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Application Of Ferric Enriched Biochar (FEB) To Capture N And P From Greywater

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A filtration test was carried out to study the nutrients (N and P) adsorption capacity of two types of biochar, i.e. the biochars from two different companies, Biolan Oy and RKP Hiili. Both biochars were used in two forms: pure and enriched with ferric sulphate (FS).

It is well known that nitrogen (N) and phosphorous (P) are the essential nutrients for the plant production; however if these nutrients are used in excessive amounts, they can leach to groundwater and streams polluting the fresh water sources. Eutrophication is one of the major threats imposed by excessive addition of these nutrients into freshwater sources. Apart from this, the use of N and P in the agricultural field is altering natural N cycle and P cycle, respectively. N cycle alteration is increasing nitrous oxide (N_2O) gas in the atmosphere, which is one of the greenhouse gases responsible for climate change. Likewise, P cycle alteration is decreasing natural P resources. Hence, this thesis is intended to extract N and P from greywater and trap these nutrients in carbon filtrate (biochar or FS enriched biochar), and after full utilization of the filtrate it can be used again for plant production. As a considerable number of studies have already proved the potentiality of biochar in plant production, the use of biochar or FS enriched biochar rich in N and P for the plant production can be one the pioneering technologies in the future. The major applications of this thesis work will be the utilization of dusty charcoal (biochar), which is considered as waste and is no longer used for BBQ, in the treatment of greywater, and the recycling of N and P to use them further in crop production along with biochar.

Greywater was made in the environmental laboratory of Helsinki Metropolia UAS., by adding a fertilizer named Yara Combi (14-11-25), which contains 14% N, 11% P and 25% K. The filtration test results showed that Biolan biochar enriched with FS was able to adsorb both nutrients N and P, especially P, in highly significant amounts. Likewise, FS enriched RKP biochar was found to adsorb only P in significant amount. However, pure biochar from both Biolan and RKP was not able to adsorb nutrients significantly. It was proved that the enrichment of biochar with FS had an effect on nutrient adsorption.

Keywords	greywater, nutrients, eutrophication, phytoplankton, biochar, ferric sulphate, filtration, adsorption, ANOVA, tukey test, pooled standard error

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Abbreviations

ADP = Adenosine diphosphate

ANOVA = Analysis of Variance

ATP = Adenosine triphosphate

BBQ = Barbeque

BD = Bulk density

C = Carbon

DNA = Deoxyribonucleic acid

FS = Ferric Sulphate [$Fe_2(SO_4)_3$]

H0 = Null Hypothesis

H1 = Alternative / Research Hypothesis

HABs = Harmful Algal Blooms

H_2 = Hydrogen gas

H_3PO_4 = Phosphoric acid

IUCN = International Union for Conversation of Nature

K = Potassium

N = Nitrogen

N_2 = Dinitrogen or nitrogen gas

NH_3 = Ammonia

NPK fertilizer = Nitrogen Phosphorous Potassium fertilizer

P = Phosphorous

RNA = Ribonucleic acid

TN = Total Nitrogen

TP = Total Phosphorous

WHOI = Woods Hole Oceanographic Institution

WHO = World Health Organization

UAS = University of Applied Science

USEPA = United States Environmental Protection Agency

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1 Introduction

Water is an essential constituent for the survival of living organisms including plants and animals. All the living creatures in the world need water to live and not surprisingly, we all living beings are made up of water. However, there is not much water on Earth at all, as mentioned by David Gallo, an oceanographer of WHOI, Massachusets. He explains that if the Earth was an apple, the water layer would be thinner than the apple skin. Hence, water covers only a larger portion of the Earth's surface, and on the basis of mass percentage, the percentage of water on the Earth is little. It has been found that oceans are 0.02 % of the total mass of the Earth (Cain, 2010). So far 72% of the Earth is covered in water, but 97.5 % of that is ocean water, which is salty and not suitable for drinking. Only 2.5 % is freshwater, but 70% of freshwater on the Earth is ice. Less than 1% of the world's freshwater is readily accessible. Therefore, on the basis of this data, it is clear that the water source is limited. Moreover, due to a massive increase in the human population, the water demand has increased, and water is becoming scarce in these days. As a result, people in different parts of the world have already been practicing the reuse and recycling of greywater (Isreal, 2010). Greywater discharged from houses is mainly water from dishwasher, kitchen sinks, and hand washing sinks, showers, and bathroom, excluding the water from toilet. The reuse of treated greywater for purposes other than drinking, such as for gardening, irrigation, and toilet flushing after disinfection can reduce the freshwater demand. Above all, the essential resources such as N and P can be recovered from the greywater (Jefferson et al., 2001).

The reuse of used water as described above can significantly decrease the water foot-print. Overall, it will be cost-effective for the people to reuse the same water, as the water bill will decrease. This will consequently decrease the energy consumption in the supply of water, as less water is supplied. Moreover, the reuse of water is environment friendly, which ultimately saves water coming from resources such as freshwater (lake, river), and maintains the groundwater level. The recycle and reuse of greywater is mostly needed in water scarce places. Studies and new inventions in technologies have already made recycling and reuse of greywater possible. However, further research is needed to make it more efficient.

With the intention of making greywater treatment highly feasible in small scale and more efficient, Biolan Oy has introduced a greywater filter, which uses adsorption technology for the treatment of greywater. In the Biolan Greywater Filter (Figure 1), water is conducted into the uppermost tray, and water flows down to the lower trays by the force of gravity through the openings at the end of the case inside the filter. Oxygen is essential for the micro-organisms to break down the organic materials; hence, there are two openings (holes) on the top and bottom of filter for the circulation of air and this circulation operates by the force of gravity; air goes in through the lower ventilation valve at the back wall and out through the upper valve. The filter is designed only for the greywater treatment; thus, it must not be used with the water from WC, rain, storm or home foundations. The efficiency of filtering material is preserved for about 100 days of use and after that period material has to be removed and replaced. The wastewater can be directly conducted into the filter or indirectly by sending wastewater first into the sedimentation basins. The main point is that filter is not able to conduct the wastewater more than 20 L per operation. When the wastewater is sent into sedimentation basins, it is operated by pump timed with a clock switch so that the pump introduces a maximum amount of 20 L of wastewater into the filter during one period of operation.

Figure 1. Diagram of Biolan greywater filter 125.

Biolan Oy is looking forward to using biochar as an alternative filtration material in its greywater filtration unit, which has already been commercialized. Biolan has so far commercialized four different prototypes, each with different capacity. They are 1) Greywater filter 125 (500L/d), 2) Greywater filter 70 (500L/d), 3) Greywater filter light (300 L/d) and 4) Sauna filter (250L/d). At the moment filtration material used in these filtration unit is a moss plant, named *Warnstorfia trichophylla*. In Finland, it is found in Savukoski. When biochar is fully utilized, the retentate can be treated in an anaerobic digester with kitchen waste and blackwater for producing compost or biogas.

Biochar is the type of charcoal derived from the thermal treatment (heating) of natural organic feed stock such as wood chip, crop waste (straw), municipal waste or manure in an oxygen limited environment. The process is called pyrolysis, in which bio-energy such as tar, oil or wood vinegar may be produced including biochar (Bridgewater, 2003). After the determination of biochar as a highly porous substance (Liang et al. 2006) with large surface area (Van Zwieten et al. 2009), it has been used especially in soil amendment and as a water-holding material. The high porosity nature of biochar makes its surface area large. The inner surface area of charcoal (pyrolysed between 400^oC and 1000^oC) ranges from 200-400 m^2 g^{-1}(Kishimoto and Sugiura, 1985, cited in Hina, 2013). Due to large surface area, biochar has capacity to adsorb nutrients. In this thesis, biochar was used as filter material.

2 Goal and Scope

As N and P are the limiting nutrients of eutrophication, removal of these nutrients during the treatment process from any source of wastewater prior to disposal into the environment is an important issue. Also due to massive use of N and P in the synthetic fertilizer for agricultural purposes, there has been alteration of N and P cycle, causing major threat to the environment and living beings. The recycle and reuse of these nutrients could possibly control these major environmental threats. This thesis project focuses on the application of biochar to capture TN and TP from greywater. The results of the thesis project can be applied in four different fields which are 1) Treatment of greywater or wastewater 2) Reuse of greywater 3) Capture of N and P in biochar from greywater and 4) Reuse of these nutrients in the agricultural field as a fertilizer. The thesis hypothesis is that biochar and FS enriched biochar is capable of adsorbing significant amounts of TN and TP from wastewater/greywater.

Biolan Oy and RKP Hiili provided the biochar needed for the experiment. Biolan funded for chemical cuvettes needed for chemical analysis. The equipment and chemicals for the filtration test (fertilizer,ferrous sulphate, filterpaper, funnel and stands) were provided by MTT Agrifood Research Finland. The laboratory scale filtration and adsorption test and chemical analysis were performed at the Helsinki Metropolia University of Applied Science. Metropolia provided other equipment needed for the experiments, such as volumetric flask, round bottom flask, pipette, bucket, water, and especially photometer for chemical analysis.

Biolan Oy is one of the major producers of charcoal (biochar) for BBQ in Finland. The company produces 2000 tons of charcoal every year. About 10% of the produced charcoal is too small for BBQ use and is disposed of as a waste every year. So the company is looking for options to utilize this charcoal. As Biolan is also the producer of the greywater filtration unit, the company is trying to manage this wood based charcoal (biochar) by utilizing it in its filtration unit as potential filtration material. Therefore, this thesis was mainly carried out to find the efficacy of biochar in the removal of the nutrients (TN and TP) from the greywater. Moreover, the RKP Hiili Oy also wanted to know the efficacy of their biochar in the adsorption of nutrients. Hence, the efficacy of Biolan Oy biochar and the RKP Hiili Oy biochar were tested in the experiment.

3 Theoretical background

3.1 Greywater

Greywater, also known as sullage or light wastewater, is the residue of washing processes; as described earlier, it has not come into contact with solid human waste, causing less risk of disease. It is also easier to break down and decompose the organic matter present in greywater than that present in blackwater, as a result greywater can be safely reused in the garden or lawn. The contents of greywater depend heavily on the household activities such as cultural habits, living standard, household demography, and type of household chemicals used (Morel and Diener, 2006). Most commonly it contains soap particles, fat and oil from cooking, hair and even flakes of human skin. However, the quantities of these contents in greywater depend on the specific sources, which is summarised in Table 1 (Morel and Diener, 2006). Most of the plants can only handle the minimum concentration of chemicals, so in order to reuse the greywater in the garden, it is wise to regulate exactly what is sent down the drain and keep the levels of household chemicals in greywater as minimal as possible. The chemical contamination can be kept to the minimum by using environmentally friendly and biodegradable soaps and detergents whenever possible.

Table 1. Specific greywater sources with specific characteristics.

Kitchen	Kitchen greywater contains food residues, high amounts of oil and fat, including dishwashing detergents. In addition, it occasionally contains drain cleaners and bleach. Kitchen greywater is high in nutrients and suspended solids. Dishwasher greywater may be very alkaline (due to builders), show high suspended solids and salt concentrations.
Bathroom	Bathroom greywater is regarded as the least contaminated greywater source within a household. It contains soaps, shampoos, toothpaste, and other body care products. Bathroom greywater also contains shaving waste, skin, hair, body-fats, lint, and traces of urine and faeces. Greywater originating from shower and bath may thus be contaminated with pathogenic microorganisms.
Laundry	Laundry greywater contains high concentrations of chemicals from soap powders (such as sodium, phosphorous, surfactants, nitrogen) as well as bleaches, suspended solids and possibly oils, paints, solvents, and non-biodegradable fibres from clothing. Laundry greywater can contain high amounts of pathogens when nappies are washed.

3.1.1 Risk related to reuse of greywater

In different parts of the world, especially in regions with water scarcity or high water prices such as the Middle East, parts of Africa and Latin America, the practice of reuse of greywater for irrigating home gardens or agricultural land is widespread. Thus, it has already been perceived and recognised that greywater is a valuable resource. However, potential drawbacks of such practices are often not taken into account. If the greywater is reused directly without treatment, it contains pathogens, salts, solid particles, fat, oil, and chemicals although it is less contaminated than other wastewater. This kind of inappropriate practice may potentially have a negative effect on human health, soil and groundwater quality. Poor irrigation with untreated greywater can cause ingestion of pathogen through consumption of raw vegetables, which is an important disease transmission route. Along with the health risk, this kind of irrigation also leads to contamination of groundwater. Moreover, it can also have detrimental effects on soil, as suspended solids, colloids and excessive discharge of surfactants can clog soil pores and change the hydro-chemical characteristics of soils. The use of greywater rich in saline and sodium for irrigation over a long period of time can cause complete and irreversible salinisation and deterioration of the topsoil, especially in the arid regions with high evaporation rates (Morel and Diener, 2006). Thus, while doing irrigation with greywater many factors should be take into account which are climate, soil characteristics, water demand of plants, and greywater characteristics. As there is a high potential risk associated with the reuse of untreated greywater, it is recommended to treat the greywater before using it for irrigation. With the purpose of greywater treatment, the use of biochar along with ferrous sulphate, mainly focussing on the removal of N and P, is experimented and discussed in this thesis.

3.1.2 Economic value of greywater

It has been researched and proved that substances that are considered as wastes such as municipal wastes are valuable sources of raw materials and energy, if recycled and utilized well. Likewise, greywater should be regarded as a valuable resource and not as a waste. The reuse of greywater has a great potential to reduce the water stress faced by the world if the risk of greywater reuse is well management. It is an effective measure for saving water on the domestic level as well as it can lead to considerable economic benefits in the place where water is scarce and expensive. For example, a study done in Cyprus indicates a 36% reduction in water bills when household greywater is reused (Redwood, 2004). Greywater may also help in crop yields and reduce the cost of buying a fertilizer. (Morel and Diener, 2006)

3.1.3 Nutrient content in greywater

The nutrients content in greywater is low in compared to that of blackwater. Nevertheless, the N and P content in greywater are the important parameters due to their fertilizing value for plants, relevance for natural treatment processes and potential negative impact on the aquatic environment. As urine is the main source of N, the greywater contains relatively low levels of N. Wastewater from the kitchen is the main source of N in domestic greywater, whereas the N levels are relatively low in bathroom and laundry greywater. N releases from ammonia-containing cleansing products and also from proteins in meats, vegetables, and protein-containing shampoos. Even the water supply might be contaminated with high concentrations of N. For example, 25mg/l of NH_4-N concentration was observed in the Hanoi (Vietnam) water supply; water originates from Hanoi's groundwater aquifers, heavily contaminated with mineralisation of peat and organic material (Hong Anh et al., 2003). Typical values of N in domestic household greywater are found within a range of 5-50 mg/l; however extreme values of 76mg/l were also observed in kitchen greywater (Siegrist et al., 1976).

The use of detergents for dishwashing and laundry are the main source of P. P content in greywater has been found high in the regions where detergents containing P have not been banned. The typical value of phosphorous in households of such regions can be as high as 45-280 mg/l, as observed in Thailand (Schouw et al., 2002) and Isreal (Friedler, 2004), whereas the typical value of P in the regions where non-phosphorous detergents are used are found within a range of 4-14 mg/l (Erikson et al., 2002).

3.2 Excess nutrients addition to the ecosystems and it's impacts

The experiment conducted by agricultural chemist Justus von Liebig in the mid-1800s showed the strong positive relationships between soil nutrient supplies and the growth yields of terrestrial plants and similarly, freshwater and marine plants are equally susceptible to nutrient inputs. The industrial revolution and other human activities during the past two centuries have caused strong alterations in the structure and function of the environment, and anthropogenic inputs of nutrients to the Earth's surface and atmosphere have increased greatly(Smith, Tilman, & Nekola, 1999). The main anthropogenic activities such as land clearing, agriculture, forestry, animal husbandry and urbanization have altered the hydrological cycles changing the globe dramatically (Vitousek et al., 1997a). The composition of many natural biological communities has been significantly altered by harvesting activities, and by the unintentional and the deliberate introduction of non-native species (Bottsford et al., 1997; Chapin et al. 1997; Dobson et al., 1997; Matson et al., 1997; Noble and Dizo, 1997). Not only this, human activities have also great impacts upon the global bio-geochemical cycles of carbon (C), nitrogen (N), and phosphorus (P) (Schlesinger and Bernhardt, 2013; Vitousek et al., 1997a, b).

3.2.1 Alteration of N cycle

Nitrogen is one of the primary nutrients necessary for the survival of all living organisms. It is a necessary constituent of many bio-molecules, including proteins, DNA, and chlorophyll. N exists in many forms including inorganic (e.g. ammonia, nitrates) and organic forms (e.g. Amino and nucleic acids). N ranks fourth behind oxygen, carbon and hydrogen as the most chemical element in living tissues. It is most often limiting plant growth in natural and agricultural systems, and the rate of internal N cycle in soil plays important factor for plant production.Even thoughN is abundantly available in the atmosphere, i.e. 78% of total air is occupied by N_2; it is largely inaccessible in this form to most organisms and plants making N as one of thelimiting factors that controlled the dynamics, biodiversity and functioning of many ecosystems. Unlike CO_2, primary producers such as plants cannot absorb N_2 directly, except for few plants belonging to Rhizobium species such as peas, soybeans and alfalfa. These plants contain bacteria nodules to fix N, eg. Rhizobium bacteria. Nitrogen gas is in a complex state held together by a strong triple bond, so most of the plants cannot take it easily. N_2 needs to be fixed in soil to make it available for plants. During nitrogen cycle, nitrogen undergoes many different transformations in biosphere, changing from one form to another, as organisms use it for growth and energy. The major transformations are nitrogen fixation, nitrification, anammox, denitrification and ammonification, as shown in Figure 2 (Bernhard, 2010). The transformation depends on the activities of organisms such as bacteria, archaea and fungi. (Vitousek et al., 1997b).

During nitrogen fixation, N_2 is converted into biologically available N. Most nitrogen fixation is carried out by prokaryotes; however, some N can be fixed abiotically by lightning or by certain industrial process, including fossil fuels combustion. The produced ammonia during nitrogen fixation is converted into nitrite (NO2-) and then to nitrate (NO3-). It is carried out aerobically by prokaryotes. The oxidation of ammonia also occurs under anoxic conditions, which is known as anammox (Strous et al., 1999, cited in Bernhard, 2010). In some areas of ocean, the anammox process is responsible for significant loss of bio-available N (Kuypers et al., 2005).

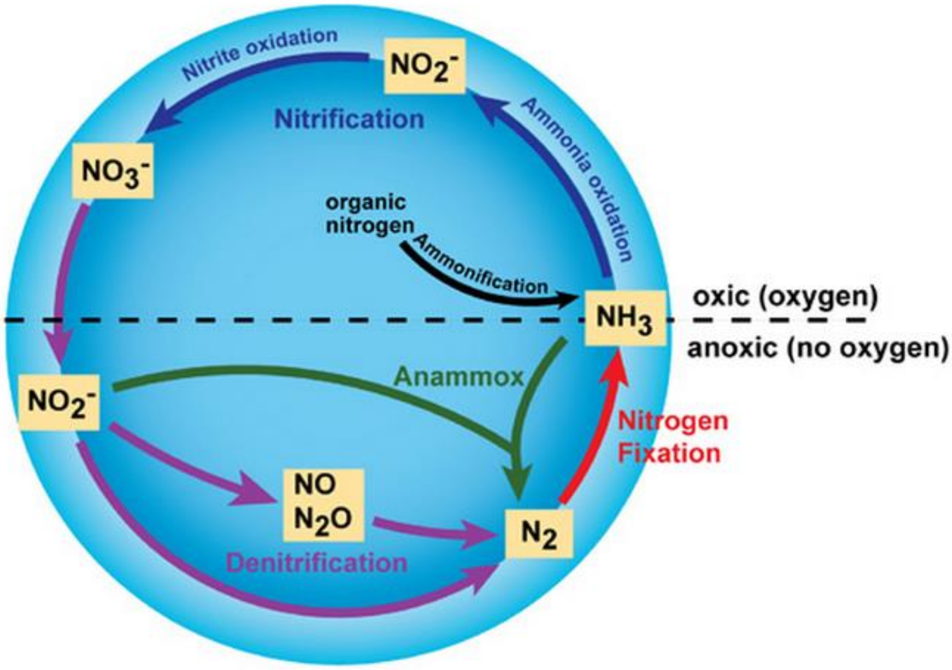

Figure 2. N cycle showing major transformations.

Denitrification is another vital process of removing bio-available N and returning it to the atmosphere, i.e. nitrate (NO3-) is converted into N_2, which is the ultimate end product of this process. However, other intermediate gaseous forms of N exist such as N_2O gas; they are greenhouse gases which react with ozone and contribute to air pollution. Finally, when organisms die or excrete waste, various fungi and prokaryotes decompose the tissue which contains organic N (e.g. amino acids, DNA) and release inorganic N back into the ecosystem as ammonia, known as ammonification. The released ammonia is available for uptake by plants or other microorganisms for growth. (Bernhard, 2010)

Human activities have been imposing threat on the alteration of global biogeochemical cycle of N. The rate of the N cycle in the terrestrial ecosystem has approximately doubled by humans, i.e. the current inputs add at least as much fixed N to terrestrial ecosystems as do all natural sources combined, and it is continuing. The change in N cycle has impact on carbon storage and soil minerals in most of the crop lands and forestry plantations. Due to importance of nitrogen in all ecosystems and significant impacts from human activities, nitrogen cycle has received great attention from ecologists. (Vitousek et al., 1997 a, b)

The global production of agricultural fertilizers is increasing vigorously. It has increased from <10 million tonnes of N in 1950 to ca. 80 million metric tonnes in 1990, and its production is predicted to exceed 135 million metric tonnes of N by 2030 (Vitousek et al., 1997b). A small fraction of total agricultural N applied to soil for plant growth may be significantly more than the required amount, and this surplus N may accumulate in soils, migrate from the land into surface waters and groundwater or enter the atmosphere via ammonia volatilization and nitrous oxide production (cf. Nolan et al., 1997; Vitousek et al., 1997b; Carpenter et al., 1998). Also the combustion of fossil fuels causes an additional emission of N into the atmosphere (Vitousek et al., 1997a) and a significant fraction of this subsequently returns to the land and ocean surface via nitrogen fixation which can be wet and dry deposition. The atmospheric deposition of N can have strong effects on the structure and function of both terrestrial and marine ecosystems (Paerl, 1995; Waring and Running, 1998)

High addition of nitrogen into the atmosphere has increased the N_2O gas, which is the one of greenhouse gas responsible for changing climate, and also there is formation of nitric oxide (NO), which increases the photochemical reaction to form smog. Alteration of nitrogen cycle also increases the loss of calcium (Ca) and potassium (K) from soil, which are responsible for the long term fertility of the soil. The excess nitrogen has caused considerable acidification of soils and water of streams and lakes. The N in the rivers eventually transports to the estuaries, seas and oceans, which is one of the major pollutant for causing eutrophication. This has caused changes in plant and animal life and ecological processes of stream and marine ecosystems and the decline of coastal marine fisheries has already been observed. It has been found that alteration of N cycle has accelerated losses of biological diversity, especially those plants that are low nitrogen dependent and afterward, the microbes and animals that depend on them (Vitousek et al., 1997b).

3.2.2 Alteration of P cycle

Like N, P is also an important element for plants and animals that make up the aquatic and terrestrial food web. However, P is present in small amount in lithosphere, hydrosphere and atmosphere. In terms of mass, P is at 11^{th} place in the lithosphere, and 13^{th} place in seawater (Smil, 2000). As P nutrient is short supply in most fresh waters, a slight increase in P supply can cause undesirable events in a stream including accelerated plant growth, algae blooms, low dissolved oxygen, and the death of aquatic animals including fish, and invertebrates (USEPA, 2012).

P is found in small amounts in the earth's biomass. P is absent in three polymers, i.e. cellulose, hemicelluloses and lignin, that make up most of woody biomass. It is also absent in proteins of living organisms, that contains amino acids in the polypeptide chain. Despite its limited presence, P in the form of phosphate (PO_4), makes up an important part of the structural framework that holds DNA and RNA together. It is essential for formation of carbohydrate polymers, proteins and nucleic acids. Teeth and bones constitute 80% of P. The P bond that reversibly moves between ADP and ATP releases energy which is consumed for synthesis of all complex molecules of life (Purves et al., 2004, cited in Bouwman et al., 2006).

The biogeochemical cycle of P consist of a very small amount of gas phase, which is different than natural N and C cycle that are driven by microorganisms and plants, and have atmospheric component (Smil, 2000). Only small amount of H_3PO_4 make their way into the atmosphere contributing in some cases to acid rain. In 1000 of years, the natural P cycle appears to be a one-way flow, with an important role of living organisms. Unlike biological N2 fixation, there is no biotic mobilization of P and the lost of P from the soil-plant cycling is replaced by the slow process of rock weathering.

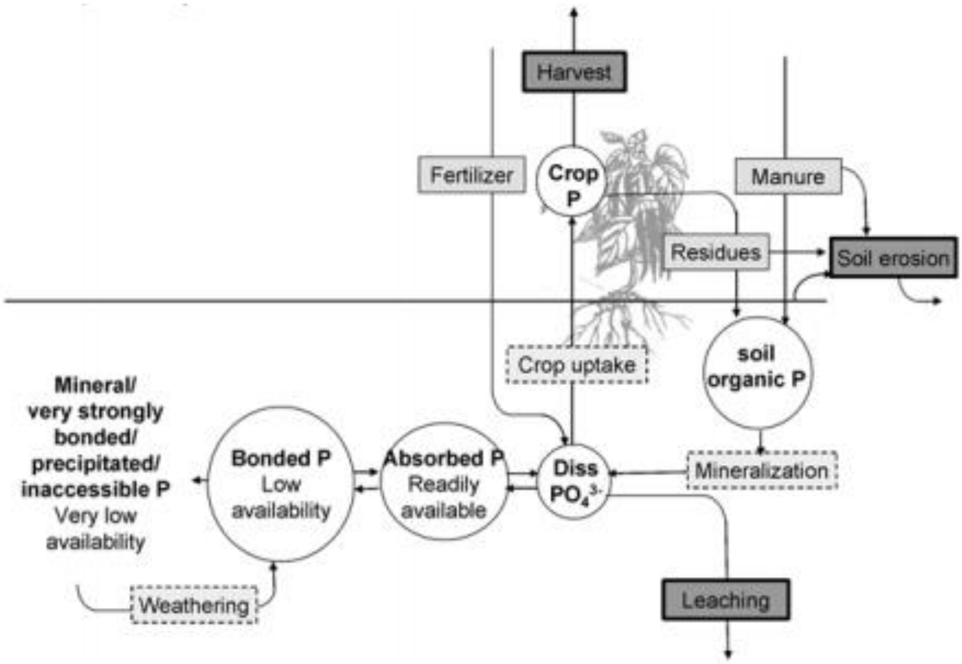

Figure 3. P cycle in soil-plant systems.

In the Figure 3, circles indicate pools, boxes with dashed lines are processes, light-grey boxes with solid lines are inputs, and dark boxes with bold lines are outputs (Bouwman et al., 2006). P cycle is driven by decomposition, mineralization and assimilation by autotrophs, as shown in Figure 3. P is found in poorly soluble form in the rocks. It is abundantly found in the rock named Apatite, calcium phosphate mineral, which contains 95% of all P in the Earth's crust. Due to rain the weathering of rock take place releasing small amount of P and this released P is usually rapidly immobilized into insoluble forms (Brady, 1990). At low pH, precipitation of phosphates occurs with alumina and with calcium in calcareous soils. Therefore, only a very little fraction of P in soils is directly available to plants as dissolved phosphate (PO_4^{3-}).The available P in soil is uptake by plants. Herbivores consume those plants and get the phosphorous needed by their body. Similarly, carnivores or omnivores get this element by consuming herbivores and plants. Phosphorous is finally discharged from the faeces and wastes of animals and the residues of dead and decay plants and animals; the mineralization of these organic P takes place. The erosion and runoff transfer soluble and particulate P to the ocean where it is eventually buried in sediments (Mackenzie et al., 2002, cited in Bouwman et al., 2006). As P has low solubility in soils, leaching of P generally occurs at low rates (Smil, 2000).

Apart from the natural source of P, there are also sources of P from human, which are wastewater treatment plants, water treatments, laundry using detergents containing phosphorous, runoff from fertilized lawns and cropland, failing septic systems, runoff from animal manure storage areas, commercial cleaning preparations, drained wetlands, and distributed land areas. All these sources are contributing more P into the earth, resulting in alteration ofP cycle. Also cutting down of tropical rain forest can alter P cycle. Rainforest ecosystems are supported through the recycling of nutrients, with the reserve of nutrients in their soil and the trees hold nutrients. When they are cut or burned, the stored nutrients are washed away by the heavy rain, making the land unfertile.The crops cannot absorb all the nutrients supplied by fertilizers, and as a result runoff of excessive nutrients into the lakes and streams take place, thus polluting freshwater sources (ELC, 2008).The alteration of P cycle, on the one hand causing major problem in the world known as eutrophication and on the other hand the natural source of P is depleting.

3.3 Eutrophication

Eutrophication refers excessive growth of aquatic plant and algal in fresh or marine water, due to high amount of one of the limiting factor needed for photosynthesis such as sunlight, carbon dioxide and nutrient fertiliser (Schindler 2006). Eutrophication occurs naturally resulting from the age of lake and increase in sediments (Carpenter 1981).

However, the rapid increase in the rate and extent of eutrophication has been noticed due to human activities through both *point-source* discharges and *non-point source* loadings of limiting nutrients, such as N and P, into aquatic ecosystems. As a result, aquatic life is affected damaging fisheries and recreational water bodies, and also polluting freshwater, the main source for drinking water (Carpenter *et al*. 1998).

According to the U.S. Environmental Protection Agency (EPA), point source is defined as“any single identifiable source of pollution from which pollutants are discharged, such as a pipe, ditch, ship or factory smokestack”. Most common types of point sources are factories and sewage treatment plants, whereas nonpoint source pollution results from agricultural runoff containing nitrates and phosphates due to moves of rain or melted snow over and through the ground. The inputs differ from watershed to watershed, depending on the local human population densities and land use (Smith, Tilman and Nekola, 1999).

The eutrophication resulting from human activities, i.e. from both point sources and non-point sources is called *cultural eutrophication*. People often eutrophicate water bodies by adding fertilizers to increase algae production for fishes, for example, aquaculture scientists and pond managers often intentionally eutrophicate ponds by adding fertilizers to increase the density and biomass of recreationally and economically important fishes via bottom-up effects on higher nutrition levels (Boyd & Tucker, 1998).Bottom-up effects in ecosystem refers to the control of ecosystem structure by the control in nutrient addition and primary producer’s production (algae). The availability of nutrients controls the plankton populations. For example, plankton populations tend to be higher in the areas where upwelling increases the nutrients concentration.

Planktons are microscopic organisms that are either prokaryote or eukaryote floating freely with oceanic currents and in other water bodies. The word plankton comes from the Greek word ‘*planktos*’ meaning ‘drifting’. These organisms are the foundation of ocean food webs. They are mainly divided into functional groups, which are phytoplankton (tiny plants)and zooplankton (tiny animals)(NatureWorks). Phytoplankton is directly linked with eutrophication. Phytoplanktons are autotrophic (primary producers), prokaryotic or eukaryotic algae that lives on the water surface where there is sufficient sunlight to support photosynthesis. The most important groups of phytoplanktons are cyanobacteria, diatoms, dinoflagellates and coccolithophores. The bloom of cyanobacteria (blue-green algae) is one of major issue linked with eutrophication.

3.3.1 Major consequences of eutrophication

The most evident consequence of cultural eutrophication is formations of dense poisonous blooms of foul smelling phytoplankton, which reduce the clarity of water and harm water quality. Eutrophication limits the penetration of light into the bottom of water body. This inhibits the growth of predators that need light to pursue and catch the prey and can even cause death of predators (Lehtiniemi, Engström-Öst, Viitasalo, 2005). Increase in rate of photosynthesis associated with eutrophication depletes the dissolved inorganic carbon, which eventually increases the pH of water body to extreme levels during the day time. The elevated level of pH can even make the sea organisms blindthat depend on the perception of chemical stimulus for their survival by diminishing their chemosensory abilities (Turner & Chislock 2010). The dense algal layer due to photosynthesis will eventually die and decompose in water. This microbial decomposition of biomass consumes much dissolved oxygen resulting in more demand of oxygen, which in turn may result hypoxic or anoxic zone, i.e. 'dead zone', lacking oxygen to support most of the organisms. The dead zones are found in many freshwater lakes, for example, the central basin of Lake Erie, the fourth largest lake of the five Laurentian Great Lakes in North America, has dead zones during summer (Arend *et a*l. 2011). Also lot of rivers and marine coastal regionsare affected by the dead zone. For example, Mississippi River and the Gulf of Mexico; Susquehanna River and the Chesapeake Bay have been affected (Diaz & Rosenberg 2008).The condition of hypoxia and anoxia as a result of eutrophication is threatening fisheries.

Algal blooms produce noxious toxins such as microcystin and anatoxin-a (Chorus and Bartram 1999, cited in Chislock, Doster, Zitomer&Wilson, 2013), which might be additional threat to organisms. The main consequences of harmful algal blooms (HABs) that have been noticed over of the past century are (1) degradation of water quality (Francis, 1878, cited in Chislock, Doster, Zitomer&Wilson, 2013), (2) devastation of economically important fisheries (Burkholder *et al*. 1992), and (3) public health risks (Morris 1999, cited in Chislock, Doster, Zitomer&Wilson, 2013). Within freshwater ecosystems, the most important phytoplanktons associated with HABs are cyanobacteria(Paerl, 1988), which are toxic in nature.The cyanobacteria including *Anabaena, Cylindrospermopsis, Microcystis*, and *Oscillatoria* (Planktothrix) dominate nutrient-rich freshwater systems due to their superior competitive abilities under high nutrient concentrations, low nitrogen-to-phosphorus ratios, low light levels, reduced mixing and high temperature (Downing *et al*. 2001; Paerl & Huisman 2009; Paerl and Paul 2012). Cyanobacteria are responsible for several off-flavor earthy-musty compounds such as methylisoborneal and geosmin found in municipal drinking water systems as well as in aquaculture and fisheries, resulting in large financial losses for regional economies (Crews & Chappell, 2007 cited in Chislock, Doster, Zitomer & Wilson, 2013). In addition of having consequences in public health risks, cyanobacteria have been linked to poor quality food for most zooplankton grazers, as shown by study done in laboratory (Wilson *et al.* 2006; Tillmanns *et al.* 2008). This eventually reduces the efficiency of energy transfer in aquatic food web and potentially prevents zooplanktons to control algal blooms.

There are number of major changes in aquatic community structure due to eutrophication. The noxious cyanobacterial blooms associated with eutrophication have been shown to cause sickness and death of zooplankton, fishes, livestock, and, sometimes, humans. Francis' (1878) first observed the dead livestock associated with a bloom of cyanobacteria (cited in Chislock, Doster, Zitomer&Wilson, 2013). The herbivore/cyanobacteria grazers (primary consumers) are important in controlling nuisance blooms of cyanobacteria in freshwaters. Such mass deaths of herbivore/cyanobacteria grazers cause harmful cyanobacteria to flourish. Therefore, understanding cyanobacteria-grazer interactions is important as they significantly influence plankton community in freshwater ecosystem. Factors such as morphological, nutritional, physiological, genetic, biochemical and molecular can influence the interactions. The results till date are unable to find the responsible factor for negative consequences associated with cyanobacteria-herbivore interactions, and more than one factor can act simultaneously on the grazer communities. Investigating and finding important factors that influence the interactions between cyanobacteria and grazing communities, especially protease inhibitors, will be helpful in providing management tools for toxic phytoplankton in freshwaters. (Agrawal & Agrawal, 2011)

The past observational studies have found that during cyanobacterial blooms, small-bodied zooplankton tend to dominate plankton communities (Porter, 1977, cited in Chislock, Doster, Zitomer&Wilson, 2013). In fish communities, piscivorous fishes, such as bass and pike, tend to dominate the fish community of nutrient-poor, oligotophic lakes, while planktivorous fishes such as shad, bream, etc. become increasingly dominant with nutrient enrichment (Jeppesen *et al*. 1997, cited in Chislock, Doster, Zitomer&Wilson,

2013). The planktivores might consume zooplankton and because of this there might lack zooplankton for the control of cyanobacterial blooms.

3.3.2 Controls

Eutrophication which results from nutrients enrichment in water bodies is deteriorating fresh and marine water systems, imposing serious threats in clean drinking water supply, fisheries, aquatic ecosystems and recreational activities. Cyanobacterial bloom has continued to rise in surface water around the world, although legislation in many countries has been implemented already to regulate point-source loading of nutrients to control eutrophication (Smith & Schindler 2009). It will be a major challenge in the near future to provide drinking water to the mass population with the predicted population growth and climate change, as this prediction has the potential to further degrade water quality and quantity. There is an immediate need of efficient water resource management system in all over the world to minimize the intensity and frequency of cyanobacterial bloom in water bodies (Paerl & Paul 2012).

3.4 Biochar technology for storing nutrients

The term ‘biochar’ is recently derived in colligation with soil management and C sequestration issues (Lehmann et al, 2006). The process of making biochar is quite similar to the production of charcoal, which is one of the most ancient industrial technologies developed by mankind (Harris, 1999 cited in Lehmann and Joseph, 2009). However, it can be distinguished from charcoal by the fact that biochar is the charred organic matter which is developed with the purpose to be applied to soil as a means of improving soil productivity, C storage, or filtration of percolating (leaching) soil water (Lehmann and Joseph, 2009). Biochar is chemically and biologically more stable than the carbon source from which it is made due to its aromatic structure. Thus, this makes biochar difficult to breakdown, remaining stable in soils for hundreds to thousands of years (Krull and McGowan, 2006).

3.4.1 History of biochar

In mid-1500's, Spanish explorer Francisco de Orellana and his crew were the first Europeans to navigate the Rio Negro and to reach the Amazon River. During their voyage they encountered large indigenous settlements, and they also discovered very large cities and fertile land. Later in 1870, American geologist and explorer James Orton noticed typically grey, acidic soils along with large patches of black, dark and fertile soil in the Amazon River basin. This drew the attention of the researchers to investigate the mysterious dark earth, or locally known as 'terra preta' (Figure 4). In 1879, Herbert H. Smith concluded that this fertile land was sheltering 1000 kitchens for 1000 years. In early twentieth century, this finding was strengthened by geologist William Katzer's by doing analysis of soil composition of terra preta, i.e. mineral residue, charred plant materials and decomposed organic matter. The correlation between the situation of the terra preta sites and the civilizations that Orellana described back in the 16th century was confirmed by the archaeological surveys.The presence of pottery shreds and food and animal waste in the soils demonstrates that they are anthropogenic in nature. It is surprising that terra preta have retained their fertility for centuries, even chemical fertilizers cannot maintain crop yields into a third consecutive growing season. A crop yield at terra preta can be four times higher than that produced in normal soil with the same parent material. Therefore, Amazonians were capable of creating a sustainable agricultural system over many centuries, supporting possibly millions of inhabitants in such limitations of their natural environment. (IUCN)

Figure 4. Comparison of nutrient poor adjacent soils (on left) and Amazonian Dark Earths, known as Terra Preta (on the right). *Photo courtesy: Rsukiennik and Bruno Glaser.*

3.4.2 Manufacture of biochar

As mentioned earlier, biochar is manufactured by the process called pyrolysis. So it is the thermochemical decomposition of organic material without the presence of oxygen. The term pyrolysis is different than the term burning. Pyrolysis is typically used for analytical procedure to investigate organic chemistry of organic matter and for bio-energy systems that capture the off-gases emitted during charring with the production of bio-oils, syngas, hydrogen, heat or electricity (Bridgewater and Radlein, 1999), whereas the term ‘burning’ is typically used when all the organic matter is converted into ash in presence of fire without any remaining of C or char. There might be some remaining of C in ash but it is negligible. The term ‘charring’ is used either when making charcoal in presence of heat or coal production from direct fire. Charring is incomplete combustion of solid materials producing char in presence of heat. Hence, the term *burning* is totally different from the terms *charring* and *pyrolysis* not only in terms of producing ash residue or char production but also in terms of gaseous production that are generated (Lehmann and Joseph, 2009). Charring and pyrolysis are quite similar. However, pyrolysis is done at a relatively higher temperature than charring.

There are three types of pyrolysis, which are partial, slow and fast pyrolysis. At partial pyrolysis we get higher yield of char (75%); at slow pyrolysis we get almost equal proportion of char, liquid and gas; whereas fast pyrolysis is used if we want high amount of liquid (bio-oil). And the pyrolysis performed at higher temperature than fast pyrolysis is called gasification, in which the organic content of the biomass is converted mostly into gas (85%). These all different types of pyrolysis with proportion yield of solid, liquid and gas in each is shown in Table 2. (Ronsse, Nachenius and Dickinson, 2012)

In summary, we can say that partial and slow pyrolysis is appropriate for biochar production. However, the end product depends on the heating rate, residence time, surrounding atmosphere and temperature, along with the types of biomass used affects both biomass volatilization and char conversion. Thus, there are mainly three factors influencing the properties of biochar: 1) biomass quality, 2) charring condition (temperature, atmosphere, heating rate) and 3) additions during the charring process.

Table 2. Pyrolysis processes showing solid, liquid and gas production by weight (%) at different pyrolysis level.

Process	Solid (wt. %)	Liquid wt. %)	Gas wt. %)
Partial pyrolysis (torrefaction) Low temperature (250 to 280^{0}C) Medium residence time (minutes)	75	20	5
Slow pyrolysis (carbonization) Low temperature (350 to 450^{0}C) Long residence time (hours)	35	30	35
Fast pyrolysis (liquefaction) Medium temperature (400 to 600^{0}C) Short residence time (seconds)	12	75	13
Gasification High temperature (750 to 1350^{0}C) Variable residence time	10	5	85

3.4.3 Biochar nutrient value

The nutrient value of biochars vary according to their origination. The animal origin (e.g. manure, sewage sludge, poultry litter) biochars are richer in nutrients (N and P) than the plant origin biochars (Lehmann and Joseph, 2009). The biochar has less mineral N in spite of significant Total N (in sewage sludge biochar) and P content is highly variable according to the biochars (Lehmann and Joseph, 2009). The nutrients present in biochar may be supplied either directly to plants or indirectly by improved soil quality increasing fertilizer use efficiency (Chan, et al., 2007; Van Zwieten, et al., 2010). Biochar also contains nutrients in ash such as K, P and other potentially important nutrients. The P content in feedstock can be fully recovered in biochars depending upon the feedstock and pyrolysis condition (Wang, 2012). Thus, biochar helps in soil P availability by indirect effect by increasing fertiliser use efficiency on soil and accessibility of mineral ash. Biochar can be highly beneficial for crop growth, especially mentioning about P availability, however, N availability can be improved simply by increasing the soil's organic matter status (Steiner, et al., 2007).

3.4.4 Applications of biochar

Biochar technology was practiced 2000 years ago to convert agricultural waste into soil enhancer, which holds carbon and increase the cation-exchange capacity of soil making it more fertile. Along with other few technologies sustainable biochar is widely applicable, relatively inexpensive and quickly scalable. The biochar may be added to soils as a soil amendment medium to achieve an agronomic and environmental benefit by improving soil functions and reducing emissions from biomass that would otherwise naturally degrade to greenhouse gases. Biochar technology helps to separate the natural C cycle. In natural C cycle plant material decomposes very rapidly after the decease of plants and this process releases carbon dioxide to the atmosphere, making the natural C cycle balance neutral. Nevertheless, these days several human activities including factories, industries work are releasing large amount of C into atmosphere, thus unbalancing the natural C cycle. Instead of allowing the plant material to decompose, biochar technology sequesters C into charcoal, a stable form of C, resistant to decomposition. Biochar technology slows the return of carbon dioxide from the soil to the atmosphere and stores C in a virtually permanent soil C pool, making it a carbon-negative process. (International Biochar Initiative)

In the past days the biochar was used only in agriculture for soil amendment. In the recent days biochar is not only limited for agricultural purpose as many findings from the research work have proven the potential use of biochar in other fields as well. Hans-Peter Schmidt has mentioned the 50 uses of biochar under different categories, which are in animal farming, soil conditioner, building sector, decontamination, biogas production, the treatment of drinking water, divers other uses, textiles and wellness (Schmidt, 2012). Due to its highly porous properties (Liang et al. 2006) and large surface area (Van Zwieten et al. 2009), biochar also has the potential to capture nutrients from wastewater.

Besides, Belcher and Mašek (2013) have categorized the uses of biochar into four main different applications: *climate change mitigation, soil conditioning, waste management, and energy*, and these may merge or overlap to form synergies. The deployment of quality biochar is needed for sustainable use in climate change mitigation with minimum negative environmental impact, and this quality biochar results from advanced technological solutions with high efficiency of feedstock conversion. The quality of biochar depends on the feedstock material type as well. (Belcher and Mašek, 2013)

3.4.4.1 Agronomic benefits

Addition of biochar in soil helps in the improvement of soil quality by making it more fertile, thus resulting in various agronomic benefits. A number of benefits have been found by the use of biochar in the place where the soil fertility and the productivity is deteriorating (Novak et al. 2009). It was reported by Steiner et al. (2007) that the yield in maize grain was doubled by the use of biochar with NPK fertilizer than just alone use of NPK fertilizer and the yields were noticed over the course of four cropping cycles on almost all plots. The rate of decline in yield was considerably less on the biochar amended plots than on those NPK amended plots. The biochar amended plots were found rich with the compounds Mg, P, K, Ca despite of the fact that these compounds disappeared after harvesting or tilling (Steiner et al. 2007, cited in Hina, 2013).

Biochar has the property of hydrophobicity, especially the biochar that is produced at a high temperature. Due to this characteristic, biochar can adsorb the organic compounds. It can adsorb organic and the plant root exudates. This adsorption capacity stimulates in nitrogen fixation in acidic tropical forest. The different organic compounds can inhibit the plants and microorganisms in nitrogen fixation and the adsorption by biochar will alleviate this inhibitory function of organic compounds (Hina, 2013).

Despite its benefits biochar can be harmful or even fatal for some of the plants, unless its limiting factor is not known. So far the amount of biochar to be added to soils is considered as a limiting factor in the use of biochar before it stops to function as a valuable soil amendment and becomes harmful for the plants (Woolf, 2008). The amount of biochar below 140 Mg C per hectare is found ineffective in the yield of crops. After the initial use, the biochar can be recycled as a soil conditioner. The biochar in soil slowly accumulates as black carbon and over a few generations the soil's biochar content could reach up to 100 t per ha (Schmidt, 2012).

3.4.4.2 Cation exchange capacity (CEC)

CEC depicts the capacity to retain vital nutrients in soil in a plant available form and minimize leaching losses; thus, it plays an essential role in the productivity of a plant (Sohi et al. 2009). The chemical structure of biochar is aromatic, but there is a possibility of formation of functional groups with net negative charge on the biochar surfaces (Schmidt and Noack, 2000). The test done in humid tropical Amazonian earth, where the leaching problem is very high, showed that Anthropols (soil enriched with biochar) is richer in cation availability than the adjacent soils with the same mineralogy (Lima et al. 2002). The formation of carboxyl groups might be the main reason for observed high CEC (Glaser et al. 2003). The formation of carboxyl groups and other functional groups with net negative charge at a range of soil pH can occur because of following two processes: (1) surface oxidation of BC particles themselves and (2) adsorption of highly oxidized organic matter onto biochar surfaces once mixed with soil (Lehmann and Rondon, 2005). It has been found that, on mass basis biochar has consistently higher CEC than whole soil (Niggusie and Kissi 2011). Due to this capacity, biochar can be used as an adsorbent like activated carbon, since adsorption process depends on the carboxyl group present on the substance as well as specific surface area of the substance.

Due to adsorption capacity of biochar, it has been reported an increase on ametryne sorption on a silty clay soil when charcoal was added (Yamane and Green 1972 cited in Hina, 2013). Biochar consolidation into soil may enhance overall sorption capacity of soils towards organic contaminants such as pesticides (NPK), herbicides, and PAHs. This property helps in control of transportation of nutrients into the water resources and groundwater. In addition, it may contribute to mitigate toxicity and reduce the effectiveness of some pesticide treatments (Kookana, 2010 cited in Hina, 2013).

3.4.4.3 Soil moisture retention

Tryon (1948) has used charcoal in soil to examine the change in water retention capacity and found an 18% increase in soil water retention upon addition of 45% (by volume) charcoal into a coarse textured sandy soil. The increase in soil moisture retention may reduce the water irrigation volume or frequency.Tryon (1948) also did research on the effect of charcoal on the available moisture content of different textured soils and found out that charcoal addition has increased the available moisture content in sandy soil, whereas available moisture content was constant in loamy soil and it was even decreased in the clayey soil in charcoal/biochar additions, which might be due to initial hydrophobicity of the charcoal. Hence, the types of soil and also the biochar quality affect the soil moisture retention capacity of biochar amended soil.

3.4.5 Biochar potential as filter material

Due to high adsorption capacity of AC, mostly Granular Activated Carbon (GAC) have been commercially used so far for a long period of time as filter medium in the treatment of drinking water to adsorb organic macro pollutants, disinfected by-products, as well as odour and taste compounds (Velten, 2008). Although AC has been found very superior in the adsorption of organic compounds, surfactants, TP and TN (Dalahmeh et al., 2012), the costly price of activation of carbon has prevented its use in wastewater treatment (Streubel, 2011). Biochar or charcoal is also produced in a similar way as AC, but without activation. Biochar and charcoal are basically same, i.e. both are produced when organic material is charred or pyrolysed in the presence of limited oxygen. However, two different terms are used separately according to their application. The term ‘biochar’ is used when applied for soil amendment, whereas the term ‘charcoal’ is used when applied as a source of energy. Like AC, biochar also has capacity to adsorb cations, anions as well as non-polar organic compounds. Thus, biochar can be alternative to AC. Biochar so far is only known for its use in soil amendment and C sequestration, biochar use as filter medium for contaminant removal is only recently gaining attraction of the scientists (Beesley et al., 2011). The highly sorption capacity of biochar is beneficial for the extraction of various organic and inorganic pollutants from solution, which can be re-utilized as valuable nutrients (Ghezzehei et al., 2014).

3.4.6 Use of Ferric Sulphate in filtration

FS is commonly used as a coagulant or flocculant for the municipal and industrial wastewater treatment leading to the coagulation and flocculation processes to separate suspended particles from the water. It forms complex compounds with P and is later removed as floc, thus helping in removal of P. It is also applied to control odour by minimizing the formation of hydrogen sulphide, and used as a sludge thickening, conditioning and dewatering agent.

$FeSO_4$ consumes 2 ppm of PO_4^{+3} for every 3 ppm of ferrous metal. The reaction can be written as follows:

$$3Fe^{+2} + 2PO_4^{+3} \longrightarrow Fe_3(PO_4)^2$$

In this thesis work biochar was enriched with FS, and a filtration experiment was carried out to study its potential in the adsorption of nutrients.

4 Experimental Part

4.1 Methodology

The experiment was carried out with 3 different filter mediums, which are i) sand, ii) sand + biochar and iii) sand + biochar + FS. Experiment was conducted with two different types of biochars from two different companies (Table 3). It means that biochar of two different qualities were used in the experiment. The filtration efficacy of these filter mediums combined with sand and FS were compared after getting the results

Table 3. Biochars from two different companies with their properties.

Companies	Feed-stock	Pyrolysis temperature	Retort	Holding time	BD	WHC	pH
Biolan Oy	Alder and Aspen sp. (hard-wood)	450^{o}C	Batch	12h	800.15g/L	68%	9.46
RPK Hiili Oy	Betula sp.	450^{o}C	Batch	23h	244.9g/L	99%	9.16

Comparatively Biolan biochar has much higher BD than RPK biochar because sand was added at the end of the pyrolysis process in Biolan biochar production. This activity affects the sorption capacity. Among these medium sand acts as filter medium and biochar along with ferrous sulphate act as adsorption medium. Before going through my thesis experiment, it is worth to know the working mechanism of filtration and adsorption. Filtration and adsorption works totally with different mechanisms.

4.1.1 Filtration

Filtration is the mechanical or physical process of separating suspended solids from fluids (liquids or gases) by allowing the latter to pass through the porous substance, known as filter. The fluid that passes out after filtration is called the filtrate. Filtration is very important and widely used in chemical technology. In chemistry, it is a physical operation used to separate materials of different chemical compositions. It may be the major part of some of the process by being simultaneously combined with other unit operations.

The filter can be any porous material such as paper, cloth, sand, cotton-wool, asbestos, slag- or glass-wool, or unglazed earthenware. However, some commercially available products such as activated charcoal and ion exchange resins are also called filters, although their principle function is adsorption. Filtration differs from the sieving, where separation occurs at single perforated layer and only big particles that cannot pass through the holes of sieve are separated. In filtration, a multilayer lattice retains those particles that are unable to follow the convoluted channel of the filter. Sometimes the blinding can occur in the filter layer, i.e. large particles may form a cake layer on top of the filter and may also block the filter lattice, preventing the fluid phase from crossing the filter.

Generally, two different types of filter mediums are used, which are surface filter and dense filter. There are several methods of filtration: simple or gravity, hot and vacuum filtrations. The selection of the appropriate method depends on the phase of the targeted material that needs to be separated, i.e. either fluid phase (dissolved form) or solid phase (suspended form).

4.1.2 Adsorption

Adsorption is the binding of molecules or particles to a surface, which is distinguished from absorption, the filling of pores in a solid. This process results the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. The material used for adsorption is called adsorbent.

The early experiments carried out by Scheele and Fontana during the eighteenth century recognized the capacity of porous solids to reversibly adsorb large volumes of vapour. However, the practical application of this property to the large-scale separation and purification of industrial process streams is relatively recent. The most common example of adsorption process is the use of an adsorbent column, packed with a suitable hydrophilic adsorbent, as a drier for the removal of traces of moisture from either gas or liquid streams. Similarly, adsorption processes are widely used on a large scale for the removal of undesirable impurities such as H_2S and mercaptans from natural gas and organic pollutants from water. The application of adsorption has been more advance in the recent days as it is capable to separate the mixtures into two or more streams, each enriched in a valuable component which is to be recovered. In the late 1950s molecular sieve adsorbents, the synthetic zeolites, became the first available on a commercial scale. Since then a wide range of zeolite structures have been synthesized and several of them have proved to be useful adsorbents, which are now available commercially. The most common available adsorbents are activated carbon, silica gel and alumina. (Ruthven, 1984)

4.2 Experimental design

Filtration test was conducted with the aim of finding the potentiality of biochar and FS enriched biochar to adsorb TN and TP. It was conducted at the Environmental Laboratory of Helsinki Metropolia UAS. Altogether filtration experiments were divided into six different categories, as shown in table 4. There were five replicates of filtration experiment from each filter medium. 2*2 factorial design was used for the experimental design, i.e. the experiment contains two factors (Biolan biochar and RPK biochar) and each factor contain two different levels (with FS and without FS). Here, sand is not considered as factor as it is used in all the experiments except the control (T1).

Table 4. Table showing the use of filter materials (sand, biochar, FS) in six different filtration experiments.

Experiments	Sand	Biochar	FS
T1	No	No	No
T2	Yes	No	No
T3	Yes	Biolan	No
T4	Yes	RPK	No
T5	Yes	Biolan	Yes
T6	Yes	RPK	Yes

The 1st experiment, i.e. T1, is the control that's why there is no use of any filter materials. The filter paper and the sponge were used in all the experiments.

4.3 Determinations of physical parameters

At first, volume of funnel and small bottle were measured. In all the filtration experiments (T2 to T6) excluding the control, the net volume occupied by the filter medium was 200ml. The dimension and volume of the materials used in the filtration experiments are shown below.

Volume of funnel ~ 600ml

Volume of small bottle ~ 250ml

Thickness of filter layer (sponge) = 2cm

Volume of sand in T2 = 200ml

Volume of sand + biochar (in T3, T4, T5 and T6) =140ml sand + 60ml biochar = 200ml

Volume of greywater = 300ml for all the experiments

The experimental setup for filtration is shown in Figure 5 (drawn using Edraw Max software). The filtration setup in the figure represents the experiments T5 and T6, i.e. biochar mixed with FS.

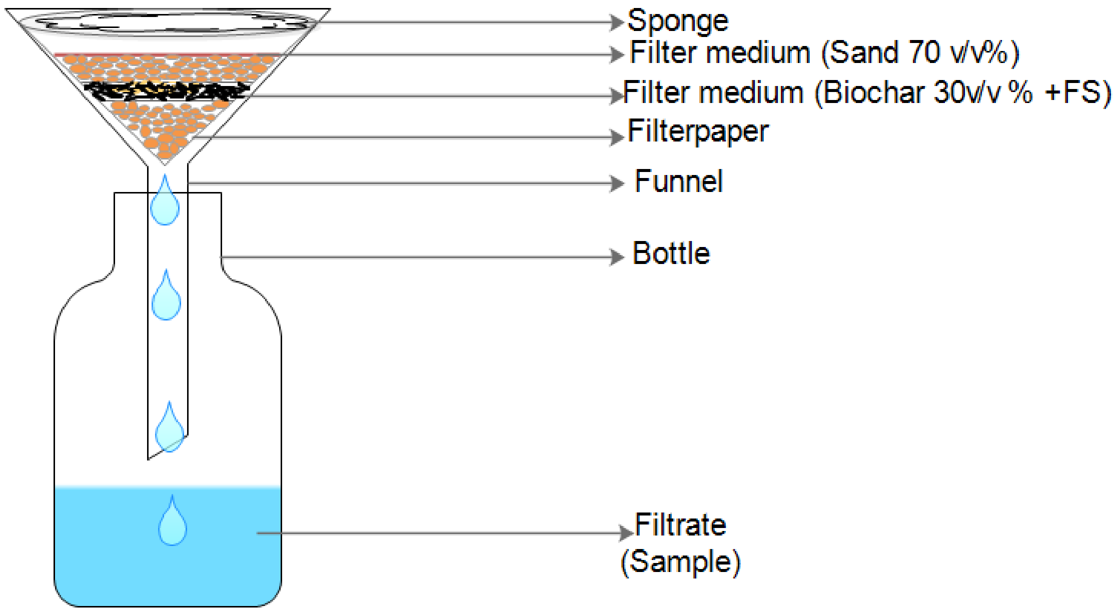

Figure 5. The diagram representing filtration test showing layer of sand and biochar in the funnel.

4.4 Moisture content and BD measurement

The moisture content of all the samples was measured. The crucibles were used to put the samples. For each sample, four crucibles were used to get the replicate measurements. At first, the oven is preheated to 105^{o}C. The crucibles were labeled properly to distinguish from each other and their masses were taken using mass balance. Then, the crucible were filled by the samples to the about half of the volume. The mass of the crucibles filled with samples were measured. After that all the crucibles containing samples were kept inside the oven at the same time. The samples were taken out after 24 hours and the mass after dry was measured. The loss in the mass of the samples is the moisture content of that sample. In it was determined by the following formula,

$$\frac{\text{loss in the mass of the sample}}{\text{actual weight of sample}} * 100\%.$$

After that bulk density (BD) of sand and biochar was measured. BD was measured based on the guideline provided by WHO to The International Pharmacopodia. Method A (Measurement in a graduated cylinder) of the guideline was used for the measurement of BD. At first the sufficient powder sample needed for the test was passed through a sieve with apertures equal to 1mm. It makes the powder more fine and break up the agglomerates. The process was done very gently to avoid the change in nature of material. Then, 100g of test sample was introduced into graduated cylinder of 250 ml. The apparent volume (V) occupied by the mass (m) of powder was leveled without compacting. Hence, the BD was determined using the formula m/V. Four replicate measurements were done for all the samples (sand and biochars).

Sometimes the powder density can be too low or too high depending on the nature of the sample making an untapped apparent volume either more than 250ml or less than 150ml. In such case, it is not possible to use 100g of test sample, therefore, different amount of test sample has to be used so that the untapped apparent volume will be from 150ml to 250ml. In this thesis, for sand 100g of test sample was used, whereas for Biolan biochar 40g and for RPK biochar 15g of test samples were used. The calculation of BD measurement was done in Excel which is shown in appendix. From the BD, the weight of sand and biochars needed in each funnel were calculated based on their volumes that will be used in the funnel, as shown in figure 5.

4.5 Greywater preparations

Greywater was prepared by contaminating the drinkable tap water of Metropolia UAS with chemical fertilizer name Yara Ferticare Combo 1 (NPK 14-5-21) (named Yara Ferticare Kombi 1 in Finnish). The fertilizer is composed of 14% N, 5% P and 21% K). The water was contaminated according to the concentration of N and P in wastewater. Usually, N and P concentrations of wastewater treatment plant are <50mg/L and <10mg/L. The total volume of water used in the filtration experiment was 9L. The volume of Yara (fertilizer) used and the concentration of N and P in the solution was calculated as follows:

If N concentration is 50mg/l in greywater then, 14% N of Yara = 50mg/l N
Therefore, concentration of Yara in 9L solution = (50/0.14)mg/l *9L =0.35 *9 g = 3.21 g
In percentage, concentration of Yara in 9L solution = 3.21g /9L = (3.21g/9000g)*100% = 0.036%
Volume of Yara used to contaminate the solution = 0.036% * 9L = 3.24mL =3.24g
Then,
Concentration of N = 14 % of 3.24g/9L = 0.14*3.24g/9L = 0.0504g/L = 50.4mg/L
Concentration of P = 5 % of 3.24g/9L = 0.05*3.24g/9L = 0.018g/L = 18mg/L

4.6 Filtration procedure

All the funnels and small bottles were cleaned and rinsed properly before using it for filtration. There were altogether 30 (six experiments each with five replicates) filtration experiments to be conducted; all the samples needed in entire filtration unit were prepared beforehand. In this case weight of sand, biochar, FS needed in each filtration unit was measured using measurement balance and these all the samples were stored in minigrip plastic bags. The filtration experiment was conducted on the next day.

9L of wastewater was prepared using fertilizer. The entire filtration test used separate funnels, but the funnels were of similar size and dimensions (same volume).Funnels were kept on the stand in a row and small bottles were fitted just down the opening of funnel to collect the filtrate, as shown in Figure 6. The filter paper was kept in the funnels to hold the filter medium sand and biochar in the funnel. Also sponge was used in the top of the funnels to spread the water evenly from all the surfaces of filter medium, as demonstrated in Figure 7.

Polluted water (Greywater) was passed slowly through filter medium using volumetric flask into the funnel; wastewater was circulated slowly through all the surface of sponge to make water evenly distribute through all the layer of filters. After few minutes water slowly start to leach out from the funnel and leachate is finally collected in the small bottle.

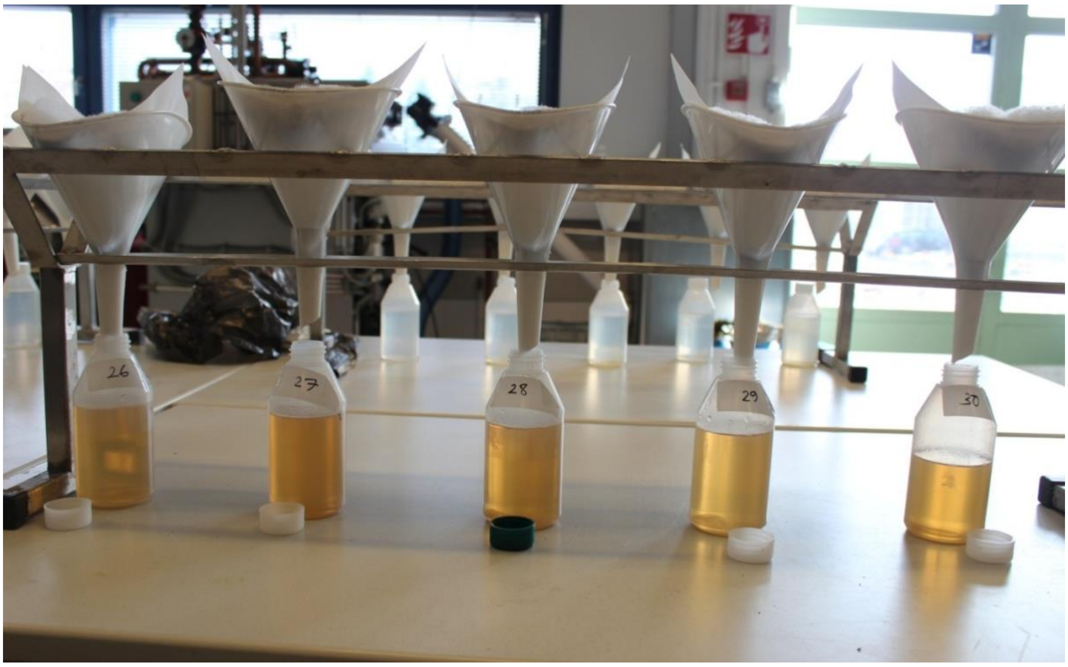

Figure 6. Filtration test using funnel, put in a row by the help of stand. Samples (yellow coloured on the front row and white coloured on the back row) are collected in the small bottles.

Figure 7. On right using sand filter and on left use of sponge on the top of filter.

Due lack of stands only 15 filtration experiments were conducted at first, which were T1, T3 and T4 and then remaining 15 experiments were conducted after 3 hours interval.

In the first experiment (T1), the control was also filtered through the filter paper + sponge, in order to know if filter paper and sponge has any significant effect on the adsorption of nutrients. Later on from the result it was found that filtration through these units has no any significant effect on adsorption of nutrients. Hence the results from T1 gave just the concentration of water soluble N and P in the polluted water.

As said earlier, the 2nd filtration unit (T2) contained only sand as filter medium. The sand was commercially available and it was not enriched with any nutrients or chemicals. The 3rd and 4th filtration unit has sand + biochar as filter medium, where the layer of sand and biochar was made in which the layer of biochar was in between the sand, as shown in figure 5. Only difference between 3rd and 4th unit was that they contained biochar from Biolan and RPK respectively. The 5th and 6th filtration unit was similar to the 3rd and 4th unit but there is addition of FS in each biochar (Biolan and RPK), i.e. making biochar enriched with FS. FS was added in dry amount mixed thoroughly with biochar.
Note that biochar and sand are not mixed, it's a separate layer just attached each other. The filtration efficiency between five (2nd, 3rd, 4th, 5th and 6th) different filtration units are compared.

4.7 Methods of addition of ferric sulphate

There are two different methods to enrich the biochar with FS which are dry and wet methods. In dry method FS is grinded into fine powder and directly mixed with biochar, whereas in wet method solution of FS is made and then the aqueous solution is mixed with dry biochar or the biochar is made wet thoroughly with the solution. After that the mixture is dried in oven

In this thesis, dry method was used for addition of FS. As mentioned earlier, FS was used mainly focusing on the removal of P. The amount of FS needed to enrich the biochar was calculated according to the guidelines provided by Kemira Ltd. The guideline illustrates that in order to remove 10mg/L concentration of P from wastewater, 180mg/L FS is needed. Hence, in my case, to remove 18mg/L of P, concentration of FS needed = (180mg/L / 10mg/L)*18mg/L = 324mg/L. As FS was used in dry form, the solution of FS was not made. It was pulverized and directly mixed with biochar instead. Hence, 324mg/L of total dry FS was needed to remove 18mg/L of P. Then, FS was added to biochar based on the water volume used per filter. In the experiment, the amount of water poured per filter is 300mL. To filter P (18mg/L) from 300ml water, FS added to biochar = 324mg/L *300mL = 97.2mg per filter (in experiments T5 and T6).

5 Experimental results

5.1 Moisture content and BD

Moisture content and BD of the filter materials were measured (Table 5).

Table 5. Moisture content and BD of filter materials.

Filter materials	Moisture content, %	BD (g/l)
Sand	0	1465.419
Biolan biochar	10.48	800.16
RPK biochar	32.74	244.9

As both biochars are produced commercially in large quantities, these biochars are kept long time in the storage. Here, RPK biochar had been kept long time in the storage area, making its moisture content higher than Biolan biochar.

5.2 Chemical analysis

The chemical content in the greywater after the filtration test was determined by the chemical analysis. Photometer was used for the chemical analysis. Hach Lange DR3900 is the name of the photometer used for the analysis of chemical content. While doing TN analysis, Hach Lange LT200 was used for heating the cuvettes. The chemical kits for TN analysis is called LCK 138 which measurement range is from 1-16 mg/l TN_b and for TP analysis is called LCK 348 which measurement range is from 0.5 – 5 mg/l PO_4–P or 1.5 – 15 mg/l PO_4. As the concentration of N and P in the greywater is beyond the range of these chemical kits, dilution of chemicals was done. 1:5 and 1:10 dilution were done for TN and TP analysis. The adsorption percentage of nutrients by pure and FS enriched biochars are shown in Table 6.

Table 6. Table showing the nutrients adsorption results in percentage by pure and FS enriched biochars.

Nutrients	Adsorption (%) by			
	Pure		FS enriched	
	Biolan	RPK	Biolan	RPK
TN	9	10	23	6
TP	27	25	39	41

5.3 Statistical analysis

The statistical analysis of the experimental results obtained from the chemical analysis was done using the software RStudio. At first, the obtained result was arranged in data matrix format, as shown in Table 7.

Table 7. Table showing the chemical content in the greywater after filtration through different filter mediums. The data are put into data matrix format.

1	Experiment	Biochar	FS	Total_N	Total_P
2	T1	no	no	9.26	6.09
3	T1	no	no	9.09	5.84
4	T1	no	no	10.9	6.41
5	T1	no	no	11.5	6.1
6	T1	no	no	11.4	6.7
7	T2	no	no	11.5	4.05
8	T2	no	no	8.6	5.18
9	T2	no	no	9.97	4.19
10	T2	no	no	8.93	4.72
11	T2	no	no	9.06	4.67
12	T3	Biolan	no	9.18	5.13
13	T3	Biolan	no	10.6	5.19
14	T3	Biolan	no	10.7	3.98
15	T3	Biolan	no	8.97	4.06
16	T3	Biolan	no	8.14	4.23
17	T4	RKP	no	10.4	4.63
18	T4	RKP	no	10.5	4.85
19	T4	RKP	no	10.3	4.55
20	T4	RKP	no	7.8	4.79
21	T4	RKP	no	7.55	4.48
22	T5	Biolan	yes	8.48	3.68
23	T5	Biolan	yes	8.77	4.18
24	T5	Biolan	yes	7.29	3.34
25	T5	Biolan	yes	8.42	4.2
26	T5	Biolan	yes	7.25	3.68
27	T6	RKP	yes	10	3.37
28	T6	RKP	yes	9.42	3.86
29	T6	RKP	yes	10.4	4.06
30	T6	RKP	yes	10.1	4.05
31	T6	RKP	yes	9.19	2.94

The chemical analysis for both TN and TP were replicated, hence forming two sets of data, i.e. data sets from original measurements and replicate measurements, as shown in appendix 2. ANOVA and Tukey test was used for the statistical analysis of original data sets. The replicated data sets were used to calculate the standard pooled variance, which clarifies the cause of variation of data.

5.3.1 Total N adsorption

The scatter plot of experimental results of TN analysis was carried out in RStudio (Figure 8).

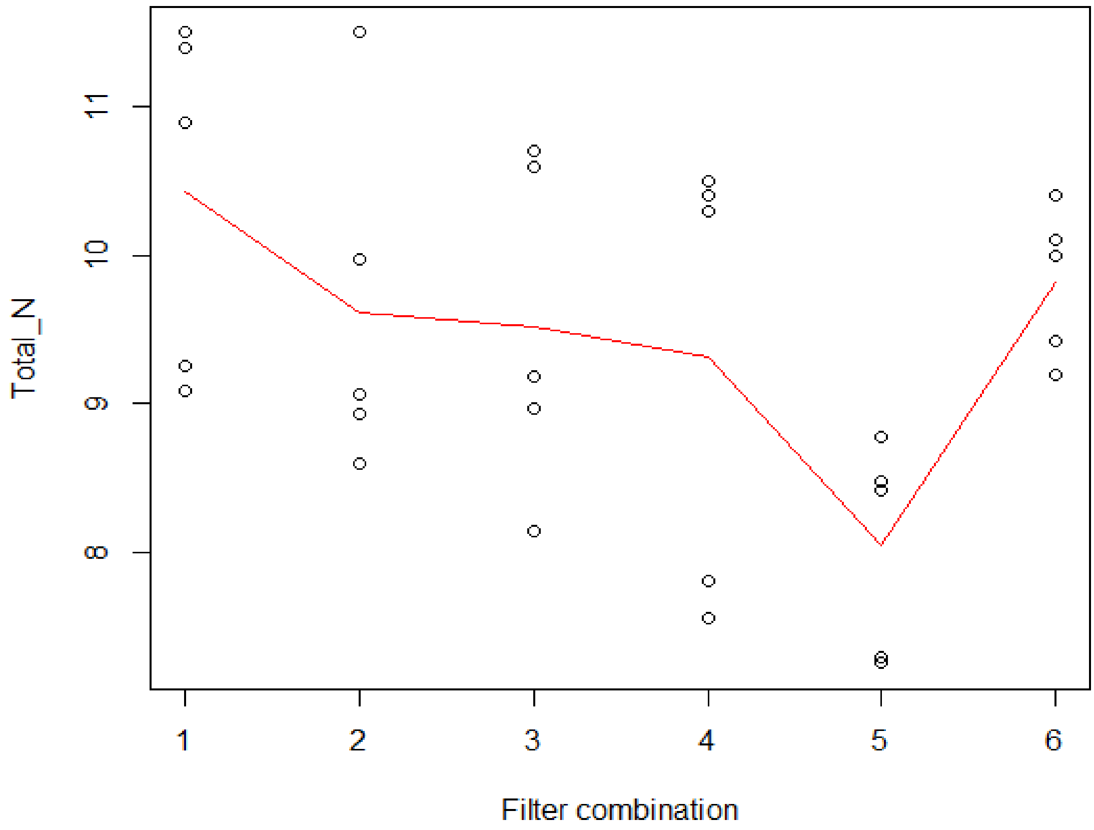

Figure 8. Plot showing the adsorption of TN by different filter combinations. X-axis represents filter combinations and Y-axis represents TN concentration in mg/l after filtration and adsorption through different filters.

Filter combinations used in the experiments are control, sand, sand + Biolan biochar, sand + RPK biochar, sand + Biolan biochar + FS and sand + RPK biochar + FS, which are represented by 1, 2, 3, 4, 5 and 6, respectively in the scatter plots (Figures 8 and 9). The red line indicates the mean value of the experimental results of each filter combination. Five replicate filtration experiments were carried out for each filter combinations and two replicate chemical analyses was done.

Before carrying out the statistical analysis, following hypothesis was made:
H0: There is no significant difference between the adsorption of TN by pure biochar and FS enriched biochar.
H1: There is significant difference between the adsorption of TN by pure biochar and FS enriched biochar.

At first, one-way ANOVA was carried out to determine whether there are any significant differences between the means of the six different filters. The statistical analysis results (Appendix 2B) showed the means of the filters were statistically significant at the significance (α level) of 0.05 (p-value = 0.0452). In simpler words, there is significant difference in the adsorption of TN by different filter groups. As only the interaction term was significant in the two-way ANOVA, it was enough to carry out the one-way ANOVA and corresponding Tukey test thereafter. The interaction of Biochar and FS was statistically significant with p-value 0.0461 (Appendix 2B), i.e. the FS enriched biochars have the significant adsorption of TN.

In order to find out specifically which filter combination shows significant result Tukey test was carried out. From the Tukey test it was found that Biolan + FS has significant effect in adsorption of TN, thus rejecting null hypothesis (H0) and concluding that there is significant difference between the adsorption of TN by pure biochar and FS enriched biochar. It is also illustrated from the scatter plot (Figure 8) that the filter combination 5, i.e. Biolan + FS has the lowest value of TN. It means that the filtration through this filter has higher efficiency of adsorbing or capturing the TN than other filter combination. However, the filter combination 6, i.e. RPK biochar + FS has no significant effect in the adsorption of TN, thus there is no enough evidence to reject H0 by FS enriched RKP biochar.

5.3.2 Total P adsorption

The scatter plot of experimental results of phosphorous analysis carried out in RStudio is shown in Figure 9.

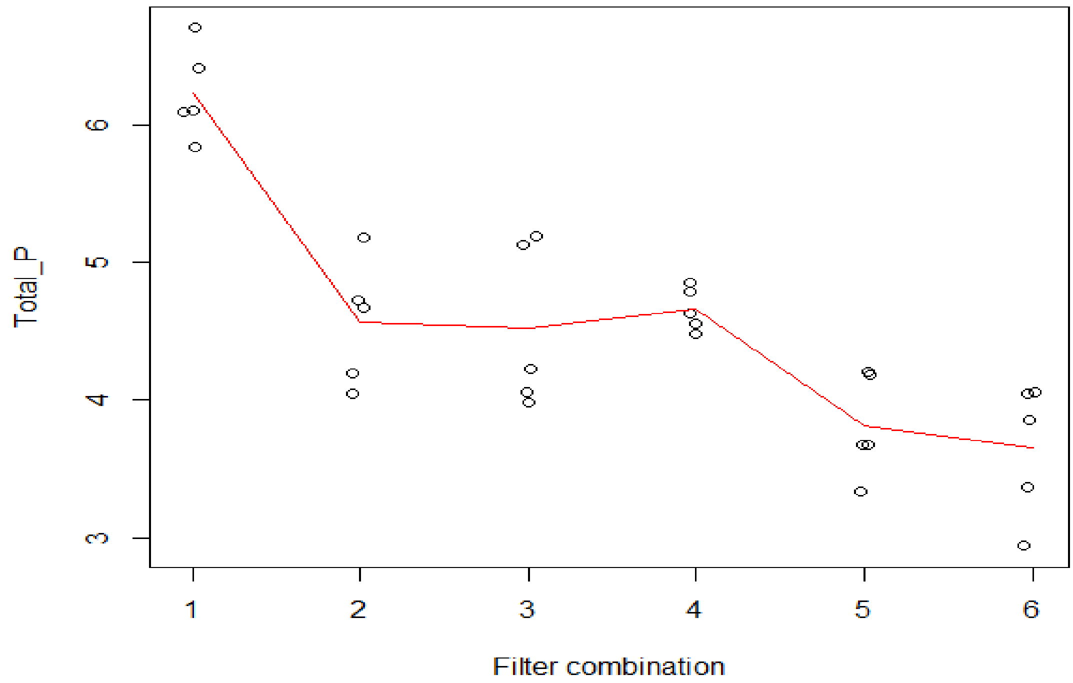

Figure 9. Plot in RStudio showing the adsorption of total phosphorous by different filter combinations. X-axis represents filter combinations and Y-axis represents total phosphorous concentration in mg/l after filtration and adsorption through different filters.

The hypothesis made in for this analysis is

H0: There is no significant difference between the adsorption of TP by pure biochar and FS enriched biochar.

H1: There is significant difference between the adsorption of TP by pure biochar and FS enriched biochar.

Similar to TN analysis, one-way ANOVA was carried out for total P adsorption to determine whether there are any significant differences between the means of the six different filters. The statistical analysis results (Appendix 2C) showed the means of the filters in the adsorption of TP were statistically highly significant at the significance (α level) of 0.001 (p-value = 1.64e-08). In simpler words, there is significant difference in the adsorption of TP by different filter groups. Similarly, only the interaction term was significant in the two-way ANOVA, hence only one-way ANOVA was carried out and corresponding Tukey test thereafter. The interaction of Biochar and FS was statistically highly significant with p-value 0.000446 (Appendix 2C), i.e. the FS enriched biochars have the significant adsorption of TN.

From the Tukey test it was found that Biolan biochar + FS and RPK biochar + FS have significant effect in adsorption of TP, thus rejecting null hypothesis (H0) and concluding that there is significant difference between the adsorption of TP by pure biochar and FS enriched biochar. It is also illustrated in the scatter plot (Figure 9) that these filters (5 and 6) have lowest concentration of TP. It means that the filtration through these filters has higher efficiency of adsorbing or capturing TP than other filter combinations.

6 Discussion

The main aim of this thesis was to determine the efficacy of biochar and FS enriched biochar in the adsorption of major nutrients (N and P) from the greywater. The adsorption of nutrients in biochar can be one of the efficient and cheapest technologies for capturing nutrients, and storing and recycling them for future use. The major benefits gained from the efficient application of this thesis work are utilization of waste dusty charcoal that is produced during the industrial manufacture of charcoal, which is not good enough to use for BBQ, treatment of greywater, recycling of N and P, control of eutrophication, prevention of global warming, carbon sequestration and plant production.

6.1 Biochar and FS enriched biochar adsorption capacity

There has already been lot of researches to investigate the biochar capacity to adsorb nutrients. For example, the biochar made from peanut hull at 600^0C used in a column of leaching experiment to assess nutrients holding ability in a sandy soil, has effectively reduced the total amount of nitrate and phosphate in the leachates by 34.0% and 20.6% (Yao et al., 2012). But there are not any publications yet studying the sorption capacity of FS enriched biochar. This thesis project was the first attempt to use FS enriched biochar as filter/sorption medium.

In the filtration test of this thesis project, the use of FS enriched Biolan biochar has reduced the total amount of nitrate and phosphate by 23% and 39% respectively. Similarly, FS enriched RKP biochar has reduced the total amount of nitrate and phosphate by 6% and 41% respectively. From the experimental results, it is clear that biochar enriched with FS has high adsorption capacity of nutrients rather than just use of pure biochar only. A 30% v/v concentration of pure biochar was also able to adsorb nutrients to some extent, and a same amount of biochar enriched with FS was able to adsorb nutrients significantly. If the volume-volume percentage of biochar is higher, then the use of pure biochar only also might have significant adsorption. Hence, it would be interesting for the further research to investigate the use of biochar at different volume levels and also with full volume of pure biochar. Just from the results of this thesis project it can be concluded that FS enriched biochar could be promising technology for capturing TN and TP.

6.2 Comparison of Biolan and RPK biochar

As mentioned earlier, FS enriched Biolan biochar adsorbed a significant amount of TN, whereas FS enriched RKP biochar showed a very low percentage of TN adsorption giving statistically very insignificant result. It is hard to give just one specific reason for it, as there might be lot of factors behind it such as feedstock, pyrolysing temperature, retort type, heat retention time, rate of change of temperature while pyrolysis process, and original Iron (Fe) content in biochar. In this thesis project, the original Fe content of both biochars is not known and this Fe content might be one of the main reasons in giving the difference in results. Hence, in this case, it would be interesting for further research to know the Fe content in each biochar. Biolan biochar uses hardwood (alder and aspen) as feedstock and pyrolysis is carried out in batch retort at 450^0C for a holding time of 12h, whereas, RKP biochar uses birch (Betula sp.) as feedstock and pyrolysis is carried out in batch retort at 450^0C for a holding time of 23h. The pH of Biolan biochar was 9.46 and RKP biochar was 9.16. The storage time of the chars were also unknown because of commercially produced biochar, aging and moisturing may change the surface area of charcoal very much.

6.3 Filtration test accuracy

In order to get highly precise results, all the experimental parts were handled in proper manner with the repeatability (replication of measurements, by single analyst using same apparatus over short period of time) of experiment. Also to get unbiased result, i.e. to get greatest reliability and validity of statistical estimates randomization was done; the cluster randomization was done in this thesis work. However, there was lot of variation of data in the results of each filter combination. This variation can be due to either experimental error or measurement error. In order to determine the source of variation, the pooled standard error was calculated from the replicate measurement of chemical analysis and statistical analysis of data was done by using ANOVA. The calculated pooled standard error represents measurement error whereas ANOVA represents the experimental error. The criteria for knowing the cause of variation is that if experimental error is slightly greater than measurement error, then the latter is the main cause of variation, whereas, if experimental error is significantly greater than the measurement error, then the former is the cause of variation.

The experimental and measurement error for TN analysis are 1.028 and 1.025, respectively. Here, the experimental error is slightly greater than the measurement error, so it is concluded that the main cause of variation is by measurement error during the chemical analysis part. It is also concluded that there is no error in the experimental part, i.e. in the filtration experiment. Similarly, for TP analysis, experiment error (0.433) is slightly greater than measurement error (0.348). Hence, it is concluded that the variation of data is the measurement error during the chemical analysis of TP. As the analysis of N and P is very sensitive, there is high probability of getting error if it is not conducted by the professionals in the laboratory. The chemical analysis of this thesis work was conducted by me under the supervision of lab teacher and thesis supervisor. If further research work is done, then I would suggest for the professionals to do a chemical analysis in order to get reliable results.

6.4 Comparison of dry and wet method of addition of FS

In the filtration experiment, the enrichment of biochar with ferric sulphate was performed by using the dry method. All the above results that has used FS in their filter combination is based on the dry method. There might be the difference in the results by the addition of FS in dry and wet state. In order to make it clear, reproducibility of the experiment but using FS in wet state, was conducted by Researcher Scientist Marleena Hagner, Helsinki University, Department of Biological and Environmental Science. The results of the reproduced experiments in percentage are shown in appendix 4. It is a bar graph illustrating P adsorption by sand, Biolan biochar, sand + FS (wet method) and Biolan biochar + FS (wet method). Using dry FS with Biolan biochar the adsorption of TP was 39% which lower than that from wet addition of FS (60%). However, the results of these two methods cannot be compared because the methods were not exactly same (particle size, volumes, leaching time etc., were varied). Hence, it cannot be concluded based on this result whether dry or wet method is better. In order to get exact comparison, further study should be done with exactly the same parameters and by same analyst.

6.5 Use of end product as carbon sequestration

Due to unique properties of biochar, it is highly stable than any other organic substances (Nguyen et al., 2008). The biochar can be the effective substance for the carbon sequestration and its addition to the soil can be useful to sink carbon for many years. From the certain amount of carbon that cycles annually through plants, about half a percentage of that carbon can be taken out of its natural cycle and can be sequestered in slower biochar cycle. The pyrolysis temperature with the residence time effects in the stability of biochar. The degree of condensation of the aromatic rings gives the information of stability of biochar in soil (Lehmann and Joseph, 2009). It has been found that the biochar derived from wood has 10-1000 times longer residence time in soils than other soil organic matter (Verheijen et al., 2010). Swift(2001) has estimated the mean residence time of biochar of 10,000 years in soils. Moreover, biochar is also found to remain integral in deep sea environment for up to 13,900 years (Masiello and Druffel, 1998).

7 Conclusion

Based on the results and discussion it can be concluded that biochar enriched with FS can be one of cost effective pioneering technology in adsorbing and capturing TN and TP from greywater or wastewater. The statistical analysis of adsorption results showed that FS enriched Biolan biochar is capable to adsorb both TN and TP significantly, whereas FS enriched RPK biochar is capable to adsorb only TP significantly. It can be concluded that the addition of FS into biochar enhances the adsorption property of biochar, especially mentioning about TP adsorption. The flocculent and magnetic properties of FS might have increased the adsorption quality of biochar by attracting nutrients easily and forming bond on porous surface of biochar.

The difference in the TN adsorption rate of Biolan (increase in adsorption significantly) and RPK (decrease in adsorption) biochars after addition of FS gave very inconclusive results. Due to contradiction in the results, it cannot be fully claimed that FS addition has increased the adsorption of TN. Further research work is needed to give better conclusion on the ability of FS enriched biochar to adsorb TN.

The filter mediums with only sand and sand + biochar (both Biolan and RPK) are able to adsorb nutrients in very little amount. The addition of only pure biochar to sand has increased the adsorption rate to some extent, but the difference is not statistically significant. The small increase in the adsorption rate might be due to use of only 30% by volume of biochar as filter medium, If the used biochar volume was higher, then the adsorption of nutrients might be significant. Therefore, further research work is needed with the use of higher volume of biochar as filter medium in order to know if only pure biochar is capable to adsorb nutrients effectively.

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Appendix 1

A. Material requirement

1. Funnels
2. Filter paper
3. Sponge (polyeurathene)
4. Small bottles
5. Stands
6. Bucket (>9L)
7. Volumetric flask
8. Pipette
9. Photometer (Hach Lange LT200)
10. Chemical kits (LCK 138 and LCK 348)
11. Beaker

B. Chemical requirement

1. Fertilizer (Yaracombi)
2. Ferrous sulfate
3. Water

C. Moisture content and BD measurement

Table 8. Moisture content and BD measurement of sand and biochars.

	Empty crucibles wt. (g)	**Wt. Before dry**	**Actual wt. Of sample (g)**	**Wt. After dry(g)**	**Moisture content (g)**	**Moisture %**		**Volume (mL)**	**Bulk Density, BD (g/mL)**	**Bulk Density, BD (g/L)**
Sand	144.8	287.3	142.5	287.7	0			69	1.449275	1449.275
	137.6	269.9	132.3	270.1	0			69	1.449275	1449.275
	138.6	295.6	157	295.7	0			68	1.470588	1470.588
	148.6	280.1	131.5	280.3	0			67	1.492537	1492.537
					0	**0**	*Average:*	68.25	1.465419	1465.419
RPK Biochar	94.2	120	25.8	111.3	8.7			61	0.245902	245.9016
	93.9	121.8	27.9	112.1	9.7			61	0.245902	245.9016
	96.9	127	30.1	116.9	10.1			62	0.241935	241.9355
	95.9	126	30.1	117.2	8.8			61	0.245902	245.9016
		Sum:	113.9		37.3	**32.74802**	*Average:*	61.25	0.24491	244.9101
Biolan Biochar	135.6	196	60.4	187.8	8.2			49	0.816327	816.3265
	140.3	219.7	79.4	211.8	7.9			51	0.784314	784.3137
	147.2	242.9	95.7	232.9	10			50	0.8	800
	143.7	213.3	69.6	207.4	5.9			50	0.8	800
		Sum:	305.1		32	**10.48836**	*Average:*	50	0.80016	800.1601

Note: In measuring volume of sand, RPK biochar, Biolan biochar the mass of sample used were 100g, 15g and 40g respectively.

Appendix 2

A. Chemical analysis of results

The data shown in red color are the repeatability, i.e. replicate measurement of chemical analysis. The highest value and lowest value from the replicate experiments were repeated.

Table 9. Chemical analysis results in excel sheet with the repeatability.

Experiment	TNb	Rep_TNb	St. Deviation	Variance	P_Total	Rep_P	St. Deviation	Variance
T1	9.26	10.1	0.593969696	0.3528	6.09	6.09		
T1	9.09	9.09			5.84	5.84		
T1	10.9	10.9			6.41	6.41		
T1	11.5	10.5	0.707106781	0.5	6.1	6.1		
T1	11.4	11.4			6.7	6.7		
T2	11.5	9.49	1.42128463	2.02005	4.05	4.5	0.318198052	0.10125
T2	8.6	8.39	0.148492424	0.02205	5.18	4.35	0.586898628	0.34445
T2	9.97	9.97			4.19	4.19		
T2	8.93	8.93			4.72	4.72		
T2	9.06	9.06			4.67	4.67		
T3	9.18	9.18			5.13	5.13		
T3	10.6	10	0.424264069	0.18	5.19	4.25	0.664680374	0.4418
T3	10.7	10.7			3.98	3.84	0.098994949	0.0098
T3	8.97	8.97			4.06	4.06		
T3	8.14	9.89	1.237436867	1.53125	4.23	4.23		
T4	10.4	10.4			4.63	4.63		
T4	10.5	10.7	0.141421356	0.02	4.85	4.85		
T4	10.3	10.3			4.55	4.55		
T4	7.8	7.8			4.79	4.79		
T4	7.55	10.3	1.944543648	3.78125	4.48	4.48		
T5	8.48	8.48			3.68	3.68		
T5	8.77	8.77			4.18	4.18		
T5	7.29	7.29			3.34	3.08	0.183847763	0.0338
T5	8.42	8.42			4.2	3.96	0.169705627	0.0288
T5	7.25	7.25			3.68	3.68		
T6	10	10			3.37	3.37		
T6	9.42	9.42			3.86	3.86		
T6	10.4	10.4			4.06	3.89	0.120208153	0.01445
T6	10.1	10.1			4.05	4.05		
T6	9.19	9.19			2.94	2.95	0.007071068	5E-05
			Pooled variance =	1.050925			Pooled variance =	0.1218
			Pooled stdev =	1.025146331			Pooled stdev =	0.34899857

B. Statistical results of total N analysis

Results of one way ANOVA, tukey test and two way ANOVA, in ascending order from top to the bottom, of total N adsorption by different filter combination.

```
            Df Sum Sq Mean Sq F value Pr(>F)
Experiment   5  15.66   3.131   2.697 0.0452 *
Residuals   24  27.86   1.161
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
  Tukey multiple comparisons of means
    95% family-wise confidence level

Fit: aov(formula = TNb ~ Experiment, data = NP)

$Experiment
        diff        lwr        upr     p adj
T2-T1 -0.818 -2.9250068  1.2890068 0.8323433
T3-T1 -0.912 -3.0190068  1.1950068 0.7614033
T4-T1 -1.120 -3.2270068  0.9870068 0.5795166
T5-T1 -2.388 -4.4950068 -0.2809932 0.0199345
T6-T1 -0.608 -2.7150068  1.4990068 0.9447025
T3-T2 -0.094 -2.2010068  2.0130068 0.9999920
T4-T2 -0.302 -2.4090068  1.8050068 0.9975627
T5-T2 -1.570 -3.6770068  0.5370068 0.2311261
T6-T2  0.210 -1.8970068  2.3170068 0.9995764
T4-T3 -0.208 -2.3150068  1.8990068 0.9995957
T5-T3 -1.476 -3.5830068  0.6310068 0.2894208
T6-T3  0.304 -1.8030068  2.4110068 0.9974852
T5-T4 -1.268 -3.3750068  0.8390068 0.4486265
T6-T4  0.512 -1.5950068  2.6190068 0.9730087
T6-T5  1.780 -0.3270068  3.8870068 0.1328049

            Df Sum Sq Mean Sq F value Pr(>F)
Biochar      1  3.089   3.089   2.924 0.1066
FS           1  1.162   1.162   1.099 0.3100
Biochar:FS   1  4.940   4.940   4.676 0.0461 *
Residuals   16 16.905   1.057
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
```

Figure 10. Statistical analysis of total N using ANOVA and Tukey test in RStudio.

C. Statistical results of total P analysis

Results of one way ANOVA, tukey test and two way ANOVA, in ascending order from top to the bottom, of total P adsorption by different filter combination.

```
            Df Sum Sq Mean Sq F value   Pr(>F)    
Experiment   5 20.818   4.164   23.43 1.64e-08 ***
Residuals   24  4.266   0.178                     
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
  Tukey multiple comparisons of means
    95% family-wise confidence level

Fit: aov(formula = P_total ~ Experiment, data = NP1)

$Experiment
        diff        lwr         upr     p adj
T2-T1 -1.666 -2.4904196 -0.84158039 0.0000251
T3-T1 -1.710 -2.5344196 -0.88558039 0.0000169
T4-T1 -1.568 -2.3924196 -0.74358039 0.0000611
T5-T1 -2.412 -3.2364196 -1.58758039 0.0000000
T6-T1 -2.572 -3.3964196 -1.74758039 0.0000000
T3-T2 -0.044 -0.8684196  0.78041961 0.9999805
T4-T2  0.098 -0.7264196  0.92241961 0.9990044
T5-T2 -0.746 -1.5704196  0.07841961 0.0923122
T6-T2 -0.906 -1.7304196 -0.08158039 0.0254123
T4-T3  0.142 -0.6824196  0.96641961 0.9942286
T5-T3 -0.702 -1.5264196  0.12241961 0.1276500
T6-T3 -0.862 -1.6864196 -0.03758039 0.0367657
T5-T4 -0.844 -1.6684196 -0.01958039 0.0426410
T6-T4 -1.004 -1.8284196 -0.17958039 0.0108424
T6-T5 -0.160 -0.9844196  0.66441961 0.9900208

            Df Sum Sq Mean Sq F value   Pr(>F)    
Biochar      1  0.000   0.000   0.002 0.963535    
FS           1  3.638   3.638  19.372 0.000446 ***
Biochar:FS   1  0.114   0.114   0.607 0.447264    
Residuals   16  3.005   0.188                     
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
```

Figure 11. Statistical analysis of total P using ANOVA and Tukey test in RStudio.

D. Wet method of addition of FS

Biochar and sand reduced P leaching about 50%. When mixed FS with sand the reduction was 88%, instead when mixed FS with biochar the reduction was about 60%. So when used FS (liquid form) the sand act better than biochar.

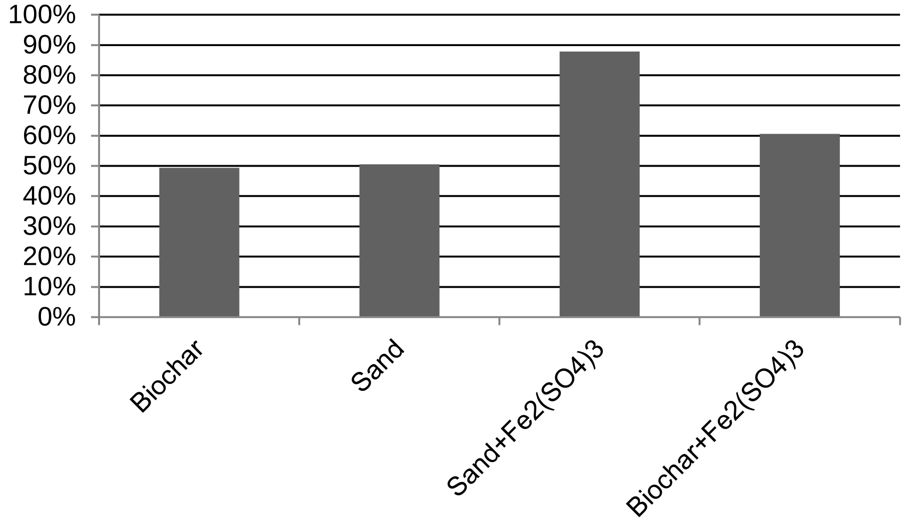

Figure 12. Plot of total P adsorption using the wet method of addition of ferric sulphate.

When comparing sand only and biochar only treatments, there is no difference → biochar had no effect on the TP concentration of leachates. When compared FS treatments, sand+FS works better than biochar+FS, i.e. by adding the biochar the reduction was decreased. So in this study the FS was the reason for decrease in TP not biochar. The particle size of used biochar was 1-10 mm.