TREATMENT OF AGRICULTURAL RUN-OFF USING INNOVATIVE CDI FILTRATION TECHNIQUES

A thesis submitted by

Salam Bakly, B Eng

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Abstract

Anthropogenic activities such as industrial discharge and agricultural run-off can negatively impact surface water quality. Agricultural run-off contaminants, other than soil particles and suspended solids are mainly nitrogen-based, phosphorus, sourced primarily from fertilisers and pesticides. Currently available treatment methods include biological treatments, aeration and filtration, however, these methods are restricted by their removal capacity, land requirement and cost. Very little research has been done on the application of capacitive deionisation (CDI) coupled with biochar in agricultural settings. This project is dedicated to investigate the capacity of this combination for removal of nitrate as a commonly existing contaminants in agriculture runoff. The application of CDI to multi-media filter layers of biochar (BC) is a promising technology to improve the nutrient adsorption capability of the BC and thus remove nutrients from the water media. The ability to easily rejuvenate the CDI-BC layers, allows for incorporation into simple backflush cycles in line with current industrial practice, whilst the increased capacity allows for a reduced number of such cycles.

This study tested the natural abilities of in-house prepared BCs sourced from agricultural waste biomass source i.e. Macadamia or as it is more traditionally known *Bauple nutshells*, in batch and column experiments targeting nitrate removal. The macadamia biochar (MBC) samples were pyrolysed at 900°C and 1000°C respectively, then characterised using standard techniques such as functional group identification using Fourier Transform Infrared Spectroscopy (FTIR) and physical structures analysis with a Scanning Electron Microscopy (SEM). Batch experiments found that 1000°C pyrolysed MBC achieved better nitrate removal around double than those of MBC pyrolyzed at 900°C.

Column test with upward flow removed more nitrate compared to downward flow, largely due to their longer contact time. Three concentrations of 5, 10 and 15 mg/L and 3 flow rates of 2, 4 and 10 ml/min were tested applying factorial design. The lowest flow rate of 2 ml/min with the highest concentration at 15 mg/L were found to be the most effective settings for nitrate removal. A laboratory scale in-house designed CDI-MBC unit was used to assess the

relative improvement to contaminant removal capacity of natural MBC. The results of these laboratory scale tests can be used to aid the future design of a pilot-scale unit, suitable for handling typical agricultural nutrient and pesticide contamination on farm. The CDI assisted MBC tests found that with the addition of CDI, the filter can remove around three times the natural MBC capability. Incorporating CDI also prolonged effective useability of the filter. CDI-MBC reached filter saturation after 72 hours usage, compared to 5.5 hrs usage of natural MBC.

Nitrate desorption was carried out after the column was saturated by being back flushed with deionised and/or tap water, using the so called 'degaussing method'. The name is derived from the approach used to remove magnetism from test equipment by applying a strong alternating voltage. In the case of CDI we applied a square waveform of frequency 100 H_z, amplitude 0.5 V and current 0.06 A during backflush to desorb nitrate. These experiments found that the 'degaussing' technique recovered around 80% of nitrate in 30 minutes, while 48% and 35% of nitrate was recovered after one hour for the backflush with deionised water and tap water respectively. The CDI- MBC regenerated filter was tested for three cycles. It was found that the fresh column was exhausted after 72 hours and the regenerated filters for cycle one and two were exhausted after 60 and 48 hours, respectively.

Certification of Thesis

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This Thesis is the work of Salam Bakly except where otherwise acknowledged, with the majority of the authorship of the papers presented as a Thesis by Publication undertaken by the Student. The work is original and has not previously been submitted for any other award, except where acknowledged.

Principal Supervisor: Senior Lecturer Les Bowtell

Associate Supervisor: Dr. Raed Ahmed Mahmood

Associate Supervisor: Dr. Vasanthadevi Aravinthan

Student and supervisors signatures of endorsement are held at the University.

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CHAPTER 1

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1. Introduction and Aims

1.1 Overview

In spite of the fact that 71% of the earth's surface consists of water, only approximately 2.5% of this water considered as fit for human consumption. This includes water found in rivers, but also ice at some lakes (USGS 2016). Overall accessible fresh water in the world is just 0.26% of the total available water. A substantial proportion of this water is at risk of contamination due to untreated runoff from factories and agricultural irrigation processes and other anthropogenic activities entering into river systems (Shiklomanov, 1998).
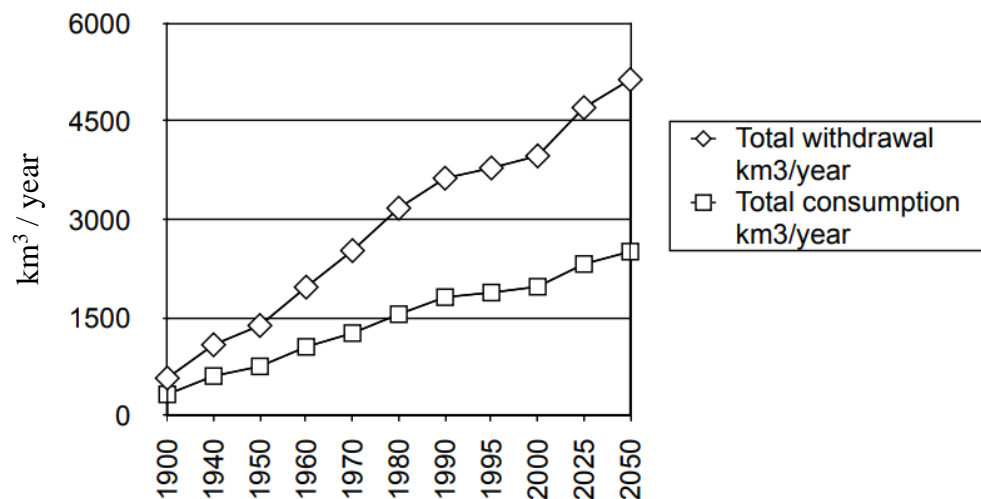
Figure 1-1: Total withdrawals water and consumption. Shiklomanov (1998)

In most farming systems around the world, untreated agricultural runoff returns nutrients, such as ammonium NH^+_4 and nitrate NO^-_3, as well as salts such as NaCl, directly into rivers through drainage systems (Silberbush and Lips, 1988). For example, sugar cane production in Australia requires around 200 kg per ha of urea-based fertilizer. Typically, more than 50% of this is lost during the irrigation process. These nutrients eventually find their way into rivers and other surface water sources (Carpenter et al., 1998). In Iraq, which is largely

considered to be an agricultural country, the majority of the irrigation systems rely on a gravity or pumped supply of surface water from the Tigris or the Euphrates for irrigation. This approach causes high water losses and allows the additional water to slowly infiltrate the soil layers and leach nutrients into nearby river systems. The salt and nitrogen groups (NG) associated with this leachate then become a complicated problem downstream, e.g. in the southern reaches of the Euphrates in Iraq the quality of drinking and irrigation water is compromised (Al-Shujairi, 2013). Several studies have attributed the deterioration in the water quality of the Euphrates River to farming water (Rahi & Halihan 2010).

In 2011, in the town of Al-Qaim, where the Euphrates river crosses the Iraq-Syria border, TDS measurements of around 760 mg/L were observed, while in Al-Simawa, a city about 280 km south of Baghdad and 770 km along the river from its entry to Iraq, TDS was measured as 3620 mg/L by AL-Thamiry et al. 2013). See Figures 1-1 and 1-2 for an Iraqi map with the two big rivers and the salinity in the Euphrates River changing from it is an entry point to 950 km along the river to the south of Iraq, respectively.
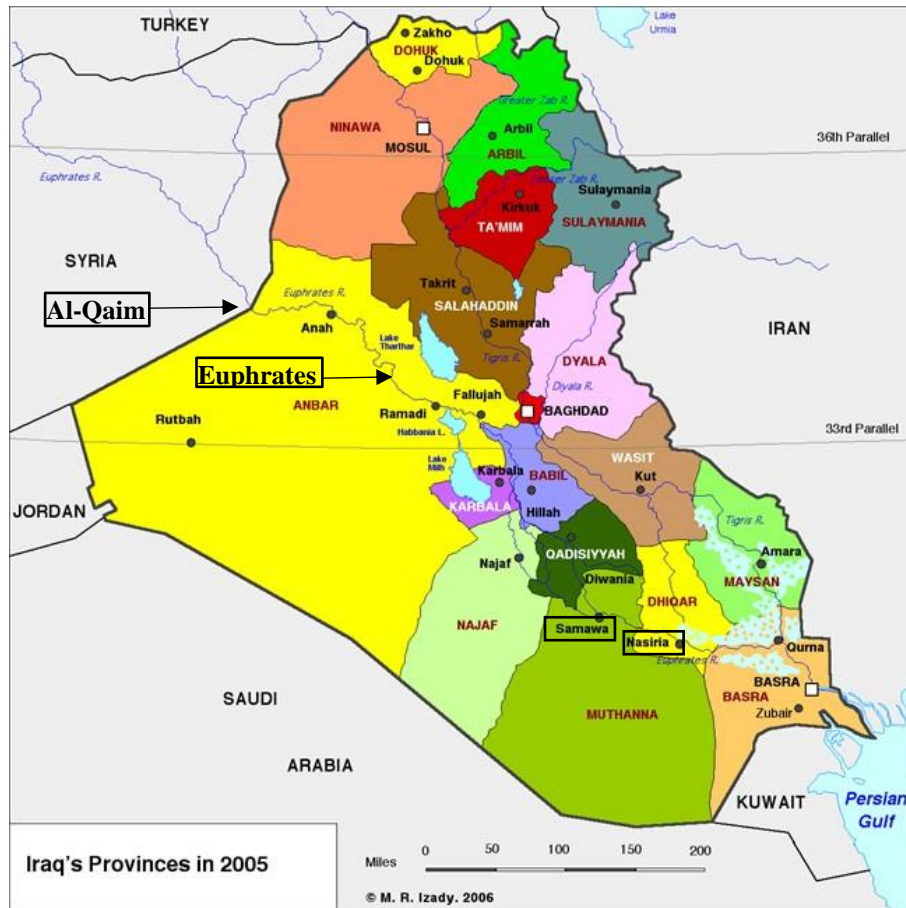
Figure 1-2: Iraq map with Tigris and Euphrates rivers (S.Seal, 2014)
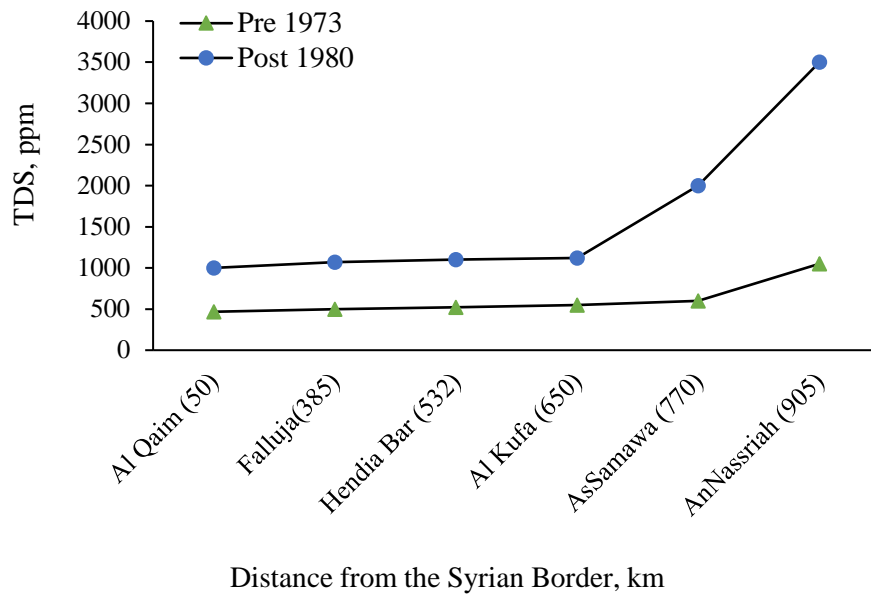
Figure 1-3: Salinity in the Euphrates (AL-Thamiry et al. 2013)

Water with Total Dissolved Salts (TDS) of the water that can be used for agricultural purposes is around 1500 mg/L before crop productivity is affected (Specification of Iraq No. 417 for maintenance of river pollution, 1967). In the Food and Agriculture Organization (FAO) guidelines, this TDS level in irrigation water is considered to be severe and will negatively affect crop productivity (FAO 1974). AL-Thamiry et al. (2013) proposed a solution to solve this problem by changing the path of the high TDS drainage water to another river and to some artificial lakes in order to reduce TDS influence on the water quality of the Euphrates. This treatment does not really solve the problem, but simply shifts it from one place to another with resulting in the continued increase of TDS in other river systems.

1.2 Techniques to reduce the effects of agricultural runoff

Contamination is the main problem for water systems these days. The major part of this problem is agricultural runoff because of uncontrolled irrigation, chemical fertilisers, pesticides, crop residue and poultry litter. Although fertilisers such as urea, nitrate or ammonia can improve crop productivity, more than 80% of applied fertiliser is lost to the soil, atmosphere or to the water system, with only 17% adsorbed by plants roots (Leach et al., 2012). After the irrigation process or heavy rainfall, water can carry the pesticide and fertiliser residue to the water system through surface runoff or seepage. This can lead to water quality degradation and requires effective treatment techniques.

There are many methods for treating agricultural runoff (with various contaminants) before it re-enters the water system: biological, chemical, filtration and bio-treatment (microorganisms primarily bacteria).

1.2.1 Constructed wetlands (CWs)

CW is one of the approaches used for water treatment. CW is a biological method that can be used to reduce pesticide and fertilizer residue as well as the salinity effects from agricultural runoff. Recently, Asia and Europe have started to use this method, especially for flat land mitigation of surface runoff (Haberl et al., 1995). It is an efficient method, for both surface and subsurface flow (vertical and horizontal), for removing pesticides such as organochlorines.

It is not able to remove urea group chemicals (NH^+_4 & NO^-_3) (Vymazal and Březinová, 2015), does not eliminate nitrogen (Vymazal, 2007) or remove TDS (Calheiros et al., 2012).

1.2.2 Filtration

Ballantine and Tanner (2010) suggested a filtration method to treat agriculture runoff, by adding natural tree bark which has the potential to act as a filter material in CWs, and enhance their ability to remove NG contaminants before returning water to the rivers (Ballantine and Tanner, 2010). Even though tree bark has an adsorption capability for many nutrients, e.g. total phosphorus, it has low capture efficiency for cations such as NH^+_4 (Bolan et al., 2004).

1.2.3 Aeration

Aeration can also be used for reducing contaminants in farming water. Bolan et al. (2004) showed that during an intermittent aeration technique, denitrification may occur while aeration is suspended, eventually transferring nutrients from agricultural runoff to gaseous nitric oxide (NO) and nitrous oxide (N_2O) which in turn emits volatiles to the atmosphere, thus changing the problem from water to air pollution (Greenhouse effects).

1.2.4 Biochar

This research project proposes the use of biochar (BC) to treat agricultural runoff. Natural BC, which is considered an environmentally friendliness and low-cost material, has the capability to capture contaminants from agricultural runoff to prevent downstream river pollution, reduce greenhouse gases, hold nutrients in the soil and keep carbon in a stable form for a long time. The project also will investigate suitable methods for the potential reuse of captured nutrients, e.g. by using granular BC as a fertilizer. Although the use of BC as an agricultural runoff amendment is reviewed by Macdonald et al. (2015) and others, there are limited studies using BC with capacitive deionisation (CDI) which may enable the BC filter to capture more nutrients, at the same time allowing regeneration of filters by reversing the supply voltage or degauss techniques.

1.3 Research questions

The essential question in this research is: Can a BC filter product made from simple materials effectively absorb nutrients by using the CDI technique? This question begs more questions which are:

- How do the surface area and porosity size affect the adsorption efficiency when using different feedstock and processes to produce BC?
- How do different feedstock impact on the adsorption/ absorption ability by changing chemical and physical properties such as porosity?
- What is the impact of the applying DC voltage as a driving force in CDI using BC?

1.4 Aim and objectives

The overall aim of this study is to investigate the ability of macadamia biochar (MBC) as a low-cost sorbent to minimize and capture nitrate before and after applying the CDI method. The main objectives are:

- To study the capability of MBC's adsorption as filter material in batch and column experiments focusing on nitrate ions
- To evaluate the efficiency of nitrate recovery methods to reuse as a soil amendment
- To investigate the performances of using an electrical technique CDI to enhance the electronegativity to attract the ions to the BC's surface
- To investigate the capability of filter regeneration with different methods such as degaussing with CDI electrodes and back flushing the system or using the deionised and tap water.

1.5 The scope of the study

This thesis focuses on investigating the characteristics and efficiency of BC to remove contaminants from agricultural run-off before allowing nutrients to enter the river system. The scope of the study includes the following:

- Macadamia nut shells will be used as a biomass source to prepare BC

- Synthetic water with the known contaminant and respective concentrations will be used to identify the absorption capability
- CDI method will be applied to enhance the absorption capability of the MBC by attracting anions and cations including NG
- Regeneration the filters and nitrate recovery by using the degauss technique and backflushing with a small amount of deionised water (DI.W)

1.6 Outline of the thesis

This thesis is laid out in five chapters:

Chapter1 gives the background of this study along with the objectives, and the scope of this study.

Chapter 2 gives an overview of the nitrate removal technologies and the reported removal controlling techniques in the literature. Extensive details about the mechanisms of the available techniques for removing nitrate including the advantages and disadvantages of each technique.

Chapter 3 introduces and discusses the material characterisation and preliminary experiment for nitrate removal using waste biomass to produce biochar and then use it in batch and column experiments to find an optimum removal condition.

Chapter 4 demonstrates the use of an old technique, capacitive deionisation (CDI), side by side with biochar to promote removal efficiency and simultaneously regenerate the filter and recover the nitrate.

Chapter 6 presents the conclusions and recommendations for future work.

<div align="right">CHAPTER 2</div>

2. Literature review

2.1 The aim of this chapter

Demand for fresh water is increasing due to population growth, but the amount of fresh water is limited and aggravated by contamination from different sources such as factories discharge and agricultural run-off. The aim of this chapter is to critically review the available techniques for treating agriculture run-off focusing on nutrients removal. The mechanisms, nutrients removal levels, advantages and disadvantages, energy requirements and cost demands of these techniques are critically reviewed. Further, this chapter will explore different techniques to remove contaminants from the agricultural runoff such as constructed wetlands, filtration, aeration, algae and woodchips. Biochar (BC) is one of the low-cost sorbents can absorb nutrient due to multi-function capability. Agricultural runoff's contaminants either dissolved or suspended solids are the basis of nitrogen, i.e. ammonia and ammonium compounds that are obtained primarily from fertilisers such as urea. Hence, this study will focus on nitrate contaminant.

This literature will compare the natural abilities of BCs sourced from a range of natural biomass sources such as Macadamia nut shells with other techniques regarding agricultural runoff focussing on nitrate removal.

2.2 Introduction

Water is essential for living creatures because it dissolves nutrients and facilitates their mobility in their bodies. Overall accessible fresh-water (rivers and lakes) around the world is just about 0.26% of the total water body which is about 71% of the total earth's surface (USGS, 2016). Half of this water is at risk of becoming saline partially because of untreated runoff from factories and agricultural irrigation processes entering into river systems (Navarro-Ortega et al., 2015).

Irrigation processes for agriculture purpose are increasingly recognized as a serious worldwide public health concern (Mateo-Sagasta et al., 2017). An agriculture runoff is responsible for a large-scale water quality degradation, because of the seepage

occurring after the irrigation process carrying some fertilisers and pesticides residue. A salt such as NaCl and NG such as NH^+_4 and NO^-_3 contaminating water resources is the primary cause of these resources becoming unsuitable for human consumption and agricultural purposes (Bouraoui and Grizzetti, 2014). In addition, the high levels of some nutrients in agricultural runoff such as phosphorus (P) along with nitrogen can cause eutrophication which may increase growing algae bloom and cyanobacteria due to the increase in nutrients concentration (Water_Online, 2017). For example, sugarcane production in Australia requires around 200 kg per ha of urea-based fertiliser. Typically, more than 50% of this is lost during the irrigation process. Bouraoui, (2014) argued that these nutrients eventually find their way into rivers and other surface water sources. Another example is Iraq, which is considered an agricultural country, most of the irrigation systems rely on gravity or pumping of surface water from the Tigris or the Euphrates for irrigation. This approach causes high water losses and allows the additional water to infiltrate slowly through the soil layers and leach nutrients into nearby river systems. To enhance the productivity of any land, farmers invariable use fertilisers containing nitrogen, phosphorus and potassium and pesticide that can wash into river system due to ineffective irrigation process, which can exceed plants need or during heavy rain. This overridden water can cause growing algae blooms, bad odour and may have a negative impact on aquatic life due to reduce oxygen from the water (U.S_EPA, 2005). Also, the U.S. Environmental Protection Agency (2005) reported that the high nitrate concentration might be a reason for many infant deaths by methemoglobinemia which is considered a danger disease (blue baby syndrome).

Nitrate was chosen to be investigated in this project due to it is available in the soil as a sort of fertiliser to enhance productivity. However, it can cause a problem if the concentration exceeds the acceptable limits in the water system after a runoff. Also, can lose some of this fertiliser (cost money) carrying by the agricultural runoff. Nitrate is considered as the main source of contaminant present in the agricultural runoff (Poe et al., 2003).

There are many applicable methods for treating agricultural runoff water. One approach is a biological method known as Constructed Wetlands (CWs). CWs can be used to reduce pesticide and fertiliser residues as well as the salinity effects from agricultural runoff. Some researchers add a filtration system to the CWs by adding

porous materials to promote NG removal from agricultural runoff (Ballantine and Tanner, 2010). Aeration can also be used for improving the treatment of farming water. Aeration pond is the common form of aeration treatment for agriculture runoff. Standard multi-media filter system (sand, anthracite and gravel or sand) is another method for removing pollutants from agriculture runoff (Samuel et al., 2014). Previous approaches can remove sediments materials, salinity, phosphorus and some other nutrients, while found to be inadequate for NG removal. From the above, finding an alternative technique with cost-effect materials are very important at this stage. Biochar (BC) can be a suitable solution for agricultural runoff remediation as a low-cost sorbent with several functionalities.

This study aims to critically review the existing techniques for agriculture runoff treatment with a focus on removal of nitrogen (N) compounds especially nitrate (NO_3^-) due to its abundance in agriculture runoff owning to its frequent use as a nutrient in agricultural activities (Oakes et al., 2000). The study will analyse the feasibility of these techniques taking into consideration contaminants removal level, cost, maintenance and other factors.

2.3 Common techniques for nutrients removal

2.3.1 Constructed Wetlands (CWs)

CWs are artificial wetlands designed to simulate a natural wetland and facilitate pesticide removal. They are also referred to as human-made, engineered or artificial wetlands. CWs are considered to be a biological method that can be used to reduce pesticide and fertiliser residue as well as salts and NG from agricultural runoff. Recently, some studies have investigated the capability of CWs to remove some nutrient and pollutant species carried by agricultural runoff before returning it to water systems such as rivers and lakes (Haverstock et al., 2017). Natural wetlands have been used as wastewater treatment since the beginning of sewage collection. After finding their ability to treat water in the early 1950s, the idea of designing a constructed wetland was born. Kadlec and Wallace started applying engineering analysis to wetland processes in the early 1970s to manage wetlands for water quality improvement (Kadlec and Wallace, 2008). Since wetlands have a high capability to retain some materials (Vymazal, 2010), constructed wetlands are expected to reduce the concentration of pesticides in agricultural runoff by acting as buffer strips between agrarian areas and the receiving surface waters.

Many developed and developing countries such as the United States of America, Australia, United Kingdom, Egypt and Zambia have started to use this method, especially for flat land mitigation of surface runoff (Vymazal, 2013a). It is an efficient method for removing pesticides such as organochlorines but, it cannot be applied to eliminate the urea group (e.g. NH^+_4), CO^-_3 (Vymazal and Březinová, 2015), total nitrogen (TN) (Vymazal, 2007) or TDS (Calheiros et al., 2012).

CWs are highly efficient in removing pesticides from agricultural runoff. Vymazal (2015) found different mechanisms to remove pesticides by using CWs. Examples of these are physical treatment (sedimentation, absorption and precipitation), chemical treatment (oxidation and cation exchange), biological (plant absorption) and biochemical processes (microbial degradation). Vymazal (2015) stated that there is no clear study that can prove, which mechanism is the best for removing pesticide as mechanisms rely on the local conditions. A previous study examined how the availability of vegetation and medium type can affect CWs' removal capability

through the use of gravel-beds and sand-beds with and without vegetation. It was found that the CW technique, using high porosity for gravel-beds encouraged nitrification and denitrification processes which improved NH^+_4 and NO^-_3 respectively. At the same time, plant uptake increased NO^-_3 removal more than unplanted beds managed to do (Yang et al., 2001). Although root zone may affect both beds' (gravel and sand) capability, vegetation may facilitate nitrification and denitrification in gravel-beds only. Also, contact time between plants and agricultural runoff during drainage inflows to the wetland, may effect on the removal efficiency of N and P in CWs (Tanner et al., 2005).

CWs were used for more than six decades to remove different kinds of contaminants from wastewater and agricultural runoff, and how they were used dependedon the macrophytes grown and the direction of the flow (Vymazal, 2010). Vymazal (2007) reported that there are four types of CWs: free-floating plants, floating plants' leaves, submerged plants and emergent plants which are also divided into two types: the free water surface and sub-surface flow. The sub-surface flow separated into a vertical and horizontal flow. The hybrid CW system is a combination of two sorts of CWs; vertical flow (VF) followed by horizontal flow to obtain better total nitrogen removal or to remove the more complex contaminants in the agricultural runoff and industrial wastewater. Hybrid CWs are mostly used in Europe and Asia (Vymazal, 2013b). Vymazal (2013) reported that in the early 1960s hybrid systems started with multi-stages of VF followed by multi-stages of HF, while in late 1990s, the hybrid systems consisting of HF-VF or HF-VF emerged. Simulating an aerobic as a vertical flow stage and an anaerobic as a horizontal flow stage may affect nutrient removal efficiency in different seasons due to microbial nitrification (a temperature sensitive-denitrification process) (Zhai et al., 2016, Wang and Li, 2015).

Figure 2-1 shows the most common CW configurations. Free-floating plant (FFP) CWs depend on the plant uptake mechanism to remove nutrients. The mechanism for removing TN and P for CWs with free water surface and with emergent vegetation (FWS) is volatilization and denitrification, while in CWs with horizontal sub-surface flows (HSSF) it is denitrification. CWs with vertical sub-surface flows (VSSF) is another mechanism for removing nutrients and has a capability for oxidating ammonia nitrogen to nitrate than HSSF.
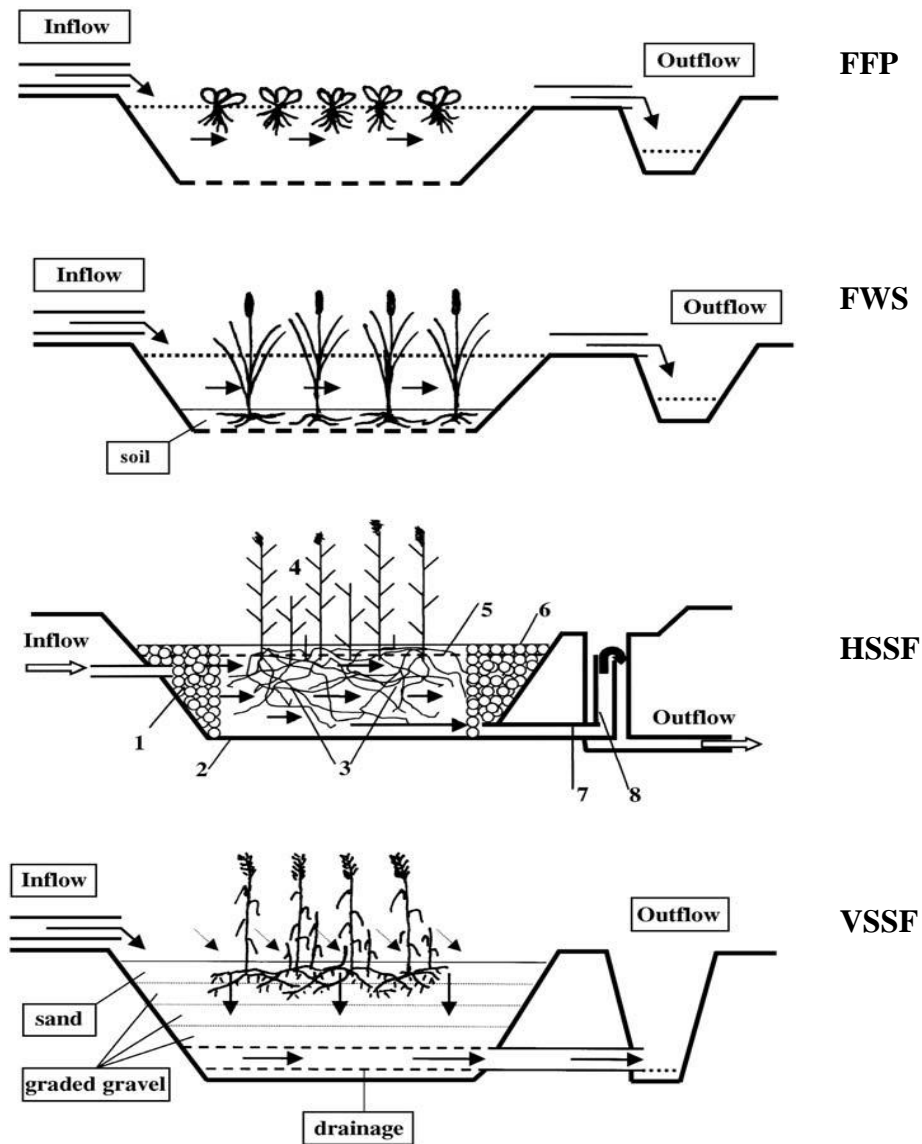
Figure 2-1: Constructed wetland basic types based on (Vymazal, 2007), 1. distribution zone filled with large stones; 2.impermeable liner; 3. filtration medium (gravel, crushed rock); 4. vegetation; 5. water level in the bed; 6. collection zone filled with large stones; 7. collection drainage pipe; 8. outlet structure for maintaining of water level in the bed. The arrows indicate only a general flow pattern (Vymazal, 2001).

The use of CWs for nutrient removal has it is advantages and disadvantages. CWs are designed to simulate natural wetlands (Kröpfelová, 2008), and are considered to be green treatment for nutrient removal from agricultural runoff (Saeed and Sun, 2012). CWs have a high capability to remove pesticides from non-point pollution (agricultural runoff). Vymazal and březinová (2015) reported that pesticide removal varies depending on the type of pesticide itself, and the process to mitigate. However, CWs

cannot entirely remove NG from agricultural runoff, but convert them into various N forms. Farmers would not prefer to use CWs to treat agriculture run-off because of the high maintenance, large land requirements and high installation cost (Reichenberger et al., 2007). Each type of CW has its benefits and drawbacks. For example, vertical flow (VF) CWs occupy a small area and have high nitrification, simple hydraulics and can quickly remove ammonia-N. However, VF has some drawbacks such as short flow distance, no denitrification, sophisticated technology requirements and ineffective P removal. In comparison, HF CWs have a long flow distance, high denitrification and nitrification, can remove N and P, but have some disadvantages such as large area requirements, low P removal, limited ammonium oxidation, and complicated for regular flow supply (clogging problems) (Luederitz et al., 2001).

Vymazal (2007) stated that some factors might have an impact on the capability of CWs to remove some nutrients such ammonia. Nutrients removal increasing with increased the initial concentration. Temperature is another factor that may affect nutrient removal by CWs. For example, 20-30°C is the most effective temperature range for the removal of biological nitrogen, due to the higher microbial activity and oxygen diffusion rates in this range compared to lower temperatures. Hydraulic residence time (HRT) has an effect on the removal of nutrients in CWs (Huang et al., 2000). Increasing HRT impacts on ammonium and total Kjeldahl nitrogen (TKN) removal positively, while there is no difference for NO^-_3 removal. Ballantine and Tanner (2010) found that the increase in phosphate removal results from a decrease in pH and an increase in ionic strength (Liu et al., 2008).

Overall, CWs have a high ability to remove pesticides, biological oxygen demand (BOD) and chemical oxygen demand (COD), but are inefficient in removing N and P nutrients. The contaminant removal efficiency of CWs relies on influent rate, contact time and pasture intensity. Tanner (2005) identified that the removal rate for TN varied between 250-840 $g.m^{-2}$ per year, and the total phosphorus (TP) removal rate was in the range of 45-75 $g.m^{-2}. y^{-1}$. Furthermore, the results of a two months study on hybrid CWs, showed removal rates of 2 $g.m^{-2}.day^{-1}$ and 1 $g.m^{-2}.day^{-1}$ for TN and TP respectively (Zhai et al., 2016).

 Few researchers have addressed the cost-effectiveness of CWs. Luederitz (2001) investigated the effect of construction materials and maintenance costs on the

feasibility of implementing CWs for sewage treatment. The technique for water treatment requires a large number of materials for wetland construction which will increases the implementation's total cost. High additional costs are subsequently incurred through vegetation management. However, CWs are regarded as energy-efficient compared to other treatment methods, such as conventional treatment systems (wastewater treatment plant (WWTP)), so the ongoing economics can overcome the construction cost within a short period after operation begins.

Land cost is another factor that can affect the implementation of CWs (Zadeh et al., 2013). Haverstock et al (2017) stated that CWs are considered to be ecologically and economically viable for rural areas seeking to reduce NO^{-3} from agricultural runoff and convert it to various N forms, especially with long residence time which reduces the capital and operating cost compared to a multitude of small wetlands (Tanner and Kadlec, 2013). However, the major drawback of CWs is the higher area demand which may, for large CWs (more than 100ha), cost about \$12,174.0 AUD/ha and for a smaller size will cost around \$60,870.0 AUD/ha (O'Geen et al., 2010, Tanner and Kadlec, 2013). Maintenance such as dredging, due to sediment accumulation, will be required after start-up. This is likely to be necessary once or twice a year and may cost around \$102.26 AUD/ha/year. Dredging is also energy insensitive; around $18,734 \times 10^3$ J (Ko et al., 2004). The expected lifetime of the traditional CW is around 25 years with refurbishment every 8-15 years due to the clogging of the media (Butterworth et al., 2013). As a pre-emptive, regeneration of CWs by changing the fouled gravel and cleaning the media before the system clogs is also necessary. In 2009, renewing a CW system of 300 m^2 cost around \$92,00000 AUD (Knowles, 2012).

2.3.2 Filtration

Filtration is a process for removing solid objects or contaminants from fluids through either mechanical, chemical or biological effects by preventing the objects from passing through the filter's structure, such as sand or screens (United States Environmental Protection Agency, 2010). The first water filtration treatment attempt dates back to 4000 BC in Ancient Greek. This method focused on turbidity removal and used water taste as a measure for water quality. The technique went through many improvements over time until the mid-1800s when scientists introduced sand filtration that was used in Europe to remove invisible contaminants (United States Environmental Protection Agency, 2000). In the early 1900s, sand filters were found to be effective for reducing turbidity, but had little effects on microbes, so chlorine was used in the United States of America and ozone in Europe, to minimise the waterborne disease outbreaks. Agricultural runoff experiences similar developments in treatment, and these began around 500 BC. Hippocrates invented the first bag filter to prevent sediments from moving through water and causing bad smells and tastes. The United States' EPA (2000) showed that treatment gradually improved in the early 1800s and scientists started to use sand as a filter to reduce the salt (which negatively affects crop productivity) in irrigation water.

In the early 1900s, the ion-exchange technique came into existence improving the efficiency of filtration methods in removing salinity and other contaminants. It is the process of replacing the anion from agriculture runoff such as replacing P^- with any anion such as Cl^- (Le, 2017, WARD and Monday, 2007).

There is a debate about the capability of CWs to remove nutrient from agricultural runoff. Some scientists have add porous materials as a filter to CWs. These materials include tree bark (Pinus radiate) and zeolite to promote adsorption (Bolan et al., 2004). Zeolite (alumina-silicate) can capture nutrients in its pore structure or by attracting cations (NH^+_4, K^+) which happens to these elements naturally. Bolan (2004) also reported that bark treatment achieved the removal of P, N, K and totally suspended solids through their porosity, and NO^-_3-N through denitrification. The advantages of bark filters are its after-use as a soil amendment and the practicality of building up such filters for pollutants' removal from industries and wastewater effluent. Figure 2-2 shows the cross-section in CWs with a filtration bed made from tree bark and the

steps taken by the water, from the inflow through each towards the outflow as treated water.
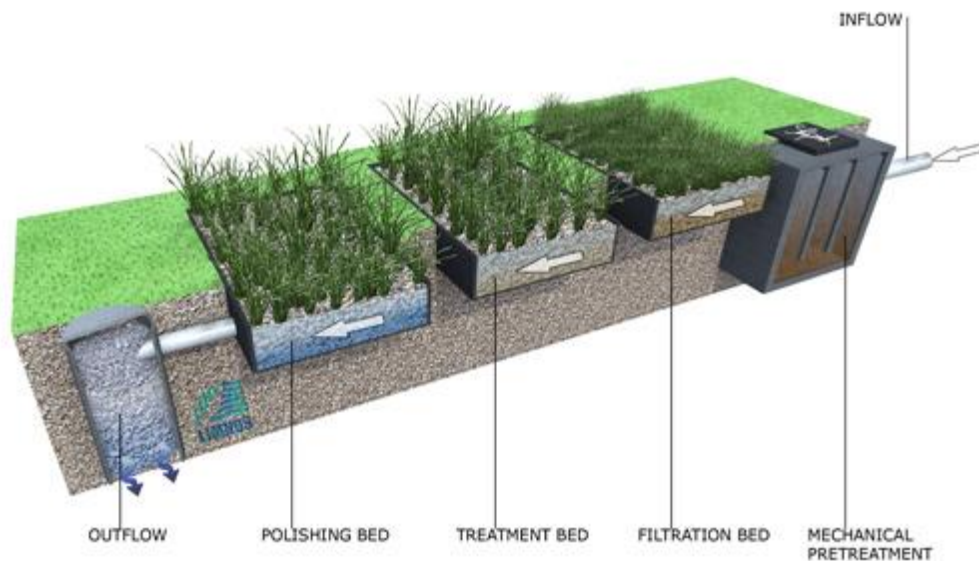
Figure 2-2: Constructed wetland with filtration bed (Browning et al., 2014)

Some filtration techniques have the benefit of being an inexpensive due to the availability of the raw materials such as sand, tree bark and limestone, is their lack of toxicity and their high P removal. However, as Ballantine and Tanner (2010) stated, these filtration techniques have some serious drawbacks: they also lack the ability to remove dissolved fluids, experience quick saturation have a high replacement cost, require maintenance and are inefficient in removing NG.

pH can have an extreme effect on the ecosystem (High or low pH solution releasing to the drainage into water system) filter material during treatment process (Allred, 2017). This will affect the product or by-product filter material will be chosen for any water treatment plant. A recent study by Allerd (2017) involved 50ppm nitrate-nitrogen (NO_3^--N) and 0.25 ppm phosphate-phosphorus (PO_4^{3-}-P) with different filter material. The average removal at pH 7.38 was found to be around 50% and 75% respectively, And the reduction in the temperature reduced the biological processing of nitrogen through (Hatt et al., 2009).

Column lifetime relies on parameters such as filter materials, flow rate and type of contaminants in the solution (Färm, 2002b). For example, natural Opoka as a filter material (to remove heavy metal from runoff) clogs after receiving 461 litres of solution (Cd, Cr and Cu), while burned Opoka, as a filtration material, clogs after 260 litres of solution. Cleaning approaches renew the filter by reversing the filtered water flow from the bottom to the top of the filter to refresh and reuse it for the second time (Clark et al., 2012, Astrom, 1999).

Using different filtration materials can remove different nutrients. For example, tree bark can effectively remove P, but it has low performance for nitrate removal. The capability to transfer nutrients can change with change to the filtration materials used. A sand filter bed combined with CW can remove around 37.70% of NO_3^- –N, 55.14% of Ns O_2^- –N, 49.37% of NH_4^+–N and 54.74% of TN from effluent through the nitrification and denitrification processes (Xiong et al., 2011). Table 2-1 shows the common types of filtration materials used to remove various solids and organic and inorganic contaminants from agriculture runoff. Based on the table, pine bark seems to be the best for P removal 98%, while limestone is the best for nitrate removal at 70%.

Table 2-1: Filter materials and percentage of mineral removal

Author	Filtration type	Percentage of the removal %					
		TN	Heavy Metal	P	NH$^+_4$	NO$^-_3$	TSS
(Shilton et al., 2005, Ugurlu and Ozturkcu, 2018)	Limestone	-	-	64	-	74	-
(Davis et al., 2001)	Sandy loam	65-75	92	80	60-80	<10	-
Bolan, (2004)	Pine bark	35	-	98	64	-	72
(Fletcher and Deletic, 2007)	Bio-filters	70	96	80	-	-	-
(Strategy, 2014), (Healy et al., 2007)	Sand	61	-	-	-	-	80
(Nick, 2018)	Compost	-	74	59-65	<20	<20	99

Bolan et al. (2004) used a survey to assess the various costs of filtration methods and found that the greatest proportion of the cost comes from the replacement of filtration materials (tree bark) in the farm scale after saturation. This means that installation of the filtration material and maintenance of the filters are the most costly portions of this method, while the feedstock is comparatively inexpensive. At the same time, a saturated porous material with nutrients can be separated and reused on the farm as a soil amendment for slow releasing of nutrients.

Le (2017) stated that using activated carbon (AC) as a filtration material to adsorb contaminants increases the cost of the filter system. Sand filtration requires 8 cents/kWh to operate an entire filtration facility with electricity using Environmental Protection Agency (EPA) calculations as a guide (Ko et al., 2004). For a sand filtration facility with a capacity of 3785 m^3/day, the total capital cost is $2.3 Million AUD. This cost consists of land, equipment, tank installation and construction, but not the periodic annual maintenance cost ($146,230.0 AUD). In terms of energy consumption, Ko et al. (2004) indicated that 2.1 TJ was required to operate and maintain the sand filtration facility for one year. While the embodied energy consumption of one year's operation of a biological filter plant with a treatment capacity of 200 m^3/day, is around 159.4 GJ (Shao et al., 2013). Membrane bioreactor (MBR) is another sort of filtration technology and has two types of submerged and side-stream MBR (Howell et al., 2004). Submerged MBRs are more popular than side-stream, because they require a low energy consumption rate of 0.2-0.4 kWh/m^3. Furthermore, the operating cost of the MBR technique with AC is $2.15 AUD per 1000 gallons treated solution (Conservation, 2007).

2.3.3 Aeration

Another method for treating agriculture runoff is aeration which was applied in conjunction with CW to enhance the ability of the latter to remove contaminants from runoff (Uggetti et al., 2016). Aeration is a process in which air is fed into the water in the form of bubbles to remove dissolved gasses or oxidise dissolved metals and organic matter (Boyle, 2002). Aeration was first used in 1882 in England with perforated tubes and pipes, and was then developed gradually by Arden and Lockett during 1914 to cover critical factors such as bubble size, placement of air flow, gas flow rate and surface contact between air and water that could influence aeration efficiency (Martin, 1927). It has been implemented in most countries around the world such as the United States of America, New Zealand, Spain, United Kingdom, Canada, Australia and China.

Aeration can be used to remove some nutrients from water through nitrification. For example, applying aeration to a hydroponic bed with a diffusor at the bottom of the bed can minimize N_2O emissions by around 50%, while reducing TN by 24.1% and having no change to NO_3^-–N concentration (Zou et al., 2017). The oxidation efficiency of NH_4^+ in aerated CWs relies on the concentration of dissolved oxygen applied to the bottom of the soil surface in CW. Figure 2-3 shows the two commonly used types of aeration configurations i) continuous and ii) intermittent. Uggetti et al. (2016) identified that, in the intermittent configuration, flow is typically set at a minimum limit of oxygen concentration so it can be controlled when the oxygen level drops below the required level, while the continuous relies on providing oxygen 24h through a specific compressor. The intermittent configuration reduces the cost of the aeration process, while with continuous configuration, the oxygen level may exceed the limit needed (Labella et al., 2015).
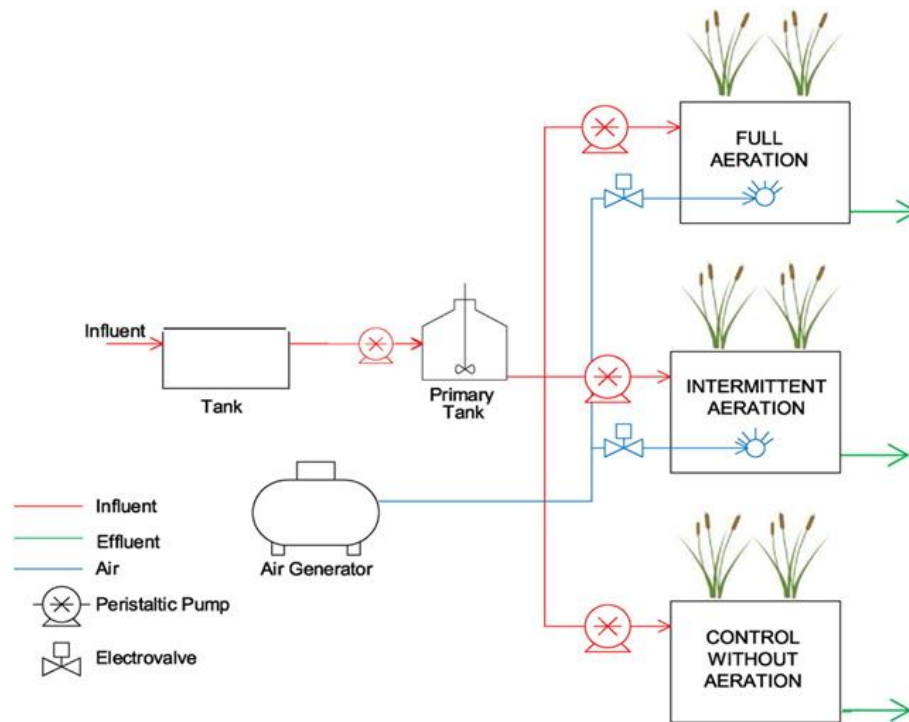
Figure 2-3: Aeration types based on Uggetti et al. (2016)

Although aeration system can efficiently remove suspended solids and carbon from farm effluents (Bolan et al., 2004), it is inefficient for nutrient (N, P and K) removal. The reduction of nitrate achieved through the intermittent aeration process may lead to the volatilization of ammonia to the atmosphere due to physical agitation and the nitrification activity (Jamieson et al., 2003, Chance and White, 2018). Denitrification can occur during an intermittent aeration technique. While aeration is suspended, it eventually transfers nutrients from agricultural runoff to gaseous nitric oxide (NO) and nitrous oxide (N_2O) which, in turn, volatiles to the atmosphere. Therefore, the technology merely changes the problem from water pollution to air pollution (Greenhouse effects) (Haustein, 2014, Tallec et al., 2008). Other contaminants such as carbon are oxidised to carbon dioxide, then released into the atmosphere causing greenhouse gases (GHG). This technique is also high cost due to installation, pumping, and maintenance. It may also cause the loss of soil nutrients (Ouellet-Plamondon et al., 2006, Wu et al., 2014).

Aeration can remove some ions, such as iron and manganese, through oxidation (aeration) or by adding some chemical oxidants (e.g. chlorine) which are then filtered

through adsorptive media (Blanchfield, 2011). Ouellet-Plamondon et al. (2006) stated that this method has a capability to remove 95% of Total Suspended Solids (TSS) during any season in planted and unplanted units, while COD removal in Winter for non-aerated mesocosms are less than Summer for both plant and unplanted units. In terms of Total Kjeldahl Nitrogen (TKN), which is the sum of NH_3 and Organic Nitrogen, artificial aeration can improve the removal for unplanted more than planted units in Summer and Winter. Even though removal by aeration for the unplanted unit is higher than the planted unit, additional aeration did not replace the absence of the plants. Intermittent aeration improves the removal efficiency of ammonium-nitrogen (NH^+_4-N) and organic pollutants and, at the same time increases TN removal through aerobic and anaerobic actions (Wu et al., 2015). Furthermore, this technique has a high percentage removal such as 96% of organic pollutants, 98% of NH^+_4-N and 85% of TN at any influent rate.

Uggetti et al. (2016) measured both components of the aeration methods (full and intermittent) and found that the intermittent type is more reliable and cost-effective than the continuous type. Comparing energy consumption between full and intermittent, intermittent was found to reduce power usage by seventy-fold for the same compressor power. Intermittent consumes less energy, has lower operating costs, use less time and maintenance, and produces higher efficiency in ammonium, TN and organic matter (chemical oxygen demand (COD)) reduction due to its ability to create suitable conditions for nitrification and denitrification (Zhou et al., 2018). Uggetti et al. (2016) calculated that the energy consumption for 24h continuous aeration with a 1.5 kWh compressor is 13.6 $kWh/m^2.d$, while the intermittent aeration required 8 pulses per day, which means 20 minutes of aeration per day, and the power usage is 0.18 $kWh/m^2.d$. Removal efficiency increases with increasing temperature because it may enhance the dissolved organic matter removal measured by COD and DOC from 2 to 13% (Labella et al., 2015). Nitrogen and phosphorous removal is affected by a positive relationship with increasing temperature due to microbial reactions such as nitrification, denitrification and organic matter decomposition which respond positively to higher temperatures, while TKN removal is slightly increased at a low temperature and NH^+_4 removal is practically constant (Stefanakis and Tsihrintzis, 2012). The pH values slightly change in the artificial aeration bed regardless of the

existence of plants and the season, while they may change dramatically in non-artificial beds (Zhang et al., 2010).

An aerobic bio-filter's expected working lifetime is five years before renewal for phosphorus removal (Heistad et al., 2006). Daily inspection and maintenance is required to prevent any clogging of the aerated pond's the diffused air system (blower and pipeline) which provides air to the bottom of the pond (U.S.EPAgency, 2011).

2.3.4 Other techniques (Algae and Woodchips)

Algae can be used to treat agricultural runoff, agro-industrial waste and human wastewater. Algae are a diverse and complex group of photosynthetic organisms, like Chlorella and (Lee, 2008). Abdel-Raouf et al. (2012) stated that using algae as a water treatment method started 75 years ago, especially in developed countries such as Australia and the USA. Algae grows rapidly, with the availability of sunlight and water, can convert CO_2 lipids through photosynthesis. Through the same process, algae convert nutrients such as N and P (available in farm water) to a complex organic structure (Lannan, 2011). Abdel-Raouf et al. (2012) consider algae an efficient means of removing N and P within one hour because they have the capability to use N and P to grow and remove toxic organic components as well as heavy metals so these cannot create secondary pollution. Figure 2-4 demonstrates the dense algal bloom growth along the shallow shoreline under the correct conditions of sunlight, excess runoff caused by rainfall, runoff in which industrial and urban waste can wash some nutrients from fertilizers (N, P, K) into water system (Roberts, 2008). In January 2019, the mass mortality of cultured fish in the Lower Darling River in NSW in Australia was caused by natural events. High temperatures can reduce dissolved oxygen levels, especially in summer, along with some algae and acidic runoff leading to fish death events (MDBA 2019).
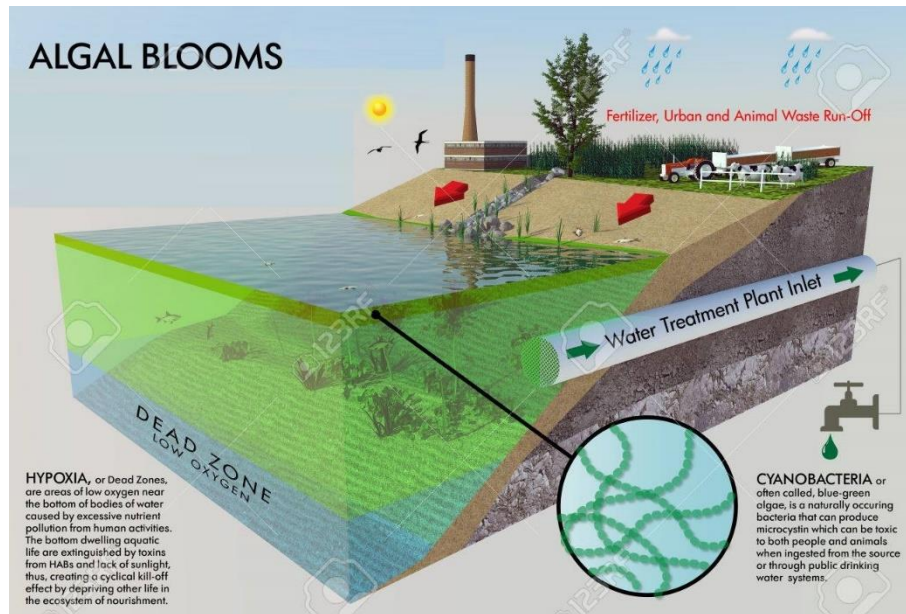
Figure 2-4: Algal blooms pond (Roberts, 2008)

Hence, some studies propose the use of a paddle wheel (raceway ponds) in the closed loop raceway channel to help keep the water moving all the time and prevent sedimentation, as illustrated in Figure 2-5 A and B (Chisti 2007; MOANA 2016).

(A)   (B)
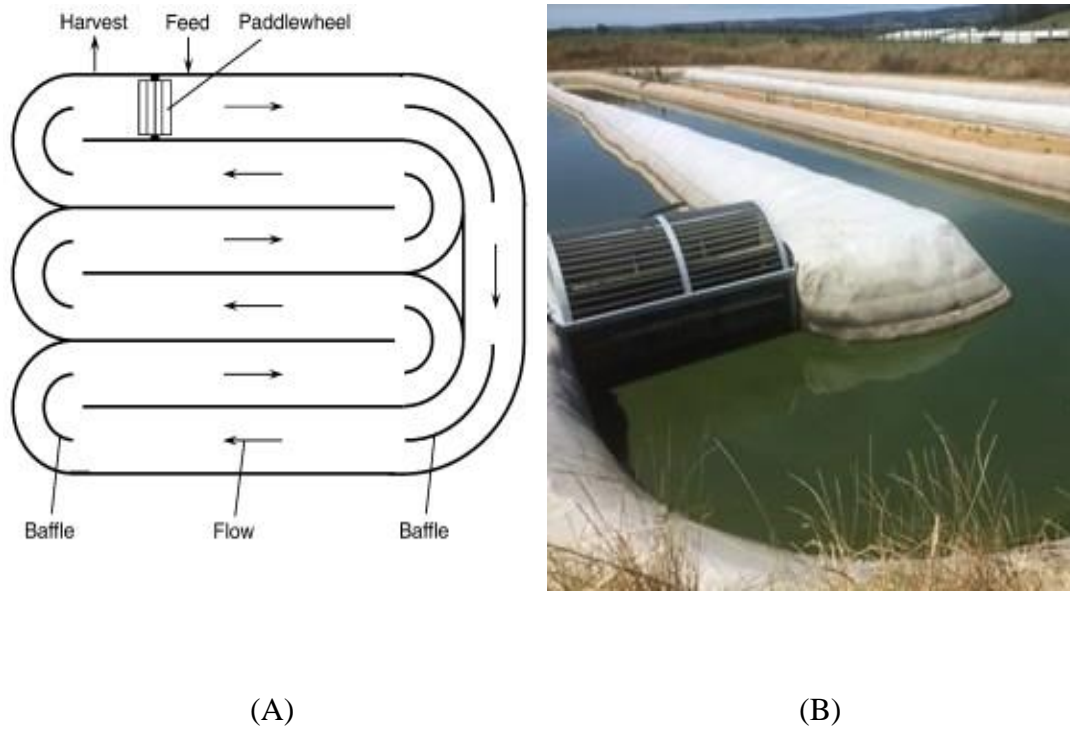
Figure 2-5: (A) Raceway of algae pond grown area based on (Chisti 2007). **(B)** Paddlewheel within the flow-way (MOANA 2016)

The benefits of using algae to treat water contamination is their rapid growth and high nutrient removal within a short period. Some researchers at the Rochester Institute of Technology named the algae treatment process as double green because it removes NO_3, PO_4, and some toxic substances from water and, at the same time, the grown algae can be used to produce biofuel (Gawlowicz, 2011). However, Abdel-Raouf et al. (2012) highlighted some drawbacks of using algae for treating agricultural runoff such as the dependence of the treatment on the type of nutrients, operating cost and bacterial decomposition of dead algae. The bacteria use oxygen for decomposing dead algae and release toxic and odorous compounds (Srivastava et al., 2013).

Algae can treat agricultural runoff from toxic minerals such as lead, arsenic, cadmium, and it is also capable of removing BOD and COD, some nutrients (e.g. N, P) and heavy metals (Kumar and Gaur, 2011). Lannan (2011) reported the removal of nitrate by 71.4%, ammonia by 81.3% and phosphate by 82.6% within three days of algae growth.

The availability and quick growth of algae make this method attractive for treating agricultural runoff. However, the high cost associated with removing algae using screening/filtration and pumping are serious concerns to be considered (Rickert and McShane, 2015). The capital cost of a station including earthworks for pond construction, paddlewheel mixing and pH controlled CO_2 addition, is $ 17.03 AUD /m^2 (Craggs et al., 2012).

Some factors affect nutrient removal, such as a higher initial algae density expected for a better removal rate. Abdel-Raouf et al. (2012) conducted a study that may lead to self-shading and minimising photosynthetic efficiency. The US EPAgency (2011) reported that the most effective and active algae for water treatment grows in water between 30-35°C. Craggs et al. (2012) showed that reducing pH to the level of less than 8.5 by adding CO_2 to wastewater treatment, may boost nutrient removal through increased algal production. Algae may affected by light and dark photoperiods which are required for maintenance because some of them might die with a long light period (Andersen, 2005). Unsuitable light: the dark system may impact negatively on the algae's growth. For example, most algae required 12:12 to 16:8 hours light: dark per day to stay active. Harvesting is the most important part of maintenance; recovering the small cell sized algae (0.2-30 µm), may cost consume 20-30% of the total biomass production costs (Christenson and Sims, 2011).

Another technique for treating agriculture runoff is solid materials such as woodchip (Christianson, 2016). Woodchip is considered a relatively new method for removing NO_3^- -N from agricultural runoff as it was implemented not more than 20 years ago. The technique is still under testing, so there is no proof that the method has the capability of working under different circumstances for a long time with the same efficiency as other methods (Hoover et al., 2016, von Ahnen et al., 2016). This process is applied by filling a large groove between the farm and the drainage tail with woodchip and running the water through the gutter. This method has been implemented in some European countries, the USA and New Zealand.

Figure 2-6 A shows a conventional and controlled drainage with wood chips structure to control the farm flow before the disposal of the water back to the river system in a schematic. Figure 2-6 B illustrates a real farm field and how to prepare the woodchips layer to treat farm water before discharging to the river system.

(A)   (B)
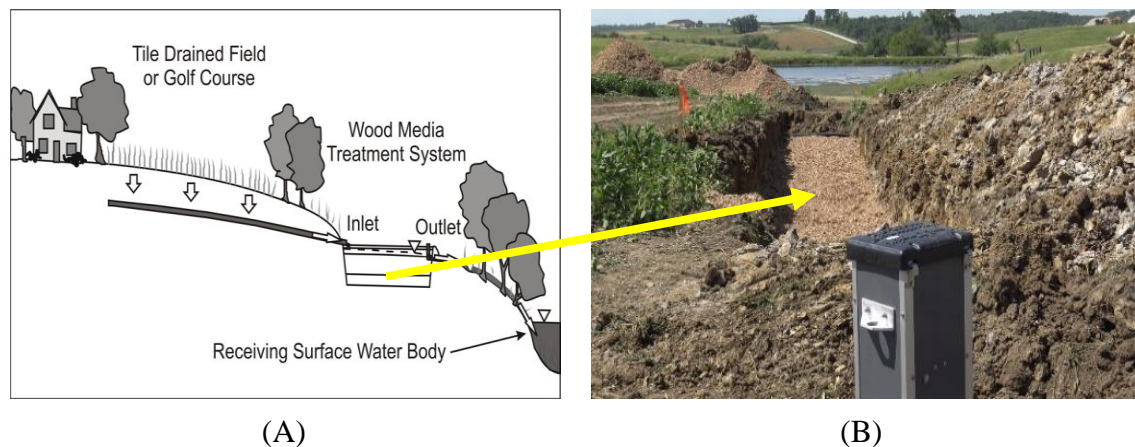
Figure 2-6: (A) Schematic of wood chips bioreactor (Van Driel et al., 2006). **(B)** Wood chips bioreactor in field scale based on Christianson (2016)

This method has some benefits such as low-cost of active materials due to the abundance of woodchip, high carbon-nitrogen ratio, high sturdiness, and simplicity of operation and maintenance (Lopez-Ponnada et al., 2017, Meffe et al., 2016). The position of woodchip bioreactors at the edge of the farm is another advantage of this method as it takes less area from the farm and doesn't affect the yield (Christianson and Helmers, 2011). However, Christianson and Helmers (2011) highlighted some drawbacks to using woodchip reactors to treat agricultural runoff such as colouring the treated water due to the leach of organic materials from the wood (Rambags et al., 2016). There is also the risk of producing toxic organic-heavy metal complexes such as methylmercury or odorous gases such as hydrogen sulphide gas. Another disadvantage of the woodchip method is the production of GHG such as nitrous oxide from the denitrification process. These negative effects might be alleviated through flow monitoring and on-line measurements of C and N concentration in the water, but this may make the method a costly option for treating agricultural runoff.

The woodchip method could also remove nitrate and phosphorous and some microbes and viruses from farm flow runoff (Rambags et al., 2016). Nitrate is removed by the woodchip bioreactor through denitrification (Moorman et al., 2010, Robertson, 2010). The average nitrate removal rate using woodchip was reported to be around 18.9 $g/m^3/d^1$ and it decreases with increasing effluent, while P removal is much less at about 0.89 $g/m^3/d$ (Hua et al., 2016).

It is considered an economical way to remove nitrate and other contaminants from agricultural runoff, due to the availability of active materials. However, this relies on the type of active elements. For example, Wildwood media has a long working life of around seven years with around 40% effects (Robertson, 2010), while wheat straw has only a half-year working life (Saliling et al., 2007). A study done for six bioreactors at Iowa University (in the USA) reported that the total installation cost for each bioreactor is between \$5,345.0 AUD and \$14,390.0 AUD, including the structure, contractor, woodchips and supplies (Christianson, 2011). The cost range for each hectare is \$240.0 AUD/ha to \$715.00 AUD/ha and, in terms of the efficiency of N removal, the range is between \$1.1 AUD/kg N to \$5.75 AUD/kg N removal. Lopez-Ponnada et al. (2017) stated that nitrification can be affected by low temperatures and low alkaline levels that will impact TN removal and NH^+_4. Christianson (2011) reported that there is annual maintenance for the bioreactor and the control structures which must be replaced every eight years. For example, a bioreactor with 13m L × 1.2m W × 1.1m D is able to remove 11.3 kg N yearly from agricultural run-off. This denitrification bioreactor system can continue for 15 years, but there is no clear study regarding the long life of NO^-_3 removal (Schipper et al., 2010).

2.3.5 Biochar (BC) filtration

BC is defined as an organic material carbonised under thermochemical conversion with no or little oxygen to produce a porous carbonaceous solid material which is suitable for the storage of carbon for a long time and use as a soil amendment (Shackley et al., 2010). BC use dates back 2500 years to civilisations in the Amazon Basin of South America, especially in regions called terra-preta, which in Portuguese means black land, because they have high fertility and high concentrations of organic matter (charcoal) (Glaser et al., 2001). Plant and animal residue were burned and buried in pits so very little oxygen can enters the process. It can also be found in smaller quantities in other soils around the world due natural vegetation fires (USBI, 2016). From these ancient methods, scientists have developed the technology of producing BC from plant waste and animal bone under similar low oxygen conditions (pyrolysis) to obtain a better quality of BC. Carbonized biomass that possesses low oxygen and high carbon content can be an ideal starting biomass for BC production (Macdonald et al., 2015). BC is considered to be a multifunctional material. It can mitigate GHG (Bolan et al., 2012), improve soil fertiliser uptake (Awad et al., 2012), sequester carbon (Joseph et al., 2009), and filter and remove contaminants from water (Ahmad et al., 2012). BC can also be used to immobilize bacteria as a high sorbent to remediate polluted soil with organic contaminants which is called the immobilized microorganism technique (Zhang et al., 2013).

Figure 2-7 demonstrates the different absorption mechanisms of BC such as a potential to absorb, oxidise and retain nutrients due to its porous nature (Bornemann et al., 2007). BC can be used as a sorbent char or soil amendment capturing nutrients such as Nitrogen (N), Phosphorus (P) and Potassium (K). The potential of BC for such uses is attributed to its cation exchange capacity (CEC), porosity, specific surface area, pH, redox reactivity, functional groups and acid neutral capacity. The increased charge density per unit area typically causes an increase in CEC on the BC surface and this leads to an increase in the oxidation of the surface and an accompanying increase in the adsorption of cations (Atkinson et al., 2010).

There is an abundance of functional groups, on the BC surface, that can provide electrostatic attraction, ion-exchange and surface complexation effects with heavy metals and other organic materials (Tan et al., 2015). For example, the mechanism of

Cr (VI) adsorption using BC takes place through three pathways: (i) positive charge of BC surface attracts negative species and vice versa (Qiu et al., 2008), (ii) hydrogen ions bonds with electron donors from BC and (iii) converted species such as Chromium (Cr) from Cr (VI) to Cr (Dong et al., 2011). The third is divided into two parts: one released into the medium and the other complexed with the functional groups on the surface of the BC. The micropore structure of BC surfaces can facilitate adsorption through pore-filling effects without the formation of chemical bonds (Han et al., 2013, Inyang et al., 2014) allowing the adsorption of organic pollutants, such as phenol and methylene blue, from agriculture runoff.

Precipitation is another BC mechanism that removes heavy metal which may occur under a high pH. The minerals react with the BC surface through metallic ions and form insoluble metallic precipitation (Inyang et al., 2016).

BC characterisation relies on many factors such as feedstock source (Corn Stover, animal litters, Woodchips, poultry manure, Bagasse and hardwood), processing temperature, pyrolysis type, heat transfer and residence time in the kiln. BC can be produced through different pyrolysis processes such as conventional pyrolysis, fast pyrolysis, gasification, hydrothermal carbonization, torrefaction and rectification processes (Mohan et al., 2014). Traditional pyrolysis (slow pyrolysis) was used thousands of years ago and is still performed using a similar method which starts with the heating of biomass in moderate temperature rising to around 500°C with a lack of air for a long residence time of hours to days. Fast pyrolysis relies on the quick heat transfer of dry feedstock with rapid increases in temperature of up to 1000°C for 1-5s of vapour residence (Lima et al., 2010). An alternative technique to traditional carbonization is hydrothermal carbonization (HTC) which can convert the biomass to char and this occurs underwater at moderate temperature (130-250°C) and pressure (10-30 bar) (Titirici et al., 2012). Torrefaction and rectification processes are used to produce BC between 230-280°C to create non-sorbent BCs. In general, the presence of many types of functional groups on the surface of any BC depends on the particular pyrolysis process, temperature and pH of the solution which can be specified through CEC assessment (Harvey et al., 2011). Gasification is another BC production method. In the gasification method, there is a relatively small amount of BC produced with 85% of gas yield and only a small amount of biomass combustion in an oxidising atmosphere (Higman and Burgt, 2008). For instance, high temperature (>550°C) and

slow pyrolysis for macadamia shells can produce highly effective BC and high Brunauer– Emmett– Teller surface areas (>400 m^2/g) (Tilman et al., 2006, Keiluweit et al., 2010). Gasification is probably the most attractive of the other BC producing methods as it has triple green effects: waste recycling, BC production and generation of useful gases.
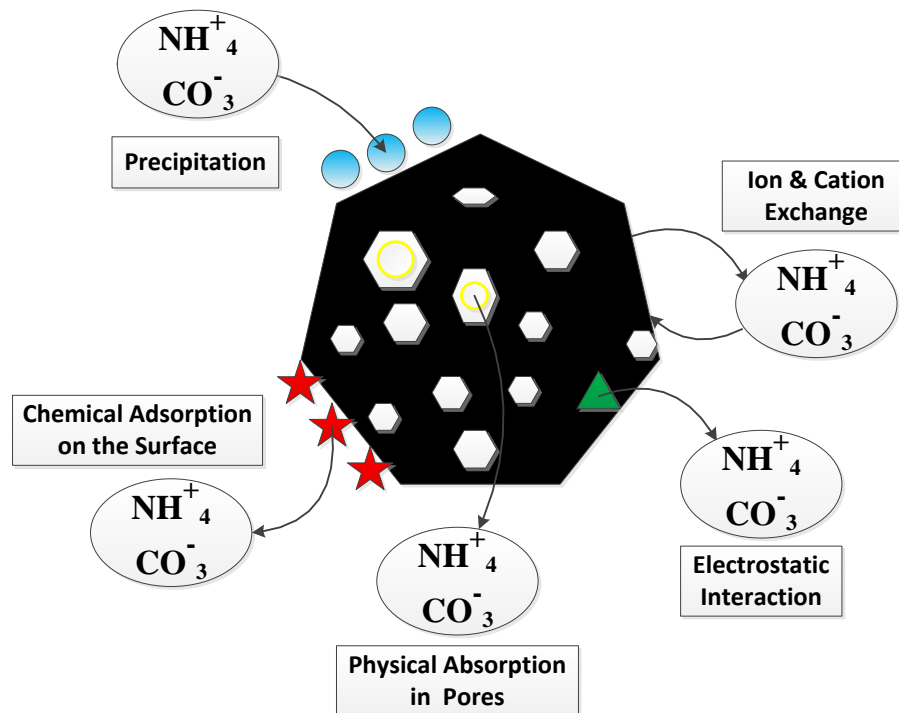
Figure 2-7: Different absorption mechanisms on biochar

BC has many notable benefits such as cost-effectiveness being from cheap feedstock (waste), environmentally friendliness as it is produced with minimal oxygen and it does not release GHG. Pyrolysis and gasification processes produce useful materials such as bio-oils and gases with high calorific values such as methane. As mentioned previously, BC has many important applications such as improving the retention of nutrients and water holding capacity (moister content) of the soil and carbon sequestration in the form of carbon dioxide (Macdonald et al., 2015). Talberg (2009) stated that BC could be produced using small or large units and this is another significant benefit. The carbon in BC stays stable longer than the raw material itself,

because of the steady aryl structures formed during the pyrolysis process. They increase the lifetime of macadamia biochar (MBC) for 1000s of years and this highlights its potential for reuse several times (Burns, 2014). BC can be used as a perfect adsorbent due to its high surface area and C content that is rich with functional groups and CEC (Zhao et al., 2018). BC has a few drawbacks mainly related to its use as soil amendments as it may negatively impact the denitrification process due to its high C: N ratio (Strock et al., 2017). Also if applied BC to the soil with lack of N supplied that will immobilize N and affect negatively on the crop productivity(Shareef and Zhao, 2016).

MBC can effectively remove N-nutrients in the form of NO^-_3, NO_2, N_2O and NH^+_4 (Major et al., 2010) and P-nutrients, minimize Aluminium (Al) (Steiner et al., 2008), sequesters C (Lehmann, 2007) and absorb CO_2 (Sohi et al., 2010, Spokas et al., 2012), and decrease Copper (Cu) (Ippolito et al., 2012). MBC can also absorb some ions due to ion exchange such as Potassium (K), Calcium (Ca), Magnesium (Mg) and Sodium (Na) (Wrobel-Tobiszewska et al., 2017). Kumar (2017) suggested that MBC (as a carbon source) can minimise iron oxides (FeO) to metallic iron (Fe), which is considered a sustainable and cleaner output of iron. The reaction equations are:

$$3Fe2O3(s) + C(s) \leftrightarrow 2Fe3O4(s) + CO (g) \tag{1}$$

$$Fe_3O_4(s) + CO (g) \leftrightarrow 3FeO(s) + CO_2 (g) \tag{2}$$

$$C(s) + CO_2 (g) \leftrightarrow 2CO (g) \tag{3}$$

$$FeO(s) + CO (g) \leftrightarrow Fe(s) + CO_2 (g) \tag{4}$$
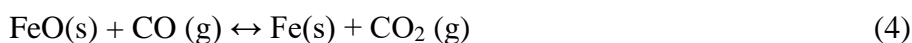
It can also remediate organic and inorganic contaminants organic pollutants can be dye pollutants from the dye industry, Phenols, solvents, miscellaneous and pesticides. Inorganic pollution can be divided to (Abdel-Raouf et al.) cations, anions such as Chromium (Cr), Copper (Cu), Lead (Craggs et al.), Cadmium (Cd), Mercury (Hg), Iron (Fe), fluoride (F), Zinc (Zn), and Arsenic (As) ions.

BC seems to be the most cost-effect technique for treating agricultural runoff, or any contaminated water for that matter. BC is produced from waste materials and this saves the cost of handling waste. In addition, the processes through which BC is made, produce other useful products such as methane gas and oils. Kumar (2017) reported that MBC could be used as a carbon resource to reduce the use of fossil-fuel in iron-making factories which are a renewable, environmental and sustainable resource. BC also has a long working life that allowing reuse for many applications such as filtration. Figure 2-8 shows how around 50% of the pyrolysis biomass can be returned to the soil as an amendment in the form of biochar, while the remainder can produce energy through gas capture.
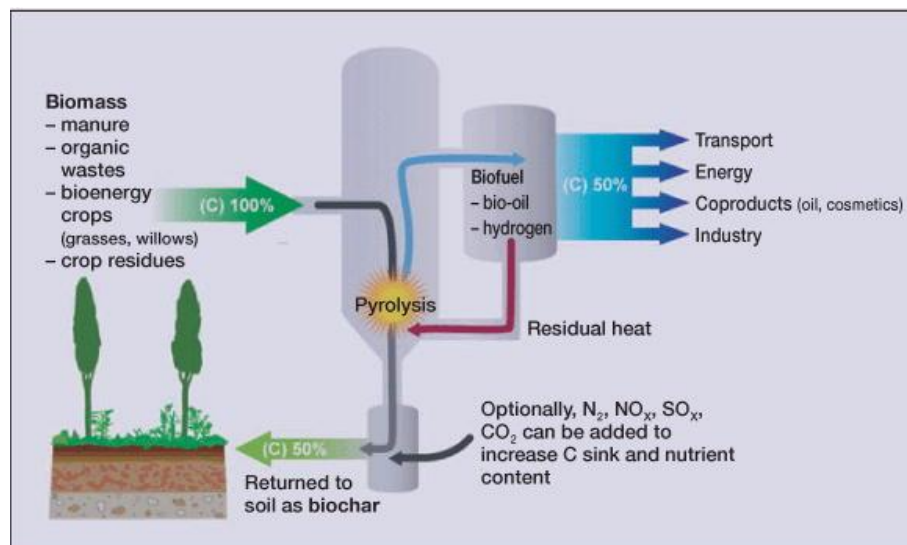
Figure 2-8: Pyrolysis biomass to produce biochar (Lehmann 2007)

Nowadays, an activated BC is considered to be an effective alternative material to AC because of its capability to adsorb different sorts of contaminants and its lower cost (Ahmad et al., 2014). The total cost of one tonne of BC production is around $346 AUD, while commercial AC available at $2,110 AUD per tonne which means that it is six times the BC cost (Maroušek et al., 2017). The main factors that may affect BC production cost are the raw feedstock prices (switch-grass $91 AUD/t, water oak wood $63 AUD/t and bio-solid 84 AUD/t (Alhashimi and Aktas, 2017)), power energy for the kiln (electricity $0.17 AUD/kWh), pyrolysis temperature and time, and the

percentage of BC production (Li and Chen, 2018). Also, Alhashimi & Aktas (2017) compared the rate of energy demand and potential global warming impact between the BC and the AC, and calculated per 1 kg production as 6.1MJ/kg and 97 MJ/kg respectively, while the average greenhouse emissions (calculated by converting their emission to the equivalent amount of CO_2) were calculated to be 0.9 kg CO_2eq/kg for BC and 6.6 kg CO_2eq/kg for AC.

2.3.6 Overall evaluation of available treatment technologies

In this section, overall evaluation is developed for treatment technologies taking into consideration important factors such as cost/energy of operation, removal capability, maintenance capability, regeneration and working lifetime. In recent years, scientists have focused on some factors that may impact the feasibility of agricultural runoff treatment techniques. The most important factors are cost, environmental effect, efficiency and sustainability respectively (Chong et al., 2010, Gómez-Pastora et al., 2017).

In terms of the cost/energy factors for the CW method, O'Geen et al. (2010) and Tanner & Kadlec (2013) stated that land and constructions is the major portion of total cost at around $60,870.0 AUD/ha for small scale, and the maintenance twice a year at about $102.26 per ha per year. Energy consumption studies are small in number but different systems have been shown to have low energy consumption (Zhang et al., 2009). In addition, it has a high capability to remove pesticides from agriculture runoff but a low capability for NG removal as Ballantine and Tanner (2010) stated. Knowles (2012) calculated that CW also has a long lifetime (about 25 years) but it requires regeneration every eight years which may cost around $90,000.00 AUD for 300 m^2.

For the filtration method, the EPA reported that a sand filtration facility with activated carbon adsorbent with a capacity of 3785 m^3/day may cost around $2 M AUD for land, construction and materials. Ko et al. (2004) stated that the facilities required 8 cents for each kW/h energy to operate the system and it consumed around 2.1 TJ to operate and maintain the facility over one year.

However, aeration can increase CWs oxygenation capacity and improve its performance. Wu et al. (2014) reported that this will increase operation and maintenance costs. Craggs et al. (2012) stated that the capital cost of the station including earthworks for ponds construction, the paddlewheel mixing and pH controlled CO_2 addition is $ 17.03 AUD /m^2. While, Christianson (2011) found that the cost range for each hectare is $240.0 AUD to $715.00 AUD including the structure, contractor, woodchips and supplies.

In BC's case, Maroušek et al. (2017) analysis found that the production of one tonne is around $346 AUD, while commercial AC is available at $2,110 AUD, which is six

times the BC cost. In addition, around $50 AUD per tonne as direct revenue can be obtained from selling the heat produced through the pyrolysis process due to synthesis gas (Meyer et al., 2011).

For the maintenance of CWs, dredging and cleaning the media due to the sedimentation and harvesting every six months can be fairly costly. For the filtration method, maintenance entails cleaning the tank and the whole media used as a filter after saturation due to clogging, and may also include digging up sediments settled in the basins (Myers, 2015). For the aeration method, maintenance includes daily inspection of the aerated ponds to prevent any clogging of the diffused air system (blower and pipeline) which provides air to the bottom of the pond (US EPA 2011). This maintenance is high cost and requires continuous monitoring of the entire system and may cause loss of soil nutrients. Harvesting is the most important part of maintenance to recover the small cell size of algae (0.2-30 µm), which may cost 20-30% of the total biomass production costs (Christenson & Sims 2011). For wood chips, the low maintenance requires once a year nutrient removal which results in low cost (Choudhury, 2017). However, using BC as a filter to reduce nutrients, requires minimum maintenance and low cost for a long period of treatment due to BC behaviour and material (from waste) replacement cost if required and backflushing for reuse.

CWs have a high ability to remove pesticides, biological oxygen demand (BOD) and chemical oxygen demand (COD), but are inefficient at removing N and P nutrients. Xiong et al. (2011) found that CW can help to remove about 35% nitrate, 50% ammonium and 55% TN through nitrification and denitrification. An aeration system can efficiently remove suspended solids and carbon from farm effluents (Bolan et al., 2004) but it is inefficient for nutrient (N, P and K) removal. Algae can treat agricultural runoff from toxic minerals such as lead, arsenic, cadmium, and it is also capable of removing BOD and COD, some nutrients (e.g. N, P) and heavy metals (Kumar and Gaur, 2011). Lannan (2011) reported the removal of nitrate by 71.4%, ammonia by 81.3% and phosphate by 82.6% within three days of algae growth. The woodchip method can remove nitrate and phosphorous and some microbes and viruses from farm flow runoff (Rambags et al., 2016). However, MBC can effectively remove N-nutrients in the form of NO_3^-, NO_2, N_2O and NH_4^+ (Major et al., 2010) P-nutrients, minimize Aluminium (Al) (Steiner et al., 2008), sequester C (Lehmann, 2007) and absorb CO_2 (Sohi et al., 2010, Spokas et al., 2012), and decrease Copper (Cu) (Ippolito

et al., 2012). MBC can absorb some ions due to ion exchange such as Potassium (K), Calcium (Ca), Magnesium (Mg) and Sodium (Na) (Wrobel-Tobiszewska et al., 2017). Kumar (2017) suggested that MBC (as a carbon source) can minimise iron oxides (FeO) to metallic iron (Fe), which is considered a more sustainable and cleaner output of iron. BC, after saturation can be used as a soil amendment with useful nutrients.

Based on the evaluation of the common techniques for nutrients removal provided above, it is fair to state the biochar treatment technology is identified as the most feasible option for treating agricultural runoff in terms of the considered factors compared to the other techniques. Gómez-Pastora et al. (2017) determined that the important factors for treatment techniques should include environmentally friendliness, low cost (originally from waste), high efficiency and sustainability.

Table 2: Advantage and disadvantages of different treatment methods

No.	Treatment Type	Advantage	Disadvantage
1	Constructed wetland	High capability to remove pesticides from non-point pollution agricultural runoff.	Cannot entirely remove NG from agricultural runoff.
		Convert nitrogen group into various N forms.	Odor & mosquito production.
		High ability to remove biological oxygen demand (BOD) and chemical oxygen demand (COD).	High maintenance, large land requirements and high installation cost.
2	Filtration	High reduction of BOD, suspended solids and pathogens.	Requires expert design and construction, particularly and require maintenance.
		Ability to nitrify due to good oxygen transfer.	Lack of ability to remove dissolved fluids.
		Low operating costs.	Inefficient in removing nitrogen group.
3	Aeration	Aeration can minimize N_2O emissions and reducing total nitrogen.	Lack of ability to remove $NO_3^-$$-N$ concentration.

#	Type	Advantages	Disadvantages
		Efficiently remove suspended solids and carbon.	Inefficient for nutrient (N, P and K) removal.
		Has a capability to remove 95% of Total Suspended Solids (TSS).	High cost due to installation, pumping, and maintenance.
4	Algae	Convert nutrients such as N and P to a complex organic structure.	Harvesting of dilute cultures.
		Remove heavy metals	Control problem in open pond.
		CO2 emissions reduction.	Light availability is a major factor affecting microalgal performance.
5	Woodchip	Low-cost of materials due to the abundance of woodchip.	Colouring the treated water due to the leach of organic materials.
		High carbon-nitrogen ratio.	Risk of producing toxic organic-heavy metal complexes such as methylmercury.
		Simplicity of operation and maintenance.	Produce of GHG such as nitrous oxide from the denitrification process.
6	BC	Cheap feedstock from macadamia nutshell waste	Applied BC to the soil with lack of N supplied that will immobilize N and affect negatively on the crop productivity
		Environmentally friendliness as it is produced with minimal oxygen	Sorption of pesticides and herbicides by the biochar can reduce their efficacy
		Improving the retention of nutrients, moister content and carbon sequestration in the form of carbon dioxide.	The fine ash associated with biochar is the perfect source for dust, posing a risk for respiratory diseases.

2.4 Agricultural runoff

Agricultural runoff and its contaminants, such as salts and nitrates, are one of the main problems that affect freshwater quality (United States Environmental Protection Agency, 1994). Agricultural runoff is the surplus water from farms after the irrigation or other activities. This water comes from different sources such as rain, melting snow and irrigation, and some of this water finds its way into surface water and eventually into groundwater. It can carry some pesticide and fertilizer residue while it is moving along the soil surface and can pollute the water that it comes into contact with by adding contaminant loads in the form of soil particles (suspended particles), dissolved organic, nutrients or salts (e.g. NO_3^- and NH_4^+) (Town, 2017). Many methods can be used to treat water from these contaminants, for instance CWs, filtration and aeration. CWs is an artificial engineering design with specific elements such as soil and vegetation that sequester pesticides from the runoff. The design of CW depends on pesticides to be treated (Vymazal, 2007). The plants growing in CWs have a major role in removing contaminants and oxidizing ammonium to nitrate as shown in the equation below:

$$NH_4^+ + 2O_2^- \Rightarrow NO_3^- + 2H^+ + H_2O \qquad\qquad (5)$$

According to Vymazal and Březinová (2015), once a year nutrient removal CW has been considered to be an effective method to remove pesticides from agricultural runoff and drainage but, it is high cost and inefficient for removal of the urea group (NO_3^- & NH_4^+) and NaCl. Another method for treating water is aeration which has been applied in conjunction with CW to enhance the ability of the latter to remove contaminants from agricultural runoff (Uggetti et al., 2016). There are two types of aeration i.) continuous and ii.) intermittent. The oxidation efficiency of NH_4^+ in aerated CW relies on the concentration of dissolved oxygen applied to the bottom of the soil surface in CW. The intermittent strategy is set at a minimum limit for oxygen concentration so it can be controlled when the oxygen level drops below the required level and this, in turn, reduces the cost of the aeration process. With the continues strategy, the oxygen level can exceed the required limit (Labella et al., 2015).

Filtration is another method that can be used to treat agricultural runoff. The application of filtration dates back to 4000BC in ancient Greek and India. These civilisations were more concerned about the turbidity of water, contaminants and microorganism in the water (Engineers, 1985). They used a basic method of filtering the water through sand and gravel and boiling it. This method is still in use, but with new materials that have a higher capacity for removing contaminants. One common example of these filters is the multilayer filter. Each layer is responsible for removing specific contaminants (suspended or dissolved) (Färm, 2002a).

2.5 CDI techniques

CDI is an electrochemical technique for removing contaminants from water. This technology started in the 1960s and the scientists have continued to work on it up to the 1990s when they began to use carbon with it to enhance the ability of carbon (high surface area and high porosity) to adsorb contaminant ions (Suss et al., 2015). This method requires two electrodes with different charges (positive and negative) on opposite sides while the water flows between the two electrodes. DC voltage applied across the two electrodes (work like capacitor plates) in a CDI cell. The anions (negatively charged ions) are attracted to the cathode (positive electrode), whereas the cations (positively charged ions) are attracted to the anode (negative electrode) (Anderson et al., 2010). CDI technology can also solve the salinity problem in water in the range of 800–10,000 mg/L. Many technologies can be used to remove contaminants however, most of them are relatively expensive in comparison to CDI. For instance, reverse osmosis and electrodialysis need about 2.25 Wh/L (8.5 Wh/gal) and 2.03 Wh/L (7.7 Wh/gal), respectively, while CDI requires only 0.13–0.59 Wh/L (0.5–2.25 Wh/gal) (Welgemoed and Schutte, 2005). CDI was found to improve the capability of BC adsorption for NG in agricultural runoff (Shi et al., 2016). It also can be used to regenerate filters after the electrodes are saturated with contaminants by a reverse charge. Then the filters are flushed with clean water. Figure 2-9 describes how the CDI technique works.

Figure 2-9: Schematic of CDI technique

CDI is a novel technology used for different water treatment applications, but mainly desalination with different forms of carbon electrodes such as conventional, porous-carbon and graphene (Ahmed & Tewari 2018). It considered to be a better technique than other existing technologies such as reverse osmosis with regard to ion removal efficiency, environmentally friendliness and energy consumption. In addition, the possibility of energy recovery through the CDI desorption operation is the most attraction feature for this researcher.

2.6 Regeneration

Regeneration may help filters remove more nutrients from contaminated water during the second cycle. Many techniques can be used to refresh filters such as the well-known back-flush with clean water. This can remove some of the ions from the filters, but it is considered an inefficient method. Reverse polarity back-flush is another technique that can be used to remove contaminants from the column after saturation. This method can use one layer for CDI, although there are some ions that may reabsorb to the opposite electrode (Uzun and Debik, 2019). Scientists have improved this method by adding an ion selective membrane after each electrode to prevent the ions being adsorbed by the opposite electrode and vice versa. Tab water (TW) will be examined and compared with the DI.W as a practical alternative for nutrient recovery on farms.

The conventional method for nutrient recovery, which is reverse polarity, has been excluded from this study because it uses multilayer column cells that will allow most of the ions to reabsorb at the opposite electrode during back-flush (Uzun & Debik 2019). Instead of this method, this study will use a novel technique from World War II (to reduce the magnetic signature of the ships) to recover nutrients (Kephart et al. 2011). This technique was called degaussing and the name comes from the unit of magnetism (Sukow et al., 2010).

In this study, we used a non-sinusoidal periodic waveform or pulse wave (square wave), similar to the degaussing technique because it can effectively dislodge absorbed nutrients with a constant frequency and equal duration between maximum and minimum. As shown in figure 2-10, a sample of square waves with duty cycles of T_{on} and T_{off} at frequency of $100H_z$ and V_L at 1.2V is used to degauss nitrate from a saturated column. This technique can help to release the ions previously adsorbed in the chemical and physical mechanism.

Figure 2-10: Square waves with duty cycle of 0.5 (El Hawary, 1986)

2.7 Conclusions

The literature pertaining relevant to treating agriculture runoff was critically analysed. The current methods for treating agriculture runoff such as CW, filtration and aeration were found to be inadequate for removing nitrate ions and expensive for construction and maintenance. This study proposes the use of a BC filter for removing nitrate ion as a part of nitrogen (N) compounds from agricultural runoff. N compounds were chosen in this study due to their abundance in agricultural runoff and their negative impact on surface and groundwater quality. Given the porous and chemically active structure of BC originally from waste, adsorption capability, interactions (electrostatic mechanism), significantly decrease runoff impacts, recovering nutrients at the same time for reuse in a cost-effective and environmentally friendliness manner without chemical substances use are the most important advantages for using BC in this study.

3. Biochar Characterisation and contaminant removal capability

3.1 Introduction

Different technologies for treating agricultural runoff, with a focus on nitrate, were critically reviewed in the previous chapter. BC was found to be the most promising option for this treatment owing to its cost-effectiveness, being environmentally friendliness and its capacity to influence nutrient retention. Therefore, macadamia biochar (MBC) as a biochar (BC) module was chosen for investigation into its capability to minimise NO_3^- from agricultural run-off.

In this chapter, the effect of MBC on the nitrates removal capability in synthetic samples scrutinized through batch and column experiments. The performance of MBC prepared at two different pyrolysis temperatures of 900 and 1000°C were investigated. The effect of the flow direction (upward and downward) on the removal efficiency in the column experiment was examined. The column experiments were used three NO_3^- concentrations with three levels of flow rate to determine the best removal parameters. The long-term performance of MBC was tested for a month. Experimental design and statistical analysis were employed to ensure the repeatability of the experimental work.

3.2 Materials and Methods

3.2.1 Solution preparation

A stock of synthetic solution was prepared by dissolving 135.4 mg Sodium Nitrate (M.W. =84.99, Analytical Reagent) in 1 L of distilled water to produce 100 mg/L of nitrate concentration (stock solution). This stock solution was prepared to save time, reduce storage space, conserve materials and improve the accuracy of the solution preparation and reagents (GHOSAL and AVASTHI, 2018). Three concentrations of 5, 10 and 15 mg/L of nitrate were applied in this study. The concentration range was chosen to cover the minimum and maximum nitrate levels expected in agricultural runoff. In most parts of the world, for example China and the USA, the maximum nitrate concentration in many sites reaches up to 15 mg/L, while the lower limit is about 3-5 mg/L (Beutel et al. 2009; Lang et al. 2013). Another study of 360 stormwater sites around the USA reported that the median limit was around 14 mg/L (Ghane et al. 2016). In addition, a report of the Department of Primary Industries in Australia indicated that the suitable NO_3^- for most plants is less than 10 mg/L (NSWPrimefact, 2014). This data informed the selection of concentration levels: a minimum level of 5 mg/L and maximum level of 15 mg/L, and their midpoint of 10 mg/L. These were considered to be best levels for obtaining the most accurate results (Beutel et al. 2009).

3.2.2 Biomass preparation

The feedstock was prepared from macadamia (Bauple) nutshell as a BC module due to its availability, affordability, being environmentally friendliness as it is a recycled product of agricultural waste, and having a high surface area compared to other shells such as pistachio, pecan, hazelnut and almond (Bae & Su 2013). Macadamia nutshell was placed into a stainless steel square container with lid 17.78W×16.51D×10.16H cm, then set it in a kiln (Rio Grande PMC Model #703-118). The kiln was programmed for the slow pyrolysis process under lack of oxygen conditions to drive the internal chamber to two temperatures 900 and 1000°C at a rate 600°C/h and holding time at the climax temperature for an hour before cooling down to room temperature. Macadamia nutshell normally loses about 65% of mass between 260-400°C due to the conversion to BC (Kumar (2017). Using higher temperatures to pyrolyse the biomass

has the advantage of reducing volatiles and obtaining more stable carbon with through a high surface area (Nick 2018). After pyrolysis was completed, MBC was cooled and later was gently crushed using a Weston hand grinder. The crushed MBC was then sieved through 1.18-2.30 mm sieve as this size range was found to be effective for sorption (Shackley et al. 2010). After that, the MBC, obtained from the above steps, was rinsed with distilled water for two hours to remove any impurities such as ash. Following this step, the BC was autoclaved at 121°C and pressure of 2.50 bars for steam sterilization using a Hirayama Manufacturing Corporation autoclave (Model HV-50L). The final product was then stored in plastic containers to be used in adsorption experiments.

3.2.3 Column preparation

A plastic column with a height of 12.20 cm and an internal diameter of 3.85 cm was used for carrying out the column experiments. The column was rinsed with DI.W, sterilised with Ethanol (C_2H_6O). Circular fibreglass mesh was laid at the bottom of the column. The column was packed with 60 g of MBC prepared at 1000°C pyrolysis temperature based on preliminary experiments which will be explained later in Section 3.3.1.1. Once the column was packed with the MBC, the top of biochar was covered with filter paper of 0.45 µm size to prevent MBC particles from leaving with the flow of the solution. The two ends of the column were covered with plastic caps and sealed with commercial silicon. The two caps had openings to accommodate the hosing of the feed and discharge lines as shown in Figure 3-1.

Figure 3-1: Schematic diagram of MBC column

3.2.4 Analytical measurements

3.2.4.1 Morphology and elemental composition

Scanning Electron Microscopy (Phenom SEM) JEOL (JCM-6000 Benchtop SEM) was used for visual comparison between the raw and pyrolysed macadamia nutshell, the structures, pore sizes and their distribution on the surface of the materials. SEM images were taken at around $\times 1000$ magnification power, secondary electron image (SEI) in a chamber pumped to high vacuum mode around 10^{-2} pa pressure in ten minutes and accelerating voltage of 5 kV.

3.2.4.2 Functional groups

Shimadzu 206-97505D/2015 Fourier Transform Infrared Spectroscopy (FTIR) was used to examine the BC structure at different conditions (pyrolysis temperatures and before and after adsorption). FTIR measurements were utilised to monitor the change in functional groups available on the BC surface as it is considered a sensitive tool for detecting any change that might happen in the composition of the functional groups on the surface of the biomass (Shen et al., 2010). Based on potassium bromide (KBr) and optics defined by the FTIR, the average record spectra was chosen from the upper limit bands at 4000 cm^{-1} to the lower bands at 400 cm^{-1} (Coates, 2000). Each band number was assigned to a specific chemical band and could help in understanding the MBC removal mechanisms of nitrate. The applied FTIR measurement conditions were as follows: % transmittance mode, no. of scans = 45, apodization is happ-genzel, and resolution of 4 cm^{-1}.

A 2 mg MBC sample was pulverized using a mortar and pestle and mixed with 200 mg Potassium bromide (KBR) to 0.1 wt.%. The mixture was pressed into a pellet of 15 mm inner diameter and 1 mm thick using manual a hydraulic press approximately 8-9 kPa for 0.5 min (Yang et al., 2017). The pellet was then placed in the FTIR instrument for a scanning test.

3.2.4.3 Ion Chromatography system (ICS-2000)

An Ion Chromatography System ICS-2000 instrument was used to analyse nitrate concentration in the samples before and after treatment. ICS-2000 works on comparing the samples to a three points calibration curve applying the standard method 4110B (Dionex, 2006). Five millilitres plastic vials with filter cap (20 µm) were used for storing the samples. The results obtained from ICS in terms of $NO_3^- - N$ were converted to NO_3^- by multiplying by a factor of 4.428.

3.2.4.4 Kinetic experiments

In this study, a batch experiment and a column experiment were used to check the adsorption capability of the BC. All experiments were conducted in triplicate and a blank sample (before adsorption) analysed as a reference for each test.

For the batch experiment, 10 mL from the stock solution prepared in Section 3.2.1 was utilised with 90 ml of distilled water to obtain a 10 ppm nitrate solution. This 100 ml solution was placed in 250 ml Pyrex beaker with 1 g of MBC prepared at 900°C and another beaker for 1000°C at an initial pH of 5.5 and a temperature of 20.9°C to compare the two. The solution was stirred for 48 hours to obtain the best equilibrium contact time between the solution and MBC particles which estimate the maximum potential of the MBC for effective removal of nitrate. These experiments were conducted in triplicate and samples were collected at 5, 15, 30, 60, 120, 180, 240, 300 and 360 minutes (Wang et al. 2017). Samples were filtered directly using a 0.45 µm paper filter to stop any reaction between the solution and MBC by removing any solid particles present in the samples.

3.2.4.5 Column experiment

A plastic column prepared in Section 3.2.3 was used with the same procedure of cleaning, sterilising and the amount of the 1000°C MBC. After the column was packed with MBC, it was rinsed with DI.W several times until the leachate pH settled indicating that the column was clean and ready for the experiments (Inyang et al.

2013). This state of cleanliness also ensured that a minimal amount of elements would be released from the biochar. In this process, upward and downward flow through the column packed with 30 gm of MBC was utilised for preliminary experiments as will be explained later in Section 3.3.2.

All of the experiments discussed below were conducted in triplicate to obtain the optimum nitrate removal concentration and flow rate per gram MBC and the results are displayed by the mean values. 20 litre sterilised plastic containers were used to carry the feed solution with three different NO^-_3 concentrations (5, 10 and 15 ppm) and filtered solution. The feed was single-pass pumped into the column through silicon tubing at three different flow rates (2, 5 and 10 ml/min) using a peristaltic pump model MasterFlex model no. 7520-47, USA and ISMATEC ecoline Model ISM1076A, Germany. Samples were collected periodically at 5, 15, 30, 60, 120, 180, 240, 300 and 360 minutes to obtain the optimum removal time. Other studies have measured the concentration of effluent at different intervals of set time to find the saturation point (Chang et al. 2006). Nitrate was measured using ICS-2000 as explained in the previous section. Equations 3-1 and 3-2 were used to calculate the percentage of the nitrate removal for each gram of MBC respectively.

$$\text{Nitrate removal (\%)} = \frac{\text{Nitrate conc. in feed water} - \text{Nitrate Conc. in column leachate}}{\text{Nitrate conc. in feed water}} \qquad (6)$$

$$\text{mg of nitrate removal per g BC} =$$

$$\frac{\text{Nitrate conc. in feed water} - \text{Nitrate Conc. in column leachate}}{\text{Nitrate conc. in feed water}} \times \text{Volume of the solution} \qquad (7)$$

Figure 3-2 shows the schematic of the plastic columns filled with MBC used for the nitrate removal experiment applying upward flow in the University's chemical laboratory.

Figure 3-2: Schematic of MBC column experiment

3.2.4.6 Statistical analyses

Statistical analysis was implemented in two stages: design of experiments and data analysis. Experimental designs and data analyses were carried out using MINITAB 17 software. The order of the experiments was randomized to obtain a normal distribution of the experimental errors. Three nitrate concentration levels and three flow rate levels were chosen. Each experiment was conducted in triplicate and, for each experiment, samples were taken after six hours to find the maximum adsorption condition in this period. Factorial design of 3^2 was performed for nitrate removal and the factors of concentration and flow rates were used in Minitab 17. The optimum nitrate removal concentration and flow rate per gram of MBC was found using three levels of nitrate concentration (5, 10 and 15 mg/L) and three levels of flow rate (2, 5 and 10 ml/min) after 6 hours with a one pass solution of upward flow through the column of MBC pyrolysed at 1000°C. The experiment's analysis program will be explained in the preliminary experiments in Section 3.3.3.

3.3 Results and discussions

3.3.1 Preliminary results

3.3.1.1 Effect of the pyrolysis temperature

Figure 3-3 shows the average nitrate removed for the three experiments in the first six hours using MBC prepared under two different temperatures (900 and 1000°C). In the first hour, NO_3^- removal measured by milligram nitrate removal per gram MBC increased for the two kinds of MBC (900 and 1000°C) with time. At around 60 minutes, they began at equilibrium status around 0.095 and 0.057 mg of nitrate removal per gram of MBC for 1000 and 900°C respectively. After 24 hours, the results of the 900°C was still around 0.059 mg/g while 0.097 mg/g for 1000°C. Higher nitrate removal was obtained with the application of 1000°C of MBC.

Figure 3-3: Nitrate removal with 10 mg/L NO_3^- concentration

Figure 3-3 above demonstrates that the first few minutes for the 1000°C MBC was a higher removal than 900°C at around doubled. After six hours the 1000°C MBC was still the highest at 0.096 mg nitrate per g MBC. This proves that the nitrate removal

capability of 1000°C MBC is much higher than the 900°C MBC. Mainly after first-hour MBC of 900°C and 1000°C start to saturate.

These results concur with the SEM images in Figure 3-4 below. Figure 3-4A and B clearly shows that the raw macadamia nutshell surface structure had closed its pores. In comparison, the macadamia nutshell after pyrolysis, Figure 3-4C and D, shows obvious the pores for MBCs pyrolysed at both 900°C and 1000°C respectively. The latter figures demonstrates that the pore size after applying pyrolysis to the raw macadamia nutshell for the 1000°C (Figure 3-4D) gives more, larger and more uniform porosity than the 900°C MBC (Figure 3-4C) under the same conditions and magnification of ×1000 (resolution of 20 µm).

(A)

(B)

(C)

(D)

Figure 3-4: A & B SEM for raw macadamia nut shell and pyrolysis MBC **C.** 900°C and **D.** 1000°C

Figure 3-5 A and B shows the weight and atomic percentage before and after the pyrolysis process using Generation 5 SEM instrument, The Phenom ProX Desktop scanning electron microscope. Obviously, there is a difference in terms of the weight and atomic percentages of the main elements of carbon and oxygen as well as Na, Ca and K present for the raw macadamia nutshell and MBC. It is clear that the carbon percentages increased while the oxygen, in the form of gas percentage, decreased in both weight and aromatic percentage when the mass moved from raw to pyrolyzed macadamia nutshell (MBC). This is the result of the strong carbon availability and stability in the BC structure. In terms of mass, the weight of the raw macadamia nut shell placed in the container of the kiln was around 370 grams and after pyrolysis, the weight was reduced to around 32% at 110 g.

(A)   (B)

Figure 3-5: Weight & atomic percentage **A.** raw macadamia nut shell and **B.** macadamia biochar

Summarising Figures 3-4 and 3-5, raw macadamia nutshell in Figure 3-4 appears with some cracks, but without any porous structure on the surface area. In terms of composition, the shells had 52.18 and 47.61 percentage of C and oxygen respectively. In the pyrolysis process, the carbon percentage was increased, driving off all the volatile materials including the oxygen contained in the raw shells. The carbonisation

process can cause the volatilisation of noncarbonated elements and development of pore structures as shown in Figure 3-4C and D. A similar process of change in porous structure and volatile compounds was reported in another study that used macadamia nutshell waste and pyrolysis at 700°C (Junior et al. 2014; Martins et al. 2015). Pyrolysis of macadamia nutshells has also been found to increase water and nutrient retention as the pyrolysis temperature increases (Shafie et al., 2012).

A FTIR test was used to define the mechanism of MBC removal by examining the functional groups present on their surfaces. Generally, the functional groups of acidity and basicity surface increase with increased pyrolysis temperatures (Kameyama et al., 2016). In Figure 3-6 below, a comparison between the MBC at 900 and 1000°C is made. Both have the same peaks positions which means they have similar functional groups that allow them to adsorb similar elements (Mandal et al., 2016). For 1000°C, some peaks are not as sharp as 900°C and that indicate the water peak in 3454.51 cm^{-1} reduced at the higher temperature. The reduction in the functional group with increasing temperature is evident through the composition analyses where the oxygen falls due to include the oxygen in a most functional group such as OH and COOH. However, as the functional group falls with higher pyrolysis temperatures, the porosity of char surface increases and conductivity might also increase which will offset the reduction in the functional group.

Figure 3-6: FTIR analysis for 900 and 1000°C MBC

3.3.2 Effect of flow direction on nitrate adsorption

As explained in Section 3.2.4.5, peristaltic pumps were used to feed the columns (in a single-passed configuration) with the nitrate solution used in Section 3.2.4.4, but in two directions (upward and downward) at a flow rate of 10 ml/min. This experiment utilised the same electro conductivity (EC) of around 20 µS/cm, ambient temperature (T) around 16.5°C and pH around 6.

Figure 3-7: Upward and downward flow column adsorption experiment for 6 hours

Figure 3-7 demonstrates that the trend for the first six hours of upward flow is very much higher than the downward flow regarding nitrate removal through the two columns and at the same time and in the same conditions. The upward started at around 80% at five minutes, while the downward started at around 12%. For the upward flow, the saturation started around the fourth hour at 20%, while for the downward it started earlier at around 5%. These results show that up-flow is a much more efficient method than the down-flow in terms of removal percentage. In addition, the upward flow has a greater uniform distribution of solution on each particle of the MBC with HRT 6.42 minutes from the inlet to outlet, which increases the contact time. The down-flow

creates a channel between the MBC particles for easy flow which reduces contact time to 2.05 minutes.

Figure 3-8 presents the FTIR spectra of particulate matter from MBC before (1000) and after (1000_Ads) nitrate adsorption. The intensity of some peaks after nitrate adsorption was substantially decreased or shifted in wavenumber (cm^{-1}) compared to those before adsorption due to the chemical bonds emerging. This means that there may be an involvement of some functional groups on the surface of the MBC in nitrate adsorption (Hafshejani et al., 2016). The peak intensity of 3454.51 cm^{-1} which is ascribed to a C-OH group within a group frequency (4000-1450cm^{-1}) is stretching vibrations and board (Baitimirova et al., 2013). The intensity decreased after adsorption indicating that the surface hydroxyl groups were involved in nitrate adsorption and chemically connected to the water. Another peak around, 2368.59 cm^{-1}, shows the stretching vibration of –C≡C– and –C–H bonds due to an alkynes group which can be attributed to the MBC component. The peak at about 1101.35 cm^{-1} also fell after adsorption and this refers to the ring skeletal C–O (a secondary alcohol) stretching (Shen et al., 2010). The decline in the peak after nitrate adsorption indicates an interaction between the functional group and NO$_3^-$ because of the powerful aromatic C–O linkages. The prominent peak at 975.98 cm^{-1} belongs to the aromatic CH plane deformation (Ma, 2017). In addition, the decline from the peak of 480.28 cm^{-1} after nitrate adsorption, indicates an interaction with the MBC functional group due to vibrations from carbohydrate and lignin (Schenzel and Fischer, 2001, Ma, 2017). Based on the aforementioned results, the falls from all peaks before nitrate adsorption can be ascribed to the interaction between the MBC functional groups and NO$_3^-$ ions to form new chemical bonds.

Figure 3-8: Compare between MBC1000°C before and after nitrate adsorption

To sum up the finding of the preliminary experiments in the previous sections, the analysis of batch triplicate experiments and SEM images shows that MBC at 1000°C pyrolysis temperature was found to cause better nitrate removal than 900°C. In addition, the upward flow column was found to be performing better in comparison to the downward flow column in terms of NO_3^- removal.

Therefore, in the next experiments for MBC 1000°C with upward flow different concentrations and flow rates were applied to the same column conditions to find the optimum condition for nitrate removal using MBC in six hours.

3.3.3 Normality and residual analyses

Table 3-1 below has the results of the nitrate removal experiments using MBC with three different concentration and three different flow rates as a Minitab software randomly chosen. Also, shows nitrate removal percentage and removal in mg/L (In-Out).

Table 3-1: Triplicate nitrate removal experiment using MBC

No.	Std. Order	Flow rate (mL/min)	Nitrate Conc. (mg/L)	Actual Feed (mg/L)	effluent (mg/L)	Removal (In-Out) mg/L	Nitrate Removal (%)	Removal NO$_3^-$ mg/L.gBC
1	16	10	5	4.90	2.80	2.10	42.73	0.04
2	19	2	5	4.90	2.74	2.16	43.36	0.04
3	8	10	10	9.50	6.74	2.76	28.59	0.05
4	2	2	10	9.50	5.01	4.49	46.84	0.07
5	11	2	10	10.20	4.60	5.60	59.40	0.09
6	21	2	15	14.70	8.95	5.75	38.82	0.10
7	5	4	10	10.20	6.20	4.00	31.26	0.07
8	23	4	10	10.20	6.76	3.44	35.77	0.06
9	3	2	15	14.50	7.80	6.70	45.83	0.11
10	1	2	5	4.70	0.80	3.90	83.95	0.07
11	20	2	10	9.40	5.10	4.30	46.13	0.07
12	24	4	15	14.60	11.50	3.10	21.77	0.05
13	14	4	10	9.90	6.72	3.18	32.16	0.05
14	17	10	10	9.60	7.01	2.59	26.71	0.04
15	4	4	5	5.10	3.02	2.08	42.30	0.03
16	7	10	5	5.10	3.50	1.60	29.81	0.03
17	6	4	15	14.60	10.30	4.30	29.48	0.07
18	15	4	15	14.90	10.70	4.20	28.39	0.07
19	22	4	5	5.01	4.07	0.94	18.69	0.02
20	10	2	5	5.10	2.54	2.56	52.57	0.04
21	18	10	15	14.80	12.18	2.62	17.68	0.04
22	13	4	5	4.80	2.90	1.90	39.85	0.03
23	27	10	15	14.60	12.00	2.60	21.43	0.04
24	25	10	5	4.70	3.04	1.66	35.33	0.03
25	26	10	10	9.80	6.94	2.86	29.20	0.05
26	12	2	15	15.10	8.53	6.57	43.52	0.11
27	9	10	15	15.10	12.07	3.03	20.05	0.05

A normal distribution is the key assumption of the statically analysis that shown the data from experiments are normally distributed (Srinivasan and Viraraghavan, 2010). Table 3-2 presents the parameters estimation of the fitted model for the mg of NO_3^- removal capability per gram of MBC. More details in the appendix A.

Table 3-2: Analysis of Variance (ANOVA) for NO_3^- Removal using Adjusted SS for Tests

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	8	0.000060	0.000008	21.79	0.000
Linear	4	0.000055	0.000014	39.43	0.000
Flow rate (mL/min)	2	0.000028	0.000014	40.12	0.000
Nitrate Conc. (mg/L)	2	0.000027	0.000013	38.74	0.000
2-Way Interactions	4	0.000006	0.000001	4.16	0.015
Flow rate (mL/min)*Nitrate Conc. (mg/L)	4	0.000006	0.000001	4.16	0.015
Error	18	0.000006	0.000000		
Total	26	0.000067			

Model Summary:

S	R-sq	R-sq(adj)	R-sq(pred)
0.0005881	90.64%	86.48%	78.94%

The normality of data was verified in terms of standardized residual as a part of the statically analysis (normal probability plot). Data normality form will be checked by drawing a normal probability plot of residuals in this experiment. Figure 3-9 shows how data fall fairly close to the fitted regression line. As observed clearly from this figure, the normal probability plot of the residuals for the nitrate removal is normality distributed population by falling all data experiments closest to the fitted line (Al-Juboori et al., 2015).

Figure 3-9: Normal distribution plot of residual for nitrate removal experiments

Figure 3-10 demonstrates the results of the diversity of the experiments with residuals and the irregular pattern for that removing nitrate residuals with fitted value. This approved the data was collected in a random distribution throughout the experiments which obviously shows randomly distributed around the zero line (Ryan et al., 2012).

Figure 3-10: Residual vs. fitted value for nitrate removal experiments

The proportional shape in figure 3-11 shown the histogram below of the residuals vs. frequency is another figure can show how the residuals of removing nitrate are normally distributed.

Figure 3-11: Residual vs. frequency for nitrate removal experiments

Further evidence for the randomly distributed of the data obtained from nitrate removal experiments shows in figure 3-12. The variation of the residuals with observation order has random data around the zero line with no obvious pattern.

Figure 3-12: residuals vs. observation order for nitrate removal experiments

3.3.3.1 Analysis of surface and contour plots

Many factors may be considered to obtain the optimum case of maximum removal of nitrate by using MBC and how it responses to each case and examine how the response conduct with each selected levels of each factor (Boubakri et al., 2014). To determine the required response values and operation conditions, this study utilised the response of the surface plots like surface and contour plots (Montgomery, 2013). The response in the contour plots showed in the two-dimensional plane and it is obvious when each contour line present a group from the same response values connected to each other. However contour plots produced a clear idea about data response, still, the surface plots displayed response values in three-dimensional view which can offer a wide exemplification. In both plots (contour and surface) can help to find the factors that have the main effects for each response through kept the variables constant except two of them and check the plots responses.

(A)

(B)

Figure 3-13: Nitrate removal by using MBC **A.** Surface plot **B.** Contour plot

Figure 3-13 shows the combined impact of three different concentrations and flow rates on nitrate removal by using MBC. NO^-_3 removal increased when influent rate become 2 ml/min and the concentration around 14-15 mg/L. It is obvious from the contour plot that the maximum adsorption happened under the 15 mg/L nitrate concentration and 2 ml/min flow rates after random experiments with various cases replicated for three times. This results matched with the experiments results at around 0.007 mg of NO^-_3/ g of MBC for an experiment number 6, 9 and 26 in table 3-1. More clear for the surface plot and easy to recognise the minimum nitrate removal around the 0.003 mg of NO^-_3/g of MBC happened in the case of 5-6 mg/L concentration and 7-10 ml/min flow rate which is in correlation with experimental results about 0.003 mg/g for the experiment number 1, 16 and 24 (table 3). The previous study by Boubakri et al. (2014) showed that the highest removal efficiency happened at high concentration and low flow rate similar to the results obtained from this study (Ebrahimi-Gatkash et al., 2017). Therefore, this technique performed better removal with increasing nitrate concentration.

3.3.4 Maximum adsorption time

The aim of the column experiment is to find the parameters required to design the adsorption column suitable for industrial purposes. Recent studies found that the capability of BC to reduce some nutrients relies on the character of the BC feedstock (Dempster et al., 2012). This removal capacity decline with time due to increasing C: N ratio of the BC from different raw material. Figure 3-14 presents the breakthrough curve for column prepared in section 3.2.3 and solution as found in section 3.3.3.1 for single-passed.

The area above the breakthrough curve represents the bed capacity (BC) and is given by the equation below (Karunarathne and Amarasinghe, 2013).

$$BC = G \int_0^T (C_o - C) \times dt \qquad\qquad (8)$$

Where G is the solution rate in L/min, C_0 and C are the inlets and outlet nitrate concentration in mg/L at time t, respectively and T in minutes is the actual time required for full bed exhaustion.

Figure 3-14: Breakthrough curve for nitrate adsorption using MBC. Ideal breakthrough curve

(IBC) at flow rate of 2 mL/min

Table 3-3: Nitrate adsorption in fixed bed column 2 mL/min flow rate and 15 mg/L initial concentration

Adsorbent weight (g)	T_s (min)	T_b (min) at $C/C_0=0.20$	LUB (cm)	Amount adsorbed at T_b		Amount adsorbed at full bed exhaustion	
				Total (mg)	mg/g	Total (mg)	mg/g
60	330	25	11.27	0.63	0.01	3.59	0.06

Ideal breakthrough curve (IBC) has been drawn in figure 3-14. In industrial practice, the operation of the column adsorption continues until reach low concentration of removal was chosen before that called breakpoint concentration at the maximum concentration of the effluent can reach. In this case, it happened around 12.50 mg/L. At this point the column is not fully saturated and can calculate the length of the unused bed (LUB) by using the equation below:

$$LUB = \frac{Z}{T_s} (T_s - T_b) \qquad\qquad (9)$$

Where Z is the height of the column, T_s the time required for full bed exhaustion at infinite rapid adsorption and T_b is the breakthrough time. BC calculation is then given by:

$$BC = G (C_o - C^*)T_s \qquad\qquad (10)$$

Where C^* is the equilibrium concentration of the effluent 60% of the lowest concentration (5 mg/L) may found in the agricultural runoff which is in this case 3 mg/L and table 3-3 tabulated the calculation of all parameters in the equations above. These results found that the effective length of the column used was 11.27 cm and the maximum nitrate removal before the bed exhausted was 3.59 mg after 330 min.

3.4 Chapter summary

The use of the MBC as environmentally friendly and cheapest sorbent investigated in this chapter. Two types of the MBC (1000, 900ºC) utilised to remove NO^-_3 ions from agricultural runoff. Batch and column experiments done with triplicate each experiment to obtain the optimum adsorption condition through changing the flowrate, concentration and flow direction. Characterisation of the MBC was done by some devices to check the differences between the two sorts of the BC used in this study. The outcomes of the experimental in this chapter are summarised below:

1. 1000°C MBC used in this experiment has more porosity and functional groups as clearly shown by SEM and FTIR sections and has more nitrate adsorption capability than the 900°C.

2. The upward flow through the MBC column experiment has more efficient direction than the downward regarding nitrate adsorption.

3. Investigated further in-depth within industries concentrations and suitable flow rates using Minitab software to manage and analyse the result of the randomly chosen samples was the effect on finding the maximum adsorption condition.

4. Triplicate the sample tests and analysed the results found that the low flow rate and high concentration performed the best around 0.007 mg NO^-_3 per g MBC. However, the intermediate removal at 0.029 mg/g with 10 mg/L and 10 ml/min for concentration and flow rate respectively. In general, for the MBC adsorption case the higher the flow the lower performance and higher concentration the better removal.

5. Working lifetime examined with time and found that the maximum nitrate adsorption was 3.59 mg after 330 min before the column exhausted and the LUB was 11.27 cm.

To fairly better assist the usability of MBC for the application of nutrients removal, further improvement for nitrate removal by MBC using the new technique. Regeneration and nutrients recovery from saturated MBC will be investigated in the next chapter.

4. Application of the CDI technique to promote contaminant removal efficiency of MBC

4.1 Introduction

In this chapter, the optimum nitrate removal conditions will be investigated with the aid of capacitive deionisation (CDI) for further improvement. Biochar regeneration and nutrient recovery with back-flush deionised water (DI.W) and tap water (TW) and degaussing technique with DI.W will also be explored in this chapter.

4.2 Materials and Methods

4.2.1 Solution preparation

The same stock solution prepared in section 3.2.1 was used in the experimental investigation presented in this chapter to prepare the diluted solution with an optimum concentration of 15 mg/L obtained from section 3.3.3.1.

4.2.2 Preparation of carbon electrode

Carbon was widely used for the CDI application electrode because it has a low contact resistance, low cost, high electrical conductivity and good process capability (Porada et al. 2013).

Carbon electrodes were extracted from new Eveready heavy duty battery 6V in this experiment. The electrodes were cleaned then sterilised with Ethanol (C_2H_6O) and covered with copper caps. The electrodes were connected to two power supplies GwInstek model GPC-3030D and Farnell Stabilised model L30-2.

4.2.3 Experimental procedure for further adsorption improvement using CDI

The plastic column prepared in section 3.2.3 was utilised in this experiment. Six holes were made on two sides of the column for embedding the electrodes into the biochar. The CDI column setup is presented in Figure 4-1. The three right holes were made at a distance of 1, 5 and 9 cm from the bottom of the column, while the three left holes distance from the bottom were 3, 7 and 11 cm, respectively. The column was packed with 46.3 g of MBC in stages where each electrode was inserted into the column at the set depth and covered with biochar. A fibreglass screen was laid on top of each layer to separate them and prevent the transport of nitrate across the layers as shown in Figure 4-1. Each electrode was glued to the column with commercial silicon to prevent leakages. The same process was repeated for the rest of the biochar layers and electrodes. Once the column is packed with MBC and the six carbon electrodes, the top of the column was covered with doubled fibreglass screen to prevent the MBC particles to leave with the flow of the solution. The column was closed with two plastic caps from the bottom and the top. The caps have openings for accommodating the hosing of the feed and discharge lines as demonstrated in Figure 4-1. The electrodes were connected to power supply (Farnell, Stabilised power supply L30-2) to provide each electrode with a voltage of 1.2 V and current of 0.2 A. The applied CDI parameters were chosen at these levels to avoid the occurrence of some problems such as the increase of pH and scale deposition on the electrodes (Lee et al., 2010), water electrolysis near the electrode and reduction energy consumption (Park et al., 2007).

Figure 4-1: MBC column with CDI technique (3cells) for nitrate removal test

The prepared columns were rinsed with DI.W several times until the leachate pH settles indicating that the column is clean and ready for the experiments (Inyang et al. 2013) and there is a minimal amount of elements released from the biochar. The supplied feed solution (prepared in section 4.2.1) was pumped through the column applying the optimum parameters found in the previous chapter. At the same time, the power supplies were turned on to start the electro-sorption process. The solution was single-passed upward through the column for 6 hours and samples were taken at 5, 15, 30, 60, 120, 180, 240, 300 and 360 min to find the best removal timeframe as this would help the industry in setting the effective operating conditions. Some studies measured the concentration of effluent at different intervals of a set time to find the saturation point (Chang et al. 2006). Nitrate removal increase with increasing the current which may speed up the oxidation-reduction reaction rate at the electrode and converted to N_2 or NH_3 gas (Vanlangendonck et al., 2005, Emamjomeh and Sivakumar, 2005). The equations below show the possible reactions at the cathode (Paidar et al., 1999).

$$NO_3^- + 3H_2O + 5e^- \rightarrow \frac{1}{2}N_2 + 6OH^- \qquad\qquad (11)$$

$$NO_3^- + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^- \qquad\qquad (12)$$

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \qquad\qquad (13)$$

4.2.4 Experimental procedure for regeneration and nitrate

recovery using back flush with DI.W and TW

The most common method for regenerating filters is back flush with water through the filter after the bed is exhausted with contaminants. It is noteworthy that two types for flushing water were applied in the regeneration step; DI.W for simulating lab environment and TW for simulating practical real-life application. Flush water was fed into the column from the bottom in an upward direction as this ensures uniform contact with MBC as explained in section 3.3.2 with the optimum flow rate of 2 ml/min was applied in this experiment. Samples were collected after 5, 15, 30, 60, 120, 180, 240, 300 and 360 minutes to check the efficiency of this method for nitrate recovery with treatment time.

4.2.5 Experimental procedure for regeneration and nitrate

recovery using a degaussing technique with backflush

Another regeneration technique, similar to the degaussing idea used in WWII, will be applied for CDI column after saturated with nitrate to remove the ions from the electrodes and MBC particles. By using Thurlby Thandar Instruments TG215 and set at frequency100 Hz, volt 7.5 Vp-p and current 0.2 A then connected the negative side to the first negative electrode and the positive side with the last positive electrode on the cells in the column as recommended as shown in figure 4-2.

Figure 4-2: MBC column with degaussing technique (3cells) for nitrate recovery

4.2.6 Nitrate removal with the regenerated MBC column

After degaussed the column and recovered nitrate ions in the previous section, regeneration efficiency will be investigated test in this reabsorptions test. The same adsorption process explained in 4.2.3 was repeated for the regenerated MBC column after nitrate was recovered from saturated MBC particles. CDI technique was applied to the column with three cells to investigate the capability of reabsorption nitrate.

4.2.7 Analytical methods

As explained in section 3.3.4, Ion chromatography ICS-2000 was applied for nitrate measurements. It worth mentioning that all experiments were conducted in triplicate.

4.3 Results and discussions

All the results presented in the following sections are expressed in mean values and the errors are depicted in the form of error bars.

4.3.1 Effect of CDI technique on the MBC adsorption capability

The difference between the performance of MBC with and without CDI was investigated in this study and the results for three days are shown in Figures 4-3. Figure 4-3A for the first few minutes showed the removal of MBC presented in mg/L of outlet concentration around 1.50 mg/L then at 30 minutes became around 3.50 mg/L, while after added the CDI technique to MBC was at 1.10 after 30 minutes. Which means adding CDI technique can improve the nitrate removal by three times more than using MBC alone. C_e/C_o was around 0.11 and it became 0.22 after 30 minutes, while with MBC-CDI nitrate removal was around 0.06 - 0.076 for the same period of time (around 93% of the initial influent concentration 15 mg/L). Similar to the results obtain from the previous study at 5 mg of nitrate per litre and 150 g of activated carbon then obtain at equilibrium time after 10 hours around 0.12 mg NO_3^-/g BC (Erickson et al., 2016). This study found at 330 min MBC achieved the equilibrium removal rate around 0.03 mg NO_3^- per g MBC (section 3.3.4), around 12.50 mg/L effluent concentration, and with CDI was improved the removal rate and the equilibrium time became at 72 hours and the effluent concentration was around 12 mg/L (80% of the influent concentration) as shown in figure 4-3B. In addition, applying CDI increased the removal by 3 times in comparison to MBC alone after six hours at Ce/Co 0.3 and 0.9 respectively. Studies investigated the use of electro-assisted biochar technique for nitrate removal by using column tests seems to be very limited (Nur et al., 2015). The available studies such as the one conducted by Mahatheva Kalaruban agree with the present study finding as both witnessed an improvement in nitrate removal (Kalaruban, 2017). However, the improvement reported by Mahatheva Kalaruban was only about 10%, in this study around 300% and this could be attributed to the different configurations of the systems applied.

(A)   (B)

Figure 4-3: Nitrate removal by natural MBC vs MBC-CDI for **A.** six hours and **B.** three days

The common NO_3^- removal mechanisms using BC are functional groups and ion exchange mechanisms and to the lesser extent the physical adsorption which is highly influenced by micro-pore volumes and surface area (Chintala et al., 2013, Kameyama et al., 2012). It is likely that the electrostatic interactions mechanisms are also involved in the removal in this study as electro-sorption capacity increases with increasing thermal pyrolysis temperature of biomass material. High temperature leads to higher graphitisation levels and minimises the electric resistance of the MBC surface and rise specific surface area (micro-porosity development, see Figure 3-4). As MBC given in this study was prepared at a high temperature of 1000°C (Lado et al., 2016).

In terms of removal mechanisms, the case with CDI can be slightly different as the electrostatic interaction is the prominent mechanisms. The capacitance of the CDI electrode was limited, however large surface area of the used BC may have enhanced the removal efficiency when combined with CDI. High surface area and good mass transfer were found to be the key points for better adsorption and electro-catalysis applications and this can explain a higher removal for CDI with MBC compared with the latter alone as studied by (Dehkhoda et al., 2016, Ahmed and Tewari, 2018).

4.3.2 Desorption and nitrates recovery by flushing deionised water

In this experiment, the capability of backflushing with DI.W on nitrate recovery from a saturated column was investigated. The flow rate applied was 2 ml/min as recommended by (Oyarzun et al., 2018). Figure 4-4 shows the results for two cycles (BF_DI.W_1 and BF_DI.W_2) along the first six hours of the flushing with DI.W Around 50% of the NO^-_3 was recovered in the first hour then reduced gradually to the 3 mg/L outlet concentration after six hours. After 24 hours more than 90% accumulative recovery was achieved at 0.80 mg/L effluent concentration. The results obtained are in agreement with the reported results by Chintalaet al. (2013) who used 1:50ml saturated materials (corn stover and switchgrass biochar) solid to DI.W ratio to desorb the nitrate ions then placed the solution into a beaker and shook up for 24 hours then samples filtered, placed in centrifuge tube and tested. This study was found that desorption increased with increasing the initial concentration of nitrate and after around one hour more than 90% recovered. Although this method was faster than desorption in the column with up-flow DI.W, it requires some technology such as centrifuge device which is not accessible for the general public.

Figure 4-4: Nitrate recovery by using deionised water

The results of adsorption and desorption experiments suggest that the adsorption of nitrate onto MBC is a faster process than desorption. This might be an attractive trait for MBC in soil amendment application, but it may be regarded as a disadvantage for MBC in filtration applications. Hence, exploring ways of speeding up the regeneration and nitrate recovery form MBC is important. This study proposes the use of degaussing coupled with the backflush for regeneration and nitrate recover which will be addressed in the following sections.

4.3.3 Desorption and nitrates recovery using Degaussing with

DI.W

Figure 4-5 presents the comparison between nitrate recoveries with average replicate degaussing coupled with DI.W backflush and flushed up-ward the DI.W alone. The experiment of degaussed nitrate from saturated column include MBC particles and carbon electrodes have resulted in a very similar unsymmetrical shape, with a rapid nitrate concentration increase for the first 30 minutes, followed by a flatter diminution. The maximum effluent of nitrate concentration peak was achieved in about 30 min for all the cycles. For the first cycle, more than 70% recovery at 11 mg/L, while around 6 mg/L for the DI.W in the previous section. For the second and third cycle became lower at the same time (30 min) at 9 and 7 mg/L. Then for the three cycles start to decline and the residue nitrate concentration approaches to 2.52, 1.77 and 1.34 mg/L after six hours for the first, second and third cycles respectively. After 24 hours the percentage of the nitrate recaptured was very close around 95 and 94% for degaussing with DI.W and DI.W alone cumulative respectively, but the improvement was notable within the first hour and that makes the degaussing quicker method and can recover more nitrate in the same time comparing with DI.W method in section 4.3.2.

Figure 4-5: Nitrate recovery by using degaussing technique

Table 4-1: Percentage of desorption using degaussing technique

Time	Cycle_1		Cycle_2		Cycle_3	
(min)	C_e(mg/L)	% of desorption	C_e(mg/L)	% of desorption	C_e(mg/L)	% of desorption
0	0	0	0	0	0	0
5	9.03	60	7.27	48	6.32	42
15	10.26	68	8.63	58	7.24	48
30	11.02	73	9.12	61	7.99	53
60	7.54	50	6.99	47	5.39	36
120	4.86	32	4.68	31	3.65	24
180	4.01	27	4.03	27	3.14	21
240	3.35	22	3.27	22	2.02	13
300	2.79	19	2.24	15	1.60	11
360	2.52	17	1.77	12	1.34	9

Table 4-1 shows that the maximum desorption for the first, second and third cycles at 73, 61 and 53% respectively in the first 30 minutes. After six hours the three cycles become less than 20% at 2.52, 1.77 and 1.34 mg/L for the first, second and third cycles respectively.

4.3.4 Tap water used for nitrate recovery

Figure 4-6 shows that the two cycles (T.W_1 and T.W_2) for nitrate recovery used TW for the first six hours treating time.

Figure 4-6: Tap water used for desorption nitrate ions

Obliviously, the maximum amount of NO^-_3 recovered between the first and the second hours by using TW with around 40% for the first cycle, while around 25% for the second cycle. Then the first and second cycles decreased to around 3 and 2.8 mg/L effluent concentration after six hours at 20% of desorption. However, after 24 hours the differences between the two cycles became very close at 2.11 and 2.19 mg/L for the first and second respectively. Although the rare study used TW for nutrients recovery, a previous study used a column saturated with lead (Pb) and obtained 22% recovery with a flow rate 25 ml/min and 20 mg/L concentration (Dimitrova, 2002). Despite the previous study was used hi flow rate and concentration compared to the new study with a different ion, higher percentage obtained for nitrate recovery using the same technique in a similar period.

To get a better understanding of the performance of the applied recovery techniques used in this study, Nitrate recovery with all three techniques was plotted and presented in figure 4-7. First of all, the three techniques were worked well and recovered nitrate ions after column saturated. The degaussing technique with DI.W was the most powerful method founded due to the ability to recover more nitrate ions in efficient time, while TW was the lowest. the maximum nitrate recovery occurred around 30 minutes, around 70% of nitrate was recovered at 11 mg/L effluent concentration for the degaussing method, while DI.W was around 48% after one hour and comparing to the TW one was around 35% at 5.3 mg/L outlet concentration. Then the curves started to decline after 30 minutes and one hour for the degaussing and the both DI.W and TW respectively. After the second hours, nitrate concentration in the outlet flow was very close for all recovery techniques around 5 mg/L, then continue to descend to about 3 mg/L after the sixth hours at 20%.

Figure 4-7: Three techniques used for nitrate recovery

A study of desorption nitrate from saturated woodchips with nitrate ions used 400 ml of 0.001M KCL solution and placed on the shaker after rinsed the samples with Nano-pure water three times. Samples taken after six hours showed that around 60% desorbed from the woodchips then after three days decreased to zero per cent and will be ready to reuse the filter (Hua et al., 2016). Mostly regenerated the filters and nutrients recovery were used chemicals in the process, while a present study conducted

to be chemical free and environmentally friendly with or without a small amount of energy (1.2 V). Although some studies used the chemical in the recovery process, the results obtained in this study were better at around 75% recovery after six hours.

4.3.5 Nitrate removal with regenerated filter

After the completion of desorption tests, the reusability of the filter for nitrate removal was examined. Figure 4-8 presents the results of nitrate removal used fresh CDI and MBC filter with two regenerated filters after desorption process used the degaussing technique with DI.W process. The results presented NO^-_3 effluent was increased by around doubled for the second regeneration filter comparing with the fresh filter within the first 30 min. Outlet concentration of nitrate was increased after six hours at 4.5, 8.2 and 9.6 mg/L for the fresh, regeneration one and two respectively. After 36 hours, the trend of the three methods were close to each other at around 10.5 mg/L of nitrate effluent concentration. The effluent nitrate concentration at full bed exhaustion (around 80% removal efficiency) was at 72, 60 and 48 hours for the fresh, regenerated one and regenerated two filters. That means the capability of reusing the filter for removal nitrate after used the degaussing method was successful.

Figure 4-8: Nitrate removal by fresh and regeneration filter of MBC with CDI **A.** six & **B.** 72 hours

This proves that the MBC filter can effectively be reused for nitrate removal at least three times after the degaussing with DI.W was used to recover nitrate ions which can practically be used as fertiliser at the same time regenerate the filter.

The results obtained in this study are in line with the trends reported in the literature. Cui et al. (2019) found that regenerating biochar synthesized with chitosan and $FeCl_3$ (LC-CF) saturated with nitrate using 0.1 M NaCl resulted in a slight declined in adsorption (Cui et al., 2019). This decline continued and reached about 5% as opposed to fresh biochar after the fifth cycle. Although the previous study used some chemical during sorption and desorption process, a present technique applied in this study has zero usage of chemicals during the adsorption and desorption process and this makes it more reliable and environmentally friendly.

4.4 Economic Analysis

Production of MBC (as a by-product) or other similar feedstock, can be used in a gasification process to primarily provide energy, approximately 9MJ/kg, as well as making high quality char at negligible cost. Alternatively, it is possible to purchase commercially available, activated carbon (coconut biochar) for around $3000/Tonne.

In the case of using MBC the calculations will be as below:

Removal rate analysis:

> Given: after 48 hours was achieved around 95% nitrate removal, this implies 14.25 mg/L was adsorbed from the 5.76 L of stock solution at an original concentration of 15mg/L.

> This gives a total of 82.1mg of nitrate absorbed by 46.3gr of MBC, giving an overall removal rate of 1.77g of nitrate / kg of MBC using CDI.

> Similarly, without CDI being used, MBC showed an overall removal rate before the bed exhausted was 0.029g / kg of MBC.

-For MBC-CDI adsorption technique:

$$Power = 0.2A \times 1.2V = 0.24W$$

$$48hr \times 0.24W = 11.25W.hr$$

$$Energy = 11.25W.hr \times 3600J = 41.47J$$

At Queensland energy price = $0.27kW.hr

$$Energy\ cost = 11.25W.hr \times \frac{\$0.00027}{(W.hr)} = \$0.00311\ AUS$$

Or, the cost of using the MBC-CDI technique to adsorb 95% of nitrate in solution is around $1.76/kg nitrate removed from solution (assuming linear scalability).

-For degaussing technique calculation:

$$Power = 0.062A \times 0.5V = 0.03W$$

$$6hr \times 0.03W = 0.18\ W.hr$$

$$Energy\ cost = 0.18W.hr \times \frac{\$0.00027}{W.hr} = \$0.000486AUS$$

The cost of using degaussing technique for 6hr to refresh more that 85% of saturated column of biochar with nitrate solution of 15mgL.

Giving an energy cost of \$0.00105/kg char used to refresh 85% of the capacity.

4.5 Chapter summary

Using CDI technique to enhance MBC column capability to remove nitrate was investigated in this chapter. Desorption NO_3^- after saturated the column test by using DI.W and TW alone as well as degaussing technique with DI.W was examined above. The experimental outcomes for this chapter epitomised below:

1. CDI with MBC has more efficient in terms of removal nitrate comparing with MBC by itself around 12 mg/L outlet of nitrate concentration (full bed exhaustion) at 72 hours and 330 minutes respectively.

2. Regards the desorption process, degaussing with DI.W (three cycles) is the most effective method in terms of quantity and rapidity comparing to DI.W flush and TW flush (two cycles). The differences in the efficiency of desorption NO_3^- between degaussing technique and the two others at the first 30 minutes was around 70, 40 and 30%, while after six hours became around 3 mg/L for the nitrate effluent concentration for all three techniques.

3. After desorbing nitrate from the saturated column, the regeneration process aimed to reuse the same CDI technique with MBC column filter found that the results for the fresh column at the first hour was around 91% removal then 80% and 70% for the regenerated one and two respectively. The differences between the fresh and the regenerated filter were about 5% for the first hour and after 24 hours. The full bed exhausted after 72, 60 and 48 hours for the fresh, regenerated one and two respectively.

4. To conclude this chapter, using CDI technique with MBC was improving the removal capability in terms of nitrate ions at the same time improving the regeneration process after degaussing with DI.W technique was presented confidant results for three cycles. Desorption through the degaussing was the best in terms of the amount of nitrate recovered in less time.

5. Conclusions and future work

Many techniques designed to reduce agricultural run-off have been suggested by a large number of researchers, including constructed wetlands, filtration, aeration, algae and the woodchip bioreactors. As demonstrated in Chapter 2, most of these suggested techniques have shortcomings that restrict their practical implementation on-farm. Biochar filters offer an effective improvement of water quality, through its potential to remove nutrient contaminants from agricultural runoff before they enter the riparian zone. However, BC suffers from rapid saturation which, in turn, diminishes its performance capability and increases operational costs. In this study, capacitive deionisation technologies have been proposed, as a new treatment technique to reduce contamination and increase the effectiveness of multi-media based BC filters, whilst also allowing filter regeneration and reclamation of the nutrients.

The experimental results presented in Chapter 3 show that the higher pyrolysis temperature (1000°C) increased nitrate removal at 0.1 mg/ g MBC by approximately double the 900°C pyrolyzed MBC. Nitrate was used in this study as a sample contaminant that exists normally in agriculture runoff. These results are supported by the SEM and FTIR analysis which showed that the 1000°C MBC is more effective than the 900°C MBC, due to higher levels of activation. In addition, the up-flow column approach was five times more effective than the down-flow column after a 30 minute interval. For the design of the experiment, three concentrations and flow rates were analysed. The highest removal was achieved with the highest concentration and lowest flow rate, and these conditions were chosen for the subsequent experiment which tested for a greater removal capability around 6.75 mg/L. Moreover, working lifetime of BC was examined within three days, and maximum nitrate adsorption was found to be 3.59 mg after 5.5hrs before the column was exhausted. At this point, the LUB was 11.27 cm.

The experimental results presented in Chapter 4 confirm that the CDI technique further enhances macadamia biochar nitrate removal by three times compared to the natural ability of the char after six hours. The breakthrough curve was found to be after 5.5hrs and 72 hrs for the natural MBC and CDI enhanced MBC filters, respectively.

Replication with other char types is required to make general statements, however this result alone is certainly promising.

Desorption experiment evaluated three techniques (degaussing, deionised water and tap water backflush). The peak nitrate desorption of 80% was achieved after 30 minutes with the degaussing method, as opposed to 48%, and 35% after 60 mins respectively for the back-flush with deionised water/tap water approaches. Regeneration of the filter after saturation with nitrate ions was tested for three cycles and filter exhaustion time was subsequently found to be after 72, 60 and 48 hours for the fresh filter, 1st regeneration and 2nd regenerations respectively.

Economic analysis for MBC or other feedstock can be used in a gasification process to make the char effectively for free and provide energy approximately 9MJ/kg, alternatively you can buy a commercial activated biochar (coconut biochar) for $4/kg by tonne.

Overall, this study concludes that CDI combined with MBC particles can be used as an effective treatment technique to reduce contamination from agricultural runoff in terms of nitrate ions by enhancing removal, desorption and filter regeneration. However, the following points are recommended for future work:

1. The effect of the pyrolysis temperatures on nitrate removal using natural MBC
2. The effect of electrical factors such as voltages and frequency on improving removal, desorption and filter regeneration using the MBC with CDI technique.
3. Comparison of the degaussing method with other innovative techniques such as ultrasonic.

References

ABDEL-RAOUF, N., AL-HOMAIDAN, A. A. & IBRAHEEM, I. B. M. 2012. Microalgae and wastewater treatment. *Saudi Journal of Biological Sciences,* 19**,** 257-275.

AHMAD, M., LEE, S. S., DOU, X., MOHAN, D., SUNG, J.-K., YANG, J. E. & OK, Y. S. 2012. Effects of pyrolysis temperature on soybean stover-and peanut shell-derived biochar properties and TCE adsorption in water. *Bioresource technology,* 118**,** 536-544.

AHMAD, M., RAJAPAKSHA, A. U., LIM, J. E., ZHANG, M., BOLAN, N., MOHAN, D., VITHANAGE, M., LEE, S. S. & OK, Y. S. 2014. Biochar as a sorbent for contaminant management in soil and water: a review. *Chemosphere,* 99**,** 19-33.

AHMED, M. A. & TEWARI, S. 2018. Capacitive deionization: Processes, materials and state of the technology. *Journal of Electroanalytical Chemistry*.

AL-JUBOORI, R. A., ARAVINTHAN, V. & YUSAF, T. 2015. Impact of pulsed ultrasound on bacteria reduction of natural waters. *Ultrasonics sonochemistry,* 27**,** 137-147.

AL-SHUJAIRI, S. 2013. Develop and apply water quality index to evaluate water quality of Tigris and Euphrates Rivers in Iraq. *International Journal of Modern Engineering Research,* 3**,** 2119-2126.

ALHASHIMI, H. A. & AKTAS, C. B. 2017. Life cycle environmental and economic performance of biochar compared with activated carbon: A meta-analysis. *Resources, Conservation and Recycling,* 118**,** 13-26.

ALLRED, B. J. 2017. Batch test screening of industrial product/byproduct filter materials for agricultural drainage water treatment. *Water,* 9**,** 791.

ANDERSEN, R. A. 2005. *Algal culturing techniques*, Elsevier.

ANDERSON, M. A., CUDERO, A. L. & PALMA, J. 2010. Capacitive deionization as an electrochemical means of saving energy and delivering clean water. Comparison to present desalination practices: Will it compete? *Electrochimica Acta,* 55**,** 3845-3856.

ASTROM, G. 1999. Method and apparatus for cleaning filter material in a filter apparatus utilizing a suction generating nozzle. Google Patents.

References

ATKINSON, C. J., FITZGERALD, J. D. & HIPPS, N. A. 2010. Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: a review. *Plant and soil,* 337**,** 1-18.

AWAD, Y. M., BLAGODATSKAYA, E., OK, Y. S. & KUZYAKOV, Y. 2012. Effects of polyacrylamide, biopolymer, and biochar on decomposition of soil organic matter and plant residues as determined by 14 C and enzyme activities. *European Journal of Soil Biology,* 48**,** 1-10.

BAITIMIROVA, M., KATKEVICS, J., BAUMANE, L., BAKIS, E. & VIKSNA, A. Characterization of functional groups of airborne particulate matter. IOP Conference Series: Materials Science and Engineering, 2013. IOP Publishing, 012025.

BALLANTINE, D. J. & TANNER, C. C. 2010. Substrate and filter materials to enhance phosphorus removal in constructed wetlands treating diffuse farm runoff: a review. *New Zealand Journal of Agricultural Research,* 53**,** 71-95.

BLANCHFIELD, D. S. 2011. Water treatment. *In:* BLANCHFIELD, D. S. (ed.) *Environmental Encyclopedia.* Detroit: Gale.

BOLAN, N. S., KUNHIKRISHNAN, A., CHOPPALA, G., THANGARAJAN, R. & CHUNG, J. 2012. Stabilization of carbon in composts and biochars in relation to carbon sequestration and soil fertility. *Science of the Total Environment,* 424**,** 264-270.

BOLAN, N. S., WONG, L. & ADRIANO, D. 2004. Nutrient removal from farm effluents. *Bioresource technology,* 94**,** 251-260.

BORNEMANN, L. C., KOOKANA, R. S. & WELP, G. 2007. Differential sorption behaviour of aromatic hydrocarbons on charcoals prepared at different temperatures from grass and wood. *Chemosphere,* 67**,** 1033-1042.

BOUBAKRI, A., HELALI, N., TLILI, M. & AMOR, M. B. 2014. Fluoride removal from diluted solutions by Donnan dialysis using full factorial design. *Korean Journal of Chemical Engineering,* 31**,** 461-466.

BOURAOUI, F. & GRIZZETTI, B. 2014. Modelling mitigation options to reduce diffuse nitrogen water pollution from agriculture. *Science of the Total Environment,* 468**,** 1267-1277.

BOYLE, W. C. 2002. A Brief History of Aeration of Wastewater. *Environmental and Water Resources History.*

BROWNING, P., GONG, M., HU, T., MARX, C. & NATAKE, T. 2014. *Water Pollution Mitigation through Constructed Wetland* [Online]. Duke University-USA. Available: https://sites.duke.edu/mpecosystem/scoring-

References

matrix/chemical-manufacturing-industry/water-pollution-mitigation/ [Accessed 2017].

BURNS, K. J. 2014. *The Effects of Biochar Additions on Soil Structure and Changes to Aged Biochar Particles in Soil.* University of Western Australia.

BUTTERWORTH, E., DOTRO, G., JONES, M., RICHARDS, A., ONUNKWO, P., NARROWAY, Y. & JEFFERSON, B. 2013. Effect of artificial aeration on tertiary nitrification in a full-scale subsurface horizontal flow constructed wetland. *Ecological engineering,* 54**,** 236-244.

CALHEIROS, C. S., QUITÉRIO, P. V., SILVA, G., CRISPIM, L. F., BRIX, H., MOURA, S. C. & CASTRO, P. M. 2012. Use of constructed wetland systems with Arundo and Sarcocornia for polishing high salinity tannery wastewater. *Journal of environmental management,* 95**,** 66-71.

CARPENTER, S. R., CARACO, N. F., CORRELL, D. L., HOWARTH, R. W., SHARPLEY, A. N. & SMITH, V. H. 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecological applications,* 8**,** 559-568.

CHANCE, L. M. G. & WHITE, S. A. 2018. Aeration and plant coverage influence floating treatment wetland remediation efficacy. *Ecological engineering,* 122**,** 62-68.

CHINTALA, R., MOLLINEDO, J., SCHUMACHER, T. E., PAPIERNIK, S. K., MALO, D. D., CLAY, D. E., KUMAR, S. & GULBRANDSON, D. W. 2013. Nitrate sorption and desorption in biochars from fast pyrolysis. *Microporous and Mesoporous Materials,* 179**,** 250-257.

CHONG, M. N., JIN, B., CHOW, C. W. & SAINT, C. 2010. Recent developments in photocatalytic water treatment technology: a review. *Water research,* 44**,** 2997-3027.

CHOUDHURY, T. 2017. *Woodchip Biofilters for Treatment of Particulate Phosphorus in Agricultural Runoff.* University of Waterloo.

CHRISTENSON, L. & SIMS, R. 2011. Production and harvesting of microalgae for wastewater treatment, biofuels, and bioproducts. *Biotechnology advances,* 29**,** 686-702.

CHRISTIANSON, L. 2016. *Reducing water pollution with microbes and wood chips* [Online]. The Conversation. Available: https://theconversation.com/reducing-water-pollution-with-microbes-and-wood-chips-58852 [Accessed].

CHRISTIANSON, L. E. 2011. Design and performance of denitrification bioreactors for agricultural drainage.

References

CHRISTIANSON, L. E. & HELMERS, M. J. 2011. Woodchip bioreactors for nitrate in agricultural drainage.

CLARK, P. A., PINEDO, C. A., FADUS, M. & CAPUZZI, S. 2012. Slow-sand water filter: Design, implementation, accessibility and sustainability in developing countries. *Medical science monitor: international medical journal of experimental and clinical research,* 18**,** RA105.

COATES, J. 2000. Interpretation of infrared spectra, a practical approach. *Encyclopedia of analytical chemistry,* 12**,** 10815-10837.

CONSERVATION, E. 2007. Wastewater Management Fact Sheet.

CRAGGS, R., SUTHERLAND, D. & CAMPBELL, H. 2012. Hectare-scale demonstration of high rate algal ponds for enhanced wastewater treatment and biofuel production. *Journal of Applied Phycology,* 24**,** 329-337.

CUI, X., LI, H., YAO, Z., SHEN, Y., HE, Z., YANG, X., NG, H. Y. & WANG, C.-H. 2019. Removal of nitrate and phosphate by chitosan composited beads derived from crude oil refinery waste: Sorption and cost-benefit analysis. *Journal of Cleaner Production,* 207**,** 846-856.

DAVIS, A. P., SHOKOUHIAN, M., SHARMA, H. & MINAMI, C. 2001. Laboratory study of biological retention for urban stormwater management. *Water Environment Research,* 73**,** 5-14.

DEHKHODA, A. M., GYENGE, E. & ELLIS, N. 2016. A novel method to tailor the porous structure of KOH-activated biochar and its application in capacitive deionization and energy storage. *Biomass and Bioenergy,* 87**,** 107-121.

DEMPSTER, D. N., GLEESON, D. B., SOLAIMAN, Z. M., JONES, D. L. & MURPHY, D. V. 2012. Decreased soil microbial biomass and nitrogen mineralisation with Eucalyptus biochar addition to a coarse textured soil. *Plant and Soil,* 354**,** 311-324.

DIMITROVA, S. 2002. Use of granular slag columns for lead removal. *Water Research,* 36**,** 4001-4008.

DIONEX 2006. ICS-2000 ION CHROMATOGRAPHY SYSTEM OPERATOR'S MANUAL.

DONG, X., MA, L. Q. & LI, Y. 2011. Characteristics and mechanisms of hexavalent chromium removal by biochar from sugar beet tailing. *Journal of hazardous materials,* 190**,** 909-915.

References

EBRAHIMI-GATKASH, M., YOUNESI, H., SHAHBAZI, A. & HEIDARI, A. 2017. Amino-functionalized mesoporous MCM-41 silica as an efficient adsorbent for water treatment: batch and fixed-bed column adsorption of the nitrate anion. *Applied Water Science,* 7**,** 1887-1901.

EL HAWARY, M. E. 1986. Principles of electric machines with power electronic applications.

EMAMJOMEH, M. & SIVAKUMAR, M. 2005. Electrocoagulation (EC) technology for nitrate removal.

ENGINEERS, J. M. M. C. 1985. Water treatment principles and design. *Water treatment principles and design.*

ERICKSON, A. J., GULLIVER, J. S., ARNOLD, W. A., BREKKE, C. & BREDAL, M. 2016. Abiotic capture of stormwater nitrates with granular activated carbon. *Environmental Engineering Science,* 33**,** 354-363.

FÄRM, C. 2002a. Metal sorption to natural filter substrates for storm water treatment—column studies. *Science of the total environment,* 298**,** 17-24.

FÄRM, C. 2002b. Metal sorption to natural filter substrates for storm water treatment—column studies. *Science of the total environment,* 298**,** 17-24.

FLETCHER, T. & DELETIC, A. 2007. Statistical evaluation and optimisation of stormwater quality monitoring programmes. *Water Science and Technology,* 56**,** 1-9.

GAWLOWICZ, S. 2011. *The Green Machine: Algae Clean Wastewater, Convert to Biodiesel*

RIT researchers take algae out of the lab [Online]. USA: Rochester Institute of Technology. Available: https://www.rit.edu/news/story.php?id=48113 [Accessed].

GHOSAL, S. & AVASTHI, A. S. 2018. *Fundamentals of bioanalytical techniques and instrumentation*, PHI Learning Pvt. Ltd.

GLASER, B., HAUMAIER, L., GUGGENBERGER, G. & ZECH, W. 2001. The'Terra Preta'phenomenon: a model for sustainable agriculture in the humid tropics. *Naturwissenschaften,* 88**,** 37-41.

GÓMEZ-PASTORA, J., DOMINGUEZ, S., BRINGAS, E., RIVERO, M. J., ORTIZ, I. & DIONYSIOU, D. D. 2017. Review and perspectives on the use of magnetic nanophotocatalysts (MNPCs) in water treatment. *Chemical Engineering Journal,* 310**,** 407-427.

References

HAFSHEJANI, L. D., HOOSHMAND, A., NASERI, A. A., MOHAMMADI, A. S., ABBASI, F. & BHATNAGAR, A. 2016. Removal of nitrate from aqueous solution by modified sugarcane bagasse biochar. *Ecological Engineering,* 95**,** 101-111.

HAN, Y., BOATENG, A. A., QI, P. X., LIMA, I. M. & CHANG, J. 2013. Heavy metal and phenol adsorptive properties of biochars from pyrolyzed switchgrass and woody biomass in correlation with surface properties. *Journal of environmental management,* 118**,** 196-204.

HARVEY, O. R., HERBERT, B. E., RHUE, R. D. & KUO, L.-J. 2011. Metal interactions at the biochar-water interface: energetics and structure-sorption relationships elucidated by flow adsorption microcalorimetry. *Environmental science & technology,* 45**,** 5550-5556.

HATT, B. E., FLETCHER, T. D. & DELETIC, A. 2009. Hydrologic and pollutant removal performance of stormwater biofiltration systems at the field scale. *Journal of Hydrology,* 365**,** 310-321.

HAUSTEIN, C. H. 2014. Oxidation-reduction reaction. *In:* LERNER, K. L. & LERNER, B. W. (eds.) *The Gale Encyclopedia of Science.* 5th ed. ed. Farmington Hills, MI: Gale.

HAVERSTOCK, M., MADANI, A., BALDÉ, H., VANDERZAAG, A. & GORDON, R. 2017. Performance of an Agricultural Wetland-Reservoir-Irrigation Management System. *Water,* 9**,** 472.

HEALY, M. G., RODGERS, M. & MULQUEEN, J. 2007. Treatment of dairy wastewater using constructed wetlands and intermittent sand filters. *Bioresource technology,* 98**,** 2268-2281.

HEISTAD, A., PARUCH, A. M., VRÅLE, L., ADAM, K. & JENSSEN, P. D. 2006. A high–performance compact filter system treating domestic wastewater. *Ecological Engineering,* 28**,** 374-379.

HIGMAN, C. & BURGT, M. V. D. 2008. *Gasification,* Burlington, UNITED STATES, Elsevier Science.

HOOVER, N. L., BHANDARI, A., SOUPIR, M. L. & MOORMAN, T. B. 2016. Woodchip denitrification bioreactors: Impact of temperature and hydraulic retention time on nitrate removal. *Journal of environmental quality,* 45**,** 803-812.

HOWELL, J., CHUA, H. & ARNOT, T. 2004. In situ manipulation of critical flux in a submerged membrane bioreactor using variable aeration rates, and effects of membrane history. *Journal of Membrane Science,* 242**,** 13-19.

References

HUA, G., SALO, M. W., SCHMIT, C. G. & HAY, C. H. 2016. Nitrate and phosphate removal from agricultural subsurface drainage using laboratory woodchip bioreactors and recycled steel byproduct filters. *Water research,* 102**,** 180-189.

HUANG, J., RENEAU JR, R. & HAGEDORN, C. 2000. Nitrogen removal in constructed wetlands employed to treat domestic wastewater. *Water Research,* 34**,** 2582-2588.

INYANG, M., GAO, B., ZIMMERMAN, A., ZHANG, M. & CHEN, H. 2014. Synthesis, characterization, and dye sorption ability of carbon nanotube–biochar nanocomposites. *Chemical Engineering Journal,* 236**,** 39-46.

INYANG, M. I., GAO, B., YAO, Y., XUE, Y., ZIMMERMAN, A., MOSA, A., PULLAMMANAPPALLIL, P., OK, Y. S. & CAO, X. 2016. A review of biochar as a low-cost adsorbent for aqueous heavy metal removal. *Critical Reviews in Environmental Science and Technology,* 46**,** 406-433.

IPPOLITO, J., STRAWN, D., SCHECKEL, K., NOVAK, J., AHMEDNA, M. & NIANDOU, M. 2012. Macroscopic and molecular investigations of copper sorption by a steam-activated biochar. *Journal of environmental quality,* 41**,** 1150-1156.

JAMIESON, T. S., STRATTON, G. W., GORDON, R. & MADANI, A. 2003. The use of aeration to enhance ammonia nitrogen removal in constructed wetlands. *Canadian Biosystems Engineering / Le Genie des biosystems au Canada,* 45**,** 1.9-1.14.

JOSEPH, S., PEACOCKE, C., LEHMANN, J. & MUNROE, P. 2009. Developing a biochar classification and test methods. *Biochar for environmental management: science and technology,* 1**,** 107-126.

KADLEC, R. H. & WALLACE, S. 2008. *Treatment wetlands*, CRC press.

KALARUBAN, M. 2017. *Nitrate removal from water using surface-modified adsorbents.*

KAMEYAMA, K., MIYAMOTO, T., IWATA, Y. & SHIONO, T. 2016. Influences of feedstock and pyrolysis temperature on the nitrate adsorption of biochar. *Soil Science and Plant Nutrition,* 62**,** 180-184.

KAMEYAMA, K., MIYAMOTO, T., SHIONO, T. & SHINOGI, Y. 2012. Influence of sugarcane bagasse-derived biochar application on nitrate leaching in calcaric dark red soil. *Journal of Environmental Quality,* 41**,** 1131-1137.

References

KARUNARATHNE, H. & AMARASINGHE, B. 2013. Fixed bed adsorption column studies for the removal of aqueous phenol from activated carbon prepared from sugarcane bagasse. *Energy Procedia,* 34**,** 83-90.

KEILUWEIT, M., NICO, P. S., JOHNSON, M. G. & KLEBER, M. 2010. Dynamic molecular structure of plant biomass-derived black carbon (biochar). *Environmental science & technology,* 44**,** 1247-1253.

KNOWLES, P. 2012. *Clogging in horizontal subsurface flow constructed wetlands.* Aston University.

KO, J.-Y., DAY, J. W., LANE, R. R. & DAY, J. N. 2004. A comparative evaluation of money-based and energy-based cost–benefit analyses of tertiary municipal wastewater treatment using forested wetlands vs. sand filtration in Louisiana. *Ecological Economics,* 49**,** 331-347.

KRÖPFELOVÁ, L. 2008. Wastewater treatment in constructed wetlands with horizontal subsurface flow, 14. Springer.

KUMAR, D. & GAUR, J. 2011. Metal biosorption by two cyanobacterial mats in relation to pH, biomass concentration, pretreatment and reuse. *Bioresource technology,* 102**,** 2529-2535.

LABELLA, A., CANIANI, D., HUGHES-RILEY, T., MORRIS, R. H., NEWTON, M. I., HAWES, P., PUIGAGUT, J., GARCÍA, J. & UGGETTI, E. 2015. Assessing the economic suitability of aeration and the influence of bed heating on constructed wetlands treatment efficiency and life-span. *Ecological Engineering,* 83**,** 184-190.

LADO, J. J., ZORNITTA, R. L., CALVI, F. A., TEJEDOR-TEJEDOR, M. I., ANDERSON, M. A. & RUOTOLO, L. A. 2016. Study of sugar cane bagasse fly ash as electrode material for capacitive deionization. *Journal of analytical and applied pyrolysis,* 120**,** 389-398.

LANNAN, E. 2011. *Scale-up of algae growth system to cleanse wastewater and produce oils for biodiesel production.* Rochester Institute of Technology.

LE, L. T. T. 2017. Removal of Phosphorus in Agricultural Run-off Water by Utilization of Lignocellulosic Biomass Filters: utilization of common reed as an adsorbent.

LEACH, A. M., GALLOWAY, J. N., BLEEKER, A., ERISMAN, J. W., KOHN, R. & KITZES, J. 2012. A nitrogen footprint model to help consumers understand their role in nitrogen losses to the environment. *Environmental Development,* 1**,** 40-66.

References

LEE, J.-H., BAE, W.-S. & CHOI, J.-H. 2010. Electrode reactions and adsorption/desorption performance related to the applied potential in a capacitive deionization process. *Desalination,* 258**,** 159-163.

LEE, R. E. 2008. *Phycology*, Cambridge University Press.

LEHMANN, J. 2007. Bio-energy in the black. *Frontiers in Ecology and the Environment,* 5**,** 381-387.

LI, S. & CHEN, G. 2018. Thermogravimetric, thermochemical, and infrared spectral characterization of feedstocks and biochar derived at different pyrolysis temperatures. *Waste Management,* 78**,** 198-207.

LIMA, I. M., BOATENG, A. A. & KLASSON, K. T. 2010. Physicochemical and adsorptive properties of fast-pyrolysis bio-chars and their steam activated counterparts. *Journal of chemical technology and biotechnology,* 85**,** 1515-1521.

LIU, H., SUN, X., YIN, C. & HU, C. 2008. Removal of phosphate by mesoporous ZrO2. *Journal of hazardous materials,* 151**,** 616-622.

LOPEZ-PONNADA, E. V., LYNN, T. J., PETERSON, M., ERGAS, S. J. & MIHELCIC, J. R. 2017. Application of denitrifying wood chip bioreactors for management of residential non-point sources of nitrogen. *Journal of Biological Engineering,* 11**,** 16.

LUEDERITZ, V., ECKERT, E., LANGE-WEBER, M., LANGE, A. & GERSBERG, R. M. 2001. Nutrient removal efficiency and resource economics of vertical flow and horizontal flow constructed wetlands. *Ecological Engineering,* 18**,** 157-171.

MA, Z. 2017. Characterization of Biomass Materials for Understanding the Processing.

MACDONALD, L., WILLIAMS, M., OLIVER, D. & KOOKANA, R. 2015. Biochar and hydrochar as low-cost sorbents for removing contaminants from water. *Water: Journal of the Australian Water Association,* 42**,** 142.

MAJOR, J., LEHMANN, J., RONDON, M. & GOODALE, C. 2010. Fate of soil-applied black carbon: downward migration, leaching and soil respiration. *Global Change Biology,* 16**,** 1366-1379.

MANDAL, S., THANGARAJAN, R., BOLAN, N. S., SARKAR, B., KHAN, N., OK, Y. S. & NAIDU, R. 2016. Biochar-induced concomitant decrease in ammonia volatilization and increase in nitrogen use efficiency by wheat. *Chemosphere,* 142**,** 120-127.

References

MAROUŠEK, J., VOCHOZKA, M., PLACHÝ, J. & ŽÁK, J. 2017. Glory and misery of biochar. *Clean Technologies and Environmental Policy,* 19**,** 311-317.

MARTIN, C. H. 1927. *Biological studies of two hymenopterous parasites of aquatic insect eggs*, Science Press.

MATEO-SAGASTA, J., ZADEH, S. M., TURRAL, H. & BURKE, J. 2017. *Water pollution from agriculture: a global review. Executive summary*, Rome, Italy: FAO Colombo, Sri Lanka: International Water Management Institute (IWMI). CGIAR Research Program on Water, Land and Ecosystems (WLE).

MEFFE, R., DE MIGUEL, Á., HERNÁNDEZ, V. M., LILLO, J. & DE BUSTAMANTE, I. 2016. Soil amendment using poplar woodchips to enhance the treatment of wastewater-originated nutrients. *Journal of environmental management,* 180**,** 517-525.

MEYER, S., GLASER, B. & QUICKER, P. 2011. Technical, economical, and climate-related aspects of biochar production technologies: a literature review. *Environmental science & technology,* 45**,** 9473-9483.

MOHAN, D., SARSWAT, A., OK, Y. S. & PITTMAN, C. U. 2014. Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent–a critical review. *Bioresource technology,* 160**,** 191-202.

MONTGOMERY, D. 2013. *Design and analysis of experiments,* USA, SAS Institute.

MOORMAN, T. B., PARKIN, T. B., KASPAR, T. C. & JAYNES, D. B. 2010. Denitrification activity, wood loss, and N 2 O emissions over 9 years from a wood chip bioreactor. *Ecological engineering,* 36**,** 1567-1574.

MYERS, R. L. 2015. *Treatment of Agricultural Stormwater Runoff by a Cascading System of Floodway Stormwater Containment Basins.*

NAVARRO-ORTEGA, A., ACUÑA, V., BELLIN, A., BUREK, P., CASSIANI, G., CHOUKR-ALLAH, R., DOLÉDEC, S., ELOSEGI, A., FERRARI, F. & GINEBREDA, A. 2015. Managing the effects of multiple stressors on aquatic ecosystems under water scarcity. The GLOBAQUA project. *Science of the Total Environment,* 503**,** 3-9.

NICK, T. 2018. Benefits of Biochar and its Applications for Runoff Water Management: Literature Review and Laboratory Report.

NSWPRIMEFACT. 2014. *Farm water quality and treatment* [Online]. NSW: Department of Primary Industries. Available:

References

https://www.dpi.nsw.gov.au/__data/assets/pdf_file/0013/164101/Farm-water-quality-and-treatment.pdf [Accessed].

NUR, T., SHIM, W. G., LOGANATHAN, P., VIGNESWARAN, S. & KANDASAMY, J. 2015. Nitrate removal using Purolite A520E ion exchange resin: batch and fixed-bed column adsorption modelling. *International Journal of Environmental Science and Technology,* 12**,** 1311-1320.

O'GEEN, A., BUDD, R., GAN, J., MAYNARD, J., PARIKH, S. & DAHLGREN, R. 2010. Mitigating nonpoint source pollution in agriculture with constructed and restored wetlands. *Advances in Agronomy.* Elsevier.

OAKES, W. C., LEONE, L. L., GUNN, C. J., DILWORTH, J., POTTER, M., YOUNG, M., DIEFES, H. & FLORI, R. 2000. *Engineering your future*, Great Lakes Press.

OUELLET-PLAMONDON, C., CHAZARENC, F., COMEAU, Y. & BRISSON, J. 2006. Artificial aeration to increase pollutant removal efficiency of constructed wetlands in cold climate. *Ecological Engineering,* 27**,** 258-264.

OYARZUN, D. I., HEMMATIFAR, A., PALKO, J. W., STADERMANN, M. & SANTIAGO, J. G. 2018. Adsorption and capacitive regeneration of nitrate using inverted capacitive deionization with surfactant functionalized carbon electrodes. *Separation and Purification Technology,* 194**,** 410-415.

PAIDAR, M., ROUŠAR, I. & BOUZEK, K. 1999. Electrochemical removal of nitrate ions in waste solutions after regeneration of ion exchange columns. *Journal of applied electrochemistry,* 29**,** 611-617.

PARK, K.-K., LEE, J.-B., PARK, P.-Y., YOON, S.-W., MOON, J.-S., EUM, H.-M. & LEE, C.-W. 2007. Development of a carbon sheet electrode for electrosorption desalination. *Desalination,* 206**,** 86-91.

POE, A. C., PIEHLER, M. F., THOMPSON, S. P. & PAERL, H. W. 2003. Denitrification in a constructed wetland receiving agricultural runoff. *Wetlands,* 23**,** 817-826.

QIU, Y., CHENG, H., XU, C. & SHENG, G. D. 2008. Surface characteristics of crop-residue-derived black carbon and lead (II) adsorption. *Water Research,* 42**,** 567-574.

RAMBAGS, F., TANNER, C. C., STOTT, R. & SCHIPPER, L. A. 2016. Fecal Bacteria, Bacteriophage, and Nutrient Reductions in a Full-Scale Denitrifying Woodchip Bioreactor. *Journal of Environmental Quality,* 45**,** 847-854.

REICHENBERGER, S., BACH, M., SKITSCHAK, A. & FREDE, H.-G. 2007. Mitigation strategies to reduce pesticide inputs into ground-and surface water

and their effectiveness; a review. *Science of the Total Environment,* 384**,** 1-35.

RICKERT, A. & MCSHANE, T. 2015. *Remediation of Agricultural Runoff using High Rate Algal Ponds* [Online]. BURDEKIN BOWEN INTEGRATED FLOODPLAIN MANAGEMENT ADVISORY COMMITTEE INC. Available: http://bbifmac.org.au/files/7414/7641/9308/HRAP_presentation.pdf [Accessed].

ROBERTS, W. 2008. *Algal Bloom Infographic* [Online]. Available: https://www.dreamstime.com/stock-illustration-harmful-algal-bloom-infographic-large-format-ecological-illustration-descriptive-text-depicts-causes-effects-image48960570 [Accessed 01/07/2018].

ROBERTSON, W. 2010. Nitrate removal rates in woodchip media of varying age. *Ecological Engineering,* 36**,** 1581-1587.

RYAN, B. F., JOINER, B. L. & CRYER, J. D. 2012. *MINITAB Handbook: Update for Release*, Cengage Learning.

S.SEAL. 2014.

Iraq to change the provincial map to be 30 provinces [Online]. Available: http://www.iraqdirectory.com/en/2014/01/12/26049/iraq-to-change-the-provincial-map-to-be-30-provinces.aspx [Accessed].

SAEED, T. & SUN, G. 2012. A review on nitrogen and organics removal mechanisms in subsurface flow constructed wetlands: dependency on environmental parameters, operating conditions and supporting media. *Journal of environmental management,* 112**,** 429-448.

SALILING, W. J. B., WESTERMAN, P. W. & LOSORDO, T. M. 2007. Wood chips and wheat straw as alternative biofilter media for denitrification reactors treating aquaculture and other wastewaters with high nitrate concentrations. *Aquacultural Engineering,* 37**,** 222-233.

SAMUEL, M. P., SENTHILVEL, S. & MATHEW, A. C. 2014. Performance evaluation of environmentally compatible stormwater filtration systems. *International Journal of Environmental Science and Technology,* 11**,** 1327-1342.

SCHENZEL, K. & FISCHER, S. 2001. NIR FT Raman spectroscopy–a rapid analytical tool for detecting the transformation of cellulose polymorphs. *Cellulose,* 8**,** 49-57.

References

SCHIPPER, L. A., ROBERTSON, W. D., GOLD, A. J., JAYNES, D. B. & CAMERON, S. C. 2010. Denitrifying bioreactors—an approach for reducing nitrate loads to receiving waters. *Ecological engineering,* 36**,** 1532-1543.

SHACKLEY, S., SOHI, S., BROWNSORT, P., CARTER, S., COOK, J., CUNNINGHAM, C., GAUNT, J., HAMMOND, J., IBARROLA, R. & MAŠEK, O. 2010. An assessment of the benefits and issues associated with the application of biochar to soil. *Department for Environment, Food and Rural Affairs, UK Government, London*.

SHAFIE, S. T., SALLEH, M. M., HANG, L. L., RAHMAN, M. & GHANI, W. 2012. Effect of pyrolysis temperature on the biochar nutrient and water retention capacity. *Journal of Purity, Utility Reaction and Environment,* 1**,** 293-307.

SHAO, L., WU, Z., ZENG, L., CHEN, Z., ZHOU, Y. & CHEN, G. 2013. Embodied energy assessment for ecological wastewater treatment by a constructed wetland. *Ecological modelling,* 252**,** 63-71.

SHAREEF, T. M. E. & ZHAO, B. 2016. The Fundamentals of Biochar as a Soil Amendment Tool and Management in Agriculture Scope: An Overview for Farmers and Gardeners. *Journal of Agricultural Chemistry and Environment,* 6**,** 38.

SHEN, Y.-S., WANG, S.-L., HUANG, S.-T., TZOU, Y.-M. & HUANG, J.-H. 2010. Biosorption of Cr (VI) by coconut coir: spectroscopic investigation on the reaction mechanism of Cr (VI) with lignocellulosic material. *Journal of hazardous materials,* 179**,** 160-165.

SHI, W., LI, H., CAO, X., LEONG, Z. Y., ZHANG, J., CHEN, T., ZHANG, H. & YANG, H. Y. 2016. Ultrahigh performance of novel capacitive deionization electrodes based on a three-dimensional graphene architecture with nanopores. *Scientific reports,* 6**,** 18966.

SHIKLOMANOV, I. A. 1998. *World water resources: a new appraisal and assessment for the 21st century: a summary of the monograph World water resources*, Unesco.

SHILTON, A., PRATT, S., DRIZO, A., MAHMOOD, B., BANKER, S., BILLINGS, L., GLENNY, S. & LUO, D. 2005. 'Active'filters for upgrading phosphorus removal from pond systems. *Water Science and Technology,* 51**,** 111-116.

SILBERBUSH, M. & LIPS, S. 1988. Nitrogen concentration, ammonium/nitrate ratio and NaCl interaction in vegetative and reproductive growth of peanuts. *Physiologia Plantarum,* 74**,** 493-498.

References

SOHI, S. P., KRULL, E., LOPEZ-CAPEL, E. & BOL, R. 2010. A review of biochar and its use and function in soil. *Advances in agronomy.* Elsevier.

SPOKAS, K. A., CANTRELL, K. B., NOVAK, J. M., ARCHER, D. W., IPPOLITO, J. A., COLLINS, H. P., BOATENG, A. A., LIMA, I. M., LAMB, M. C. & MCALOON, A. J. 2012. Biochar: a synthesis of its agronomic impact beyond carbon sequestration. *Journal of environmental quality,* 41**,** 973-989.

SRINIVASAN, A. & VIRARAGHAVAN, T. 2010. Oil removal from water by fungal biomass: a factorial design analysis. *Journal of Hazardous Materials,* 175**,** 695-702.

SRIVASTAVA, A., SINGH, S., AHN, C.-Y., OH, H.-M. & ASTHANA, R. K. 2013. Monitoring Approaches for a Toxic Cyanobacterial Bloom. *Environmental Science & Technology,* 47**,** 8999-9013.

STEFANAKIS, A. I. & TSIHRINTZIS, V. A. 2012. Effects of loading, resting period, temperature, porous media, vegetation and aeration on performance of pilot-scale vertical flow constructed wetlands. *Chemical engineering journal,* 181**,** 416-430.

STEINER, C., GLASER, B., GERALDES TEIXEIRA, W., LEHMANN, J., BLUM, W. E. & ZECH, W. 2008. Nitrogen retention and plant uptake on a highly weathered central Amazonian Ferralsol amended with compost and charcoal. *Journal of Plant Nutrition and Soil Science,* 171**,** 893-899.

STRATEGY, N. 2014. 9.9 SAND FILTERS.

STROCK, J., RANAIVOSON, A., FEYEREISEN, G., SPOKAS, K., MULLA, D. & ROSER, M. 2017. *Nutrient Removal in Agricultural Drainage Ditches*, Minnesota Department of Agriculture.

SUKOW, D. W., GAVRIELIDES, A., ERNEUX, T., MOONEYHAM, B., LEE, K., MCKAY, J. & DAVIS, J. 2010. Asymmetric square waves in mutually coupled semiconductor lasers with orthogonal optical injection. *Physical Review E,* 81**,** 025206.

SUSS, M. E., PORADA, S., SUN, X., BIESHEUVEL, P. M., YOON, J. & PRESSER, V. 2015. Water desalination via capacitive deionization: what is it and what can we expect from it? *Energy & Environmental Science,* 8**,** 2296-2319.

TALLEC, G., GARNIER, J., BILLEN, G. & GOUSAILLES, M. 2008. Nitrous oxide emissions from denitrifying activated sludge of urban wastewater treatment plants, under anoxia and low oxygenation. *Bioresource Technology,* 99**,** 2200-2209.

References

TAN, X., LIU, Y., ZENG, G., WANG, X., HU, X., GU, Y. & YANG, Z. 2015. Application of biochar for the removal of pollutants from aqueous solutions. *Chemosphere,* 125**,** 70-85.

TANNER, C., NGUYEN, M. & SUKIAS, J. 2005. Nutrient removal by a constructed wetland treating subsurface drainage from grazed dairy pasture. *Agriculture, ecosystems & environment,* 105**,** 145-162.

TANNER, C. C. & KADLEC, R. H. 2013. Influence of hydrological regime on wetland attenuation of diffuse agricultural nitrate losses. *Ecological engineering,* 56**,** 79-88.

TILMAN, D., HILL, J. & LEHMAN, C. 2006. Carbon-negative biofuels from low-input high-diversity grassland biomass. *Science,* 314**,** 1598-1600.

TITIRICI, M.-M., WHITE, R. J., FALCO, C. & SEVILLA, M. 2012. Black perspectives for a green future: hydrothermal carbons for environment protection and energy storage. *Energy & Environmental Science,* 5**,** 6796-6822.

TOWN, T. 2017. Agricultural Runoff. *ENVIRONMENTAL HEALTH CONCERNS AND TOXIC CHEMICALS WHERE YOU LIVE, WORK, AND PLAY*.

U.S.EPAGENCY. 2011. *Principles of Design and Operations of Wastewater*

Treatment Pond Systems for Plant Operators, Engineers,

and Managers [Online]. Available: https://www.epa.gov/sites/production/files/2014-09/documents/lagoon-pond-treatment-2011.pdf [Accessed].

U.S_EPA, E. P. A. 2005. *Protecting Water Quality From Agricultural Runoff* [Online]. USA. Available: https://webcache.googleusercontent.com/search?q=cache:a__uqU5kjWMJ:https://www.epa.gov/sites/production/files/2015-09/documents/ag_runoff_fact_sheet.pdf+&cd=1&hl=en&ct=clnk&gl=au [Accessed 2018].

UGGETTI, E., HUGHES-RILEY, T., MORRIS, R. H., NEWTON, M. I., TRABI, C. L., HAWES, P., PUIGAGUT, J. & GARCÍA, J. 2016. Intermittent aeration to improve wastewater treatment efficiency in pilot-scale constructed wetland. *Science of the Total Environment,* 559**,** 212-217.

UGURLU, A. & OZTURKCU, S. D. 2018. Treatment of Nitrocellulose Industry Watewaters by Upflow Denitrification Filter: Effect of Packing Media and Recirculation. *Environmental Processes,* 5**,** 81-94.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY, E. 1994. Water Quality Standards Handbook.

References

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY, E. 2000. *History of Drinking Water Treatment* [Online]. Available: https://nepis.epa.gov/Exe/ZyNET.exe/P1002SMN.txt?ZyActionD=ZyDocument&Client=EPA&Index=2000%20Thru%202005&Docs=&Query=&Time=&EndTime=&SearchMethod=1&TocRestrict=n&Toc=&TocEntry=&QField=&QFieldYear=&QFieldMonth=&QFieldDay=&UseQField=&IntQFieldOp=0&ExtQFieldOp=0&XmlQuery=&File=D%3A%5CZYFILES%5CINDEX%20DATA%5C00THRU05%5CTXT%5C00000019%5CP1002SMN.txt&User=ANONYMOUS&Password=anonymous&SortMethod=h%7C-&MaximumDocuments=1&FuzzyDegree=0&ImageQuality=r75g8/r75g8/x150y150g16/i425&Display=hpfr&DefSeekPage=x&SearchBack=ZyActionL&Back=ZyActionS&BackDesc=Results%20page&MaximumPages=1&ZyEntry=1 [Accessed].

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY, E. 2010. *Waste and Cleanup Risk Assessment Glossary* [Online]. Office of Land and Emergency Management Available: https://ofmpub.epa.gov/sor_internet/registry/termreg/searchandretrieve/glossariesandkeywordlists/search.do?details=&glossaryName=Waste%20and%20Cleanup%20Risk%20Assess#formTop [Accessed 18/12 2017].

USBI. 2016. *Biochar Then & Now* [Online]. Building the Future from the Ground Up. Available: http://biochar-us.org/biochar-then-now [Accessed].

USGS. 2016. *How much water is there on, in, and above the Earth?* [Online]. USA: USA. gov. Available: https://water.usgs.gov/edu/earthhowmuch.html [Accessed 27/04 2017].

UZUN, H. I. & DEBIK, E. 2019. Economical approach to nitrate removal via membrane capacitive deionization. *Separation and Purification Technology,* 209**,** 776-781.

VAN DRIEL, P., ROBERTSON, W. & MERKLEY, L. 2006. Denitrification of agricultural drainage using wood-based reactors. *Transactions of the ASABE,* 49**,** 565-573.

VANLANGENDONCK, Y., CORBISIER, D. & VAN LIERDE, A. 2005. Influence of operating conditions on the ammonia electro-oxidation rate in wastewaters from power plants (ELONITA™ technique). *Water research,* 39**,** 3028-3034.

VON AHNEN, M., PEDERSEN, P. B., HOFFMANN, C. C. & DALSGAARD, J. 2016. Optimizing nitrate removal in woodchip beds treating aquaculture effluents. *Aquaculture,* 458**,** 47-54.

VYMAZAL, J. 2007. Removal of nutrients in various types of constructed wetlands. *Science of the total environment,* 380**,** 48-65.

References

VYMAZAL, J. 2010. Constructed wetlands for wastewater treatment: five decades of experience. *Environmental science & technology,* 45**,** 61-69.

VYMAZAL, J. 2013a. Emergent plants used in free water surface constructed wetlands: a review. *Ecological engineering,* 61**,** 582-592.

VYMAZAL, J. 2013b. The use of hybrid constructed wetlands for wastewater treatment with special attention to nitrogen removal: a review of a recent development. *Water research,* 47**,** 4795-4811.

VYMAZAL, J. & BŘEZINOVÁ, T. 2015. The use of constructed wetlands for removal of pesticides from agricultural runoff and drainage: a review. *Environment international,* 75**,** 11-20.

WANG, L. & LI, T. 2015. Effects of seasonal temperature variation on nitrification, anammox process, and bacteria involved in a pilot-scale constructed wetland. *Environmental Science and Pollution Research,* 22**,** 3774-3783.

WARD, F. & MONDAY, J. 2007. Canadian Content Forums> Themes> Science & Environment> Climate Change> How the GW myth is perpetuated.

WATER_ONLINE. 2017. *About Nutrient Removal* [Online]. Water Online. Available: https://www.wateronline.com/solution/nutrient-removal [Accessed 2017].

WELGEMOED, T. & SCHUTTE, C. 2005. Capacitive deionization technology™: an alternative desalination solution. *Desalination,* 183**,** 327-340.

WROBEL-TOBISZEWSKA, A., BOERSMA, M., SARGISON, J., ADAMS, P., SINGH, B., FRANKS, S., BIRCH, C. & CLOSE, D. 2017. Nutrient changes in potting mix and Eucalyptus nitens leaf tissue under macadamia biochar amendments. *Journal of Forestry Research***,** 1-11.

WU, H., FAN, J., ZHANG, J., NGO, H. H., GUO, W., HU, Z. & LIANG, S. 2015. Decentralized domestic wastewater treatment using intermittently aerated vertical flow constructed wetlands: impact of influent strengths. *Bioresource technology,* 176**,** 163-168.

WU, S., KUSCHK, P., BRIX, H., VYMAZAL, J. & DONG, R. 2014. Development of constructed wetlands in performance intensifications for wastewater treatment: a nitrogen and organic matter targeted review. *Water research,* 57**,** 40-55.

XIONG, J., GUO, G., MAHMOOD, Q. & YUE, M. 2011. Nitrogen removal from secondary effluent by using integrated constructed wetland system. *Ecological Engineering,* 37**,** 659-662.

References

YANG, J., LI, H., ZHANG, D., WU, M. & PAN, B. 2017. Limited role of biochars in nitrogen fixation through nitrate adsorption. *Science of The Total Environment,* 592**,** 758-765.

YANG, L., CHANG, H.-T. & HUANG, M.-N. L. 2001. Nutrient removal in gravel- and soil-based wetland microcosms with and without vegetation. *Ecological engineering,* 18**,** 91-105.

ZADEH, S. M., HUNT, D. V., LOMBARDI, D. R. & ROGERS, C. D. 2013. Shared Urban Greywater Recycling Systems: Water Resource Savings and Economic Investment. *Sustainability,* 5**,** 2887-2912.

ZHAI, J., XIAO, J., RAHAMAN, M. H., JOHN, Y. & XIAO, J. 2016. Seasonal variation of nutrient removal in a full-scale artificial aerated hybrid constructed wetland. *Water,* 8**,** 551.

ZHANG, D., GERSBERG, R. M. & KEAT, T. S. 2009. Constructed wetlands in China. *Ecological Engineering,* 35**,** 1367-1378.

ZHANG, L.-Y., ZHANG, L., LIU, Y.-D., SHEN, Y.-W., LIU, H. & XIONG, Y. 2010. Effect of limited artificial aeration on constructed wetland treatment of domestic wastewater. *Desalination,* 250**,** 915-920.

ZHANG, X., WANG, H., HE, L., LU, K., SARMAH, A., LI, J., BOLAN, N. S., PEI, J. & HUANG, H. 2013. Using biochar for remediation of soils contaminated with heavy metals and organic pollutants. *Environmental Science and Pollution Research,* 20**,** 8472-8483.

ZHAO, B., O'CONNOR, D., ZHANG, J., PENG, T., SHEN, Z., TSANG, D. C. & HOU, D. 2018. Effect of pyrolysis temperature, heating rate, and residence time on rapeseed stem derived biochar. *Journal of Cleaner Production,* 174**,** 977-987.

ZHOU, X., JIA, L., LIANG, C., FENG, L., WANG, R. & WU, H. 2018. Simultaneous enhancement of nitrogen removal and nitrous oxide reduction by a saturated biochar-based intermittent aeration vertical flow constructed wetland: Effects of influent strength. *Chemical Engineering Journal,* 334**,** 1842-1850.

ZOU, Y., HU, Z., ZHANG, J., FANG, Y., LI, M. & ZHANG, J. 2017. Mitigation of N2O Emission from Aquaponics by Optimizing the Nitrogen Transformation Process: Aeration Management and Exogenous Carbon (PLA) Addition. *Journal of agricultural and food chemistry,* 65**,** 8806-8812.

Appendix A

Appendix A

General Factorial Regression: Nitrate Removal (mg/g ... e Conc. (mg/L)

Factor Information

Factor	Levels	Values
Flow rate (mL/min)	3	2, 4, 10
Nitrate Conc. (mg/L)	3	5, 10, 15

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	8	0.000060	0.0000008	21.79	0.000
Linear	4	0.000055	0.000014	39.43	0.000
Flow rate (mL/min)	2	0.000028	0.000014	40.12	0.000
Nitrate Conc. (mg/L)	2	0.000027	0.000013	38.74	0.000
2-Way Interactions	4	0.000006	0.000001	4.16	0.015
Flow rate (mL/min)*Nitrate Conc. (mg/L)	4	0.000006	0.000001	4.16	0.015
Error	18	0.000006	0.0000000		
Total	26	0.000067			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.0005881	90.64%	86.48%	78.94%

Coefficients

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	0.003595	0.000113	31.76	0.000	
Flow rate (mL/min)					
2	0.001387	0.000160	8.66	0.000	1.33
4	-0.000378	0.000160	-2.36	0.030	1.33
Nitrate Conc. (mg/L)					
5	-0.001355	0.000160	-8.46	0.000	1.33
10	0.000343	0.000160	2.14	0.046	1.33
Flow rate (mL/min)*Nitrate Conc. (mg/L)					
2 5	-0.000562	0.000226	-2.48	0.023	1.78
2 10	-0.000207	0.000226	-0.92	0.372	1.78
4 5	-0.000113	0.000226	-0.50	0.625	1.78
4 10	0.000217	0.000226	0.96	0.351	1.78

Regression Equation

Nitrate Removal (mg/g MBC) = 0.003595 + 0.001387 Flow rate (mL/min)_2
- 0.000378 Flow rate (mL/min)_4
- 0.001009 Flow rate (mL/min)_10
- 0.001355 Nitrate Conc. (mg/L)_5
+ 0.000343 Nitrate Conc. (mg/L)_10
+ 0.001012 Nitrate Conc. (mg/L)_15
- 0.000562 Flow rate (mL/min)*Nitrate Conc. (mg/L)_2 5
- 0.000207 Flow rate (mL/min)*Nitrate Conc. (mg/L)_2 10
+ 0.000769 Flow rate (mL/min)*Nitrate Conc. (mg/L)_2 15
- 0.000113 Flow rate (mL/min)*Nitrate Conc. (mg/L)_4 5
+ 0.000217 Flow rate (mL/min)*Nitrate Conc. (mg/L)_4 10
- 0.000104 Flow rate (mL/min)*Nitrate Conc. (mg/L)_4 15
+ 0.000674 Flow rate (mL/min)*Nitrate Conc. (mg/L)_10 5
- 0.000009 Flow rate (mL/min)*Nitrate Conc. (mg/L)_10 10
- 0.000665 Flow rate (mL/min)*Nitrate Conc. (mg/L)_10 15

Fits and Diagnostics for Unusual Observations

Obs	Nitrate Removal (mg/g MBC)	Fit	Resid	Std Resid	
10	0.004160	0.003065	0.001095	2.28	R

R Large residual

Means

Term	Fitted Mean	SE Mean
Flow rate (mL/min)		
2	0.004981	0.000196
4	0.003217	0.000196
10	0.002586	0.000196
Nitrate Conc. (mg/L)		
5	0.002240	0.000196
10	0.003937	0.000196
15	0.004607	0.000196

Flow rate (mL/min)*Nitrate Conc. (mg/L)

2 5	0.003065	0.000340
2 10	0.005116	0.000340
2 15	0.006763	0.000340
4 5	0.001749	0.000340
4 10	0.003776	0.000340
4 15	0.004124	0.000340
10 5	0.001906	0.000340
10 10	0.002919	0.000340
10 15	0.002933	0.000340

Flow rate (mL/min)*Nitrate Conc. (mg/L)