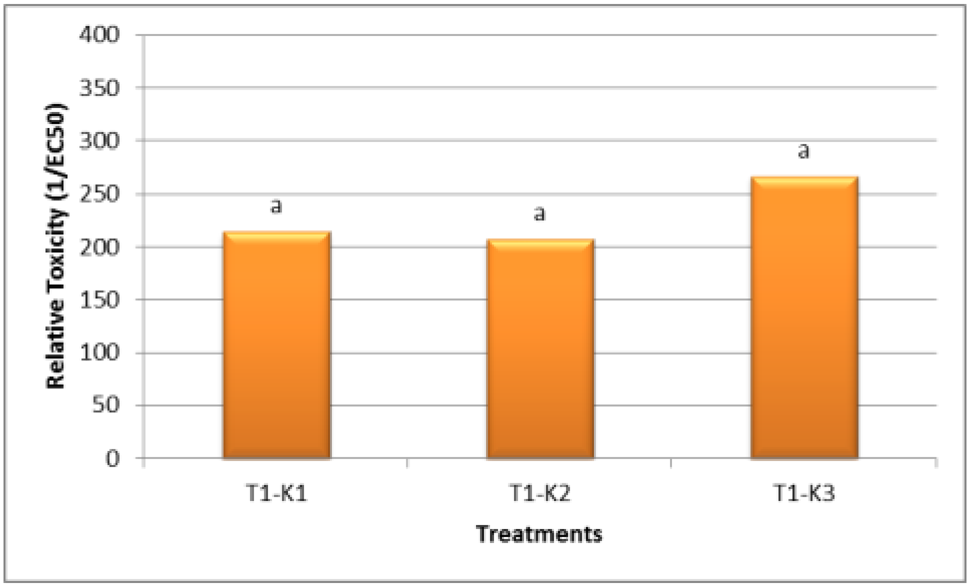

Figure 18 Toxicity differences among three columns of treatment one.

Different letters indicate significant difference in toxicity at the P=0.05 level of significance for a given treatment.

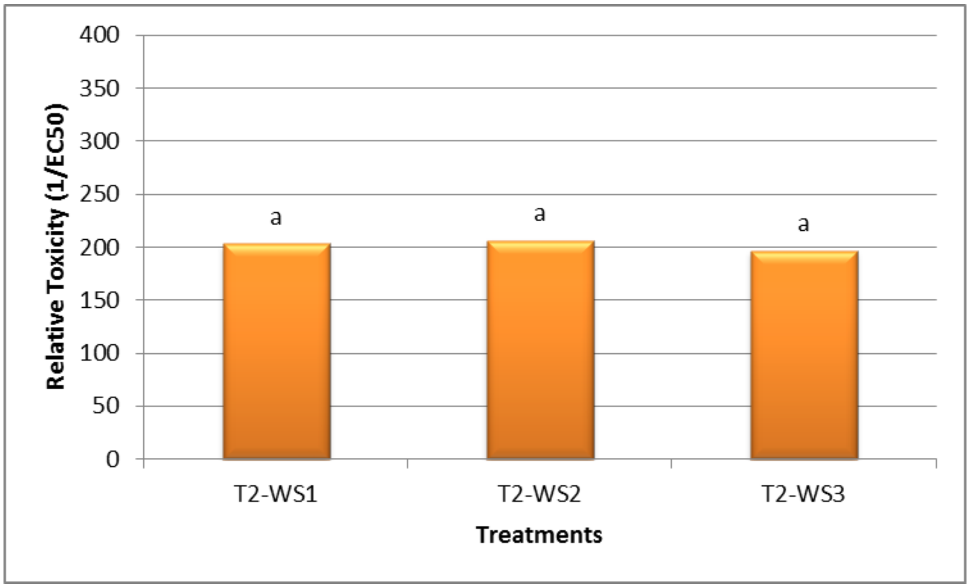

Figure 19 Toxicity differences among three columns of treatment two.

Different letters indicate significant difference in toxicity at the P=0.05 level of significance for a given treatment.

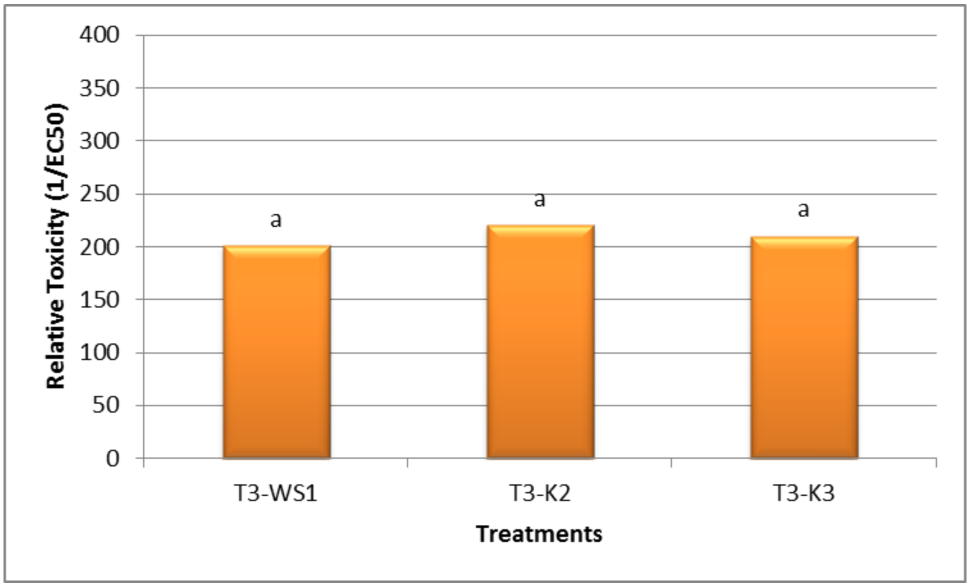

Figure 20 Toxicity differences among three columns of treatment three.

Different letters indicate significant difference in toxicity at the P=0.05 level of significance for a given treatment.

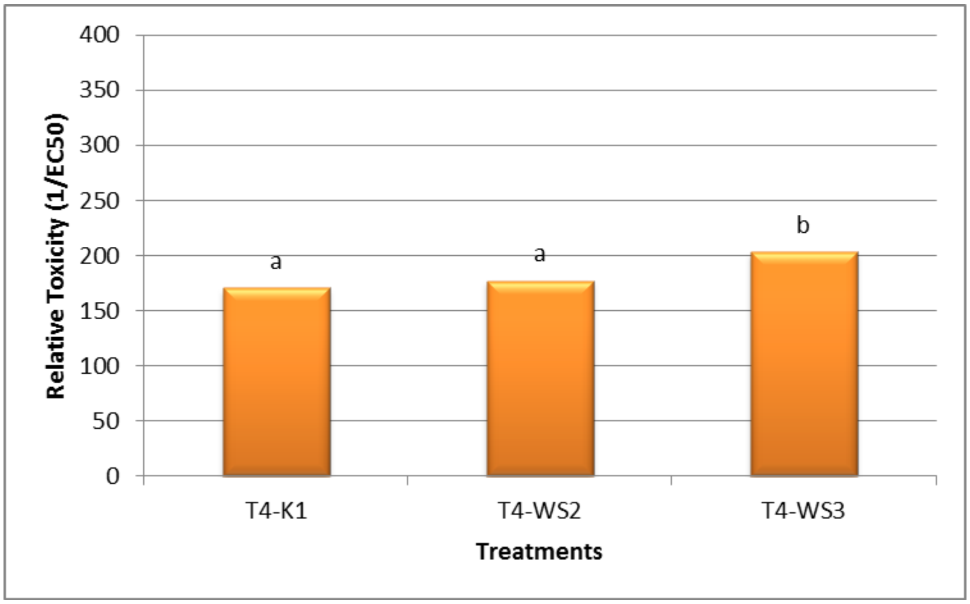

Figure 21 Toxicity differences among three columns of treatment four.

Different letters indicate significant difference in toxicity at the P=0.05 level of significance for a given treatment.

Oil and Grease Concentrations of Bio-treated Filtrates

The addition of air significantly decreased the oil and grease concentrations in the filtrate water (Figure 22), when compared to the control filtrate water which received no aeration as well as the starting water. Although the addition of bacteria with aeration, decreased the oil and grease concentration compared to aeration alone, this decrease was not significant. Percent reductions in oil and grease for the bio-treatment are shown in Figure 23. Compared to the starting water, the aeration treatments showed a decrease of 57% for air alone and 67% for air plus bacteria. Once again, the reduction in the two aeration treatments was significantly greater than the control.

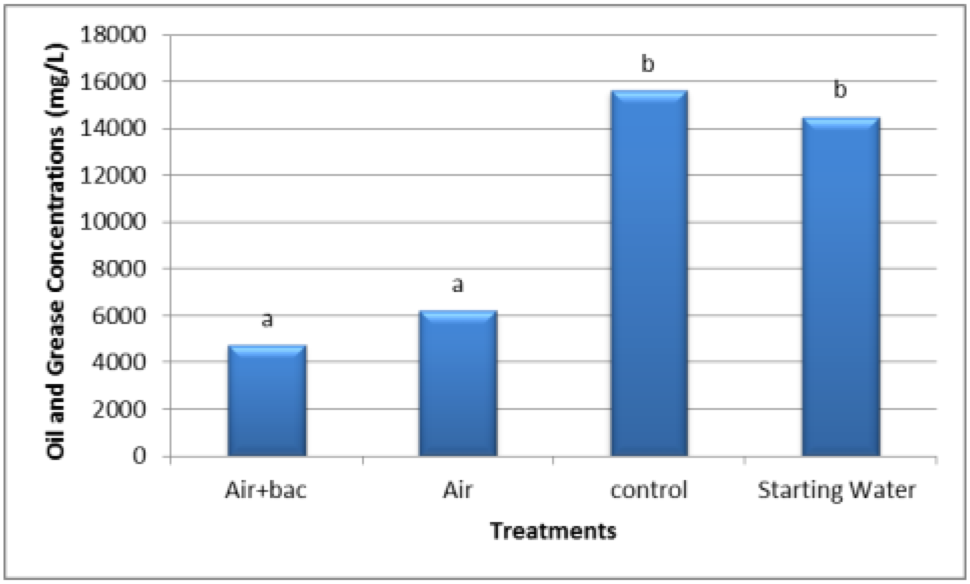

Figure 22 Oil and grease concentrations (mg/L) after bio-treatment.

Different letters indicate significant difference in oil and grease concentrations at the P=0.05 level of significance for a given treatment.

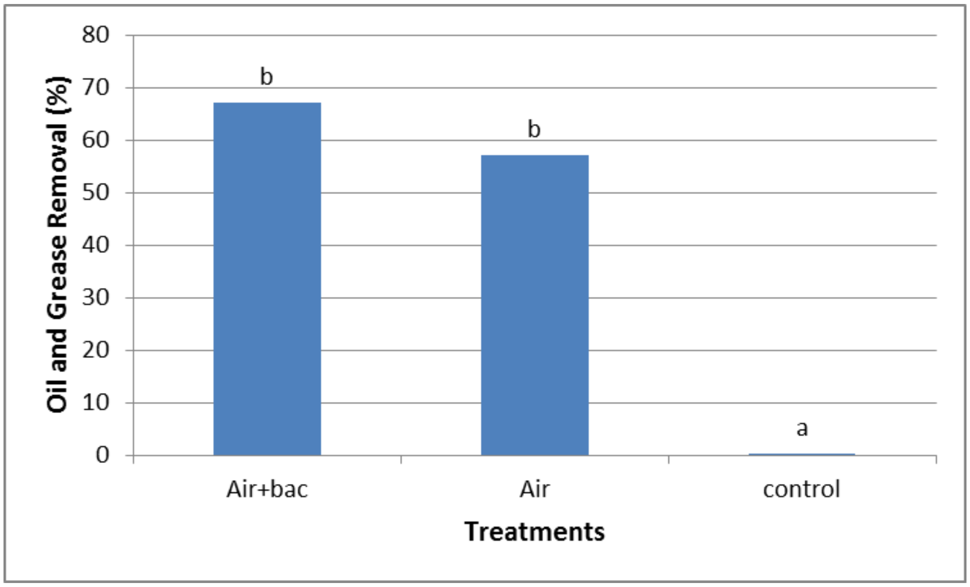

Figure 23 Percent oil and grease reduction rate after bio-treatment.

Different letters indicate significant difference in percent oil and grease reduction rate at the P=0.05 level of significance for a given treatment.

Toxicity Results of Bio-treated Filtrates

The results of toxicity of bio-treatment are shown in Figure 24. Statistical analysis indicated that all treatments significantly decreased the toxicity of the contaminated water when compared to the untreated control. Even though, there were no statistically significant differences between the three treatments; the bacteria plus air treatment decreased the toxicity more compared to the air alone.

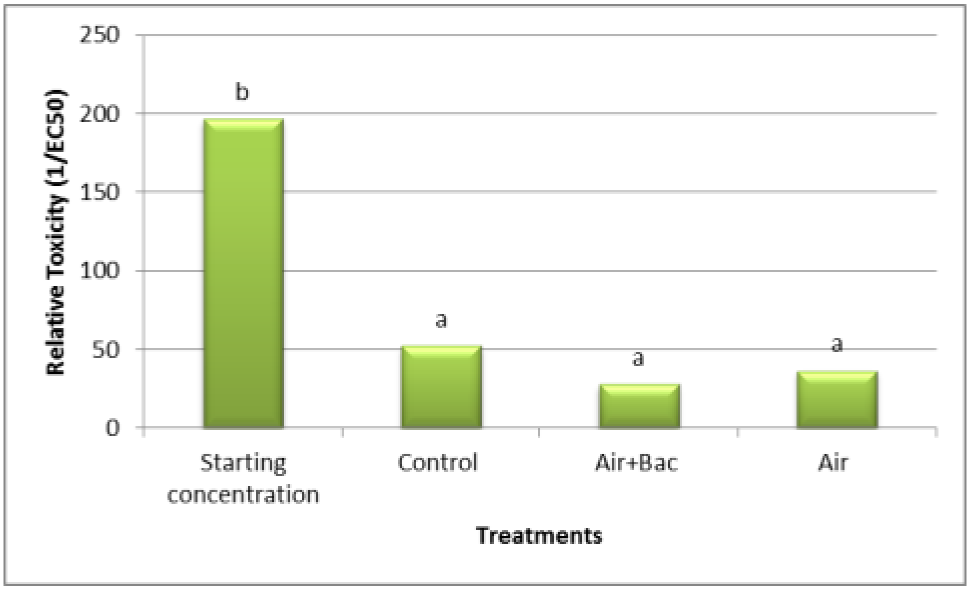

Figure 24 Toxicity differences in bio-treatments.

Different letters indicate significant difference in toxicity at the P=0.05 level of significance for a given treatment.

Oil and Grease Concentrations in Compost Samples

Composting significantly reduced the oil and grease concentrations by day 45 when compared to the control for both kenaf (Figure 25) and wood shavings (Figure 26). There was no significant difference between day 45 and day 90 for either of the two matrices. Although not significantly different, kenaf consistently removed more oil and grease compared to the wood shavings (Figure 27). The greatest percent removal of oil and grease was kenaf at day 45 (80% removal) followed by kenaf at day 90 (76%), wood shavings at day 45 (68%) and wood shavings at day 90 (62%) (Figure 28). Kenaf may be a more effective composting matrix for many reasons including; it supports a greater concentration and diversity of microorganisms; it has a higher surface area thus contact between the pollutant and microbes is greater; it may help maintain higher oxygen levels; and it breaks down easier thus stimulates a more rapid composting process.

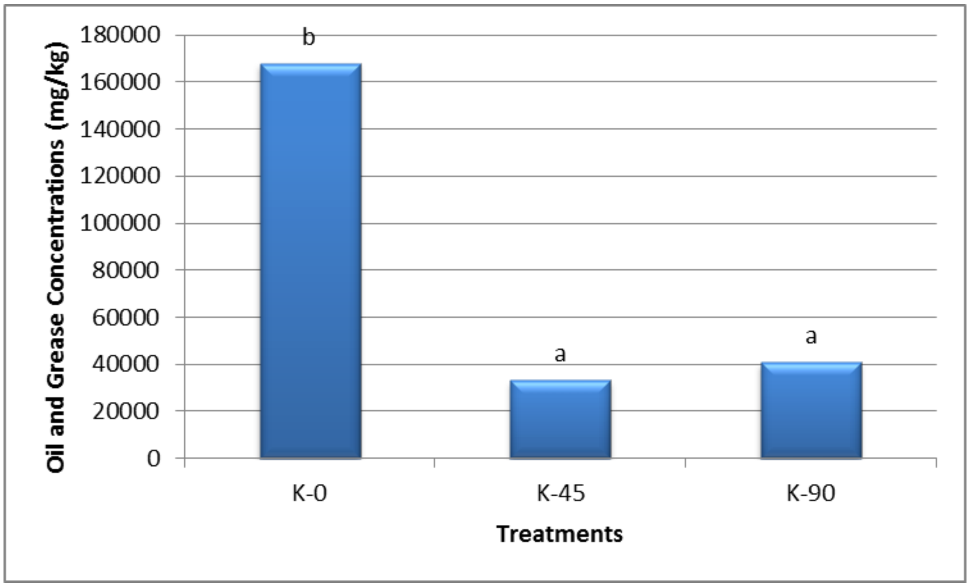

Figure 25 Oil and grease concentrations in kenaf after composting for day 0, 45, and 90.

Different letters indicate significant difference in oil and grease concentrations at the P=0.05 level of significance for a given treatment.

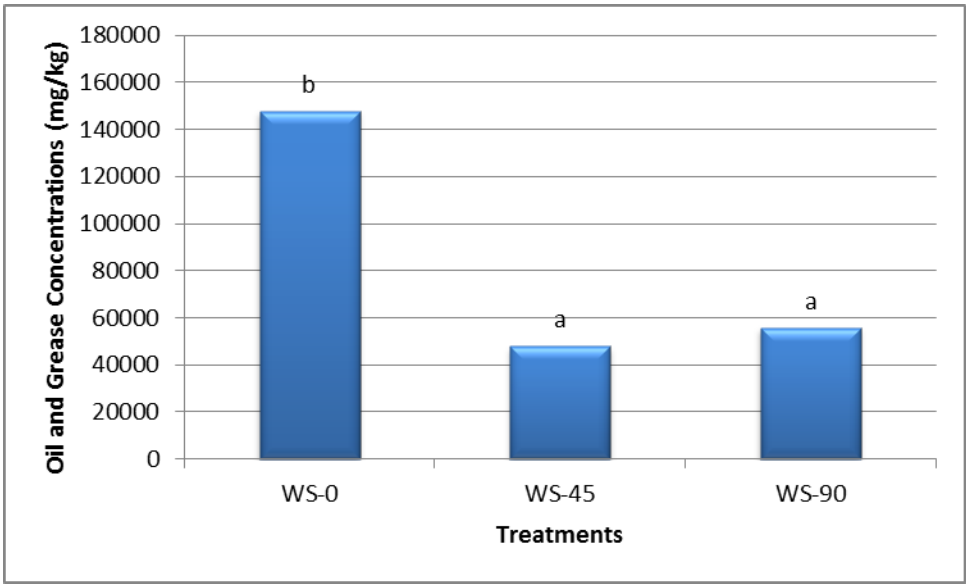

Figure 26 Oil and grease concentrations in wood shavings after composting for day 0, 45, and 90.

Different letters indicate significant difference in oil and grease concentrations at the P=0.05 level of significance for a given treatment.

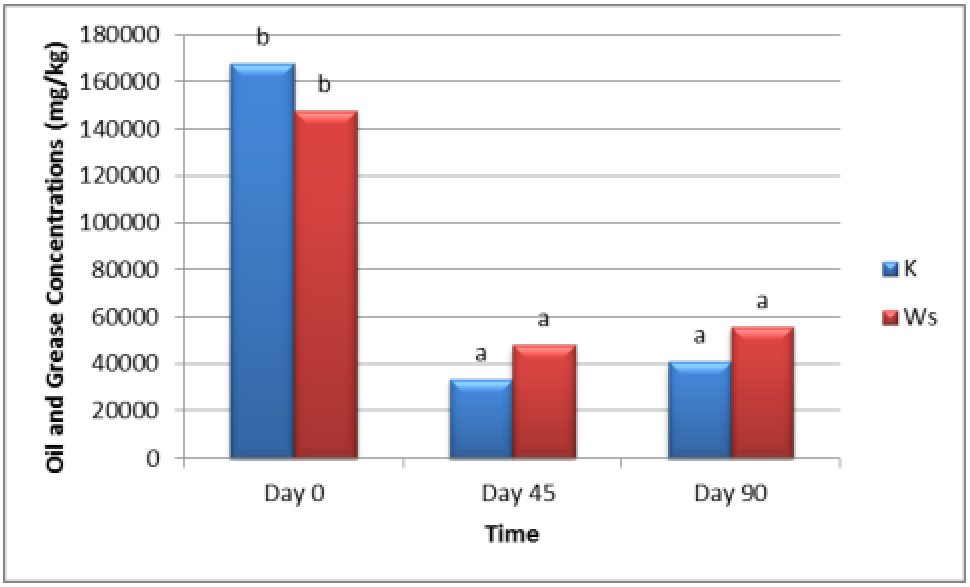

Figure 27 Oil and grease concentrations in kenaf and wood shavings after composting for day 0, 45, and 90.

Different letters indicate significant difference in oil and grease concentrations at the P=0.05 level of significance for a given treatment.

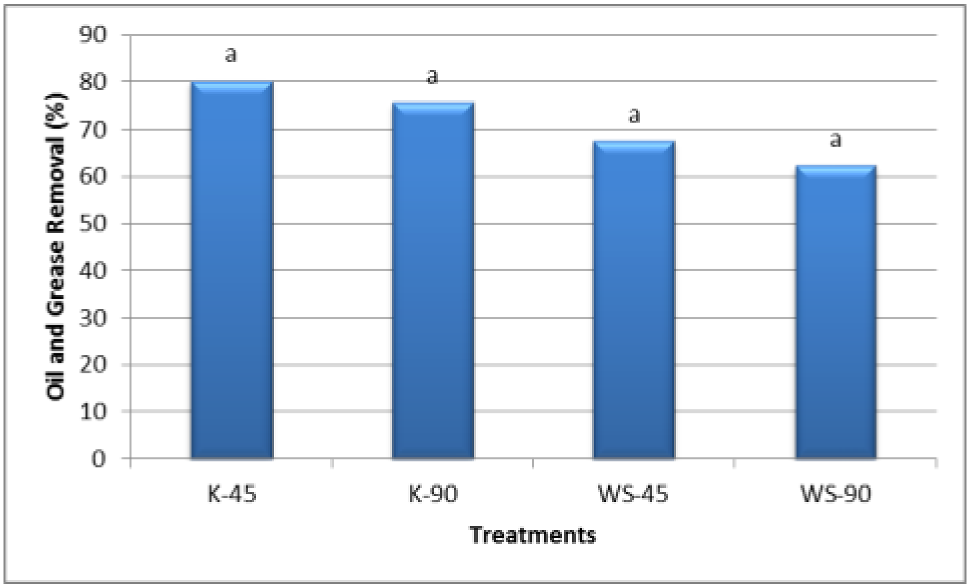

Figure 28 Percent oil and grease reduction rate in kenaf and wood shavings after composting for day 45 and 90.

Different letters indicate significant difference in percent oil and grease reduction rate at the P=0.05 level of significance for a given treatment.

Toxicity Results of Composts

Composting resulted in a decrease in the overall toxicity of the kenaf and wood shavings composts (Figures 29 through 31). Figure 29 compares kenaf compost for day 0, 45, and 90. Composting for the different duration times significantly affected the removal of contaminants when compared to day 0. However, there were no significant differences between day 45 and 90.

Figure 30 compares composting of wood shavings for day 0, 45, and 90. The two different duration times significantly decreased the toxicity of wood shavings when compared to day 0. However, there were no statistically significant differences between day 45 and 90.

Figure 31 compares all kenaf and wood shavings composts for day 0, 45, and 90. All kenaf and wood shavings significantly decreased the toxicity compared to day 0. However, there were no significant differences between kenaf and wood shavings for day 45 and 90.

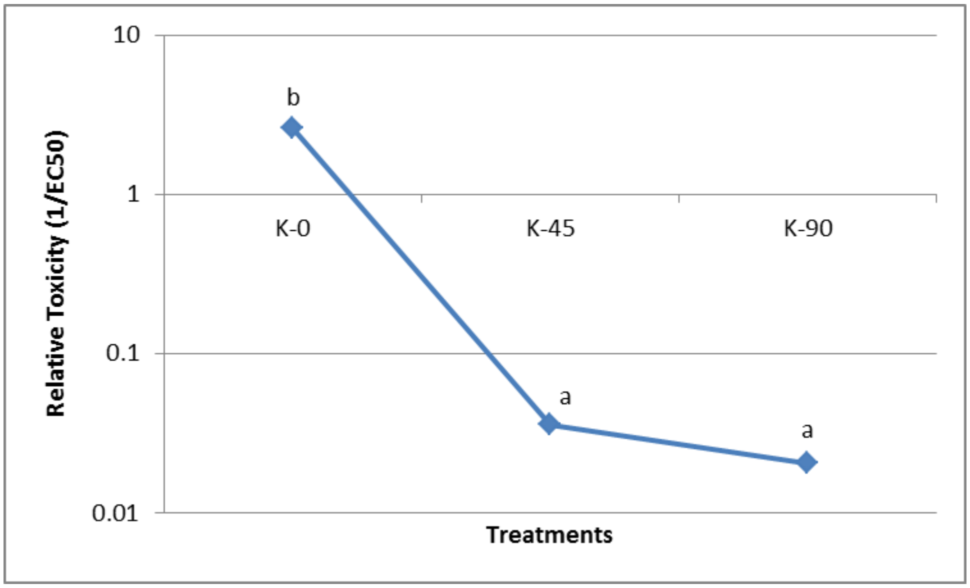

Figure 29 Relative toxicity differences of kenaf composts at day 0, 45, and 90.

Different letters indicate significant difference in toxicity at the P=0.05 level of significance for a given treatment.

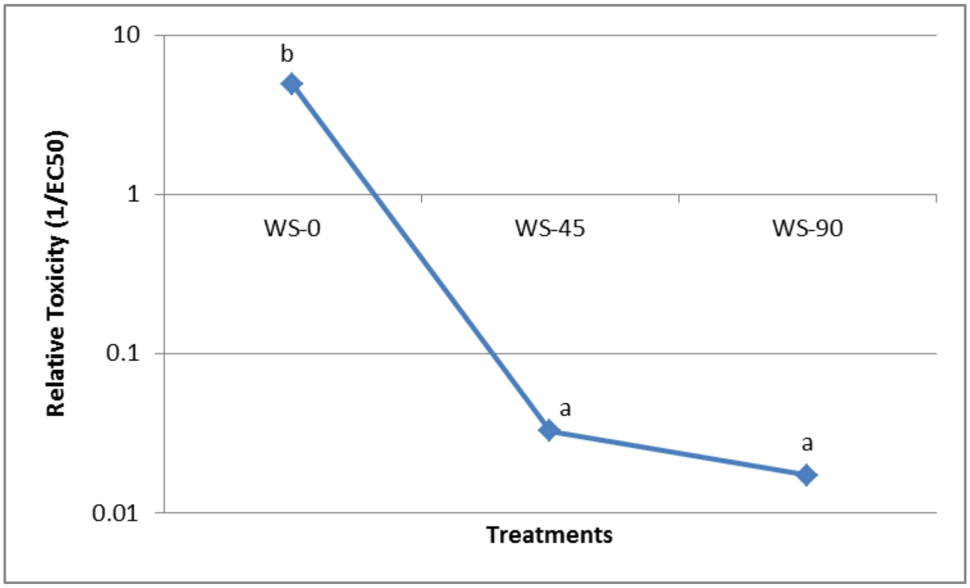

Figure 30 Relative toxicity differences of wood shavings composts at day 0, 45, and 90.

Different letters indicate significant difference in toxicity at the P=0.05 level of significance for a given treatment.

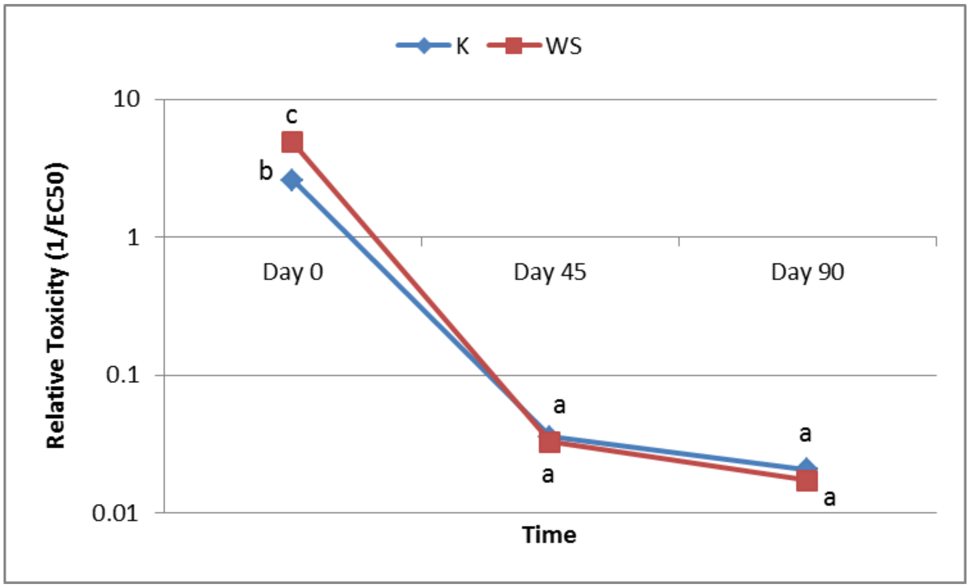

Figure 31 Relative toxicity differences between kenaf and wood shavings at day 0, 45, and 90.

Different letters indicate significant difference in toxicity at the P=0.05 level of significance for a given treatment.

Weight Loss Results of Compost Samples

The weight loss results of the composts based on the dry weights for day 0, 45, and 90 are shown in Figure 32 and 33. All composts indicated observable weight reductions after 45 and 90 day. The kenaf showed 52% weight reduction after 90 days and wood shavings showed 47% weight reduction after 90 days (Figure 33).

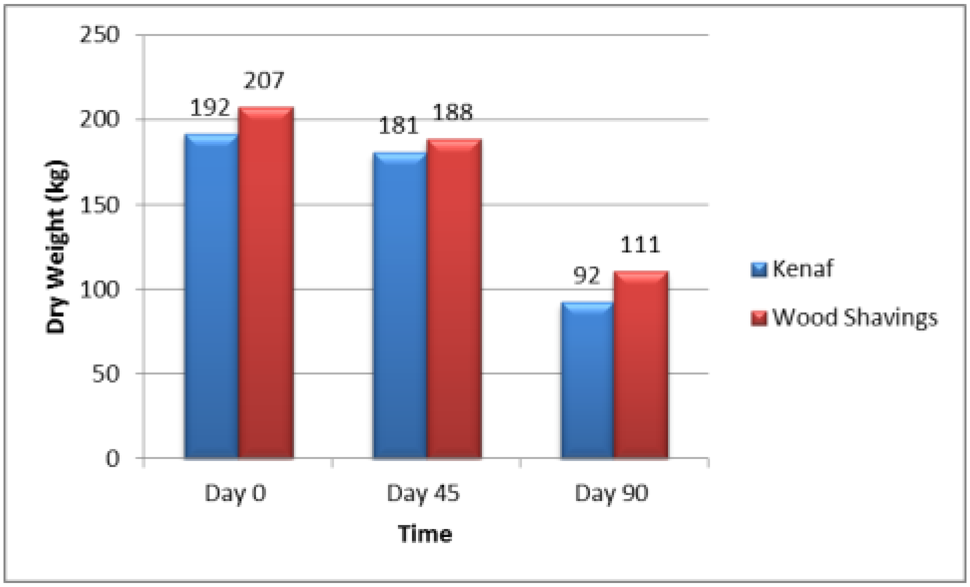

Figure 32 Dry weight of composts for day 0, 45, and 90

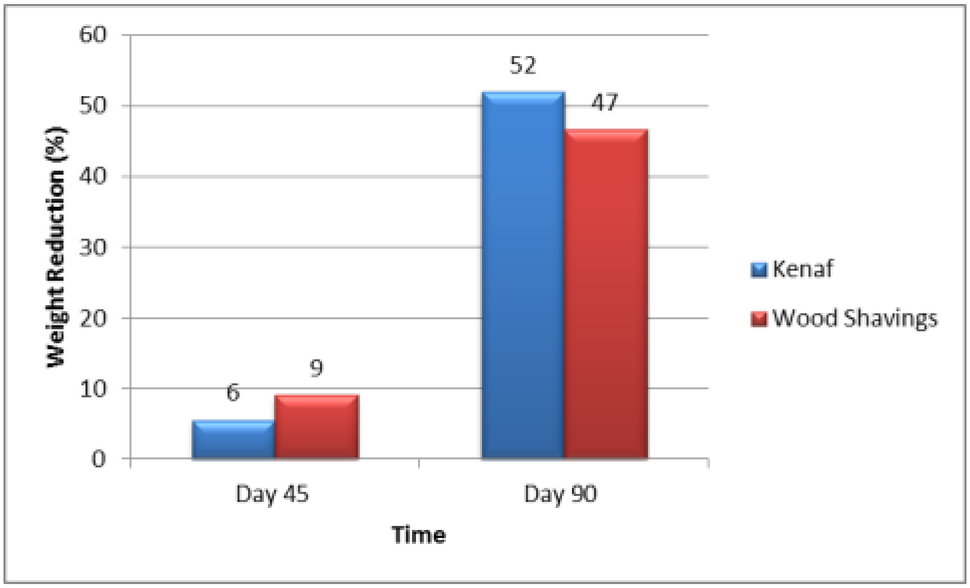

Figure 33 Percent weight loss for kenaf and wood shavings on day 45 and 90

Compost Maturity Test

The signs that showed the composts were matured by day 90 included darker color, shrinkage in the original volume of the compost, and smooth and fine texture of the compost (Figure 34). Also, the radish seed germination tests indicated that the composts were matured by day 90 (Figures 35 and 36). Radish seed germination tests for all samples are summarized in Table 3. Composts of day 0 showed no germination rate due to the toxic material from filtration. However, composts of day 45 and 90 illustrated considerable germination rates. The reason could be due to degradation of toxic contaminants by microorganisms and weathering. In addition, contaminants could be converted to nutrients.

Table 3 Radish seed germination rate % in compost

Sample ID	Germination Rate % Day 0	Germination Rate % Day 45	Germination Rate % Day 90
Kenaf	0	78	100
Wood Shavings	0	83	94
Control Potting Soil	100	100	100

Figure 34 Compost samples of day 0, 45, and 90

Figure 35 Control samples (potting soil)

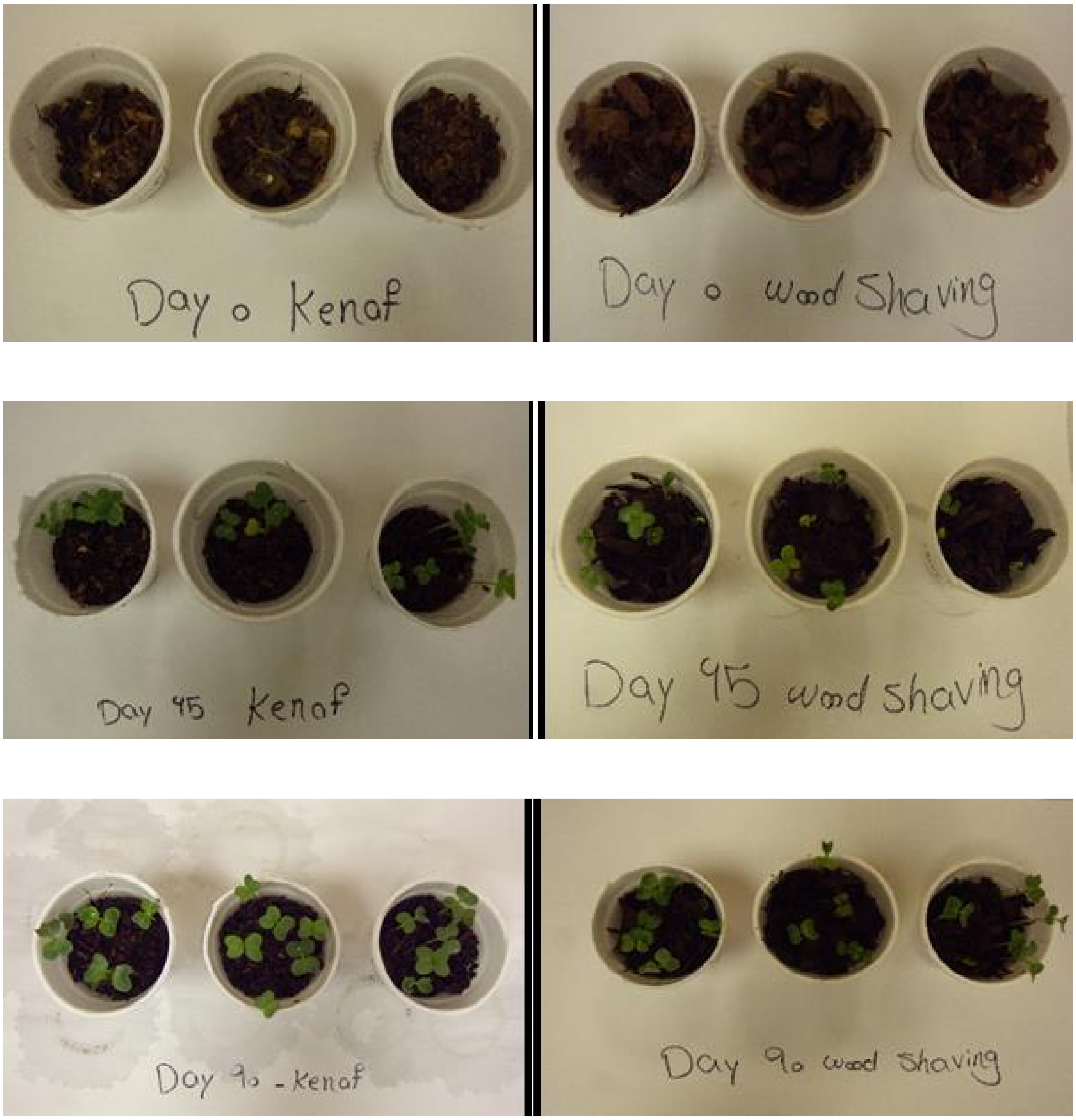

Figure 36 Germination test with radish seeds

Figures from top to bottom are: germination tests for day 0, 45, and 90

Phase II Filtration

Oil and Grease Concentrations of Filtrates

The results of oil and grease concentrations for phase II filtrations are shown in Figures 37 through 44. Figure 37 compares the concentrations of oil and grease in the water after the first column of each treatment. All four treatments significantly removed oil and grease when compared to the unfiltered control. However, there were no statistically significant differences among the four treatments; the wood shavings columns (Treatments 2 and 3) removed more oil and grease compared to the kenaf columns (Treatment 1 and 4). These differences are shown in Figure 38. The two wood shavings columns removed 40% of the oil and grease from the water, while the kenaf removed about 36%.

Figure 39 compares the concentrations of oil and grease in the water after the second column of each treatment. All four treatments significantly removed oil and grease when compared to the unfiltered control. There were no significant differences among the four treatments; however, in this case the columns containing kenaf removed slightly more oil and grease than the wood shavings columns. This is shown in Figure 40. The kenaf columns (Treatments 1 and 3) removed 33-38% of oil and grease compared to 33-35% removed by wood shavings columns (Treatments 2 and 4).

Figure 41 compares the oil and grease concentrations after passing through the third column of each treatment. Once again all four treatments were significantly less than the unfiltered control. However, there were also some differences among treatments. Figure 42 indicates that the wood shavings column of treatment 2 removed significantly more oil and grease when compared to the kenaf column of treatment 1. Percent removal of oil and grease ranged from 28% in the treatment 1 to 40% in the treatment 2.

Figures 43 and 44 compare the oil and grease reduction among three columns of each treatment. Statistical analysis indicated that there were no significant differences among three columns of each treatment as well as among all treatments.

Note: one of the replications in T1 column 3 was removed, but it was replaced with the average of the other two replications.

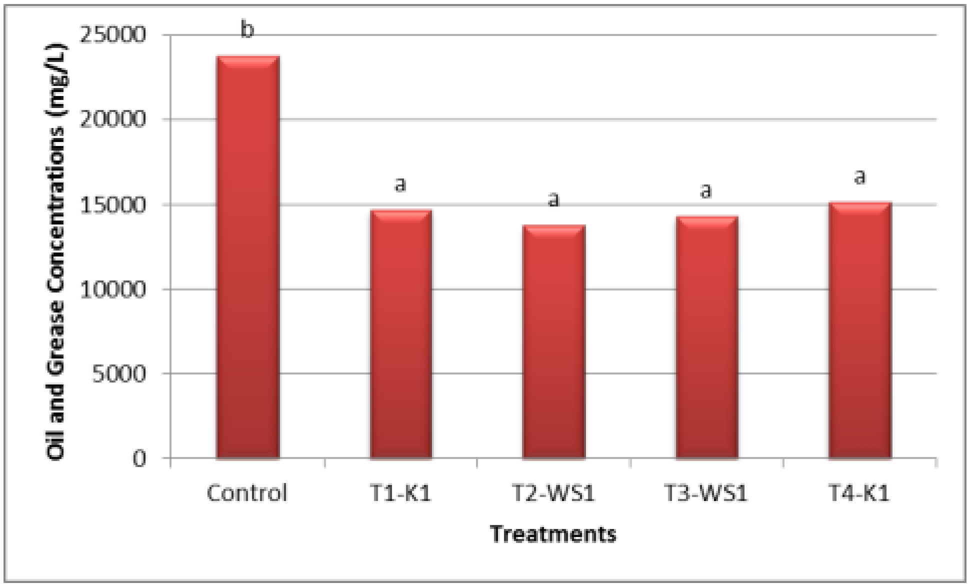

Figure 37 Oil and grease concentrations (mg/L) after filtration for first column in each treatment.

Different letters indicate significant difference in oil and grease concentrations at the P=0.05 level of significance for a given treatment.

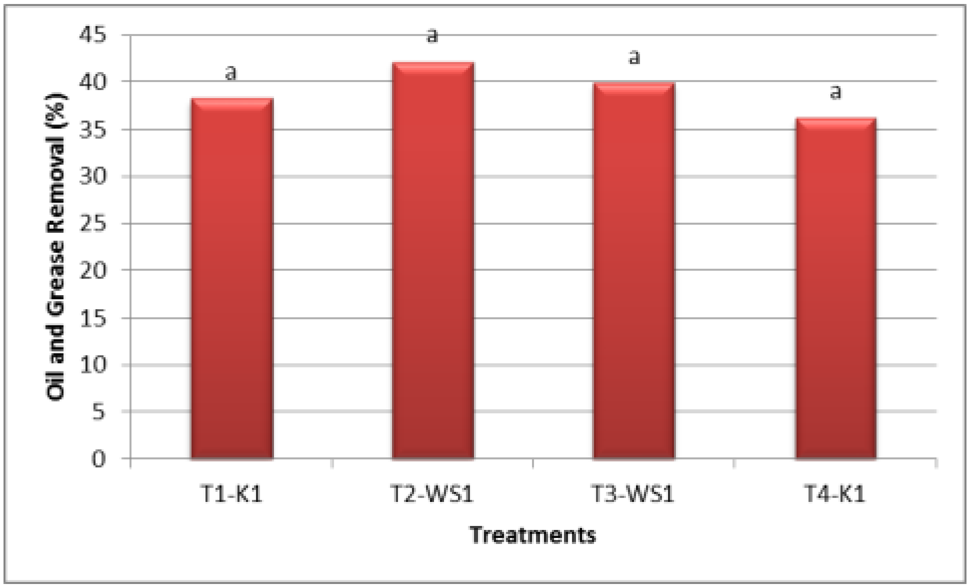

Figure 38 Percent oil and grease reduction rate after filtration for first column in each treatment.

Different letters indicate significant difference in percent oil and grease reduction rate at the P=0.05 level of significance for a given treatment.

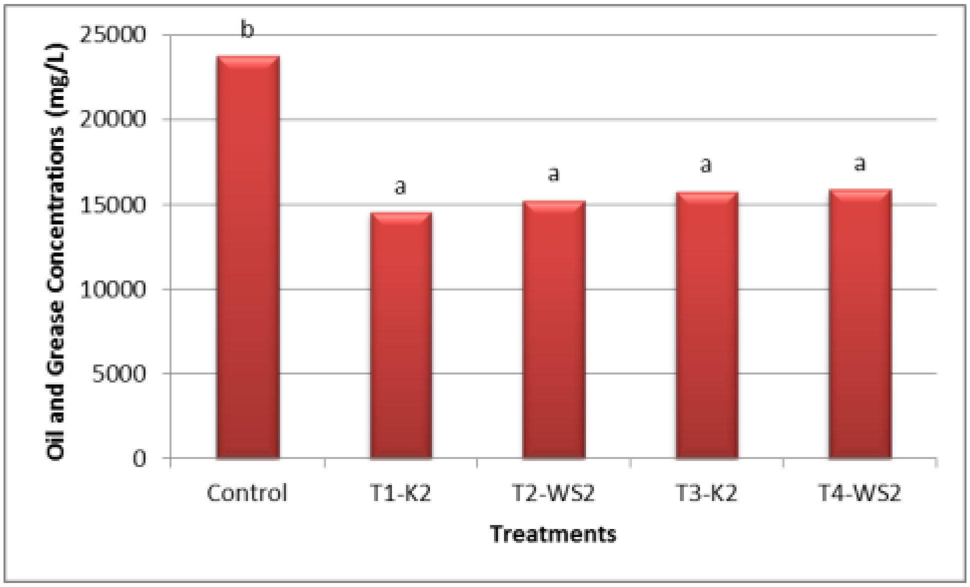

Figure 39 Oil and grease concentrations (mg/L) after filtration for second column in each treatment.

Different letters indicate significant difference in oil and grease concentrations at the P=0.05 level of significance for a given treatment.

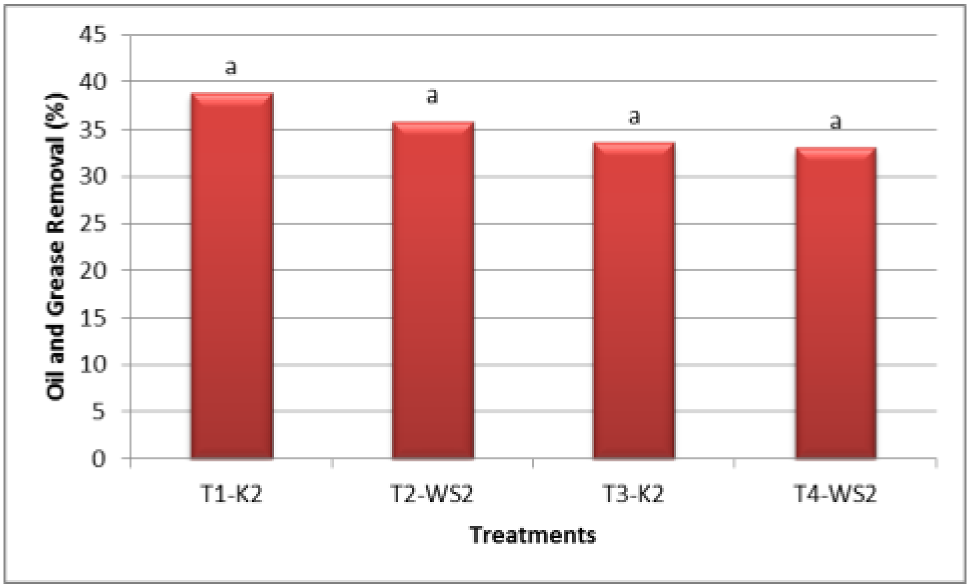

Figure 40 Percent oil and grease reduction rate after filtration for second column in each treatment.

Different letters indicate significant difference in percent oil and grease reduction rate at the P=0.05 level of significance for a given treatment.

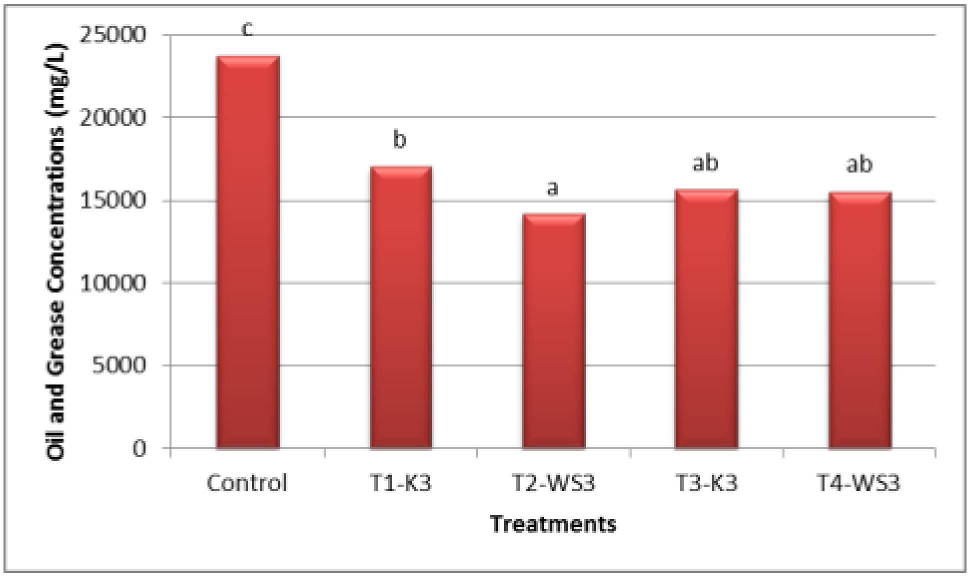

Figure 41 Oil and grease concentrations (mg/L) after filtration for third column in each treatment.

Different letters indicate significant difference in oil and grease concentrations at the P=0.05 level of significance for a given treatment.

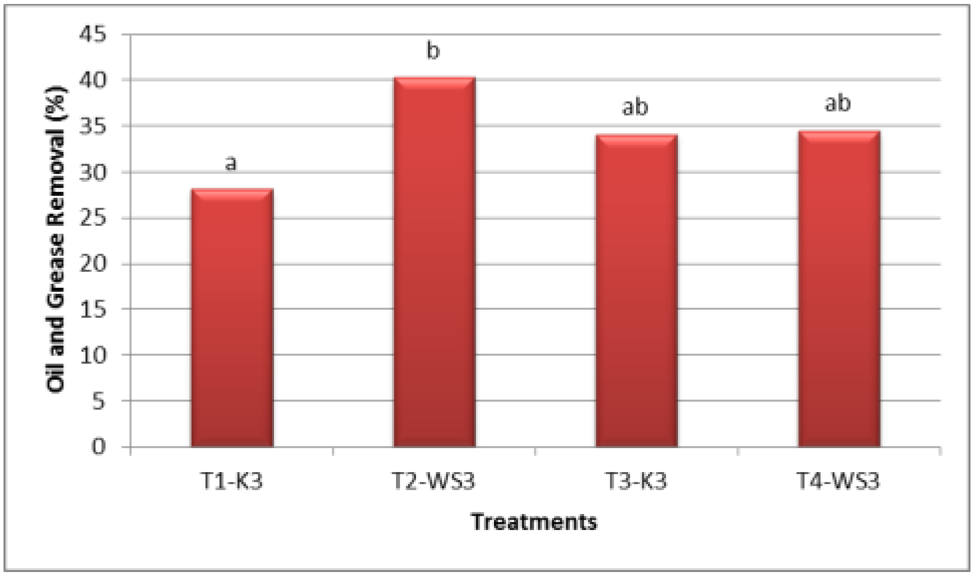

Figure 42 Percent oil and grease reduction rate after filtration for third column in each treatment.

Different letters indicate significant difference in percent oil and grease reduction rate at the P=0.05 level of significance for a given treatment.

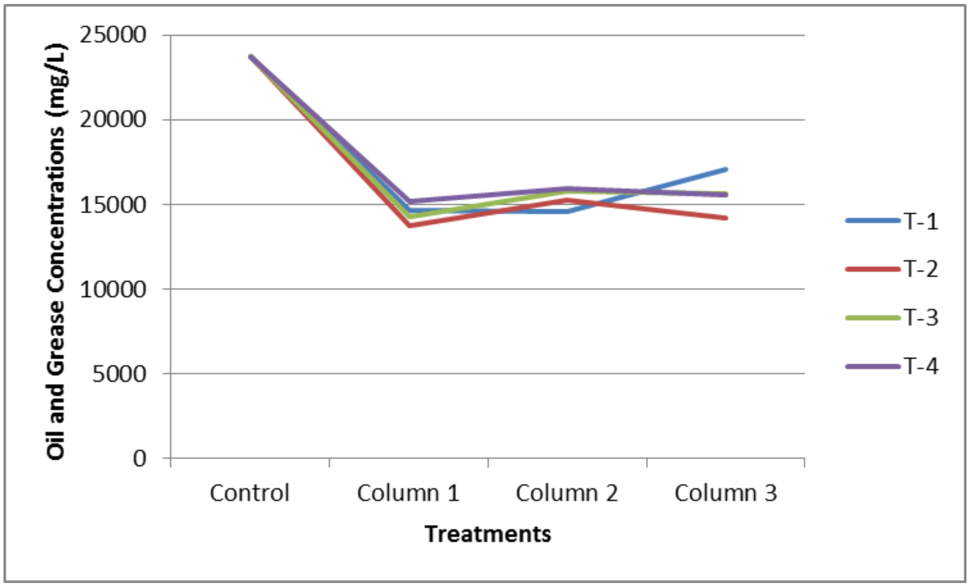

Figure 43 Comparison of oil and grease concentrations of three columns of each treatment

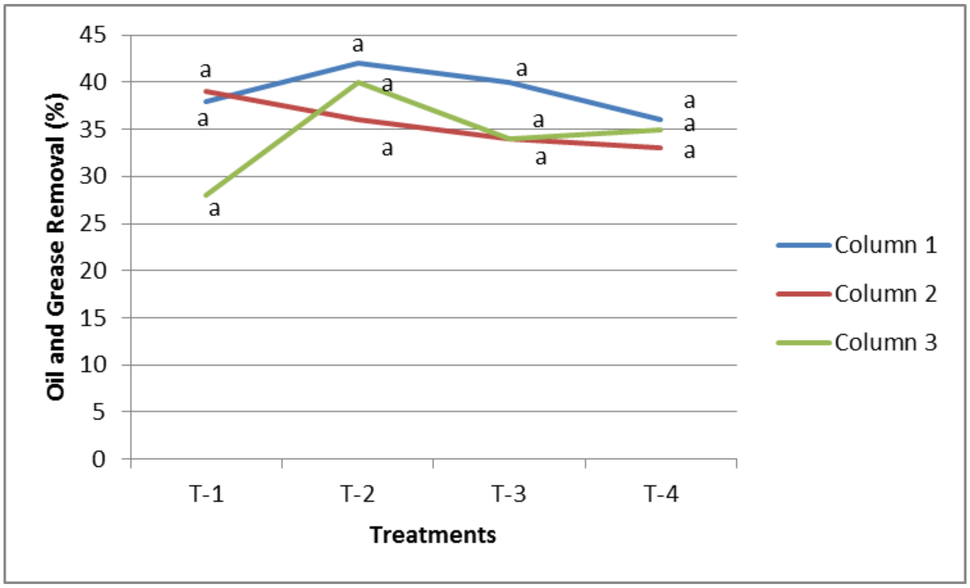

Figure 44 Comparison of percent oil and grease reduction rate of three columns of each treatment.

Different letters indicate significant difference in percent oil and grease reduction rate at the P=0.05 level of significance for a given treatment.

Toxicity Results of Filtrates

The results of toxicity of filtrates for phase II filtration are shown in Figures 45 through 51. Figure 45 compares the toxicity of the water after the first column of each treatment. All four treatments significantly reduced the toxicity of the water when compared to the unfiltered control. Even though statistical analysis indicated that there were no significant differences among the four treatments; the kenaf column in treatment 1 and the kenaf column in treatment 4 removed more toxicity compared to the wood shavings in treatments 2 and 3.

Figure 46 compares the toxicity of the water after the second column of each treatment. Once again all treatments significantly decreased the toxicity of the water compared to the unfiltered control. However there were no significant differences among the treatments; the wood shavings column in treatment 2 and 4 decreased the toxicity more compared to the kenaf columns in treatments 1 and 3.

Figure 47 compares the toxicity of the water after the third column of each treatment. All four treatments significantly decreased the toxicity of the water when compared to the unfiltered control. However, there were no significant differences among the treatments. The wood shavings in treatment 2 removed slightly more toxicity compared to the other three treatments.

Figure 48 compares the toxicity differences among three columns of treatment one. The statistical analysis demonstrated that the kenaf in column one removed more toxicity compared to column 2. The relative toxicity ranged from 130 in column 1 to 233 in column 2.

Figure 49 compares the toxicity differences among the three columns of treatment two. The statistical analysis showed that there were no significant differences among the columns. However, the wood shavings in the third column removed more toxicity compared to the wood shavings in the columns 1 and 2. The relative toxicity ranged from 157 in column 3 to 181 in column 1.

Figure 50 compares the toxicity differences among the three columns of treatment three. The statistical analysis indicated that there were no significant differences among the three columns. However, the kenaf in column 3 decreased toxicity to about 167.

Figure 51 compares the toxicity differences among the three columns of treatment four. The statistical analysis showed that there were no significant differences among the three columns. The relative toxicity ranged from 145 in column 1 to 176 in column 2.

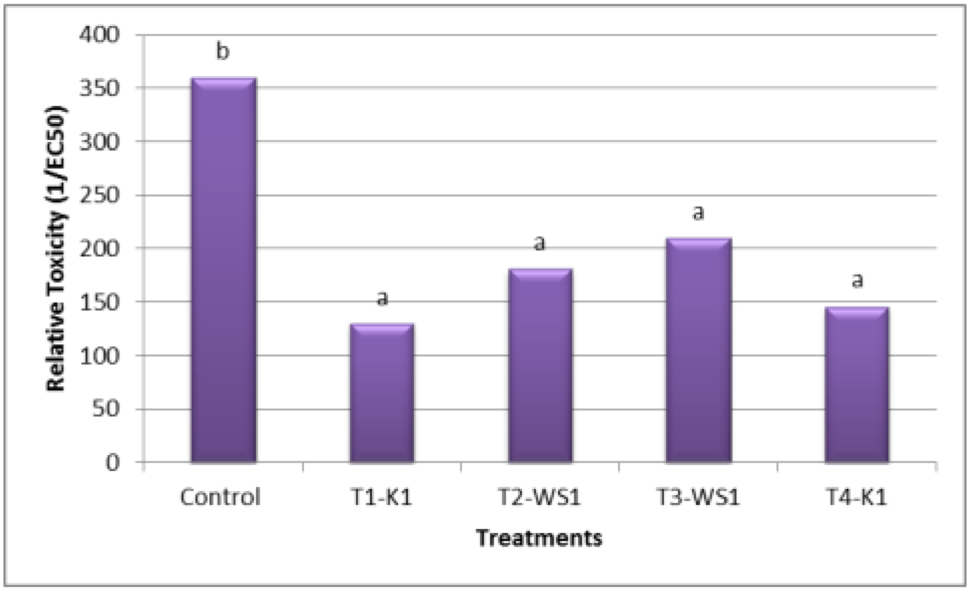

Figure 45 Toxicity differences in column one for four treatments.

Different letters indicate significant difference in toxicity at the P=0.05 level of significance for a given treatment.

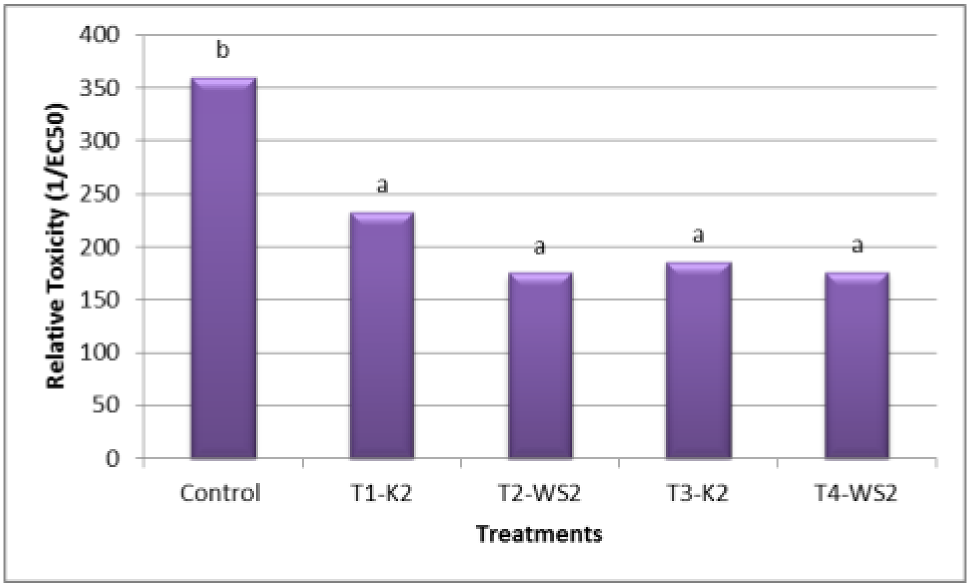

Figure 46 Toxicity differences in column two for four treatments.

Different letters indicate significant difference in toxicity at the P=0.05 level of significance for a given treatment.

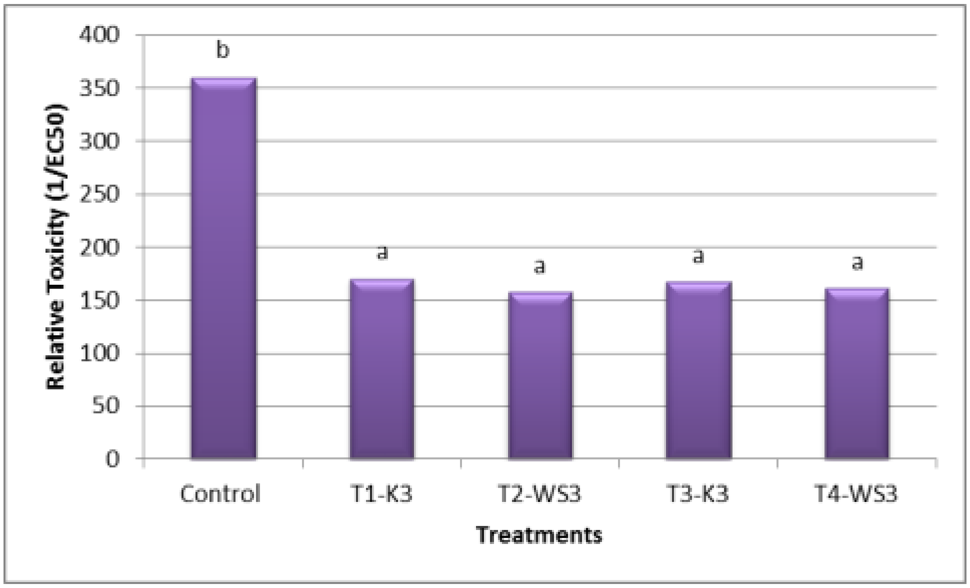

Figure 47 Toxicity differences in column three for four treatments.

Different letters indicate significant difference in toxicity at the P=0.05 level of significance for a given treatment.

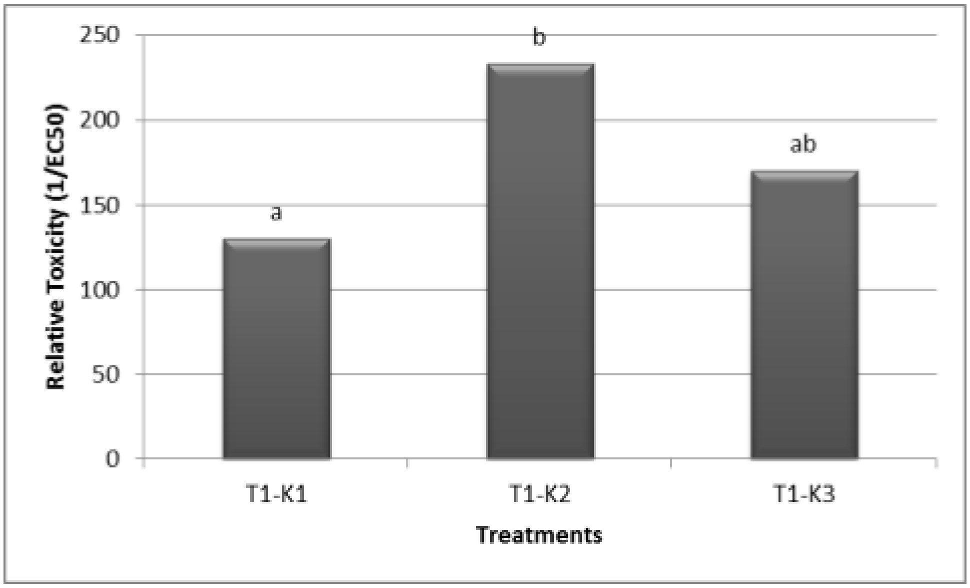

Figure 48 Toxicity differences among three columns of treatment one.

Different letters indicate significant difference in toxicity at the P=0.05 level of significance for a given treatment.

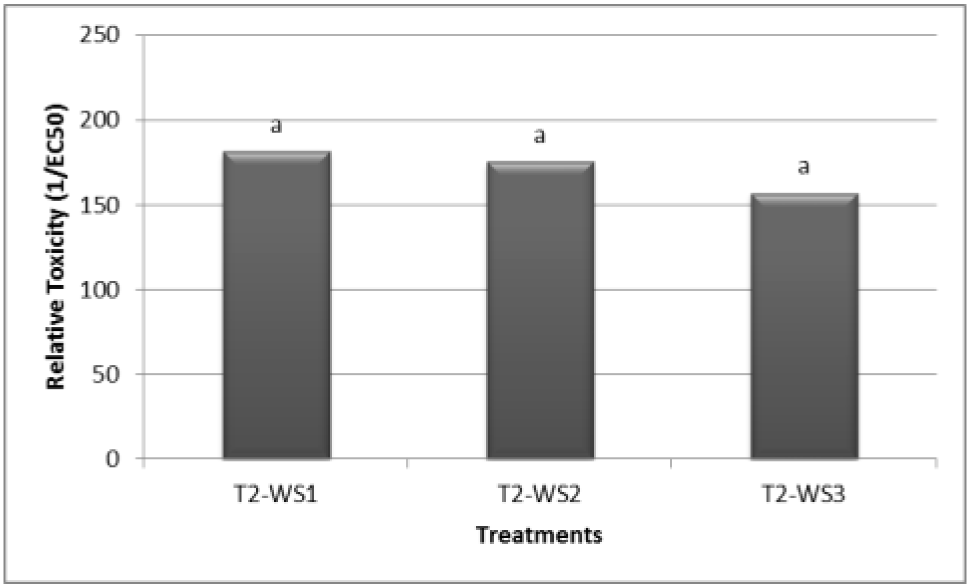

Figure 49 Toxicity differences among three columns of treatment two.

Different letters indicate significant difference in toxicity at the P=0.05 level of significance for a given treatment.

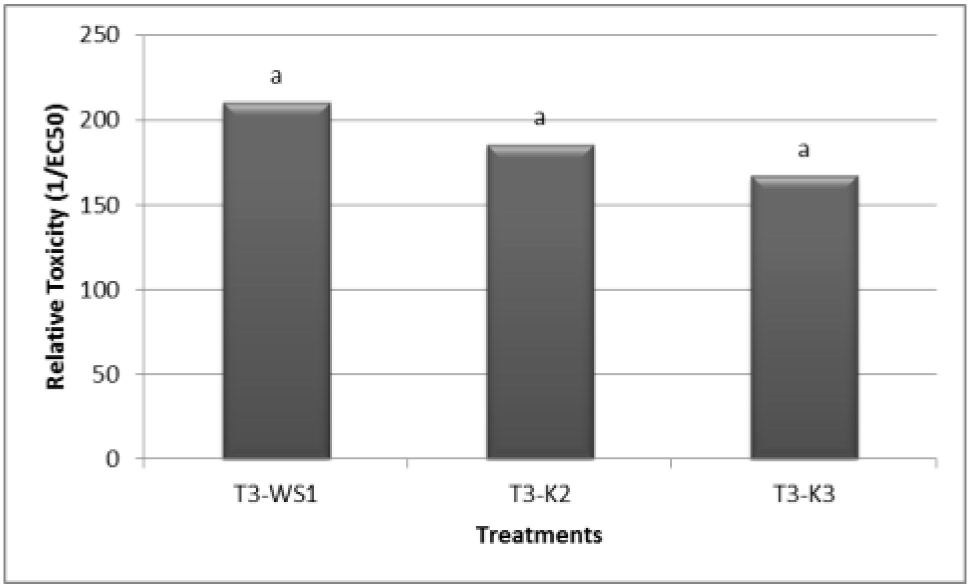

Figure 50 Toxicity differences among three columns of treatment three.

Different letters indicate significant difference in toxicity at the P=0.05 level of significance for a given treatment.

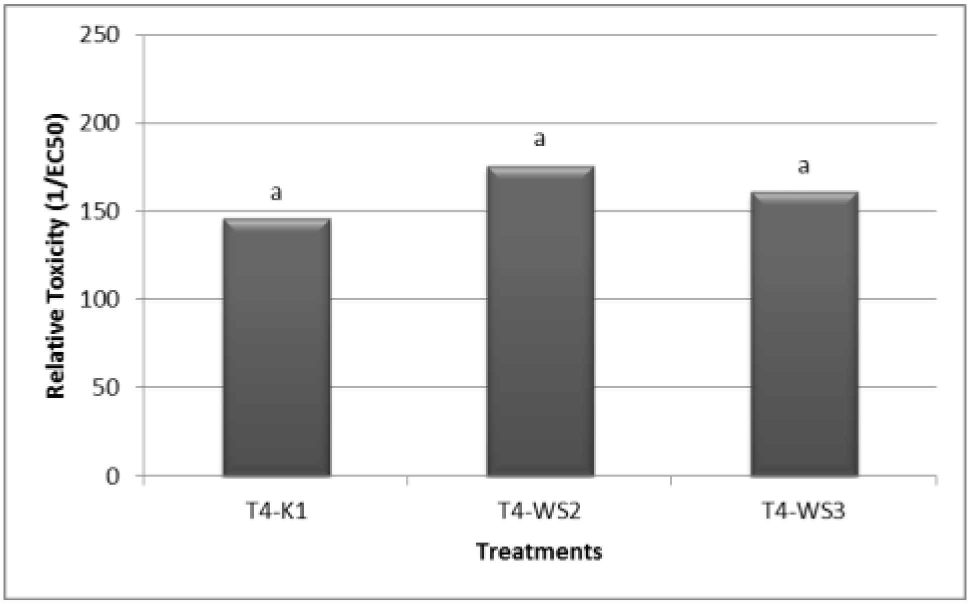

Figure 51 Toxicity differences among three columns of treatment four.

Different letters indicate significant difference in toxicity at the P=0.05 level of significance for a given treatment.

Comparison of Oil and Grease Removal of Phase I and II

The comparison of oil and grease removal for phase I and II are shown in Figure 52. The statistical analysis indicated that there were no significant differences between phase I and II. However, treatment two in both phases I and II significantly removed more oil and grease when compared to treatment 1.

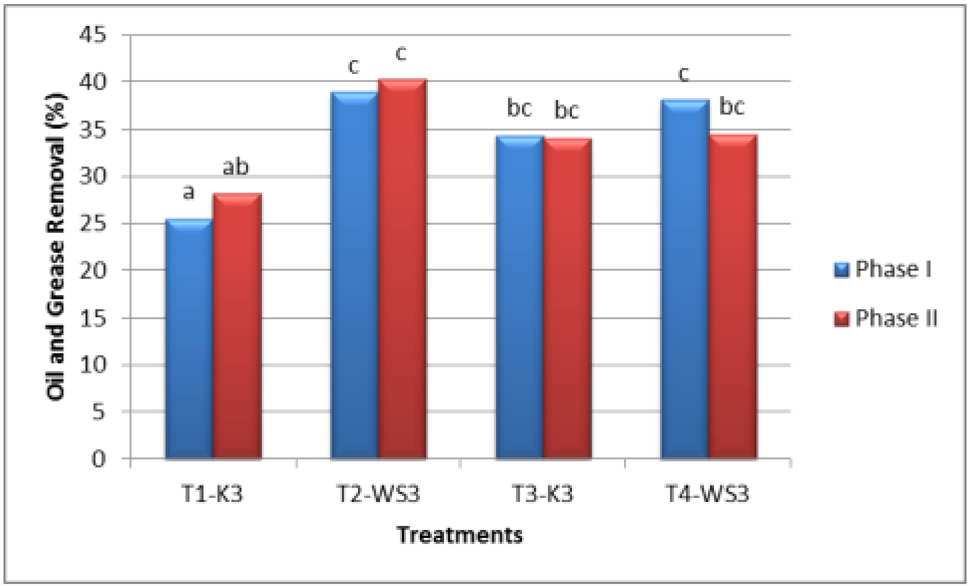

Figure 52 Comparison of percent oil and grease reduction rate for phase I and II filtration.

Different letters indicate significant difference in percent oil and grease reduction rate at the P=0.05 level of significance for a given treatment.

Comparison of Relative Toxicity of Phase I and II

The comparison of toxicity results for phase I and II are presented in Figure 53. The statistical analysis indicated that there were no significant differences between phase I and phase II relative toxicity. However, treatment 1 in phase I showed significantly more toxicity compared to the other treatments in phase I as well as phase II.

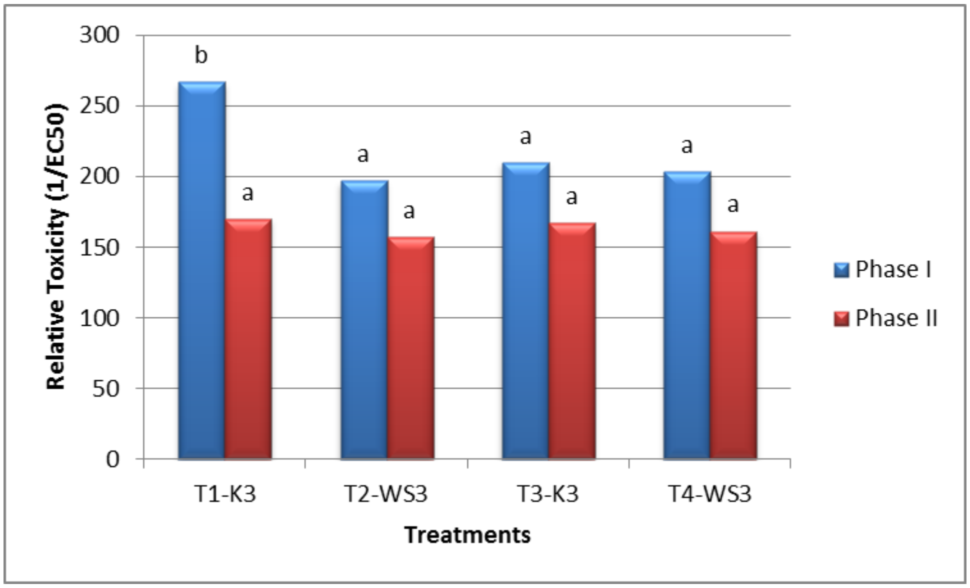

Figure 53 Comparison of toxicity differences in treatments for phase I and II filtration.

Different letters indicate significant difference in toxicity at the P=0.05 level of significance for a given treatment.

CHAPTER V

CONCLUSIONS

This study was conducted to evaluate the effectiveness of bio-filtration followed by bioremediation of process water from a bio-oil manufacturing facility. The bio-filtration through kenaf and wood shavings reduced the oil and grease concentrations by approximately 35-40% and the bioremediation of the filtrate water reduced the concentration another 67%. These treatments reduced the original oil and grease concentrations by 80%. Toxicity of the water also decreased by 44% after bio-filtration and another 86% after bioremediation resulting in an overall decrease in toxicity of 91-92%. Composting of the used bio-filtration matrix also significantly decreased the toxicity and oil and grease concentrations.

When comparing kenaf to wood shavings as bio-filtration matrices, both products effectively removed 35-40% of the oil and grease. Adsorption by kenaf was not significantly different from adsorption by the wood shavings. A majority of the removal of the oil and grease was accomplished after passing through the first column. The additional columns did not remove additional concentrations of oil and grease. Again there was no statistical difference between additional columns containing kenaf and additional columns containing wood shavings. There was however noted differences in the toxicity levels of the water that passed through kenaf versus wood shavings. Process water passing through some columns containing wood shavings had statistically less toxicity compared to treatment 1 in which all columns contained kenaf.

For the bioremediation phase of the study, the addition of air significantly decreased the concentration of oil and grease compared to the starting material and the un-aerated control. The addition of bacteria and air did not statistically decrease the oil and grease levels compared to air alone. The fact that the oil and grease levels decreased by 67% with only 1 week of aeration are impressive given the high levels in the starting material. Bio-treatment with air also significantly decreased the toxicity levels (an 86% decrease from the filtrate water). Interestingly, the toxicity of the control water also significantly decreased during this week. The control was not aerated, yet toxicity levels dropped to almost the same level as the other treatments. Since oil and grease concentrations in the control did not decrease, the resulting drop in toxicity must be due to other contaminants in the water.

Composting of the bio-filtration matrices significantly reduced the oil and grease concentrations by day 45, but there was no decrease between day 45 and day 90. Overall, composting decreased the oil and grease levels by 80%. Toxicity levels also significantly decreased by day 45. There was no significant difference between kenaf and wood shavings in either oil and grease or toxicity reductions. Interestingly, there was only a 6-9% decrease in weight by day 45, but by day 90 there was close to a 50% reduction in weight. The compost maturity test reflected this result in that there was less germination in the day 45 compost compared to the day 90 compost. So even though oil and grease and toxicity levels were down by day 45, the compost had not yet fully matured.

Increasing the flow rate through the bio-filtration columns (Phase II) did not change the concentrations of oil and grease that were removed when compared to the slower rate of Phase I, however, it did reveal some differences between the kenaf columns and the wood shavings. In general, the kenaf when used in the first column tended to remove more oil and grease and show less toxicity than the wood shavings. However, when kenaf is used in subsequent columns 2 and 3, it tended to remove less oil and grease and show more toxicity compared to wood shavings used in the same columns. The only significant differences between the kenaf and wood shavings for both removal of oil and grease and toxicity were seen in column 3.

In conclusion, bio-filtration followed by bioremediation was able to remove over 80% of the oil and grease from the process water and decrease the toxicity by 90%. Both kenaf and wood shavings were similar in their abilities to adsorb the contaminants. The second and third columns of the bio-filtration system did not contribute to the removal of oil and grease, however, the oil and grease capacity of a column was not determined thus eventually a column will be saturated and need to be replaced. It is likely that if the bioremediation stage was longer, a greater reduction of oil and grease would be possible. Composting of the used kenaf and wood shavings successfully reduced the oil and grease concentrations as well as toxicity of the matrix material. Oil and grease levels after 90 days were still high, but the compost did not appear to be toxic to plants if used as ground mulch.

Suggestions for the future work could be the use of different bacteria such as acidophilus bacteria that can tolerate the highly acidic environment of the wastewater as well as bacteria that are able to degrade different chemical compounds presenting in the wastewater. Also, addition of various nutrients to the wastewater could assist the growth of the bacteria and consequently enhance the biodegradation of the wastewater contaminants.

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APPENDIX A

PHASE I FILTRATION

Table 4 Oil and Grease Concentrations of Column One for Four Treatments

Sample ID	Oil and Grease Concentrations (mg/L)	Percent Removal %
T1-K1-A	14519	39
T1-K1-B	13553	43
T1-K1-C	14732	38
T2-WS1-A	13783	42
T2-WS1-B	15581	34
T2-WS1-C	16536	30
T3-WS1-A	13783	42
T3-WS1-B	15581	34
T3-WS1-C	16536	30
T4-K1-A	14519	39
T4-K1-B	13553	43
T4-K1-C	14732	38
Control-A	23420	-
Control-B	24302	-
Control-C	23545	-

Table 5 Oil and Grease Concentrations of Column Two for Four Treatments

Sample ID	Oil and Grease Concentrations (mg/L)	Percent Removal %
T1-K2-A	16865	29
T1-K2-B	16986	28
T1-K2-C	15233	36
T2-WS-2-A	13539	43
T2-WS-2-B	15354	35
T2-WS-2-C	17310	27
T3-K2-A	16193	32
T3-K2-B	17476	26
T3-K2-C	17330	27
T4-WS-2-A	15893	33
T4-WS-2-B	15946	33
T4-WS-2-C	15304	36
Control-A	23420	-
Control-B	24302	-
Control-C	23545	-

Table 6 Oil and Grease Concentrations of Column Three for Four Treatments

Sample ID	Oil and Grease Concentrations (mg/L)	Percent Removal %
T1-K3-A	17557	26
T1-K3-B	17824	25
T1-K3-C	14603	39
T2-WS3-A	14328	40
T2-WS3-B	12867	46
T2-WS3-C	14665	38
T3-K3-A	15943	33
T3-K3-B	15887	33
T3-K3-C	14945	37
T4-WS3-A	14376	39
T4-WS3-B	14321	40
T4-WS3-C	15407	35
Control-A	23420	-
Control-B	24302	-
Control-C	23545	-

Note: The highlighted values were replaced with the average of the other two replications

Table 7 Oil and Grease Concentrations of Bio-treatments

Sample ID	Oil and Grease Concentrations (mg/L)	Percent Removal %
Air+bac 1	4786	67
Air+bac 2	3436	76
Air+bac 3	5991	59
Air 1	4433	69
Air 2	7020	52
Air 3	7109	51
Control 1	15520	0.1
Control 2	13991	0.1
Control 3	17401	0.1
Starting Water 1	14328	-
Starting Water 2	14496	-
Starting Water 3	14665	-

Table 8 Oil and Grease Concentrations of Composts

Sample ID	Oil and Grease Concentrations (mg/L)	Percent Removal %
K-0-1	169290	-
K-0-2	172870	-
K-0-3	161351	-
WS-0-1	170476	-
WS-0-2	126115	-
WS-0-3	146495	-
K-45-1	29432	82
K-45-2	33972	80
K-45-3	36162	78
WS-45-1	43206	71
WS-45-2	49250	67
WS-45-3	51158	65
K-90-1	37750	78
K-90-2	39184	77
K-90-3	45447	73
WS-90-1	52558	64
WS-90-2	65143	56
WS-90-3	49318	67

Table 9 Relative Toxicity of Phase I Filtrates

Sample ID	Relative Toxicity	Sample ID	Relative Toxicity
T1-K1-A	238	T3-WS1-A	179
T1-K1-B	210	T3-WS1-B	185
T1-K1-C	194	T3-WS1-C	240
T1-K2-A	236	T3-K2-A	180
T1-K2-B	217	T3-K2-B	265
T1-K2-C	169	T3-K2-C	217
T1-K3-A	244	T3-K3-A	232
T1-K3-B	256	T3-K3-B	202
T1-K3-C	300	T3-K3-C	196
T2-WS1-A	179	T4-K1-A	162
T2-WS1-B	185	T4-K1-B	173
T2-WS1-C	245	T4-K1-C	177
T2-WS2-A	222	T4-WS2-A	186
T2-WS2-B	202	T4-WS2-B	178
T2-WS2-C	195	T4-WS2-C	167
T2-WS3-A	220	T4-WS3-A	191
T2-WS3-B	169	T4-WS3-B	214
T2-WS3-C	201	T4-WS3-C	205
Control-A	353	Control-A	353
Control-B	347	Control-B	347
Control-C	379	Control-C	379

Table 10 Relative Toxicity of Bio-treatments

Sample ID	Relative Toxicity
Air+Bac 1	35
Air+Bac 2	23
Air+Bac 3	25
Air 1	30
Air 2	29
Air 3	30
Control 1	43
Control 2	65
Control 3	49
Starting Water 1	220
Starting Water 2	169
Starting Water 3	201

Table 11 Relative Toxicity of Composts

Sample ID	Relative Toxicity
K-0-1	1.4
K-0-2	3
K-0-3	3.4
WS-0-1	4.8
WS-0-2	5.4
WS-0-3	4.5
K-45-1	0.04
K-45-2	0.04
K-45-3	0.03
WS-45-1	0.04
WS-45-2	0.03
WS-45-3	0.03
K-90-1	0.02
K-90-2	0.02
K-90-3	0.02
WS-90-1	0.01
WS-90-2	0.02
WS-90-3	0.02

APPENDIX B

PHASE II FILTRATION

Table 12 Oil and Grease Concentrations of Column One for Four Treatments

Sample ID	Oil and Grease Concentrations (mg/L)	Percent Removal %
T1-K1-A	14662	38
T1-K1-B	14961	37
T1-K1-C	14374	39
T2-WS1-A	13743	42
T2-WS1-B	16073	32
T2-WS1-C	12293	48
T3-WS1-A	14594	39
T3-WS1-B	14435	39
T3-WS1-C	13798	42
T4-K1-A	12874	46
T4-K1-B	14737	38
T4-K1-C	17851	25
Control-A	23420	-
Control-B	24302	-
Control-C	23545	-

Table 13 Oil and Grease Concentrations of Column Two for Four Treatments

Sample ID	Oil and Grease Concentrations (mg/L)	Percent Removal %
T1-K2-A	13855	42
T1-K2-B	16199	32
T1-K2-C	13593	43
T2-WS-2-A	15244	36
T2-WS-2-B	16052	32
T2-WS-2-C	14849	37
T3-K2-A	15497	35
T3-K2-B	16374	31
T3-K2-C	15418	35
T4-WS-2-A	14882	37
T4-WS-2-B	15259	36
T4-WS-2-C	17542	26
Control-A	23420	-
Control-B	24302	-
Control-C	23545	-

Table 14 Oil and Grease Concentrations of Column Three for Four Treatments

Sample ID	Oil and Grease Concentrations (mg/L)	Percent Removal %
T1-K3-A	14262	40
T1-K3-B	17469	26
T1-K3-C	16656	30
T2-WS3-A	14186	40
T2-WS3-B	15170	36
T2-WS3-C	14200	40
T3-K3-A	15014	37
T3-K3-B	14993	37
T3-K3-C	16952	29
T4-WS3-A	14888	37
T4-WS3-B	15280	36
T4-WS3-C	16489	31
Control-A	23420	-
Control-B	24302	-
Control-C	23545	-

Note: The highlighted value was replaced with the average of the other two replications

Table 15 Relative Toxicity of Phase II Filtrates

Sample ID	Relative Toxicity	Sample ID	Relative Toxicity
T1-K1-A	143	T3-WS1-A	291
T1-K1-B	89	T3-WS1-B	221
T1-K1-C	158	T3-WS1-C	119
T1-K2-A	191	T3-K2-A	167
T1-K2-B	209	T3-K2-B	173
T1-K2-C	299	T3-K2-C	217
T1-K3-A	167	T3-K3-A	149
T1-K3-B	186	T3-K3-B	189
T1-K3-C	157	T3-K3-C	163
T2-WS1-A	218	T4-K1-A	110
T2-WS1-B	145	T4-K1-B	133
T2-WS1-C	181	T4-K1-C	194
T2-WS2-A	161	T4-WS2-A	158
T2-WS2-B	178	T4-WS2-B	194
T2-WS2-C	187	T4-WS2-C	176
T2-WS3-A	172	T4-WS3-A	156
T2-WS3-B	150	T4-WS3-B	170
T2-WS3-C	149	T4-WS3-C	157
Control-A	353	Control-A	353
Control-B	347	Control-B	347
Control-C	379	Control-C	379