THE EFFICACY OF TWO BIOCHAR VARIANTS AS FILTRATION MATERIAL FOR THE IMPROVEMENT OF RIVER WATER QUALITY

By

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DECLARATION

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ABSTRACT

The safety of irrigation water from rivers is continuously diminishing and has a direct effect on the safety of fresh produce. Not only can irrigation water be the source of pathogenic contamination, but it can also be a source of other physical and chemical contamination into the food system. The reduction or removal of these contaminants from river water for irrigational use may be achieved using a combination of water treatments. One such treatment includes the alternative use of biochar as a filtration media to improve the river water quality. Little is known about biochar as a possible adsorbent of contaminants from water mediums in filtration systems. The aim of the study was thus to determine the efficacy of biochar filtration to improve the river water quality.

Open-ended filtration columns were constructed with two variants of biochar and compared to granular activated carbon (GAC). Untreated river water was exposed to these columns and analysed to determine the quality of the treated water both microbiologically and physicochemical. The pine and black wattle biochar, as well as the GAC, did not improve the microbiological quality of the untreated river water. In certain runs the heterotrophic plate count (HPC), faecal coliforms and *Enterobacteriaceae* were increased by the treatments, possibly due to the formation of biofilms in the columns. The pine biochar did, however, have the least negative effect on the microbial status of the untreated river water. Furthermore, the pine biochar was also more effective than the black wattle biochar and GAC at improving the COD, TSS, VSS, turbidity and UVT% of the untreated river water. The pine biochar filtration showed the most promising results and showed the most effective improvement on the UVT% of the untreated river water (from 33.9% to 97.7%). As a result of this improvement it was decided to expose the untreated river water to filtration and UV irradiation. The combined treatment with the biochar filtration and UV treatment lead to more effective and efficient reduction of microorganisms and the removal of STEC.

Closed filtration columns were then constructed to enable complete saturation of the pine biochar filtration media. Untreated river water was filtered using these columns and the microbiological and physicochemical characteristics of the filtrates were analysed. The pine biochar filtrates only reduced the faecal coliforms from the untreated river water and more so when the filtrate was resting in the column for three days. The GAC filtrates did not indicate reduction of faecal coliforms. The physico-chemical properties of the untreated river water were best improved by the pine biochar filtration media. The UVT% and turbidity were improved as effectively as with the with open-ended columns. Both these properties of the

untreated river water were further improved when the river water sample remained exposed to the columns for three days.

Furthermore, improvement of the untreated river water using biochar filtration systems is dependent on the type of biochar as well as the design of the filtration columns. The filtration with biochar alone could not improve the untreated river water to conform to standards for irrigational use. This may be achieved when using it in combination with other treatments such as UV irradiation.

UITTREKSEL

Die veiligheid van besproeiingswater vanaf riviere word gedurig verminder en het 'n direkte invloed op die veiligheid van varsprodukte. Nie net kan besproeiingswater die bron van patogeniese kontaminasie wees nie, maar dit kan ook 'n bron van ander fisiese en chemiese besmetting in die voedselstelsel wees. Die vermindering of verwydering van hierdie kontaminante van rivierwater vir besproeiings gebruik kan bereik word met behulp van 'n kombinasie van waterbehandelings. Een so 'n behandeling sluit in die alternatiewe gebruik van biochar as 'n filtrasie media om die rivierwatergehalte te verbeter. Daar is min studies bekend oor die gebruik van biochar in filtrasie stelsels as 'n moontlike alternatief vir die absorpsie van kontaminante vanaf watermediums. Die doel van die studie was dus om die doeltreffendheid van biochar-filtrasie te bepaal om die rivierwatergehalte te verbeter.

Oop geëindig filtrasie kolomme is gebou met twee variante van biochar en met korrel geaktiveerde koolstof (GAC) vergelyk. Onbehandelde rivierwater is aan hierdie kolomme blootgestel en ontleed om die gehalte van die behandelde water, beide microbiologies en fisiochemies, te bepaal. Die denne-en swart wattel-biochar, asook die GAC, het nie die mikrobiologiese gehalte van die onbehandelde rivierwater verbeter nie. In sekere gevalle is die heterotrofiese plaattelling (HPC), fekale kolivorme en *Enterobacteriaceae* verhoog deur die behandelings, moontlik as gevolg van die vorming van biofilms. Die denne-biochar het egter die minste negatiewe uitwerking op die mikrobiese status van die onbehandelde rivierwater gehad. Verder was die denne-biochar ook meer effektief as die swart wattel biochar en GAC met die verbetering in COD, TSS, VSS, turbiditeit en UVT% van die onbehandelde rivierwater. Die denne-biochar filtrasie het die mees belowende resultate getoon en het die mees effektiewe verbetering op die UVT% (97,7%) van die onbehandelde rivierwater (33,9%) gehad. As gevolg van hierdie verbetering was daar besluit om die onbehandelde rivierwater aan biochar filtrasie en UV-bestraling bloot te stel. Die gekombineerde behandeling van die biochar filtrasie en UV behandeling lei tot meer effektiewe en doeltreffende vermindering van mikro-organismes en die verwydering van STEC.

Geslote filtrasie kolomme was daarna gebou om volledige versadiging van die denne biochar filtrasie media te verseker. Onbehandelde rivierwater was met behulp van hierdie kolomme gefiltreer en die mikrobiologiese en fisikochemiese eienskappe van die filtrate was geanaliseer. Die denne biochar filtraat het slegs die fekale kolivorme van die onbehandelde rivierwater verminder en meer nog toe die filtraat vir drie dae in die kolom rus. Die GAC filtrate het nie die vermindering van fekale kolivorme aangedui nie. Die fisicochemiese

eienskappe van die onbehandelde rivierwater was die beste verbeter deur die denne-biochar filtrasie media. Die verbetering van UVT% en turbiditeit was net so effektief soos met die oop geëindig kolomme. Beide hierdie eienskappe van die onbehandelde rivierwater was verder verbeter toe die rivierwatermonster vir drie dae lank aan die kolomme blootgestel was.

Verder is die verbetering van die onbehandelde rivierwater met behulp van biochar-filtrasie stelsels afhanklik op die tipe biochar, asook die ontwerp van die filtrasie kolomme. Die filtrasie met biochar alleen kon nie die onbehandelde rivierwater verbeter om te voldoen aan standaarde vir die gebruik as besproeiingwater nie. Dit kan egter bereik word deur die gebruik van die biochar filtrasie kolomme in kombinasie met ander behandelings, soos UV bestraling.

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ABBREVIATIONS

ADRV	Adult Diarrhoea Rotavirus
CEC	Cation Exchange Capacities
CFU	Colony Forming Units
COD	Chemical Oxygen Demand
DAF	Dissolved Air Flotation
DOC's	Dissolved Organic Carbon's
E. coli	*Escherichia coli*
EC	Electrical Conductivity
GAC	Granular Activated Carbon
HPC	Heterotrophic Plate Count
HUS	Haemolytic-Uraemic Syndrome
MF	Microfiltration
NF	Nanofiltration
NOM	Natural Organic Matter
NP	Nano particle
PAA	Peracetic Acid
PCA	Plate Count Agar
RO	Reverse Osmosis
ROS	Reactive Oxygen Species
SAR	Sodium Adsorption Ratio
STEC	Shiga-Toxin producing *E. coli*
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
UF	Ultrafiltration
UV	Ultraviolet
UVT%	Ultraviolet Transmission percentage
VRBA	Violet Red Bile Agar
VRBGA	Violet Red Bile Glucose Agar
VSS	Volatile Suspended Solids
WHO	World Health Organisation
WWF	World Wildlife Fund

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This thesis is presented in the format prescribed by the Department of Food Science at Stellenbosch University. The structure is in the form of one or more research chapters (papers prepared for publication) and is prefaced by an introduction chapter with the study objectives, followed by a literature review chapter and culminating with a chapter for elaborating a general discussion and conclusion. Language, style and referencing format used are in accordance with the requirements of the *International Journal of Food Science and Technology*. This thesis represents a compilation of manuscripts where each chapter is an individual entity and some repetition between chapters has, therefore, been unavoidable.

CHAPTER 1

INTRODUCTION

BACKGROUND

Water is an essential component to the sustainment of all life and ecosystems on earth. It is thus just as essential to maintain and regulate fresh water sources as best as possible to ensure that wastage and pollution of the fresh water is decreased. This can become problematic due to climate change and the increase in the human population (Fischer-Jeffes *et al.*, 2017; WHO, 2017).

Climate change is occurring rapidly and leads to an annual rise in the temperature of the earth's surface, which results in a decrease in the water supply and the scarcity thereof, specifically in developing regions such as South Africa (Bizikova *et al.*, 2015; Nyamwanza & Kujinga, 2016). The demand for alternative water sources leads to the need for an effective treatment of wastewater and recycling thereof (Qadir *et al.*, 2010; Ganeshamurthy & Raghupathi, 2013). Not only will climate change aid in the decrease of natural water sources but also reduce the quality of the water as a result of the increased concentration of natural organic and inorganic pollutants present in the air (DWAF, 2005; Fabris *et al.*, 2008; Sampathkumar *et al.*, 2010).

These pollutants can occur naturally and can also be a result of wastewater deposits from industrial effluents and domestic wastes which are increasing due to the ever-increasing world population (DWAF, 2005; Park *et al.*, 2015). Natural organic matter (NOM) plays a major role in reducing the quality of water by reacting with chloride molecules (forming unwanted by-products), transporting hydrophobic organic compounds and metals, and contributing to the growth of bacteria, slime and increased corrosion (Matilainen *et al.*, 2004). Microbial pathogens such as *E. coli* and *salmonella* may be the greatest threat to the hazardous status of any source of water (Forsythe, 2010). The consumption of any pathogen may result in the occurrence of food borne illnesses and is therefore one of the primary contaminants of water, which should be removed (WHO, 2016). Treatments involved in reducing microbial contamination and removal of pathogens include chemical disinfectants and ultraviolet (UV) radiation (Schug, 2016; WHO, 2017). Heavy metals pose a great risk to the quality and safety of water due to its toxic and carcinogenic potential (Qadir *et al.*, 2010; Ahmed *et al.*, 2016). Some metals are challenging to reduce or completely remove from contaminated water due to the inability of the metal ion to bio-transform or biodegrade (Ali, 2010). Treatments of water to reduce or remove metal ions and organic compounds can be achieved using chemical, photochemical and physical treatments (Parsons & Jefferson, 2006; WHO, 2017). A commonly used method is chemical precipitation, which involves the use of hydroxide, sulphide, phosphate and carbonate (Son *et al.*, 2015; Schug, 2016; Tsai *et al.*, 2016). This treatment, however, results in the production of sludge which can lead to disposal problems. Furthermore, activated carbon, made from coal or biomass, is a form of physical treatment that is used in a filtration system which acts as an adsorbent (Schug, 2016). Although previous studies have shown that this method of treatment does adsorb pollutants from contaminated water, the production of the activated carbon is quite costly (Rivera-Utrilla *et al.*, 2001; Kearns *et al.*, 2014; Mohan *et al.*, 2014). These treatments (chemical precipitation and filtration with activated carbon) are used in series to obtain a quality of water suitable for both agricultural use and potential drinking water.

The quality of water, which should conform to irrigational guidelines, are resulting in a great demand for the treatment of contaminated ground and surface water. In Quebec, a province in Canada, for example, the regulation requires the treated water to have low amounts of trihalomethane levels (less than 80 $\mu g.L^{-1}$), low turbidity levels, and the absence of pathogenic microorganisms such as faecal coliforms, *Escherichia coli* (*E. coli*), *Enterococcus* bacteria, and coliphage viruses (Niquette *et al.*, 2011). The presence of these pathogenic microbes in water are of a particular problem in the rural communities worldwide where the water is untreated or limited treatment is available. This could result in a higher prevalence of infectious diseases in these regions (Hunter *et al.*, 2009; WHO, 2016). It is thus essential that treatment of irrigation water not only results in the complete removal of waterborne, pathogenic microbes but also be efficient, easy to operate and increase the re-usability of water sources (Qadir *et al.*, 2010). The removal of such contaminants are of major concern due to the carryover of pathogenic microorganisms onto the irrigated crops and thereby entering into the food chain. Contaminants such as inorganic matter may play a role in reducing the plant growth and thereby reducing the yield, resulting in increased crop loss (Ganeshamurthy & Raghupathi, 2013).

Activated carbon as mentioned earlier is an effective adsorbent for the reduction or elimination of heavy metals, however, it requires an extensive amount of energy to produce due to the high level of carbonisation required (Yang & Jiang, 2014; Schug, 2016). An alternative to activated carbon is the use of biochar which undergoes significantly less carbonisation and does not require an activation phase during production (Inyang & Dickenson, 2015; Tan *et al.*, 2015). Biochar is used to improve the properties of soil by increasing nutrient availability, microbial activity, soil organic matter, water retention and crop yield whilst it decreases fertiliser needs, greenhouse gas emissions, nutrient leaching and erosion (Dempster *et al.*, 2012; Mohan *et al.*, 2014; Iqbal *et al.*, 2015; Park *et al.*, 2015). It is produced from plant matter which is thermally degraded in the absence of air, a process formerly known as pyrolysis (Lehmann & Joseph, 2015; Santos *et al.*, 2015; Ahmed *et al.*, 2016).

Pyrolysis and the adjustment of parameters such as temperature and residence time during this process, can result in the production of biochar with varying characteristics, which may influence its absorbance capability (Inyang & Dickenson, 2015; Tan *et al.*, 2015). This relates to many characteristics of the biochar such as the degree of porosity and surface area thereof. The higher the temperature that is reached during pyrolysis and the longer this temperature is maintained will result in a greater degree of porosity within the biochar. This in turn will result in a larger surface area, which plays a role in increasing the adsorption of pollutants from contaminated water (Tang *et al.*, 2013; Jin *et al.*, 2016). The surface area of the biochar is increased further when exposed to water and thus increases possible binding sites for contaminants, as a result of relaxometric properties and the nonconventional hydrogen bonds (Conte *et al.*, 2013; Cernansky, 2015). Pyrolysis also influences the number of aromatic carbon molecules within the biochar structure. The aromatic carbons are in larger abundance in biochar than in other organic matter and specifically fused aromatic carbon structures. At lower pyrolysis temperatures the formation of amorphous fused aromatic carbon tends to occur whilst turbostratic fused aromatic carbon occurs at high pyrolysis temperatures. These aromatic carbon molecules play an important role in the chemical stability of the biochar structure. This stability is partially dependent on the type of biochar and influences the ability of microbes to utilise leached carbon, nitrogen or nutrients which have been mineralised, as an energy source (Lehmann *et al.*, 2011). The type of aromatic structure of different biochar organic matter, therefore, plays a role in stimulating or inhibiting the growth of microorganisms.

An influential characteristic of biochar is its electrostatic interactions with heavy metals, ionic and ionisable organic compounds, adding to the adsorption potential of the biochar (Tang *et al.*, 2013; Inyang & Dickenson, 2015). This is largely dependent on the net charge of the biochar surface as well as the cation exchange capacities (CEC). Higher pyrolysis temperatures, which result in greater surface area and loss of volatiles, lead to a decrease of potential CEC and charge density (Lehmann & Joseph, 2015). The CEC of soil is initially high and thus interacts with positively charged metals, however, upon the addition of biochar to the soil, an increase in pH occurs which results in the immobilisation of these heavy metals and optimally leads to the precipitation thereof (Tang *et al.*, 2013).

These characteristics can also aid in the reduction or complete removal of water-borne bacteria such as *E. coli*. Through the steric interactions, hydrophobic attraction and straining of a potential biochar filter, bacteria attachment occurs rapidly to the biochar. These interactions are largely influenced by the pH difference and change between the biochar and interacting water (Mohanty & Boehm, 2014). Furthermore, the use of transition metal oxide nano particle (NP) together with biochar increases its potential to remove pathogenic bacteria from contaminated water (Inyang & Dickenson, 2015).

This study was limited to one water source which was potentially polluted from industrial effluents and domestic waste. This will give an indication of the biochar adsorptive capacity and efficacy. Furthermore, the use of low technology filters will be used to estimate the potential efficacy of the biochar in a rural environment where funding for purification systems may not be available. The study could, therefore, contribute in providing clear results which may motivate the use of biochar as an alternative to activated carbon as a filtration media. This provides greater opportunities for rural farmers to implement filtration systems to increase their quality of water and may result in an increase in crop quality and yield. Furthermore, the use of biochar could reduce the use of other chemical treatments used in the purification of water and thus less raw chemical from the earth sources will be needed. The study may also indicate the importance of physical treatments in improving the status of water for subsequent treatments which it may benefit. This may increase the efficacy and efficiency of other treatments and thereby reduce energy and time which results in a more cost-effective system. Additionally, the biochar could potentially be used as a soil amendment after filtration, which would further increase the efficient use thereof.

The aim of the study was, therefore, to investigate the potential use of biochar as filtration media for the effective removal of contaminants from untreated river water. The first objective of the study was to investigate the difference in efficacy of two variants of biochar and a commercially produced activated carbon as filtration media. The second objective of the study was to investigate the potential that the pine biochar filtration system will have on the effective and efficient use of ultraviolet radiation on reducing microbial counts. Lastly, the adsorptive potential of biochar when increasing exposure time through the development of a closed filtration system was investigated.

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CHAPTER 2

LITERATURE REVIEW

2.1 GENERAL INTRODUCTION

Water, the source of life.

A crucial substance required in our everyday lives, yet not accessible to a substantial amount of people. Ocean water adds up to an estimated 98% of the total global water resource whilst less than 1% originates from surface water (rivers, dams, biological waters and soil moisture). Surface water is, for obvious reasons, on a much higher demand whilst the world population increases and especially within Third World countries. This surface water is the only accessible source of water which is used by all sectors of a country. Just like most semi-arid and arid countries in Africa, the water crisis in South Africa is becoming a major national problem (Bizikova *et al.*, 2015; Nyamwanza & Kujinga, 2016; Fischer-Jeffes *et al.*, 2017). According to The Department of Water and Sanitation of South Africa, a reduction in water levels as much as 26.9% has been observed in major water catchment areas between the years 2011 and 2017 (DWAF, 2013; DWA, 2016). An average water level of 64% from the South African water catchment areas for 2017, is not nearly sufficient to sustain the growing population of the country which is estimated to be over 56 million people for the same year (DWA, 2016; STATS SA, 2017). As the country's population increases at an annual rate of 1.61%, there is an obvious growing demand for water supplies whilst the limited supply from the water catchment areas remains limited and under pressure. It furthermore, creates pressure within the different sectors of South Africa (WWF SA, 2016; STATS SA, 2017). There are ten water supply systems operating in South Africa, of which the integrated Vaal River system supplies up to 80% of the nation's water (DWA, 2016).

National water usage is divided into a variety of sectors which include, irrigation, urban use, rural use, mining, bulk industry, power generation, and afforestation (DWAF, 2004). The South African agricultural sector, which predominantly consists of irrigation activities, consumes up to 63% of the nation's water supply (WWF-SA, 2017). This sector uses the majority of a nation's accessible water and relies mostly on rain-fed water and large-scale irrigation systems. The rain-fed water can be distinguished into two types of water resources. These resources include the runoff in streams, rivers and aquifers and the other source is related to the water embedded in the soil (Rijsberman, 2006). Due to water scarcity, the agricultural sector, with its demand for large quantities of water, can not only rely on the direct use of renewable water but has to consider all water sources and its interactive constituent in relation with water recycling (Rijsberman, 2006). The water used for irrigation, however, has to be of a certain quality to prevent crop-loss and foodborne illnesses. According to the South African Water Quality Guidelines, as indicated in Table 2.1, water which conforms to the given guidelines can be used for the following agricultural activities: production of commercial crops; irrigation water applications and distribution; home gardening; production of commercial floriculture crops; and potted plants (DWAF, 1996a; DWA, 2013).

Table 2.1. Agricultural Irrigation water quality guidelines indicating the ideal limitations of selected variables for acceptable water use

Variable	limits
pH	6.5 – 8.4
TDS/ Electric conductivity	< 40 $mS.m^{-1}$
Faecal coliforms	< 1 000 CFU per 100 mL
Sodium Adsorption Ratio (SAR)	< 2
Suspended solids	< 50 $mg.L^{-1}$

Reduction in water resources results in water-scarce areas due to environmental and economic stressors such as climate change, poor water system management and population increases (WHO, 2017b). The change in climate has a global impact on the availability of water resources as a result of the ever-increasing evaporation rate as the average surface air temperature increases annually (Nyamwanza & Kujinga, 2016). This can further lead to diminishing water quality due to increased concentration of pollutants. The change in climate also contributes greatly to other phenomena which can result in severe occurrences of water scarcity such as water table changes, droughts, floods, storms and erratic rainfall (Rijsberman, 2006; Nyamwanza & Kujinga, 2016). These environmental stressors, as well as the change in acidification levels in soil, plays a major role in influencing the quality of water by increasing natural organic matter (NOM) within water resources (Fabris *et al.*, 2008). The increasing demand for water resources due to the increased population creates a great deal of pressure on water supply systems (Rijsberman, 2006).

More specifically, certain key conditions such as safe and affordable water; sanitation; rural use; reduced groundwater in aquifers; and rivers unable to flow into seas and oceans, all contribute to the increased demand for water resources (Rijsberman, 2006). Restricted and limited financial investments in infrastructural development for the improvement of water scarcity, such as building more dams in newly identified water catchment areas, do not overcome the challenges of meeting the ever-increasing water demand, realising a backlash in water infrastructural maintenance and investments. The focus should, however, be on improving overall water productivity rather than depending on raw resources as the only supply of usable water (Rijsberman, 2006).

A water-scarce area is classified as a region with water availability of fewer than 500 m^3 per year per capita (FAO, 2018). Water scarcity is most prominent in semi-arid areas such as in Southern-, Western-, Eastern Africa and South Asia (Bizikova *et al.*, 2015). Particularly, developing countries such as in Sub Saharan Africa, experience a great deal of water scarcity and decreased water quality. These countries do not have the required infrastructure to manage water productivity effectively (Sampathkumar *et al.*, 2010; Nyamwanza & Kujinga, 2016). The influence of climate change on water scarcity is a complex one and it would thus be wise to invest in the increased development of water-related institutions (Nyamwanza & Kujinga, 2016). This may provide the stimulus for great innovations to improve sustainable water management, as well as lead to the development of proactive institutions (Nyamwanza & Kujinga, 2016). For South Africa, the World Wildlife Fund (WWF) suggests that becoming successful in reaching important goals would improve the future of water in the country (WWF-SA, 2017). These goals include the following:

- Become a water conscious country with sufficient knowledge and skill in the water sector.
- Implement strong water governance with resilient stakeholder partnerships that advance the more explicit 2nd phase of the National Development Plan to achieve water security under climate change.
- Manage water supply and demand regulations more rigorously and protect water resources.
- Become a water-smart economy and a leader in Africa in commercialising the low-water technology for industry and agriculture.

Pollution of water resources can originate from various sources and can result in unsafe and hazardous water. In South Africa, the greatest threats to the ever-diminishing water quality are mainly pollutants by acids originating from mine drainage and electricity production (McKee *et al.*, 2007; Muruven & Tekere, 2013; Rodda *et al.*, 2016). Surface water quality is also threatened by excessive nutrient inflow due to untreated wastewater from domestic lands, treated wastewater from the industrial sector, as well as sewage treatment works (McKee *et al.*, 2007; Rodda *et al.*, 2016). Untreated sewage water becomes a major problem and concern due to rural and urban migration which predominantly results in increased urban-dwelling within slums, as well as limited and poorly maintained water- and sanitation systems (Rodda *et al.*, 2016). The agricultural sector also plays a role in increasing the level of pollution in the water resources by the run-off from agricultural lands and uncontrolled disposal of wastewater from informal settlements (McKee *et al.*, 2007; Rodda *et al.*, 2016). In South Africa, the rivers and dams are mainly threatened by industrial effluent discharge, mining activities, alien plants and high evaporation rates (Rodda *et al.*, 2016).

The quality of water is determined by a set of important parameters in order to prevent the use of toxic or disease-causing water. Water quality is dramatically decreased by activities resulting in heavily polluted water resources which include, domestic wastes as well as industrial activities (Sampathkumar *et al.*, 2010). The pollutants found in water can significantly affect the acidity or alkalinity, chlorine content and turbidity of water resources, as well as the microbiological environment (DWAF, 2005). For example, in certain areas in India, which also exhibits high rates of population growth, it has been reported that many resources of surface water, as well as groundwater, are unsafe for human consumption, nor suitable for irrigation or industrial purposes (Sampathkumar *et al.*, 2010). The effect of these pollutants on water used for irrigation results in reducing plant growth and quality. Irrigation water which has specific microorganisms such as pathogenic bacteria, viruses and parasites, holds a major health risk to consumers of raw fruits and vegetables due to the increased probability of foodborne illnesses (Qadir *et al.*, 2010; Allende & Monaghan, 2015; Johannessen *et al.*, 2015). Irrigation water can thus become a major health concern due to its potential transfer of microbes to irrigated plants. There are, however, preventative actions which could be taken to reduce the microbial load or inhibit growth thereof within irrigation water (Jongman & Korsten, 2017). These preventative actions include water treatments such as; sodium hypochlorite; calcium hypochlorite; chlorine dioxide; ultrasound; UV-C; and membrane filtration pre-irrigation (Parsons & Jefferson, 2006; Li *et al.*, 2013; Allende & Monaghan, 2015; Schug, 2016; WHO, 2017b; WHO, 2017a).

Water resources with high levels of organic and inorganic trace elements can also become a health risk potentially resulting in acute or chronic health effects when transferred from irrigation water to the plant and ultimately to the consumer. These elements include heavy metals such as cadmium, chromium, nickel, lead and iron (Qadir *et al.*, 2010; Ahmed *et al.*, 2016). Organic matter and other nutrients including nitrogen, potassium and phosphorus compounds found in irrigation water, can result in the increased growth of certain vegetables (Abegunrin *et al.*, 2016). According to Paghupathi & Ganeshamurthy (2017), however, the occurrence of high levels of dissolved salts found in irrigation water could hinder the growth of plants due to the salts' toxic effect on the plant's physiological processes as well as playing a role in the nutritional disorder. These dissolved salts include major cationic salts such as sodium, calcium and potassium, whilst the major anionic salts include chloride, sulphate, bicarbonate, carbon trioxide and nitrate (Ganeshamurthy & Raghupathi, 2013). The quality of irrigation water could be improved by exposing it to certain treatments. These treatments, however, are not always feasible in developing countries. Alternative treatments such as water stabilisation ponds, constructed wetlands, infiltration percolation and up-flow anaerobic sludge blanket reactors could be used to improve irrigation water quality (Qadir *et al.*, 2010).

2.1.1 Detrimental factors influencing the quality and safety of the water.

The quality and safety of a specific water source can be determined by several measurable factors. These factors indicate whether the quality of water is suitable for drinking, irrigation or other activities which do not require the highest quality or specific guidelines. In addition, these factors also indicate the microbiological, biological, physical, chemical and hydrological characteristics of water.

2.1.1.1 Microorganisms and their water environment

Microorganisms are most likely the most direct threat to the safety of water (Forsythe, 2010). According to the World Health Organization (WHO), one-third of deaths in developing countries are caused by the consumption of contaminated water. The risk of acquiring a water-borne infection is dependent on the dose of pathogenic microorganisms within the water. Groundwater can be contaminated with bacteria, protozoa and viruses of which all have certain families and strains which can result in serious infection or disease. (Forsythe, 2010; Olivier, 2015; Ramirez-Castillo *et al.*, 2015; WHO, 2016; Sivhute, 2019).

Bacteria

Escherichia coli (E. coli)

One of the most common and fatal pathogens found in water is pathogenic *E. coli* such as *E. coli* O157: H7, which is a Shiga-toxin-producing *E. coli (*STEC) and is commonly known as Enterohaemorrhagic *E. coli (Cabral, 2010; Ramirez-Castillo et al., 2015)*. *E. coli* is a gram-negative, facultatively anaerobic bacterium which is not spore-forming and is part of the *Enterobacteriaceae* genus. It naturally occurs in the gastrointestinal tract of warm-blooded animals (Cabral, 2010; Forsythe, 2010). If this pathogen were to be consumed in a low dosage of up to 10 cells or less, it may lead to an infection resulting in severe illness such as bloody diarrhoea, haemorrhagic colitis, haemolytic-uraemic syndrome (HUS) and thrombotic thrombocytopenic purpura (Cabral, 2010; Forsythe, 2010; Ramirez-Castillo *et al.*, 2015). The STEC pathogen is responsible for many fatalities of children living in low and mid-income countries (Bortman *et al.*, 2002; Francis *et al.*, 2015). Other strains of *E. coli* such as Enterotoxigenic *E. coli* can also lead to infection resulting in mild illness after consuming up to 10^8-10^{10} cells (Cabral, 2010; Ramirez-Castillo *et al.*, 2015). Although there are many other pathogens from the *Enterobacteriaceae* family such as *Salmonella, Listeria monocytogenes*, and *Vibrio*, *E. coli* is the most prominent microbe and is thus the primary indicator organism when analysing water samples for microbial contamination (DWA, 2013; Francis *et al.*, 2015; WHO, 2016).

Salmonella

Salmonella species are of significant importance as pathogenic bacteria due to their causes of morbidity, mortality and economic loss (Forsythe, 2010). *Salmonella* is a genus of the *Enterobacteriaceae* family and has the following characteristics: Gram-negative, facultatively anaerobic, non-spore forming, short rods of which some have peritrichous flagella (Cabral, 2010; Forsythe, 2010; Willey *et al.*, 2011b; Ramirez-Castillo *et al.*, 2015). This pathogen is responsible for causing the disease known as salmonellosis and is the most frequently reported foodborne decease in the world. The symptoms of salmonellosis are diarrhoea, nausea, abdominal pains, mild fever and chills, sometimes vomiting, headaches and malaise. This pathogen can lead to a chronic condition which includes the cause of gastroenteritis (*S. enteritidis* and *S. typhimurium*), enteric fever (*S. typhi* and *S. paratyphi*) and invasive systemic disease (*S.cholerasuis*) (Cabral, 2010; Forsythe, 2010; Sherwood *et al.*, 2011; Ramirez-Castillo *et al.*, 2015). The infective dose of Salmonella can be as low as 1 000 cells. The low pH of the stomach, however, inhibits the growth and may result in a low dosage of 10^5 bacteria cells (Cabral, 2010; Forsythe, 2010).

Listeria monocytogenes

Listeria monocytogenes is a pathogen of great concern due to its specific cause of illness to immune-compromised beings (Forsythe, 2010; Sherwood *et al.*, 2011). *Listeria* is Gram-negative, non-spore forming bacteria with flagella and is thus a motile bacterium. The dangers of *L. monocytogenes* are reasonably problematic as a result of the bacterium's growth between the temperature range of 0 and 42 degrees Celsius (Forsythe, 2010). It is, therefore, able to grow at slow rates in refrigeration temperatures, making this pathogen rather unique and dangerous. The infective dose of *L. monocytogenes* is as low as 1 000 organisms and may result in a disease known as listeriosis (Forsythe, 2010; Sherwood *et al.*, 2011). Initial symptoms of listeriosis include influenza-like symptoms, fever, severe headaches, vomiting, nausea and sometimes may lead to symptoms of delirium or result in a coma (Forsythe, 2010). Listeriosis could also become chronic and may result in septicemia in a pregnant woman, fetuses or neonates as well as result in internal or external abscesses, meningitis or sepsis (Forsythe, 2010).

Vibrio cholerae

Vibrio cholerae is another dangerous pathogen which may result in infection after the consumption of water contaminated with faecal matter (Cabral, 2010; Forsythe, 2010; Sherwood *et al.*, 2011). This pathogen is another facultative anaerobic, gram-negative rod with flagella and produces an exotoxin called cholera toxin. This toxin has an effect on the mucosal surface of the small intestine (Cabral, 2010; Forsythe, 2010; Willey *et al.*, 2011b). The cholera disease results from the physiological actions of the toxin and is characterised by profuse watery diarrhoea, electrolyte imbalance, vomiting and leg cramps and may even lead to gastroenteritis (Cabral, 2010; Forsythe, 2010; Sherwood *et al.*, 2011; Ramirez-Castillo *et al.*, 2015).

Protozoa

The Most common pathogenic protozoans found in water are *Endamoeba histolytica, Giardia intestinalis, Cryptosporidium spp.* and are found to exhibit great resistance to various water treatments (Bortman *et al.*, 2002; Willey *et al.*, 2011a; Ramirez-Castillo *et al.*, 2015). These protozoa obtain their pathogenic characteristics by passing through the gastrointestinal tract of humans or animals and influence the nutritional uptake by the intestinal epithelium (Forsythe, 2010; Sherwood *et al.*, 2011). For instance, food or water contaminated by rodent, deer, cattle or household pet faeces or person-to-person contact, has been reported to result in infection from these pathogens (Forsythe, 2010; Willey *et al.*, 2011a). The target group for these pathogenic protozoa are young children and immune-compromised individuals and if infected, may result in persistent diarrhoea (Forsythe, 2010). The most common of these protozoa are *Cryptosporidium parvum* and if cysts or spores of this pathogen are ingested, may lead to crytosporosis (Forsythe, 2010; Sherwood *et al.*, 2011; Ramirez-Castillo *et al.*, 2015). Infected individuals may experience symptoms such as fever, diarrhoea, abdominal pain, nausea, vomiting and anorexia (Ramirez-Castillo *et al.*, 2015). Immune compromised individuals who are infected face a more dangerous situation which may result in death if untreated (Forsythe, 2010).

Viruses

Viruses such as the rotaviruses and enteroviruses found in water sources around the world are responsible for many deaths (Bortman *et al.*, 2002; Forsythe, 2010; Ramirez-Castillo *et al.*, 2015). The rotaviruses result in the death of many children worldwide, particularly in developing countries such as Bangladesh where 15 000 – 30 000 children die from this virus annually (Forsythe, 2010; Willey *et al.*, 2011d). The infectious dose of the rotavirus is approximately 10 – 100 viral particles, transmitted by the faecal-oral route or person-to-person contact and may lead to gastroenteritis which is characterised by watery diarrhoea, vomiting and a low-grade fever (Forsythe, 2010; Willey *et al.*, 2011d; Ramirez-Castillo *et al.*, 2015). The rotavirus is categorised into seven serological groups of which group A, B and C are infectious to humans. Group A rotavirus is responsible for the leading cause of diarrhoea amongst children of which more than half are hospitalised. It is thus considered as a worldwide endemic (Forsythe, 2010). Group B rotavirus is also referred to as adult diarrhoea rotavirus (ADRV) and leads to infected individuals of all ages experiencing severe diarrhoea (Forsythe, 2010). Group C rotavirus is associated with diarrhoea resulting from rare and sporadic cases. The initial symptoms start with vomiting, followed by diarrhoea and may even cause a temporary condition of lactose intolerance (Forsythe, 2010).

Human enteroviruses such as the poliovirus, Groups A and B coxsackieviruses, echoviruses and enteroviruses serotype 68 – 71, usually occur in human faeces and are thus associated with sewage and the treatment thereof (Bortman *et al.*, 2002; Forsythe, 2010). The poliovirus is one of the most common enteroviruses and once ingested, initial phases of replication of the virus begin in the throat or the small intestine and invade the tonsils, lymph nodes of the neck and the end of the small intestine (Forsythe, 2010; Willey *et al.*, 2011c). The virus may result in a brief illness characterised by a fever, headaches, sore throat, vomiting and loss of appetite. The virus can also enter the bloodstream causing viremia (Willey *et al.*, 2011c; Ramirez-Castillo *et al.*, 2015). Although it is unlikely to happen, the viremia may be persistent and the virus may enter the central nervous system causing paralytic polio (Willey *et al.*, 2011c).

2.1.1.2 Physicochemical properties of water

The physicochemical properties of water provide an indication of, biological, physical, chemical and hydrological characteristics of river water and have a significant influence on the quality of water.

Natural organic matter

Natural organic matter (NOM) plays a major role as a substrate for the growth of microorganisms and can also influence watercolour, taste and odour quality (Fabris *et al.*, 2008). NOM's originate from organic and inorganic matter which are both subjected to oxidation when a desired amount of oxygen is available. This oxygen level is referred to as the chemical oxygen demand (COD) of a specific water sample and is defined as the number of specified oxidants that react with a sample under controlled conditions. The COD parameter is one of the measurable parameters used to determine the level of pollution in water samples (Bortman *et al.*, 2002; APHA, 2005; DWA, 2013). The level of NOM's in water samples is irregular and unpredictable between seasons, which can become a problem with certain water treatment systems and the extent of treatment needed to reduce or eliminate these NOM's (Fabris *et al.*, 2008). The detection or determination of NOM is accomplished by using correlations with UV absorbance to detect the aromatic content within a given water sample. This can now be used to correlate the level or degree of pollution with NOM's (Fabris *et al.*, 2008).

Dissolved organic carbons

The dissolved organic carbon's (DOC's) within the NOM plays a major role in its distinctive characteristics. Mundane derived DOC's exhibit high quantities of phenolics and aromatic carbons, whilst DOC's derived from aquatic algae exhibit lower levels of phenolics and aromatic carbons but an increased nitrogen content (Fabris *et al.*, 2008; Schug, 2016).

Turbidity

Turbidity is an important parameter for the determination of the water quality with a designated focus on the clarity of the water (Bortman *et al.*, 2002; Schug, 2016). An increase in turbidity is realised from an increase of suspended and colloidal matter within a given sample and thereby results in a decrease in clarity. An increased concentration of suspended and colloidal matter within any fluid results in increased reflection and absorption of light of the specific sample and directly correlates with the level of turbidity (APHA, 2005).

Total solids

The total solid content within water samples can result in an unfavourable physiological reaction if consumed due to its influence on palatability. Total solids refer to the remaining residues in water samples after complete evaporation and include both total suspended solids and total dissolved solids. Water high in suspended solids could result in unsatisfactory water quality for household use (DWAF, 1996b). Volatile solids are mineral salts which are lost during ignition due to volatilisation or decomposition. The analysis of solids is important for the management of biological and physical water treatment systems and processes for the purpose to ensure water standards are acquired (Bortman *et al.*, 2002; APHA, 2005; Schug, 2016).

Conductivity

Another important parameter of water is the measurement of conductivity (Schug, 2016). Conductivity is the ability for the current to be carried through an aqueous solution and gives an indication of the organic and inorganic compound content in a given sample. This is dependent on the ion constituents of the organic or inorganic content as well as the ions total concentration, valence, mobility and temperature. Organic compounds in aqueous solutions are poor conductors and will thus result in a decreased conductivity of a water sample, whilst increased inorganic content will significantly increase the conductivity (APHA, 2005; DWA, 2013).

pH and alkalinity

The measurement of the pH of a given sample is the most important and is the most used measurement during analyses of water (DWA, 2013). It gives an indication of the intensity of basic or acid conditions of the water and is used in many acid-base equilibrium measurements, including alkalinity and carbon dioxide measurements (APHA, 2005; Schug, 2016). The measurement of pH of a water sample is important due to its potentially corrosive effect and influences on other water treatment efficacies if the pH is not maintained or altered (Bortman *et al.*, 2002; Sampathkumar *et al.*, 2010; Schug, 2016).

Alkalinity is an aggregate property of water which indicates its buffer capacity for the neutralisation of acids within the sample. Carbonate, bicarbonate and hydroxide content are the responsive molecules which give an indication of alkalinity in surface water. This factor and the measurement thereof is used for interpretation and management in the process of treating water supplies (APHA, 2005; Schug, 2016).

2.2 WATER TREATMENTS FOR THE IMPROVEMENT OF WATER QUALITY

Water quality determines the uses of water for designated activities. Pollutants may prevent the use of water unless a specific treatment has been used to remove or reduce the pollutants. Many treatment methods can be employed to reduce pollutant loads in water. These treatments are summarised in Table 2.2. and include chemical, photochemical and physical treatments which are usually used together in combination to improve water quality to an optimal level. Different water supply sources can be treated with different combinations of treatments depending on the nature of the pollutants within the water that need to be reduced or removed. Though the main purpose of this study is directed to the elimination of pollutants in order to provide water with a quality suitable for irrigation purposes, most of the water treatments are briefly discussed in this section. This water treatment for irrigation as well as for drinking water quality and industrial activities.

Table 2.2. Variation of water treatments used to improve the quality of polluted water

Chemical treatments	Photochemical Treatments	Physical Treatments
Agglomeration and Clarification/Settling	Ultraviolet (UV) light	Dissolved Air Flotation (DAF)
Chlorine-based disinfectants		Membrane processes.
Bromine-based disinfectants		Filtration systems
Hydrogen Peroxide based disinfectants		
Ozone-based disinfectants		
Peracetic acid (PAA) based disinfectants		

2.2.1 Chemical treatments

2.2.1.1 Agglomeration and Clarification/Settling

Agglomeration is the process of adding a coagulant to the water sample followed by clarification or settling which improves the turbidity of water by removing natural organic matter and other soluble organic and inorganic matter (Parsons & Jefferson, 2006). The addition of a coagulant results in destabilised particles which can collectively form into small agglomerates. An example of effective coagulants includes lithium iron phosphate and nanoparticles which can be composed of copper oxide (Son *et al.*, 2015; Tsai *et al.*, 2016). After the coagulation step, the sample is usually exposed to a flocculation process driving these agglomerates to collide with each other to form floccules. These floccules are removed from the water sample via clarification.

The settling out of suspended solids in passive water conditions with gravity as the driving force of separation is known as clarification and is seen as a physical water treatment. Many impurities are removed by the process of clarification which would have remained in suspension due to the turbulent flow of water. The use of lamella plates or a bed of course stones or gravel in the process of clarification enhances the process by establishing high rate sedimentation or increasing floccules density respectively (Parsons & Jefferson, 2006; von Sperling, 2007; Schug, 2016).

2.2.1.2 Disinfection treatments for water

Chemical disinfection is the use of chemical agents to prevent the spread of water-borne diseases by deactivating or destroying pathogenic microorganisms found in water (Parsons

& Jefferson, 2006; Schug, 2016). The disinfection process is usually the final process in a combination of treatments by eliminating all risk of pathogenic microorganisms which might have resisted any other water treatment systems (WHO, 2017b). The efficacy of the disinfection process is dependent on contact time of the disinfection agent with the microorganisms and the concentration of that disinfection agent (Parsons & Jefferson, 2006; Schug, 2016; WHO, 2017a). A certain by-product of chemical disinfectants is produced when reacting with organic and inorganic molecules within the water (Momba *et al.*, 2008.). This by-product can become carcinogenic when consumed and has shown to cause cancer in tested animals (Parsons & Jefferson, 2006). Chlorine is without a doubt one of the most commonly used chemical disinfectants. There are, however, other alternatives which prove to be more beneficial such as bromine, hydrogen peroxide, ozone and peracetic acid.

Chlorine-based disinfectants

Chlorine is one of the most common disinfecting agents used in water treatment which not only eliminates pathogens but also acts as a preservative for the water by reducing the growth of the pathogenic microorganism (Parsons & Jefferson, 2006). Chlorine can be utilised in water for the disinfection thereof in the following forms: It can be utilized as gaseous chlorine (elemental chlorine), a liquid sodium hypochlorite or solid calcium hypochlorite (Raudales *et al.*, 2014; Olivier, 2015). Each form of chlorine and the use thereof has it's advantageous and disadvantageous. The decisive use thereof, however, will depend on the availability of local chemicals as well as dosing and treatment facilities of the treatment plant (Olivier, 2015).

The mechanism of interaction chlorine has with pathogens, results in the destruction of the microbial cell wall (Olivier, 2015). Chlorine molecules firstly react with water molecules to form hydrochloric and hypochlorous acid. Dissociation of these acids results in the formation of hypochlorite and hydrogen atoms. The hypochlorite and hypochlorous acid are referred to as free chlorine and are the responsible oxidants for disrupting and destruction of the bacteria cell walls which consequently leads to cell death (Olivier, 2015).

There are many advantages of using chlorine as a disinfecting treatment. The cost of the initial infrastructure for water treatment with chloride is fairly low compared to other treatment plants (Momba *et al.*, 2008.; Olivier, 2015). The chloride substance is easy to handle, measure and dose, and has a high solubility resulting in increased effectiveness (Momba *et al.*, 2008.; Olivier, 2015). A low dosage of the substance results in a reduction of microbial content by three log reduction and due to the oxidation potential of the substance, results in the removal of undesirably foul-tasting and odour compounds (Olivier, 2015). The dosage of the chlorine used for chemical disinfection is dependent on the pathogenic microorganisms, its characteristics as well as its growth rate and load (Parsons & Jefferson, 2006; WHO, 2006).

Bromine-based disinfectants

Bromine is not as common as chlorine and is usually used to reduce bacteria and algae in pool water and cooling towers (Momba *et al.*, 2008.). The mechanism of bromine reacting with water and resulting in cell death of the microbes is similar to that of chlorine. Bromine, however, results in the presence of foul taste and odour compounds after water treatment. Bromine is most commonly utilized as sodium bromine and is often added to sodium hypochlorite to form hypobromous acid. The hypobromous acid is the substance responsible for the disinfection properties of bromine. Disrupting the microbial cell in a similar way to that of the hypochlorous acid with an additional benefit that hypobromous acid is less influenced by pH levels of the water (Momba *et al.*, 2008.). Bromine utilisation for the treatment of water for agriculture is also likely to be more beneficial than chlorine due to its persistent disinfectant properties when bound to nitrogen-based compounds. In the water that is used for agriculture, these nitrogen-based substances such as ammonia, are not uncommon and therefore bromine would be the ideal disinfectant. Bromine disinfectant also has greater biocidal activity than that of chlorine and thus results in the increased reduction and cell death of enteric viruses (Momba *et al.*, 2008.; Olivier, 2015).

Hydrogen Peroxide based disinfectants

Hydrogen peroxide is another oxidizing agent with great potential as a disinfectant. It is usually added to water and decomposed into water molecules and oxygen which results in the production of reactive oxygen species (ROS) (Joshi *et al.*, 2013; Olivier, 2015). These ROS have the ability to disinfect water by acting as a toxin to the microbial cell which disrupting its DNA, proteins and lipids and eventually resulting in cell death. Along with a catalyst, hydrogen peroxide can result in increased oxidation potential due to its conversion to hydroxyl radicals and superoxide radicals (Olivier, 2015).

Ozone-based disinfectants

Ozonation is a commonly used treatment to improve the microbiological quality as well as the physicochemical and sensory quality of water. Naturally occurring as an activated form of oxygen, ozone is also produced by activating the oxygen by means of discharging high voltage and thereby converting oxygen gas into ozone gas (Momba *et al.*, 2008.; Olivier, 2015). The use of ozone has many advantages and improves many water quality parameters such as taste, odour and colour compounds, turbidity, total organic carbon and levels of disinfected by-product precursors in water (Burns *et al.*, 2006). Disinfection of water using ozone is usually achieved by diffusing the ozone gas into the water where it rapidly decomposes and forms free radicals responsible for its disinfectant properties (Momba *et al.*, 2008.; Olivier, 2015). Hydroperoxyl and hydroxyl free radicals show disinfectant properties particularly to bacteria and parasites such as *Cryptosporidium, Giardia lamblia* and *Escherichia coli* (Burns *et al.*, 2006). The mode of action that these disinfecting radicals have on such microorganisms, is a result of its oxidising potential. These radicals disrupt the genetic material of microbes and thereby their replicable processes, as well as lysis of pathogenic cell walls and consequently resulting in cell death (Burns *et al.*, 2006; Momba *et al.*, 2008.; Olivier, 2015).

Peracetic acid (PAA) based disinfectants

Peracetic acid and the use thereof for the disinfection treatment of water is an alternative to chlorine and hydrogen peroxide due to its greater oxidation potential and less hazardous by-product formation (Luukkonen *et al.*, 2014; Olivier, 2015). Peracetic acid consists of a stable mixture of 5 to 15% (w/w) of acetic acid and hydrogen peroxide, which is the active compounds within the solution (Luukkonen *et al.*, 2014; Olivier, 2015). In addition to its great oxidation potential, peracetic acid and the mode of action is less influenced by physicochemical parameters such as total dissolved solids and organic material (Luukkonen *et al.*, 2014). Upon addition of PAA to aqueous solutions, the molecules degrade into its initial constituents; acetic acid, hydrogen peroxide, water and oxygen. These constituents play an important role in damaging the outer membrane of microorganisms due to its oxidising potential (Olivier, 2015). This mode of action, like most chemical disinfectants, lead to cell death by resulting in increased membrane permeability and denaturation of proteins.

2.2.2 Photochemical treatments

2.2.2.1 Ultraviolet (UV) light

The use of Ultraviolet light as radiation for the disinfection of water has shown promising results and can aid in producing potable water free from disinfectant by-products (Olivier, 2015; Van Rooyen, 2018). Ultraviolet radiation is a form of electromagnetic radiation and inhibits further growth of pathogenic microorganisms in water by manipulating their replication process. This is achieved as the UV light with wavelengths of between 200 and 280nm is absorbed by DNA/RNA and thus penetrates the microbial cell, directly manipulates the nucleus DNA of the microbe (Olivier, 2015). The disruption of the cell's DNA disables it from continuing the replication process and thus preventing the growth of these pathogens. The UV light is produced with the use of xenon lamps, antimony and mercury vapour and can be directly used as a form of water treatment (Parsons & Jefferson, 2006; WHO, 2017a).

2.2.3 Physical treatments

2.2.3.1 Dissolved air flotation (DAF)

The purpose of DAF is to decrease the density of suspended solids in water which results in the coagulation and buoyancy of these particles after which it can be removed by skimming at the surface of the water (Parsons & Jefferson, 2006; von Sperling, 2007). This process is achieved by incorporating air bubbles into the agglomerated particles and thereby decreasing their densities. The rate of the process is thus dependent on the number of bubbles attached to these agglomerates and the formation of a sludge layer at the surface of the water (von Sperling, 2007; Schug, 2016). The use of a saturator provides the bubbles which attach to the particles for flotation. The efficacy of the process depends both on whether enough bubbles are generated and the nature of the mechanism influencing binding of agglomerated and bubbles (Parsons & Jefferson, 2006; von Sperling, 2007; Schug, 2016).

2.2.3.2 Membrane processes.

The membrane process, which is also a form of filtration, is the use of a specific semi-permeable membrane to inhibit the flow-through of suspended, colloidal and dissolved solids (Parsons & Jefferson, 2006). The physical characteristics such as size, diffusivity and affinity for specific contaminants, are the driving forces for its potential of removal (Parsons & Jefferson, 2006; Olivier, 2015). A semi-permeable membrane is a thin porous layer of material which can retain specific solids from water depending on the pore size. The pore size is the key parameter for removing unwanted pollutants. The separation is dependent on the physical characteristics of these pollutants as well as the mechanism thereof which in turn, is driven by low pressure (Parsons & Jefferson, 2006; Momba *et al.*, 2008.; Abegunrin *et al.*, 2016).

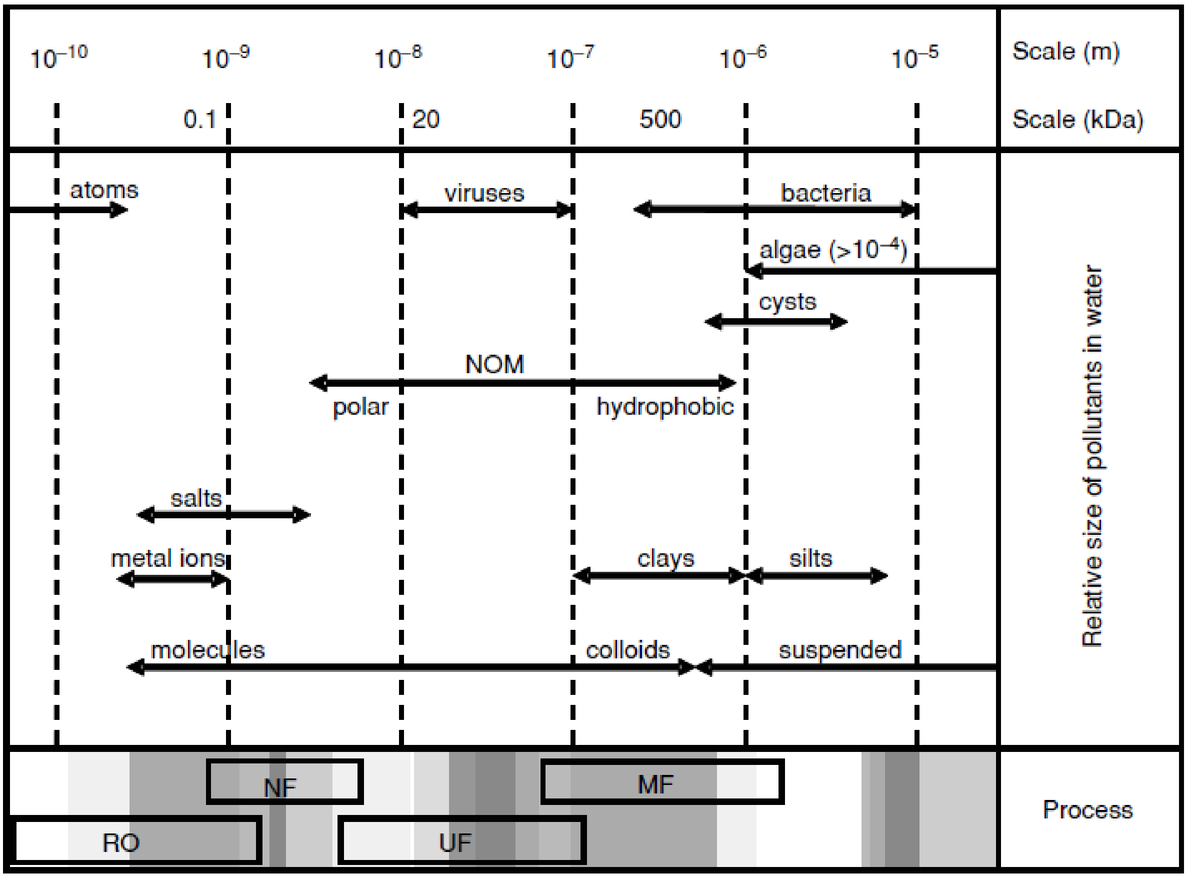

Figure 2.1. Indication of the relative size of pollutants in water and the membrane treatments as RO (reverse osmosis), NF (nanofiltration), UF (ultrafiltration) and MF (microfiltration) for those types of pollutants (Parsons & Jefferson, 2006).

Reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) are all examples of membrane processes which are used as potable water treatments (Parsons & Jefferson, 2006; Schug, 2016). Each type of treatment is used for the reduction or removal of specific types of pollutants as indicated in Figure 2.1. Ultrafiltration has gained much interest due to its potential of effectively reducing certain viruses, bacteria and protozoa cysts from water sources (Parsons & Jefferson, 2006; Momba *et al.*, 2008.; Konieczny & Rajca, 2009). Amongst the membrane process, Ultrafiltration is the most commonly used treatment due to its wide spectrum of potential pollutant it may eliminate from water as well as the retention of these pollutants for further isolation (Parsons & Jefferson, 2006).

2.2.3.3 Filtration systems

The process of filtration is the physical flow of water through granular filter media, whereby it adsorbs and removes undesirable constituents such as microorganisms, organic and metal ion precipitates, salts and clays (Kubiak *et al.*, 2015; Schug, 2016). The adsorptive mechanism between the granular media and the undesirable constituents involves both collision and attachment within the molecular interactions (DWAF, 2004; Parsons & Jefferson, 2006; Schug, 2016). The most influential part of filtration is likely the biofilm layer formed above the granular layer, referred to as the *Schmutzdecke* (Kubiak *et al.*, 2015; Pfannes *et al.*, 2015). This biofilm consists of a community of fungi, algae, nematodes, protozoa, bacteria and other organisms as well as organic and inorganic matter and is formed by the continuous flow of groundwater through the filtration system (Zheng, 2014; Kubiak *et al.*, 2015; Pfannes *et al.*, 2015). The mechanism of action consists of a combination of physical, chemical and biological activity of the biofilm with organic constituents, and may result in the increased removal of certain pathogens (Kubiak *et al.*, 2015; Pfannes *et al.*, 2015).

Slow sand filtration

Slow sand filtration, unlike chemical and photochemical treatments, is a low-tech and inexpensive filtration system which is still in use by cities such as London and Zurich, for purification of water with high microbial load (Kubiak *et al.*, 2015; Pfannes *et al.*, 2015). Not only do slow sand filtration improve water quality by reducing total suspended solids (TSS) and turbidity, but also by reducing pathogenic content adsorbed on the biofilm and captured in the pores of the sand particles (Zheng, 2014; Olivier, 2015). A study completed on the elimination of faecal bacteria by slow sand filtration columns with a grain size of 0.25 mm indicated a log reduction of 1.6 - 2.3, of which most removals occurred in the *Schmutzdecke* (Pfannes et al., 2015). It should be noted that although faecal bacteria are typical indicator organisms, one cannot predict the removal or reduction potential of the slow sand filtration for all microorganisms, due to the variation in physical microbial size and the pore size of the sand granules (Zheng, 2014).

Other microorganisms such as *Xanthomonas* spp. (bacteria), *Fusarium* spp. (fungi), *Phytophthora* spp. (Ascomycota), *Pythium* spp. (Ascomycota), *Pelargonium* flower break virus and tobacco mosaic virus which are plant pathogens and are also shown to be reduced using slow sand filtration for treatment of irrigation water (Kubiak *et al.*, 2015). Kubiak *et al.* (2015) indicated that using slow sand filtration systems for the treatments of irrigation water resulted in the removal of *Fusarium solani* and *pythium sterile* by 80 – 90% and the removal of *Xanthomonas campastris, Pseudomonas syringae* and *Rhizobium radiobactor* by 70%. Although these microorganisms are only pathogenic to plants, it is important to note that the biofilm formed during sand filtration is complex and adsorbs a large spectrum of microorganisms.

Activated carbon filtration

Although sand filtration may be beneficial, there are many other alternative filter media which have greater adsorption potential. The separation and adsorption of a variety of undesirable hazard from water samples can be achieved using a charcoal-like material called activated carbon. In the water industry, activated carbon is particularly used for the removal of undesirable tastes, odours, algal toxins, pesticides and natural organic molecules and inorganic matter (Rivera-Utrilla *et al.*, 2001; Mohan *et al.*, 2014; WHO, 2017a). Activated carbon is produced from a wide variety of substances such as coconut shell, coal, lignite, wood and bone and results in an extremely porous substance with a large internal area (Schug, 2016).

The process of adsorption is based on a four-phase process and the efficacy of absorption is dependent on the specific characteristics of the carbon material and the molecules being adsorbed (Redman *et al.*, 2001; Parsons & Jefferson, 2006). During the first phase, the pre-adsorbed pollutant must first travel to and surround a film of carbon particles out of the liquid phase. The second phase consists of the mobility of the pollutant to travel through this surrounding film, entering the interstitial void of the carbon. The diffusion of the pollutant through the carbon void and into the carbon solid phase is the third phase, followed by the adsorption of the pollutant onto the carbon which is the fourth phase. The efficacy of adsorption is a function of pH, concentration and temperature of both the activated carbon and the pollutant. Adsorption of these pollutants can result from a physical or chemical interaction between the pollutant and activated carbon (Redman *et al.*, 2001; Parsons & Jefferson, 2006). Physical adsorption involves weak van der Waals forces which bind pollutants on the surface of the carbon particles. During chemical adsorption strong covalent or ionic bonds are formed between the pollutant and activated carbon as a result of electron density rearrangement (Parsons & Jefferson, 2006).

The thermal process of producing activated carbon consists of a two-phase process (Parsons & Jefferson, 2006; WHO, 2017a). The first phase consists of the carbonisation of derived material into a char-like substance at approximately 700ºC or higher, in the absence of oxygen (pyrolysis). This process reduces the volatile content of the derived material as it comforts to char. In the second phase, the activated carbon is steamed under controlled oxygen levels up to 1 000ºC. The purpose of the steam is to create a large internal area, by oxidising internal carbon atoms as it penetrates the carbon particles, and thereby activating the carbon (Parsons & Jefferson, 2006; WHO, 2017a). Activated carbon is, however, a complex substance and dependent on the biomass from which it is made, it may have a major influence on its adsorbent properties (Rivera-Utrilla *et al.*, 2001). Rivera-Utrilla *et al.* (2001) indicated that whilst one variation of activated carbon could adsorb up to 100% of *Escherichia coli,* another could only absorb 20% of the microorganism. This result is likely due to the pH and pore difference between the two activated carbons (Rivera-Utrilla *et al.*, 2001). Moreover, Rivera-Utrilla *et al.* Indicate that the adsorption of *E. coli* resulted in increased removal of lead as a result of the uptake of oxides by microbes, exhibiting a decrease in hydrophobicity. Commercially produced activated carbon also has the potential to adsorb herbicides and pesticides according to Kearns *et al.* (2014), however, the intermediate co-product after the first phase of production of activated carbon, known as biochar, shows comparable results as adsorptive media to that of activated carbon (Kearns *et al.*, 2014).

Biochar as filtration media

Biochar is referred to as the non-activated form of activated carbon as the process of production is halted before activation (Inyang & Dickenson, 2015; Tan *et al.*, 2015). The temperature required for the carbonisation of activated carbon is also higher than the production of biochar and along with the removal of the activation process, the biochar production results in a potentially low-cost and effective adsorbent as an alternative to activated carbon (Inyang & Dickenson, 2015; Tan *et al.*, 2015). Biochar has many advantages due to its production process and has comparable characteristics to that of activated carbon (Kearns *et al.*, 2014; Tan *et al.*, 2015). One such advantage is that developing regions which traditionally produced charcoal fuels from the kiln, and agricultural biochar soil conditioners, can use this char for water quality improvement due to its activated carbon-like properties (Kearns *et al.*, 2014). This will be discussed in more detail in the section that follows.

2.3 BIOCHAR PRODUCTION AND CHARACTERISATION

2.3.1 Introduction to Biochar

Biochar is a charcoal-like substance, rich in carbon and aromatic compounds, with a large surface area due to its porous crystalline structure (Santos *et al.*, 2015; Tan *et al.*, 2015). The biochar is produced similarly to that of activated carbon, which is used in many water filtration systems for the significant reduction of natural organic matter and heavy metals

(Rivera-Utrilla *et al.*, 2001). The process of pyrolysis is used to convert the organic matter, the content of wood, manure or leaves, via thermochemical reactions, in an oxygen-deprived chamber or environment to produce biochar (Ahmad *et al.*, 2014). This process results in the production of a highly porous substance, biochar, which has the potential to absorb many pollutants due to the chemical and physical transformation which the derived material undergoes (Ahmad *et al.*, 2014; Santos *et al.*, 2015; Tan *et al.*, 2015; Ahmed *et al.*, 2016).

Compared to activated carbon, biochar is potentially a cost-effective alternative filtration media and adsorbent, due to its lower pyrolysis temperature and the added activation treatments which biochar does not need to be exposed to (Tan *et al.*, 2015). Pyrolysis temperature and residence time of pyrolysis play the primary role in distinguishing biochar characteristics from each other, whilst the derived plant material the biochar is produced from contributes to the enhancement of specific characteristics (Keiluweit *et al.*, 2010; Ahmad *et al.*, 2014). The derived plant matter from which biochar is produced and specifically the lignin content of that plant matter determines the aromatic content of the biochar (Keiluweit *et al.*, 2010). The aromatic content of the biochar, in turn, determines the adsorptive potential for pollutants such as heavy metals and natural organic matter. An increased amount of lignin content in plants results in a greater increase of aromatic content post-pyrolysis. Plant matter such as wood, which are higher in lignin content, and specifically coniferous wood such as pine, is reported to contain extremely high lignin content (Keiluweit *et al.*, 2010).

2.3.2 The process of pyrolysis

2.3.2.1 Combustion

The thermochemical production of biochar is accomplished with a form of combustion reactions during pyrolysis. Combustion is the process of synthesising an energy source needed to convert plant matter into highly dense char and is thus important to understand the mechanism of this process (Brewer *et al.*, 2012; Bridgwater, 2012). The initial step of combustion according to Brewer *et al.* (2012), begins with the evaporation of water from the raw or processed biomass by drying the material. Drying requires less energy than a fire source and thus low amounts of energy are needed to reach the relatively low evaporation temperature of the water, which will result in the release of the steam out of the biomass. The second step of combustion results in the breaking of chemical bonds and increasing the ease of vaporisation of smaller molecules out of the biomass (Brewer *et al.*, 2012; Bridgwater, 2012). During this step, no oxygen is required and is thus referred to as volatilisation. The third step is gas-phase oxidation, where volatiles which has vaporised out of the biomass are exposed to oxygen, resulting in an exothermic reaction and eventually igniting (Brewer *et al.*, 2012). The final phase of combustion occurs after all the volatiles have been oxidised and removed, resulting in solid glowing coal. In this step the process is slow and a flame is not visible, due to the slow diffusion of oxygen from the oxidising volatiles to the surface of the coal. The process is complete when all the free carbon is oxidised into carbon dioxide and the ash, which is non-combustible material, remains in the char (Brewer *et al.*, 2012).

The extent of pyrolysis is determined by the extent of combustion which can be manipulated by controlling available energy supplied to the system, oxygen availability in the chambers, the residence time of the biomass and the quantity of biomass to be pyrolysed (Brewer *et al.*, 2012; Bridgwater, 2012). With the ability to manipulate these variables, the thermal-chemical reactions have been categorised into five distinct processes used to produce different products and are summarised in Table 2.3.

Slow pyrolysis

According to Brewer *et al.* (2012), there are five different types of thermochemical processes. Slow pyrolysis and traditional charcoal making are accomplished at moderate to high temperatures in the absence of oxygen (Brewer *et al.*, 2012; Joubert, 2013; Hodgson *et al.*, 2016). The production of biochar from the thermochemical process is an energy-dense high carbon solid char product, whilst producing pyroligneous acid (wood tar) and low-energy combustible gasses as co-products (Brewer *et al.*, 2012; Joubert, 2013; Hodgson *et al.*, 2016).

The physical structures developed to complete such combustible reactions are referred to as a kiln or pyrolyser. Kilns are built from metal, brick, or concrete to create greater insulation and control of the environmental parameters. An example of an efficiently used kiln is a so-called rotary kiln, which is a continuous production unit and provides increasing consistency (Kunii & Chisaki, 2008a; Nielsen *et al.*, 2012). The rotary kiln is divided into three zones and relies on a rotary paddle to mobilise the biomass from one zone to the next, down a spiral-like internal structure. The top zone of the kiln is the drying zone whereby hot air from the lower zones is used to dry the biomass. In the middle zone or combustion zone, the oxygen supply is limited due to the gasses released during combustion and results in the transformation of biomass into char.

Table 2.3. Illustrating the difference between thermochemical processes (Brewer *et al.*, 2012)

Thermo-chemical process	Temperature range (^{0}C)	Residence time	Heating rate	Primary product
Slow pyrolysis	350 - 800	Hours - days	Slow	Char
Terrefraction	200 - 300	Minutes - hours	Slow	Stabilised friable biomass
Fast pyrolysis	400 - 600	Seconds	very fast	Bio-oil
Flash pyrolysis	300 - 800	Minutes	fast	Biocarbon/ char
Gasification	700 - 1500	Second - minutes	Moderate - very fast	sun gas/ producer gas

This zone is followed by the cooling zone where the temperature is reduced as the transformed biomass transcends out of the kiln. The char-like substance exits the bottom of the kiln whilst the unrecyclable gasses produced during combustion are diverted to an afterburner as soon as it reached the top of the kiln (Kunii & Chisaki, 2008a; Brewer *et al.*, 2012; Nielsen *et al.*, 2012).

Torrefaction

Torrefaction and feedstock pretreatment is a process similar to low-temperature slow pyrolysis and results in the removal of water, volatile molecules and readily available carbon structures from the biomass with the aim to improve grinding, transport and storage (Basu, 2010b; Brewer *et al.*, 2012; Mohan *et al.*, 2014; Nsaful, 2018). If the biomass is not treated by torrefaction and contains high moisture content, it becomes more flexible and thus more energy is required to crumble such biomass for further use. Transportation also becomes costly as the biomass would have a low bulk energy density and thus large volumes of biomass would need to be produced (Brewer *et al.*, 2012; Nsaful, 2018). High moisture content would also play a major role in the microbial contamination and growth of spoilage organisms and would decrease the biomass storage life significantly. Torrefaction is thus an ideal pretreatment to prevent above-mentioned phenomena and results in the production of a brown char which is slightly hydrophobic and thus more stable during storage (Basu, 2010b; Nsaful, 2018). The char produced is, however, not used as a form of Biochar, but rather serves a purpose in the preservation of easily managed feedstock which can be available all year round (Brewer *et al.*, 2012).

Fast pyrolysis

Fast pyrolysis is a much more rapid form of pyrolysis and results in the additional production of bio-oils (Bridgwater, 2012; Joubert, 2013). Whilst slow pyrolysis relies on the thermodynamically controlled processes, fast pyrolysis uses an alternative controlled process via kinetics. This is usually accomplished at high temperatures, extreme heating rates and short residence time, to inhibit the produced vapours from condensing and becoming carbonised (Brewer *et al.*, 2012; Bridgwater, 2012; Mohan *et al.*, 2014). During fast pyrolysis, the drying and vaporisation phase occurs instantaneously and volatiles are rapidly expanded out of the biomass. The volatiles are extracted from the reaction zone via a vacuum or flow of inert sweep gasses (Joubert, 2013). These vapours hereafter are separated from the carbonised material using filtration methods or cyclones, after which the vapours are condensed out of the gas phase via cooling and results in the formation of bio-oils (Bridgwater, 2012; Joubert, 2013). Bio-oils are most commonly used as an alternative to heavy oils used in boilers, as it is energy-dense and exhibits fewer complications. The bio-oils are bio-renewable for gasification and petroleum in the purpose of producing asphalt (Bridgwater, 2012). There are many other potential extracts which can be obtained from bio-oils however, many more extraction processes are needed and the science of separation of these extracts from bio-oils are not well known or are extremely costly (Brewer *et al.*, 2012).

Flash pyrolysis

Flash pyrolysis, which is another thermo-chemical process, and differentiates from the other processes by using moderate pressure to decrease reaction time and significantly increase the yield of biocarbon. Flash pyrolysis, differentiates specifically from fast pyrolysis as it induces condensation of both volatiles and formation of char (Basu, 2010b; Brewer *et al.*, 2012; Mohan *et al.*, 2014). The process of flash pyrolysis works similar to that of a retort in the food industry for sterilization (Brewer *et al.*, 2012). A large vessel is filled with canisters packed with biomass which can withstand high pressures. The vessel is semi-sealed after which compressed air is pumped into the chamber and the combustion process is initiated at the bottom of the vessel by electric heaters. As the canisters at the bottom of the vessel begin to heat up it initiates a cascade of events leading to the combustion of the biomass at the bottom, and eventually through thermal conduction and convection, to the biomass at the top of the vessel. During combustion, the oxygen will eventually become depleted and the biomass will be transferred into char whilst any vented gasses are used for the potential production of heat or electricity with the use of afterburners. This process is thought to be energy efficient due to the use of pressure, as it will result in less energy usage, in the form of heat, which therefore shifts the thermodynamic equilibrium in the favour of producing char using decreased reaction time (Basu, 2010b; Brewer *et al.*, 2012). Flash pyrolysis can effectively be used to produced activated carbon and other coal replacements, however, a strong shift in the potential use of flash pyrolysis for "waste-to-carbon" processes, agricultural applications, and biochar horticulture is being focused upon (Brewer *et al.*, 2012).

Gasification

The final thermochemical process is gasification, which has extremely high process temperatures in the presence of a little amount of oxygen which is needed for stoichiometric combustion (Nsaful, 2018). The product referred to as syngas is produced during gasification and mostly consists of carbon monoxide and hydrogen together with other functional groups (Basu, 2010a; Brewer *et al.*, 2012; Mohan *et al.*, 2014). Syngas is used as an alternative to natural gasses such as methane, due to its significantly lower energy density and can also be used to synthesise chemicals and petroleum (Basu, 2010a). During gasification, the combustion is not able to reach the gas-phase or the solid-phase and does not reach thermodynamic equilibrium as a result of limited oxygen and significantly reduced reaction time (Basu, 2010a; Aldana *et al.*, 2015; Nsaful, 2018). The by-product resulting from the process is viscous, sticky tar which can become problematic in reactors due to clogging. The gasification process can be completed in a variety of reactor configuration such as circulating fluidized beds, downdraft reactors and bubbling fluidized beds (Brewer *et al.*, 2012; Aldana *et al.*, 2015; Nsaful, 2018).

2.3.3 Factors influencing Biochar physical characteristics during pyrolysis

The temperature of pyrolysis plays an important role in the properties of the biochar. The higher the pyrolysis temperature is the more chemical transformation there is of the plant biomass, which results in increased aromatic ring structures. Hereafter smaller aromatic units are condensed into large conjugated sheets (Keiluweit *et al.*, 2010). The higher the temperature, retention time and increased concentration of oxygen the greater yield of char with aromatic properties will be produced (Santos *et al.*, 2015). Furthermore, particle size of pre-pyrolysed biomass has a significant effect on the biochar's chemical composition as well as the aromatic and pore structure of the biochar, which in turn could affect adsorption potential (Mohan *et al.*, 2014) Although overall biochar yield decreases with increased temperature, there is an improvement in fixed carbon content and thus producing higher quality char (Santos *et al.*, 2015)

A unique study completed on the molecular structure of biochar by Keiluweit *et al.* (2010), distinguished biochar into four specific char categories. These categories are determined by the crystalline transitional phases of the biochar as it transforms during combustion, and the influence of temperature on the charring intensity, as seen in Figure 2.2. All Biochar originates from plant material and during the initial phases of thermal combustion remains unchanged. The plant's native structure such as cellulose, hemicelluloses, lignin content and molecular structure is preserved whilst only dehydration occurs resulting in the removal of water (Basu, 2010b; Keiluweit *et al.*, 2010).

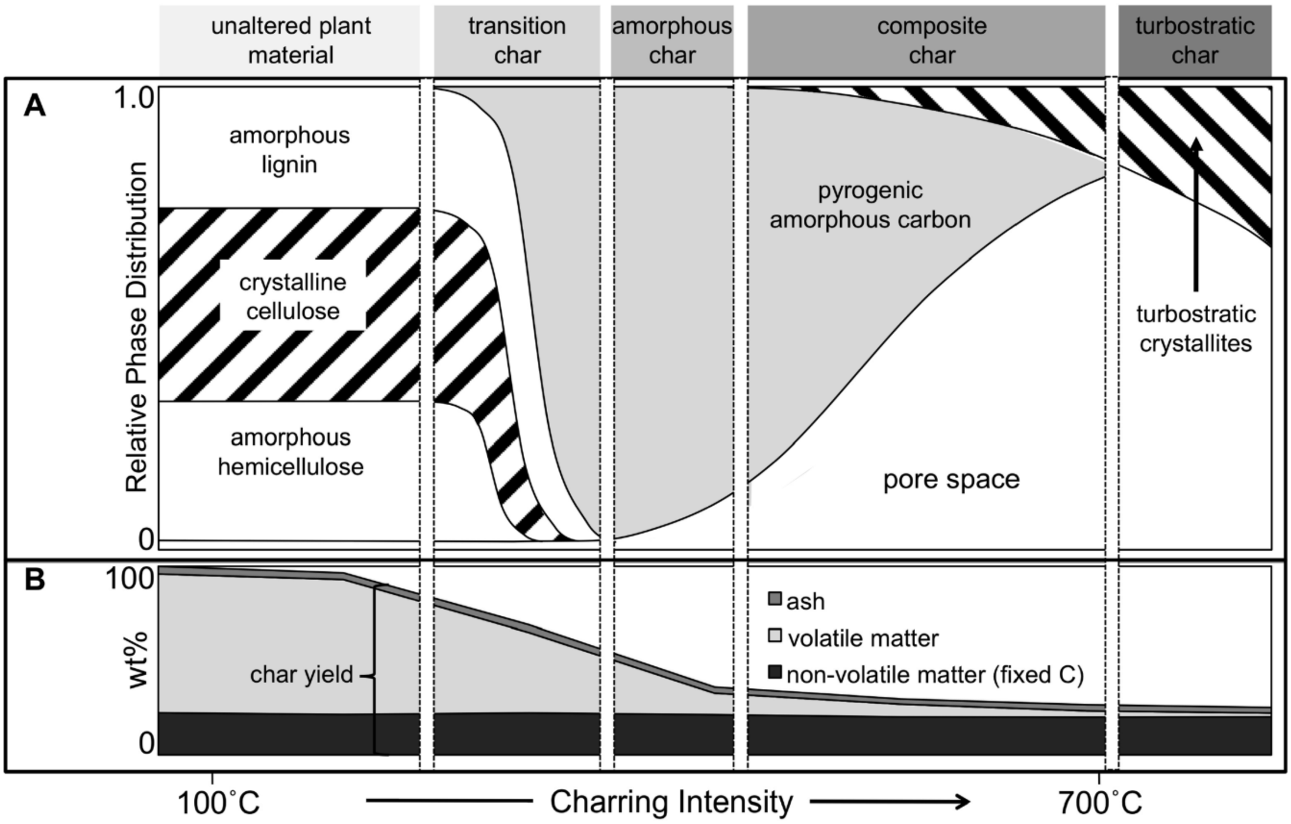

Figure 2.2. A diagrammatic indication of pyrolysis temperature and transition phase of plant material into char (Keiluweit et al., 2010).

Transition chars

Transition chars, which are the first category of char, results in the production of small volatile products due to the further dehydration and initial depolymerisation of the plant matter, which can be illustrated on the second region of Figure 2.2. The detection of higher levels of ketones, aldehydes and carboxyl carbons during this phase of charring intensity is an indication of the depolymerisation of the lignin within the biomass (Kunii & Chisaki, 2008b; Basu, 2010b; Keiluweit *et al.*, 2010). The increase in carboxyl carbons plays a role in providing amorphous centres to initiate the synthesis of the crystalline matrix structure involved in char formation (Keiluweit *et al.*, 2010).

Amorphous chars

As the charring intensity increases the development of amorphous chars results from the significant increase of aromatic carbon units, which are ordered randomly as condensation continuous and can be seen in region three of Figure 2.2. During this transition stage, the formation of intermediate molecules such as phenols, quinones, pyrroles, furans, anhydrosugars, pyramids and small aromatic units are evident at these charring intensities (Basu, 2010b; Keiluweit *et al.*, 2010). The aromatic carbons from lignin are enriched due to the loss of less heat-resistant compounds. These compounds are responsible for the significant decrease in char yield and non - carbon atoms (Keiluweit *et al.*, 2010).

Composite chars

Composite chars result in further heating of the amorphous chars, which increase the degree of condensation and result in the formation of turbostratic crystallites as seen in the fourth region of Figure 2.2. At this transition stage, the atomic pore size within the carbon crystalline layers, as well as the recondensation and trapping of volatile components, results in an increased surface area of the crystal. Therefore aromatic, aliphatic, and the oxygen-containing volatile matter is retained in the char matrix, surrounding the turbostratic crystal with a low-density amorphous matrix (Basu, 2010b; Keiluweit *et al.*, 2010).

Turbostratic chars

Turbostratic char transition stage occurs due to increased temperatures during thermal combustion whilst condensation also increases. During this phase turbostratic crystals increasingly grow in a long-range order which strengthens the crystalline matrix. This elongation of crystals results in the development of graphene-like sheets which continuously lead to a greater loss of amorphous carbons and results in the significantly increased surface area of the crystal. The conversion of these amorphous carbons form into dense turbostratic chars and lead to the formation of nanopores (Keiluweit *et al.*, 2010). The nanopores crystalline matrix together with the aromatic carbon structure and the trapped volatile matter, are what result in the final characteristics associated with what is commonly known as biochar (Basu, 2010b; Keiluweit *et al.*, 2010).

Increased recovery of liquid products during pyrolysis can be accomplished using fast pyrolysis. Low heating rates, however, result in the higher rates of thermal combustion once the pyrolysis chamber reaches a specific temperature. This results in a slow output of newly formed components within the system. Remaining in the system under higher temperatures for a longer time period results in further decomposition of these liquid components. Components of lower molecular weight together with the volatile constituents are thus produced (Santos *et al.*, 2015).

2.3.4 Biochar variants and its adsorption specificity

The type of plant material biochar originates from, as well as the temperature of the pyrolysis process used during the production of these biochars, can significantly influence its adsorption specificity. This results from a molecular change which occurs between constituents of the carbonous graphene-like compounds (Inyang & Dickenson, 2015; Tan *et al.*, 2015). The constituent of the biochar can vary to such an extent that it can selectively adsorb specific pollutants or contaminates. The extent of specificity is determined by the plant or waste derivative, as well as the temperature used during pyrolysis which alternatively determines pore size. A variety of biochars produced at specific temperatures which are selective for specific contaminants or pollutants are illustrated in Table 2.4.

Table 2.4. Biochar variants and selectivity of these biochar's for specific contaminants or pollutants

Biochar Type	Pyrolysis Temperature (°C)	Pollutants/Contaminants	Reference
Bamboo	400, 600	Sulfamethoxazole	Yao *et al.* (2012)
Coconut Coir	250-600	Chromium	Shen *et al.* (2012)
Eucalyptus	400	Methylene blue dye	Sun *et al.* (2013)
Pinewood	300	Lead	Liu and Zhang (2009)
Rice Husk	300	Lead	Liu and Zhang (2009)
Rise husk	350	Lead, copper, sink, Cadmium	Xu *et al.* (2013)
Spartina alterniflora	400	Copper	Li *et al.* (2013)
Dairy manure	200	Atrazine	Cao *et al.* (2009)
Oak	400	Catechol	Kasozi *et al.* (2010)
Pig manure	700	Carbaryl	Zhang *et al.* (2013)
Grass	300	Fluridone	Sun *et al.* (2011)
Loblolly pine chips	300	Carbamazepine, diclofenac and ibuprofen	Jung *et al.* (2013)
Hardwood litter	600	Sulfamethazine	Teixidó *et al.* (2011)
Pine needles	550	trichlorobiphenyl	Wang *et al.* (2013)
Pine needles	700	Nitrobenzene	Chen *et al.* (2008)
HCL-treated willow wood	600	DNA	Wang *et al.* (2014)
Steam activated wood	300	E. *Coli*	Mohanty and Boehm (2014)
Maize	400	Perfluorooctane sulfonate	Chen *et al.* (2011)

2.4 BIOCHAR AS A FILTRATION MATERIAL

2.4.1 Adsorbent capability

The use of biochar as a filtration media is a form of low cost and effective technology for the removal of organic and inorganic contaminants from aqueous solutions (Park *et al.*, 2015; Santos *et al.*, 2015). Compared to activated carbon, biochar is less carbonised and thus not only more cost-effective to produce but also stores more oxygen and hydrogen within the biochar, together with the ash originating from the biomass used during biochar production. Biochar can thus result in the effective adsorption of hydrocarbons, other organics, and some inorganic metal ions. Through these adsorptive properties, biochar can thus be used in water purification systems (Mohan *et al.*, 2014). Biochar can be introduced as a bio adsorbent material for several contaminants such as pigments, dyes, heavy metals, naphthalene, 1-naphtol, atrazine, phosphorous and some macro and micronutrients (Santos *et al.*, 2015). Additionally, biochar has been suggested as a good sorbent for heavy metals by rapidly changing the properties of these specific heavy metals and thereby decreasing the mobility and bioavailability of the contaminant (Park *et al.*, 2015).

The sorption of heavy metals is, however, dependent on the competitive metal systems and the involved biochar sorption site, which determines the affinity of the biochar for a specific metal (Park *et al.*, 2015). The adsorption capacity of biochar for a single heavy metal isotherm is dependent on how readily that specific metal is adsorbed, with cadmium being the most readily absorbed, following by chromium, zinc, lead and copper. When these heavy metals are, however, introduced to the biochar in a multi-metal isotherm, lead retention is significantly increased whilst the cadmium significantly lost most retention capacity (Park *et al.*, 2015). The biochar can furthermore be exposed to different pre-treatments to enhance its affinity for a specific heavy metal (Jing *et al.*, 2014; Yang & Jiang, 2014; Tan *et al.*, 2015).

Biochar also has the potential to absorb and eliminate organic contaminants such as volatile organic compounds, natural organic matter and disinfection by-products, as well as perfluoroalkyl acids, pesticides from agricultural run-off, and down the drain chemicals such as pharmaceuticals and personal care products (Inyang & Dickenson, 2015). The use of biochar as potential adsorbent of these contaminants out of polluted river water can result in water quality sufficient for use in agricultural systems whilst obtaining stimulating benefits.

A study completed by Takaya *et al.* (2016), on the phosphate and ammonium sorption capacity of biochar, indicates that chars with the lower surface area did indeed vary significantly in adsorption ability than those with the high surface area. This may suggest that surface area is not the only characteristic which results in effective adsorption of these specific compounds (Takaya *et al.*, 2016). Char calcium and magnesium content are believed to play an important role in the effective adsorption of phosphates according to Xue *et al.* (2009). According to the results obtained by Takaya *et al.* (2016), however, a correlation between calcium and magnesium content and the effective adsorption of these two compounds could not be made. Therefore further research should be done on the effective adsorption of phosphates based on the calcium and magnesium content within the char.

The presence and functionalities of phenolics and quinones in biochar as a functional group can react with free radicals such as hydrogen peroxide. By transferring a single electron to the radical and reducing it to hydroxyl radicals, exploitation of these radicals for mineralisation of organic pollutants can occur (Inyang & Dickenson, 2015). Biochar is capable of adsorbing any polar or non-polar organic compounds and it is dependent on the specific type of biochar which is used. For selective adsorption of a specific contaminant, a certain biochar could be used, as indicated in Table 2.4 (Inyang & Dickenson, 2015).

Although most research focuses on the adsorptive interaction of biochar and non-microbial constituents, Carbonaceous media produced by pyrolysis such as biochar has shown to have a strong potential to remove faecal indicator bacteria from stormwater (Mohanty & Boehm, 2014).

2.4.2 Factors playing a role to increase water quality

Attraction forces and particle shape

The effect of biochar on the removal and remobilisation of *E. coli* can be as effective as a 95% reduction. The mobilisation of these microorganisms from biochar columns was reduced to only 2% according to a study done by Mohanty and Boehm (2014). This could be a result of the significantly high attractive forces present in the biochar such as hydrophobic and steric interactions, as well as the rough surface and irregular shape of biochar which can promote bacterial attachment by straining (Mohanty & Boehm, 2014; Inyang & Dickenson, 2015). Furthermore, a concentration of *E. coli* as high as 10^7 CFU. mL^{-1} began to oversaturate the adsorptive attachment sites of the biochar. This may have started resulting in the decreased affectivity for adsorption of bacteria (Mohanty & Boehm, 2014).

Particle size and removal of bacteria

The effect of biochar particle size indicates that smaller char particles, smaller than 125 µm, rather than larger particles, are responsible for the significant adsorption of *E. coli* by trapping the microorganism. This could be due to the decreased surface area or attachment sites on large char particles than it is on fine char particles. Bacterium attaches to the outer surface or internal wall of pores of the biochar particles which are larger than bacterium cells. Fine biochar particles may also increase the compactness of the biochar bed and thus result in increased removal of bacteria by straining (Mohanty & Boehm, 2014).

Infiltration rate and bacteria adsorption

Furthermore, the infiltration rate and the effect thereof on adsorption of bacteria should indicate that, with an increase in infiltration rate, a decrease in adsorption of bacteria is expected. This is, however, not the case as the effective removal of *E. coli* remained at 91%

at slow and fast infiltration times. This provides a great advantage to possible production of pathogenic free water rapidly through a biochar filter and is thus considered as an attractive biofilter amendment (Mohanty & Boehm, 2014).

Deactivation and removal of bacteria

Additionally, during infiltration between successive runs, it might have been expected that an increase in the growth of *E. coli* might have occurred, however, the period of time between runs resulted in a decrease in concentration of *E. coli*. This could have been a result of the removal of *E. coli* by a rate-limited process such as deactivation. The mineral ash and organic carbon constituents of the biochar attach bacteria at different rates and could lead to the removal of *E. coli* during slow attachment of the bacteria on the hydrophobic carbon surfaces (Mohanty & Boehm, 2014).
Inactivated carbon, due to its significantly higher affinity for adsorption potential, results in the increasing amount of sediments, and thus results in fouling of anthropogenic contaminants or dissolved natural organic matter. This leads to a significant and rapid decrease of adsorption potential due to the clogging effect caused by biofilm formation, or the presence of small particles in the filtration media during ageing. This, however, is not the case for biochar due to its reduced affinity for contaminant adsorption (Hale *et al.*, 2011; Mohanty & Boehm, 2014; Mohanty *et al.*, 2014).

Paramagnetic centres

The nature of water-biochar interface interactions can influence the resulting adsorption of pollutants due to the diffusive flow of water through paramagnetic centres of the biochar. Biochar is rich in paramagnetic centres and can have an organic and inorganic nature. Inorganic paramagnetic centres originate from metals such as iron, copper and manganese, which are usually present in the biomass used for pyrolysis during the production of biochar (Conte *et al.*, 2013). The organic paramagnetic centres are generated during the charring process due to unpaired electrons of delocalised pi - systems. These paramagnetic centres are distributed in the char among surface sites as well as bulk-sites, and the diffusion of water through and between these sites can be stalled by pore size and solid-liquid interactions, thus increasing the contact time for water-biochar interactions (Clarkson, 1998; Conte *et al.*, 2013). The water interacts with the biochar by binding to these sites via non -

conventional hydrogen bonds and are the responsive interactions which influence the adsorption of contaminants out of the water (Conte *et al.*, 2013; Inyang & Dickenson, 2015).

Surface area and pores size

Biochar has a large surface area and a microporous structure which is an ideal characteristic to increase its beneficial adsorption potential. This creates excellent potential as an adsorbent to be used as filter media for total suspended solids, nutrients, heavy metals, polycyclic aromatic hydrocarbons and pathogens (Reddy *et al.*, 2014; Inyang & Dickenson, 2015).

The pore size of biochar plays a dominant role in the mechanism of pore filling and thus water-biochar interactions. Porous carbons such as biochar consist of a pore network consisting of large macropores, smaller mesopores and significantly smaller micropores. The pore size influences the surface area of the char significantly and is suggested that smaller pores, thus micropores and small mesopores, are responsible for the effective reduction or removal of organic compounds (Inyang & Dickenson, 2015).

Partitioning and Hydrophobicity

Partitioning contributes greatly to the adsorption of organic chemicals containing hydrophobic molecules. Partitioning occurs in biochar where adsorbed organic compounds solubilise within the organic matter matrix and thereby enhance their adsorption (Inyang & Dickenson, 2015).

The hydrophobicity of the biochar contributes to the adsorption of hydrophobic organic compounds or neutral inorganic entities by partitioning or hydrophobic interactions. Fresh biochars with low surface oxidation levels are hydrophobic. The greater the hydrophobic interaction there is a greater increase in adsorption of contaminants there are (Inyang & Dickenson, 2015).

Graphitisation and pollutant adsorption

The level of graphitisation, which refers to a microstructural change, of biochar plays a crucial role in the adsorption of planar aromatic compounds as a result of the aromatic-pi and cation-pi interactions within the graphene-like biochar surface (Inyang & Dickenson, 2015). Aromatic-pi systems are produced if lower pyrolysis temperatures are used (500ºC) during biochar production. These pi-systems contain electron-withdrawing entities that can accept electrons and thus adsorb contaminant which can readily donate an electron.

Complete graphitisation of biochar results from pyrolysis temperatures exceeding 1 100ºC during biochar production and results in the formation of polycondensed aromatic rings or high electron-rich graphene sheets. This may serve as a π-donor that binds electron-withdrawing molecules such as chlorine substituent in atrazine (Inyang & Dickenson, 2015).

Electrostatic interactions and pollutants adsorption

Electrostatic interactions are a key factor to the adsorption of ionic and ionisable organic compounds as a result of the surface charge of the biochar. The adsorption of ionic contaminants or molecules are attracted to the surfaces of the biochar with an opposite charge. This enables cationic organic compounds to bind to the negatively charged sites on the biochar surfaces, whilst anionic contaminants will bind to a positively charged site on the biochar such as the paramagnetic centres (Inyang & Dickenson, 2015).

2.4.3 Factors playing a role to decrease water quality

Leaching of volatile compounds

During pyrolysis, the condensation or recondensation of liquids and gases increase the organic compound content of specific biochars and are released before reaching pyrolysis temperatures. These organic compounds may be a form of contaminants which can be leached out of the biochar (Mohanty & Boehm, 2014). These volatiles, in either gaseous or liquid phase, when dissolved in water, are highly mobile and result in great toxicity leading to inhibition of plant growth and germination (Buss & Masek, 2014).

Large surface area

Biochar does not exhibit good adsorption potential for nitrates and phosphates due to the large surface area resulting in a large negative charge. This decreases even more so with biochar produced at high temperatures (Park *et al.*, 2015). During hydrophobic interactions, the adsorption of contaminants becomes competitively bound and results in certain contaminants not binding as strongly. This is particularly a problem as the biochar becomes more saturated with pollutants. The adsorbed apolar molecules and water molecules are selectively adsorbed, whilst the hydrophobic molecules are adsorbed on biochar surfaces with low hydration energy, and can thus be distinguished from partitioning (Inyang & Dickenson, 2015).

Induced microbial environment

During the use of filtration, in between runs of intermittent flow of water samples through a biochar column, the time period between each run whilst filtration does not occur plays an important role for the stimulation of growth of microorganisms or even pathogens. It could either induce the growth or the microorganism could potentially decay due to inactivation (Mohanty & Boehm, 2014).

Time-dependent

Diffusion or partitioning of water through biochar can be a slow process and can thus be the rate-limiting step specifically when using biochar with a biofilm developed on the surface due to ageing (Inyang & Dickenson, 2015).

2.5 BIOCHAR AS AN AMENDMENT IN SOIL

Biochar is a rather complex and amorphous substance and is used specifically as a soil additive to increase plant growth inducers and decrease plant growth inhibitors. There has been an increasing interest in research of this soil amendment due to the great influence and effects it has on water retention, removal of pollutants, the microbial community and the reduction of emissions of greenhouse gasses in a soil environment. It may, therefore, serve as a strong amendment for soil which is degraded or fertiliser scarce as it helps the soil to retain any nutrients available (Cernansky, 2015).

2.5.1 Plant growth and ideal soil characteristics

Plant growth is largely dependent on the nutrients found within the soil in which it is anchored. This essential nutrient can be categorised into two groups namely, macronutrients and micronutrients. Macronutrients such as nitrogen, phosphorus, magnesium, potassium, carbon, hydrogen and oxygen are required by plants in large quantities, as it plays a major role in the growth and development of cellular components such as proteins, nucleic acid and larger organic molecules of the plant cell (Morgan & Connolly, 2018). Micronutrients are used by the plant as cofactors for enzyme activity and include nutrients such as iron, zinc, manganese and copper (Morgan & Connolly, 2018). The adsorption of these nutrients from the soil is not always that easy as the chemical composition and physical attributes of the soil, as well as the chemical form in which the nutrient can influence the uptake thereof by the plant roots (Duong *et al.*, 2012; Morgan & Connolly, 2018).

An increased level of nitrogen and phosphorus content within the soil plays an important role in enhancing the plant's roots and shoot biomass, as well as the area of the leaf and fruit yields in plants such as wheat & tomatoes (Agele *et al.*, 2011; Duong *et al.*, 2012). Usually, plants acquire nitrogen from the soil in the form of ammonia or nitrates, however, when the sources of nitrogen are depleted certain species of plants from the Fabaceae family initiate symbiotic relationships with nitrogen-fixing bacteria called Rhizobia (Francioli *et al.*, 2018; Morgan & Connolly, 2018). The bacteria are able to convert nitrogen gas from the atmosphere into ammonia for the plant and in exchange, the plant provides the bacteria with carbohydrates derived from photosynthesis, which the microbe uses to produce energy (Morgan & Connolly, 2018). If there is a deficiency of phosphates it can also be absorbed by the plant by relying on the mycorrhizal symbiotic relationship. This symbiosis relies on fungal microorganisms which increases the roots surface area for the adsorption of the nutrient (Francioli *et al.*, 2018; Morgan & Connolly, 2018).

Furthermore, according to Duong *et al.* (2012), an increased electric conductivity, as well as a pH between the range of 6 and 9, would be beneficial to soil quality and play a role in increasing the yield of plant biomass. Soil with acidic pH usually results in either deficiency or unusable form of essential micronutrients by plants, whilst the micronutrients increase to toxic levels for most plant species (Medinski, 2007). Soils with a basic pH of over 8 could result in a deficiency of these micronutrients, which can indicate the presence of phytotoxic boron (Medinski, 2007).

The salinity of soil also plays an important role in water availability and water-soluble nutrients, which are associated with plant growth and yield (Medinski, 2007). Soils containing high salt content reduces moisture availability to plants and may lead to dehydration due to the osmotic potential created in the soil and results to the greater energy expenditure of the plant to absorb water (Medinski, 2007). As a result, nutrient uptake by plants associated with water may be largely influenced by the salinity of the soil.

The macronutrient, potassium, is the most abundant cation within the plant cell and plays major roles in balancing the charges of cellular anions, enzyme activation, control of stomatal gateways and serves as an osmoticum for cellular growth. Plants which do not adsorb enough potassium usually result in browning or yellowing of leaves, curling of leaf tips and reduced growth and fertility (Morgan & Connolly, 2018).

Iron is an example of a micronutrient which is rather essential as a cofactor for proteins which are involved in processes such as photosynthesis and respiration (Morgan &

Connolly, 2018). Iron is one such nutrient which is not readily available for the plant to absorb. Iron forms insoluble complexes in aerobic and neutral soils, and can results in plant mobilisation of the iron in the rhizosphere before it can be absorbed into the plant (Morgan & Connolly, 2018). Plants which are iron deprived usually display interveinal chlorosis, which is a condition of the leaves where the veins remain green whilst the areas of the leaf between these veins are yellow (Morgan & Connolly, 2018).

The excess uptake of micronutrients can also contribute to the production of reactive oxygen species (ROS) and can lead to plant tissue damage (Morgan & Connolly, 2018). In addition, the plant uptake system may not be able to distinguish between all essential nutrients and may lead to the adsorption of toxic elements such as lead and cadmium. Not only do these toxins result in the reduced uptake of essential nutrients and plant growth, but also enter the food cycle and could potentially result in the exposure of these toxins to consumers (Morgan & Connolly, 2018).

2.5.2 Biochar influence in soil biota for plant growth

Within a soil environment, the physical and chemical properties of biochar particles influence the water mobility between the different kind of soil grains, thus influencing the water retention in the soil available for plant growth (Govender *et al.*, 2011; Cernansky, 2015). The soil type dramatically influences the potential for plant growth, and biochar can improve the quality of any type of sand. Biochar also contributes to the inhibiting effect of pathogenic damage to plant roots by binding to possible signalling molecules that bacterial cells secrete to coordinate their pathogenic activity (Masiello *et al.*, 2013; Cernansky, 2015).

A study completed on the impact of Biochar on development and productivity of pepper and tomato grown in fertigated soilless media by Graber *et al.* (2010), indicated that biochar affects the microenvironment of the rhizosphere by shifting the microbial growth towards beneficial plant growth-promoting fungi or rhizobacteria, as a result of the physical or chemical characteristics of the biochar (Srinath *et al.*, 2003; Harman *et al.*, 2004; Kloepper *et al.*, 2004; Gravel *et al.*, 2007; Graber *et al.*, 2010). That study also hypothesises that the chemical constituents in the biochar resulted in stimulating plant growth, whilst inducing systemic resistance of pathogenic plant microorganisms by a dose - responses phenomenon is known as Hormesis (Calabrese & Blain, 2009). These chemical constituents include organic compounds such as hydroxyl acid, acetoxy acid, benzoic acids, diols, triols, phenols and *n*-alkanoic acid which appear in low dosage in biochar (Graber *et al.*, 2010). A study completed by Dempster *et al.* (2012), on the effect of Eucalyptus biochar in coarse-textured soil on the microbial biomass, however, indicated an overall decrease of microorganisms even when the pH of the soil increased to a more optimal level for microbial growth (Dempster *et al.*, 2012). This could be due to the pore size of the biochar particles which are favourable for the habitation of microorganisms (Strong *et al.*, 1998).

The significance of plant growth is also dependent on the nutrition in the soil available and not only water. Soil treated with biochar affects the nutritional properties of soil by increasing the availability of potassium as well as other nutritive organic matter (Liu *et al.*, 2013; Cernansky, 2015). Whilst the nutrients in the soil is retained by the biochar, the pollutants in the soil such as heavy metals can bind to the biochar particles and keep it from reaching the plants and inhibiting their growth (Cernansky, 2015). A study completed by Park *et al.* (2011) on the effect of chicken manure-derived biochar and green waste derived biochar on promoting plant growth whilst evaluating immobilisation of metal, indicate a significant reduction in ammonium nitrate, cadmium, copper and lead concentration in the soils due to the immobilisation of these metals (Park *et al.*, 2011). Both types of biochar not only reduced these negative affecting compounds but also increased the availability of nutrients such as phosphorous and potassium which together increased the yield of plant dry biomass (Uchimiya *et al.*, 2010; Park *et al.*, 2011).

A study completed by Iqbal *et al.* (2015), in the effect of biochar on leaching of soil nutrients from compost in bio-retention systems, indicated that biochar produced at 600ºC did not significantly retain nutrients such as organic carbon, nitrogen and phosphorous, however, it did indeed retain metal contaminants. These soil nutrients may be leaching out into the bio-retention systems used to treat stormwater. The organic carbons in the system did not adsorb in the presence of the biochar due to the possible contact time and insufficient biochar saturation, which reduced the effective adsorption of dissolved organic carbons (Iqbal *et al.*, 2015). The nitrogen, nitrates, and nitrites were not significantly adsorbed due to the negative charge of biochar, which would only reduce ammonia volatilisation, however, other research indicates that a pinewood - derived biochar produced at temperatures higher than 600ºC could adsorb these contaminants (Knowles *et al.*, 2011; Mukherjee *et al.*, 2011; Clough *et al.*, 2013). The leaching of phosphorous through the biochar is likely due to the low concentration of aluminium oxide, and iron oxide present in the biochar, which are the limiting properties for phosphorus leaching (Iqbal *et al.*, 2015).

The addition of biochar to soil also reduced the concentration of pesticides, such as imidacloprid, isoproturon, and arsine in pore water, according to a study completed by Jin *et al.* (2016). According to the results obtained by this study, the specific biochar and the increasing pyrolysis temperature had a significant correlation with surface area and organic carbons, which are the primary characteristics for increasing adsorption of these pesticides.

Jin *et al.* (2016) also found that plant-based biochar was more effective at adsorbing these pesticides than waste-based biochar, due to the increased surface area of the biochar produced from rice and wheat straw (Jin *et al.*, 2016). In addition, higher temperature biochar's play a detrimental roll in reducing the phytoavailibity of pesticides such as chlorpyrifos and carbofuran from the soil, as a result of sequestering of pesticide residues, according to a study completed by Yu *et al.* (2009). This significant study indicates that the addition of biochar to a soil environment reduces plant uptake of pesticides.

2.6 CONCLUSION

It is clear that as important as water is in our everyday lives, it is found more and more often that water sources are becoming more and more polluted. This results from numerous events occurring such as global warming and increased water pollution. In South Africa, water sources are becoming increasingly scarce as the population rises annually and applies a great amount of pressure on the country's infrastructure. The cascade of events which occur as a result of population increases only further, worsening the situation, leading to polluted waters. The pollutants can be extremely dangerous and can even result in a fatal situation such as the consumption of specific pathogenic bacteria and viruses. Other pollutants can result in acute or chronic conditions as a result of high levels of heavy metals within the water. This condition or fatalities do not only occur if the polluted water is consumed but also any other consumable which may have been in contact with such polluted water such as fresh produce. It is, therefore, a high priority to ensure water which is consumed or used for agricultural purposes are as hazardous free as possible.

In order to achieve a quality of water suitable for irrigation, the water can be exposed to a variety of treatments which may improve microbiological, biological, physical, chemical and hydrological properties of the water. Many of these treatments can be used as a disinfectant and eliminate pathogenic microorganisms and others can improve the physicochemical parameter of the water. All these treatments have many advantages and usually fewer disadvantages, however, these disadvantages may result in other problems such as disinfectant byproduct production, which is known to be potentially carcinogenic, or even the cost of certain treatment may not be feasible and investors might thus not be interested.

Filtration systems seem to show much potential, although there is a large variety of filtration media which has not yet been documented, many may prove to be beneficial in adsorption potential. Biochar is one such filtration media which could be extremely beneficial to improving the overall quality of water as a result of its adsorption properties. A key aspect of biochar is the quality of production thereof, which include residence temperature and residence time during the production of this media. Another important aspect is the granular size of the biochar. The smaller the particles the better, due to increased pore size and surface area. These together with aromatic compounds of the biochar, which is dependent on the plant matter from which the biochar is produced from, are responsible for the adsorption potential. Biochar is more commonly used in soil and it proves to be extremely beneficial in this environment by adsorbing all the desired nutrient components for increased plant growth. The adsorption potential may be used in a water filtration system in the same way thereby adsorbing pollutants out of the water. Therefore the investigative use of biochar as a water filtration media to improve the quality of polluted water in the current study will give a greater indication of the beneficial potential of biochar.

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CHAPTER 3

DETERMINING THE EFFECTIVE ADSORPTION POTENTIAL OF TWO BIOCHAR VARIANTS IN RIVER WATER FILTRATION COLUMNS, AND THE EFFECT ON ULTRAVIOLET TREATMENT

3.1 ABSTRACT

Water being a crucial substance is polluted by everyday activates and leads to the diminishing quality of water. This disqualifies the use of this water for irrigational use and increases the demand for improving water quality. Filtration media such as biochar could be used as a potential treatment of this polluted water to increase its microbiological and physicochemical quality. Biochar can originate from many different kinds of plant material. For this study, however, pine and black wattle were chosen as biochar filtration media. The biochar was produced by pyrolysis and used in a column filtration process through which untreated river water was filtered. Granular activated carbon (GAC) and silica sand were also used as a reference/control filtration. The untreated river water and filtrates from each column were analysed microbiologically and physicochemically. Results of microbial content indicated that the biochars were only effective in the first run (initial treatment of polluted river water), after which the microbial count in the filtrate increased, at times even above the initial level of the untreated river water. The biochar had the strongest and most positive impact on the TSS, VSS, COD, turbidity and UVT% of the untreated river water. The pH and alkalinity of the river water were intermediately affected whilst the TDS and EC were negatively impacted by the biochar. The second part of the study involved the pine biochar filtrates being exposed to UV treatment. The improved UVT% of the river water from the pine biochar enabled the UV treatment to be more effective at removing microbial content from the filtrates at lower dosages. An improved UVT% of the filtrate results in a decreased exposure time and dosage strength needed for the UV treatment. From the results, it was clear that both the biochar filtration and UV treatment was most effective when used in sequence. Although the treatments in Trial 1 and 2 improved the quality of water for certain properties such as microbial content, COD, TSS, VSS, turbidity and UVT%, it remained insufficient for use as agricultural irrigation water.

3.2 INTRODUCTION

Fresh groundwater and the availability thereof is decreasing rapidly around the world. Without water, life on earth would not be sustainable and therefore is considered as one of the most crucial substances known to man. Although the earth is surrounded by water, less than 1% is easily available for the use of activities associated with agricultural irrigation. In South Africa, the availability and quality of surface water, which is used for agricultural irrigation, is deteriorating rapidly as a result of climate change and ever-increasing population growth (DWA, 2016; Nyamwanza & Kujinga, 2016; Fischer-Jeffes *et al.*, 2017; WHO, 2017b; Bizikova *et al.*, 2015). This can put significant stress on the food chain due to the possible health risk certain pollutants may cause as well as the insufficient water supply for stimulating plant growth (Rijsberman, 2006; Fabris *et al.*, 2008).

The most direct threat to the safety of water is likely the microbial content within the water. Specifically, pathogenic microbes, which could result in harmful infection if a high enough dose were to be consumed, making them the greatest risk in the food chain (Qadir *et al.*, 2010; Allende & Monaghan, 2015; Johannessen *et al.*, 2015). Considering the possible transfer of pathogens from irrigation water to crops and ultimately to the consumer, the specific guidelines for agricultural irrigation water only indicates a limit of faecal coliforms (no more than 1 000 cfu per 100 mL)(DWA, 2013), and does not include a limit for pathogens. In South Africa, this limit is often exceeded and serves as an indication of the microbial status and therefore the quality of surface water which is ideally used for irrigation. Other indicators of the water quality include the content of organic and inorganic matter as well as the total solids within the water which may result in acute conditions and undesirable characteristics (DWAF, 1996; Fabris *et al.*, 2008; Rice *et al.*, 2012; DWA, 2013; Schug, 2016). It is therefore essential to manage water supply systems with the necessary treatments to reduce problematic pollutants. There are a wide variety of treatments that can be used to reduce or remove undesired contaminants from water (Parsons & Jefferson, 2006; Li *et al.*, 2013; Allende & Monaghan, 2015; Schug, 2016; WHO, 2017b; WHO, 2017a). In the production of potable water, a combination of treatments are usually used to ensure safe drinking water. For the treatment of irrigation water, this is not always economical and thus less or cost-effective treatments are of primary interest (Qadir *et al.*, 2010).

A treatment such as biochar filtration has been gaining much interest due to its activated carbon-like properties and the benefits which it provides as a soil amendment (Inyang & Dickenson, 2015; Tan *et al.*, 2015). Biochar is a carbon-rich char produced from plant material and with its aromatic compounds and porous crystalline structure, it provides the ideal environment for adsorption (Santos *et al.*, 2015; Tan *et al.*, 2015). Biochar can serve as a cost-effective alternative to granular activated carbon(GAC) filtration processes which are used to eliminate undesirable contaminants from water (Tan *et al.*, 2015).

Table 3.1. South Africa water quality guidelines: Agricultural use of irrigation water indicating the ideal limitations of selected variables for acceptable water use (DWAF, 1996; DWA, 2013)

Variable	Limits
pH	6.5 – 8.4
TDS/ Electric conductivity	< 40 $mS.m^{-1}$
Faecal coliforms	< 1 000 cfu per 100 mL
Sodium Adsorption Ratio (SAR)	< 2
Suspended solids	< 50 $mg.L^{-1}$

Pyrolysis is used to produce the biochar via thermo-chemical combustion whilst the plant matter is oxygen-deprived (Brewer *et al.*, 2012; Bridgwater, 2012; Hodgson *et al.*, 2016). The production method, plant material from which it is produced and size of the biochar particles plays a major role in its effective adsorption potential (Keiluweit *et al.*, 2010; Mohan *et al.*, 2014; Mohanty & Boehm, 2014; Inyang & Dickenson, 2015; Santos *et al.*, 2015; Tan *et al.*, 2015). Biochar is primarily produced via slow pyrolysis which results in temperatures of 350 – 800ºC during combustion and has a residence time which varies from hours to days (Brewer *et al.*, 2012; Joubert, 2013; Hodgson *et al.*, 2016). The higher the temperature of pyrolysis the greater the porosity of the biochar will be (Keiluweit *et al.*, 2010). The type of plant material influences the aromatic compounds within the biochar. The higher the lignin content of the material the higher quantity of aromatic compounds will be bound in the biochar (Keiluweit *et al.*, 2010). The particle size of biochar influence the sedimentation of pollutants through a filtration system (Mohanty & Boehm, 2014). The smaller the particles the greater the surface area will be and thus the increased contact time and contact surfaces there will be between pollutant and biochar particle. These key properties of biochar are the driving force to the adsorption of unwanted pollutants from an aqueous environment.

The use of biochar as filtration media may also result in sufficient improvement of water quality to enhance the benefits of other treatments. Biochar could, for example, be used to improve the ultraviolet transmission of the water (Park *et al.*, 2015; Santos *et al.*, 2015), followed by exposure to ultraviolet (UV) light treatment, which can reduce the microbial load. The UV light is known to reduce pathogenic microbes from water due to its mode of action which directly influences the microorganisms DNA/RNA and thus inhibits growth thereof (Olivier, 2015; WHO, 2017a; Van Rooyen, 2018). High organic and aromatic content can influence the absorbance of UV by microbes and will thus require higher UV doses and longer exposure times to be effective. The use of a biochar filter may, however, be used to adsorb these interfering contaminants and thus reduce the dose and exposure time required for the removal of microbes. This would result in a more efficient and cost-effective UV treatment due to the reduction in energy use and time.

This study investigated the adsorption potential of two variants of biochar within a low-cost filter to improve the quality of polluted river water. The objective of this study was firstly to determine the microbial and physicochemical properties of the Plankenburg river water and secondly to determine the quality of the river water after treatment with filtration media variants. The most effective filtration media was then selected as a physical treatment of the river water after which a photochemical treatment was applied (UV treatment). This was investigated to determine the combined effect of both treatments on the microbial content of the river water.

3.3 MATERIALS AND METHODS

3.3.1 Research study design

It is understood that biochar and the plant material from which it originates, may have an influence on the adsorptive capacity for possible pollutants from river water. Part of the study was to compare two different biochars originating from different plant materials, namely pine and black wattle. By distinguishing between river water which interacts with these two biochars through a column packed filtration system, a conclusion can be drawn whether the plant material from which the biochar is made would have an influence on the adsorption potential. This was accomplished by constructing filtration columns with the same dimensions and the same volume of filtration media. The samples that were filtered through all the columns were of the same quality and originated from the same sampling site. These two filtration media variants were, furthermore, compared with a commercially produced granular activated carbon (GAC) which is a commonly used filtration media in filtration systems to improve water quality. This was carried out to determine the potential for these two variants of biochar as filtration media in the removal of a pollutant from, or improving the water quality of the river water. The GAC serves as a positive control to analyse the efficacy of each of the variants of biochar and a conclusion can thus be drawn to determine which variant of biochar may be ideal for the improvement of water quality.

Filtration systems are known to improve water quality to some extent. However, it may not necessarily improve polluted river water by such extremes to deem the water viable for irrigation purposes. These standards may, however, be achieved by combining filtration systems with a photochemical system such as ultraviolet (UV) treatment. The purpose of the biochar filtration would be to improve certain physicochemical properties of the river water before being exposed to UV treatment to reduce the microbial content. By using these two forms of treatment, it can be determined whether the treatments in combination would improve water quality to a greater extent than using either of the individual treatments alone. By improving certain physicochemical properties, UV treatment may also become more efficient at destroying microorganisms.

The study consisted of two distinct trials where different sized untreated river water samples were exposed to different water treatments. The first trial, Trial 1, consisted of sampling 15 L of untreated river water every three days. This continued for 30 days, thereby sampling a total of 450 L untreated river water over the course of ten sampling runs as can be seen in Figure 3.1. This water was used in two parts of Trial 1. The first part (Part 1) consisted of analysing 2 L of the untreated river water on the day of sampling, to determine the water quality thereof. These results were then compared to the South African water quality guidelines. The second part (Part 2) consisted of constructing filtration columns with different filtration media (silica sand, GAC, black wattle biochar and pine biochar) which would be used to filter the untreated water on the day of sampling. A total of 12 L of the untreated river water that was sampled was divided equally and filtered using these columns. There was thus 2 L of untreated river water which was filtered through each column every three days. The filtrates were collected after filtration runs and were analysed.

The second trial, Trial 2, consisted of sampling 15 L of untreated river water every three days. This, however only continued for ten days, thereby sampling a total of 150 L of untreated river water over the course of four sampling runs, as seen in Figure 3.2. Similar to Trial 1, the untreated river water that was collected was used in two parts of Trial 2, where Part 1 consisted of analysing the untreated river water before exposure to any filtration and UV treatments. to determine the water quality thereof. These results were then compared to both the raw, untreated river water, and the South African water quality guidelines.

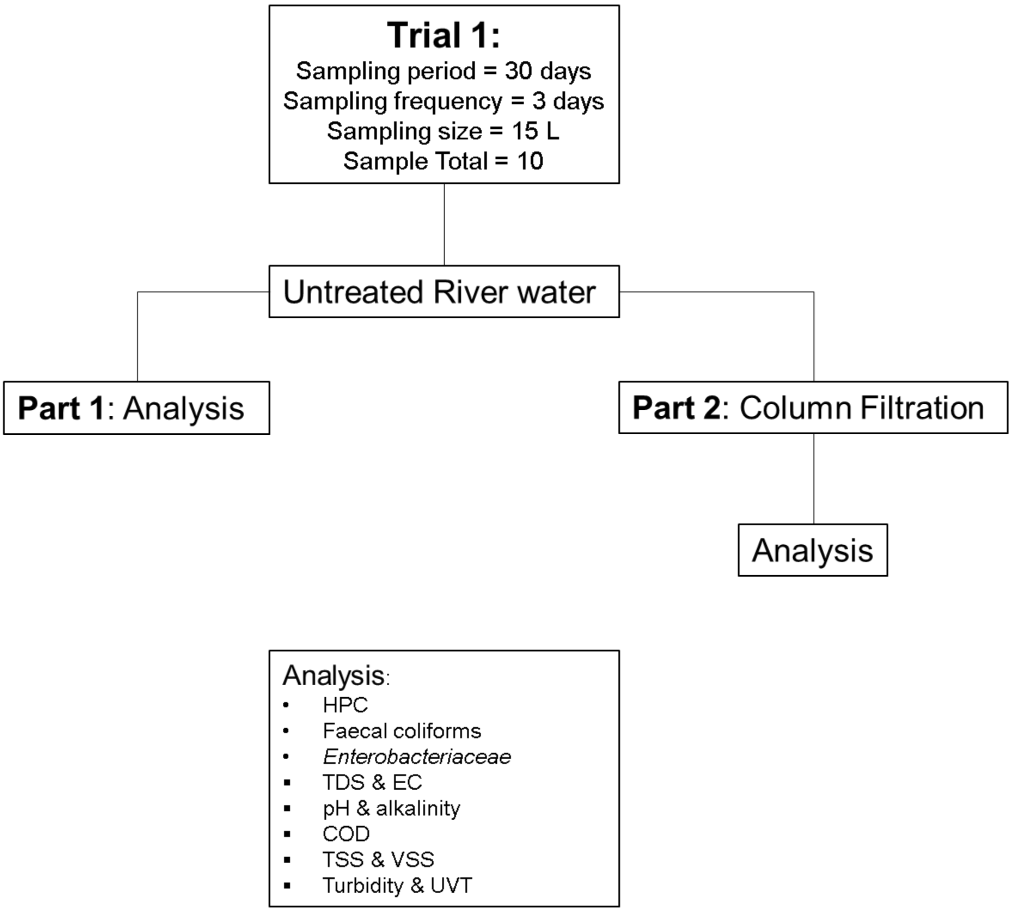

Figure 3.1. Trial 1 indicating the process flow of experimentation and analysis as per the research study design

Part 2 of this trial consisted of determining the water quality after the untreated river water was exposed to UV treatment, filtration treatment and both treatments used in sequence. Two filtration columns with pine biochar were constructed for Part 2 of this trial. Through each column, 2 L of untreated river water was filtered each day for a period of ten days. Only the filtrates that were collected every third day was analysed and exposed to UV treatment. A raw sample of untreated river water was also exposed to UV treatment. The UV treatments for both samples (raw untreated river water and filtrate collected on the third day of filtration) were carried out on the same day. The results obtained from the filtrates and UV treated river water were compared to the quality of the untreated river water as well as the South African water quality guidelines.

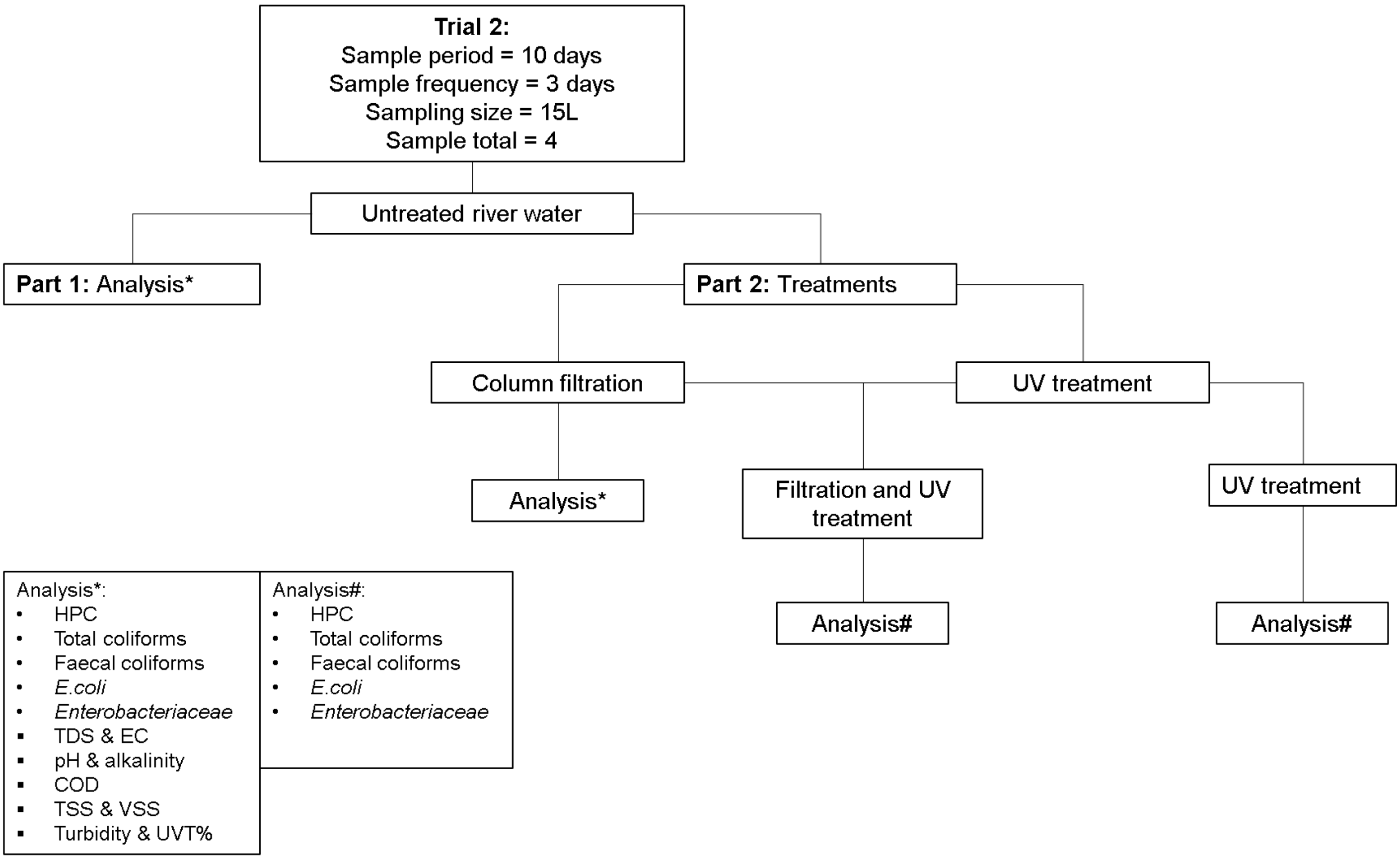

Figure 3.2. Trial 2 indicating the process flow of experimentation and analysis as per the research study design.

3.3.2 Trial 1

Part 1: Untreated river water quality: Microbiological and physicochemical characteristics

The microbial analysis included the determination of heterotrophic microorganisms, faecal coliforms and *Enterobacteriaceae* concentration within the untreated river water. This was determined by performing two serial dilutions of the untreated river water samples. The serial dilutions were plated in duplicates on PCA, VRBA and VRBGA pour plates for the enumeration of heterotrophic microorganisms, faecal coliforms and *Enterobacteriaceae,* respectively, after which they were plated and enriched with the selected agar. The plates were incubated at the selected temperature and time for the desired microorganism after which the plate counts were recorded. The physicochemical analysis consisted of a range of tests and included total dissolved solids (TDS), electrical conductivity, pH, alkalinity, chemical oxygen demand (COD), total suspended solids (TSS), volatile suspended solids (VSS), turbidity and ultraviolet transmission (UVT).

Part 2: Filtration of untreated river water: Differentiating between the efficacy of pine and black wattle biochar and comparing it with GAC as filtration media

In this part of the study, a total of six glass filtration columns, open at both ends, were used for packing duplicate pine biochar, duplicate black wattle biochar, granular activated carbon (GAC) and silica sand filtration columns as can be seen in Figure 3.3. These filtration columns were exposed to the untreated river water under gravitational flow. The cylindrical glass columns had a length of 65 cm and an inside diameter of 8.5 cm. The glass columns were sterilised and closed at one end with a thin layer of sterilised glass wool and wired mesh with the aid of autoclaved cable ties. This was used to prevent the filter media from falling through the column whilst maintaining the flow of the filtrate.

The columns were packed with a layer of 100 g sterilised acid-washed sand, followed by a layer of 2 L of filter media after which another layer of 200 g sterilised acid-washed sand was added to the top of the filter media. A filtration column with sterilised acid-washed sand (300 g) only served as a negative control.

The GAC was a commercially produced GAC from coconut shells with a granular size of 0.6 – 2.36 mm. The coconut shell GAC was acquired from AQUAMAT South Africa (Pty) Ltd. The pine and black wattle biochar were both produced by Adsorb Technologies (Pty) Ltd. at 800 ºC with a granular size of 0.6 – 1.2 mm. The purpose of the two layers of sand was to prevent movement or floatation of the filtration media within the column as filtrate passes through. A circular sponge type material made from PVC was placed above the sand layer to evenly distribute flow and prevent channelling. The columns were placed in a wooden frame to keep them upright and rested on sterilised glass funnels with their spout into a 2 L sterilised reagent bottle. Columns were rinsed with 10 L of sterilised distilled water to remove any leached constituents of the filtration media.

After rinsing of the columns, 2 L of untreated river water was poured from the top of the column to pass through the filter media and was collected at the bottom of the column as a filtrate. This was done once every three days. The top of the column remained closed with sterilised foil at all times between successive runs to avoid any external contamination. It should be noted that during all ten runs of the filtration process the filtration columns remained in place and were not altered in any way. The 2 L filtrates (taken every third day) from each filtration column were collected and analysed microbiologically and physicochemically.

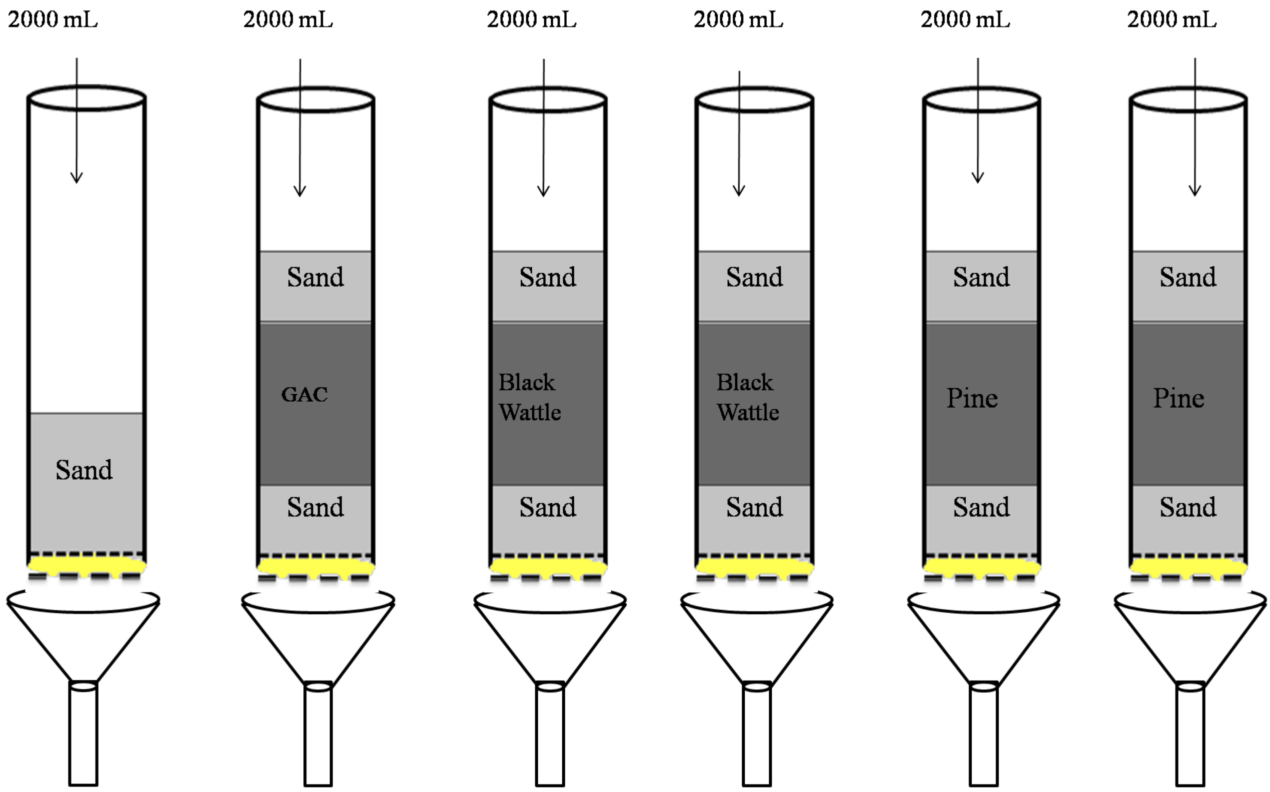

Figure 3.3. Diagram illustrating the six filtration columns used in Part 2 of trial 1 through which 2 L of untreated river water was treated every three days. The following filtration media were used: silica sand (1), GAC (1), black wattle biochar (2) and pine biochar (2).

For the microbiological analysis of the pine and black wattle biochar filtrate, only one serial dilution per column was completed (pine and black wattle biochar columns were in duplicate). For the untreated river water and the filtrate from the GAC and silica sand columns, duplicate serial dilutions were completed. Therefore, a total of two serial dilutions were completed per treated and untreated river water after which it was plated and enriched with the selected agar for the enumeration of heterotrophic microorganisms, faecal coliforms and *Enterobacteriaceae*. All treated samples were analysed physicochemically in duplicate for TDS, EC, pH, alkalinity, COD, TSS, VSS, turbidity and UVT%.

3.3.3 Trial 2

Part 1: Untreated river water quality: Microbiological and physicochemical characteristics

In this part of the study, untreated river water was sampled on days 1, 4, 7 and 10. On these days, part of 1 L of untreated river water was used to analyse the microbiological and physicochemical status of the untreated river water. The microbiological analysis was completed by performing duplicate serial dilutions of each collected sample of the untreated river water. With each serial dilution, a series of pour plates were performed in duplicate of PCA and VRBA for the enumeration of heterotrophic microorganisms and faecal coliforms, respectively. The microbial analysis also consisted of STEC detection and enumeration of *E. coli,* total coliforms and *Enterobacteriaceae* of the untreated river water. This was completed by the Food Science Department, Stellenbosch University. The untreated river water was also analysed physicochemically in duplicates for TDS, EC, pH, alkalinity, COD, TSS, VSS, turbidity and UVT%.

Part 2: Filtration and UV of untreated river water: Influence of using pine biochar water filters as a physical treatment on the improved efficacy of ultraviolet water treatment on microbial reduction

For this part of the study, the remaining part of the 1 L untreated river water used in Part 1, was exposed to a UV dose to determine the microbial reduction of the UV treatment on the untreated river water. The UV treatment of the untreated river water comprised of a dose of UV at 40 $mJ.cm^{-2}$, followed by a reactivation step which was done in conjunction with Sivhute (2019). Two pine biochar columns identical to those used in Trial 1 were constructed. These columns were exposed to 2 L of river water samples for 10 consecutive days. The river water which had been filtered by the pine biochar columns were also treated with UV at 40 $mJ.cm^{-2}$, followed by a reactivation step, on days 1, 4, 7 and 10. These water samples which were treated with UV and biochar filtration were analysed microbiologically and physicochemically as indicated in Figure 3.3.

The microbial analysis was completed by performing duplicate serial dilutions of each sample collected from the biochar filtration alone and from the combined treatment of the river water with the biochar filtration and UV treatment. With each serial dilution, a series of pour plates were performed in duplicate on PCA, VRBA and VRBGA for the enumeration of heterotrophic microorganisms, faecal coliforms and *Enterobacteriaceae*, respectively. Additional microbial analyses were conducted on the same samples by Sivhute (2019) and included *E. coli*, *Enterobacteriaceae* and total coliforms counts and STEC detection. Both the filtrates and the filtrates treated with UV were analysed physicochemically in duplicates for TDS, EC, pH, alkalinity, COD, TSS, VSS, turbidity and UVT%.

3.3.4 General Methods

3.3.4.1 River water sampling

Raw river water was sampled from the Plankenburg River in Stellenbosch (33°55'52.1"S 18°51'06.1"E), according to the SANS method 5667-6 (SANS, 2006). A sterilised 1 L glass beaker and extension pole was used to submerge the beaker into the river and collect the water sample, after which it was transferred into sterilised 5 L reagent bottles. The 5 L reagent bottles were filled and transferred into cooler boxes for transport. This was then stored at 4ºC until used.

3.3.4.2 Sterilised acid-washed sand

The purpose of acid washing the silica sand was to remove volatile constituents which could influence the physicochemical and microbiological analysis. Silica sand was acquired from AQUAMAT South Africa (Pty) Ltd. with a granular size of 0.6 – 1.2 mm. The silica sand (600 g portion) was acid washed twice with 300 mL of 0.1 N hydrochloric acid, after which the sand was rinsed off with 500 mL aliquots of distilled water four consecutive times. The acid washed silica sand was autoclaved at 121ºC for 20 min and dried for 24 hours at 100ºC. After drying the acid washed silica sand was ready for use in the filtration columns.

3.3.4.3 Ultraviolet (UV) treatment

Ultraviolet treatment was completed by Sivhute (2019) using a bench-scale collimator instrument (Bersons, Netherlands). The instrument was used to expose 20 $mJ.cm^{-2}$ and 40 $mJ.cm^{-2}$ of UV light to 25 mL of water sample before and after filtration. The UV exposure time was dependent on the UVT% of untreated and filtered river water and was calculated using the following formula (Hallmich & Gehr, 2010):

$$\mathrm{Iavg}, \lambda\ (\mathrm{mW.cm} - 2\ ) = \mathrm{I0}\lambda[\frac{1- e\mathrm{dln}(\mathrm{UVT}(\lambda))}{-\mathrm{dln}(\mathrm{UVT}(\lambda))}]\ [1]$$

$$\text{Desired dose } (\mathrm{mJ.cm} - 2\ )\ = \text{Average intensity } (\mathrm{mW.cm} - 2\ )\ \times \text{Exposure time } (\mathrm{s})\ [2]$$

Where:

I_{avg}, λ = average intensity of UV light over the sample depth, d

$UVT(\lambda)$ = UV transmission at wavelength, λ, determined using an optical path length of 1 cm

$I_0\lambda$ = intensity of UV light measured at the surface of the sample.

After UV treatment the samples were exposed to a three-hour reactivation phase to compensate for repairing of microbial DNA (Sivhute, 2019).

3.3.4.4 Microbiological methodology and analysis

The microbiological methods consisted of completing serial dilutions (10^0 – 10^{-6}) in Ringer solution of the samples according to SANS 6887-1 method (SANS, 1999), and duplicate pour plates of these dilutions for the enumeration of selected groups of microorganisms on Plate Count Agar (PCA), Violet Red Bile Agar (VRBA) and Violet Red Bile Glucose Agar (VRBGA) were completed.

Heterotrophic plate count (HPC)

The heterotrophic group of microorganisms were enumerated by following the SANS 4832 method (SANS, 2007). Serial dilutions (10^0 – 10^{-6}) were made of the water samples before and after the filtration treatment. All the series dilutions were plated in duplicate with 1 mL of the dilutions and BIOLAB® PCA was used to perform the pour plates (Merck, South Africa). The PCA plates were incubated at 30ºC for 48 hours after which the colonies were counted on each plate representing a count between 25 – 250 cfu.mL^{-1} and recorded.

Faecal coliforms and Enterobacteriaceae

The enumeration of the faecal coliforms and *Enterobacteriaceae* was performed by following the method set out by Schraft and Watterworth (2005), and SANS 21528-2 respectively (SANS, 2005). The exact same serial dilutions used for the HPC counts were used for both faecal coliform and *Enterobacteriaceae* enumeration. After adding 1 mL of each dilution to duplicate plates, pour plates were made using BIOLAB® VRBA and VRBGA in duplicate and incubated at 44ºC and 35ºC, respectively for 24 hours (Merck, South Africa). After incubation, colonies were counted on plates containing 25 – 250 cfu.mL^{-1} and recorded.

3.3.4.5 Physicochemical methodology and analysis

The river water samples were all analysed physicochemically before and after the filtration treatment. These analyses included total dissolved solids (TDS), electrical conductivity (EC), pH, alkalinity, chemical oxygen demand (COD), total suspended solids (TSS), volatile suspended solids (VSS), turbidity and ultraviolet transmission percentage (UVT%). The recorded measurements were compared to the irrigation water quality guidelines as seen in Table 3.1.

3.3.4.6 Total dissolved solids (TDS) and Electric conductivity (EC)

TDS and EC were determined using a TDS-3 meter (HM DIGITAL, USA) and HI8733 conductivity meter (HANNA instruments, USA), respectively. The TDS meter was calibrated using a solution made up with sodium chloride at 90 parts per million whilst the EC meter was calibrated using a conductivity standard solution of 12 880 $uS.cm^{-1}$ (HANNA Instruments, USA). Distilled water was used as a blank for both TDS and EC meters.

3.3.4.7 pH and Alkalinity

The pH and alkalinity for each sample was determined by using a WTW® pH 3110 SET 2 meter and SenTix® 41 pH probe (WTW, Germany). The pH meter was calibrated using standard buffer solutions to a two-point calibration. The determination of alkalinity of the samples was performed in the same 20 mL used for pH determination by titrating with 0.1 N sulphuric acid to a pH of 4.4 (APHA, 2005). The volume of sulphuric acid used for the titration was recorded and the alkalinity of the sample was calculated using the following formula (APHA, 2005):

$$Alkalinity = \frac{A \times N \ \times 50\ 000}{mL\ sample}$$

Where:

A = standard acid used and

N = normality of standard acid

3.3.4.8 Chemical oxygen demand (COD)

The COD of the samples was determined using Spectroquant® COD Cell Test Kit of the range of 4.0 – 40.0 $mg.mL^{-1}$ (Merck). To each test tube containing COD solution, 3 mL of the sample was added. The contents of the test tubes (COD solution and 3 mL sample) were then mixed together and placed in a digestion block, at 150ºC for 2 hours. Together with the duplicate samples, a blank sample (distilled water) and a standard solution sample (20 $mg.mL^{-1}$ COD) were digested. After digestion, the test tube contents were mixed and cooled, after which the samples were measured in a Spectroquant® NOVA 60 spectrophotometer (Merck).

3.3.4.9 Total suspended solids (TSS) and Volatile suspended solids (VSS)

TSS and VSS were determined in duplicate using the filtration method as proposed by (APHA, 2005), where 70 mm (1.6 µM) prepared and pre-weighed Munktell® micro-glass fibre paper (LASEC, South Africa), was used to filter 250 mL of a water sample using a 70 mm Whatman® vacuum filter. After filtration, the filter paper was placed in an oven at 100ºC for 2 hours and reweighed. This weight was recorded for the determination of TSS by using the following formula (APHA, 2005):

$$mg\ total\ dissolved\ solids\ per\ L = \frac{(A - B) \times 1000}{sample\ volume, mL}$$

Where:

A = Weight of dried residue + dish, mg, and
B = Weight of dish, mg

After the filter paper was weighed it was placed in a muffle furnace at 550ºC for 2 hours after which it was cooled and reweighed. The weight was recorded for the determination of VSS by using the following formula (APHA, 2005) :

$$mg\ volitile\ solids\ per\ L = \frac{(A - B)\ \times 1000}{sample\ volume, mL}$$

Where:

A = weight of residue + dish before ignition, mg, and

B = weight of residue + dish after ignition, mg

3.3.4.10 Turbidity and Ultraviolet transmission percentage (UVT%)

The turbidity was determined using a portable Orion AQUAfast 3010 turbidity meter (Thermo Scientific, USA) by placing 15 mL of water sample in the test tube which was placed in the turbidity meter. Duplicate samples were completed and recorded. The turbidity meter was calibrated using standard solutions of 0.02, 20.0, 100.0 and 800.0 NTU and distilled water was used as a blank. The UVT% was determined using a portable Berson Sense® T254 handheld UVT meter (Berson, Netherlands) by placing the probe into 300 mL water samples which were placed in a 500 mL beaker. The UVT% was recorded in duplicate and distilled water was used as a blank at 100% UVT.

3.3.4.11 Data Analysis

All raw results were captured and processed using Microsoft Excel. The standard means and standard deviation between duplicates were determined using Sigmaplot® 14. Diagrams were created using Sigmaplot® 14, to show the effect which the different filtration media had on the untreated river water.

3.4 RESULTS AND DISCUSSION

3.4.1 Trial 1

Part 1: Untreated river water quality: Microbiological and physicochemical characteristics

The Plankenburg river water was specifically sourced at a site where it may have been polluted from upstream industrial outflow and rural activities. The microbial content of the water, as well as the physicochemical characteristics, resulted in water quality which would not meet the irrigation water guidelines. The river water contained a large variety of different microorganisms which can be seen from the high heterotrophic plate count (HPC) in Table 3.2, ranging from 4.14 - 5.22 log cfu.mL^{-1}, for Run 6. This is not nearly as high as 6.4 cfu.mL^{-1} which was the result of HPC counts in the Plankenburg River by Olivier (2015).

A high count of faecal coliforms are usually an indicator of potential contamination with pathogens and may thus be hazardous (Blumenthal *et al.*, 2000; Edberg *et al.*, 2000; Ashbolt *et al.*, 2001). According to the irrigation water quality guidelines, the limit for faecal coliforms may not exceed 1 000 cfu per 100 mL (DWAF, 1996; DWA, 2013). This limit was indeed exceeded in the Plankenburg river for Runs 1 - 10 and reached up to 3.89 log cfu.mL^{-1} (785 000 cfu.100 mL^{-1}), as seen in Table 3.2. It has been shown by both Olivier (2015), and Van Rooyen (2018), that the faecal coliform counts in the Plankenburg river can reach up to 6.4 and 6.5 cfu.100 mL^{-1}, respectively.

The *Enterobacteriaceae* count of the river water from Runs 1 - 10 ranged between 3.17 - 4.38 log cfu.mL^{-1} as seen in Table 3.2. According to Van Rooyen (2018) and Sivhute (2019), the Plankenburg River can become contaminated with higher levels of *Enterobacteriaceae*, reaching as high as 6.5 and 5.3 cfu.mL^{-1}, respectively. The limit for *Enterobacteriaceae* according to Forsythe (2010), resulting in safe to eat foods, should not exceed that of 1 000 cfu.mL^{-1} (3.0 log cfu.mL^{-1}). Although the limit above is for consumable goods it provides a good indication for the safe consumption of water as well as the safe use of that water for irrigation. This is important as microbial content could be transmitted from the untreated river water onto the fresh produce during irrigation, thereby increasing the probability of high *Enterobacteriaceae* counts in the food chain.

The exceedingly high count of *Enterobacteriaceae* is concerning as it could consist of many pathogens such as Shiga-toxin-producing *E.coli* (STEC), *Salmonella, Listeria monocytogenes* and *Vibrio* and could thus enter into the food chain via irrigation.

The physicochemical characteristics were also monitored. The electrical conductivity of the river water was in the range of 0.43 – 0.76 mS.cm^{1} as seen in Table 3.2, thus indicating that it does not conform to the irrigation water guidelines (below 0.4 mS.cm^{-1}). According to Duong *et al.* (2012), however, a higher conductivity within irrigation water may be beneficial for increasing plant biomass. The pH of the river samples varied to the extent that it would either be within the recommended range or it would fall below the minimum pH of 6.5 and even as low as to 5.7. An acidic pH of irrigation water could influence plant growth negatively and result in a decreased yield of harvested crops (Medinski, 2007). According to Spellman (2008), the ideal levels of alkalinity for irrigation water should not exceed 80.0 mg.L^{-1}. The results obtained for alkalinity exceeded these levels and could play a role in reducing plant biomass. The level of alkalinity was between 120.0 – 280.0 mg.L^{-1} for Runs 1 – 10 as seen in Table 3.2.

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Table 3.2. Untreated river water quality of the Plankenburg river before treatment with different filtration media for Sampling plan A

Runs	1	2	3	4	5	6	7	8	9	10
HPC (log cfu.mL^{-1})	4.33	5.02	4.27	4.73	4.98	5.22	4.17	4.14	4.17	4.52
Faecal coliforms (log cfu.100 mL^{-1})	3.39	3.89	3.70	3.35	3.75	2.87	2.78	2.06	3.30	3.22
***Enterobacteriaceae* (log cfu.mL^{-1})**	3.81	4.38	4.11	3.53	4.18	3.60	3.42	3.26	3.17	3.83
TDS (mg.L^{-1})	369.50	398.50	276.00	266.50	278.50	313.50	185.00	453.50	436.00	458.50
EC (mS.cm^{-1})	0.68	0.76	0.52	0.60	0.62	0.73	0.43	0.76	0.72	0.73
pH	7.14	5.92	5.72	6.19	7.03	6.75	7.04	6.38	6.00	7.13
Alkalinity (mg.L^{-1})	271.50	170.00	122.25	139.00	212.75	250.00	139.00	185.75	125.00	191.25
COD (mg.L^{-1})	50.15	50.55	53.85	54.90	55.80	54.95	33.85	52.50	49.50	31.40
TSS (mg.L^{-1})	18.20	13.00	32.60	10.00	12.20	21.60	6.00	15.20	9.20	14.80
VSS (mg.L^{-1})	11.60	10.80	21.40	10.00	10.20	13.40	4.00	11.40	7.00	9.60
Turbidity (NTU)	16.01	21.65	28.85	16.78	18.91	45.50	8.70	43.25	47.00	19.14
UVT (%)	33.85	21.10	24.75	40.70	37.90	26.50	54.90	31.75	17.80	30.10

The water from the Plankenburg River water had a COD range of 31.4 – 55.8 $mg.L^{-1}$. The level of COD within the water samples gives an indication of the natural organic matter (NOM) content as a result of the oxidation of NOM's which occurs in the presence of oxygen. In the samples obtained from the Plankenburg river, the NOM content may play a role in increased microbial growth as well as water colour, taste and odour quality (Fabris *et al.*, 2008; Rice *et al.*, 2012).

The TSS of the untreated river water was the only physicochemical characteristic which was mostly within the limits of the irrigation water guidelines. The TSS of the untreated river water remained below the irrigation water guideline of 50.0 $mg.L^{-1}$ for all of the samples. It is important to note that there was no rainfall during this 30 day sampling period which indicates that the TSS levels are not a result of any climate conditions but merely the fluctuation of solids within the river. The VSS levels of the river water samples were no more than 21.4 $mg.L^{-1}$ in Run 3, as seen in Table 3.2. VSS gives an indication of the inorganic salts which form part of NOM and it is clear that the high level of NOM's was not a result of these inorganic salts. This could, therefore, be a result of contaminants of a more organic nature. This can be observed by comparing the VSS and COD results. By eliminating the VSS from the COD, the remaining result indicated the level of organic matter. Whilst the VSS of all the runs were low, the COD was rather high and thus indicated a high level of organic matter in the river water.

The turbidity guideline for irrigation water indicates that the levels should not exceed 10 NTU (Ayers & Westcot, 1994; Hanseok *et al.*, 2016). The results obtained indicate that the turbidity of the untreated river water varied between 8 - 47 NTU as seen in Table 3.2. The runs which exceed the NTU limit of 10 could have resulted from external contamination upstream which could result in increased organic material in the river water. The ultraviolet transmission percentage (UVT%) of the river water ranged between 17.8 - 54.9 UVT% as seen in Table 3.2. The poor UV transmission percentage could result from phenolic compounds within the river water such as tannins and lignins which could originate from plant material along the river. Although some samples reached a high of 55% the majority remained below 50% and as mentioned by Sigge *et al.* (2016), this would contribute negatively to the efficacy of water treatments such as UV treatments.

The results of the physicochemical characteristics of the Plankenburg River water are comparable to other studies completed by Olivier (2016) and Van Rooyen (2018).

Part 2: Filtration of untreated river water: Differentiating between the efficacy of pine and black wattle biochar and comparing it with GAC as filtration media

Microbial reduction efficacy in filtrates

The results obtained for the HPC in the untreated and treated river water are shown in Figure 3.4. The HPC in the untreated river water in Run 1 was 4.3 log cfu.mL^{-1}. The silica sand filtration only reduced this value of HPC to 4.2 log cfu.mL^{-1} in Run 1, as seen in Figure 3.4. This count of heterotrophs was further reduced by the GAC and black wattle biochar filters to 3.6 log cfu.mL^{-1} and 3.5 log cfu.mL^{-1}, respectively. The pine biochar filtration reduced the HPC most effectively in Run 1 to 2.7 log cfu.mL^{-1}. This trend of reduction was, however, not maintained during the remaining Runs (1 - 10) as can be observed in Figure 3.4. In fact, during Run 2 – 10, the treated river water showed higher counts or negligible reduction of HPC from the untreated river water.

The results obtained for the faecal coliform log counts in the untreated and treated river water are shown in Figure 3.5. The log count of faecal coliforms for the untreated river water was 3.4 log cfu.mL^{-1} in Run 1 and was reduced by the silica sand filtration to 2.8 log cfu.mL^{-1}. The GAC and black wattle filtration also reduced the faecal coliform counts of the untreated river water in Run 1 to 2.6 log cfu.mL^{-1} and 1.3 log cfu.mL^{-1}, respectively. The pine biochar filtration was most effective at reducing the faecal coliforms as it did with the HPC. The pine biochar filtration reduced the faecal coliform count in the untreated river water to 0.2 log cfu.mL^{-1} in Run 1, as seen in Figure 3.5. This indicates that the pine biochar seems to reduce the faecal coliform more effectively than the black wattle biochar, GAC and silica sand. In Run 2, the log count of faecal coliforms in the untreated river water increased to values as high as 3.9 log cfu.mL^{-1}.

The silica sand, GAC and black wattle filtration reduced the faecal coliform count of the untreated water to a negligible amount. It was only the pine biochar filtration which reduced the faecal coliform count in the untreated river water to 2.5 log cfu.mL^{-1}, as seen in Figure 3.5. After Run 2, reductions minimised and, in some cases, counts increased. Reduction of faecal coliforms was not improved by any of the treatments from Run 3 – 10, according to Figure 3.5.

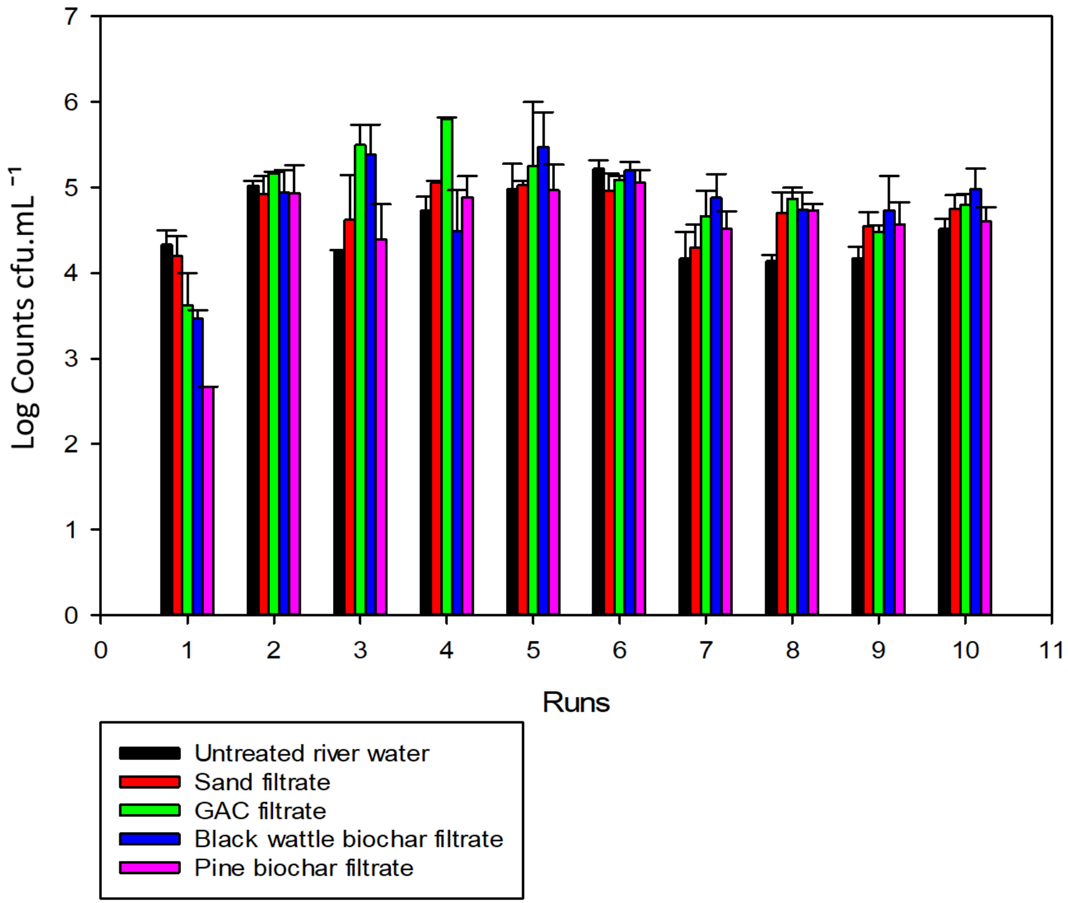


Figure 3.4. Heterotrophic plate counts (HPC) of untreated and treated river water with the following filters: Pine biochar, Black wattle biochar, GAC and silica sand.

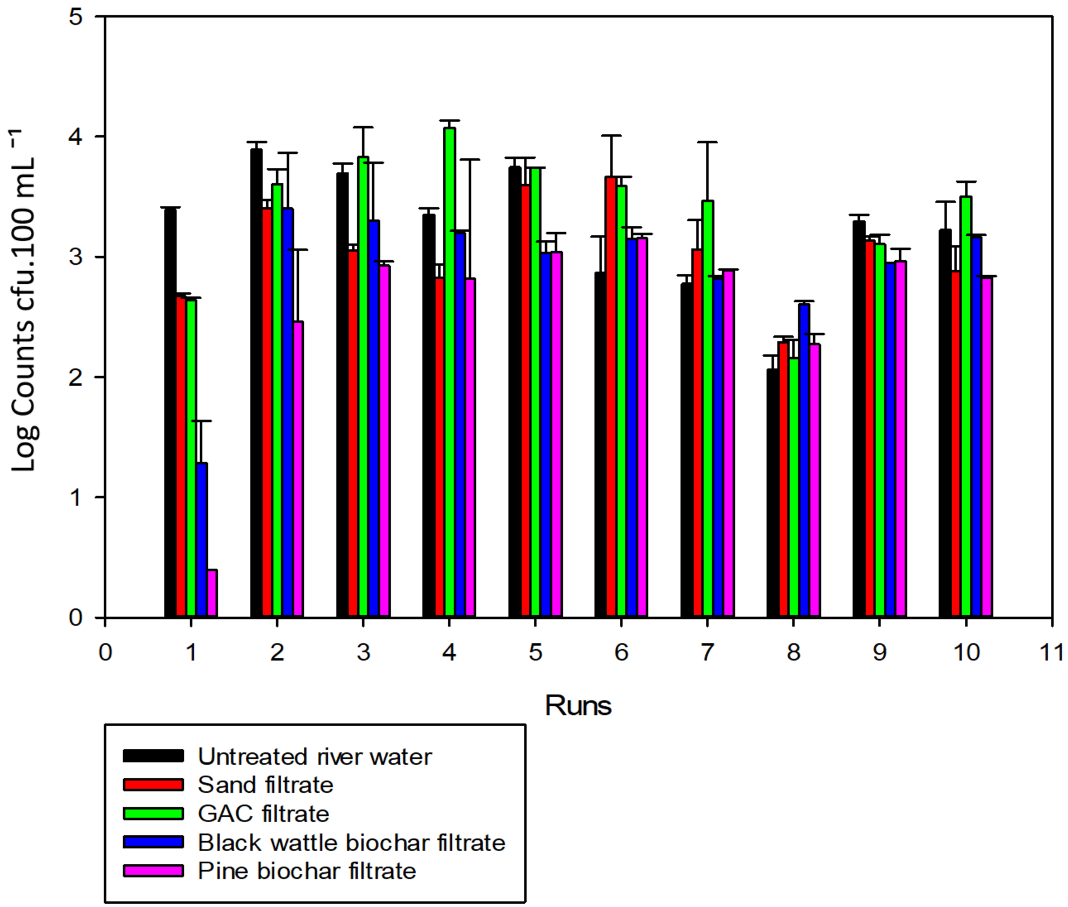


Figure 3.5. Faecal coliform log counts of untreated and treated river water with the following filters: Pine biochar, Black wattle biochar, GAC and silica sand.

The *Enterobacteriaceae* log counts of the untreated and treated river water are shown in Figure 3.6. In Run 1, the untreated river water had a log count of 3.8 log cfu.mL^{-1} according to Figure 3.6. The sand filtration reduced the *Enterobacteriaceae* counts of the untreated river water in Run 1 to 3.72 log cfu.mL^{-1}. The GAC filtration also had a low reduction in the *Enterobacteriaceae* counts from the untreated river water in Run 1 to a count of 3.65 cfu.mL^{-1}. The black wattle filtration was more effective at reducing the *Enterobacteriaceae* counts of the untreated river water in Run 1 to a log count of 1.8 log cfu.mL^{-1}. The pine biochar was yet again the most effective filtration treatment in the removal of *Enterobacteriaceae* according to Figure 3.6 and resulted in reductions in the untreated river water to 0.5 log cfu.mL^{-1} in Run 1. It was only in Run 1 that this reduction by both black wattle and pine biochar filtration was so effective. In Run 2, according to Figure 3.6, the untreated river water had an *Enterobacteriaceae* count of 4.4 log cfu.mL$^{-1,}$ with little reduction thereof by the silica sand and GAC filtration. The black wattle biochar filtration only reduced these *Enterobacteriaceae* counts in the untreated river water to 3.5 log cfu.mL^{-1}. The pine biochar filtration was also not as effective in Run 2 according to Figure 3.6, but did indeed have a notable reduction of the untreated river water counts to 2.6 log cfu.mL^{-1}. From Run 3 – 10 there were no severe reductions in the microbial counts of the untreated river water from any of the filtration treatments as seen in Figure 3.6.

The initial load of HPC in Run 1 could have resulted in the pore filling of the biochars and GAC, resulting in the saturation of the micropores within the biochar and GAC with microbes. During the three day rest period, before the next run (Run 2), the filter media may have created an ideal growing environment for the microbes. Thus, when Run 2 was completed, the three day cultured microbes were washed out of the column and into the filtrates.

The filter media did not remain saturated with river water, instead, it had the opportunity to allow oxygen to pass through the column, thereby enhancing the ideal growing environment for the microbes. The oxygen may also negatively affect the micropore filling by the river water during gravitational flow due to its own occupancy within the micropores, thereby inhibiting the binding or effective filtration of microbes present in subsequent Runs (Keiluweit *et al.*, 2010; Mohan *et al.*, 2014; Mohanty & Boehm, 2014; Inyang & Dickenson, 2015; Santos *et al.*, 2015; Tan *et al.*, 2015).

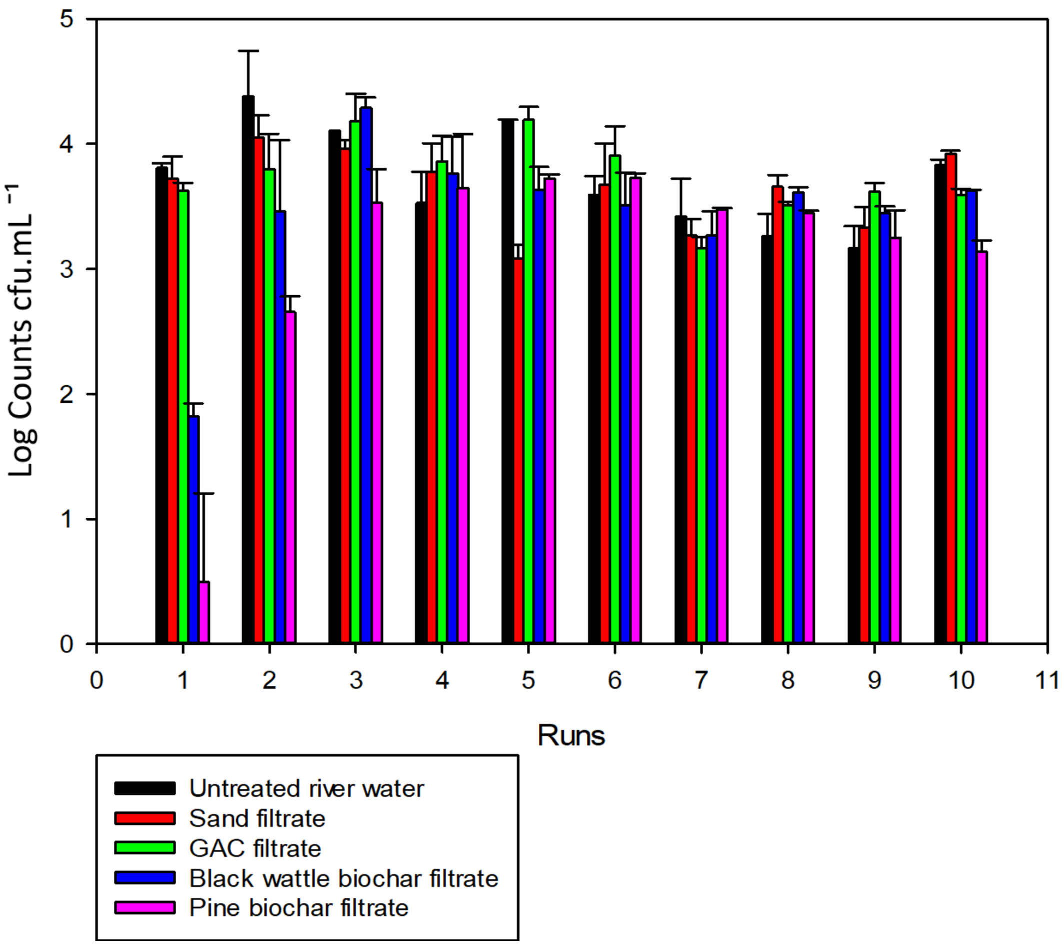


Figure 3.6. *Enterobacteriaceae* log counts of untreated and treated river water with the following filters: Pine biochar, Black wattle biochar, GAC and silica sand.

The unsaturated filter media could have also resulted in the formation of multiple biofilms on the water surfaces in between the micropores of the biochar filtration media. Although a biofilm is another source of nutrients and energy for the growth of microorganisms, they can be dislodged by the interrupted flow of water as well as the degradation which occurs during each run(Simpson, 2008). This would contribute greatly to the increase in log counts after filtration. Furthermore, the growing environment can be further enhanced by possible nutrient adsorption by the filtration media, which the microbes can make use of as a source of energy.

When observing the results in Run 1 for all the types of microbiological analysis, pine biochar reduced the microbes most effectively. This could be due to the larger surface area of the pine biochar in comparison with that of black wattle biochar, GAC and silica sand (WHO, 2004). Another characteristic which may have influenced the efficacy of adsorption of the biochars and GAC is the exposure time between the water molecules and contaminant with the biochar molecules and aromatic functional groups (Who, 2004; Simpson, 2008). Increased exposure time can result in further penetration of the river water into the micropores of the biochar and binding of the contaminants to aromatic groups and carbon structures within the biochar. This may explain why the microbes were not adsorbed by the filter media during Run 2 - 10. The exposure time of the contaminated water with the intermolecular structure of the biochar was not sufficient to result in effective binding of these pollutants with the functional groups. As mentioned previously, the columns are rinsed prior to the start of Run 1, the effective reduction of the microbes observed in Run 1 may, therefore, be as a result of this rinsing step. According to the results obtained by Reddy *et al.* (2014), in determining the potential of using biochar as a filtration media, *E.coli* was not effectively adsorbed during filtration. This contributes to the ineffective adsorption of microorganism by biochar.

In a study completed by Mohanty and Boehm (2014), when using biochar as geomedia for a biofilter, an average of 96% *E.coli* was removed from the urban stormwater. The reduction by this biofilter could result from the specific column design and the continuous flow of polluted water through the geomedia, as well as the backwashing step before filtration which removed colloidal particles (Mohanty & Boehm, 2014). Furthermore, Van Rooyen (2018), also indicated an effective reduction in microbial content in untreated river water, however, only one run was completed for each filtration.

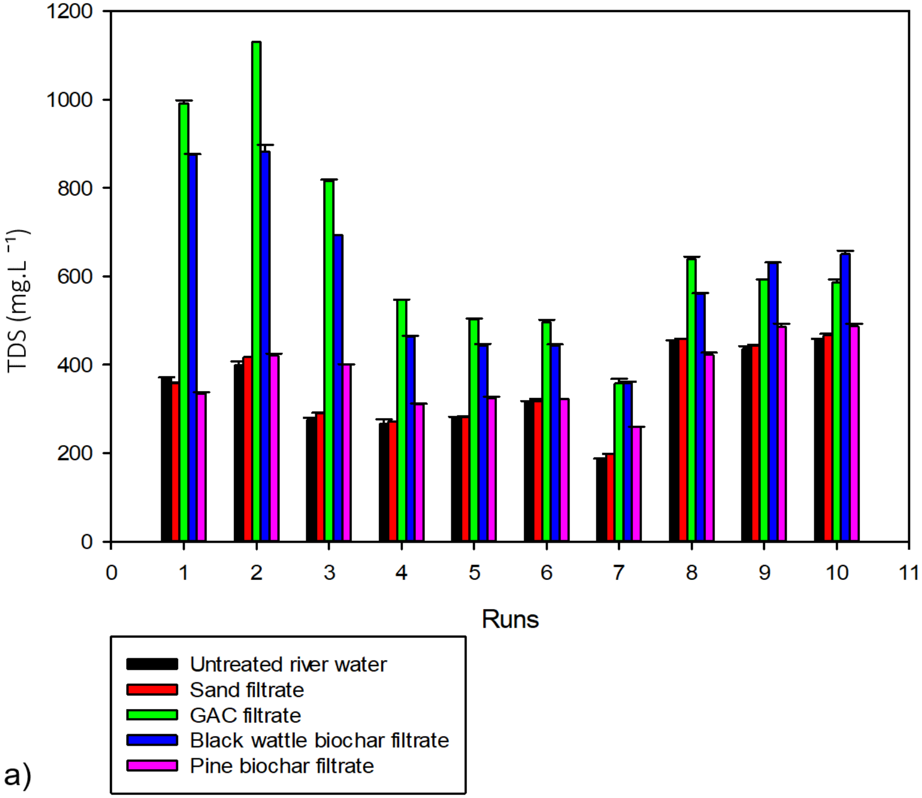
The high microbial load in the washout indicated that only the initial run would result in effective reduction of microorganisms whilst subsequent runs would not. The filtration column design used in this study limits the exploration of continuous flow and backwashing as well as different infiltration rates to improve the microbial status of the untreated river water. It should, therefore, become an objective for further studies to experiment with filtration design to facilitate these features.

Physicochemical efficacy of filtrates

The results obtained for the TDS and EC of the treated and untreated river water are shown in Figure 3.7. The untreated river water in Run 1 for both TDS and EC had a level of 368.5 mg.L^{-1} and 0.68 mS.cm^{-1}, respectively. The results obtained for the silica sand filtration initially showed a slight reduction in both the TDS and EC readings, reaching a level of 361.3 mg.L^{-1} and 0.67 mS.cm^{-1}, respectively. This was seen for Run 2 – 10 where either a slight reduction or increase in both the TDS and EC readings was observed. A similar trend was observed for the pine biochar filtration, which showed a slight reduction in the TDS reading (363.4 mg.L^{-1}) initially whilst a slight increase in the EC reading (0.7 mS.cm^{-1}) was seen initially. This was followed by either an increase or reduction for both readings in subsequent Runs. An increase in both the TDS and EC readings of the treated river water with the GAC and black wattle biochar filtration was observed for Run 1 -10, as seen in Figure 3.7.

The TDS and EC readings for the GAC filtrate in Run 1 reach values of 989.4 mg.L^{-1} and 1.56 mS.cm^{-1}, respectively, whilst the black wattle biochar filtrate had a reading of 842.6 mg.L^{-1} and 1.38 mS.cm^{-1}, respectively. The largest increase in both the TDS and EC readings was seen in Run 2 in Figure 3.7 for both the GAC and black wattle biochar filtrate. Although the result obtained for the untreated river water is bordering on the required standard for EC of lower than 0.4 mS.cm^{-1}, there is not an observable effect on the untreated river water by the silica sand and pine biochar treatment.

The results obtained from the black wattle biochar and GAC treatments indicated a negative effect with TDS values reaching as high as 882 mg.L^{-1} and 1 130 mg.L^{-1}, respectively. Similarly, a negative effect can be seen on the EC results for both treatments, with readings reaching values as high as 1.42 mS.cm^{-1} and 1.61 mS.cm^{-1}, respectively (Figure 3.7). A study completed by Van Rooyen (2018), also indicated an increase (54.5 to 125.1 mS.m^{-1}) in EC after the untreated river water was treated with pine biochar in a filtration system. This could be an indication of leached out dissolved solids from the GAC and black wattle biochar which was not removed during the rinsing phase.



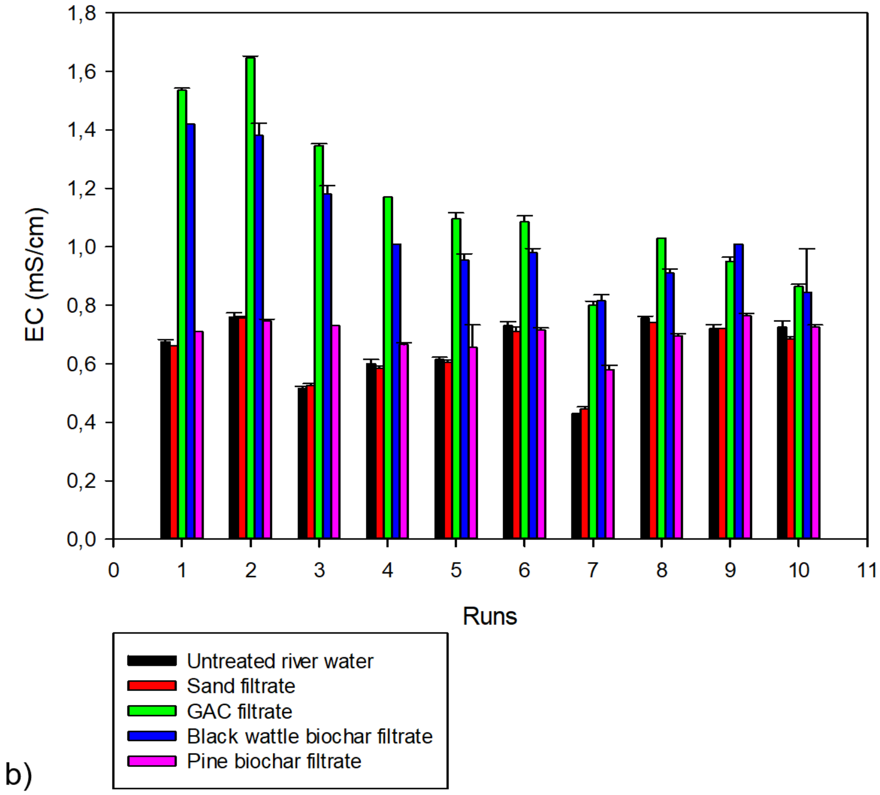


Figure 3.7. a) TDS and b) EC, of untreated and treated river water with the following filters: Pine biochar, Black wattle biochar, GAC and silica sand.

These dissolved solids may have originated from the biochar through pyrolysis, which was made available for hydrophilic interactions to occur with the water molecules during filtration and thereby increasing the washout of these solids into the filtrate. Furthermore, the levels of TDS and EC remain high from Run 8 - 10 and thus negatively affected the quality of water in this aspect. The surface area and pore size may also play a role in the efficacy of each biochar and GAC treatment (Reddy *et al.*, 2014; Inyang & Dickenson, 2015). This may also explain the high level of leach out that occurred with the black wattle biochar and GAC treatments. The larger pore size may result in weaker binding of these dissolved solids, in comparison to the stronger binding within the pine biochar with its smaller pores. The pine biochar, however, did not improve the levels of TDS and EC of the untreated river water which could be explained by the phases of unsaturation between runs and the exposure time between the pine biochar and dissolved solids. This could result in the minimal leach out of solids from the pine biochar each time the char becomes saturated, resulting in the removal of dissolved solids and thus inhibiting the adsorption of pollutants from the untreated river water. These results are in correlation with those of Reddy *et al.* (2014) where the EC readings of the effluents after treatment with biochar was increased and thus not improving the EC and TDS of synthetic stormwater. This may result from leached ionic constituents from the biochar (Reddy *et al.*, 2014).

The results obtained for the pH and alkalinity of the untreated and treated river water are shown in Figure 3.8. The pH and alkalinity of the untreated river water in Run 1 was 7.14 and 271.5 $mg.L^{-1}$, respectively. The results obtained for the silica sand filtration showed either very slight increases or decreases on both pH and alkalinity for Run 1 – 10, therefore indicating that the treatment had little to no effect on the pH and alkalinity of the river water. In contrast to this, the pH of the untreated river water was increased for Run 1 – 10 when treated by the GAC, black wattle and pine biochar filtration. The largest increase was observed in Run 1, reaching a pH of 8.52, 9.45 and 9.38 for the GAC, black wattle and pine biochar, respectively. The black wattle biochar showed the highest increase in pH, for Run 1 – 10, between these three filtration media. The result of the pH of the treated river water are not similar to those in a study completed by Zipf *et al.* (2016), where a high increase in pH was not observed, but rather a small reduction from 7.60 to 7.57, when using a sand and GAC filter.

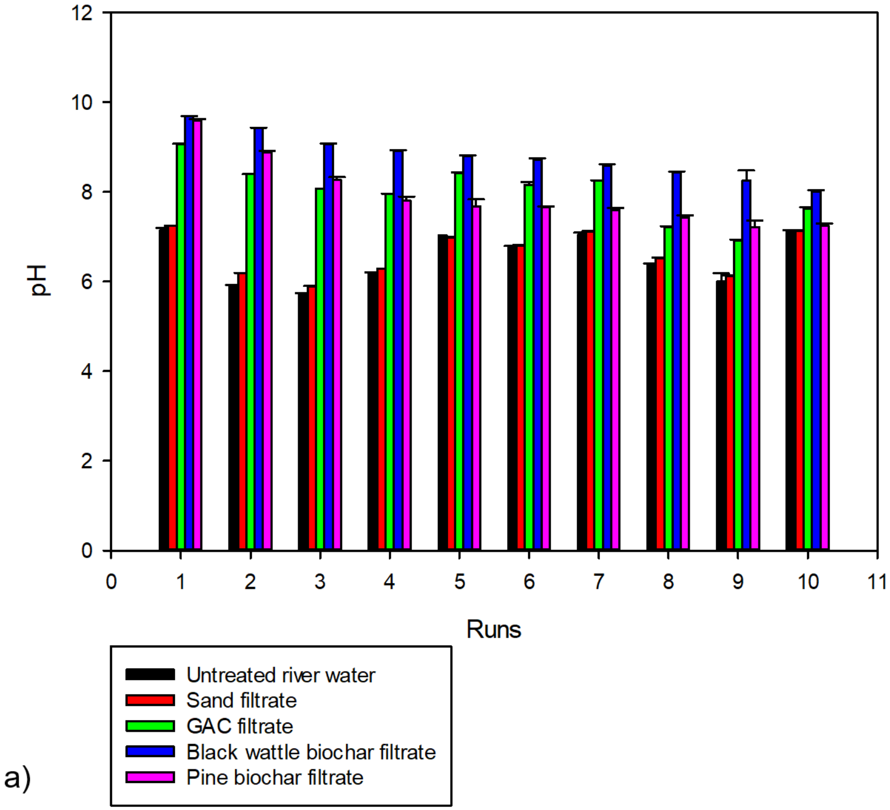
Furthermore, a large increase on the alkalinity was observed with the GAC and black wattle biochar filtration whilst the pine biochar showed an increase to a much lesser extent. The largest increase in alkalinity was again seen in Run 1 reaching 709.6 $mg.L^{-1}$, 668.5 $mg.L^{-1}$and 327.8 $mg.L^{-1}$ for the GAC, black wattle and pine biochar, respectively.

Alkalinity readings provide an indication of a solutions buffer capacity. This high buffer capacity, which reduced during the runs, could be an indication of high levels of carbonate, bicarbonate and hydroxide within the molecular structure of the filtration media which leaches out and in turn results in increased alkalinity of the filtrates (Rice *et al.*, 2012; Schug, 2016). Although fluctuations on both the pH and alkalinity were observed for the untreated river water for Run 1 – 10 in Figure 3.8, the pH and alkalinity of the GAC, black wattle and pine biochar filtrates were always higher compared to that of the untreated river water. Furthermore, the largest increase in both the pH and alkalinity were observed in Run 1.

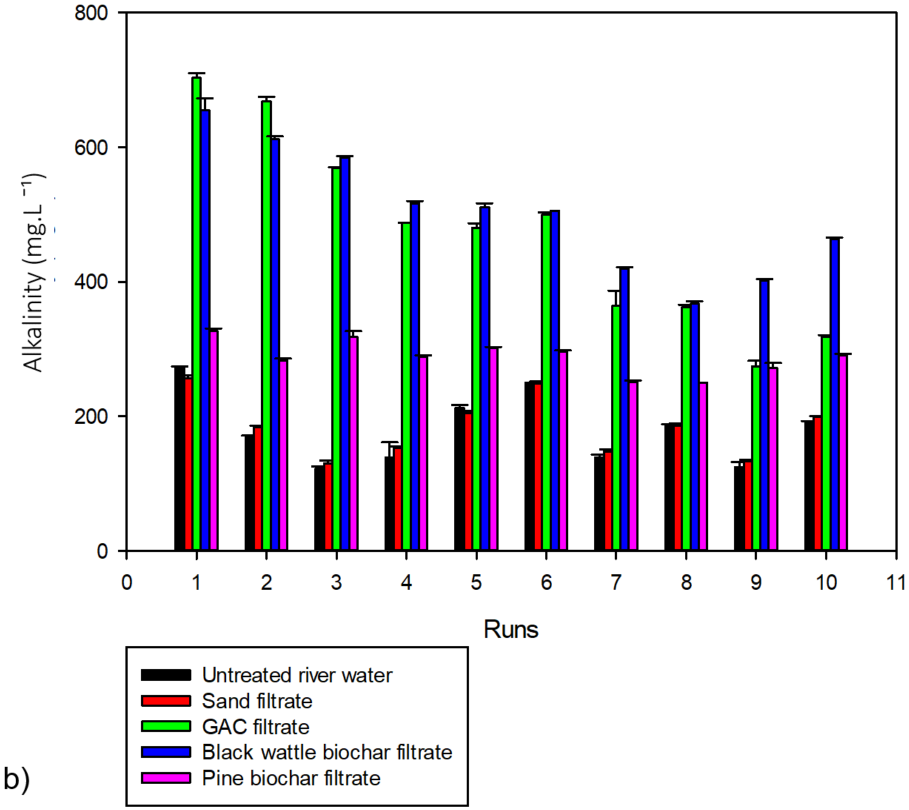
Similar fluctuations in pH were also be observed for the GAC filtrate in Figure 3.8a. Although the pH of the GAC filtrate was higher than that of the untreated river water, these fluctuations in pH correspond with the fluctuations observed for the untreated river water. This indicates that the pH level of the filtrate is dependent on the pH level of the untreated river water. The pH of the pine biochar and black wattle biochar filtrate, however, did not follow this trend which indicated that the pH obtained was as a result of the internal properties of the biochars and was thus independent of the pH levels of the untreated river water.

The pine biochar, as from Run 3, effected the pH of the untreated river water to such a degree that it remained within the limits for irrigational use, despite the acidic levels which the untreated river water reached at Run 3 and 9. This range was only reached at Run 9 for the black wattle filtrate (Figure 3.8.). According to Reddy *et al.* (2014), an increase in pH in the initial runs is not uncommon and could contribute to the initial reduction in microorganisms.

As mentioned previously, the alkalinity of the filtrates remained higher than that of the untreated river water for Run 1 – 10, with the GAC and black wattle filtrate having a much higher increase in alkalinity than the pine biochar filtrate. This could be due to its carbonate, bicarbonate and hydroxide content that is bound to the biochar much more strongly as a result of the smaller pore size and greater surface area of the pine biochar (APHA, 2005; EL-Gawad, 2014). These compounds thus could leach out at a much slower rate when compared to both the GAC and black wattle biochar, resulting in a reduced increase in alkalinity. The alkalinity of the untreated river water further showed fluctuations for all the runs which corresponds with the pH fluctuations that was observed in Figure 3.8a.



a)



b)

Figure 3.8. a) pH and b) alkalinity, of untreated and treated river water with the following filters: Pine biochar, Black wattle biochar, GAC and silica sand.

These fluctuations were again observed with the GAC filtrate, although seen at much higher levels and again indicated that the levels of alkalinity of the GAC filtrate was dependent on the levels of the untreated river water. The alkalinity of the pine and black wattle biochar filtrates, furthermore, did not follow this trend in fluctuations as observed in Figure 3.8b. This could be due to the internal properties of these biochars which is less influenced by the alkalinity of the untreated river water.

The results obtained for the COD of the untreated and treated river water are shown in Figure 3.9. In Run 1 the untreated river water had a COD value of 50.15 mg.L^{-1}. The COD of the untreated river water was initially reduced in Run 1 by the silica sand, GAC and pine biochar filtration media, whilst an increase was seen for the black wattle biochar. The pine biochar filtration media showed the most effective reduction in Run 1, giving a reading of 34.6 mg.L^{-1}. Although an initial reduction in the COD of the untreated river was observed when treated with the silica sand, GAC and pine biochar filtration media, the COD value remained unchanged (or is slightly increased) at Run 2, 4, 6, 8 and 9. Similarly, treatment with the black wattle biochar filtration media resulted in slight increases in the COD of the untreated river water over these runs, as shown in Figure 3.9.

Furthermore, notable reductions in the COD of the untreated river water was observed at Runs 5, 7 and 10 with the pine biochar filtration media and at Runs 7 and 10 with the black wattle biochar filtration media. The smaller pore size of these filtration media compared to that of the GAC and silica sand may result in clogging (WHO 2004), which is present due to sedimentation and ageing within the filtration media and thus could result in the reduction of COD that is observed in Figure 3.9.

Additionally, the presence of different inorganic and organic material in the untreated river water on the specific day of sampling might have interacted differently with the filtration media, which could also explain the reduction in COD that is observed at these runs and would thus require further investigation. From Figure 3.9, a large increase in the COD value was observed for the silica sand at Run 10. This could be explained by the disruption of sediments that accumulates within the biochar in previous runs, which then leaches out when the untreated river water is filtered through the filtration media. Furthermore, the fluctuation and variation in trends and levels of COD of the untreated river water could be explained by the type of organic or inorganic matter within the untreated river water on the day of sampling and thus the specific run.

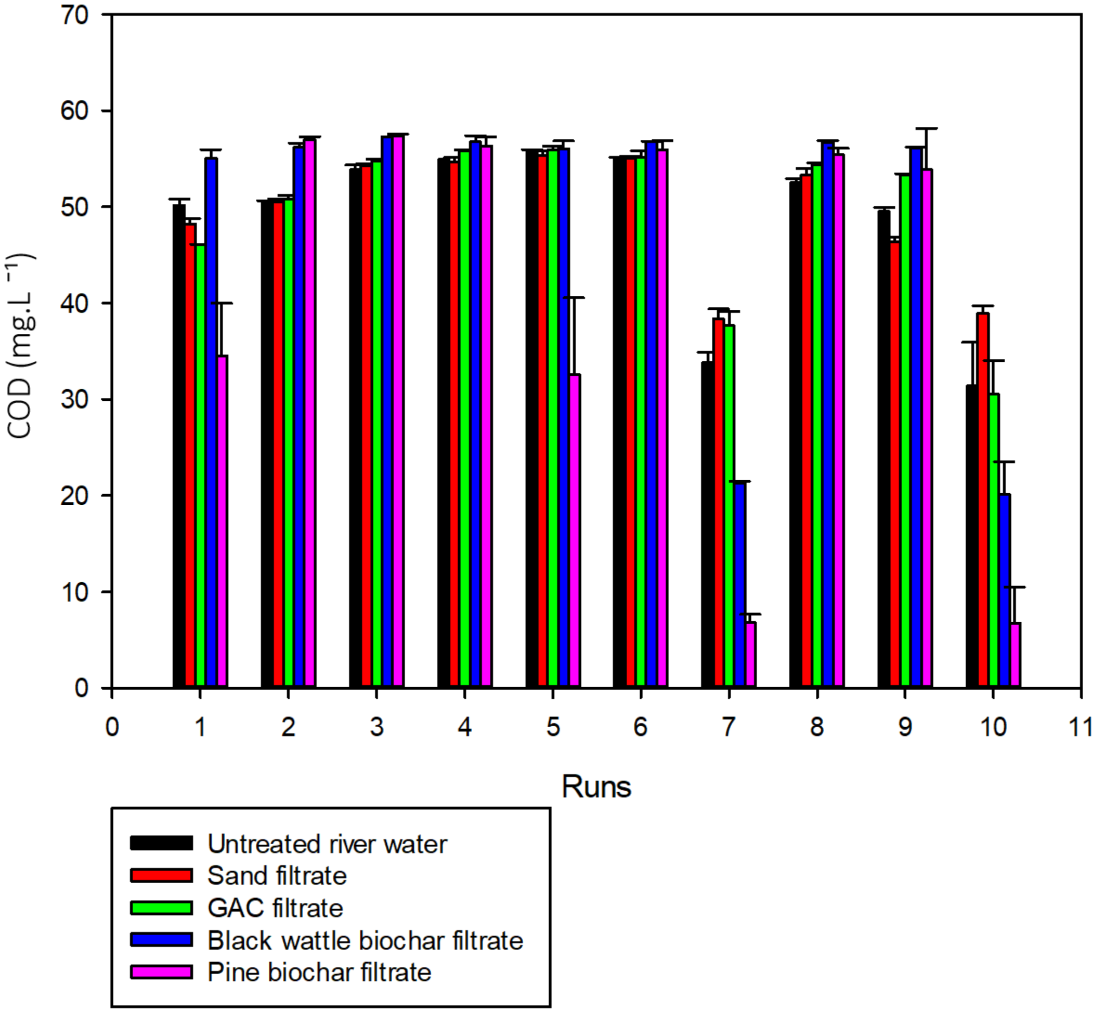


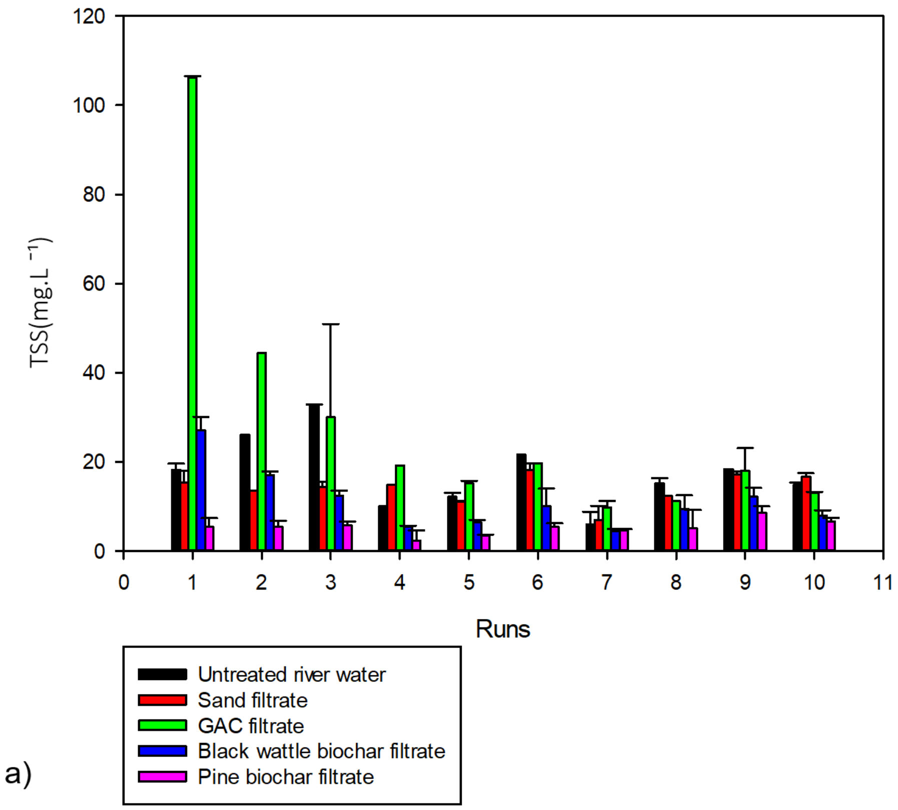
Figure 3.9. COD of untreated and treated river water with the following filters: Pine biochar, Black wattle biochar, GAC and silica sand.

This could further be explained by domestic and industrial effluent which occurs during different days between subsequent runs. The days in which domestic and industrial effluent are present within the river water results in increased organic and inorganic matter and could thus result in the increased adsorption that is observed. Studies completed by Van Rooyen (2018), also indicated a fluctuation of COD between trials when determining the effect of pine biochar on untreated river water. Radhi and Borghei (2017) and Zipf *et al.* (2016), however, both show results of COD which was reduced when using GAC as filtration media of up to 78% and 41%.

The TSS and VSS results obtained for the untreated and treated river water are shown in Figure 3.10. In Run 1 the untreated river water had a TSS and VSS value of 18.20 $mg.L^{-1}$ and 11.60 $mg.L^{-1}$, respectively. The TSS value was reduced when treated with silica sand and pine biochar filtration media whilst an increase was observed when treated with GAC and black wattle filtration media in Run 1. The VSS value, in contrast, showed a reduction with the pine biochar filtration media whilst the silica sand, GAC and black wattle filtration media had an initial increase in the VSS value in Run 1. For both the TSS and VSS a general trend can be observed in subsequent runs where a notable reduction in both values occurred when treated with the silica sand, black wattle and pine biochar filtration media.

The GAC filtration media, however, showed an increase in both the TSS and VSS over Run 1 – 5 after which a reduction in both values occurred to a much lesser extent when compared to both the black wattle and pine biochar filtration media. This initial increase in both VSS and TSS when treated with the GAC filtration media could be due to the leach out of residual GAC particles that were not completely removed in the initial rinsing step.

As a result, a reduction was thus only observed from Run 6, as can be seen in Figure 3.10. Overall, the pine biochar was the most effective at reducing the TSS and VSS of the untreated river water throughout Run 1 – 10. It should be noted although slight decreases in both the TSS and VSS were observed for the silica sand, only the black wattle and the pine biochar filtration showed notable reductions in the TSS and VSS values of the untreated river water from Runs 2 – 10, as shown in Figure 3.10. This indicates that both filtration materials are not only capable of removing larger (>45 microns.) solids in suspensions as indicated by the TSS results, but are also able to remove organic material, as indicated by the VSS results, which may be small and easily passed through the filter.



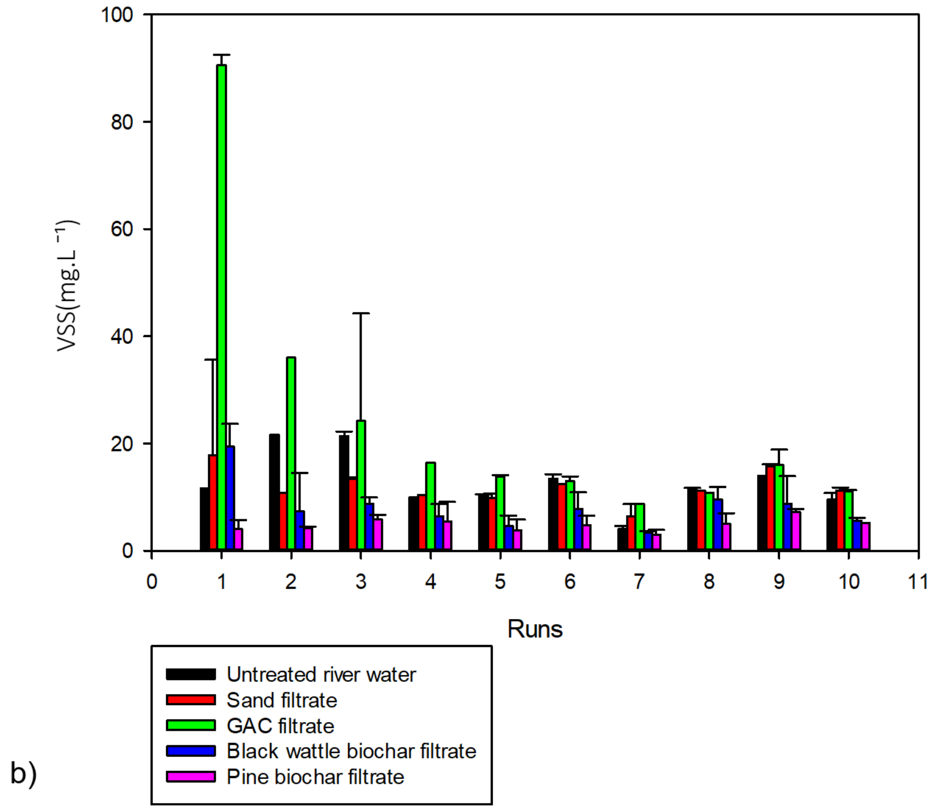


Figure 3.10. a) TSS and b) VSS, of untreated and treated river water with the following filters: Pine biochar, Black wattle biochar, GAC and silica sand**.**

This reduction could be a result of infiltration, electrostatic interactions, partitioning and hydrophobicity that are present with these specific media, which play a major role in the adsorption of suspended and volatile solids (Mohanty et al., 2014; Inyang & Dickenson, 2015). The pine and black wattle biochar further reduced the TSS to values below 50 $mg.L^{-1}$ for the use as irrigation water. Furthermore, other studies using biochar as filtration media have also showed an effective improvement in TSS of polluted water (Reddy et al., 2014).

The results obtained from turbidity and UVT% for the untreated and treated river water are shown in Figure 3.11. The turbidity and UVT% of the untreated river water in Run 1 was 16.01 NTU and 33.5 %, respectively. A similar trend was observed for the turbidity of the treated water where both the silica sand and pine biochar filtration media showed a reduction in turbidity in Run 1 whilst the GAC and black wattle filtration media showed an increase. The turbidity was then reduced in subsequent runs when treated with the silica sand, black wattle and pine biochar filtration media. The GAC filtration media showed increases from Run 1 – 5 and a reduction was again only observed from Run 6 in Figure 3.11a. The UVT %, in contrast, resulted in large increases for both the black wattle and pine biochar filtration media whilst treatment with the silica sand filtration media only resulted in slight increases or decreases in the UVT% for Runs 1 – 10.

The GAC filtration media showed an initial decrease in the UVT% after which only slight increases were observed for Run 2 – 10. This could be a result of aromatic compounds which leach out of the GAC filtration media during filtration in the initial runs and thereby influence the reading that is obtained for both the turbidity and UVT% (APHA, 2005). In both cases, the pine biochar filtration media showed the most effective reduction in turbidity and improvement in UVT% giving values of 6.1 NTU and 91.7% in Run 1, respectively.

Although not as effective as the pine filtration media, the black wattle filtration media also resulted in improved turbidity and UVT% reading. The turbidity of the filtrate indicated that the clarity of the untreated river water was improved. This could be a result of the suspended and colloidal solids which were adsorbed by the biochars. These solids which were adsorbed could have imparted diffraction of light in the untreated river water which initially reduced the clarity of the river water. This would explain the high turbidity reading of the untreated river water as well as the reduced reading after filtration. The UVT% provides an indication of the amount of UV light that is absorbed by the constituents within the water samples. Therefore, a lower UVT% indicates that there are more UV absorbing constituents such as aromatic compounds within the water sample which could negatively affect the irrigation water quality.

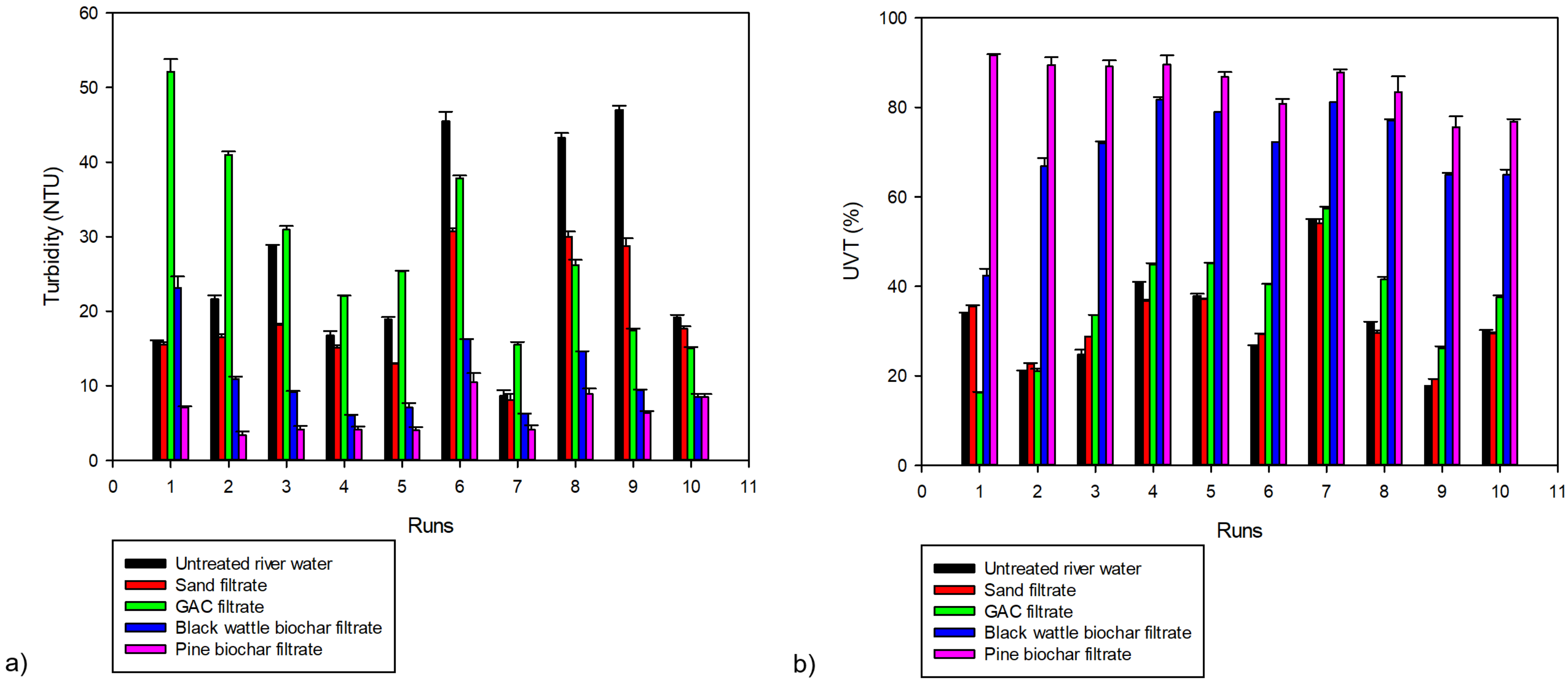


Figure 3.11 a) Turbidity and b) UVT%, of untreated and treated river water with the following filters: Pine biochar, Black wattle biochar, GAC and silica sand.

Furthermore, the increased UVT% by the biochar filtration indicates that the UV absorbing constituents could have been reduced from the untreated river water and would thus explain the high UVT% readings. These filtration media have the potential to adsorb suspended and colloidal solids, pigmentations, organic, inorganic or aromatic compounds from the river water which thus may have resulted in the improved results obtained for both the turbidity and UVT% in Figure 3.11. (Keiluweit *et al.*, 2010).

The ability of the biochars to improve the UVT% of the untreated river water could be beneficial as a pre-treatment to other water treatments, such as UV treatment, which may improve the microbial status of the river water. The efficacy of UV treatments is dependent on the amount of UV absorbing constituents within the water sample. By reducing these constituents through the biochar filtration treatments, the UV treatment could be more effective in reducing microbial counts within the untreated river water. Thereby improving the water quality for possible irrigation use.

The results for the physicochemical properties are in strong correlation with the studies completed by Van Rooyen (2018), which used columns of the same dimension and similar procedure for the filtration of untreated river water. Both this study and the study done by Van Rooyen (2018) indicated that using biochar as a potential filtration media that is produced at a high pyrolysis temperature would result in improving COD, TSS, VSS, turbidity and UVT% of the initial 20 L of the untreated river water. Furthermore, both studies reveal that the initial run of this study would negatively impact the EC, pH and alkalinity of untreated river water. This study also showed a comparison of two variants of biochar filtration with GAC and silica sand filtration media and the effect each of these filtration media had on the contaminated river water. From the results obtained in this study, it is clear that the individual filtration media each has a different effect on the river water. This could either be as a result of its potential to adsorb certain contaminants from the river water or leaching out of organic and aromatic compounds that are present within the filtration media itself.

The results for the filtered water samples were also compared to the irrigation water quality standard and recommendations. Although all the filtration media did improve certain characteristics of the river water such as pH, faecal coliforms, TDS and TSS and thereby improve the water quality, not all the recommended limits for the irrigation quality guidelines as seen in Table 3.1, were achieved. These include both the pH which fall outside the range of 6.4 – 8.4 and TDS values which were higher than the recommended value of 40 $mS.m^{-1}$.

3.4.2 Trial 2

Part 1: Untreated river water quality: Microbiological and physicochemical characteristics

The results for the microbiological and physicochemical analysis of the untreated river water are shown in Table 3.3. The HPC results obtained for the untreated river water range between 3.06 log cfu.mL^{-1} and 4.85 log cfu.mL^{-1} for Run 1 - 4. The total coliform count (Sivhute, 2019) for the untreated river water had a range of 2.07 - 3.95 log cfu.mL^{-1} while a range of 0.30 – 2.65 log cfu.mL^{-1} was observed for the faecal coliform count for Run 1 – 4 as shown in Table 3.3. The microbial count for *E. coli*, which was an additional microbial analysis that was carried out by Sivhute (2019) in Trial 2, ranged from 0.75 - 2.94 log cfu.mL^{-1}. The *Enterobacteriaceae* counts ranged between 2.17 and 4.01 log cfu.mL^{-1} for Run 1 – 4 (Table 3.3). Although the microbial counts were lower in this part of the study, similar results were obtained for the microbial count in Trial 1. The highest faecal coliform count in Trial 1 was seen at Run 2 in Table 3.2 reaching 3.86 log cfu.mL^{-1}. The faecal coliform count in Trial 2, however, was the highest at Run 3 with a value of 2.65 log cfu.mL^{-1} (Table 3.3). Similarly, the *Enterobacteriaceae* count is highest at Run 2 in Trial 1 and at Run 3 in Trial 2 reaching 4.38 and 4.01 log cfu.mL^{-1}, respectively (Table 3.2 and 3.3). The difference in the microbial counts between the two trials could be explained by the seasons in which the samples were collected. In this study the samples in Trial 1 were collected during the summer period while the samples in Trial 2 were collected during the winter period of this region. The reduced temperature and increased rainfall during the winter period in this region results in increased river flow and thus may lead to a lower microbial count observed in these samples.

Furthermore, the TDS and EC results obtained for the untreated river water in Run 1 - 4 had a range of 171.5 – 239,0 mg.L^{-1} and 0.26 – 0.37 mS.cm^{-1}, respectively as shown in Table 3.3. The pH and alkalinity of the untreated river water ranged between 6.7 and 7.2, and 61.0 mg.L^{-1} and 95.0 mg.L^{-1}, respectively. The COD resulted in a range of 12.5 - 39.3 mg.L^{-1} for Run 1 – 4 while the TSS and VSS ranged from 9.8 – 132.4 mg.L^{-1} and 4.0 – 23.6 mg.L^{-1}, respectively (Table 3.3). Lastly, the turbidity and UVT% for these samples ranged from 16.5 – 198.0 NTU and 8.9 – 53 %, respectively for Runs 1 - 4.

Table 3.3. Untreated river water quality of the Plankenburg river before treatment exposure for Sampling plan B

Runs	1	2	3	4
HPC (log cfu.mL^{-1})	3.96	4.85	4.85	3.06
Total coliforms (log cfu.mL^{-1})*	3.07	3.36	3.95	2.07
Faecal coliforms (log cfu.mL^{-1})	2.15	2.07	2.65	0.30
E. coli* (log cfu.mL^{-1})	1.94	2.52	2.94	0.75
***Enterobacteriaceae* (log cfu.mL^{-1})**	2.77	3.48	4.01	2.17
TDS (mg.L^{-1})	201	239	203	171.5
EC (mS.cm^{-1})	0.31	0.37	0.32	0.26
pH	6.70	6.97	7.06	7.15
Alkalinity (mg.L^{-1})	95.00	84.75	78.00	61.00
COD (mg.L^{-1})	39.3	27.9	18.6	12.45
TSS (mg.L^{-1})	9.8	104.8	132.4	16.8
VSS (mg.L^{-1})	4.0	16.2	23.6	4.4
Turbidity (NTU)	16.5	108.4	198.0	22.95
UVT (%)	47	8.9	14	53

* Sivhute (2019)

The characteristics of both the microbiological and physicochemical quality of the untreated river water in Trial 2, are similar to the results obtained in Trial 1. This can be expected as the sampling of the untreated river water was completed at the exact same coordinates as in Trial 1. Although the results are affected by the seasonal change, the water quality was similar to Trial 1 and thus do not conform to the South African quality guideline for irrigation water as seen in Table 3.1.

Part 2: Filtration and UV treatment of river water: Influence of using pine biochar water filters as a physical treatment on the improved efficacy of ultraviolet water treatment on microbial reduction

Microbial reduction efficacy of filtrates

The HPC results for the treated and untreated river water are shown in Figure 3.12. In Run 1 the untreated river water had an HPC of 3.9 log cfu.mL^{-1}. The HPC was reduced by the biochar filtration to 3.1 log cfu.mL^{-1} in Run 1 whilst the UV treatment resulted in an HPC of 2.1 log cfu.mL^{-1} . The UV treatment reduced the HPC by 1.8 log cfu.mL^{-1}, which is similar to the results as indicated by Olivier (2015), which reached a log reduction of up to 1.78 when using a UV dose of 10 mJ.cm^{-2}. The two treatments used in combination, biochar filtration and UV, was most effective at reducing the HPC resulting in a count of 0.3 log cfu.mL^{-1} in Run 1 (Figure 3.12). Similarly, reductions for all three treatments were observed in the HPC of both Run 2 and 3. The HPC results obtained in Run 4, however, showed an increase in the microbial count when treated with the biochar filtration while both the UV treatment and the treatment used in combination showed reductions to a similar extent. This increase that was observed for the filtration media could be as a result of the dislodging of possible biofilm containing HPC microbes into the filtrate.

Additionally, saturation of the filtration media could prevent the removal of the HPC microbes from the river water resulting in an increase in the HPC that was observed in Figure 3.12. Between the two treatments, pine biochar filtration and UV, it is clear from Figure 3.12 that the UV treatment was responsible for the greater reduction in the HPC.

The results obtained for the faecal coliform counts for the untreated and treated river water are shown in Figure 3.13a. In Run 1 the untreated river water had a faecal coliform count of 2.15 log cfu.mL^{-1}. The faecal coliforms were reduced by the pine biochar filtration to 0.82 log cfu.mL^{-1} in Run 1 and were further reduced by the UV treatment to 0.78 log cfu.mL^{-1}. Similarly, the results of both Olivier (2015) and Van Rooyen (2018), indicated that the UV treatment of the Plankenburg River at 10 and 13 mJ.cm^{-1}, respectively, resulted in 2.46 and 4.67 log reductions of faecal coliforms, respectively. The two treatments in combination resulted in the complete reduction of the faecal coliforms present in the untreated river water for Run 1 - 4.

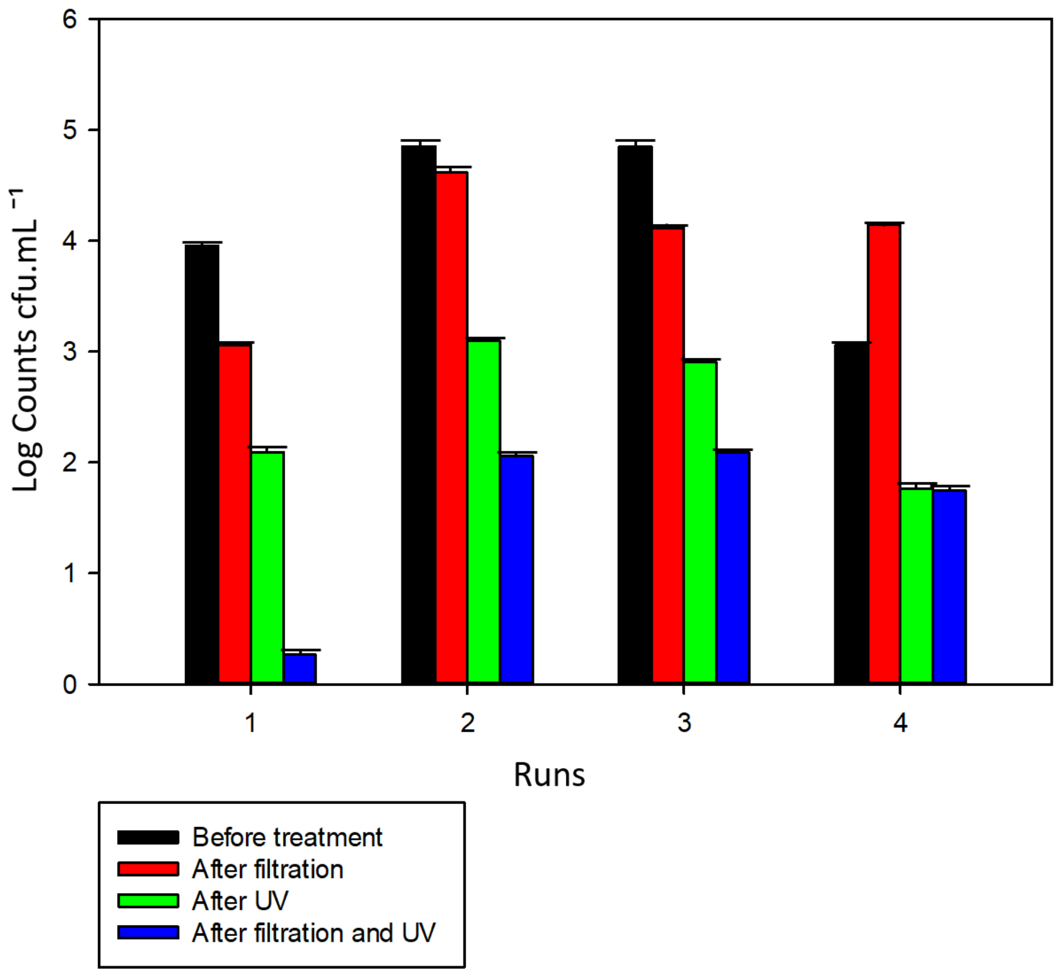


Figure 3.12. Heterotrophic plate count (HPC) of river water and treated river water with the following: pine biochar filtration, UV at 40 mJ.cm^{-2} and a combination of both.

Similarly, Run 3 and 4 resulted in the complete reduction of the faecal coliforms when the river water underwent UV treatment. The pine biochar filtration, furthermore, only resulted in the reduction of the faecal coliform count in Run 1 – 4 in comparison to the complete reduction that was observed for both the UV treatment and treatment used in combination (Figure 3.13a).

The *Enterobacteriaceae* counts for the untreated and treated river water are shown in Figure 3.13b. In Run 1, the untreated river water had a count of 2.77 log cfu.mL^{-1}. The pine biochar filtration reduced these counts to 0.88 log cfu.mL^{-1}. Both the UV and the filtration with UV treatments conducted in conjunction with Sivhute (2019) resulted in the complete reduction of the *Enterobacteriaceae* from the untreated river water. The reduction of the *Enterobacteriaceae* by UV treatment is as effective as another part of the study completed by Sivhute (2019), where a reduction from 5.29 to 1.78 log cfu,mL^{-1} was reported after treating Plankenburg River water with a UV dose of 40 mJ.cm^{-2}. In Run 2 - 4 all the treatments resulted in a reduction in the *Enterobacteriaceae* counts, however, it was only the filtration with UV treatment which resulted in complete reduction of *Enterobacteriaceae* from the untreated river water (Figure 3.13b).

The total coliform counts of the treated and untreated river water are shown in Figure 3.13c. The total coliform counts in the untreated river water were reduced by the pine biochar filtration in Run 1 – 4, with the greatest reduction seen at Run 1 to 0.5 log cfu.mL^{-1}. Complete reduction was observed for both the UV treatment and treatment used in combination in Run 1 (Sivhute, 2019).

The UV treatment and the effective reduction of total coliforms is similar to studies completed by Olivier (2015), Van Rooyen (2018) where there were log reductions of up to 2.7 and 4.9 respectively, at a UV dose of 10 and 13 mJ.cm^{-2}, respectively The UV treatment, furthermore, showed reductions in the total coliform count in Run 2 and 3 while complete reduction was observed in Run 4 (Sivhute, 2019). Similarly, the treatment used in combination resulted in the complete reduction in the faecal coliform count over all four runs (Figure 3.13c).

The results for the *E. coli* counts of the treated and untreated river water are shown in Figure 3.13d. These results are similar to those seen for the total coliform counts, where the treatment used in combination (both with the pine biochar filtration and UV treatment) resulted in the complete reduction over all four runs.

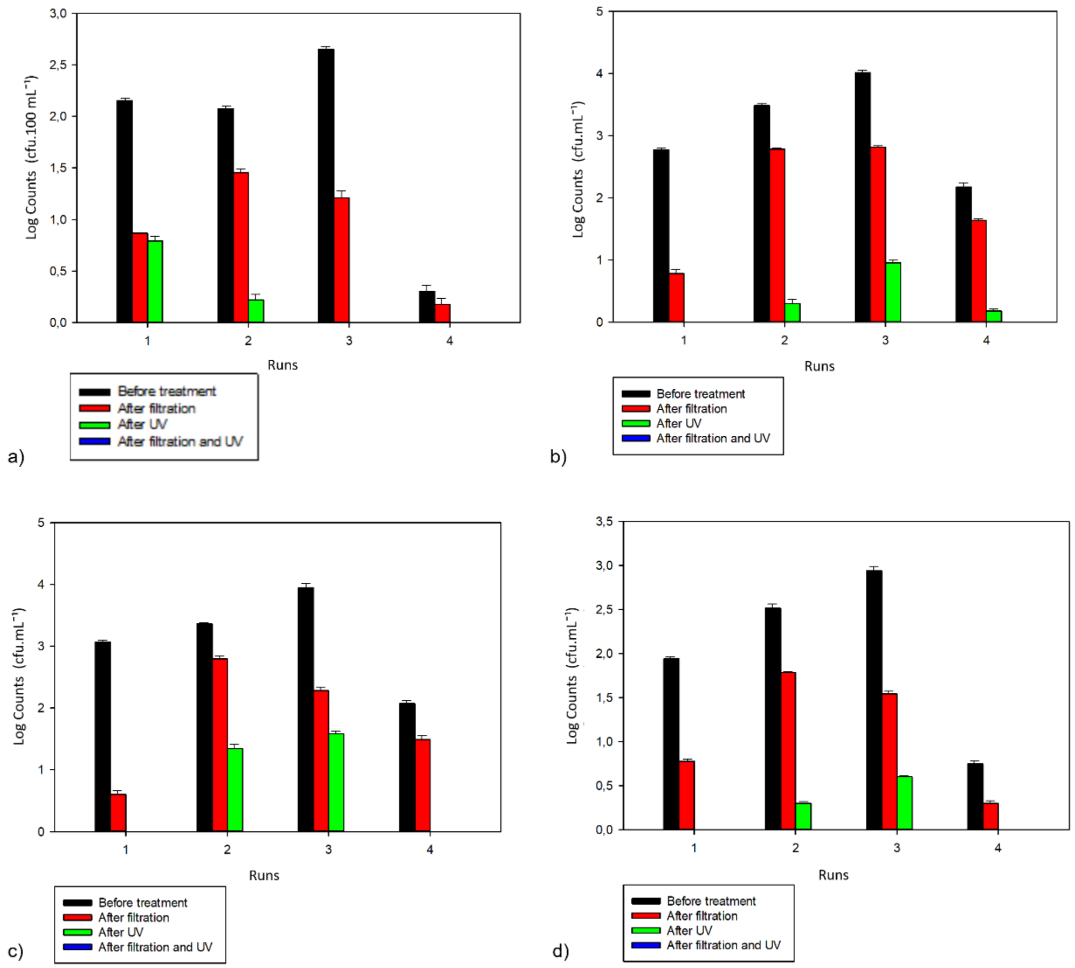


Figure 3.13. The effect of UV treatments at 40 mJ.cm^{-2}, pine biochar filtration and the combination of both on a) faecal coliforms, b) *Enterobacteriaceae*, c) total coliforms (Sivhute, 2019) and d) *E.coli* in the untreated river water (Sivhute, 2019).

The pine biochar filtration resulted in the reduction of the *E.coli* count over all four runs. In Run 3 the *E. coli* in the untreated river water reached a high count of 2.94 log cfu.mL^{-1} which was reduced by the pine biochar filtration to 1.58 log cfu.mL^{-1} and further reduced by the UV treatment to 0.63 log cfu.mL^{-1}. According to a Sivhute (2019), an effective reduction of *E.coli* was also observed at a UV dose of 40 mJ.cm^{-2} where it is reduced from 5.22 to 1.54 log cfu.mL^{-1}. It was only in Run 1 and 4 where the UV treatment alone, resulted in the complete reduction of the *E. coli* from the untreated river water.

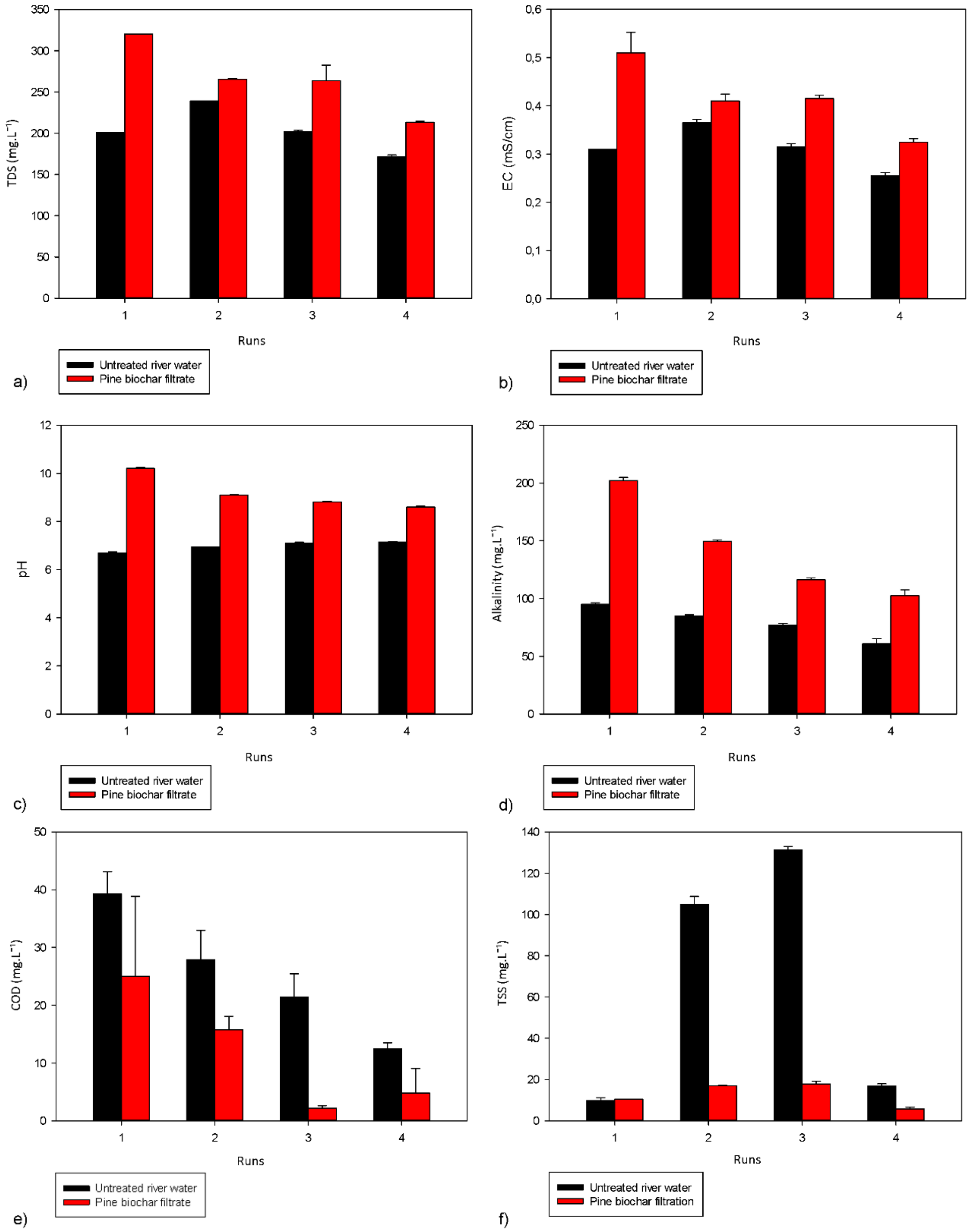
The results shown in Figure 3.13, furthermore, showed that the combined treatment of UV and pine biochar filtration resulted in the complete removal of all these microorganisms from the river water. The highest log counts for all four groups of microorganisms can be observed at Run 3 for the untreated river water, which was 2.6, 4.0, 4.0 and 3.0 cfu.mL^{-1} for faecal coliforms, *Enterobacteriaceae*, total coliforms and *E. coli,* respectively. Although these counts were the highest at Run 3, the combination of both UV treatment and pine biochar filtration reduced the counts for all of these microorganisms to 0.0 cfu.mL^{-1}.

In addition to the *Enterobacteriaceae* that was present in the untreated river water, *E. coli* was also detected to levels almost as high as the *Enterobacteriaceae* as shown in Figure 3.13 b and d. Furthermore, it was indicated by Sivhute (2019) that Shigella Toxic - producing *E.coli* (STEC) was also present in the Plankenburg River water. From her study, the use of UV treatment and pine biochar filtration resulted in effective and efficient removal of STEC (Sivhute, 2019).

As indicated by Olivier (2015), the effect of UV treatment may be obscured by other UV adsorbing contaminants within river water. These contaminants include phenolics compounds such as lignin and tannins. The biochar filtration of river water with these phenolics may be an essential process in reducing these contaminants. This will provide less scattering and adsorption of UV by these pollutants and greater adsorption by microorganisms which ultimately results in an efficient reduction thereof. It is clear from the results obtained on the microbial characteristics of the treated and untreated river water that the filtration influences the efficiency of the UV treatments. This may have resulted due to the potential of the biochar to remove UV adsorbing contaminants and thereby expose the microbes in the water to a greater extent of UV. This did not only reduce the microbial content but also improved the efficiency of the UV treatment.

Physicochemical efficacy of filtrates

The trends seen in the results of the physicochemical efficacy in this part of the study correlate to those seen in Trial 1. The results from Trial 2 for TDS and EC are shown in Figure 3.14a and b. Run 1 – 4 showed no improvement in these results for Trial 2 and in fact, showed that filtration negatively affected the untreated river water (Figure 3.14a and b). The pH and alkalinity of the filtered river water was reduced from 10.2 to 8.4 and 202.0 to 119.2 mg.L^{-1} over Run 1 to 4, respectively (Figure 3.14c and d). The COD results shown in Figure 3.14e, are not similar to the results in Trial 1, as the COD in Trial 2 showed a decrease from Run 1 – 4 after the river water underwent filtration. The trends for TSS, VSS, turbidity and UVT% are similar to those in Trial 1, as these parameters were improved after filtration (Figure 3.14 Figure 3.14. f – i). As a result of excessive rainfall in between sampling periods of different runs, the TSS of the untreated river water resulted in a rapid increase to values higher than the limit of 50 mg.L^{-1} (Figure 3.14f). The TSS increased to levels as high as 131.2 mg. L^{-1} and can be a result of the higher water levels resulting from the excessive rainfall that took place during the sampling period. This may have led to water contamination due to the suspended solids that were previously present on the river bank. Although the levels of TSS increased to such a high extent, a reduction to levels below 50 mg.L^{-1} (irrigation guidelines) was observed with the pine biochar filtration treatment. Furthermore, it is important to note that the UVT% is an important parameter in determining the exposure time of UV treatment. It is therefore clear that the improved UVT% of the untreated river water obtained by filtration results in a reduced exposure time, which in turn increases the UV treatments efficiency. The higher the UVT% the less UV exposure time is needed to reach a specific dose to become effective. As mentioned earlier, this could be due to the ability of the biochar to absorb phenolics compounds from the river water.


TDS (mg.L^{-1})
Runs
Untreated river water
Pine biochar filtrate
a)
EC (mS/cm)
Runs
Untreated river water
Pine biochar filtrate
b)
pH
Runs
Untreated river water
Pine biochar filtrate
c)
Alkalinity (mg.L^{-1})
Runs
Untreated river water
Pine biochar filtrate
d)
COD (mg.L^{-1})
Runs
Untreated river water
Pine biochar filtrate
e)
TSS (mg.L^{-1})
Runs
Untreated river water
Pine biochar filtration
f)

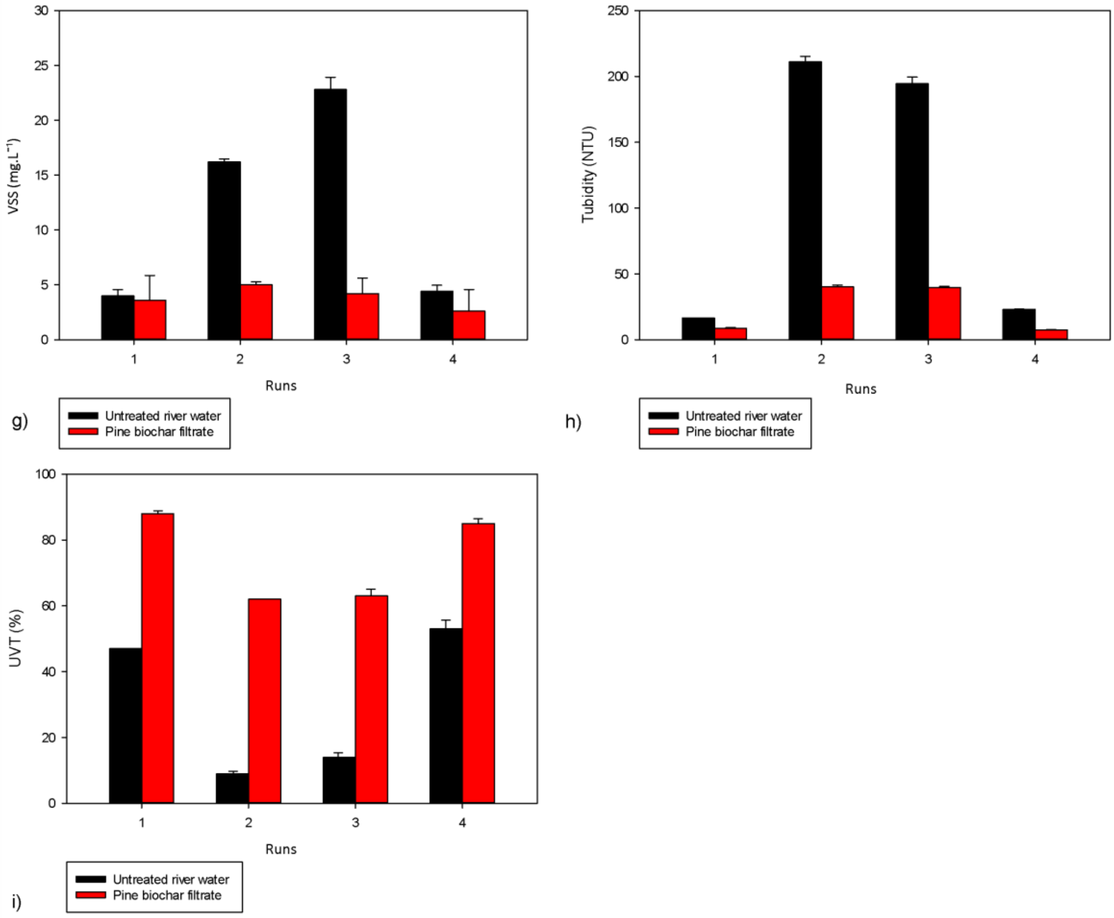


Figure 3.14. The effect of UV treatments, pine biochar filtration and the combination of both on a) TDS, b) EC, c) pH, d) alkalinity, e) COD, f) TSS, g) VSS, h) turbidity and i) UVT% of the untreated river water.

3.5 CONCLUSION

In this study, GAC and two variants of biochar, both produced at the same pyrolysis temperatures, were used as filtration media. The overall results indicated a definite difference in the efficacy of these media to adsorb pollutants. Of the three media (GAC, black wattle and pine biochar), it was pine biochar which was most effective at adsorbing pollutants from the untreated river water. This was clear when observing the physicochemical properties such as the COD, TSS, VSS, turbidity and UVT%. The pine biochar additionally, showed to be beneficial for the adsorption of heterotrophic microorganisms, *Enterobacteriaceae* and faecal coliforms from the contaminated water. This efficacy was, however, limited to the quantity of water that passes through the filtration media. Furthermore, the pine biochar influenced the quality of the untreated river water least negatively when observing the TDS, EC, pH and alkalinity properties. Although the black wattle biochar improved the quality of the river water to a better degree when compared to the GAC filtration media, the pine biochar proved to be most beneficial in all aspects of improving water quality and was, therefore, used in the second part of the study (Trial 2) as the biochar filtration media.

In Trial 2 of the study, the pine biochar was used as filtration media in combination with UV treatment to determine the efficacy and influence the pine biochar will have on improving the water quality of the river water. It is clear that a combination of the two treatments was most effective. The pine biochar filtration resulted, not only in improving the physicochemical properties of the river water but also improved the UVT% to such an extent that the UV treatment successfully eliminated STEC, *E. coli, Enterobacteriaceae* and faecal coliforms at a decreased exposure time. This, in turn, resulted in a more effective UV treatment at a lower dosage strength.

The differences in efficacy observed for both the pine and black wattle biochar are likely as a result of the variation in functional groups, porosity and therefore surface area of the specific biochar. As both the pine biochar and black wattle biochar were produced at the same pyrolysis temperature, the temperature of biochar production cannot be the primary aspect that resulted in the variation in efficacy observed. It is thus as a result of the origin of the biomass from which the biochar is made. In this study, the origins were pine and black wattle. There are, however, many more different kinds of plant material which could be converted to biochar and used as a filtration media. The efficacy of both pine and black wattle, however, did not improve the overall quality of the river water to the recommended standard for irrigational use. This may not necessarily be improved by using different filtration media but rather by improving the flow of water through the biochar media itself. Water-biochar interactions are most effective when the exposure time of these interactions are increased. In this study, gravitational flow was used, and the biochar did not remain saturated between the runs. This may have resulted in reduced infiltration and increased oxidation reactions which may have influenced the effect of absorption of pollutants from the river water negatively. It is clear that much research about biochar can be completed to find the best plant origin and filtration method to improve the quality of water most effectively. It is also clear that a combination of treatments for the improvement of the water quality are most effective together and thus opens many research topics for the exploration of all the possibilities.

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CHAPTER 4:

DETERMINING THE EFFICACY OF PINE BIOCHAR IN A CLOSED FILTRATION SYSTEM TO IMPROVE RIVER WATER QUALITY FOR AGRICULTURAL IRRIGATION

4.1 ABSTRACT

Filtration systems have been used for the adsorption of contaminants in water for many years. The efficacy of the filtration system plays an important role to determine the efficacy of the filtration media. Biochar may serve as a cost-effective alternative to granular activated carbon (GAC) in filtration systems. In this study, pine biochar was used as filtration media as it has added benefits for the treatment of polluted river water for use in agricultural irrigation. The exposure time of filtration media with untreated river water may play an essential role in the effective adsorption of contaminants. From the results obtained, it is clear that the pine biochar used as filtration media improved the untreated river water best, in comparison with the GAC. Furthermore, it is also clear that the exposure time of both the filtration media with the untreated river water had a greater effect on the adsorption of certain contaminants. Certain properties of the water were influenced by an exposure time of three days with the filtration media, whereas the water properties of the filtrates with little exposure time, were not. The pine biochar filtrates which had an exposure time of three days to the filtration media effectively adsorbed faecal coliforms from the untreated river water and improved the turbidity and UVT% properties more than the filtrates with little exposure time. Although the increased exposure time provided a positive effect, it also increased the TDS, COD and alkalinity to an undesired quality. It is clear that the exposure time may indeed contribute to the effective adsorption of certain contaminants.

4.2 INTRODUCTION

Up to 63% of South Africa's water supply is used for agricultural irrigation (WWF-SA, 2017). It is thus important to maintain a certain standard of irrigation water quality to improve plant growth and nutrition as well as to prevent crop loss from contaminants such as spoilage microorganisms (DWAF, 1996; DWA, 2013). It is also essential to inhibit the presence of pathogenic microorganisms in irrigation water due to the hazardous conditions it might bring to the food chain (Forsythe, 2010a; Jongman & Korsten, 2017).

With the current problems of diminished water quality as a result of the ever-increasing population and climate change, it is important to develop new strategies to improve water quality (Rijsberman, 2006; DWA, 2016; Nyamwanza & Kujinga, 2016; STATS SA, 2017; WHO, 2017). Filtration systems are a form of physical water treatment used to improve the overall quality of water (DWAF, 2004; Parsons & Jefferson, 2006; Schug, 2016). This water treatment is usually one phase of many when water is purified for safe consumption. It is therefore suggested that filtration could be used as a feasible treatment for irrigation water in maintaining the quality thereof, according to the guidelines as given in Table 4.1 (Kubiak *et al.*, 2015; Pfannes *et al.*, 2015).

Table 4.1. South Africa water quality guidelines: Agricultural use of Irrigation water indicating the ideal limitations of selected variables for acceptable water use (DWAF, 1996; DWA, 2013)

Variable	limits
pH	6.5 – 8.4
TDS/ Electric conductivity	< 40 $mS.m^{-1}$
Faecal coliforms	< 1 000 cfu per 100 mL
Sodium Adsorption Ratio (SAR)	< 2
Suspended solids	< 50 $mg.L^{-1}$

The process of filtration includes the flow of an aqueous medium through granular media and through collision and attachment mechanisms, which results in the adsorption of undesired contaminants (DWAF, 2004; Parsons & Jefferson, 2006; Schug, 2016). These mechanisms of absorption may lead to the formation of a biofilm, otherwise known as a *Schmutzdecke* when polluted water is filtered continuously through a filtration system (Kubiak *et al.*, 2015; Pfannes *et al.*, 2015). This biofilm is usually a thin layer formed above the filtration media and consists of a community of microorganisms as well as organic and inorganic matter (Kubiak *et al.*, 2015; Pfannes *et al.*, 2015). It may play a significant role in attaching and adsorbing spoilage and pathogenic microorganisms through physical, chemical and biological activity with the organic matter. The organic matter in the biofilm serves as a nutrition and energy source for microorganisms and is continuously expanded by the ongoing attachment of microbes (Kubiak *et al.*, 2015; Pfannes *et al.*, 2015). The rapid formation of the biofilm in the filtration system may be dependent on the type of filtration media that is used. Biochar is one such media which may promote the formation of a biofilm. With its hydrophobic and steric interactions as well as rough surfaces, biochar may promote the binding of organic material, including microorganisms, during straining (Conte *et al.*, 2013; Mohanty *et al.*, 2014; Reddy *et al.*, 2014; Inyang & Dickenson, 2015).

Biochar is a carbon-rich substance that is used as a soil amendment to adsorb many undesired constituents which may diminish the soil quality, thereby improving plant growth and nutrition (Keiluweit *et al.*, 2010; Santos *et al.*, 2015; Tan *et al.*, 2015). These contaminants include heavy metals such as ammonium nitrate, cadmium, copper and lead as well as nitrogen, other nitrates, nitrites and pesticides, such as imidacloprid, isoproturon, and arsine (Iqbal *et al.*, 2015; Park *et al.*, 2015; Jin *et al.*, 2016; Takaya *et al.*, 2016). In addition to these contaminants, microorganisms could be removed from the polluted water as a result of the biochar properties which include attraction forces, particle shape, paramagnetic centres, surface area, pore size, partitioning, hydrophobicity, graphitisation and electrostatic interactions (Clarkson, 1998; Hale *et al.*, 2011; Conte *et al.*, 2013; Mohanty & Boehm, 2014; Reddy *et al.*, 2014; Inyang & Dickenson, 2015). Biochar could thus be used as a filtration media not only to remove microorganisms but also to remove a large spectrum of contaminants (Mohanty *et al.*, 2014).

This study explored the use of biochar as a filtration media in a closed filtration system using a pump to pump untreated river water through the system. This would possibly lead to the formation of a *Schmutzdecke* and additionally aid in establishing a controlled flow rate of polluted water through the filtration media. The objective of this study was firstly to determine the microbiological and physicochemical characteristics of the Plankenburg River water. The second objective was to assess the river water quality after treatment with the pine biochar in a closed system, whilst maintaining saturation. Therefore, the effect that a prolonged exposure time will have on the effective adsorption of the contaminants was investigated.

4.3 MATERIALS AND METHODS

4.3.1 Research study design

The biochar used in this study was produced from pinewood via pyrolysis at 800ºC. From filtration optimisation and previous experience from Chapter 3 of this study, one can assume that an increased exposure time may improve the adsorption of the filter. This could have been due to the porosity of the pine biochar which was so small that the infiltration of possible pollutants could not have occurred effectively (WHO, 2004a; Simpson, 2008). By keeping the filtration columns saturated with the untreated river water the increased exposure time for infiltration into the micropores could have occurred. A closed system would have provided the vacuum to inhibit gravitational flow and, therefore, have lead to an increased exposure time of untreated river water with the biochar. A closed system which was sterilised would also have been less affected by the external microbial environment and therefore result in a less biased system. Furthermore, a closed system enables the controlled flow of a medium through the columns at a controlled flow rate with the aid of a pump. This was experimented with to determine the ideal flow rate which provided the ideal exposure time between the aqueous environment and the biochar for the most effective adsorption. It is, however, important that the sample of untreated river water which was pumped through the columns was of the same quality and was therefore collected on the same day as the run. The flow rate was also the same for all columns used to ensure that the deviation between duplicate columns as well as differentiation between different kinds of filtration media was less biased.

This study consisted of sampling a total of 20 L of untreated river water from the Plankenburg River every three days for 30 days (10 runs) as seen in Figure 4.1, therefore ten samples of untreated river water. This study consisted out of two parts, Part 1 and Part 2, wherein this untreated river water would be used. The initial part (Part 1) of the study was to determine the microbiological and physicochemical quality of the untreated river water which would pass through the filtration system used in Part 2 (Figure 4.1). Part 2 of the study consisted of constructing closed filtration columns packed with pine biochar through which the untreated river water would have been filtered. This part also consisted of filtering the untreated river water through these columns at a specific flow rate with the aid of a pump after which samples were collected and analysed microbiologically and physicochemically as seen in Figure 4.1. The samples collected from the filtration columns included both a direct sample which passed through the filtration column and a sample which remained in the column for three days, before being analysed.

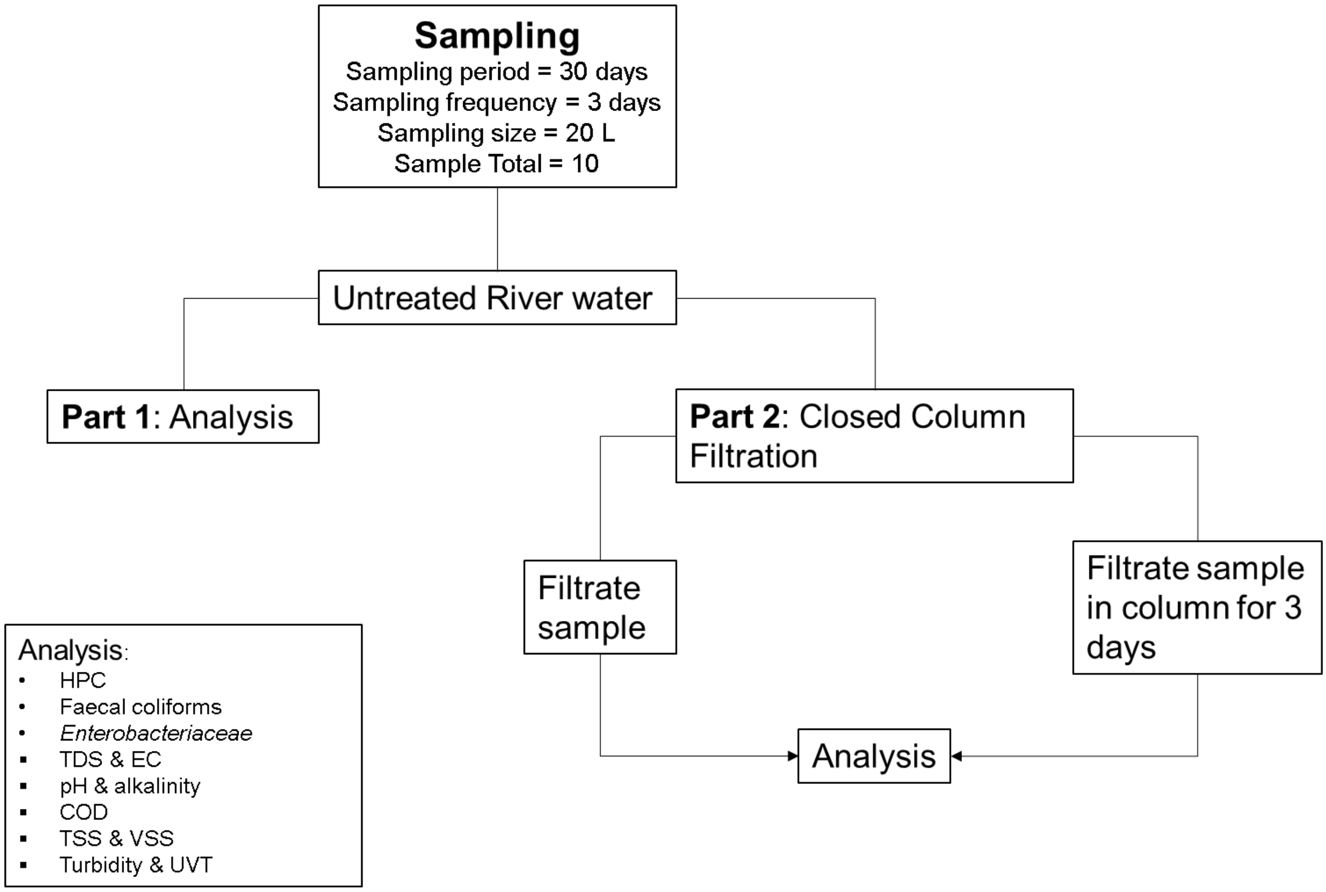


Figure 4.1. Research study design indicating the process flow of experimentation and analysis.

Part 1: Plankenberg River water quality: Microbiological and physicochemical characteristics

In this part of the study, 2 L of the untreated river water was used for the microbial and physicochemical analysis of the river water quality. The microbial analysis consisted of the enumeration of heterotrophic colonies (HPC), faecal coliforms and *Enterobacteriaceae* according to the standard methods as described under General Methods. This was completed by performing a duplicate serial dilution of each sample of untreated river water, after which duplicate pour plates of each dilution were prepared for each group of bacteria. After incubating, the colony forming units (CFU) per millilitre were counted and recorded. The physicochemical analysis consisted of duplicate tests of total dissolved solids (TDS), pH, alkalinity, chemical oxygen demand (COD), total suspended solids (TSS), volatile suspended solids (VSS), turbidity and ultraviolet transmission percentage (UVT%) according to standard methods as described under General Methods.

Part 2: Assessing river water quality treated by a closed water filtration system using biochar for the removal of contaminants

In this study, a total of four filtration systems were used of which three had pine biochar as filtration media and the last had granular activated carbon (GAC) as filtration media. Each system was exposed to 4 L of untreated river water every three days, over a period of 30 days. Therefore, a total of 10 runs were passed through each column. The first 2 L of each run was used for the flushing of the columns. The following 2 L was filtered through the filtration media and collected for analysis as seen in Figure 4.1. An additional sample of 0.5 L was collected from the filtration columns after three days which was left resting in the filtration column for that time. This was collected before the start of the next run. Therefore, each run consisted of three samples of biochar filtrate, three samples of biochar filtrate resting for three days, a sample of GAC filtrate, and a GAC filtrate resting for three days. A flow rate of 0.41 $L.min^{-1}$ was used for Runs 1 - 4, after which the flow rate was reduced to 0.26 $L.min^{-1}$. This difference in flow rate could have been used to determine how sensitive the efficacy of the filtration media would be when the duration of exposure time was slightly reduced. These samples provided an ideal indication of the effect the exposure time of the untreated river water to the filtration media would have had on the adsorption potential of these contaminants.

For the microbial analysis, a serial dilution was made for each filtrate from the pine biochar columns whilst two serial dilutions were completed for the filtrate from the GAC column and the untreated river water. These serial dilutions were plated into duplicate petri dishes in which PCA, VRBA and VRBGA pour plates were completed. For the physicochemical analyses, all filtrates from the biochar columns were analysed. The GAC filtrates, as well as the untreated river water, were analysed in duplicates.

For the filtration process, the biochar media was packed in the same columns and in the same ratio following the methodology described in Chapter 3 of this thesis. The columns were sealed at both ends (top and bottom) with a PVC plug. These plugs had a built-in nozzle with an inside diameter of 0.8 cm as seen in Figure 4.2. Before attaching these plugs to the columns, which had been filled with filter media, the plugs were sterilised with a 10% (v/v) Milton sterilising fluid. At the bottom of the columns, between the silica sand layer and the plug, a thin layer of sterilised glass wool was placed to filter small media particles, which could have passed through into the filtrate.

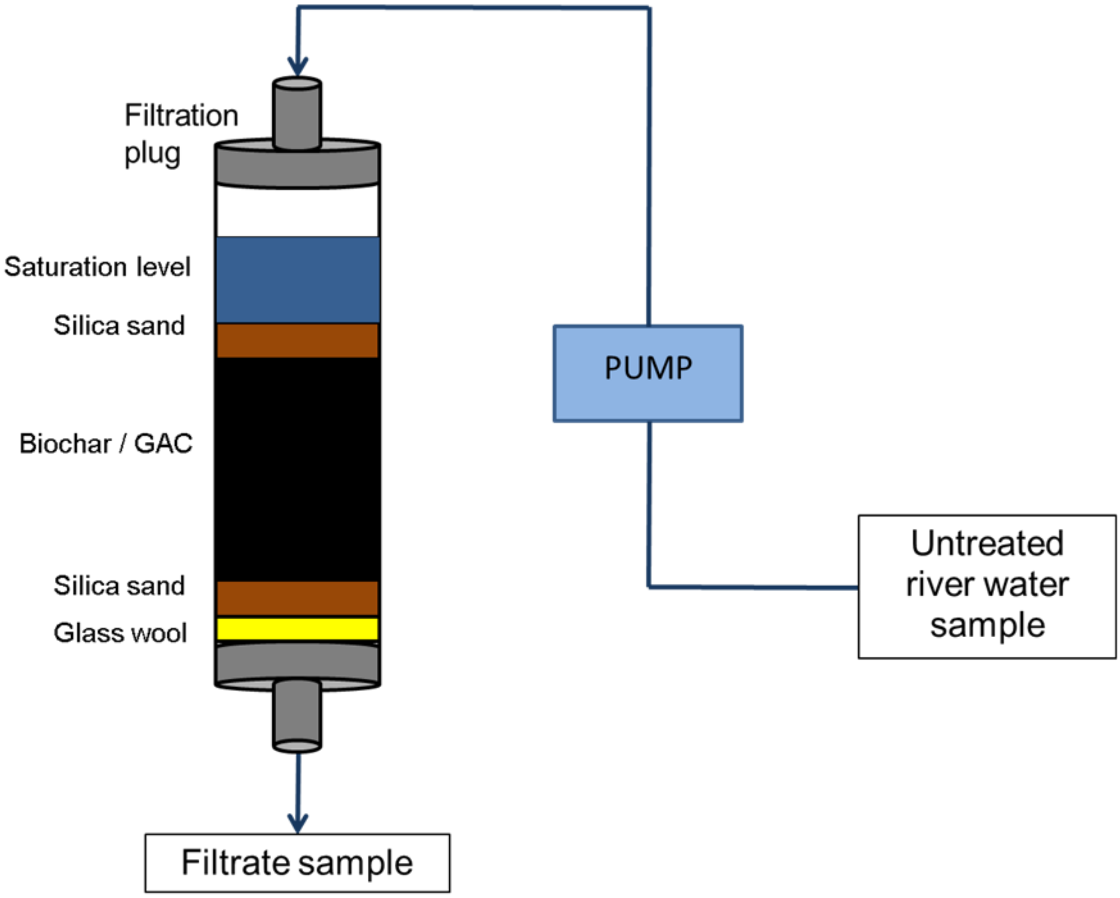


Figure 4.2. Filtration system for the determination of the efficacy of pine biochar when saturated with untreated river water.

PVC pipes with diameters of 0.8 cm were attached to the nozzles, which were used for the pumping of the untreated river water through the columns, directing the filtrates into 2 L sterilised reagent bottles. These PVC pipes were sterilised with the plugs in a 10% (v/v) Milton sterilising fluid. A Watson Marlow 323 peristaltic pump was used to pump the untreated river water through each column, providing a flow rate of 0.41 $L.min^{-1}$ through the columns.

Before using the columns for the filtration of the untreated river water, they were rinsed with 10 L of sterilised distilled water. For the rinsing of the columns, distilled water was pumped into the columns whilst the outlet pipe was clamped. The columns were filled, leaving a headspace of approximately 15 cm after which a vacuum was formed inside the columns by reversing the flow of the pump. The purpose of the vacuum was to control the flow of river water into the columns whilst the same volume of filtrate was pumped into the reagent bottles as filtrates. The vacuum also assisted in keeping the filtration media saturated at all times as well as in the partial removal of air pockets in the pores of the filtration media. After the vacuum was formed the remaining 10 L of distilled water was pumped through the columns. The columns were, however, kept saturated with the distilled water. Before the first experiment for each run, 2 L of the untreated water was first used to flush the column from residual solutions interacting with the filtration media. This was followed by another 2 L of the untreated water from the same batch which was collected for analysis. The purpose of the flushing with the untreated river water before the first run was to ensure that the distilled water in the column, which kept the columns saturated after rinsing, would be flushed out and would therefore not influence the results. The flushing occurred before each subsequent experimental run to ensure that the untreated river water from the previous run would not influence the results of the next run. This was a rather important step as the river water batches were collected on different days for each run and therefore any difference in the river water properties may have influenced the consistency of the results obtained by the filtrates.

4.3.2 General methods

4.3.2.1 River water sampling

The sampling of river water from the Plankenberg River in Stellenbosch (33°55'52.1"S 18°51'06.1"E) was completed using the same SANS method 5667-6 as indicated in Chapter 3 (SANS, 2006). These samples were collected in 5 L reagent bottles which were filled and transferred into cooler boxes for transport and stored at 4ºC till use.

4.3.2.2 Filtration media

The 2 L media used for filtration was pine biochar produced at 800ºC with a granular size of 0.6 – 1.2 mm and was sourced from Adsorb Technologies (Pty) Ltd. The controlled media was granular activated carbon (GAC) produced from coconut shell with a granular size of 0.6 – 2.36 mm and was sourced from AQUAMAT South Africa (Pty) Ltd.

4.3.2.3 Microbiological methodology and analysis

The methodology used in Chapter 3 of this thesis for the enumeration of heterotrophic colonies, faecal coliforms and *Enterobacteriaceae* was used in this study. Serial dilutions (10^{0} – 10^{-6}) were completed using Ringer solution according to SANS 6887-1 method (SANS, 1999). From these serial dilutions, 1 mL was used to prepare pour plates in duplicate with plate count agar (PCA), violet red bile agar (VRBA) and violet red bile glucose agar

(VRBGA) for the enumeration of heterotrophic colonies, faecal coliforms and *Enterobacteriaceae,* respectively (SANS, 2005; SANS, 2007). These pour plates, PCA, VRBA and VRBGA were incubated for 48 hours at 30ºC, 24 hours at 44ºC and 24 hours at 35ºC, respectively, after which the colonies were counted, recording counts between 25 and 250 cfu per plate.

4.3.2.4 Physicochemical methodology and analysis

The methodology and instrumentation used in Chapter 3 of this thesis for the analysis of total dissolved solids (TDS), pH, alkalinity, chemical oxygen demand (COD), total suspended solids (TSS), volatile suspended solids (VSS), turbidity and ultraviolet transmission percentage (UVT%) were used in this study (APHA, 2005).

The total dissolved solids, when calculated using the electric conductivity value in Table 4.1, should not exceed 260 ppm. This was done with the aid of the following formula:

$$Electricalconductivity\ (mS.m^{-1}) \times 6.5 = TDS\ (mg.L^{-1}). \qquad \text{eq.1}$$

4.3.2.5 Data Analysis

All the recorded data was captured through Microsoft Excel after which it was processed in Sigmaplot®14 for the construction of Figures. The standard means and standard deviation between duplicate and triplicate samples were determined and line graphs we constructed to demonstrate the effect of the different treatments of untreated river water for all the runs.

4.4 RESULTS AND DISCUSSION

Part 1: Plankenberg River water quality: Microbiological and physicochemical characteristics

Table 4.2 shows the microbial and physicochemical results of the untreated river water. The heterotrophic plate count (HPC) of the untreated river water before filtration is shown in Table 4.2. The range of HPC of the untreated river water between Runs 1 and 10 was 3.19 - 4.81 log cfu.mL^{-1}. This was not the case in studies completed by (Olivier, 2015), indicating a much higher HPC count of up to 6.4 cfu.mL^{-1}. The faecal coliform count of the untreated river water ranged between 0.57 log cfu.100 mL and 2.79 log cfu.100mL. According to Table 4.1, the faecal coliform load should not exceed 1 000 cfu per 100 mL sample. Recalculating this value to determine the log counts of faecal coliforms in 1 mL would result in 1 log cfu.100mL. Only the results for water used in Run 8 indicated a faecal coliform count of 0.57 log cfu.100 mL, which did not exceed the limit of 1 log cfu.100mL. The water used in the remaining runs had loads with values as high as 2.79 log cfu.100 mL (Run 6) (Table 4.2). These fluctuations of faecal contamination may result from the daily variation of rainfall or runoff from rural and industrial activities along the river (Sampathkumar *et al.*, 2010; Nyamwanza & Kujinga, 2016). The high count of faecal coliforms in the Plankenburg River was not nearly as high as those from studies completed by Olivier (2015) and Van Rooyen (2018), which indicated counts as high as 6.4 and 6.5 cfu.100 mL^{-1}, respectively.

The faecal coliform count of the river water only gives an indication of the microbial contamination in the water. It is seen in Table 4.2 that the *Enterobacteriaceae* counts were higher than the faecal coliforms with a range of 1.86 – 3.59 log cfu.mL^{-1}, which was expected, as the faecal coliforms form part of the greater family of *Enterobacteriaceae*. These counts were not as high as those indicated in studies completed by Van Rooyen (2018) as well as by Sivhute (2019), on the Plankenburg River where counts reached as high as 6.5 and 5.3 cfu.mL^{-1}, respectively.

It is important to note how much higher the *Enterobacteriaceae* was than the faecal coliforms. According to Table 4.2, the difference between faecal coliform and *Enterobacteriaceae* range from 0.53 – 2.09 log cfu.mL^{-1}, and therefore indicates that there were many other microorganisms from the *Enterobacteriaceae* family present in the untreated river water. This is concerning as there are many pathogenic microorganisms such as Shigella Toxic-producing *Escherichia coli* (STEC), *Vibrio cholera, Salmonella thyphi,* non-typhoid *Salmonella* spp and many more which are part of this family (Forsythe, 2010b). Pathogens may not only induce disease or illness via fresh produce but could also find its way through the food chain.

It is clear in Table 4.2 that the TDS of Runs 4, 6, 8, 9 and 10 conformed to the guidelines, as referred to in Table 4.1, whilst run 1, 2, 3, 5 and 7 exceeded this limit and reached values as high as 386 ppm in Run 2. Although there were variations on the borderline of the limit for TDS, the higher values obtained in these runs could have been a result of upstream activities such as residential and agricultural runoff, sewage or industrial effluents as well as chemicals which were used in water treatment processes. Leached constituents from soil could also have resulted in an increased TDS (Barnes, 2003; Olivier, 2015).

Table 4.2. Untreated river water quality of the Plankenberg River before filtration treatment

Runs	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
HPC (log cfu.mL^{-1})	4.47	3.96	4.45	4.77	3.62	4.81	3.92	3.19	3.70	3.59
Faecal coliforms (log cfu.100 mL^{-1})	2.95	2.26	2.19	1.99	1.33	2.79	1.51	1.57	1.82	1.03
Enterobacteriaceae (log cfu.mL^{-1})	3.40	3.25	3.26	3.24	1.86	3.59	2.97	2.66	2.69	2.51
TDS (ppm)	332.00	386.00	272.00	245.50	355.00	242.50	306.50	236.00	236.00	244.00
pH	7.00	7.02	6.76	6.86	7.30	7.24	7.32	7.10	7.10	7.12
Alkalinity (mg.L^{-1})	155.00	182.00	101.00	113.50	130.75	115.00	129.50	86.75	86.75	108.75
COD (mg.L^{-1})	109.00	N/A	342.00	213.60	631.20	263.40	428.40	610.20	610.80	328.40
TSS (mg.L^{-1})	20.00	16.80	4.40	54.60	8.60	57.20	24.60	20.20	20.20	24.60
VSS (mg.L^{-1})	10.40	9.20	4.00	13.40	3.60	12.60	6.00	7.00	7.00	7.40
Turbidity (NTU)	21.80	34.80	23.00	49.70	13.07	85.70	40.30	19.28	19.28	17.18
UVT (%)	37.60	35.70	41.10	25.40	39.90	7.00	26.95	48.95	48.95	53.75

The results obtained for the physicochemical properties of the untreated river water in Table 4.2 indicate that with a pH range of 6.8 – 7.3, the quality of river water conformed with the irrigation pH guidelines of 6.5 – 8.4. In Table 4.2 all the runs exceeded the guideline limit as suggested by Spellman (2008), of 80,0 mg.L^{-1} for alkalinity. This indicates that the carbonate, bicarbonate and hydroxide content within the river water was not adequate to be used as irrigation water. The range for alkalinity through all the runs was between 86.8 mg.L^{-1} and 182,0 mg.L^{-1}. Increased alkalinity in river water could have resulted from uptake and reduction of strong anionic acids which occur naturally and well as corroded rock which was high in carbonates. Other contributing factors which could have increased the alkalinity could include exchange reaction within the soil in the river water, precipitation of evaporated minerals and the mere mobility of dust particles (Spellman, 2008).

The chemical oxygen demand (COD) of the untreated river water is shown in Table 4.2. With the highest value for the river water reaching 631.2 mg.L^{-1}, the lowest COD level of the untreated river water was 109,0 mg.L^{-1}. The higher level of COD could have resulted from increased microbial growth. This may be due to organic substrates which could be a source of nutritious for microbial growth. The content of the total suspended solids (TSS) for all the samples collected from the Plankenburg River, excluding those collected for Run 4 and 6, conformed to the guidelines on irrigation water which may not exceed 50,0 mg.L^{-1}. The results obtained for Run 4 and 6 were 54.6 mg.L^{-1} and 57.2 mg.L^{-1}, respectively. Although these water samples exceeded the irrigation water guidelines for TSS by a margin of a few milligrams, a lower level of TSS in water contributed to greater benefits for better quality water. The volatile suspended solids (VSS) in the river water compared to the COD was not higher than 13.4 mg.L^{-1}. The high values of COD (Table 4.2) indicated that the contaminants which contributed greatly to the COD levels are of an organic nature (APHA, 2005).

The turbidity of the river water should preferably not be more than 10 NTU according to Hanseok *et al.*, (2016). The untreated river water, before filtration, had turbidity values ranging from 13.7 to 85.7 NTU for all 10 samples that were collected from the Plankenburg River (Table 4.2), and therefore did not conform to this recommendation. The difference in turbidity was rather large and was highly dependent on the content within the water which influences the clarity thereof. This could have included organic and inorganic matter as well as dissolved and suspended solids. These contaminants and the fluctuation thereof in river water may be greatly influenced by periods of rainfall, industrial dumping activities as well as rural activities (Sigge *et al*, 2016; Barnes, 2003).

Ultraviolet transmission percentage (UVT%) is another parameter similar to turbidity, however, the result was influenced not only by content which influences the clarity but any compounds which absorb ultraviolet light. It, therefore, gives an indication of the quality of water and the level of constituents within the water which absorbs UV light. The UVT% of the river water was rather poor when considering that a UVT% level lower than 50% would influence other photochemical treatments negatively (Sigge *et al.*, 2016). It is clear from Table 4.2 that the UVT% of the samples collected from the Plankenburg River, only conformed to this recommended limit for Run 10, with a UVT% of 53.8%. The remaining samples of river water had not conformed to this recommended limit as the UVT% ranged between 7.0% and 48.95%. The results obtained in this study for the physicochemical status of the Plankenburg River water is similar to the results shown in other studies (Olivier, 2015; Van Rooyen, 2018; Sivhute, 2019). From these results obtained on the untreated river water in this study, it is clear that it had not conformed to all the guidelines and recommendations and therefore should not be used directly for fresh produce irrigation without the proper treatment.

Part 2: Assessing river water quality treated by a water filtration system using biochar for the removal of contaminants

Microbial reduction efficacy of filtrates

The HPC of the treated and untreated river water is presented in Figure 4.3. The microbial counts of the treated river water indicated that the biochar filtration reduced the HPC in Run 1 from 4.5 log cfu.mL^{-1} to as low as 1.9 log cfu.mL^{-1}, as seen in Figure 4.3. The biochar filtration with a three day resting period in the column resulted in the complete reduction of the HPC in the river water in Run 1. The GAC filtration as well as the GAC filtration with a three day resting period in the column, only reduced the HPC of the river water by a negligible value (4.46 log cfu.mL^{-1} and 4.03 log cfu.mL^{-1}). Although a large reduction in the HPC of Run 1 was seen in the biochar filtrate as well as the biochar filtrate collected after a three day resting period in the column, this treatment was not as effective in subsequent Runs. In Run 2 a reduction from 3.96 log cfu.mL^{-1} to 2.94 log cfu.mL^{-1} was observed in the filtrate collected directly after the biochar filtration, whilst an increase to 4.87 log cfu.mL^{-1} in the biochar filtrate resting for three days in the column, was observed.

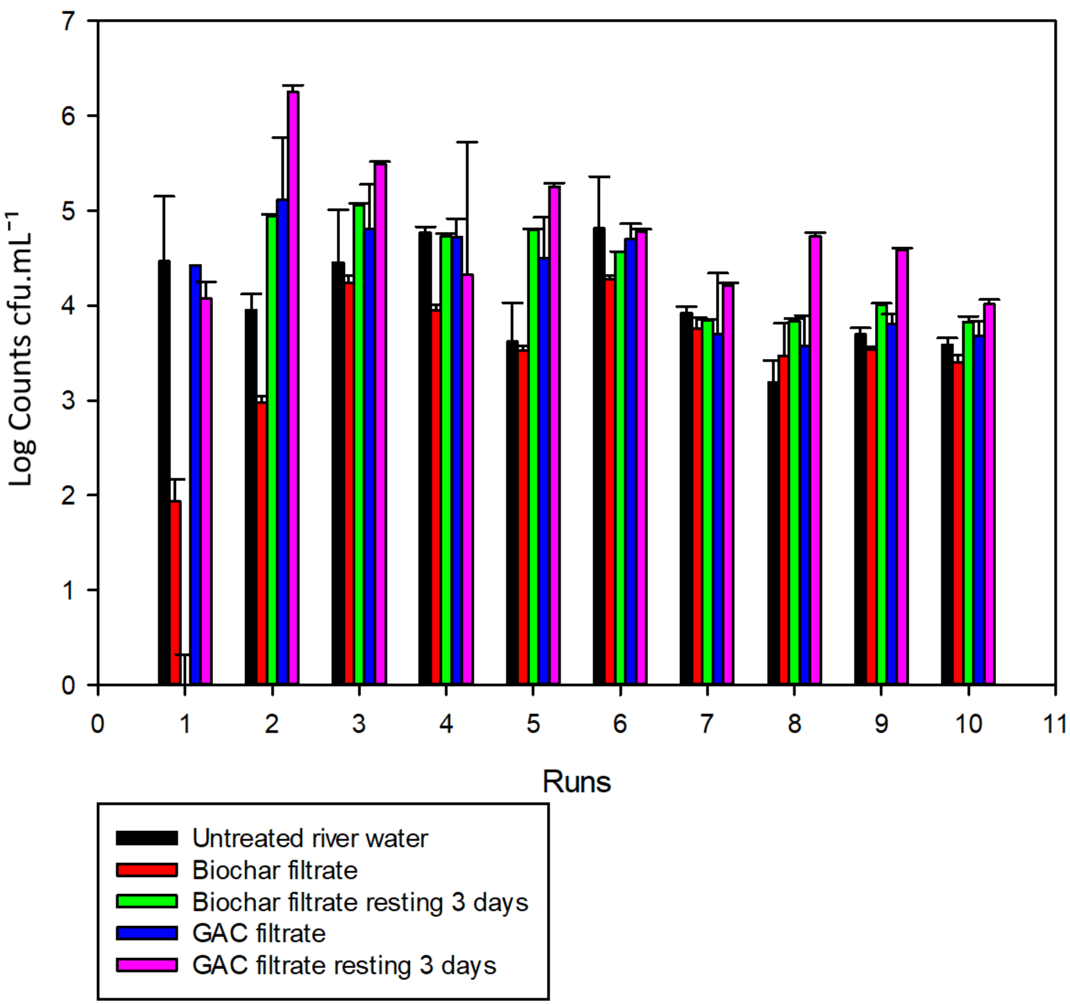


Figure 4.3. Heterotrophic plate counts (HPC) of untreated and treated river water with biochar and GAC filtration system.

Both the immediate GAC filtration and the GAC filtration that included a three day resting period in the column resulted in an increase of the HPC in the filtrate in all Runs except Run 1, 4 and 6. From Run 3 – 10 the filtration treatments (both direct filtration and with the three day resting period in the column) from both the pine biochar and the GAC did not contribute to notable reductions in HPC from the untreated river water as seen in Figure 4.3. Biochar gave a slight reduction or no change, while biochar resting for three days, GAC and GAC resting for three days all resulted in increased counts.

The biochar filtration system thus only reduced the heterotrophic microorganisms in the first 8.0 L (Run 1 and 2) of untreated river water. Furthermore, the biochar filtrate which rested for three days indicated an HPC of zero in Run 1. This, however, drastically increased to higher counts compared to the samples of untreated river water that were collected for Run 2, to values as high as 4.9 log cfu.mL^{-1}.

It is possible that the moist environment within the columns provided the ideal growing conditions for heterotrophic microorganisms. This may have led to the formation of a biofilm within the columns which in turn, further influenced the microbial environment (Simpson, 2008). The GAC filtration did not contribute in reducing the heterotrophic microorganisms and in fact resulted in an increase above the levels that were present in the samples collected from the Plankenburg River for Runs 2, 3 and 5 – 10. These results thus indicated that there was a greater reduction of HPC by the biochar than by the GAC.

In both Run 1 and 4 slight decreases can be seen for both the GAC filtrate and GAC filtrate resting for three days. This could be as a result of the initial adsorption of the HPC which could play a role in the formation of a biofilm. If a biofilm had occurred in the filtration column, it could explain why there was no reduction of HPC after Run 1. Biofilms and the microorganisms within biofilms are prone to degradation and result in the breaking down of the biofilm (Simpson, 2008). The breaking down of the biofilm could thus have resulted in increased microbial counts within the filtrates. In Run 3, however, the biofilm might have been less prone to degradation and therefore did not result in increased HPC levels. On the contrary, the biofilm could have been more prone to degradation and may have leached out in the pre-rinse step and therefore would not have been detected in the HPC counts of this Run**.**

The results obtained for the counts of faecal coliforms in the treated and untreated river water are shown in Figure 4.4. From the results obtained, it was observed that the faecal coliform count in the untreated river water (2.95 log cfu.100 mL^{-1}) was completely reduced by the biochar filtration system for both sampled filtrates, in Run 1 (Figure 4.4).

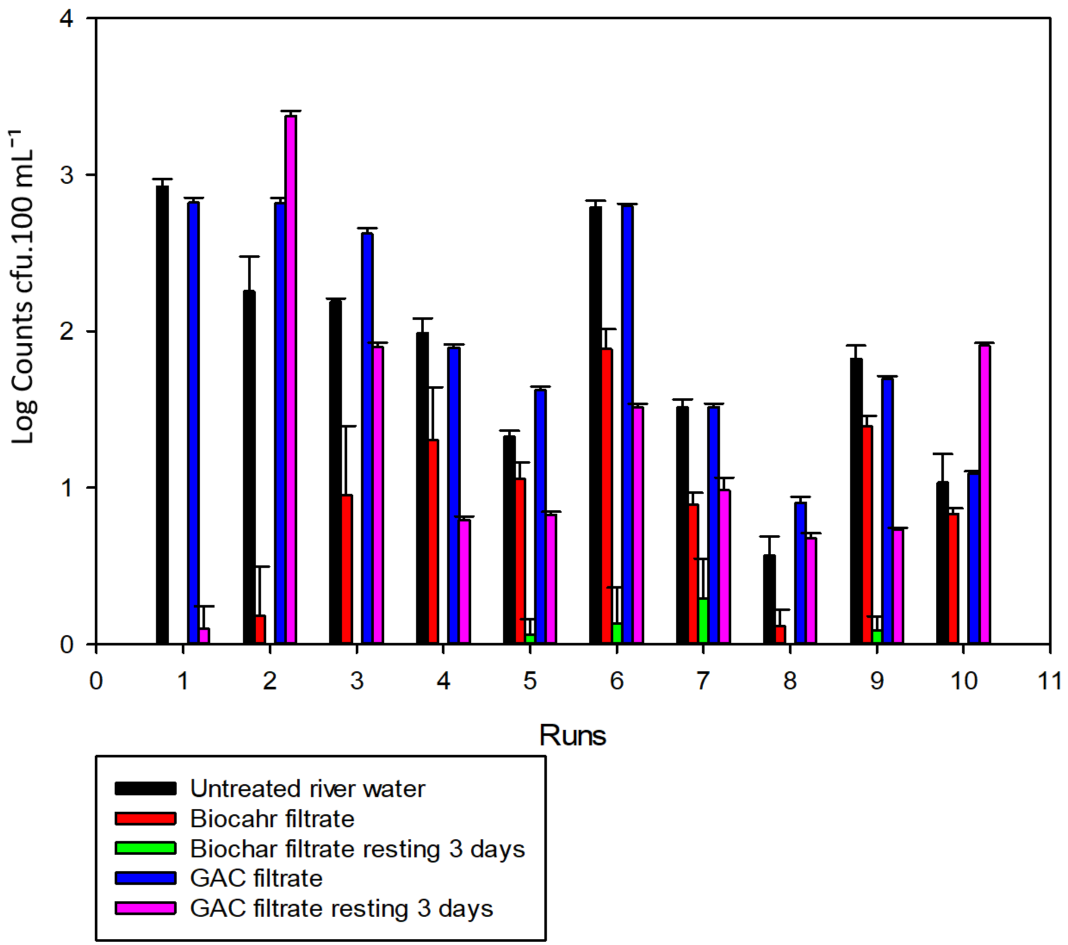


Figure 4.4. Faecal coliform count of untreated and treated river water with biochar and GAC filtration systems.

The GAC filtration only resulted in a slight decrease in faecal coliforms in the untreated river water to a count of 2.83 log cfu.100 mL^{-1}, in Run 1

The GAC filtration, with a three day resting period in the column, resulted in an effective reduction of faecal coliforms in the untreated river water to 0.12 log cfu.100 mL^{-1} in Run 1. The results obtained for Run 2 indicated that the pine biochar filtration resulted in a reduction of faecal coliforms in the untreated river water from 2.3 to 0.2 log cfu.100 mL^{-1} whilst the biochar filtration with a three day resting period in the column, resulted in the complete removal of the faecal coliforms. Both the GAC filtration samples (GAC filtration and GAC filtration with a three day resting period in the column) resulted in increasing the faecal coliform counts to above the counts in the untreated river water in Run 2.

The faecal coliform count of the biochar filtrate remained at all times below that of the untreated river water, with the lowest reduction of 0.3 log in Run 5, as seen in Figure 4.4. All Runs following Run 5 indicated that the faecal coliform counts of the biochar filtrate followed a similar trend to that of the untreated river water at lower levels. This could indicate that the reduction in the biochar filtration systems was highly dependent on the initial faecal coliform counts within the untreated river water.

The biochar filtration with a three day resting period in the column, reduced the faecal coliforms in the untreated river water in most of the Runs to a near-zero value, as seen in Figure 4.4. The formation of a biofilm, as well as the size of the different types of microorganism and the pore size of the filtration media, could have played a role in the reduction of the faecal coliforms (WHO, 2004b; Simpson, 2008).

This would explain why faecal coliforms may be reduced to such extremes whilst heterotrophic microorganisms are using the biofilm as a food source for increased growth as shown in Figure 4.3. According to a review by Simpson (2008), microorganisms are able to proliferate on GAC media and form a biofilm as they feed on organic matter, other microorganisms and waterborne nutrients. The GAC was not as effective in reducing the faecal coliform count as compared to the biochar filtration. Only the GAC filtration with a three day resting period in the column indicated a reduction of faecal coliform from 2.93 log cfu.100 mL^{-1} to 0.68 log cfu.100 mL^{-1} in Run 4 (after Run 1), as seen in Figure 4.4. The only Runs where the GAC filtration with a three day resting period in the column, did not reduce the faecal coliforms of the untreated river water was in Run 2, 8 and 10. This reduction could have also resulted from the formation of a biofilm rich in faecal coliforms which were less prone to degradation. These results are comparable to those obtained in a study completed by Mohanty and Boehm (2014), where a reduction in *E.coli* of up to 96% was observed in the treatment of urban stormwater with biochar biofilters. Furthermore, a study completed by Radhi and Borghei (2017), indicated that the aeration of untreated water and filtering thereof with GAC filtration media is up to 56.7% effective at removing faecal coliforms. These studies mentioned and the results obtained in this study indicates that biochar was more effective than GAC as filtration media for the removal of faecal coliforms.

The *Enterobacteriaceae* counts of the treated and untreated river water are shown in Figure 4.5. In Run 1 the biochar filtration reduced the *Enterobacteriaceae* counts of the untreated river water from 3.40 log cfu.mL^{-1} to 0.4 log cfu.mL^{-1}. The pine biochar filtration with a three day resting period in the column resulted in the complete removal of *Enterobacteriaceae* from the untreated river water. The GAC filtration resulted in a minor increase of the *Enterobacteriaceae* from the untreated river water whilst the GAC filtration with a three day resting period in the column, reduced the *Enterobacteriaceae* to 2.37 log cfu.mL^{-1} in Run 1.

This can be explained by the large standard deviation of the untreated river water as seen in Figure 4.5. In Run 2 only the pine biochar filtration and the pine biochar filtration with a three day resting period in the column, resulted in a reduction of *Enterobacteriaceae* from the untreated river water from 3.25 log cfu.mL^{-1} to 1.54 log cfu.mL^{-1} and 2.71 log cfu.mL^{-1}, respectively (Figure 4.5). The GAC filtration and GAC filtration with a three day resting period in the column resulted in an increased count of *Enterobacteriaceae* compared to the untreated river water. From Run 3 onwards, the efficacy of filtration varied. Counts were slightly reduced or even increased, but with no clear trends visible. It is clear that the reduction of *Enterobacteriaceae* was not as effective after Run 1.

These counts showed a similar trend to the HPC as indicated in Figure 4.3. After Run 4 the counts tend to vary and this trend can also be seen in the biochar filtrate resting for three days. As with the HPC, the *Enterobacteriaceae* may have been feeding off of the waterborne nutrients, organic matter and other microorganisms which form part of the biofilm and thereby increased their growth (Simpson, 2008). For both these groups of microorganisms, the latching mechanism which was used to form part of the biofilm was possibly not as strong as for faecal coliforms due to possible microbial size (Simpson, 2008; WHO, 2004). This could have been a result of increased degradation of these microorganisms and therefore lead to the breakdown of the biofilm segments. This may have resulted in an increase in the microbial counts each time the biofilm is degraded at each run where these biofilm particles were leached out.

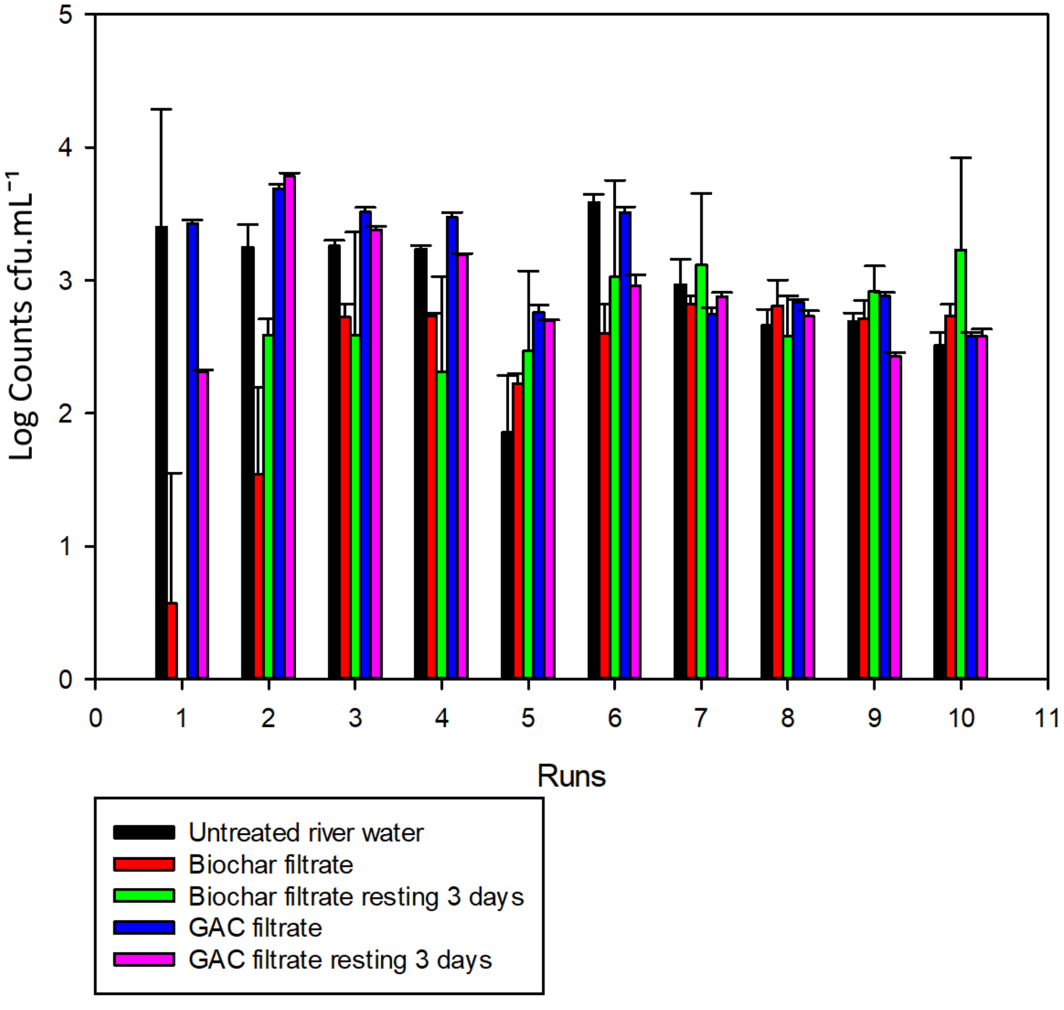


Figure 4.5. *Enterobacteriaceae* of untreated and treated river water with biochar and GAC filtration systems.

Physicochemical efficacy of filtrates

The treatment of the river water with either pine biochar or GAC and the effect it had on the physicochemical properties of the water was analysed and shown in the Figures below. The total dissolved solids (TDS) of the treated and untreated river water is shown in Figure 4.6. The TDS of the untreated river water in Run 1 had a value of 332 ppm and is reduced slightly by the biochar filtration. The biochar filtration with a three day resting period in the column as well as the GAC filtration also had not influenced the TDS of the untreated river water by a notable amount. The GAC filtration with a three day resting period in the column increased the TDS in Run 1 to 1 120 ppm. The results of the treatments in the following Runs had not deviated in any notable way from the results found in Run 1. The only exception is that as the Runs went on, the increase in TDS in the GAC and three day filtrates had become smaller (i.e. by Run 10 the TDS had only increased from 280 ppm to 470 ppm (40%), compared to the 70% increase in Run 1).

TDS is a property of the untreated river water, which is not influenced by either treatment, as shown in Figure 4.6. Although pine biochar and GAC filtrates had higher values of TDS through all the Runs in comparison with the untreated river water, the difference was no larger than 88 ppm between the treated and untreated water in Run 1 (Figure 4.6). When the untreated river water was exposed to the filtration media for three days, an increase in the TDS was observed. The TDS after exposure to the GAC filtration media for three days resulted in the highest TDS value of 1 120 ppm obtained from Run 1. Although a reduction to 478 ppm was observed in Run 4, where the untreated river water was 245.5 ppm, the TDS value remained higher than the untreated river water in all Runs with the lowest difference of 184.5 ppm observed in Run 7. The pine biochar filtration where the river water was exposed to the filtration media for three days only began to increase above expected values in Run 4 to 428 ppm, where the untreated river water was 245 ppm. The highest TDS value obtained for the pine biochar filtrates resting for three days is 523 ppm where the untreated river water was 242.5 ppm in Run 6, as can be seen in Figure 4.6.

The filtration media influencing the water quality over the three day period may have been a result of the increased exposure time between the filtration media and water molecules. This may have resulted in a greater effect of water infiltration into the intermolecular space in both the biochar and GAC filtration media, resulting in the binding of water molecules to unbound carbonous material in the micropores of the filtration media.

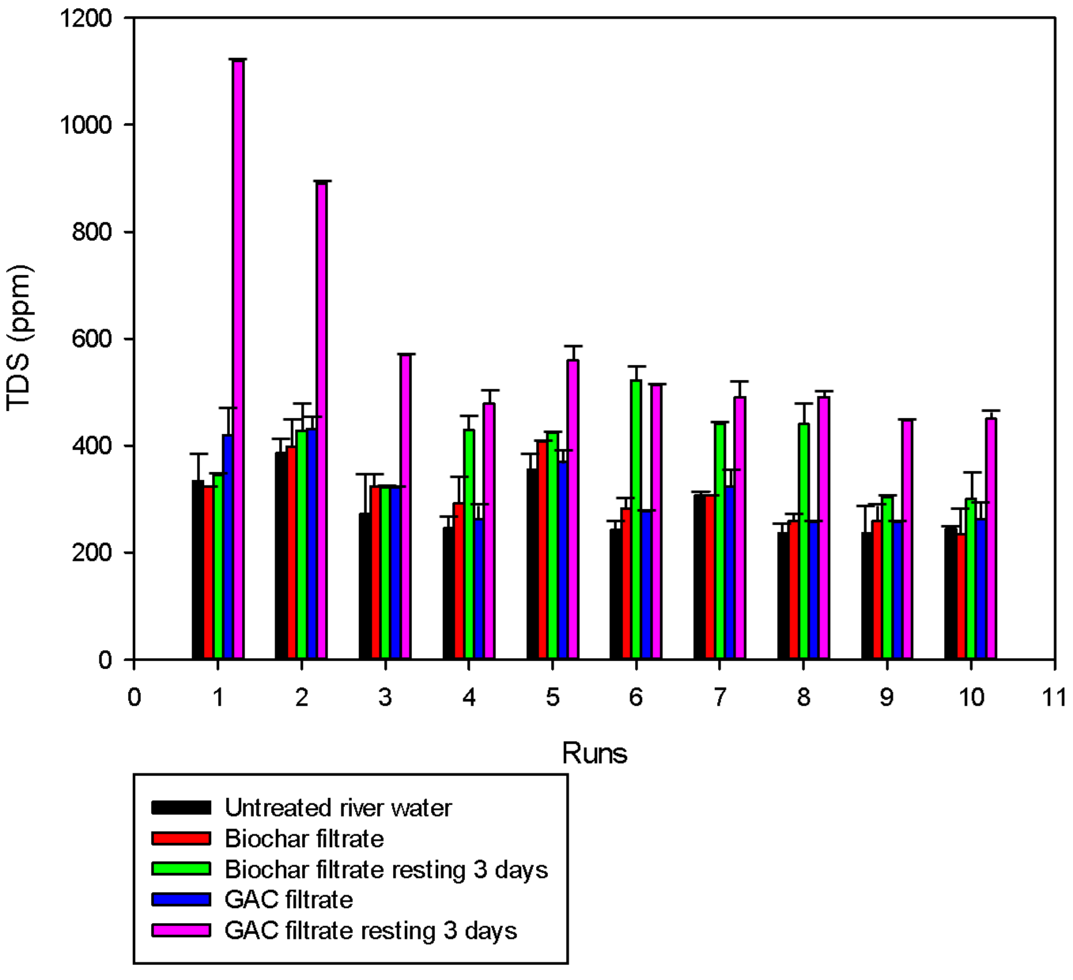


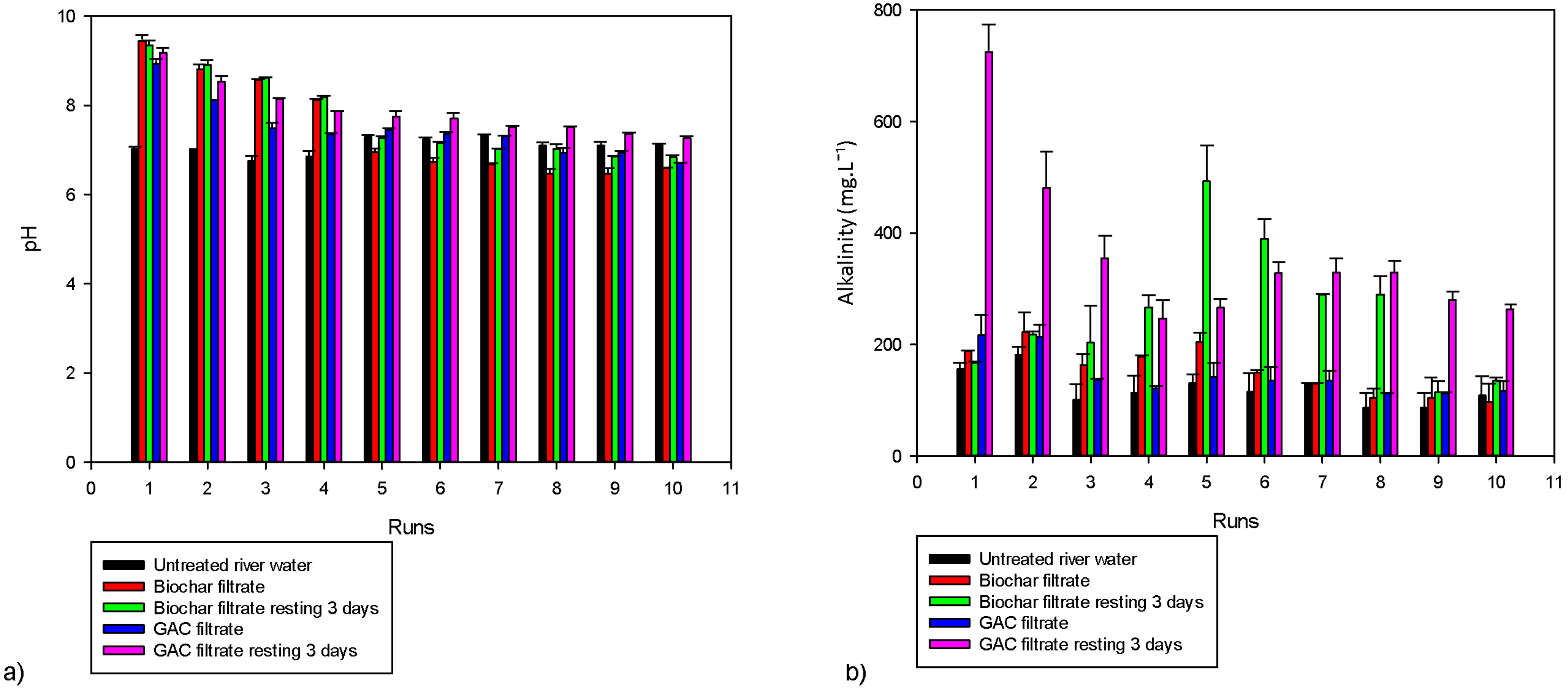
Figure 4.6. TDS of untreated and treated river water with biochar and GAC filtration system

This could have been the reason for increased carbonous material to leach out into the water and lead to an increase in TDS levels when the untreated river water is exposed to the filtration media for three days.

It is therefore unexpected that the first three Runs of the pine biochar filtrate resting for three days had not shown a high TDS value. This could be explained by the rinsing step before the untreated river water was filtered, which may have removed most of the dissolved solids from the micropores. The increase in Run 4 may have been as a result of some dissolved solids which may have been trapped in the micropores and were only released during the subsequent runs. Nevertheless, the filtration media had not improved the TDS of the untreated river water to below the guideline of 260 ppm. Therefore, both pine biochar and GAC influence the TDS quality of water negatively.

The results obtained for the TDS by the biochar filtration media are similar to the results that were obtained by Van Rooyen (2018), where the Electric Conductivity (EC) increased from 54.5 to 125.1 $mS.cm^{-1}$ before and after treatment with the pine biochar filtration, respectively. As indicated in the methodology section, EC is related to TDS and a conversion factor can be used to illustrate the TDS values theoretically. The TDS value would thus have increased from 327.0 to 75.6 ppm before and after treatment with the pine biochar, filtration respectively. The effect of the GAC in reducing TDS in this study was, however, not similar to the results obtained by Hanan (2014), where a decrease of up to 55% of TDS from surface water was observed. It should thus be noted that the filtration design, as well as the production process of the different filtration media, may play a role in influencing its efficacy towards adsorption properties.

The results obtained for the pH and Alkalinity of the untreated and treated river water are shown in Figure 4.7a and b. The pH of the untreated river water in Run 1 is 7.0 (Figure 4.7a). The pH of both the biochar filtrate and the biochar filtrate resting for three days indicated a rather high pH of 9.4 and 9.3 in Run 1, respectively. By Run 5, however, the pH of both these filtrates had dropped to below that of the untreated river water (pH of 7.3) to 6.9 and 7.3, respectively. The ideal pH range for irrigation water is between 6.5 and 8.4. It is clear that once constituents of the biochar, with a basic nature, which influence the pH was leached out, the media had the opposite effect, resulting in a decrease in the pH to acidic levels. A similar trend can be seen for the GAC filtrates. The pH value, however, did not drop by such a large extent below the untreated river water as compared to the pH drop of the pine biochar filtrates. This was not the case in a study completed by Zipf *et al.* (2016), where the pH of greywater treated with sand and GAC filtration had not lead to increases in pH as observed in this study.



a) b)

Figure 4.7. a) pH & b) alkalinity, of untreated and treated river water with biochar and GAC filtration system.

Instead, the sand and GAC filter resulted in a decrease of pH from 7.60 to 7.57. A relationship may exist where the adsorption of pH influencing constituents are dependent on the leach out of constituents from the filtration media it-self as well as the composition of these constituents. If carbonous material was the result of the increased TDS levels within the filtrate it may also explain why the pH was high in the initial Runs. Carbonous material could have increased the pH due to leaching out of these constituents and as the constituents within the char matrix reduced, the leach out of these constituents reduced. This would have lead to a reduction in pH in the filtrates over the trial period.

The alkalinity of the untreated river water in Run 1 was 155,0 mg.L^{-1}. The alkalinity was not notably influenced by the pine biochar filtration, pine biochar filtration with a three day resting period in the column and the GAC filtration as seen in Figure 4.7b. Only the GAC filtration with a three day resting period in the column increased the alkalinity of the untreated river water to 724.0 mg.L^{-1}. The pine biochar filtration and the GAC filtration had not influenced the alkalinity of the untreated river water by a notable difference from Run 1 - 10. The pine biochar filtration with a three day resting period in the column notably increased the alkalinity of the untreated river water in Runs 4 – 8 whilst the GAC filtration with a three day resting period in the column decreased from Run 1 – 4 after which it stabilised. The GAC filtration with a three day resting period in the column, however, still remained at higher levels of alkalinity than the untreated river water throughout all the Runs.

Analysis of the alkalinity of the water resting for three days in both filtration media resulted in a larger observable difference between the treated and untreated river water. These results could have correlated with the TDS results seen in Figure 4.6. The fluctuations in alkalinity could have been a result of the level of carbonate, bicarbonate and hydroxide content in the filtrates (APHA, 2005; Hanan, 2014). The high alkalinity of 725,0 mg.L^{-1} of the GAC filtrate resting for three days in Run 1 and 167.7 mg.L^{-1} of the pine biochar filtrate resting for three days in Run 5, as seen in Figure 4.7b), possibly indicate that the carbonate, bicarbonate and hydroxide content originated from the filtration media itself. This may have been due to the dissolved solids which are referred to in Figure 4.6.

The chemical oxygen demand (COD) of the treated and untreated river water is shown in Figure 4.8. The COD of the untreated river water in Run 1 was 109,0 mg.L^{-1}. This was reduced by the pine biochar filtration to a value of 14.6 mg.L^{-1}. The pine biochar filtration with a three day resting period in the column increased the COD value of the untreated river water to 178.5 mg.L^{-1}. The GAC filtration did not improve the COD level in Run 1 of the untreated river water. The GAC filtration with a three day resting period in the column increased the COD of the untreated river water to 204.6 mg.L^{-1}.

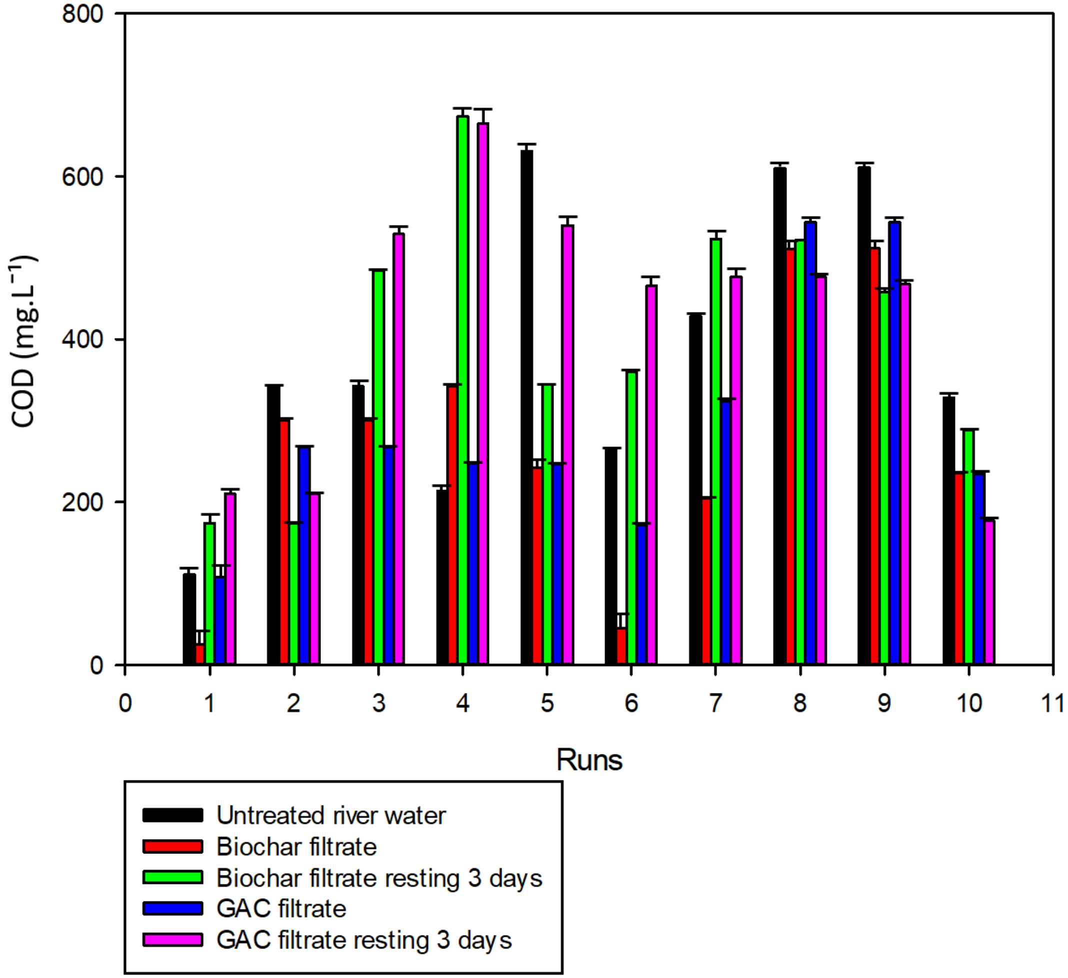


Figure 4.8. Chemical oxygen demand (COD) of untreated and treated river water with biochar and GAC filtration systems.

The COD of the untreated river water varies from Run 1 -10 and was reduced by the pine biochar filtrate and the GAC filtrate in all the runs except in Run 4. This was not the case for the filtrates of pine biochar and GAC resting for three days where the fluctuations of the filtrate COD from the untreated river water varies.

The COD gives an indication of the organic and inorganic material in a sample. It is clear from Figure 4.8, that the COD of the untreated river water was reduced by the pine biochar and GAC filtration media. It is only in Run 4 that the COD value for both filtration media is higher than that of the untreated river water sample. The highest reduction of COD by the pine biochar and GAC is to 389.2 $mg.mL^{-1}$ and 385.2 $mg.mL^{-1}$ in Run 5, respectively. Similarly, a study completed by Van Rooyen (2018), using pine biochar as a filtration media, also indicated variation in the trials where COD reduction occurred whilst in other trials it did not. However, the study done using Eucalyptus type biochar as filtration media indicated that this type of biochar was effective at reducing the COD from values as high as 120.6 to 16.2 $mg.L^{-1}$ (Van Rooyen, 2018). A study completed by Radhi and Borghei (2017), on the filtration of river water with the use of a GAC as filtration media, in contrast, indicated a gradual reduction of up to 77.5% efficiency in COD.

Furthermore, a study completed by Zipf *et al.* (2016), on the efficacy of a sand and GAC filter on greywater systems, also indicated a reduction of COD from 128.0 $mg.L^{-1}$ of the raw greywater to 52.1 $mg.L^{-1}$. It should be noted that both the studies which indicate an effective reduction in the COD made use of a different filtration design and procedures. The biggest difference being that the sampled water was continuously flowing through the filtration and at no point did the flow thereof stop.

This decrease in COD may result from the sieving and straining of larger particles of organic and inorganic matter. Most runs for the pine biochar and GAC followed a similar trend to the untreated river water and indicated small decreases in the filtrates. This may indicate that if there is a carbonous filtration media with a large surface area, the filtration of organic and inorganic matter will occur. From Figure 4.8, the COD of the river water was generally decreased when treated with the biochar and GAC filtration media, with Run 4 showing the only increase over all the runs. Furthermore, when the river water was treated with the pine biochar with a three day resting period a general increase in the COD value was seen in Run 1-7 whilst a decrease was observed for Run 8-10. Similarly, an increase was observed in Run 1-7 when treated with the GAC filtration media with a three day resting period whilst a decrease was observed in Run 8-10. The reduction of COD by both the biochar and the GAC which was observed between Run 8 and 10 could be a result of the development of the microbial environment which could be utilising the organic constituents, resulting in degradation thereof (WHO, 2004; Simpson, 2008).

The analysis of these filtrates indicated that organic and inorganic matter would not be absorbed as effectively when the river water was not exposed to the media for three days. Further research is required to determine if the ongoing filtration of untreated river water by biochar and GAC filtration media would result in a significant decrease in COD levels.

The filtrates resting for three days had high levels of COD in Run 3, 4, 6 and 7 which were above the COD values of the untreated river water, as seen in Figure 4.8. The variation of increases and decreases in the COD values could only be explained by the interaction which the filtration media had with the constituents of the organic and inorganic matter. It may also be explained by the over-saturation of these contaminants in the micropore spaces after which it was discarded when the water surfaces are disrupted three days later (Simpson, 2008). The three day filtrates might thus be a representation of a secondary form of rinsing, which may be leaching out constituents that were cleaved during the three day duration. It is, however, clear that there is different interaction in the untreated river water when it was exposed to the filtration media for a much longer duration.

The results obtained for the total suspended and volatile suspended solids in the treated and untreated river water are shown in Figure 4.9. The TSS of the untreated river water in Run 1 was 20.0 $mg.L^{-1}$. The biochar filtration reduced the TSS of the untreated river water to 2.6 $mg.L^{-1}$ in Run 1 and the pine biochar filtration with a three day resting period in the columns, reduced this value to zero. The GAC filtration reduced the TSS of the untreated river water to 4.8 $mg.L^{-1}$ in Run 1, as seen in Figure 4.9a. The GAC filtration with a three day resting period in the column also showed complete removal of TSS from the untreated river water in Run 1. In Run 2 the TSS of the untreated river water was notably reduced by all the filtration media as seen in Figure 4.9a. In Run 3 the TSS of the untreated river water had a low reading of 4.4 $mg.L^{-1}$ and as a result thereof only the pine biochar filtration reduced the TSS to 0.4 $mg.L^{-1}$. The pine biochar filtration with a three day resting period in the column had no notable reduction in the TSS whilst the GAC filtration and the GAC filtration with a three day resting period in the column, increased the TSS value of the untreated river water to 15.4 $mg.L^{-1}$ in Run 3. In Runs 4 - 10 the TSS of the untreated river water varied, however, both filtrates (direct filtration and filtrate resting for three days) of the two treatments (pine biochar and GAC) notably reduced the TSS.

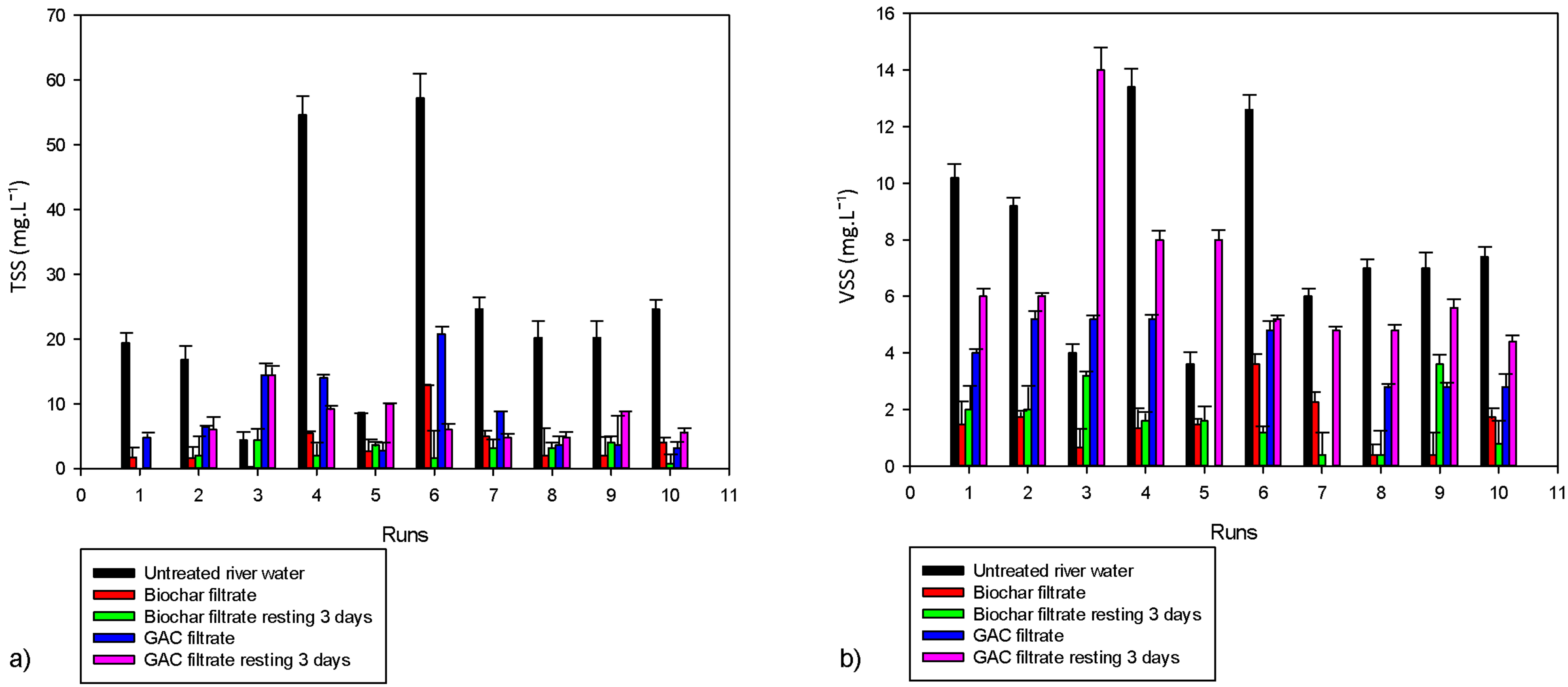


Figure 4.9. a) Total suspended solids (TSS) and b) volatile suspended solids (VSS) of untreated and treated river water with biochar and GAC filtration system.

Pine biochar filtration was most effective at reducing the TSS in the river water even with the high peaks of the untreated river water in Run 4 and 6. Both the filtration and filtration with a three day resting period in the column reduced the TSS to values below the guidelines of 50.0 mg.L^{-1} for irrigation water (Table 4.1). In fact, the highest TSS value of all the filtrates was in Run 6 of the GAC filtrate with a value of 20.8 mg.L^{-1}, and the lowest was in Run 1 of the pine biochar filtrate and GAC filtrate resting for three days with a complete reduction in the suspended solids, as can be seen in Figure 4.9a. TSS gives an indication of the total amount of solids within the untreated and treated river water which is larger than 0.45 micron. These solids can thus consist of a variety of materials which could be polluting river water (Woodard & Curran, 2006).

The VSS of the untreated river water in Run 1 had a value of 10.4 mg.L^{-1} which was reduced by the biochar filtration and the biochar filtration with a three day resting period in the column, to 1.4 mg.L^{-1} and 1.9 mg.L^{-1}, respectively, as seen in Figure 4.9b. The VSS of the untreated river water was also reduced by the GAC filtration and the GAC filtration with a three day resting period in the column to 2.9 mg.L^{-1} and 5.9 mg.L^{-1}, respectively. In Run 2 - 10 the VSS of the untreated river water was continuously reduced by all the filtrations except in Run 3 and 5, where the GAC filtration with a three day resting period in the column, increased the VSS of the untreated river water as seen in Figure 4.9b. The VSS of a water sample gives an indication of the organic material which may be present in the specific sample (Woodard & Curran, 2006).

A similar trend to the TSS can be seen in the VSS, where the pine biochar seems to be most effective at reducing the number of volatile solids in the untreated river water. It is clear from Figure 4.9b that only for Run 5 and 7, the GAC filtration showed better reductions compared to the biochar filtration and the biochar filtration with a three day resting period in the columns. This is not the same with the corresponding GAC filtration with a three day resting period in the column, in Run 5, where the VSS was increased to above the level present in the untreated river water from 3.6 mg.L^{-1} to 8.0 mg.L^{-1}. This is rather interesting due to the GAC filtrate in Run 5 and 7, which had the lowest value of 0.7 mg.L^{-1} of all the filtrates and in all the runs. The biochar filtration did prove to be most beneficial due to its smaller range of variability in reducing VSS. Both the biochar filtration and biochar filtration with a three day resting period in the column reduced the VSS to a range of 0.4 - 3.6 mg.L^{-1} and 0.1 – 3.6 mg.L^{-1}, respectively, whilst the corresponding ranges for the GAC filtration was 0 – 5.2 mg.L^{-1} and 4.8 – 14.0 mg.L^{-1}, as seen in Figure 4.9b. Properties in the biochar such as the infiltration, electrostatic interactions, partitioning and hydrophobicity interaction that exist between the biochar and suspended solids may result in the effective adsorption of these contaminants (Mohanty & Boehm, 2014; Inyang & Dickenson, 2015). The adsorption of suspended solids originating from organic matter may contribute to the reduction of faecal coliforms as seen in Figure 4.4.

The results of the turbidity of the untreated and treated river water are shown in Figure 4.10a. The turbidity of the untreated river water in Run 1 had an NTU reading of 21.8 NTU (Figure 4.10a). This turbidity was reduced by both the biochar filtration and the biochar filtration after resting for three days in the column to a near-zero value. The GAC filtration and the GAC filtration with a three day resting period in the column also resulted in reducing the turbidity of the untreated river water in Run 1 to 14.5 NTU and 20.4 NTU, respectively. In Run 2 – 10 the turbidity levels of the untreated river water were consistently reduced by all four filtration systems. Turbidity provides an indication of the clarity of the water and according to Figure 4.10a, the pine biochar was most effective at reducing the turbidity of the untreated river water. The pine biochar filtrate did not exceed a turbidity value of 27.5 NTU (Run 6) whilst the GAC filtrate reached a value of up to 57.8 NTU in Run 6, as seen in Figure 4.10a. Although both media reduced the turbidity of the untreated river water (reaching the highest level of 85.7 NTU in Run 6) in all the runs, it is clear that the pine biochar was most effective as seen in Figure 4.10a.

These results are similar to those seen in a study by Zipf *et al.* (2016), where the turbidity of greywater (21.55 NTU) was reduced by sand and GAC filtration to 7.0 NTU. According to Van Rooyen (2018), however, the pine biochar used as filtration media resulted in increased turbidity from values of 14.0 to values as high as 42.3 NTU. Although this is unexpected, it should be noted that the pine biochar which was used in the study by Van Rooyen was pyrolyzed and produced at a much lower temperature. The efficacy of the biochar is extremely sensitive to the temperature at which it is produced. In most cases, the higher the production temperature of the biochar the larger the increase in efficacy there is to adsorb contaminants due to smaller pore size and larger surface area (Mohanty & Boehm, 2014; Reddy *et al.*, 2014; Inyang & Dickenson, 2015).

Furthermore, it is clear that both filtration media were more effective when untreated river water was resting for three days in the columns. It is important to note that the only filtrate which remained below the recommended guideline for irrigation, considering turbidity of less than 10 (Ayers & Westcot, 1994; Hanseok *et al.*, 2016), is the pine biochar filtrate resting for three days. This may indicate that organic matter which is suspended in the untreated river water with a level of up to 57.2 $mg.L^{-1}$ (TSS of untreated river water), may be the largest contributing factor which may be influencing the clarity of the water.

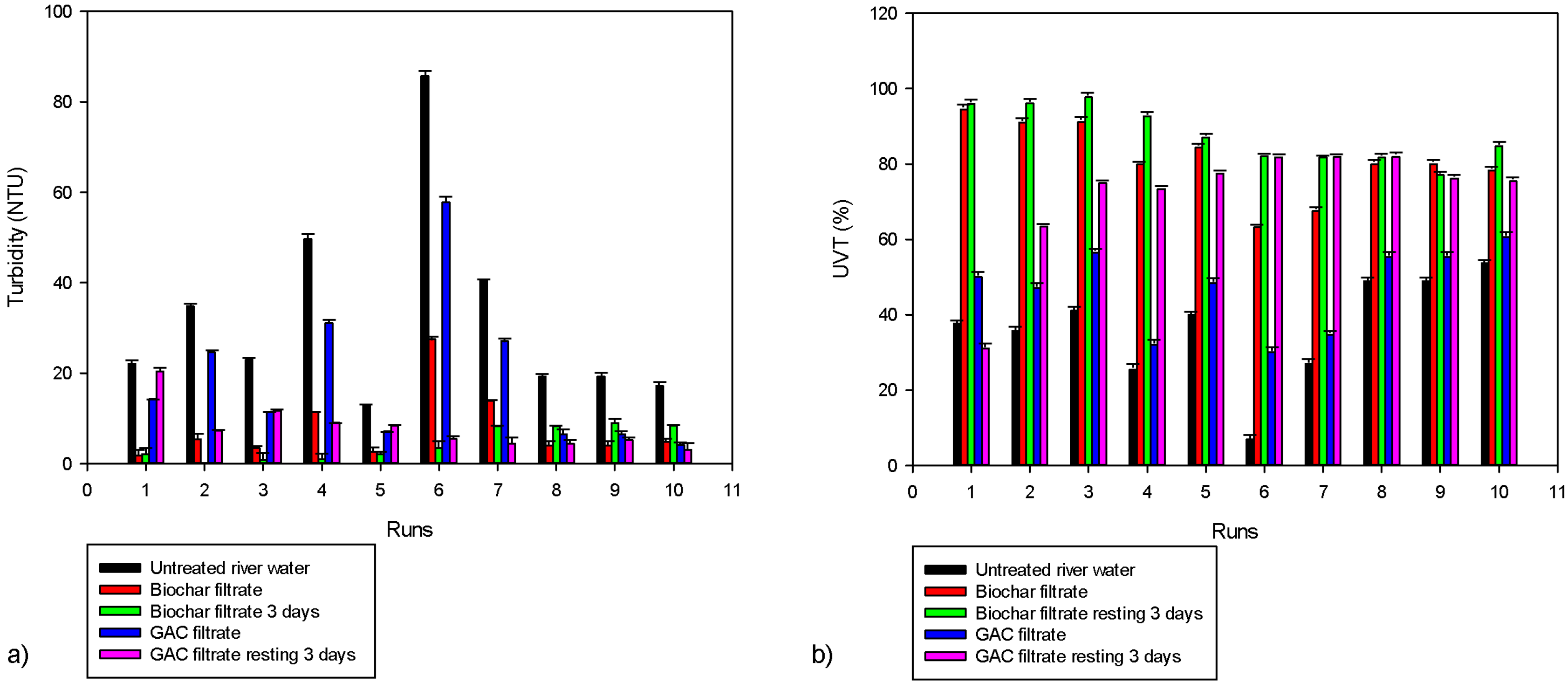


Figure 4.10. a) Turbidity and b) ultraviolet transmission percentage (UVT %) of untreated and treated river water with biochar and GAC filtration systems.

The pine biochar may thus be improving the clarity by reducing the suspended and volatile solids as seen in Figure 4.9a and b.

The UVT results of the treated and untreated river water are shown in Figure 4.10b. The UVT of the untreated river water in Run 1 was 37.6%. The biochar filtration and the biochar filtration with a three day resting period in the column, improved the UVT of untreated river water to 94.8% and 95.9%, respectively, in Run 1 (Figure 4.10b). The GAC filtration also improved the UVT of the untreated river water to 49.2% whilst the GAC filtration with a three day resting period in the column, reduced the UVT of the untreated river water to 32.4%. In Run 2 – 10 the UVT of the untreated river water was consistently improved by all the filtration systems as seen in Figure 4.10b.

The UVT results of the untreated river water were improved most effectively by the pine biochar filtration, biochar with a three day resting period in the column and the GAC filtration with a three day resting period in the column as seen in Figure 4.10b as from Run 5 - 10. Between the pine biochar and the GAC filtration, the pine biochar filtration improved the UVT of the untreated river water most effectively. This can be observed through all Runs from 1 to 10 and is most clearly observed in Run 6, where the untreated river water has a UVT of 0.7%. The pine biochar filtration improved the UVT to 62.3% whilst the GAC filtration only improved the UVT to 30%. The biochar filtration and the biochar filtrate resting for three days were very effective at improving the UVT% of the untreated river water from Run 1. GAC filtrate and GAC filtrate resting for three days always improved the UVT% of untreated river water, but less than that of the biochar filtration and biochar filtrate resting for three days. The GAC and GAC resting for three days did gradually improve at increasing the UVT% and from Run 5 – 6 it was very similar to that of the biochar and biochar resting for three days. If it was organic matter which influenced the turbidity of the untreated river water most, it may explain why the filtration media which reduced the turbidity most would likely increase the UVT% most effectively. This may be explained by the ability of organic matter, and more specifically aromatic compounds within the organic matter as well as faecal coliforms to adsorb ultraviolet light (APHA, 2005). Furthermore, UV treatments have shown promising results in the improvement of the microbial status of untreated river water, (Olivier, 2016; Van Rooyen, 2018; Sivhute, 2019). The UVT% is used to determine the amount of UV absorbing contaminants in the water in order to adjust the dosage of the UV treatment accordingly. The improvement in the UVT% by the pine biochar filtration indicates the potential use thereof as a pre-treatment to improve river water quality.

4.5 CONCLUSION

The analysis on the microbial and physicochemical status of the Plankenburg river water indicated signs of highly contaminated river water not suitable for irrigational use. It is, therefore, essential for this water to undergo treatment before it can be safely utilised for irrigation. Pine biochar was used in this study as a filtration media and compared to the commercially produced and used GAC filtration media. The filtration system was designed to pump water through the filtration media which was housed in a closed column. This filtration media was kept saturated during the entire time period between all the runs. The filtration system was crucial to determine if the exposure time would influence the efficacy of adsorbing contaminants from the untreated river water. From the results obtained it is clear that the pine biochar was a more effective filtration media as compared to the GAC. The pine biochar filtration indicated that it was more beneficial than the pine biochar filtration with a three day resting period in the column when considering the COD, alkalinity and TDS improvement of the filtrates. The pine biochar filtration with a three day resting period in the column did, however, improve the faecal coliform counts, turbidity and UVT% of the untreated river water more effectively than the pine biochar filtration immediately after treatment with the pine biochar. Although the flow rate was reduced from Run 5, it is clear that only when the untreated river water was exposed to carbonous filtration media for three days that it will affect the adsorption of contaminants. Although the exposure of the river water to the filtration media for periods as long as three days proves to be beneficial, it may not be feasible to filter untreated river water this slowly. Further research would be required in the design of the filtration systems and the continuous flow of untreated river water through the column for a duration of days to weeks. This would provide information which can be used to determine the quantity of water which can be filtered with the biochar before it has no beneficial effect on the quality of water.

The carbonous material, pine biochar, has many benefits for the adsorption of contaminants out of untreated river water, however, it was not effective at reducing the microbial load of untreated river water to acceptable levels. The biochar and the efficacy thereof were directed towards the improvement of the physicochemical characteristics of the untreated river water. This could have a great effect on the reduction of microorganism by treatments such as UV light if used after filtration. Biochar filtration, therefore, has an indirect contribution to the improvement of the microbial status of the untreated river if it is used together with other water treatments such as the UV light, and coagulation treatment. This may reduce the dissolved solids as well as improve the microbial quality of the untreated river water. It should be noted that although the faecal coliform count was reduced by the pine biochar filtration, the mechanism of this adsorption is not yet understood and therefore further research should be conducted in the specific analyses of the organic adsorption of the pine biochar. Using this system in a series of treatments should put less strain on the pine biochar filtration alone. Therefore, the pine biochar might prove to be a more beneficial treatment focussing on the adsorption of specific contaminants. This may also increase the duration of the effective use of the biochar.

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CHAPTER 5

GENERAL DISCUSSION AND CONCLUSION

Irrigation water is a key ingredient to the growth of safe, fresh produce. The microbial and physiochemical quality of the water influences the growth potential and the health risk these consumables may have when contaminants are carried over from the water to plant matter (Qadir *et al.*, 2010; Allende & Monaghan, 2015; Johannessen *et al.*, 2015). Rivers and dams are one of the largest sources of irrigation water and it is clear that these water sources are becoming increasingly polluted with many hazardous contaminants in South Africa (Qadir *et al.*, 2010; Allende & Monaghan, 2015; Johannessen *et al.*, 2015). The microbial status of the water most likely contributes the most immediate threat to the safe consumption of fresh produce (Forsythe, 2010; Hoyle *et al.*, 2018). It is evident that untreated river water from a source such as the Plankenberg River in Stellenbosch is not the ideal quality for the growth of plant matter according to both studies completed in Chapter 3 and 4 of this thesis. It is thus essential to develop cost effective treatments for these contaminated sources to prevent not only contaminants which may enter into the food chain but also inhibit the negative effect of these contaminants on plant growth.

In South Africa the agriculture sector uses up to 63% of the country’s water catchment area predominantly for irrigation use (WWF-SA, 2017). The Vaal River System comprises up to 80% of the country’s water supply and when these sources are contaminated with faecal matter it can place a great deal of pressure and stress on the agricultural sector (Department of Water and Sanitation, 2016). If irrigation water does not conform to certain guidelines it is not suggested to be used. In 2018 the Vaal river catchment area had a high *E. coli* count of up to 6 000 CFU per 100 mL, where water contaminated with more than 400 CFU per 100 mL, according to Bega (2018), and would be hazardous for human contact and thus indicates how hazardous it could be as irrigation water (Bega, 2018). With this high count in the water catchment area it is not recommended to use this water as irrigation for plants without having gone through a treatment which significantly reduces the microbial load (DWA, 2013).

There are a number of treatments which can be used to not only reduce microbial load for the safe use of irrigation water, but also improve the physicochemical properties of the water (Parsons & Jefferson, 2006; Schug, 2016; Van Rooyen, 2018) . This is usually accomplished in combining a number of treatments to achieve the reduction and improvement of water quality. One such treatment which could improve the water quality both microbially and physicochemically is the use of biochar as a filtration media (Keiluweit *et al.*, 2010; Jing *et al.*, 2014; Mohanty & Boehm, 2014; Yang & Jiang, 2014; Inyang & Dickenson, 2015; Park *et al.*, 2015; Santos *et al.*, 2015; Tan *et al.*, 2015). Biochar has many benefits to improving water quality by adsorbing certain contaminants due to its large surface area and functional groups. Biochar is produced from plant matter and could have the potential of adsorbing undesirable contaminants from irrigation water (Inyang & Dickenson, 2015; Tan *et al.*, 2015). Usually activated carbon is used in filtration systems, however, biochar may be a cost-effective alternative. The overall purpose of this study was to investigate the effect of biochar as a filtration media on the microbiological and physicochemical status of untreated river water.

In the first phase of the study filtration columns were packed with filtration media to evaluate the efficacy of these selected media. The media was exposed to untreated, contaminated river water as it passed through the columns. Two different types of biochar were used, pine and black wattle, whilst granular activated carbon (GAC) and silica sand were used as a positive and negative control, respectively. Each column was exposed to ten runs. Samples were collected after each run, which consisted of passing 2 L of untreated river water through the column. Although the results indicated a reduction in the microbial count in the initial runs, the reduction was not nearly as effective as the number of runs increased. The results indicated that not one of the filtration treatments improved the microbial status of the untreated river water. The pine biochar was, however, more effective at reducing the microbial counts compared to the black wattle biochar, GAC and silica sand. The pine biochar also proved to be more effective at improving certain physicochemical properties of the untreated river water as compared to the other filtration media. These include improvement of pH, alkalinity, total suspended solids, total volatile solids, turbidity and ultraviolet transmission (UVT). The results indicate that biochar is not an effective treatment to reduce microbial content, but could serve as an effective pre-treatment to other water treatment processes.

With a large improvement observed in the UVT results of the untreated river water, treatment with the pine biochar filtration was combined with ultraviolet radiation treatment. The purpose of biochar filtration was firstly to reduce the microbial activity and secondly to improve the physicochemical properties of the water. This resulted in the improvement of both the efficacy and efficiency of the UV treatment. Not only did the biochar filtration result in more reduction of microorganism by the UV treatment in the untreated river water but, it also resulted in requiring a lower UV dose to achieve similar results.

Furthermore, the ineffective ability of the filtration media to adsorb certain pollutants such as microbes and other organic and inorganic matter from the contaminated water, may result from the filtration design itself. The pine biochar has a large surface area due to its porosity. A longer exposure time of the untreated river water with the biochar may be required for a better absorption of the pollutants from the contaminated water.

The second phase of the study therefore aimed to improve the filtration design and increase the exposure time of the contaminated water with the biochar. This was accomplished by closing the filtration columns and managing the flow rate through the column with the aid of a pump. The main differences between the first and second phase of the study was that the columns were saturated at all times with untreated river water and an additional 2 L of this water was used to flush out the saturate before samples were collected. The pine biochar was chosen as filtration media due to the positive results obtained in the first phase of the study, with the GAC chosen as a positive control. It is clear, from the results obtained, that saturating the biochar with the untreated river water and reducing the flow rate improved the quality of water to a greater extent compared to the first phase of the study. These changes both played a role in increasing the exposure time of the polluted water with the biochar. In the first phase of the study gravitational flow was used for all columns, which had a flow rate of 1.3 $L.min^{-1}$ whilst the second phase of the study had a flow rate of 0.41 $L.min^{-1}$ using a closed filtration system. This large reduction in the flow rate not only improved the water quality to a greater extent but was also achieved with larger quantities of water. A total amount of 20 L of untreated river water was passed through the filtration columns in the first phase of the study whilst a total of 40 L of untreated river water was filtered through the columns in the second phase of the study. Although the quantity of water doubled, the closed filtration system was more effective at improving the water quality than the gravitational flow columns used in the first phase of the study. This was particularly observed in the following water quality parameters; faecal coliform count, pH, alkalinity, COD, turbidity and UVT measurements.

The improved reduction in the faecal coliform count observed in the second phase of the study lead to reduction thereof in each run when observing the results for the pine biochar column and was further reduced to near zero values for the biochar filtrate resting for three days. This may be as a result of the development of a biofilm in the column. This may have resulted as saturation was maintained between runs. Furthermore, an increase in the microbial count of the *Enterobacteriaceae* and heterotrophic microorganisms suggests that the environment within the biochar stimulated the growth thereof. This could be the result of biofilm formation. The guidelines only indicate that the faecal coliform count is the only group of microorganisms which need to be conformed to, for the safe use of the water. Although faecal coliforms are reduced (or low) in the biochar filtrates, it is not an ideal indication of other *Enterobacteriaceae* bacteria which does not form part of the irrigation water quality guidelines. This is rather concerning due to the prevalence of pathogenic microorganisms within this family, which could find their way into the food chain via irrigation water. The physicochemical improvement of the irrigation water compared to the first phase of the study was likely a result of the organic and inorganic contaminants' filtration into the biochar micropores. The improved adsorption of these contaminants into the micropores are due to the increased exposure time of the contaminated water with the biochar. This was achieved by reducing the flow rate through the biochar. This may have improved the effectiveness of the biochars infiltration, electrostatic interactions, partitioning and hydrophobicity interactions which occur between the biochar compounds and water contaminants and would thus result to increased adsorption of the pollutants. Although these filtration systems were more effective than those used in the first phase of the study, the treated river irrigation water still did not conform to the South African Water quality guidelines (DWAF, 1996; DWA, 2013). This is as a result of the inability of biochar to improve total dissolved solids and electric conductivity. This, in turn, could be as a result of the strong molecular bonds formed between the water and the dissolved contaminants within the water, which the biochar is not able to interact with. This problem, however, could be overcome with the use of a coagulate as a treatment to remove dissolved contaminants before it undergoes filtration treatment. In the first phase of the study UV treatment was used in combination with biochar filtration. As a result, all the microorganism in the water were reduced effectively and efficiently in addition to the removal of STEC. A combination of treatments involving biochar filtration, UV treatment, and coagulant treatment could thus result in obtaining irrigation water safe enough for the use thereof.

Although the biochar filtration did not lead to a reduction in the microbial count of the river water, a clear reduction in the physio-chemical parameters was observed. The biochar filtration media would thus be more suited at reducing the physio-chemical parameters of contaminated water which would be beneficial to other water treatment processes, such as UV treatment. The biochar filtration thus has the potential to contribute in the reduction of certain physio-chemical parameters of contaminated water and act as pre-treatment to other water treatment processes. Compared to GAC, biochar is a better substitute, as it was more effective in improving water quality and is more efficient to produce. Although pine and black wattle biochar could not lead to the improvement of water quality to conform to irrigational guidelines, it did prove beneficial in the removal of specific contaminants.

RECOMENDATIONS FOR FUTURE STUDIES

It would be ideal to determine the effect which saturation alone might have on the efficacy of biochar. From the results obtained in the second phase of the study, it is clear from the saturate that was analysed that there are other interactions that are present between the untreated river water and the biochar when the exposure time was increased to three days. To compare the effect of saturation, the flow rate of the closed system should be identical to the gravitational flow rate as in the first phase of the study. This, however, was limited by the increasing internal pressure within the columns which can result in possible rupturing of the column itself. This could be rectified by using a stronger material for the design of the filtration column as well as increasing the internal diameter of the nozzles at the bottom end of the column. The pressure within the system might have played a role in the interfiltration of untreated river water into the micropores of the biochar. If pressure does play a role to this interaction, further research can be done in the design of a stronger and more sophisticated filtration system. Further research with this filtration design would involve a continuous flow of untreated river water through the biochar columns. This would indicate how effective the biochar would be as a physical treatment for large quantities of water specific for irrigation. Additionally, the effect the biofilm formation will have on the microbial environment can be determined. This may be a unique study as a continuous flow will most likely result in the formation of the biofilm directly on the biochar granules. This will increase the surface area of the biofilm, which could increase the adsorption of microorganisms but may also become more prone to degradation of the biofilm which could end up in the filtrate. The concept of continuous flow would enable backwashing of the filtration system. This may result in the increased removal of biochar constituents influencing the quality of water whilst maintaining saturation during filtration.

It should also be noted that the filtration columns were only exposed to one river source. This limits the study exclusively to the excessive high contamination levels of the Plankenburg River water. Further research can be conducted where the filtration columns are exposed to multiple sources. This could give an indication of how effective the biochar filters would be when exposed to less contaminated water or more contaminated water. This could give specific insight on the microbial activity in filtrates that had initial low levels. Furthermore, the plant source of the biochar plays an important role in the specific removal of certain contaminants and therefore studies using different plant sources of biochar can be conducted to find the most optimal form of biochar for the use in a filtration system. This could include one type of biochar from one plant source or a combination of biochars from different plant sources to potentially adsorb a large spectrum of contaminants. Research in this aspect may open many opportunities to experiment with different types of biochar. This could give an indication of which type of biochar would best affect the quality of water through the removal of specific contaminants. The molecular structure of the different biochars will be the leading assumption to why certain biochars are more effective at adsorbing contaminant than others. Further research could also be conducted to determine the molecular structure of the biochar through the use of mass spectroscopy and X-ray diffraction (XRD). This kind of study can also be used to determine the mechanism of binding of certain contaminants to the phenolic compounds of the biochar. It would also give an indication of the charge and polarity of the biochar which would ideally be used in the filtration system. This could be an important aspect as attraction forces are dependent on the charge and polarity of the molecular structure of the biochar as well as the different contaminants.

The mechanism of the biochar to adsorb microbial contaminants such as faecal coliforms are not clearly understood. The first question which needs to be answered is whether the biochar removes the bacterial contaminants or whether it inhibits the growth of those contaminants. The second question would have to do with the mechanism in which this occurs; Is the reduction as a result of the formation of a biofilm or is the mechanisms of filtration through the biochar micropores or is it both which contribute to such reductions. Further research can be conducted to determine the specific types of microorganisms which are best adsorbed by the biochar as well as determine if the biochar is capable of just merely removing adsorbed microbes or if the biochar contains growth inhibitors which retard the growth of microorganisms.

The use of biochar as a filtration media can be beneficial in a series of treatments to improve untreated river water quality as is seen in Chapter 3 of this thesis. The biochar filtration system should be closed, and saturation of the filtration media should at all times be maintained. To potentially improve untreated river water that is as contaminated as the Plankenburg River to a standard which can be used for irrigation water, biochar filtration alone would not be able to accomplish this. Biochar filtration could rather be used as a pre-treatment, to improve certain physicochemical characteristics of the water such as UVT%, before the use of UV treatments for specific improvement of the microbial status of the river water. Furthermore, the use of a coagulants may better improve the EC and TDS of the untreated river water before filtration occurs. Therefore, further research can be conducted in experimenting with coagulants which can improve the TDS and EC of untreated river water. In a series of treatments, this treatment could occur first, followed by treatment with continuous filtration with pine biochar as filtration media. Lastly an in-line UV treatment at a specific dose could be utilised all to improve the quality of untreated river water to conform to South African water quality guidelines for irrigational use.

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