RETENTION OF WATER CONTAMINANTS BY

FLY ASH AMENDED PERVIOUS CONCRETE BLOCKS

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ABSTRACT

RETENTION OF WATER CONTAMINANTS BY FLY ASH AMENDED

PERVIOUS CONCRETE BLOCKS

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Fly ash amended pervious concrete has been demonstrated not to leach the hazardous compounds in the fly ash and may offer additional advantages by filtering out some contaminants. A series of experiments were conducted using five different types of fly ash amended pervious concrete blocks- 0% fly ash, 20% fly ash-high carbon content, 20% fly ash-low carbon content, 30% fly ash-high carbon content and 30% fly ash-low carbon content, to investigates the potential for biodegradation improvement of motor oil by pervious concrete blocks, and to what extent the pervious concrete blocks could retain water contaminants like PO_4^{3-} from urban runoff. Ion Chromatography (IC) was used to measure the retention of PO_4^{3-}. Biodegradability was measured as the ratio of biochemical oxygen demand (BOD) to chemical oxygen demand (COD).

The range of BOD_5/COD values for leachate motor oil samples were 0.7 to 0.9, suggesting good biodegradation. The BOD_5/COD ratio improved with increasing motor oil retention as the percentage of fly ash increased in pervious concrete block. Phosphate leaching studies revealed that the 20% fly ash low carbon content and the 30 % fly ash high carbon content pervious concrete block did not leach any phosphate.   The 0% fly

ash, 20% fly ash high carbon content and 30% fly ash low carbon content concrete blocks

ash, 20% fly ash high carbon content and 30% fly ash low carbon content concrete blocks

leached phosphate. However, all five fly ash amended concrete blocks showed the ability

to remove 99% of phosphate from high concentration phosphate solution (750 ppm).

ACKNOWLEDGEMENTS

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CHAPTER 1

INTRODUCTION

Human activities are directly and indirectly creating a drastic change in the environment. As infrastructure (roads, sidewalks, commercial and residential structures) increases, impervious surfaces increase, which in turn radically decreases the rate of water infiltration. As a result, the volume of water runoff increases and disrupts the natural hydrologic cycle; this leads to flooding, erosion, habitat degradation, and water quality impairment.

Stormwater runoff has been identified as one of the major causes of water quality degradation in urbanizing water sheds.[1] Pollutants generated or derived from everyday activities will blend in with stormwater runoff as nutrients, sediment, heavy metals, hydrocarbons, gasoline additives, pathogens, herbicides, and pesticides. Usually these pollutants are bound up in soil that prevents or slows the spreading of the contamination into the water table until microbial degradation or plant uptake can happen. However, with the use of impervious concrete, pollutants cannot be absorbed into the soil. Instead, deposit on the surfaces often drain directly into rivers or lakes, bypassing the natural filtration abilities of soil. The use of pervious surfaces rather than impervious concrete

and asphalt can help to prevent these problems by allowing the runoff to pass through the pavement and eventually into the subsurface. The underlying subsurface contains native soil, which is a filter to remove water pollutants before groundwater is recharged, or before waters can enter nearby natural water bodies.

In recent years, pervious concrete has been increasingly used in the United States, as well as other parts of the world. The U.S. Environmental Protection Agency (EPA) has recommended it as a Best Management Practices (BMP). The performance of pervious concrete can be improved by substituting some of the cement with fly ash. Fly ash has been shown to increase adsorption of water contaminants, improve the later-age strength of concrete, and increase freeze-thaw durability of concrete.[2]

Objectives

The objective of this research was to investigate the potential of pervious concrete containing fly ash to remove contaminants commonly found in urban stormwater runoff. Five different sets of pervious concrete-fly ash mixture were examined: 0% fly ash, 20% fly ash low-carbon content, 20% fly ash high-carbon content, 30% fly ash low-carbon content, and 30% fly ash high-carbon content. The specific goal was, to investigate if any of the five sets of pervious concrete-fly ash could remove water contaminants like nutrient anion PO_4^{3-}, and hydrocarbons such as motor oil from urban runoff generated from storm events. Another objective of this research was to measure the BOD_5/COD ratio as an indication of biodegradability of motor oil in urban runoff and the impact pervious concrete may have on its reduction.

Contaminants of Urban Runoff Water

Urban water runoff is being reported as a substantial source of surface water pollution. Because of the impervious surface of many urban areas, water runs off instead of soaking in, causing more stormwater in urban areas.[3] Although there are many pollutants in urban stormwater, the major categories are as follows: total suspended solids, heavy metals, polycyclic aromatic hydrocarbons (PAHs), petroleum products, particulates and nutrients.[4] Sources of pollutants are wide and varied but are mostly due to increased numbers of people, vehicles, roads, building materials, soil erosion, household chemicals, industrial processes, human and animal wastes, fertilizers, etc.[4] The focus of the research presented here is on Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), oil and grease and nutrient contaminant such as phosphate in urban runoff.

Biodegradation

Biodegradation is the metabolic or enzymatic processes of living microorganisms used to break down organic substrates into smaller compounds.[5] Biodegradation of petroleum compounds occurs when they are converted into food and energy to sustain microbial growth. It is very important natural attenuation since many important compounds of petroleum hydrocarbon contamination can be changed into less hazardous or benign substances.

There are several options available to determine the biodegradability of organic compounds in aqueous medium including shake-flask batch tests measuring biogas

production, activated sludge simulation, biochemical oxygen demand (BOD), static

test(zahn-wellens method), respirometry, dissolved organic carbon (DOC), total organic

carbon (TOC), chemical oxygen demand (COD) metabolism and identification of

transformation products. In this project, BOD_5 and COD have been used to evaluate the

biodegradability of motor oil. Below are details on both tests.

Biochemical Oxygen Demand

Biochemical Oxygen Demand (BOD) refers to the amount of oxygen required by

bacteria if all the biologically degradable organic matter in a specified volume of water

where biodegraded. With the growing concern of effective pollution control, added

importance has been placed on Biochemical Oxygen Demand. The Environmental

Protection Agency (EPA) uses BOD_5 levels as a measurement of effluent strength and

establishes an effluent guideline as required by the Federal Water Pollution Control Act.[6]

BOD$_5$ is defined by Sawyer and Mccarty[7] as a wet oxidation procedure in which

bacteria serve as the medium for oxidation of the organic matter to carbon dioxide and

water. The BOD_5 test is used to measure the amount of biologically oxidizable organic

matter present in a sample and determine the oxidation rate. In order to make the test

work, the sample must be sealed properly and then placed in a controlled environment for

a preselected period. In the standard test, a given volume of sample water is seeded with

bacteria and nutrients (nitrogen and phosphate) in 300 mL BOD bottle and then incubated

at 20°C for five days in the dark. The BOD_5 is then calculating by subtracting the final

dissolved oxygen (DO) from the initial dissolved oxygen concentration.

Usually BOD_5 level depends on oxygen demand. If there is a large quantity of organic waste present in water, there will also be a large number of bacteria in there to decompose this waste. In this case, the demand for oxygen will be high as will the BOD_5 level. As the waste is consumed, BOD_5 levels will start to decline. When BOD_5 levels are high, dissolved oxygen (DO) levels in water decrease because the bacteria are consuming the available dissolved oxygen.

Dissolved oxygen is one of the most important water quality parameters because sufficient DO is crucial for the survival of fish and other aquatic life. Oxygen measured in its dissolved form is called "Dissolved Oxygen". Oxygen is dissolved into water from the atmosphere and from aquatic-plant photosynthesis. DO is measured in mg/L or "Percent Saturation". Milligram per liter refers the amount of oxygen in a liter of water. Percent saturation refers the amount of oxygen in a liter of water compare to the total amount of oxygen that water can hold at that temperature.[8] The concentration of DO in a water sample is dependent on:

 (a) Temperature: As water temperature increases, DO decreases.

 (b) Salinity: As water salinity increases, it holds less oxygen and as a result DO decreases.

 (c) Atmospheric pressure: DO decreases when atmospheric pressure is low.

The 18th Edition of "Standard Methods for the Examination of Water and Wastewater" introduces two methods for the determination of DO in wastewater.[9]

They are the Winkler method (azide modification) and the electrometric method that uses membrane electrodes and a DO meter. The Winkler method is based on the capability of the DO in a sample to oxidize chemicals that are added to the sample.

The membrane electrode method uses a meter and electrode, and is based on the rate at which oxygen molecules pass through a membrane covering a set of electrodes. The oxygen molecules react with an internal filling solution and develop a small electrical charge between the electrodes, which appears on a meter. The reading on the meter is the amount of DO present in the sample.

The BOD_5 test is used widely in measuring waste loadings of treatment plants and the efficiency of treatment processes, but it is of limited use in industrial wastewater containing toxic metal substances that is harmful to the microorganisms. Usually BOD_5 tests use the same type of bacteria that is commonly found in municipal plants, although it may be ineffective to degrade the organic found in peppermills or refineries systems. In addition, BOD_5 values of complex hydrocarbons; particularly contaminants that are made up of many different compounds, such as crude oil or petroleum are found to be lower and indicate less biodegradability. Groenewold et al.[10] studied 12 long and short-chain fatty acids. They reported that since BOD_5 is a bioassay test and utilizes bacteria to oxide organic substances, complete oxidation is not very likely to happen and therefore, BOD_5 values are usually less than the ThOD (Theoretical oxygen demand) value.[10] The theoretical oxygen demand of a given compound is the calculated maximum amount of oxygen needed for the oxidization of this compound. Sometimes this hard to degrade

organic material needs more than five days to breakdown. Therefore, a five day BOD standard test may give an inaccurate result about the amount of pollution present in a waste stream. Moreover, in some cases the organic material may simply not be biodegradable.

Chemical Oxygen Demand

Natural organic detritus, organic waste from industrial and agricultural runoff, wastewater treatment plants, and failing septic systems act as a prime source of organic matter. If discharged into natural water bodies, organic matter can cause complete deficiency of dissolved oxygen causing mortality to the aquatic organisms.

In environmental chemistry, the Chemical Oxygen Demand (COD) is a quick, easy means to determine the water quality. Chemical Oxygen Demand (COD) refers to the amount of oxygen needed to consume the organic matter content of a sample and convert it into carbon dioxide and water under aerobic conditions. It is expressed in milligram per liter (mg/L) which signifies the amount of oxygen consumed, during the oxidation of organic matter, per liter of aqueous sample. In the oxidation process, a strong oxidant (potassium dichromate) is used in the presence of a catalyst (silver) and strong acid (sulfuric acid) to convert most of the carbon to carbon dioxide, while any hydrogen present in the organic matter is converted to water.[11]

Organic matter + Oxidant $\rightarrow CO_2 + H_2O$
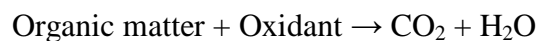
Chemical Oxygen Demand has some disadvantages. The oxidation step of this procedure cannot distinguish between organic and inorganic carbons. Usually the

organic carbon fraction of the sample is necessary for correlation with Biochemical

Oxygen Demand (BOD) and Total Organic Carbon (TOC). Therefore, unknown

oxidizable inorganic carbon can produce positive error and alter any attempt to directly

substitute COD for BOD or TOC.

Determination of organics in aqueous sample can be made by several approved

methods-EPA Method 410.4, Hach Method 8000 and Standard Method 520D. Hach

Method 8000 has some advantages over other methods. Since it is a micro method, it

needs smaller sample sizes, reduced reagents and obviously less waste disposal. This

method uses digestion/analysis vials with pre-measured amounts of necessary reagents

which are commercially available.

The Hach 8000 Method requires several steps; digestion is the first step.[12]

Concentrated sulfuric acid (H_2SO_4) is the primarily digestion catalyst and silver sulfate

(Ag_2SO_4) is the secondary catalyst. Most of the organic compounds except volatile

straight chain aliphatic compounds oxidize almost completely. The use of sealed

ampules limits the amount of vaporization and maximizes the amount of oxidation. In

addition, aliphatic compounds are oxidized largely in the presence of a catalyst such as

silver, which increases the accuracy of the COD value.

In the digestion process, the sample's organic carbon is oxidized with the

hexavalent dichromate ion ($Cr_2O_7^{2-}$) of potassium dichromate ($K_2Cr_2O_7$). This reaction

reduces the dichromate ion ($Cr_2O_7^{2-}$) to green chromate ion (Cr^{3+}). The amount of Cr^{3+}

produced is proportional to the amount of organics present.[13]   Colorimetric method is

used for determining the amount of chromium in a particular valence state. Colorimetric analysis works because dichromate ion and trivalent chromium absorb at different wavelengths. The dichromate ion absorbs at 420 nm whereas, Cr^{3+} ion absorb around 600-620 nm.[14] In general, low range COD (<150 ppm) analysis measures the remaining yellow Cr^{6+} and high range COD (<15,00 ppm) analysis measures the amount of green Cr^{3+} produced. The presence of chlorine ion in the sample interferes with the oxidation of the organic matter, but it can be overcome by complexing chloride with mercuric sulfate ($HgSO_4$).

Oil and Grease

The oil and grease detected in runoff water can be classified as hydrocarbons between C_{10} to C_{40}.[15] These include aromatics, polar hydroxyl acids, cyclic hydrocarbons, ketones, esters, and some other unresolved complex mixtures. Most hydrocarbons found in stormwater runoff are derived from petroleum products like used motor oil.

Motor oils consist of a base lubricating oil (a complex mixture of hydrocarbons, 80% to 90% by volume) and various additives that improve the oils performance (10% to 20% by volume). Motor oil also contains chemicals because of the breakdown of additives, contaminations that produce are during combustion, and the addition of metals from the wear and tear of the engine. Therefore, it is difficult to characterize the exact composition of used motor oil. Used oils consist of aliphalic and aromatic hydrocarbons, such as phenol, naphthalene, benz(a) anthracene, benzo(a) pyrene, and fluoranthene, that

are considered to be the most toxic compounds of petroleum products and are also associated with chronic and carcinogenic effects.[16] Used oils contain up to 30% aromatic hydrocarbons, with as much as 22 ppm benzo(a) pyrene (a PAH). Inorganic components found in used motor oil include chlorine, sulfur, phosphorus, bromine, nitrogen, and metals like zinc, magnesium, barium, and lead.[16]

Since large amounts of used motor oil the enters aquatic ecosystem through water runoff, it is a contaminant of concern. As mentioned earlier, PAHs, heavy metals, additives, and antioxidants, trace levels of chlorinated solvents, and PCBs are the main compounds in used motor oil. Sharma et al.[17] studied sources of PAHs in street sediments. They found that in Sault Ste.Marie, Ontario, vehicles and coke ovens are the major contributors to PAHs. Latimer et al.[18] investigated sources of petroleum hydrocarbons in urban runoff.   They reported that hydrocarbons were mainly originated from used motor oil, with a small amount of fuel oil detected at industrial sites. Used mineral-based motor oil enters into the environment by several means. Usually oil enters the air through the exhaust system of the automotive engine. It may also enter the soil or water by leaking from cars onto streets or parking areas. The hydrocarbon compounds of the oil usually attach to the soil surfaces. Some hydrocarbons evaporate into the air quickly while others evaporate slowly. The rest of the hydrocarbon compounds enter surface water and adhere to settleable solids of the water and eventually settle to the bottom. Some metals in used oil dissolve in water and discharge directly into surface water and groundwater. Another way used oil enters the aquatic environment is through

improper disposal of it. Many car owners change the car motor oil by themselves instead of having it done professionally and they do not dispose of used oil properly.

Heavy metals are of particular concern in stormwater runoff because of their toxicity, widespread occurrence and since they are not chemically transformed easily, they remain in the system long enough to threaten the environment. The effects of these motor oil contaminants include harming environments and potentially affecting human health. Aromatics are considered one of the most toxic components of petroleum products, and are related with chronic and carcinogenic effects. Naphthalene is a compound found in motor oil that is associated with harmful effects on kidney, liver, heart, lung and nervous system.[19] Laboratory tests demonstrated that exposure to used motor oil produced an induction of EROD enzymes in the liver of fish. Used oil also has been shown to have some effects on amphibian reproduction.[19]

The presence of many metals in urban runoff is directly correlated with the volume of traffic in streets.[19]   They not only violate water quality standards but also create human health problems and are toxic to aquatic life.

Nutrient Contaminant

Nutrients (e.g., nitrogen, phosphate) are vital elements to aquatic ecosystems. When these nutrients are found at excessive levels, they can set off a whole chain of undesirable events in aquatic systems. Such nutrients lead to the eutrophication of water bodies. Eutrophication results from the increase of nutrients in aquatic systems, which in turn, create excessive algae and plant growth. When the nutrients are used up, the great

biomass of algae die and decompose. Various microbes that feed on dying plants also thrive and consume too much of dissolved oxygen in the water body leaving fish and many species of aquatic life to die.

The nutrient of interest in this research is phosphate (PO_4^{3-}). Phosphates are found in three forms: orthophosphate, polyphosphate and organic bound phosphate.[20] Each of them contains phosphorous in a different chemical formula. Orthophosphate are produced by natural processes and are found in sewage. Polyphosphates are found in synthetic substances like detergents whereas organic-bound phosphate are found in amino acids, peptides and proteins.[20]

Fertilizer applied to agriculture land, lawns, gardens, golf courses, and landscape areas are a huge source of phosphate in urban runoff.[21] When phosphates are applied to soils, they are quickly absorbed onto the soil particles and in case of soil erosion, these soil-bound phosphates contribute to pollution. Sometimes, fertilizer is over-spread or spilled onto streets, driveways and sideways and is washed with rain through storm drains into natural and manufactured bodies of water. Another source of phosphate in urban runoff is grass clippings and decaying tree leaves.[22] Research studies indicate that most of the phosphorous from urban areas that comes from grass clippings and falling leaves end up in street gutters, and eventually release their phosphorous on hard surfaces through the decaying process. When a storm event occurs, the urban runoff carries the phosphate away to bodies of water; this can generate a high concentration of bio-available phosphorous and can lead to eutrophication of bodies of water.

Pervious Concrete

Pervious concrete, also known as porous, gap-graded, or enhanced concrete, is a special kind of concrete that is created with reduced or no fines. It contains Portland cement, water, various admixtures and aggregate. However, the aggregate is single-sized; there is no sand and fines filling the voids between large particles. The single-sized aggregate particles leave open voids that give the material its porosity and permeability. Compared with regular concrete, its porosity is higher and has a total void space of between 15 and 35 percent, with an average of 20 percent.[23] The rates of water flow though permeable concrete from 0.2 cm/s to > 1 cm/s.[24]

Improper design, installation, and lack of maintenance can reduce the permeability of the pervious pavement system. Since the installation process of permeable concrete differs from conventional concrete, it requires trained and experienced construction contractors. Potential clogging of the pervious concrete pores is another concern. To prevent this, regular observation and a maintenance schedule should be followed. Any fine particles like sediment or grass clipping must be removed before they clog the filtration system.[24]

Pervious pavements have been demonstrated as effective solutions to an urban environmental problem by managing stormwater runoff from paved surfaces. When large amounts of land are used as impervious parking lots, driveways or transit areas, runoff has traditionally been controlled with the use of containment methods such as infiltration basins. This allows runoff to remain until it is absorbed into the ground.

Although this solution can reduce abrasion and flood, it is costly to implement. Pervious concrete omits the need for retention ponds and other runoff collection by providing drainage.

In an impervious pavement system, contaminants collect over time on road surfaces resulting in storm events with runoff containing high pollutant loads; these often drain directly into rivers, lakes and streams without any removal of contaminants, and disrupt natural aquatic life. Common urban pollutants can be treated by pervious concrete, which acts as a hydrocarbon trap.[25] Usually automobile corrosion and wear release cadmium and lead which can be captured in pervious pavement's voids and the minute sediment particle to which the ions are attached.[26] As a result, metals will not be flowing into streams and accumulating in the environment. Brattebo and Booth[27] in their six-year study period, found a similar result. The concentration of sample constituents in filtrated water were as follows: motor oil, 0.10 mg/L; copper, 1.0 µg/L; zinc, 5.0 µg/L whereas, in asphalt runoff the concentration of sample were motor oil, 0.164 mg/L; copper, 12.0 µg/L; and zinc 34.0 µg/L.[27]

While traditional, impervious surfaces deliver stormwater runoff swiftly to sewer systems and watercourses, pervious pavement tend to slow the discharge of the stormwater runoff to the final destination; trapping pollutants in the void spaces. The research has shown that permeable pavement has performed as an effective *in situ* aerobic bioreactor, where oil leaked from automobiles is broken down by naturally occurring microorganisms, leaving little but carbon dioxide and water.[28]

One environmental concern is global warming which has accompanied and

increased with urbanization. It refers to the fact that manufactured structures tend to

attract and retain heat at a higher rate, which increases the ground-level ozone production

by as much as 30%. Because of the black or gray surface, asphalt absorbs sunlight and

retains it for long periods of time.[29]   Pervious concrete, on the other hand has a light

color that reflects more ultraviolet rays from sun and absorbs less heat than asphalt. The

voids in pervious concrete allow air to circulate within, resulting in even lower heat

retention.

Fly Ash

Fly ash is the particulate residue generated in combustion of coal that rises with

the flue gases. It is a by-product of coal-fired power generating plants. Fly ash particles

are spherical in shape and their size range is between 0.5 µm and 100 µm. The American

Society for Testing and Materials, (ASTM) defines two classes of fly ash: class F fly ash

and class C fly ash.[30] Both classes contain pozzolans, material that can react with

calcium hydroxide in the presence of water and produce cementitious compounds. The

main difference between these classes is the quantity of calcium, silica, alumina, and iron

content in the ash. The chemical properties of the fly ash are mostly dependant on the

chemical content of the coal burned. F fly ash is produced from burning harder, older

anthracite or bituminous coal, whereas class C ash is normally produced from burning

younger lignite or subbituminous coal. Although both class C and class F fly ash have

pozzolanic properties, only class C has cementitious properties because of increasing concentration of calcium oxide from lignite coal.

In the past, fly ash was usually disposed in landfills. In recent decades, under growing pressure, more environmentally friendly controls have been implemented. The average yearly production of fly ash is about 61 million metric (MT) tons and 70% to 80% of fly ash is disposed of in landfils.[31] Typically 75% of the remaining fly ash is incorporated into concrete as a cement replacement.[31] This has economic benefits in addition to the added advantages of a safe disposal means for the fly ash. Since fly ash has a high concentration of both heavy metals and organic contaminants such as PAH's, some have expressed concerns about metal leaching when considering alternative uses for the ashes. Kim et al,[32] based on their experiment, showed that only arsenic, calcium and potassium are soluble in basic solutions, whereas, barium, cadmium, iron, lead, antimony, and selenium were insoluble. The common metals that are usually found in fly ash are aluminum, copper, potassium, magnesium, manganese; sodium, nickel and zinc all were only slightly soluble under acidic conditions. Since cement is basic, it is indicated that when fly ash is bound to cement, the potential leaching of heavy metals is not a threat.

Adding fly ash to cement can add to the concrete's final strength and increase its chemical resistance and durability. It can replace from 15-35 wt% all the way up to 70 wt% for large structures such as dams, walls, parking areas, etc. Because of spherical fly ash particles, it increases workability of cement while reducing water demand.

CHAPTER 2

MATERIALS AND METHODS

Five-Day Biochemical Oxygen Demand of Motor Oil

BOD_5 measurements involve diluting and seeding a test sample, storing the sample for a specific time and recording the initial and final dissolved oxygen (DO) values. In the BOD_5 experiments, at least three different dilutions and seedings are set per sample to cover the expected range of BOD_5. They are called dilution water blank and seed control. When less than a 300.0 mL sample is to be analyzed, sample volume is added to dilution water blank to bring the total sample volume to 300.0 mL. In addition, the pH of the dilution water should be maintained in a range suitable for bacterial growth (pH 6.5 to 7.5). Sulfuric acid or sodium hydroxide may need to be added to the dilution water to lower or raise the pH (Figure 1).

Meter

A HACH Portable Multiparameter meter with temperature probe conductor (SensIon156, Hach Company, Loveland, CO) was used to measure dissolved oxygen and temperature. A waterproof pH meter (Hach Company, Loveland, CO) was used to measure pH.

Figure 1. BOD$_5$ Analysis Setup: DO Meter, Probe And pH Meter

Dilution Water

      Dilution water is used to provide nutrients to microorganisms and to dilute samples to a measurable BOD_5 range. HACH BOD_5 nutrient buffer pillow (HACH CO, Loveland, CO) was added to 3.0 L of deionized water in the preparation of dilution water for all BOD_5 tests. Each pillow contains buffer and nutrients specified by the U.S. Environmental Protection Agency (USEPA) and American Public Health Association (APHA) in the Standard Methods for Examination of Water and Wastewater (1999).

      Dilution water in 3 L volumetric flask was shaken for about one to five minutes to dissolve the slurry and to saturate the water with oxygen. Dilution water had to be checked for quality control and was determined by its DO uptake. The initial and final (after 5 days $\pm$ 4 hours) DO tests of the dilution water were determined and recorded simultaneously with each batch of samples. The DO depletion of dilution water blank must not be more than 0.2 mg/L in 5-day incubation period.

Seed Control

      Polyseed solution was prepared by mixing one polyseed capsule (InterLab, Woodlands, TX) in 300 mL dilution water. The solution was aerated by stirring. The polyseed solution will remain active up to six hours with continual aeration. The varying concentrations of seed were prepared in the BOD_5 bottles using 10.0-mL, 15.0-mL, and 20.0-mL aliquots of seed and diluted to 300.0 mL with the dilution water to determine the correct volume of seed needed for the seed control. The DO uptake for the seed control should be between 0.6 and 1.0 mg-O_2/L.

Two BOD_5 bottles, one amber and one clear, with a 300 mL capacity, (Fisher Scienfic, Fair Lawn, NJ) were prepared for each seed concentration. The clear bottle was used to measure the initial temperature and the initial dissolved oxygen. The amber bottle was used to determine the temperature and final amount of oxygen present after 5 days incubation. The difference between the initial DO and final DO was calculated to determine the amount of seed needed to consume between 0.6 and 1.0 mg-O_2/L.

Glucose-Glutamic Acid Standard

The glucose-glutamic acid check was made using 6.0 mL of the glucose-glutamic acid solution (HACH CO, Loveland, CO) and 10.0 mL aliquots of seed, which was then added directly into the 300 mL BOD_5 bottles and filled with dilution water. Two bottles were prepared for the standard glucose-glutamic acid check and DO uptake was determined. The BOD_5 was calculated according to the standard method and its' accepted BOD_5 is 198 ± 30.5mg/L. The BOD_5 standard (glucose-glutamic acid test, GGC) is used to be a reference point for evaluation of dilution water quality, seed effectiveness, and analytical technique.

BOD Incubator

All BOD_5 bottles were placed in Max Q 4000 incubator (Thermo Scientific, USA) in the absence of light for five days at 20 ± 1° C. All bottles had glass stoppers that fitted into the necks of the bottles to form a water-seal and a cap to act as a vapor seal over the top of the bottles to ensure no evaporation of the water-seal.

BOD$_5$ Measurements of Motor Oil

The BOD$_5$ method (Standard Method 5210 B) was tested using a series of different mass of 10W-40 motor oil mixed with deionized water. Motor oil /deionized water samples were prepared by adding an analytically determined quantity of 10W-40 motor oil to 1000.0 mL of deionized water. Then the sample was stirred adequately on an electric stirring plate. The volume of motor oil sample was measured using a 100.0 mL graduated cylinder and then diluted with dilution water to meet the method criterion. The sample dilutions should result in a DO residual of at least 1.0 mg/L and there should be at least 2.0 mg/L DO change between the initial and the final reading to produce the most reliable result. The correct dilutions were determined experimentally. The motor oil samples were prepared in two BOD bottles. Each BOD bottle was filled with sample, control seed and dilution water. The amber bottle was incubated for five days at 20°C. The clear bottle was used to analyze the initial temperature and the amount of DO present. At the end of the incubation period, the final temperature and the amount of DO present was recorded.

BOD is calculated using the following equation;

$$BOD_5 = [(D_1 - D_2) - (B_1 - B_2)\ f] / P \qquad \rightarrow \qquad (1)$$

Where D_1 is the initial DO of the sample, D_2 is the final DO of the sample, B_1 is the initial DO of the seed control, B_2 is the final DO of the seed control, f is the ratio of seed in the sample to seed in the seed control, (% seed in D_1 / % seed in B_1) and P is the decimal volumetric fraction of sample used (mL of sample, Vs / 300 mL).

Chemical Oxygen Demand (COD) Measurements

Chemical Oxygen Demand (COD) was analyzed using HACH COD vials which were prefilled with necessary reagents in 16×100 mm culture tubes (HACH, Loveland, CO). The total volume of the premeasured reagents was 3.3 mL. They contained greater than 75% sulfuric acid, less than 2% mercuric sulfate, less than 1% silver sulfate, less than 1% potassium dichromate, and greater than 20% deionized water. For COD Test, a 2.0-mL aliquot was added to each COD vials. The vials were then tightly capped and inverted several times for complete mixing. They were wiped with a damp towel and placed in the HACH digestion block (model 45600 COD reactor) at 150±2°C for 2 hours to reflux (Figure 2). Before measuring the absorbance, the samples were allowed to cool at room temperature. The samples were inverted several times to loosen the solids that adhere to the COD vial. The samples were then allowed to settle and the exterior of the COD vials dried with Kimwipe® before measuring the absorbance. An analytical balance (model AB104, Mettler-Toledo, Highstown, NJ) was used for all measurements.
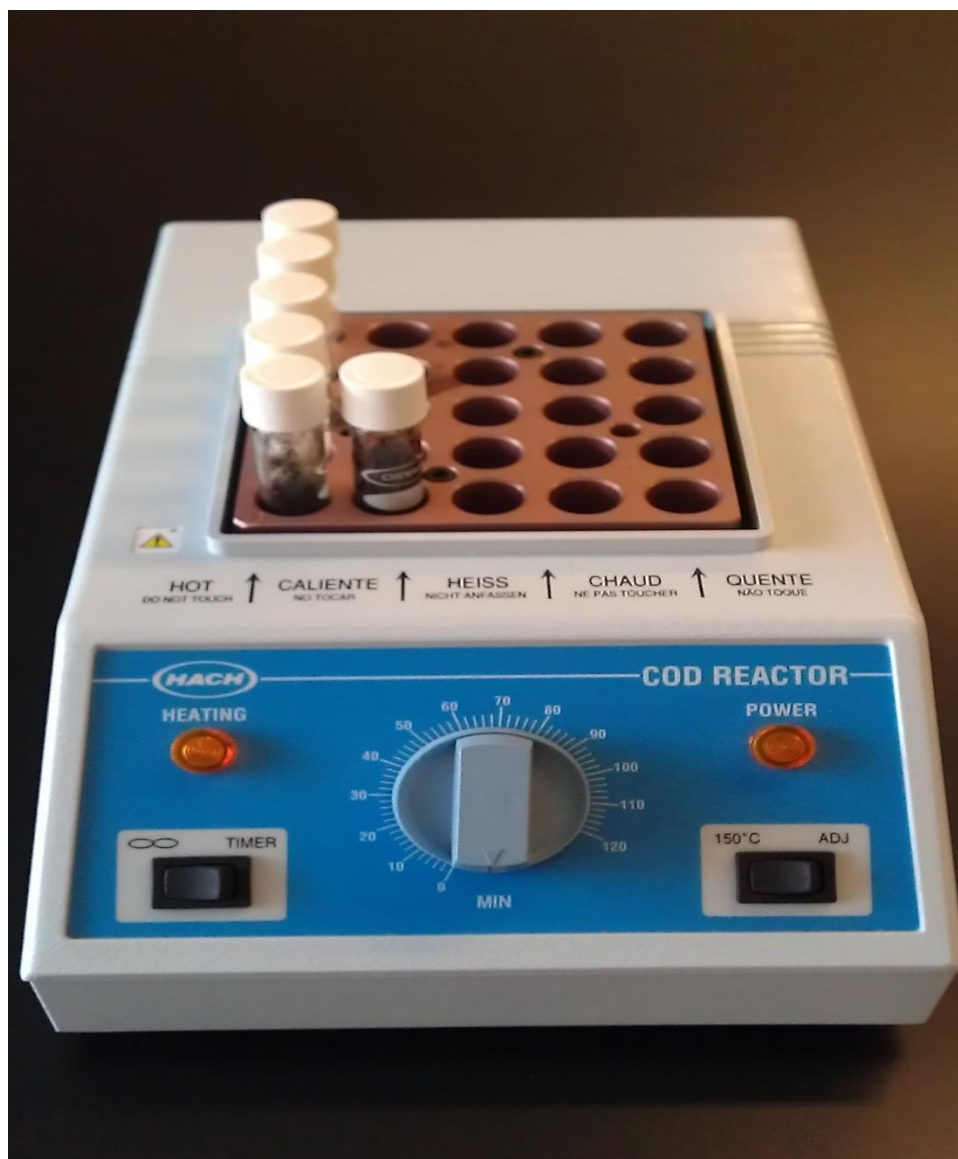
Figure 2. HACH COD Reactor

UV/Vis Spectrophotometer Analysis

HACH DR/2400 Spectrophotometer with wavelength range between 400 to 800 nm was used for all COD analysis and absorbance (Figure 3). The spectrometer was set at 620 nm and 100% transmittance for all COD mg/L measurements. Before each use, the spectrophotometer was calibrated with deionized water and a zero value was recorded from blank.

COD Calibration

The COD method was calibrated by measuring the COD of potassium hydrogen phthalate (KHP) standards. The standard curve was created for motor oil samples with high range COD vials (0-1500 mg/L) and used to convert the measured absorbance (620 nm) to COD in mg/L. The absorbance was plotted against COD concentration for each KHP concentration (certified A.C.S.grade, Fischer Scientific, Fairlawn, NJ). A KHP stock solution, with a COD of 900 mg/L, was prepared by dissolving 765 mg of crushed and dried (120°C, overnight) KHP in deionized water and brought to total volume to 1000 mL. All other standards were prepared from this solution with COD ranging from 18 mg/L to 900 mg/L in 100.0 mL volumetric flasks using class ''A" pipettes. The standards can be refrigerated for up to 3 months. Sample preservation is usually acidification using concentrated (18 M) sulfuric acid to a pH below two. They can be stored at 4° C for up to 28 days.
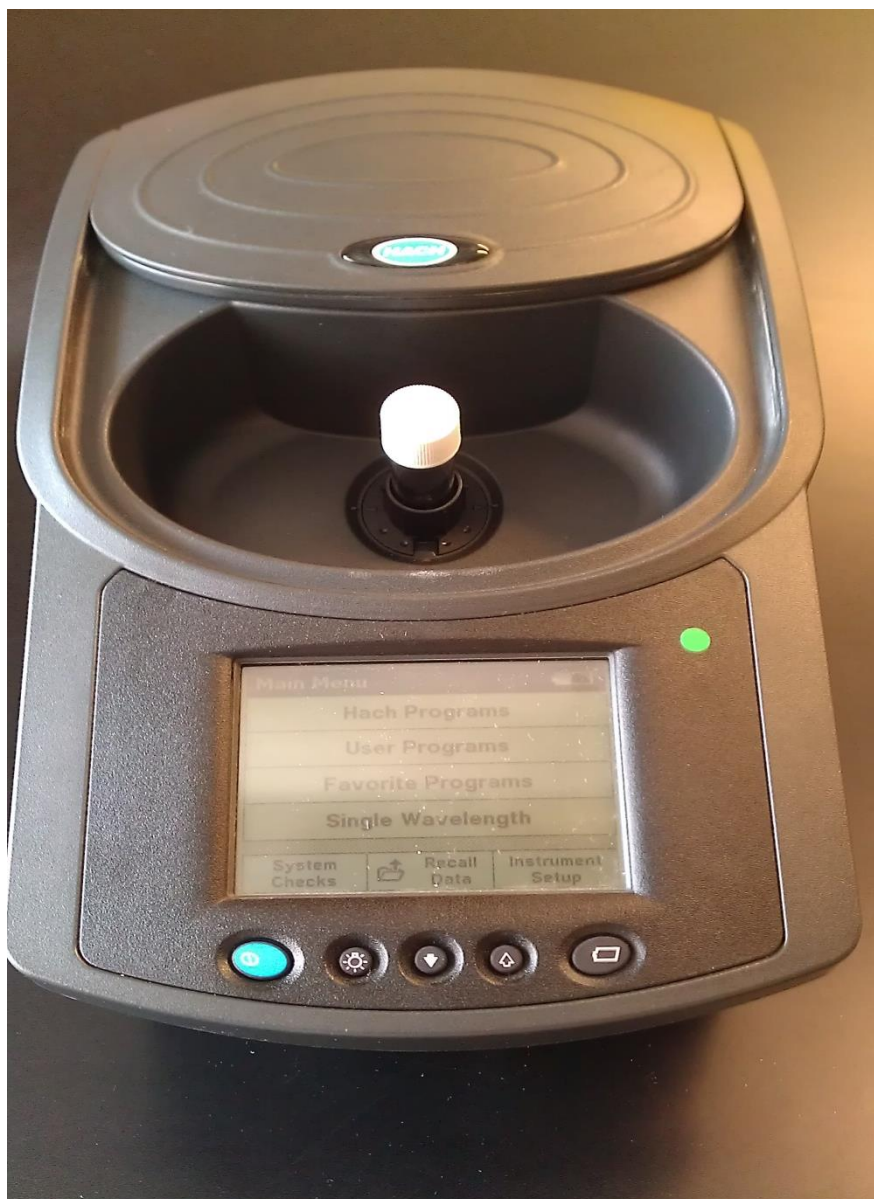
Figure 3. HACH DR/2400 Spectrometer

COD Measurements of Motor Oil

Motor oil /deionized water emulsions were used as samples. The samples were prepared by adding an analytically determined quantity of 10W-40 motor oil to 100.0 mL of deionized water. Then the sample was stirred adequately on an electric stirring plate. High range (0-1500 mg/L) COD vials were used for measurements. The COD was measured in triplicate for motor oil/deionized water samples. The KHP standard curve for this COD range was created using reagent blank and the following concentrations: 90, 135, 225, 450, 675 and 810 mg/L. An example trend line from KHP standards used to convert absorbance to COD is shown in Figure 4.
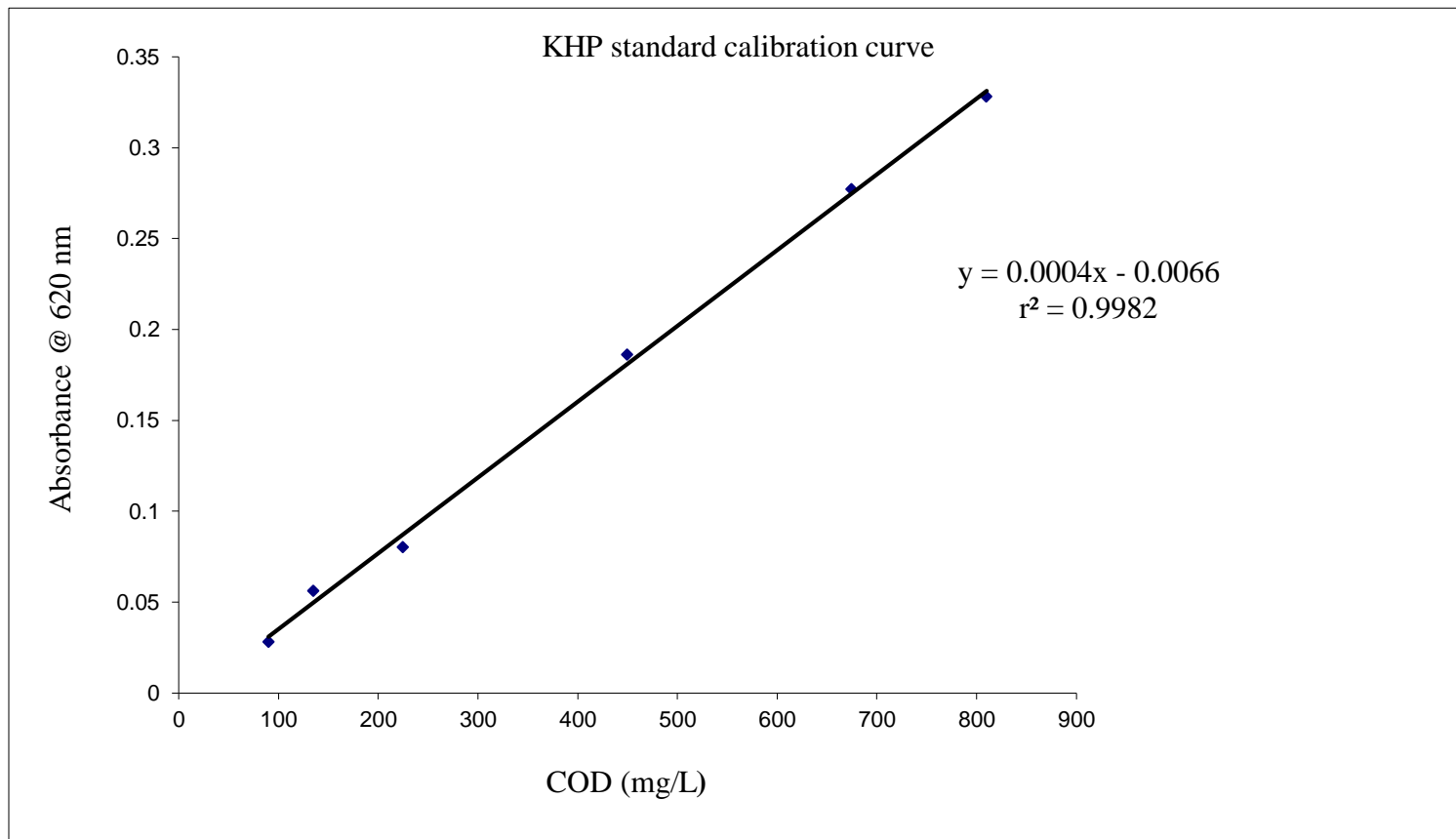
Figure 4. Absorbance vs. COD of KHP Standards.

Phosphate Retention Study

Five different types of fly ash amended pervious concrete cores were used for phosphate retention studies, provided by Dr. Heather Brown of Concrete Industry Management Department at Middle Tennessee State University. They were 0% fly ash, 20% fly ash low carbon content, 20% fly ash high carbon content, 30% fly ash low carbon content and 30% fly ash high carbon content. Beside the fly ash, Type I ordinary Portland cement was used along with water and limestone coarse aggregate to form these concrete cores. Each of them was pre-treated by running tap water over it in a sink about 10 minutes. The core was then left to dry in the lab before being used in experiments.

Rain Simulator

The rain simulator was made of a series of PVC pipes to disperse the water over the pervious concrete cores. It is connected to an Aqua Source® Showerhead with a 9.5 L/min maximum flow rate by a PVC pipe valve, which was used to control the flow rate. A wooden stand was constructed to hold a glass funnel which would hold the concrete core. A 1L glass beaker was placed underneath the glass funnel to collect the resulting solution passing through the pervious concrete core.

Phosphate Adsorption Method

All five types of fly ash amended-pervious concrete cores were used in the initial phosphate adsorption step. A 8L 750 ppm phosphate (potassium phosphate certified A.C.S.Fisher Scientific) sample solution was made in a 15 L plastic bucket using 8 liters deionized water with six grams of potassium phosphate. Then a pervious concrete core was slowly submerged in the phosphate sample solution. The set up was placed on a stir

plate and a magnetic stir bar was added to the bucket for constant movement. The bucket was held on that position for about 210 hours. After that period, 6 mL phosphate solution was taken from the bucket using a 0.45 μm filter and stored in a glass vial, in a refrigerator for 48 hours. The concrete core was removed from the bucket and let dry in the lab overnight. The core was then placed on the glass funnel and 3 1L deionized water washes were poured into the rain simulator allowing it to flow over the core slowly until the stream slowed to drops. Each sample collected was filtered via a 0.45 μm filter and 6.0 mL was transferred to a glass vial. They were stored in a refrigerator until analyzed by IC within 48 hours.

Phosphate Calibration Curve

A 100 ppm phosphate (potassium phosphate, certified A.C.S. Fisher Scientific) standard stock solution was made. Six calibration standards were made from the 100 ppm stock solution; 2, 5, 10, 15 20, 30, and 40 ppm. A calibration curve was created by plotting the calibration standards with area on the X axis and concentration on the Y axis. The concentration of phosphate in each sample was calculated by comparing the area of each peak to the calibration curve.

Ion Chromatography (IC)

Ion Chromatography (Dionex ICS-2000) was used to determine the phosphate concentration. IC measures concentration of ionic species by separating them based on their interaction with a resin. The eluent for anion separation used with the Dionex IC system is a hydroxide solution with a concentration of 25 mM. In this research potassium

hydroxide (KOH) was chosen as a electrolyte at a concentration of 45 mM for the first

16.200 min and 20 mM for the remaining 3.30 min to get more prominent phosphate

peak. The flow rate was set at 1.00 mL/min. Although 1.00 mL samples were manually

injected with a 3.00 mL plastic syringe, only 25 μL of sample was analyzed, the rest was

removed. The instrument detection limit for phosphate was previously determined to be

0.731 ppm.[33]

CHAPTER 3

RESULTS AND DISCUSSIONS

Water quality is a term used to define the condition or environmental health of a water body.[34] It is described in the Clean Water Act as the standard of purity that is necessary for the preservation of fish, shellfish and wildlife populations in the aquatic environment, and for recreational uses in and on the water. Two parameters often monitored to measure water quality in urban runoff are Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD).[35] Both the BOD_5 and the COD tests are a measure of relative oxygen-depletion effect of a wastewater contaminant, and have been widely accepted as measures of pollution effect. The COD test uses strong chemicals to oxidize organic matter, while the BOD_5 test relies on microorganisms to oxidize readily available organic matter.[36] The COD test is not a direct substitute for the BOD_5 test and it always gives a higher concentration reading than BOD_5 for a particular sample. However, a ratio can be correlated between the two tests. Parallel BOD_5 and COD testing are found beneficial because the COD test can be used in aiming a specific BOD_5 range, thus minimizing the necessity of multiple BOD_5 dilutions.

The BOD_5/COD ratio are also used as a measurement of biodegradability, where a value of zero reflects nonbiodegradability and an increase in the ratio indicates biodegradability improvement.[37] Lower BOD_5/COD ratio (< 0.1) reflects the resistance to conventional biological treatment.[37] Gys Mtui [38] stated that the ratio of BOD_5/COD between 0.4-0.5 is considered as an indicator of good biodegradability.

To determine the BOD_5 and COD of motor oil samples, several tests were conducted to develop a method. The results are summarized and discussed below.

BOD_5 Results

There is no absolute BOD_5 value of a sample. It is based on the parameters of the test method, and not on any "true" BOD_5 value.[39] Below are the requirements that must be met for a valid BOD method: Dilution, Dissolved Oxygen, Seed control, and Glucose-Glutamic Acid standard. A series of experiments for each requirement were conducted, and the results are shown and discussed as below.

BOD_5 Method Results: Dilution and Dissolved Oxygen

The BOD_5 method involves diluting and seeding a test sample, storing and recording the initial and final dissolved oxygen (DO). Three different dilutions were set in the preliminary test to choose the appropriate dilution for BOD_5- 0%, 33% and 50% dilutions. According to the standard method, the DO change between the initial and the final readings should be at least 2.0 mg/L.[9] The data for determining the dilutions is shown in Table 1. High level of DO suggests the lack of oxidizable materials in samples,

and low level of DO indicates the influence of oxidizable materials. Significant oxygen depletion suggests that sufficient biodegradation that may have occurred. The results from 5-day BOD experiment showed insufficient oxygen depletion in all 12-ppm motor oil samples, indicating inadequate biodegradation. Continued concerns about the low oxygen depletion by the microbial population led to a change in seed preparation procedure. One suggested method to improve the oxygen depletion level is by reducing the polyseed rehydration water by 200 mLs.[40] Therefore, the polyseed was mixed in 300 mL BOD water instead of 500 mL BOD water. The data presented in Table 2 represents reduced polyseed rehydration water improving the DO depletion and BOD_5 values of motor oil samples.

Table 1. BOD$_5$ Results for Preliminary Method Development of Motor Oil Samples

Sample (mg/L)	Dilution (%)	Seed Vol (mL)	Sample Vol(mL)	DO initial (mg/L)	DO final (mg/L)	Delta DO (mg/L)	Avg Delta DO (mg/L)	BOD$_5$ (mg/L)
12 ppm	0%	10.0	290	7.33	8.05	-0.72	-0.84	--
12 ppm	0%	10.0	290	7.23	8.38	-1.15		--
12 ppm	0%	10.0	290	7.45	8.09	-0.64		--
12 ppm	33%	10.0	194	7.23	7.12	0.11	0.32	--
12 ppm	33%	10.0	194	8.04	8.00	0.04		--
12 ppm	33%	10.0	194	7.92	7.12	0.80		--
12 ppm	50%	10.0	145	7.59	8.69	-1.10	-0.20	--
12 ppm	50%	10.0	145	7.85	9.16	-1.31		--
12 ppm	50%	10.0	145	7.51	8.71	-1.20		--
12 ppm	0%	20.0	280	7.87	7.30	0.57	0.017	--
12 ppm	0%	20.0	280	7.91	7.50	-0.41		--
12 ppm	0%	20.0	280	8.01	7.90	-0.11		--
12 ppm	33%	20.0	187	7.52	8.36	-0.84	-0.67	--
12 ppm	33%	20.0	187	7.78	8.40	-0.62		--
12 ppm	33%	20.0	187	7.68	8.22	-0.54		--
12 ppm	50%	20.0	135	8.04	7.90	0.14	-0.11	--
12 ppm	50%	20.0	135	7.73	8.34	-0.61		--
12 ppm	50%	20.0	135	7.98	7.83	0.15		--
SeedCtrl	--	10.0	0	8.10	7.45	0.65	0.41	--
SeedCtrl	--	10.0	0	8.20	8.12	0.08		--
SeedCtrl	--	10.0	0	7.94	7.44	0.50		--
SeedCtrl	--	20.0	0	8.45	6.97	1.48	1.58	--
SeedCtrl	--	20.0	0	8.37	6.80	1.57		--
SeedCtrl	--	20.0	0	8.40	6.70	1.70		--
BWblnk	--	0	0	8.36	8.16	0.20	0.23	--
BWblnk	--	0	0	7.45	7.36	0.09		--
BWblnk	--	0	0	9.00	8.61	0.39		--
GGCStd	--	10.0	6	8.04	3.20	4.84	3.73	242
GGCStd	--	10.0	6	7.07	4.73	2.34		117
GGCStd	--	10.0	6	7.80	3.79	4.01		201

BOD$_5$ Method Results: Seed Control, and GGA Standard

To determine the amount of seed needed for the seed control, several BOD$_5$ tests were run with 10.0 mL, 15.0 mL and 20.0 mL of seed and the oxygen uptake was determined in each case. According to the Standard Method, the oxygen depletion should be between 0.6 to 1.0 mg/L. The average DO depletion for the 10.0 mL seed control was 0.94 mg/L, which was within the expected range. However, seed controls of 15.0 mL and 20.0 mL exhibited an average of 1.2 mg/L and 1.58 mg/L DO depletion respectively. These values were higher than the recommended range (Table 2). This indicates that 10.0 mL of seed is sufficient for BOD$_5$ analysis.

After reducing the rehydration water, two different sample dilutions were run to select the correct dilution by comparing their DO results. The delta DO values obtained by 50% diluted motor-oil samples were higher than 0% diluted samples. The 50% diluted samples exhibited the desirable results, showing at least 2 mg/L DO reduction and having a minimum DO residual of 1 mg/L (Table 2). The BOD$_5$ values obtained by 50% diluted motor-oil samples were higher than 0% diluted samples. The calculated BOD$_5$ values obtained by the 50% diluted motor-oil samples with 10.0 mL seed produced 1.41 $\pm$ 0.76 mg/L and with 15.0 mL seed produced 5.02 $\pm$ 0.82 mg/L. These numbers were higher than those calculated for 0% diluted samples with 10.0 ml seed, at 0.20 $\pm$ 0.88 mg/L and 15.0 mL seed, at 1.29 $\pm$ 0.51 mg/L (Table 2). The hypothesis is that BOD$_5$ values increased with the dilution because less diluted samples were toxic to the microorganisms. Alvares et al.[37] experienced the same fact while working on the partial

oxidation of textile azo dyes by ozone. In the BOD_5 tests, they used three different dilutions for each sample. They found that toxic samples with a high dilution factor gave a high BOD_5 result due to diluted toxicity effects, while less diluted samples gave lower BOD_5 results because of a more intensified toxicity effect.

The GGC standard is used as a reference point for evaluation of dilution water quality, seed effectiveness, and analytical technique. A test was set-up to choose the amount of seed needed for GGC standard. For this intention, 10.0 mL and 15.0 mL of seed with 6.00 mL of stock solution and BOD water were added to BOD bottles. The resulting average BOD_5 exhibited by these standards was 176 mg/L and 177 mg/L by 10.0 mL and 15.0 mL of seed added, respectively (Table 2). Both values were within recommended range (198 mg/L$\pm$ 30).[9]

Table 2. BOD$_5$ Results for Method Development of Motor Oil Samples.

Sample Conc. (mg/L)	Dilution (%)	Seed Volume (mL)	Sample Volume (mL)	DO initial (mg/L)	DO final (mg/L)	Delta DO (mg/L)	BOD$_5$ (mg/L)	Avg BOD$_5$ (mg/L)	BOD$_5$ STDEV
12 ppm	0%	10.0	290	8.50	7.92	0.58	-0.37	0.20	
12 ppm	0%	10.0	290	8.51	6.40	2.11	1.21		0.88
12 ppm	0%	10.0	290	7.94	7.24	0.70	-0.25		
12 ppm	0%	15.0	285	8.53	6.65	1.88	0.72	1.29	
12 ppm	0%	15.0	285	8.48	5.65	2.83	1.72		0.51
12 ppm	0%	15.0	285	8.41	5.85	2.56	1.43		
12 ppm	50%	10.0	145	7.70	6.29	1.41	0.97	1.41	
12 ppm	50%	10.0	145	7.77	6.37	1.40	0.95		0.77
12 ppm	50%	10.0	145	8.56	6.51	2.05	2.30		
12 ppm	50%	15.0	143	8.88	5.65	3.23	4.27	5.02	
12 ppm	50%	15.0	143	8.83	4.83	4.00	5.90		0.82
12 ppm	50%	15.0	143	8.39	4.86	3.53	4.90		
GGCStd	--	10.0	6.00	8.07	3.74	4.33	169	176	
GGCStd	--	10.0	6.00	8.26	4.09	4.17	161		20.0
GGCStd	--	10.0	6.00	7.95	3.96	3.99	199		
GGCStd	--	15.0	6.00	8.57	3.58	4.99	189	177	
GGCStd	--	15.0	6.00	7.99	4.15	3.84	132		40.4
GGCStd	--	15.0	6.00	7.90	2.50	5.40	210		

Sample Conc. (mg/L)	Dilution (%)	Seed Volume (mL)	Sample Volume (mL)	DO initial (mg/L)	DO final (mg/L)	Delta DO (mg/L)	BOD$_5$ (mg/L)	Avg BOD$_5$ (mg/L)	BOD$_5$ STDEV
SeedCtrl	--	10.0	0	8.37	7.85	0.52	--	--	
SeedCtrl	--	10.0	0	8.74	7.69	1.05	--	--	
SeedCtrl	--	10.0	0	7.74	6.49	1.25	--	--	
SeedCtrl	--	15.0	0	7.91	6.92	0.99	--	--	
SeedCtrl	--	15.0	0	8.03	6.80	1.23	--	--	
SeedCtrl	--	15.0	0	7.61	6.23	1.38	--	--	
BWblnk	--	0	0	8.04	7.80	0.24	--	--	
BWblnk	--	0	0	8.39	8.23	0.16	--	--	
BWblnk	--	0	0	8.14	7.90	0.24	--	--	

The results of all four motor oil samples for BOD_5 are summarized in Table 3. Each

sample was replicated three times. Samples of 18 ppm had an average BOD_5 of 3.11 ±

0.59 mg/L, and 12 ppm samples had an average BOD_5 of 4.10 ± 0.19 mg/L. Motor oil

samples of 8 ppm had an average BOD_5 of 5.81 ± 0.41 mg/L, and 4 ppm motor oil

samples had the highest average BOD_5 value of 8.79 ± 0.59 mg/L. These results indicate

that the BOD_5 values increased as the motor oil concentrations decreased. The results

indicate that the biodegradation of the motor oil samples by microorganisms is successful

at lower concentration and that higher concentrations are toxic to the microorganisms.

The GGC standard samples with 10.0 mL seed had an average BOD_5 of 201

± 3.33 mg/L and the average DO of BOD-water blank was 0.12mg/L (Table 3).

Table 3. BOD$_5$ Results of Four Different Motor Oil Samples.

Sample (mg/L)	Dilution (%)	Seed Volume (mL)	Sample Volume (mL)	DO initial (mg/L)	DO final (mg/L)	Delta DO (mg/L)	BOD$_5$ (mg/L)	Avg BOD$_5$ (mg/L)	BOD$_5$ STDEV
18 ppm	50%	10.0	145	8.71	6.20	2.51	3.25		
18 ppm	50%	10.0	145	8.53	6.40	2.13	2.46	3.11	0.59
18 ppm	50%	10.0	145	8.90	6.21	2.69	3.62		
12 ppm	50%	10.0	145	8.17	5.15	3.02	4.31		
12 ppm	50%	10.0	145	8.16	5.30	2.86	3.98	4.10	0.19
12 ppm	50%	10.0	145	8.10	5.23	2.87	4.00		
8 ppm	50%	10.0	145	8.46	4.59	3.87	6.07		
8 ppm	50%	10.0	145	8.02	4.50	3.52	5.34	5.81	0.41
8 ppm	50%	10.0	145	8.75	4.90	3.85	6.02		
4 ppm	50%	10.0	145	8.11	2.81	5.30	9.03		
4 ppm	50%	10.0	145	8.20	2.89	5.31	9.05	8.70	0.59
4 ppm	50%	10.0	145	7.90	3.10	4.81	8.01		
BWblnk	--	0	0	8.64	8.01	0.13	--	--	--
BWblnk	--	0	0	8.59	8.52	0.09	--	--	--
BWblnk	--	0	0	8.47	8.32	0.15	--	--	--
GGCstd	--	10.0	6.00	7.70	3.69	4.01	200		
GGCstd	--	10.0	6.00	7.95	3.99	3.96	198	201	3.33
GGCstd	--	10.0	6.00	8.16	4.07	4.09	205		

Preliminary COD Method Testing

To determine Chemical Oxygen Demand of motor oil/deionized water mixture, several tests were performed. The preparation of the motor oil/ deionized water mixture samples was somewhat difficult because of their "immiscible-nature". First, the sample was prepared by adding an analytical determined quantity of oil to a specific amount of deionized water and mixed for about 15 minutes on an electrical stirring plate.

The calibration curve with a good linearity with a correlation coefficient, r^2, of 0.99 for the KHP standards was used to convert absorbance to COD. Figure 1 represents the calibration curve for KHP standards.

COD results from the preliminary test were analyzed to determine the applicability of the method for homogenizing the samples (Table 4). The mass of the motor oil was not consistent with COD results. Analyzing the COD results, it was clear that COD values were not corresponding with motor oil mass. It is expected that COD values will increase linearly as the mass of motor oil increases. However, COD values did not always exhibit a linear correlation with motor oil mass. For example, 59.9 mg motor-oil samples showed an average COD of 108 mg/L, and 65.5 mg motor-oil samples gave an average COD of 98.2 mg/L. Also all the COD values were lower than the ThOD of motor oil values (Figure 5). ThOD value of a given material is the calculated maximum amount of oxygen needed to completely oxidize any organic material to CO_2 and H_2O. One possible explanation for inconsistent COD values is that samples were not homogenized well.

Theoretical Calculation of Oxygen Demand (ThOD)

The following chemical equation expresses the relationship between any organic compound and the amount of oxygen required for the conversion of this compound.

$$C_nH_aO_bN_c + (n + a/4 - b/2 - 3/4c)\ O_2 \rightarrow nCO_2 + (a/2 - 3/2c)\ H_2O + cNH_3 \qquad (2)$$

Using this equation, the ThOD of motor oil is found to be approximately 3.4 mgO_2 per mg of motor oil. Motor oils consist of a base lubricating oil (a complex mixture of hydrocarbons, 80% to 90% by volume), various additives and chemicals. Therefore, there is not any exact chemical formula of motor oil. It is a mixture of compounds with a general formula around $(C_{40}\ H_{82})$.[15]

The stoichiometric relation for the ThOD of motor oil is given as follows-

Chemical Formula of motor oil $(C_{40}\ H_{82})$ Molecular weight: 56,2000 mg/mol

$C_{40}\ H_{82} + 60.5\ O_2 \rightarrow 40\ CO_2 + 41\ H_2O$
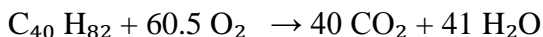
(60.5 mol O_2/mol motor oil) * (32,000 mg O_2 /mol O_2) = 193,600 mg O_2/ mol oil.

(193,600 mg of O_2/ mol motor oil) / (56,2000 mg motor oil / mol motor oil)

3.44 mg O_2/mg motor oil.

ThOD = 3.4 mg O_2/ mg motor oil.

Table 4. Preliminary COD Results.

Sample (mg/L)	COD(mg/L)	Ave COD (mg/L)	ThOD Value (mgO$_2$)	COD STDEV
7.90 ppm 7.90 ppm 7.90 ppm	9.30 9.40 9.70	9.46	26.9	0.21
19.2 ppm 19.2 ppm 19.2 ppm	18.3 13.6 20.3	17.4	65.3	3.44
32.9 ppm 32.9 ppm 32.9 ppm	28.7 38.3 29.0	32.0	112	5.40
35.7 ppm 35.7 ppm 35.7 ppm	65.1 43.8 34.7	47.9	122	15.6
42.5 ppm 42.5 ppm 42.5 ppm	67.5 36.6 75.7	59.9	145	20.6
49.1 ppm 49.1 ppm 49.1 ppm	83.8 79.8 81.3	81.6	167	2.02
54.9 ppm 54.9 ppm 54.9 ppm	118.9 OVERRANGE 96.8	108	187	15.6
65.5 ppm 65.5 ppm 65.5 ppm	89.8 82.0 123	98.2	223	2.20

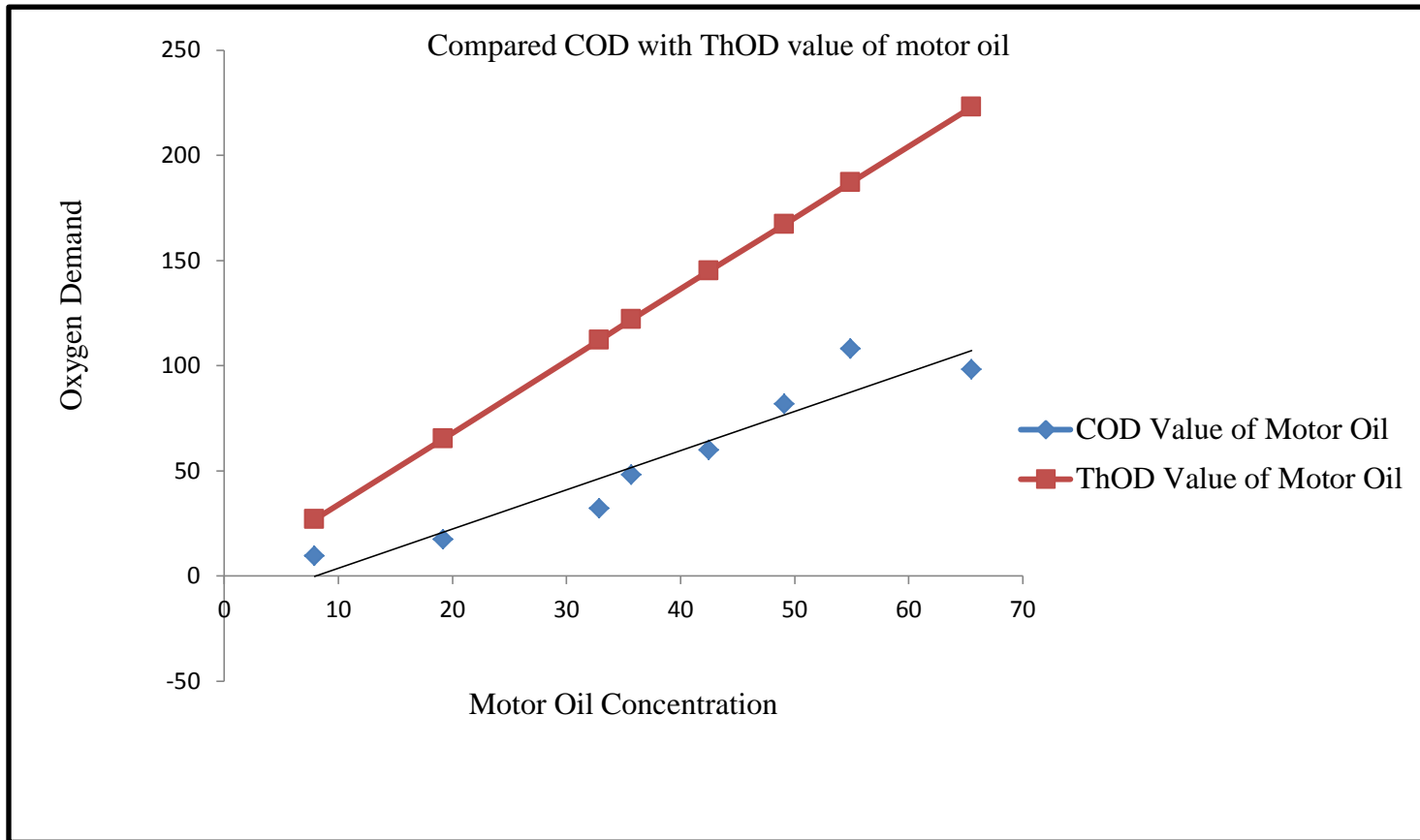Calculated Theoretical Oxygen Demand of Motor Oil is Approximately 3.4 mg O$_2$/ mg of motor oil

Figure 5. Comparison Between COD Value and ThOD Value of Motor Oil.

COD Measurement with Increased Time and New Homogenize- Methods

Because of the 'immiscible-nature' of the samples, in the preliminary experiments, COD values were not correlated well with motor oil mass (Table 4). Therefore, the effect of sample homogeneity and its corresponding COD value was tested. Samples were homogenized in three different ways.

Each method was replicated six times. A mass of 39.4 mg of motor oil, the median mass determined from the Table 4, was used to prepare the samples.

(A) Homogenize the samples for 3 hours on stirring plate.

(B) Homogenize the sample for 1 hour on stirring plate.

(C) Homogenize the sample for 40 minutes with vortex shaker.

The COD results obtained by using three different methods were compared with ThOD Values (Theoretical Oxygen Demand) of motor-oil and examined their correlation with mass (Table 5 and Figure 6). Among the three methods, the three hours-homogenize method produced more precise results and more accurate when compared to ThOD values (Table 5). Three hours homogenize-method exhibited an average COD of 99.6 ± 9.06 mg/L, which gave the best agreement with the ThOD value of 133 mg/L and had the lowest experimental error of 24.8%. Two hours homogenize-method produced an average COD of 24.1 ± 10.3 mg/L with 81.8% error, while forty minutes-homogenize-method, using vortex shaker produced only an average COD of 5.90 ± 2.54 mg/L with 95.6% error.

Table 5. Comparison of the Three COD Methods

Method ID	Sample Conc (mg/L)	COD (mg/L)	Avg. COD (mg/L)	ThOD Value (mgO$_2$)	% Error	COD STDEV
A	39 ppm	85.2				
	39 ppm	103				
	39 ppm	94.4				
	39 ppm	102	99.7	133	24.8	9.06
	39 ppm	112				
	39 ppm	101				
B	39 ppm	4.20				
	39 ppm	17.4				
	39 ppm	18.9				
	39 ppm	21.4	24.1	133	81.8	10.3
	39 ppm	40.9				
	39 ppm	41.7				
C	39 ppm	7.40				
	39 ppm	10.2				
	39 ppm	3.40				
	39 ppm	3.90	5.90	133	95.6	2.54
	39 ppm	5.70				
	39 ppm	4.70				

ThOD = Calculated Theoretical Oxygen Demand of Motor Oil is found approximately 3.4 mg O$_2$/ mg oil
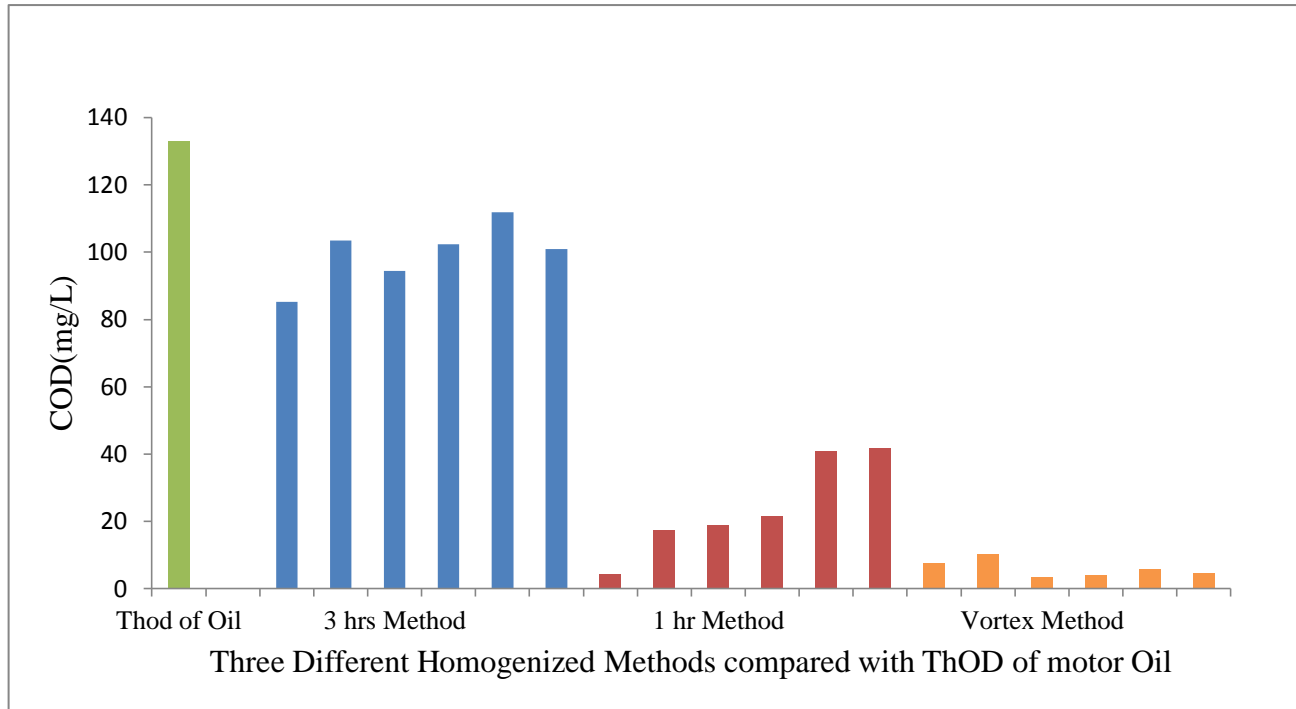
Figure 6. COD Results of Three Different Homogenization Methods.

COD of Motor Oil Samples

   Since the three-hour homogenized method produced encouraging results, another

COD test was run to confirm the reliability of this method. Six motor oil samples of

different concentration were tested this time. Each sample was replicated three times.

The measured COD values of motor-oil samples are listed in Table 6.   COD calculations

were made based on the calibration curve from KHP (Figure 1). The COD values were

all correlated with motor oil mass. A graph of motor oil concentration versus the

chemical oxygen demand of the samples was plotted to determine their correlation

(Figure 7). The coefficient of determination (r^2) is 0.83.

Table 6. COD Analysis of Motor Oil Samples

| Sample (mg/L)	COD (mg/L)	Avg COD (mg/L)	COD STDEV
4.2 ppm 4.2 ppm 4.2 ppm	10.2 13.2 7.15	10.2	3.00
8.0 ppm 8.0 ppm 8.0 ppm	19.3 18.6 20.6	19.5	1.01
12.7 ppm 12.7 ppm 12.7 ppm	22.2 27.9 22.7	24.2	3.71
18.0 ppm 18.0 ppm 18.0 ppm	24.2 29.0 25.4	26.2	2.49
20.0 ppm 20.0 ppm 20.0 ppm	25.4 24.7 31.2	27.1	3.55
26.0 ppm 26.0 ppm 26.0 ppm	36.2 36.7 31.9	34.9	2.64
35.0 ppm 35.0 ppm 35.0 ppm	43.2 47.4 45.1	45.3	2.12
39.0 ppm 39.0 ppm 39.0 ppm	86.7 92.7 79.2	86.2	6.76
51.0 ppm 51.0 ppm 51.0 ppm	141 130 153	141.3	11.76
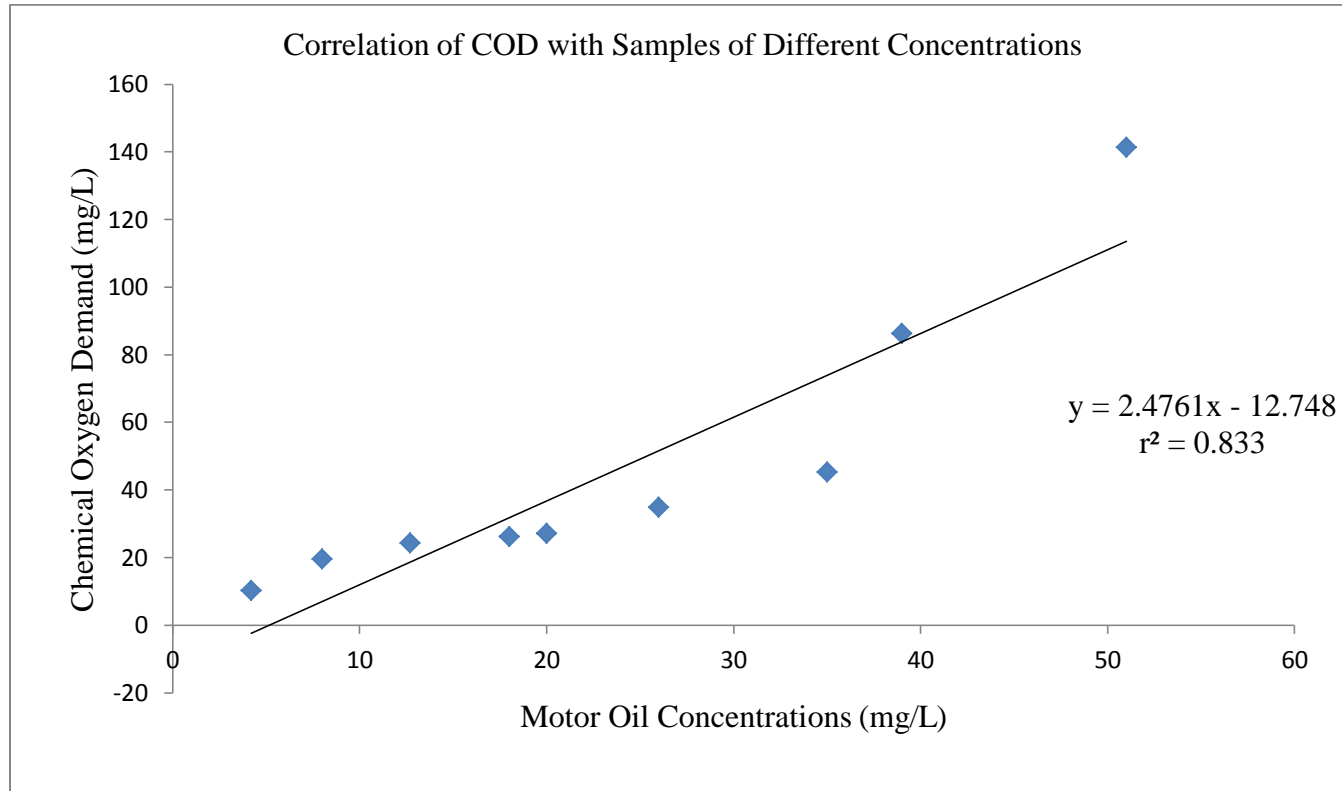
Figure 7. Correlation of COD with Motor Oil Samples of Different Concentrations.

Final Incorporation of BOD$_5$, COD and Motor Oil Samples

A comprehensive incorporation of all BOD$_5$, COD values and calculations are given in Table 7 and Figures 8, 9 and 10. The BOD$_5$ values used in the final analysis and calculation of biodegradability were taken from the final BOD$_5$ analysis run (Table 3). The COD values used for final incorporation were taken from Table 6.

Table 7. BOD$_5$, COD Results and Calculated BOD$_5$/COD Ratios for Motor Oil Samples.

Sample (mg/L)	Avg BOD$_5$ (mg/L)	BOD$_5$ STDEV (mg/L)	95% Confidence limit	Avg COD (mg/L)	COD STDEV (mg/L)	95% Confidence limit	BOD$_5$/ COD
4.0 ppm	8.70	0.59	0.67	10.2	3.0	3.39	0.853
8.0 ppm	5.81	0.41	0.46	19.5	1.01	1.14	0.298
12.0 ppm	4.10	0.19	0.21	24.2	3.71	3.53	0.169
18.0 ppm	3.11	0.59	0.67	26.2	2.49	2.81	0.119

Samples with low oil concentration provided higher BOD$_5$ results than higher concentration motor oil samples (Table 7 and Figure 8). Therefore, the BOD$_5$ values increase as the sample concentrations decrease. Possibly, high concentrated, less diluted motor oil sample is too toxic for microorganisms to degrade. Another explanation is that bacteria need more than five days to acclimate to higher concentration samples.

Biodegradability of hydrocarbons depends on type and size of the hydrocarbon molecule. In general, alkanes with intermediate chain length (C_{10}-C_{24}) often degrade

more rapidly than the long chain alkanes.[41] Usually, crude oil and petroleum made up of

complex, long chain hydrocarbons, alkanes ($> C_{24}$), are increasingly resistant to

microbial degradation.[41]   Ijaha et al.[42] who conducted studies on light crude oil, stated

that since the biodegradation of hydrocarbons is hindered by their limited bioavailability,

the crude oil is hardly degraded by microorganisms in nature.   Complex hydrocarbons

like crude oil and/or petroleum requires the cooperation of multiple species, because

individual microorganisms can biodegrade only a limited range of hydrocarbon

substrates, while mixed cultures with overall broad enzymatic capacities can increase the

rate of biodegradation. This phenomenon showed that each strain or genera have its role

in hydrocarbon transformation processes. Rambeloarisoa et al.[43] evaluated the

biodegradation of used motor oil by a mixed culture, containing 8 strains of 6 genera.

Their results showed that the mixed cultures degraded used motor oil more effectively.

Although, only 5 strains among them could grow as pure cultures on different

hydrocarbons; when the other 3 strains were removed from the culture the effectiveness

of the mixed culture was remarkably decreased. These results suggest that each strain or

genera in a microbial community has a significant role and may be dependent on the

presence of the other species for surviving. It is possible that one strain or genera can

remove the toxic metabolites of the other strain or genera, or degrade some compounds

better than others.[43]

The COD values are usually higher than the BOD_5 results because COD oxidizes

both inorganic and organic compounds that are not degraded by microorganisms within

5 days (Table 7).   In general, oxidation efficiency depends on the condition of the microorganism, which is susceptible to pH, temperature, and other variables in the samples. On the contrary, COD test uses a strong chemical oxidizing agent that oxidizes materials regardless of water conditions. A graph of COD versus the motor oil concentration was plotted to determine their correlation (Figure 9). The coefficient of determination (r^2) is 0.85.

The BOD_5/COD ratio is used to measure the biodegradability improvement. It is suggested that the BOD_5/COD quotient of 0.4 to 0.5 is considered an indicator of biodegradability.[38]   The BOD_5/COD ratios obtained in this study were 0.1 to 0.9 (Table7).   The lowest concentration, 4ppm motor oil sample had the highest BOD_5/COD value of 0.853. It simply indicates that the lower concentration sample has higher rate of biodegradability due to its less toxicity. A graph of BOD_5/COD versus the motor oil concentration was plotted to determine their correlation (Figure 10). The coefficient of determination (r^2) is 0.73.
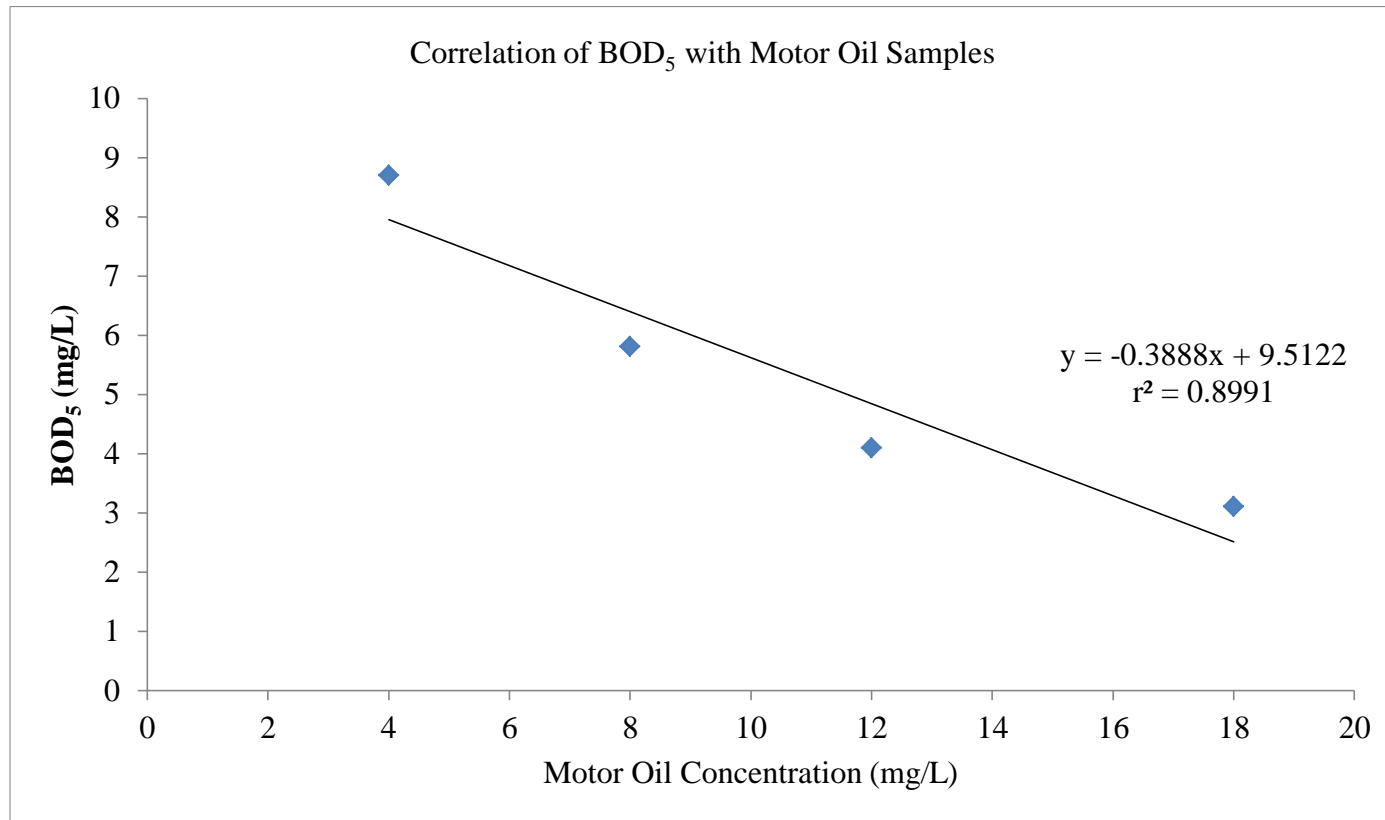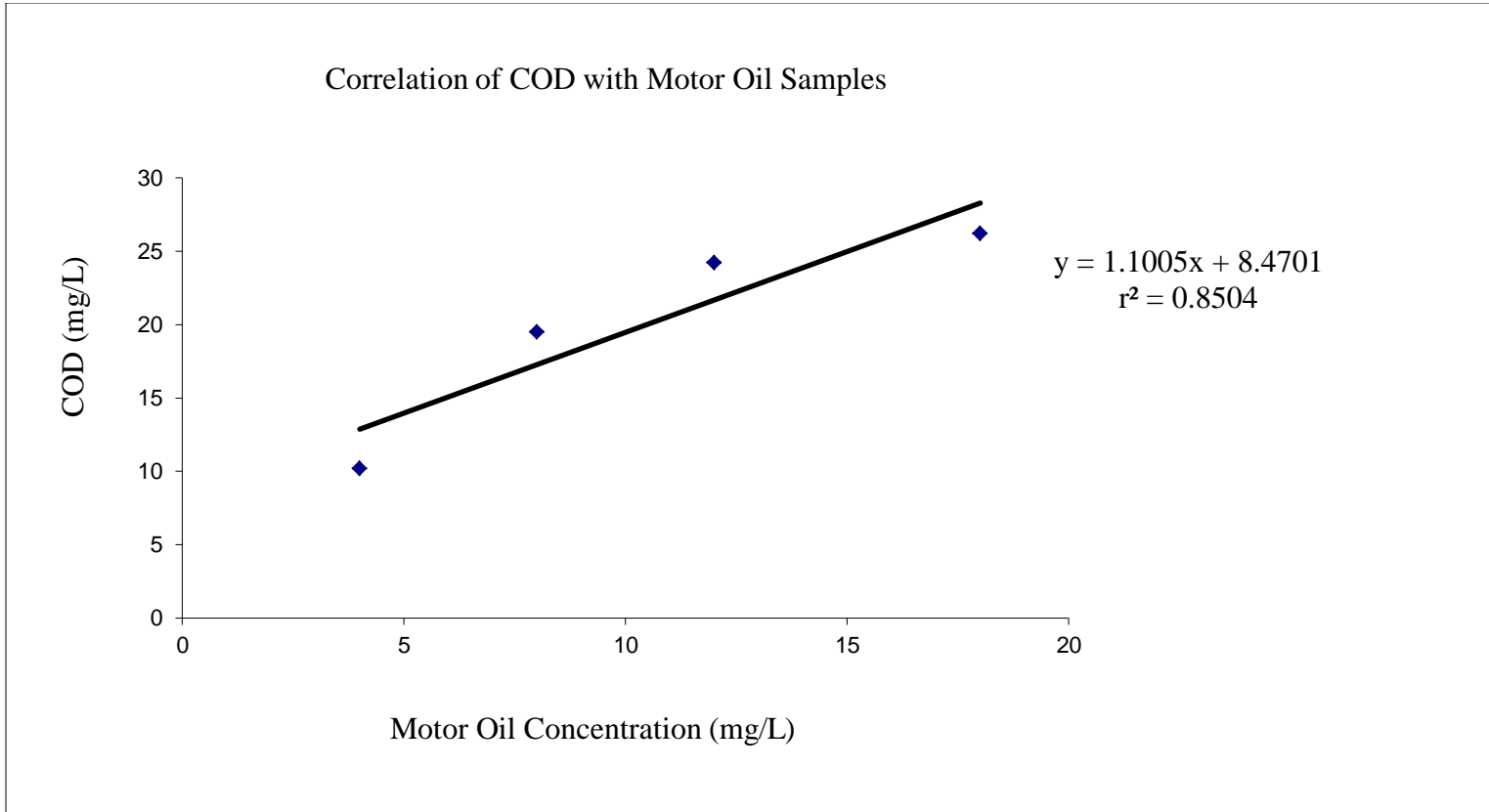
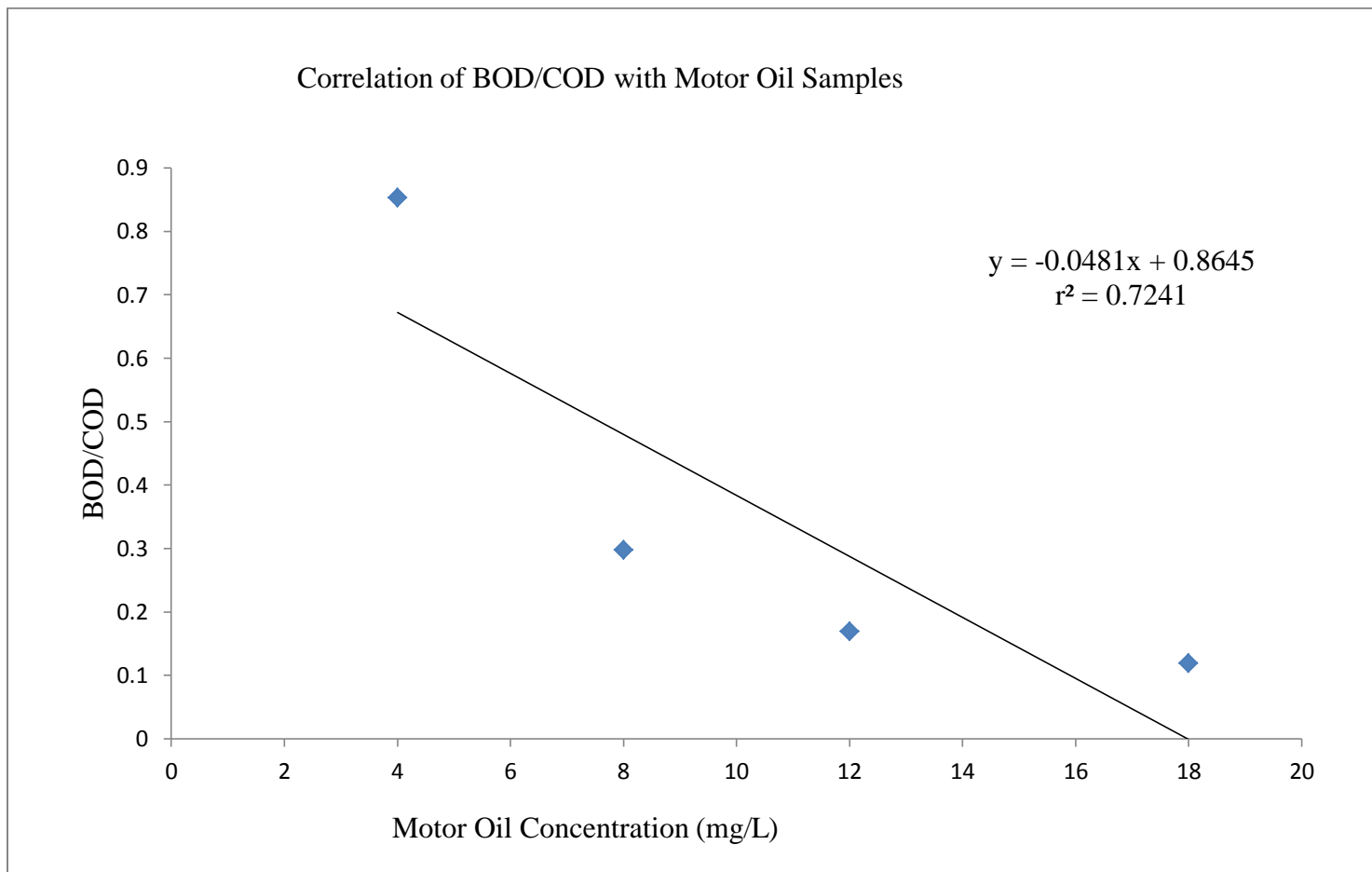Figure 8. BOD vs. Motor Oil Samples.

Figure 9. COD vs. Motor Oil Samples

Figure10. BOD$_5$/COD vs. Motor Oil Samples

BOD$_5$ and COD of Leachate Motor Oil

Previously conducted experiments in our lab by Jessie Weatherly on percentage

adsorption of motor oil by fly ash amended pervious concrete were used as the basis to

calculate the BOD$_5$ and COD values of leachate motor oil concentrations in this study.[44]

Tables 9, 10 and 11 summarize the data. Figures 11 and 12 represent the results of BOD$_5$

and COD analysis of motor oil, using pervious concrete blocks containing various

percentages of fly ash. To calculate the BOD$_5$ values for motor oil samples, a calibration

curve was created by plotting the motor oil standards with BOD$_5$ values on the Y axis

and concentration on the X axis for each of the standard samples (Figure 8). The

calibration curve was then used to convert the leachate concentrations to BOD$_5$ values.

The same approach was followed to obtain the COD values of motor oil samples. A

calibration curve was created by plotting the motor oil standards with COD values on the

Y axis and concentration on the X axis for each of the standard samples (Figure 9). The

calibration curve from the COD standards was used to convert the leachate

concentrations to COD values.

The 0% fly ash concrete block retained the least amount of motor oil. It retained

82.7% of the motor oil and leached 2.88 ppm motor oil after 20 liters of water passed

through the block, giving the highest COD value of 11.55 mg/L. The 20% fly ash

concrete block had 89.6% of the motor oil remaining on the block and leached 1.21 ppm

oil after 20 liters water wash which gave a COD value of 9.80 mg/L. The 30% fly ash

retained 92.0% of the motor oil and leached only 0.68 ppm motor oil which showed the lowest COD value of 9.21 mg/L after 20 liters water passed through the block.

The 0% fly ash concrete block gave the lowest BOD_5 value, 8.42 mg/L after 20 liters of water passed through the blocks. It gave the lowest BOD_5 value because it leached the highest volume of motor oil and higher concentrated motor oil is more toxic to microorganisms. The 20% fly ash concrete block gave the BOD_5 value of 9.04 mg/L. The 30% fly ash concrete block showed the highest BOD_5 value of 9.25 mg/L because it leached the lowest volume of motor oil after 20 liters water passed through the block and lower concentration sample has the higher rate of biodegradability due to its less toxicity.

Since high concentration motor oil is toxic to bacteria, we calculated COD reduction and looked at the increase of biodegradability after passing through the pervious concrete blocks, because it is necessary for Best Management Practices (BMP). COD reduction of motor oil leachate is shown in Table 8. Percentage of COD reduction increases as the percentage of fly ash increased in pervious concrete.

Table 8. COD Reduction Of Motor Oil Leachate.

% Fly ash	Mass of oil on Block(mg)	COD of oil(mg/L)	Conc. In leachate (mg/L)	COD of Leachate (mg/L)	COD reduction (mg/L)	COD reduction (%)
0%	413.32	463.33	2.88	11.55	451.78	97.5%
20%	447.22	500.64	1.21	9.80	450.84	98.0%
30%	450.53	504.23	0.68	9.22	495.03	98.2%

The BOD_5/COD ratio, which is a parameter of biodegradability improvement, produced some encouraging numbers (Tables 9, 10 and 11). The 0% fly ash, 20 % fly ash, and 30% fly ash amended pervious concrete blocks gave BOD_5/COD values ranging from 0.7 to 0.99, indicating good biodegradation.[38] This suggests that these blocks have the potential to reduce the oil concentrations below toxic levels and allow the leachate to be biodegraded by the soil bacteria in the subsurface.

Typically, unpolluted surface waters have BOD_5 values of 2 mg/L or less and COD values less than 20 mg/L.[34] However, the concentration levels of BOD_5 and COD found in urban runoff water are very high. A study was conducted by Marquette municipality in Wisconsin to measure the amount of pollutant from stormwater runoff being discharged to lakes and streams.[45] They found a median BOD_5 concentration of 15.4 mg/L and a median COD concentration of 66 mg/L in stormwater discharge. In fact, studies in our own lab in Rutherford County Tennessee showed that the BOD_5 of the runoff samples collected within the Murfree Spring basin ranged from 8.3 to 60.6 mg/L and the average COD for the samples was 152 mg/L.[46]

Horner et al.[47] conducted another important study. They found that the concentrations of pollutants in urban runoff are directly related to degree of development within the watershed. In commercial area, the median BOD_5 and COD concentration were 62 mg/L and 420 mg/L respectively and parking lots contained a median concentration of 47 mg/L of BOD and a median concentration of 270 mg/L of COD.

Several studies highlight the important role pervious concrete systems could play in contaminants adsorption. Usually oil and diesel fuel contaminants are frequently detected on asphalt and other non-permeable surfaces. Nevertheless, these contaminants were not detected on pervious surfaces assessed by Bratterbo and Booth; mostly because particle bound contaminants are largely retained by the surface and subbase of pervious pavement.[27]

Pervious pavements can act as efficient hydrocarbon traps and powerful *in-situ* bioreactors. Coupe et al.[25] domenstrated that a pervious concrete system specifically inoculated with hydrocarbon-degrading microorganism does not successfully retain a viable population of organisms for the purpose of increased hydrocarbon degradation over the years. However non-inoculation, naturally developed microbial communities degrade oil successfully.

Wilson et al.[48] incorporated an oil interceptor into a porous surface construction and carried out some tests. They combined the worst pollutants with strong rain events to assess how the system retains pollutants within its structure. The results successfully demonstrated that this system can retain hydrocarbons, and can offer improved water outflow.

The results obtained from these motor oil leaching studies agree with all the previous research mentioned above. The percentage leaching of the first ten motor oil samples shown in Table 10 was 0.485%, indicating 92% of motor oil was removed by the 30% fly ash. Based on this data, further calculations were done to determine the maximum

concentration of motor oil that could enter the block and still result in a biodegradable effluent concentration. 1,500 ppm was the calculated maximum level of motor oil concentration that could be biodegradable after 92% motor oil removal. The pervious concrete block would reduce the concentration to 7.2 ppm in the urban runoff with the BOD_5/COD value of 0.41, significantly lowering the concentration to the biodegradable range of 0.4-0.5.[38]

The data in Figure 13 shows that the BOD_5/COD ratio improved with the increasing motor oil retention as the percentage of fly ash increased in pervious concrete. The 0% fly ash concrete block had the lowest BOD_5/COD value of 0.73 after 20 liters of water passed through the block (Table 9). The 20% fly ash amended pervious block gave the BOD_5/COD value of 0.92 and 30% fly ash amended pervious concrete block had the highest BOD_5/COD value of 0.99 after 20 liters of water passed through the block (Tables 10 and 11). So using the 30% fly ash amended concrete block in place of impervious concrete in low impact areas could potentially lower oil concentration to a level where it would be biodegraded by the microbial communities successfully.

Table 9. Data for COD and BOD_5 Values of Motor Oil Leaching from 0% Fly Ash Amended Concrete Block.

Liters of water	Concentration in Leachate (mg/L)	Mass of Oil on Block(mg)	% of Oil on Block	COD(mg/L)in Leachate	BOD_5(mg/L) in Leachate	BOD_5/COD(mg/L)
0	NA	499.8	100.0	NA	NA	NA
1st 1L	2.22	497.5	99.05	10.91	8.65	0.79
2nd 1L	5.68	491.8	98.42	14.72	7.30	0.50
3rd 1L	3.95	487.9	97.63	12.82	7.98	0.62
4th 1L	9.00	478.9	95.83	18.37	6.01	0.33
5th 1L	8.36	470.5	94.15	17.67	6.27	0.35
6th 1L	9.59	460.9	92.23	19.02	5.78	0.30
7th 1l	2.95	458.0	91.64	11.72	8.37	0.71
8th 1L	5.98	452.0	90.45	15.05	7.19	0.48
9th 1L	7.64	444.4	88.92	16.88	6.54	0.39
10th 1L	3.87	440.5	88.14	12.73	8.00	0.63
11th 1L	1.93	438.6	87.76	10.59	8.76	0.83
12th 1L	3.66	434.9	87.02	12.49	8.09	0.65
13th 1L	1.52	433.4	86.72	10.14	8.92	0.88
14th 1L	4.94	428.4	85.73	13.90	7.59	0.55
15th 1L	5.66	422.8	84.60	14.69	7.31	0.50
16th 1L	1.80	421.0	84.24	10.45	8.81	0.84
17th 1L	2.42	418.6	83.75	11.13	8.57	0.77
18th 1L	1.24	417.4	83.50	9.830	9.03	0.92
19th 1L	1.24	416.1	83.26	9.830	9.03	0.92
20th 1L	2.80	413.3	82.70	11.55	8.42	0.73

Table 10. Data for COD and BOD_5 Values of Motor Oil Leaching from 20% Fly Ash Amended Concrete Block

Liters of Water	Concentration in Leachate (mg/L)	Mass of Oil on Block(mg)	% of Oil on Block	COD (mg/L) in Leachate	BOD_5(mg/L) in Leachate	BOD_5/COD
0	NA	489.9	100.0	NA	NA	NA
1st 1L	1.87	497.0	99.62	10.52	8.79	0.84
2nd 1L	5.81	491.2	98.46	14.86	7.25	0.49
3rd 1L	7.44	483.8	96.97	16.66	6.62	0.40
4th 1L	5.93	477.8	95.78	14.99	7.21	0.48
5th 1L	5.02	472.8	94.77	13.99	7.56	0.54
6th 1L	218	470.6	94.34	10.87	8.66	0.80
7th 1l	3.77	466.8	93.58	12.62	8.05	0.64
8th 1L	3.47	463.4	92.89	12.29	8.16	0.66
9th 1L	2.70	460.7	92.34	11.44	8.46	0.74
10th 1L	2.37	458.3	91.87	11.08	8.59	0.78
11th 1L	1.60	456.7	91.55	10.23	8.89	0.87
12th 1L	1.34	455.4	91.28	9.940	8.99	0.90
13th 1L	1.25	454.2	91.03	9.850	9.03	0.92
14th 1L	0.91	453.2	90.85	9.470	9.16	0.97
15th 1L	1.00	452.2	90.65	9.950	9.12	0.92
16th 1L	0.56	451.7	90.54	9.090	9.29	1.02
17th 1L	0.69	451.0	90.40	9.230	9.24	1.00
18th 1L	1.13	449.9	90.17	9.710	9.07	0.93
19th 1L	1.43	448.4	89.99	10.04	8.96	0.89
20th 1L	1.21	447.2	89.65	9.800	9.04	0.92

Table 11. Data for COD and BOD$_5$ Values of Motor Oil Leaching from 30% Fly Ash Amended Concrete Block

| Liters of water	Concentration in Leachate (mg/L)	Mass of Oil on Block(mg)	% of Oil on Block	COD(mg/L)in Leachate	BOD$_5$(mg/L) in Leachate	BOD$_5$/COD
0	NA	489.9	100.0	NA	NA	NA
1st 1L	2.82	487.1	99.43	11.57	8.42	0.73
2nd 1L	2.87	484.2	98.84	11.63	8.39	0.72
3rd 1L	2.58	481.6	98.31	11.31	8.51	0.75
4th 1L	3.59	478.1	97.58	12.42	8.12	0.65
5th 1L	2.28	475.8	97.12	10.98	8.63	0.79
6th 1L	1.88	473.9	96.73	10.54	8.78	0.83
7th 1l	2.11	471.8	96.30	10.79	8.69	0.80
8th 1L	2.04	469.7	95.88	10.72	8.72	0.82
9th 1L	1.83	467.9	95.51	10.48	8.80	0.84
10th 1L	1.64	466.3	95.18	10.27	8.87	0.86
11th 1L	3.26	463.0	94.51	12.06	8.24	0.68
12th 1L	2.16	460.9	94.07	10.85	8.67	0.80
13th 1L	2.01	458.9	93.40	10.68	8.73	0.82
14th 1L	1.28	457.6	93.40	9.880	9.01	0.91
15th 1L	0.93	456.1	93.21	9.490	9.15	0.96
16th 1L	1.55	455.1	92.89	10.18	8.91	0.88
17th 1L	1.31	453.8	92.63	9.910	9.00	0.91
18th 1L	1.04	452.7	92.41	9.610	9.11	0.95
19th 1L	1.53	451.2	92.10	10.15	8.92	0.88
20th 1L	0.68	450.5	91.96	9.220	9.25	0.99
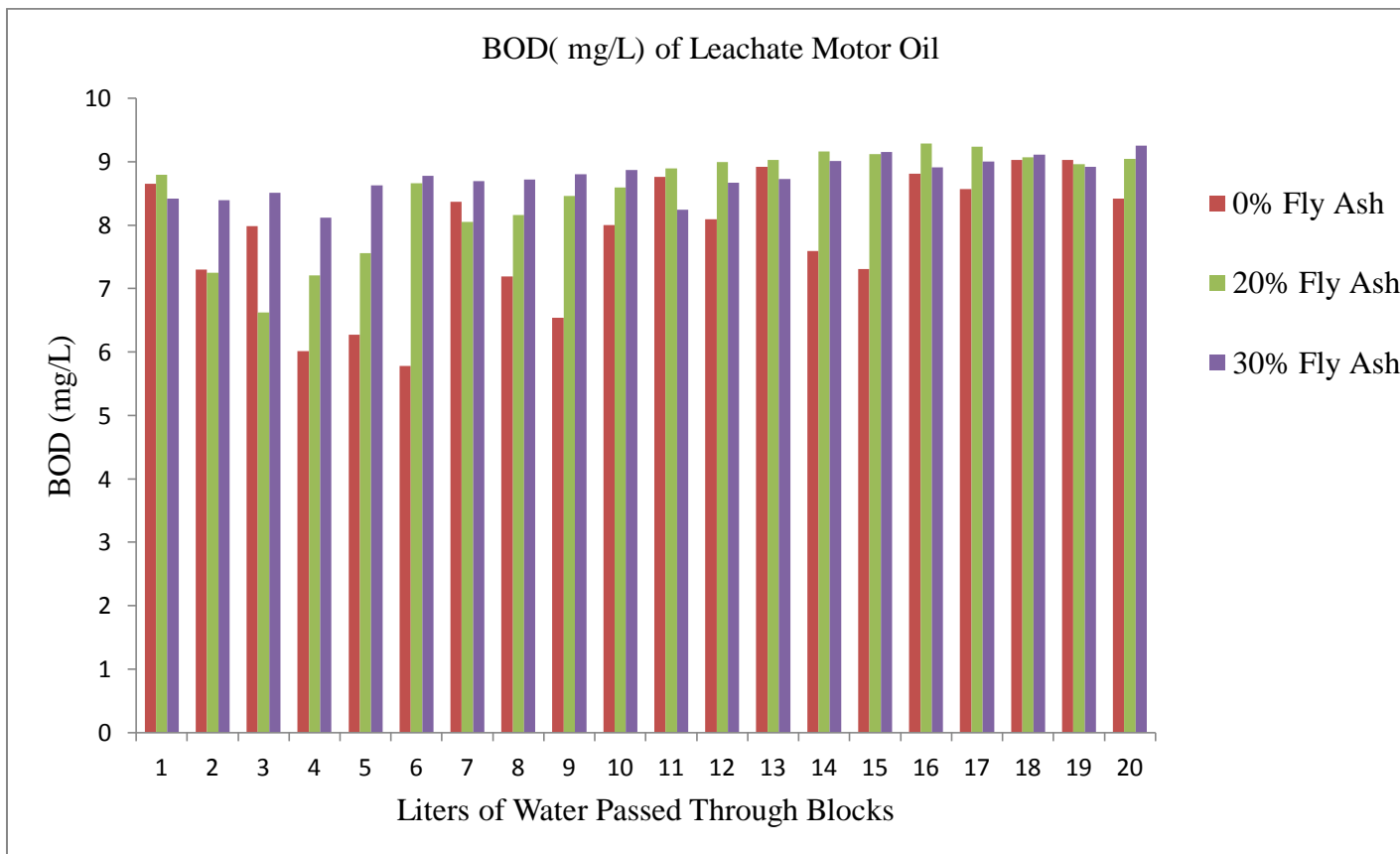
Figure 11. BOD_5 (mg/L) of Motor Oil Leaching by Blocks
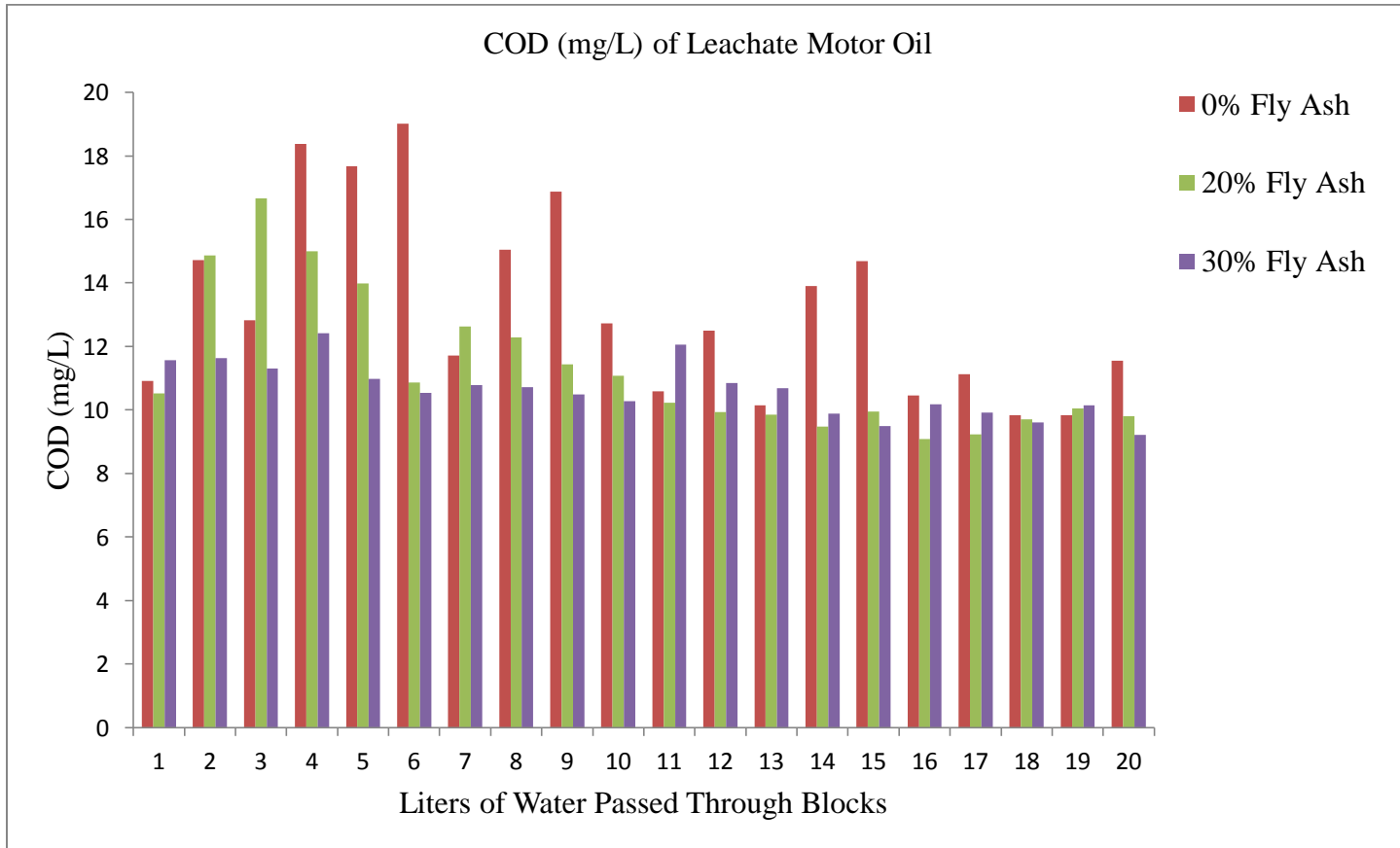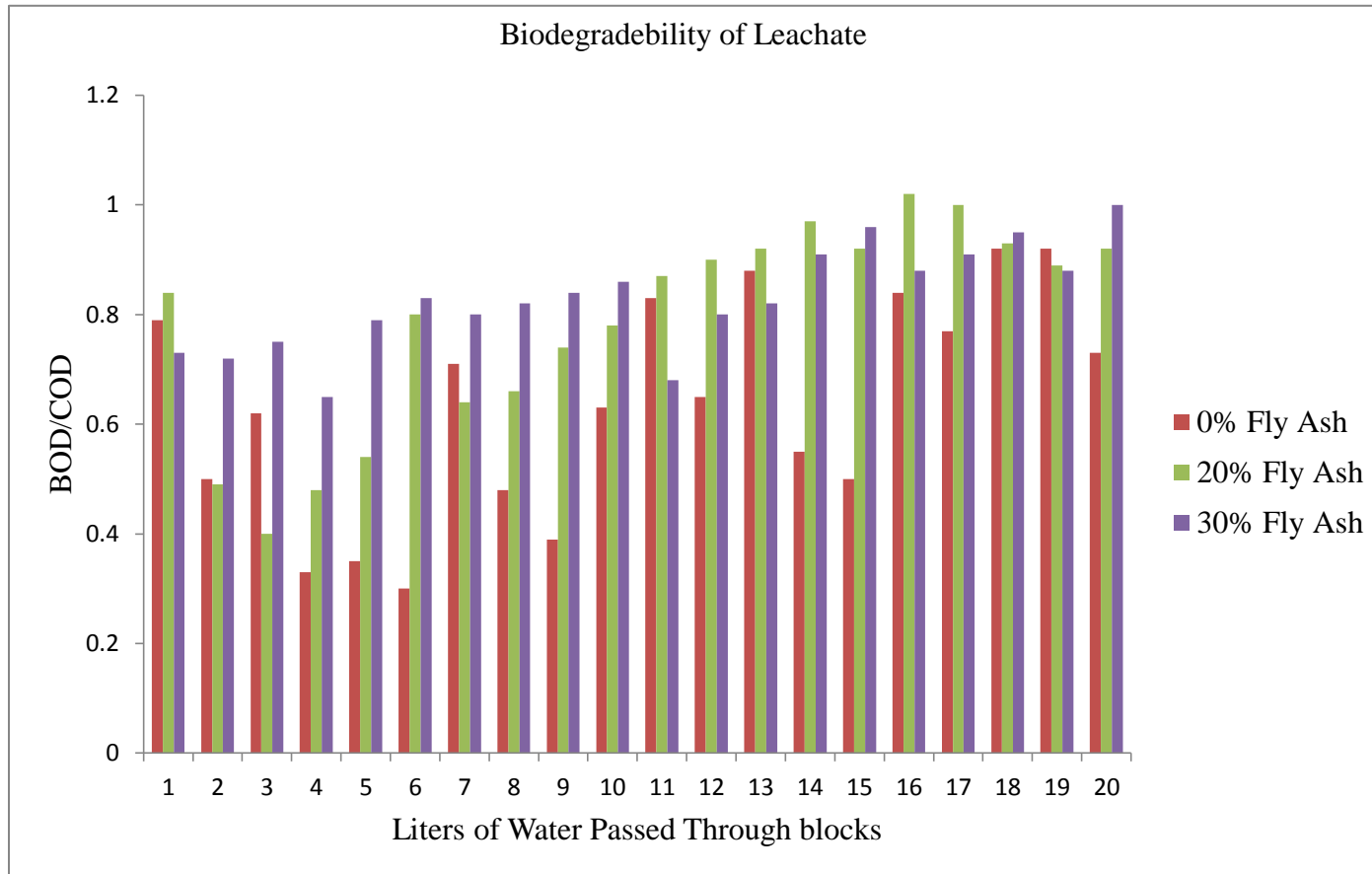
Figure12. COD (mg/L) of Motor Oil Leaching by Blocks

Figure 13. Biodegradability of Motor Oil Leaching from Blocks

Phosphate Adsorption Study

Five types of fly ash-amended pervious concrete were soaked in 750-ppm phosphate solution. Then they were washed with 3 1L deionized water rinses. The main purpose of this study was to determine how much phosphate is retained on the concrete cores since the previous studies in our lab demonstrated the ability of pervious concrete to adsorb large amounts of phosphate.[33] The 20% fly ash low carbon pervious concrete block and the 30 % fly ash high carbon pervious concrete block did not leach any phosphate (Table 12). No phosphate was observed in any of the 3 1L water flushes. Both of these two concrete blocks retained 100% phosphate. The 0% fly ash pervious concrete block gave an average phosphate leaching of 0.55 mg/L after 3 liters of water passed through the block. The 20% fly ash high carbon content concrete block leached an average 11.4 mg/L and the 30% fly ash low carbon pervious concrete block gave an average phosphate leaching of 11.3 mg/L after 3 liters of water passed through the block. Considering the highly concentrated phosphate solution (750 ppm) used in the adsorption study, the percentage of leaching from 20% and 30% fly ash amended block was only1.5%. Both of the 20% fly ash high carbon content and the 30% fly ash low carbon content pervious concrete blocks showed the ability to remove 98.5% of phosphate from 750 ppm phosphate solution. The 0% fly ash pervious concrete block retained 99.9% phosphate after 3 liters of water passed through the block.

The USEPA does not list nutrient anion phosphate under any primary or secondary drinking water standards.[49] However, to help control the eutrophication of

bodies of water, they recommend that the concentration of total phosphate should not exceed 0.05 mg/L in a stream that is entering a body of water; for streams that do not enter a body of water, the total phosphate concentration should not exceed 0.1 mg/L.[49]

Natural concentrations of phosphate in surface water usually range from 0.005 to 0.020 mg/L, which is lower than the phosphate concentrations found in urban runoff.[34] Dierkes et al[50] measured possible ranges of pollutant concentrations in rain, roof and road runoff, in sixty cities throughout the Europe. Among other pollutants, they found concentrations of phosphate range from 0.01 to 0.19 mg/L. Usually runoff from roads contains higher pollutant concentrations than roof runoff. Results from NURP (Nationwide Urban Runoff Program) indicate that there is a significant difference in pollutant concentrations in runoff from urban sources than that produced from non-urban areas.[47] They found that residential areas contained a median concentration of 0.38 mg/L of phosphate, commercial areas contained a median concentration of 0.20 mg/L of phosphate and non-urban areas contained a median concentration of 0.12 mg/L of phosphate.[47] Another important study was conducted by Tengne Wondie to assess the magnitude of the pollutant load in urban runoff imposed by Bahir Dar City on Lake Tana.[51] The samples were collected from six urban runoff events during the 5-month study period. The study found a mean concentration of 0.46 mg/L of total phosphorus (which is same as phosphate), a median concentration of 0.58 mg/L of total phosphorus (phosphate) and a maximum total phosphorus (phosphate) concentration of 0.69 mg/L

during the study period. The runoff collected from business and commercial areas had elevated values of phosphate than the non-urban runoff.

All these studies indicate that the level of concentrated phosphate found in urban runoff is potentially harmful to receiving waters. Once they enter the bodies of water, they will cause contamination and eutrophication. The pervious concrete blocks demonstrated the ability to removed 99% of phosphate, so using it instead of impervious concrete in low impact areas could lower the urban runoff volume, as well as concentration of phosphate in runoff water.

Table 12. Phosphate Retention Data

Block ID	Sample	Avg Concentration in Leachate (mg/L)	STADEV of Leachate	% of Phosphate Adsorption	95% Confidence Level of Leachate
0% Fly Ash	Sample Solution	0.757	0.14	--	0.16
	1st wash	0.235	0.20	99.97	0.23
	2nd wash	0.459	0.09	99.93	0.10
	3rd wash	0.551	0.13	99.92	0.15
20% High FA	Sample Solution	3.55	0.81	--	0.93
	1st wash	2.405	1.08	99.68	1.23
	2nd wash	2.501	1.19	99.66	1.35
	3rd wash	11.47	2.09	98.45	2.28
20% Low FA	Sample Solution	2.251	--	--	--
	1st wash	NF	--	100	--
	2nd wash	NF	--	100	--
	3rd wash	NF	--	100	--
30% High FA	Sample Solution	NF	--	--	--
	1st wash	NF	--	100	--
	2nd wash	NF	--	100	--
	3rd wash	NF	--	100	--
30% Low FA	Sample Solution	25.108	0.28	--	0.33
	1st wash	1.140	0.05	99.85	0.06
	2nd wash	2.182	0.92	99.71	1.04
	3rd wash	11.35	0.04	98.47	0.05

CHAPTER 4

CONCLUSIONS

Pervious concrete has been used in the area of storm water management because of its high porosity. The advantage of pervious concrete can be enhanced by substituting some of the cement with fly ash which has shown promising results to increase the overall performance of concrete. To explore the possibility of removal of urban runoff contaminants, a series of experiments were conducted using five different types of fly ash amended pervious concrete blocks. The following conclusions were drawn from the results.

- COD values of motor oil samples correlate well with increasing oil concentrations indicating that high concentration hydrocarbons are degraded easily by strong chemical oxidant.

- BOD values of motor oil samples did not correlate with increasing oil concentrations at the high concentration end suggesting high oil concentrations are inhibitory to the biodegrading microorganism. There were indications that low-concentration hydrocarbons biologically degraded better than high-concentration hydrocarbons.

- The BOD/COD values of motor oil, leached from pervious concrete blocks were 0.7 to 0.8, suggesting good biodegradation. The BOD/COD values showed trends that would point out that the fly ash plays an important role in the biodegradability.   It is found that the 1,500 ppm is the maximum motor oil concentration that would be biodegradable after 92% of motor oil would be retained by the 30% fly ash amended concrete block. So using pervious concrete blocks in place of impervious concrete blocks could help to reduce the concentration of motor oil in urban runoff at a lower level, where degradation of motor oil would be achieved.

- Leaching study of the five types of fly ash amended pervious blocks revealed that 20% fly ash low carbon and 30% fly ash high carbon concrete blocks did not leach any phosphate. The 0% fly ash pervious concrete block gave an average phosphate leaching of 0.55 mg/L after 3 liters of water passed through the block. The 20% fly ash high carbon content concrete block leached an average 11.4 mg/l and the 30% fly ash low carbon pervious concrete block gave an average phosphate leaching of 11.3 mg/L after 3 liters of water passed through the block. Considering the high concentrated phosphate solution (750 ppm) used in the adsorption study, the percentage of leaching was only 1.5%. However, all five different fly ash amended concrete blocks showed the ability to remove an average of 99% of phosphate.

- Future work could be performed to determine if the multiple species of microorganisms could increase the amount of hydrocarbon biodegradation and determine if the higher percentage of sample dilution for higher concentration motor oil would be beneficial in obtaining BOD_5 values.

REFERENCES

1. Water Quality Conditions in the United States: A Profile from the 1996 National Water Quality Inventory Report to Congress; USEPA 1998; Office of Water, U.S Government Printing Office: Washington, DC, 1998.

2. American Coal Ash Association. Federal Highway Administration, Fly Ash Facts for High Engineers, FHWA-03-013, 2003, 6(13).

3. Rushton T, Betty. Low-Impact Parking Lot Design Reduces Runoff and Pollutant Loads. *J. Water Res. Planning and Management*. **2001**, 127(3), 172-179.

4. Davis P, Allen.; Shokouhian, Mohammad. Liading Estimates of Lead, Copper, Cadmium, and Zinc in Urban Runoff from Specific Sources. *Sci. Direct*. **2001**, 44(5), 997-1009.

5. Eugene R, Weiner. *Applications of Environmental Aquatic Chemistry*; CRC Press: Florida, 2008; Chapter 3, 243-245.

6. Progress in Water Quality: An Evaluation of the National Investment in Municipal wastewater treatment; EPA-832-R-00-008; U.S. Environmental protection agency, Office of water: Washington, DC, 2000.

7. Sawyer, C.N.; McCarty, P.L. *Chemistry for Environmental Engineering;* McGraw Hill: New York, 1978.

8. Penn R, Michael.; Pauer J, James. Biochemical Oxygen Demand . *Environmental and Ecological chemistry*, Wiley and Sons: New York, 2012.

9. Standard Methods for the Examination of Water and Wastewater, 19th ed; APHA-AWWA-WPCF, Washington, DC. 1995; 4-98 to 5-16.

10. Groenewold, John C.; Pico, Richard F.; Watson, Kenneth S .Comparison of BOD Relationships for Typical Edible and Petroleum Oils. *Water Pollution Control Federation*. **2012**, 54(4),398-405.

11. Eugene R,Weiner. *Application of Environmental Aquatic Chemistry*; CRCPress: Florida, 2008; Chapter 3,79-81.

12. Shepherd G, H.L. Time-dependent Retardation Model for Chemical Oxygen Demand Removal in a Subsurface-Flow Constructed Wetland for Winery Wastewater Treatment. *Water.Environ. Research*. **2001,** 56-60.

13. Baker, J.R. Relationship between Chemical and Theoretical Oxygen Demand for Specific Classes of Organic Chemicals. *Water Research*.**1999**, 33(2), 327-334.

14. Wikipedia, the free encyclopedia.http;//en.wikipedia.org/wiki/chemical oxygen demand.

15. Eganhouse, R.P.; Simoneit, B.R.T.; Kaplan, I.R. Extractable Organic Matter in Urban Stormwater Runoff. 2. Molecular Characterization. *Environ. Sci. Technol.***1981**, *15* (3), 315-326.

16.   R.H.Schlosberg.; J.W.Chu.;G.A.Knudsen.; E.N.Suciu and H.S.Aldrich. High Stability Esters for Synthetic Lubricant Applications. *lubrication Eng*. **2001**, 21-26.

17.   M. Sharma.; E.A.McBean.; J. Marsale. Source Characterization of Polycyclic Aromatic Hydrocarbons in Street and Creek Sediments. *Water Qual.Res.J.* **1997**, 32(1),23.

18.   Latimer S, James.; Hoffman J, Eve.; Hoffman, Gerald.; Fasching L, James.; Quinn G, James. Source of Petroleum Hydrocarbons in Urban Runoff. *Water Air Soil Pollution.* **1990**, 52 (2), 1-21.

19.   Okeola, F.O.; Odebunmi,E.O.; Aremu,J. Comparative Assessment of Physicochemical Properties of Common Automobile Consumable Oils. *Advances in Environ. Bio*. **2011**, 5(1), 1-4.

20.   Aryal, R.; Vigneswaran, S.; Kandasamy, J.; Naidu, R. Urban Stormwater Quality and Treatment. *Korean J. Chem. Eng.* **2010**, *27*(5) 1343-1359.

21.   King, K.W.; Balogh, J.C.; Hughes, K.L.; Harmel, R.D. Nutrient Load Generated by Storm Event Runoff from a Golf Course Watershed. *J. Environ. Qual*. **2007**, *36*, 1021-1030.

22.   Wallace, T.A.; Ganf, G.G.; Brookes, J.D. A Comparison of Phosphorus and DOC Leachates from Different Types of Leaf Litter in an Urban Environment. *Freshwater Biology*. **2008**, *53*, 1902-1913

23. Delatte, N.; Mrkajic, A.; Miller, D.I. Field and Laboratory Evaluation of Pervious Concrete Pavements. *Transportation Research Record: J. Transportation Research Board*. **2009**, 132-139.

24. Stormwater Technology fact Sheet: Porous Pavement; Environment Protection agency, U.S. Government Printing Office: Washington, DC.1999.

25. Coupe, S.J.; Smith, H.G.; Newman, A.P.; Piehmeier, T. Biodegradation and Microbial Diversity within Permeable Pavements. *Euro.J. Protistology.* **2003**, 39, 495-498.

26. Ferguson, Bruce K. Porons Pavement: The Overview. University of Georgia School of Enviromental Design, Athens, GA.

27. Brattedo, B.O.; Booth, D.B. Long-term Stormwater Quality and Quality Performance of Permeable Pavement Systems. *Water Res*. **2009**, 37, 4369-4376.

28. Pratt,C.J.; Newman.A.P.; Bond, P.C. Mineral Oil Bio-degradation Within a Permeable Pavement: long Term Observations. *Water Sci.Tech.* **1999**, 39,103-109.

29. Georgia Stormwater Management Manual; Atlanta Regional Commision: Atlanta, GA, 2001; Vol.2.

30. ASTM, C 618-03. Standard Specification for Fly Ash and Raw or Calcined Natural Pozzolans for Use in Concrete. Philadelphia, PA.2003.

31. Fly ash Application in Pervious concrete. Na Jin, B.E. M.S. Thesis, The Ohio State University, Ohio, 2010.

32. Kim, A. G.; Kazonich, G.; Dahlbert, M. Relative Solubilty of Cation in Class F Fly Ash. *Environ. Sci. Technol*. **2003**, 37, 4507-4511.

33. Nutrient Anion Sorption and Leaching in Fly-Ash Mixed Pervious Concrete. Buchner, Brian A. M.S.Thesis, Middle Tennessee State University, Murfreesboro, Tennessee.2011.

34. Bates, B.; Kundzewicz, Z.W.; Wu, S. Climate Change and Water ; IPCC: Switzerland, 2008.

35. Untreated Highway Runoff in Western Washington. www.wsdot.wa.gov/NR/.../BA_Untreated Hwy RunoffWestWA.pdf(accessed March, 2008)

36. Koch, M. Ozonation of Hydrolyzed Azo Dye Reactive Yellow 84(Cl). *Chemosphere.* **2002**, 109-113

37. Alvares, A.B.C.; C, Diaper.; S.A, Parsons. Partial Oxidation of Hydrolysed Texile Azo Dyes by Ozone and the Effect on Biodegradability. *Trans. Inst.Chem.Eng*. *2001*, 103-108.

38. Mtui, Gys. Combined Chemical and Treatment of Recalcitrant Industrial Effluents: A Case Study on Kraft Pulp Wastewater. *Tanz .J. Sci*. **2001**.

39. BOD Test Requirements. file:// G:/BOD%20 Test% 20Requirements.html.(accessed 2003)

40. Biochemical Oxygen Demand. www.polyseed.com.

41. Bagherzadeh-Namazi, A.; Shojaosadati, S.A.; HashemiNajafabadi,S.
     Biodegradation of Used Engine Oil Using Mixed and Isolated Cultures.
     Int.J.Environ.Res. **2008**, 2(4), 431-440.

42. Ijaha,U.J.J.; Antaib, S.P.; Removal of Nigerian Light Crude Oil in Soil Over a 12-
     Month Period. *Int.Biodeterio.* **2003**, 51, 93-99.

43. Rambeloarisoa, E.; Rontani, J.F.; Giusti G.; Duvnjak, Z.; Bertrand, J.C.
     Degradation of Crude oil by a Mixed Population of Bacteria Isolated from Sea-
     surface Foams. *Marine Biol.* **1984**,78, 194-199.

44. Leaching and Adsorption of Contaminants Associated with Fly Ash Pervious
     Concrete. Weartherly, Jessie. M.S.Thesis, Middle Tennessee State University,
     Murfreesboro, Tennessee.2008.

45. Total Suspended Solids: the How & whys of Controlling Runoff Pollution,
     UWEX PUBGWQ055, Wisconsin. 2009.

46. Quantifying Organic Constituents of Urban Runoff in Murfreesboro, Tennessee:
     Potential Impact on Spring Water Chemistry. James, Rebecca R. M.S.Thesis,
     Middle Tennessee State University, Murfreesboro, Tennessee.2003

47. Preliminary Studies/ stormwater/USEPA.
     www.epa.gov/waterscience/stormwater/(accessed 2012)

48. Wilson, S.; Newman, AP.; Puechmeier, T.; Shuttleworth, A. Performance of an
     Oil Interceptor Incorporated into a Pervious Pavement. Proceedings of the
     Institution of Civil Engineers-Engineering Sustainability. **2003**, 51-58.

49. United States Environmental Protection Agency, 2011 edition of the Drinking Water Standards and Health Advisories. EPA 820-R-11-02. Office of Water, U.S. Environmental Protection Agency, Washington D.C. Winter 2011. Revised: January 2011.

50. Scholz, Miklas.; Grabowiecki, Piotr. Review of Permeable Pavement Systems. *Sci.Direct.***2007,** 3830-3836.

51. The Impact of Urban Storm water Runoff and Domestic Waste Effluent on Water Quality of Lake Tana and Local Groundwater Near the City of Bahir Dar, Ethiopia. Wondie, Tenagne Addisu. M.S.Thesis, Cornell University, Ithaca, N,Y, May 2009.