UTILIZATION OF BIOCHAR PRODUCED FROM AGRICULTURAL RESIDUES FOR THE REMOVAL OF PESTICIDE AND PHARMACEUTICAL MICROPOLLUTANTS IN SURFACE WATER BIOFILTRATION

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Abstract

In recent years, there has been a growing interest in exploring possible agro-based biochar for use in different remediation applications. This thesis therefore investigated the feasibility for biochar produced from rice straw (RSBC), corn cob (CCBC), coconut husk (CHBC) and coconut shell (CHBC) to immobilize micropollutants in water, with the aim of finding a better alternative to activated carbon (GAC). First, 3% (w/w) amendment applications of the selected adsorbents were set up to evaluate their influence on leachate properties. Results showed significant increase in pH (>8) in biochar leachates which decreased leachability of metals, while GAC with lower pH (<6) showed greater metal leaching. Also, all amendments increased hydraulic conductivity (K) by 11.6%, except for CHBC and CCBC that decreased K by 54.7% and 36.9%, respectively. The characteristics of the biochars in batch adsorption studies were compared to evaluate their adsorption of four pharmaceuticals and two herbicides micropollutants. Although, removal efficiencies were feedstock type dependent, RSBC exhibited significantly higher sorption capacity of 12.81±0.13 mg/g (at 0.5 g/L and 10 days contact time) for oxytetracycline (OTC), compared to that of GAC of 19.11±0.72 mg/g for the same compound. Partition coefficient (K_d) values were used to compare how effective the different adsorbents are in the reduction of micropollutants availability and transfer in aqueous solution. Comparatively, the kinetic study indicated that RSBC and CHBC showed better adsorption for most micropollutants than other biochars. CHBC amendment of sand biofilters showed a reduction in hydraulic flow from 24.48 m/day in fresh fine sand (FISA) to 1.87 m/day in CHBC amended fine sand, which facilitated the micropollutant biodegradation process. All measured compounds were attenuated by a combination of sorption and biodegradation processes, however, pharmaceuticals were removed more significantly ($p<0.05$) than herbicides in both amendment types. Overall, biodegradation accounted for >90% removal in CHBC and <60% for FISA columns. Microbial analysis confirmed a shift in bacterial community composition for CHBC versus FISA columns, but depth as the most critical community structuring factor. In this work, RSBC and CHBC were shown to have potential for cheap, and environmentally friendly amendments to enhance removal of micropollutants in surface water biofiltration.

Acronyms and Abbreviations

ACM:	Acetaminophen
ANOVA:	Analysis of Variance
As:	Arsenic
ASTM:	American Society for Testing and Materials
ATR:	Atrazine
B:	Boron
BC:	Biochar
C:	Carbon
Ca:	Calcium
CCBC:	Corn Cob Biochar; Corn Cob Biochar + fine sand
Cd:	Cadmium
CEC:	Cation Exchange Capacity
CHBC:	Coconut Husk Biochar; Coconut Husk Biochar + fine sand
Cr:	Chromium
CSBC:	Coconut Shell Biochar; Coconut Shell Biochar + fine sand
Cu:	Copper
DIC:	Diclofenac
DNA:	Deoxyribonucleic Acid
DRN:	Diuron
EBCT:	Empty Bed Contact Time
FC:	Fixed carbon
Fe:	Iron
FISA:	Fine Sand
FTIR:	Fourier-Transform Infrared
GAC:	Granular Activated Carbon; Granular Activated Carbon + fine sand
GC-MS:	Gas Chromatography Mass Spectrometry
GHG:	Greenhouse Gas
Hg:	Mercury
HPLC:	High-performance liquid chromatography
HTT:	Highest Temperature of Treatment
ICP-MS:	Inductively Coupled Plasma-Mass Spectrometer

K:	Potassium
LOI:	Loss on Ignition
Mg:	Magnesium
Mn:	Manganese
N:	Nitrogen
Na:	Sodium
NDWQS:	National Drinking Water Quality Standard
OTC:	Oxytetracycline
P:	Phosphorus
Pb:	Lead
PCR:	Polymerase Chain Reaction
PSD:	Particle Size Distribution
qPCR:	Quantitative Polymerase Chain Reaction
RNA:	Ribonucleic Acid
rpm:	Revolutions per minute
rRNA:	Ribosomal RNA
RSBC:	Rice Straw Biochar; Rice Straw Biochar + fine sand
S:	Sulphur
SD:	Standard deviation
SEM:	Scanning Electron Microscopy
SUDS:	Sustainable Urban Drainage System
TC:	Tetracycline; Total Carbon
TDS:	Total dissolved solids
TOC:	Total Organic Carbon
TSS:	Total Suspended Solids
UKBRC:	United Kingdom Biochar Research Centre
US:	United States
VM:	Volatile Matter
WHO:	World Health Organization
WSBC:	Wheat Straw Biochar
WSP:	Wheat Straw Pellets
WWTP:	Wastewater Treatment Plant
Zn:	Zinc

Dedication

I dedicate this PhD Thesis to God Almighty who has been my source and strength. The One who is faithful to His Word in Matthew 28:20 that has kept me throughout my education journey. May His name be praised forever. I also dedicate this work to my wife, Mrs Ibitoroko Emmanuel Johnson, and our children, Tonye, Tokoni and Tekena for being great pillars of support and encouragement, every day.

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Chapter 1. General introduction, aims and scope of the thesis

1.1 Problem statement

The usefulness of water to both human and biological systems cannot be overemphasized. Since the start of the Industrial Revolution, an increase in population together with a corresponding increase in living standards as well as an increase in the demand for industrial and agricultural products also increased the demand for water (Gani and Kazmi, 2017). For many developing economies, the agricultural sector accounts for up to 90% of freshwater use while only about 10% of the generated wastewater in these countries undergoes proper treatment (Kaetzl *et al.*, 2020). Thus, the increase in agricultural activities with high fertilizer and pesticide use may also increase the dispersion of nutrients and pollutants into water bodies. Urbanization is known to be a major contributor to environmental pollution as it leads to problems such as increased flooding, altered groundwater recharge by blocking infiltration of water into the ground, and additional environmental challenges by generating wide-spread non-point source pollution in surface water (Hatt, Fletcher and Deletic, 2007; Aryal *et al.*, 2010; Ulrich *et al.*, 2015; Segismundo *et al.*, 2017; Shrestha, Hurley and Wemple, 2018; Kaetzl *et al.*, 2020).

Over the past few decades, there has been an increasing awareness of the unintentional presence of new groups of pollutants in the aquatic environment at concentrations capable of causing harm to human and aquatic organisms (Derksen, Rijs and Jongbloed, 2004; Kot-Wasik, Debska and Namieśnik, 2007; Ebele, Abou-Elwafa Abdallah and Harrad, 2017). As reported in recent reviews, this group of pollutants are a large number of chemicals compounds that includes pharmaceuticals and pesticides, among others that are not commonly monitored in the environment but have become a global concern in both developed and developing countries (Kot-Wasik, Debska and Namieśnik, 2007; Gasperi *et al.*, 2014; Mailler *et al.*, 2014; Geissen *et al.*, 2015; Inyang and Dickenson, 2015a; Ebele, Abou-Elwafa Abdallah and Harrad, 2017; Rodriguez-Narvaez *et al.*, 2017). Research has shown that conventional contaminated water treatment technologies that play a major role in limiting the release of pollutants into aquatic environments are insufficient for the complete elimination of micropollutants, and their fate, behaviour and potential effects in water are not yet fully understood (Matamoros *et al.*, 2012; Geissen *et al.*, 2015).

Due to the increase in the demand for food production, the need to manage the waste generated from agriculture and related agro-industries efficiently and sustainably is a growing priority. Evidence suggests that large volume wastes are associated with agriculture by-products of crop production such as husk, shells, straw and cobs, and they constitute over 80% of total agricultural biomass generated (Wijitkosum and Jiwnok, 2019) for which the waste treatment and management in developed countries cost billions of dollars (Parmar, Nema and Agarwal, 2014). Hence, they are found to be unutilized and discarded in landfills or burnt in the open in many developing countries. Thus, as far as biomass availability is concerned, these agriculture residues are available to be valorized for local biochar production in order to exploit for example the benefits of using it as a filter medium to enhance water quality in onsite applications.

1.2 Water pollution and environmental concerns

Water pollution in the natural environment is regarded as the release of pollutants into the environment through surface runoff from agricultural sites, liquid spills, effluent discharge and leakage from hospitals and households into groundwater (as shown in Figure 1-1) in such a way that it results in a threat to the global ecosystem (Pal *et al.*, 2010; Sui *et al.*, 2015). Water pollutants refer to materials and/or chemical compounds that contaminate water and the severity of their effects is determined by their chemical nature, available concentration, and persistence in the environment. In recent years, urbanization has increased the number of communities drawing on water from sources that are directly or indirectly replenished by effluents from contaminated non-point sources. This has led to an increased concern that chemical micropollutants from diverse anthropogenic sources may contaminate surface or groundwater supplies and cause adverse effects on humans and aquatic lives. While the occurrence and treatability of conventional water pollutants have been widely discussed, limited attention has been given to organic micropollutants in the environment. These micropollutants represent a class of toxic chemicals including natural or synthetic chemicals, whose environmental concentrations are generally unknown because they have been newly introduced into the environment and so are unregulated or not commonly monitored.

Research attention has been directed at pharmaceutical and pesticide compounds as surface and groundwater micropollutants, because these compounds have been frequently detected due to their widespread use in many households and agriculture (Kot-Wasik, Debska and Namieśnik, 2007; Matamoros *et al.*, 2012; NIEA, 2014; Geissen *et al.*, 2015; Mrozik *et al.*, 2019), and also because these chemicals have been purposefully designed to have a biological effect. Hence, they raise concerns, even at low concentration levels. A review by Gani and Kazmi (2017) on the distribution of publications on water source pollutants in India showed that 74% of reported research articles were related to pharmaceutical and pesticide micropollutants. Sui et al. (2015) reported that the mobility of these micropollutants is influenced by their physicochemical properties, as well as other environmental factors. The author also added that chemicals with strong adsorption tendencies have lower leaching potential, however, those with weak adsorption are more likely to permeate into groundwater (Sui *et al.*, 2015). It is clear that a wide range of pharmaceutical and pesticide micropollutants are present in urban runoff (Ulrich *et al.*, 2015). Therefore, this study focused on the fate and removal of four widely used pharmaceuticals; acetaminophen, tetracycline, diclofenac and oxytetracycline, and the two pesticides; atrazine and diuron.

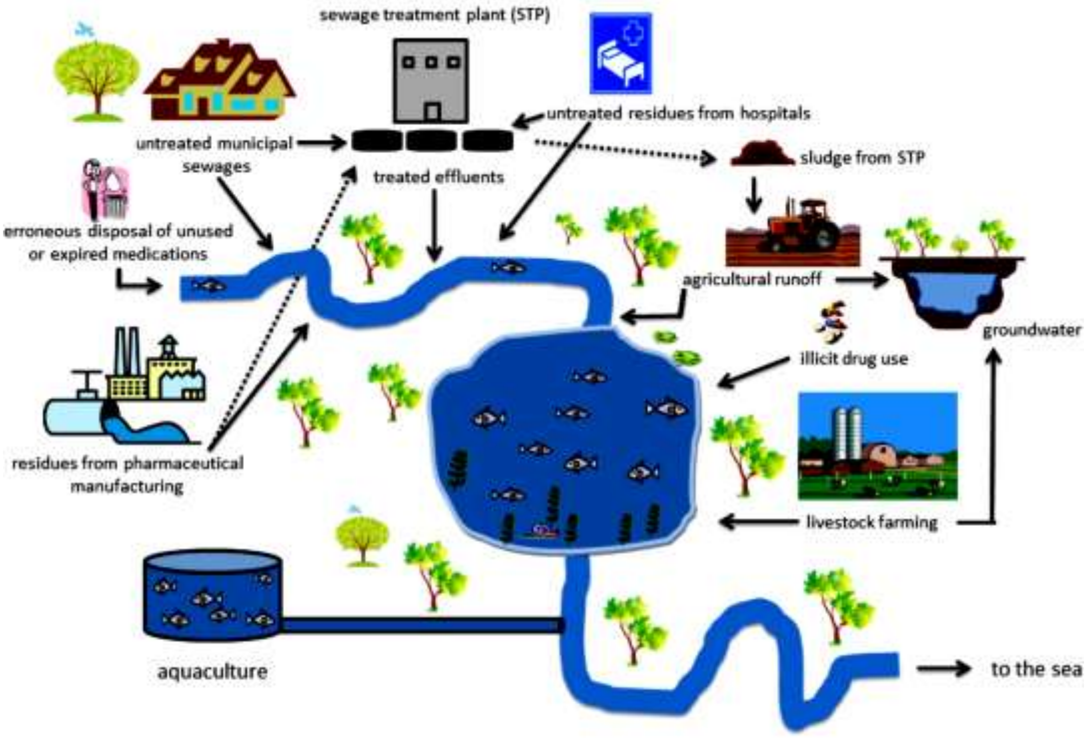


Figure 1-1 Origin and fate of water pollutants in the environment (source: Matozzo, 2014)

1.3 Sand filtration system and the potential enhancement with biochar amendments

To ameliorate water treatment challenges, several studies have proposed new water treatment technologies for the removal of micropollutants. These proposed solutions range from individual or field-scale actions to global geo-engineering approaches. The development of varying solutions is due to differences in experimental methodologies (e.g., pollutants type, sampling procedures, and analytical methods), with variable consideration of the effectiveness and affordability of the technologies for pollutants removal. Technologies should be environmentally friendly and accessible to remote communities in developing regions of the world (Kearns *et al.*, 2018).

One technique that is long-established in water purification and used globally is the sand filtration system, and this technique is increasingly adapted for the design of stormwater treatment systems (Kaetzl *et al.*, 2020). Such filtration systems use sand as a filter medium, often supported with gravel layers, and operate by vertical filtering of contaminated influent through the filter media (Glaister *et al.*, 2017; Segismundo *et al.*, 2017; Shrestha, Hurley and Wemple, 2018). While the main role of gravel is to prevent clogging of the systems and support collection or ground infiltration of the filtrate, the sand in the system is to reduce dissolved micropollutant concentrations via a combination of physicochemical and biological processes and removal of suspended solids. This centuries-old technique is considered a sustainable practice for the removal of micropollutants from water and at the same time a very favourable tertiary treatment option for secondary effluents of wastewater treatment plants (Kaetzl *et al.*, 2020). However, treating contaminated water using the old-fashioned method may result in suboptimal efficiencies (Boehm et al. 2020). Hence, the need to improve the sand media physical properties to increase the micropollutant removal efficiency by employing an amendment application to the sand, with materials that are efficient, environmentally friendly and readily available, as has been proposed in recent publications (Herath, Camps-Arbestain and Hedley, 2013; Perez-Mercado *et al.*, 2018).

In recent decades, studies on eco-friendly environmental remediation technologies have proposed the use of biochar; a by-product of biomass pyrolysis, as a sustainable sand amendment in treating contaminated water, gaining much attention globally (Zhang *et al.*, 2013; Inyang and Dickenson, 2015a; Kaetzl *et al.*, 2020). In particular, the application of biochar is attractive due to the abundance of waste biomass that can be used for its production, and it could be widely used in a range of filtration and sand or soil amendment applications. It is one technology that has the potential to ameliorate the four environmental problems identified above (i.e., total suspended solids, nutrients, organic micropollutants, and heavy metals). Also recently, the lower cost of the biochar combined with its positive effects in sandy soil quality improvement have generated research interest into the adsorption capabilities of biochar produced from various feedstocks as a potential soil amendment (Hale *et al.*, 2013; Smebye *et al.*, 2016). While the variety of agronomic benefits of the use of biochar as soil amendment are mainly derived from its fertilizer value influence on pH and effects on the improvement of soil physical properties (Herath, Camps-Arbestain and Hedley, 2013), the biofiltration benefits mostly involve reducing the concentrations of TSS, organic micropollutants, and heavy metals from wastewater (Boehm et al., 2020; Kaetzl et al., 2020). Although the ability of biochars to adsorb organic micropollutants largely depends on their physio-chemical properties, which vary dramatically with the pyrolysis condition of the feedstock and the type of feedstock (Sigua, Novak and Watts, 2016a; Sun *et al.*, 2016a), the efficient utilisation of biochar as an adsorbent for removing various micropollutants, including heavy metals, nutrients, and organic compounds (Zhang *et al.*, 2013) compares favourably with the conventional treatment adsorbents in sand infiltration systems (Perez-Mercado *et al.*, 2018).

1.4 Biochar sources and properties

Biochar is the black carbon-rich solid product of heating biomass to high temperatures (250–800°C) in oxygen-limited conditions – a process which is known as pyrolysis (Inyang and Dickenson, 2015a; Perez-Mercado *et al.*, 2018; Piscitelli *et al.*, 2018). Biochar can be produced from any type of biomass material, and it is characterized by several factors, including high porosity and a high-specific surface area, that makes it a good amendment material for micropollutant adsorption from water and as a support for the attachment of bacteria (Piscitelli et al., 2018; Boehm et al., 2020). There is a growing interest in exploring agro-based biochar due to its unique properties for use in different environmental applications.

Generally, biochar exhibits a great potential to efficiently remove micropollutants from water considering the wide availability of biomass material characterised by having large surface area, low density and high porosity, and/or favourable physicochemical surface characteristics. It is a soil amendment material and the changes it creates in the soil physical environment could influence the number of services the soil provides (Blanco-Canqui, 2017). Although studies on biochar’s influence on the physio-chemical and hydraulic properties of the soil media have reported with mixed results (Lim *et al.*, 2016a; Novak *et al.*, 2016), these properties have been known to be soil texture dependent and the effect of the different biomass sources type, particle size and soil additions have not been exhaustively studied (Lim *et al.*, 2016b). This suggests that biochars from different sources may exhibit different property parameters and therefore different adsorption characteristics. Also, the consideration of biochar effects on hydraulic properties of the soil or filter medium is particularly important in water filtration applications (Trinh, Werner and Reid, 2017).

1.5 Research aims and objectives

The goal of this thesis was to study the role of biochar produced with inexpensive methods using agricultural waste biomass as a potential replacement for activated carbon in the removal of micropollutants from contaminated surface water. To this end, the micropollutant adsorption abilities of biochars produced with a low-cost drum kiln method from four agricultural wastes (corn cob, coconut shell, coconut husk and rice straw) were investigated. To provide a point of reference, activated carbon was used. The research evaluated acetaminophen, oxytetracycline, tetracycline and diclofenac (as exemplary pharmaceutical micropollutants), and diuron and atrazine (as exemplary pesticide micropollutants). Column studies evaluated the effect of the biochars and activated carbon amendments in the sand on infiltration rates and water quality in biofiltration systems, considering first the potential release of biochar/activated carbon associated pollutants into clean water, and then the removal of micropollutants from contaminated water. The main study objectives were as follows:

Objective 1

The objective of this study was to determine whether the application of biochars in water treatment systems could have detrimental impacts on water management such as the leaching of biochar associated nutrients, heavy metals and fine particles into groundwater, and/or reduced water infiltration rates. Specific steps to achieve this objective were to:

- Use laboratory fixed-bed columns to investigate the potential influence of selected biochar amendments present in sand on effluent quality via comparison with the UK/EU/WHO recommended standards for drinking water quality.
- Evaluate the hydraulic properties of amended sand filters compared with the unamended sand filter
- Monitor and compare the above-mentioned effects in a long-term flushing process under alternate drying and wetting hydraulic loading conditions.
- Conduct a field lysimeter study to evaluate the influence of wheat straw pellet versus wheat straw biochar applications to soil on leachate quality.

Objective 2

The objective of this study was to understand and compare the adsorption abilities of the selected biochars versus activated carbon to remove a mixture of the selected micropollutants from aqueous solutions. Specific steps to achieve this objective were to:

- Measure the adsorption capacities of the biochar adsorbents relative to activated carbon in batch adsorption studies.
- Quantitatively assess the adsorption kinetics of the adsorption processes.
- Identify through the interpretation of the batch study data the adsorption processes by which micropollutants interact with the adsorbents.

Objective 3

The objective of this study was to systematically examine the adsorption, chemical and biological degradation of a mixture of micropollutants from contaminated surface water using unamended versus biochar-amended laboratory biofiltration column experiments. Specific steps to achieve this objective were to:

- Evaluate the removal of selected micropollutants spiked into pond water using coconut husk biochar-amended sand filters versus unamended sand filters operated under biotic gravity flow conditions (i.e., passive treatment).
- Identify using a mass-balance approach the relative contribution of the possible attenuation mechanisms (i.e., adsorption and/or biodegradation) responsible for the micropollutant removal in biofiltration experiments.
- Establish the effects of biochar amendment on the hydraulic properties (i.e., hydraulic conductivity, empty bed contact time, flow rates, etc.) of the filters under continuous loading versus alternate drying and wetting conditions.
- Establish the effects of operating conditions on the micropollutant removal performance (i.e., continuous flow versus alternate drying and wetting flow conditions).
- Investigate the response of the indigenous microorganisms occurring within different biofilter media types using 16S rRNA gene sequencing techniques.

1.6 Research hypothesis

The main hypothesis of this study was that low-cost biochar produced from agricultural waste biomass such as corn comb, coconut shell, coconut husk and rice straw, can enhance the removal of selected organic micropollutants from aqueous solution, and could therefore be a beneficial amendment to sand in a biofiltration system. The working hypotheses guiding specific research objectives in this thesis were as follows:

Hypothesis 1

A starting hypothesis of this thesis is that biochar and activated carbon amendments application to soil influence the hydraulic flow and leachate quality of the filtration system. Directly, by changing the physio-chemical qualities of resulting leachates such as their pH, suspended solids, and chemical composition and indirectly through changing the hydraulic conductivity of biofiltration systems.

Hypothesis 2

Biochar from agricultural waste biomass is a suitable micropollutant adsorbent with performance comparable to commercially available activated carbon.

Hypothesis 3

The amendment of sand with biochar from agricultural waste biomass enhances the removal of micropollutants in biofiltration systems.

1.7 Research scope and limitation

Since this research focused on potential applications of biochar as a low-cost water treatment in developing countries, all biochars used were obtained from the partner research team in Thailand (KMUTT) and produced with a drum kiln method appropriate for implementation by ordinary farmers. The data on the biochar characterisation was obtained as part of a research collaboration with KMUTT, and therefore, the procedures used to measure the biochar properties are not presented in this study. Also, due to the potential application of biochar in Thai aquaculture to remove micropollutants from surface water, pond water was used in the column experiments. Moreover, the selection of micropollutants to be studied was focused on compounds found to be present in Thai surface water.

1.8 Structure of the thesis

The chapters in this thesis are presented as largely self-contained work packages with their own summaries, methodologies, obtained results and conclusions. This thesis is organised into six chapters, each addressing a different facet of the project, and brief details of each chapter are as follows:

Chapter 1: *Overarching introduction, aims and scope of the thesis*

This chapter provided the background to the environmental challenges in water management, biochar and its use in micropollutant remediation. It also outlined the research activities; their motivation, the research aim, objectives and hypotheses.

Chapter 2: *Overarching literature review*

Following on from the introduction in chapter 1, this second chapter reviews the existing literature of interest in more detail, covering biochar definition, properties and its potential influence on nutrients, heavy metals and leaching, as well as the adsorption of organic micropollutants in biofiltration systems. It also identifies research gaps and inconsistencies, and areas for further research.

Chapter 3: *Investigating the influence of biochar and activated carbon amendments on the chemical properties of leachate from soils and biofilters*

This chapter presents laboratory columns and field lysimeter experiments to probe potential undesirable impacts of biochars and activated carbon amendment in sand and soil on water management. It addresses the concerns that the proposed adsorbents may themselves leach micropollutants into percolating water and negatively affect the hydraulic properties of biofiltration systems.

Chapter 4: *Comparison of biochars derived from different feedstocks with activated carbon as potential adsorbents for organic micropollutant removal from multiple-pollutant solutions*

This chapter contains results of batch experiments that were conducted to investigate the suitability of biochar and activated carbon as adsorbent materials for selected micropollutants. It includes the characterization of the different adsorbents with respect to their interaction with the different micropollutants, using sorption models to suggest the interactions and the diffusion mechanisms that influence the removal processes, and also evaluates the influence of contact time on the adsorption process.

Chapter 5: *Understanding the fate of organic micropollutants in a biofiltration system with fine sand versus coconut husk biochar-amended fine sand*

The chapter presents data to demonstrate the benefits of coconut husk biochar amendment for micropollutant removal from contaminated water in sand biofilters. It discusses the fate and transport of micropollutants in column studies and the dependency on the flow rate, influent concentration, and empty bed contact time. It also discusses the contribution of adsorption and biodegradation to micropollutant removal.

Chapter 6: *Overarching thesis discussion, conclusion and suggested future research*

This chapter summarises the key findings of the preceding experimental chapters and provides recommendations for future work. It also acknowledges the limitations of the research and suggests follow-up studies that may be able to provide further insights into the gaps identified in this study.

Chapter 2. Literature Review

2.1 Introduction

Numerous studies have reported on various filter materials used for the removal of pollutants from surface water, stormwater, groundwater, and industrial effluents. These filter materials include natural, manufactured and waste/recycled materials, and studies have been critical in determining environmentally benign, easily available, and inexpensive filter materials for water remediation. But there remain some uncertainties and knowledge gaps. Few studies have specifically reported on the performance of biochar-augmented biofilters for removing multiple pollutants from surface water. Thus, this chapter provides an overview of literature relevant to the remediation of organic pollutants in water using biochar. The review covers the impact of biochar on the fate of micropollutants with emphasis on the sorption of pollutant compounds that are ubiquitous and are designed to cause biological effects in the environment. This chapter ends with a summary of the major research gaps and how these feed into the study objectives of this thesis.

2.2 Surface water and groundwater quality

Surface and ground water are the world's most extracted raw materials (Andrade *et al.*, 2018). In many parts of the world, surface water is the direct source of drinking water to serve an increasing urban population, while in other parts, the abstraction of groundwater is the main source of drinking water. Both water sources represent separate water quality management challenges. The unsustainable use of water is greatly affecting the limited freshwater resources, partially due to urbanization which has degraded the quality and quantity of water resources (Jackson *et al.*, 2001; Ulrich *et al.*, 2015). Freshwater is just a small percentage (2 – 3%) of the global water resources, of which less than 0.01% is available to meet human demand (Jackson *et al.*, 2001; Baron, 2008; Altaner, 2012). All over the world, large volumes of wastewater are being discharged into surface waters on a daily basis. Hence, the direct introduction of these wastes into surface water and runoff causes pollution, consequently allowing these pollutants to also gain access to groundwater sources. The worst cases of water pollution are reported in developing countries where about 70% of untreated effluents and 90% of raw sewage are being discharged into surface water (Kathuria, 2006; Kumi-Larbi *et al.*, 2018; Ferronato and Torretta, 2019; Pantha *et al.*, 2021).

Major contributors to water pollution are the discharges of chemical pollutants from both point and non-point sources into water bodies. Generally, these water-polluting waste streams are produced from domestic and industrial sources, and the extensive use of agrochemicals in agricultural activities are also major sources of water pollution (Aryal *et al.*, 2010; Scheurer *et al.*, 2015; Ferronato and Torretta, 2019; Aldana *et al.*, 2020). A list of major contributors to water pollution also includes industries such as steel, pharmaceuticals, fertilizer factories, food industries, and petrochemicals (Faucette *et al.*, 2005; Bushnaf, 2013; Parmar, Nema and Agarwal, 2014; Zhang *et al.*, 2016; S. He *et al.*, 2018; Ramírez-Malule, Quiñones-Murillo and Manotas-Duque, 2020), releasing anions such as chloride, carbonates, nitrites, nitrates and several other pollutants (Vikrant *et al.*, 2018), and cations such as sodium, potassium, calcium and toxic heavy metals like arsenic, cadmium, lead, nickel, iron, mercury, chromium, zinc, copper, magnesium and cobalt that are produced from their operations (Marcovecchio, Blanca and Freije, 2007; Abdel Salam, Reiad and ElShafei, 2011).

Although some identified water pollutants such as copper, manganese, chromium are essential micronutrients for humans, if their presence in water exceeds set threshold values, they become harmful and can cause severe health problems in humans and other organisms. Their undesirable environmental effects may result from their impacts on sensitive receptors and have led to calls for strict regulations on their discharge concentration levels to receiving waters (Zhang *et al.*, 2013; Geissen *et al.*, 2015; Inyang and Dickenson, 2015a; Sui *et al.*, 2015; Ulrich *et al.*, 2015; Gani and Kazmi, 2017; Rodriguez-Narvaez *et al.*, 2017; Gogoi *et al.*, 2018; Dalahmeh, Alziq and Ahrens, 2019). There have also been reports of water pollution contributing to more people being at risk of carcinogenic diseases in places where cancer cases are exceptional (Gavrilescu *et al.*, 2015; Rahmanian *et al.*, 2015; Gwenzi, 2018). To reduce the effects of pollutants on surface and groundwater, several countries have created mitigation techniques with the aim to protect the ecosystem. Also, the European Union (EU) member states have adopted the EU Water Framework Directive, which concisely and critically sets out limits of chemicals for good status of water bodies (Kallis and Butler, 2001; European Commission, 2002; NIEA, 2014). However, there also exists an increasingly recognized hazard posed by yet to be prioritised compounds, also known as pollutants of emerging concern (Vrana *et al.*, 2006).

2.3 Micropollutants in the aquatic environment

As reported in the previous section, several studies have identified many substances as water pollutants generally comprising groups of organic chemicals, heavy metals and other forms of pollutants that are of emerging concern, some of which belong to a large group of active compounds found in water bodies (Matamoros *et al.*, 2012; Cederlund *et al.*, 2016; Mrozik *et al.*, 2019; Ramírez-Malule, Quiñones-Murillo and Manotas-Duque, 2020) and typically detected at trace concentrations ranging from µg/L to below ng/L (Kim and Zoh, 2016). Given their relatively low concentration levels, they are collectively termed as "micropollutants" (Gasperi *et al.*, 2014; Das *et al.*, 2017), comprising pharmaceuticals (Kot-Wasik, Debska and Namieśnik, 2007; Pal *et al.*, 2010; Jing *et al.*, 2014; Ahmed, 2017) and pesticides (Ulrich *et al.*, 2015; Cederlund, Börjesson and Stenström, 2017; Mandal and Singh, 2017; PETTER *et al.*, 2017; Aldana *et al.*, 2020), among others, which may have effects even at low concentrations.

Micropollutants are ubiquitous and are often used to improve human life (Kim and Zoh, 2016). Thus, due to the diverse origins of micropollutants, it is often difficult to control the sources of the compounds in the water environment. For example, multiple reports show that sources of many micropollutants in urban stormwater may include wastewater effluents from hospitals and/or chemical manufacturing plants, as well as wastewaters from agriculture (Pal *et al.*, 2010; Matamoros *et al.*, 2012; Ulrich *et al.*, 2015; Kearns *et al.*, 2018). Common among the groups of active water-soluble micropollutants that include a wide variety of poorly or undocumented pharmaceuticals, pesticides, and various metals of concern (Gasperi *et al.*, 2014). Although micropollutants vary in mobility, degradability, solubility and toxicity, their physicochemical properties and bioavailability can affect their persistence and ability to remain dissolved in natural waters (Gasperi *et al.*, 2014; Kim and Zoh, 2016; Rogowska *et al.*, 2020). Their existence in the aquatic environment is controlled by five main factors, which are their physicochemical properties, environmental factors, transport and retention, biotransformation, and bioaccumulation. Additional factors include the volatility, water solubility, stability of the chemical structure, and particulate distribution characteristics (Kim and Zoh, 2016).

It should be noted that the degradation and transformation products of certain micropollutant compounds in the environment can have unknown structures and properties (Rogowska *et al.*, 2020). Hence, this section provides a brief overview of the fate, occurrence, and behaviour of pharmaceutical and pesticide micropollutants, as well as concerns on their adverse effect in the aquatic environment.

2.3.1 Pharmaceuticals in the environment

Pharmaceuticals constitute a large group of medicinal compounds such as acetaminophen, oxytetracycline, tetracycline and diclofenac, which are used globally in many ways to support human and animal health (Ahmed, 2017), with specific modes of action in the body (Gogoi *et al.*, 2018). Many pharmaceuticals are excreted from the body, and commonly found pharmaceuticals in the environment are classes of antibiotics which are used for inhibiting bacterial infection; analgesics which are used for reducing pains; antiseptics which are used for preventing microbial infection; and hormonal drugs (Jing *et al.*, 2014; Ahmed, 2017; Ramírez-Malule, Quiñones-Murillo and Manotas-Duque, 2020). Pharmaceuticals are considered pseudo-persistent pollutants and have been entering the environment for many years at very low concentrations (Gogoi *et al.*, 2018). According to Jing et al. (2014):

> *"The spread of these bioactive compounds can potentially lead to long-term adverse consequences on various ecosystems, including acute and chronic toxicity and propagation of antibiotic resistance in microbes."*

Pharmaceutical pollutants can enter the environment in main two ways: by their addition in normal waste, which is avoidable; and via feces or urine after their consumption by humans and animals, which is almost unavoidable (Rivera-Utrilla, Sánchez-Polo, *et al.*, 2013). Studies show that over 160 different pharmaceuticals have been detected in aquatic environments such as surface and groundwater (Gogoi *et al.*, 2018). For example, reported concentrations for antibiotic residues are usually of ng/L to µg/L levels in domestic effluents to higher concentrations of up to 100 – 500 mg/L in hospital and pharmaceutical manufacturing effluents (Jing *et al.*, 2014). Pharmaceutical drugs are frequently used in homes, hospitals, drug stores, and convenience stores; some of which are available without prescription (e.g., acetaminophen, tetracycline, oxytetracycline and diclofenac). While they are produced for human and animal consumption, they are not utilized completely in the body and residual pharmaceuticals and their metabolites are excreted into wastewater. Also, another source of pharmaceuticals in the environment is discarded waste from expired drugs and industrial processes (Kim and Zoh, 2016).

Although, the main routes of human exposure to pharmaceutical pollutants are via food, and occupational exposure, some researchers have argued that many pharmaceuticals are endocrine disruptors (Varjani and Sudha, 2020). The adverse effects of various pharmaceutical compounds found in the environment have been investigated in recent reports (Gogoi *et al.*, 2018), but there is still not enough knowledge about the eco-toxicological impacts of these compounds on human and aquatic lives, as the analysis of their impacts remains insufficient (Rogowska *et al.*, 2020).

2.3.2 Pesticides in the environment

Pesticides are chemical substances used in agriculture to kill, repel, or control certain forms of plants or animal life that are considered as pests in an effort to increase crop yields and assure an efficient food supply to an increasing world population (Sun *et al.*, 2016b; Pérez-Lucas *et al.*, 2019). Classes of pesticides include herbicides which are used for destroying unwanted plants; insecticides which are used for controlling a variety of crop-destroying insects; fungicides which are used to prevent the growth of fungi, parasites, and other biological organisms; disinfectants which are used for preventing the spread of bacteria; and other compounds used for controlling mice and rats. Although pesticide use has been instrumental, a recent review by Kearns et al. (2018) reported that "pesticide pollution" appeared twice in the top 10 of *The World's Worst Toxic Pollution Problem Report 2011*. Also, Ulrich et al. (2015) and Kim and Zoh (2016) reported detected herbicide concentrations of diuron and atrazine at µg/L levels in roadside and roof runoff, respectively, while Mrozik et al. (2019) reported detected herbicides, pesticides in canals and pond water, which indicate that pesticides are widely present in surface water at potentially harmful levels (Ulrich *et al.*, 2015). The intensification of agriculture with high fertilization rates and pesticides use have been the major reason for the increased discharge of pesticide pollutants into the aquatic ecosystems (Matamoros *et al.*, 2012):

> *"The widespread occurrence of these pollutants in freshwater is potentially a major problem with consequences that are yet to be fully understood*."

Although water pollutants follow many pathways to enter the environment, it is reported that pesticide compounds typically bind to particulate matter in wastewater and are finally deposited in the sediment (Vrana *et al.*, 2006), for which higher pesticide concentrations have also been reported on sediments acting as reservoirs with the aquatic environment (Carazo-Rojas *et al.*, 2018). In spite that pesticides are probably the most studied pollutants in the aquatic environment (Köck-Schulmeyer *et al.*, 2013), their occurrence and behaviour in wastewater treatment and drinking water production plants in relation to reuse of water resources has been very seldom studied (Petrović, Gonzalez and Barceló, 2003; Gómez *et al.*, 2012; Köck-Schulmeyer *et al.*, 2013; K'oreje *et al.*, 2018).

2.3.3 Micropollutants of emerging concerns

The increasing consumption and manufacturing processes have increased the amount of industrial chemical compounds, which are released deliberately into the environment and are key problems prevalent in today's society. Although these compounds bring many benefits, they have been found ubiquitously in natural waters, and leave a trace as "emerging" environmental micropollutants. In the last decades, the variety and severity of these traced micropollutants have attracted more attention from environmental administrative authorities as potentially hazardous to the environment. Among these micropollutants, pesticides and pharmaceuticals are of great importance due to their low aqueous solubilities and hydrophobic nature (Vrana *et al.*, 2006). And because conventional wastewater treatment plants (WWTP) are not designed to remove them, they can persist in the treatment of effluent water (Borrull *et al.*, 2020), and as a result, they present in aquatic environments including surface and groundwater supplies (Hijosa-Valsero *et al.*, 2013; Kim and Zoh, 2016). Therefore, people can become unconsciously exposed to these micropollutants even with tap water collected for domestic use since micropollutants in surface waters can enter WWTPs, and their presence in drinking water can still be detected (Kim and Zoh, 2016; Tröger *et al.*, 2018).

Research has shown that many emerging micropollutants enter the environment, disperse, and persist to a greater extent and they may pose at least an equivalent hazard to the environment in the long run as do they on humans (Rivera-Utrilla, Sánchez-Polo, *et al.*, 2013). In the European Union alone, there are more than 100,000 of these chemical compounds registered, of which 30,000–70,000 are in use daily (Loos *et al.*, 2009; Brack *et al.*, 2018). Due to their hazards, a ranking system was established based on their effect on aquatic life, human health, potential of exposure, and other subjective public concerns (Rytwo *et al.*, 2007). Although exposure patterns and routes may vary among different people, Colosio, Rubino and Moretto (2016) reported that about 4% of accidental poisoning related deaths in developing countries are due to pesticides. Consequently, the focus of many environmental regulatory agencies like the Water Framework Directive (WFD) has been to identify these micropollutant compounds and to reduce the risk of these compounds entering drinking water supplies (Allan *et al.*, 2006; Rogowska *et al.*, 2020). More so, there are growing concerns that even at low concentrations, some emerging micropollutants have far-reaching possible consequences because:

1. they are toxic for chronic and occupational exposure to human beings (Colosio, Rubino and Moretto, 2016).
2. they bioaccumulate in the food chain (Diamanti-Kandarakis *et al.*, 2009; Mrozik *et al.*, 2019; Rogowska *et al.*, 2020).
3. they are designed to have biological effects (e.g. endocrine disruption or cancer) (Diamanti-Kandarakis *et al.*, 2009; Sossalla *et al.*, 2020).
4. they may contribute to the risk of environmental antimicrobial resistance (Pruden *et al.*, 2013).
5. there are uncertainties about the effects of long-term exposure to combinations/mixtures of micropollutants on the environment and human health (Rogowska *et al.*, 2020).

While there are not enough consistent data to show, other areas of concern for micropollutant compounds in the environment could include their impact on endocrine disruption, reproductive health, and neurological effects (Colosio, Rubino and Moretto, 2016). Unless appropriate development and implementation of highly effective remediation/conversion techniques are applied to eliminate micropollutants in WWT, they will remain a problem for water resources.

2.4 The concept of biochar technology and production properties

Research relating to biochar has been ongoing for many years now. The traditional use of biochar has been long practised by many countries, for example, evidence of past use of biochar is drawn from the discovery and characterisation of patches of dark, highly fertile soils called *terra preta* found in the Amazon Basin (Zama *et al.*, 2018). Apart from the ecological benefits biochar has in CO_2 capture and storage from the atmosphere, many researchers have reported that biochar applications to soil improve soil functions (Shackley *et al.*, 2010; Berek and Hue, 2013; Cornelissen *et al.*, 2013; Parmar, Nema and Agarwal, 2014; Sigua, Novak and Watts, 2016a; Agegnehu, Srivastava and Bird, 2017; Deng *et al.*, 2017; Li *et al.*, 2019; Tisserant and Cherubini, 2019; Borah *et al.*, 2020). In particular, some researchers also reported the influence of biochar application in the treatment of wastewater and management of water cycles (Ahmed *et al.*, 2016; Huggins *et al.*, 2016; Li *et al.*, 2016; Dalahmeh *et al.*, 2018; Perez-Mercado *et al.*, 2018; Kaetzl *et al.*, 2020). In recent years, biochar has been reported as a potential replacement for activated carbon in environmental remediation and water treatment due to its low cost, relative abundance, and desirable adsorptive abilities (Beesley *et al.*, 2011; Inyang and Dickenson, 2015a; Thompson *et al.*, 2016; Oliveira *et al.*, 2017). Thus, this section reviews the various concepts of biochar and provides an overview of biochar production and properties.

2.4.1 What is biochar?

Biochar is the porous, carbon-based solid material derived from biomass pyrolysis (Shackley *et al.*, 2010; Freddo, Cai and Reid, 2012; Khan *et al.*, 2014; Jiang *et al.*, 2016; Deng *et al.*, 2017; Zama *et al.*, 2018). It is a charcoal-like material produced from renewable biomass such as agricultural bio-waste (Fan *et al.*, 2020) and has been reported to show great potential as a low-cost activated carbon (Huggins *et al.*, 2016; Weber and Quicker, 2018). Biochar has been produced and utilized for several thousand years and is best known as charcoal (when produced from woody biomass) (Shackley *et al.*, 2010; Weber and Quicker, 2018). Although the applications of biochar are very diverse, ranging from an attempt to reduce greenhouse gas emissions to use in heat and power production, biochar has gained popularity in agriculture and remediation applications in the past few years as a replacement for activated carbon in several of these applications (Weber and Quicker, 2018).

2.4.2 Biochar production

For biochar production, the choice of different feedstocks materials will be dependent on their local availability and ease of utilization of the huge biomass wastes produced from agricultural areas. Biochar is produced in a thermo-chemical conversion, known as pyrolysis, of carbonaceous biomass such as agriculture residues, forest residues, manures, activated sludge, etc., at high temperature (300 – 900 °C) and under O_2-limiting conditions (Inyang and Dickenson, 2015a; Cha *et al.*, 2016; Hussain *et al.*, 2017; Oliveira *et al.*, 2017; Ndirangu *et al.*, 2019; Yaashikaa *et al.*, 2020).

The term pyrolysis is the word used to describe the thermal separation or decomposition of organic matter at higher temperatures with limited oxygen. Specifically, pyrolysis converts the biomass into a liquid oil, gas and a carbon-residue generically referred to as char (Sohi *et al.*, 2010; Mohanty and Boehm, 2014). It has also been reported that pyrolysis processes widely used for biochar production have been continuously improved dated back to the ancient Egyptian centuries when tar for caulking boats and certain embalming agents were made using pyrolysis. However, it is only in the last two decades that plant pyrolysis liquid yields were increased by employing "fast pyrolysis" where the biomass is heated at a rapid rate to about 400 – 500 °C (Mohan et al., 2014; Wijitkosum and Jiwnok, 2019). Hence, pyrolysis processes are divided into slow pyrolysis and fast pyrolysis depending on the heating rate of the reactor. Cha et al. (2016) and Weber and Quicker (2018) reported that in slow pyrolysis (i.e., low heating rate and moderate temperature), the vapours reside in the reactor for a long time at low temperatures, and this increases the char yield, while the char produced at higher heating rate has a lower volatile matter content. The authors concluded that a high heating rate is desirable for quality biochar production. Thus, the type of biochar obtained in the process depends largely on the temperature, the heating rate, surrounding atmosphere and residence time (Cha *et al.*, 2016). In addition, the type of biomass also affects both biomass volatilization and char conversion (Oni, Oziegbe and Olawole, 2019).

Also, Parmar, Nema and Agarwal (2014) and Wijitkosum and Jiwnok (2019) suggested that since the waste generated in agriculture and related agro-industries have the potential to supply feedstock for biochar production, converting residual biomass from farm and food processing industry into biochar can help in achieving long-term beneficial effects in environmental management.

2.4.3 Biochar physical properties and characterisation

The composition of biochar is an important indicator for determining its application. Biochars may have a high surface area due to a large distribution of micro or mesopores. Several authors have observed that biochars' large specific surface area, porous structure, enriched surface functional groups and mineral components make it possible for it to be used as a proper adsorbent to remove pollutants from aqueous solutions (Tan *et al.*, 2015; Sizmur *et al.*, 2017). Moreover, the greater the number of micropores, the greater the surface area of the biochar and the more surface sites upon which pollutants can be absorbed (Sizmur *et al.*, 2017). However, Hussain et al. (2017) have argued that biochars from different feedstock sources or pyrolysis methods differ in pore size and surface area and, therefore, behave differently in contrasting applications owing to their varying adsorption behaviour and biological activity. In addition, biochar may have similar porous structure to activated carbon, which is commonly used as an efficient adsorbent for the removal of diverse pollutants from water (Tan *et al.*, 2015).

The three main factors are influencing the properties of biochar are (Domingues *et al.*, 2017; Hussain *et al.*, 2017; Weber and Quicker, 2018; Silos-Llamas *et al.*, 2020): (i) feedstock type used for pyrolysis (ii) the pyrolysis process, and (iii) the interacting environment (e.g., pyrolysis temperature). The type of feedstock strongly influences the elemental composition of the biochar, its porous structure, accompanying ash, and adsorption properties of the resulting biochar (Oni, Oziegbe and Olawole, 2019; Hassan *et al.*, 2020). The main elements of biochar are carbon (C), hydrogen (H), oxygen (O), ash, and trace amounts of nitrogen (N) and sulfur (S), which can be used to assess variation in properties of biochar between samples and to document the process of ageing in the environment. The elemental ratios of C/H, O/H, and O/C are found to provide reliable measures of both the level of oxidative alteration of biochar in application and the extent of the pyrolysis, which are relatively simple to ascertain (Nartey and Zhao, 2014).

Changing the chemical composition of biochar compared to that of its raw biomass, most of all by increasing the carbon content, is one main aim of biochar production (Weber and Quicker, 2018). However, the biochar elemental composition varies according to the type of raw biomass material used for biochar production and the characteristics of the carbonization process (Cha *et al.*, 2016; Yaashikaa *et al.*, 2020). Also, the nature of the functional groups on the biochar surface is intimately connected to the surface chemical composition of the biochar which plays an important role in its adsorption property. Functional groups such as carboxyl (−COOH), hydroxyl (−OH), and lactonic groups abundantly present at the surface of biochar essentially increase its sorption properties (Klasson, 2017; Yaashikaa *et al.*, 2020). Currently, several modern techniques have been reported for characterizing biochar such as Fourier transform infrared spectroscopy (FTIR) can also be used for determining surface functional groups present in biochar, Scanning electron microscopy (SEM), X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), proximate and ultimate analysis, etc. (Nartey and Zhao, 2014; Klasson, 2017; Yaashikaa *et al.*, 2020). Tan et al. (2015) and Sohi et al. (2010) reported that the results from FTIR characterization demonstrate qualitative differences in the surface functional groups of biochar due to both differences in the original feedstocks and the pyrolysis conditions, suggesting that pyrolytic temperature also had a significant influence on the surface functional groups of biochars. There tends to be a reduction in most bands as the pyrolytic temperature is increased, which indicates reduced heterogeneity of the surface chemical structures of biochars produced at high temperature based on the corresponding peaks of FTIR spectra (Tan *et al.*, 2015).

2.4.4 Agro-waste biochar production

Generally, all biomass material, unprocessed or processed, can be used as feedstock for charcoal/biochar production (Parmar, Nema and Agarwal, 2014; Kuppusamy *et al.*, 2016). Feedstock types currently used in commercial and research production facilities include wood biomass such as wood chip, wood pellets, tree bark; crop residues such as corn cob, straws, shells, husks and hulls; organic wastes including sugarcane bagasse, dairy manure, and sewage sludge (Sohi *et al.*, 2010; Hussain *et al.*, 2017; Klasson, 2017; Muhammad *et al.*, 2018; Panwar, Pawar and Salvi, 2019; Yaashikaa *et al.*, 2020). However, practically, the continuous harvesting of wood and mangrove forest products for charcoal production can have negative impacts on the ecosystem providing them (James Rotowa *et al.*, 2019). Charcoal production has been reported to have devastating ecological and environmental impacts in tropical regions of the world (Chidumayo and Gumbo, 2013; Sedano *et al.*, 2016; Scales and Friess, 2019). Thus, instead of high-quality wood biomass, waste from agriculture residues and organic matter that does not find any other useful application should be used as pyrolysis feedstock for biochar production.

In many agricultural systems, waste is generated in significant amounts from field crop residues such as shells, cobs, husks, and straws (Wijitkosum and Jiwnok, 2019). According to López-Cano et al. (2018), the wide range of agriculture residues available for biochar production could be beneficial to biochar produced from woody biomass, as woody biochar represents a trade-off between the detrimental impact of charcoal production from forest/mangrove ecosystems and the competition with food production systems. However, Obia et al. (2019), in a report suggested that biomass used for biochar production should be restricted to agricultural waste such as food cobs, shells and husks. Agricultural residues are by-products of crop production and are generated within the farm, whereas residues from other sources are normally produced outside the farm (Parmar, Nema and Agarwal, 2014; Wijitkosum and Jiwnok, 2019). Normally, agricultural residues are simply left in the field to decompose or burned, but instead of burning to emit greenhouse gases (GHG) that could impacts severely on air quality, biodiversity and human health, farmers can conveniently, quickly and cost-effectively convert large volumes of crop residues into biochar using slow pyrolysis (Wijitkosum and Jiwnok, 2019). It is evident that agro-waste residues such as nutshells, straw and husk of various farm crops are therefore the most favourable feedstock for the production of biochar. Hence, utilizing this residual biomass from agriculture to produce biochar is a viable solution to manage waste by minimizing the burning of agricultural wastes in fields, which is otherwise related to air pollution and risk other environmental concerns.

2.5 Benefits of biochar and potential applications

Biochar is receiving increasing attention as an emerging economical substitute to activated carbon to remove diverse organic pollutants due to its distinctive benefits in agricultural and environmental applications (Zheng *et al.*, 2015; Oliveira *et al.*, 2017; Zama *et al.*, 2018; Tisserant and Cherubini, 2019). The section focused on the potential effects of biochar considering two key benefits: (1) its social and economic impact, and (2) its effects on water treatment.

2.5.1 Social and economic benefits

A number of agronomic benefits have been reported with biochar applications particularly, in the capture, treatment, and recharge of urban runoff which can augment water supplies for water-scarce cities (Luthy, Sharvelle and Dillon, 2019). As reported by Boehm et al. (2020), biochar has the potential of giving social communities environmental benefits via stormwater and biofiltration applications. Also, the application of biochar as an urban soil amendment can, in some circumstances, provide multiple benefits that include increases in plant growth by reducing abiotic impact factors, such as drought by enhancing water holding capacity or nutrient preservation by growing cation exchange capacity (Thomas *et al.*, 2013; Häring *et al.*, 2017; Chen *et al.*, 2018; Paz-Ferreiro *et al.*, 2018; Blanco-Canqui, 2019; Song *et al.*, 2020; Kumar *et al.*, 2021). Being a renewable resource and due to its economic and environmental benefits, biochar contributes additionally to a broader effort of greening urban infrastructures to improve run-off management, which includes more street trees, parks, drainage systems and green roofs (Field *et al.*, 2013; Qian *et al.*, 2015; Oni, Oziegbe and Olawole, 2019; Zhang *et al.*, 2019; Boehm, Bell, Fitzgerald, Gallo, Higgins, Hogue, Luthy, Portmann, B. A. Ulrich, *et al.*, 2020; Matuštík, Hnátková and Kočí, 2020). Hence, there exists a co-benefit of biochar being used as biofilters in green infrastructures such as swales, soak-aways, stormwater retention ponds and infiltration wells for groundwater recharge (Mohanty and Boehm, 2014; Mohanty *et al.*, 2014, 2018; Ulrich *et al.*, 2015; Lau *et al.*, 2017; Sun *et al.*, 2020). For example, due to population growth, economic expansion, and the impacts of climate change, many developed cities of the world face challenges with managing urban stormwater runoff to control nutrient loads and pollution in the environment (Luthy, Sharvelle and Dillon, 2019). The beneficial use of urban stormwater will help cities reduce dependence on unsustainable groundwater withdrawals. Some information is available on the costs, benefits, and risks of urban stormwater use, but in general, such practical information beyond the simplest applications is limited.

Biochar application to agricultural soil interacts with the environment and climate system in multiple complex ways, which is typically found essential in stabilizing global rising temperatures and often cited as an important potential benefit for its carbon sequestration (Xu *et al.*, 2012; Gul and Whalen, 2016; Kavitha *et al.*, 2018; Shaaban *et al.*, 2018; Tisserant and Cherubini, 2019; Dai *et al.*, 2020). In addition to these carbon sequestration benefits, biochar amendment to soil has also been reported to bring benefits in terms of soil physical, chemical and biological attributes; with several authors reporting enhanced plant growth (Ahmad *et al.*, 2014; Nartey and Zhao, 2014; Dai *et al.*, 2020). The variety of agronomic effects of soil biochar additions on crop yields have been shown in many studies (van Zwieten *et al.*, 2010; Xu *et al.*, 2012; Kuppusamy *et al.*, 2016). In a health risk assessment research by Khan et al. (2014) to mitigate potentially toxic elements contamination in rice farmed on cancer-prone fields, biochar application to soil significantly reduced the risk of lifetime cancer associated with the consumption of rice by 66%. Even though the exact mechanism is not fully known, the improvement of crop productivity has been attributed to the increase in soil available nutrients and enhanced soil physical properties (e.g., decrease in soil bulk density, increase in water holding capacity) after the incorporation of biochar (Lim *et al.*, 2016b).

Other benefits include the low production cost of biochar (Homagain *et al.*, 2016; Choudhary, Kumar and Neogi, 2020; Pandey, Daverey and Arunachalam, 2020). Converting agricultural waste into biochar in many agricultural countries such as Thailand offers a potential solution to manage massive quantities of crop residues generated after harvest (Wijitkosum and Jiwnok, 2019). Biochar costs vary widely, depending on the feedstock, transport, pyrolysis operation, and other factors, but are estimated to range from $350 to $18,000 per metric ton (Boehm et al., 2020). The current cost of biochar is significant compared to construction sand, which is typically used as biofilter media and cost about $8.6 per metric ton in 2015, but potentially lower than activated carbon at $2000 per metric ton (Boehm et al., 2020).

2.5.2 Applications of biochar for water treatment

There have been an increasing number of reports on the adsorption of various pollutants on biochar in the past few years (Tan *et al.*, 2015; Jiang *et al.*, 2016; J. J. Zhao *et al.*, 2019). Biochar has been demonstrated as an attractive material for the capture of suspended particulate matter, and the sorption and/degradation of pollutants in wastewater treatment (Zama *et al.*, 2018). Some of these pollutants include trace metals, organic pollutants, and other pollutants. According to a review by Tan et al. (2015) on the distribution of available literature on biochar application in water treatment, about 46% of the studies are concerned with the ability of biochar to remove heavy metals versus 39% for organic pollutants, 13% for nutrients, and 2% for other pollutants. Sigua, Novak and Watts (2016) reported that specific biochars could be designed to target the removal of a specific chemical compound, but no single biochar type has yet been developed to resolve all environmental issues. Cheung et al. (2007) pointed out that adsorption affects the availability, leaching and behaviour of organic or inorganic chemicals, and controls the toxicity, fate and transport of organic micropollutants in the environment. Hence, the adsorption isotherms and kinetics are of great significance to evaluating the performance of a given biochar and to gain insight into the underlying sorption mechanisms such as reaction rates, and the interactions that occur between the adsorbent and micropollutants (Dotto, Vieira and Pinto, 2012). There are, however, several conditions that are responsible for the high sorption capacity of biochar for specific pollutants, such as the kind of feedstock, its mineral composition and its pyrolysis condition, which makes agriculture waste biomass more effective than wood biomass (Sizmur *et al.*, 2017; J. J. Zhao *et al.*, 2019).

In water treatment, it is also important to consider biochar impacts on hydraulic conductivities. Although the impact of biochar on the soil hydraulic properties is a texture-dependent complex interaction of soil and biochar physical properties, several other studies have reported that the incorporation of biochar to soil increased the saturated hydraulic conductivity (K_{sat}) while other studies have observed decreased K_{sat} following biochar additions (Lim *et al.*, 2016a). This improves the soil bulk density, water holding capacity and promotes soil aggregation (possibly in combination with soil biological effects), which may be temporary or long term (Shackley *et al.*, 2010). Also, studies have reported that biochar showed excellent ability to remove contaminants such as heavy metals, organic pollutants, and other pollutants from aqueous solutions. In general, biochar is a promising resource for environmental technology used for environmental treatment. Specifically, biochar loaded with ammonium, nitrate, and phosphate is also proposed to be a slow-release fertilizer to enhance soil fertility, as biochar after adsorption may contain an abundance of valuable nutrients (Tan *et al.*, 2015). Meanwhile, several biochars exhibit comparable or even better adsorption capacity than commercially activated carbon (Ulrich *et al.*, 2015; Tomczyk, Sokołowska and Boguta, 2020).

2.6 Impact of biochar production techniques

There are significant institutional and environmental concerns associated with the production of biochar. Biochar indeed offers many socio-economic benefits, and in modern industrial systems, the production of biochar can be controlled with minimal gas emissions, but in rural tropical environments, the same results are difficult to achieve (Smebye *et al.*, 2017). A variety of biochar production methods exist in low-income rural areas. Also, it is reported that biochars used for research (Kuśmierz and Oleszczuk, 2014) and farm (Wijitkosum and Jiwnok, 2019) purposes are usually produced at local conditions, with different medium-sized traditional kilns using slow pyrolysis (Pandit *et al.*, 2017). These traditional techniques used for biochar production are simple, convenient, quick, cost-effective, allow fast preparation of the farm for the next rotation, and can be applied in countries that do not have advanced technologies (Wijitkosum and Jiwnok, 2019).

According to a recent report by Khawkomol *et al.* (2021), the drum kilns are a very popular traditional method widely used for biochar production in the rural areas of Thailand and other parts of Asian countries, as they are more efficient than other traditional kilns. However, apart from the risk associated with deforestation with regards to using woody biomass, using unmodified, traditional low-tech kilns have two main issues: (1) the emission of air pollution like greenhouse gases (GHG), particularly carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), PAHs, particulates, etc., and retains relatively small propositions of carbon in the feedstock (Sohi *et al.*, 2010; Nartey and Zhao, 2014; Pandit *et al.*, 2017; Tisserant and Cherubini, 2019; Wijitkosum and Jiwnok, 2019); and (2) the loss thermal energy produced during pyrolysis – this is a waste of fuel (Sohi *et al.*, 2010; Pandit *et al.*, 2017). Specifically, the emission of these toxic compounds formed which are usually released during biochar production, pose potential threats to both humans and the health of the ecosystem health (Wijitkosum and Jiwnok, 2019), and they end up in the food chain (Ndirangu *et al.*, 2019; Tisserant and Cherubini, 2019). These circumstances negatively affect the potential benefits of biochar production and currently, there are no socio-economic studies that have addressed such situations (Sohi *et al.*, 2010). Also, it is possible that there may be non-monetary costs associated with the distribution of feedstocks for pyrolysis, such as disruptions of schedules and soil disturbance.

Although it is expected that a growing understanding of the relationship between the availability of feedstock source, the manipulation of the pyrolysis conditions, and the social application of biochar should all be considered when selecting biochar, as this will ultimately enable biochar to be “modified” to provide the balance of benefits most appropriate for any particular application at variable locations (Sohi *et al.*, 2010; Hussain *et al.*, 2017). Moreover, a report by Ndirangu *et al.* (2019) recommended taking into account environmental protection and health safety factors when designing technologies for biochar production, so as to minimise the emissions of pollutants that are harmful to humans. Since biochar could be produced at a large scale, it is important to carefully assess its potential negative effects on occupational health, water quality, and food safety. In general, only a few studies have considered the human health effects of biochar production technologies using traditional kilns methods. Nevertheless, the lack of knowledge and awareness about the measure of the balance between the many possible environmentally friendly benefits of biochar as against its negative implications and harmful effects on the ecological system is a key challenge to be addressed by further research.

2.7 Research gaps and justification

The widespread occurrence of these contaminants in water is potentially a major problem with consequences that are yet to be fully understood (Matamoros *et al.*, 2012). Therefore, while biochars properties may be potentially attractive for water pollution amelioration, there are uncertainties around:

1. Impact biochars from different feedstock may have on soil and biofilter hydraulic conductivities and leachate quality via release of biochar associated soluble compounds.

2. Relationship between biochar properties and its potential to immobilise organic water pollutants in the laboratory and the use of the results to predict the expected influence of biochar application in the field remains unclear and does not always allow the establishment of appropriate process conditions to produce biochar with desired characteristics (Sigua, Novak and Watts, 2016).

3. Benefits of biochar in surface water biofiltration systems, especially with regards to its performance for mixtures of micropollutants in a real surface water matrix.

4. Impacts of biochar amendment in biofiltration systems on the micropollutant biodegradation and microbial communities.

Overall, the effect of the different feedstock sources, the particle size of biochar and soil conditions have not yet been fully studied. Also, research on biofilter performance considering interactive processes occurring with pollutant mixtures or under field conditions is limited and additional research is needed (Boehm *et al.*, 2020).

Chapter 3. Investigating the influence of biochar and activated carbon amendments on the chemical properties of leachate from soils and biofilters

Abstract

Biochar and activated carbon have been increasingly promoted globally as potential amendment materials for a wide range of environmental applications, including retaining pollutants in biofilters and bioactive soil horizons. However, their unexpected influence on hydraulic properties and leachate fluxes from the amended porous media in terms of pollutants leaching behaviour has not yet been thoroughly discussed. This work investigated the impacts of biochar types and activated carbon amendments and compared lysimeter soil amended with wheat straw biochar (L-WSBC) versus wheat straw pellets (L-WSP), on hydraulic conductivity and leachate quality, in order to assess if chemical ions released from these sorbents present a risk to groundwater quality. The research was motivated by the need to verify a ‘no harm’ position of amendment application in soils to groundwater. First, the saturated hydraulic performances of sand columns with biochar/activated carbon amendments were evaluated relative to the sand only control. Coconut shell biochar (CSBC), rice straw biochar (RSBC) and granular activated carbon (GAC) amendments increased saturated hydraulic conductivity (*K*) by 11.6%, while coconut husk biochar (CHBC) and corn cob biochar (CCBC) decreased *K* by 54.7% and 36.9%, respectively. Biochar amendments increased pH (>8) of the effluents and decreased the leachability of metals, while GAC with lower pH (<6) showed greater solubility and increased leaching of Cu, Ni, Cd, As, Cr, Ba and Sr, as compared to the sand only control, however, their concentrations declined after multiple leaching cycles. Next, two long-term outdoor field lysimeter studies were used to assess the change in the chemical properties of leachate under more natural conditions, before and after adding wheat straw biochar and wheat straw pellets amendments to man-made urban topsoil. Overall, changes in dissolved metals, carbon and nutrients in leachate from the lysimeters was unaffected by the addition of the soil amendments over the period under investigation. However, the leachate pH and nutrient content were reduced significantly after the amendment addition. Thus, the impacts of the amendments in the laboratory study were feedstock type-dependent, while the field study leachate composition was variable and dependent on a range of other factors. Overall, hydraulic conductivities could be maintained within a desirable range, and leachate quality was consistent with drinking

water quality standards demonstrating that the biochar amendments did not result in leachate that would represent an environmental problem.

3.1 Introduction

Sand filtration systems are one of the oldest practices in water purification that is still broadly used in today's world. This filtration system mimics the natural cleansing processes of the subsurface for the removal of contaminants from water such as chemicals, toxins, and total suspended solids (Vignola *et al.*, 2018). At the same time, sand filters are a very favourable tertiary treatment option for secondary effluents of wastewater treatment plants (Kaetzl *et al.*, 2020). Sand filtration systems have a layer of sand supported with gravel (medium to large-sized grains) and the technology is one of the most efficient for the design of stormwater filtration systems (Glaister *et al.*, 2017; Segismundo *et al.*, 2017; Shrestha, Hurley and Wemple, 2018). The gravel is in the system mainly to prevent clogging of the filter and provide support for the sand, while the primary role of the sand in the filter is to reduce dissolved contaminants in water via biological processes and remove suspended solids. The filtration rate is a key property of the sand filter in establishing how fast the water flows downward through the sand for use in irrigation water or groundwater recharge, with a relatively high hydraulic loading rate being desirable as confirmed by several studies (Kaetzl *et al.*, 2020). However, treating contaminated water using sand may result in poor filtration efficiency for chemical pollutants. Hence, improving the filter media properties to increase contaminant removal efficiency through amendments to sand has been proposed in recent publications (Herath, Camps-Arbestain and Hedley, 2013).

Application of amendments is widely used in a range of filtration and remediation applications and the use of biochar; a by-product of biomass pyrolysis, as a sustainable filter or soil amendment in treating contaminated water has gained much attention globally (Peake, Reid and Tang, 2014; Kaetzl *et al.*, 2020). Biochar can be produced from any type of biomass material, and it is characterized by a number of properties; including high porosity and high specific surface area, that make it a good amendment material for water purification (Piscitelli *et al.*, 2018). Recently, the lower cost of the biochar combined with its positive effects in soil quality improvement and carbon sequestration have generated wide research interest into utilizing the adsorption capabilities of biochar produced from various feedstocks as a potential soil amendment (Hale *et al.*, 2013). The agronomic benefits are mainly derived from the fertilizer value of biochar and its effects on the improvement of soil physical properties (Herath, Camps-Arbestain and Hedley, 2013) while the biofiltration technology benefits mostly involve reducing the concentrations of total suspended solids (TSS), organic pollutants, and heavy metals from wastewater or stormwater (Boehm et al., 2020; Kaetzl et al., 2020). Biochar is also considered to be a potential soil amendment as the changes it creates in the soil physical environment could influence the number of services the soils provide (Blanco-Canqui, 2017). Regardless of whether biochar is used as an amendment in stormwater management systems, or in agricultural applications, the implications of biochar amendment on the physical and hydraulic properties of the amended porous medium need to be better understood.

According to Obia et al. (2019), the effect of biochar on water transport in porous media is commonly measured in terms of hydraulic conductivity, which is the physical property that denotes the capacity of a porous material to allow water flow through pore spaces (Diminescu, Dumitran and Vuţă, 2019). Hydraulic conductivity is dependent on soil type, biochar type and particle size. Lee et al. (2013) also commented that the effects of biochar and the requirements on its properties for soil amendment are difficult to predict because they are influenced by numerous parameters which may depend on biochar pyrolysis conditions, which often result in strongly context-specific and method-dependent results (Fidel *et al.*, 2017). Despite the promising benefits of biochar, there are concerns that the addition of nitrogen (N), carbon (C) and phosphorus (P) from biochar could influence the N-C-P balance through leaching or runoff (Barnes et al., 2014; Yang et al., 2019; Boehm et al., 2020). Indeed, nutrient leaching is not uncommon when biofilters are amended (Boehm et al., 2020). Mannino and Harvey (2004), Masiello (2004), Major et al. (2010) and Jaffé et al. (2013) all reported that applied C loss through leaching from soils contribute significantly to global riverine C fluxes. Other reports pointed out that the physical, chemical and structural properties of biochar vary greatly depending on the type of biomass used and the pyrolysis conditions (Perez-Mercado *et al.*, 2018). Hence, it is difficult to anticipate the influence of soil amendment with biochar on leachate quality, and an investigation of soil amendment properties and leachate components to understand the relationships between the two is necessary (Yang *et al.*, 2019).

Although many papers have reviewed the potential impacts of biochar amendment on the removal of organic and inorganic contaminants, understanding of the implications of biochar application itself on the physical and hydraulic properties of soil and leachate quality is lacking and long-term studies are needed to understand potential impacts on groundwater resources. According to Hale et al. (2013), it is important to first consider what effects the amendment materials themselves may have before considering their benefits for pollutant removal. Many leaching studies are carried out through repacked laboratory soil columns, however, a few researchers have adopted an intermediate approach, using undisturbed soil amendments that are larger than the usual laboratory columns and submitted to natural boundary conditions for water fluxes and solutes infiltration beyond the root zone (Schoen et al., 1999). This lysimeter study differed from the laboratory column tests in which conditions were not representative of field conditions, as they do not consider the spatial variability of the soil properties, because of soil repacking, small column sizes and controlled boundary conditions. Based on this discussion, the present work is aimed at evaluating the impacts of biochar as an amendment to sand in laboratory column studies and soil amendment in a field lysimeter experiment, on hydraulic properties and the leachate quality generated from the percolation of clean water such as rainfall. While the biochar amended sand column studies mimicked purposefully designed sustainable urban drainage systems (SUDS) components such as soak-aways and infiltration basins/wells, the lysimeter studies mimicked biochar amendment of urban topsoil which may be used more widely for landscaping in the construction of swales and green buffer zones in SUDS. The study compared the impact of amendments of activated carbon and biochars produced from four different feedstocks on leachate quality against drinking water recommended standards, to understand potential impacts on groundwater as a resource for drinking water production. In addition, it evaluated amendment impacts on the saturated hydraulic conductivities (K) versus unamended pure sand to understand amendment impacts on water infiltration rates in SUDS components such as soak-aways.

In this context, it was hypothesised that the application of biochar or activated carbon amendments to sand or soil would not detrimentally alter the quantity and quality of leachates from SUDS. Short-term, small-scale laboratory column experiments quantified the effects of 3% (by mass) amendment on the saturated hydraulic conductivity (K) of sand, as well as the effects of these amendments on leachate quality. Field lysimeter experiments were then conducted to evaluate amendment effects on leachates produced from a man-made soil used for the landscaping of the UK National Green Infrastructure Facility at the Helix Site in Newcastle upon Tyne. Outdoor lysimeter experiments are valuable as there is an insufficient number of long-term monitoring field-performance studies for biochar amended soils available in the literature. Overall, the experimental results obtained will thus address important knowledge gaps by providing new quantitative data on how biochar amendments change hydraulic properties of porous media and the chemistry of related leachates; thus before considering amendment benefits in the next chapters, this work first addresses the need to demonstrate “no harm” from the amendments on the intended ecosystem services of SUDS, namely reducing surface run-off and groundwater pollution risks.

3.2 Precursor Material Analysis

While biochar is known for its many functions, previous research has led to contrary conclusions on the influence of physicochemical properties on its application. Although their physicochemical properties depend on their feedstock type (Sun *et al.*, 2017; Maaz, Hockaday and Deenik, 2021) and pyrolysis condition (Pugalendhi and Gopal, 2017), studies have shown that biochar can possess water-soluble compounds during pyrolysis that can impact on the environment negatively during application (Buss and Mašek, 2014). The data obtained from the preparation condition, proximate and ultimate analyses of CC, CH, CS, RS, AC are summarised in Table 3-1 and Table 3-2, respectively. Studies also showed that pyrolysis at low temperatures produced slightly acidic biochar, while high temperatures produced slightly alkaline biochar (Sun *et al.*, 2017). Thus, it is expected that RS with the lowest temperature values (Table 3-1) would produce leachate with low pH values compared to the rest of the biochar materials.

Table 3-1. The maximum heating temperature during carbonization and yield of various biochars used in this study. Data obtained from KMUTT.

Biomass	Max. Temp in Chamber (°C)	Weight (kg)		% Yield	Heating value (MJ/kg)	Bulk density (g/cm^3)
		Before	After			
CC	480	18.4	5.9	32.1	22.1	0.70
CH	378	10.4	3.5	33.7	26.1	0.66
CS	704	34.0	8.1	23.8	28.7	1.14
RS	303	10.0	1.0	10.0	14.1	1.69

Table 3-2. Physical characteristics of the different adsorbents used in this study were synthesized under different conditions. Data obtained from KMUTT. Abbreviation: M – Moisture content, A – Ash content, VM – Volatile matter, FC – Fix carbon content.

Biomass Type	M (%)	A (%)	VM (%)	FC (%)	BET surf. Area (m^2/g)	Iodine Number (mg/L)	pH (DI water)	%C	%H	%N	%S	%O	Molar Ratio O/C	Molar Ratio H/C	Molar Ratio (O+N)/C
CC	18.7	6.33	49.0	26.0	<0.1[a]	32.3	8.97	60.4	3.03	1.81	0.12	34.7	0.43	0.60	0.46
CH	1.69	8.6	5.99	83.8	11	68.4	9.75	68.5	3.53	0.06	0.15	27.8	0.30	0.62	0.31
CS	2.96	4.4	38.6	54.0	<0.1[a]	13.1	9.02	68.6	3.69	0.25	0.02	27.4	0.30	0.65	0.30
RS	1.91	36.0	33.4	28.9	14.6	3.06	8.94	53.6	2.50	1.74	0.33	41.8	0.58	0.56	0.61
AC	9.99[*]	14.9[*]	14.6[*]	18.8[†]	760[*]	-	6.8[*]	77.1[*]	1.41[*]	0.41[*]	0.06[†]	44.5[†]	0.43	0.22	0.44

[a] data too small to be measured

[*] Source: Kołodyńska, Krukowska and Thomas (2017)

[†] Source: Duan et al. (2012)

Also, Table 3-1 presents the different biochar feedstock subjected to carbonization at different temperatures ranging from 300 to 700°C. It showed that while the yield (%) on a dry weight basis decreased with increased pyrolysis temperature, the proximate analysis presented in Table 3-2 showed CC had the lowest fixed carbon content of 26%, the highest moisture of 19%, and highest volatile matter content, following an order of magnitude with others prepared from the same kiln: CC > CS > RS > CH. The volatile matter content of biochar is a measure of its thermal alteration, which has a direct effect on nitrogen and carbon dynamics in soil (Maaz, Hockaday and Deenik, 2021). Although biochar samples exhibited large variations in the proximate and ultimate analysis, especially in the ash content (Table 3-2), Buss and Mašek (2014) suggested that biochar containing high ash content can impact negatively on soil and leachate. The solid residues obtained from pyrolysis also contain pollutants that originated from the initial inorganics content of raw biomasses (Uras-Postma, Carrier and Knoetze, 2014). Therefore, RS contained the highest ash content (36%), whereas the rest of the samples; CC, CH, and CS, had ash contents of less than 9% which makes them unlikely to cause toxicity on leachates. Again, given the high ash content RS has, it is expected that the feedstock will release more soluble nitrogen species into leachate water compared to other feedstocks. Soluble nitrogen (N) represented are nitrogen in the form of ammonium (NH_4^+), nitrate (NO_3^-), and nitrite (NO_2^-) in the leachate.

Since the pH of biochar directly impacts on filtration process during application (Stella Mary *et al.*, 2016), a neutral pH is generally preferred. Biochar generally has alkaline pH (Stella Mary *et al.*, 2016) and the biochar samples in this study also recorded alkaline pH values (8.94 – 9.75). Activated carbon (AC), on the other hand, which is commercially obtained from coconut shell, usually have low pH values (Kołodyńska, Krukowska and Thomas, 2017). The controlled thermal activation of AC allows it to obtain a high surface area and porous structure (Kołodyńska, Krukowska and Thomas, 2017). As there are currently no locally operating AC production systems, which is why it is very difficult to assess the AC characteristics prepared under the same production condition as that of biochar for comparison, hence, a number of assumptions are made to create the basis for comparison between biochar and AC. The proximate analysis data for AC in Table 3-2 used for this comparison were derived from Abdeljaoued *et al.* (2018) with is similar data also presented in Duan *et al.* (2012).

As can be noted from Table 3-2, the BET surface area of AC, 760 m^2/g is considerably higher, followed by RS and CH with 15 and 11 m^2/g, respectively, and it is in the range of a commercial AC (500–1500 m^2/g) (Abdeljaoued *et al.*, 2018). This high surface area is as a result of increased temperatures during carbonization which often form the pore structures during the charring (Al-Wabel *et al.*, 2018). Although at high temperatures, the collapse of pores may lead to a decrease of surface area (Al-Wabel *et al.*, 2018), hence the situation with CS and CC with BET surface areas being too small to be measured. The chemical and physical characteristics of the precursor materials are crucial sources of information for knowing the best candidate for a low leachate hazard pathway. A limited amount of literature has been published discussing the chemical properties of biochar and its effects on leaching chemical properties. Also, previous studies have shown that the type of feedstock biomass has a significant influence on leaching nutrients biochar amendment, in addition to the heavy metal content. Ions released from each material amendment were also investigated using methods stated later.

3.3 Aims and objectives

A primary aim of this thesis was to assess the short-term and long-term effects of soil amendment application on leachate quality. The study tried to establish how different biochar types and properties could influence porous media leachate quality and hydrology in the context of using biochar amendment in SUDS. The research will focus on using selected biochar types and activated carbon as a reference amendment, and it was intended that the results will give insight into the potential effects of these amendments on water infiltration rates and leachate quality in SUDS.

The objectives of this study were to investigate the influence of amendments of four biochar types produced from four agriculture wastes (corn cob, coconut shell, coconut husk and rice straw) on vertical flow biochar filters, compared with sand filters, in regards to the hydraulic conductivity and leaching of nutrients and heavy metals. Specific objectives were to assess the physical, chemical, and hydraulic properties of amended sand or soil and their leachates for the different types of amendments in the short-term and long-term, under drying and wetting hydraulic loading conditions.

3.4 Materials and methods

This section outlines the testing of different soil amendments and their impacts on leachate qualities, experimental set-ups, procedures and analytical methods for both laboratory and field experiments.

3.4.1 Experimental Design

To address the different objectives of this study, two different types of experiments namely laboratory-scale work and fieldwork were tested to assess the effects of sand amendment on hydraulic properties and leachate quality for different types of biochar or activated carbon amendments using continuous gravity downward flow. The amendments tested were granular activated carbon (GAC), biochars produced from different feedstocks and wheat straw pellets.

Laboratory-scale work was first carried out with small-scale fixed-bed laboratory columns. In these laboratory experiments, biochar and fine sand column filters were packed in glass columns and operated at room temperature. Before mixing the media, the following properties of the sand were determined: effective size and uniformity coefficient, and particle density. After packing the columns, the following filter properties were determined: Bulk density, porosity, and hydraulic residence time. Varying-head hydraulic conductivity testing was determined only for the sand, biochar and activated carbon filters. These trials in the laboratory helped in understanding the basic influence of biochar amendment on soil hydraulic properties. In addition, amendment impacts on leachate quality were assessed by measuring nutrient, metal and suspended solid concentrations.

Based on the laboratory results, further large-scale outdoor trials were subsequently carried out using field lysimeter experiments. Lysimeters are typically some iron-based media (stainless steel tanks or containers) that define a specific boundary to contain experimental soil for measuring the volume of water percolating vertically and its quality (Kondo *et al.*, 2019). This field research was useful to complement the laboratory work by considering a more complex type of soil (man-made loam used for surfacing a new development site with SUDS in Newcastle City Centre), alternative amendment types (wheat straw pellets versus wheat straw biochar), natural rainfall and ambient weather conditions.

3.4.2 Biofiltration materials

Biochar

Due to local availability, cost-effectiveness, and institutional collaboration with partners in Thailand on agricultural waste valorisation, the biochars used for this laboratory column study and later in this thesis were derived from four main feedstocks; coconut shells, coconut husks, corn cobs, and rice straw. These biochars were prepared locally using low-cost drum kiln reactor (shown in Figure 3-1) at the Centre for Energy and Environmental Engineering Centre (EEEC), Faculty of Engineering, Kasetsart University Kamphaeng Saen Campus. The horizontal drum with 0.2 m^3 capacity used for the biochar production was designed and operated in accordance with specifications by Khawkomol et al. (2021). The different biochar types used for the experiments were then delivered by the research collaborators at King Mongkut's University of Technology Thonburi (KMUTT), Thailand. These feedstocks materials were chosen to represent a range of natural agricultural waste biomass sources as well as to provide a diversity of feedstock chemistries with varying particle shapes and sizes.

Figure 3-1. Biochars production using oil drum kiln and pyrolysis reactor (source: Energy and Environmental Engineering Center (EEEC), Kasetsart University Kamphaeng, Thailand).

The physicochemical properties obtained for the selected biochar samples as measured by the collaborators at KMUTT are shown in Table 3-1 and Table 3-2 above. The higher C contents of the biochar versus their feedstocks were due to the fact that cellulose and lignin in the feedstock had undergone carbonization throughout pyrolysis (Yang *et al.,* 2019). The particle sizes of the biochar samples were uneven, and therefore in order to obtain more uniform sizes, these materials were crushed into smaller pieces using a mortar and pestle in the fume cupboard and were sieved in a shaker to obtain effective particle size for water filtration (see Figure 3-2). The purpose was to have a similar particle size distribution between 212 – 1180 µm in each column.

For the lysimeter study, since a larger amount of biochar was required to scale up the experiments and the biochar species could not be obtained in large quantity in the UK, wheat straw biochar obtained from the UK Biochar Research Centre (UKBRC), University of Edinburgh, UK, was utilized for the lysimeter experiments. The biochar was produced from wheat straw pellets as shown in Figure 3-3(d), was used as the benchmark specimen biochar in this study as it was commercially available and can be obtained in large quantities. Further details of the biochar production and composition can be found at (https://www.biochar.ac.uk/standard_materials.php; accessed 22/04/2020). The wheat straw pellets of the original feedstock (Figure 3-3(c)) were also obtained in large quantity as an alternative soil amendment, to compare data between applications of feedstock and feedstock biochar.

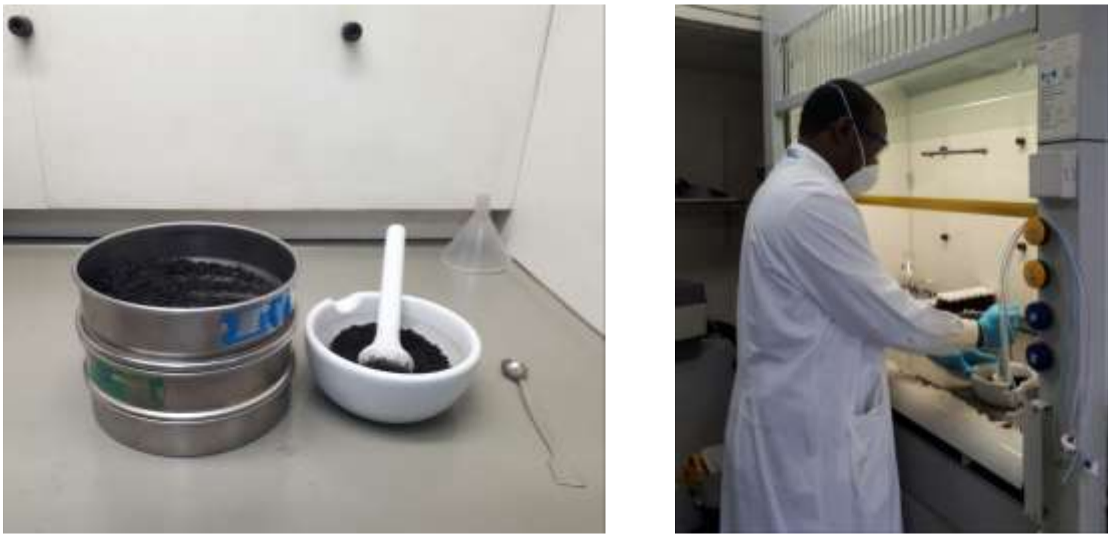

(a) (b)

Figure 3-2. (a) Manual crushing and sieving of biochar (b) crushing biochar in the fume cupboard

Figure 3-3. Soil amendment materials used in the study: (a) coconut shell biochar; (b) rice straw biochar; (c) wheat straw pellets; (d) wheat straw biochar. Sources: *images obtained from KMUTT **mages are assessed from https://www.biochar.ac.uk/standard_materials.php

Activated Carbon

Activated carbon use for environmental remediation has been extensively tested and the benefits have been studied under laboratory and field-scale conditions in terms of sequestering contaminants in soil, water and wastewater (Hale and Werner, 2010; Hale *et al.*, 2012). Granular activated carbon (GAC) produced from coconut shells by Norit was used as a conventional adsorbent for comparison in this study, and it was used in all experiments contained in other chapters of this thesis. The GAC was donated by Norit, with particle sizes ranging from 420 – 840 µm, and its BET surface area of 975 m^2/g and other physical property characterisations have been reported by Han et al. (2015).

Sands

The two types of support materials used for the laboratory column experiments were coarse-grained and fine sand. The particle size distribution (PSD) for both sand aggregates were determined using dry sieving analysis in accordance with the ASTM C136-14 (2014) standard tests methods. U.S. sieve numbers 18, 34, 46, 74, 84, 120, and 250 (sieve opening sizes: 1.180 mm, 0.600 mm, 0.425 mm, 0.250 mm, 0.212 mm, 0.150 mm, and 0.063 mm, respectively) were used for the fine sand PSD analysis while only sieve numbers 18, 34, 46, 74, and 84 were used for the coarse sand PSD analysis. Plots of cumulative per cent passing versus particle size were created as shown in *section 3.4.1* and from the plots, the effective size (D_{10}) and uniformity coefficient (C_u) for both sand types could be determined. While C_u is the ratio of D_{60} and D_{10} and is primarily used to determine the gradation of the sand, D_{10} is commonly the diameter from the particle size distribution curve at 10% finer material.

Soils

The soil sample used for the lysimeter field studies which were located near the Urban Sciences building in Newcastle University, Newcastle, United Kingdom, was sandy loam soil. This was man-made topsoil purchased for the landscaping of the UK National Green Infrastructure Facility and acted in this study as a case study urban soil media in a SUDS. Information on the soil characteristics and application procedure in the lysimeter can be seen in Appendix A.

Wheat straw pellets and wheat straw biochar

The lysimeter experiments used wheat straw pellets (WSP) and wheat straw biochar (WSBC) produced and provided by the UK Biochar Research Centre (UKBRC) at the University of Edinburgh, UK. The wheat straw was provided in small square pellets, while the biochar was produced using a pilot-scale rotary kiln pyrolysis unit, at a nominal peak temperature of 550°C. Further details of the physicochemical characteristics of the production of the materials can be found in Figure A1 and at (https://www.biochar.ac.uk/standard_materials.php; accessed 22/04/2020).

3.4.3 Laboratory column set up

The filter media generally used in water filtration systems are sand and gravel. Sand is primarily used as a filtering medium to remove suspended solids and chemicals via biological activity on attached biofilms, while gravel is used to prevent clogging of the system. To quantify the influence of biochar amendment on the hydrological properties of sand columns and the quality of their leachate, a small column laboratory experiment was conducted across six filter media. The column experiment was run in duplicates (n=2), and columns content were fine sand only (unamended control), fine sand+coconut shell biochar mixed, fine sand+coconut husk biochar mixed, fine sand+corn cob biochar mixed, fine sand+rice straw biochar mixed, fine sand+granular activated carbon mixed and were labelled FISA, CCBC, CHBC, CCBC, and GAC, respectively. The biochar and activated carbon both have distinctive properties (i.e., higher absorbing capacity than sand) that can make them valuable additions to the system. Images of the media materials used in this study are presented in Figure 3-3. Columns were set up using 3% dry masses of each amendment material to the base – fine sand (i.e., 3% biochar or activated carbon, 97% fine sand). These amendment doses were similar to previous works by Kloss et al. (2014) and Ulrich et al. (2015).

Although, certain systems may benefit from the application of biochar in distinct layers rather than mixed with the sand, for example during landscaping for C sequestration or retaining some pollutants (Cederlund, Börjesson and Stenström, 2017), this column study, however, demonstrates using the conventional practice of biochar application in mixture with sand or soil in order to ascertain results close to real-life applications. In effect, sand has its physical properties, but when biochar is added to it in a mixture, the physical characteristics of biochar will, directly and indirectly, affect mixture systems. Its contribution to the change in the physical and chemical nature of the system is significant; affecting the texture, structure, porosity, pore and particle-size distribution, density, and packing, thus modifying aeration, soil hydrology, microbial activity and nutritional status of the sand (Joseph et al., 2010; Liu et al., 2016; Rawat, Saxena and Sanwal, 2019). The laboratory filter column material consisted of a glass column 120 mm high and with 50 mm inner diameter, with a funnel-shaped outlet. Columns were packed by gently pouring the homogeneously mixed media into each replicate column, after first clogging the outlet with glass wool and filling the funnel-shaped bottom with coarse sand. No compaction was applied to avoid media breakage. About 140 g of filter media was homogenised by hand and manually poured directly into each column to a bed height of 50 mm, sandwiched within 10 mm layers of coarse sand both at the base and at the top surfaces of the media cores (as shown in Figure 3-4(a)) to facilitate drainage and minimize soil disturbance when filling the column with water.

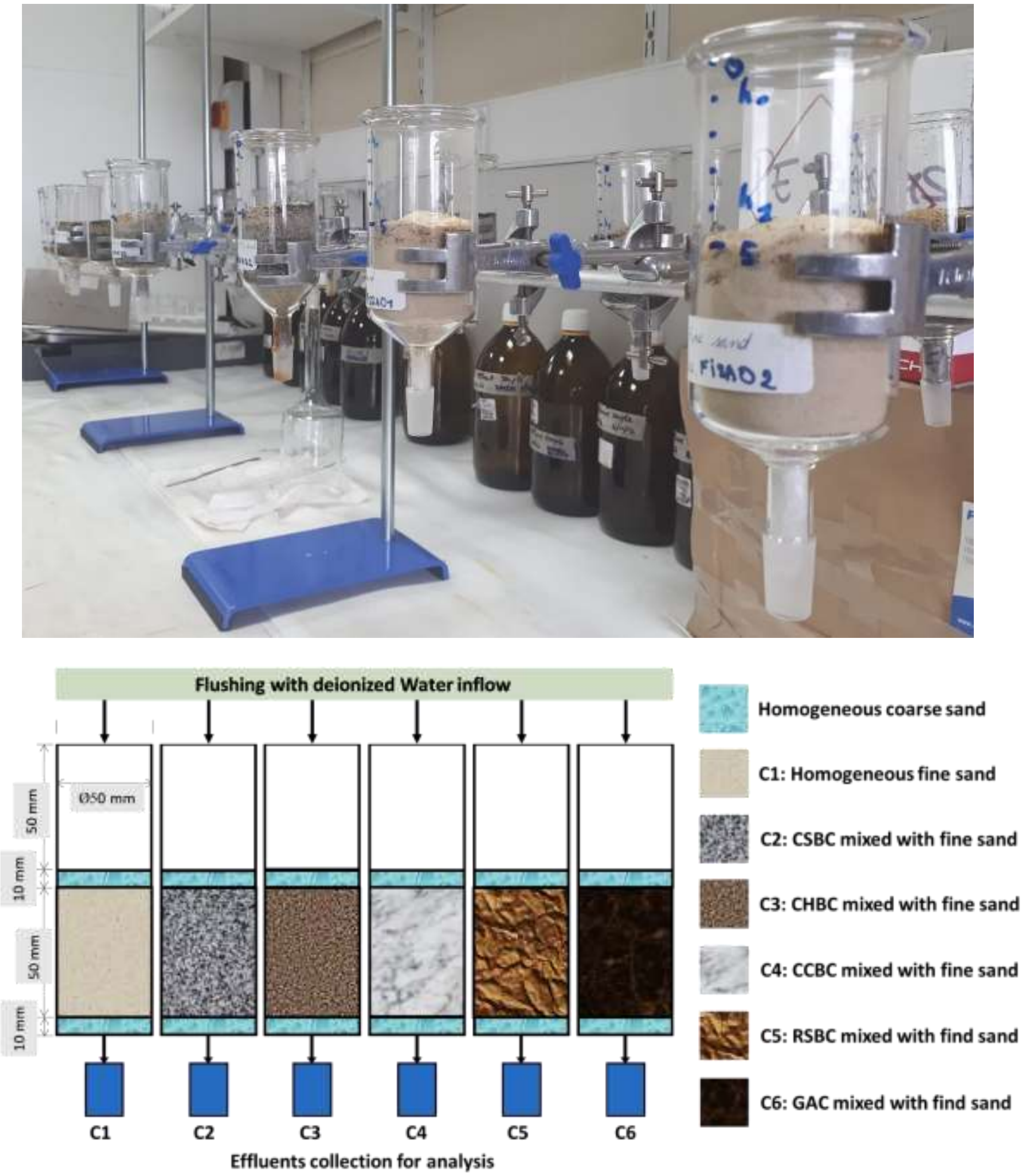


Figure 3-4 Illustration of the column media set-up with sand, biochar, and activated carbon in four different configurations for the leaching experiments and the column dimensions. Each column configuration was duplicated in the experiment.

3.4.4 Field lysimeter set up

The lysimeter study aimed at evaluating the long-term release of chemicals from the amendment materials and soil into leachate in conditions close to those prevailing in a SUDS. Leaching of surface-applied amendments is of interest to researchers, as the quality of the underlying groundwater is also of concern. Hence, the field lysimeter experiments were run on large intact soil submitted to natural boundary conditions for water fluxes to compare data with that of laboratory experiments.

Two tank-types lysimeters; Lysimeter 1 (L-WSBC) and Lysimeter 2 (WSP), was set up in Newcastle University's Green Infrastructure Research Facility, UK, study site (54º58'24" N, 1º37'31" W) located behind the Urban Science Building (USB) of the University (Figure 3-5). The ambient climate condition in this area is the continental type and the minimum winter temperature was as low as −9 °C while the average summer temperature rose to above 29 °C during the field study. The average monthly rainfall was about 59.8±6.97 mm (reports of weather conditions can be accessed at https://en.climate-data.org/europe/united-kingdom/england/newcastle-upon-tyne-72)). The background characteristics of the leachates from the soil in the lysimeter experiment were determined at the beginning of the experiment, i.e., before the amendment of the topsoil.

Figure 3-5 Picture of actual lysimeters set-up located behind *USB, Newcastle University*

Each lysimeter set up consisted of a large stainless-steel cell with an open area of 10 m^2 and a volume of approximately 7 m^3, with a central, inverted pyramid-shaped drainage system for collecting percolating water into a leachate container fitted at the bottom side of the tank. Further details of the lysimeter layout and dimensions are presented in Figure A2. The inverted pyramid-shaped bottom of the lysimeter was filled with fine gravel to a height of about 10 cm with a gravel grain size of 8 mm. Thereafter, the lysimeters were filled with sand (< 4 mm) of bulk density 1762 kg m^{-3}, filling 70 cm of the total lysimeter volume space and leaving the top 30 cm layer filled with the sandy loam soil of bulk density of 1,600 kg cm^{-3} filled to about 3 m^3 of the total lysimeter volume (Gamage *et al.*, 2016; Obia *et al.*, 2016). The lysimeters were left exposed to the atmosphere for the entire period of the experiment, and the WSBC and WSP amendments were mixed into the top 30 cm layered soil on June 21, 2018.

Since studies have shown that soil amendment applications of 1 – 2% by weight is sufficient to change the soil physicochemical properties (Ajayi and Horn, 2016; Głąb *et al.*, 2016), wheat straw biochar was uniformly mixed *in situ* with the sandy loam soil of the topsoil layer of Lysimeter 1 (L-WSBC) at a rate of 2% (w/w) while in lysimeter 2 (WSP), wheat straw pellets were applied to the topsoil layer with the same carbon weight as the biochar, using a shovel for the placement until a homogenous mixture was obtained **(**see Figure 3-6). A total of about 43.2 kg of wheat straw biochar was used to amend the sandy loam soil in the L-WSBC, whereas the amount of wheat straw pellet that was added to WSP was 64.4 kg. The lysimeters were seeded with a mixture of clover, wildflowers and grasses. The study lasted for 22 months with a regular collection of leachates for analysis.

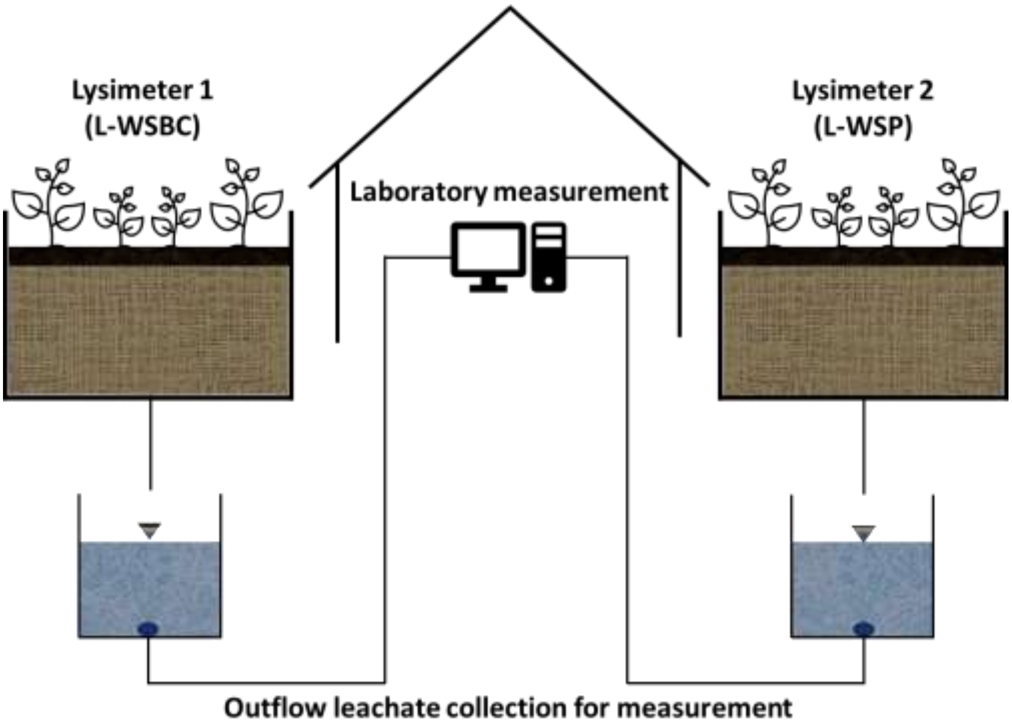


Figure 3-6 Schematic lysimeter set-up for leachate monitoring and testing

3.4.5 Sampling collection and preparation

In this research, experimental sample collection was carried out in accordance with the recommended standard method for the examination of water and wastewater (Baird, Eaton and Rice, 2017). Samples were collected in 1 L non-reactive amber glass bottles with PTFE- lined caps that had been rinsed carefully with deionised water and oven-dried before use.

Column sampling

For each column experiment, the column was first flushed with 18 MΩ-cm MilliQ deionised water, allowing it to flow into the porous medium by gravity in a downward flow mode for 2 hours to equilibrate it before collecting leachate samples. The same experimental procedure was used for all columns with the six filtration materials for inter-comparison. Once fully saturated, the columns were loaded with deionised water (in total about 10 L was flushed through each column throughout the period under investigation) and the drainage was simulated under varying head flow conditions. Effluent samples were then collected at different time intervals using reagent bottles. The rate of flow was determined by measuring the flow of effluent samples in mL per minute at regular intervals of time. All the columns were run at room temperature and the leachate samples collected were immediately stored at 4°C for further analysis. Also, aliquots of 50 mL effluent were taken, filtered through sterile 25 mm single-use 0.45 µm PTFE membrane syringe filters obtained from VWR International (Leicestershire, UK) into 60 mL amber vials closed with Teflon screw caps, to remove suspended solids and stored at 4°C until analysis. This process was repeated to maintain continuous flow through the columns until all columns were completely drained.

Lysimeter sampling

Leachate samples were collected weekly (at 7-day intervals) from both lysimeters between May 2018 and March 2020. The leachate collections were first carried out on each lysimeter for 5 weeks before the addition of wheat straw pellet and wheat straw biochar amendments each to the topsoil layer of each lysimeter soil. The volume of leachate collected weekly was recorded for each lysimeter and aliquot samples of 50 mL were immediately filtered through sterile 25 mm single-use 0.45 µm PTFE membrane syringe filters obtained from VWR International (Leicestershire, UK) into 60 mL amber vials closed with Teflon screw caps, to remove suspended solids and stored at 4 ^{o}C until analysis.

Leachate quality testing was carried out independently for each lysimeter to measure specifically the leaching of solids, organic and inorganic contaminants from the soil.

3.4.6 Analytical measurements

Determination of the materials physical and chemical properties, porosity, bulk densities, total suspended solids (TSS) and carbon content analysis was performed according to the Standard Methods for the Examination of Water and Wastewater (Baird, Eaton and Rice, 2017). Inorganic analyses of anions and cations were carried done using standard laboratory instruments as explained below. The pH measurements of liquid samples were also determined using a portable laboratory portable Mettler Toledo Quattro MP220 pH meter.

Porosity and bulk density

The porosity of the sample is the measurement of how much of its volume are pore spaces and its values can be calculated from the bulk density and the particle density of the samples. The average particle size of each of the biochar used in the column study is about 0.7 mm, while the characteristic parameters of the sand used can be found in Table 1. The bulk density of each column media was determined by dividing the known mass of the dry media sample by the measured volume of the sample in the column. In its natural state, a porous medium volume includes the solids and pores within, therefore, measurements must be taken without compacting or crumbling the samples to correctly determine the bulk density.

Turbidity

Samples for turbidity testing were collected and measured using a HACH® Model TL2350 Portable Turbidity Meter EPA according to the manufacturer’s instructions, repeating the analysis two to three times.

Total Suspended Solids (TSS)

The concentration of suspended solids (SS) in effluent samples was determined in accordance with the established standard method set by American Public Health

Association (2017). The sample bottles were shaken to agitate settled sediments and at the end of mixing the suspended solids were determined by vacuum filtration through pre-weight 0.45 µm Whatman® glass microfibre membrane standard glass fibre filter (GFF) papers to filter out the suspended sediments from the samples. The weighing of filter papers was done using a laboratory analytical balance with precision to 0.1 µg.

Leachate nutrients analysis

The chemical concentration of sulphate ions (SO_4^{2-}), chloride ions (Cl^-), bromide ions (Br^-) in leachate were determined from filtrate samples following the suggested method by Ro et al., (2016) using an ion chromatography - Thermo fisher ICS-100mion chromatography system, the column was a Dionex Ion Pac AS14 (4 x 250 mm) and a guard column also AG14A (4x50mm), while the suppressor was Dionex AERS 500 (Dionex, Sunnyvale, CA, USA), located in the Environment Engineering Research Laboratory at Newcastle University. Instrumental quantification was calibrated using standard nitrite, nitrate and phosphate solutions for a three-point calibration. Aliquots of the samples were extracted using 1 mL single-use sterile syringes and then filtered through 0.2 µm PTFE membrane syringe filters obtained from VWR International (Leicestershire, UK).

Also, nitrogen (N) in form of ammonium (NH_4^+-N), nitrate (NO_3^--N) and nitrite (NO_2^--N) were determined from filtrate samples using the HACH cuvette tests kits LCK 304, LCK 541, and LCK 341, respectively, and measured using Hach® Model Lange benchtop photometer (DR6000 UV-VIS spectrophotometer with RFID technology) to read the samples in accordance with manufacturer's instruction. This enabled an understanding of how much of the chemical ions were leaching into effluent water flowing through the sand filtration system.

Leachate Metals analysis

For cation analyses, first, the effluent solutions were filtered using 0.2 µm PTFE membrane syringe filters obtained from VWR International (Leicestershire, UK) prior to the analysis and preserved by acidifying the samples with concentrated HNO_3 at pH less than 2. The concentration of metals in the acidified effluent solutions were then determined using Varian Vista MPX axial Induced Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) located in the Environment Engineering Research Laboratory at

Newcastle University, operated according to standard methods for the examination of water and wastewater. The difference between the concentrations of metal contaminants in the control and the amended columns was used to calculate the metals leaching in the amended soils. The analysis was initiated immediately as soon as the samples arrived at the laboratory following the methods by Quina, Bordado, and Quinta-Ferreira (2011). The analysed metals include nickel, iron, lead, chromium, manganese, cadmium, and arsenic which were considered as potential threats to the groundwater supply (Quina, Bordado and Quinta-Ferreira, 2011; Kloss *et al.*, 2014).

pH measurement

A laboratory portable Mettler Toledo Quattro MP220 pH meter was used to determine the pH of the unfiltered leachate samples at laboratory room temperature. The use and calibration of the instrument were done according to the manufacturer’s instructions. To take readings, the pH probe was inserted into the samples and the values were recorded after the electrode stabilised. The results of the pH were then compared and analysed.

Total carbon (TC), total organic carbon (TOC) and total inorganic carbon (TIC)

The total dissolved organic carbon (DOC) content in the leachates, as well as the solid total organic content (TOC) of the filtered residues, were measured using their respective carbon analysers. A Leco CS230 Carbon/Sulphur analyser (LECO Corporation, Michigan, USA) located at the Newcastle University laboratories was used to measure total carbon (TC) in the solid (residue) samples. To measure the TOC, after the suspended solids had been extracted from the leachate by filtering the solution using a 0.45 µm Whatman® glass microfiber filters (GFF) paper, the residue was oven-dried at 550°C for 12 hours to convert the organic compounds in solid samples into CO_2 before TC analysis. The residue samples and GFF filter paper were manually transferred and weighed into quartz crucibles and recorded to the nearest 0.1 mg. An empty crucible and GFF paper were also weighed and recorded to the nearest 0.1 mg as method blank. The crucibles were then placed in a crucible tray prepared for analysis as shown in Figure 3-7(a). Calibration of the method was done using a minimum of 5 standards of known carbon content before measuring the samples and method blanks. Measurements were performed in triplicate and the percentage total carbon (TC) content was then calculated for the samples as follows:

$$TC(\%) = \frac{Carbon\ (g)}{W(g)} \tag{3.1}$$

Also,

$$TOC(\%) = \frac{Organic\ Carbon\ (g)}{W(g)} \tag{3.2}$$

Where W(g) is the weight of the dry sediment in grams.

Therefore,

$$TIC(\%) = TC(\%) - TOC(\%) \tag{3.3}$$

On the other hand, the dissolved TOC in the filtrate samples was also measured using the Shimadzu TOC-5050A analyser with ASI-5000A-S-P autosampler liquid analyser located at Newcastle University. This method is a simple direct application by loading up to 8 mL of each of the samples in the auto-sampler shown in Figure 3-7(b) and following the protocol for the measure. Also, a calibration of the machine was done using known standard concentrations.

Figure 3-7 (a) Preparing samples for quantifying the particulate carbon (b) dissolved carbon analyser

3.4.7 Other analytical procedures

Saturated hydraulic conductivity analysis

The hydraulic conductivity (K) is an important hydraulic parameter in measuring soil permeability as it affects infiltration and consequently estimation of contaminant travel time through the soil. Hydraulic conductivity for saturated soil can be evaluated using the equation based on Darcy's law that illustrates the relationship between Darcy's flow velocity of a homogeneous fluid in a porous medium to the applied hydraulic gradient (Desiderio, 2014). The constant of proportionality is Darcy's permeability (or hydraulic conductivity). In that sense, the hydraulic conductivity of the column test materials was determined using a simplified falling-head permeability test technique for the flow which used the level difference between the free water surfaces based on an adaptation from Diminescu et al. (2019) method suitable for fine sand particles as showed in Figure 3-8. Deionised water was gently poured into the column until it was full (of height 11 cm above media height of column) and hydraulic testing was performed after steady flow conditions were attained, usually after 3 – 4 times repetitive flushing of the entire column. In total, about 10,000 mL of leachate was infiltrated during the period of the investigation and K describes the ease of fluid flow through saturated porous media and it can be measured with flow-through experiments or estimated using theoretical or empirical models.

The water flow measurements through each test column were taken 3 times, and the arithmetic mean of the drop in hydraulic head over a known time was used to calculate the K value for each sample (Barnes *et al.*, 2014; Lim *et al.*, 2016b). Hence, the saturated hydraulic conductivity (K) from falling-head data was calculated using the equation (Stibinger, 2014; Liu et al., 2016):

$$K = \frac{L}{t} \cdot \ln\left(\frac{h_1}{h_2}\right) \tag{3.4}$$

Where K is hydraulic the conductivity (cm/s), L is length (cm) of the soil sample in the column, h_1 and h_2 are the initial and final heights (cm) of the free water surfaces in the column measured from the outlet, respectively, and t is time (s) elapsed to decrease water the level from h_1 to h_2. The variables h and t are the changing parameters in the hydraulic conductivity calculation. The porosity was also measured because it is directly related to permeability. The effluent volume was calculated by using the equation:

$$V_{eff} = Qt_{total} \tag{3.5}$$

Where V_{eff} is the effluent volume collected (cm^3), Q is the volumetric flow rate (cm^3/s) and t_{total} is the total flow time (s). After replicate measurements were taken, the samples columns were then air-dried under laboratory room condition overnight. Afterwards, the samples columns were rewetted by flushing with deionised water and the *K* was measured again. The wetting and drying process of the columns and their respective *K* measurements was repeated five times (to avoid too much material losses particularly in the CSBC and CHBC substrates). Simultaneously, for each flush, effluents samples with collected and stored at 4 for further analytical measurements.

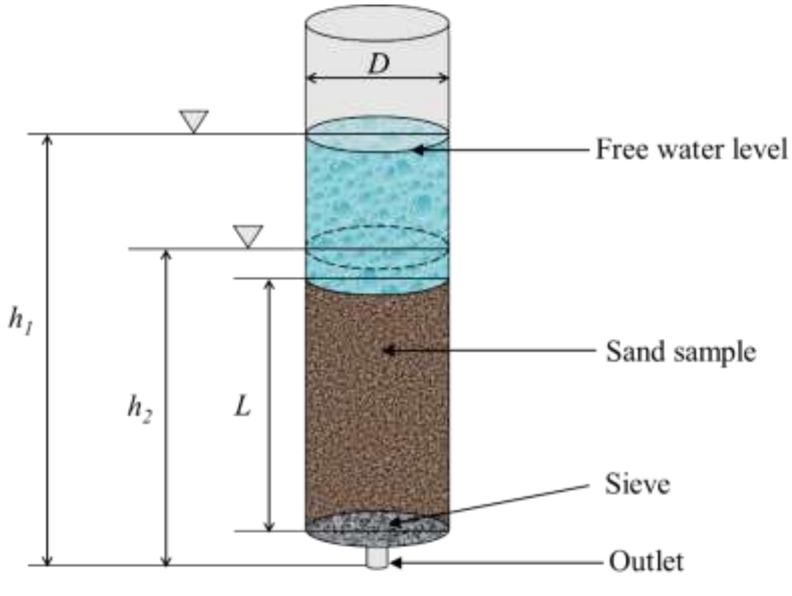


Figure 3-8 Schematic diagram for the measurement of the saturated Hydraulic Conductivity by a falling-head method.

3.4.8 Statistical analysis

To determine the influence of sand amendment on leachate properties over time, the statistical assessments of possible differences among the physical parameters between the various treatments were determined. All data were statistically analysed using means, standard deviations, analysis of variance (ANOVA) in Microsoft Excel 365. Occasionally, means were compared using student *t*-tests with a level of significance ($p < 0.05$) were used to determine differences between the treatments. Different letters in the figures indicate significant differences between the treatments. P-values in the legends indicate the error probability of an effect of the amendments on the respective parameters. The obtained values of each parameter were compared with the global standard values set by the World Health Organization (WHO), as well as local standards such as UK Drinking Water Inspectorate (DWI) and the European Union guidelines.

3.5 Results and discussion

This section outlines the results and significant findings of the short-term laboratory column testing as well as long-term lysimeter testing. Long-term testing was essential in this study to determine the changing of the leachate characteristics through the filtration system over a period. The column studies were run in duplicates while the sampling and measurements taken were also done in triplicates. The data are thus presented as mean ± SD (standard deviation).

3.5.1 Physical characterisation of the column media materials

Important factors which influence the leachate hydraulic performance in a column filtration system are the media solid composition and compaction. Generally, the hydraulic permeability with similar column media types may be different due to differences in compaction and operational conditions. The proximate and ultimate analysis results of the different biochar types after pyrolysis have been reported in Section 3.4.2 above. However, the basic physical properties of the sand used in this study are summarised in Table 3-3. The other basic properties of the different amendment mixtures, including density and porosity, were measured and the results are shown in Figure 3-9.

Table 3-3 Physical properties of the fine sand

Properties	Units	Fine sand
Mean grain size, D_{50}	(mm)	0.361
Coefficient of uniformity, $C_u=D_{60}/D_{10}$	-	2.332
Coefficient of graduation, $C_c=(D_{30})^2/(D_{10}*D_{60})$	-	0.656
Hydraulic conductivity, K	(cm/s)	0.011
Bulk density	(g/cm^3)	2.620
Porosity (%)	(%)	38.9

Bulk density and porosity

Bulk density for each tested filter media was determined using the dry masses of each sample and the volume of water displaced by the sample. Although bulk density lower than 1.00 will float in water (Khawkomol *et al.*, 2021), the amended sand media columns had lower bulk densities (1.89, 2.09, 1.63, 1.67, and 2.48 g/cm^3 for the CSBC, CHBC, RSBC, CCBC, and GAC, respectively) than the FISA control (2.62 g/cm^3). Also, the initial porosity measurements of the amended materials are as shown in Figure 3-9.

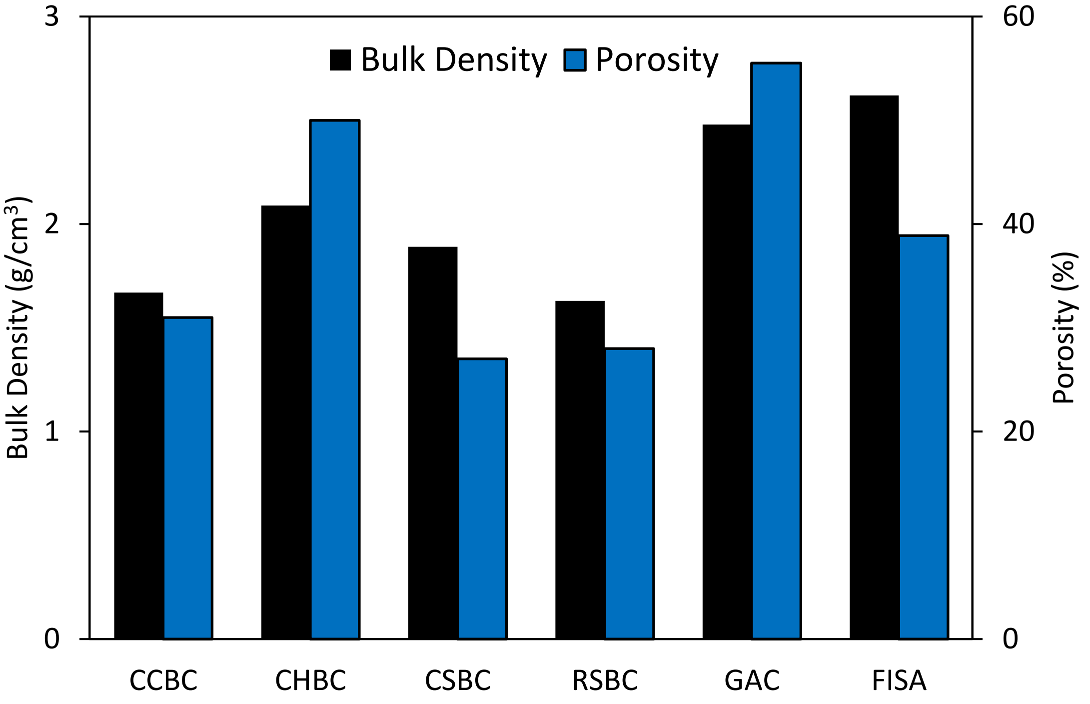


Figure 3-9 Measured density and porosity values for the different amendments, following the addition of biochar (3%) to fine sand. Abbreviation: CCBC, corn cob biochar; CHBC, coconut husk biochar; CSBC, coconut shell biochar; RSBC, rice straw biochar; GAC, activated carbon; FISA, unamended control.

Particle size distributions of fine and coarse sand

Figure 3-10 shows the particle size distribution for the fine sand and coarse sand used in this study. The fine sand curve followed a good distribution with particles generally constricted to 150 – 425 µm and distribution over a range of 63 – 1180 µm. The coarse sand particles on the other hand are somewhat larger, with mean particle sizes occurring near 600 – 1180 µm and distribution over 250 – 2000 µm. From the results (Figure 3-10), coarse sand had a D_{10} of 0.33 mm and C_u of 3.00 while the fine sand had a D_{10} of 0.19 mm and C_u of 2.33. D_{10} is the effective size of the particles equivalent to particle diameter at which 10% of particles are smaller, while D_{60} is the particle diameter below 60%.

Uniformity Coefficient (C_u), on the other hand, is a measure of the uniformity of the particle sizes and is defined as the ratio of D_{60} to D_{10}. Previous studies with sand filters (Carty and Bourke, 1995; Huisman and Wood, 2015; Grace, Healy and Clifford, 2016) suggested that for sand selection for a filtration system, the D_{10} should be in the range of 0.15 – 0.35 mm and C_u should be less than 3. Therefore, following the recommended values, the D_{10} values for coarse and fine sand are within the range. However, the C_u value for the coarse sand exceeds the limit which placed the fine sand material as a better option for the sand component of the sand amendment used in all column experiments in the thesis.

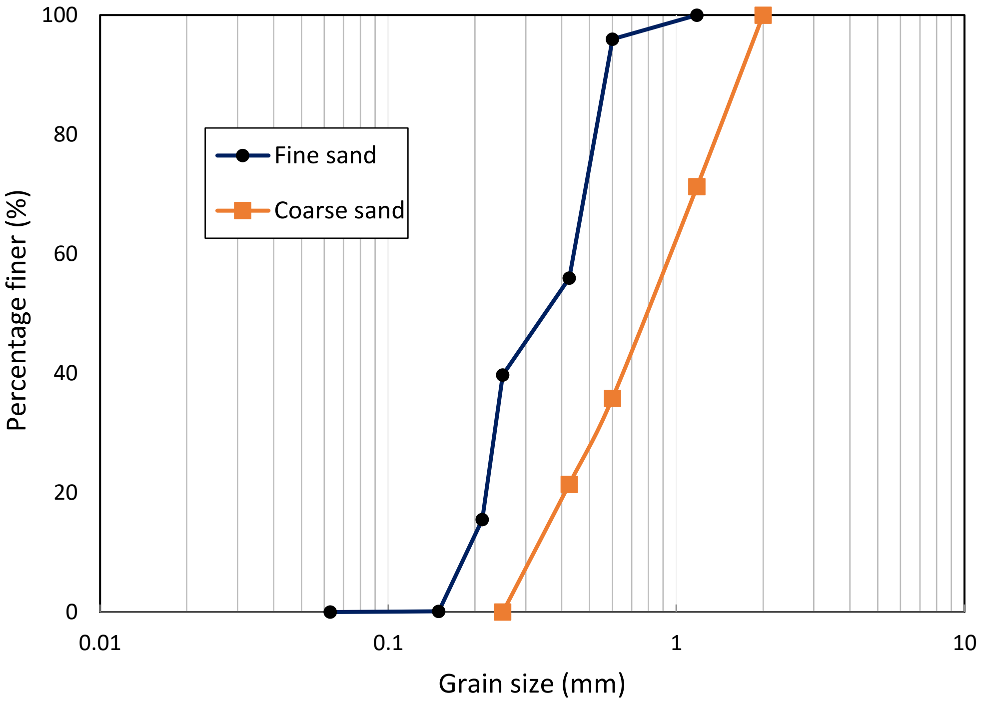


Figure 3-10 Particle size distribution for fine sand and coarse sand materials.

3.5.2 Influence of amendments on leachate quality and hydraulics in laboratory column study

The individual fixed-bed columns were tested to analyse the effect of biochar and activated carbon amendment on the hydraulic conductivity of each column and the impact each has on the chemical properties of the leachate collected in terms of pH, anion and cation composition.

Influence on hydraulic characteristics in columns

The addition of biochar and activated carbon amendment to sand changed a number of physical properties in the amended columns which would affect their hydraulic properties (Barnes *et al.*, 2014). The daily flow results from the experiment are presented in Figure 3-11 and showed the impact of the amendment on K in the different filters. The results showed significant statistical differences ($P<0.05$, 95% confidence level) in the average K values of the CCBC and CHBC columns, which decreased K by 54.7% and 36.9%, respectively, compared with the unamended FISA. This difference is justified by the increased turbidity (which is discussed in the later section), and the resulting clogging effect due to the leaching of fine BC particles into the media pore spaces. Although the results in Table 3-4 showed an apparent increase in the average K values of CSBC, RSBC and GAC amendments which corresponded to 11.6% ($p=0.119$), 11.3% ($p=0.046$) and 11.5% ($p=0.245$), respectively, no significant statistical differences ($P>0.05$) were observed compared to the unamended FISA.

The trend in the volumetric flow rate for each amendment appeared to follow the hydraulic conductivity for each column as shown in Table 3-5. Table 3-4 showed the hydraulic conductivity values for each column test taken for 2 weeks and it also showed that although the hydraulic conductivity fluctuated slightly throughout the 12 daily cycles, the results when comparing amendments using a one-way ANOVA are statistically significant ($p<0.001$), which justifies the influence of the different amendment types and particle size on the hydraulic performance of the filters (Barnes *et al.*, 2014). Although the average flow rates for CCBC, CHBC, CSBC, RSBC, and GAC was 0.015, 0.009, 0.022, 0.022, 0.030, and 0.020 L/min, respectively, are too low based on various filtration design models, as they fall outside the prescribed range 0.6 – 1.0 L/min of according to Elliott et al. (2008). This, according to the author, indicated that the particle size of the media was too small and requires further washing before use. The decline in the flow rate over time as observed was due to filter maturation, compression of the filter media and the increment of head-loss of the filtration system as shown in Figure A4. Flow rates are highly dependent on the sand grain distribution, sand depth and quality of raw water (Elliott *et al.*, 2008).

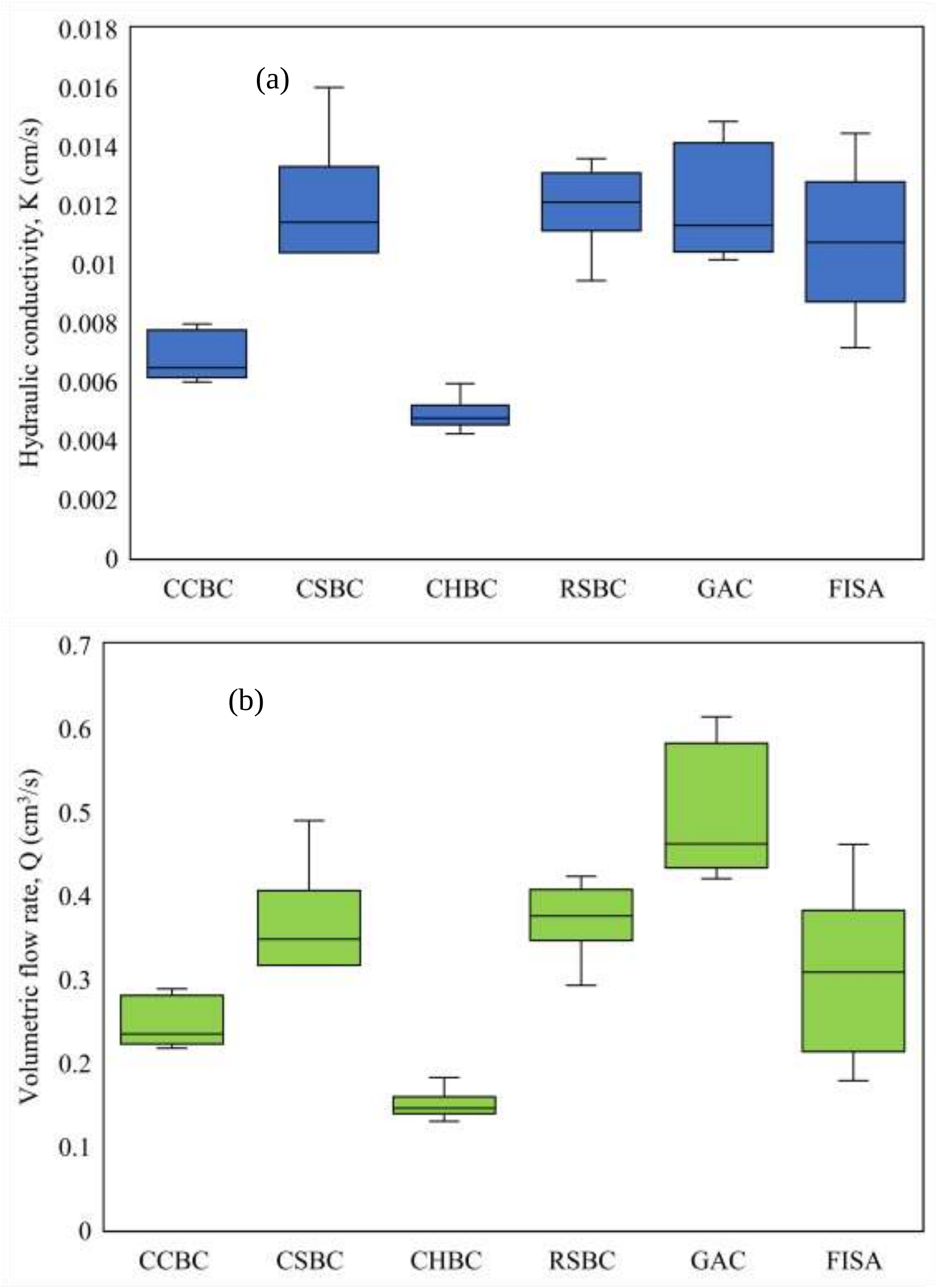


Figure 3-11 Box-and-whisker plots for comparing the (a) hydraulic conductivity and (b) volumetric flow rates for all columns test measurements, following the addition of biochar (3%) to fine sand. Abbreviation: CCBC, corn cob biochar; CHBC, coconut husk biochar; CSBC, coconut shell biochar; RSBC, rice straw biochar; GAC, activated carbon; FISA, unamended control.

Table 3-4 Falling head permeability test results, following the addition of biochar (3%) to fine sand. Abbreviation: CCBC, corn cob biochar; CHBC, coconut husk biochar; CSBC, coconut shell biochar; RSBC, rice straw biochar; GAC, activated carbon; FISA, unamended control.

Type of sand amendment	Day	CCBC	CHBC	CSBC	RSBC	GAC	FISA
K (cm/s)	1	0.00609	0.00642	0.02020	0.00651	0.01010	0.01250
	2	0.00542	0.00522	0.00977	0.00490	0.00989	0.00331
	3	0.00633	0.00708	0.00963	0.00951	0.01250	0.00456
	4	0.00544	0.00660	0.00946	0.00990	0.01520	0.01000
	5	0.00488	0.00581	0.00873	0.01116	0.01340	0.00533
	6	0.00488	0.00581	0.00873	0.01224	0.01470	0.00577
	7	0.00925	0.00332	0.01180	0.01713	0.01020	0.01640
	8	0.00653	0.00322	0.01320	0.01395	0.01110	0.01100
	9	0.00957	0.00476	0.01310	0.01519	0.00959	0.01390
	10	0.00804	0.00329	0.01534	0.01595	0.01450	0.01230
	11	0.00748	0.00343	0.01200	0.01220	0.00971	0.01920
	12	0.00748	0.00343	0.01200	0.01490	0.01310	0.01490
Average (cm/s)		0.00678	0.00487	0.01200	0.01200	0.01200	0.01080
StdDev		0.00160	0.00148	0.00330	0.00377	0.00213	0.00507

Table 3-5 Volumetric flow rates of the different amendment types, following the addition of biochar (3%) to fine sand. Abbreviation: CCBC, corn cob biochar; CHBC, coconut husk biochar; CSBC, coconut shell biochar; RSBC, rice straw biochar; GAC, activated carbon; FISA, unamended control.

Type of sand amendment	Day	CCBC	CHBC	CSBC	RSBC	GAC	FISA
Q (cm^3/s)	1	0.2310	0.1940	0.6230	0.2050	0.3780	0.4160
	2	0.2060	0.1580	0.3010	0.1540	0.3700	0.1100
	3	0.2400	0.2140	0.2970	0.2990	0.4690	0.1530
	4	0.2070	0.2000	0.2910	0.3120	0.5680	0.3340
	5	0.1850	0.1760	0.2690	0.3510	0.5010	0.1780
	6	0.1850	0.1760	0.2690	0.3860	0.5490	0.1930
	7	0.3240	0.1040	0.3560	0.5290	0.4610	0.5060
	8	0.2290	0.1010	0.3980	0.4310	0.5040	0.3380
	9	0.3360	0.1500	0.3950	0.4690	0.4360	0.4280
	10	0.2820	0.1030	0.4640	0.4920	0.6590	0.3770
	11	0.2620	0.1080	0.3630	0.3770	0.4410	0.5890
	12	0.2620	0.1080	0.3630	0.4600	0.5960	0.4590
Average (cm^3/s)		0.2457	0.1500	0.3660	0.3720	0.4940	0.3400
StdDev		0.0496	0.0427	0.1000	0.1150	0.0870	0.1520

The relationships between volumetric flow rate (Q) and hydraulic conductivity (*K*) are illustrated in Figure 3-12 for the different media types. The plots of the average volumetric flow showed a nearly perfect proportional relationship to *K* (R^2>0.99) for most amended columns. However, GAC has most data points scattered far from the fitting line with an R^2 value of 0.69. The order of proportionality for the individual column tested seen to be RSBC > CHBC > FISA > CSBC > CCBC >> GAC. Using Darcy's law which says that as the volumetric flow rate increases, the hydraulic conductivity also increases, it then follows that the flow in all the media columns appears to be Darcian.

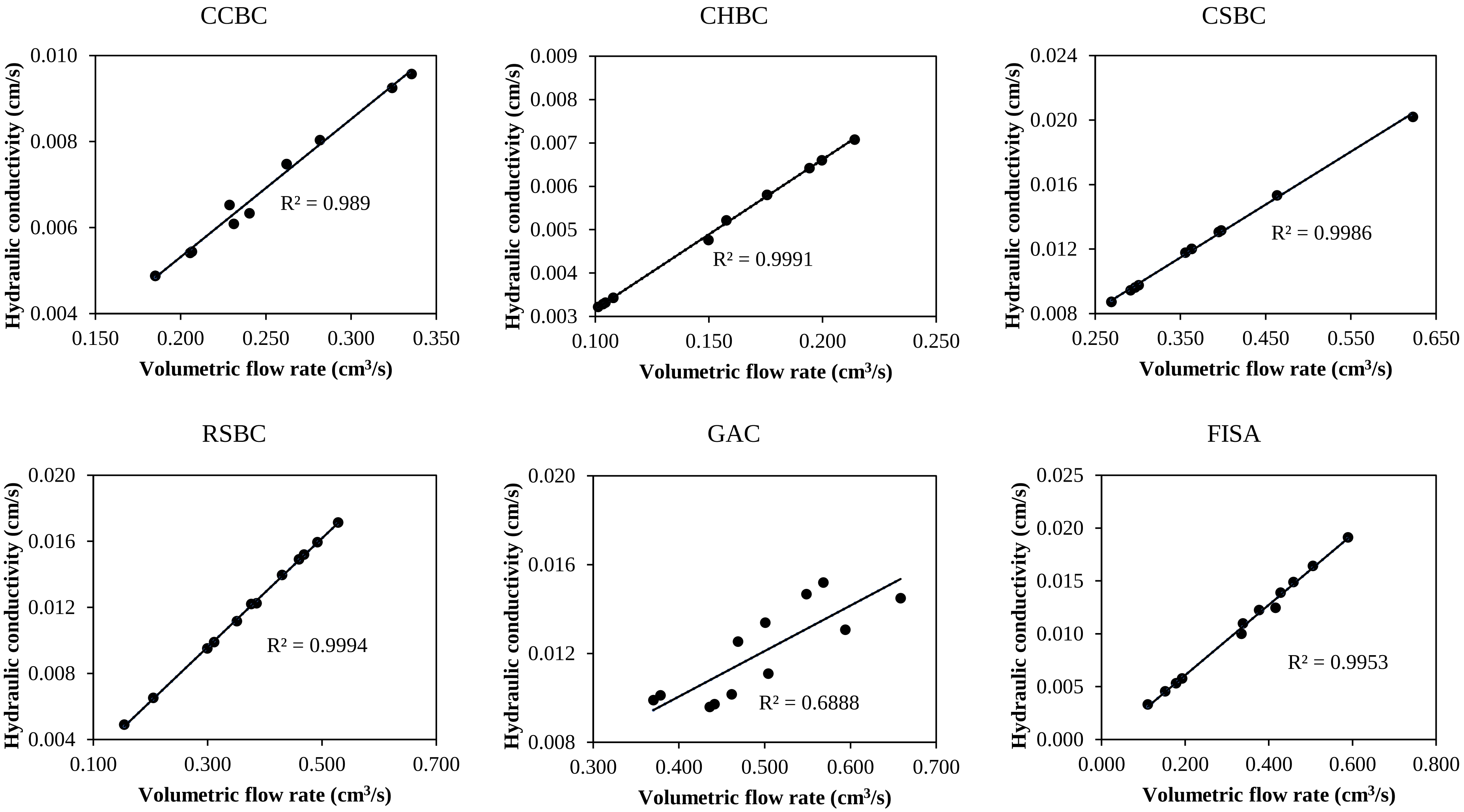


Figure 3-12 Correlations between the hydraulic conductivity and volumetric flow rates for the flow through the different amendment types, following the addition of biochar (3%) to fine sand. Abbreviation: CCBC, corn cob biochar; CHBC, coconut husk biochar; CSBC, coconut shell biochar; RSBC, rice straw biochar; GAC, activated carbon; FISA, unamended control. Data points represent the relationships between both quantities at the various sampling intervals throughout the continuous flow experiment.

Influence on leachate TSS and turbidity in columns

TSS and turbidity are the most important physical parameters of raw water quality. The concentration of suspended solid matter in the leachates was measured for each amendment type throughout the period investigated. The mean level of TSS in the leachates was analysed as shown in Figure 3-13. However, the suspended solids in the leachates fluctuated over the 6 weeks of measurement as shown in Figure 3-14. Moreover, the leachate TSS concentrations were higher for CCBC, CHBC and CSBC amendments. It is likely that the destabilization of particles during saturation creates more mobile, finer particles that migrated through the pore spaces resulting in high peaks of leachate turbidity. The same features are seen in the microscopy image of TSS on filters for the different amendments shown in Figure A3. Although the author could not find set standards for TSS for WHO and UK (Table 3-6), Rahmanian et al. (2015) suggested a maximum recommended TSS limit set by National Drinking Water Quality Standard (NDWQS) is 25 mg/L, which makes all leachates TSS of no concern, as they are well below the maximum standard limit of 25 mg/L. Also, Arden and Ma (2018) reported that the allowable TSS concentration for discharge effluents is set to 30 mg/L, again suggesting the TSS in leaching effluents from all amendments in the experiments are within allowable means and are not a concern to groundwater recharge.

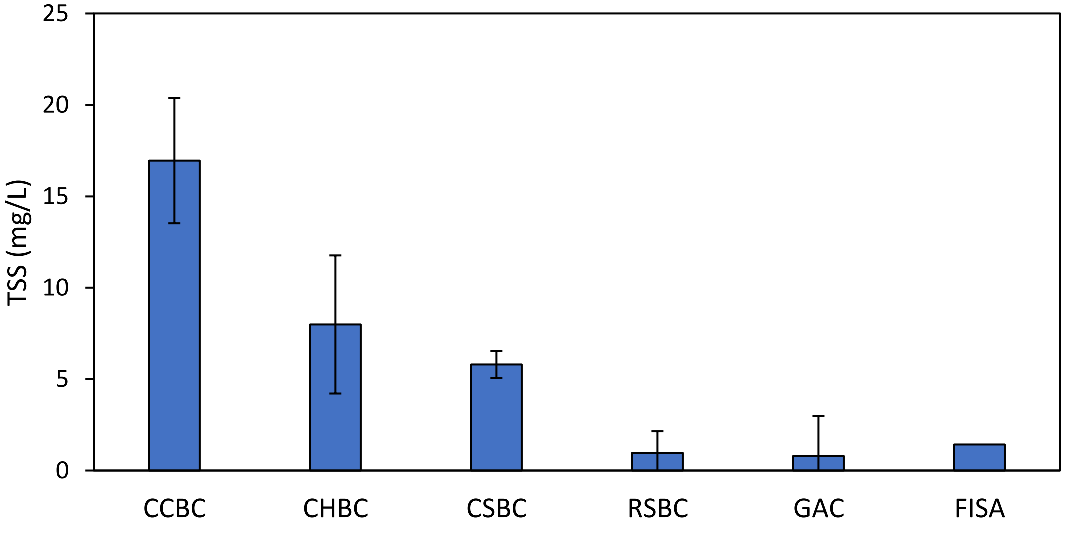


Figure 3-13 Average values of total suspended solids (TSS) in leachate samples from the column experiments over the investigation period, following the addition of biochar (3%) to fine sand. Abbreviation: CCBC, corn cob biochar; CHBC, coconut husk biochar; CSBC, coconut shell biochar; RSBC, rice straw biochar; GAC, activated carbon; FISA, unamended control.

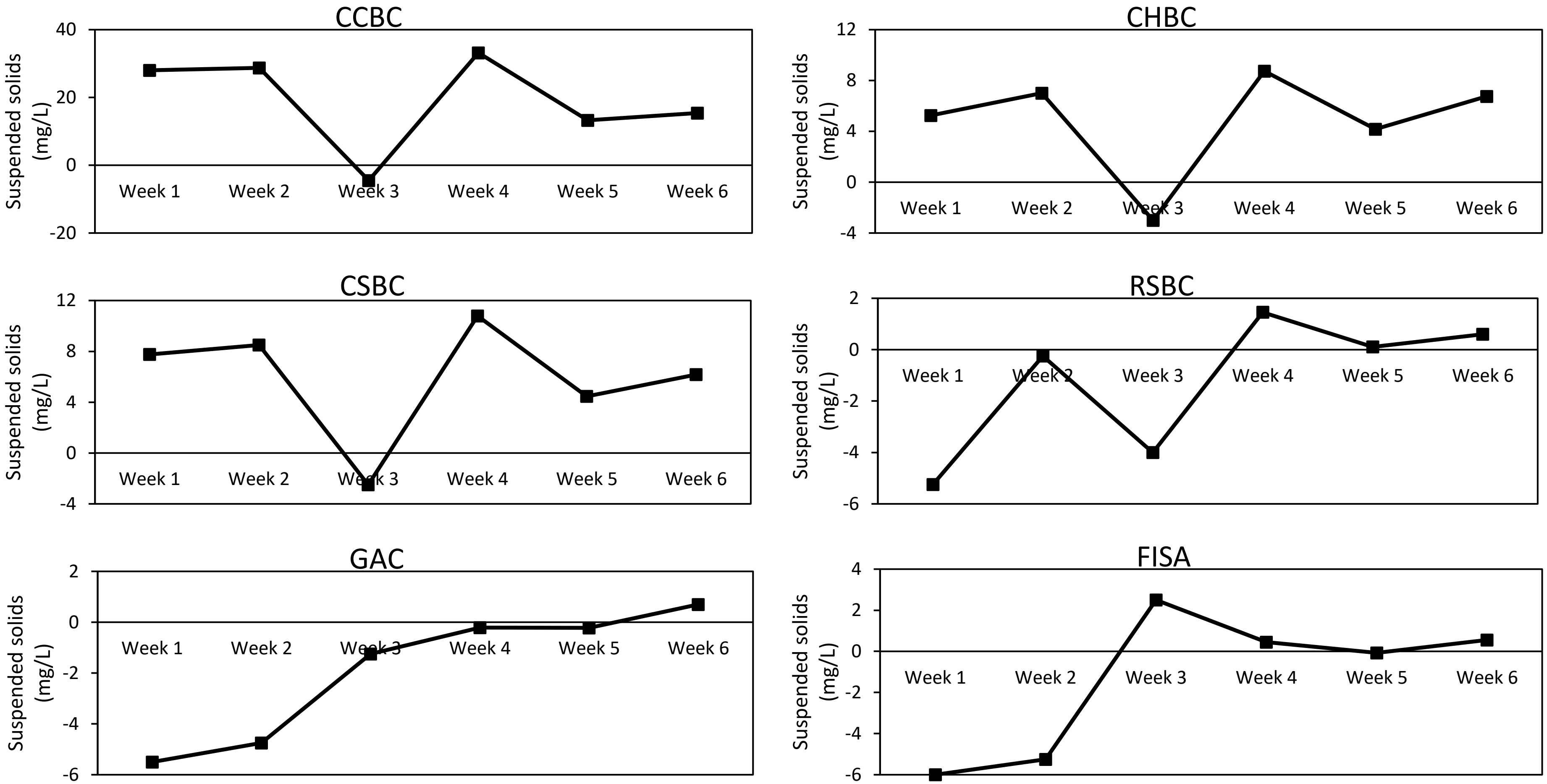


Figure 3-14 Suspended solids concentrations in leachates during the experimental period, following the addition of biochar (3%) to fine sand. Abbreviation: CCBC, corn cob biochar; CHBC, coconut husk biochar; CSBC, coconut shell biochar; RSBC, rice straw biochar; GAC, activated carbon; FISA, unamended control. Negative values are errors due to the difficulty of measuring small differences in the filter weight before and after the filtration and drying.

Table 3-6 Comparative WHO and EU/UK water quality recommendations for drinking water in comparison with leachates characterisations from the different biofilters, following the addition of biochar (3%) to fine sand. Abbreviation: CCBC, corn cob biochar; CHBC, coconut husk biochar; CSBC, coconut shell biochar; RSBC, rice straw biochar; GAC, activated carbon; FISA, unamended control. WHO and EU do not have set guidelines or standards for TSS, pH and turbidity in drinking water. Where measured values exceed guidance values this has been indicated in bold.

Parameters	WHO[1,5,6,7]	EU/UK[1,2,3,4]	CCBC	CHBC	CSBC	RSBC	GAC	FISA
Physical parameters**								
TSS (mg/L)	n.a	n.a	17.0	5.8	8.0	1.0	0.8	1.4
Turbidity (NTU)	<5*	4	**17.4**	**7.40**	**5.03**	1.03	0.37	0.29
pH	6.5-9.5*	6.5 - 9.5	**10.6**	**10.8**	7.8	**11.0**	**5.8**	**7.3**
Chemical parameters (mg/L)								
NO_3-N	50	50	<10	<10	<10	<10	<10	<10
NO_2-N	0.5	0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
NH_4-N	1.5	0.5	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Cl	250	250	<100	<100	<100	<100	<100	<100
SO_4	500	250	<20	<20	<20	<20	<20	<20
Br	n.a	0.01	n.d	n.d	n.d	n.d	n.d	n.d
As	0.01	0.01	**>0.01**	**>0.01**	**>0.01**	**>0.01**	**>0.01**	0.01
Cd	0.03	0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Pb	0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	2	2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Fe	0.3*	0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Zn	3	n.a	<1	<1	<1	<1	<1	<1
Mn	0.5	0.05	<0.01	<0.01	<0.01	<0.01	**0.07**	<0.01
Cr	0.05	0.05	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ni	0.02	0.02	<0.01	<0.01	<0.01	<0.01	<0.02	<0.01
Al	0.1	0.2	**0.11**	**0.12**	**0.10**	<0.1	**0.14**	<0.1

1. Anon (2016) 2. Fawell (2012) 3. Drinking Water Inspectorate (2017) 4. NIEA (2014)
5.Rickwood (2007) 6. WHO (World Health Organization) - regional office for Europe (2017) 7. Kumar (2012)
n.d – not detected n.a – not available or does not set a standard * Desirable
** No WHO/EU set standards for drinking water (www.lenntech.com/who-eu-water-standards.htm, sourced 20/03/21

In terms of turbidity, although leachate from RSBC, GAC and FISA reliably met the 4 NTU criteria for drinking water reuse, the change in leachate turbidity also appeared to be in line with the change in TSS for the different amendments. Although the average turbidity values for CCBC, CHBC and CSBC are higher than the control unamended sand (FISA) as shown in Figure 3-15, they are observed to be higher than the recommended limit for drinking water by over 350%, 138% and 57%, respectively. These significantly high turbidity values are a concern for field soil applications of the biochars as they could potentially influence the quality of percolating leachate and groundwater supply.

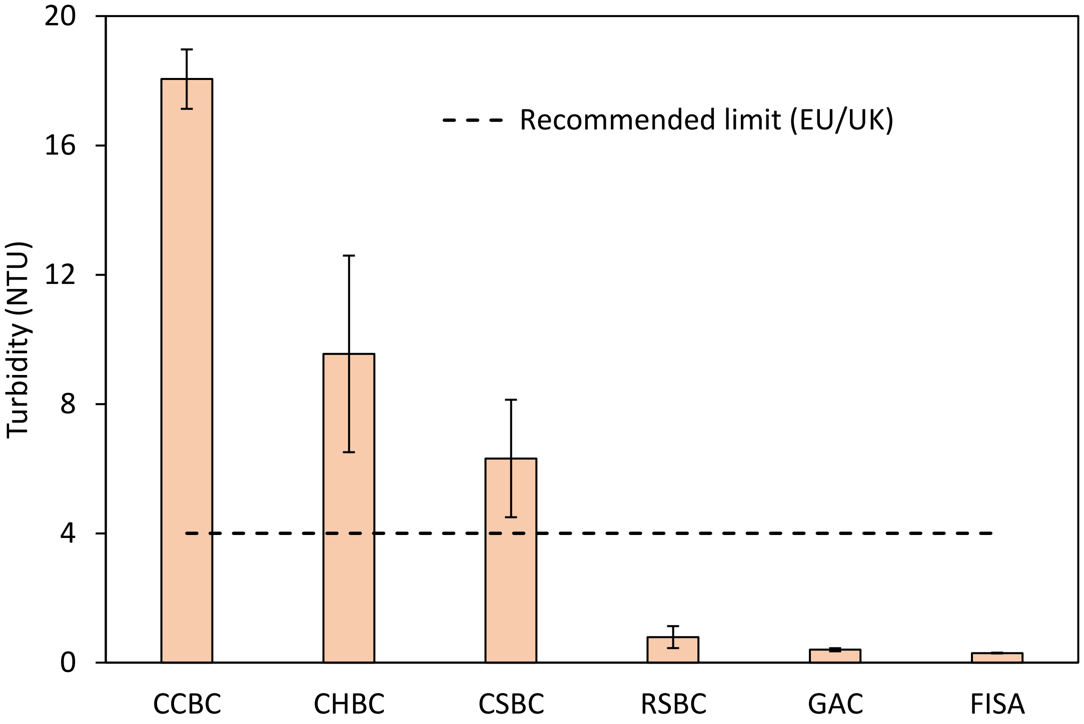


Figure 3-15 Turbidity measurements of effluent samples from the column experiments, following the addition of biochar (3%) to fine sand. Abbreviation: CCBC, corn cob biochar; CHBC, coconut husk biochar; CSBC, coconut shell biochar; RSBC, rice straw biochar; GAC, activated carbon; FISA, unamended control. Broken lines showing the recommended limit for drinking water.

Influence on leachate pH in columns

The pH is an important parameter of leachate, which influences the availability and usefulness of water in the ecosystem. Researchers have shown that the pH of soil media can influence the soil properties and metals leaching ability of the soil. In this study, the pH of the sand was slightly lower with GAC amendment (<7), whereas it became more alkaline with biochar amendment due to the biochars rich content of alkaline minerals, mainly carbonates of Ca^{2+}, Mg^{+} and K^{+} (Vamvuka, Esser and Komnitsas, 2020). The data presented in Figure 3-16 indicated that the biochar sand amendments were all alkaline with pH values ranging from 7.90 (± 0.66) to 10.15 (± 0.86) in the order CSBC < CCBC < CHBC < RSBC. This order of increase in pH correlated positively with the increase in ash content of the different biochars as shown in Table 3-2. This finding is in line with those of Berek and Hue (2013) and Tomczyk, Sokołowska and Boguta (2020), which explained that the pH values of biochars are associated with the formation of ash content and oxygen functional groups that occur during pyrolysis. It can also be noticed that the maximum pH values were slightly higher than the EU/UK recommended MCL for drinking water in . For most of the leaching events throughout the study, the RSBC and CHBC leachate pH measurements were higher than for the other amendment types, and the GAC leachate pH was lower than that from columns containing the biochar. Several previous studies indicated that the alkalinity of biochar is attributed to the presence of alkaline components such as organic anions (Yuan, Xu and Zhang, 2011), carbonate and other inorganic alkalis (Lee *et al.*, 2013; Fidel *et al.*, 2017; Tomczyk, Sokołowska and Boguta, 2020), and functional groups (Yuan, Xu and Zhang, 2011; Kinney *et al.*, 2012; Berek and Hue, 2013).

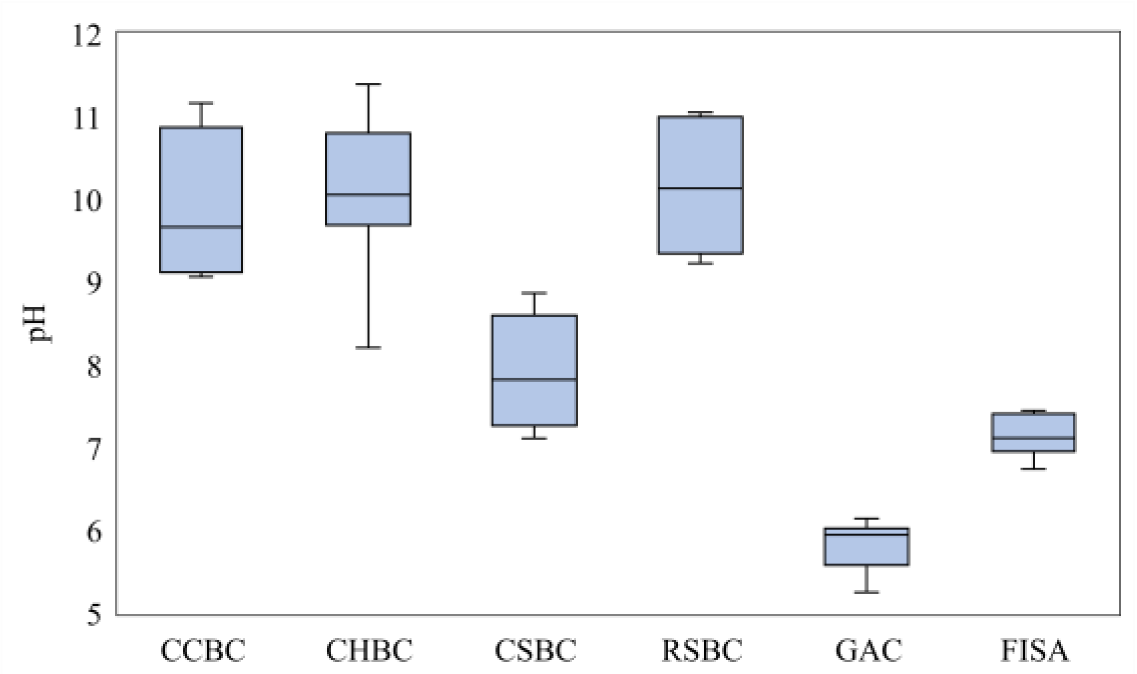


Figure 3-16 Box-and-whisker plots for comparing the pH analysis of the effluent samples for the different column amendments collected throughout the experiments (n=3), following the addition of biochar (3%) to fine sand. Abbreviation: CCBC, corn cob biochar; CHBC, coconut husk biochar; CSBC, coconut shell biochar; RSBC, rice straw biochar; GAC, activated carbon; FISA, unamended control.

The plots showed that the amendment of sand with biochar or GAC significantly altered the pH of the leachates. The leachate pH for GAC was lower than for the control, with a pH of 5.82 (±0.02). This observation could explain the data from Figure 3-16, where the leachate samples from GAC had the highest metals concentration and thus, it became apparent that the pH is a critical parameter of filter medium amendments, which impacts on pH-sensitive water-porous media interactions (Fidel *et al.*, 2017) and the ability for the amended matrix to adsorb and retain cations (Yuan, Xu and Zhang, 2011). It could be observed in general that there was only a slight change in pH with time for all the measured leachate samples throughout the experiment, as represented in Figure 3-16.

Influence on leaching nutrients in columns

Figure 3-16 show the results of the leaching of ammonium, nitrite, nitrate, chloride, and sulphate, respectively, from the different sand amendments at the start and end of the experiments. The test results shown are an average of four measurements obtained based on replicate tests. The control column tests were conducted with fine sand alone while, in addition, a blank test was conducted using deionised water.

The test results also showed that the nutrient concentrations leaching out of all sand amendments used in this experiment were within acceptable limits for drinking water as indicated in Table 3-6. However, the initial concentrations of chloride in leachate samples from the RSBC, CCBC and CHBC with high pH were shown to be fairly high with 127±20.5 mg/L, 139±10.3 mg/L and 148±17.2 mg/L, respectively, nearing the 250 mg/L MCL benchmark. This is over 98% higher than for the rest of the sand amendments used in this study.

Leachate from sand amended with GAC is observed to have higher concentrations of sulphate ion (97.04±4.48 mg/L) at the start of the experiment. The standard deviation value was relatively small, indicating that within duplicate column test measurements, the variation was minimal. Clearly, all the columns released ions in this experiment but at different rates for different amendments. Notably, the concentration of anions released was reduced by up to 95% between the start and end of the experiments, as represented in Figure 3-16 for the leaching of sulphate ions by GAC. Therefore, the impact of nutrient leaching from the sand amendments would be temporary.

Not surprisingly, cumulative leaching throughout the study for all three nitrogen (N) parameters tended to follow the same pattern in the concentration reduction between the start and end of the experiment as shown in Figure A5. Nitrate and nitrite ions tend to be highly soluble, so chemical precipitates are unlikely to form. Hence, the leaching out of these ions from all amendment types may be attributed to their hydrophilic property to interact with water molecules in the sand. In contrast to the sand only column, the addition of CSBC to the sand did not significantly increase the release of NO_3–N, NO_2–N and NH_4–N in the leachate as shown in Figure 3-17. This suggests that while the biochar and activated carbon added leachable ions to the sand, these amendments are also capable of adsorbing and mitigating some ions from the influent and thus leaching out from the porous matrix. In this study, deionized water was used as an influent, and therefore only the effect of the amendments on the nutrient release into leachate became apparent.

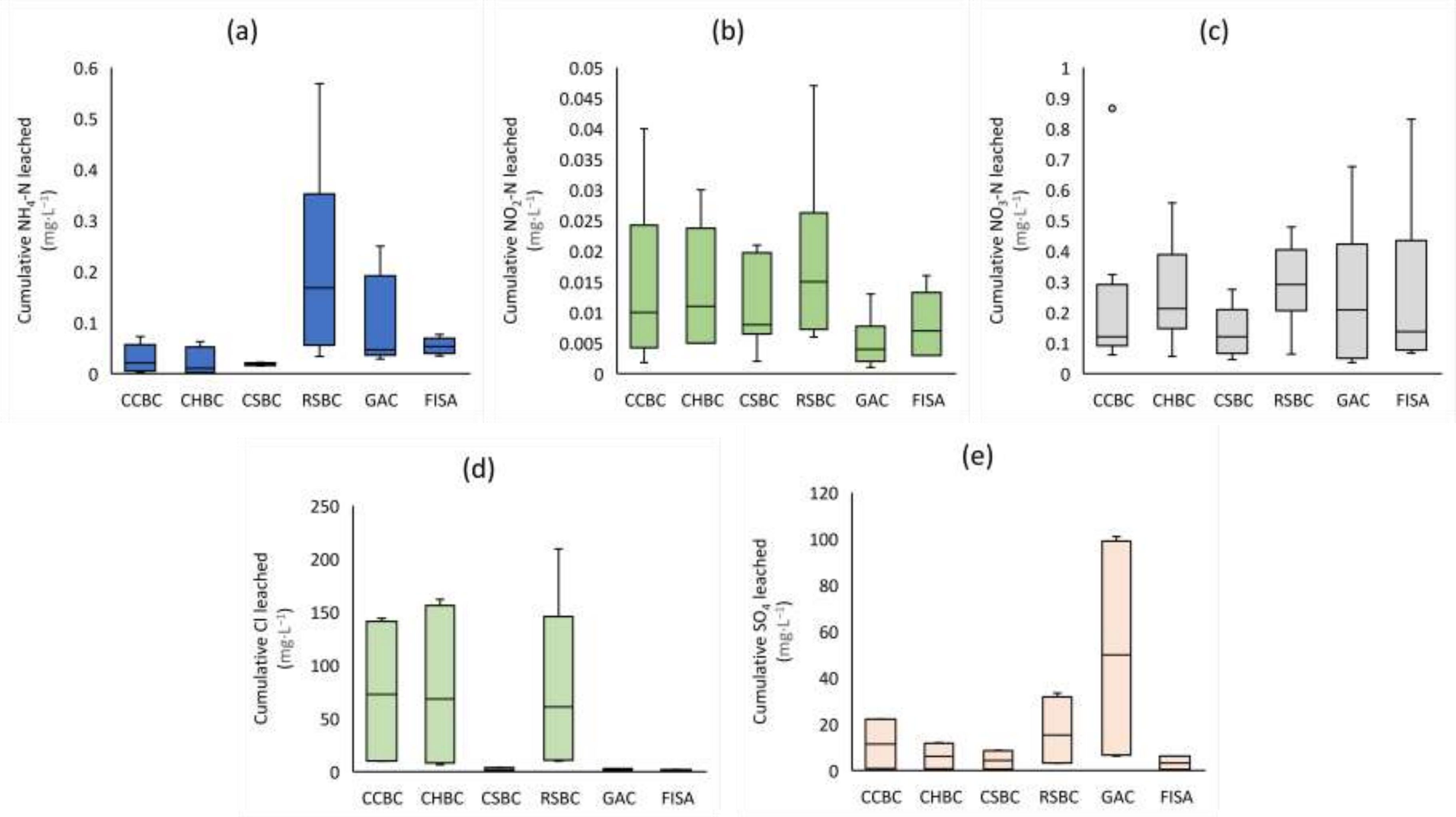


Figure 3-17 Cumulative quantities of (a) NH_4–N (b) NO_2–N (c) NO_3–N (d) Cl and (e) SO_4 leached from the columns (n=3), following the addition of biochar (3%) to fine sand. Abbreviation: CCBC, corn cob biochar; CHBC, coconut husk biochar; CSBC, coconut shell biochar; RSBC, rice straw biochar; GAC, activated carbon; FISA, unamended control.

Influence on leaching of metals and trace elements in columns

The influence of sand amendments applications on the concentrations of metals in the leachates is represented in Figure 3-18. Despite the difference in the quantity of leached metals at the start of the experiment between the unamended sand control and the amended sand as illustrated in Figure 3-19, the results showed the effect of the different sand amendment types on the leaching behaviour of the different metals. In general, the results of the leachate analyses (Figure 3-18 and Figure 3-19) showed that the application of sand amendments significantly increased the concentration of metals in the leachates relative to the control, with GAC leachate having a higher leached concentration of most toxic metal ions (such as Cu, Cd, Zn, Ni, Mn) leached out than other sand amendments. As stated earlier in this study, this difference agrees with the low pH value of GAC compared to all other amendment combinations. Furthermore, the variations in the leached concentrations are partly due to differences in the solubility of the various compounds containing these elements, and partly due to differences in pore structure and sizes (Vamvuka, Esser and Komnitsas, 2020).

While the release of Ca is reduced in all biochar amendment applications, most metal significantly increased in the leachates of columns after amendment application. The most prevalent among the leached metals are As, Al, Fe and K with an increase of 40 – 150%, 100 – 2000%, 100 – 6000%, and 1000 – 60000%, respectively, relative to the unamended sand. Among the numerous factors affecting the leaching of trace elements from biochars such as mineralogical and chemical compositions, various reaction kinetics, permeability and cation exchange capacity (CEC), the high pH of leachates for the biochar amendments, as previously shown, was a key factor for the low metal extractability (Alaboudi, Ahmed and Brodie, 2019). As can be seen from Figure 3-19, Ca, Al, Zn, Cu, Ba, and Mn were extracted at higher concentrations from GAC amended sand, while CHBC has the lower leached concentrations for most measure species. Overall, the findings suggest that despite the differences between the controls and the amended sands observed for all measured metals, and given the decline in leached concentrations over time, most measured leached out metals for all amendments (except As for all amendments, and Mn and Al for GAC amendment) were below the EU/UK set out standards for drinking water and so do not pose a reasonable risk to groundwater supply or the environment in a long-term application, as shown in Table 3-6.

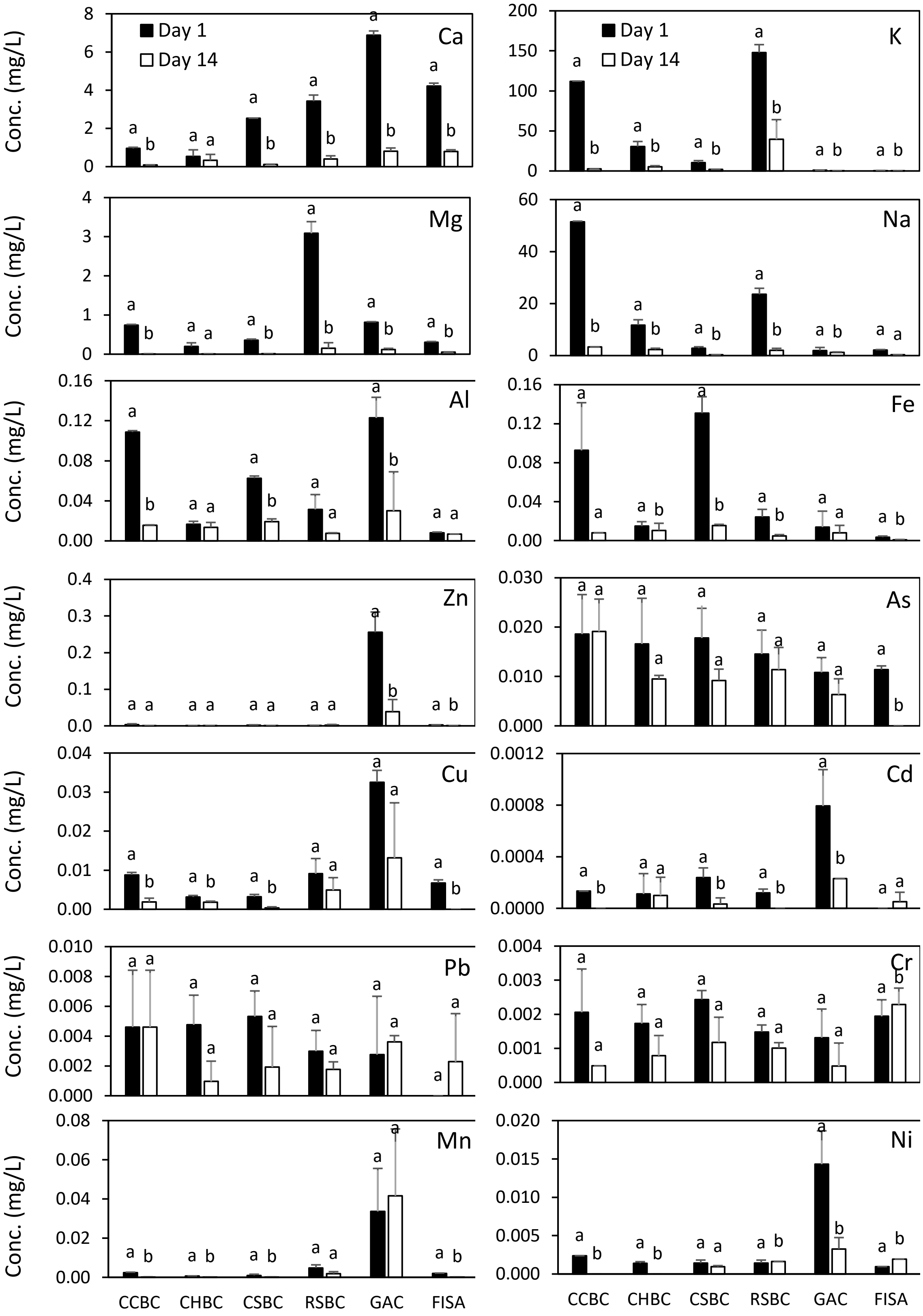


Figure 3-18 Comparing the metals concentrations in leachates from different column amendments collected 1 and 14 days after the start of the experiments. Data are the mean with SD (error bar). Abbreviation: CCBC, corn cob biochar; CHBC, coconut husk biochar; CSBC, coconut shell biochar; RSBC, rice straw biochar; GAC, activated carbon; FISA, unamended control.

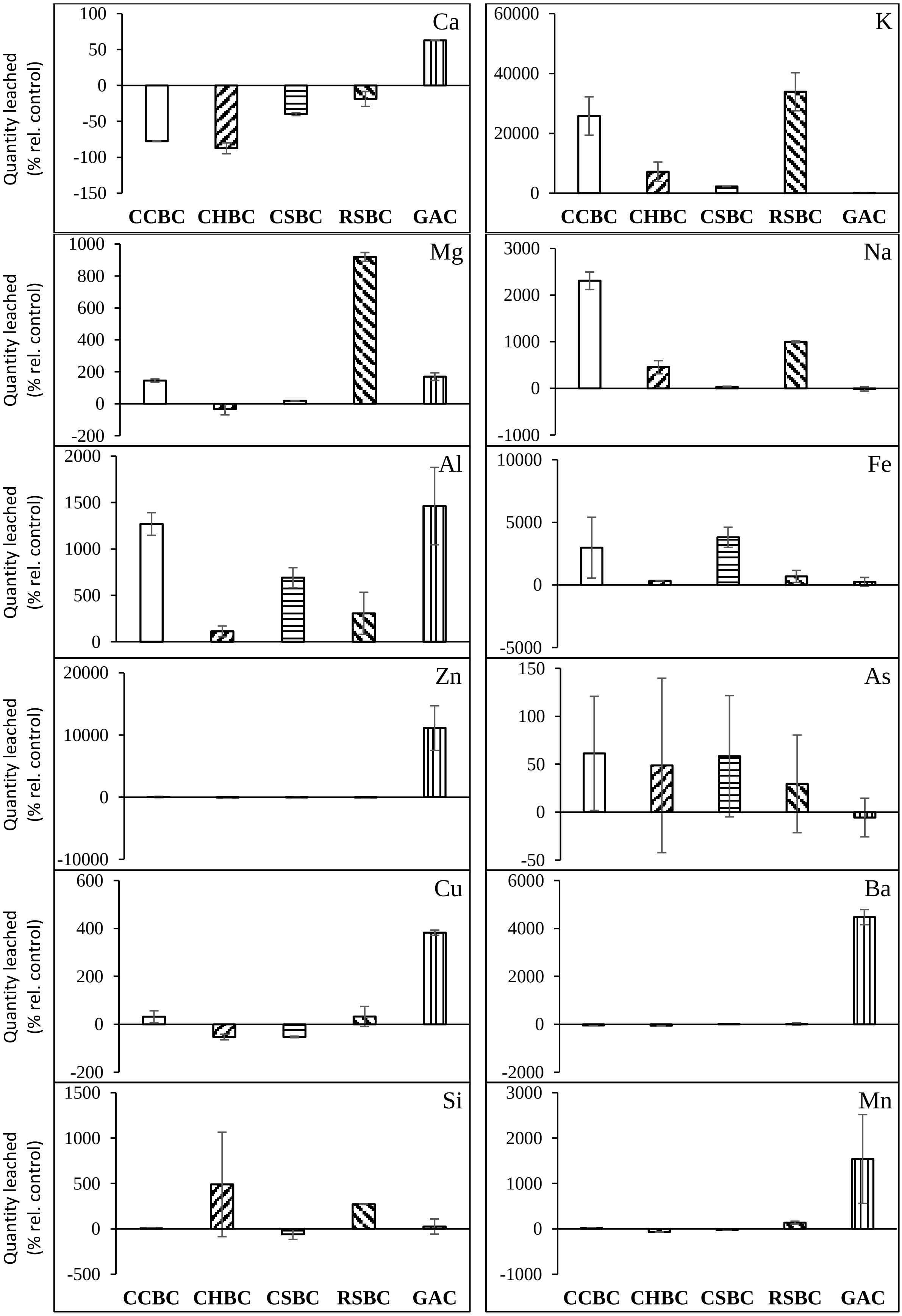


Figure 3-19 Metals leached (%) from the columns at the start of the experiment relative to the unamended sand control (FISA), following the addition of CCBC, CHBC, CSBC, RSBC, and GAC to dissimilar sand columns. Error bars are percentage standard deviations (n=3).

3.5.3 Influence of amendments on leachate quality in the lysimeter field study

To estimate the long-term impacts of soil amendment with biochar on leachate quality under natural climatic conditions, a lysimeter investigation on leachate quality was carried out and the results from observations were recorded below. The two lysimeters under study were L-WSBC – soil+wheat straw biochar; L-WSP – soil+wheat straw pellets.

Leachate pH analysis over the experimental period

The variation of pH with time for each leachate obtained from both lysimeters for the period of the field experiment is represented in Figure 3-20. Despite no statistically significant differences ($p<0.05$) in leachate pH in both lysimeters, it can be observed from the results that the pH decreased by 7.5 % in L-WSBC and over 10% in L-WSP after adding the soil amendments on 21/06/2019, suggesting that the amendments themselves may have contributed to reducing leachate pH of the unamended soil samples. However, not enough data exists to statistically quantify these observations. Similar results were obtained before the addition of wheat straw pellets in LB. In contrast to the pH analysis in the column study, the addition of biochar amendments did not have a significant influence on the pH of the leachate collected, However, the L-WSBC leachate had higher pH in the long term, which is in line with the findings in the column study.

Release of soil nutrients from lysimeters

In general, soil nutrients are naturally occurring ions that are part of life’s cycle (Kumar and Puri, 2012). However, researchers have shown that the release of nutrients from the biochar amended soils is particularly influenced by the desorption characteristics of the biochar. Figure 3-21 and Figure 3-22 present nutrient anions in the lysimeter leachates monitored for 10 weeks from 15/05/2018 to 06/08/2018 with soil amendment added in-between on 21/06/2019.

The results showed that there was a significant difference in the leaching of the different anions from the lysimeters after the addition of wheat straw biochar (WSBC) and wheat straw pellets (WSP) to the soils. This result was further tested using a one-way ANOVA for the measured data and it showed to be statistically significant ($p<0.001$). Researchers have argued that the application of amendments like biochar which has the potential to stimulate nitrification in soil, could promote high nutrient availability in the soil (Hale *et al.*, 2012). But the results agree with a previous work by Kuo, Lee and Jien (2020), demonstrating a significant decrease in the measured parameters after week 5 for both lysimeters, suggesting that the addition of amendments to the soil significantly influenced the concentration of leached out anions in the leachate measurements. Thus, the observations suggest that the overall influence of the amendment in the lysimeter leachate quality was not of concern, as anion concentrations were below drinking water standards.

Lysimeter trace metals analysis

Figure 3-23 showed the cumulative comparison of the concentrations of trace metals ranging in size from Al to Zn extracted from the lysimeter leachates. The concentrations of As, Cd and Hg were not quantified in the leachate extractions from both lysimeters as their concentrations were below ICP-OES detection limits (<0.0001 mg/L). All values (except Al and Ni) were below the EU/UK recommended limit for drinking water as shown in Table 3-6. As can be seen, Ca^+, Na^{2+}, Mg^+ and K^+ were extracted in higher amounts from both lysimeters. Although, the data reported showed that leached out concentrations throughout the experiments suggest no significant concern to drinking water standards in contrast with the previous column study, Figure 3-23 agrees with the report by Kloss et al. (2014) which showed that the application of soil amendment to the soils in both lysimeters did not significantly change the metal concentrations in the leachates as opposed to previous studies that found decreased metal concentrations in leachates (Novak *et al.*, 2009; Beesley *et al.*, 2011; Fellet *et al.*, 2011).

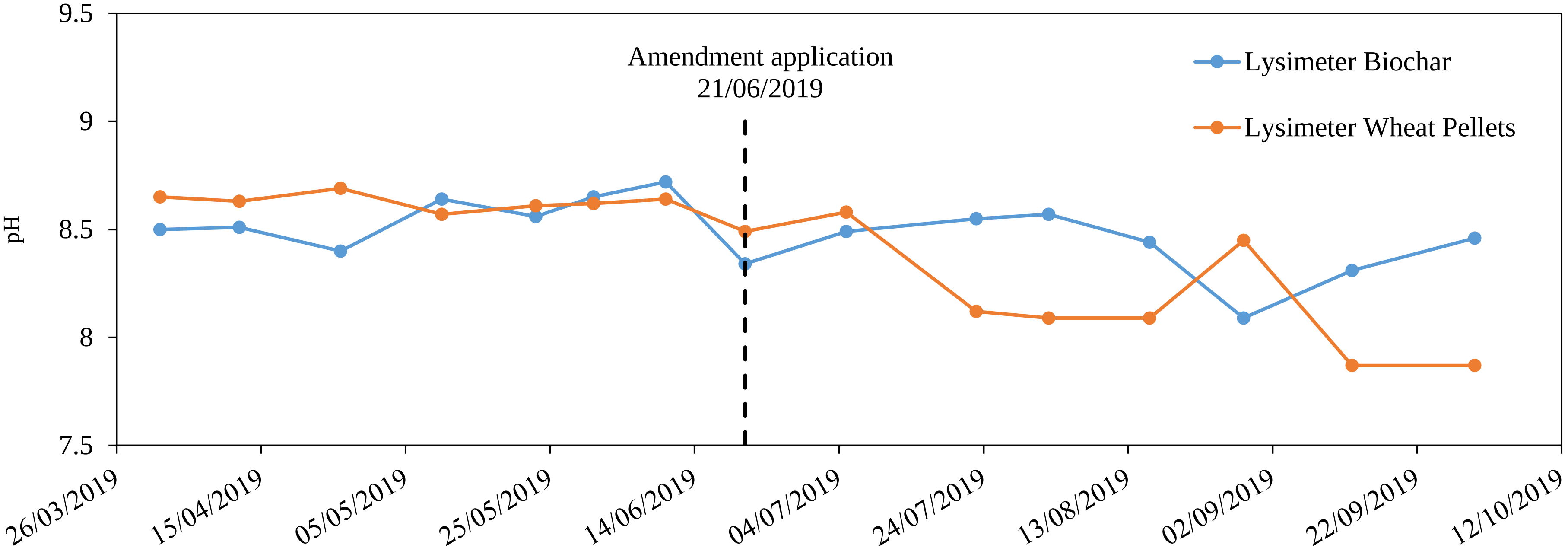


Figure 3-20 pH variation of leachates and sampling times in the different lysimeters collected from the start of the experiment and after the addition of soil amendments.

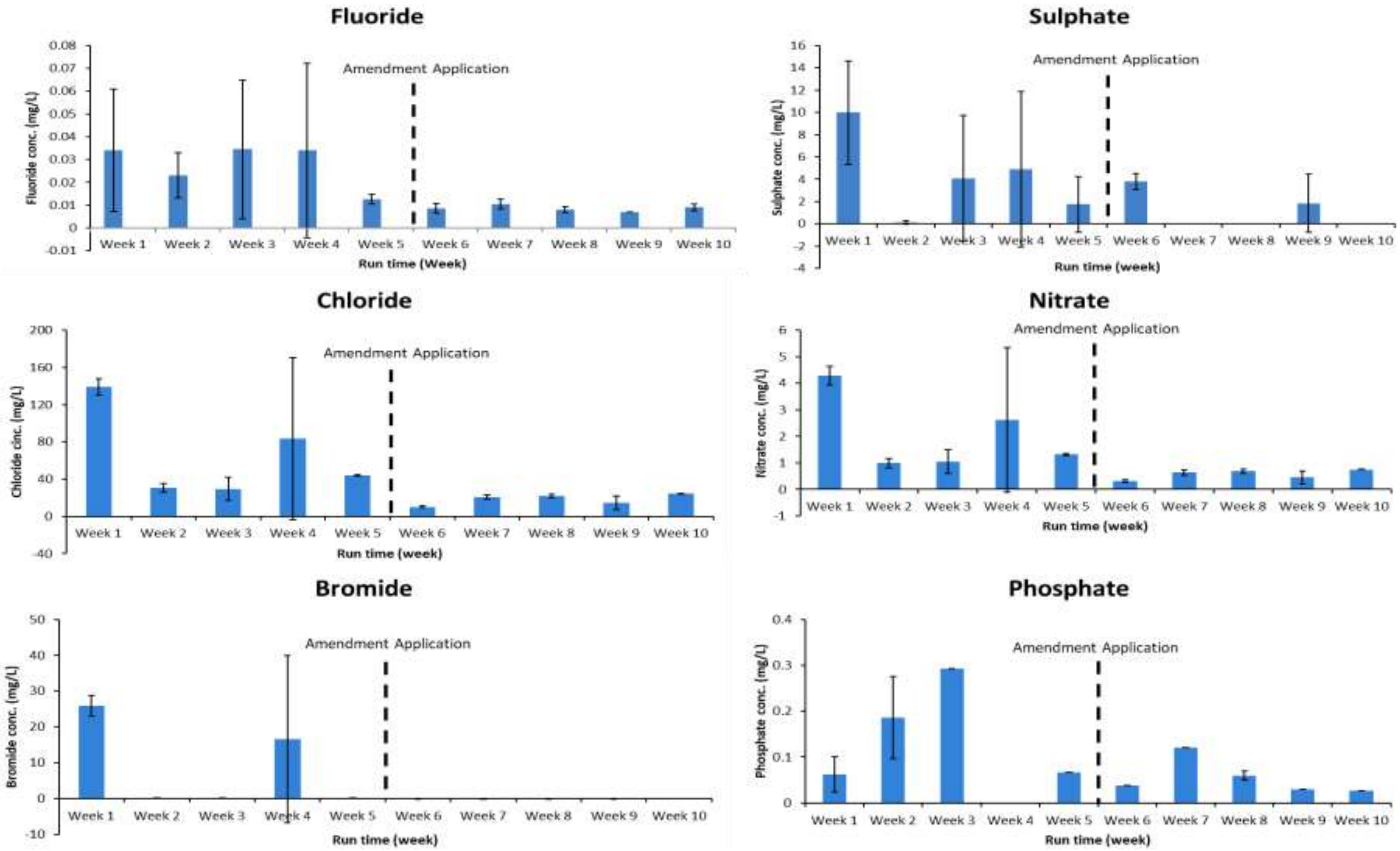


Figure 3-21 Measured nutrient concentrations in L-WSBC leachate samples. Samples collection before and after wheat straw biochar amendment application.

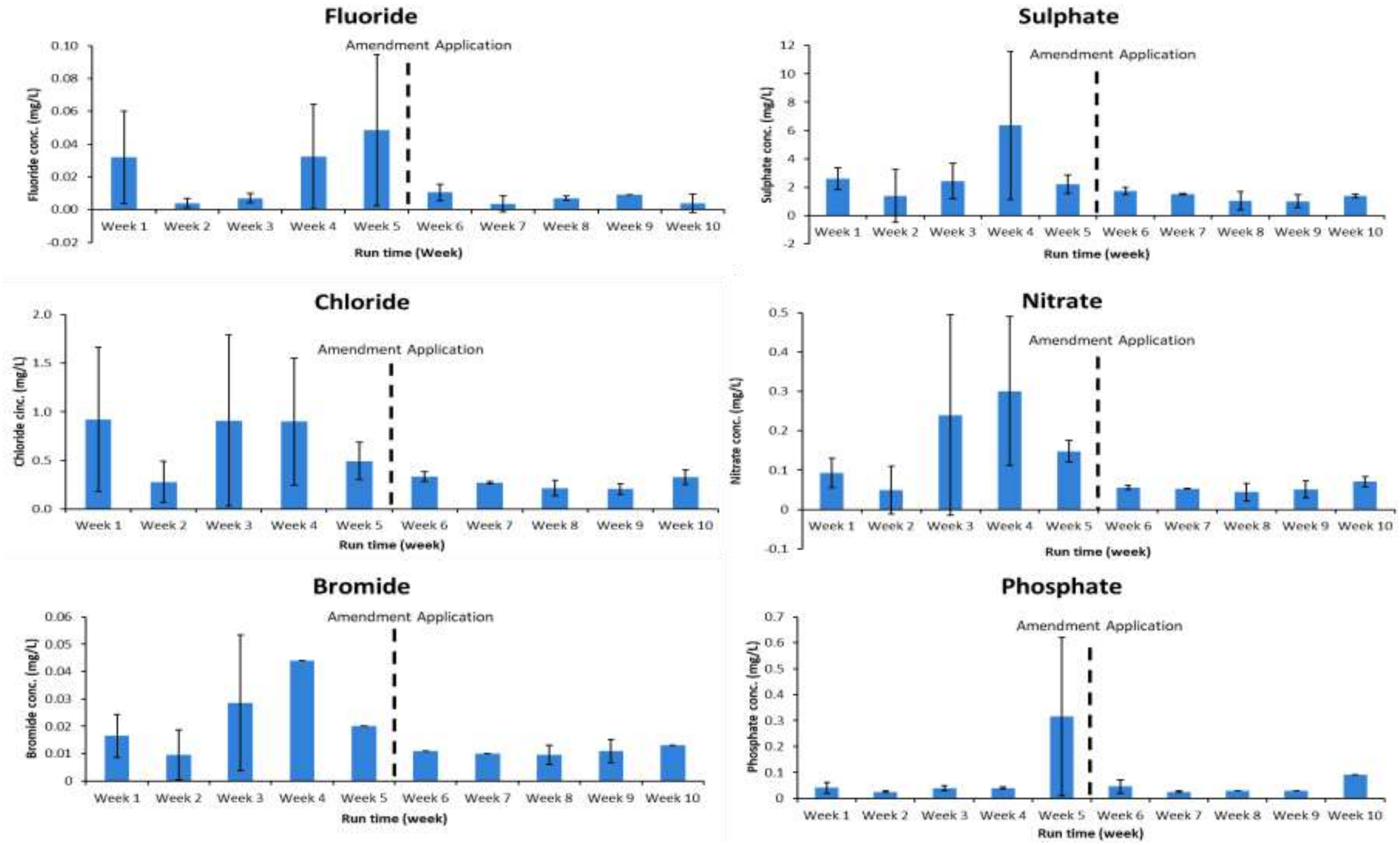


Figure 3-22 Measured nutrient concentrations in L-WSP leachate samples. Samples collection before and after wheat straw pellet amendment application.

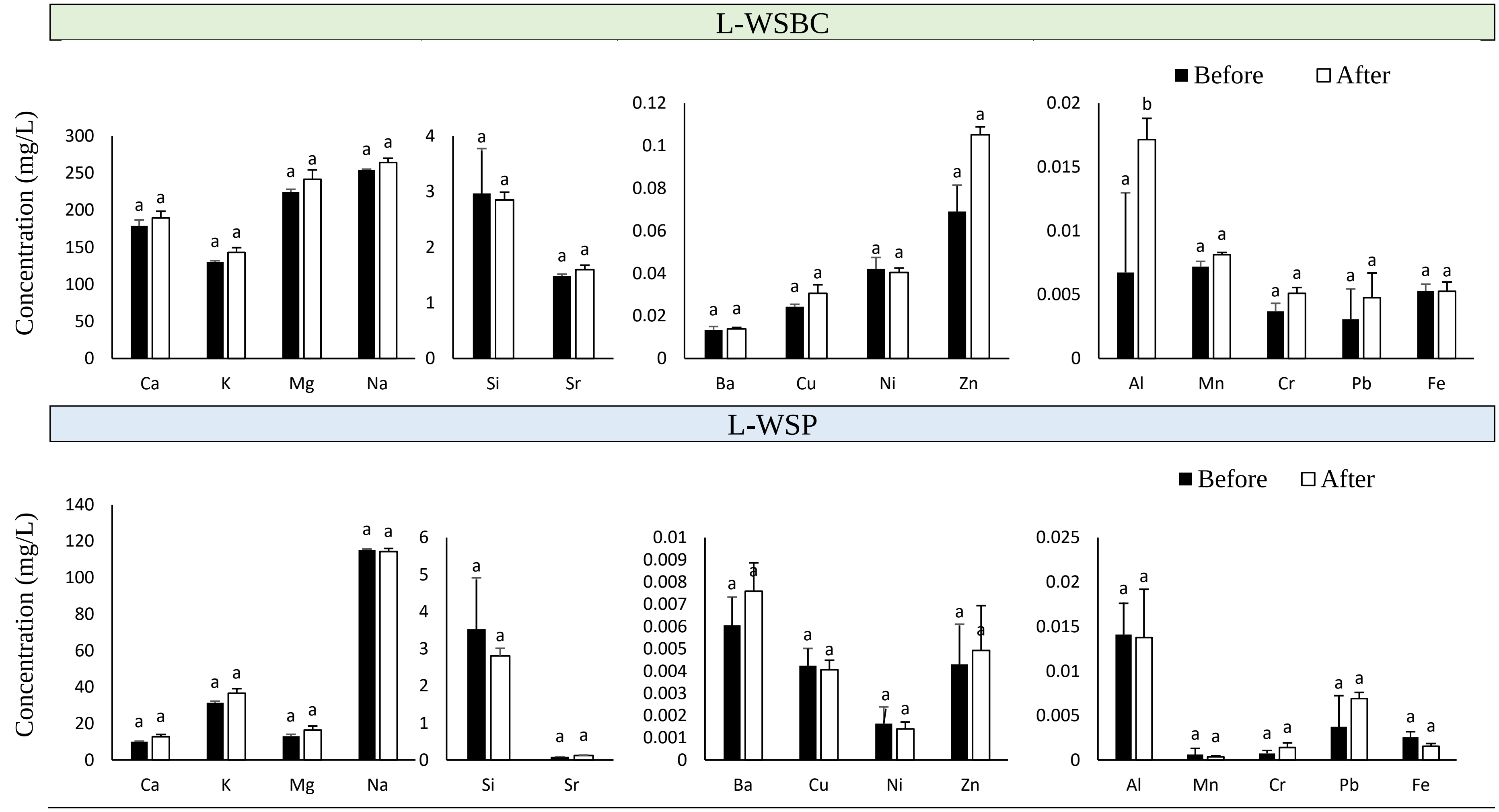


Figure 3-23 Comparing the trace metals concentrations in leachates from different lysimeters soil (a) L-WSBC (b) L-WSP, measured before and after amendment addition in the soils. Statistical evaluation included student t-test with the factor sampling time; different letters indicate significant differences ($p < 0.05$) within one panel. Error bars are standard deviations of mean values (n=3)

3.6 Conclusions

Biochar and activated carbon amendments have been proposed to improve soil physical properties such as water permeability, water infiltration, and drainage and to enhance the removal of physical, chemical and microbial contaminants in biofiltration systems. The purpose of this study was to understand the impact of these soil amendments themselves on leachate parameters and hydrology to address concerns that they may present a risk to groundwater resources. The experimental design was broad but built around the first hypothesis that the amendments could adversely affect the physicochemical properties of biofiltration systems such as hydraulic conductivity. The study also examined if the employed amendment materials had an impact on leaching water quality like the pH, hydraulic conductivity, flow rate, physical and chemical composition. The results data supported the hypothesis by showing that the application of most amendments had a significant change in the investigated parameters compared to the control. However, overall, the hydraulic conductivities could be maintained within a desirable range, and leachate quality was consistent with drinking water quality standards demonstrating that the impacts of the amendments are not of concern from a biofiltration design or public health perspective.

As shown by the results of the laboratory experiments, depending on the amendment type, the addition of different amendments to sand either increased or decreased the saturated hydraulic conductivity (K) when compared with that of the sand only control. This is indicative that CSBC, RSBC and GAC increased the soil porosity and permeability which increased K (0.01196 – 0.01199 cm/s) compared to the control (0.01075 cm/s) than CHBC and CCBC. A similar trend was observed in the volumetric flow rates and the pH measurements in the experiments, except for GAC that had a lower pH range. The results demonstrated that biochar amendment application to soil, particularly CHBC and RSBC, could potentially alleviate soil acidification.

Although, the turbidity and TSS were below WHO and EU/UK drinking water standards, indicating a significant loss of amendment particles being leached into leachate samples. This could be attributed to the presence of finer amendment particles that were washed out in the flush. Furthermore, the effluent permeability declined over the period of the experiments. Reduction in water flow rates may be due to clogging of media pores caused by the biochar physical disintegration over time. Hence, the fine-grain particles are likely changing the porosity and K of the amended soil by hindering the water flow through the column pores. Other mechanisms may additionally act to alter *K* on long-term analysis, including increased microbial activity and increased bioturbation. These examinations provide the impetus for further examining the effects of amendment particle sizes on soil hydraulic properties.

Our laboratory experiments also illustrate that biochar and activated carbon addition to soils increase the leaching of chemical ions from the amended systems. The results showed that the concentration of the leached chemical ions reduced significantly throughout the experiments. However, for the outdoor lysimeter experiments, the chemical leaching was unaffected by the addition of soil amendment type over the long-term testing period which may be attributed to the fact that macro and micronutrients released by the amendments would be recycled through the biological activity in the topsoil layer, so less likely to leach into the groundwater. The results showed that the concentrations of all the chemicals ions in leachates from the laboratory experiments met the limits set out by the EU/UK for drinking water, however, the concentrations of Al in L-WSP and Ni in L-WSBC before the addition of soil amendments slightly exceeded these limits. Overall, there was no evidence that the amendments would cause groundwater pollution.

Finally, these results show that pollutant compounds contained in biochar after production can be dissolved easily into water, which could potentially leach into groundwater and/or be taken up by soil microorganisms. While the research efforts were already substantial for this project, future research should address the complex interactions between amendment types (varying feedstock, pyrolysis type, and particle size) and soil hydrology, chemical ions cycling, as well as different soil types, to further understand the amendment rates that control these processes.

Chapter 4. Comparison of biochars derived from different feedstocks with activated carbon as potential adsorbents for organic micropollutant removal from multiple-pollutant solutions

Abstract

Biochar application has been suggested for reducing the concentration levels of a wide range of micropollutants in contaminated water and enhancing treatment processes in a variety of applications. This study compared the sorption characteristics of four different types of biochar locally produced from agro-waste biomass; coconut shell biochar (CSBC), corn cob biochar (CCBCBC), coconut husk (CHBC), and rice straw rice (RSBC), with the conventional adsorbent granular activated carbon (GAC), for the removal of organic micropollutants from aqueous solutions. The work forms a basis for the application of biochar produced in inexpensive kilns conditions for water treatment and environmental remediation. Batch adsorption experiments were carried out to investigate the removal of mixed micropollutants comprising acetaminophen (ACM), tetracycline (TC), diclofenac (DIC) and oxytetracycline (OTC), and atrazine (ATR) and diuron (DRN), in aqueous solutions. The adsorption suitability of the biochar was also analysed using results of their proximate, ultimate, and elemental characteristics to understand their morphology and physicochemical properties. RSBC exhibited significant OTC uptake with maximum saturated adsorption capacities of 12.8±0.13 mg/g adsorbent (at 22°C, pH 8.62, initial pollutant concentration of 10 mg/L, agitation speed of 170 rpm, and at a dosage of 0.5 g/L) compared to GAC which has a capacity of 19.1±0.72 mg/g adsorbent for the same conditions. The investigation also indicated that the adsorption capacities (q_e) and the distribution coefficients (K_d) decreased in the order GAC>> RSBC> CHBC> CSBC> CCBC for most micropollutants. The kinetics adsorption data were fitted to the pseudo-first-order and pseudo-second-order models to describe the adsorption processes, and the adsorption data showed a good fit with the latter model. The rate parameters of the film and intraparticle diffusion models for adsorption were also evaluated and compared for the different adsorbents to identify the underlying sorption mechanism. This study showed that low-cost biochar produced from common agricultural waste materials are suitable engineered adsorbents for water treatment applications, such as reducing toxic levels of micropollutants and/or predicting the fate of micropollutants in biochar-amended soils.

4.1 Introduction

Global population growth has triggered agricultural and industrial growth for the sustenance of the day to day demands of the world's population. This increase has led to a corresponding growth in the use of chemicals, some of which are now increasingly being detected as emerging pollutants in the environment, posing a threat to global water security. Pesticides and pharmaceuticals are the two main classes of emerging pollutants (Gavrilescu *et al.*, 2015; Gogoi *et al.*, 2018) which are widely found in the environment, raising concerns for both human and environmental health (Sui *et al.*, 2015; Alahabadi and Moussavi, 2017; Ebele, Abou-Elwafa Abdallah and Harrad, 2017). They are frequently found in surface water, groundwater and wastewaters because of their extensive use in a wide range of human activities from industrial and non-industrial sectors; uncontrolled manufacturing (factories area), storage (factories and agricultural area) and uses (Taha *et al.*, 2014; Gavrilescu *et al.*, 2015; J. Bedia *et al.*, 2018). Their presence has also been detected in food products because they are used in animal food production and preparation (Petrie, Barden and Kasprzyk-Hordern, 2014). These pollutants, even if detected in low concentrations in water and wastewater treatment plants, could still be a hazard to the ecosystem and human health given their molecular design to alter metabolic processes (Sophia A. and Lima, 2018). Conventional methods for the removal of pollutants from wastewater include adsorption onto solid substrates, chemical coagulation, disinfection, filtration, and UV treatment (Cheung, Szeto and Mckay, 2007).

Adsorption techniques are considered to be one of the most effective physical techniques applied for environmental remediation because they are inexpensive and easy to manage (Qiu *et al.*, 2009; Dotto, Vieira and Pinto, 2012; Liu *et al.*, 2015). According to Cheung et al. (2007), adsorption affects the availability, leaching and behaviour of organic or inorganic chemicals, and controls the toxicity, fate and transport of organic pollutants in the environment. Adsorption kinetics is of great significance to evaluating the performance of a given adsorbent and to gain insight into the underlying mechanisms because they lead to information on the factors that affect the reaction rate, and the interactions that occur between the adsorbent and adsorbate (Dotto, Vieira and Pinto, 2012). Adsorbents commonly used in industry include activated carbon (J. Bedia *et al.*, 2018), whereas biochar (Han *et al.*, 2016; S. Zhang *et al.*, 2018) is nowadays being evaluated as a lower-cost and more sustainable adsorbent alternative. Activated carbon is the most studied and widely used adsorbent for removal of organic contaminants in industrial wastewater treatment (Alahabadi and Moussavi, 2017) owing to desirable properties such as large specific surface area, high micropore volumes, rapid adsorption capability through a well-developed macro, meso and micropore network, and selectivity towards organic molecules (Yates, Blanco and Martín-Luengo, 2002).

Biochars can be produced from agricultural and other waste biomass and have been shown to also have the potential to control the fate of pesticides and other organic pollutants in the environment (Cederlund *et al.*, 2016; Hu *et al.*, 2019). Organic micropollutants like pesticides and pharmaceuticals have been shown to adsorb more strongly to biochar (Liu *et al.*, 2012; Rivera-Utrilla, Gómez-Pacheco, *et al.*, 2013; Inyang and Dickenson, 2015b; Mandal, Singh and Purakayastha, 2017) than other mineral soil particles and soil organic matters. The high micropollutant capacity of biochar for some micropollutants appears to stem from a combination of physical and chemical attributes. The high porosity of many biochars essentially stems from the preservation of the biomass feedstock cell structure, and the generation of high surface area in the pyrolysis process (Cederlund *et al.*, 2016). Biochar is generally less of a pure carbonaceous material than activated carbon, and as such, its surface chemistry is a complex heterogeneous chemical composition which often depends on the type of biomass material used and pyrolysis conditions (Zama *et al.*, 2018). Although, Han et al. (2015) and Jiang and Xu (2013) reported that sorbent adsorption potentials is not always correlated with the BET surface areas, suggesting that functional groups and volatile matter were found to be more essential than the carbon surface area in the adsorption of some pollutants. Fundamentally, biochar structure is supported by carbon (C) arranged hexagonally in a “honeycomb” pattern without oxygen or hydrogen and exhibits acidity (mainly supplied by carboxyl and hydroxyl groups), and basicity (mainly supplied by O and N functional groups) in conjunction with some hydrophilic and hydrophobic properties that increase the immobilization of pollutants through different mechanisms (Jiang and Xu, 2013; Han *et al.*, 2015). Hence, the diversity of functional groups on biochar surfaces facilitates pollutants binding via mechanisms such as hydrogen bonding and electrostatic interactions.

When adsorption is concerned, kinetic performance and kinetic mechanisms of a given adsorbent are of great significance for the analysis of the solute uptake rate, which determines the residence time required for completion of adsorption reactions in water treatment applications. At present, several mathematical models have been widely used to describe adsorption data, for example, a pseudo-second-order rate equation based on chemical sorption was employed to describe organic pollutants adsorption onto numerous adsorbents (Boudrahem, Aissani-Benissad and Aït-Amar, 2009; Ndi Nsami and Ketcha Mbadcam, 2013; Nethaji, Sivasamy and Mandal, 2013; Kuśmierek and wia¸tkowski, 2015; Ahmed, 2017; Boukhemkhem and Rida, 2017; Mandal, Singh and Purakayastha, 2017; R. He et al., 2018). Also, the distribution coefficient is a useful parameter for comparing the adsorptive capacities of different adsorbent materials for any particular adsorbate when they are measured under the same experimental conditions. Although, there is disagreement regarding the effectiveness of the mathematical models to interpret adsorption data, some parameters of these models, such as maximum adsorption capacity and the distribution coefficient are widely acceptable in characterising pollutants adsorption capacity of different adsorbent materials (Shaheen, Derbalah and Moghanm, 2012). Biochars from different sources would exhibit different properties parameters and therefore different adsorption characteristics. The effects of the key parameters on the removal of pollutants by the biochars and activated carbon mentioned above were therefore evaluated using batch study experiments and biochars produced from typical agricultural waste biomass in Thailand.

4.2 Feedstock and pyrolysis effects on biochar and organic pollutants adsorption chemistry

In the last decade, biochar has been extensively tested for its adsorption capabilities (Islam, Li and Cheng, 2021). Many researchers have manipulated different parameters during pyrolysis to attain a functionalized biochar, but studies that investigated in depth the properties which regulate its ability to adsorb specific micropollutants has not been established yet (Zama *et al.*, 2017; Hassan *et al.*, 2020; Islam, Li and Cheng, 2021). It is evident that the adsorption of adsorbate onto biochar depends on several factors, such as the affinity between the specific adsorbate and biochar, the specific surface area of biochar exposed to adsorbate, the concentration of the adsorbate/ biochar in solution (Zama *et al.*, 2017). Nonetheless, comparing the adsorption performance of biochar from a range of feedstock types is quite challenging because of variations in equipment, experimental conditions, and insufficient data from homogeneous systems. At present, efforts are still being made to understand how the various biochar feedstock types produced at varying conditions and properties bring about changes to their adsorption behaviour and how they can be optimized to enhance micropollutants adsorption, specifically for pesticides and pharmaceuticals (Ahmad *et al.*, 2014; Hassan *et al.*, 2020). In this section, special attention was paid to the characterization of biochars produced from agricultural biomass and commercial activated carbon (AC) and comparing the adsorbents.

4.2.1 Proximate and ultimate analysis of the biochars

Although biochar yield depends on the feedstock type, pyrolysis temperature, and heating rate (Ahmad *et al.*, 2014; Luo *et al.*, 2022), different feedstock types studied are found to present different properties at their different maximum pyrolysis temperatures (Hassan *et al.*, 2020). Hence, exploring the relationships between biochar preparation and their characteristics is paramount for understanding the ideal physicochemical properties for specific micropollutants adsorption. Table 3-1 and Table 3-2 in the preceding chapter summarized the key parameters collected from the different biochar feedstocks studied and their characteristics. The elemental analysis such as total carbon, hydrogen, nitrogen, and oxygen was also calculated. Due to the inconsistency in the maximum pyrolysis temperatures (Table 3-1), the degree of carbonization for the different feedstock types also differs, showing variations in their physical characteristics, including ash content, volatile content, and the generation of surface area. Also, Devi and Saroha (2015) agreed that the pyrolysis temperature strongly influence the adsorption behaviour of the adsorbents.

It can be noticed from Table 3-2 that the volatile content in the biochars was found to decrease with an increase in the pyrolysis temperature ranging from 300 to 700 °C, while the fixed carbon content was found to increase with an increase in pyrolysis temperature. The ash content and the Brunauer–Emmett–Teller (BET) surface area in the biochar were found to decrease as well with an increase in pyrolysis temperature. Although the surface areas of CCBC and CSBC biochars were too small to be measured using the method, RSBC and CHBC biochars were found to be higher at temperatures < 400 °C. Also, the pH of biochar ranged from 8.94 to 9.75, indicating alkalinity, and followed an order: CHBC > CSBC > CCBC > RSBC.

The resulting analysis of biochars used in this study showed that the elemental carbon (C) content of the biochar ranged from 54 to 69%. This is because, during the pyrolysis process around 50% of the carbon is retained with charred biomass (Pugalendhi and Gopal, 2017). The total C content is higher with the biochar with the highest pyrolysis temperature and followed an order: CSBC > CHBC > CCBC > RSBC, nonetheless, more ash content was found in RSBC biochar at 36%. Comparatively, the table showed that

RSBC has very high ash content, low fix carbon, very low iodine number and very high BET surface area, as against CHBC with low ash content, very high fix carbon, very high iodine number and high BET surface area. On the other hand, studies have shown activated carbon to have higher C and ash contents of >77% and 15%, respectively (Kołodyńska, Krukowska and Thomas, 2017). The amount of C observed in the different biochar types are a function of several factors such as the pyrolysis temperature, residence time, moisture content of the biomass, and most importantly, the feedstock type (Srinivasan and Sarmah, 2015). From this result, it inferred that biochar with low pyrolysis temperatures contains fewer volatile compounds when compared to biochar with higher pyrolysis temperatures; this means that the biochars became less hydrophilic with weaker polar groups as pyrolysis temperatures increased (Zama *et al.*, 2017).

4.2.2 Elemental content analysis

The elemental contents of carbon (C), hydrogen (H), nitrogen (N), and oxygen (O) in biochars are indicators of carbonization, hydrophobicity, and polarity of the biochar (Zama *et al.*, 2017; Hassan *et al.*, 2020). While C is the key element for biochar yield (Hassan *et al.*, 2020), O is associated with functional groups, and H is associated with surface functional groups in biomass feedstocks (Bakshi, Banik and Laird, 2020). The systematic changes in the elemental composition are also reflected in the inverse relationships between H/C and O/C molar ratios and pyrolysis temperature (Bakshi, Banik and Laird, 2020). The calculated H/C, O/C, and (O + N)/C molar ratios are used as indexes for aromaticity, hydrophobicity, and polarity (Zhao et al., 2019), respectively, if the molar ratio of H/C is less than 0.5 (Kołodyńska, Krukowska and Thomas, 2017), which is indicative of long-term stability of the biochar in the environment (Srinivasan and Sarmah, 2015; Stella Mary *et al.*, 2016; Zama *et al.*, 2017). Also, recent studies have shown biochar’s affinity for hydrophobic organic compounds, pesticides, pharmaceuticals and other micropollutants (Mrozik *et al.*, 2021). Therefore, the analysis results in Table 3-2 showed the varying contents of C, H, O and N in the different biochar feedstocks.

The molar ratios of these elements in Table 3-2 for O/C and (O + N)/C are higher for RSBC biochar than other adsorbents, suggesting the lower hydrophobicity and higher polarity (Z. Zhao *et al.*, 2019). Moreover, the molar ratios H/C for the biochar adsorbents remained almost stable for the different feedstocks (Table 3-2) between 0.56 and 0.65. These amounts are higher than the calculated values for activated carbon (AC) which was 0.22, derived from the study by Kołodyńska, Krukowska and Thomas (2017). Also, the

H/C ratios for the different biochars decreased in the order: CSBC > CHBC > CCBC > RSBC. Additionally, the molar ratio O/C of adsorbents is used as an indicator for surface hydrophilicity because it is indicative of the polar group content in adsorbents (Samsuri, Sadegh-Zadeh and Seh-Bardan, 2014). The O/C and (O + N)/C ratios of the biochar adsorbents were similar as the values decreased in the order: RSBC > CCBC > CHBC > CSBC. Hence, RSBC had a higher polarity index than other biochar species, which indicates a higher concentration of surface polar functional groups in the RSBC (Samsuri, Sadegh-Zadeh and Seh-Bardan, 2014). Furthermore, comparing the chemical composition of each type of biochar feedstock, the analysis of all four biochar samples confirmed that overall, the biochars functionality as adsorbents is not only influenced by C, H, and O, which varies depending on the feedstock types but the aromaticity (H/C) and polarity (O/C and N/C) present in the precursors. Although studies also suggest that adsorption may increase due to an increase in the microspore volume of biochar (Ahmed *et al.*, 2016).

4.2.3 Structure and functionalities of biochars

The structural chemistry of feedstocks influences the mass yield and elemental composition of biochars (Bakshi, Banik and Laird, 2020). It can be noticed that the BET surface area of the biochars in Table 3-2 decreased with an increase in pyrolysis temperature which favours the generation of surface area (Devi and Saroha, 2015). Comparatively, while AC has a much higher surface area of 760 m^2/g, the BET surface areas of CHBC and RS biochars were low at 11 and 15 m^2/g, respectively, whereas the BET surface areas for CCBC and CSBC biochars could not be established. AC is essentially charcoal treated with oxygen to increase the surface area and porosity (Islam, Li and Cheng, 2021). Since biochar also contains non-carbonized fractions such as the O-containing carboxyl and hydroxyl surface functional groups that may interact with contaminants and make biochar more effective in binding certain contaminants from water (Ahmad *et al.*, 2014; Islam, Li and Cheng, 2021), it has the potentials to act as a very effective adsorbent for organic and inorganic contaminants found in water due to its multi-functional properties. Additionally, it is reported that while biochars produced at higher pyrolysis temperatures have a greater affinity towards pollutants because of their higher aromaticity and specific surface area, biochars produced at lower pyrolysis temperatures have more oxygenic functional groups, and so can still be effective for pollutants adsorption through complexation (Islam, Li and Cheng, 2021).

4.2.4 Adsorption interaction of biochar

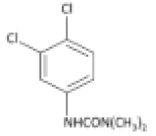
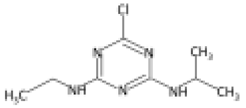
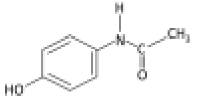
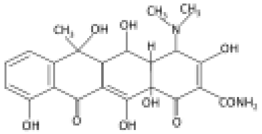
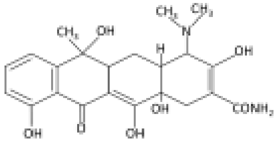
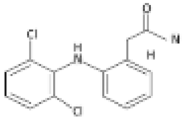
As discussed earlier, the adsorption properties of biochar are heavily influenced by the feedstock type and pyrolysis conditions (such as residence time, heat transfer rate, and pyrolysis temperature), it is, therefore, crucial to select the appropriate biochars for different conditions. Adsorption has been widely used as a pollution mitigation technique, and biochar's significance has been fully recognized in the treatment of pesticide and pharmaceutical micropollutants (Ahmad *et al.*, 2014; Ahmed, 2017; Islam, Li and Cheng, 2021), because of its heterogeneous surface, high surface area, and aromatic properties (Ahmad *et al.*, 2014; Tomczyk, Sokołowska and Boguta, 2020; Islam, Li and Cheng, 2021; Mrozik *et al.*, 2021; Luo *et al.*, 2022). From the analysis data in Table 3-2, the adsorption of iodine in aqueous solution (iodine numbers) showed that CCBC, CHBC, CSBC, and RSBC biochars were 32, 68, 13, and 3 mg/L, respectively. It is worth noting that the iodine number is a method used to investigate the adsorption of iodine on the biochar. It was reported that the higher the number the better the approximation of the surface area of the adsorbent (Mianowski, Owczarek and Marecka, 2007). Comparatively, it showed that CHBC which has the higher iodine number is a much better adsorbent candidate than other biochar species for the adsorption of micropollutants from water.

4.2.5 Micropollutants – water interactions

As with adsorbents, the physicochemical properties of an adsorbate also have a crucial effect on their adsorption, because the capacity and rate of adsorption are influenced by the type of molecules adsorbed (Karanfil and Kilduff, 1999; Ania *et al.*, 2008; Uras-Postma, Carrier and Knoetze, 2014; Luo *et al.*, 2022). Understanding the correlation between these influencing factors and the characteristics of biochar is paramount for the development of biochar with optimal properties for the adsorption of targeted pollutants (Luo *et al.*, 2022). In general, the interactions between adsorbents and adsorbates are controlled by the physicochemical properties of the adsorbent, the molecular structure of the adsorbate, and the solution chemistry (Uras-Postma, Carrier and Knoetze, 2014). Also, adsorbates with higher molecular weight are adsorbed faster than adsorbates with lower chains. Specifically, physisorption (physical), chemisorption (chemical), and electrostatic interactions have been identified as the main types of interaction between adsorbates and the carbon surface (Moreno-Castilla, 2004). Since hydrophobic compounds tend to accumulate at solid-water interfaces, chemical compatibility among micropollutant molecules and water is the primary factor that determines solubility (Karanfil and Kilduff, 1999; Karanfil and Dastgheib, 2004). Hence, as the chain length of organic subunits increases, the solubility of an organic compound decreases, resulting in higher adsorption onto carbon surfaces (Weber and Beck, 1973).

Table 4-1 showed the structure and characteristics of the micropollutant compounds used for the study. The table showed that ACM has a higher solubility in water, and this is indicative of the fact that ACM will be the least adsorbed compared to other compounds. The solubility values for each compound decreased in the other ACM > DRN > ATR > OTC > TC > DIC. From this comparison, it can be predicted that DIC will be highly adsorbed given its low solubility. In terms of the molecular weight of each adsorbate, the table showed to decrease in the other OTC > TC > DIC > DRN > ATR > ACM. From this comparison, it hypothesised that OTC will be adsorbed faster than other adsorbates. Therefore, in addition, the micropollutants adsorption mechanism in this present study aims at understanding how the chemical nature of feedstocks can be related to the adsorption properties of agro-waste-based biochar obtained from low-tech pyrolysis process and comparing to that of a commercially obtained activated carbon.

Table 4-1. Characteristics and structure of organic micropollutants.

Name Abbr.	Use/ Occurrence	MW (g/mol)	Aq. Sol. (mg/L) (25°C)	Log K_{OW}	Henry's Law Constant (atm-m^3/mol)	Chemical Formula	Structure Formula	Literature
DRN	Herbicides/ Agricultural watershed	233	36.4	2.85	5.04×10^{-10}	$C_9H_{10}Cl_2N_2O$		Field et al. (2003) Hladik and Calhoun (2012) EL-Nahhal, Kerkez and Heen (2015)
ATR	Herbicides/ Agricultural watershed	216	28	2.61	2.63×10^{-9}	$C_8H_{14}ClN_5$		Brand and Mueller (2002) Paschke et al. (2004) Dalrymple (2005)
ACM	Analgesics/ Environmental waters	151	14×10^4	0.46	8.93×10^{-10}	$C_8H_9NO_2$		Harris and Logan (2014) Chang et al. (2015)
OTC	Antibiotics/ Environmental waters	460	17	-1.12	1.70×10^{-25}	$C_{22}H_{24}N_2O_9$		Ahmed (2017) Conde-Cid et al. (2020) Xu et al. (2021)
TC	Antibiotics/ Environmental waters	444	22	-1.25	4.66×10^{-24}	$C_{22}H_{24}N_2O_8$		Ahmed (2017) Conde-Cid et al. (2020) Xu et al. (2021)
DIC	Analgesics/ Environmental waters	318	4.47	4.51	4.73×10^{-12}	$C_{14}H_{11}Cl_2NO_2$		Scheytt et al. (2005) Williams et al. (2009) Lonappan et al. (2016)

4.3 Aims and objectives

This study aims to understand and compare the abilities of biochars produced from four agriculture wastes (corn cob, coconut shell, coconut husk and rice straw) and activated carbon to remove pharmaceutical and herbicide pollutants from contaminated water. Although the research will primarily focus on pesticides and pharmaceuticals detected in Thai surface waters (Mrozik *et al.*, 2019), it is intended that the results are transferable to other organic contaminants and environments. The primary objectives of this study were:

- to elucidate the potentials of selected biochars for the removal of a mixture of acetaminophen, diuron, oxytetracycline, atrazine, tetracycline and diclofenac from aqueous solution to compare and understand their hydrophobicity effect.
- to measure the adsorption capacities of the biochar adsorbents relative to activated carbon.
- to identify the kinetic processes through which micropollutants are transported and investigate any specific interactions with the sorption sites on adsorbents.

4.4 Materials and methods

This section presents the selection of materials used and their sources, the various experimental procedures and pieces of analytical equipment and methods used to generate the results discussed in this chapter.

4.4.1 Adsorbents Preparation

The four biochars used in this study were prepared by collaborators at the King Mongkut’s University of Technology Thonburi (KMUTT), Thailand, under limited oxygen conditions as described in *Section 3.4.2* of Chapter 3. All samples were pyrolyzed with temperatures reaching 303 – 704 °C, depending on the outside chamber temperature conditions (as shown in Table 3-1 of Chapter 3). The biochars were produced from agro-waste feedstocks namely Corn Comb, Coconut Shell, Coconut Husk, and Rice Straw, and were abbreviated as CCBC, CSBC, CHBC and RSBC, respectively. KMUTT researchers have characterised many physicochemical properties of these biochars, including the C, H, N, S and O contents, bulk densities, iodine numbers, BET surface areas, and pH, shown in Table 3-2 of Chapter 3**.** Biochar properties varied, though all had high pH values (>7.1), high carbon contents (>53%) and relatively low BET surface areas (Khawkomol *et al.*, 2021). The samples received from KMUTT were ground using a mortar and pestle, sieved through a test sieve with aperture sizes of 0.212mm >Ø> 1.18mm, then transferred into air-tight PTFE containers and stored at room temperature. Notably, RSBC had a significantly higher surface area and higher ash content than the other adsorbents. These properties will influence the adsorption characteristics and behaviour of the biochars.

Granular activated carbon (GAC) produced from coconut shells by Norit was included as a conventional adsorbent for comparison in the study due to its superior surface area and porosity. The adsorbent was ground and not subjected to any further pre-treatment before use. The surface area and other property characterisation have been carried out by Han et al. (2015).

4.4.2 Chemicals

All chemicals used in this work were analytical grade and used as received. HPLC-grade acetonitrile (CAS [75-05-8], ≥99.6%) was obtained from Thermo Fisher Scientific™ UK. Methanol (CAS [67-56-1], ≥99.9%) and Acetone (CAS [67-64-1], ≥99.5%) were purchased from VWR International (Lutterworth, UK). Deionized water (≥18.2MΩ·cm) was supplied by a Millipore water purification system (Milli-Q). The seven certified compounds used for this study were: acetaminophen (CAS [103-90-2], ≥99.0%), diuron (CAS [1912-24-9], ≥98.0%), oxytetracycline hydrochloride (CAS [2058-46-0], 95.0 %), atrazine (CAS [1071-83-6], 98.9%), tetracycline (CAS [60-54-8], ≥98.9%) and diclofenac sodium salt (CAS [15307-79-6], 98.5 %) obtained from Sigma-Aldrich International and abbreviated as ACM, DRN, OTC, ATR, TC and DIC, respectively. A summary of the compounds and some of their key properties can be found in Table 4-1.

Amber glass vials of 60 mL obtained from VWR (Lutterworth, UK) were used with Teflon-lined screw-top caps providing leak-tight, inert closure (Figure 4-1). A Terumo sterile syringe was used to inject samples while syringe filters with PVDF membrane of pore size 0.2 µm and diameter 13 mm, also obtained from Thermo Fisher Scientific™ UK, was used to filter adsorbent from the collected sample solutions.

4.4.3 Adsorbates standard preparation

Stock solutions were prepared by first dissolving 10 mg of individual adsorbate salts (micropollutant) each in 10 mL of analytical grade methanol obtained from VWR International (Lutterworth, UK) at concentrations of 1000 mg/L and kept closed in the dark at 4°C. Then, a standard solution containing the mixture of the six adsorbates standards was prepared by spiking the 10 mL each of the individual stock solution into a pre-determined volume of sterilized deionized water to a concentration of 100 mg/L for each compound and also kept at 4°C. The standard solution was then diluted further to provide five concentrations prepared for calibration curves; 0.1, 1, 2.5, 5, and 10 mg/L.

4.4.4 Calibration curve for HPLC analysis

The standards concentrations were run chromatographically under ideal conditions. A High-Performance Liquid Chromatography (HPLC) was used to determine the concentrations of target chemical compounds in solution and a direct relationship between the peak area and concentration of the target compound was established for the quantification of unknown concentrations from the measured peak areas. The HPLC system (Shimadzu; Kyoto, Japan) consisted of an LC-10AD VP pump, SIL-10A VP autosampler, SPD-10A VP UV detector, and SCL 10 A-VP controller unit. Data were acquired and processed by CLASS-VP V 5.032 software. The stationary phase was a Gemini-NX 150 x 4.6 mm, 5µ, C18, 110 E column (Phenomenex, USA). The mobile phase consisted of acetonitrile and water (50: 50 % v/v), at an isocratic flow rate of 1 mL/min. The elution profiles were recorded at 254 nm, and the injection volume was 10 µL.

4.4.5 Batch Adsorption Experiments

The batch adsorption experiment was conducted to study the behaviour of the selected organic micropollutants on biochars and GAC in a competitive sorption system at a room temperature of 22°C. This provides a straightforward method of analysing the characteristics of the adsorption system and its response to internal and external changes. The samples were prepared in triplicates as shown in Figure 4-1 with mixed micropollutants concentrations of 10 mg/L for all pollutant compounds studied as follows: 100 mg/L stock solution containing all studied chemical compounds have been prepared before beginning the experiment.

An accurate amount of the studied adsorbent (25 mg, oven-dry basis) was each added to 60 mL capacity amber glass vials Teflon-lined screw caps supplied by VWR (Lutterworth, UK) containing 45 mL deionized water (≥18.2MΩ·cm) supplied by a Millipore water purification system (Milli-Q). The vials were closed using the screw cap and the sample was autoclaved. The desired initial batch micropollutant concentrations were then obtained by spiking each autoclaved vial with 5 mL of the prepared stock solution to obtain a 50 mL aqueous solution containing 10 mg/L mixture of micropollutants of equal concentration without any pH adjustment. Blank controls containing the same concentration micropollutants (adsorbates) solution only (without adsorbents) were simultaneously run in parallel with the samples to check for loss of micropollutants through sorption to the glass vials or possible degradation. The amber glass vials closed with Teflon screw caps were then returned to the laboratory shaker (KS 4000i by IKA) and allowed to shake at 170 rpm following the suggestion of Kuśmierek and wia¸tkowski (2015) under the conditions stated before for 10 days at room temperature.

A schematic of the methodology for the adsorption studies is given in Figure 4-2, and the purpose of the analysis are summarised in Table 4-2. After the desired shaking time, aliquot samples were extracted from the batches using 1 mL sterile syringes and then filtered through sterile, single-use 13 mm PVDF membrane syringe filters of 0.2 µm obtained from Thermo Fisher Scientific™ UK into 2 mL amber GC-vials closed with blue 9 mm white silicone/red PTFE screw caps to remove suspended solids. The filtered aqueous samples were carried out carefully to reduce external microbial influence and analysed using HPLC to determine the residual concentration of adsorbates in the filtrate (C_t in mg/L) were extracted and measured after the agitating time intervals of 10 and 30 min, 1, 2, 3, 7, 12, 22, 56, 80, 100, 126, 150, 170 and 240 hrs for kinetic sorption studies. An external standard method was used to calibrate the machine beforehand. Under these conditions, the retention times observed for ACM, DRN, OTC, ATR, TC, DIC, were 2.619±0.008, 8.022±0.045, 5.026±0.022, 7.483±0.031, 5.435±0.024, and 9.012±0.009 min, respectively. Based on the results of the analysis, equilibrium was assumed to have been reached after 240 hours of agitation tests.

The amount of micropollutants adsorbed per unit weight of adsorbent was computed using the difference between equilibrium concentrations of treatment and control samples. All the experiments were conducted in triplicate and data were presented as mean ± SD (standard deviation). The record showed that no adsorption for any of the adsorbates occurred in the control glass vials.

Figure 4-1. Batch experiments showing 60 mL amber vials with screw-top caps with PTFE liner.

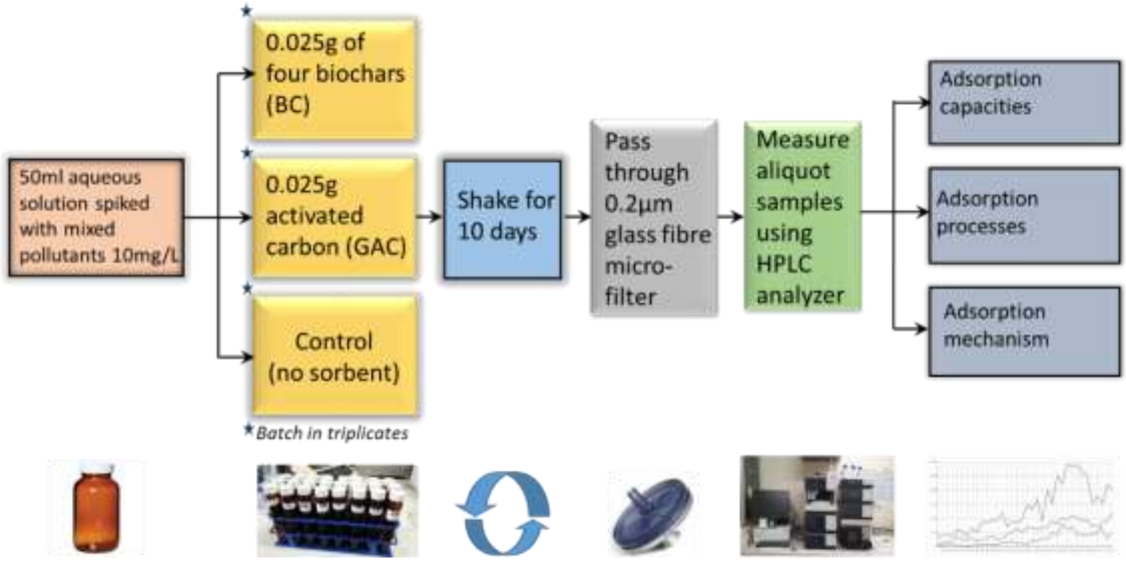


Figure 4-2. A schematic of the methodology for the adsorption studies

Table 4-2. Summary of batch adsorption tests carried out and their purposes

Analysis	**Description**	**Models**	**Purpose**
Adsorption capacity	Adsorption of adsorbates to the adsorbents over time	• Adsorption efficiency • Adsorption capacity	To determine the uptake efficiency, affinity, and capacity
Adsorption kinetics	Sorption processes of the different adsorbents for the different adsorbates	• Pseudo-first-order • Pseudo-second-order • Elovich	To determine the adsorption rates
Adsorption mechanism	Sorption interactions, rate-controlling steps	• Film diffusion • Intraparticle diffusion	To determine the rate-limiting steps

4.4.6 Modelling of kinetic data

Adsorption capacity determination

The adsorption capacity of each adsorbent with respect to each micropollutant was calculated using experimental data based on the mass balance process. Applying the assumption that $q_0 = 0$, the amount of adsorption at equilibrium was obtained, q_e (mg/L), i.e., at the final incubation time, when equilibrium was assumed to have been reached, was calculated using the following equation:

$$q_e = \frac{V(C_0 - C_e)}{m} \tag{4.1}$$

Where C_0 and C_e are the initial and final liquid concentrations (mg/L), respectively, and V and m are the liquid volume (L) and the weight of dried adsorbent (g) in the batches, respectively.

The final sorption percentage (% removal) of micropollutants from aqueous solution was computed using the following equation:

$$Removal\ (100\%) = 100\ \frac{(C_0 - C_e)}{C_0} \tag{4.2}$$

Equations (4.3) and (4.4) below describe the data evaluation for the contact time experiments:

$$q_t = \frac{V(C_0 - C_t)}{m} \tag{4.3}$$

and

$$\% \, removal = 100 \, \frac{(C_0 - C_t)}{C_0} \tag{4.4}$$

Where C_0 and C_t are the initial and time t concentrations of the adsorbates (i.e., C_t is the concentration at time t); V (L) is the volume of the batch; m is the dosage of adsorbent (grams).

Distribution coefficient (K_d) determination

The distribution or adsorption coefficient K_d as estimated using Equation (4.5) is the partitioning of an analyte associated with the solid and aqueous phase and is defined as the ratio of the amount of adsorbate adsorbed per mass of adsorbent to the amount of adsorbate remaining in the aqueous phase when the system is at equilibrium (EPA, 1999; US EPA, 2004).

$$K_d = \frac{q_e}{C_e} \tag{4.5}$$

Where K_d, q_e and C_{eq} are the sorption coefficient (L/g), the equilibrium adsorption capacity (mg/g) and the equilibrium aqueous phase concentration of the pollutant (mg/L), respectively.

High values of K_d indicate that the adsorbate is strongly absorbed by the solid phase, and also indicating that the adsorbate is probably hydrophobic and highly insoluble as well, although there are exceptions (Wauchope *et al.*, 2002; Shaheen, Derbalah and Moghanm, 2012). Similarly, low values of K_d indicate that a high adsorbate amount remains in the solution (Shaheen, Derbalah and Moghanm, 2012).

Adsorption diffusion models

These adsorption diffusion models are mainly constructed to describe the process controlled by film diffusion and/or intraparticle diffusion. According to McMillan (2018), the adsorption rate controlled by film diffusion suggests that the interactions at the sorption sites are the rate-limiting step, while the adsorption rate controlled by intraparticle diffusion suggests that the time taken for micropollutants to reach the adsorption sites is the rate-limiting step. Itodo et al. (2010) also added that the structure of the solid and its interaction with the diffusion substance influences the rate of transport. The adsorbent may be in the form of porous barriers and solute movement may be by diffusion from one fluid body to the other by a concentration gradient. Thus, the film diffusion model uses Boyd's intraparticle diffusion model, which is currently one of the most widely used models for studying the adsorption mechanisms (Viegas *et al.*, 2014), to determine the relative influences of the rate-controlling steps. The Boyd parameters are calculated by using the model equations assuming all the particles were uniform spheres of radius *r*, under the conditions where particle diffusion was the sole rate-controlling process (Boyd, Adamson and Myers, 1947):

$$F = \frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \times \sum_{n=1}^{\infty} \frac{1}{n^2} \times e^{-n^2 \times B_t} \qquad \textbf{(4.6)}$$

$$B = \frac{\pi^2 D_i}{r^2} \qquad \textbf{(4.7)}$$

Where *F* is the fractional attainment of equilibrium at time t. Based on the *F* values, the corresponding values of B_t were obtained from Reichenberg's transformation to obtained the approximations given by the following equations (Reichenberg, 1953):

$$B_t = -\ln\frac{\pi^2}{6} - \ln\left(1 - F(t)\right) \qquad \text{for F(t)} > 0.8 \qquad \textbf{(4.8)}$$

$$B_t = \left(\sqrt{\pi} - \sqrt{\pi - \frac{\pi^2 F(t)}{3}}\right)^2 \qquad \text{for F(t)} \leq 0.85 \qquad \textbf{(4.9)}$$

Following Boyd's model (equation on Table 4-3), the linearity test of B_t versus time plots drawn for the different adsorbate adsorption is employed to distinguish between film diffusion and particle diffusion. From the slope of the straight-line graphs (B) obtained from B_t versus time plots, the values of the effective diffusion coefficient (D_i) may be determined provided the Boyd plot passes through the origin, which happened only for most of the adsorbents. The slope of the linear proportion indicates the rate of the adsorption; the lower slope corresponds to a slower adsorption process and vice versa. Also, if a plot is nonlinear or linear but passes through the origin it suggests that sorption is controlled by intraparticle diffusion, while from deviations from this it can then be concluded that the limiting step is the film diffusion or intraparticle diffusion, both are significant in the case.

Kinetic adsorption models

To evaluate the kinetics of adsorption, models were fitted to the data in order to evaluate and compare their respective fits: the pseudo-first-order model, the pseudo-second-order model, the Elovich model, the intraparticle diffusion model, and the film diffusion model. The equations for these models are given in Table 4-3, where q_t represents adsorption at time t; q_e represents adsorption at equilibrium; and k_1, k_2, α, β, k_i and C_i are fitting parameters of the respective models. In order to estimate film diffusion and intraparticle diffusion values, experimental data were fitted with the film diffusion model by plotting the Boyd Number, B_t, against time, t. The intraparticle diffusion model plots were generated by fitting a two-step linear model to a plot of q_t vs. $t^{1/2}$ based on the theory of Weber and Morris (1963). This was used to evaluate the diffusion mechanisms and rate-controlling steps in the adsorption of adsorbates onto the different adsorbents. The first step described the initial rapid chemical adsorption phase, while the second step described the slower, intraparticle diffusion phase. The two lines were fitted by minimising the squares of the errors between the observed values and the fitted model. Values of q_e(cal) were calculated from plots of $ln(q_e-q_t)$ versus t, and t/q_t versus t, as opposed to the experimentally determined values. The Boyd plots were generated using the film diffusion model by fitting B_t, as calculated using the equation in Table 4-3 against time, t. Finally, the model results were compared for the goodness of fit using the statistical p-value and 95% confidence intervals determined using the ANOVA regression analysis package in Excel.

Table 4-3. Summary models and equations fitted to kinetic adsorption data

Kinetic models	**Equation**	**Linearized equation**	**Plot**
Pseudo-first order	$q_t = q_e[1 - \exp(-k_1 t)]$	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$q_t \; vs \; t$
Pseudo-second order	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	$\frac{t}{q_t} \; vs \; t$
Elovich	$q_t = \frac{1}{\beta}\ln(1 + \alpha\beta t)$	$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t$	$q_t \; vs \ln t$
Intraparticle diffusion	$q_t = k_{id} t^{0.5}$	$q_t = k_{id} t^{0.5} + C_i$	$q_t \; vs \; t^{0.5}$
Film diffusion	$B_t = \left(\sqrt{\pi} - \sqrt{\pi - \frac{\pi^2 F(t)}{3}}\right)^2$ since F(t) ≤ 0.85	$B_t = B(t) + C$	$B_t \; vs \; t$

4.4.7 Statistical methods

Statistical analysis of the obtained data was carried out using Microsoft Excel 365. All samples were analysed in duplicate to ensure accuracy and repeatability.

4.5 Results and discussion

4.5.1 Overview

This section discusses the results of the adsorption characterization of the different adsorbents with respect to their interaction with the different adsorbates. The characterizations included the adsorption capacities of the biochars and GAC towards micropollutants, the removal efficiencies in the batch tests, the kinetic adsorbate uptake processes and diffusion mechanisms. Replicate measurements were in general very reproducible within ±10%.

4.5.2 Comparative study of the dynamic adsorption capabilities and the biochar-water partition coefficients (K_d)

The interaction time needed for adsorption to reach equilibrium is very important for industrial applications. Ideally, adsorbents should rapidly remove adsorbates in the first few minutes of interaction with the solutions to be treated. The results obtained from the interaction time study is represented in Figure 4-3, while the K_d (L/g) values for the biochar adsorbents are presented in Figure 4-4 and the adsorption capacities of the adsorbents are measured as a function of time q_t (mg/g) and the removal efficiencies for the adsorbed compounds are presented in Figure 4-5 and Figure 4-6, respectively.

Acetaminophen adsorption

As agitation time increased, ACM removal increased initially, but then gradually approached a constant value, denoting the attainment of adsorption equilibrium. The results reveal that the uptake of ACM by the adsorbents was changing with increasing contact time. Although all biochars showed rapid increases in ACM adsorption in the first 30 minutes to 12 hours of the contact period, thereafter, it became slower and approached equilibrium at which time the rate of sorption was found to be nearly constant. With respect to the contact time, GAC reached saturation after 22 hrs, while CSBC, CCBC, CHBC and RSBC reached saturation after 12, 12, 56 and 126 hrs respectively, which represented their optimum contact times. Among the four biochars, CHBC exhibited the highest adsorption capacity (Figure 4-3(a)) followed by RSBC, CCBC and CSBC. Based on the K_d values (Figure 4-4(a)), although GAC had very high K_d (133±56 L/g, not shown in plot), the biochar adsorbents can be ranked in the order of ACM sorption as CHBC > RSBC > CCBC > CSBC. Notably, as the contact time was increased from 10 to 30 mins, the adsorption ability of CSBC was reaching equilibrium (1.27±0.123 mg/g), and after that mainly kept stable. In contrast, there was an increase in adsorption by GAC from 0.72±2.58 mg/g to 16.9±1.70 mg/g in 10 - 720 mins. This sharp increase of adsorption for GAC could be the result of the high initial concentration of solute in the solution and the large number of available adsorption sites on the adsorbent surface (Dutta *et al.*, 2015).

Oxytetracycline adsorption

The higher initial concentration of solute in solution increases the driving force and collisions between the adsorbents and micropollutants, and the available adsorption sites were attractive to mobile molecules (Hou *et al.*, 2016). The micropollutant removal efficiency of GAC for OTC reached its maximum after 22 hrs with a capacity of 19.1±0.7 mg/g. In Figure 4-3, it can be observed that all biochar adsorbents had increasing adsorption capacities until the end of the experiments. This indicated that the maximum adsorption equilibrium for the biochar adsorbents was not attained for OTC. However, it was clear from the plots that RSBC was the best OTC adsorbent with a final adsorption capacity of 12.8±0.1 mg/g, followed by CHBC, CSBC and CCBC (Figure 4-5(b)). This same order was observed in the K_d determination values, as RSBC showed to be the better OTC biochar-based adsorbent in Figure 4-4.

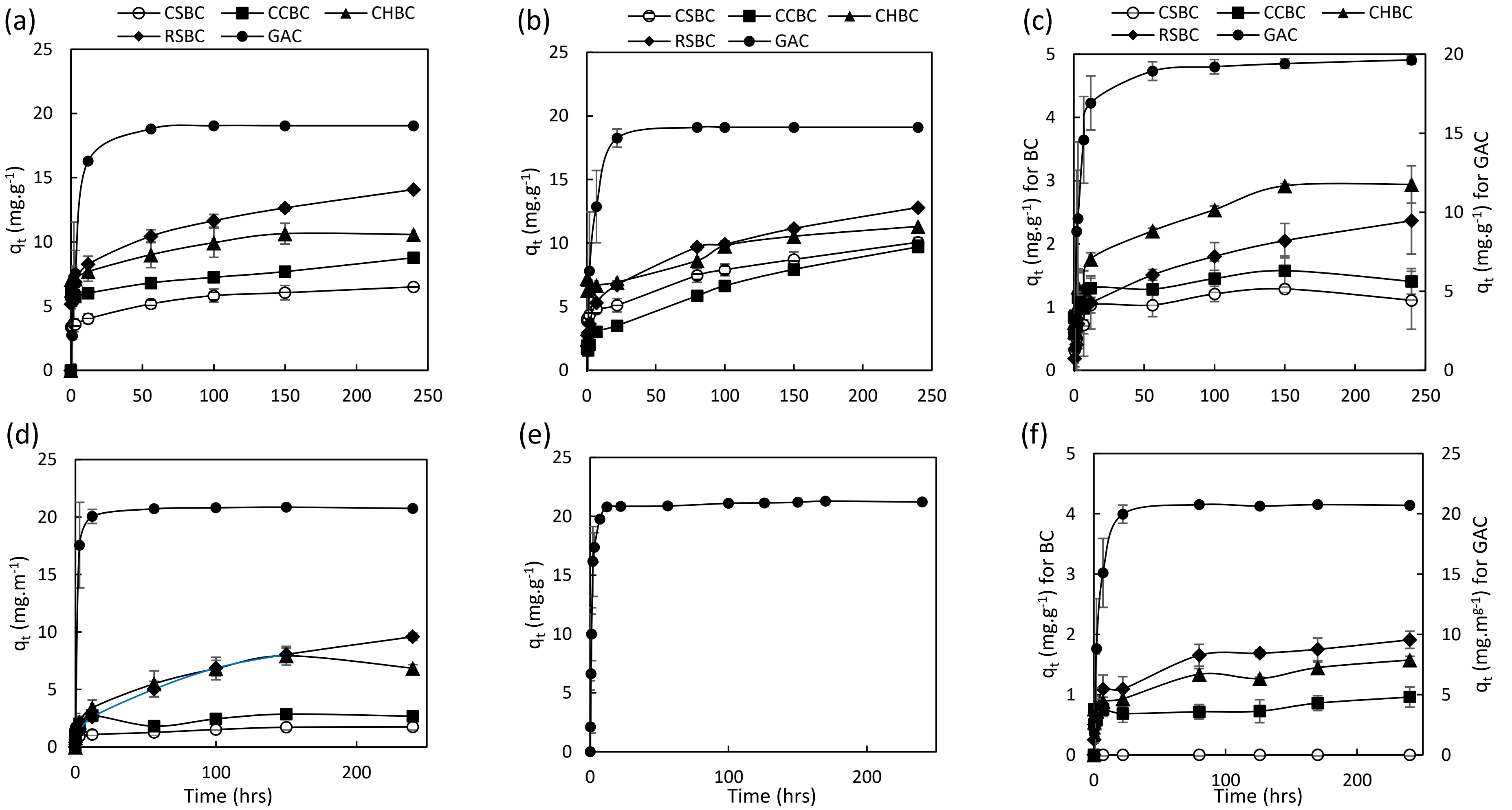


Figure 4-3. Comparison of the different treatments (mean ± standard deviation, n=5) on adsorption capacities for (a) TC (b) OTC (c) ACM (d) DRN (e) DIC and (f) ATR in the multiple-pollutant aqueous system. Initial pollutant concentration of 10 mg/L of each pollutant compound, contact time of 240 hours, and 25 mg of adsorbent in 50 mL of the initial solution. Error bars indicate one standard deviation of three batch-test measurements. All data points are plotted on a single axis except ACM and ATR with a split axis for GAC.

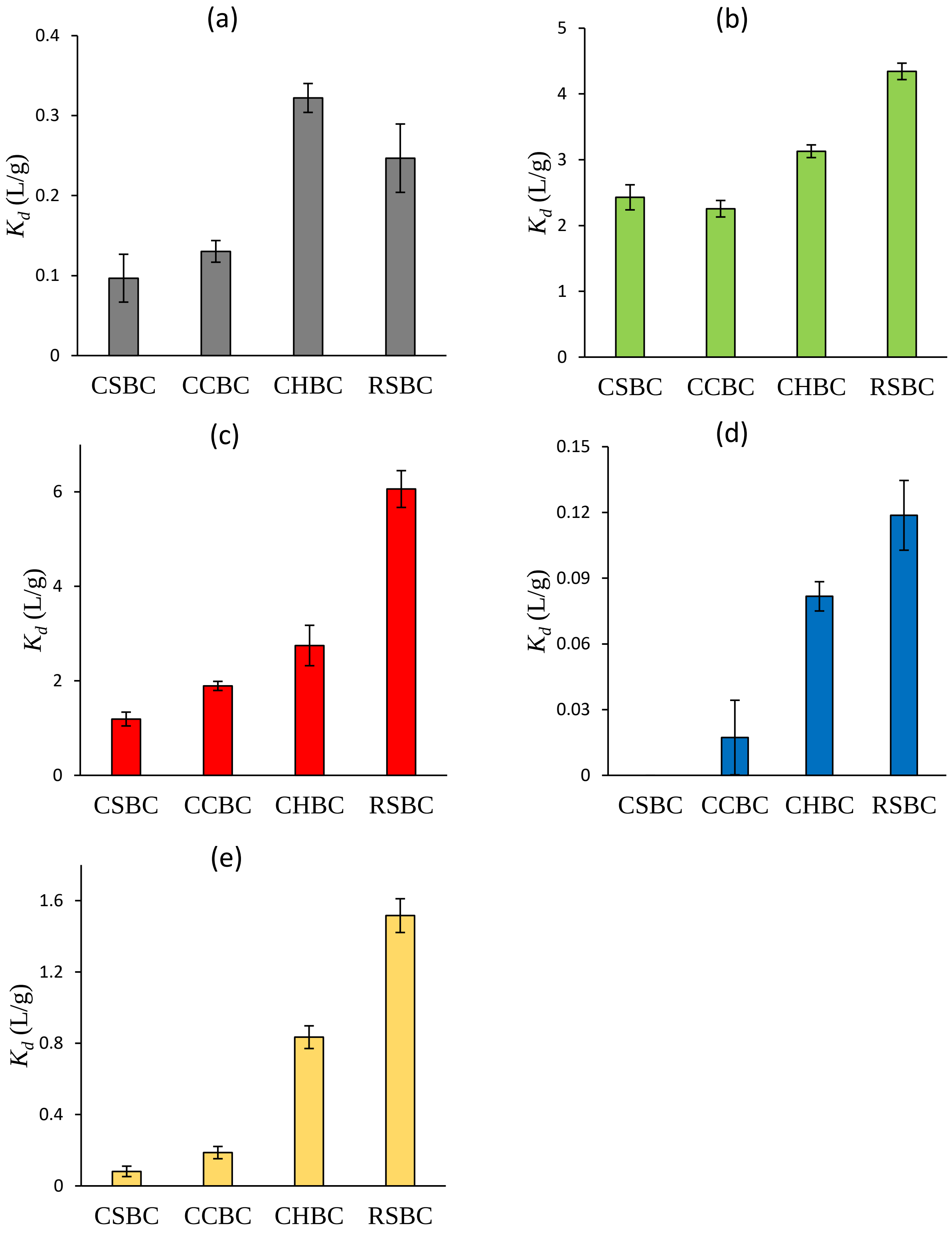


Figure 4-4 Partitioning coefficient for sorption of (a) ACM (b) OTC (c) TC (d) ATR and (e) DRN on the biochar-based adsorbents in the multiple-pollutant aqueous system. Initial pollutant concentration of 10 mg/L of each pollutant compound, contact time of 240 hours, and 25 mg of adsorbent in 50 mL of the initial solution. Error bars indicate one standard deviation of three batch-test measurements. (The experimental conditions are the same).

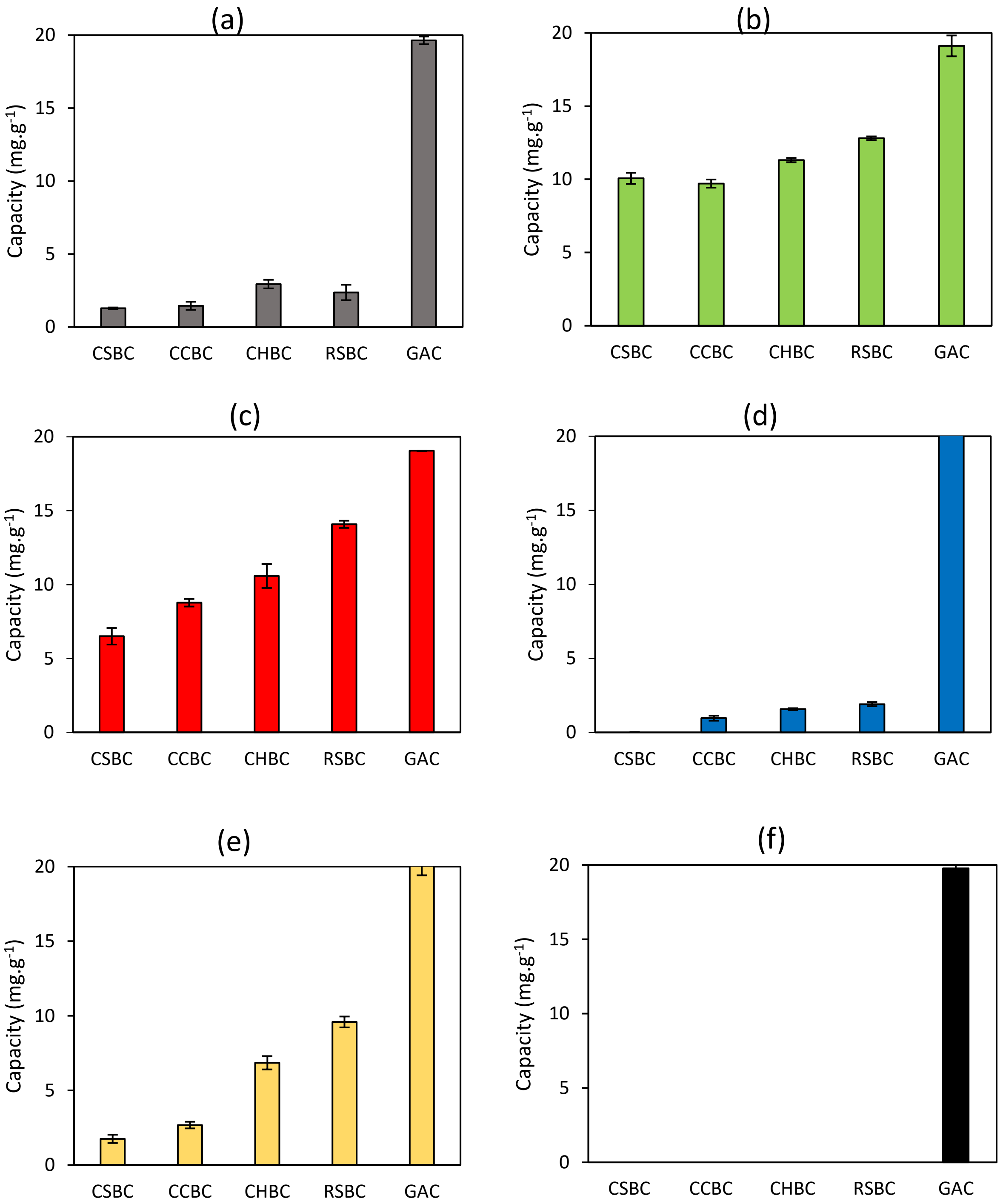


Figure 4-5. A summary adsorption capacity of the different adsorbents for (a) ACM (b) OTC (c) TC (d) ATR (e) DRN and (f) DIC in the multiple-pollutant aqueous system. Initial pollutant concentration of 10 mg/L of each pollutant compound, contact time of 240 hours, and 25 mg of adsorbent in 50 mL of the initial solution. Error bars indicate one standard deviation of three batch-test measurements. (The experimental conditions are the same).

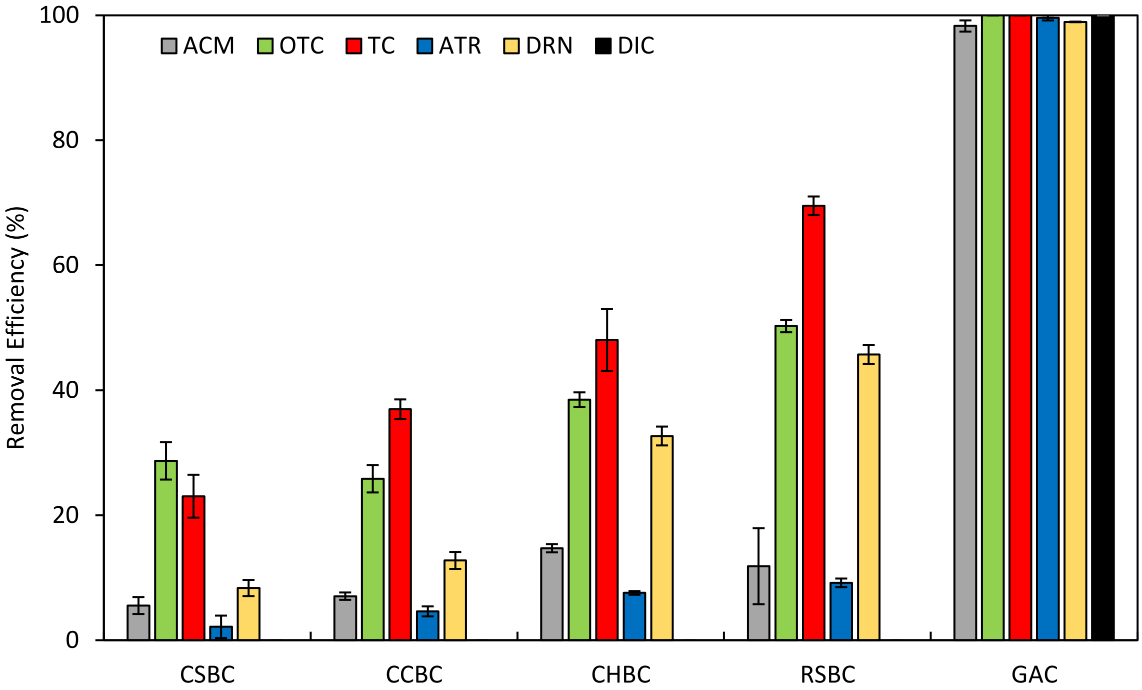


Figure 4-6. A summary of the adsorbate removal efficiencies for the different adsorbents in the multiple-pollutant aqueous system. Initial pollutant concentration of 10 mg/L of each pollutant compound, contact time of 240 hours, and 25 mg of adsorbent in 50 mL of the initial solution. Error bars indicate one standard deviation of three batch-test measurements.

Tetracycline adsorption

TC was adsorbed by both the biochar and the GAC, and removal efficiencies increased with increasing interaction time with these adsorbents (Figure 4-3(c)). The result showed in Figure 4-7(c) revealed that adsorption of TC on adsorbents was very rapid as significant uptakes of over 85.6±9.3% adsorption, equivalent to 16.3±1.8 mg/g, was achieved for GAC; while 43.4±3.4%, 40.4±2.8%, 31.6±0.5% and 21.2±1.6% was recorded for RSBC, CHBC, CCBC and CSBC respectively within the first 12 hours of contacting the adsorbents with the aqueous solutions. Thus, the adsorption capacity of the adsorbent types is ranked as follows for TC: GAC>> RSBC> CHBC> CCBC> CSBC. The highest adsorption capacities of TC by the biochars was observed for RSBC (14.1±0.2 mg/g) and CHBC (10.6±0.8 mg/g). TC showed the highest partitioning with RSBC (6.1±0.4 L/g) in Figure 4-4, while other adsorbents showed 2.7±0.4 L/g, 1.9±0.1 L/g, and 1.2±0.1 L/g, for CHBC, CCBC and CSBC, respectively.

Atrazine adsorption

Experimental results showed that GAC attained equilibrium adsorption in 12 hrs (20.7±0.1 mg/g). However, the adsorption of ATR onto RSBC proceeded more slowly (during the first 1 hr it was 2.7%), whereas adsorption onto CHBC and CCBC proceeded faster as 3.6 – 4.0% adsorption was observed within the first 1 hr. Thereafter, the rate of adsorption by RSBC was observed to increase (3.0 – 9.8%) eventually reaching its equilibrium capacity of 1.9±0.1 mg/g. Although the results showed that there was no measurable adsorption of ATR by CSBC for the period under investigation, CHBC and CCBC reached low adsorption capacities of 1.6±0.1 mg/g and 1.0±0.2 mg/g, respectively. These observations also agree with the sorption of ATR to the biochar adsorbents (K_d) as they can be ranked in the order of RSBC > CHBC >> CCBC >>> CSBC.

Diuron adsorption

Diuron adsorption kinetics were characterized by rapid adsorption in the first 12 hrs followed by a slow phase (Figure 4-7). The kinetic adsorption results suggest that while adsorption may not have reached completion after 12 hrs, the adsorption rate slowed substantially within this period except for RSBC and CHBC. The equilibration time for each adsorbent was checked after 10 days of agitation, from which time onwards there was no change in the adsorption for CSBC and CCBC. Ideally, an equilibrium time should be chosen to fairly reflect the maximum adsorption capacity of a given adsorbent, however, should be as small as feasible to facilitate experimentation and realistic contact times in water treatment. Regardless of the agitation time, the lowest adsorption was observed in the treatments with CSBC and CCBC with capacities 1.8±0.3 mg/g and 2.7±0.3 mg/g respectively. GAC was observed to completely adsorb DRN by up to 99.0±0.02% removal from the aqueous solution, followed by RSBC and CHBC with 45.7±1.5% and 32.7±1.5% removal respectively (see supplementary information). Based on the K_d value, the biochar adsorbents can be ranked in the order DRN uptake as RSBC >> CHBC >> CSBC > CCBC. The nonlinear adsorption characteristic behaviour of diuron adsorption kinetic as reported by Petter et al., (2017) is related to the gradual filling of available sorption sites. According to the author, the difficulty in occupying the vacant surface sites during the slow phase is caused by the repulsion between the molecules of the solute in the solid phase and the molecules in solution, which results in reducing the forces of attraction of solute molecules in solution for a sorbate-sorbent interface.

Diclofenac adsorption

Experimental results showed that equilibrium was reached at 98.8±0.4% removal from the aqueous phase for GAC with a recorded initial rapid adsorption for the first 12 hrs. However, there was no measurable DIC adsorption on the biochar adsorbents to be able to determine other parameters. According to Laksmono et al. (2018) increasing the adsorbent dosage will considerably enhance the removal efficiency of DIC on biochar adsorbents. In another study, the author (Lonappan *et al.*, 2018) had the opinion that raw biochar showed low removal efficiency for DIC at 10 mg/L whereas higher removal efficiencies are obtained at a lower DIC concentration of 0.5 mg/L.

4.5.3 Adsorption kinetics studies

Adsorption kinetics studies are widely used to understand the mechanisms involved in adsorbent and adsorbate interactions and provide insights into the transport of micropollutants molecules to sorption sites. Adsorption processes typically depend on the physicochemical characteristics of the adsorbents such as its pore versus solid matrix structure as well as the migration of the adsorbate (mass transfer) within these domains. In studies reported in the literature, five mechanisms have been proposed to govern the adsorption of chemicals by biochar from aqueous solutions, namely, complexation, ion exchange, precipitation, electrostatic interactions, and chemical reduction (J. J. Zhao *et al.*, 2019). However, the role that each mechanism plays for each adsorbate varies considerably depending on the target micropollutants and adsorbents. It is also important to find the adsorption rate for a given treatment system to design for its application. The adsorption kinetic data were therefore interpreted with the linear forms of the pseudo-first-order, pseudo-second-order, and Elovich models, and the calculated kinetic parameters for these three models are given in Table 4-4. Kinetic equations and theoretical aspects involved in the models are given in Table 4-3.

In the comparison of the different kinetic models, the GAC adsorbent exhibited good fitting of the experimental data with the pseudo-first-order, the pseudo-second-order and Elovich kinetic models (square correlation coefficients obtained were $R^2 > 0.91$, $R^2 > 0.99$, and $R^2 > 0.84$ respectively) for all adsorbates except for DRN. In contrast, it was observed from Table 4-4 that the pseudo-first-order kinetic model did not fit the biochar experimental data. The adsorption experimental data for the biochar adsorbents fitted well with the pseudo-second-order kinetic model with high correlation coefficients ($R^2 > 0.98$), except for the adsorption of ATR, DRN and DIC. The best-fitting model was evaluated based on both the square correlation coefficient (R^2) and the q_e(cal) value, i.e., the calculated value of adsorption at equilibrium. The values of q_e(cal) for the pseudo-first-order model were low compared to experimental values (q_e(exp)), while the q_e(cal) values for the pseudo-second-order model closely match that of the experimental values (q_e(exp)). This is important because q_e(exp) described the ultimate adsorption at equilibrium. Also, the correlation coefficient R^2 were relatively higher for the pseudo-second-order models in comparison with the pseudo-first-order model, thereby indicating that the pseudo-second-order kinetic model should be used to predict the characteristics of adsorption for ACM, OTC, and TC. The pseudo-second-order kinetics indicated that the removal is a chemical reaction, such as precipitation, complexation, and electron exchange (Hien, 2018; Hu *et al.*, 2019). The pseudo-first-order model was not considered an accurate model in this case, and the rate constants associated with it were not considered for further analysis. Remarkably, Table 4-4 also showed that the first-order (k_1) and second-order (k_2) adsorption rate constants values were closer to each other in higher R^2 plots for GAC (0.12 and 0.02) and RSBC (0.013 and 0.0012) than for the other adsorbents, suggesting similar initial uptake of their respective adsorbates onto the adsorbents for these two materials.

As stated earlier, the Elovich model is suitable to describe the adsorption behaviour that concurs with the nature of chemical adsorption (Wu, Tseng and Juang, 2009). The model evaluates chemisorption mechanisms, such as chemical bonding between micropollutants and heterogeneous surfaces of the adsorbents. The Elovich model had a much stronger fit in the kinetic adsorption data on GAC ($R^2 > 0.84$) for all adsorbates than the biochars. Notably, the RSBC also had a good fit ($R^2 > 0.90$) for the removal of most micropollutants except for DIC which experimentally showed no adsorption onto any of the biochar adsorbents. CHBC, CCBC, and CSBC obtained fluctuating R^2 values which were relatively low for most of the adsorbates, ranging from 0.09 to 0.92 and suggesting a nonchemical adsorption mechanism (McMillan, 2018). This is likely due to the differences in the chemical properties of the adsorbents from different sources.

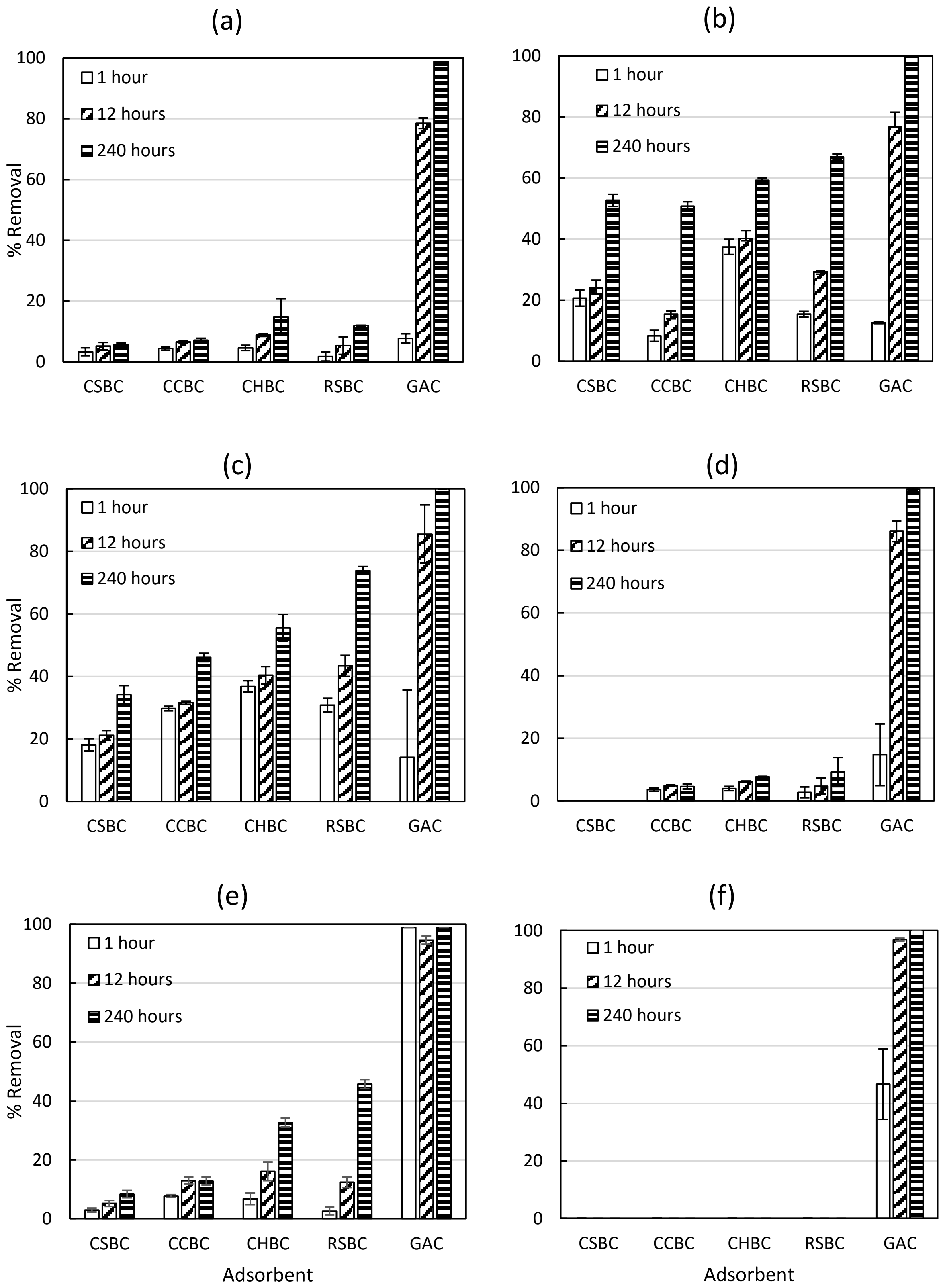


Figure 4-7. Comparison of the removal efficiencies for the different adsorbents for different time intervals (a) ACM (b) OTC (c) TC (d) ATR (e) DRN and (f) DIC in the multiple-pollutant aqueous system. Initial pollutant concentration of 10 mg/L of each pollutant compound, contact time of 240 hours, and 25 mg of adsorbent in 50 mL of the initial solution. Error bars indicate one standard deviation of three batch-test measurements.

4.5.4 Adsorption diffusion models

Since the pseudo-first-order or pseudo-second-order model could not always be used to understand the diffusion mechanisms and rate-controlling steps affecting the adsorption kinetics, the kinetic adsorption data were fitted to film diffusion and intraparticle diffusion models. Weber and Morris (1963) found using an empirical model that in many adsorption cases, solute uptake varies almost proportionally with $t^{1/2}$ rather than being linearly related to the contact time t. According to the Weber-Morris model, the intraparticle diffusion plots should be a straight-line plot going through the origin, with a slope (diffusion rate constant, k_{id}) when the intraparticle diffusion is a rate-limiting step. However, this was not always the case in this study as the plots were not linear over the whole time range, implying that the adsorption process may be controlled by both film diffusion and intraparticle diffusion simultaneously. Cheung, Szeto and Mckay, (2007) argued that the variate nature of these plots could be explained by boundary layer diffusion, which gave the first portion and the intraparticle diffusion that gave the further two linear portions. In general, the adsorbent plots given in Figure 4-8 showed a clear distinction between these two different phases of adsorption, and the final equilibrium phase was not reached in some cases. The relatively good fitting of the model parameters (given in Table 4-4) suggest that the microporous regions are generally playing a significant role in the adsorption process. One could observe that since the slope of the plots corresponded to rates of the adsorption process, the diffusion in the bulk phase to the exterior surface of adsorbents (boundary layer diffusion) controlled kinetics at the onset of the process and was fast for most of the adsorbents. This then implied that the intraparticle diffusion of adsorbate molecules into micropores of the adsorbents was the rate-limiting step, particularly over long contact periods. There is a clear slow diffusion phase from $t^{0.5} \approx 4$ to 17 $\text{hours}^{0.5}$, which suggests that intraparticle diffusion does play a role in the adsorption process.

In comparing the plots of different adsorbents and different adsorbates, the slopes generally increased in the order GAC>>> CHBC> RSBC> CCBC> CSBC, which corresponded to enhanced diffusion of adsorbate molecules from the exterior surface of the adsorbent through the micropores. In general, the initial adsorption rate of GAC is 10 times faster than for the best biochar adsorbent (RSBC and CHBC) used in this study. These results fit closely with the adsorption efficiency observed in the adsorption kinetics studies.

Table 4-4. Adsorption kinetics parameters for the adsorption of selected micropollutants onto the various adsorbents

Adsor-bate	Adsor-bent	Pseudo First-Order				Pseudo Second-Order				Elovich Model		
		K_1 (min^{-1})	q_e (exp) (mg/g)	q_e (cal) (mg/g)	R^2_{adj}	K_2 (g/mg·hr)	q_e (exp) (mg/g)	q_e (cal) (mg/g)	R^2_{adj}	β (g/mg)	α (mg/g·min)	R^2
ACM	CSBC	0.0228	1.1182	0.6825	0.6894	0.4105	1.1184	1.1184	0.9871	8.4104	9.9772	0.6521
	CCBC	0.0333	1.3982	0.8057	0.8135	0.2426	1.3790	1.3791	0.9831	8.0128	42.6528	0.5707
	CHBC	0.0207	2.9382	2.2673	0.9164	0.0267	2.9382	2.9621	0.9870	2.6295	2.6209	0.8884
	RSBC	0.0137	2.3582	1.5385	0.9578	0.0439	2.3582	2.2769	0.9839	3.1726	1.2415	0.9335
	GAC	0.1600	19.6382	18.1687	0.9755	0.0176	19.6382	19.8807	0.9997	0.3230	17.4015	0.8974
OTC	CSBC	0.0102	10.9600	6.0394	0.9973	0.0125	10.9600	10.4058	0.9857	1.0128	66.9774	0.7205
	CCBC	0.0098	10.6000	7.8452	0.9946	0.0066	10.6000	10.0000	0.9633	0.8610	8.1918	0.8261
	CHBC	0.0098	12.2000	4.6000	0.9351	0.0176	12.2000	11.7233	0.9920	1.5382	90427	0.8219
	RSBC	0.0134	8.6200	8.6470	0.9646	0.0012	8.6200	11.1607	0.9690	0.4974	0.4625	0.9545
	GAC	0.1406	19.1400	18.0347	0.9912	0.0212	20.0000	20.2840	0.9997	0.2510	44.6096	0.8451
TC	CSBC	0.0125	7.4600	2.6639	0.8885	0.0589	7.4600	6.8918	0.9978	2.1993	7426	0.8843
	CCBC	0.0075	9.7200	2.9991	0.9788	0.0526	9.7200	8.7413	0.9971	1.9463	374847	0.9248
	CHBC	0.0120	11.5200	3.4535	0.8235	0.0249	11.5200	11.3250	0.9950	1.6510	52338	0.6299
	RSBC	0.0129	15.0200	8.1165	0.9353	0.0128	15.0200	14.5138	0.9930	0.8086	248.4767	0.9786
	GAC	0.1607	20.0000	18.5588	0.9973	0.0208	20.0000	20.2840	0.9997	0.2345	4.3000	0.9801
ATR	CSBC	-	-	-	-	-	-	-	-	-	-	-
	CCBC	-0.0055	0.1800	0.1720	0.3430	718663	0.1800	0.0398	0.1192	10.1626	0.0029	0.0876
	CHBC	-0.0009	0.7800	0.2842	0.0038	57.9322	0.7800	0.8891	0.7656	5.5371	0.0629	0.5440
	RSBC	0.0037	1.1200	0.6852	0.0152	0.0117	1.1200	1.3012	0.8207	4.0225	0.0550	0.9077
	GAC	0.0529	19.9200	11.1217	0.9148	0.0159	19.9200	20.3252	0.9990	2.6660	0.0000	0.9192
DRN	CSBC	0.0143	0.7800	1.2181	0.8729	0.0059	0.7800	1.1956	0.3364	2.2795	0.1230	0.8811
	CCBC	0.0063	1.7000	1.1147	0.1367	-0.0943	1.7000	1.3317	0.5435	5.0736	0.8454	0.5369
	CHBC	0.0102	5.8800	4.4786	0.5116	0.0038	6.8400	6.7340	0.9048	0.8595	0.6900	0.8696
	RSBC	0.0134	8.6200	8.6469	0.9646	0.0012	8.6200	11.1607	0.9690	0.4974	0.4625	0.9545
	GAC	0.0142	19.8400	1.4174	0.3406	0.0827	19.8400	19.8807	1.0000	0.2689	51.8794	0.9062
DIC	CSBC	-	-	-	-	-	-	-	-	-	-	-
	CCBC	-	-	-	-	-	-	-	-	-	-	-
	CHBC	-	-	-	-	-	-	-	-	-	-	-
	RSBC	-	-	-	-	-	-	-	-	-	-	-
	GAC	0.1838	20.0000	19.1538	0.9946	0.0185	20.0000	20.3252	0.9998	0.2493	18.0664	0.9472

Table 4-5. Adsorption mechanism parameters for the adsorption of selected micropollutants onto the various adsorbents

Adsorbate	Adsorbent	Intra-particle Diffusion Model			Boyd Kinetic Model		
		K_{id} (mg/g·hr$^{0.5}$)	*I* (mg/g)	R^2	B	D_i (x10^{-11} m^2/s)	R^2
ACM	CSBC	0.0517	0.5208	0.5995	0.0033	51.4640	0.3433
	CCBC	0.0554	0.7157	0.5454	0.0026	40.5474	0.2388
	CHBC	0.1651	0.7239	0.9006	0.0008	12.4761	0.0868
	RSBC	0.1434	0.3797	0.9384	0.0123	191.8205	0.8051
	GAC	4.5381	0.1861	0.9346	0.0290	452	0.8551
OTC	CSBC	0.4860	3.7821	0.8480	0.0031	48	0.9345
	CCBC	0.5703	1.8278	0.9679	0.0101	158	0.9804
	CHBC	0.4138	6.1896	0.5960	0.0107	167	0.8351
	RSBC	0.6470	-0.6400	0.9780	0.0134	209	0.9646
	GAC	5.2243	-0.5836	0.9646	0.1406	2193	0.9912
TC	CSBC	0.2794	3.631	0.6698	0.0021	33	0.8164
	CCBC	0.2791	5.5291	0.4684	0.0025	39	0.9642
	CHBC	0.3937	6.2887	0.564	0.0038	59	0.9125
	RSBC	0.6764	5.7513	0.8166	0.0083	129	0.9912
	GAC	5.2343	-0.4054	0.9833	0.2299	3585	0.9881
ATR	CSBC	-	-	-	-	-	-
	CCBC	0.0154	0.0370	0.0767	0.0000	0.4679	0.0660
	CHBC	0.0557	-0.0836	0.6592	0.0002	3.1190	0.7313
	RSBC	0.0798	-0.9065	0.9458	0.0002	3.1190	0.8356
	GAC	4.8396	0.0319	0.9346	0.0282	440	0.7709
DRN	CSBC	0.0927	-0.4670	0.9457	-0.0069	-108	0.7422
	CCBC	0.0808	0.3514	0.4621	-0.0126	-196	0.2820
	CHBC	0.4462	-0.0180	0.9057	-0.0093	-145	0.6223
	RSBC	0.6387	-0.5419	0.9741	-0.0100	-156	0.7356
	GAC	2.5525	9.1321	0.8418	-0.0007	-11	0.2823
DIC	CSBC	-	-	-	-	-	-
	CCBC	-	-	-	-	-	-
	CHBC	-	-	-	-	-	-
	RSBC	-	-	-	-	-	-
	GAC	4.5175	0.3536	0.9647	0.1607	2506	0.9973

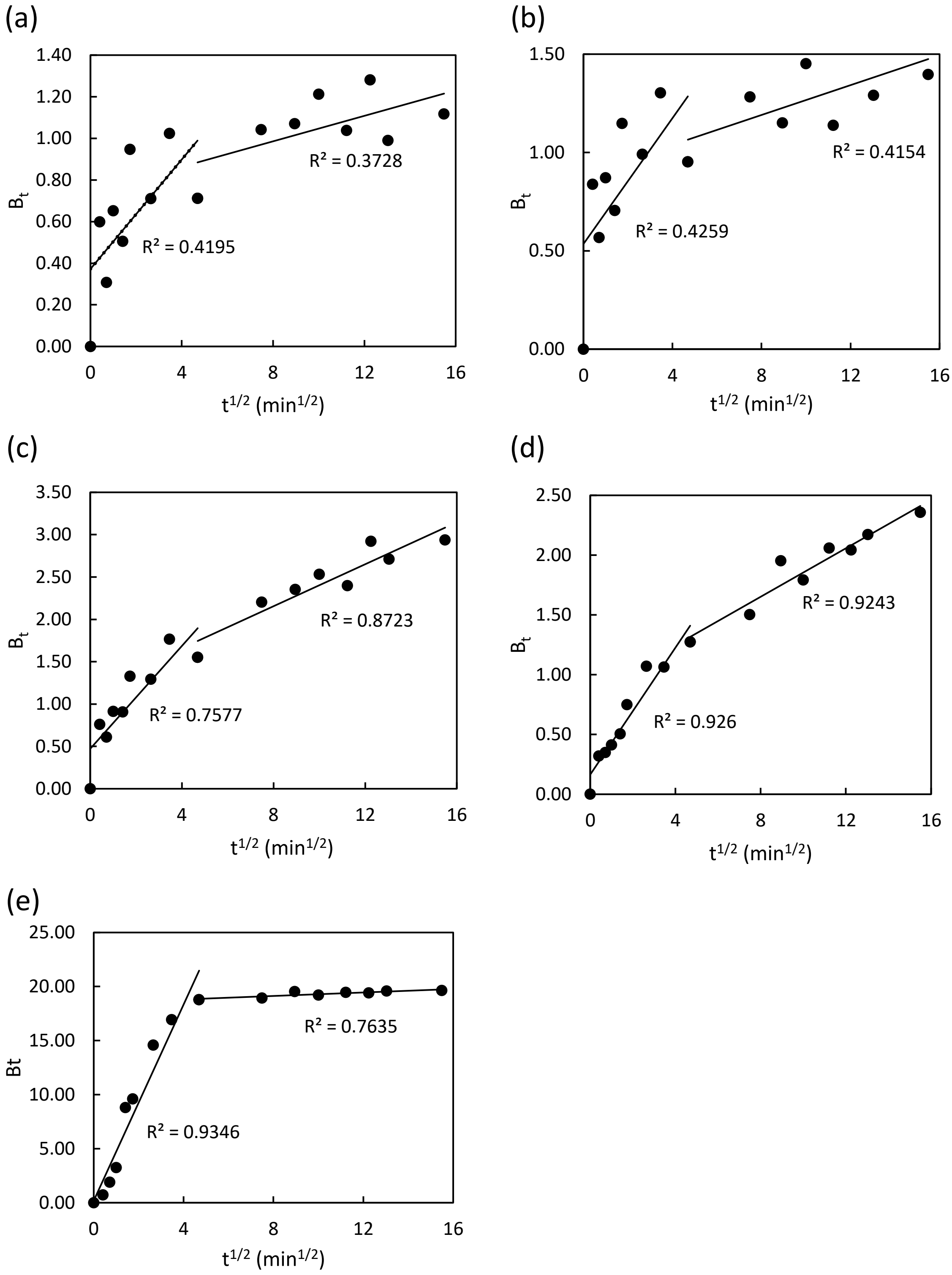


Figure 4-8. Boyd kinetic plots for ACM adsorption onto the five adsorbents; (a) CSBC (b) CCBC (c) CHBC (d) RSBC (e) GAC in the multiple-pollutant aqueous system. Initial pollutant concentration of 10 mg/L of each pollutant compound, contact time of 240 hours, and 25 mg of adsorbent in 50 mL of the initial solution.

4.6 Conclusions

In this study, competitive adsorption characteristics of adsorbed ACM, DRN, OTC, ATR, TC and DIC, were assessed on biochar produced from four feedstocks and compared to that of activated carbon. The four biochars produced from agricultural biomass residues in Thailand showed relatively good adsorption capacities for TC, OTC and DRN in aqueous solution. However, the batch experiments demonstrated that the GAC had better adsorbent kinetic properties than the biochar-based adsorbents with more than 10 times the adsorption rate of the best biochar adsorbent used in this study. Comparatively, the kinetic study indicated that biochars derived from rice straw (RSBC) and coconut husk (CHBC) showed better adsorption capacity than biochars derived from coconut shell (CSBC) and corn cob (CCBC) as illustrated by their respective K_d values. The results showed that the different adsorption profiles of each biochar were largely a result of their different chemical and physical properties, and their adsorption was found to be dependent on the contact time with the adsorbates. In general, the batch adsorption studies have indicated that pore filling is a significant process in the immobilisation of micropollutants onto the biochars, particularly for RSBC and CHBC, and that the adsorption mechanism was predominantly intraparticle diffusion. The Boyd and Weber diffusion models were best able to distinguish between these effects.

From these results, it can be concluded that the potential of biochar for micropollutants immobilization is feedstock type-dependent, and it is important that these are explored before using the biochar as amendments for pollutants removal. As mentioned earlier, an adsorbent's pores and surfaces determine its availability for adsorption, while its surface chemistry influences its chemical affinity to adsorbates. Likewise, the presence of the functional groups, molecular conformation, weight, size, polarity, and solubility of an adsorbate affect the adsorption. The results showed that TC and OTC with higher molecular weights are the most removed adsorbates by the different biochar species, while DIC with the lowest solubility is the least adsorbed by the biochar. The results agreed with the hypothesis set for the most adsorbed micropollutant.

Overall, the results suggested that RSBC and CHBC biochars could be environmentally sustainable alternatives to GAC for micropollutant removal from wastewater, as their use could cost less; however, net benefits also depend on biochar production conditions and treatment capabilities. Also, although the kinetic adsorption plots suggest that the removal efficiency trends of biochar-based adsorbents can be evaluated from the batch adsorption studies, batch experiments usually are conducted under ideal conditions, which may not reflect the ‘real’ adsorption efficiency of the adsorbents under dynamic conditions.

Although this chapter investigated the competitive removal of micropollutants using biochar under limited or no microbial interference, the proceeding chapter presents investigations into the influence of CHBC sand amendment biofiltration system on micropollutant removal using real wastewaters and under varied operational conditions. This will further give insights into the fate and transport of micropollutants in column studies and the dependency of micropollutants removal on the flow rate, influent concentration, and empty bed contact time. Additionally, it will help in providing useful data that can be used in the design of a biochar-based biofiltration system from such realistic conditions.

Chapter 5. Organic micropollutant removal in surface water biofiltration using fine sand with and without coconut husk biochar amendment

Abstract

In this study, biofilters with fine sand (FISA) or 10% w/w coconut husk biochar-amended fine sand (CHBC) were comparatively assessed for their potential to remove six micropollutants (four pharmaceutically active compounds and two pesticides compounds). The micropollutants covering a range of sorption properties and biodegradation pathways were spiked as a mixture (each at 100 µg/L) into pond water for laboratory column filtration experiments. Continuous flow and alternate drying and wetting cycles were investigated at 22°C under gravity flow conditions to mimic passive treatment systems such as constructed subsurface flow wetlands with the vertical flow. In the continuous flow study, the hydraulic flow velocities started at 24.5 m/day and 1.87 m/day for the FISA and CHBC columns, respectively. The resulting differences in the empty bed contact times (EBCT) were 12 to 20 mins in FISA versus 150 to 240 mins in CHBC. The micropollutants were attenuated by a combination of adsorption and biodegradation processes in the columns. TC and OTC were generally attenuated more significantly ($p<0.05$) than ATR and DRN in both filter media types. Total removal efficiency (25 – 60%) obtained in the FISA columns was significantly less than the total removal efficiency (97 – 100%) obtained in the CHBC columns, likely because the enhanced EBCT in the CHBC media provided more time for pollutant biodegradation as the water passes through the column. From the breakthrough plots, a high removal variability between the two media types was observed, but not between the flow conditions. Microbial analysis including cluster and principal component analyses confirmed an effect of the filter media type on the composition of the associated bacterial community, although the distance from the surface was identified as the most important factor in shaping the filter bed bacterial communities. The findings suggest that the micropollutant adsorption by the biochar did not inhibit the micropollutant biodegradation processes, since most of the micropollutant mass was removed via biodegradation (>90% in CHBC). The results, therefore, conclude that CHBC is a promising filter medium amendment for robust removal of emerging pollutants from surface water.

5.1 Introduction

Micropollutants represent a wide variety of chemical compounds detected in the aquatic environment which originate from anthropogenic practices such as agricultural, municipal and industrial discharges, but often go unnoticed due to low concentrations ranging from below detection to the µg/L level (Kim *et al.*, 2007; Suárez *et al.*, 2012; Anjum, Gill and Tuteja, 2017; Ramírez-Malule, Quiñones-Murillo and Manotas-Duque, 2020). The occurrence and continuous discharge of non-regulated organic trace pollutants, known as emerging micropollutants, in the environment and their potentially harmful impacts on both human and aquatic life are now an issue of global concern as their removal during the conventional wastewater treatment is only partial or incomplete (Gros *et al.*, 2010). Besides pesticides that are widely used for pest control in agriculture may also end up in the environment. Pharmaceutical compounds originating from animal husbandry, municipal, hospitals or laboratory wastewaters nowadays also contribute to the list of micropollutants that increasingly cause contamination of surface water bodies (Kot-Wasik, Debska and Namieśnik, 2007). To protect surface waters, the European Commission adopted a Water Framework Directive (2000/60/EC) and established a watch list of priority substances as a control policy measure against contaminated water (Comissão Europeia, 2001). This regulation harmonises quality standards and emission controls of certain substances to achieve a good ecological and chemical status in surface waters among member states. Because of advances in analytical techniques extremely low concentrations of micropollutants can nowadays be measured in water (Kim *et al.*, 2007; Kot-Wasik, Debska and Namieśnik, 2007). In addition, a variety of physical, chemical and biological technologies have recently been proposed to remove or degrade residues of micropollutants in wastewater (Ahmed *et al.*, 2017; Anjum, Gill and Tuteja, 2017). However, the mechanisms determining the fate of these micropollutants and their removal in biological treatment systems are complex and not yet well understood.

The fate of micropollutants in biological treatment systems and the environment depends on several factors, including diffusion, convection, evaporation, adsorption-desorption, transformation, biodegradation, etc. (Zhang et al., 2018; Zhao et al., 2020) and is regulated by the interplay of both microbial and physicochemical processes (De Wilde *et al.*, 2009). The adsorption of many micropollutants to suspended solids during wastewater treatment was reported in Zhang et al. (2018) and as a result, they are found in sludge through sedimentation, which suggests that adsorption of micropollutants to solids occurs almost immediately upon contact. However, they added in the same study that the high bioavailability and degradation associated with some pollutants were a result of low adsorption capacity, and hence biodegradation is equally important as a removal process. Mrozik et al. (2019) and Acharya et al. (2019) agreed that the transportation and bioavailability of micropollutants for degradation is dependent on their unique chemical binding modes, the type of degrading microbial community, and the environmental conditions (i.e., aerobic and anaerobic). Ultimately, whereas adsorption can remove micropollutants from water, it will create a micropollutant loaded adsorbent as by-product and waste management challenge, whereas bacteria in biological treatment processes will consume micropollutants and eventually convert them into carbon dioxide (Ahmed *et al.*, 2017; Palansooriya *et al.*, 2019). Hence, biological treatment is by far the most widely used technology for micropollutants removal from wastewater (Ahmed et al., 2017; Zhang et al., 2018).

Biofiltration is a fixed bed technique that combines physical retention and biological attenuation processes to remove dissolved pollutants from water. This method often involves the trickling of polluted water through biological sand filters in biotic conditions. Although several recent studies have focused on the removal of micropollutants in biofiltration systems from the action of mixed cultures of microorganisms (Lou *et al.*, 2015; Paredes *et al.*, 2016; Palansooriya *et al.*, 2019), more studies have reported that the efficiency of microorganisms toward degradation can be enhanced by optimizing the various physiochemical parameters in the filtration processes (Anjum, Gill and Tuteja, 2017; Palansooriya *et al.*, 2019). Sand biofiltration is a cost-effective technology due to the low cost of sand but recently, different materials such as activated carbon, biochar, etc., have been proposed as biological filter media amendments due to their perceived advantages: great potential to adsorb micropollutants and improve the quality of effluent by lowering pollutants concentration and minimising transformation products (Ulrich et al., 2017; Paredes et al., 2016; de Castro et al., 2018; Wolfand et al., 2019; Boehm et al., 2020). Although the selection of media should be based on numerous parameters, in reality, media with good support properties for biodegradation and lower production cost tend to be selected. Therefore, biochar exhibits several advantages due to its low costs and desirable physicochemical properties and characteristics that are largely governed by the biochar feedstock types, pyrolysis conditions, modification techniques, and resulting ability to host and stimulate indigenous microbial activities (Palansooriya *et al.*, 2019). Despite these strengths, biofiltration in biochar amended filters remains poorly studied regarding the mechanisms of micropollutant removal in biofilters operated under bioactive environmental conditions.

For a more comprehensive understanding of the fate of micropollutants in a biofiltration system under varying conditions, column displacement experimental set-ups are recommended (De Wilde *et al.*, 2009; Mandal, Singh and Purakayastha, 2017) with varying filtration media types and applied conditions. In this study, tetracycline, oxytetracycline, atrazine, diuron, acetaminophen, and diclofenac were chosen as the model pollutants spiked into pond water to mimic naturally contaminated surface water, while fine sand and coconut husk biochar were selected to constitute the filtration media. Although results from Chapter 3 of previous column studies showed specifically that, leachates from coconut husk biochar showed very high TSS content and very low hydraulic conductivity and very poor volumetric flow compared to all other tested adsorbents, Chapter 4 experiments demonstrated that coconut husk biochar is also a good candidate for micropollutants adsorption. Moreover, coconut husk biochar adsorbent has been successfully used in a field trial to remove a range of pesticides and pharmaceuticals from surface water at a dose of 10% (Mrozik *et al.*, 2021). Hence, the objective of the column studies was to extend the work by Mrozik et al. (2021) over more filtration cycles to understand the respective contributions of adsorption and biodegradation in micropollutant removal in the laboratory, since the application of biochar to sands changes the physicochemical properties and drives the hydraulic properties and microbial community that influences the adsorption and biodegradation performance of the blended media (Palansooriya *et al.*, 2019). The vast majority of the studied literature published in the field of pollutants elimination from water only focuses on the overall efficiency of the eliminating media, in which the raw influent and final effluent were sampled in order to determine the overall removal of pollutants from the liquid phase. Less attention was given to the main mechanisms involved in biofiltration (i.e. adsorption versus biodegradation) (Suárez *et al.*, 2012; Paredes *et al.*, 2016). Also, most laboratory column studies used pumps to maintain constant and equal flows through various filter media compositions, whereas low-cost passive treatment systems more typically are designed to operate under gravity flow. This study explored the relative contribution of sorption and biodegradation to the micropollutant removal for two different filter media (fine sand versus fine sand amended with biochar) using an integrated mass balance calculation (Suárez *et al.*, 2012; Lou *et al.*, 2019). In addition, filter media effects on hydraulic parameters under gravity flow conditions, and the microbial communities associated with the two media were also investigated. Comparison of the community level genetic profiling data derived from 16S rRNA gene amplicon sequencing allowed evaluation of the shift in the microbial community within the soil column and expression of the microbial diversity in the two media types. The information generated from this research regarding the biofiltration performance for fine sand versus fine sand amended with biochar will improve understanding of the biochar amendment effects on the fate of micropollutants in biochar-amended sand media, and ultimately assist in improving the design of low-cost and nature-based treatment systems such as, for example, subsurface flow constructed wetlands.

5.2 Aims and objectives

This study aimed to demonstrate the benefits of biochar amendment for enhanced micropollutant removal from contaminated water in sand amended biofilters. The main objective of this study was to extend this work by Mrozik et al. (2021) in the laboratory over more filtration cycles, using coconut husk biochar which is shown from literature to have the best universal sorption properties (Mrozik *et al.*, 2021), to understand the respective contributions of adsorption and biodegradation in the micropollutant removal.

Specific objectives were to:

(i) Evaluate the removal efficiency of six selected micropollutants from surface water in fine sand biofilters operated under gravity flow conditions, with and without coconut husk biochar amendment.

(ii) Establish the relative contribution of sorption versus biodegradation as attenuation mechanisms for the micropollutant removal.

(iii) Establish the effects of biochar amendment on the hydraulic properties of the filters and micropollutant removal under constant head versus wetting and drying conditions.

(iv) Investigate the effects of biochar amendment on the biofilter microbial communities.

The experimental work tested the following hypotheses:

i. The amendment of sand with biochar enhances the removal of micropollutants in biofiltration systems.

ii. Biochar amended sand biofilters have the potential to stimulate biodegradation activities needed to degrade micropollutants in biofiltration systems.

iii. At 10% amendment of sand, biochar amended filters operate with slower filtration rates for gravity flow conditions as compared to pure sand.

iv. Biochar amended sand biofilters have distinct microbial communities compared to the unamended sand.

5.3 Materials and methods

5.3.1 Chemicals, stock solution and influent solution preparation

Analytical grade chemicals and reagents were used for the experiments. The six test chemicals (micropollutants) were selected from a previous chemical dataset as described in Chapter 4, Section 4.4.2, considering that these selected chemicals cover a range of emerging micropollutants (pesticides and pharmaceuticals) found in surface water (Jorge Bedia *et al.*, 2018) with variable biodegradation pathways. The micropollutants have been detected in surface water used for aquaculture in Thailand, where biofiltration with or without biochar produced from local agricultural waste material might provide an inexpensive treatment accessible to small scale aquaculture farmers (Mrozik *et al.*, 2019). To mimic contaminated surface water, a mixture of the six micropollutants was spiked into natural surface water obtained from a pond located in Newcastle Exhibition Park, UK (54°59′08.6″N, 1°36′59.7″W) near Newcastle University (NU). The spiked surface water was then used in the laboratory to investigate the pollutant attenuation under gravity flow conditions.

A stock solution of the six micropollutant compounds was prepared by dissolving predetermined amounts of each compound in methanol to obtain a concentration of 1000 mg/L and was kept closed in the dark at 4°C. Then a mixed pollutant solution of 100 mg/L for each of the different compounds was prepared by diluting the stock solution ten-fold with distilled water and stored at 4°C. Also, a working solution concentration (C_0) of 100 µg/L was prepared by spiking 1 L of the pond water with 1 mL of the mixed pollutants solution and used as the influent solution to study the ability of the filter media to remove the different micropollutant concentrations as reported in Table 5-1. The standard solution was then diluted further to provide each analyte with six concentrations prepared for calibration curves: 0.1, 1, 5, 10, 50, and 100 µg/L.

5.3.2 Sand and biochar preparation

The fine sand was obtained from the Geotechnical Laboratory of the School of Engineering, Newcastle University campus (UK) and the coconut husk biochar from collaborators at King Mongkut's University of Technology Thonburi in Thailand. The sand and biochar properties were already described in Chapter 3, Section 3.4.2 and Section 3.4.3 of this Thesis.

Table 5-1. The initial concentrations of the studied compounds and a summary of their key properties (also provided in Table 4.1 of this thesis)

Name Abbr.	Use	Henry's Law Constant (atm-m^3/mol at 25 °C)	Chemical Formula	MW (g/mol)	Influent Concentration (µg/L)
DRN	Pesticides	5.04 X 10^{-10}	$C_9H_{10}Cl_2N_2O$	233	100
ATR	Pesticides	2.63 X 10^{-9}	$C_8H_{14}ClN_5$	216	100
ACM	Pharmaceut.	8.93 X 10^{-10}	$C_8H_9NO_2$	151	100
OTC	Pharmaceut.	1.70 X 10^{-25}	$C_{22}H_{24}N_2O_9$	481	100
TC	Pharmaceut.	4.66 X 10^{-24}	$C_{22}H_{24}N_2O_8$	444	100
DIC	Pharmaceut.	4.73 X 10^{-12}	$C_{14}H_{11}Cl_2NO_2$	318	100

5.3.3 Laboratory column set up

A column study was conducted by using vertical columns with open ends made of borosilicate glass about 500 mm high and 20 mm inner diameter. The bottoms of the funnel-shaped end of each column were plugged with glass wool to make a support for the filter media particles and prevent their loss during filter operation. The columns were homogeneously and gently packed with fine sand or sand amended with biochar. The sand amended columns were set up using 10% dry masses of coconut husk biochar (i.e., 10% biochar or activated carbon, 90% fine sand). The amendment dose is similar to previous works by Novak et al. (2009), Fellet et al. (2011), Khan et al. (2014) and Mrozik et al. (2021).

Dry-packing was chosen rather than wet-packing as biochar floats during wet-packing which may prevent uniform distribution of the media in the filter (Mohanty *et al.*, 2014). This experiment was operated under gravity flow conditions to simulate a passive treatment system that allows the influent to trickle down without pumping whilst enabling contact between the adsorbate and the adsorbent (Chauhan and Talib, 2017). About 55 g of fine sand and 32 g of amended filter media material was manually poured directly into each column to achieve an equal bed height of 200 mm and was sandwiched between 10 mm layers of coarse sand both at the top and at the bottom of the media core (as shown in Figure 5-1). The coarse sand reduced clogging to allow drainage flow and also reduced media suspension during filter loading with influent water. Henceforth, these columns were referred to as 'Fine Sand' (FISA) and 'Coconut Husk Biochar' (CHBC) columns even though the CHBC column also contains 90% (by weight) fine sand. The columns were set up in triplicate for each medium (n=3), and after packing were left undisturbed at 20±2°C for 48 hours to allow for natural settlement of the media.

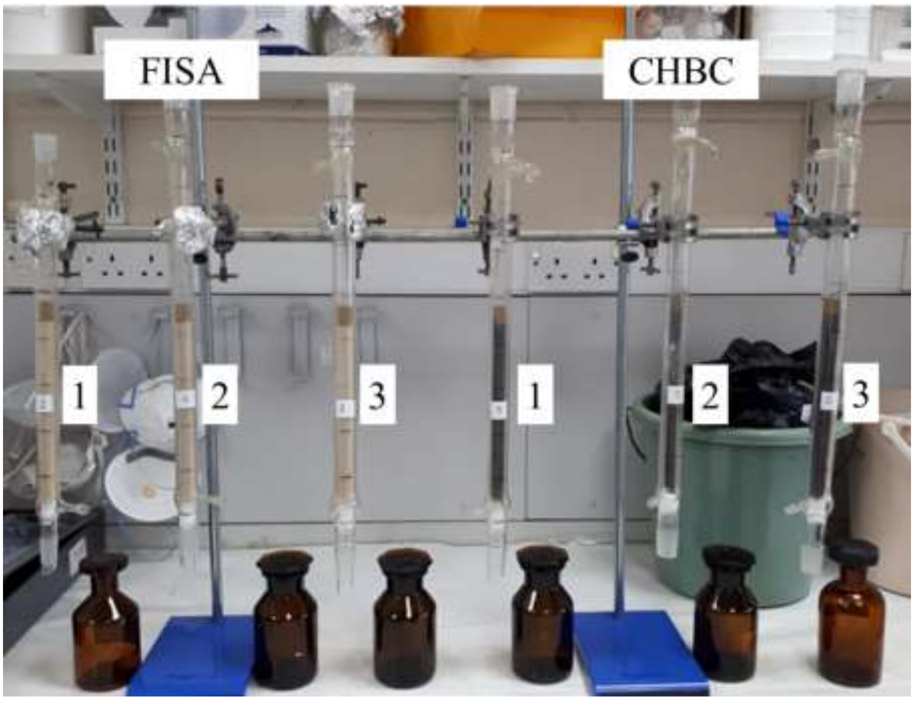


Figure 5-1: Laboratory column setup for the biofiltration system.

5.3.4 Gravity flow column studies

The attenuation of the selected organic pollutants on the two filter media was studied. The columns were first continuously flushed with 18Ω-cm MiliQ deionised water flowing through the porous medium under gravity for 2 hours to equilibrate and wash out impurities from the system. After that period, freshly prepared influent of the required micropollutant concentrations was quickly added to the filtration columns and allowed to percolate under gravity (Ding *et al.*, 2010; Chauhan and Talib, 2017). The influent flow rate during the experiments was influenced by the characteristic of the column media and was determined by measuring the volume of effluent in mL per unit time at regular intervals. The concentrations of the different analytes were determined in samples from both the columns inlets and outlets at regular time intervals. Figure 5-2 presents schematics of the experimental setup for the column studies. All the column experiments were run at room temperature (20±2°C) for two flow conditions:

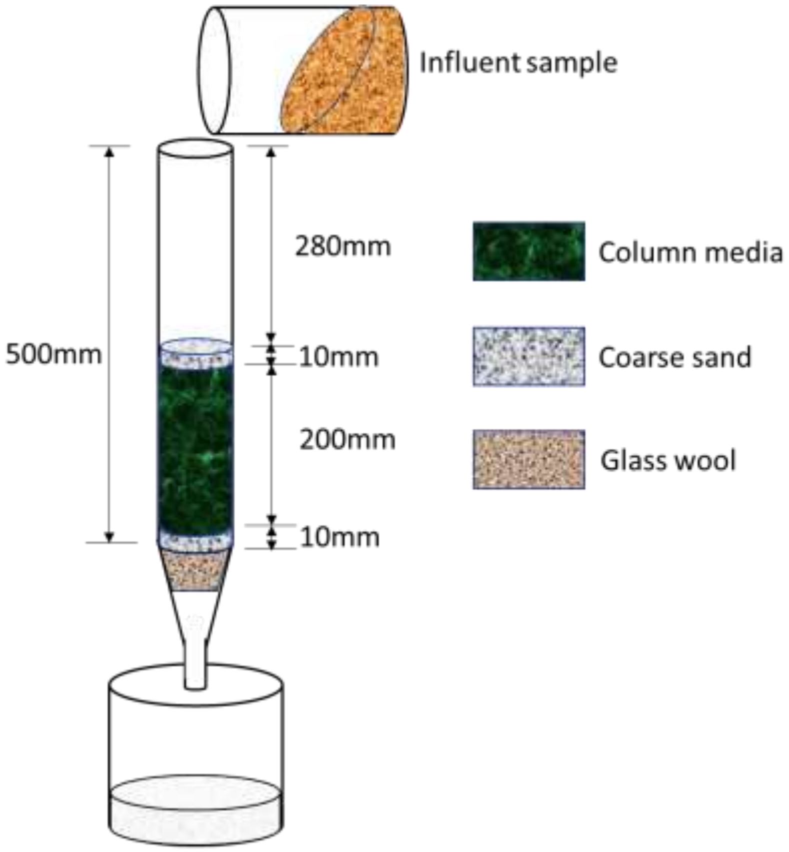


Figure 5-2: Schematic of laboratory column setup for micropollutant removal in wastewater.

Column Experiment 1 (Continuous flow): In this study, the contaminated water was allowed to flow continuously (Liu *et al.*, 2006) under gravity through the columns (Hu *et al.*, 2016; Chauhan and Talib, 2017). A constant head was maintained by regularly topping up the columns to maintain a water level of about 20 cm above the filter. Once the experiment started running, influent and effluent samples were collected at 30 minutes time intervals and stored using amber glass reagent bottles, while the filtration process continued for 12 hours. Samples were then drawn from the reagent bottles and were immediately filtered through sterile syringe filters (pore size 0.2 µm, diameter 13 mm PVDF membrane) into 2 mL amber GC-vials to remove suspended solids. The samples were immediately capped with blue 9 mm white silicone/red PTFE septa screw caps and stored at -4°C to hinder bacterial activity while the times taken to collect samples were recorded. The filtered aqueous samples were analysed using liquid chromatography-tandem mass spectrometry (LC-MS/MS) as described below.

Column Experiment 2 (Wetting and drying cycles): In this second study, similar columns to the first experiment were also run while the water application frequency was varied to simulate natural flow variability as might be observed in passive treatment systems (Hatt, Fletcher and Deletić, 2007). This experiment investigated the effects of repeated column wetting and drying cycles on the micropollutant removal and explored the longer-term performance of the biofilters. These draining and wetting steps were repeated daily for 40 days, mimicking frequent but irregular loading as might occur for frequent heavy rainfall in stormwater treatment systems, or the daily treatment of canal water used to “top up” aquaculture ponds and compensate for evaporative water losses. During the ‘wetting period’, each column was loaded daily with 20 mL of micropollutant spiked pond water, which was then drained by gravity. Water samples were collected from the inflow and outflow and analysed for the micropollutants. Samples were collected at the column inlets and outlets on a daily basis and were immediately filtered through sterile syringe filters into close amber GC vials (pore size 0.2 µm, diameter 13 mm PVDF membrane) to remove suspended solids and stored at 4°C to hinder bacterial activity. The concentrations of the analytes in collected samples were determined first using LC-MS/MS following the standard operating protocols described below.

5.3.5 Analytical methods

Effluent samples analysis

The concentrations of the selected micropollutants in Experiment 1 were analysed at NU using an LC-MS/MS system (Waters, Elstree, UK) equipped with an ACE C-18 PFP column (2.1x100 mm, 1.7 µm, HiChrom, Theale, UK) following previously described methods (Mrozik *et al.*, 2019). The separation column was thermostated at 40 ºC during the runs. The mobile phase consisted of solvent A (water with 0.1% formic acid) and B (acetonitrile with 0.1% formic acid). The flow rate was 0.4 mL/min. The gradient eluting protocol was applied as follows: 0-0.25 min: 10% B; 0.25-9.5 min: 98% B; 9.5-10.5 min: 98% B; 10.5-11.5 min: 10% B; 11.5-14 min: 10% B (equilibration between samples). A Triple Quad Waters Xevo – TQS mass analyser (Waters, Elstree, UK) was used for MS/MS quantitative analysis. The system was equipped with an electrospray ionization (ESI) source and operated in positive ionization mode. The operating parameters were: capillary voltage, 3.0 kV; source temperature, 150°C; desolvation temperature, 600°C; cone gas flow, 150 Lh^{-1}; desolvation gas, 1000 Lh^{-1}; collision gas, 0.15 $mLmin^{-1}$ and nebuliser gas, 7.00 bar. Quantification of each target compound was performed in multiple reaction monitoring (MRM) mode. MassLynx 4.1 software (Waters, Elstree, UK) was used to acquire and process all data.

In order to assess the concentration of the micropollutants in Experiment 2, aqueous samples collected at the column inlets and outlets were analysed using LC-MS/MS. The selected micropollutants were analysed by a Thermo Fisher Ultimate 3000 UPLC system. It consisted of a binary pump, autosampler, column compartment and UV detector. The analysis was carried out at 230 nm wavelength. The column, ACE C-18 PFP column (2.1x100 mm, 1.7 µm, HiChrom, Theale, UK), was thermostated at 40 ºC during the runs. The mobile phase consisted of solvent A (water with 0.1% formic acid) and B (acetonitrile with 0.1% formic acid). The flow rate was 0.4 mL/min. The gradient program was applied as follows: 0-0.25 min: 10% B; 0.25-9.5 min: 98% B; 9.5-10.5 min: 98% B; 10.5-11.5 min: 10% B; 11.5-14 min: 10% B (equilibration between samples). The injection was set at 80 µL and external standards were used for calibration.

Chemical analysis of column materials

At the completion of the continuous flow study (Experiment 1), the filter medium samples were immediately collected from each column and then manually homogenized, weighed, and stored at –20°C to terminate bacterial activity awaiting further chemical or microbial analysis. Depending on the probable analyte and grams of soil sample required to carry out the analysis, the determination and quantification of residual micropollutant compounds adsorbed in the soil samples in Experiment 1 (Continuous flow) were carried out commercially by the Royal Pharmaceutical Society (RPS), UK.

DNA analysis of column materials

Filter medium samples at the end of Experiment 2 (Wetting/Drying flow) were collected in subsamples sections according to their depth positions in the filtration column and were prepared for microbial community analysis. The filter media subsamples collected from different sampling depths of the columns were well mixed before 3 random 1 g aliquot samples were collected from each sample for the analysis of bacterial communities by 16S rRNA gene amplicon sequencing. DNA extraction is a critical step in determining the composition of constituent bacterial communities (Maksimov *et al.*, 2017). The DNA was extracted from the freeze-dried soil aliquots as described by Kennedy et al. (2014) and Maksimov et al. (2017) using a commercially available soil DNA extraction kit (FastDNA^{TM} SPIN kit for soil) and was carried out as recommended in the manufacturer's instruction (MP Biomedicals, UK). Subsequently, the eluted or extracted DNA was transferred to a sterile Eppendorf tube and preserved at –20 °C until use. The total extracted DNA was then sent to the Department of Applied Biology, Cellular and Molecular Sciences, Northumbria University, UK, for 16S rRNA gene amplicon sequencing and were sequenced on the MiSeq Illumina Sequencing Platform using their established protocol as described previously in Kozich et al. (2013).

PCR analysis and 16S rRNA gene sequencing

Real-time polymerase chain reaction (PCR) assays were performed on a BioRad CFX C1000 System (BioRad, Hercules, CA USA) to quantify the template bacteria 16S rDNA gene fragments following procedures outlined by Shamurad et al. (2019). The primers used are summarized in Table 5-2. The amplification (PCR) was carried out using 2 µl template DNA in a reaction mixture containing 7.5 µl 2 × SsoAdvanced Universal SYBR Green Supermix (Bio-Rad), 300 nmol l^{-1} of each forward (1055F) and reverse (1392R) primer, and Qiagen nuclease-free water (Qiagen 129114) to a final volume of 15 µl. Reaction conditions set for quantification of the 16S rRNA gene were 98°C for 3 min (1×), then 98°C for 15 s, and 60°C for 60 s (40×). All samples were run in triplicate and H_2O replaced template in control reactions. To avoid inhibitor effects, DNA samples were diluted to a working solution of 5 ng/ul and an internal control DNA was used in SYBR green reactions.

Table 5-2: Primers and probes used in this study

Target	Primer	Sequence (5'-3')	Length (bp)	Product size (bp)	Reference
16S rRNA	1055f	ATGGCTGTCGTCAGCT	16	337	(Harms *et al.*, 2003)
	1392r	ACGGGCGGTGTGTAC	15		

5.3.6 Analysis of column data

Hydraulic conductivity

The Hydraulic Conductivity (K) parameter was used to estimate how the filter medium permeability affects infiltration and the travel time of micropollutants through the filter bed. This important parameter for saturated porous media can be evaluated using Darcy's equation and the simplified falling-head permeability test technique which is suitable for fine sand particles (Diminescu, Dumitran and Vuţă, 2019) and illustrates the relationship between Darcy's flow velocity of a homogeneous fluid in a porous medium and the applied hydraulic gradient (Desiderio, 2014). The saturated hydraulic conductivity (K) was calculated from falling-head data using the equation:

$$K = \frac{L}{t} \cdot \ln\left(\frac{h_1}{h_2}\right) \tag{5.1}$$

Where K is the hydraulic conductivity in cm/s, L is the length of the soil column in cm; t is time, measured in seconds, taken for the free water surfaces in the column to flow from h_1 to h_2 which are the initial and final heights of the water level, respectively, measured from the outlet of the column in cm.

The instantaneous effluent volumetric flow rate at each effluent collection interval was calculated by using the equation:

$$Q_i(t) = \frac{V_i(t)}{t} \tag{5.2}$$

Where, Q_i(t) is the volumetric flow rate in mL/min associated with period i, V_i(t) is the effluent volume collected in mL during period i, and t is flow duration in period i in seconds.

Empty Bed Contact Time (EBCT)

EBCT provides a measure for the contact time of the target compounds to be absorbed, or adsorbed and biodegraded in the filter bed, and is represented by the following equation:

$$EBCT = \frac{Volume\ of\ bed}{Volumetric\ flow\ rate} = \frac{V_{bed}}{Q} = \frac{A \times H}{Q} \tag{5.3}$$

Where, $EBCT$ is the empty bed residence time (s), V_{bed} is the volume of the filter medium in the column (cm^3), A is the cross-sectional area of the cylindrical bed column (cm^2), H is the height of the bed column (cm) and Q is the effluent flow rate (cm^3/s).

Chemical Mass-balance calculations

Based on the results from the column studies, the fate of micropollutants in both the control and biochar-amended soils was interpreted with a mass balance. Some assumptions were made during the mass balance calculation regarding physical properties of the experimental materials and the dynamics of the micropollutants removal in a continuous flow experiment:

I. The filter media samples are homogenously packed in the columns.
II. The diameter of the cylindrical column was assumed constant over the whole column length and filled with the porous medium.
III. A uniform distribution of voids in the soil column was assumed.
IV. The physical properties of the solid and liquid phases were assumed to be constants during the treatment process.
V. Changes in the influent concentrations throughout the experiment were assumed to be negligible.
VI. Effluent concentration variations between sampling time intervals were assumed to be negligible.
VII. Changes in the volumetric flow rates between sampling time intervals were assumed to be negligible.

VIII. Particulate proportions in influent and effluent were assumed to be negligible in the analysis.

IX. Adsorption of each micropollutant compound in the column is ascribed to the desorbed concentration at the end of the experiments.

X. Degradation of each micropollutant compound in the column is the missing proportion of the chemical mass balance.

A theoretical mass balance method is frequently used to estimate the presence of biodegradation under steady flow conditions (Zheng, Aagaard and Breedveld, 2002; Suárez *et al.*, 2012; Zhao *et al.*, 2020; Zhiteneva *et al.*, 2020). In this study, the main removal processes considered for micropollutants during their passage through the soil column are adsorption and biological degradation (Suárez *et al.*, 2012) and the chemical mass balance for the different filtration columns were calculated at the end of each experiment assuming the total influent volume is equivalent to the total effluent volume as in Eq. (5.1), and there is an insignificant mass loss for the trace micropollutants due to volatilisation. Hence, to calculate the mass loading for each trace micropollutants, the following were accounted for: (i) the mass of micropollutants entering the soil column at the start of the experiment, (ii) the amount retained in the soil column as residue at the end of the experiment, (iii) the amount leaving in the effluent samples, and (iv) the amount degraded/transformed during the experiment (Egiarte *et al.*, 2006; Fernandez-Fontaina *et al.*, 2012; Zhao *et al.*, 2020).

$$V_{in,total} = V_{eff,total} \tag{5.4}$$

Where $V_{in,total}$ and $V_{eff,total}$ are the total influent volume added and effluent volume collected (mL) at the end of each column experiment.

The total influent/effluent volume throughout the experiment was calculated from the summation of all the effluent volumes collected during each period *i* (of 0.5 hrs) for a 12 hour continuous flow experiment using the equation:

$$V_{eff,total} = \sum_{i=1}^{N} V_i(t) \tag{5.5}$$

Where;

$$V_i(t) = Q_i(t) \times t \tag{5.6}$$

Where, N is the number of the aliquots collected during the event, $V_{eff,total}$ is the total effluent volume collected in mL, while Q_i(t) and V_i(t) are the volumetric flow rate (mL/min) and effluent volume (mL) during the period i, respectively, and t is the duration of the period i (mins).

According to Kim et al., (2014), assuming no significant mass loss to volatilization in the filtration process, the total mass loading for each trace micropollutant with the influent, equals the mass adsorbed within the filter bed, leached out of the filter with the effluent samples, and used up as substrates or transformed during the filter passage:

$$M_{in,total} = M_{sorb,total} + M_{eff,total} + M_{deg,total} \tag{5.7}$$

Where $M_{in,total}$, $M_{sorb,total}$, $M_{eff,total}$ and $M_{deg,total}$ are the total masses of the micropollutant in influent samples, filter bed samples, effluent samples and degraded/transformed (µg), respectively.

Also, the total mass recovered in each column for a trace micropollutant compound at the end of the experiment was calculated using the equation:

$$M_{in,total} = \frac{C_0 V_{in,total}}{1000} = \frac{C_0 V_{eff,total}}{1000} \tag{5.8}$$

$$M_{sorb,total} = C_{sorb}\, W_{filter\ medium} \tag{5.9}$$

$$M_{eff,total} = \sum_{i=1}^{N} \frac{C_i(t)\, V_i(t)}{1000} \tag{5.10}$$

Where, N is the number of aliquots collected during the event, C_0 and C_i(t) are the initial influent and effluent concentrations of the micropollutant (µg/L) associated with period i, respectively. C_{sorb} is the sorbed concentration of the micropollutant (µg/kg), $W_{filter\ medium}$ is the weight of the filter bed solids in the column (kg), V_i(t) is the effluent volume (mL) collected during the period i, while $V_{in,total}$ and $V_{eff,total}$ are the total influent and effluent volume (mL) flowing through each column, respectively.

The equations applied to derive an integrated mass fraction, *F* (%), of trace micropollutants that were discharged through final effluent and partitioned to filter bed solids, were:

$$F_{eff}(\%) = \frac{M_{eff,total}}{M_{in,total}} 100 \tag{5.11}$$

$$F_{sorb}(\%) = \frac{M_{sorb,total}}{M_{in,total}} 100 \tag{5.12}$$

$$F_{deg}(\%) = \frac{M_{deg,total}}{M_{in,total}} 100 \tag{5.13}$$

Where F_{eff} , F_{sorb} and F_{deg} are the removal mass fractions in leached effluent, sorbed, and degraded/transformed, respectively.

The difference between the total micropollutant mass that enters the columns and the total mass adsorbed and leaving the columns can be attributed to the amount degraded/transformed due to biological transformation. Hence, from Eq. (5.7) the total mass degraded/transformed was estimated by subtracting the total influent mass from the combined mass of sorption and effluent mass:

$$M_{deg,total} = M_{in,total} - (M_{sorb,total} + M_{eff,total}) \tag{5.14}$$

This implies that the degradation/transformation mass fraction can be estimated by subtracting the influent mass fraction (100%) from the combined mass factions of sorption and effluent using the equation:

$$Degradation\ or\ transformation\ (\%) = 100\% - F_{eff}(\%) - F_{sorb}(\%) \tag{5.15}$$

Interpretation of breakthrough curves

The breakthrough point and curve were obtained from the data generated from continuous flow column experiments and used to compare and evaluate the adsorption performance of filtration media under various conditions (Zhou *et al.*, 2013). The analysis of the various parameters associated with the column breakthrough time and shape of the curve was used to determine the operation lifespan of a fixed bed column and the dynamic response of the adsorption process (Samarghandi, Hadi and McKay, 2014).

The breakthrough time is commonly expressed in terms of normalized concentration, which is defined as the ratio between influent concentration and effluent concentration at different times *t* which was calculated from Eq. (5.16), and then used to construct the breakthrough curve plot.

$$Normalized\ concentration = \frac{C_i(t)}{C_0} \tag{5.16}$$

Where C_0 is the influent concentration and C_i(t) is the effluent concentration associated with period *i*.

Using the breakthrough curve analysis, key points to consider are the saturation point, which is the point reached when the effluent concentration, C_i(t), becomes equal to the influent concentration, C_0, i.e. the micropollutant is no longer effectively adsorbed or removed from the water. The saturation point will only be reached if there is no pollutant biodegradation in the column. The breakthrough point is the time when the effluent concentration, C_i(t), is up to 5% of the influent concentration, C_0, (commonly stated as $0.01C_0<C_i(t)<0.05C_0$), and the adsorption exhaustion point is the point reached when the effluent concentration, C_i(t), is about 90–95% of the influent concentration, C_0 (Patel, 2019).

Analysis of Soil Bacterial Communities

One way to gain insight into the microbial community structure that causes the micropollutant biodegradation is to analyse the compositions and diversity of the microorganisms in the filter bed. Next-generation sequencing can quantify the relative abundance of thousands of operational taxonomic units (OTU) making up the microbial community. Since it is computationally very demanding to run an all-against-all comparison of the OTU datasets, graphical representation of the bacterial communities for the different filter media types and sampling positions were performed using several non-metric multivariate analytical procedures as described by Shamurad et al. (2019). Representation of communities using dendrograms to link samples into hierarchical groups and the similarities between samples were mapped in ordination plots using non-metric MDS where the position of each sample is determined by its distance from all other points in the analysis (Wu *et al.*, 2008). A square root transformation was applied to the data before construction of the similarity and differences matrices were carried out between samples to down weight the high relative abundance OTUs in the community structure analysis.

5.3.7 *Statistical analysis*

All statistical analysis for the mathematical data was performed using Microsoft Excel 365. Determinations for each analysis were done in replicates and expressed using the mean values ± standard deviation. For all parameters, multiple comparisons were conducted using a one-way analysis of variance (ANOVA). A comparison of the relative abundance of identified bacterial groups at the beginning and end of the experiments for individual columns, and between samples collected at different locations was conducted using STAMP software. Other non-metric multivariate analyses procedures for evaluating the microbial community structure, including cluster and MDS analysis, were conducted using the Primer-7 software at NU, UK.

5.4 Results and Discussion

5.4.1 *Influence of biochar amendment on the hydraulic performance of biofilters*

The study investigated the effect of coconut husk biochar amendment on the hydraulic performance parameters such as flow rates, HLR, hydraulic conductivity, and EBCT by comparing FISA and CHBC biofilters in the continuous flow experiment. The average values of the hydraulic parameters are presented in Appendix A. Figure 5-3 shows that the hydraulic conductivity results of both FISA and CHBC columns decreased significantly ($p<0.001$) over the 12 hours of the event. The change in flow rates was noticeable in both filter types (Figure 5-4) and could be explained by the impact of pore-clogging by fine particles from the pond water, especially near the filter surface which agrees with Trinh, Werner and Reid (2017). Interestingly statistical analysis of the data (including ANOVA and t-tests) from FISA and CHBC columns all showed significant differences between the filter media types ($p<0.001$). As already observed in Chapter 3, CHBC amended columns are prone to release of numerous small particles from the biochar which can fill pore spaces and clog the flow path of the filter thereby reducing its hydraulic conductivity (Trinh, Werner and Reid, 2017). This generates restricted flow which may, however, also be beneficial, as it creates sufficient contact time between the CHBC media and the micropollutants (Hina, 2013). While the obvious reduction in hydraulic conductivity over time (>61%) was to be expected in the CHBC filters, the change in hydraulic conductivity was less obvious in the FISA filters (<19%), and it is evident that FISA columns had a higher flow rate than CHBC columns (Figure 5-4). Bratières et al. (2010) pointed out that the continuous pouring of contaminated water into the columns in large amounts disturbs the surface clogging layer, which however reforms every time, and therefore keeps the flow rates in the columns fluctuating as shown in Figure 5-4. From this point in time onwards, the flow rate was probably governed by the presence of the clogging layer at the surface of the media and transport of smaller (disintegrated) particles to available pore spaces.

EBCT is an important consideration for filtration processes, because it states the time available for adsorption and adsorption efficiency is directly correlated with the contact time (Paredes *et al.*, 2016). Chowdhury, Abd Hamid and Zain (2015) also reported that at a higher flow rate, a lower empty bed contact time (EBCT) was obtained, which may then imply that for the micropollutants in the FISA columns, there may be insufficient contact time for the adsorption mechanism to occur between the micropollutants and the sand solids. However, it was previously observed that sand is anyway not a good adsorbent material for micropollutants, therefore the lower the EBCT values as shown in Figure 5-5 may have only minor impacts on the retention of micropollutants by the fine sand media (Chowdhury, Abd Hamid and Zain, 2015). Hence, the influence of EBCT on micropollutants removal depends on the type of filtering material (Paredes *et al.*, 2016) as longer EBCT also means more opportunity for the bacteria in the biofilter to biodegrade the trapped micropollutants in the media pores spaces. The EBCT results showed that there is a significant difference (t-test, $p<0.001$) between the different filter media types, which is an important consideration for the discussion of biofiltration efficiency.

Paredes et al. (2016) had established that the reduction in EBCT values has two contrary effects on the treatment efficiency: one positive (increased loading rates fed to biofilters which means smaller filter footprints) and one negative (decreased contact time for adsorption and biotransformation). Both effects were observed during this study and the importance of one over the other will depend on the biodegradability of each compound (Paredes *et al.*, 2016). Previous works by Kalkan et al. (2011) and Chowdhury, Abd Hamid and Zain (2015) demonstrated the efficiency of full-scale biofilter columns to remove micropollutants. However, the removal efficiencies largely depended on the operational conditions applied, removal mechanisms and EBCT.

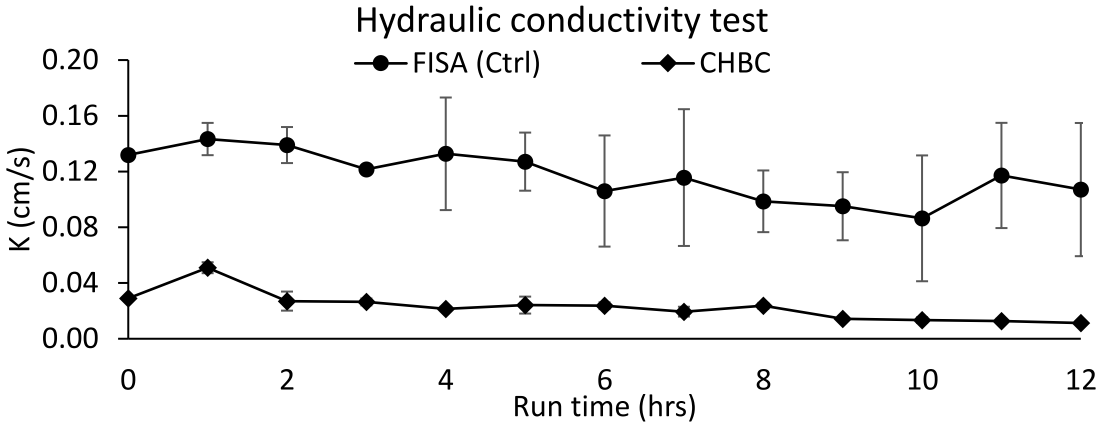


Figure 5-3. Hydraulic conductivity test analysis for the filter columns. Symbols and error bars represent mean ± standard deviation (n=2).

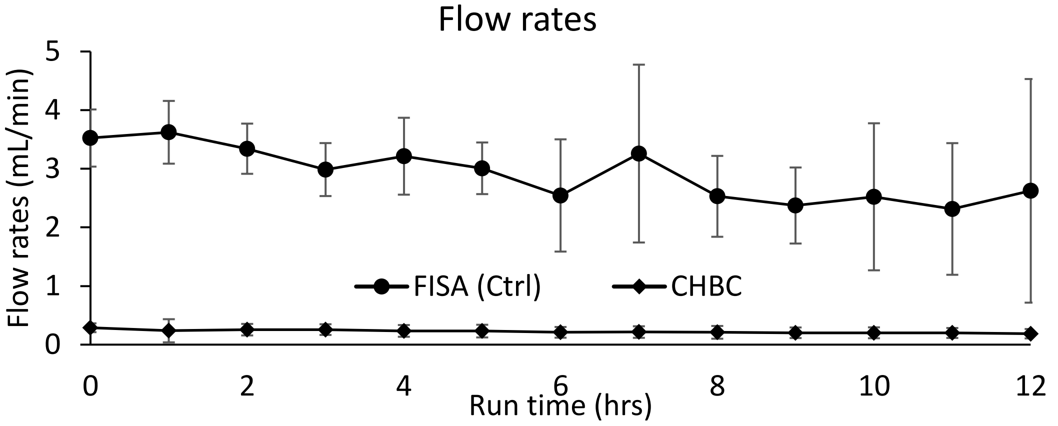


Figure 5-4. Flow rate analysis for the filter columns. Symbols and error bars represent mean ± standard deviation (n=2).

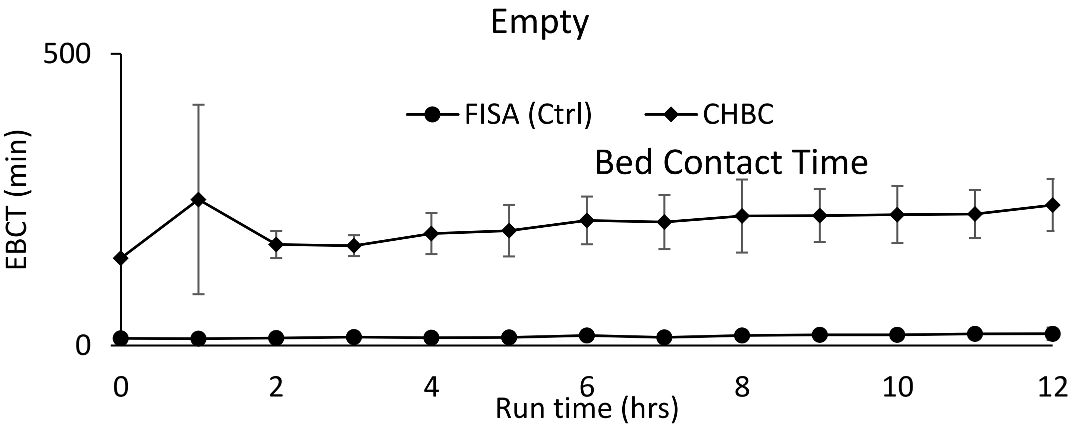


Figure 5-5. EBCT analysis for the filter columns. Symbols and error bars represent mean ± standard deviation (n=2).

5.4.2 The fate of micropollutants in the biofilters

In previous work, the fate of micropollutants differed for different soil types (Aldana *et al.*, 2020). In this study, Table C 1 to Table C 7 summarised the removal pattern of micropollutants from both experiments considering the whole set of influent and effluent concentrations of micropollutants in the liquid phase. The CHBC filters showed greater removal of micropollutants than FISA filters in all experiments (Figure 5-7), which indicate a higher adsorption/degradation of organic pollutants on biochar amended filters than on unamended sand. The concentration profiles during the filtration of the six different chemicals at a fixed inlet concentration (i.e., 100 µg/L) are shown in Table C 1 to Table C 6. All chemical concentrations were reduced or completely removed in the effluent relative to the influent, as shown in the breakthrough curves. TC, OTC, ATR, DRN, ACM, and DIC were removed or reduced in CHBC columns to concentrations below the detection limits of the measuring instruments, and therefore, their efficiency values could not be exactly calculated. Using the limit of detection (≥ 10µg/L) of the instrument, the removal efficiency for non-detectable compounds can be said to be at least 90%.

5.4.3 Continuous flow biofiltration experiment

In this study, the biodegradation efficiencies of compounds were influenced by the different filter media types (Dai *et al.*, 2019) and to a much lesser extent by the different operational conditions – the discontinuous loading with wetting and drying cycles versus continuous flow experiments. In the continuous flow condition, effluent samples collected from the unamended (FISA) columns showed a high concentration of leached pharmaceuticals relative to the inlet concentration (TC: 67.7±9.3% and OTC: 40.2±7.3%) and pesticides (ATR: 79.4±19.3% and DRN: 66.2±14.9%), while lower concentrations or concentrations below the limit of quantification were recorded for the tested compounds in the biochar-amended (CHBC) columns (Figure 5-6). Similar removal patterns were also observed in the concentration profiles of other compounds as shown in Table C 1 to Table C 6. The data obtained in this study support the initial research hypothesis that biochar-amended sand could enhance micropollutants removal from contaminated solution under gravity flow conditions.

Breakthrough curve analysis for continuous flow

By plotting the solute concentration (in µg/L) in the effluent i.e. C_t/C_o against time, typical experimental breakthrough curves were obtained as shown in Figure 5-7. Fiorentin et al. (2015) reported that the breakthrough curve shape and the breakthrough point are important in understanding column's dynamic behaviour which can be influenced by operational conditions. However, from the experimental data, the curve shape of the breakthrough plots did not follow the characteristic S-shaped profile produced in ideal adsorption plots, a behaviour which is ascribed to complex causes as reported by Park and Knaebel (1992), such as feed flow rate and the rapid biodegradation/transformation of the target molecules. In an ideal situation, the adsorption process continues until equilibrium is established between the solute present in the liquid phase and the solute adsorbed to the adsorbent and the column is completely exhausted, $C_0 \approx C_t$. However, in this study, complete equilibrium was never established at any stage between the solute present in the solution and the amount adsorbed. For continuous flow, it was observed that all the trace micropollutants were effectively attenuated in the CHBC columns, resulting in low concentrations of solute in the effluent. This is evident in the breakthrough curves obtained for CHBC columns, in which biodegradation occurred, as indicated by the plateaus at lower C_t/C_0 values of around 0.026, 0.029 and 0.038 for ATR, DRN and DIC, respectively, while pharmaceutical compounds such as TC and OTC plateaued at the zero baselines of the plots. This behaviour is consistent with the impact of degradation on micropollutant transport.

In contrast to the observations for the CHBC columns, the breakthrough curves obtained with the unsterile FISA columns reached much higher C_t/C_0 values, in which some level of biodegradation also occurred as indicated by $C_t/C_0 < 1$ in the mid-section of the run. Values of $C_t/C_0 \sim 1$ early on in the run indicated rapid micropollutant breakthrough in the FISA columns, whereas the C_t/C_0 minimum in the middle of most runs indicated that biodegradation was most effective at that time with reducing effectiveness towards the end of the run (Figure 5-7). Under continuous flow, biodegradation/transformation of micropollutants thus took place with a short delay after the start of the experiment, likely due to a lag phase in the biodegradation. However, after about 2 hours of continuous runs, the C_t/C_0 values raise again incrementally towards the saturation point. Zhiteneva et al. (2020) reported that pharmaceuticals are poorly removed via adsorption mechanism in biofilters studies but are well biodegraded in the system. The breakthrough curves of TC, OTC and DRN from the FISA filters follow a similar trend with evidence for biodegradation after a lag phase, that was most effective in the mid-section of the run, whereas ATR, ACM and DIC maintained a fairly plateaued breakthrough curve shape near C_t/C_0 ~ 1 with little evidence for biodegradation for the duration of the experiment. Comparing the results from the mass balance shown in Figure 5-6 and the breakthrough curves shown in Figure 5-7, it was observed that biodegradation alone accounted for the > 97% total removal of TC and OTC, and > 91% total removal of ATR and DRN in the CHBC columns. Whereas, while adsorption was nearly negligible for TC and OTC removal, biodegradation was the dominant removal mechanism which accounted for between 32 – 60% removal of TC and OTC, and 5 – 28% removal of ATR and DRN in the FISA columns. This is in line with the aforementioned reduced efficiency of biological removal in the FISA filters, and further supports the research hypothesis that both adsorption and biodegradation are the removal mechanism in the CHBC filters

Chemical mass balances analysis

Chemical mass balances calculations were applied to understand how the fate of the micropollutants was affected by the filter media types under continuous flow conditions. Figure 5-6 showed that the adsorption of micropollutants onto the biofiltration columns was almost negligible for TC and OTC in the FISA column, and small, but measurable, for TC, OTC, ATR and DRN at 2.03%, 2.30%, 6.89% and 2.03% of the influent mass, respectively, in the CHBC columns. Hence, over 93% of the removal of the tested compounds in the CHBC columns was attributed to biodegradation, which is in agreement with other authors, who found that under biotic conditions these compounds are readily biodegradable (Fernandez-Fontaina *et al.*, 2012; Suárez *et al.*, 2012; Paredes *et al.*, 2016; Ahmed *et al.*, 2017).

This analysis also showed that biodegradation/transformation alone achieved a significant removal of 90 – 98% of the total mass of micropollutants in the aqueous phase in the CHBC column, compared to a 5 – 60% in the biodegradation removal in the unamended control (FISA) column. Remarkable, Table 5-3 also revealed that the maximum removal by adsorption (16% for ATR and 6% for DRN) was noticed for the unamended sand (FISA); apparently, the real adsorption amounts of ATR and DRN on CHBC were higher than the calculated adsorption amounts. Moreover, the attenuation effect was more obvious in CHBC with the increase in the total removal in an aqueous solution. This further proved that the microbes would interact more with the biochar/soil components to influence the biodegradation capacity of biochar-amended for micropollutants removal. In particular, the differences between the adsorption and biodegradation amounts of the micropollutants were much higher for CHBC than those for FISA, which indicated that the interaction of microorganisms with the micropollutants was higher in CHBC, and this will be explained further in the proceeding sections. This was because CHBC has higher EBCT, which was influential toward biodegradation due to the increase in contact for biodegradation to occur. Although the studies had suggested that media pore blockage may reduce biochar adsorption capacity during flow events (Trinh, Werner and Reid, 2017), this results indicated that biodegradation/biotransformation plays an essential role in the micropollutants removal process. Therefore, biodegradation/transformation was identified to be the dominant removal mechanism in both filter media types, with much greater overall removal in the CHBC column. The mass balance calculations assumed that volatilizations of compounds were negligible, which is reasonable given their low Henry coefficients in Table 5-1.

Table 5-3. Summary of each micropollutant removal mechanism and efficiency for each biofiltration material at approximate quantities.

Micropollutants	**Media**	**Removal fraction (%)**		**Total removal (%)**
		Adsorption	**Biodegradation**	
TC	FISA	≈ 0.33	≈ 31.98	≈ 32.31
	CHBC	≈ 2.03	≈ 96.95	≈ 98.98
OTC	FISA	≈ 0.29	≈ 59.53	≈ 59.82
	CHBC	≈ 2.30	≈ 97.70	≈ 100.00
ATR	FISA	≈ 15.52	≈ 5.04	≈ 25.56
	CHBC	≈ 6.89	≈ 90.67	≈ 97.56
DRN	FISA	≈ 5.82	≈ 28.01	≈ 33.83
	CHBC	≈ 2.03	≈ 94.68	≈ 96.71

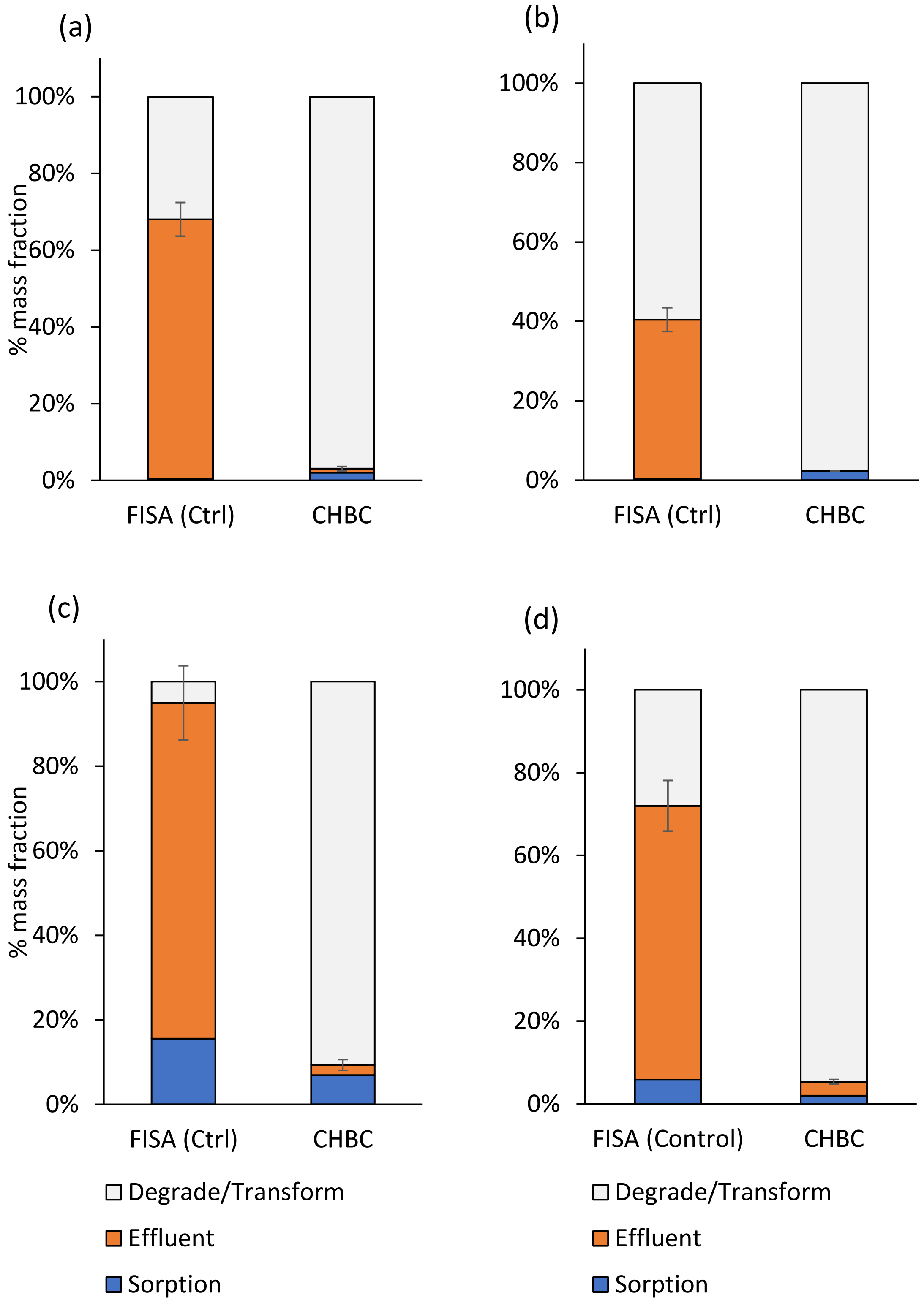


Figure 5-6. Removal mass fraction distribution of (a) TC, (b) OTC, (c) ATR, and (d) DRN in the column filtration analysis. Colours and error bars represent mean ± standard deviation for the mass distribution analysis. n=2 for effluent, n=1 for soil.

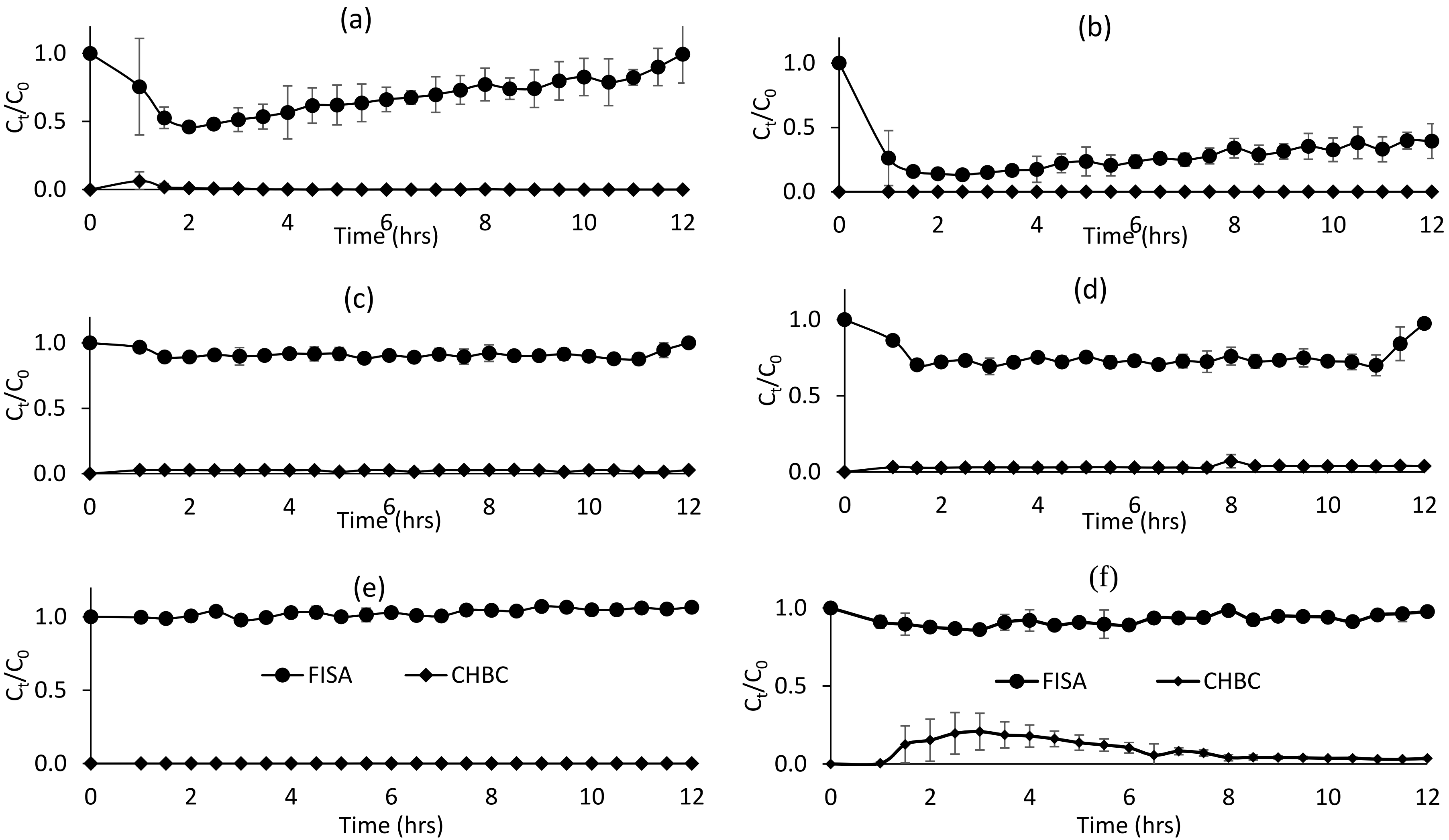


Figure 5-7. Real breakthrough curve for the transport of (a) TC, (b) OTC, (c) ATR, (d) DRN, (e) ACM, and (f) DIC through the FISA and CHBC columns for the removal of different micropollutants from contaminated pond water measured in the continuous flow experiments. The influent concentration was approximately 100 µg/L and the error bar indicates the standard deviation of measurements (n=2).

5.4.4 Wetting and drying cycles biofiltration experiment

The simultaneous interaction of adsorption and biodegradation that occurred during micropollutant transport was also studied by performing different column experiments under alternate drying and wetting flow conditions. A breakthrough experiment at room temperature was performed with the same influent micropollutant concentrations.

Breakthrough curve analysis for alternate wetting and drying flow in biofiltration experiments

Breakthrough curves for micropollutant transport through biofilter columns under alternate wetting and drying cycles were generated as shown in Figure 5-8. In these experiments, the total influent volumes and pollutant loadings of the FISA and CHBC columns were the same, even if the water flowed faster through the FISA columns due to their higher hydraulic conductivity. Similar to the continuous flow experiment, the breakthrough curves remained at C_t/C_0 values of ≈0 for CHBC columns, and near or slightly below C_t/C_0 values of ≈1 for the FISA columns, which suggested better performance of the CHBC columns, regardless of the flow conditions. It was also observed that micropollutant removal remained consistently high in the CHBC columns throughout the duration of the experiment, even after many wetting and drying cycles, indicating that biodegradation was the predominant removal process, as micropollutant breakthrough would otherwise have eventually occurred. If adsorption processes had determined the shape of the breakthrough curves, they would have followed a characteristic S-shaped effluent concentration profile, reaching C_t/C_0 values of 1 after the filter medium sorption capacity had been exhausted. However, in addition to the slower water filtration due to the lower hydraulic conductivity of the CHBC column, adsorption may still have benefitted the pollutant biodegradation in the CHBC columns. According to Vijayanandan, Philip and Bhallamudi (2018), the benefit could be that the microbial population might be less numerous or metabolically inactive at the start of the experiment. At that point, the micropollutants may have been retained in the filter medium by adsorption, to be released at a later stage in the experiment as the microbes had grown and adapted their metabolism (i.e., overcome the lag phase). The removal of the micropollutants would then result from the synergistic interaction of adsorption and biodegradation, as was previously demonstrated for VOC biofiltration experiments (Bushnaf *et al.*, 2017).

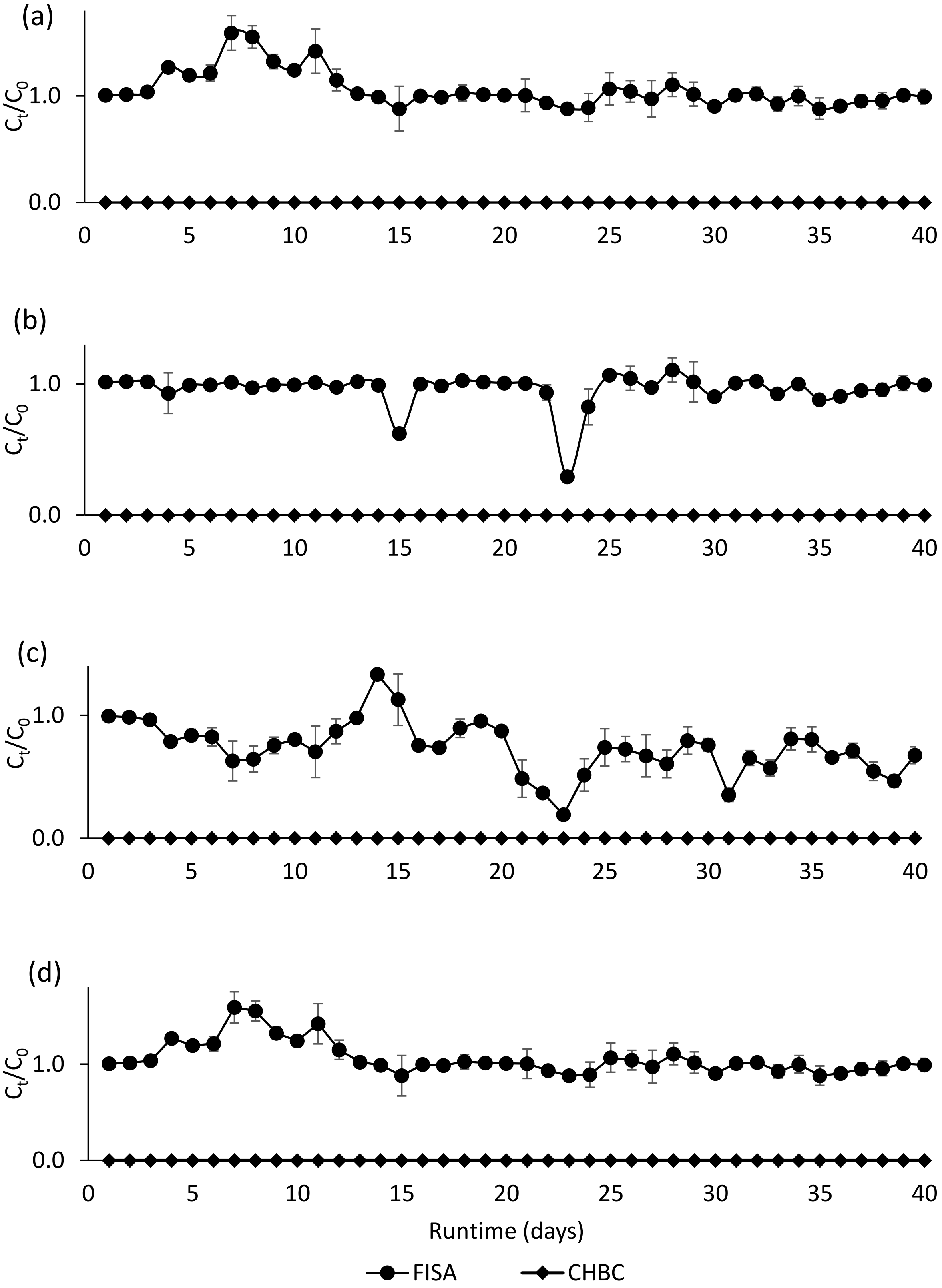


Figure 5-8. Effect of drying and wetting cycles on the breakthrough curve for (a) ATR, (b) DRN, (c) ACM, and (d) DIC transport in contaminated pond water through FISA and CHBC columns. The influent concentration was approximately 100 µg/L and the error bar indicates the standard deviation of measurements (n=3).

5.4.5 Microbial community composition

It was hypothesized that the variation in the micropollutants attenuation results between the CHBC and FISA columns would be reflected in distinct microbial communities for the two filtration systems, including for specific degraders responsible for degrading certain compounds. Lou et al. (2015) reported that during pollutants treatment processes, the application of biochar results in a complex process of adsorption-biodegradation-transformation of pollutants and changes in the microbial community structure in the system. Another study by Cheng et al. (2017) observed that biodegradation of micropollutants can be influenced by both the microbial abundance and enzymatic activities, and additionally stated that only bioavailable pollutants can be mineralized by microorganisms (Anderson *et al.*, 2011; Khodadad *et al.*, 2011; Tong *et al.*, 2014; Dai *et al.*, 2021; Zhang *et al.*, 2021). Therefore, 16S rRNA gene sequencing analysis was used to characterize the microbial diversity and inter-relationship between communities associated with the two biofilter media types for various locations in the filter.

Comparing the degradation mechanism in the different column types under the alternate drying and wetting conditions, it was observed that there is a positive correlation between the presence of soil microorganisms growth and the increased biodegradation efficiencies in the unsterilized biochar amended soil as reported by Lou et al. (2015), Elzobair et al. (2016), Cheng et al. (2017), Palansooriya et al. (2019), Zhu, Mao and Chen (2019) and Gorovtsov et al. (2020), which significantly increased removal of micropollutants in the CHBC columns compared to the FISA columns. The results in this study agree with a number of studies that found that biochar amendment could influence microbial community structure significantly in the soil (Anderson *et al.*, 2011; Khodadad *et al.*, 2011; Tong *et al.*, 2014; Cheng *et al.*, 2017; Mrozik *et al.*, 2021; Zhang *et al.*, 2021). Although in this study, there was not enough data to justify the significant association of biochar with the bacterial community composition, biochar could indirectly, rather than directly, affect the soil microbial community structures through the effect of CHBC on micropollutants biodegradation, bioavailability, and toxicity. Also, previous studies indicated that only bioavailable contaminants can be utilized by microorganisms, and it had been suggested that the free state of hydrophobic micropollutants might provide a direct measure of the microbial degradable contaminant fraction in the water (Cheng *et al.*, 2017).

In this filtration system, adsorption-desorption of micropollutants and microorganisms to CHBC, microbial growth, and biodegradation of micropollutants exist simultaneously (Cheng *et al.*, 2017). To analyse the observed diversity variation among samples at different levels in the soil column horizon, the hierarchical cluster analysis was performed (Figure 5-9) to show the major trends within the data set. The samples clustered into two distinct populations with a shared overlap of CHBC and FISA on both clusters, indicating that the biochar was not a major determinant in microbial community composition. Although, in general, the diversity of the bacterial community was higher in the top layers than the bottom of the column soil horizon, which agrees with the study by Truu et al. (2005).

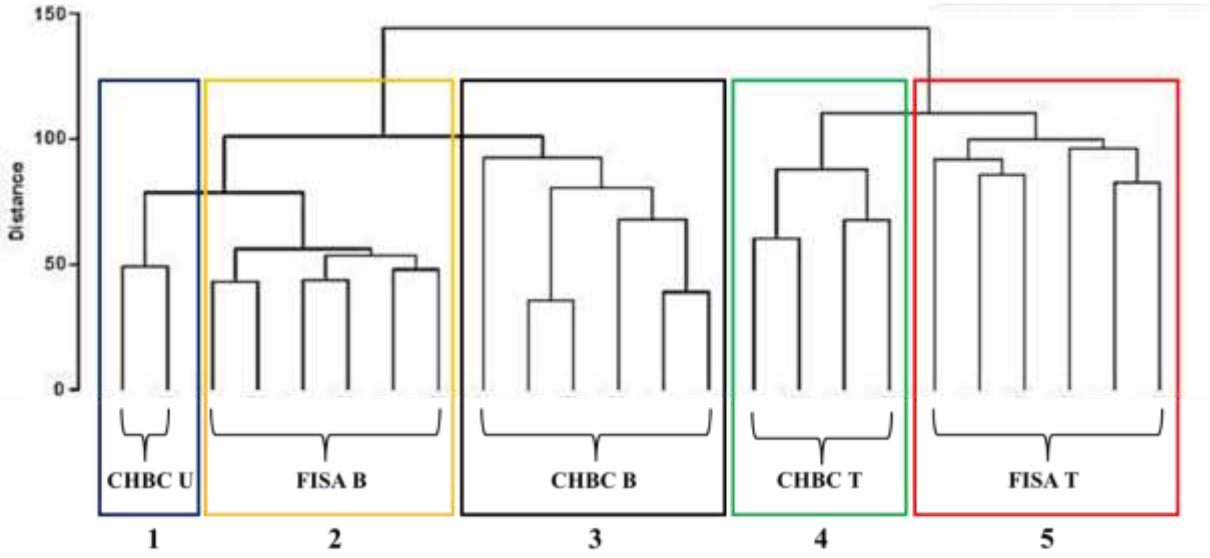


Figure 5-9. Dendrograms of soil bacterial community profiles of 16S rRNA sequencing of samples collected from unsaturated (not spiked) biochar media (cluster 1), the bottom (cluster 2 and cluster 3) and top (cluster 4, cluster 5) of two replicate media columns; FISA (control) and CHBC. Clusters for duplicate samples and the same sampling depths are circled separately. Samples collected from column top, bottom and unsaturated (not spiked) media are noted by 'T', 'B', and 'U' after the sample names, respectively.

It can be seen that cluster 4 and cluster 5, each represent distinct microbial communities from the top section of either the FISA or CHBC columns, respectively, but were more similar to each other as compared to other clusters, representing microbial communities from the bottom section of the FISA and CHBC columns. This suggests effluent addition at the top of the media was the most important factor in shaping the microbial communities, with the FISA and CHBC filter media type being the next most relevant factor (Plaimart *et al.*, 2021). However, cluster 1, cluster 2 and cluster 3 were quite similar to the initial microbial community, which suggests that there is a smaller change in microbial community composition at the bottom of the CHBC filters before and after the experiment. Similarly, the MDS plot shown in Figure 5-10 indicated how MDS1 separated samples according to their location in the biofilters, whereas MDS2 separated FISA samples (blue triangles) away from the communities of the CHBC samples (red triangles). Overall, the plot revealed that top (T) versus bottom (B) location in the biofilter, and filter media type (FISA versus CHBC) were microbial community shaping factors, which is identical to the principal component analysis outcomes (PCA) in Figure 5-11.

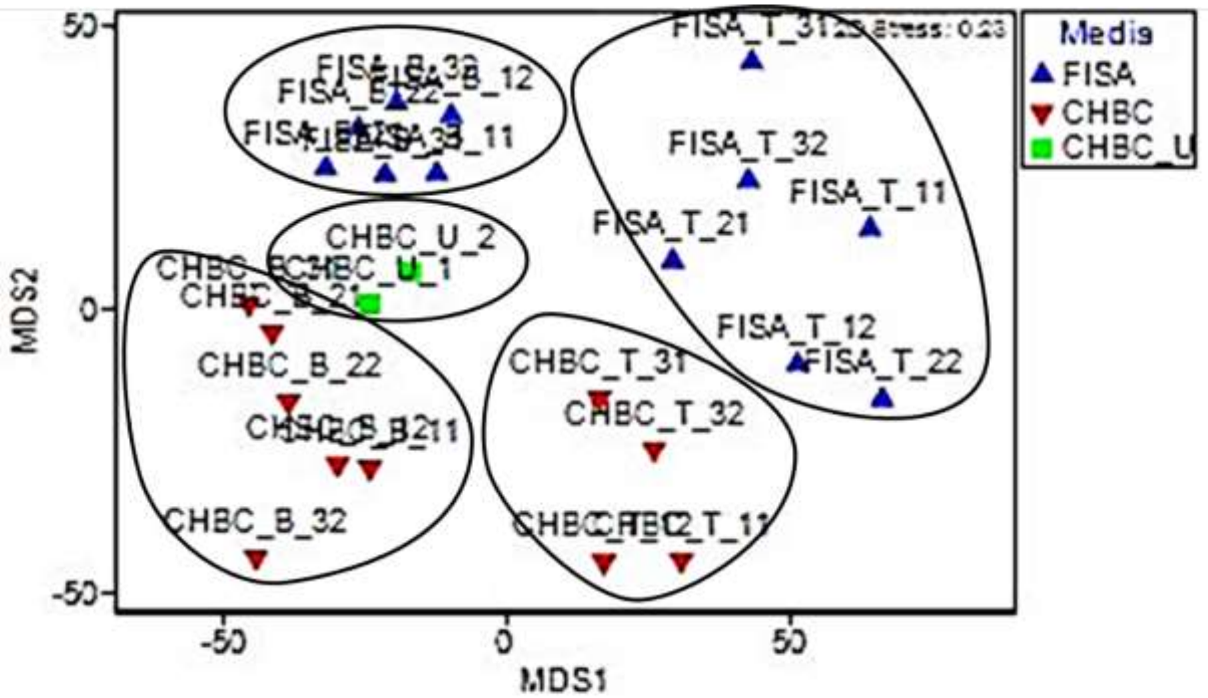


Figure 5-10. Multidimensional scale (MDS) plot generated with Primer-7 showing the variability in bacterial communities between replicate samples at genus level in the column experiments before and after micropollutants degradation. Clusters for duplicate samples and the same sampling depths are circled separately. Samples collected from column top, bottom and unsaturated (not spiked) media are noted by ‘T’, ‘B’, and ‘U’, respectively. The later numbers represent replicates.

5.4.6 Microbial species determinants and functions in biodegradation system

The goal of this study was to identify the geochemical drivers of microbial community composition within biofilter medium samples as the results obtained from the data set appeared to affect the dominance of certain families and genera. Hence, the PCA plot in Figure 5-11 was used to assess similarities in community composition among the different samples. The two principal components (PCs) derived accounted for 76.86% of the variance inherent in the data set. Observations and variables plot of the PCA is shown for the dominant bacteria genera in the Illumina derived 16S rRNA gene sequence libraries. A close visual inspection of the plot showed a clear pattern of demarcation of the filter medium samples classed into different quadrants, which revealed that samples from the top and bottom were separated along PC1, while samples from the bottom of FISA and bottom of CHBC were separated along PC2 (Figure 5-11). On PC1, filter medium samples from the bottom of both filters were partitioned into the positive range of the axis corresponding to the high relative abundance of the genera *Flavobacterium*, *Massilia*, *Rhodoferax*, *Methylobacillus*, *Symbiobacterium*, and *Nesterenkonia*, while samples from the top of both filters were partitioned into the negative range of the axis of PC1 corresponding to the high relative abundance of the genera *Crenothrix*, *Hyphomicrobium*, *Methylobacterium*, and *Planctomyces*. From the data, given the distance in separation, it could be deduced that there is a significant difference in sample community at the top of FISA and the top of CHBC. However, the sample communities associated with the bottom of both filters are only slightly different.

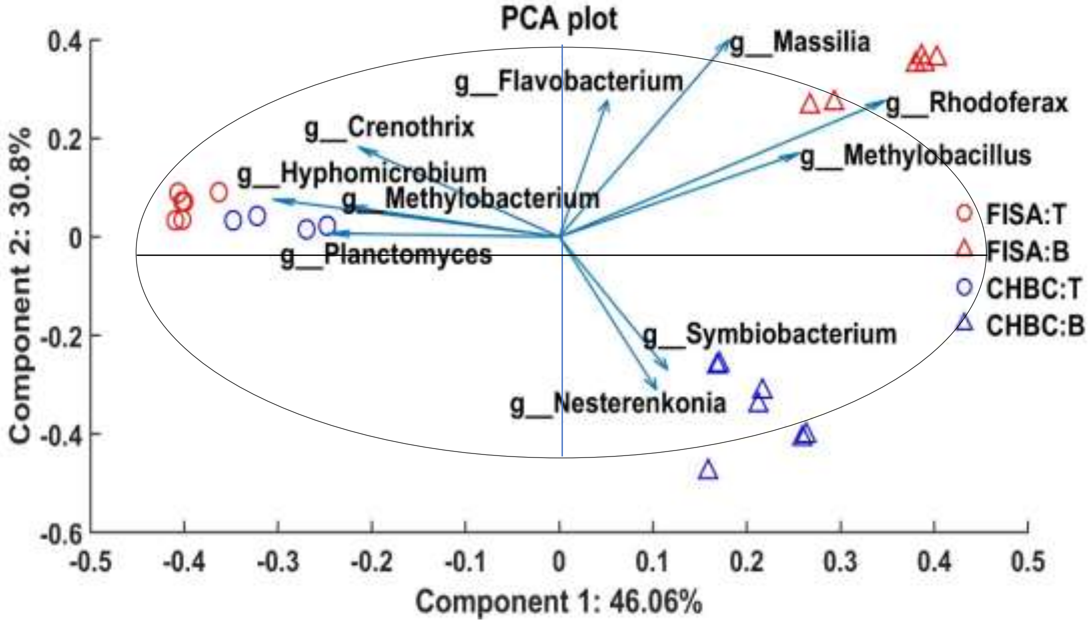


Figure 5-11. A principal component analysis (PCA) plot of the relative abundances of dominant OTUs at the genus level (square root transformed data) of the 16S rRNA-sequencing dataset. The direction of vectors indicates the direction of change of each variable so that the observation samples clustered together have similar microbial communities.

At the end of the biofiltration process, the percentage abundance of the different families and genera was significantly changed throughout the experiment (Figure B 2, Figure B 3 and Figure B 4), which suggests a shift in the microbial community structure in the different filters. STAMP plots generated at genus level taxonomy in Figure 5-12, showed the comparison of the bacterial profiles at the top and bottom of representative column treatment after biofiltration ((a) and (b)), and before and after biofiltration (c) of the compounds over the period of the alternate wetting and drying flow experiments. There was a significant difference with respect to the relative abundances of the OTUs between the top segment and bottom segment of the individual biofilter media. Furthermore, the microbial community of the unsaturated biofilter media samples differed at the end of the experiment from the initial samples (Figure 5-12(c)). This suggests that the microbial community shifted in response to available substrates in the applied pond water over time and the subsequent enrichment and/or reduction of competing genera. Interestingly, while there was a significant distinction between microbial community structures represented by 16S rRNA genes, the overall results revealed that the application of contaminated pond water at the top of the biofilters was the main factor affecting the shift in microbial community structures (Li *et al.*, 2010).

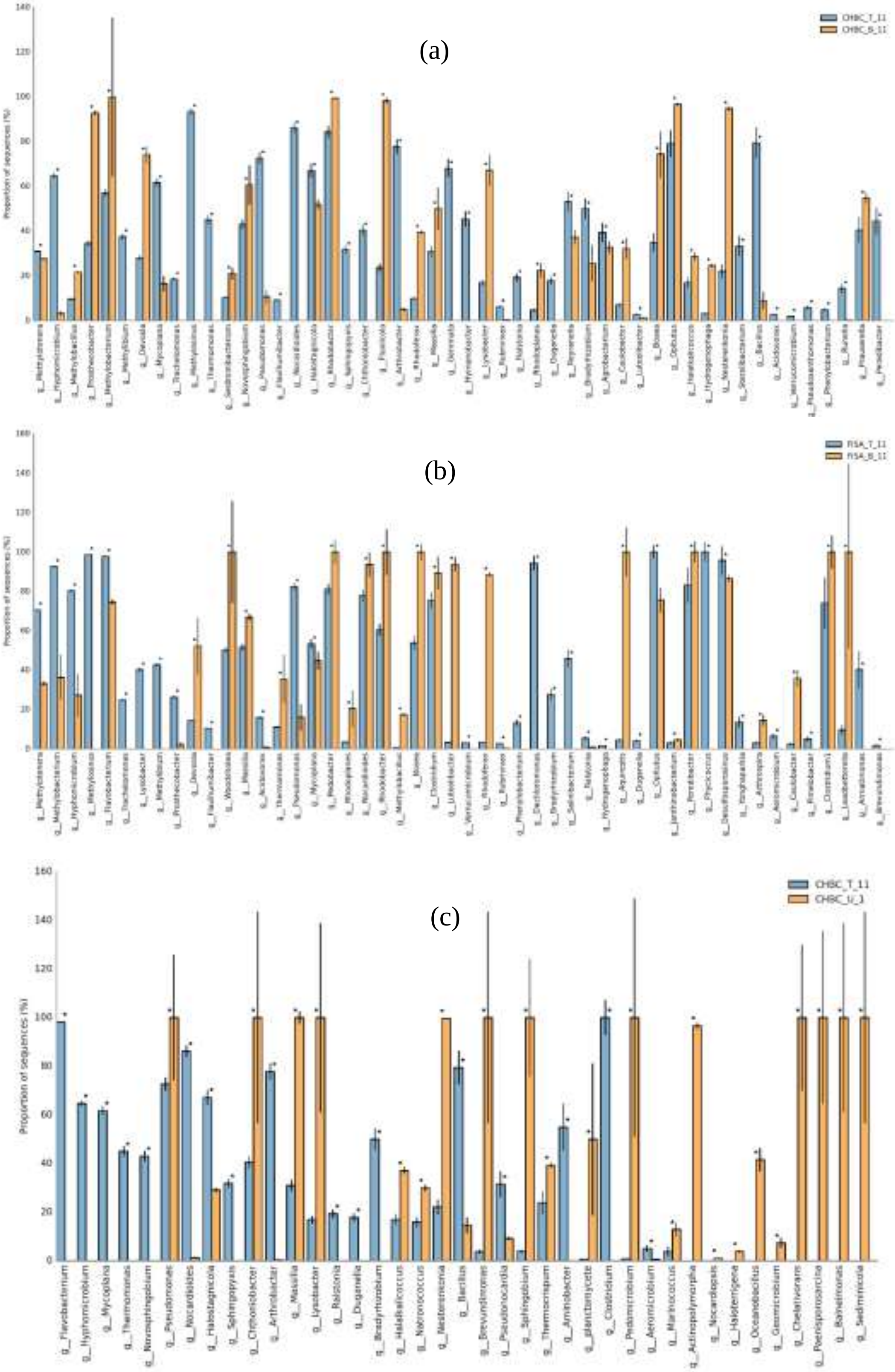
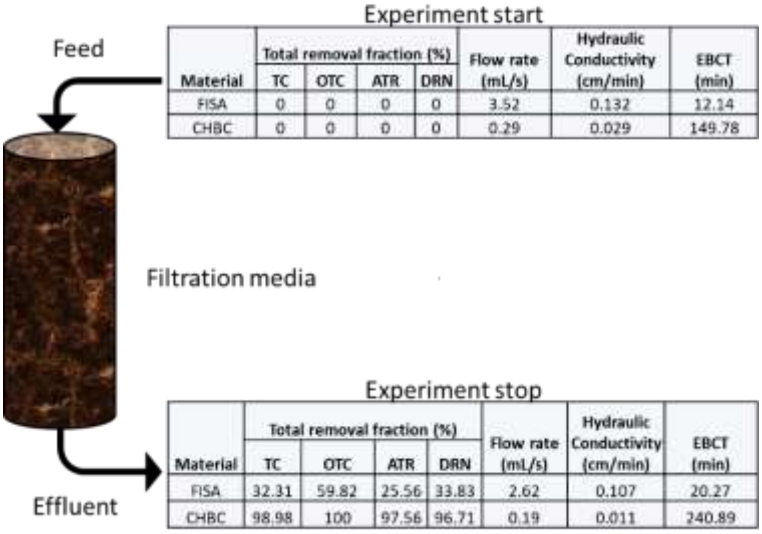


Figure 5-12. Summary comparison plots generated using STAMP software of OTUs between the top and bottom of (a) FISA, (b) CHBC columns at the end of the experiment, and (c) top of CHBC media before and after saturation. Samples collected from column top, bottom and unsaturated (not spiked) media are noted by 'T', 'B', and 'U', respectively. The later numbers represent replicates.

5.5 Conclusions

In conclusion, the application of a biochar sand biofilter can significantly improve the quality of raw contaminated water, as shown by the decreased concentration of micropollutants in the effluent samples. Experimental and analytical investigations carried out on the removal of the selected micropollutants from the unamended sand (FISA) and CHBC columns, operated under continuous flow and wetting/drying flow test conditions, suggested that the 10% CHBC amendment dose significantly reduced the hydraulic conductivity of the fixed-bed columns which helped improve the micropollutant removal by the combined effects of adsorption and biodegradation (Figure 5-13). The hydraulic retention time effects on pollutant removal efficiency and treated water quality were observed for both, continuous flow and discontinuous filter loading with wetting and drying cycles. The study revealed that the fate of micropollutants in pond water passed by gravity flow through the column leaching tests significantly enhanced their removal and also reduced water infiltration rates in the biochar amendment soil by up to 93%, thereby reducing pollutant leaching risks by increasing the EBCT up to 1100%.



Experiment start

Material	Total removal fraction (%)				Flow rate (mL/s)	Hydraulic Conductivity (cm/min)	EBCT (min)
	TC	OTC	ATR	DRN			
FISA	0	0	0	0	3.52	0.132	12.14
CHBC	0	0	0	0	0.29	0.029	149.78

Experiment stop

Material	Total removal fraction (%)				Flow rate (mL/s)	Hydraulic Conductivity (cm/min)	EBCT (min)
	TC	OTC	ATR	DRN			
FISA	32.31	59.82	25.56	33.83	2.62	0.107	20.27
CHBC	98.98	100	97.56	96.71	0.19	0.011	240.89

Figure 5-13. Summary data from the continuous flow column experiment

In the continuous study, the removal of micropollutants from aqueous solution was considerably enhanced due to the biochar amendment; moreover, this enhancement was dependent on the microbial activities present in the biochar. In addition, and similar to the continuous flow experiment, the breakthrough curves values obtained from the alternate wetting and drying flow study was negligible for CHBC columns, and near or slightly below 1 for the FISA columns; which suggested a better performance of the CHBC columns for micropollutants removal, regardless of the flow conditions. While the CHBC column performed better than the FISA column in terms of micropollutant removal in all flow conditions, the significant decline in flow rate observed in the CHBC column over the period of the study was due to pore blockage by biological layer maturation and fouling in the media. More so, it should be noted that the about tenfold reduced flow rate under gravity implies a tenfold greater filter footprint for equivalent volumetric throughput. Nonetheless, the results of this laboratory study agree with the fieldwork carried out by Mrozik et al. (2021) that the amendment application of the coconut husk biochar, as a low-cost adsorbent material, to sand improved the retention and/or removal of micropollutants from surface water in a real-life coastal aquaculture farm for possible synergistic interactions between agriculture, biochar producers, and aquaculture in the rural economy.

The study also examined the effects of CHBC on micropollutant biodegradation in biofilters. As a result, the effects of CHBC on micropollutants and microorganisms were used to determine whether CHBC reduced or promoted micropollutant degradation. It was found that CHBC affected microorganisms by changing the toxicity of micropollutants and microbial quantity, activity, rather than by altering the microbial community structure. The taxonomic analysis showed a significant change in the metagenomic profile in the inocula and the bacterial libraries clustered differently at the different sampling depths. Several genera known to degraders of these chemical compounds including *Flavobacterium*, *Massilia*, *Rhodoferax*, *Methylobacillus*, *Symbiobacterium*, and *Nesterenkonia*, were enriched significantly after the biodegradation assay and their proportion of sequence increased when compared to the un-spiked control. These findings supported our working hypothesis that the CHBC amendment influences the soil microbial composition and promotes the growth of specific taxa.

Overall, biofiltration involves many complex physical and chemical processes dealing with a highly variable inflow - urban stormwater. The main removal mechanism is biodegradation in the biochar amended biofilter, whereas both biodegradation and adsorption occurred in both the amended and unamended biofilters. The results showed that biochar amendments could be useful applications as stormwater filters and other soil applications to reduce pollutant leaching. However, there could be an optimal biochar percentage in the biochar-amendment system which can enhance hydraulic loading through the soil column and accelerated adsorption-biodegradation coupled bioremediation. Hence, additional biochar testing is necessary with the aim of optimizing effluent flow rates through soil columns and avoiding flow clogging, by removing biochar fines via prewashing of the biochar before application.

Chapter 6. General Thesis Discussion, Conclusion and Suggested Future Research

6.1 Background

Biochar has been receiving attention as an environmental adsorbent and what has emerged from modern research so far is a complex multifactorial picture of adsorbents produced from different types of biomass with different methods. Many of the factors determining biochar properties are intrinsically associated with the biochar feedstock type and pyrolysis conditions. In this thesis, various kinds of agricultural residue biomass were converted into biochar and studied as potential adsorbents for the removal of emerging environmental pollutants and were compared with activated carbon (GAC). Agricultural waste like Corn Cob (CCBC), Coconut Shell (CSBC), Coconut Husk (CHBC) and Rice Straw (RSBC) was used to create the biochars investigated in this study. The purpose of the various studies presented in the earlier chapters was to obtain more information regarding the applicability and adsorption characteristics of the biochars, with particular reference to their ability to retain emerging contaminants in bioactive sand filter media. In addition, the research tested to what extent the studied adsorbents themselves leach pollutants into water, in both laboratory-scale column and field-scale lysimeters experiments. Biochar impacts on the hydraulic conductivity of bioactive sand filter media were also investigated. In this way, the research in this thesis focussed on testing the suitability of different agricultural waste produced biochars in removing pollutants from an aqueous solution comprising pharmaceuticals; acetaminophen (ACM), tetracycline (TC), diclofenac (DIC) and oxytetracycline (OTC), and herbicides; atrazine (ATR) and diuron (DRN) in a bioactive filtration system. This chapter will therefore review and integrate the results and discussions of the preceding chapters of this thesis, to consider the extent to which the results support the use of biochar as an amendment in bioactive filtration systems, and to identify the remaining knowledge gaps and focus areas for future work.

6.2 General Discussion

In any discussion of experimental results, it is important to revisit the purpose of the experiment and the expected outcome. The results of three experiments have been presented and discussed; experiments to investigate the influence of biochar derived from four main feedstock and activated carbon on the physical and chemical properties of leachates produced by percolating clean water through small-scale fixed-bed laboratory columns and an outdoor lysimeter trial with biochar-amended soil, a batch study experiment comparing the biochar types used in the first experiment with activated carbon for organic micropollutants removal from a multiple-pollutant solution, and finally, regarding stormwater or surface water treatment with respect to understanding the fate of organic micro-pollutants in a biofiltration system comparing fine sand media versus coconut husk biochar-amended fine sand media. The systematic investigation carried out in this study has provided detailed information on the adsorption characteristics of the use of coconut husk, coconut shell, corn cob and rice straw biochar in removing emerging pollutants in aqueous solution. The measurement of many variables, physical, chemical and biometric, and in different ways, allowed a variety of hypotheses and statistical techniques to be considered.

6.2.1 Chapter 2

In this chapter, an in-depth review of previous research showed that, although efforts have been taken globally to identify the most suitable adsorbents for water pollutants, finding inexpensive adsorbents with high uptake capacity remains an area of research and development. The review found that there was no definitive report on the methodology for selecting adsorbent among the vast options available. Also, while the characteristics and mechanisms of adsorption are not yet fully understood, the role of the adsorption mechanisms in enhancing organic contaminant removal in biochar-amended porous media, and the pollution risk to groundwater caused by the adsorbents themselves over long-term remediation periods has received little attention. This chapter explored the use of low cost, environmentally friendly and readily available materials as adsorbents to remove the emerging pollutants from contaminated water. In particular, it highlighted the use of biochar technology for remediating organic contaminants and identified several inconsistencies and gaps in the efforts to date. However, the review suggested that the main constraints for the adoption of biochar are the production cost and other environmental challenges resulting from the application of biochar to soil. Navia and Crowley (2010), Dumroese et al. (2011) and Gaunt and Atwood (2013) all agreed that the dustiness of the biochar and the potential release of polyaromatic hydrocarbon (PAH) during production are major deterrents to the use of biochar for environmental management.

To overcome these constraints, there has been extensive research to date into providing evidence of the suitability of various feedstocks in biochar production that can provide additional benefits that would increase its value. Many researchers reported that the application of biochar can, in some circumstances, have multiple benefits to soil physicochemical properties, as well as soil biological properties which may directly or indirectly affect the sustainability of the agro-ecosystems. Biochar technology has more potential for use in countries with large agricultural activities, which produce large quantities of waste biomass as a potential feedstock. A parallel literature survey of biochar application opportunities in stormwater treatment revealed that there remains a need to develop a greater understanding of biochar impacts on the functioning of water biofilters. Passing stormwater through bioactive filters prior to discharge will reduce the pollutant loading of surface water, in particular, via the treatment of polluted stormwater before it reaches a water body such as rivers and lakes. The literature survey indicated that biological activities in the open filters play a major role in the treatment processes, highlighting that organic contaminants can be adsorbed by biochar, but implications on the pollutant biodegradation in the filter remain poorly understood.

6.2.2 Chapter 3

Before considering biochar as a water filtration medium, it is important to investigate the potential leaching of pollutants from the biochar itself and biochar impacts on the hydraulic properties. This chapter was guided by two main hypotheses; change in ‘effluent quality’ and ‘hydraulic condition’ due to amendment application, the results considered in this chapter go a long way in addressing the first hypothesis:

- Biochar and activated carbon amendments could adversely affect the physical and chemical properties of biofiltration systems such as pH, hydraulic conductivity, flow rate, the physical and chemical composition of leachate quality of soils to which the biochar was added.

The chapter discussed the results and significant findings of the laboratory column testing as well as long-term field testing of pollutant leaching from biochar amended sand and soil, respectively. The individual fixed-bed column was tested to ascertain the impact of each biochar and activated carbon amendment on the physical and chemical properties of the leachate percolating through the columns. A preliminary investigation showed that the addition of biochar and activated carbon amendment to sand changed several physical properties in the amended columns which affected their hydraulic properties. The bulk densities of the amended sand decreased in the order GAC > CHBC > CSBC > CCBC >

RSBC, however, this order did not correlate well with the results from the volumetric flow (*Q*) and hydraulic conductivity (*K*) testing that showed higher values of *K* and *Q* in GAC and RSBC compared to other amendments. The relationships between *Q* and *K* when tested on the individual columns was also seen to have best-fit proportionality in the order RSBC > CHBC > FISA > CSBC > CCBC >> GAC which indicated the flow in the media columns appeared to be Darcian. However, results from the turbidity and suspended solids analyses on leachate samples took a different trend with CCBC >> CHBC > CSBC >>> RSBC > GAC > FISA, indicating a significant loss of fine biochar particles released into leachate. Visual investigations on filter paper used in filtering leachate samples provided similar evidence, and this could be attributed to the presence of finer (or broken down) biochar particles that were washed out of the column media pore spaces, with CCBC being the most friable biochar.

On the chemical side of the analysis, the results showed that leachate from the biochar amended columns was all alkaline with pH values ranging from 7.9 (± 0.7) to 10.2 (± 0.9), while the pH of leachate from GAC was lower than for the control (FISA), with a pH of 5.8 (±0.02). The pH values from the results only changed slightly throughout the experiments. This, according to Fidel et al. (2017) and Yuan, Xu and Zhang, (2011), played critical roles in the ability of pH-sensitive water-porous media to adsorb and retain cations. The results showed that the application of sand amendments significantly increased the concentration of trace metals in the leachate samples, with leachates from GAC having higher metal ions leached out than biochar amendments. GAC amended sand released Fe, Cu, Ni, Mn, Ba and Sr in higher concentrations than the biochars, likely because of the more acidic pH. Vamvuka, Esser and Komnitsas (2020) agreed that among the numerous factors affecting the leaching of trace elements from biochar-amended sands, high leachates pH, as previously shown, was a major factor for their low extractability. The authors also added that the variations in the leached concentrations are partly due to differences in the solubility of the various compounds containing these elements, and partly due to differences in pore structure and sizes. In addition, the concentrations of all investigated trace metals in leachates from the laboratory experiments were below the recommended limits set out by the EU/UK for drinking water, indicating minimal risks to groundwater resources.

According to the first hypothesis, the leaching of soil nutrients from the column study, as previously shown, proved leaching of ammonium, nitrite, nitrate, chloride, and sulphate from most of the amended sand columns at the start and a significant reduction in leached concentration at the end of the experimental period. This suggests that while the biochar and activated carbon added leachable ions to the sand, such an impact would be time-limited. However, in comparison with the FISA column, the addition of CSBC to the sand did not significantly increase the release of nitrogen ions in the leachate. The lysimeter leachate analysis also showed a similar trend to the column study as the results showed that there was a significant difference in the leaching of the different anions from the lysimeter after the addition of wheat straw biochar and wheat straw pellets to the soils in Lysimeter 1 (L-WSBC) and Lysimeter (L-WSP), respectively. As was seen in the metal investigations, Ca^{2+}, Na^{+}, Mg^{2+} and K^{+} were leached in higher amounts from both lysimeters soil mixtures, however, all metals concentrations in leachate samples investigated were below the EU/UK recommended limit for drinking water, except for Al (in L-WSP) and Ni (in L-WSBC).

6.2.3 Chapter 4

This chapter investigated the adsorption capacities of biochar and activated carbon for a wide range of organic micropollutants in aqueous solution, using the same biochar and activated carbon used in the previous chapter. The aim was to understand and compare the abilities of biochars produced from the four agricultural wastes biomass and activated carbon to remove pharmaceutical and herbicide from sterilized aqueous solution using batch adsorption experiment. The main objective of this research was to evaluate the adsorption performance of the different biochars and compare them with activated carbon. Hence, the second hypothesis was that:

- Specific adsorption behaviours would correlate with specific adsorbent characteristics such as the functional group chemistry, which may allow optimization of biochar selection for maximal effect,
- Biochar from agricultural waste biomass is a better alternative to activated carbon.

The analysis highlighted the overall adsorption characterization of the different adsorbents with respect to their interaction with the different micro-pollutants, using predictive models to suggest the interactions and the diffusion mechanisms that influenced the removal processes. The results of ACM adsorption revealed that all biochars showed a rapid increase in adsorption within the first 12 hours of the contact time, with the adsorption capacities in the order GAC>>>CHBC>RSBC>CCBC>CSBC. However, a similar analysis for DRN, OTC, ATR, and TC compounds showed capacities in the order; GAC>>RSBC>CHBC>CCBC>CSBC, except for DIC that was adsorbed to activated carbon only. This showed that in comparison, the adsorption rate of GAC is 10 times faster than for the best biochar used in this study.

Also, the results showed a relatively good fitting of the model parameters which suggested that the microporous regions are generally playing a significant role in the adsorption process. Again, the data showed that since the slope of the plots corresponded to rates of the adsorption process, the diffusion to the exterior surface of adsorbents controlled the kinetics at the onset of the process and was fast for most of the adsorbents. This then implied that the intraparticle diffusion of micro-pollutants into micropores of the adsorbents was the rate-limiting step, and the diffusion phase suggested that intraparticle diffusion does play a role in the adsorption process. Although batch experiments are generally conducted under ideal conditions, which may not reflect ‘real’ adsorption efficiency of the adsorbents under dynamic conditions, the overall study suggested that RSBC and CHBC biochars could be environmentally sustainable alternatives to GAC for micropollutant removal from water as they may have appropriate adsorbent characteristics depending on particular conditions. To validate this hypothesis further, column displacement experiments were performed in Chapter 5, where transport of pesticide and pharmaceutical micropollutants was studied using environmental wastewater in the presence of environmental microorganisms.

6.2.4 Chapter 5

The observed strong adsorption of micropollutants to biochar found in previous studies (Chapter 4) presents potential implications for micropollutants biodegradation in sand biofilters, while biochar application could impact the sediment microbial ecology. However, comprehensive studies on the effects of biochar on micropollutants biodegradation coupled with microbial ecology are rarely documented. In Chapter 5 of this thesis, the effects of biochar on the biodegradation of the selected pharmaceutical and pesticide compounds were investigated using 2 different flow-through systems in sand amended with coconut husk biochar (CHBC).

This chapter aimed to demonstrate the benefits of the CHBC amendment for enhanced micropollutant removal from contaminated water using a biologically active sand filtration in the laboratory, with a particular focus on evaluating the removal efficiency of the selected micropollutants from surface pond water operated in a continuous gravity flow conditions, and also with wetting and drying cycles. The aim was to evaluate the removal efficiency of selected micropollutants used in the preceding chapter from surface water in fine sand biofilters operated under gravity flow conditions. To start with, a working hypothesis was generated for this third study:

- The addition of 10% (w/w) CHBC will significantly influence the removal of selected micropollutants in a sand biofiltration system,
- A breakthrough point will be achieved for the biofiltration system under continuous flow,
- Biodegradation of micropollutants will increase with the addition of CHBC to the sand biofilter.

The CHBC amended sand filters showed improved performance in the retention of micropollutants as compared to the sand only control FISA, which often showed almost immediate breakthroughs of the tested compounds. The results in this chapter confirmed the results from the previous chapter that biochar adsorbs organic micropollutants and the micropollutants removal in the column study were found to be dependent on the flow rate, influent concentration, and EBCT, and the removal mechanisms are mainly adsorption and subsequent biodegradation. The removal efficiency increased as expected with the addition of biochar in the column and this was partially related to the change in the hydraulic performance of the biofilters, i.e. reduced flow rate in the CHBC amended sand. Also, only a small percentage of the adsorbed micropollutants could be extracted from the biochar media at the end of the experimental study indicating the presence of significant microbial activities leading to micropollutant biodegradation in the media as the main removal mechanism.

The results from the continuous flow biofiltration experiment revealed over 61% reduction in hydraulic conductivity throughout the experimental period indicating that the flow rate in CHBC biofilters was probably governed by increased clogging of the media and the transport of fine biochar particles to clog available pore spaces. The increase in EBCT by over 60% showed an increase in the contact time that would influence the adsorption and biodegradation. The fate of TC, OTC, ATR, and DRN was established in the study by mass balance. The results showed that TC, OTC, ATR and DRN removal in sand biofilter increased by 66.7%, 40.2%, 77.0% and 62.9%, respectively, due to the addition of 10% w/w CHBC-amendment to the biofilter, with over 90% of the removal in CHBC biofilter being due to biodegradation. This was also evident in the breakthrough curves obtained for the CHBC columns, in which biodegradation occurred, as they exhibited plateaus at lower C_t/C_0 values of around 0.026, 0.029 and 0.038 for ATR, DRN and DIC, respectively, as compared to a near or slightly below C_t/C_0 values of ≈1 in the unamended sand (FISA) columns, while pharmaceutical compounds such as TC and OTC always remained below the detection limit. This behaviour suggests consistency in the impact of degradation on micropollutant transport.

Similar to the continuous flow experiment, breakthrough curves from an alternate drying and wetting analysis remained at C_t/C_0 values of ≈0 for CHBC columns, and near or slightly below C_t/C_0 values of ≈1 for the FISA columns, which suggests that micropollutant removal remained consistently high in the CHBC columns throughout the experiment, even after many wetting and drying cycles, and indicating that biodegradation was the predominant removal process. Microbial community structure analysis carried out on filter media samples taken from selected locations in the column showed an increase in the microbial community before and after the experiment, especially in the top filter layer of each column. This suggests that the microbial community shifted may be due to competition on available substrates in the applied contaminated pond water over time and the subsequent enrichment and/or reduction of competing genera. Interestingly, while there was a significant distinction between microbial community structures represented by 16S rRNA genes in CHBC and FISA biofilters, the overall results revealed that the application of contaminated pond water at the top was the main factor affecting the shift in microbial community structures in both types of biofilters.

6.3 General Conclusions

In concluding any experimental results, it is important to revisit the purpose of the experiment and the expected outcome. The purpose of the research carried out in this study was twofold, both exploratory and hypothesis-testing, and there are set working hypotheses for specific research in this thesis. This section reviews the outcomes of the data analysis of the different experimental chapters and the wider implications of the outcomes. For example, although, biochar and activated carbon amendments promise to improve soil physical properties such as water permeability, water infiltration, and to enhance the removal of physical and chemical contaminants in biofiltration systems, This confirms the hypothesis that the application of 3% (w/w) biochar from four main feedstocks to sand either increased (CSBC, RSBC and GAC) or decreased (CHBC and CCBC) the saturated hydraulic conductivity (K) when compared with the sand only control. Leaching of fine biochar particles was evident and supported by the turbidity report for CCBC, CHBC and CSBC which showed NTU values of 18.1±0.9, 9.6±3.0, and 6.3±1.8, respectively, several times above the UK/EU/WHO recommended limit for drinking water of 4 NTU. Or to say it the other way around: Even though the pH values and the leaching metals and anions were generally higher than in fine sand (FISA), they remained below Drinking Water standards, so are not really of significant concern. A long-term investigation in outdoor lysimeters further substantiated these findings.

The results in Chapter 4 and models analysis of the adsorption data considered showed that each biochar was unique depending on its feedstock type, pyrolysis conditions, and surface characteristics, which resulted in distinct pharmaceuticals and pesticides removal from aqueous solution. The best micropollutant adsorbent from the study was activated carbon, however, its production requires sophisticated pyrolysis technology, which is not yet within reach of rural farmers in developing countries. Nonetheless, RSBC and CHBC showed promising adsorbents for multiple micropollutants removal in aqueous solution.

The batch study demonstrated that the activated carbon had better adsorbent kinetic potentials than the biochar-based adsorbents with its adsorption capacity more than 10 times the adsorption capacity of the best biochar (RSBC) for ATR adsorption, more than 6 times the best of biochar (CHBC) for ACM adsorption, more than 2 times the best of biochar (RSBC) for DRN, more than 1.6 times the best of biochar (RSBC) for OTC adsorption, and more than 1.4 times the best of biochar (RSBC) for TC adsorption, respectively used in this study. Comparatively, the kinetic study indicated that RSBC and CHBC showed better pollutant removal efficiency than CSBC and CCBC for the tested pollutants (RSBC > CHBC > CCBC > CSBC). However, CHBC tends to remove more pollutants from aqueous solution within the first 12 hours than all other biochar-based adsorbents. Conclusively, the different adsorption profiles of each biochar are largely a result of their different chemical and physical properties, and their adsorption was found to be dependent on the contact time with the micropollutants. Also, the studies have indicated that pore filling is a significant process in the immobilisation of micropollutants onto the biochars, particularly for RSBC and CHBC, and that the adsorption mechanism was predominantly intraparticle diffusion. Taken together, therefore, the second hypothesis put forward is partly accepted (specific biochar have better removal efficiency than others for a specific micropollutant) and partly rejected (activated carbon remains a better adsorbent for all tested micropollutants). Overall, the results in Chapter 3 and Chapter 4 suggested that CHBC and RSBC could be environmentally superior alternatives to the other tested biochar-based adsorbents for micropollutant removal from aqueous solutions.

Although previous studies had indicated that only bioavailable contaminants can be utilized by microorganisms, it had been suggested that the free state of hydrophobic micropollutants might provide a direct measure of the microbial degradable contaminant fraction in the water (Cheng *et al.*, 2017). The results obtained in Chapter 5 of this study indicated that CHBC amendment significantly influenced the soil microbial composition and promotes the growth of specific taxa, however, reduced the hydraulic conductivity of the biofilter which helped improve the micropollutant removal by the combined effects of adsorption and biodegradation. The results agree with the number of studies that found that biochar amendment could influence microbial community structure significantly in the soil (Anderson *et al.*, 2011; Khodadad *et al.*, 2011; Tong *et al.*, 2014; Cheng *et al.*, 2017; Mrozik *et al.*, 2021; Zhang *et al.*, 2021). Although, in this study, there was not enough data to justify the significant association of CHBC with the bacterial community composition in the biofilters. These effects were observed for both continuous flow and discontinuous filter loading with wetting and drying cycles. Based on the results three broad conclusions can be stated:

1. CHBC amendment changed the physical and hydrological properties of the sand biofiltration system, most notably it reduced hydraulic conductivity.
2. Reduced hydraulic conductivity and micropollutant retention by the CHBC amendment benefitted the micropollutant biodegradation.
3. Adsorption-desorption of micropollutants and microorganisms to CHBC, microbial growth, and biodegradation of micropollutants exist simultaneously.
4. Despite many positive influences on the flow-through effluent, the removal mechanism was largely due to biodegradation rather than chemical changes in the system.

Following on from the observation for the 3% w/w CHBC amendment of sand (Chapter 3), the hydraulic conductivity values determined using DI water decreased with the 10% w/w CHBC amendment of sand (Chapter 5) and using real pond water. This decrease could be as a result of increased suspended solids from the fine biochar particles and pond water that contributed to clogging the pores of filter media. However, not enough data exist to clarify this point, so it is recommended that more research is conducted on the influence of amendment rates and influent characteristics on hydrological properties of biochar amended filter media. Evidence was also found that biofiltration media with CHBC amendment are conducive for the biodegradation of micropollutants, which is consistent with the view presented elsewhere suggesting that biochar increases the population of indigenous microbes responsible for biodegradation activities (Luo *et al.*, 2017; Dai *et al.*, 2021; Zhang *et al.*, 2021). The results from the molecular dynamics were broadly in agreement with the chemical mass balance analysis which indicated that the major micropollutants removal mechanism is via biodegradation. The microbial community is expected to be distinctively different in the two systems, as a result of the different filtration media and substrate compositions, although this was not further examined in this study. Measurements of microbial assays suggest that the microbial community diversity in the biofilter was altered by the CHBC amendment, but stratification (filter top versus bottom) had the greatest impact on the biofilter microbial communities.

6.4 Broader implications of current research

Based on the results of this study investigating four types of biochar at doses up to 10% (w/w), and their usability in water treatment, four broad implications can be stated:

1. The effects of applying biochar on leachate quality (anions and metals) were predominantly non-harmful and this supports the utilization of agricultural waste biomass derived biochar for environmental remediation and recycling. Biochar influences on leachate quality were significantly higher than the unamended sand in terms of turbidity, pH, organic and inorganic pollutants leaching, however, the leached out concentrations were largely in line or below the very stringent drinking water standards, so not really of concern. However, the mobility of fine biochar particles in the subsurface needs to be further investigated.

2. At a 3% w/w application rate, biochar of certain feedstocks can increase the hydraulic conductivity of the filtration medium which could help reduce flooding for surface water runoff. However, at a 10% w/w application rate, the results of this work showed that hydraulic conductivity tends to decrease, which will have implications on biochar applications in stormwater biofiltration.

3. Biochar amendment was beneficial in enhancing the micropollutant removal in biofilters, although that was partially due to the reduction in hydraulic filtration rates, and hence longer empty bed contact time and opportunity for micropollutant biodegradation.

From the results of this work, it can be said that biochar amendment of sand biofilters is a promising approach for enhanced stormwater treatment in infiltration systems because the biochar itself does not detrimentally impact leachate quality but improves micropollutant removal. However, the leaching of fine biochar particles from the filter is a potential concern. One characteristic finding was that specific biochar adsorbent types showed an affinity for the adsorption of specific micropollutant compounds. This potential was demonstrated experimentally by measurements and the responses in adsorption ability of the four biochar adsorbents. Also, there are trade-offs between enhanced micropollutant removal in the biochar amended biofilters and reduced hydraulic conductivity which need to be considered in the design of biochar amended stormwater treatment systems.

6.5 Suggestions for further work

In addition to providing useful results, this work also highlights some research questions which are yet to be answered going forward and this should form the basis for the suggestions for future work. Research should be continued into the influence of agricultural-based absorbents on the availability, degradation and transportation of emerging micropollutants, as well as the retention of inorganic nutrient and metals. Based on the outcome of the current research, suggested specific examples of areas where further work is needed are discussed next.

This study focused on selected micropollutants spiked in DI water or pond water and experiments have also been carried out under carefully controlled laboratory conditions to facilitate the interpretation of outcomes via mass balance calculations, etc. But for future work, the systems should also be tested in outdoor conditions with real contaminated water under variable temperatures, etc., in order to assess the effect of adsorption competition and climatic impacts on biodegradation processes.

Although this study investigated the use of raw biochars to identify their specific adsorption characteristics, many studies have investigated how modification of biochar can improve the adsorption capacity. Future studies should therefore carefully consider the net advantages of the use of cheap chemical modifiers to improve the tested biochar as well as the potential risks of the modifiers in contaminating the environment. Additionally, studies such as life cycle analysis or other decision-making tools should be considered in these cases to determine the net benefits of using biochar versus conventional adsorbents such as activated carbon.

It is important also to be aware of the potential for biochar to introduce contaminants into the amended soil profile as seen in the results from this thesis. The results of the study showed that biochar with finer particle sizes are easily leached out of the media of biofiltration systems and are sources of clogging particles for the pores spaces of the media. There is also a risk that the fine biochar particles could become carriers for adsorbed pollutants. Very fine particles (colloids) can be mobile in groundwater, and a lot of biochar colloids could enhance the mobility of adsorbed pollutants. This should be further investigated with various particle sizes of biochar tested to identify the suitability for use of adsorption and biofiltration design purposes.

A balance needs to be struck between good adsorbents and the need to reduce the risk of leaching pollutants or the biochar to groundwater during heavy rainfall events and to trade-off these risks with the significant environmental advantages of biochar. Finally, the molecular study done in this thesis can be improved further, for example, looking at functional genes responsible for degrading specific micropollutants and how their abundance and expression are influenced by biochar addition. Because micropollutant degrading bacteria may only be a small proportion of the overall microbial community, their abundance changes are not easily recognized with 16S rRNA gene sequencing methods, which survey the entire bacterial community.

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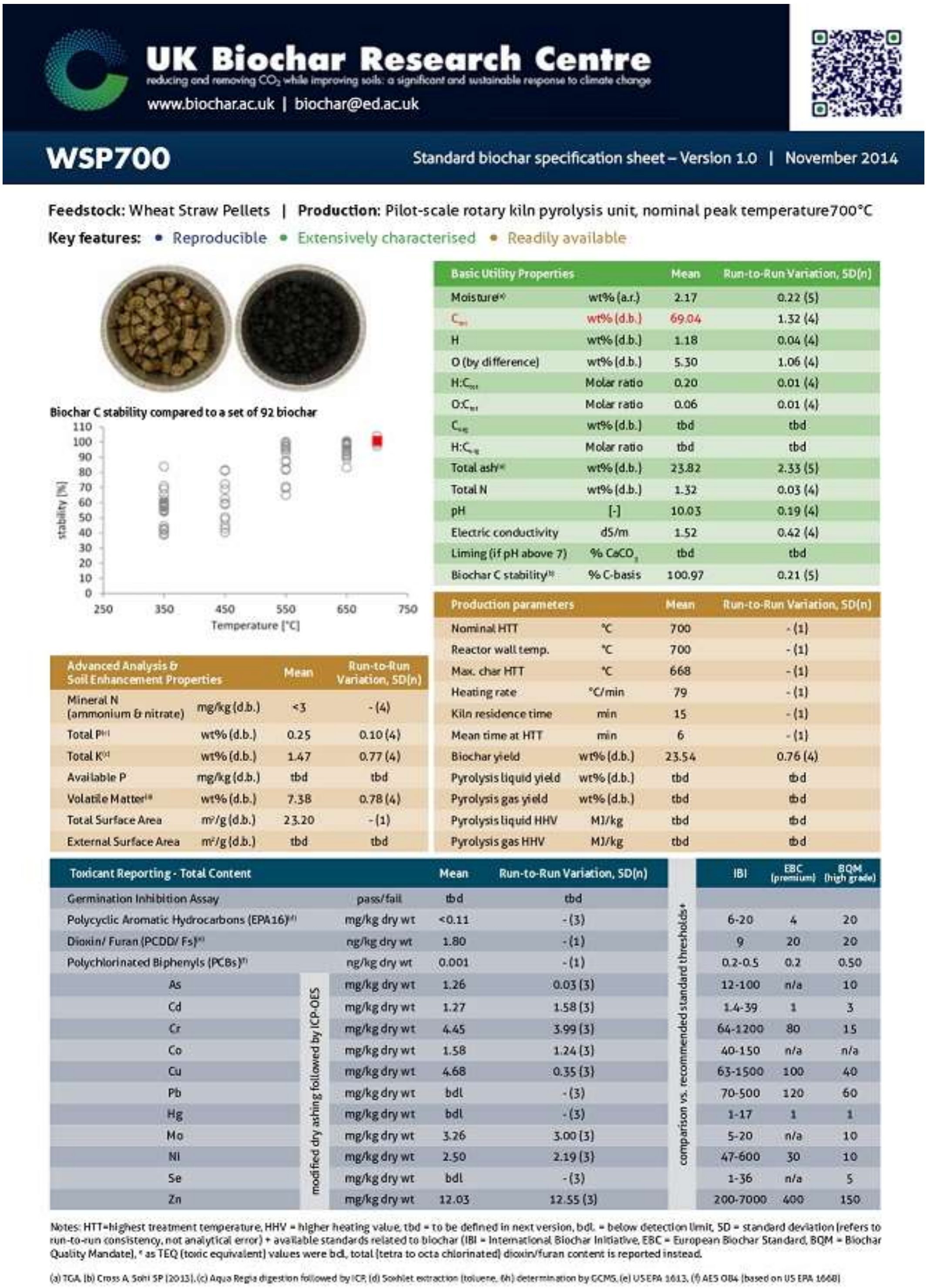
Appendices

Appendix A



UK Biochar Research Centre

reducing and removing CO_2 while improving soils: a significant and sustainable response to climate change

www.biochar.ac.uk | biochar@ed.ac.uk

WSP700

Standard biochar specification sheet – Version 1.0 | November 2014

Feedstock: Wheat Straw Pellets | **Production:** Pilot-scale rotary kiln pyrolysis unit, nominal peak temperature700°C

Key features: • Reproducible • Extensively characterised • Readily available

Biochar C stability compared to a set of 92 biochar

Basic Utility Properties		Mean	Run-to-Run Variation, SD(n)
Moisture[a]	wt% (a.r.)	2.17	0.22 (5)
C_{tot}	wt% (d.b.)	69.04	1.32 (4)
H	wt% (d.b.)	1.18	0.04 (4)
O (by difference)	wt% (d.b.)	5.30	1.06 (4)
$H:C_{tot}$	Molar ratio	0.20	0.01 (4)
$O:C_{tot}$	Molar ratio	0.06	0.01 (4)
C_{org}	wt% (d.b.)	tbd	tbd
$H:C_{org}$	Molar ratio	tbd	tbd
Total ash[a]	wt% (d.b.)	23.82	2.33 (5)
Total N	wt% (d.b.)	1.32	0.03 (4)
pH	[-]	10.03	0.19 (4)
Electric conductivity	dS/m	1.52	0.42 (4)
Liming (if pH above 7)	% $CaCO_3$	tbd	tbd
Biochar C stability[b]	% C-basis	100.97	0.21 (5)

Production parameters		Mean	Run-to-Run Variation, SD(n)
Nominal HTT	°C	700	- (1)
Reactor wall temp.	°C	700	- (1)
Max. char HTT	°C	668	- (1)
Heating rate	°C/min	79	- (1)
Kiln residence time	min	15	- (1)
Mean time at HTT	min	6	- (1)
Biochar yield	wt% (d.b.)	23.54	0.76 (4)
Pyrolysis liquid yield	wt% (d.b.)	tbd	tbd
Pyrolysis gas yield	wt% (d.b.)	tbd	tbd
Pyrolysis liquid HHV	MJ/kg	tbd	tbd
Pyrolysis gas HHV	MJ/kg	tbd	tbd

Advanced Analysis & Soil Enhancement Properties		Mean	Run-to-Run Variation, SD(n)
Mineral N (ammonium & nitrate)	mg/kg (d.b.)	<3	- (4)
Total P[c]	wt% (d.b.)	0.25	0.10 (4)
Total K[c]	wt% (d.b.)	1.47	0.77 (4)
Available P	mg/kg (d.b.)	tbd	tbd
Volatile Matter[a]	wt% (d.b.)	7.38	0.78 (4)
Total Surface Area	m²/g (d.b.)	23.20	- (1)
External Surface Area	m²/g (d.b.)	tbd	tbd

Toxicant Reporting - Total Content			Mean	Run-to-Run Variation, SD(n)		IBI	EBC (premium)	BQM (high grade)
Germination Inhibition Assay		pass/fail	tbd	tbd	comparison vs. recommended standard thresholds+			
Polycyclic Aromatic Hydrocarbons (EPA16)[d]		mg/kg dry wt	<0.11	- (3)		6-20	4	20
Dioxin/ Furan (PCDD/ Fs)[e]*		ng/kg dry wt	1.80	- (1)		9	20	20
Polychlorinated Biphenyls (PCBs)[f]		ng/kg dry wt	0.001	- (1)		0.2-0.5	0.2	0.50
As	modified dry ashing followed by ICP-OES	mg/kg dry wt	1.26	0.03 (3)		12-100	n/a	10
Cd		mg/kg dry wt	1.27	1.58 (3)		1.4-39	1	3
Cr		mg/kg dry wt	4.45	3.99 (3)		64-1200	80	15
Co		mg/kg dry wt	1.58	1.24 (3)		40-150	n/a	n/a
Cu		mg/kg dry wt	4.68	0.35 (3)		63-1500	100	40
Pb		mg/kg dry wt	bdl	- (3)		70-500	120	60
Hg		mg/kg dry wt	bdl	- (3)		1-17	1	1
Mo		mg/kg dry wt	3.26	3.00 (3)		5-20	n/a	10
Ni		mg/kg dry wt	2.50	2.19 (3)		47-600	30	10
Se		mg/kg dry wt	bdl	- (3)		1-36	n/a	5
Zn		mg/kg dry wt	12.03	12.55 (3)		200-7000	400	150

Notes: HTT=highest treatment temperature, HHV = higher heating value, tbd = to be defined in next version, bdl. = below detection limit, SD = standard deviation (refers to run-to-run consistency, not analytical error) + available standards related to biochar (IBI = International Biochar Initiative, EBC = European Biochar Standard, BQM = Biochar Quality Mandate), * as TEQ (toxic equivalent) values were bdl, total (tetra to octa chlorinated) dioxin/furan content is reported instead.

(a) TGA, (b) Cross A, Sohi SP (2013), (c) Aqua Regia digestion followed by ICP, (d) Soxhlet extraction (toluene, 6h) determination by GCMS, (e) US EPA 1613, (f) AES OB4 (based on US EPA 1668)

Figure A1 Details of the materials physicochemical characteristics of wheat straw pellets (WSP) and wheat straw biochar (WSBC) used for the Lysimeter experiments.

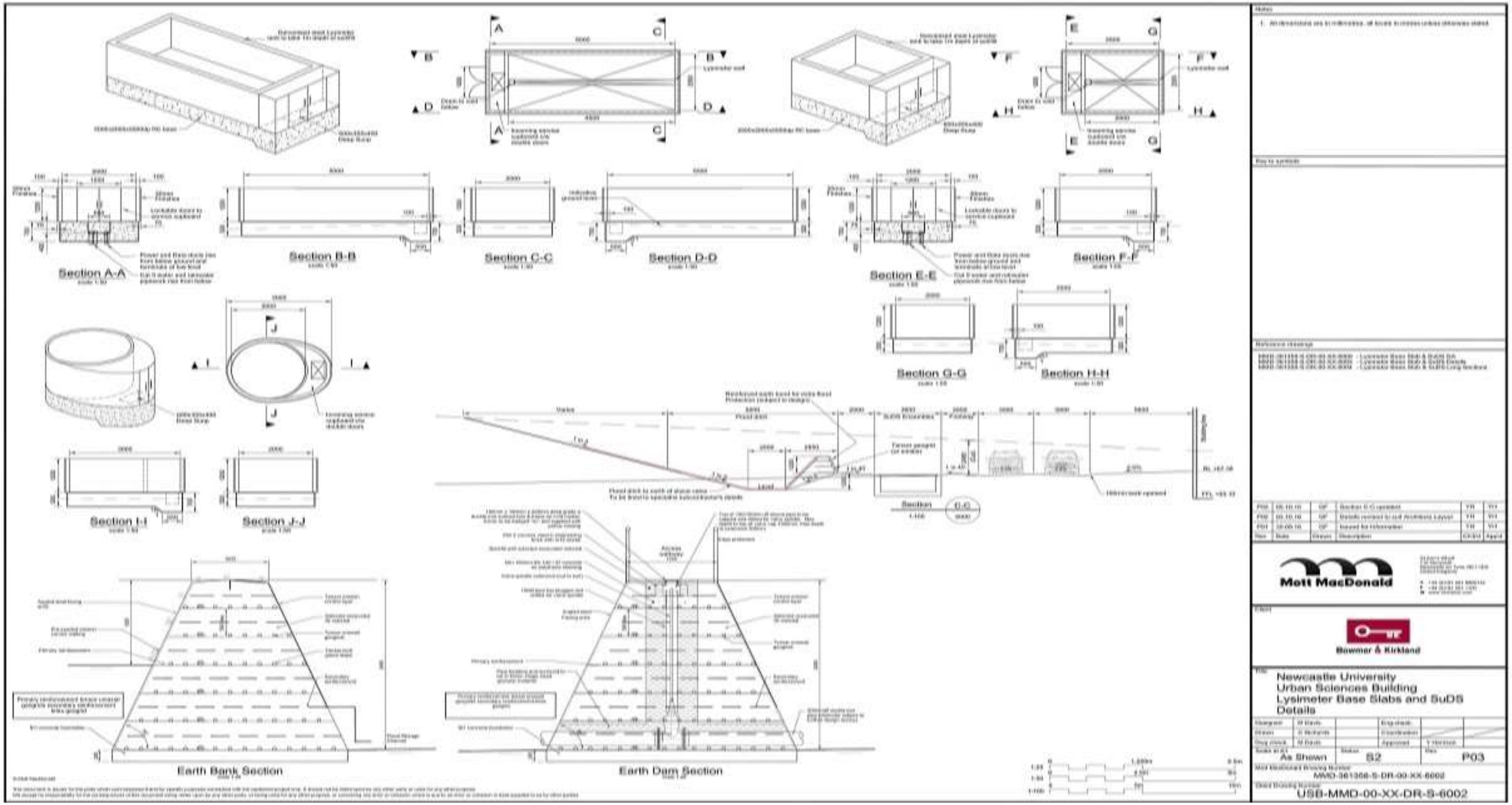


Figure A2 Construction details of the lysimeter - layout and dimensions.

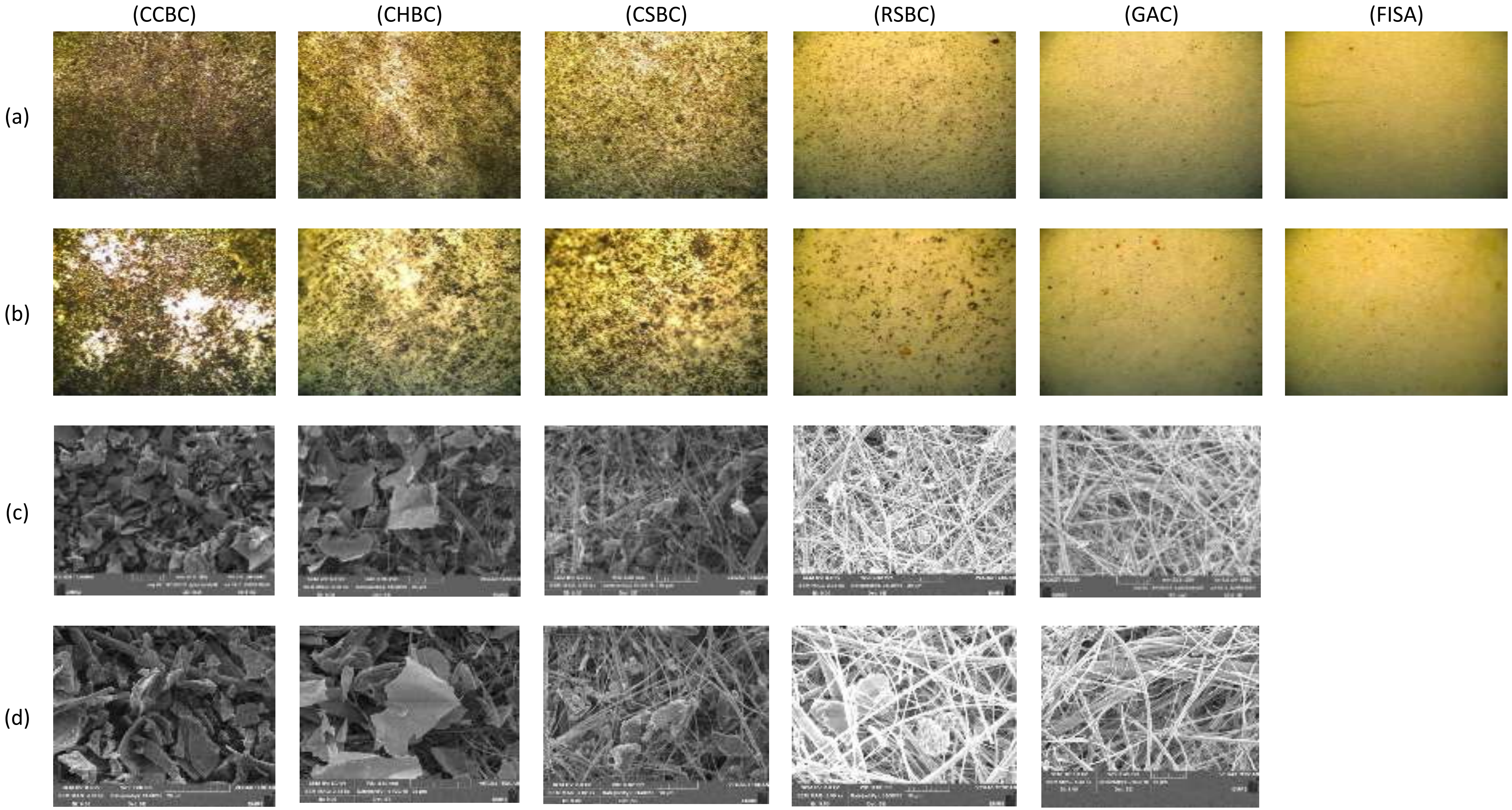


Figure A3 Residue image of suspended solids in effluent samples for the different amendments. In ascending magnification order: (a) microscopy magnification 4X; (b) microscopy magnification 10X; (c) SEM image magnification 2000X; (d) SEM image magnification 5000X

Table A1 Proximate analysis and properties of biochar the materials (Source: KMUTT).

Parameters	**Units**	**Corn Cob (CCBC)**	**Coconut Husk (CHBC)**	**Coconut Shell (CSBC)**	**Rice Straw (RSBC)**
Moisture	(%)	18.67	1.69	2.96	1.91
Ash	(%)	6.33	8.56	4.42	35.75
Volatile Matter	(%)	48.97	5.99	38.63	33.41
Fix C	(%)	26.03	83.76	53.99	28.93
Heating value	(MJ/kg)	22.05	26.12	28.65	14.13
C	(%)	60.36	68.48	68.63	53.63
H	(%)	3.03	3.53	3.69	2.50
N	(%)	1.81	0.06	0.25	1.74
S	(%)	0.12	0.15	0.02	0.33
O	(%)	34.68	27.78	27.41	41.80
Pyrolysis Temp.	(°C)	480	378	704	303
Yield	(%)	32.07	33.65	23.82	10.00
Bulk density	(g/cm^3)	0.70	0.66	1.14	1.69
Iodine Number	(mg/g)	32.31	68.36	13.17	3.06
pH (DI water)	-	8.97	9.75	9.02	8.94

Table A2 Lysimeter soil characteristics

Parameter	Result
Soil Class	Sandy loam
pH	7.8
Phosphorus (ppm)	24
Potassium (ppm)	227
Magnesium (ppm)	149
Calcium (ppm)	3396
Sulphur (ppm)	111
Manganese (ppm)	42
Copper (ppm)	27.2
Boron (ppm)	1.78
Zinc (ppm)	75.3
Molybdenum (ppm)	0.1
Iron (ppm)	542
Sodium (ppm)	100
C.E.C. (meq/100g)	15.8
Organic matter (%)	8.8
Organic Carbon (%)	5.12
Silt (%)	34.54
Clay (%)	12.11
Sand (%)	53.35

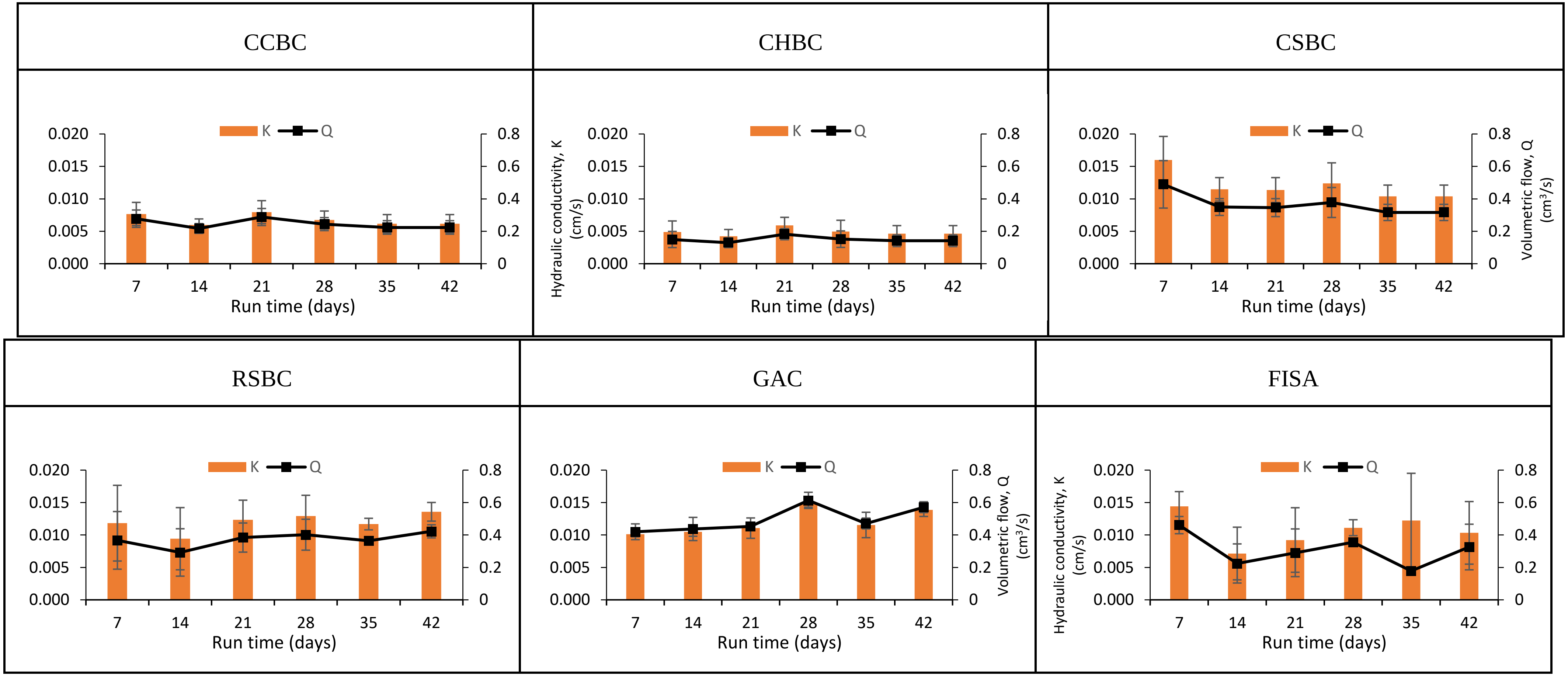
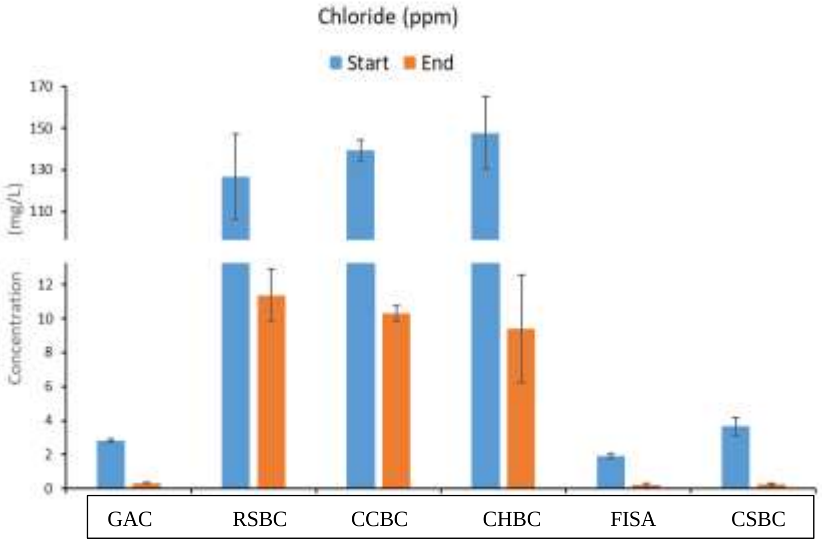
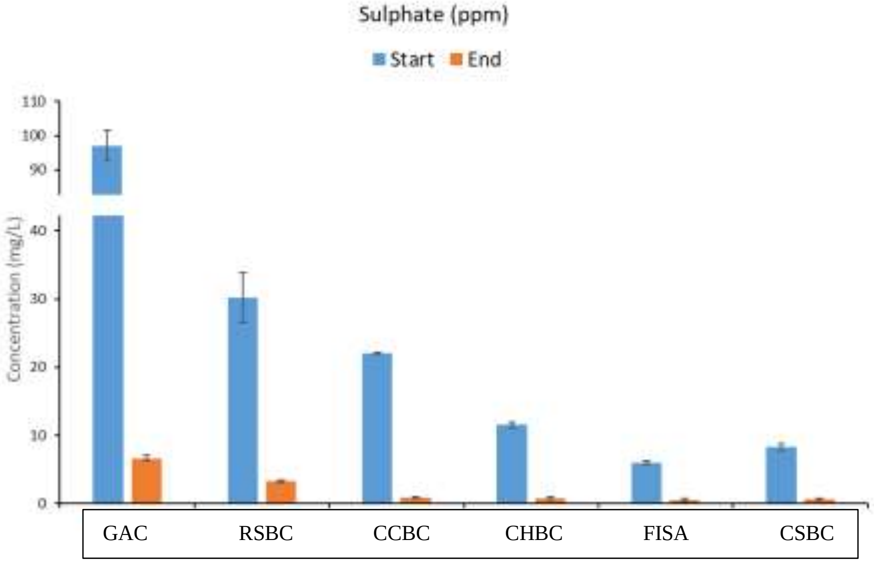
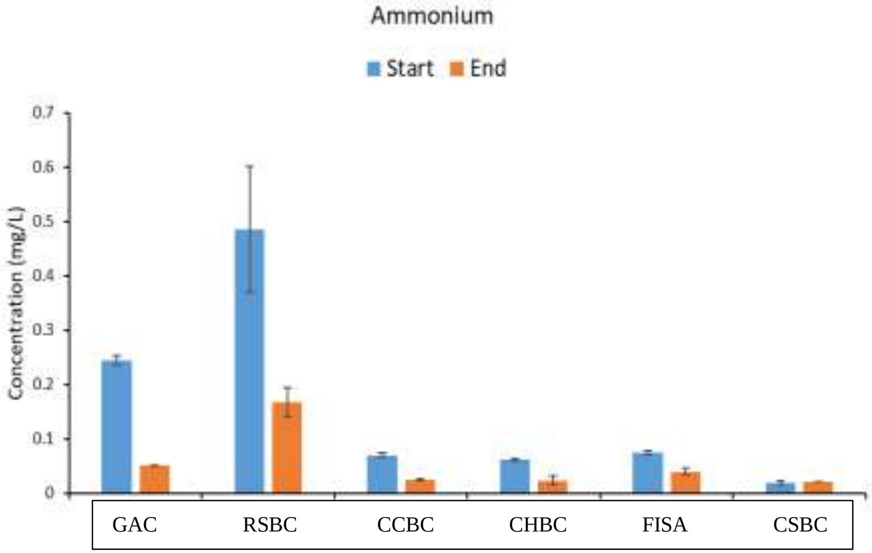
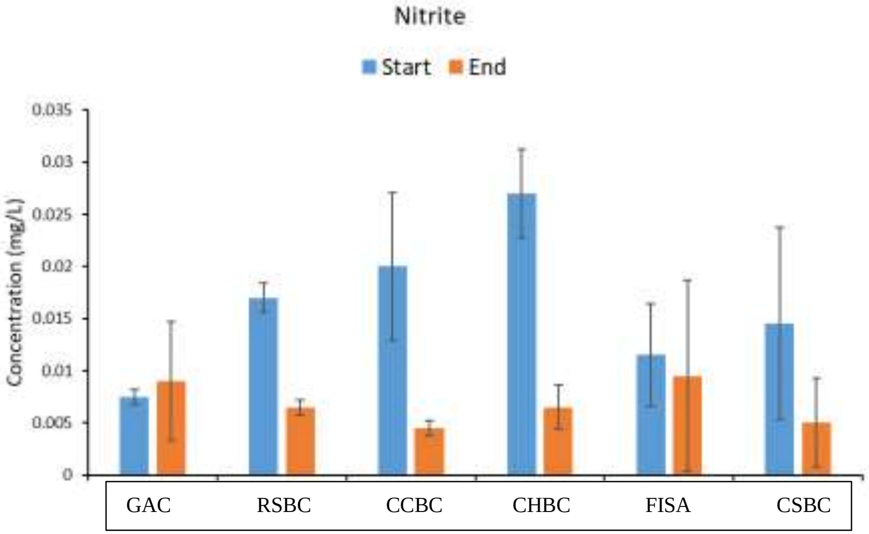


Figure A4 Variation in saturated hydraulic conductivity (*K*) and the volumetric flow rate (*Q*) in the sand column, following the addition of biochar (3%) to fine sand. Abbreviation: CCBC, corn cob biochar; CHBC, coconut husk biochar; CSBC, coconut shell biochar; RSBC, rice straw biochar; GAC, activated carbon; FISA, unamended control. The *K* is measured using simplified falling head experiments for six soil treatments over subsequent flushing events.


Chloride (ppm)
Start
End
170
150
130
110
12
10
8
6
4
2
0
Concentration (mg/L)
GAC
RSBC
CCBC
CHBC
FISA
CSBC


Sulphate (ppm)
Start
End
110
100
90
40
30
20
10
0
Concentration (mg/L)
GAC
RSBC
CCBC
CHBC
FISA
CSBC


Ammonium
Start
End
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Concentration (mg/L)
GAC
RSBC
CCBC
CHBC
FISA
CSBC


Nitrite
Start
End
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
Concentration (mg/L)
GAC
RSBC
CCBC
CHBC
FISA
CSBC

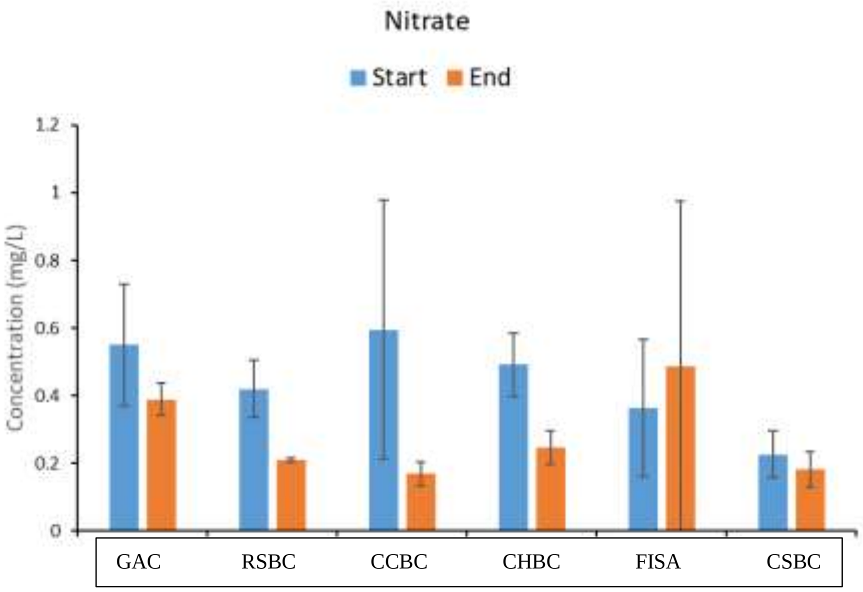
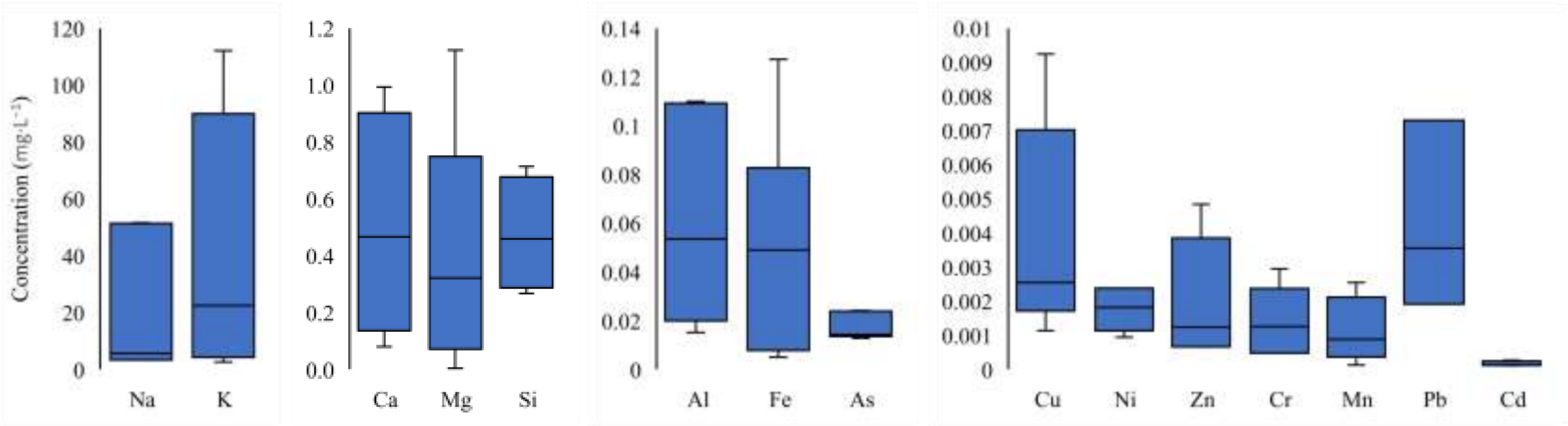
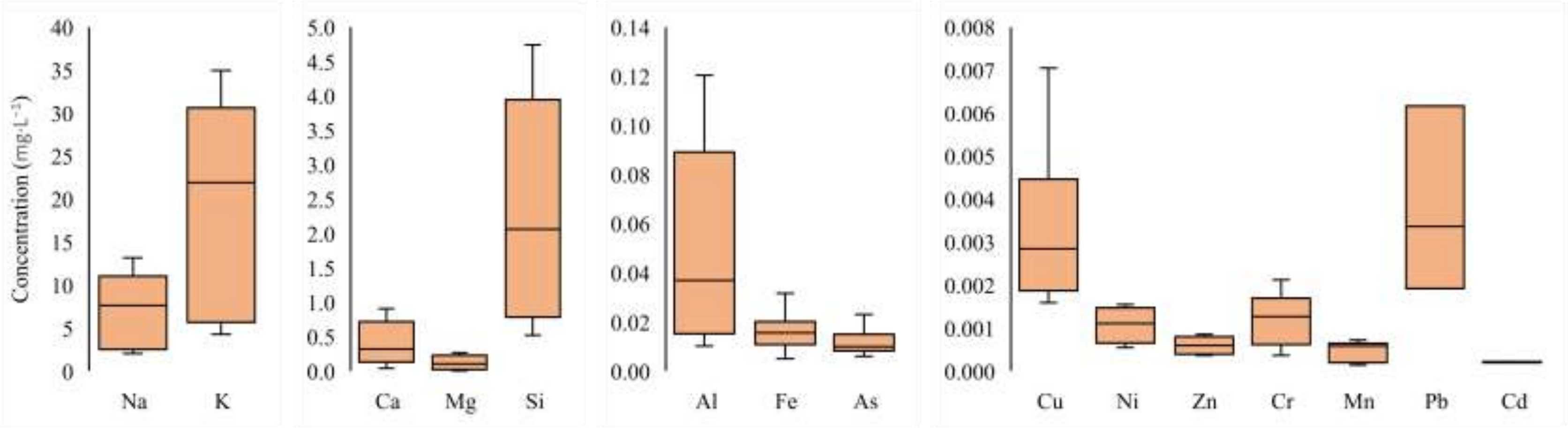


Figure A5 Concentrations of nutrients leaching from the different amendments measured at the start and the end of the experiments, following the addition of biochar (3%) to fine sand. Abbreviation: CCBC, corn cob biochar; CHBC, coconut husk biochar; CSBC, coconut shell biochar; RSBC, rice straw biochar; GAC, activated carbon; FISA, unamended control.

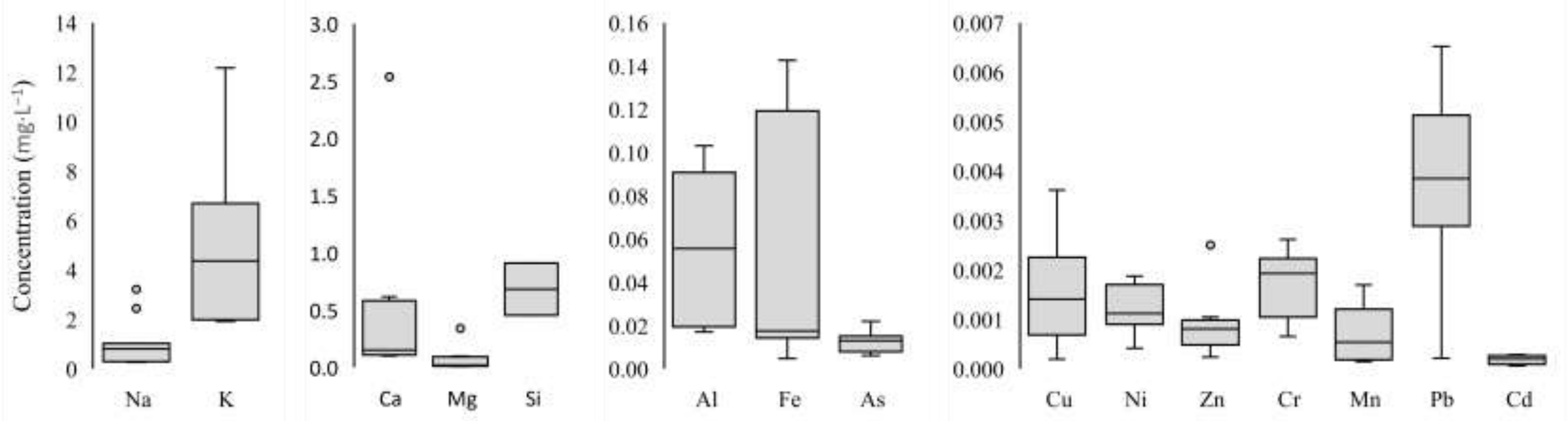
CCBC



CHBC



CSBC



RSBC

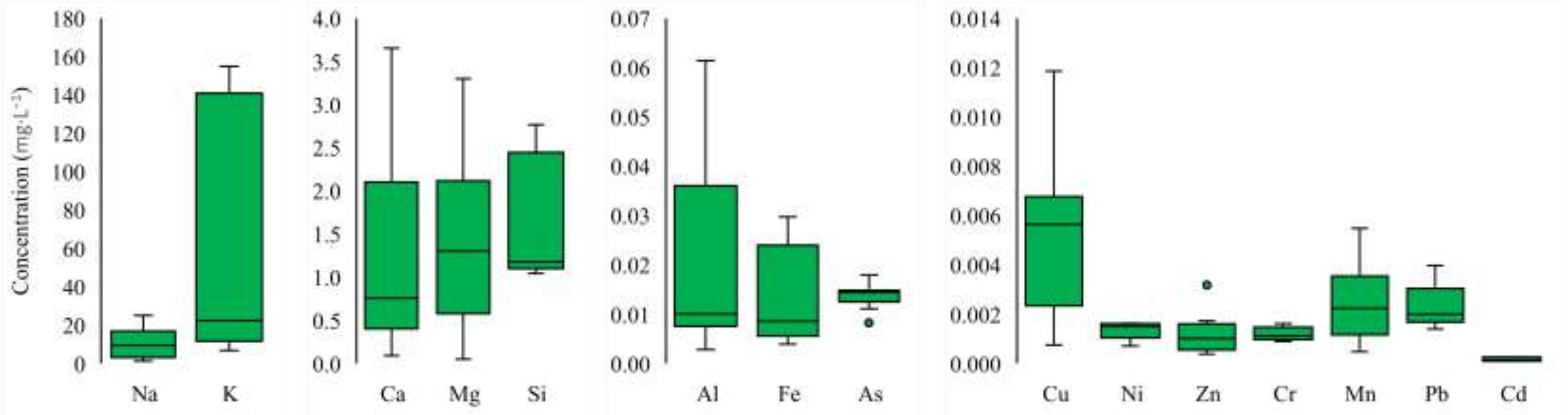


Figure A6 Box-and-whisker plots for comparing metals leaching for the different column amendments collected over the period of the experiments.

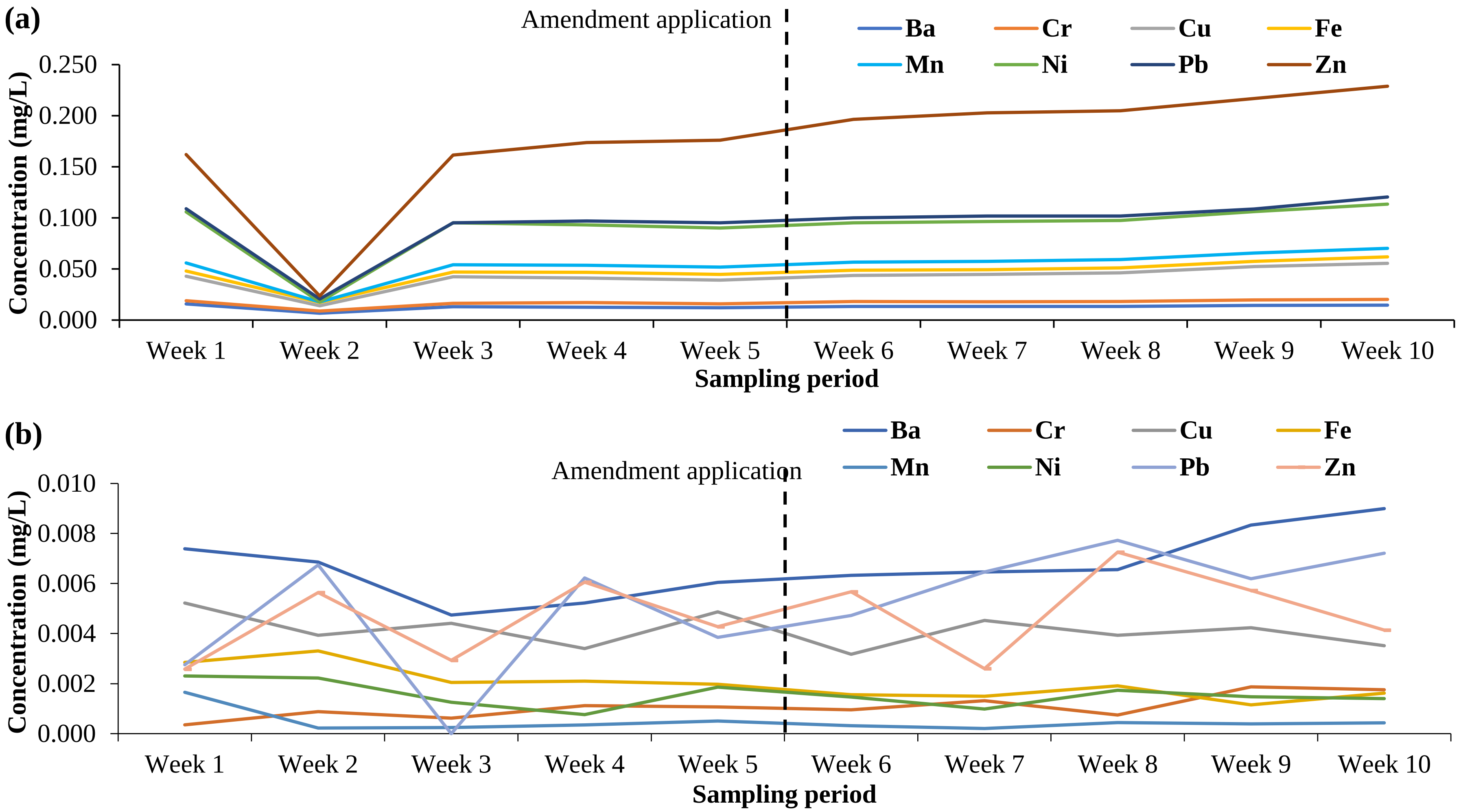


Figure A 7 Trace element concentrations (Ba, Cr, Cu, Fe, Mn, Ni, Pb, Zn) in the leachates of the different lysimeters soil (a) L-WSBC (b) L-WSP, measured for the experiments with amendment applied after Week 5.

Appendix B

Table B 1 A summary of the p-values and 95% confidence intervals for the y-intercept of the Boyd plots. A p-value of less than 0.05 provides significant evidence against the null hypothesis of the y-intercept being equal to zero.

Adsorbate	Adsorbent	Significant Level		
		P-value	Lower 95%	Upper 95%
ACM	CSBC	0.0453	0.0001	0.0066
	CCBC	0.0902	0.0005	0.0056
	CHBC	0.2680	0.0007	0.0022
	RSBC	0.0032	0.0009	0.0037
	GAC	0.0000	0.0196	0.0318
OTC	CSBC	0.0001	0.0016	0.0037
	CCBC	0.0000	0.0093	0.0110
	CHBC	0.0000	0.0078	0.0135
	RSBC	0.0000	0.0119	0.0150
	GAC	0.0000	0.1288	0.1525
TC	CSBC	0.0000	0.0033	0.0056
	CCBC	0.0000	0.0023	0.0040
	CHBC	0.0082	0.0011	0.0061
	RSBC	0.0000	0.0031	0.0055
	GAC	0.0001	0.0561	0.1111
ATR	CSBC	0.0000	0.0000	0.0000
	CCBC	0.0000	0.0023	0.0012
	CHBC	0.3307	0.0028	0.0010
	RSBC	0.0801	0.0020	0.0001
	GAC	0.0203	0.0021	0.0002
DRN	CSBC	0.0002	0.0022	0.0009
	CCBC	0.2654	0.0022	0.0007
	CHBC	0.1891	0.0018	0.0004
	RSBC	0.5433	0.0010	0.0018
	GAC	0.1492	0.0037	0.0006
DIC	CSBC	0.0000	0.0000	0.0000
	CCBC	0.0000	0.0000	0.0000
	CHBC	0.0000	0.0000	0.0000
	RSBC	0.0000	0.0000	0.0000
	GAC	0.6845	0.0115	0.0078

Appendix C

Table C 1 Profile of mean values ± standard deviation of leached TC concentrations, for FISA and CHBC biofilters in the continuous flow experiments, following the addition of biochar (10%) to fine sand. Abbreviation: CHBC, coconut husk biochar; FISA, unamended control.

Runtime (mins)	FISA (μg/L)	CHBC (μg/L)
30	75.55±35.41	6.26±6.78
60	52.66±7.86	1.81±2.56
90	46.00±0.81	1.17±1.66
120	41.18±2.02	0.78±1.10
150	51.31±8.74	0.78±1.10
180	53.51±9.13	0.16±0.24
210	56.69±19.47	0.13±0.19
240	61.68±13.01	N.D
270	62.09±14.58	0.13±0.18
300	63.69±13.84	N.D
330	66.14±8.94	0.05
360	67.64±4.93	N.D
390	69.73±13.09	N.D
420	73.13±10.56	N.D
450	77.13±11.97	0.21
480	74.07±7.89	N.D
510	74.09±13.86	N.D
540	79.81±14.11	N.D
570	82.64±13.67	N.D
600	78.80±17.89	N.D
630	82.32±5.73	N.D
660	89.97±13.68	N.D
690	99.38±21.23	N.D

N.D = Not Detected

Table C 2 Profile of mean values ± standard deviation of leached OTC concentrations, for FISA and CHBC biofilters in the continuous flow experiments, following the addition of biochar (10%) to fine sand. Abbreviation: CHBC, coconut husk biochar; FISA, unamended control.

Runtime (mins)	FISA (µg/L)	CHBC (µg/L)
30	26.18±21.36	N.D
60	15.82±0.66	N.D
90	13.91±0.66	N.D
120	13.21±2.66	N.D
150	14.87±3.89	N.D
180	16.64±4.05	N.D
210	17.43±10.12	N.D
240	22.09±7.27	N.D
270	23.58±11.26	N.D
300	20.52±8.13	N.D
330	23.35±5.21	N.D
360	25.84±1.38	N.D
390	24.95±5.01	N.D
420	27.82±6.08	N.D
450	33.83±7.63	N.D
480	28.8±7.43	N.D
510	31.44±5.94	N.D
540	35.32±10.02	N.D
570	32.62±9.16	N.D
600	38.02±12.32	N.D
630	33.049.72	N.D
660	39.75±6.46	N.D
690	39.40±13.55	N.D

N.D = Not Detected

Table C 3 Profile of mean values ± standard deviation of leached ACM concentrations, for the FISA and CHBC biofilters in the continuous flow experiments, following the addition of biochar (10%) to fine sand. Abbreviation: CHBC, coconut husk biochar; FISA, unamended control.

Runtime (mins)	FISA (µg/L)	CHBC (µg/L)
30	99.59±1.92	N.D
60	98.81±1.44	N.D
90	100.61±0.83	N.D
120	103.66±2.28	N.D
150	97.67±1.07	N.D
180	99.41±0.31	N.D
210	102.77±1.92	N.D
240	102.99±4.17	N.D
270	100.06±3.27	N.D
300	101.28±4.58	0.04±0.07
330	102.74±0.87	N.D
360	100.93±0.5	N.D
390	100.48±1.47	N.D
420	104.52±1.38	N.D
450	104.33±0.5	N.D
480	103.9±2.21	N.D
510	106.96±1.83	N.D
540	106.47±0.14	N.D
570	104.68±2.27	N.D
600	104.81±3.83	N.D
630	106.04±0.03	N.D
660	105.23±1.84	N.D
690	106.41±3.01	N.D

N.D = Not Detected

Table C 4 Profile of mean values ± standard deviation of leached ATR concentrations, for the FISA and CHBC biofilters in the continuous flow experiments, following the addition of biochar (10%) to fine sand. Abbreviation: CHBC, coconut husk biochar; FISA, unamended control.

Runtime (mins)	**FISA (µg/L)**	**CHBC (µg/L)**
30	100.19±97.99	N.D
60	91.36±89.78	N.D
90	92.86±88.01	N.D
120	92.63±92.14	N.D
150	96.56±85.61	N.D
180	93.5±90.45	N.D
210	95.52±91.25	N.D
240	97.67±89.04	N.D
270	97.36±89.34	N.D
300	88.84±89.92	N.D
330	94.20±89.8	N.D
360	93.18±87.58	N.D
390	96.65±89.12	N.D
420	95.58±86.15	N.D
450	99.19±88.70	N.D
480	94.20±88.96	N.D
510	93.48±89.73	N.D
540	96.67±89.46	N.D
570	94.48±87.87	N.D
600	91.21±86.65	N.D
630	92.3±85.26	N.D
660	92.02±101.20	N.D
690	105.97±100.07	N.D

N.D = Not Detected

Table C 5 Profile of mean values ± standard deviation of leached DRN concentrations, for the FISA and CHBC biofilters in the continuous flow experiments, following the addition of biochar (10%) to fine sand. Abbreviation: CHBC, coconut husk biochar; FISA, unamended control.

Runtime (mins)	**FISA (µg/L)**	**CHBC (µg/L)**
30	84.98±87.62	2.09±4.25
60	68.61±72.14	1.66±3.91
90	73.32±71.18	1.79±3.77
120	71.59±74.77	1.82±4.11
150	73.11±65.5	1.82±4.16
180	71.27±72.95	1.88±4.01
210	75.29±75.08	1.73±4.13
240	74.91±69.69	1.97±3.97
270	76.74±73.98	1.88±4.37
300	69.3±74.91	1.96±4.24
330	75.52±70.44	2.03±3.82
360	72.92±68.21	1.69±4.01
390	75.88±69.63	1.66±4.19
420	77.33±67.35	1.63±4.29
450	80.09±71.83	10.11±4.02
480	75.68±69.44	4.00±3.96
510	72.43±74.25	4.18±3.99
540	79.11±70.7	3.63±4.00
570	73.6±71.85	4.29±3.32
600	75.74±68.63	4.30±3.63
630	74.82±65.17	4.13±3.42
660	76.32±91.91	4.08±4.14
690	100±94.89	3.79±3.92

Table C 6 Profile of mean values ± standard deviation of leached DIC concentrations, for the FISA and CHBC biofilters in the continuous flow experiments, following the addition of biochar (10%) to fine sand. Abbreviation: CHBC, coconut husk biochar; FISA, unamended control.

Runtime (mins)	FISA (µg/L)	CHBC (µg/L)
30	88.17±93.91	0.96±0.01
60	84.57±94.57	20.94±4.18
90	86.1±89.3	24.78±5.72
120	84.52±88.9	29.07±10.2
150	84.41±87.77	29.07±12.38
180	87.17±94.36	24.56±12.68
210	87.11±96.86	22.92±12.89
240	89.7±88.24	19.62±12.58
270	90.8±90.56	17.16±10.21
300	83.17±96.04	14.95±9.36
330	87.59±90.51	12.79±8.03
360	93.89±93.25	10.78±0.52
390	94.15±93.01	9.76±6.62
420	94.94±92.6	8.42±5.64
450	99.45±97.18	2.66±5.49
480	90.95±93.8	3.03±5.39
510	95.82±93.66	3.41±4.91
540	93.44±95.56	3.32±4.60
570	94.03±93.89	3.41±3.91
600	92.55±90.01	3.14±4.24
630	97.53±93.53	3.33±2.84
660	92.79±100	3.21±2.88
690	97.13±98.27	4.10±2.97

Table C 7 Micropollutants adsorbed to soil solids in amount/kg soil and percentage removal mass fraction at approx. 0.07095kg FISA soil and 0.0357kg CHBC soil, following the addition of biochar (10%) to fine sand. Abbreviation: CHBC, coconut husk biochar; FISA, unamended control.

Compound	FISA Column		CHBC Column	
	µg/kg	%	µg/kg	%
TC	(10)	0.33	(10)	2.03
OTC	(10)	0.29	(10)	2.30
ATR	480	15.53	30	6.89
DRN	200	5.82	(20)	2.03
ACM	-	-	-	-
DIC	-	-	-	-

Analysis on compounds with (-) could not be performed as at the time of the experiment.
Values in brackets are at the detection limit of the analysis performed

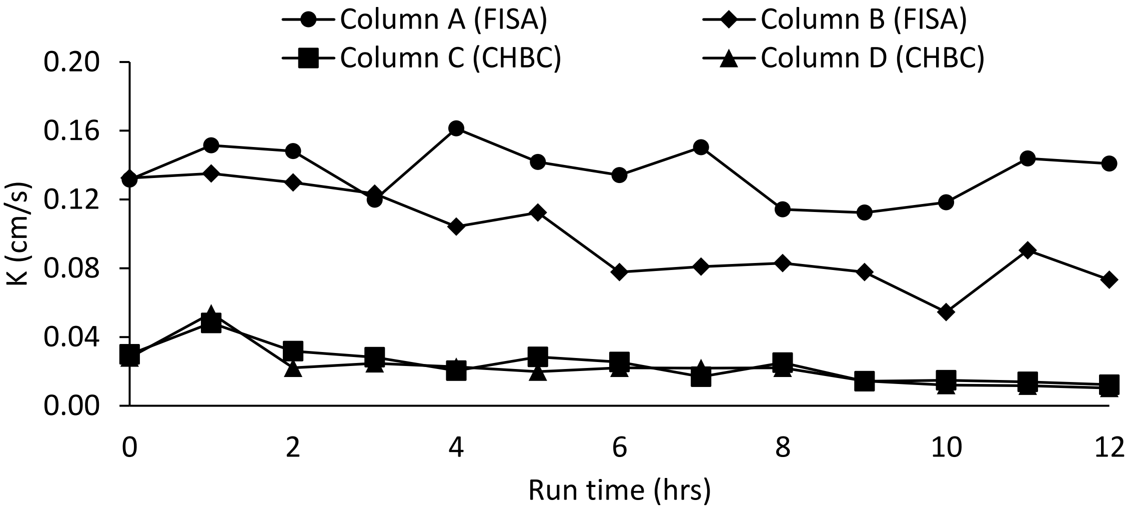


Figure C 1 Hydraulic conductivity analysis measured for each column, following the addition of biochar (10%) to fine sand. Abbreviation: CHBC, coconut husk biochar; FISA, unamended control.

Table C 8 Summary hydraulic performance parameters mean values ± standard deviation (n=2) for the different filter columns, following the addition of biochar (10%) to fine sand. Abbreviation: CHBC, coconut husk biochar; FISA, unamended control.

Flow Time (hrs)	Influent Conc. (μg/L)	Bed Height (cm)	Flow Rate (mL/s)		Empty Bed Contact Time (EBCT) (mm/hr)		Hydraulic Conductivity (cm/min)		Hydraulic Loading (cm/min)	
			FISA	CHBC	FISA	CHBC	FISA	CHBC	FISA	CHBC
0	100	20	3.52±0.49	0.29±0.08	12.14±1.44	149.78±0.92	0.132±0.006	0.029±0.001	1.66±0.20	0.13±0.00
1	100	20	3.62±0.54	0.24±0.20	11.81±1.29	250.34±162.53	0.143±0.012	0.051±0.004	1.70±0.19	0.10±0.07
2	100	20	3.34±0.43	0.26±0.10	12.80±1.65	173.24±23.40	0.139±0.013	0.027±0.007	1.58±0.20	0.12±0.02
3	100	20	2.99±0.45	0.26±0.09	14.33±1.52	171.13±17.86	0.122±0.003	0.026±0.002	1.41±0.15	0.12±0.01
4	100	20	3.21±0.66	0.23±0.10	13.35±0.70	191.73±35.04	0.133±0.040	0.022±0.002	1.50±0.08	0.11±0.02
5	100	20	3.01±0.44	0.23±0.11	14.22±1.57	197.03±44.36	0.127±0.021	0.024±0.006	1.41±0.16	0.10±0.02
6	100	20	2.54±0.96	0.21±0.09	17.36±2.21	214.44±40.98	0.106±0.040	0.024±0.002	1.16±0.10	0.10±0.02
7	100	20	3.26±1.52	0.21±0.10	13.96±3.12	211.56±46.18	0.116±0.049	0.019±0.004	1.47±0.10	0.10±0.02
8	100	20	2.53±0.67	0.21±0.11	17.09±0.31	221.99±62.64	0.099±0.022	0.024±0.002	1.17±0.02	0.10±0.03
9	100	20	2.37±0.65	0.20±0.09	18.22±0.34	222.90±45.10	0.095±0.024	0.014±0.000	1.10±0.02	0.09±0.02
10	100	20	2.52±1.25	0.20±0.09	18.28±4.73	224.54±48.81	0.086±0.045	0.013±0.002	1.13±0.29	0.09±0.02
11	100	20	2.31±1.12	0.20±0.08	19.81±4.86	225.49±40.82	0.117±0.038	0.013±0.002	1.04±0.26	0.09±0.02
12	100	20	2.62±1.91	0.19±0.08	20.27±10.55	240.89±44.37	0.107±0.048	0.011±0.001	1.14±0.59	0.08±0.02

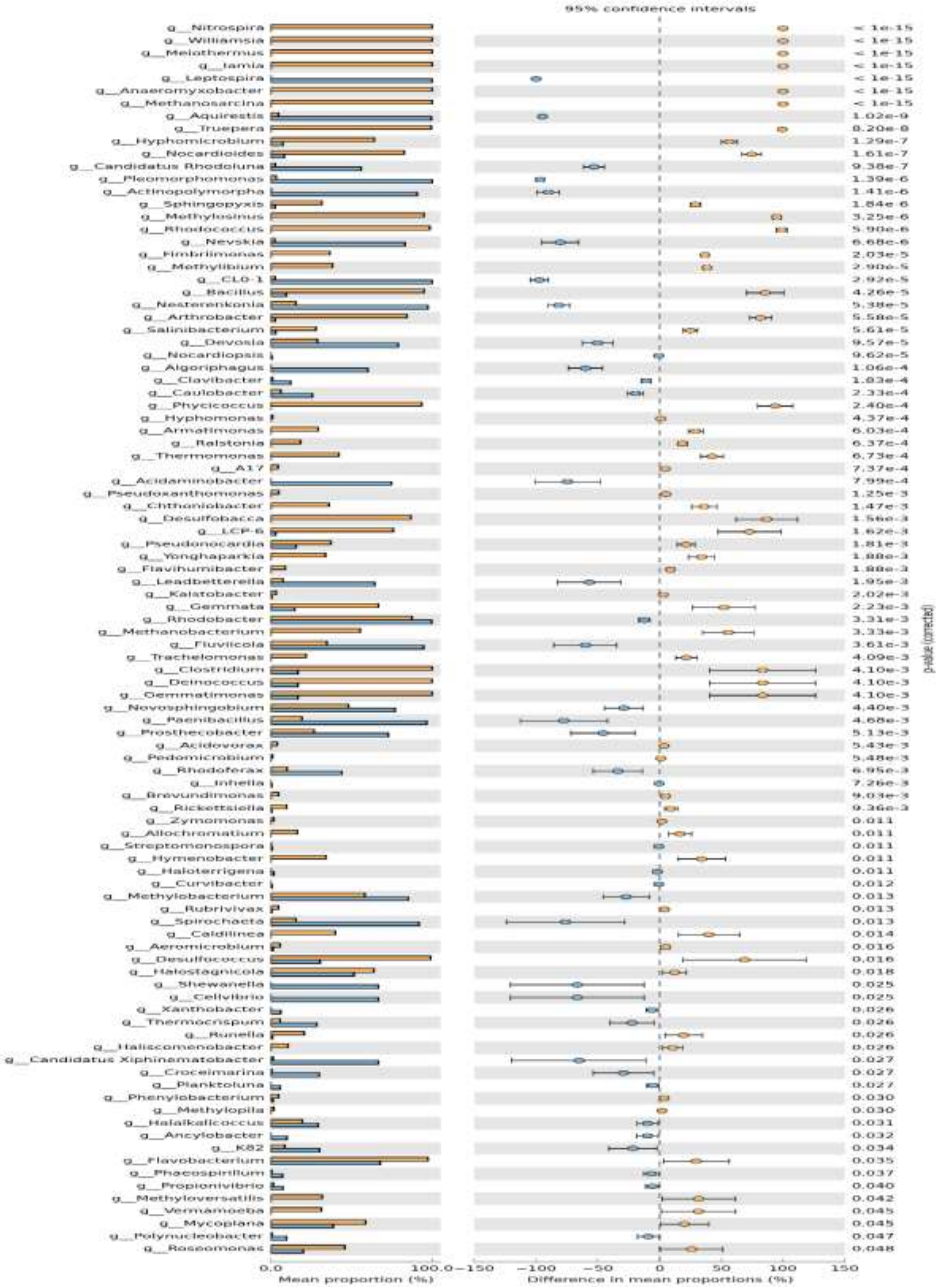


Figure C 2 Extended error bar plot of CHBC top (green) vs CHBC bottom (green) considering the abundance profile of microbial domains in the 16s rRNA amplicon sequencing data for micropollutants degradation assay in spiked pond water, The bacterial domain that increased or decreased significantly (G-test, p<0.05) over the duration of the assay are reported in the plot.

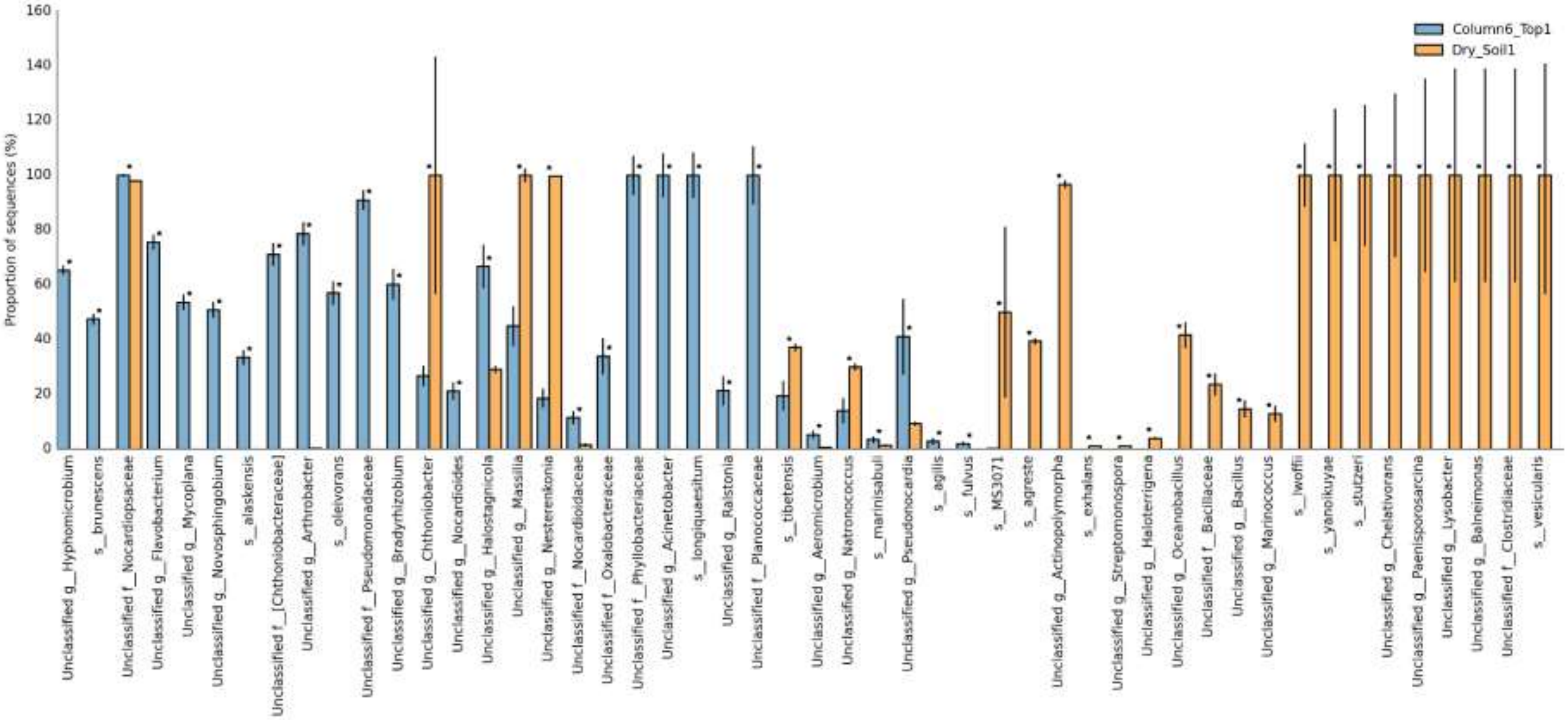


Figure C 3 Extended error bar plot of CHBC top (blue) vs CHBC unsaturated (green) considering the abundance profile of microbial domains in the 16s rRNA amplicon sequencing data for micropollutants degradation assay in spiked pond water. The bacterial domain that increased or decreased significantly (G-test, p<0.05) over the duration of the assay are reported in the plot.

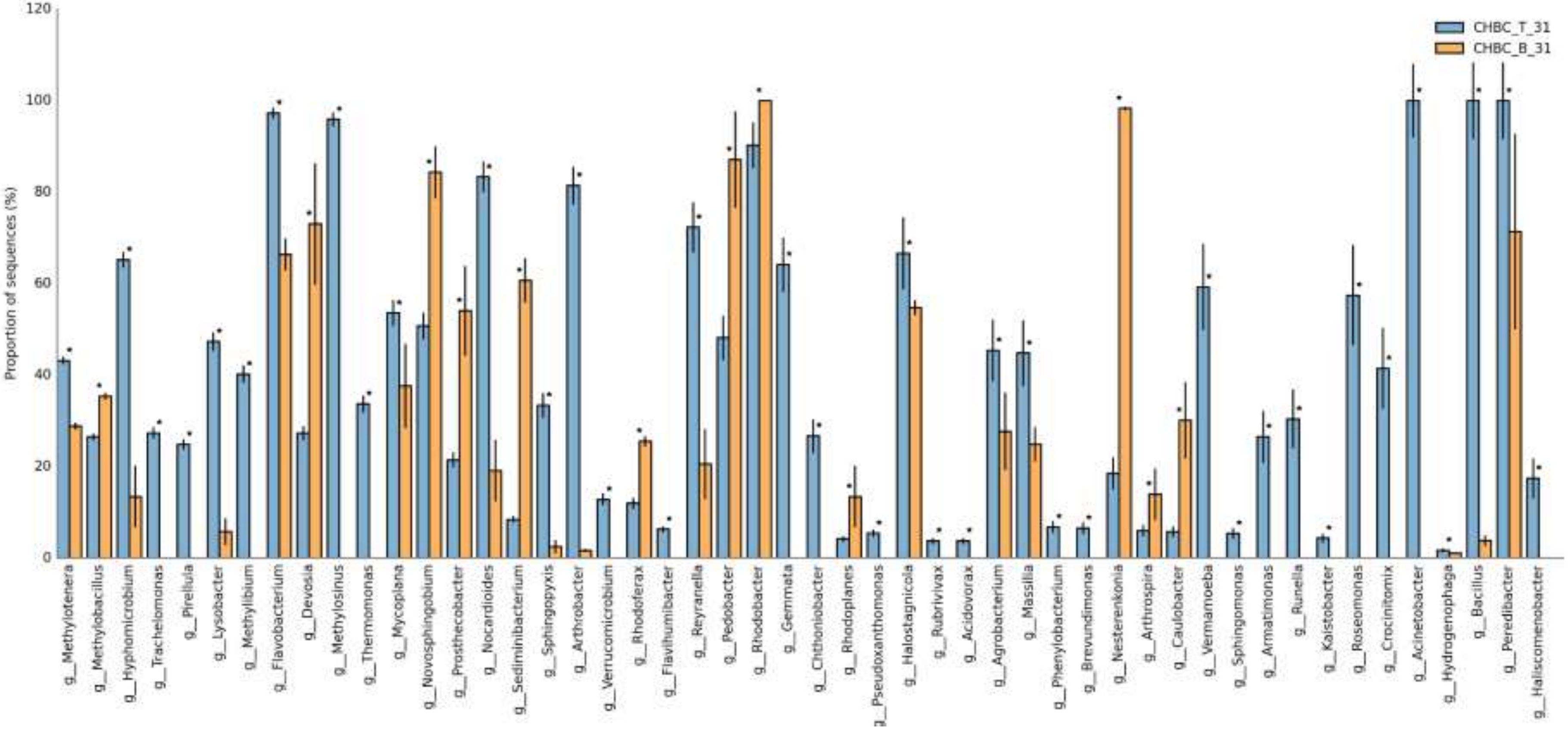


Figure C 4 Extended error bar plot of CHBC top (blue) vs CHBC bottom (green) considering the abundance profile of microbial domains in the 16s rRNA amplicon sequencing data for micropollutants degradation assay in spiked pond water.

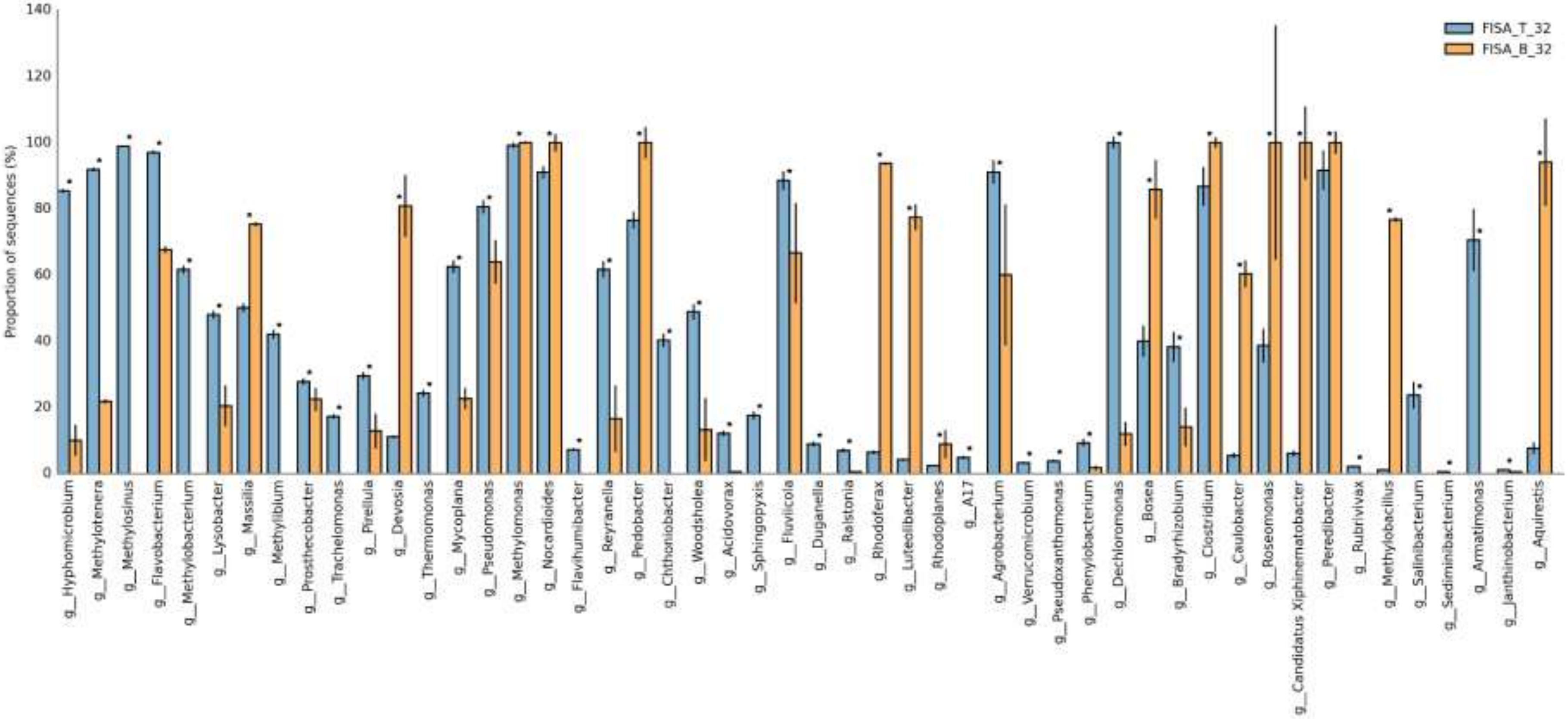


Figure C 5 Extended error bar plot of FISA top (blue) vs FISA bottom (green) considering the abundance profile of microbial domains in the 16s rRNA amplicon sequencing data for micropollutants degradation assay in spiked pond water, following the addition of biochar (10%) to fine sand. Abbreviation: CHBC, coconut husk biochar; FISA, unamended control.

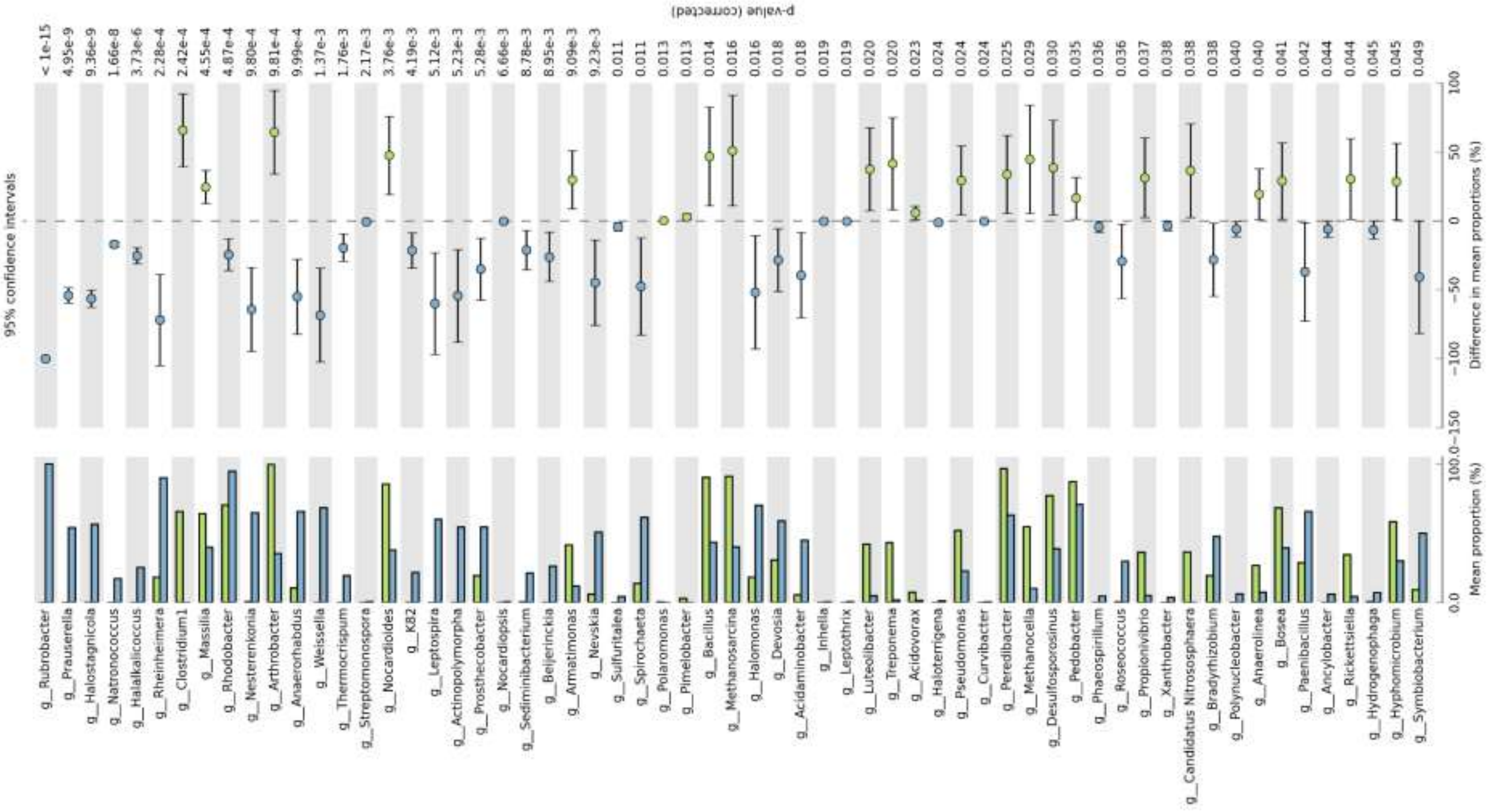


Figure C 6 Extended error bar plot of FISA top (blue) vs CHBC top (green) considering the abundance profile of microbial domains in the 16s rRNA amplicon sequencing data for micropollutants degradation assay in spiked pond water,