UNIVERSITY OF SOUTHERN QUEENSLAND AUSTRALIA

THE EFFECT OF BIOCHAR ADDITION ON PLANT MAJOR NUTRIENT UPTAKE IN HYDROPONIC SYSTEMS

A thesis submitted by

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ABSTRACT

Farming is a vital part of people's lives worldwide. New methods for increasing agricultural productivity, such as aquaponics and aeroponics can be costly and slow to implement. Whereas conventional approaches tend to use more fertiliser to increase productivity, significantly impacting the environment and human health.

This study examines if the ancient technology of hydroponics, can benefit from the addition of biochar (BC) in its growth media. Measurements included effects on pH, electrical conductivity (EC), and macronutrients, coupled with the effects on plant chlorophyll, photosynthesis, dry weight, leaf area, height and nutrient contents.

Prior to selecting coconut shell biochar (CSBC), the CSBC was applied at four rates (0, 5, 25, and 50%) using two types of growth media (washed river sand and peatmoss). Initial tests used a largely inert growth media to eliminate as many variables in the system under test. Later column tests used CSBC mixed with more commercially representative mixtures of sand and peatmoss.

Tests were initially conducted at a small laboratory scale, then under temperature-controlled conditions in a glasshouse, before making final observations with a small farm trial. Throughout these tests, CSBC's effects on pH, EC and macronutrients (nitrate, phosphate, potassium, calcium, magnesium and sulphate) retention and release were monitored. In the Glasshouse tests, CSBC's effect on the previously optimised parameters were measured for the two irrigation solutions (hydroponic nutrient solution and pure water). Plant physiochemical characteristics (nitrate, phosphate, potassium, calcium, magnesium, sulphate, leaf area, plant height, dry weight, photosynthesis, and chlorophyll) were monitored, with a commercial SCADA package used to control the system.

As CSBC rates increased pH increased and EC decreased, most nutrient retention increased, except for potassium and magnesium, e.g. the highest release of nutrients (56 - 60 $mg.L^{-1}$) was from the control (0% BC) whereas the lowest was from the 25-50% BC (100 - 108 $mg.L^{-1}$). For commercial usage it was determined that the 5 - 10% BC rate showed the most positive combination of effects on plant growth and nutrient sorption/desorption.

THESIS CERTIFICATION

This Thesis is entirely the work of Mohammed Taha Haraz except where otherwise acknowledged. The work is original and has not previously been submitted for any other award, except where acknowledged.

Principal Supervisor: Dr Les Bowtell

Associate Supervisor: Dr Saddam Al-Lwayzy

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

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LIST OF SYMBOLS

BC	Biochar
CSBC	Coconut Shell Biochar
PSBC	Pecan Shell Biochar
MSBC	Macadamia Shell Biochar
PSBC900	Pecan Shell Biochar prepared at 900 °C
MSBC900	Macadamia Shell Biochar prepared at 900 °C
PSBC500	Pecan Shell Biochar prepared at 500 °C
MSBC500	Macadamia Shell Biochar prepared at 500 °C
BaBC	Banana skin Biochar
WoBC	Wood Biochar
NS	Nutrient Solution
DW	Deionised water
SD	Standard Deviation
H_2O	Water
TNS	Treated hydroponic solution
Ctrl	Control

CHAPTER 1 INTRODUCTION:

Water retention and soil pollution pose a significant problem to the sustainability of crop production and food security (Falkenmark and Lannerstad, 2004, Jonathan et al., 2005, Awad et al., 2017). Besides, the world population subjected to reach 9.7 billion by 2050. Also, it was estimated that 50% of the cultivable land worldwide will not be farmable (www.un.org/development, 2017). Increasing world population resulted in more demand for food, hence, a new system should be introduced to cover the rapidly growing demand of food with minimum use of natural resource and less cost (Gashgari et al., 2018). As farming is one of the vital aspects in any community's life, and as it is one of the most significant water demanding and environment polluting activities (Falkenmark and Lannerstad, 2004, Jonathan et al., 2005), more attention has been paid to solving such problems.

Hydroponics or soilless culture was introduced as the new-old cultivation method to solve such problems. Hydroponics is a method of growing plants without using soil where the plants are fed by supplying them with a nutrient solution (Figure 1.1). To support plants, different growth media are used such as peatmoss, sand, wool, etc. Hydroponic showed an increase in plant productivity and more effective management of water and fertilisers (Sharma et al., 2018, Gashgari et al., 2018). It is well known that plants quantity and quality is higher in hydroponics than in the traditional methods of growing plants (Davidson and Szmidt, 1992, Olle et al., 2012).

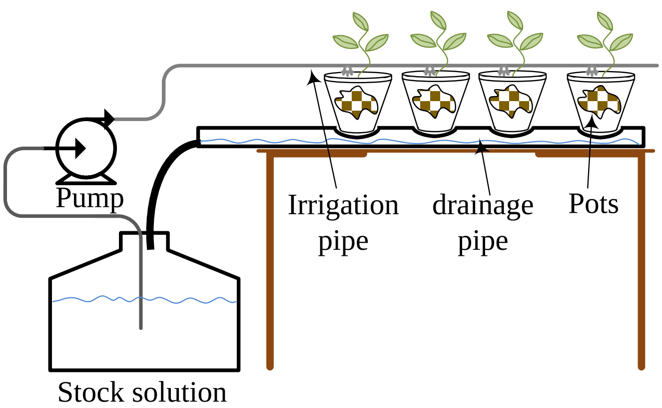


Figure 1.1: Closed Hydroponic System

Nutrients applied to plants can be lost in various ways such as leaching individually or by precipitated with organometal complexes, volatilising, and bound to organic matter. Approximately, half of the applied nutrients are taken by plants and the rest can be lost (Liu et al., 2010, Adesemoye et al., 2009). Around 160 kg of N and 30 kg of P are lost from agriculture soils annually by leaching from traditional system (Herzog et al., 2008, Sims et al., 1998) (Figure 1.2). There are few studies on nutrients loses in hydroponic. Antón et al. (2004) demonstrated that fertilisers' amendment for hydroponic crops has the most negative impact on the environment. Bugbee (2003) stated that the recovery of some nutrients (50% of calcium and 70% of nitrogen) was low in recirculating systems. Sanjuan-Delmás et al. (2020) reported that there is a gap in the nutrient retention in hydroponic growth media. Stated by Yoshihara et al. (2016) that volatilisation might be a major source of nutrient loss in hydroponics. Nitrogen loss in a form of N_2O can be around 16% (Hashida et al., 2014b, Yoshihara et al., 2016) (Figure 1.3).

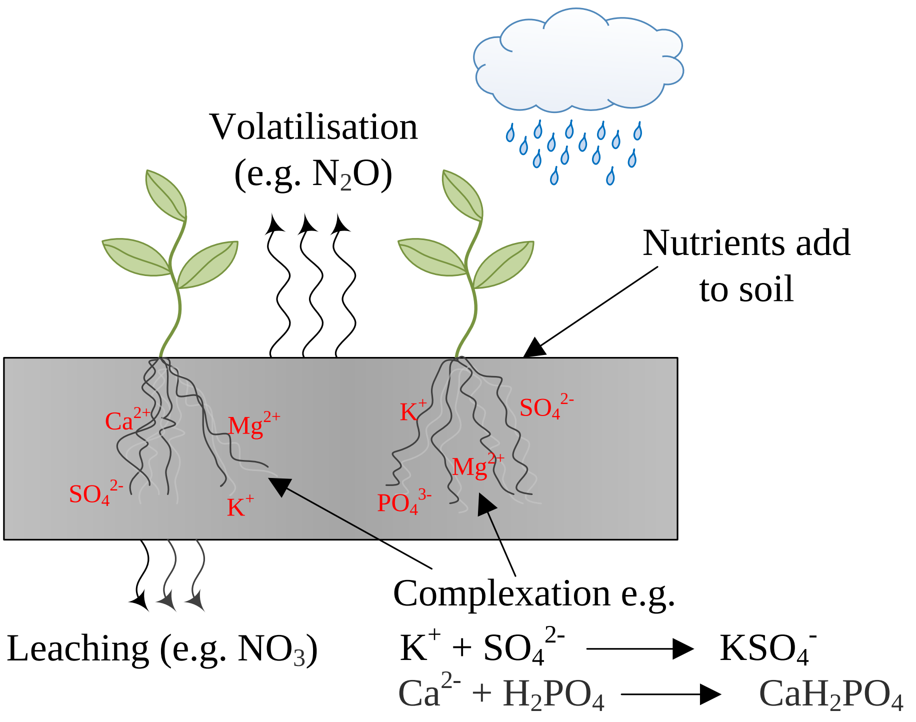


Figure 1.2: Nutrient Loss Pathways in Soil

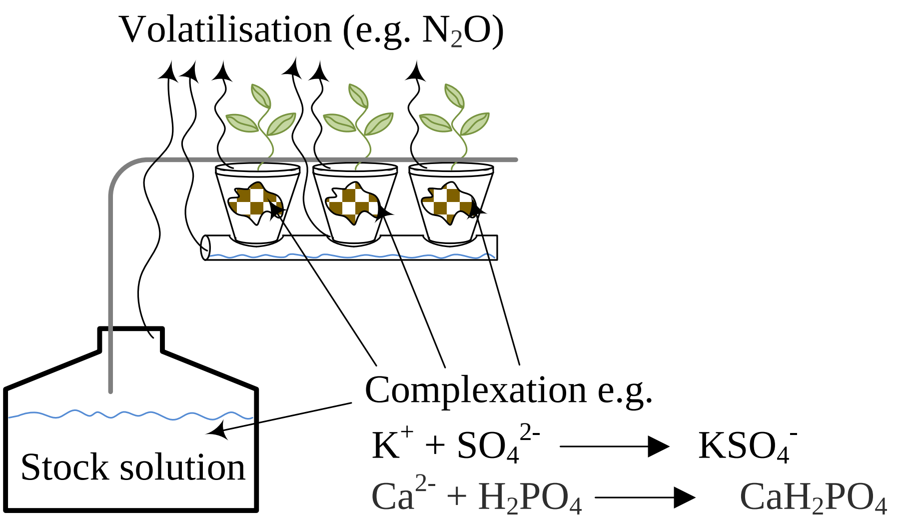


Figure 1.3: Hydroponic System Nutrient Loss Pathways

Hydroponics has also shown early plant production compared to soil cultivation (Valenzano et al., 2008). There are many types of hydroponics, in this project, the recycling effluents used as it is the best eco-friendly system (Bar-Yosef, 2008) also to increase nutrient and water use efficiency as well as reduce the cost of production (Grewal et al., 2011, Rouphael et al., 2004). It was also shown that recycling nutrients save water and fertiliser, while reducing water pollution (Savvas, 2002, Carmassi et al., 2005). Comparing between hydroponics and traditional cultivation, the former is considered better due to its potential to cover future food needs in a sustainable way (Gashgari et al., 2018). The traditional cultivation has drawbacks such as high land and water requirements, high pesticides, nutrient runoff, and soil degradation (Killebrew and Wolff, 2010). In a study conducted by Barbosa et al. (2015), comparing conventional agriculture to hydroponics using lettuce as a test plant, hydroponics offered 11 ± 1.7 times higher yield than traditional one. There was also another study to compare tomato cultivation plants in hydroponics and soil, hydroponic closed-cycle was better in term of yield and water use efficiency (Valenzano et al., 2008). The yield of lettuce grown hydroponically is around 10 times higher than conventional agricultural methods (Barbosa et al., 2015). Water savings with hydroponics can reach as high as 85-90% compared to conventional agriculture (Sharma et al., 2018). Gashgari et al. (2018) reported that hydroponics have higher plant growth rate and can achieve a 20-25% higher yield than traditional systems. A closed hydroponic system is the most effective system in reducing water and fertiliser use while increasing plant productivity (Maboko et al., 2011).

However there are several advantages of hydroponics, there are some drawbacks such as environment pollution by inorganic minerals and substrates. The common practice of using concentrated nutrient solution in hydroponics can be problematic as cultivators may have to discard the solution after utilising it for certain number of planting cycles. Christie and Nichols (2014) showed that around 8000 litres of hydroponic solutions discarded each time (planting cycle). This can occur daily in summer and weekly in winter. Discarded solution is a significant issue that can cause environmental pollution. Additionally, growers need to replenish nutrients in the solution tanks, hence there is an additional cost to grow the plants. Another issue is that the demand for soilless growth media has increased recently with the rise in concern for the environment, especially for a non-renewable substrate such as peat. This factor led to seeking out alternative materials (Fascella, 2015). The media which is going to be used should be of low-cost and high-quality as peatmoss price has increased (Fascella, 2015). Allaire et al. (2001) and Allaire et al. (2005) drew researchers' attention to various elements required in any new substrate (sourced of organic and recyclable material which are easy to obtain and dispose of; more cost-effective; and, suitable for plant growth). Neocleous and Polycarpou (2010) suggested materials that minimise environmental impact and transportation costs. Locally sourced materials are recommended to be used in hydroponics.

Biochar is inexpensive, a rich carbon product, and eco-friendly and available worldwide. It is produced by heating biomass (wood, leaves or manure) at 450° - 1000 °C in a closed or semi-closed space with a limited amount of air, or no air at all (Lehmann and Joseph, 2015, Lehmann, 2007). Biochar types, chemical and physical properties can vary depending on pyrolysis conditions and feedstocks (Keiluweit et al., 2010). Many researchers have pointed out the advantages of using BC plants grown in soil and improving microbial activity (Kloss et al. 2014; Mohamed et al. 2017; Woldetsadik et al. 2016). Other researchers have shown some BC influences on reducing plant nutrients in leachate (Borchard et al., 2012c, Knowles et al., 2011, Troy et al., 2014, Yao et al., 2012a, Uchimiya et al., 2010). Biochar can be used to reduce water usage and can help plants to resist the drought (Mulcahy et al., 2013, Basso et al., 2013). In environmental application BC has the ability to ameliorate soil and wastewater contaminants (Houben et al., 2013, Kim et al., 2015, Fahmi et al., 2018), carbon sequestering (Steinbeiss et al., 2009), as well as reducing of gaseous emissions (Karhu et al., 2011, Zhang et al., 2010, Jia et al., 2012). Dumroese et al. (2011) stated that 25% BC of growth media improved water retention. Biochar could provide farmers with a cost-effective, supplement substrate fertiliser (Dunlop et al., 2015). Biochar can be used as organic protection for plants (Gravel et al., 2013). Using BC in a strawberry farm reduced the plant resistance and demonstrated a significant effect of BC on reducing plant disease (Harel et al., 2012). The effect of BC on plant productivity are heavily dependent upon the rate and BC type (Alburquerque et al., 2014a).

While the use of BC in soils is widely researched, there is far less research on the use of BC in hydroponics. Moreover, the influence of BC on hydroponically grown plants is still not fully understood. Using material such as BC can not only reduce the additional cost of using more nutrients, it also reduces environmental harm by reducing carbon emission being a product of recycled waste (Adeyemi and Idowu, 2017). Ain Najwa et al. (2014) reported the advantages of using BC with various soilless growth media with cherry tomato. Also, BC can provide plants with nutrient sustenance (Song et al., 2014). Graber et al. (2010) stated that there was a significant improvement in sweet pepper Maccabi (Hazera Genetics, Israel) productivity and growth by adding wood-derived BC growth media. The combination of peatmoss with BC has shown a significant impact on plant productivity and nutrient retention. Ismail et al. (2004) and Ismail et al. (2001) stated that cauliflower and Pak Choy showed high yield and better growth when BC mixed with peatmoss compared to peatmoss alone. Various vegetables (tomato, cucumber, and lettuce) grown in a mixture of hydroponic media demonstrated a higher yield than when grown in soil (Olle et al., 2012). Nutrients such as K, Mg, Mn, and Zn can be released from BC which can act in the plants' favour (Akhtar et al., 2014). Biochar can also be used as a host for microorganism which enhances nutrient uptake (Kim et al., 2017, Rehman et al., 2016, Lee et al., 2015). Biochar can aid in the maintenance of favourable aeration and moisture at the plant root system (Akhtar et al., 2014). Abiven et al. (2015) stated that BC increased the root biomass to roughly twice the size of non-BC treated plants. It was noticed that BC increased micronutrients in maize as well as plant height, shoot dry matter and root length (Puga et al., 2015). Adeyemi and Idowu (2017) reported that BC can increase microbar activity, nutrient retention capacity and high carbon sequestration ability. Beck et al. (2011) showed that the amendment of greenroof media with 7% BC decreased phosphate and nitrate in runoff and increased water retention.

1.1 Aims

This project is aimed to investigate the effect of Coconut Shell Biochar (CSBC) on: **1)** plant macronutrients in a hydroponic nutrient solution and **2)** plants productivity in hydroponics using washed river sand and peatmoss as growth media. Leafy vegetables are the most promising plants to harvest using a hydroponic system (Sharma et al., 2018). Thus Rocket (*Eruca sativa*) was selected as a model plant in this study.

1.2 Hypotheses

Biochar has shown a significant impact on plant nutrients elements, plants productivity, soils characteristics, biotic and environment with soil-grown plants. The hypotheses of this project is that BC may have a similar impact on nutrients, plants, growth media, biotic and the context in hydroponics as the one in soils.

1.3 Objectives

1. Preform preliminary tests to select appropriate BC for further trials
2. Using a contrive approach (column tests) to limit confounding issues to determine the nutrient retention and release characteristics of the chosen BC using washed river sand on macronutrient in a lab environment.
3. Using the same approach in the second objective but with more realistic growth media (peatmoss) in a lab environment.
4. Evaluate the impact of BC on plants and their macronutrient elements in a glasshouse hydroponic farm.
5. Confirm previous lab and contrive synthesis system results on a real farm environment.

1.4 Project Overview

The project was divided into three phases to achieve the objectives (Section 1.3).

1.4.1 Stage I (Preliminary Tests)

To select the best BC for nutrient adsorption and release and BC effects on pH and EC through preliminary tests (Chapter 3) using three types of BC; coconut shell biochar (CSBC), pecan shell biochar (PSBC) and macadamia shell biochar (MSBC) layer with washed river sand.

This stage required:

- Biochar preparation (Section 3.1.2)
- Characterisation of BCs and sand
- Column tests (preliminary tests)

Five trials were conducted at this stage (preliminary tests):

- The effect of BC and sand (raw BC and sand) on pH, EC and nitrate without washing the BC or the sand.
- The effect of BC r and sand on pH, EC and NO_3 after washing both BC and sand with distilled water for 4 times. Prior to that, the sand was washed 4 times with tap water to get rid of any organic or clay in the sand.
- The effect of BC and sand on pH, EC and NO_3 after washing and sterilisation (using an autoclave) of both the sand and BC. The BC was washed with deionised water for 4 times to remove any flow. The sand was washed with tap water 3-4 to remove bulk contaminants then finally flashed with deionised water to remove any residual contaminants.
- Measure changes in pH level, EC level, and NO_3 concentration with different flow rate. Three flow rates were used (3, 5, and 10 ml/min) to observe pH, EC and NO_3 concentration affects.
- Observe CSBC rate effects on pH, EC and NO_3 in a nutrient solution. Three rates of BC were mixed with the growth media (25%, 50%, and 100% of a column size) compared to the configuration used in test number 2 and 3 which was 1.8% of the column. Observing a column of ~300 ml (40 mm diameter 250 mm height).

1.4.2 Stage II (Column Tests)

In this stage, the effect of the best-performed CSBC from the prior tests was tested for pH, EC and plant macronutrient retention and release.

This stage contains two laboratory experiments:

- Using CSBC with an inert washed river sand to monitor plant macronutrient retention and release as well as pH and EC measurement in the form of column tests (Chapter 4). This stage was conducted as follows; sand was sieved and washed with tap water to minimise any presence of organic and clay materials followed by further rinsing with deionised water to reduce pH and EC levels as well as reduce the presence of other nutrients. Biochar also was washed to reduce pH and EC level as well as reduce ash content. Both the BC and sand were sterilised using an autoclave. Biochar was mixed with and sand in 4 rates (0, 5, 25, and 50%).
- Testing the effect of CSBC mixed with peatmoss on plant macronutrients retention and release as well as pH and EC in column tests (Chapter 5). This stage was conducted as follows:

  Biochar was washed and sterilised then mixed in 4 ratios (as in the previous) with the peatmoss. In both tests (BC with sand and BC with peatmoss) peristaltic pumps were used to water the columns then the outcome to the same container (closed hydroponic system). The nutrient solution and the peatmoss were provided by K Farm. This test was conducted using an industry standard hydroponic media of peatmoss to observe any noticeable difference between a standard growth media and sand.

1.4.3 Stage III (Glasshouse and Farm Experiments)

The effect of CSBC on rocket plants (*Eruca sativa*) and irrigation solutions was tested in two experiments:

- The effect of CSBC on the rocket (*Eruca sativa*) in a glasshouse hydroponic farm (Chapter 6). Changes in plants nutrient content (NO_3, PO_4, K, Ca, MG, and SO_4) as well as chlorophyll, photosynthesis, leaf area, plant height, overground-dry weight. Changes in the stock solution, pH, EC NO_3, PO_4, K, Ca, MG, and SO_4 of the stock solution were monitored during the experiment.
- The impact of CSBC on the rocket (*Eruca sativa*) in a local hydroponic farm (Chapter 7). Changes in plants nutrient content (NO_3, PO_4, K, Ca, MG, and SO_4), chlorophyll, photosynthesis, leaf area, plant height, and overground-dry weight were measured in this experiment.

CHAPTER 2 LITERATURE REVIEW:

Poor agricultural practices, deforestation, overgrazing, and industrialization are growing global concerns. These days, increasing soil-nutrient depletion which is leading to plant nutrient deficiencies has been reported everywhere. In recent times BC has become of interest for soil nutrient management including contaminated soils, with many other applications in environmental remediation and carbon sequestration.

Scientists and researchers desire to increase the productivity of the crop, for the purpose of improving the quality and quantity of the products, and for the undamaged and unspoiled environment. Hydroponics is one of the solutions which can be an alternative method to soil cultivation. Some remedial organic biomass (biochar) materials have been suggested to solve these kinds of problems. Key evidence shows an improvement of water efficiency and plant productivity by using it properly. The main objective of this study is to assist in the reduction of problems like nutrient runoff (Lehmann and Rondon, 2006); algal bloom growth in nutrient solutions; and, reducing water contamination mainly carried out by heavy metals and pesticides. This chapter will provide insights for future research directions in order to establish effective BC uses in hydroponics.

2.1 Introduction

Hydroponic or soilless culture is a method of growing plants using water-based, nutrient-rich solution. Plants are fed with water-soluble macronutrient and micronutrient such as N, P, K, Ca, Mg, S, Fe, B, Zn, Cl, Mo, Ni, Cu, and Mn. Hydroponics can be a solution for salinity and lack of water dilemmas for countries in arid and semi-arid regions in the world. Soilless culture has led to better yield quantity and quality (Davidson and Szmidt, 1992). Hydroponics show better management of water and improvement of plant productivity (Rouphael et al., 2004). However, there are still some drawbacks such as the cost of constructing and maintaining hydroponic farms; the cost of using special growth media; and the discarding of nutrient solutions after being used. Even with all these drawbacks of hydroponic farms, they are still much better than using soil cultivation because fruits' quality and quantity are higher in hydroponics than soil cultivation. This results in more income. From the previous statement on hydroponic drawbacks, especially dealing with nutrients and their effects on the environment and the outcome, BC is the targeted material to solve or elevate some of the hydroponic problems. Biochar shows significant results of improving plant productivities; nutrient availability and reducing their leaching; soil microbial activities; decreasing water consumption; reducing greenhouse gas emissions; and positively affecting soil chemical and physical characteristics (Jia et al., 2012, Lehmann and Joseph, 2015, Hashida et al., 2014a). A brief review of BC usage in soils will be shown in this article followed by a review of using BC in hydroponic cultivation.

2.2 Biochar

Biochar and activated carbon are biomass product produced in a limited or no oxygen environment (Lehmann and Joseph, 2015, Lehmann and Rondon, 2006). In other words, BC is the remnant carbonaceous material when biomass is heated (from 400 up to 1000 °C) in a closed space with little or no air (Lehmann and Joseph, 2012). The characteristics and properties of BC depend on three main factors: feedstock, pyrolysis temperature and residence time (Lehmann and Joseph, 2015, Singh et al., 2010, Tang et al., 2013). Biochar prepared under low or variable temperature can have phytotoxic characteristics (Mukherjee and Lal, 2014). The pH value of BC is contingent on the feedstock and the process temperature. Plant derived BC tends to be acidic with low (200 – 400 °C) pyrolysis temperatures and alkaline with high (750 – 1000 °C) pyrolysis temperatures (Zhang et al., 2011). As BC is largely inert carbonations material it generally resist any further decomposition especially that made at higher temperatures (Biederman and Harpole, 2013). Figures 2.1, 2.2, and 2.3 show three types of BC structure and porosity observed with Phenom Prox Desktop Scanning Electron Microscope, from Thermo Scientific (SEM-P) at the University of Southern Queensland. The three types of were produced coconut, pecan and macadamia shell feedstocks.

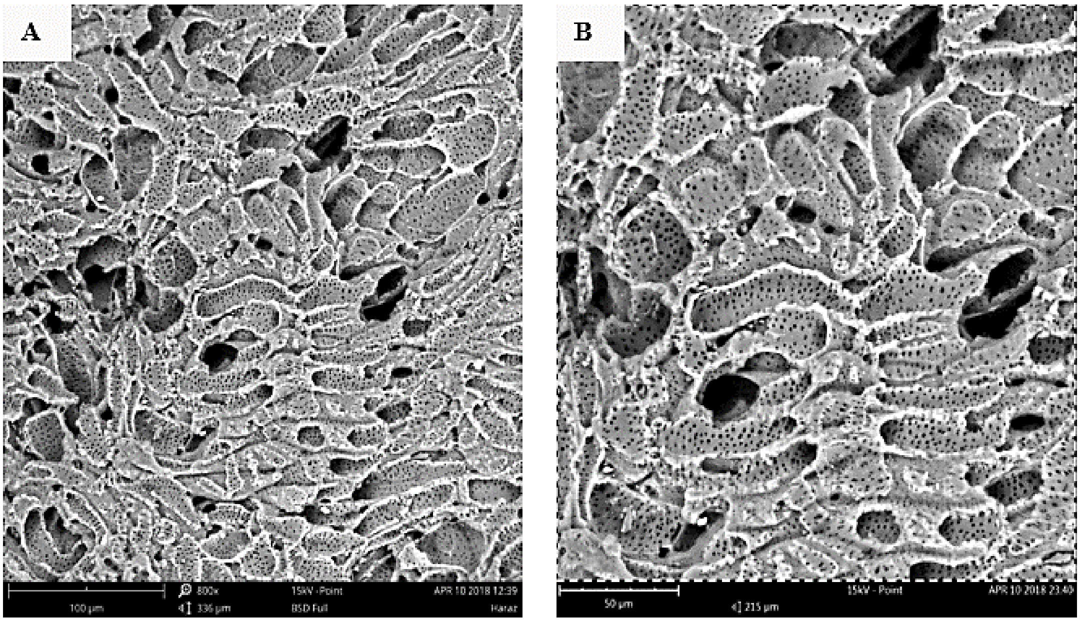


Figure 2.1: A (100µm) and B (50 µm), Morphology of Coconut Shell Biochar (CSBC)

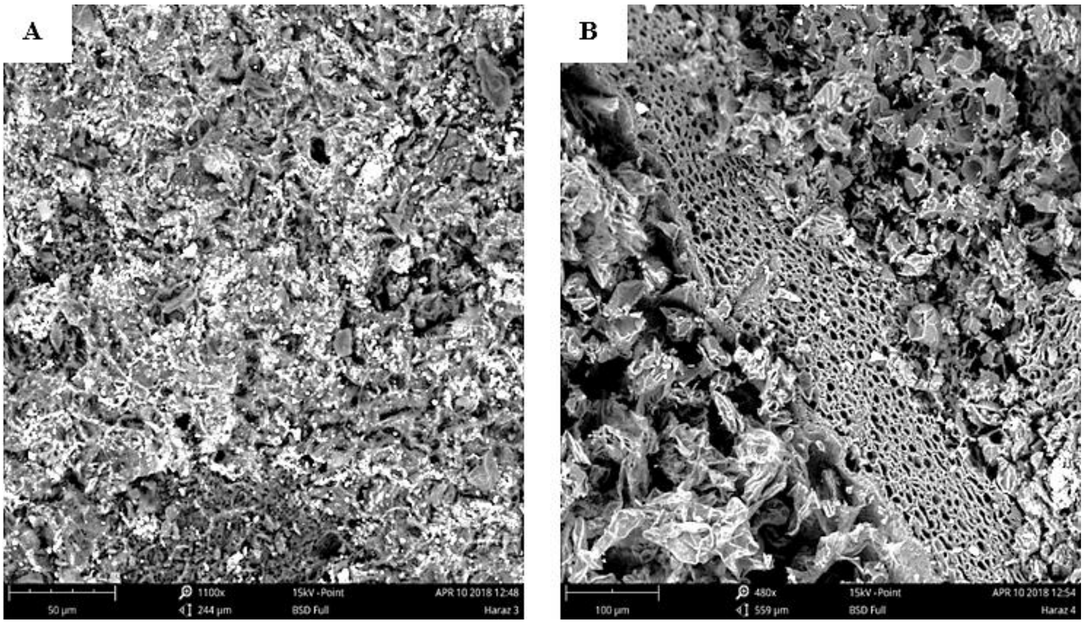


Figure 2.2: A (100µm) and B (50 µm), Morphology of Pecan Shell Biochar (PSBC)

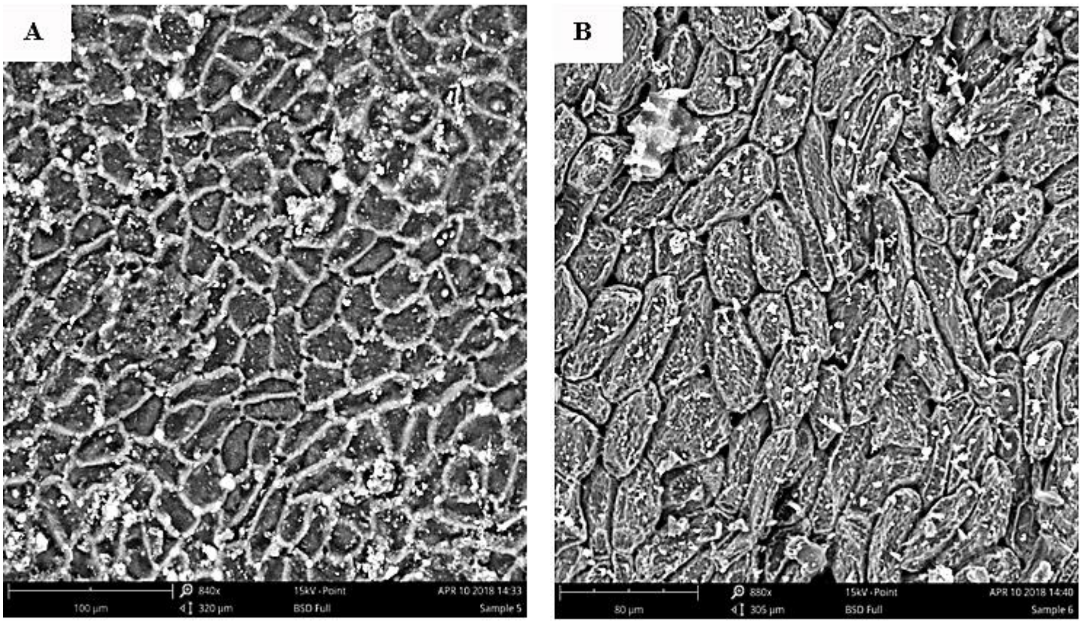


Figure 2.3: A (100µm) and B (50 µm), Morphology of Macadamia Shell Biochar (MSBC)

2.3 Biochar Properties

Feedstock characteristics and pyrolysis conditions largely control the physicochemical properties (such as particle size, pore size distribution and composition) of the resulting biochar, which in turn to determine the suitability for a given application (Lehmann and Joseph, 2015, Lehmann and Rondon, 2006, Mukherjee and Lal, 2014).

2.4 pH, EC and CEC

pH can affect elemental cycles in nature as shown by (Zou et al., 2016) on the nitrogen cycle. Nitrification increases with pH level 6. The application of BCcan increase soil pH due to the pH of the BCitself and through enhancing the retention of cations within the soil e.g., Ca^{2+}, Mg^{2+}, and K^{+} (Novak et al., 2009a, Angst and Sohi, 2013). Biochar produced at higher temperature has a higher pH. This is due to the release of alkali salts from the organic matrix of the feedstock (Ahmad et al., 2012). pH level can affect plant growth and developments as stated by Chen and Li (2006). When six levels of pH (ranging from 4-9) were used on Gerbera jamesonii bolus, the result demonstrating pH level 6 was the most effective level on nutrient retention in the experiment (cabdirect.org/cabdirect/abstract/ 20113016 981). In another study high pH (8-9) decreased the yield of dill, cabbage and red lettuce (Awad et al., 2017).

Electrical Conductivity (EC) is an indication of salt ion concentration in solutions. Adsorption of macronutrients was the lowest with 3.5 $ms.cm^{-1}$ and the highest with 3.8-4.1 $ms.cm^{-1}$ (Amalfitano et al., 2017). They also stated that water consumption and yield was high with 3.8 $ms.cm^{-1}$ as well as fruit quality. Wortman (2015) claimed that crops grown in high EC resulted in a higher yield compared with low EC. Four levels of EC were examined by Rosadi et al. (2014), the results showed that 3 $ms.cm^{-1}$ EC level increased tomato yield.

Many research projects have shown the advantages of adding BCinto the soil, as will be demonstrated in the following review. In the following table (Table 2.1), we highlighted the most relevant research that used BCin hydroponics.

Table 2.1: Summary Using of Biochar in Hydroponics

Biochar type	Quantity of BC	Pyrolysis temperature	Particle size of biochar	Growth media	Plant used	Reference
-	150 g	Date were not available	Date were not available	Coco peat, oil palm fruit branch,	Cherry tomato	(Ain Najwa et al., 2014)
Commercial rice husk biochar (RB)	1:1 ration of RB:PL. V/V	500 °C	≤2 mm	Perlite (PL)	Seedlings of dill, cabbage, red lettuce, tatsoi, and mallow	(Awad et al., 2017)
Tomato crop green west	BC:SD ratio 0:100 25:75 50:50 75:25 100:0	440° to 550 °C	Date were not available	Biochar (BC) and pine sawdust (SD)	Tomato	(Dunlop et al., 2015)
Citrus wood	0, 1, 3, or 5% by weight	Date were not available	>0.5 mm	Coconut Fibre: Tuff	Pepper and tomato	(Graber et al., 2010)

2.5 Biochar Effects on Plant Productivity

By enhancing water retention in soil, BC can be used for enhancing crop productivity in dry and semi-dry areas (Akhtar et al., 2014). Soil water holding capacity, can typically be improved by 11% with the addition of BC in agricultural soils (Karhu et al., 2011). Another study conducted by Mulcahy et al. (2013) verified that BC could be a material to be used to solve water scarcity through improved plant water use efficacy. In a study with wood-based BC added to tilled soils, an increase of >13% water holding capacity was observed (Troy et al., 2014). Experiments undertaken by the above researchers have shown that plant productivity of some elements has increased by the use of BC mixed with other materials. Another study on the effects of BCon plant growth and soil quality by Schulz and Glaser (2012) revealed a positive impact on plant growth, while the levels of total organic carbon (TOC) and potassium (K) content in the plant tissue increased. In the Schulz and Glaser (2012) study, BC had a positive effect on soil organic matter content and fertility that led to increased plant growth. Biochar addition to agricultural soils generally results in increased crop yields and plant green biomass (Biederman and Harpole, 2013). Rouphael et al. (2004) proved that soilless cultivation increased the yield and harvest index of zucchini plants (*cucurbita pepo* l.) ‘Aphrodite’, compared to those soil cultivated. A combination of pulverised wood and BCpellets, used with peat moss as a growth substrate showed better results than using media by itself for nursery plant production (Dumroese et al., 2011). The addition of wood BCto tilled soil helped to reduce NO_3 and organic C leaching in surface soil classified as an Acid Brown Earth (Troy et al., 2014). Another study about the effect of BCon macronutrient leaching in hydroponically grown plants, showed that the rate of nutrient (PO_4 and K) was increasing by increasing the rate of BC(Altland and Locke, 2012). In summary, BCcan work in both ways - it can store nutrient elements as well as release them so they can be used by the plants as well as increase water holding capacity in the media.

2.6 Biochar Effects on Plant Nutrients

This section will discuss the effects of BCon increasing nutrient and their availability. Borchard et al. (2012a) and (Lehmann et al., 2011) stated that adding BCto the soil enhanced the available nutrients concentration and soil fertility.

2.6.1 Soil Nitrate Forms and Physical Effects

Nitrate is an essential ion for growth and development of plants. It is claimed by Crab et al. (2007) that only 25% of nitrogen input is retained by organisms and the rest is discharged into the surrounding environment. Many researchers have proven that BC can improve NO_3 availability. Soil nitrification may be enhanced by adding BC (Rondon et al., 2006), reported that the total N recovery in crops is higher in charcoal amended plots compared to compost treated plots, 18.1% versus 16.5% respectively. Steiner et al. (2008) also reported increased N retention by charcoal versus compost soil amendments. The application of poultry litter BC without N fertiliser, resulted in yield increases for radish plants from 42 to 96% in comparison with the control, indicating enhanced N availability and plant uptake (Chan et al., 2007). These researchers have proven that BC additions significantly increase plant tissue N concentrations. At BC application rates of 10 tonnes/ha, plant N uptake increased from 41% to 45% compared to the control, while N uptake increased further with increasing application rate. Correspondingly, research findings of Uzoma et al. (2011) indicated that the rate of BC application had an effect on plant nutrient efficacy, showing an improved rate of N uptake in maize. Nitrate decreased in the leachate at first 10 days of the experiment (Nelson et al., 2011). Nitrification was increased by 10-69% with addition of silage maize biochars (Nelissen et al., 2012). N requirement to grow maize decreased with the use of BC (W. H. Utomo et al., 2012). Researchers have suggested that enhanced N uptake at higher BC addition rates can be attributed to the increased K, since K is considered as the counter cation accompanying the uptake of N as nitrate ions (Chan and Xu, 2009).

2.6.2 Phosphorus Availability with Biochar

Phosphate (PO_4) is a form elemental phosphorus which used by plants and plays a vital role in plants. Since only 25% of PO_4 can be recovered by organisms (Crab et al., 2007), other methods need to be applied to retain these ions to prevent their leaching. Many researchers believe that BC is an effective material which can reduce PO_4 from being leached. Biochar prepared from peanut hull and Brazilian pepperwood at 600 °C, reduced PO_4 in the leachate by 20.6% (Yao et al., 2012a) et al., 2012). Lehmann et al. (2003a) and Lehmann et al. (2003b) also revealed that increasing BC application rates also increase P concentration and uptake in plants. Further, an increase in grain yield has been recorded after the addition of BC to rice fields with low available P (Asai et al., 2009). Researchers have clarified that microbial biomass is crucial for organic P to be bioavailable and biochar-amended soils are rich in microbial biomass carbon (Lehmann et al., 2011, Masto et al., 2013). High microbial biomass carbon starts to get high amounts of ortho-P for its metabolic functions, leading to having high concentrations of bioavailable P in soil (Masto et al., 2013).

On the other hand, P uptake by plants may depend on the association between plants and mycorrhizal fungi which secretes extracellular phosphatases and P-solubilizing organic acids, making organic P plant available. Several researchers revealed that BC encourages mycorrhizal colonization of plant roots by facilitating habitats for them and thereby indirectly promoting P solubility (Gul et al., 2016, Warnock et al., 2007). Alternatively, nutrients in BC increase the production of P-solubilising organic acids (Deb et al., 2016) and have stated that this effect is more significant in nutrient-poor soils than in fertile soils. Cow manure BC has been attributed as the cause of increased dynamic P availability, as a result of increased soil pH (Uzoma et al. 2011).

2.6.3 Potassium Plant Availability

Potassium ions are considered a macronutrient in plant fertilisers. Several studies claimed that BC enhances potassium availability in plant growth media. Peanut shell BC increased potassium in the soil , which increased the K level and benefits to the plants (Gaskin et al., 2010). Biochar produced from prosopis had high potassium content (Shenbagavalli and Mahimairaja, 2012). An experiment on soybeans showed that available potassium levels increased as the level of added BC increased (Yin et al., 2012). Biederman and Harpole (2013) stated that BC increased soil and plant potassium, in agreeance with (Nigussie et al., 2012) who stated that BC significantly increased the plants' uptake of potassium. Several researchers proposed that increased potassium availability in soil could be attributed to the enhanced soil pH by the addition of BC (Manolikaki et al., 2016, Smider et al., 2014). The increase in soil pH may encourage the less available K^{+} ions firmly attached to clay particles, to be released into the soil solution. An increase of rice and cowpea biomass by the potassium provided from BC has also been reported (Lehmann et al. 2003a). Biochar produced from plant biomass increased potassium uptake in common beans (Rondon et al. 2007). Some researchers have suggested that the high availability of potassium for plants with BC may be temporary and not persist beyond a year after application (Steiner et al. 2007).

2.6.4 Calcium Responses to Biochar Addition

Soil has the potential to exchange Ca^{2+} with plant roots, a significant increase in exchangeable Ca (Ca^{2+}) levels and enhanced Ca uptake after the addition of cow manure was reported by (Uzoma et al. 2011). In spite of the increased plant uptake, Ca becomes more readily available in the soil after the application of biochar. Biochar has a greater negative surface charge, charge density, and higher surface area than other organic amendments (Sombroek et al., 1993). However, the Ca content in BC may replace monomeric Al species in soil mineral or soil organic matter exchangeable sites, enhancing Ca availability for plants (Novak et al. 2009). According to some research findings, excess Ca levels in the soil after harvesting indicates that Ca release from BC may exceed even plant requirements (Ma et al., 2013).

2.6.5 Sulphurs Relationship to Biochar

Sulphurs is one of the three secondary nutrients along with Ca and Mg required by plants for normal, healthy growth. The balance between N and S is significant to plant health, i.e. without enough sulphurs, plants cannot efficiently use nitrogen and other nutrients to reach their full potential. Nevertheless, there are limited studies which detail the effects of BC addition on S uptake. Although studies have outlined the changes caused by BC that might increase S availability, some studies indicated that there was a decrease in available S observed after adding small amounts, (0.36 - 0.5% v/v) of BC to the field (Namgay et al., 2010). Increased soil pH after the application of BC amendments may negatively affect S oxidation. Biochar might add S uptake inhibitors to the soil, or inhibit microbial activities of S oxidation. Furthermore, organic amendments with high C/S ratios (e.g. rice husk) have been found to result in severe S plant deficiency, due to S immobilisation in the soil (Chowdhury et al. 2000).

2.6.6 Magnesium Plant Availability

Magnesium (Mg) is an essential element for the photosynthesis process. Magnesium ions are readily available for plant uptake (Uzoma et al., 2011). The amount of Mg that can be absorbed by plants in soil, heavily depends on soil pH. Soil Mg absorption decreases under low pH conditions. Since most BC applications increase soil pH, there is a significantly high level of exchangeable Mg in biochar-amended soils (Uzoma et al. 2011). Consequently, research shows that cow manure BC is responsible for increased Mg concentrations in maize grain. This was attributed to the increased levels of exchangeable Mg in soils with higher BC application rates. Alternatively, some researchers reported that the addition of BC reduced the uptake of Mg and reduced the yield of corn silage (Lentz and Ippolito, 2012). In many instances where low temperature biochars have been applied, results can be inconsistent, especially in the first cropping cycle after application. In subsequent seasons volatile phyto-toxic components which may have previously negatively affected the yield, are no longer present, while the carbon components of the BC persist.

2.7 Nutrient Availability and Concentrations

Generally, BC derived from biomass is high in carbon and containing a range of plant macronutrients (N, P, K, Ca, Mg, and S) and micronutrients (Cu, Fe, Mn, and Zn) (Chan and Xu 2009; Hossain et al. 2011). Research has shown that the nutrient content of BC is generally attributed to the feedstock type (Chan et al. 2008a) and conversion process parameters of temperature and holding time. Specifically, total P and N contents were found to be higher in BC derived from feedstocks of animal origin e.g., sewage sludge, broiler litter, than those from plants e.g., wood/green waste (Chan et al. 2008a). However, the nutrient elements from animal feedstocks tend to mineralise, co-stabilize with carbon, or volatilise to form condensable products during pyrolysis. For instance, P and K are largely conserved after converting into their inorganic forms. Whereas N is volatilised in proportion to available carbon or becomes associated with C in the residual fraction (Chan and Xu 2009). Both P and K vaporise at pyrolysis temperatures above 760°C, whereas Mg and Ca are lost above 1107°C and 1240°C, respectively. Therefore, recent studies have suggested that the BC produced at low temperatures is suitable for agricultural uses, whereas high-temperature (>1107) derived BC can be effectively used for contaminant adsorption in soils (Agrafioti et al., 2013).

2.8 Biochar as a Soil Amendment

Biochar has been reported as a soil amendment in terms of increased crop yield and improved soil quality (Haefele et al., 2011, Major et al., 2010). Biochar has been heralded as an extremely stable soil amendment which improves nutrient availability beyond any fertiliser effect. Consequently, researchers have indicated that BC is not comparable with other types of compost or manure used for improvement of soil properties, as it is much more efficient than any other organic soil amendment in improving soil quality (Lehmann and Joseph 2015).

A varied range of soil constraints such as:

1- Soil structure and nutrient availability
2- Bioavailability of organic and inorganic pollutants
3- Cation exchange capacity (CEC)
4- Retention of nutrients can be influenced by the application of biochar. Pesticides, nutrients and minerals in the soil can also adsorb by biochar,

limiting the movement of such chemicals into groundwater or surface water and the subsequent degradation of these waters from agricultural activity.

2.9 Removal of Heavy Metals from Contaminated Soil and Water

In 2013 experimental work carried out by Houben et al. (2013) showed that BC can improve the soil quality and reduce heavy metals such as Cd, Zn, and Pb in contaminated soils. Steinbeiss et al. (2009) proved that different types of BC exhibit different effects on soil properties. Application of BC to soil is generally beneficial in terms of carbon sequestration and soil fertility (Peng et al., 2011). Mohan et al. (2007) evaluated BC made from pine wood, pine bark, oak wood and oak bark for their capacity to remove As, Cd, and Pb from water/wastewater. They found that all of these could effectively remove heavy metals if used at sufficiently high rates. Biochar has also been reported to be a suitable sorbent of organic compounds (Beesley et al., 2010, Brändli et al., 2008).

2.10 Biochar effects on Microflora

It is generally accepted that the activity of soil microorganisms is enhanced by the addition of BC (Pietikäinen et al., 2000). Since BC is a very porous material and the pore size varies with the type of biochar, a suitable BC is able to act as a habitat for microbes and can protect them from predation and desiccation, whilst also providing the necessary nutrients and diverse carbon sources (Warnock et al., 2007). The high porosity of BC increases its water holding capacity (Pietikäinen et al., 2000) and thus causes an overall increase in the soil's water holding capacity when amended with biochar. Biochar with high ash content becomes more porous as the residual ash leaches away. However, the increased water holding capacity of BC provides a surface for microbes to grow and colonise. Micro-pores usually retain capillary soil water longer than larger pores (i.e. larger than 10μm to 20μm). Water is very well known for being a biological solvent and the presence of water in BC can therefore correlate to increasing the chance of microbial colonisation (Lehmann and Joseph, 2009). As an example, the use of BC on clover increased mycorrhizal growth in bioassay plants by providing suitable conditions for colonisation of plant roots (Warnock et al, 2007).

2.11 Physiochemical and Biological Properties of Hydroponic Growth Media.

It has been claimed that BC has positive effects on physicochemical and microbial properties of hydroponic substrates. Kim et al. (2017) stated that there was increased nutrient retention, CEC, water holding capacity and 150% increase in plant dry weight, when rice hull based BC was mixed with growth media. In order to improve porosity, water holding capacity and bulk density to the required levels, 20% w/v BC was added to green compost waste (Zhang et al., 2014). Previous tests on adding BC to plant growth media have shown significant advantages in the resultant media's physical properties. Specifically, the addition of BC to three types of hydroponic growth media (coir dust, perlite, and vermiculite) at three percentages (w/w) 0, 1, 2, and 5% by (Kim et al., 2017).

Chemically, BC has generally demonstrated improved chemical properties of growth media according to the limited available references discussed in this chapter. CEC tended to increase in the presence of BC in the growth media (Liang et al., 2006). Higher CEC was gained when BC was mixed with vermiculite (Headlee et al., 2014). pH also seemed to be affected by BC addition, or at least the presence of mineralised ash contaminants in the biochar. pH was increased from 3.8 to 6.8 after BC addition (Chen and li, 2006). Electric conductivity (EC) also increased during the stage of plant growth, when fly ash-amended substrates were added (Chen and li, 2006). Green-waste based BC had reduced media degradation (Tian et al., 2012). A combination of 0.7% and 20% BC to composted green waste gave the highest quality of growth media and it was the opposite when non-BC was added (Zhang et al., 2014). A range of nutrients (K, Zn, Mg, Mn, Na, Ca, and Fe) increased in leafy vegetable leaf matter raised in media treated with a combination of BC and perlite (Awad et al., 2017). A brief description of BC effects on nutrient sorption is in the following sections.

Biologically, soil organic C plays a pivotal role in the nutrient cycle and in improving plant available water reserves, soil buffering capacity and soil structure (Horwath, 2007). Soil hardening and soil density is reduced by the addition of biochar, accompanied by increases in cation exchange capacity and soil aeration. Changes in soil consistency and structure through the changes in physical and chemical properties were also noted (Rawat et al., 2019). Compared to other organic matter, BC greatly enhances the process to reclaim degraded soils. Because of its negative surface charge, charge density and large surface area, it has a greater ability to adsorb cations per unit C of C. This offers the possibility of improving yields while offering a wide balanced variety of life forms, including bacteria, fungi, protozoa, nematodes, arthropods, and earthworms, thereby resulting in good healthy soil. At a smaller scale, by providing space for soil microbes, BC has been reported to increase the microbial respiration rate of the soil (Rawat et al., 2019).

2.12 Hydroponically Grown Plant Productivity.

While there are many soil-based studies including biochar, there is limited research on BC effects on plant productivity in hydroponic systems. In Kim et al., (2017), BC was mixed with vermiculite to use as a growth media. The mixture of BC with vermiculite increased the tree shoots' K as well as root/shoot biomass compared to the control treatments (Headlee et al., 2014). The nutrition and growth of *calathea insignis* was investigated by Zhang et al. (2014) for its response to 3 rates of BC (0, 20, and 35%) and 3 percentages of humic acid (0, 0.5, and 0.7%). Shoot/root fresh and dry weight, the number of leaves, plants heights, crown breadth and total root length were increased as well as total of K, P, N, chlorophyll contents of the leaves when 20% of BC and 0.7% of humic acid mixed with compost green waste comparing with planting in 100% green compost waste. Plant growth was greatest with original peat substrate (OP) + plant green waste (BGW) total biomass, for example, increased by 22% in OP + BGW relative to peat alone (Tian et al., 2012). Canopy widths and heights as well as dry weights and shoot fresh of plants produced from fly ash-amended substrates were comparable to those produced from the dolomite-amended substrate but significantly different from those produced from the basal substrate (Chen and li, 2006). Biochar seemed to have the ability to solve the problem of algal growing with hydroponic by decreasing their spread in nutrient solution (Awad et al., 2017).

CHAPTER 3 LABORATORY EXPERIMENTS:

3.1 Preliminary Tests

Preliminary work involved the selection of the most appropriate BC for field testing. This was done by conducting initial experiments in a laboratory environment. Polyethylene columns, pipes and plastic containers were used to create an open-loop hydroponic system. Peristaltic pumps (Master flex L/S Digital Drive, 600 rpm; 115/230 VAC) were used to deliver the solution from the stock tank into the vertically orientated columns. The out-going liquid (leachate) of the column was collected by 200 ml containers. Washed river sand was used as the growth media. Three types of feedstock-based BC were used to test BC effects on pH, EC and NO_3 in the open-loop hydroponic system. Biochars used in the experiment were derived from coconut shell (CSBC), macadamia shell (MSBC) and pecan shell (PSBC). The design of the

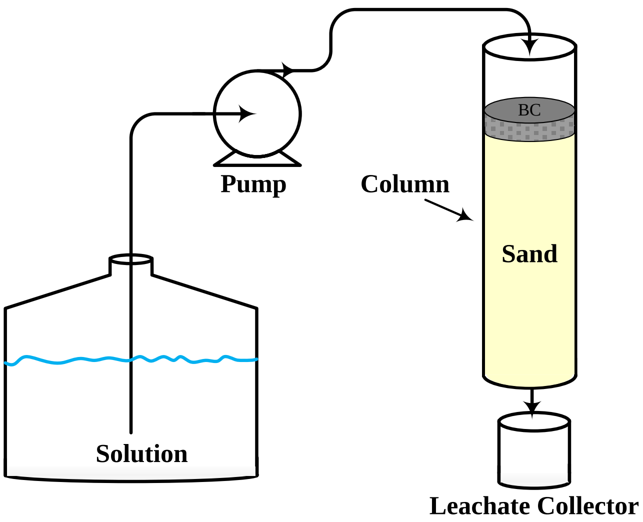


Figure 3.1: General Layout of the Column Tests

experiment is shown in Figure 3.1 .

Biochar morphology was examined using the Phenom Prox Desktop Scanning Electron Microscope, from Thermo Scientific (SEM-P). Biochar morphology images of BC made at various temperatures and with various holding times are shown in figures 3.2 - 3.6 and mineral compositions are shown in tables 3.1 - 3.5. In general, there were mainly two elements (C and O) present in the surface region for all BC types. There were other elements on the BC surface, but they were typically less than

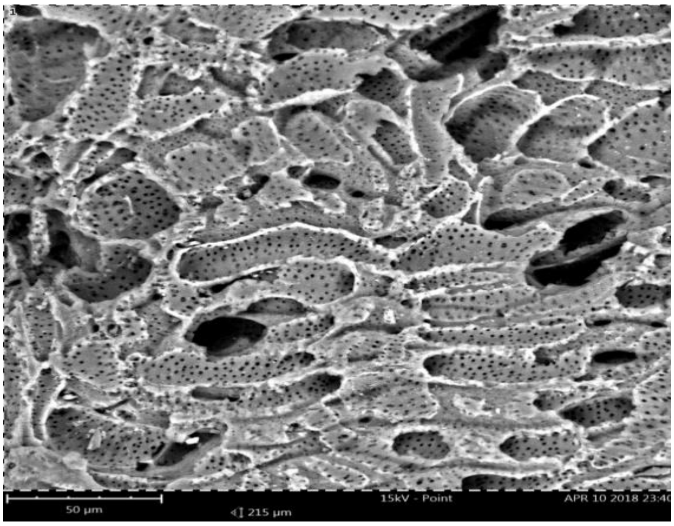


Figure 3.2: CSBC Morphology

1% concentration, so their impact on adsorption properties was not considered.

Table 3.1: Surface Element Contents of CSBC

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	92.83	90.67
8	O	Oxygen	7.17	9.33

Table 3.2: Surface Element Contents of PSBC900

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	67.98	56.11
8	O	Oxygen	25.97	28.55
19	K	Potassium	3.31	8.90
20	Ca	Calcium	1.57	4.34

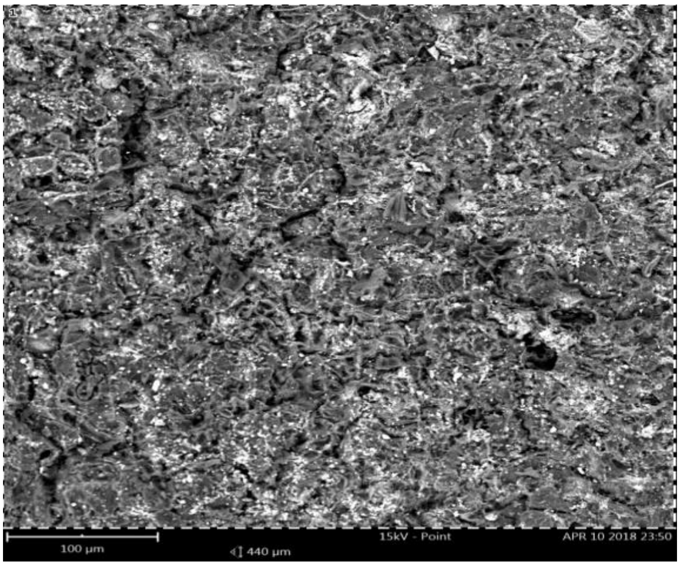


Figure 3.3: PSBC 900 °C Morphology (1h hold time)

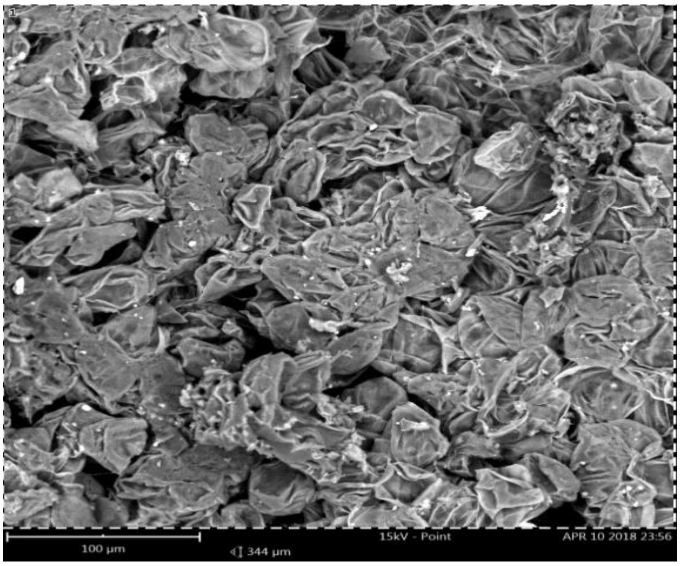


Figure 3.4: PSBC 500 °C Morphology (1h hold time)

Table 3.3: Surface Element Contents of PSBC500

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	82.28	75.51
8	O	Oxygen	16.12	19.71
19	K	Potassium	1.60	4.78

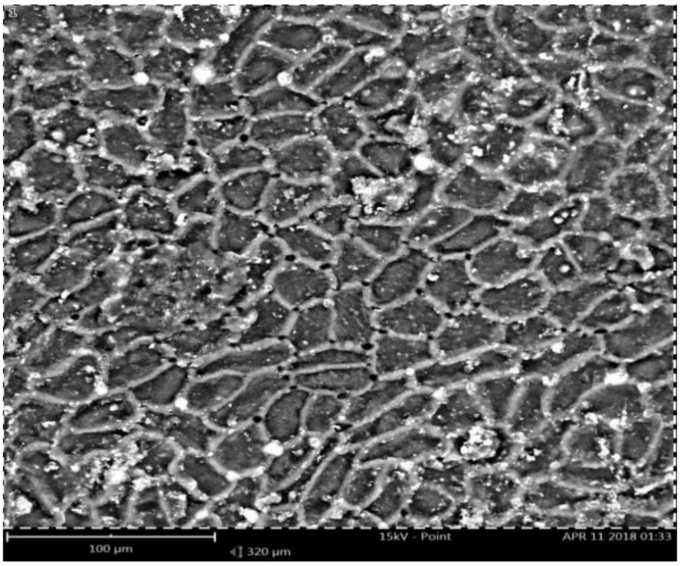


Figure 3.5: MSBC 900 °C Morphology (1h hold time)

Table 3.4: Surface Element Contents of MSBC900

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	89.79	85.46
8	O	Oxygen	8.88	11.26

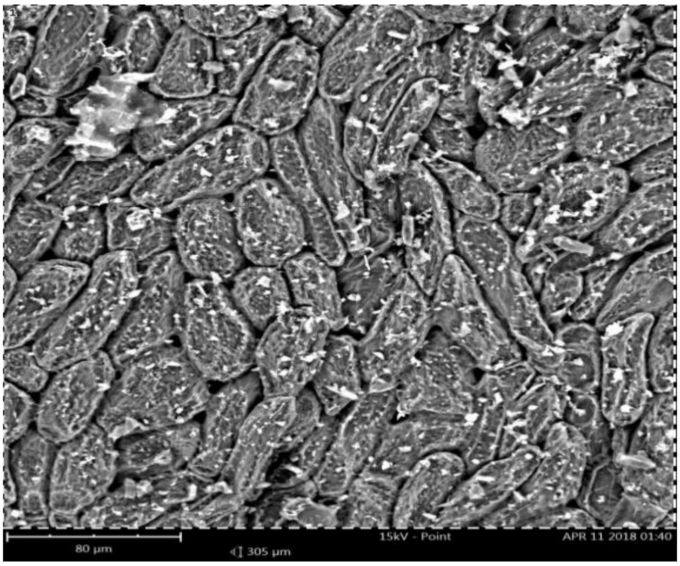


Figure 3.6: MSBC 500 °C Morphology (1h hold time)

Table 3.5: Surface Element Contents of MSBC500

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Con
6	C	Carbon	83.32	78.36
8	O	Oxygen	16.27	20.39
19	K	Potassium	0.41	1.25

Tests were conducted on the three types of BC with 3 replicates of each considered. Commercial grade coconut BC was provided by Clarence Water Filters in NSW, Australia. The other two types of BC were prepared in the laboratory at the University of Southern Queensland, Toowoomba (Section 3.1.4. Biochar preparation and analysis). Washed river sand that was used as a growth media in the initial test was provided by a local landscape supplier. Polyethylene columns and irrigation pipes were used to deliver the stock solution from the holding tank to the columns. Peristaltic pumps (Masterflex) were used to deliver the nutrient solution from the holding tank to the columns. Individual test details will be explained in the following sections.

3.1.1 Column Preparation

Solid polyethylene columns (140 mm in height by 40 mm diameter) were used (in triplicate for each BC type). Three columns were filled with sand only (control treatment). The process reported by Yao et al. (2012b) was adopted with a slight change in how the hydroponic media was used. Columns were filled with sand and tapped gently a few times to allow the media to settle, before the BC was loaded. Biochar was then added, and another layer of sand was placed on the top of the BC to keep it in the place. A small layer of fine sand was then placed on the top of coarse sand to separate the solution around the media and BC on top of the column. After the BC was loaded the columns were moistened with distilled water and then placed in their respective holder. Four peristaltic pumps (Master flex L/S Digital Drive, 600 rpm; 115/230 VAC) with 12 heads were used to deliver the solution to the columns (i.e. each column was treated as individual trial).

3.1.2 Biochar and Sand Preparation and Analysis

A muffle furnace at the USQ laboratory was used to prepare BCs. Two types of feedstock (pecan and macadamia shell) were loaded into the furnace which was set to 900 °C, with a heating rate of 600 °C/h and holding time of one hour. After allowing cooling to ambient temperature, the BC was crushed and sieved with two sieves in series (2mm and 0.3 mm) and then stored in closed containers in a dry environment. The particle size of between 2 and 0.3 mm was used in this research as being appropriate for agricultural purposes without any special handling equipment being required. BCs were scanned with SEM-P at USQ (Figures 3.2 - 3.6). The BCs were then tested to determine their content NO_3, P, K, Ca, Mg, and S. Moisture content, mobile matter and ash content were measured following ASTM (2003). Table 3.1 shows some physical and chemical properties of the BC and sand tested. The procedure below was used to characterise both the char and the sand components.

Washed river sand was used as plant growth media, after being analysed for its content of N, present as NO_3. A ratio of 1:5 w/w sand to water was used to determine the rate of NO_3 in the sand, i.e. 5 g of sand was added to 25ml of deionised water. The sample was shaken for one hour before being inserted into a centrifuge for 10 min at 3000 rpm. Finally, the extraction solution was tested by using Ion Chromatography (ICS-2000) to determine NO_3 concentration. The measured NO_3 concentration in the sand was found to be approximately 0.065 $mg.L^{1-}$. The fertiliser effect of the sand was neglected as it was present at such a low trace level, it was therefore unlikely to have any perceivable effect on the trial results.

Table 3.6: Biochar and Sand Characteristics

	Coconut biochar	Pecan biochar	Macadamia biochar	Sand
NO_3 $mg.L^{-1}$	0.0250	0.0222	0.0259	0.0563
pH	6.5	7.9	7.4	6.2
EC $\mu S.cm^{-1}$	9.90	32.3	3.3	3.1
Pore size µm	2.24 - 4.03	2.26 - 4.19	2.13 - 3.95	n/a
Moisture %	0.088	0.077	0.08	n/a
volatile matter	0.055	0.076	0.047	n/a

3.1.3 Sample Collection and Measurement

200 ml of sand and BC leachate were collected from each treatment, once per day for a period of 1 week. This is a similar scenario to irrigation approaches in a closed loop hydroponic system. Collected samples were similar for all treatments except columns seven and eight of test number four (Section 3.1.7). Samples of leachate from the columns, as well as samples from the stock solution were collected daily. Collected solution's pH and EC were measured as soon as the samples were collected during the study, with EUTECH INSTRUMENTS pH and EC meters, type PC 2700, pH/mV/conductivity /°C/°F meter. The samples were then stored at 4 °C on the collection day for later measurement of NO_3 once all samples were collected. Nitrate (NO_3) samples were measured every third day of sample collection to detect any changes in the stock solution (such as variations in NO_3 concentration) which may occur after 48 hours of storage. An ICS-2000 Ion Chromatograph was used to measure NO_3 levels, following standard industrial methods of water and waste-water analyses.

3.1.4 Initial Test Part 1 (Unwashed Biochar and Sand)

The three types of BCs and the sand were used in the test without washing. Biochars were used in a layer in each column. The BC to sand ratios were 5:95% sand (v/v). The columns were treated with NO_3 from a KNO_3 source, to determine the effect of BC on pH, EC and NO_3 retention in hydroponic substrate (sand). BCs and sand used were prepared as mentioned in the above Section 3.1.2. A filter paper (Whatman 45 µm) was placed on the bottom of the column to prevent the media in the columns being washed away (Figure 3.7).

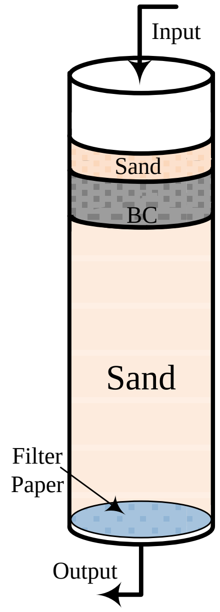


Figure 3.7: Column Setup for First Test

3.1.5 Initial Test Part 2 (Washed Substrates)

The difference between the first and second test was that in this subsequent test, the media (sand and BC) were both washed with distilled water 4-5 times in order to reduce pH and EC for both BCs and the sand. Thus, minimising BCs particulate ash, as well as cleaning the sand of residual organic and clay particles. The substrate was washed in the subsequent tests because the results in the first test were odd. A mesh was used instead of the filter paper at the bottom of the column because the filter paper started to block the flow of solution into the columns and did not allow the solution to move as smoothly as would happen in a normal hydroponic system.

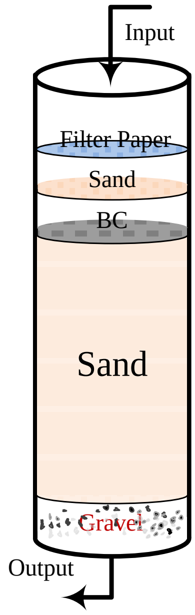


Figure 3.8: Column Set-up for Secondary Tests

3.1.6 Initial Test Part 3 (Biochar Mixed with Sand)

There were some changes observed in this test (Figure 3.9) compared to previous tests. Biochar and sand were both washed with deionised water 4 times (for the reasons mentioned in Section 3.1.5) and sterilized with an autoclave (HICLAVE, HV-50L) to make sure there were no biological effects reflected in the results such as fungi or bacteria which might grow in such an environment. Also, one column out of the three columns were used for each treatment in the test mixed with one type of BC instead of one layer of BC (one column has a mixture of sand with BC while the other two have BC in a layer above the sand). Hence, three columns were mixed as follows: sand mixed with 5% CSBC, sand mixed with 5% PSBC, and sand mixed with MSBC. To observe whether a layer or a mixed configuration can better affect the retention of NO_3 as well as the effect on pH and EC. Additionally, a filter paper was placed on the top of each column to make sure the solution was even distributed around the media (sand and BC) in the column. The third test was conducted in case there was channelling in the columns as sand is conducive to channelling.

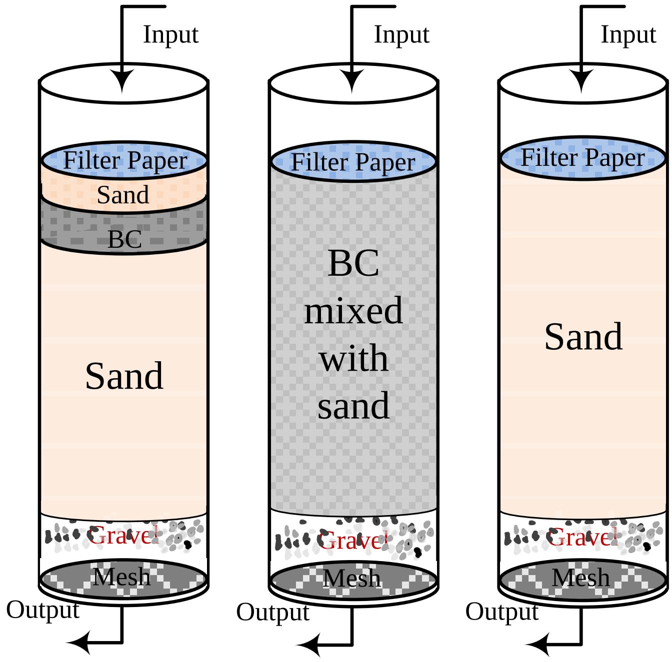


Figure 3.9: Column Set-up for Third-stage Tests

3.1.7 Initial Test Part 4: (High Biochar Rates with a Range of Flow Rates)

In this test, CSBC was used and the other two types of BC (PSBC and MSBC) were excluded, due to the fact that they had sub-optimal adsorption parameters. This test was conducted with eight columns as follows: the first three columns were designed like the one in the third test (Section 3.1.6.) but the flow rate was different. It was 3, 5, 7 ml.min^{-1} for the first, second and third columns respectively. The other three columns (fourth, fifth, and sixth) were used to know the optimum amount of BC that have positive effect on NO_3, pH and EC. Columns (fourth, fifth, and sixth) were designed as follows: 25%, 50%, and 100% BC to sand (v/v) for the fourth, fifth, and sixth columns respectively using the old flow rate 10 ml/min. The last two columns (seventh and eighth) were designed as follows: the seventh column was filled with CSBC, and 10 ml/min flow rate was used. The solution was running constantly for 11 days. In the eighth column 5% (old configuration, 5:95 BC:sand v/v) of CSBC and 10 ml/min flow rate was used. The solution was also running constantly for 11 days.

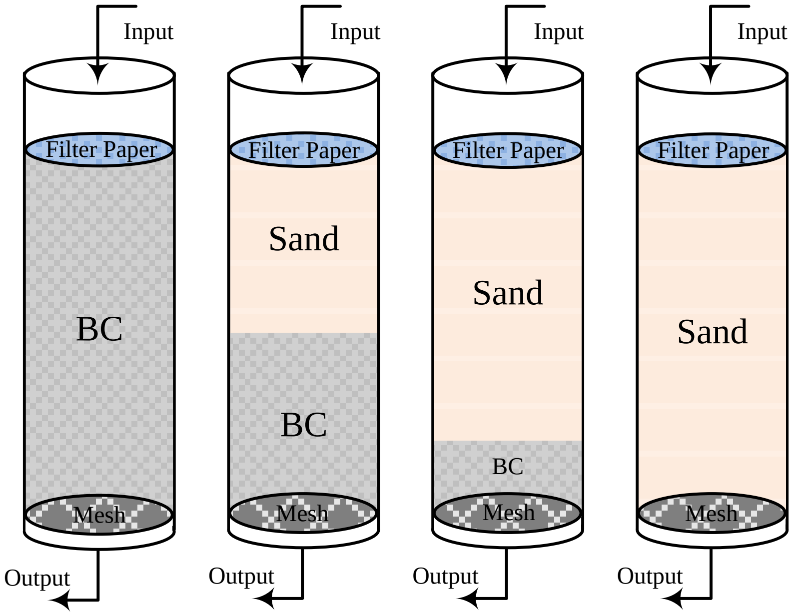


Figure 3.10: Column Set-up for Fourth-stage Tests

3.2 Results and Discussion

From the first test, it was found that unwashed BC can affect the pH and EC in a way which is undesirable for a hydroponics experiment (results are not presented). In the second test (Figure 3.8), the sand and BC were washed which thus resulted in a reasonable outcome (Figures 3.11, 3.12, and 3.13) for pH, EC, and NO_3 adsorption respectively. pH and EC were measured for the three types of BC in order to select the most suitable types of BC to be used in the next tests. The type of BC that was planned to use should have less effect on pH. At the same time it should have a positive effect on EC. Figure 3.11 presents the effect of three types of BC on pH level. The results show that macadamia and pecan BC increased pH level to around 7.2 and 7.5 respectively.

Coconut BC also increased pH level, but it was less than the other two types of BC by around 0.4. The EC is presented in figure 3.12, where CSBC performed better than the other two BCs. Figure 3.13 shows NO_3 retention with the three types of BCs. As shown, CSBC retained more NO_3 than the other BCs. This being the case, we selected CSBC to conduct the next tests. In order to investigate which type of BC react better to pH, EC, and NO_3 retention, we utilised 50 mg/L of NO_3.

In the third test (Figure 3.8), BC was mixed with the growth media as this is what farmers usually use in commercial hydroponic systems. There was not little difference from the second test results and results are not discussed here further.

In the fourth test, three flow rates (3, 5, and 10) ml/min were used to monitor the effect of flow rates on the studied parameters, with a larger amount of BC used in this test (Figure 3.10). The results showed that 5 and 10 ml/min performed better than 3 ml/min. Increased BC resulted in more adsorption of NO_3 and reduced EC in the leachate and increased pH level to around 7, slightly above the normal level used in commercial hydroponic systems. However, this slight increase does not have any dramatic side effects on plant growth, as confirmed by some researchers (Dunlop et al., 2015).

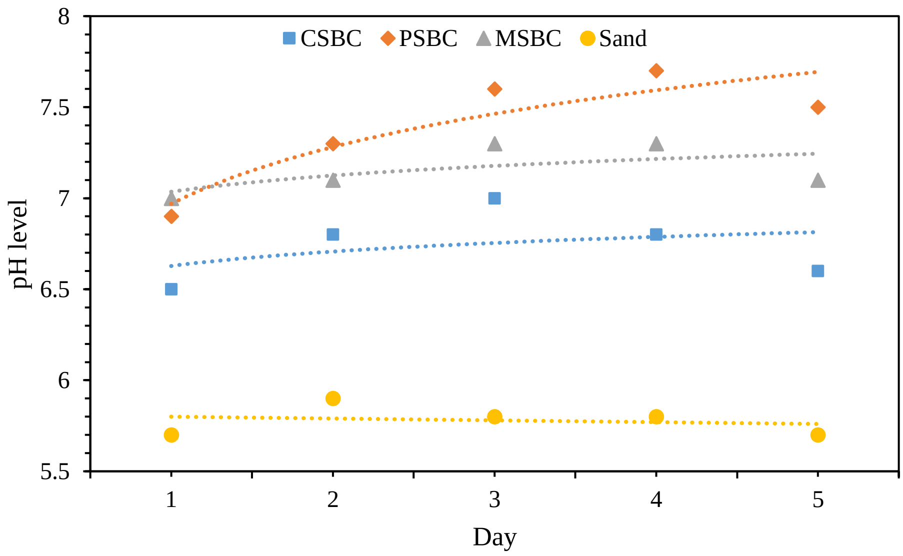


Figure 3.11: Biochar Types Effect on pH

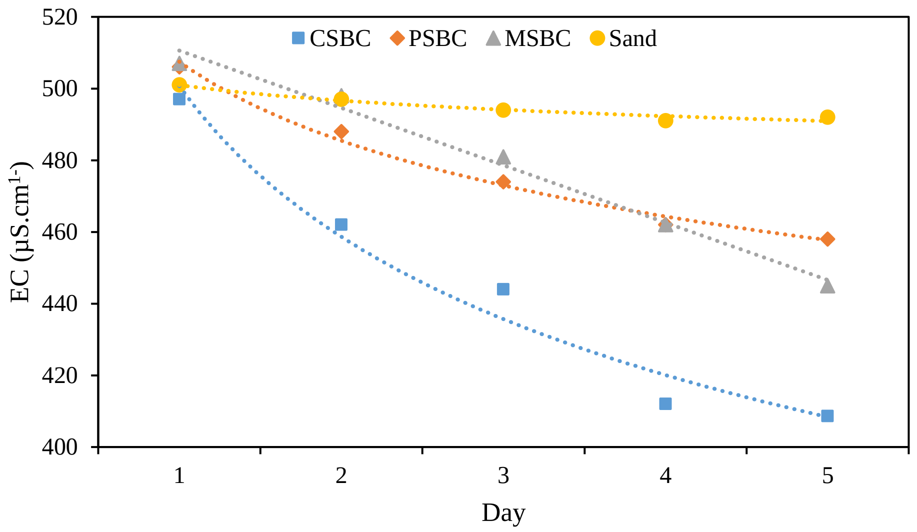


Figure 3.12: Biochar Types Effect on EC

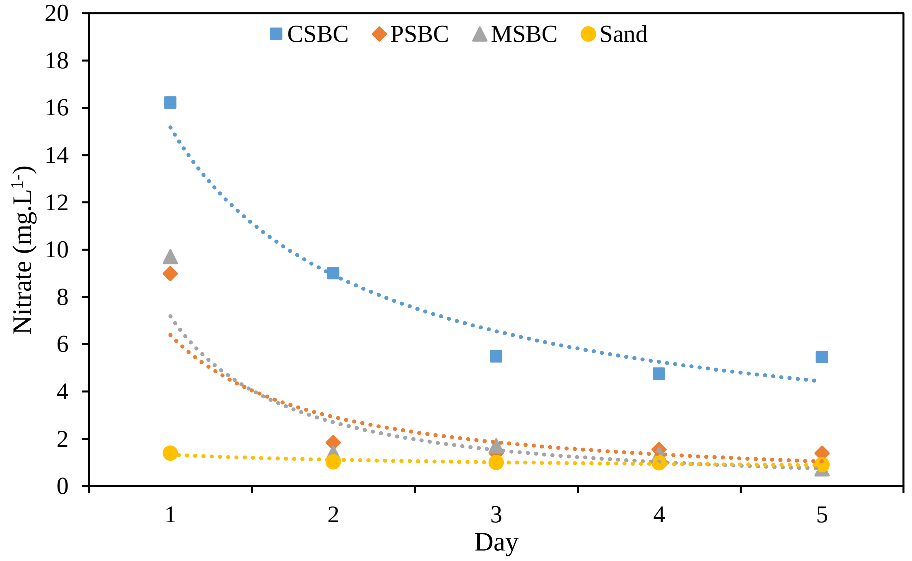


Figure 3.13: Biochar Types Effect on Nitrate

CHAPTER 4 INITIAL COLUMN TESTS:

4.1 Biochar and Sand Samples

The CSBC and washed river sand were the substrates used in this study. CSBC was provided by Clarence Water Filters Australia. According to the manufacturers report (Clarence Water Filters) https://www.clarencewaterfilters.com.au CSBC was prepared from coconut shell at 450 $^{\circ}$C, activated with steam at high temperature, then washed with acid to enhance the nutrient absorption ability. The CSBC was washed with DW four times to minimise any mineralised ash then saturated with DW overnight to reduce pH and EC effects down to a level suitable for hydroponics.

The sand was obtained from a local landscape firm. The sand was washed five times with tap water to remove any organic particles and clay that may affect the treatments before being washed three times with DW to reduce EC and pH levels. Both CSBC and sand samples were kept dried and stored prior to analysis.

4.2 Physiochemical Properties of CSBC

The pH and EC were measured at a solid : water rate of 1:5 w:v for CSBC or sand to DW. Samples were weighed into 5 g lots, then 25 ml DW was added. The mixture of CSBC with DW was shaken for 5 min on a RATEK shaker at 100 rpm before pH and EC were measured using a PC 2700 from EUTECH INSTRUMENTS. All the measurements were performed following the Standard Methods outlined in (Baird et al., 2017).

4.2.1 Scanning Electron Microscopy

CSBC was scanned with a SEM-P to examine the surface structure, porosity and pore size (Figure 4.2).

4.2.2 Surface Functional Groups

The functional groups of the CSBC were examined using a Fourier Transform Infrared Spectrophotometer (FTIR) from SHIMADZU, system No: 4-00468. Oven-dried CSBC samples were mixed with potassium bromide (KBr) in a ratio of ~1:99 CSBC to KBr. The mixture was then compressed to obtain a thin semi-clear layer, loaded in the device to examine the functional group of the CSBC (Figure 4.3). All tests were conducted in triplicate to reduce experimental error.

4.2.3 Cation Exchange Capacity

The cation exchange capacity (CEC) was measured using the method presented by Shen et al. (2015). 1 g of CSBC was mixed with 20 ml of 0.5 M BaCl and shook for 2 h at 200 rpm. The mixture was then filtered with 45 µm filter paper before the exchangeable nutrients were measured using an Atomic Adsorption Spectroscopy (AAS) and an Ion Chromatography System (ICS-2000). Nutrients measured were K, Mg, and Ca with the AAS and NO_3, PO_4, SO_4 with the ICS2000.

4.2.4 Zeta Potential

CSBC zeta potential (ZP) was measured as follows:

Samples were ground and sieved through a 0.2 mm sieve. The sieved sample outcome (>0.2 mm) was taken and washed with DW to reduce EC below 50 $\mu S.cm^{-1}$. Finally, 5 g of each sample was added to 50 ml DW. Samples were then agitated to have the small particles suspended in solution when added to the ZP device's cell to measure. These tests were all conducted in triplicate.

4.2.5 Nutrient Assay for Sand and Biochar

The nutrient content of CSBC and sand were measured as follows:

a) sand, 1 part sand to 5 part (w/v) of DW were loaded into a container and shaken for 1 hour before being centrifuged for 10 min at 3000 rpm. The centrifuged solution was filtered with Whatman 45 µm filter paper before measuring K, Mg, and Ca by the AAS while NO_3, PO_4, SO_4 were measured by the ICS.

b**)** Coconut shell biochar, the mixture of CSBC:DW was used to measure pH and EC then it was further shaken for 24 h before measuring nutrients. The mixture was filtered with Whatman 45 µm filter paper and taken to the ICS to measure NO_3, PO_4, SO_4 and the AAS to measure K, Mg, and Ca.

4.2.6 Stock Solution

The stock solution was obtained from a local hydroponic farm (K Farm in Toowoomba). The studied parameters, EC, pH, NO_3, PO_4, K, Ca, Mg and SO_4 were measured (Table 4.1). The reason for using a nutrient solution from a local hydroponic farm was, to allow a realistic comparison of our results with a standard hydroponic farming practices.

Table 4.1: The Stock Solution Characteristics

Parameter	Properties
pH level	6.1
EC ($mS.cm^{-1}$)	1.803
Nitrate ($mg.L^{-1}$)	80.121
Phosphate ($mg.L^{-1}$)	40.88
Potassium ($mg.L^{-1}$)	150.176
Calcium ($mg.L^{-1}$)	93.783
Magnesium ($mg.L^{-1}$)	24.746
Sulphate ($mg.L^{-1}$)	50.727

4.2.7 Batch Tests

Batch tests for CSBC with nutrient solution (NS) were conducted to evaluate the ability of BC to retain or release nutrients while observing any changes in pH and EC. Batch tests were conducted in triplicate using 100 ml containers for each BC ratio. The BC: nutrient solution percentages (w/v) were prepared as follows:

CSBC was loaded into the containers containing nutrient solution and shaken for 24 h at100 rpm using a RATEK shaker. Prior to being filtered with Whatman 45 µm filter paper. The extract was frozen until ready for analysis. The PC 2700 was used to measure pH and EC; the AAS and ICS2000 were used to measure the nutrients. Table 4.2 shows the ratio of BC to NS in the batch tests.

Table 4.2: Biochar Ratios in the Batch Tests

Treatments (n = 3)	CSBC (g)	CSBC ratio (%)	NS ratio (ml)
1 Control	0 g CSBC	0%	50
2	2.5 g CSBC	5%	47.5
3	12.5 g CSBC	25%	37.5
4	25 g CSBC	50%	25

4.2.8 Column Tests

The CSBC and sand mixture were packed into columns with a capacity of around 300 ml (40 mm in diameter and 250 mm in length). CSBC was used with four volumetric percentages of 0, 5, 25 and 50% (v/v). A closed hydroponic system was used to run the tests as per (Figure 4.1). The tests consisted of 4 treatments, each tested in triplicate. Five litres of DW and five litres of NS were used for each treatment. On the first day of the experiment, the columns were irrigated with DW for around 36 min with 15 $ml.min^{-1}$ flow rate. The water pump duty cycle was on for 12 mins and off for 10 mins. The process was repeated three times each day, for 10 events (E1-E10) five times with DW and five times with NS. The test process cycle used was one day with DW followed by one day with NS according to the method reported by (Altland and Locke, 2012). Samples were taken daily from the solution tanks for each treatment, with EC and pH measured immediately after collecting samples, then samples were frozen until they were analysed. After collecting the leachate, the columns left open overnight allow them to drain fully. In short term processes (two weeks) the ability of BC to retain and release nutrient was thus tested.

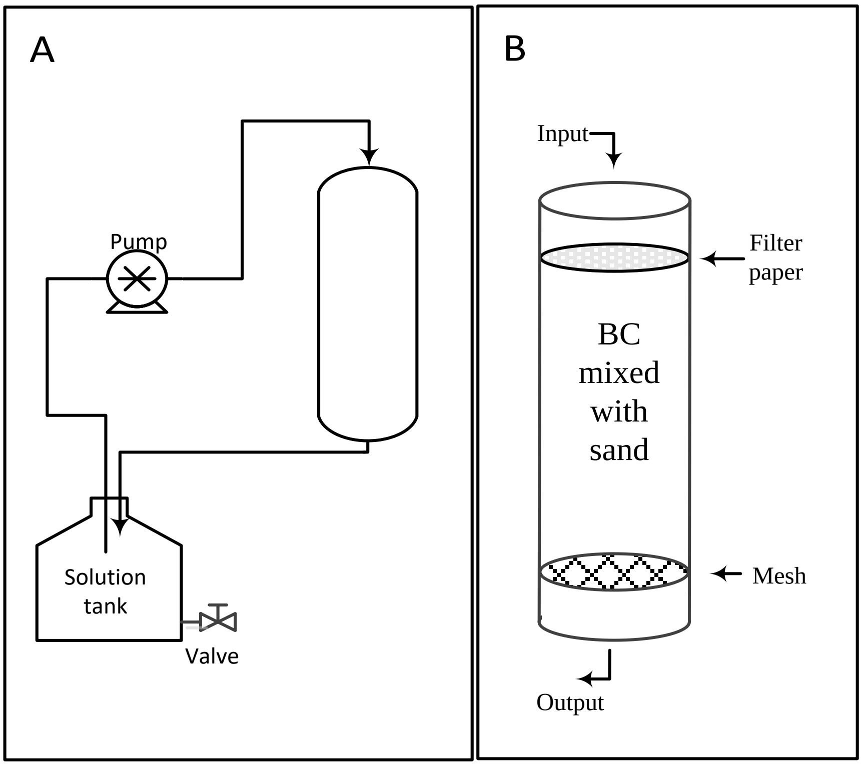


Figure 4.1: A) General Experimental Setup, B) General Column Details

4.2.9 Statistical Approach Used

The data points display the replicate mean (n = 3) with standard error bars shown. IBM SPSS Statistics version 24 was used to analyse the data, using two-way factorial analysis and Duncan's significant differences test, at a significance level of P <0.05. The corresponding correlation coefficient (R^2) values are shown within the figures.

4.3 Results and Discussion

4.3.1 Biochar and Sand Characteristics

Table 4.1 shows CSBC properties as provided by the manufacturer. Tables 4.3, 4.4 and 4.5 show the CSBC and sand characteristics. CSBC morphology was examined using SEM-P (Figure 4.2). SEM-P results showed that CSBC was very porous with a pores sizes range 2.24-4 µm. SEM-P also showed that CSBC has an irregular shape. The CSBC tested has a high surface area (Table 4.3). These features increased CSBC nutrients adsorption ability (Park et al., 2003).

Table 4.4: Sand Basic Characteristics

Parameters	Sand properties
pH level	5.6
EC ($\mu S.cm^{-1}$)	2.01
Nitrate ($mg.L^{-1}$)	-
Phosphate ($mg.L^{-1}$)	0.0015
Potassium ($mg.L^{-1}$)	0.0012
Calcium ($mg.L^{-1}$)	0.3308
Magnesium ($mg.L^{-1}$)	0.0133
Sulphate ($mg.L^{-1}$)	0.5215

Table 4.3: Biochar Properties as Provided by Clarence Water Filter, Australia

Parameter	CSBC properties
Moisture content max	5%
Total ash content max	1%
Apparent density min	460 $kg.m^{-3}$
pH level	5-7
Hardness min	98%
Surface area	1050 $m^2.g^{-1}$
CTC activity	55%
Apparent density	5353 $kg.m^{-3}$
Apparent density, backwashed and drained	455 $kg.m^{-3}$

Table 4.5: Measured CSBC Characteristics

Parameters	CSBC properties
pH level	6.3
EC ($\mu S.cm^{-1}$)	9.90
Zeta potential (mV)	-43.9
CEC (coml $_{(c)}$ kg^{-1} by ($BaCl_2$)	21.548
Pore size (μm)	2.24 - 4.03
TN ($mg.L^{-1}$)	0.0260
Nitrate ($mg.L^{-1}$)	0.0250
Phosphate ($mg.L^{-1}$)	0.0210
Potassium ($mg.L^{-1}$)	0.0894
Calcium ($mg.L^{-1}$)	0.0409
Magnesium ($mg.L^{-1}$)	0.1840
Sulphate ($mg.L^{-1}$)	0.0312

4.3.2 Functional Groups

The FTIR spectra (Figure 4.3) using IRAffinity-1S from SHIMADZU showed that CSBC has functional groups such as carboxyl (C-O), aromatic (C-C), acyclic (monosub. alkenes) C-C, acyclic (1,1-disub. alkenes) C-C, amides, primary amines (N-H), and alcohols O-H. These functional groups were also found by Angalaeeswari

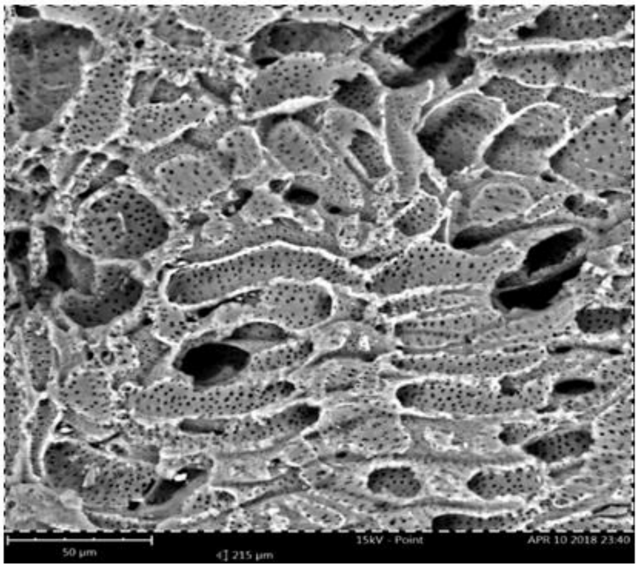


Figure 4.2: Biochar Surface Morphology

and Kamaludeen (2017).

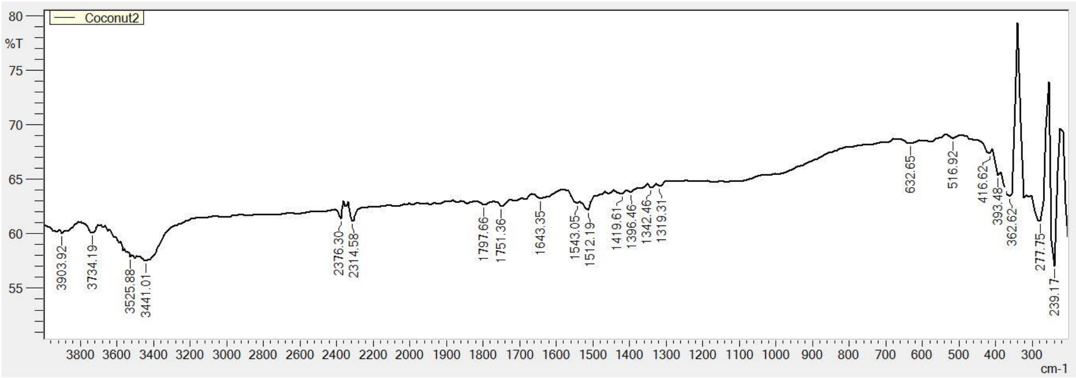


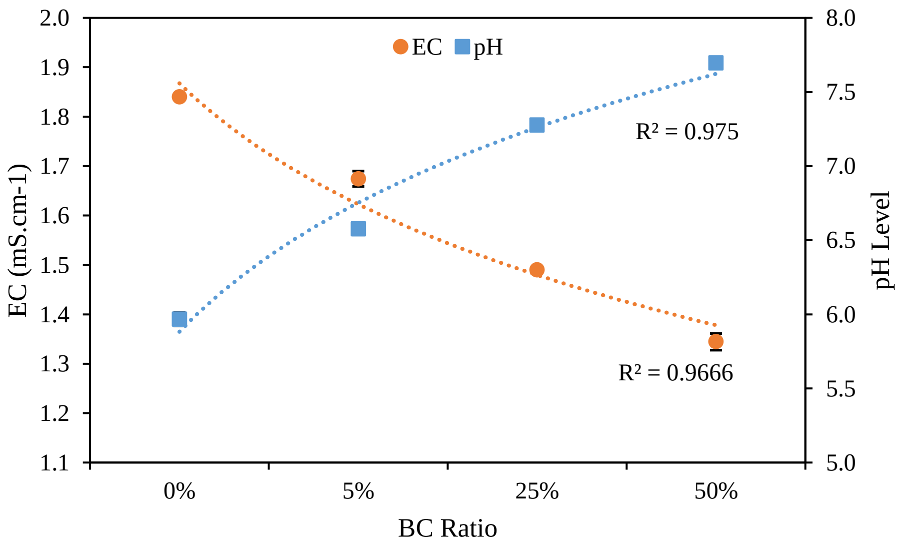
Figure 4.3: FTIR of CSBC Showing Functional Groups

4.4 Batch Adsorption Tests with Nutrient Solution

Initial batch tests were conducted to gain an idea about the ability of CSBC to effect pH, EC, nutrient retention and release. A summary of the results of these batch tests is shown in the following section.

4.4.1 pH and EC Changes with BC Addition

Figure 4.4 displays pH and EC changes in the batch test. In general, pH increased as the BC rate increased while the opposite occurred with EC.



4.4.2 Macronutrient Adsorption

Figure 4.5 illustrates the retention of macronutrients in batch tests. Nitrate levels in the batch tests generally decreased as the CSBC rate increased. With 50% CSBC, NO_3 concentration decreased to around 4 mg.L^{-1}, while with 25% CSBC mg.L^{-1} it was 12 mg.L^{-1} and around 33 mg.L^{-1} with 5% CSBC.

Phosphate retention increased as the amount of CSBC increased in the solution. Levels of 11, 18, and 27 mg.L^{-1} of PO_4 were recorded for 5, 25, and 50% CSBC, respectively.

Unlike other nutrients there was a release of K observed, instead of a retention. There was around 55 mg.L^{-1} of K released in the solution with 50% CSBC. The other two treatments 25 and 5% released around 40 and 8 mg.L^{-1} respectively. The Ca concentration in the solution was reduced by around 59, 42 and 17 mg.L^{-1} with 50, 25 and 5% CSBC ratios respectively.

Biochar concentration did not affect Mg concentration in the solution. Sulphate was also affected by CSBC concentration in the solution, where 50% CSBC retained around 16 mg.L^{-1}. The reduction of SO_4 was less with 25 and 5% CSBC treated solutions, around 10 and 2 mg.L^{-1} respectively.

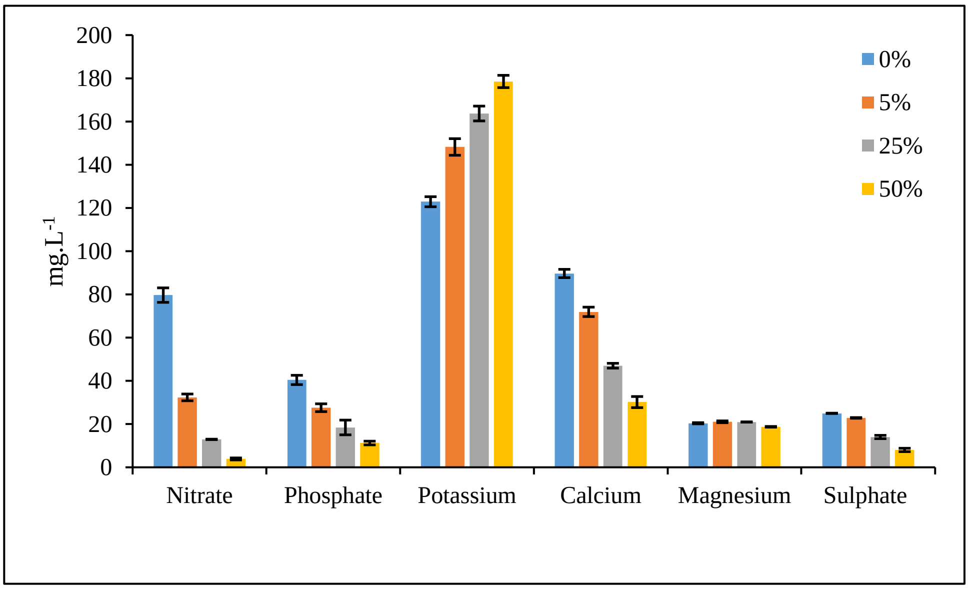


Figure 4.4: Nutrient Retention in Batch Tests

4.5 Column Tests

4.5.1 pH Level Changes

In general, the addition of BC increased pH level in all treatments when the nutrient solution was used (Figure 4.6). The highest pH was obtained from 50% BC treated media while the lowest was recorded by the control treatment. The pH of the nutrient solution was 6.1 at the beginning of the tests, increasing to 7.1, 7.4 and 7.5 at the end of the respective treatments of 5, 25 and 50% BC treated media, while a pH of 6.7 was recorded for the control treatment. Overall, as expected, pH trended upwards as the BC rate increased in the media (Figure 4.6).

Figure 4.7 shows pH levels when DW was applied. Generally, the pH trends for all treatments increased. With the control treatment pH increased to reach 6.1 (compared to the initial pH in the DW 5.6 - 5.8) but it was higher with 50% treated columns, it reached 6.9 and it was 6.5, 6.4 for 25% and 5% treated column respectively. The results were significant in both tests at $P<0.001$.

The reults are in line with findings shown in other studies which examined BC effect on pH level (Chen and Li, 2006, Brockhoff et al., 2010, Kaudal et al., 2016). The reasons behind the increase of pH can be due to the BC has some mineralised ash and nutrients such as K, Ca, Mg (Table 4.1) which can rise pH level up (Bruun et al., 2012), also it could be because of the functional group mention in Section 3.1.1. (Bruun et al., 2012, Yuan et al., 2011).

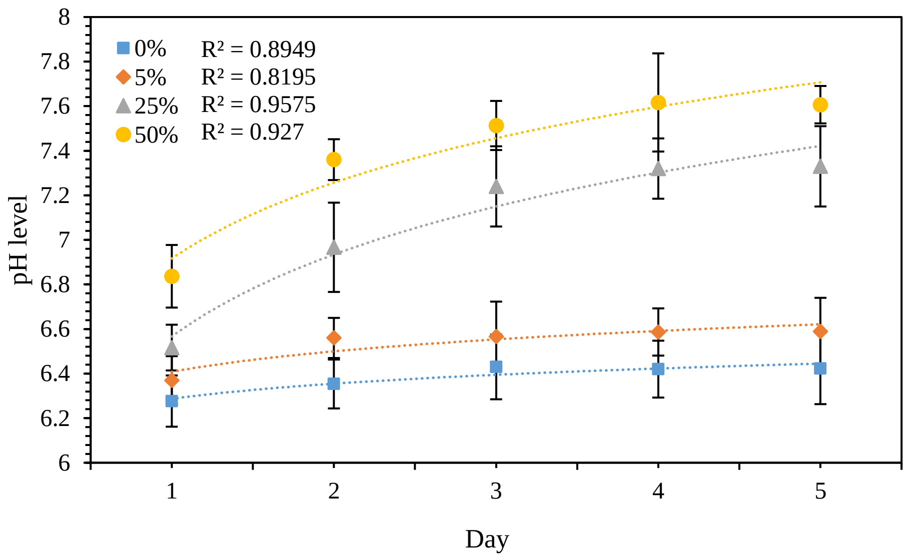


Figure 4.5: Changes of pH as Nutrients from the Hydroponic Nutrient Solution are Absorbed by the Char

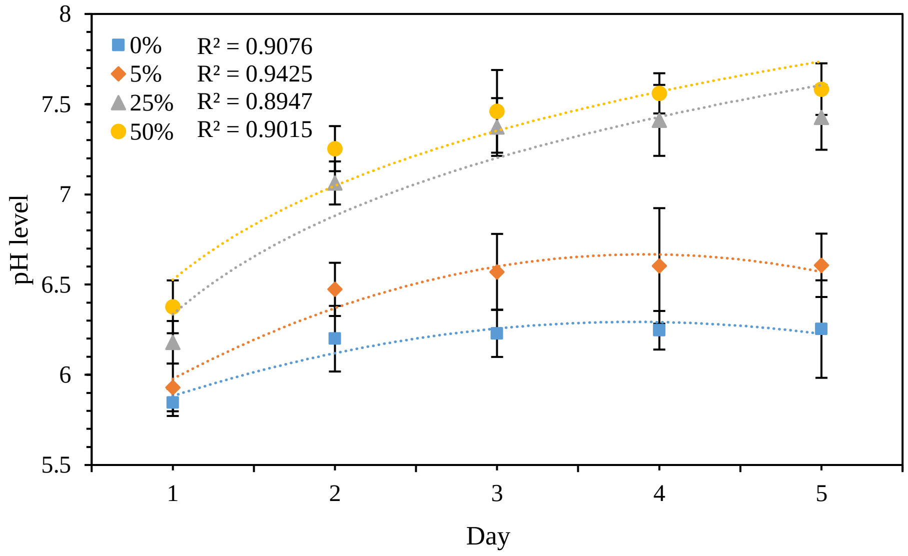
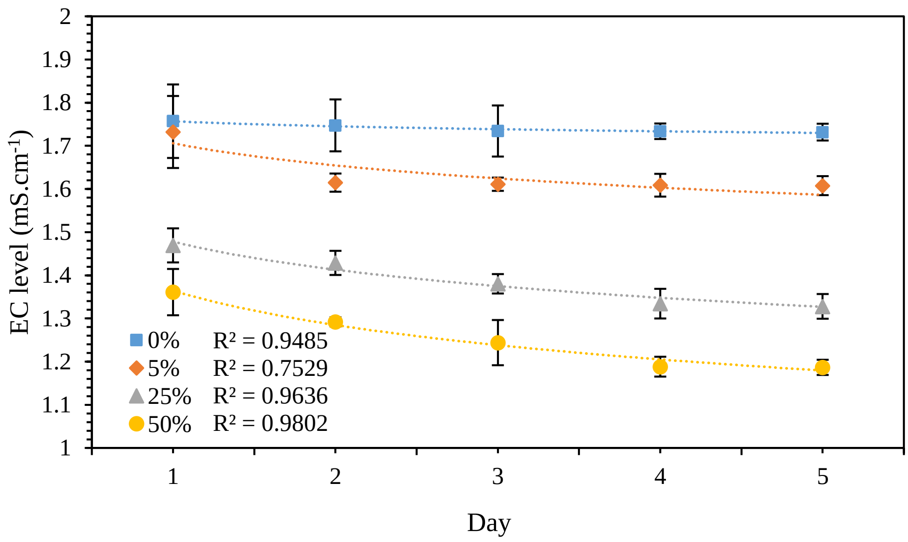


Figure 4.6: pH Response with Alternate Use of Deionised Water and Nutrient Solution

4.5.2 Electrical Conductivity Change

Biochar significantly affected the EC level in both solutions. In figure 4.8 it can be seen that there is only a slight variation over the five days in the control treatment and that is partly due it is suspected to some volatilisation to the atmosphere also there may be some random biological or contaminant in the sand mixture which may adsorb small amount of nutrient. The EC was reduced by 0.2, 0.47 and 0.61 $mS.cm^{-1}$ for 5, 25, and 50% BC respectively. As EC was reduced in the leachate from the nutrient solution, it was increased in the leachate from DW (Figure 4.9). 50% BC treatment gave the highest value of EC, but the lowest was from the control treatment. Increasing the EC of solution when BC rate increased could be due to the element released from the CSBC especially Mg and K (Angst and Sohi, 2013). This finding is in line with other studies finding (Brockhoff et al., 2010, Kaudal et al., 2016, Vaughn et al., 2013, Chen and Li, 2006).



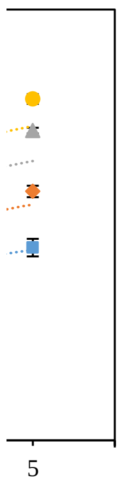


Figure 4.7: Electrical Conductivity Changes as Nutrients are Adsorbed

Figure 4.8: Electrical Conductivity Changes as BC Releases Nutrients

4.5.3 Biochar Effect on Nitrate

Figure 4.10 shows that BC significantly reduced the concentration of NO_3 in the leachate. With 0% percentage of BC in the media, NO_3 concentration was higher in the leachate than other BC treatments during the experiment events and the recovered NO_3 was only 13 $mg.L^{-1}$. The retention of NO_3 increased to be 21, 31 and 36 $mg.L^{-1}$ for 2, 25, and 50% respectively. Similar results were obtained from the batch test (Figure 4.5). As stated by several researchers that BC addition increased NO_3 retention

(Ota et al., 2013, Wang et al., 2015, Shenbagavalli and Mahimairaja, 2012). More BC led to less release of NO_3 (Altland and Locke, 2012). Altland and Locke (2012)

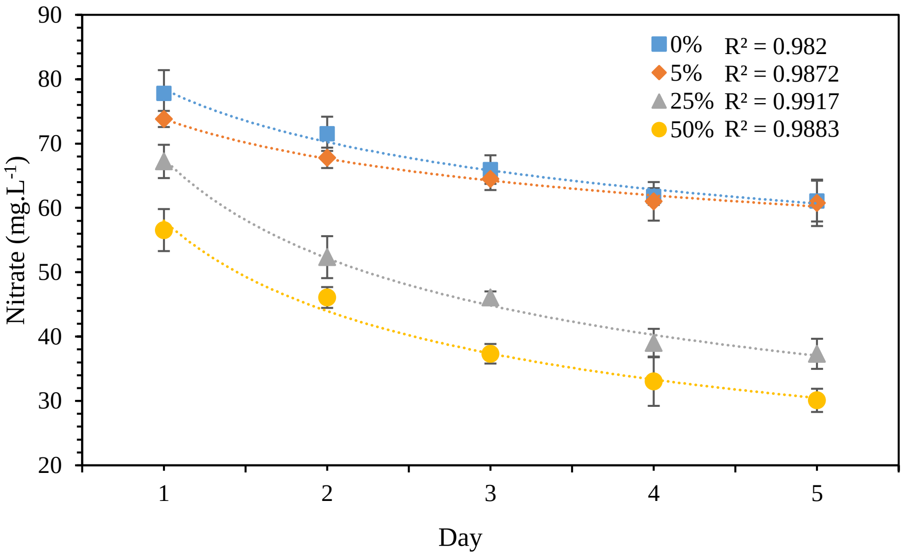


Figure 4.9: Change in Nutrient Solution Nitrate Concentration over 5 Days

claimed that BC absorbs NO_3 and releases it slowly over time and that is what was observed in this test. Nitrate was released slowly when DW was applied to mimic a natural nutrient cycle fluctuation (Figure 4.11), with similar results obtained by (Hale et al., 2013). While NO_3 was retained from the nutrient solution, it was subsequently released in the leachate, with the application of DW (Figure 4. 11). Nitrate releases reduced as the amount of the BC increased. The control treatment (0% biochar) released the highest amount of NO_3 9.3 mg.L^{-1} during the experiment time while 50% BC released only 0.9 mg.L^{-1}. The other treatments, 5 and 25% released 5.4 and 2.5 mg.L^{-1} respectively. The trend of the release was liner with all treatments. CSBC utilises NO_3 retention could be by its high surface area and high porosity. Another reason can be functional groups (Figure 4.3) such as carboxyl which is an effective group on NO_3 adsorption (Borchard et al., 2012c).

4.5.4 Biochar Effect on Phosphate

In general, phosphate concentration in the leachate from the columns was reduced with the addition of BC (Figure 4.12). The retention of phosphate was less at the first day (event) then increased with the time. The lowest recovery was 4 mg.L^{-1} in the control treatment and the highest was achieved for 50% BC treated media 23 mg.L^{-1}. 5 and 25% retained 9 and 23 mg.L^{-1} respectively. The result was in line with the batch test.

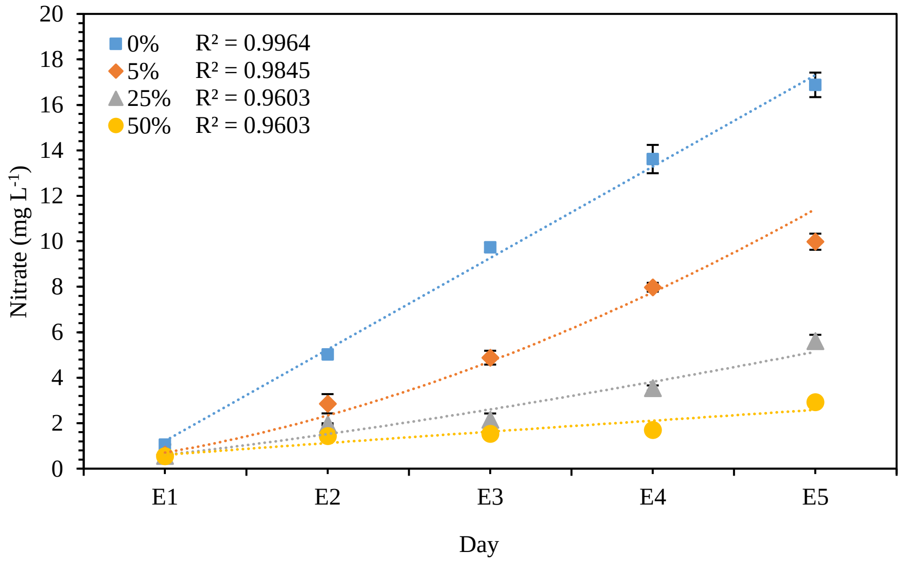


Figure 4.10: Nitrate Release into the Deionised Water over 5 Days

Phosphate concentration was low when the BC rate increased in the media. In term of releasing phosphate (Figure 4.13), the highest release was 14 mg.L^{-1} from the control treatment while the lowest value was 10 mg.L^{-1} from media with 50% biochar. 5 and 25% BC treated media released 11 and 12 mg.L^{-1} respectively. The reduction of phosphate may refer to the surface functional group (Carboxyl C-O). Based on the preliminary tests (Chapter 3) of this project, after five times of exposing CSBC to nutrients, BC adsorption gets slower and that is when back flash is needed to reuse the BC again and increase the adsorption of elements. In this way, BC can be used longer than the normal process which is just adding nutrient solution. That may depend on the concentration of nutrients, the amount of BC in a treatment and BC type. The results were in line with Hale et al. (2013). The results are in line with Zhong et al. (2019) who stated that phosphate adsorption was enhanced by coconut shell biochar. Marshall et al. (2017) also claimed that phosphate was recovered by the addition of BC to an aqueous solution.

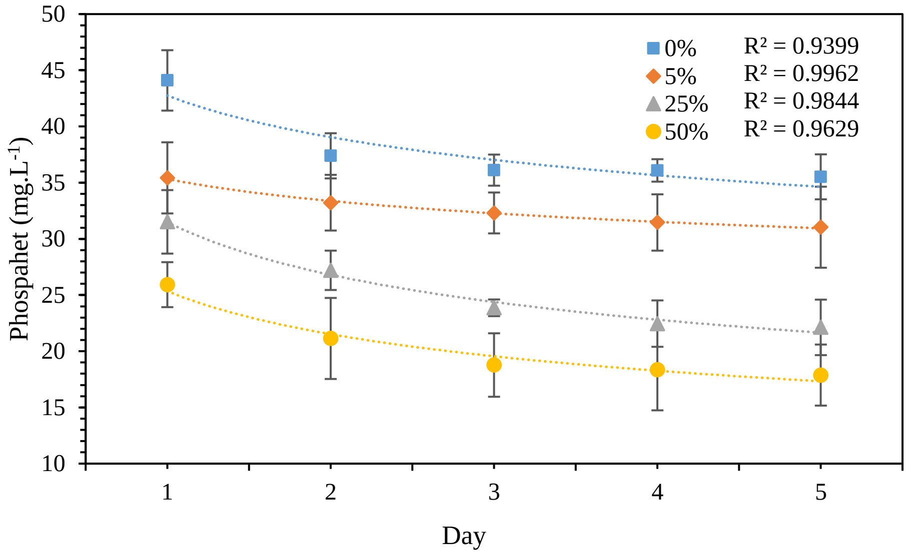


Figure 4.12: Change in Nutrient Solution Phosphate Concentration over 5 Days

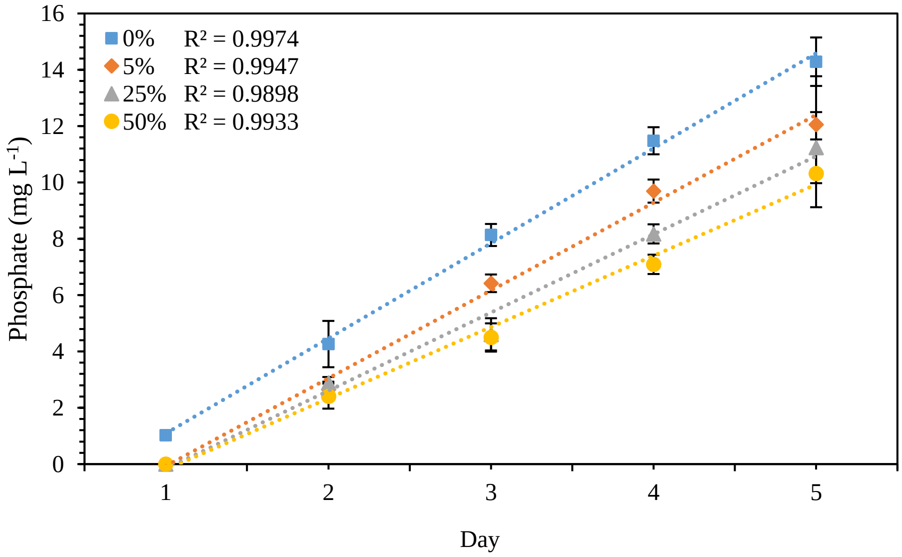


Figure 4.11: Phosphate Release into the Deionised Water over 5 Days

4.5.5 Biochar Effect on Potassium

Contrary to findings for other nutrients, K levels showed a different trend as BC increased above 25% in the media, with K retention decreasing (Figure 4.14). The addition of CSBC increased K in the solution, indicating that K might have been withdrawn from the CSBC structure, rather than being absorbed into it. The highest K retention was 17 mg.L^{-1} obtained from 25% CSBC amended media, while the lowest recovery was 6 mg.L^{-1} obtained from 50% CSBC amended media. With the 0 and 5% column amended char, the retention was 9 and 15 mg.L^{-1} respectively.

Increasing K levels by using coconut shell carbon has been reported by (Gaskin et al., 2010, Yin et al., 2012, Biederman and Harpole, 2013). The increase in K concentration could be due to CSBC being made of plant waste, which is often rich in K (Shenbagavalli and Mahimairaja, 2012). In the batch test (Figure 4.5) the result was similar to the column tests, except that the 25% and 50% CSBC treated media showed almost identical K retention. Potassium released (Figure 4.15) was higher as the CSBC rate increased in the substrate. The lowest release was obtained from 0% CSBC amended media until event 4 but at the last event, 5% released (41 mg.L^{-1}) less than the rest of the treatments. The highest release was 57 mg.L^{-1} from the 50% CSBC mixed media during the experiment events.

The adsorption of K could be mainly due to the carboxyl group in the CSBC (Wang et al., 2015). The CEC could be another plausible reason for a decrease in this element

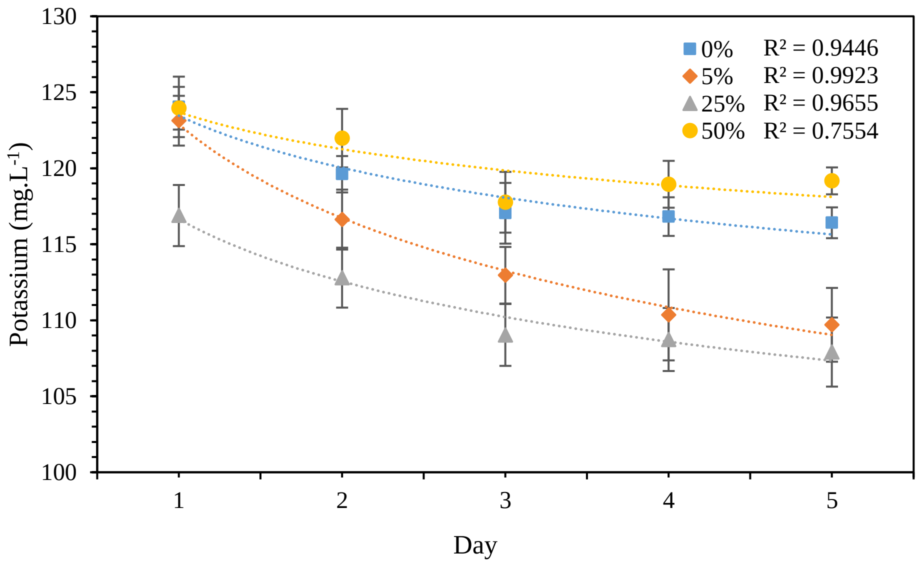


Figure 4.13: Change in Nutrient Solution Potassium Concentration over 5 Days

in the leachate (Nelson et al., 2011). Therefore, according to these results, BC can be used as an organic source of K fertiliser rather than use of inorganic compounds. Thus, CSBC can leveraged as an eco-friendly source of K in hydroponics.

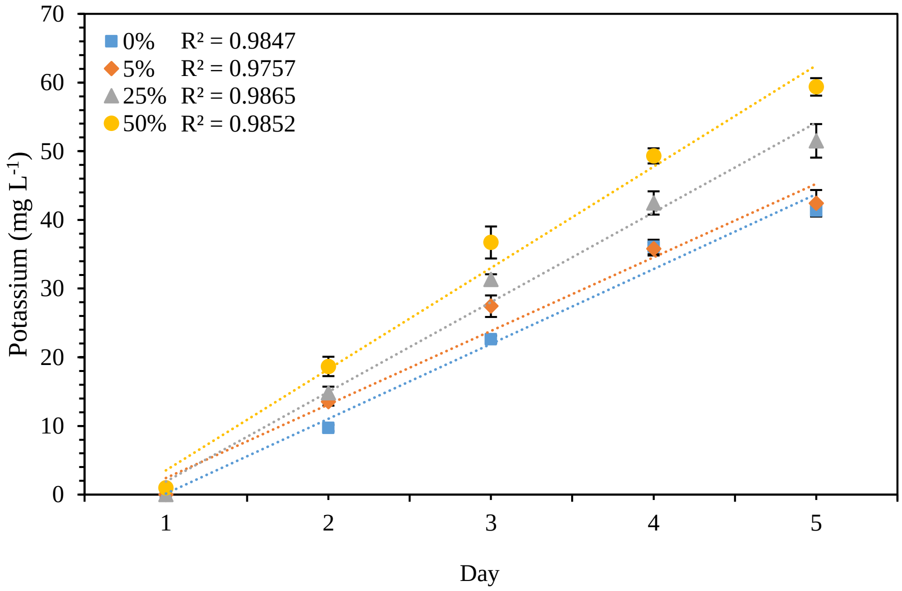


Figure 4.14: Potassium Release into Deionised Water over 5 Days

4.5.6 Biochar Effect on Leachate Calcium

The addition of CSBC reduced Ca concentration in the leachate in all events (Figure 4.16). The highest retention of Ca was into the columns with 50% CSBC while the lowest was into the control columns. The control and 5% CSBC treated media had a similar trend of Ca recovery. This could be because of 5% CSBC is a small amount to affect Ca retention thus, the trend of Ca recovery was directed by the sand, not biochar. The 25 and 50% CSBC amended media recovered 27 and 34 mg.L^{-1} respectively. Calcium releases (Figure 4.17) increased in the leachate during experimental period. Calcium like most of the other nutrients can be adsorbed by CSBC then released slowly over time. Biochar typically is a source of Ca as it is plant based product. There is a limited number of data on the effect of BC on Ca in a solution. Some paper showed that BC increased Ca in soils, thus increased Ca in plant tissues (Sorrenti et al., 2016).

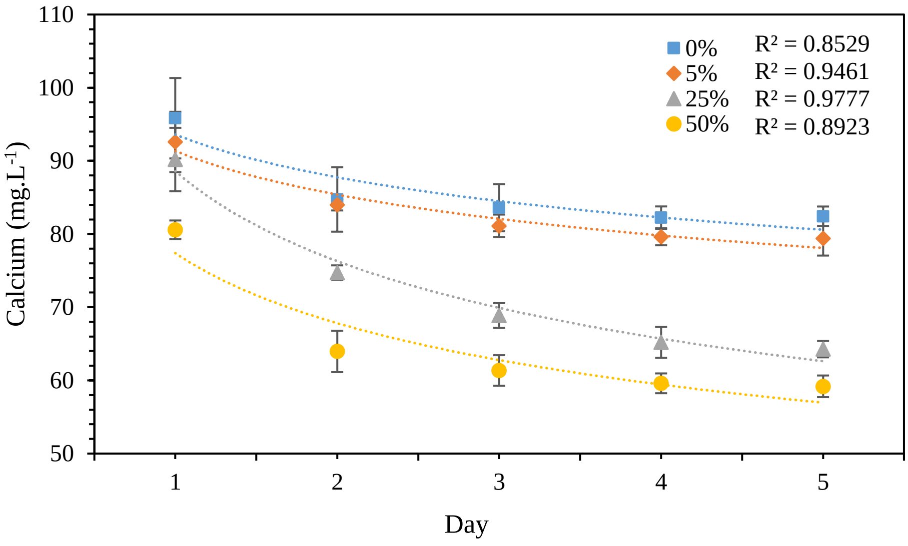


Figure 4.15: Change in Nutrient Solution Calcium Concentration over 5 Days

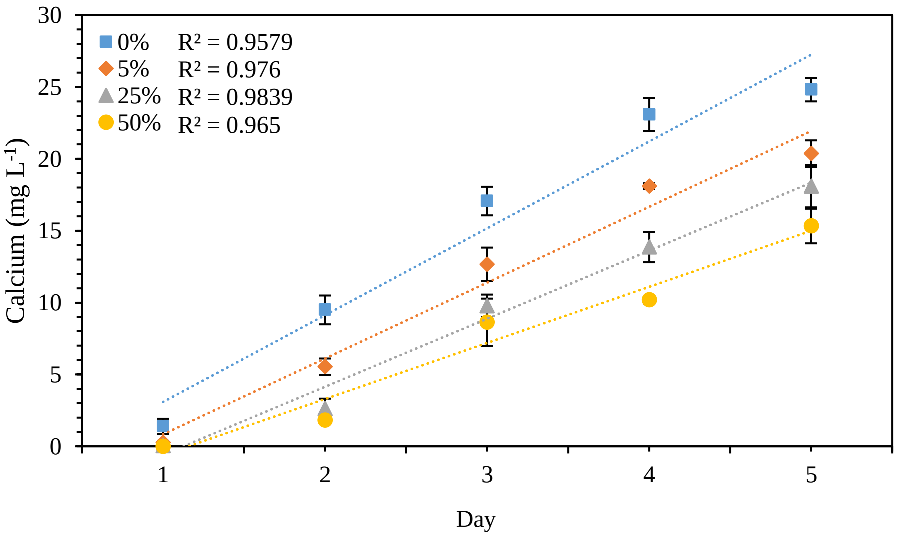


Figure 4.16: Calcium Releases into Deionised Water over 5 Days

4.5.7 Biochar Effect on Magnesium

The retention of Mg was negligible by CSBC during the experiment (Figure 4.18). All the CSBC ratios had a similar effect between 23.3, 23.4, 23.6 and 23.8 mg.L^{-1} for 50, 25, 5,and 0% BC, respectively. There were no effects from CSBC on Mg retention in the batch tests or in the column tests. The release of Mg increased in the leachate over time, but it showed little variation with CSBC ratios (Figure 4.19). In general, the control treatment released more than other treatments. The release was somewhat similar with the 5 and 25% treatments. At the end of the test, all treatments released a similar amount of Mg between 12-13 mg.L^{-1}. However, the results indicated that CSBC was not a desirable source of Mg retention, as BC released Mg slowly over the experiment time rather than being washed. The results are in line with Sorrenti et al. (2016) who reported that BC did not retain Mg in enriched solutions.

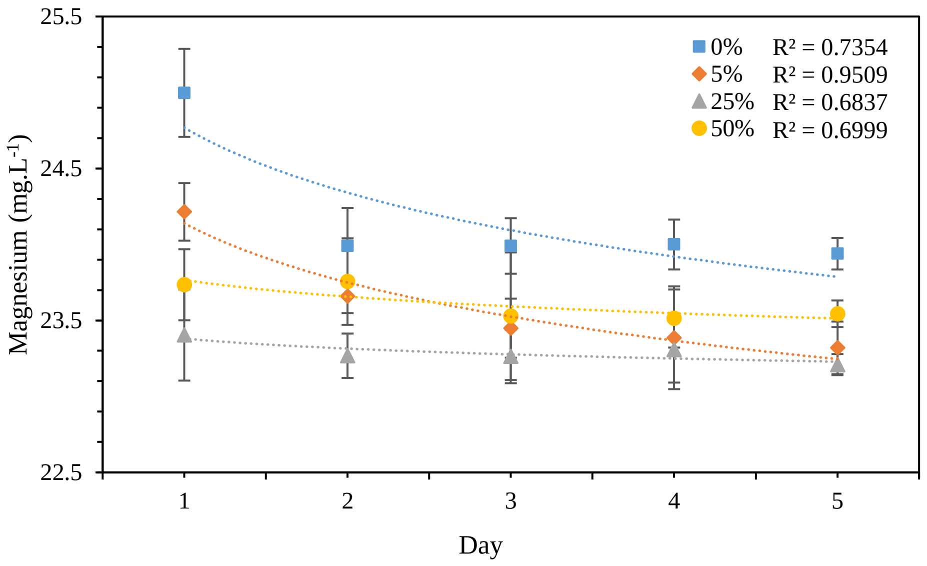


Figure 4.17: Change in Magnesium Nutrient Solution Concentration over 5 Days

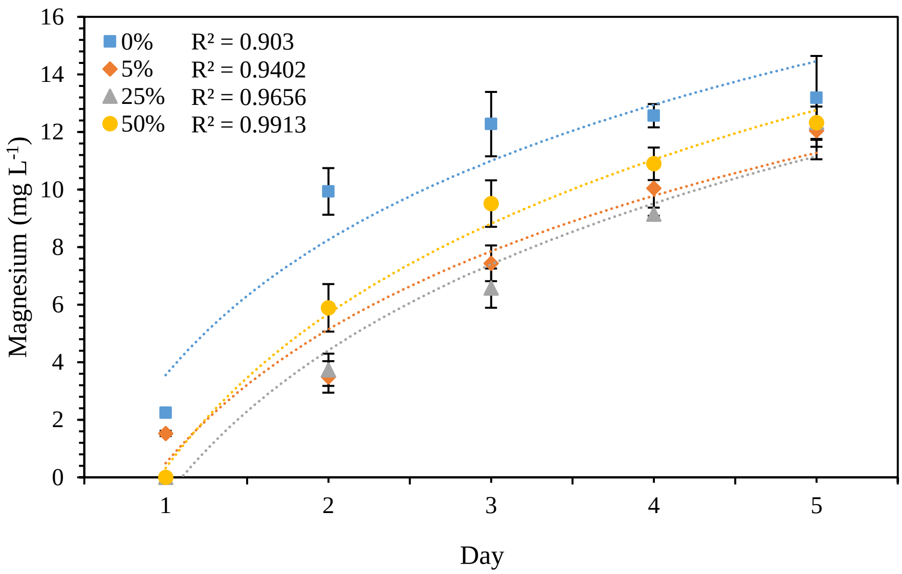


Figure 4.18: Magnesium Release into the Deionised Water over 5 Days

4.5.8 Biochar Effect on Sulphate

Sulphate concentration was reduced in the leachate during the experiment and by increasing the CSBC ratio (Figure 4.20). The lowest retention was 20 mg.L^{-1} from the control treatment, while the highest retention was 35 mg.L^{-1} from 50% CSBC amended media. The 5 and 25% CSBC treated columns retained 26 and 38 mg.L^{-1} respectively. The recovery of SO_4 was affected directly by the BC ratio. As the BC ratio increased, the retention of SO_4 also increased. Similar results were obtained from the batch test (Figure 4.5).

The release of SO_4 in the leachate was affected by the amount of CSBC in the media during the trial (Figure 4.21). In general, the highest release was 43 mg.L^{-1} from the control treatment while the lowest was 36 mg.L^{-1} from both 25 and 50% treatments. The 5 CSBC treated media released 40 mg.L^{-1}. Once again, the surface functional groups could prove to be the main reason behind the SO_4 adsorption (Borchard et al., 2012a). Coconut shell activated carbon was washed with acid, hence, that may have made functional groups on the CSBC actived. Thus, the retention of nutrients can be due to the presence of carboxyl groups.

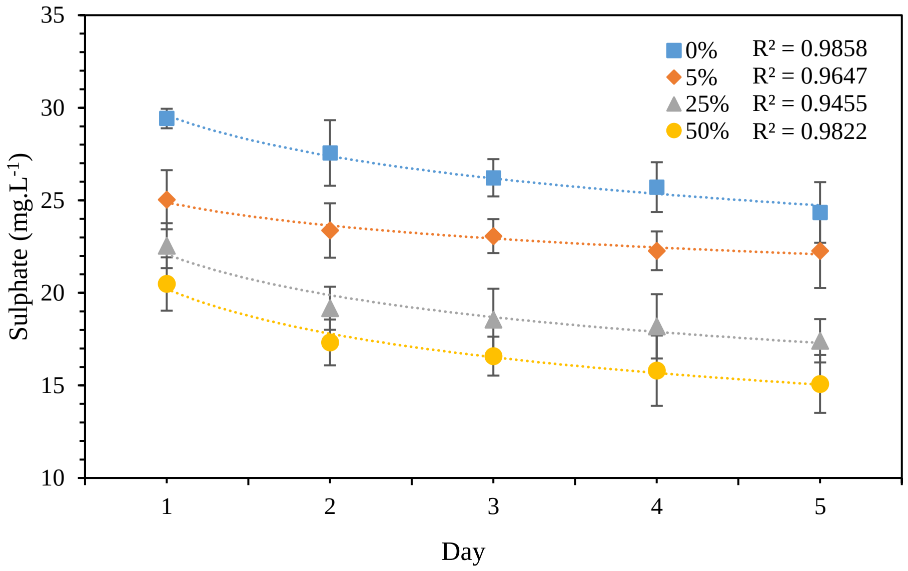


Figure 4.19: Change in Nutrient Solution Sulphate Concentration over 5 Days

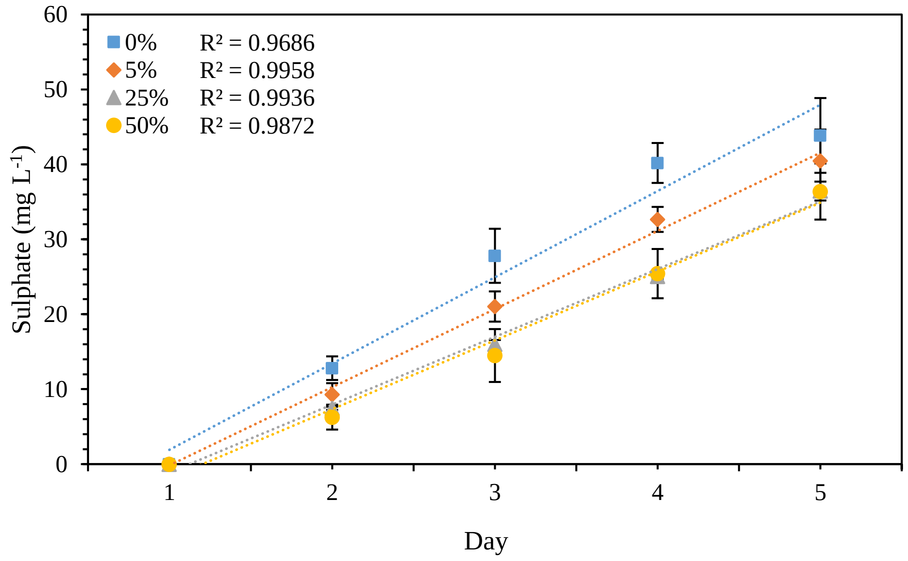


Figure 4.20: Sulphate Release into the Deionised Water over 5 Days

4.6 Steady State Nutrient Behaviour

Allowing the system long enough to settle i.e. 5-6 days, shows that 25 - 50% CSBC treated media have the highest retention and the lowest release of all nutrients in this study, with the exception of K. It was also shown that media without BC had the highest nutrient release, once again with the exception of K. From a plant science perspective, it is recommended to use no more than 25% CSBC in the media, as there was little difference between this ratio and the 50% ratio, in terms of nutrient retention. Also, the 25% and 50% CSBC treated media released similar amounts of nutrients, such as PO_4, Mg and SO_4. Another benefit of using the 25% ratio is that it reduces the on-going production costs of hydroponic farms.

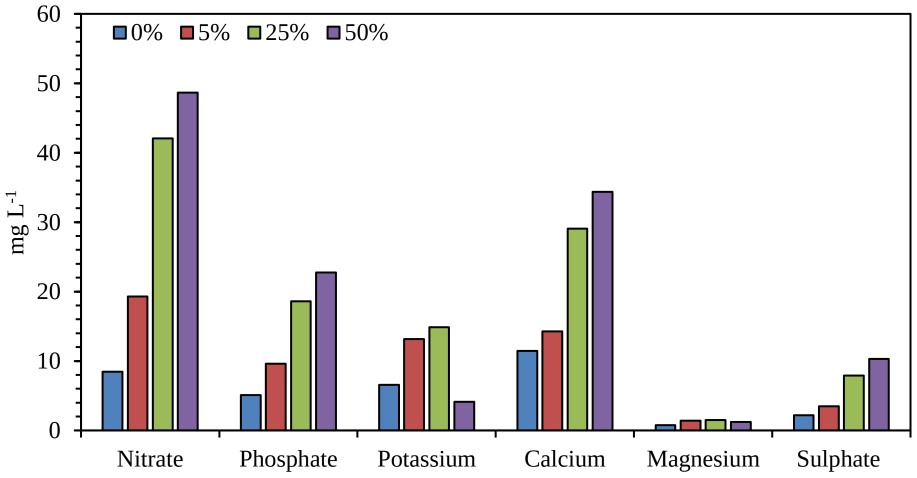


Figure 4.21: System Steady-State Nutrient Retention

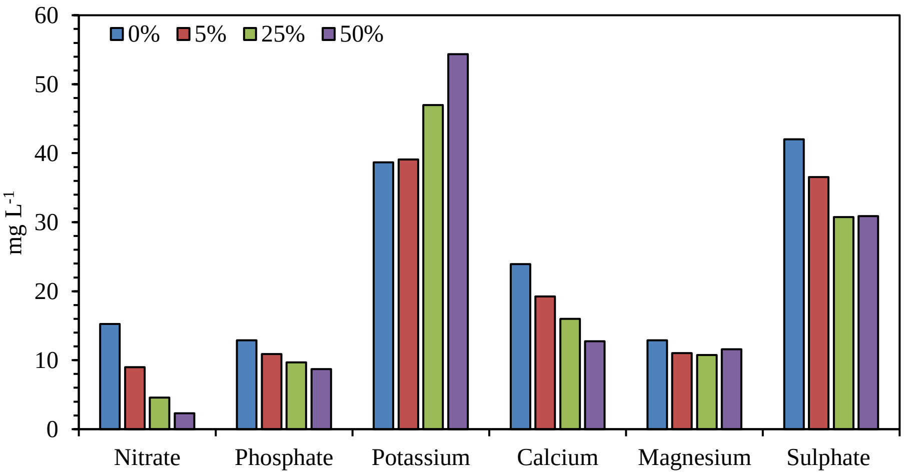


Figure 4.22: System Steady-State Nutrient Release

4.7 Sand Filter Media Behaviour

From the previous figures (Figures 4.10 - 4.21) on the adsorption and desorption of macronutrients, it can be seen that the sand also had effect on the nutrient retention and release. As shown in the literature, sand is one of the materials which have been traditionally used for water filtration. Sand was used to minimise both inorganic and organic components in the water. Wathugala et al. (1987) reported that a sand filtration system removed 69 and 6 $g.m^{-2}$ of NO_3 and PO_4, respectively, from wastewater. another study about Cd(II) ion adsorption onto beach sand conducted by Taqvi et al. (2007) showed that around 66% of Cd(II) was adsorbed. Rauf et al. (1996) stated that ytterbium in dilute acidic solution was removed by sand. All of the aforementioned observations explain the change in macronutrients concentration as the solution passes through the sand.

4.8 Nutrient Trends with Biochar Addition

Biochar storage and release capability with the time generally showed common trends amongst macronutrients. An exponential trend ($y = m\ e^{cx}$) was found with the nutrient adsorption for NO_3, PO_4, K, Ca, and SO_4. Whereas in the desorption phase, the trend typically linear ($y = mx - c$) for NO_3, PO_4, Ca and SO_4. The remaining nutrients (K and Mg) fitted with logarithmic trend ($y = m\ (x) + m$).

CHAPTER 5 SECOND COLUMN TESTS:

5.1 Materials and Methods

5.1.1 Experiment Setup

The experiment was set up as follows:

- Four triple head peristaltic pumps (Thermo Scientific™ DB3000A) were used to 12 spray units, supplying DW and nutrient solution alternately to the columns.
- The water or the nutrient solution was supplied from holding tanks (Icon Water Carrier 15L) to each column.
- 24 containers (12 containers filled with DW, and the other 12 containers filled with nutrient solution) with each column linked to two containers, one with DW and another one with nutrient solution.
- 12 columns, three of them filled with peatmoss only (0% the control treatment) and the other nine columns filled with 5, 25 and 50% v/v biochar/peatmoss.
- The columns were first irrigated with DW on the first day (E1) for around 38 min ± 1 min (the pumps were on for 12 x 3 min intervals and off for 10 x 2 min intervals)
- Samples from the DW containers were taken and frozen for later analyses.
- On the second day (E2), the columns were irrigated with stock solution for 38 min ± 1 min (as the above process with DW) and samples from the stock solution containers were taken and frozen for later analyses.
- The process continued with alternate: one day with DW and the other day with the stock solution until 15 events (8 events with DW and 7 events with the stock solution) achieved.

This process times chosen (as per Figure 5.1and Table 5.1) are in accordance with what farmers use in commercial hydroponic farms. The standard setup is a closed-loop system that offers the most economic and eco-friendly option compared to other hydroponic growing systems (Bar-Yosef, 2008, Grewal et al., 2011).

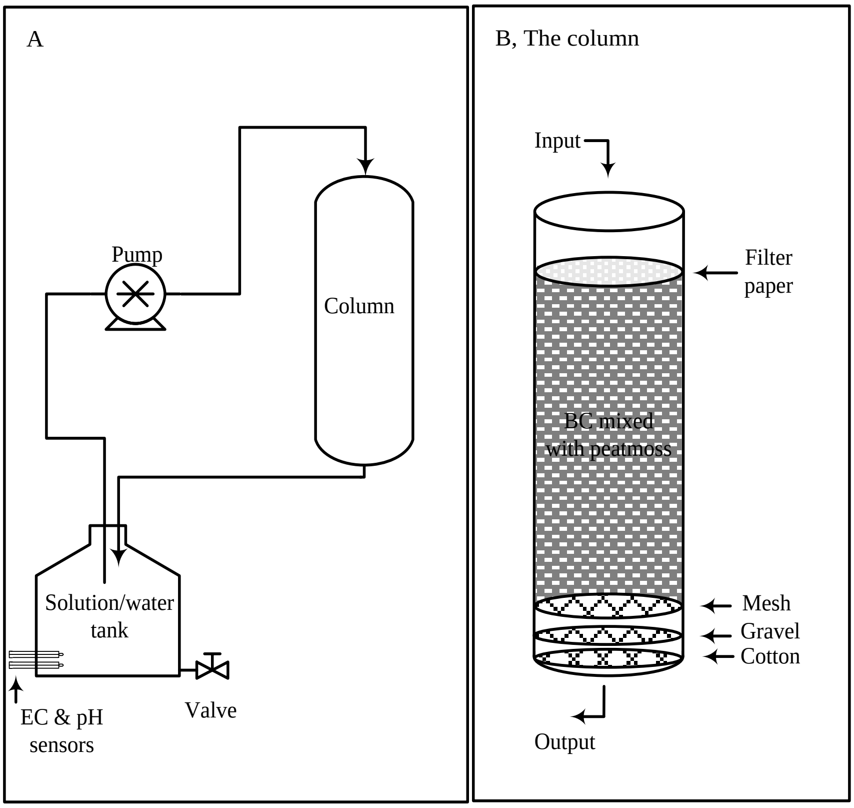


Figure 5.1: (A) General Experimental Setup. (B) Column Design

5.1.2 Substrate Types

The substrates used in this work comprised of coco-peat (peatmoss) obtained from a local farm (K Farm, Toowoomba, Australia) provided by Aussie Environmental-Australia and BC provided by Clarence Water Filter, Australia. BC was washed for 4 times to bring the hydroponic solution pH level down to 5.5 - 6.5 and ensure as much as possible, the stoppage of caustic mineralised ash releases into the solution. BC and peatmoss were sterilised at 120 °C for 30 min using an autoclave (HICLAVE, HV-50L) to minimise biological activity, then oven-dried at 70 °C for 24 h. Finally, the prepared substrate was stored in a dry environment in closed containers until they were used.

Table 5.1: Irrigation Experiment Timing over 15 Days

Biochar ratio	Replicates	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	Day 8	Day 9	Day 10	Day 11	Day 12	Day 13	Day 14	Day 15
0% CSBC	R1	*DW	*NS	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW
	R2	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW
	R3	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW
5% CSBC	R1	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW
	R2	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW
	R3	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW
25% CSBC	R1	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW
	R2	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW
	R3	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW
50% CSBC	R1	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW
	R2	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW
	R3	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW	NS	DW
*** DW = Deionised water**																
***NS = Nutrient solution**																

5.1.3 Column Preparation

The columns were constructed from polyvinyl chloride (PVC) pipe measuring 250 mm in height and 40 mm in diameter. PVC and polyethylene fittings sized 9, 13, and 15 mm were used to connect the columns to the pumps and to the stock solution input and output lines. A layer of cotton swabs was placed at the bottom of each column, then a plastic mesh (fibreglass fly screen) with 60 µm pore size was laid on the top of the cotton layer. A layer of gravel-sized 2-4 mm was then added on the top of the mesh. The three layers were used to prevent substrates of being washed by the solution at the same time to filter the outcome. The peatmoss was mixed with BC (total mixture depth was 200 mm of the column height) in 4 rates of 0:100, 5:95, 25:75, and 50:50 v/v BC/peatmoss, respectively. The mixture was then packed into the columns. The columns were gently tapped a few times to let the media settle. A filter paper (Whatman 45 µm) was placed on top of the media to ensure a good distribution of the solution in the column packing materials Figure 5.1 (B). The columns were closed from both ends with plastic caps that have opening for connecting the inlet and outlet lines simulating a closed hydroponic system, as shown in Figure 5.1 (A). The columns were then placed in their respective holders and connected to the stock solution containers, via the input and output pipes.

5.2 Substrates and Stock Solution Characterisation

The characteristics of the substrate and stock solution (provided by a local commercial hydroponic farm K Farm, Toowoomba, Qld, Australia) such as pH, EC and the concentration of NO_3, PO_4, K, Ca, Mg and SO_4 were examined using pH and EC (PC 2700 from EUTECH INSTRUMENTS) meters along Ion Chromatography System ICS-2000 and Atomic Absorption Spectrophotometer AAS-7000 (SHIMADZU, Australia) following the standard methods described in (Eaton et al., 2005). The results for peatmoss and stock solutions are presented in Tables 5.2 and 5.3. It is worth mentioning that all of the applied measurements were conducted in triplicate to ensure the accuracy of the results.

DW was used as an extraction solution for the peatmoss constituents. Peatmoss was mixed with DW in a ratio of 1:20 (w/w, peatmoss to DW) and loaded into 100 ml plastic vials. The mixture was shaken at 100 rpm/min for 24hrs. The resultant mixture was then filtered through filter paper (Whatman 45 µm). The filtrate was then used for performing the analyses. Biochar pH and EC were also measured following (Wang et al., 2015) where 1:20 ratio for BC to DW was used. Figure 5.2 shows the surface morphology of the CSBC used in this test.

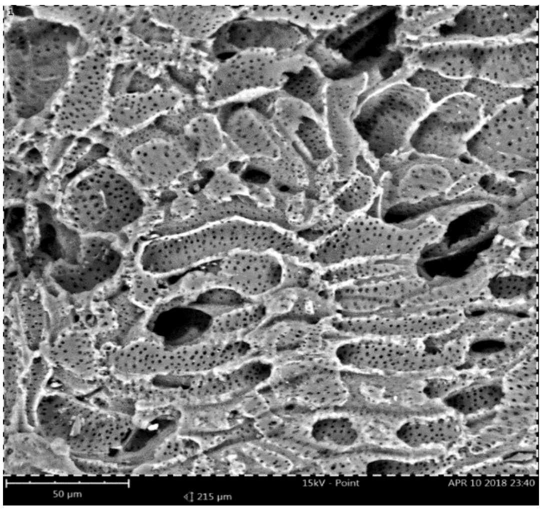


Figure 5.2: CSBC Surface Morphology

5.2.1 pH and EC Measurements

The pH and EC were measured at a solid/water ratio of 1:20 w/v for CSBC or sand to DW. Samples were weighed into 5g lots, then 25ml DW was added. The mixture of CSBC and DW was shaken for 5 min on a RATEK shaker at 100 rpm before pH and EC were measured using a PC 2700 from EUTECH INSTRUMENTS. All the measurements were performed following the Standard Methods outlined in (Baird et al., 2017).

5.2.2 Nutrient Assay

The nutrient content of CSBC and sand were measured as follows; **1)** sand, 1 part sand to 5 part DW were loaded into a container and shaken for 1 hour before being centrifuged for 10 min at 3000 rpm. The centrifuged solution was filtered with Whatman 45 µm filter paper before measuring K, Mg, and Ca with the AAS and NO_3, PO_4, and SO_4 with the ICS. **2)** CSBC, the mixture of CSBC:DW (Section 2.2.1) was used to measure pH and EC was further shaken for 24h before measuring nutrients. The mixture was filtered with Whatman 45 µm filter paper and taken to the ICS to measure NO_3, PO_4 and SO_4 and the AAS to measure K, Ca and Mg. Table 5.2 and 5.3 show the stock solution characteristics the basic properties of the peatmoss that used in this test.

Table 5.2: Stock Solution Characteristics

pH level	6.2
EC (mS.cm^{1-})	2.3
Nitrate (mg.L^{1-})	300.97
Phosphate (mg.L^{1-})	32.91
Potassium (mg.L^{1-})	136.63
Calcium (mg.L^{1-})	140.12
Magnesium (mg.L^{1-})	18.01
Sulphate (mg.L^{1-})	157.01

5.3 Results and Discussion

5.3.1 Biochar Impacts on Leachate pH

Figures 5.3 and 5.4 show the effect of BC on the pH of leachate from the column with nutrient solution and DW, respectively for retention and release events. It can be seen that pH increased in all treatment scenarios, except for nutrient solution without biochar. This could be attributed to the acidic nature of peatmoss (pH of 4.34). The pattern of pH increase during treatment events was different for the two tested solutions. The level of pH had a sharp increase with nutrient solution for the first day (event) especially with high BC ratio. Then the increase almost plateaued. In comparison, the increase of pH level with DW exhibited a logarithmic growth curve for all BC rates. The maximum pH increase of 1.2 was achieved with DW using 50% biochar.

Table 5.3: Basic Properties of Peatmoss

pH level	4.34
EC (mS/cm)	2.3
TN (mg.L^{1-})	5.32
Phosphate (mg.L^{1-})	0.20
Potassium (mg.L^{1-})	0.31
Calcium (mg.L^{1-})	1.72
Magnesium (mg.L^{1-})	1.02
Sulphate (mg.L^{1-})	0.11

Given the acidic nature of peatmoss, BC addition can help to bring the pH to a more neutral level. As the level of pH is increased over 7, this can affect plant growth and productivity negatively, as stated by Wortman (2015) where pH should be kept in the range of 5.5-6. The effect of pH on plants was invested by Koehorst et al. (2010) where low (4.5) and high (8.5) pH significantly reduced plants productivity. Raviv et al. (2019) showed that biochars were able to increase pH level to suit the majority of plant groups in soilless cultivation. Increasing pH level by adding BC to the growth media could be due to a number of factors. The main one being that BC ash contains many base cations, such as Ca, Mg, K and Na, so the exchange of ions reduces the media's hydrogen concentration (Novak et al., 2009b).

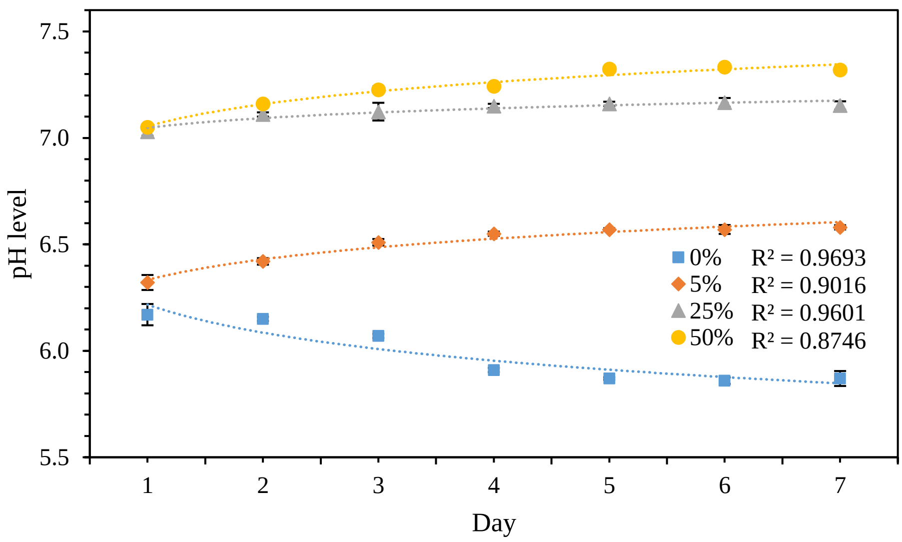


Figure 5.3: Nutrient Solution pH Level over 7 Days. P<0.001, n=3

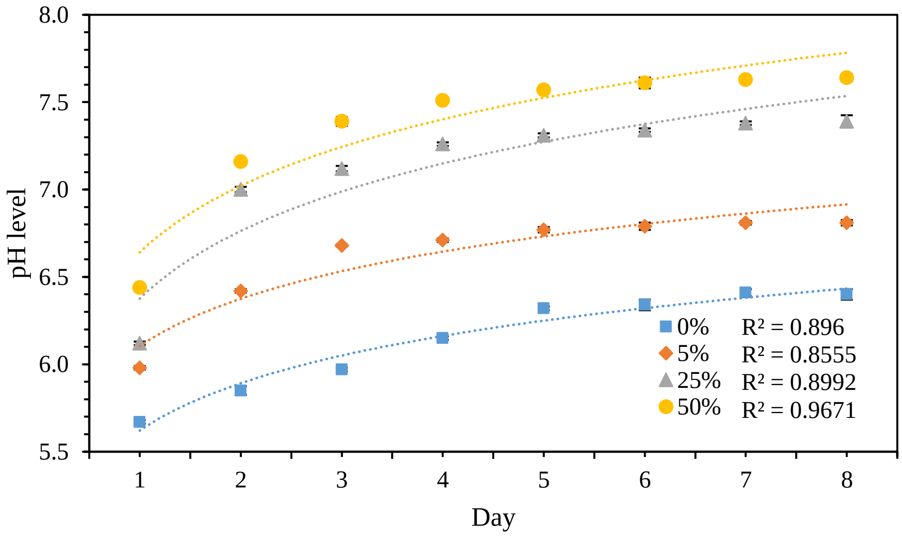


Figure 5.4: Deionised Water pH Level over 8 Days. P<0.001, n=3

5.3.2 Biochar Impact on EC Level

Figures 5.5 and 5.6 illustrate the effect of BC on EC during retention and release events. It can be noticed that the retention events led to reducing EC in the columns effluent and vice versa with release events. The variation in EC reflects the change in nutrients and anions concentration in the passing solution through the columns. In general, the increase of the effluent EC with the release events was higher than the decrease with retention events. The maximum decrease of EC of approximately 837 µS was achieved with 50% BC, whereas the maximum increase in EC of 977 µS was achieved with 0% BC. This is due to the strong stripping effect of DW and the sorption capacity of BC, as shown by Raviv et al. (2019).

Proper nutrient factors such as EC, the type of nutrient, composition of irrigated nutrient solution and so on are key factors to improve yield quality. Savvas (2001) stated that EC is considered to be one of the most important properties of the nutrient solutions used in soilless cultivation. If the EC of a nutrient solution is too low, the supply of some nutrients to the crop may be inadequate. Similarly, when the EC is too high, the plants are exposed to salinity effects. However, the yield response of the plants to the EC of the nutrient solution may vary widely among different species. Therefore, for each cultivated plant species, the terms "too low" and "too high" need to be quantitatively defined based on experimental results. (Putra and Yuliando, 2015). Electrical conductivity was significantly affected by the BC rate and with the experiment time. Electrical conductivity of peat was raised by adding $CaCO_3$ and by mixing with biochars that contained soluble salts and carbonates; in particular, in P-BC+peat, the salinity was increased fourfold. In any case, EC levels were well below the threshold (<300 mSm^{-1}) recommended for soilless substrate fertilising solutions (Raviv and Lieth 2008).

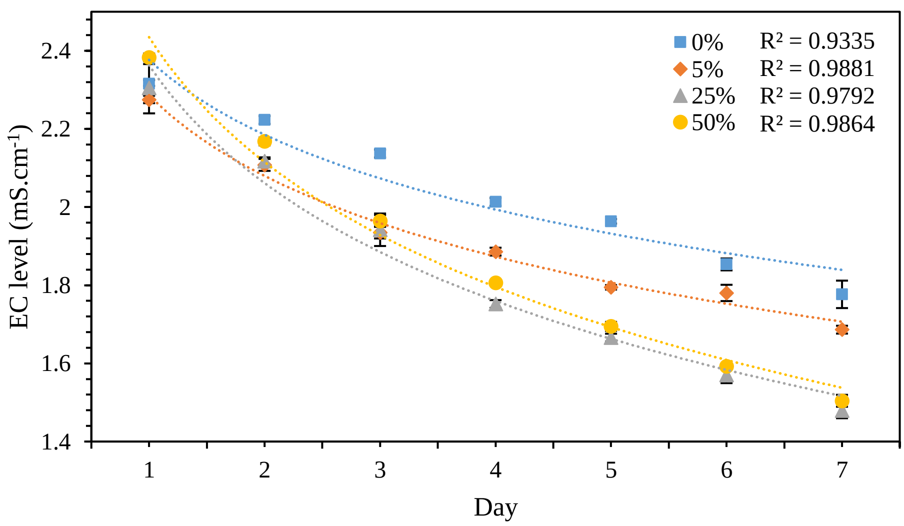


Figure 5.5: Nutrient Solution EC Level over 7 Days. P<0.001, n=3

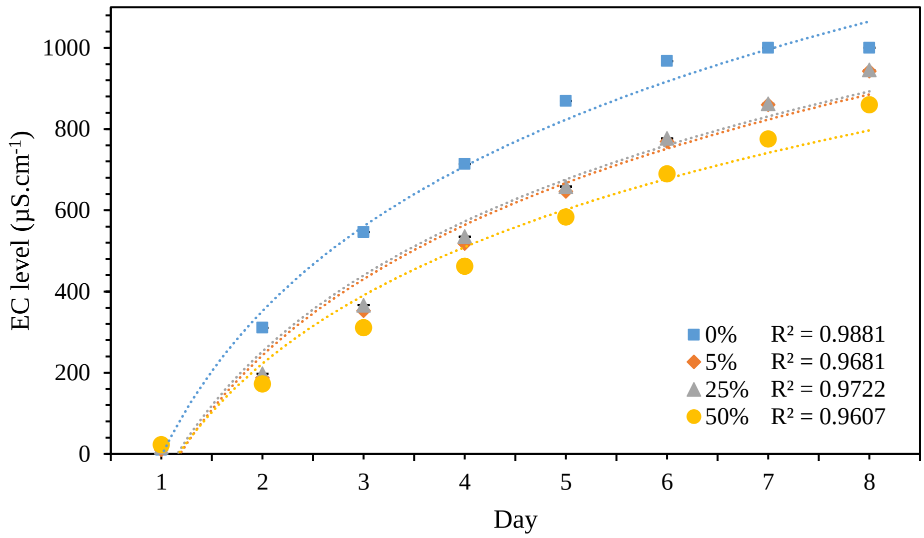


Figure 5.6: Deionised Water EC Level over 8 Days. P<0.001, n=3

5.3.3 Biochar Impact on Nitrate Concentration

The results presented in this section are expressed in mean values of three measurements and the error bars represent that standard error of these measurements.

The retention of NO_3 onto column packing materials and its subsequent release are illustrated in Figures 5.7 and 5.8. The retained NO_3 concentration had a linear correlation with the frequency of the events. It is apparent that the presence of BC increased the retention of NO_3 in the column. Nitrate retention increased with increasing biochar rate. The release of NO_3 was the highest for 0% biochar. The amount of NO_3 release decreased with increasing BC rate. This is closely related to the holding capacity of BC for NO_3. It can be noticed that the released amount of NO_3 with 0 % BC does not follow a linear trend and it plateaued after the sixth day. The recovered amount of NO_3 from peatmoss decreases after a certain number of release events. The addition of BC reduced NO_3 in the leachate which is in line with the findings reported in (Altland and Locke, 2012, Yao et al., 2012b, Gai et al., 2014, Ding et al., 2010). Beck et al. (2011) also showed that adding BC to trays increased NO_3 retention. The retention of NO_3 onto BC could be attributed to the electrochemical interaction with the basic functional groups of the char (Wang et al., 2015). Steam activation of BC almost doubled the positive effects of biochars for nutrient retention, and this highlights the need for further investigation for effective application of BC in hydroponic systems (Borchard et al., 2012c).

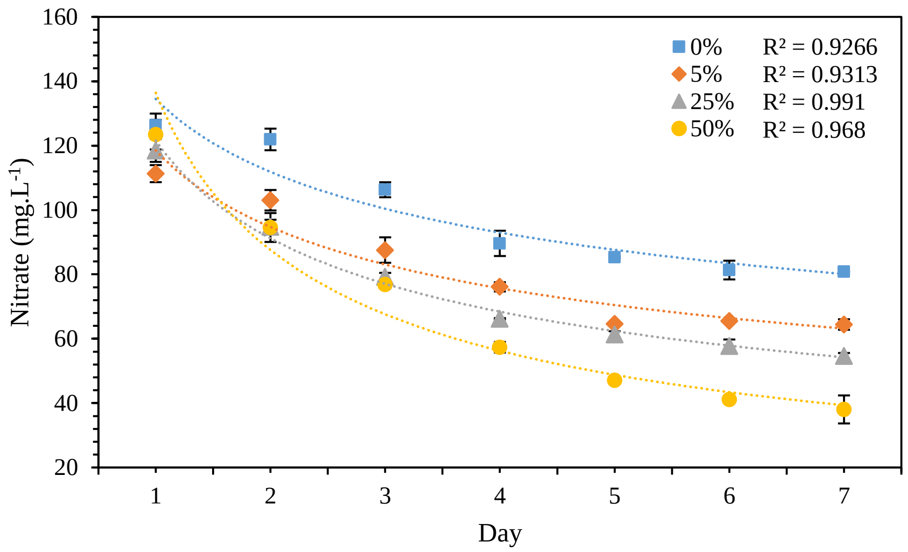


Figure 5.7: Nutrient Solution Nitrate over 7 Days. P<0.001, n=3

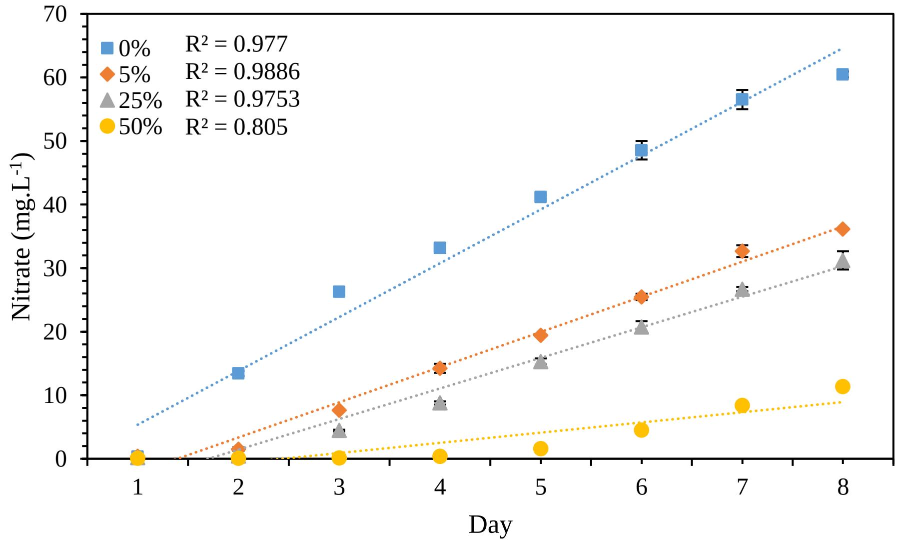


Figure 5.8: Deionised Water Nitrate over 8 Days. P<0.001, n=3

5.3.4 Biochar Impact on Phosphate Concentration

Phosphate was retained and released as shown in Figures 5.9 and 5.10 respectively. It can be noticed that the amount of PO_4 absorbed and released by BC is much less than that of NO_3. This is ascribed to the high concentration and the co-existence effect of NO_3 (Zhong et al., 2019, Palanivell et al., 2020). A study conducted by (Palanivell et al., 2020) showed that BC has a greater absorption capacity of nitrogen than its desorption capacity compared to phosphorous and K especially for acid media. Given the acidic nature of peatmoss, this explains the observed difference in NO_3 behaviour as opposed to PO_4 and K (will be addressed in the following section. Similar to NO_3, the adsorption and release exhibited liner correlations with the frequency of the events.

In general, higher rate of BC in the media resulted in more retention of PO_4 and less releasing. The control treatment retained around 7 $mg.L^{-1}$ whereas 50% BC retained around 22 $mg.L^{-1}$. The 5 and 25% treatments retained around 13 $mg.L^{-1}$ and 18 $mg.L^{-1}$ respectively (Figure 5.9). As PO_4 was retained by BC, it was released slowly over the experiment time (Events). The highest release of PO_4 was from the control treatment while the lowest was from 50% BC. It was around 27 $mg.L^{-1}$ for 0% BC and around 17 $mg.L^{-1}$ for 50% BC. The 5% and 25% BC treated media released around 22 $mg.L^{-1}$ and 23 $mg.L^{-1}$, respectively. The results of this study are aligned with the findings reported in the literature as BC was found to be capable of absorbing and slowly releasing PO_4 in the leachate (Nelson et al., 2011). However, the capacity of BC on controlling the mobility of PO_4 depends on feedstock and pyrolysis conditions of the char (Yao et al., 2012b). CSBC was acid washed biochar, this might have improved the retention ability of BC.

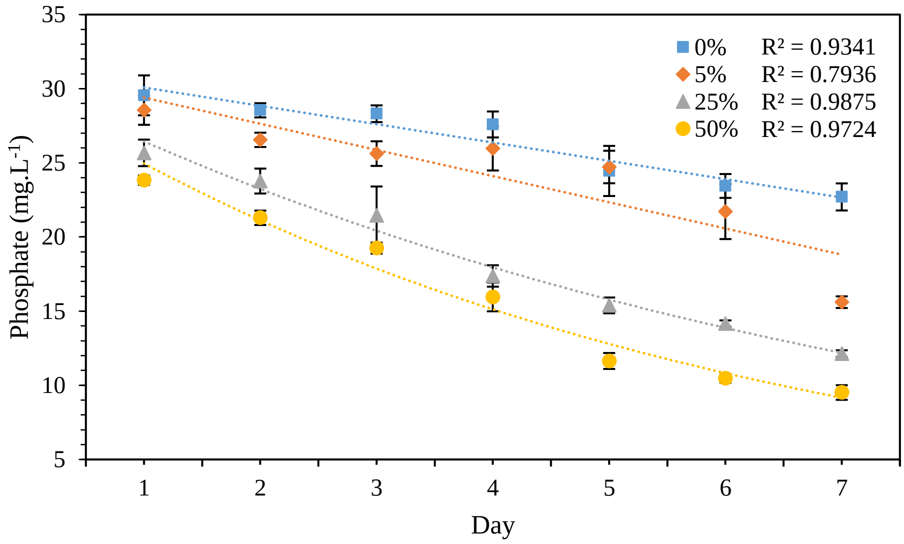


Figure 5.9: Nutrient Solution Phosphate over 7 Days. P<0.001, n=3

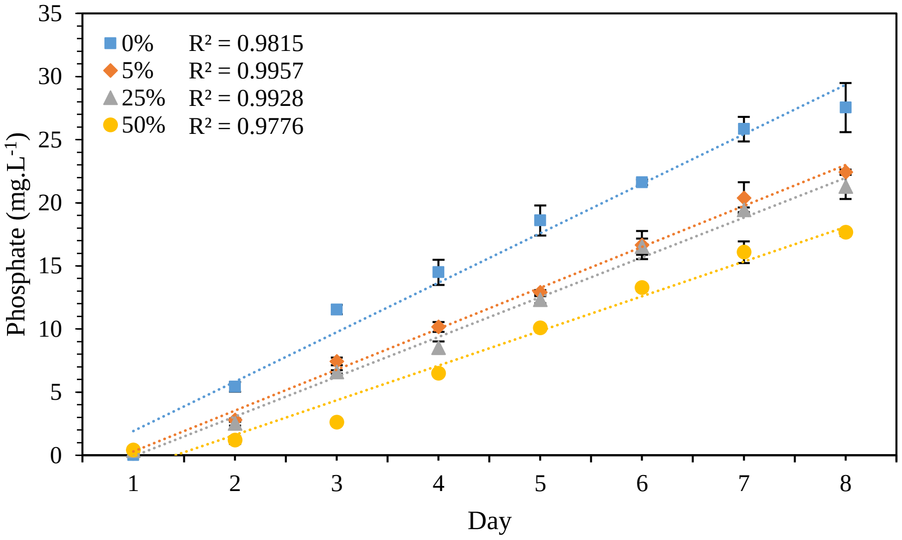


Figure 5.10: Deionised Water Phosphate over 8 Days. P<0.001, n=3

5.3.5 Biochar Impact on Potassium Concentration

The effect of BC addition on K availability in the media is demonstrated in Figures 5.11 and 5.12, unlike NO_3, SO_4 and K retention and release which follow exponential decay and logarithmic growth patterns. Comparing the concentration of K in the solution which was 136 mg.L^{-1}, the reduction of K in the leachate at the end of the test was approximately 19, 21, and 25-26 mg.L^{-1} with 50, 25 and 5% BC respectively. It can be noticed that the small rate of BC of 5% had no effect on the retention of K as it had similar retained amount of K as that of peatmoss. Interestingly, the medium rate of BC of 25% stopped absorbing K after the fourth event and started releasing small amounts of K after that. Some K release from media with 5 % was also noticed at the end of the retention events. This indicates that for effective retention of K in the media, a high rate of BC of at least ≥ 50 % needs to be applied.

With regards to the release experiments, media with and without BC had similar results for events at the beginning and the end. The highest release of K was from 50% BC treated columns whereas the lowest was from the control treatment. 50% BC released around 100 mg.L^{-1}, the other treatments released 95-97 mg.L^{-1}. For the events in the middle, the release was higher with the higher concentration of BC. It can also be noticed that the amount of K released is higher than the absorbed K indicating the leaching of K form BC structure. Similar results were reported by (Zhong et al., 2019, Palanivell et al., 2020) . This can be an attractive trait for both hydroponic and soil based agriculture as BC can reduce the amount of K added to plants. Wu et al. (2019) found that the addition of BC increased the availability of dissolved and bioavailable K in the soil.

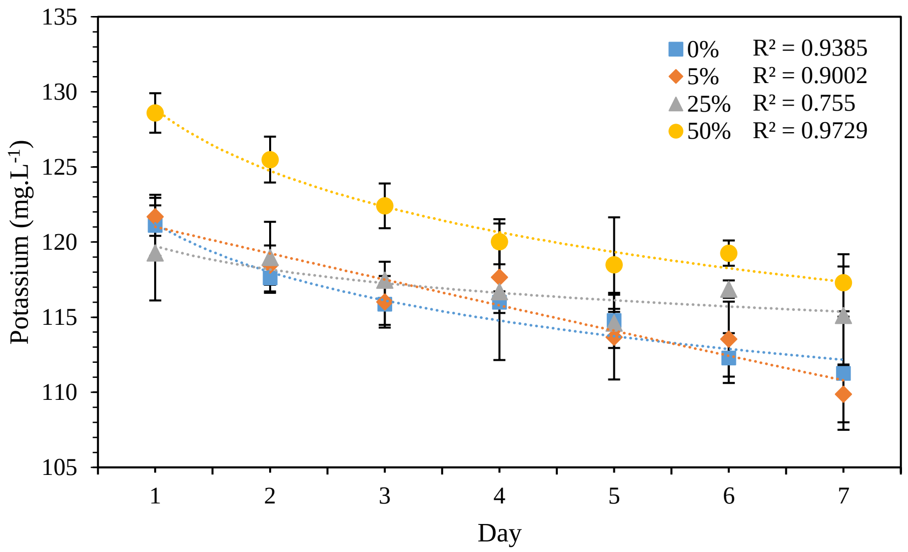


Figure 5.11: Nutrient Solution Potassium over 8 Days P<0.001, n=3

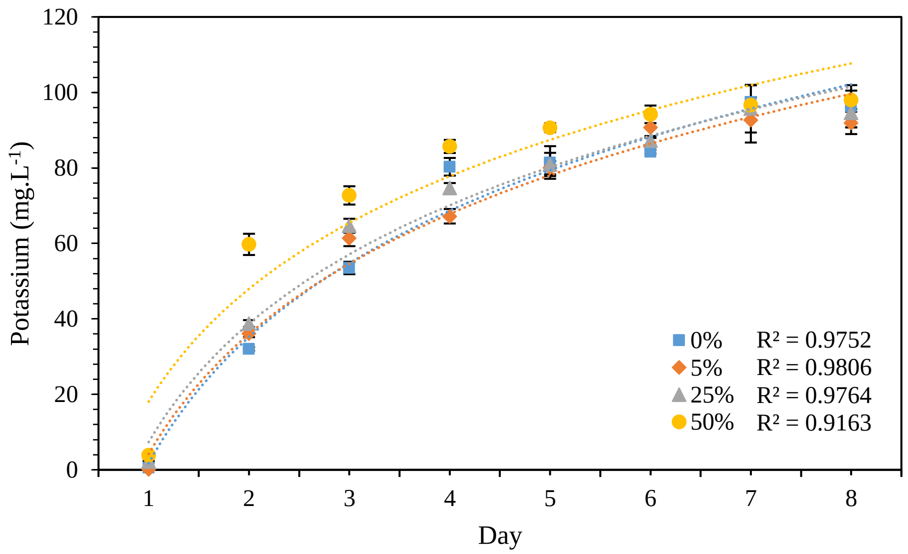


Figure 5.12: Deionised Water Potassium over 7 Days P<0.001, n=3

5.3.6 Biochar Impact on Calcium Concentration

The effect of BC on Ca interaction with the media is depicted in Figures 5.13 and 5.14. Ca concentration in the effluent of the column followed a liner correlation with retention events in the case of 0% BC and exponential decay in the case of BC incorporation into the media. Interestingly, 5% of BC had the highest retention of Ca followed by 25% BC and then 50% BC. This might could be attributed to Ca release from BC structure when the applied BC rate is high. When DW was passed through the column for recovering adsorbed Ca, the resultant concentrations exhibited linear correlations with the frequency of release events. A considerable amount of Ca remained in the column even after eight washes with DW. None of Ca was released in the first two events for all treatments. In comparison to the other measured nutrients so far, 0% BC had the closest release amount of the absorbed element as opposed to other treatments. This suggest that peatmoss is effective in storing Ca. From the above, it can be said the combination of peatmoss and BC can effectively be used in hydroponics in order to reduce the use of fertiliser. There are limited research papers on BC effects on Ca concentration in a solution, however, many authors have shown that BC can enhance Ca availability in soils. Our results showed that CSBC can adsorb Ca then slowly release it in the DW.

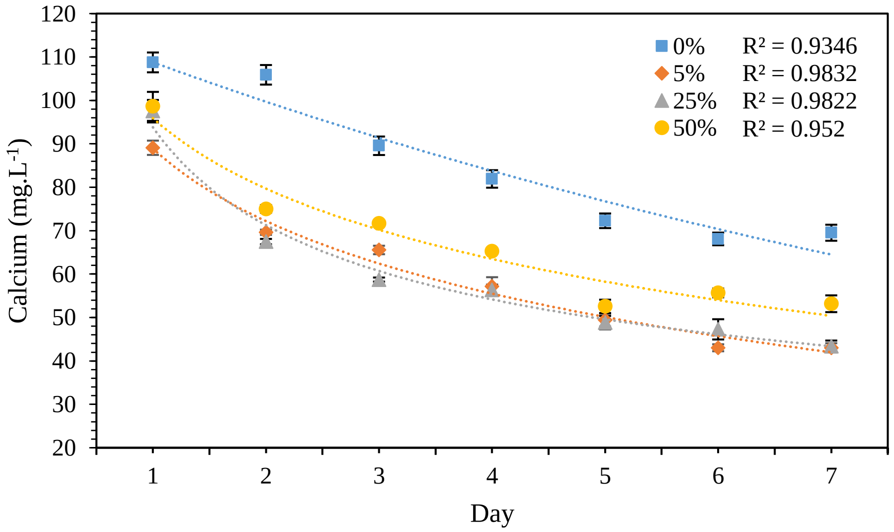


Figure 5.13: Nutrient Solution Calcium over 7 Days. P<0.001, n=3

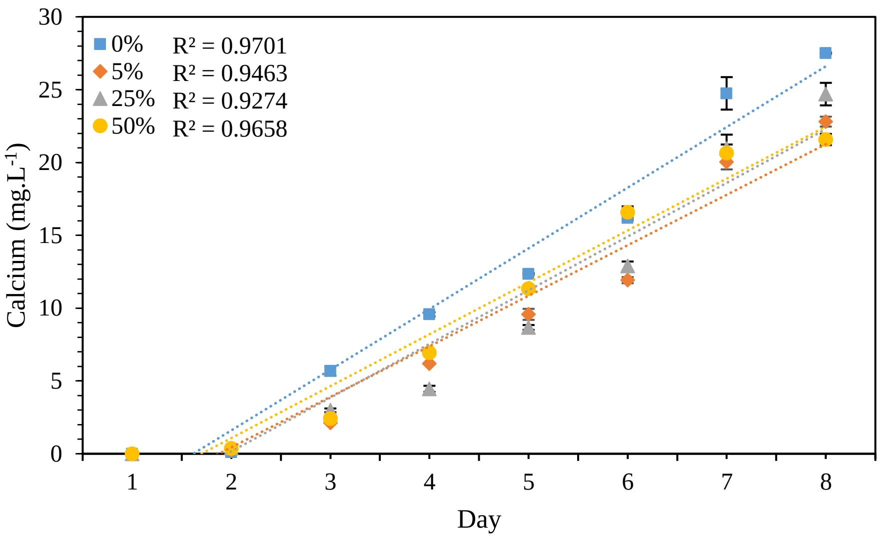


Figure 5.14: Deionised Water Calcium over 8 Days. P<0.001, n=3

5.3.7 Biochar Impact on Magnesium Concentration

The retention and release patterns of Mg are demonstrated in Figures 5.15 and 5.16. It is clear that BC did not affect Mg concentration in the nutrient solution. The difference between the control treatment (0% BC) and the other treatments was around 1 $mg.L^{-1}$. There was virtually no difference between Mg concentrations in the effluent of the column for all of the treatments with biochar. However, surprisingly there was a release of Mg when DW was used. The release exhibited a logarithmic growth trend. The released Mg was higher as BC ratio increased in the media. The highest release was around 15 $mg.L^{-1}$ with 50% BC, and it was around 13-14 $mg.L^{-1}$ with the other treatments. This suggests that DW stripped off Mg from the structure of peatmoss and biochar. These results are in line with the findings of Angst and Sohi (2013). It was also shown by Kuhlbusch and Crutzen (1995) that burning biomass lead to producing ash which has Mg. This could be the reasons why the mixture did not adsorb Mg, rather released it. Mukherjee and Lal (2014) observed that Mg concentration decreased with increasing rate of BC amendment.

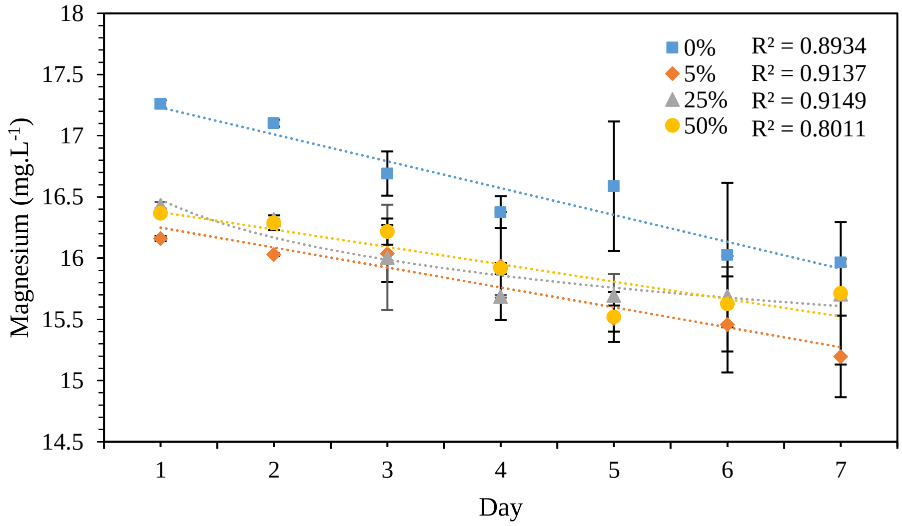


Figure 5.15: Nutrient Solution Magnesium over 7 Days. P<0.001, n=3

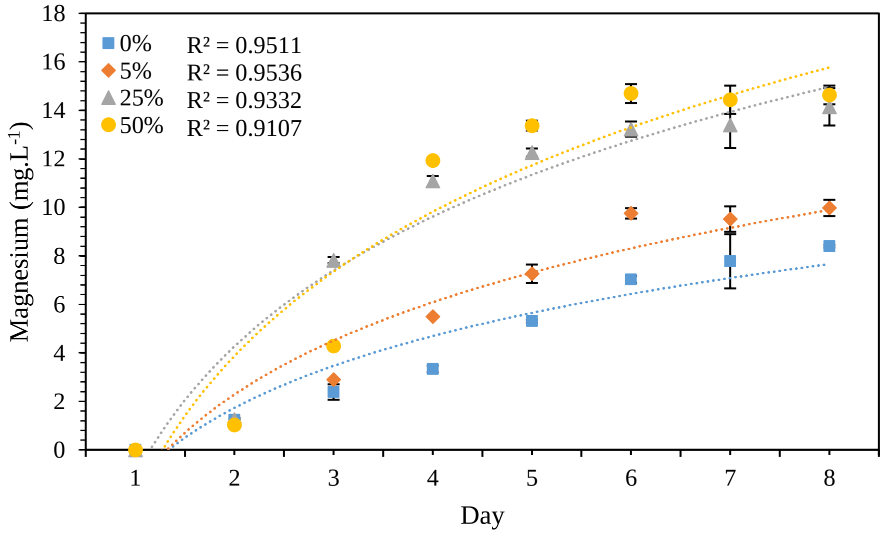


Figure 5.16: Deionised Water Magnesium over 8 Days. P<0.001, n=3

5.3.8 Biochar Impact on Sulphate Concentration

Figures 5.17 and 5.18 illustrate the effect of BC ratio on PO_4 sorption and desorption during 7 events. In general, BC improved the retention of Mg and this improvement is directly related to the rate of used BC. Compared to the initial concentration of SO_4 (140 mg.L^{-1}), the retention was around 60 mg.L^{-1} in the control treatment while it was around 100 mg.L^{-1} with 50% BC. The 5% and 25% BC treatments retained around 77 mg.L^{-1} and 84 mg.L^{-1} respectively.

In term of SO_4 release during 8 events, 0% BC released more PO_4 than other treatments. The release of SO_4 was around 60 mg.L^{-1}, 37 mg.L^{-1}, 30 mg.L^{-1} and 11 mg.L^{-1} from 0%, 5%, 25% and 50% treatments respectively. The retention of SO_4 could be due to the surface functional groups such as carboxylic group (Wang et al., 2015), which is available in BC made from coconut shell (CSBC) as it is the case of this study. The retention of SO_4 could also be attributed to the high surface area (1050 m^2.g^{-1}, taken from the specification sheet) and porous structure of such char (Verheijen et al., 2010, Lehmann and Joseph, 2015).

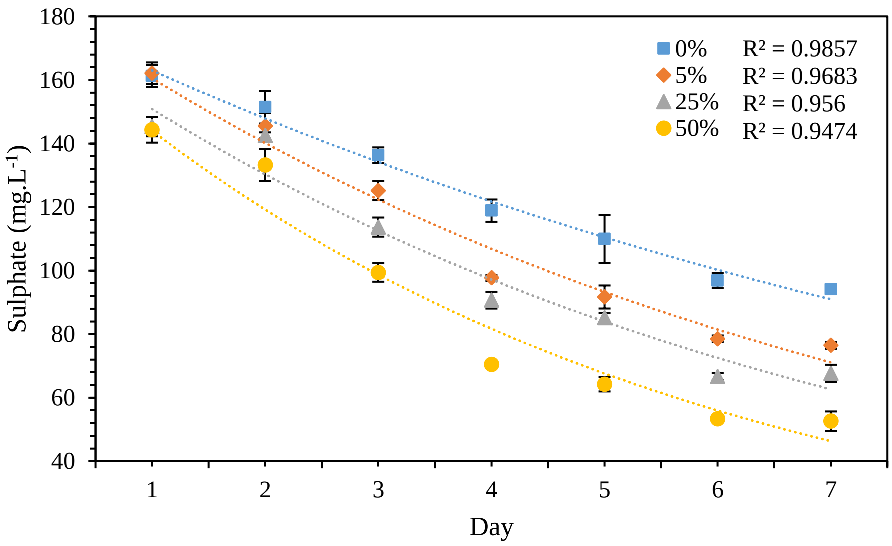


Figure 5.17: Nutrient Solution Sulphate over 7 Days. P<0.001, n=3

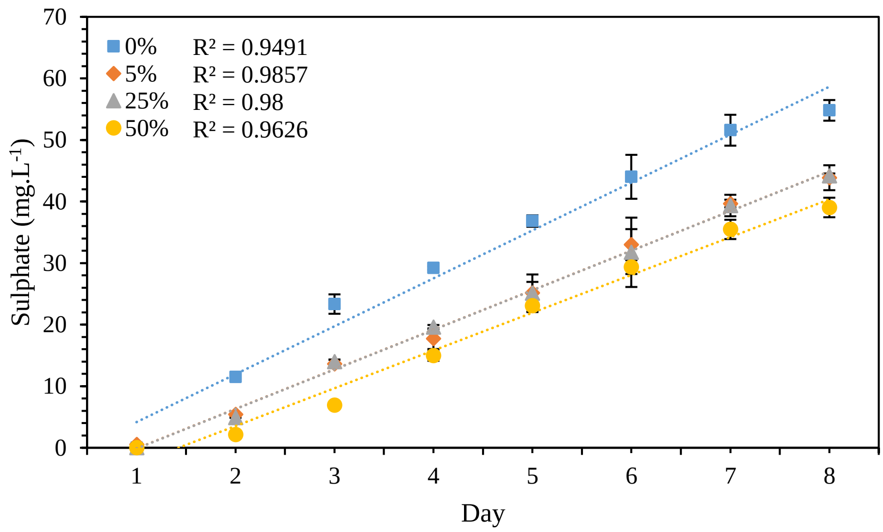


Figure 5.18: Deionised Water Sulphate over 8 Days. P<0.001, n=3

5.4 Nutrient Trends with Biochar Addition

Macronutrients adsorption and desorption on BC exhibited different trends with time. The trends were either exponential ($y = m\ e^{-cx}$) and power ($y = m\ x^{-c}$) for adsorption whereas linear ($y = mx+c$) and logarithmic ($y = m\ ln\ (x) + c$) were observed for desorption. Adsorption of PO_4 and SO_4 fitted with an exponential trend as well as K at 0 and 5% BC and Ca at 0% BC level. In comparison, NO_3, K at 25 and 50% BC as well as Ca at 5, 25 and 50% BC levels fitted well with the power trend. Magnesium was the only element which fitted with a linear trend. At the desorption phase, all nutrients fitted showed linear trends except K at all BC levels and Mg at 25 and 50% BC levels were fitted with logarithmic trends.

CHAPTER 6 GLASSHOUSE EXPERIMENTS:

6.1 Material and Methods

The experimental system consists of Polyvinyl chloride (PVC), irrigation pipes (Holman 13mm Black Poly Irrigation Tube), drippers (Pope Veri-Flow Threaded Trickler Dripper), 12-unit x 20L stock's storage containers (Icon Water Carrier with Bung 20L) and plastic pots (REKO 510mm Black Round Plastic Growers Pot). There were 5 replications of each treatments (five pots of each biochar ratio). Growth substrates consisted of washed river sand/BC mixtures. The sand was provided by a local landscape supplier and the BC was provided by Clarence Water Filter Australia. The water pumps were 24V 130PSI 5.5L/min High-Pressure Diaphragm Self-Priming Water Pump Boat Caravan. Rocket (*Eruca sativa*) seeds were provided by K Farm/Toowoomba. The nutrient solution commercially known as CULTIPLEX MAX NITRO GROW 1kg 2 PART POWDER 1000L provided by Sunstate Hydroponics, Gold Coast, Australia.

6.1.1 Growth Media and Potting Preparation

CSBC and sand were used as hydroponic growth media to grow Rocket in a glasshouse hydroponic experiment. Biochar was washed with tap water 3-4 times, then washed 3 times with DW to minimise ash content. The sand was sieved firstly with a 1.7 mm sieve and a 0.3 mm sieve. Thereafter, the sand was washed 3 - 4 times with tap water followed by 3 washes with DW, to ensure the removal of organic materials and clay from the growth media. BC and sand were sterilised at 120 °C for 30 min using an autoclave (HICLAVE, HV-50L) to minimise the presence of bacteria and fungi. BC and the sand (CSBC:Sand) were used in four rates at Table 6.1. As the char is lighter than the sand, the substrates were mixed using volume/volume (v/v) CSBC/sand. The media were first loaded in plastic bags (56 bags) then shaken to mix properly. Each plastic bag was then loaded into one pot. Prior to loading the media into the pots, a cotton ball wad was placed into the bottom of each pot with a piece of fibreglass flyscreen mesh to prevent the media from being washed. The pots were then weighed and seeds sown at depth of 2 - 3 mm.

Table 6.1: Percentages of Sand/Biochar

Growth media	Percentages
Sand	100% sand (control)
Sand + CSBC	5% BC + 95% sand 25% BC + 75% sand 50% BC + 50% sand

6.1.2 Water Circulation Procedure

Water circulation was performed by alternating the fed water to the hydroponic system between water with nutrients and only tap water. The nutrient solution was prepared by adding CULTIPLEX MAX NITRO GROW into 5L x 2 DW containers, then shaken properly to achieve well mixed solution. The concentration of the different constituents of the stock nutrient solution are shown in Table 2. Twelve pre-cleaned plastic containers were used to carry the circulating water and nutrient solution. Four containers were filled with tap water (15L in each container) and the other eight containers were filled with hydroponic nutrient solution (15L in each container). Four nutrient solution containers (one container for each BC treatment) were used to irrigate the plants as a control. The other four nutrient solution containers were used alternately with the four water containers. The nutrient solution containers were used in the first week to irrigate the plants and in the second week the water containers were used to irrigate the plants.

Table 6.2: Nutrient Content in the Stock Solution

Nutrients	Concentration ($mg.L^{1-}$)
NO_3	180
PO_4	80
K	180
Ca	108
Mg	70
SO_4	106

6.1.3 Seedlings

Rocket seeds were sown on the 15th of July 2019 into pots inside the glasshouse at a temperature of 17 °C ± 2 °C until germination (two days). After germination, the pots were placed into the PVC holders which were prepared to secure the pots and collect the effluent.

6.1.4 Experiment Design

A closed hydroponic system shown in Figures 6.1 and 6.2 was utilised to conduct the test utilising dripping irrigation system to water the plants. The PVC pipes were cut to one meter each piece and connected to each other, then holes were made to secure the pots. Fittings and irrigation pipes were connected to the PVC to collect the drainage from the pots. The water containers were used to store the stock solution/water and collect the outlet. The amount of water, flow rate and the pressure were controlled using pumps with set times as explained in the following section. The pots were irrigated three times a day for three intervals-9am, 12pm and 3pm (Table 6.3).

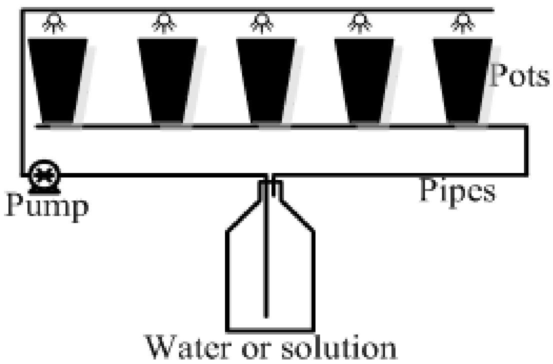


Figure 6.1: Closed Hydroponic System Design

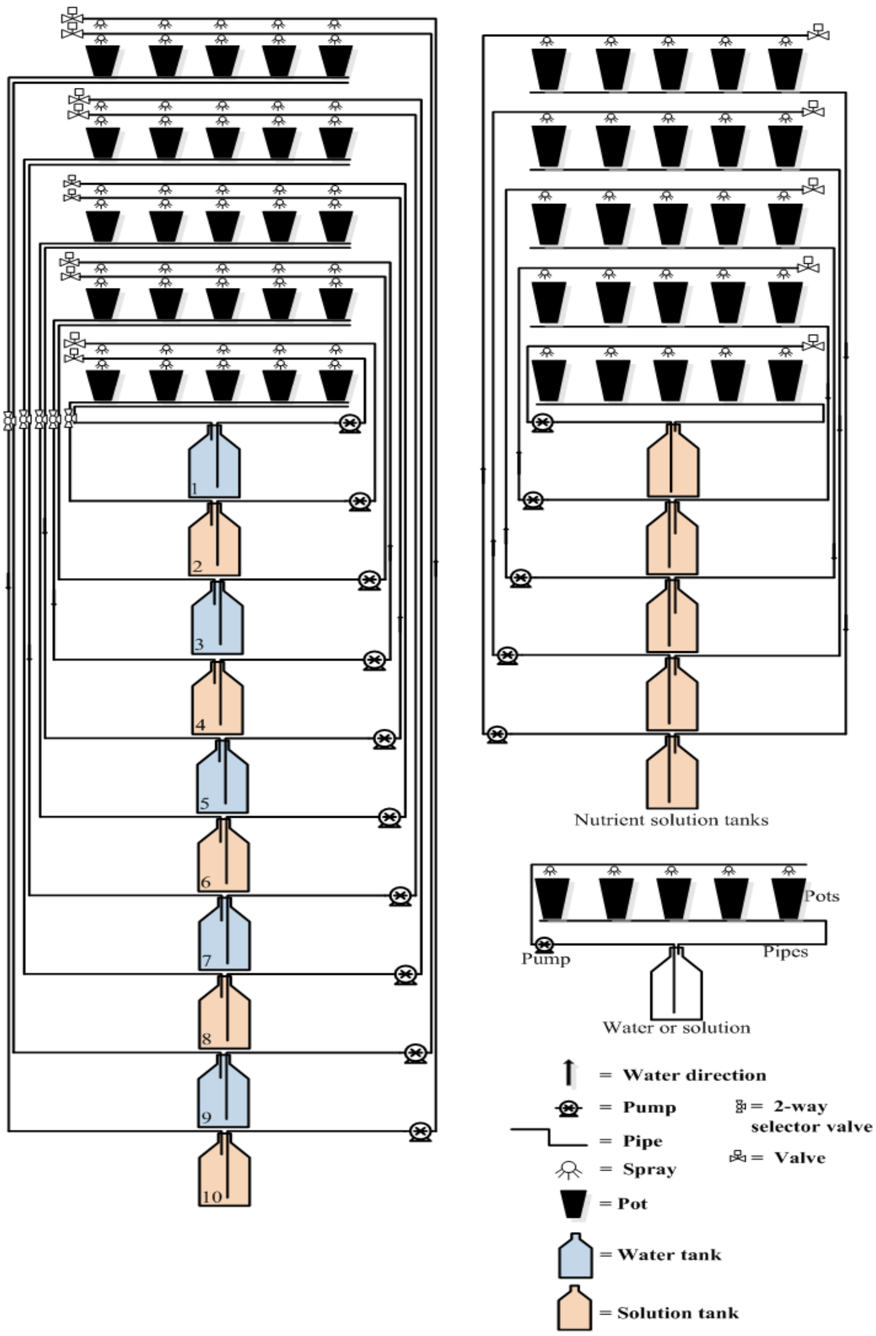


Figure 6.2: Experimental Setup

6.1.5 Irrigation Time and Programs

Table 6.3 and figure 6.3 show irrigation weekly timing. Pumps numbered 1-4 were running every day until the end of the test. Pumps numbered 5-8 were running during the first week to supply nutrient solution to the plants. During the second week, pumps numbered 5-8 were turned off and pumps numbered 9-12 were turned on in order to supply tap water to the pots. The process continued until the end of the experiment.

Table 6.3: Daily Irrigation Timing

	Pumps 1 to 4	**Pumps 5 to 8**	**Pumps 9 to 12**
1st week	**On (NS)** 3 times a day for 5min 9am, 12noon, 3pm	Off	**On (NS)** 3 times a day for 5min 9am, 12noon, 3pm
2nd week	**On (NS)** 3 times a day for 5min 9am, 12noon, 3pm	**On (NS)** 3 times a day for 5min 9am, 12noon, 3pm	Off
3rd week	**On (NS)** 3 times a day for 5min 9am, 12noon, 3pm	Off	**On (NS)** 3 times a day for 5min 9am, 12noon, 3pm
4th week	**On (NS)** 3 times a day for 5min 9am, 12noon, 3pm	**On (NS)** 3 times a day for 5min 9am, 12noon, 3pm	Off
5th week	**On (NS)** 3 times a day for 5min 9am, 12noon, 3pm	Off	**On (NS)** 3 times a day for 5min 9am, 12noon, 3pm
6th week	**On (NS)** 3 times a day for 5min 9am, 12noon, 3pm	**On (NS)** 3 times a day for 5min 9am, 12noon, 3pm	Off

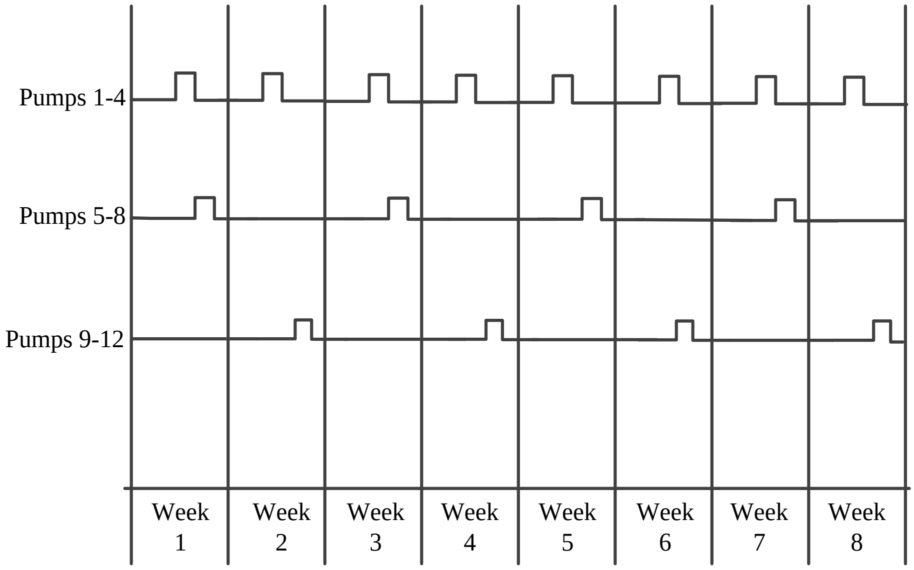


Figure 6.3: Weekly Irrigation Timing

6.1.6 Plant Sample Regime

The leaves from each harvested treatment were immediately processed after harvest. They were washed in tap water to remove residuals and the surface water was removed. The samples were placed in labelled paper bags then placed in the oven at 72 °C for 72 h. Samples were weighed few times before the dry matter weight was recorded. Leaf nutrient content (NO_3, PO_4, K, Ca, Mg, SO_4) was measured in the dry matter. Chlorophyll and photosynthesis were measured the day prior to harvesting the plants. Leaf area was measured at the end of the test.

6.1.7 Analytical Measurements

The following parameters were measured during the course of this study, leaf area, chlorophyll, photosynthesis, dry weight, plant height and dry tissue nutrient content. Leaf area was measured using leaf area scanning (LI-COR [LI-3100C AREA METER]). Chlorophyll content in the leaves was measured at the end of the test (week 8) using an atLEAF CHL PLUS Chlorophyll meter (Novichonok et al., 2016). Photosynthesis was measured using LI-6400XT Portable photosynthesis system following the method reported by Akhtar et al. (2014), however in this study, photosynthesis was measured once only. The pH, EC, NO_3, PO_4, K, Ca, Mg, SO_4were measured where pH and EC measured using a PC2700 from EUTECH INSTRUMENTS. K, Mg and Ca were measured using an Atomic Absorption Spectrophotometer AA-7000 (SHIMADZU, Australia). NO_3, PO_4 and SO_4 were measured using an ion chromatography system ICS-2000 following the standard methods described in (Eaton et al., 2005). Plant nutrient content was measured by an external laboratory at the University of Queensland, Gatton, Australia.

6.2 Results and Discussion

6.2.1 Leaf Area Behaviour with Biochar Addition

Leaf area was negatively influenced by the increase of BC rate in the media (Figure 6.4). In general, there was not much difference in the leaf area between the control and the treated plants grown in 5% biochar. The highest leaf area in both treated and non-treated plants was from plants grown on 5% BC, whilst the lowest was from plants grown on 50% BC in the control treatment. In the 0% BC treated media, the leaf area was approximately 7 cm^2 higher than that of the treated media, however it was only approximately 3 cm^2 with 5% BC. The difference between the control treatments and the treated plant's leaf area was between 2-3 cm^2 in the 5% BC. The review of previous research indicated that plants responded differently to BC treatments depending upon BC type, amount and plant type. Awad et al. (2017) have investigated the effect of BC on leafy vegetables and their results showed that the addition of BC affected some plants but not others. Their results showed that the leaf area of dill and lettuce significantly increased while the leaf area of mallow, cabbage were not affected. Another study found that the Arabidopsis leaf area significantly increased by 130% (Viger et al., 2015). Biochar type could also affect plant leaf area positively or negatively (Alburquerque et al. (2014a). Three levels of BC were used by Graber et al. (2010) on pepper and tomato. The results demonstrated a significant increase in the leaf for both types of plants at all BC levels on pepper and tomato.

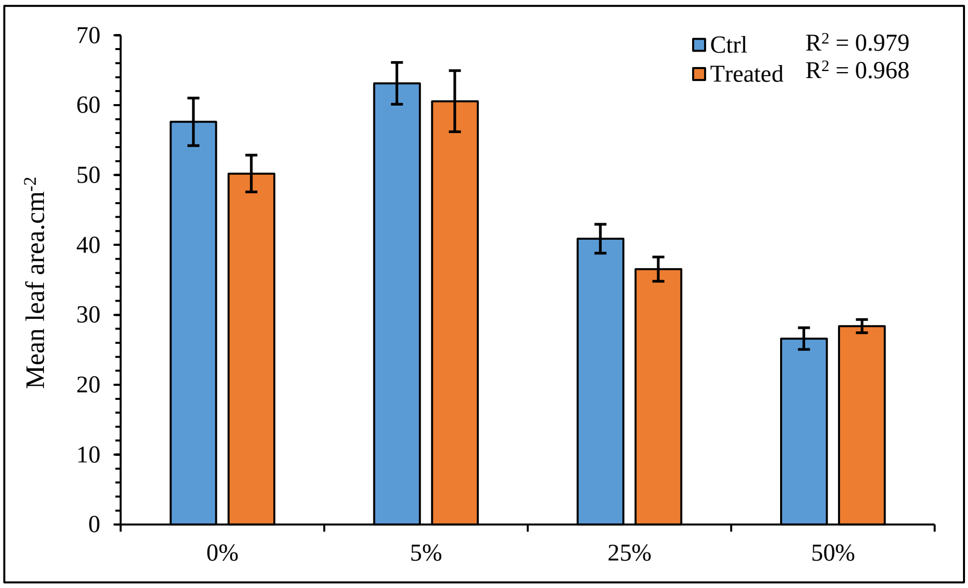


Figure 6.4: Effect of BC Ratios and Irrigation Scheme on Plant Leaf Area

6.2.2 Plant Height Behaviour with Biochar Addition

Biochar ≥ 25% in the media affected plant height negatively as shown in Figure 6.5. Plants grown on 5% BC in the control recorded the highest plant height whilst the lowest was from plants grown on 50% BC in the control as well. Plant height was reduced by approximately 6 cm and 3 cm for 50% and 25% BC in both irrigation solutions, respectively. The irrigation solution did not affect plant heights except in the 5% BC as plants were taller than the control treatment. The results showed that alternate tap water/nutrient solution use showed no changes in plant height. A number of researches have reported that BC increased plant height. The effect of citrus wood BC at 1- 5%, w/w was tested on tomatoes (*Solanum lycopersicum*) and peppers (*Capsicum annuum*) growth and results showed BC increased plant height (Graber et al., 2010). Biochar addition at 0, 20, and 35% to composted green waste increased plant height at 20% BC by 45.2% compared to control (Zhang et al., 2014). Another study by Webber III et al. (2018) showed that plant height responded differently to BC type (standard sugarcane bagasse BC and pneumatic sugarcane bagasse biochar) and amount where 50% by vol. of pneumatic sugarcane bagasse BC increased plant height, but the other BC had an insignificant effect on plant height. Gu et al. (2013) investigated pinewood BC mixed at 5 - 30% v/v with peat-based media on gomphrena (*Gomphrena globosa*) growth. The results showed that plants grew taller in the (BC + Media) than plants grown in the control media only.

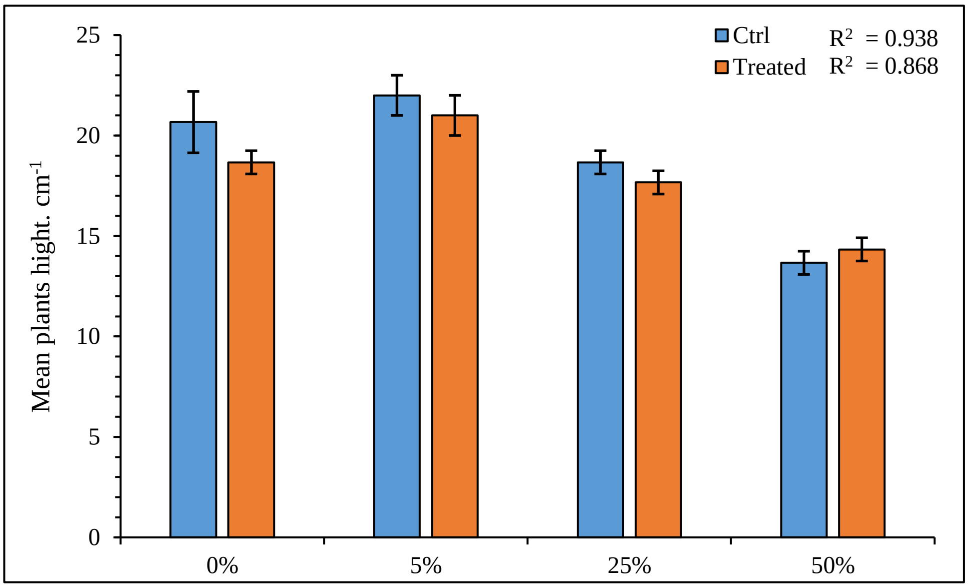


Figure 6.5: Effect of BC Ratios and Irrigation Scheme on Plant Height

6.2.3 Photosynthesis Behaviour with Biochar Addition

Figure 6.6 displays the effect of BC on photosynthesis in both treated and non-treated plants with different rates of biochar. In general, the addition of BC did not affect photosynthesis significantly either in the control treatment or the treated mixture, but photosynthesis slightly decreased with increasing BC rate in the media. The Figure also shows that changing the irrigation solution did not affect plant photosynthesis which proves that tap water could be used alternately with a nutrient solution in the presence. The highest photosynthesis rate was 17.4 μmol.m^{-2}.s^{-1} at the control in 0% BC whilst the lowest was 14 umol.m^{-2}.s^{-1} at the TNS in 50% BC. A number of studies have reviewed the effect of BC on photosynthesis. Younis et al. (2015) reported that using cotton feedstock derived BC (3% and 5% BC) increased photosynthesis, but photosynthesis level was lower compared to it is level in the control treatment (0% BC). Akhtar et al. (2014) and Baronti et al. (2014) reported that BC enhanced photosynthesis in tomato under drought stress. Viger et al. (2015) claimed that there was a limit effect of BC on the gen controlling photosynthesis. Other scholars have reported that BC did not affect photosynthesis. Alburquerque et al. (2013) and Thomas et al. (2013) reported that BC did not affect photosynthesis under fertiliser treatment and salinity.

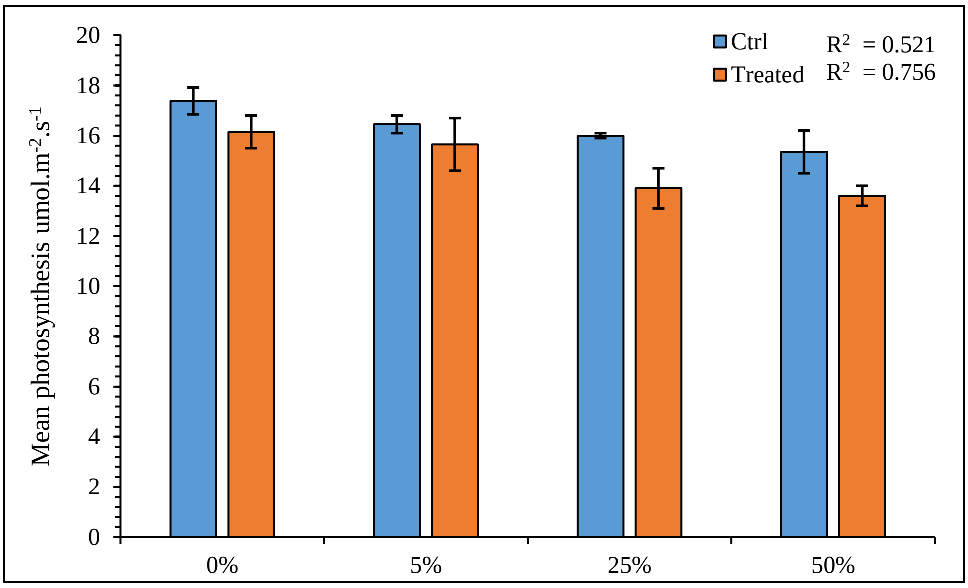


Figure 6.6: Effect of BC Ratios and Irrigation Scheme on Plant Photosynthesis

6.2.4 Dry Matter Behaviour with Biochar Addition

For alternate cycles plant dry matter was significantly affected by BC rate, as in Figure 6.7. The highest dry matter achieved was with plants grown on 5% BC with both solution (control and treated) whilst the lowest was from 50% BC. Alternating the irrigation solution demonstrated a significant effect on plant dry matter with 0% BC but was insignificant with the remaining treatments with BC. This indicated that BC presence positively affects dry matter and it is also demonstrated that plain water could be used alternately to irrigate plants if BC is added to the growth media. From the review of previous studies on BC effects on dry matter, Viger et al. (2015) reported that the effect of poplar wood chips BC (50 $t.h^{-1}$) on lettuce productivity showed a significant increase in dry matter. BC effect was investigated on two types of plants (spinach [*Spinacia oleracea* L.] and mustard [*Sinapis alba* L.]) by Pavlíková et al. (2017). The results showed that BC increased dry biomass compared to the control. Awad et al. (2017) reported that BC reduced plant (cabbage, dill, and red lettuce) dry mass when used by itself as a growth media, whereas dry mass increased when BC was used in combination with perlite. Other studies have stated that BC increased plant biomass. Biochar was used by Younis et al. (2015) on spinach with a 3% increase in biomass by around 4 g. Viger et al. (2015) investigated the effect of BC on the model plant *Arabidopsis* and lettuce (*Lactuca sativa* L.) and they found that BC increased biomass for both species.

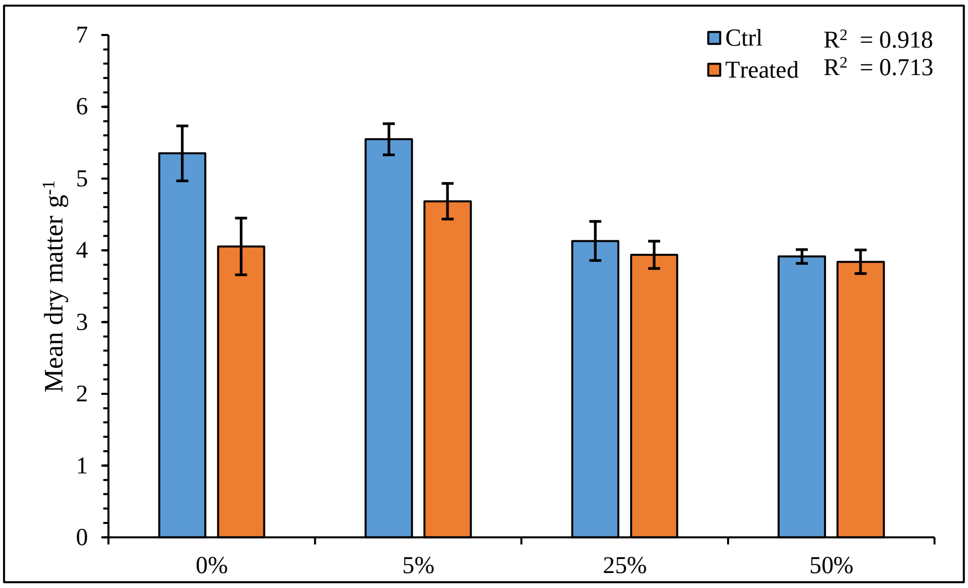


Figure 6.7: Effect of BC Ratios and Irrigation Scheme on Plant Dry Matter.

6.2.5 Chlorophyll Behaviour with Biochar Addition

Chlorophyll was negatively affected by BC addition to the media, but the effect was insignificant with a changing irrigation solution as presented in Figure 6.8. Comparing the results of the highest ration of BC to the control (0% BC), it can be observed that chlorophyll was around 22 µmol.m^{-2} lower in the plants grown on 50% BC and TNS, while it was 5 µmol.m^{-2} higher with control irrigation. There was an insignificant difference between control and TNS with different BC ratio except at 0% BC. The results were in line with the findings reported by Awad et al. (2017) where BC addition significantly reduced chlorophyll content by 17-24% compared to plants (dill, mallow, and red lettuce) grown on perlite only. Another study by Akhtar et al. (2014) showed that the addition of BC significantly reduced chlorophyll content in tomato. In contrast, Rehman et al. (2016) stated that BC increased total chlorophyll content in maize (*Zea mays* L.). Thomas et al. (2013) reported that there was no effect of two rates of BC (5 and 50 t .ha^{-1}) on chlorophyll in herbaceous plants *Abutilon theophrasti* and *Prunella vulgaris*. The decrease in the total chlorophyll content in this study could be due to less intake of NO_3 (Figure 6.17) which resulted in the deficiency of chlorophyll, as N is one of the main compounds in chlorophyll structure (Awad et al., 2017).

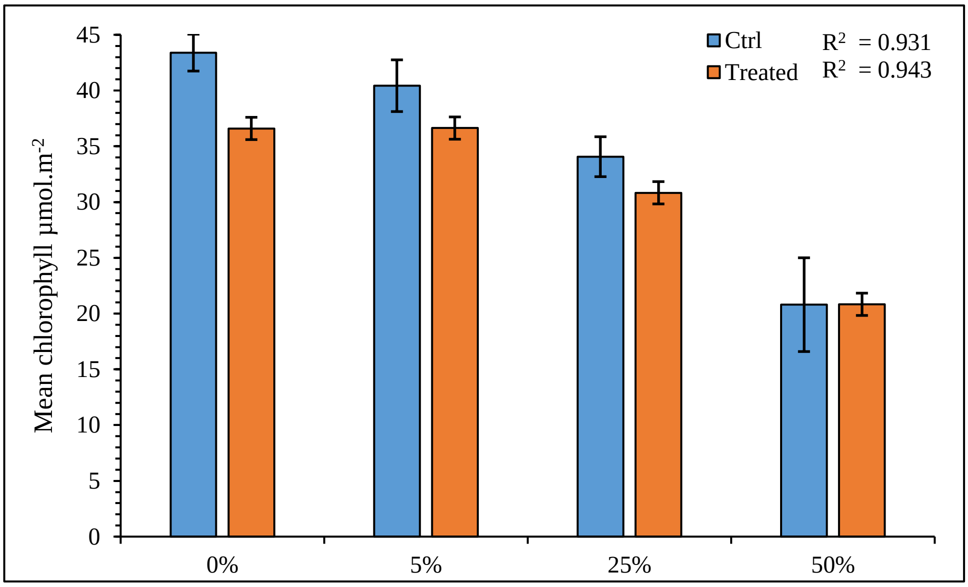


Figure 6.8: Effect of BC Ratios and Irrigation Scheme on Plant Chlorophyll

6.2.6 Plant Nitrate Contents

Plant NO_3 concentration was significantly affected by BC addition but not with changing the irrigation solution as revealed in Figure 6.9. Nitrate dropped from 30 $mg.kg^{-1}$ in the control with 0% BC to be 15 $mg.kg^{-1}$ in the plants treated with tap water and nutrient solution (TNS) with 50% BC. It can be seen that the reduction between 0% and 50% was half. Changing the irrigation solution did not demonstrate any effect on NO_3 in 25% and 50% BC, but there was a small difference in the 0% and 5% with both control and TNS where plants in control had 1.5-2 $mg.kg^{-1}$ higher NO_3 than TNS. Effect of BC NO_3 content in plants was investigated by Akhtar et al. (2014) on tomato plants. They reported that the N content was significantly reduced when BC was added to tomato growth substrate. Other studies conducted by (Jones et al., 2012, Deenik et al., 2010) showed the adsorption process of NO_3 by BC resulted in plant nutrient deficiency. Kammann et al. (2011) found that the addition of BC in different rates (0, 100, and 200 $t.ha^{-1}$) decreased NO_3 in pseudo-cereal Chenopodium quinoa Willd.

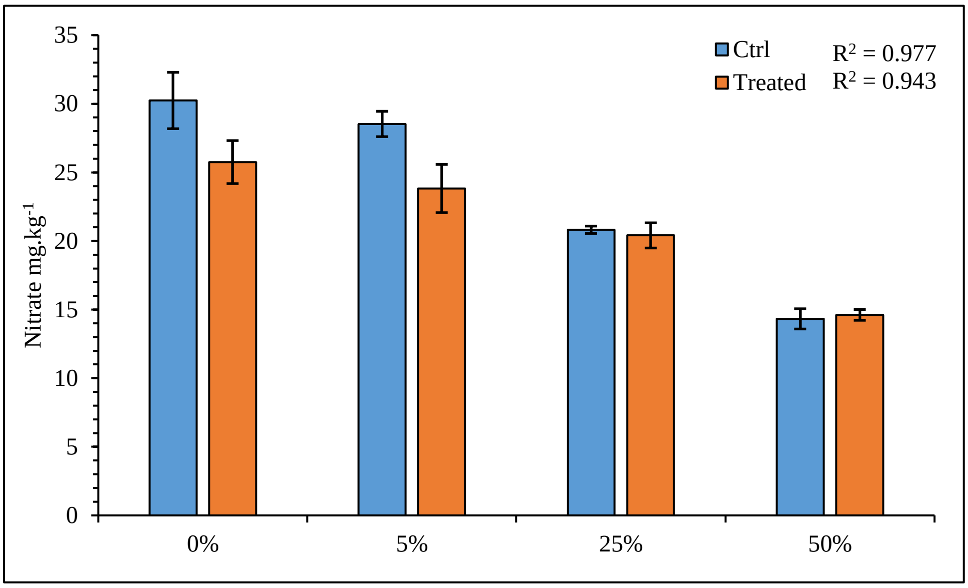


Figure 6.9: Effect of BC Ratio and Irrigation Scheme on Plant Nitrate Content

6.2.7 Plant Phosphate Contents

Figure 6.10 demonstrates the effect of BC and irrigation solution on PO_4 concentration in plant tissue. This figure illustrates that the presence of BC reduced the effect of changing irrigation solution on PO_4 concentration in plants. In the 0% BC, PO_4 concentration was 1.7 $mg.kg^{-1}$ higher in the control than the TNS. It is important to mention that the highest concentration of PO_4 concentration in the TNS was from plants grown on 5% BC. Biochar effect on spinach (*Spinacia oleracea* L.) and mustard (*Sinapis alba* L.) content of PO_4 was investigated by Pavlíková et al. (2017). The results showed that BC limited PO_4 content in plants. Kammann et al. (2011) also reported that PO_4 was decreased when BC was used with pseudo-cereal Chenopodium quinoa Willd. Bornø et al. (2018) utilised three BC based feedstocks (oilseed rape [OSR], rice husk [RH] and softwood [SW]). They reported that phosphorus response to BC addition can be variable, depending on BC type. Cassava stem BC produced at 350 °C mixed with soil was used to grow green beans (*Vigna radiata* L.). it was found by another study that BC addition did not affect phosphorus content in plants (Prapagdee et al., 2017). Altland and Locke (2017) reported that 15-20% of gasified rice hull BC mixed with soilless media (peatmoss) provided a sufficient P for tomato and geranium plants for 5-6 weeks.

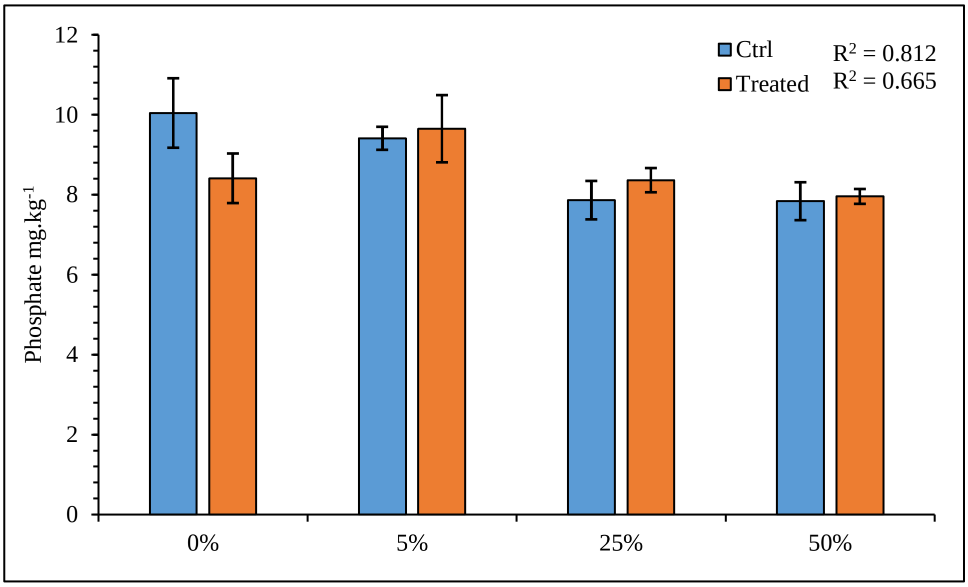


Figure 6.10: Effect of BC Ratio and Irrigation Scheme on Plant Phosphate Content

6.2.8 Potassium Content in the Plant

Potassium concentration in the plant tissue was significantly affected by BC addition when the irrigation solution was not altered as illustrated in Figure 6.11. The highest K content was 71 mg.kg^{-1} in the plant grown in 50% BC with both irrigation solutions. K concentration was slightly higher in the plants irrigated with nutrient solution only. There was a gradual increase in plant K content as BC rate increased in the media. There was 5 mg.kg^{-1} ± 1 mg.kg^{-1} of K in the 25% BC with control and in the 50% BC in both solutions. The results are in line with several studies that reported an increase of plant K content grown on mixed media. Several studies reported an increase of K content in plants with BC addition to the growth media. Biochar produced from cassava stem at 350 °C added (1-20% w/w) to green bean (*Vigna radiata* L.) soil increased K content in plants (Prapagdee et al., 2017). There was an increased K content in mustard (*Sinapis alb*a L.) and spinach (*Spinacia oleracea* L.) with 5% BC per mass of soil as stated by Pavlíková et al. (2017). Blok et al. (2017) reported that Gasification BC added a high and stable level of K to the growth media (peatmoss). Altland and Locke (2017) stated that gasified rice hull BC can provide K to some plants but not to all. Rice husk BC in a nutrient film technique hydroponic system was used alone or mixed with perlite growing tatsoi, mallow, dill, red lettuce, and cabbage.

This showed an increase of K content in plants grown in BC mixed with perlite (Awad et al., 2017).

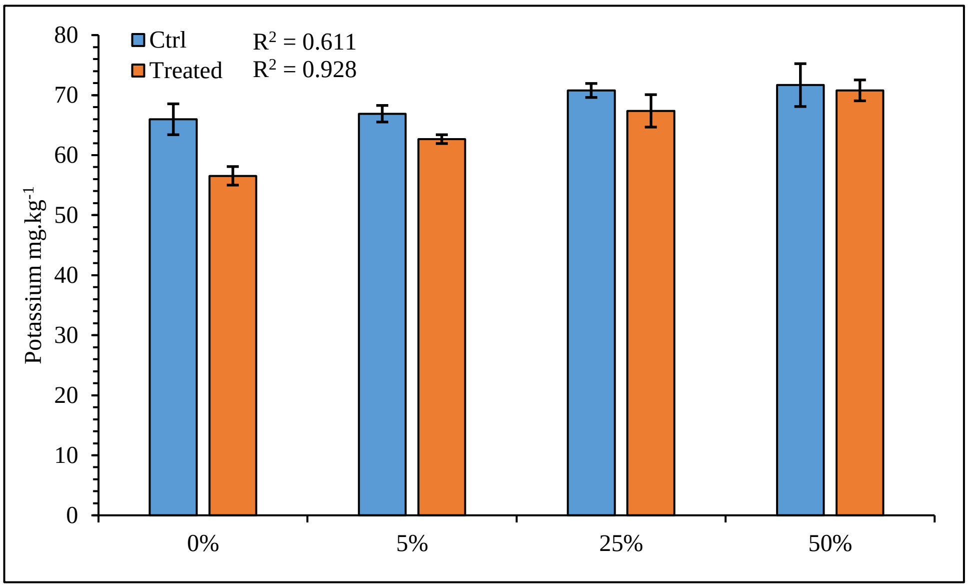


Figure 6.11: Effect of BC Ratio and Irrigation Scheme on Plant Potassium Content

6.2.9 Calcium Contents in Plant matter

Biochar affected Ca concentrations in the nutrient solution and in plant matter, Figure 6.12. Comparing the results of BC addition to control, it can be observed that BC showed more effect on plant Ca than irrigation solution Ca. The concentration of Ca in plants was higher in the control than treated samples. The highest concentration occurred with (0% BC) control. The lowest Ca content occurred in plants grown on 50% in both solutions, with the TNS lower than all other treatments. The difference in Ca content was 6-8 mg.kg^{-1} between the control and TNS with 50% BC and 0% BC ratios respectively. The difference in Ca content was about 0.5-3 mg.kg^{-1} between the 5% and 25% BC in both solutions. The effect of BC on plant Ca content was investigated and the results varied as some demonstrated an increase and in others a slight decrease. Awad et al. (2017) invested BC effect on plant Ca content using hydroponically grown dill, cabbage, red lettuce, mallow, and tatsoi with rice husk BC and perlite. Pavlíková et al. (2017) reported that there was a decrease of 45% and 30% in spinach grown in Spring and Autumn respectively and with mustard by 34%. The control treatment showed higher Ca contents. BC similarly effected corn Ca leaf content, reported by Brantley et al. (2016). Hardwood-derived BC enhanced Ca content in soybean (Waqas et al., 2017). Butnan et al. (2015) described a decrease in plant Ca content after applying two types of eucalyptus derived BC to corn crops grown in a silty, clay-loam *Oxisol* and a loamy-sand *Ultisol*.

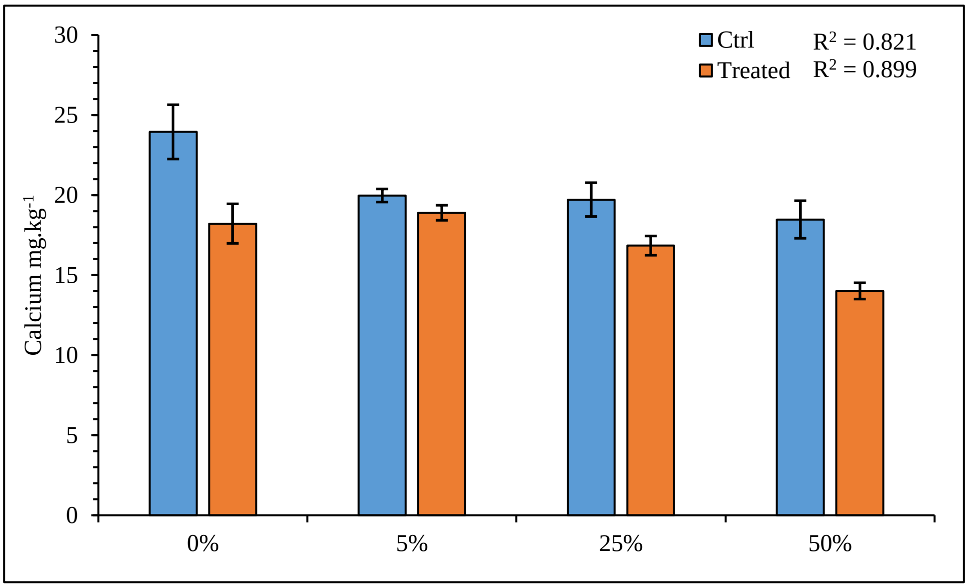


Figure 6.12: Effect of BC Ratio and Irrigation Scheme on Plant Calcium Content

6.2.10 Magnesium Content in Plants

Magnesium levels were affected by both BC ratio and irrigation solutions as in Figure 6.13. In general, the highest reduction in Mg content in plants was with 50% BC, whilst the highest content was in plants grown in 5% and 25% BC mixtures. There was an increase of 1.5-2 ± 0.2 mg.L^{-1} in Mg content in plants grown on 5% and 25% BC c.f. the control. The Mg content increased by 0.9- 1.2 ± 0.15 mg.L^{-1} in plants grown on 5% and 25% BC with TNS. Literature has shown that BC could increase or reduce Mg content depending on the plant and BC type and application rate (Huang and Gu, 2019). Waqas et al. (2017) stated that using BC alone as growth media increased Mg content in soybean (*Glycine max* [L.] Merr.) compared to BC mixed with *G. geotrichum* WLL1 and control treatments. Spinach (*Spinacia oleracea* L.) and mustard (*Sinapis alba* L.) were used to assess BC addition at 5% per mass to soil on plant Mg content showed that BC reduced Mg content in plants (Pavlíková et al., 2017). Awad et al. (2017) investigated the effect of rice husk BC alone or mixed with perlite on red lettuce, dill, mallow, tatsoi, and cabbage grown hydroponically. They stated that BC did not significantly affect Mg in tatsoi and lettuce, whereas Mg in mallow, cabbage, and dill plants grown in BC significantly increased. Biochar produced from animal waste added to soil at 0, 5 and 10 $Mg.ha^{-1}$ exhibited a decrease in Mg content in corn (*Zea mays* L.) leaf Brantley et al. (2016).

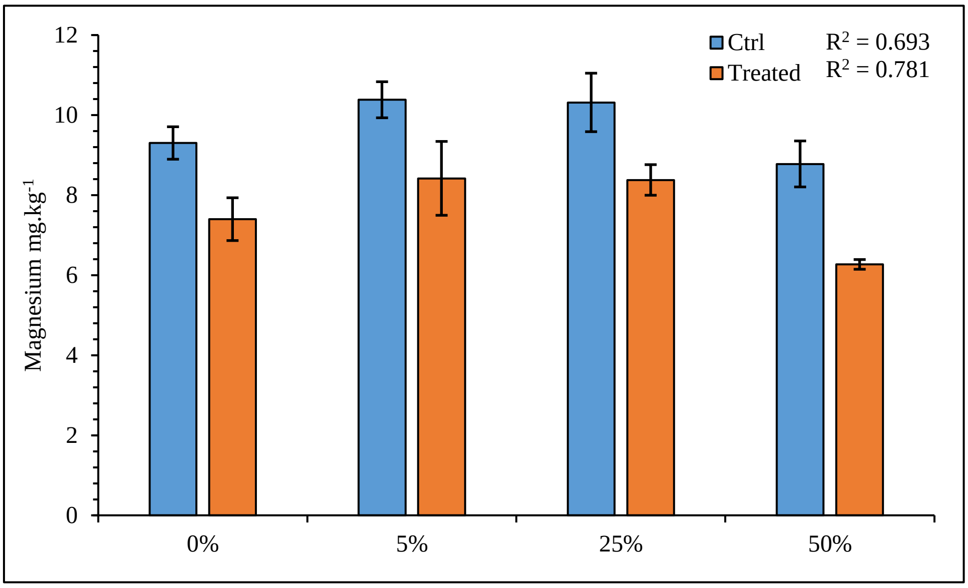


Figure 6.13: Effect of BC Ratio and Irrigation Scheme on Plant Magnesium Content

6.2.11 Sulphate Content in Plants

Sulphate content in plant tissue is shown in Figure 6.14. In general, the highest content of SO_4 was (13 $mg.kg^{-1}$) in the control with 0% BC while the lowest was 6.4 $mg.kg^{-1}$ in the control as well with 50% BC. The effect of BC was higher than the effect of changing the irrigation solution. Scarce studies exist regarding the effect of BC on SO_4 content in plants as well as the effect of BC on SO_4 retention and release. Kammann et al. (2011) investigated BC effect at 0, 100 and 200 t ha^{-1} on pseudo-cereal *Chenopodium quinoa* Willd grown in a sandy soil and reported that BC increased SO_4 in the plants. A study was conducted by Borchard et al. (2012b) to assess BC effect on SO_4 absorption. The results showed that SO_4 absorption was negligible with composted and non-composted biochars.

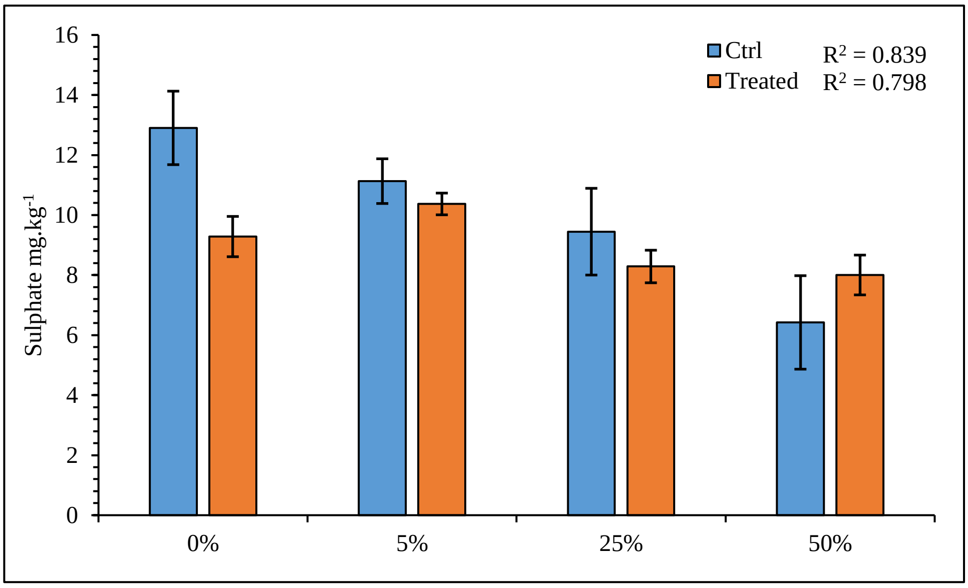


Figure 6.14: Effect of BC Ratio and Irrigation Scheme on Plant Sulphate Content

6.2.12 Irrigation Solution pH

The pH level was affected by increasing BC ratio in the growth media as well as by the duration of the experiment as shown in Figure 6.15. With regard to the control treatment (using hydroponic nutrient solution only), pH level decreased from 6.2 to 6.1 with 0% CSBC treated media. This was the only treatment where the pH level decreased. In 50% BC, pH level increased from 6.2 to reach approximately 6.8 in the last week. As shown in the previous chapters, pH level increased as BC rate increased with time. pH was a little higher with tap water and this is due to the fact that DW is slightly more acidic than tap water. This effected the pH level over the time of the test. The pH level with TNS was fairly close to the pH level of the control for most of the time. The highest pH level was 6.9 at the completion of the test for 50% BC in the third week. The pH level could affect plant productivity as reported by many researchers. Koehorst et al. (2010) stated that pH level over 8.5 or lower than 4.5 could significantly reduce plant root and shoot dry mass and total dry mass. Chlorophyll was effected by pH level and increased over 7 (Koehorst et al., 2010). It was also reported by Deng et al. (2012) that there was a significant decrease in plant productivity with pH level over 7. Increasing pH levels in the presence of BC could be attributed to the ash content and some minerals such as K (Kim et al., 2012). Alkalinity in BC could be effected by pyrolysis temperature, carbon crystallization (Yuan et al., 2011)

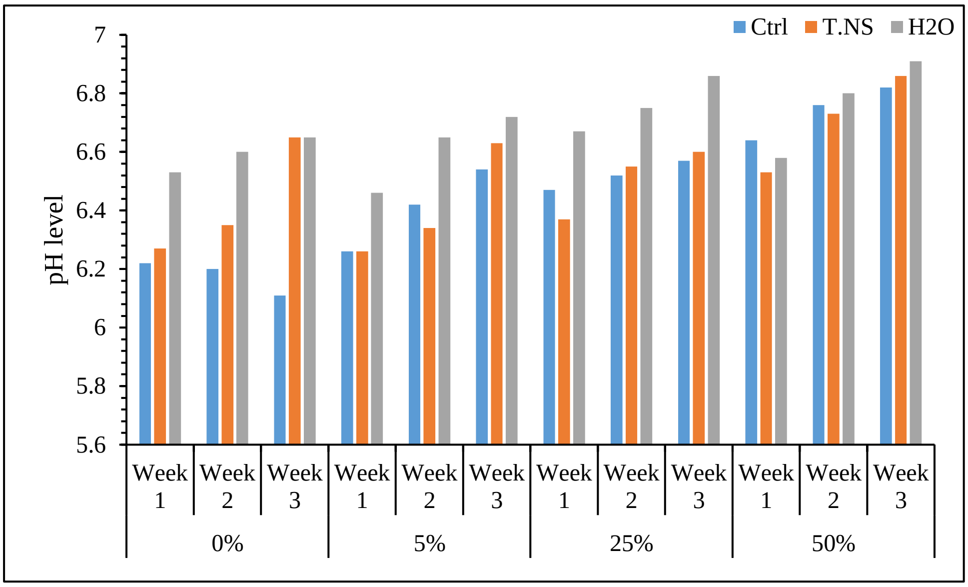


Figure 6.15: pH Changes Effected by BC Ratio

6.2.13 EC of Nutrient Solution

Biochar amount significantly affected EC level in the control and TNS solutions. EC was reduced by 0.8-0.9 mS.cm^{-1} in the 50% BC compared to the 0% BC. The reduction was lesser for low BC rates. From figure .16, it can be noticed that the reduction was linear with the prolonged treatment and with the BC rate in the control and TNS solutions whereas there was a linear increase in EC for tap water. The results are in line with the outcomes reported earlier in Chapters 4 and 5. There was a reduction in EC level, but EC did not drop below a critical level which could affect plant productivity. The lowest EC level which is attributed to the nutrient retention in the control and TNS was observed in the last week for 50% BC treatment. The effect of EC level on plants was seasonally tested by Amalfitano et al. (2017) and demonstrated a high level of increased yield in summer but a low level indicating an enhanced effect in winter. Wortman (2015) reported that there was a reduction by 76% and 44% in marketable yield of kale and basil a low EC solution, respectively. The EC effect on tomato in hydroponics was tested by Rosadi et al. (2014) and the results showed that an EC level over 3 dSm^{-1} decreased the yield. The EC for in a nutrient solution varied by crop species, planting density, growth stage and hydroponic system but it is in generally between 1-3 mS.cm^{-1} (Rouphael and Colla, 2005).

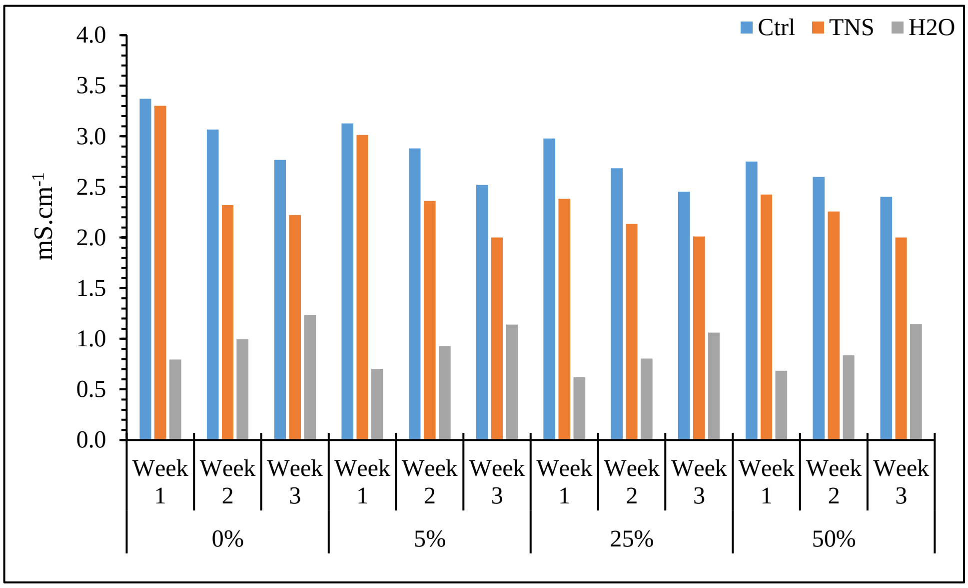


Figure 6.16: EC Changes Effected by BC Ratio

6.2.14 Nitrate Behaviour in Nutrient Solution

In general, NO_3 was reduced as CSBC increased in the growth media. Figure 6.17 illustrates the effect of BC rate on NO_3 over a duration of three weeks. The 50% CSBC in the growth media reduced NO_3 to more than half of its original concentration in the stock solution (control, Figure 6.17). The reduction occurred as well in other treatments, but it was less than the sample containing 50% CSBC. The 50% BC retained 108 mg.L^{-1} where 25% CSBC retained the NO_3 by approximately 85 mg.L^{-1}. The 5% CSBC and the control treatments reduced NO_3 by approximately 57 and 44 mg.L^{-1}, respectively. In the TNS treatments, NO_3 retention was less by 24, 19, 14 and 10 mg.L^{-1} for 0, 5, 25, and 50% BC, respectively. As NO_3 was retained by BC, it was released over time with the use of tap water. The results were in line with other results from previous tests (Chapter 4 and 5). As NO_3 was absorbed, it was released again when water was used. The release was approximately 59, 42, 29, and 20 mg.L^{-1} with 0, 5, 25, and 50% treatments, respectively. The release of NO_3 was steadier with BC treated media than the control treatments and the results were in accordance with previous studies. Agegnehu et al. (2017) stated that NO_3 was significantly reduced in the leachate with the presence of Brazilian pepperwood BC in the media. Nitrate was reduced with the addition of 10 Mg. ha^{-1} BC to soil (Yao et al., 2012b). Biochar reduced NO_3 leachate was also reported by Gai et al. (2014) and Ventura et al. (2013). Adeyemi and Idowu (2017) stated that NO_3 content was significantly reduced in plots amended with biochar. Pine-woodchip and wheat-straw biochars decreased soil NO_3 (Alburquerque et al., 2014b). Wood-derived BC reduced NO_3 ratio in the peat (Sorrenti et al., 2016), and it could also replace 20% of peat without affecting plant growth (Blok et al., 2017).

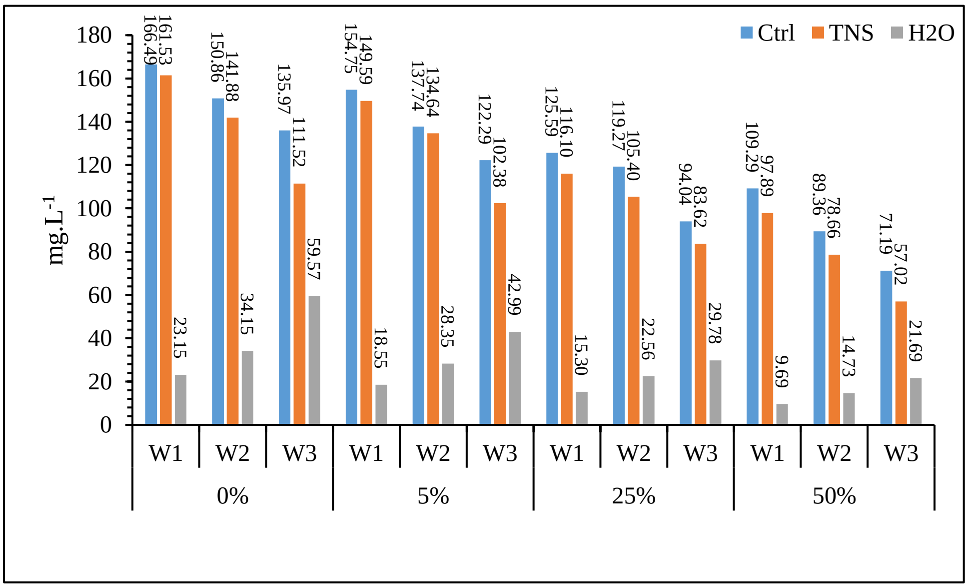


Figure 6.17: Nitrate Changes Effected by BC Ratio

6.2.15 Phosphate Behaviour in Nutrient Solution

Phosphate concentration reduced more in the TNS than control solution but BC presence reduced the effect of changing the irrigation solution on PO_4 concentration in the solutions as illustrated in Figure 6.18. The reduction of PO_4 was rapid in the 0% BC in both solutions compared to the other BC treatments. The highest retention of PO_4 was in the 50% BC treated with TNS, whilst the lowest was in the 0% BC treated with TNS. The results showed that tap water can be used alternately with a nutrient solution to irrigate plants in hydroponics. The addition of Brazilian pepperwood BC to the media significantly reduced PO_4 by 20.6% in the leachate as described by Agegnehu et al. (2017). Adeyemi and Idowu (2017) reported that BC is a very efficient absorber for dissolved PO_4. Phosphate absorption and de-absorption was investigated by Morales et al. (2013) using fast pyrolysis BC (a mixture of three types BC-sugar cane leaves, elephant grass and sawdust), and slow pyrolysis BC produced from Amazonian tree species (Lacre, Ingá and Embaúba). The results showed that the ability of adsorbing and de-absorbing PO_4 varied according to BC type and pyrolysis conditions.

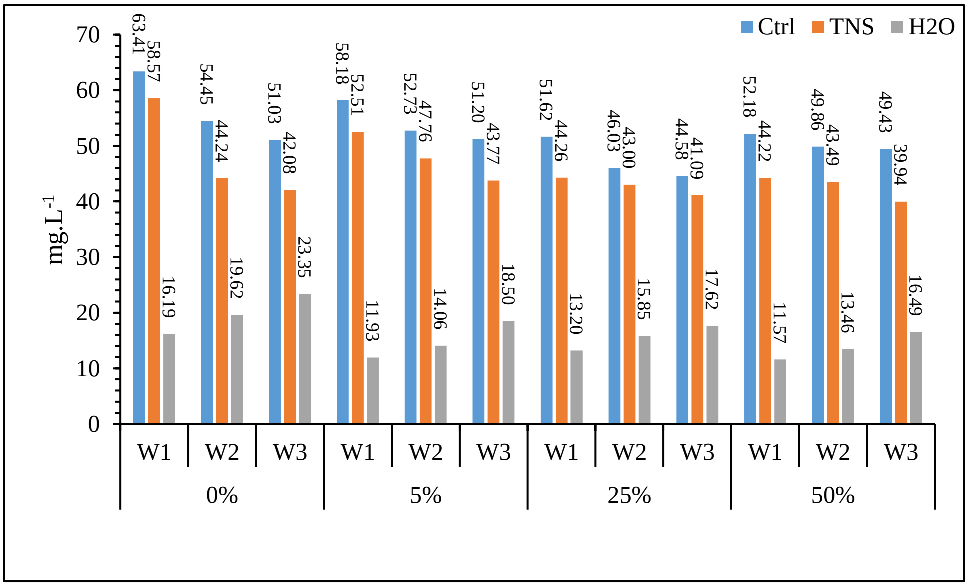


Figure 6.18: Phosphate Changes in the Irrigation Solution versus BC Ratio

6.2.16 Potassium Behaviour in Nutrient Solution

Potassium concentration in the irrigation solutions are displayed in Figure 6.19. The results indicate that K concentration in the 0% and 5% BC decreased in both control and TNS but it was increased in tap water with all BC ratios. Potassium concentration in 25% and 50% BC increased with the control and H_2O but was reduced in the TNS. Comparing the results of K concentration in the 0% BC and control to the rest of the treatments, it can be seen that there was 40 $mg.L^{-1} \pm 2$ $mg.L^{-1}$ reduction in K concentration in BC treatments and TNS. 50% BC and control treatments increased K concentrations, along with 25% BC and control. Biochar of cassava stem produced at 350 °C was applied at a rate of 20% to the green bean soil and increased K concentration in the soil (Prapagdee et al., 2017). Soil analysis also showed an increase in K content after the addition of gasified poplar wood chips (Viger et al., 2015). An examination of nutrient retention and release of softwood and hardwood biochars, demonstrated that pore water K increased with both biochars, to a lesser extent with hardwood BC (Bedussi et al., 2015). Schulz et al. (2014) reported a significant increase in K content in sandy soil with 50 and 250 $t.ha^{-1}$ BC added, while 10 $t.ha^{-1}$ produced a negative impact. Headlee et al. (2014) reported that applying plant growth media with 25% BC supplied greater K availability and retention. Application of BC to soil increased K concentrations in the soil, compared to the control treatment (Biederman and Harpole, 2013). Yin et al. (2012) claimed that with the increased amount of BC available, K rose significantly by 7.56 $g.kg^{-1}$ compared to the control.

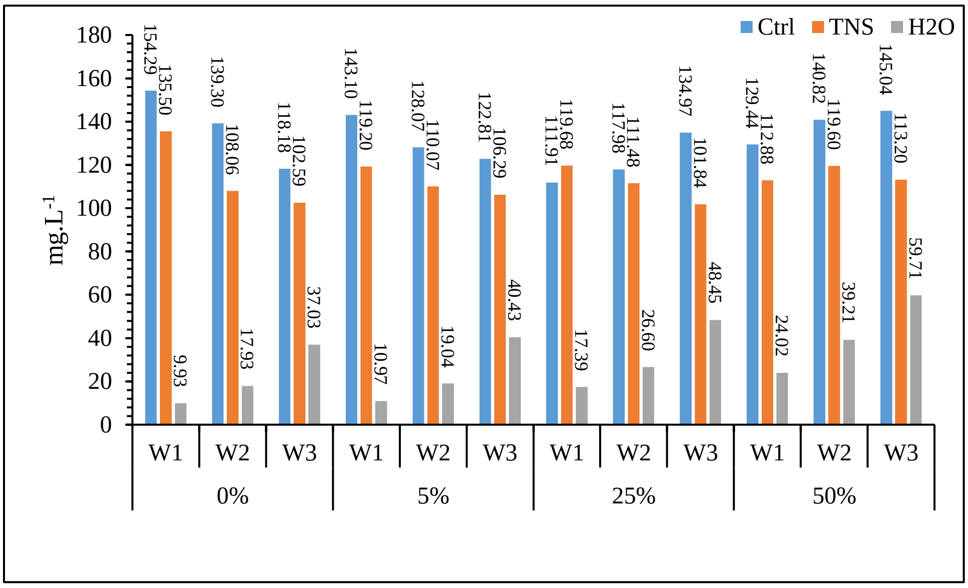


Figure 6.19: Potassium Changes in the Irrigation Solutions versus BC Ratio

6.2.17 Calcium Behaviour in Nutrient Solution

The effect of BC on Ca was higher than the effect on irrigation solution as illustrated in Figure 6.20. The retention of Ca had a linear trend with increasing BC ratio in the media. The lowest retention was recorded with the 0% BC for both control and TNS. In fact, Ca retention was slightly higher in TNS than the control. The concentration of Ca in the solution was always higher in the control than TNS with all BC ratios. This is due to the fact that tap water was used to irrigate plants, therefore Ca was washed away. The highest retention rate was with 50% BC in the TNS. The results were in line with the results in Chapters 3 and 4. Some researchers have reported an increase in Ca whilst others claimed that there was a decrease in Ca content/concentration with the use of BC in growth media. Waqas et al. (2017) reported that Ca content was decreased as a result of adding 10:90 (w/w) hardwood-derived BC to soybean substrate. Butnan et al. (2015) invested two types of BC (eucalyptus wood-derived biochar) at four w/w rates of 0, 1, 2, and 4% to a *silty-clayloam Oxisol* and a loamy-sand *Ultisol* on two consecutive corn crops. The results showed that Ca decreased in the growth media, resulting in reducing Ca in plants. Agegnehu et al. (2015) reported that there was a significant reduction in Ca leachate when acacia and willow was mixed with compost. Colombian *savanna Oxisol* was applied at 20 $t.ha^{-1}$ to soil and the results indicated that Ca decreased in the leachate (Major et al., 2012).

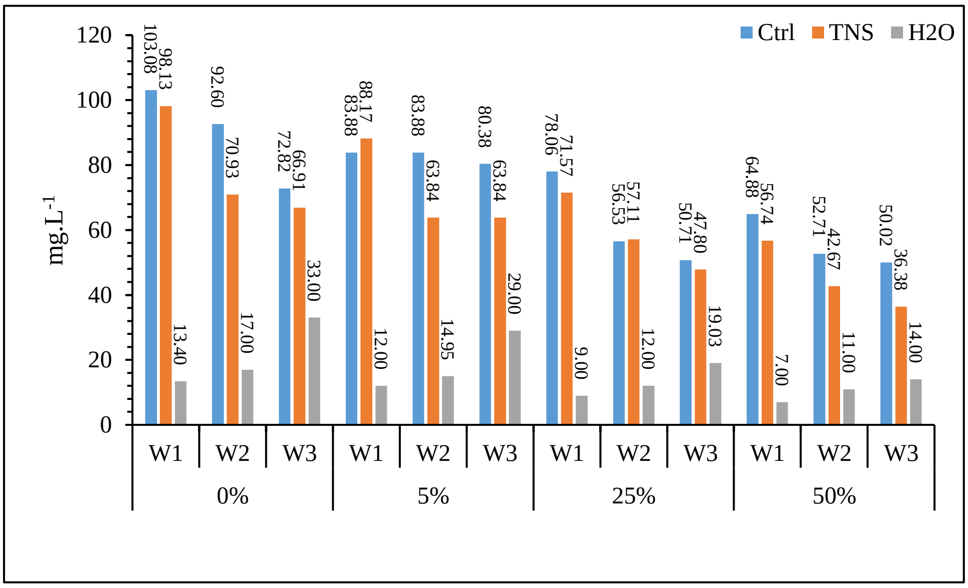


Figure 6.20: Calcium Changes in the Irrigation Solutions versus BC Ratio

6.2.18 Magnesium Behaviour in Nutrient Solution

Figure 6.21 illustrates the change in Mg concentration in the irrigation solution. In general, both BC and the irrigation solution affected Mg concentration in the solutions. The highest retention of Mg was with 25% BC in both control and TNS solutions, whilst the lowest retention was with 0% BC with TNS. The 50% BC released Mg instead of retaining it. The difference in Mg concentration in the control and TNS was higher in 0% and 5% BC than in 25% and 50% which indicates that Mg might be released from 25% and 50% BC treatments. The literature revealed that the addition of BC could increase Mg in a growth media/solution. The Mg content in the soybean growth media was decreased when BC was mixed with the growth media, but it was increased when using BC alone as growth media (Waqas et al., 2017). Magnesium was reduced when BC was added to a typical Midwestern agricultural soil (Laird et al., 2010). A 20 $t.ha^{-1}$ of Colombian *savanna Oxisol* was applied to a field soil with the result that Mg decreased in the leachate (Major et al. (2012). Magnesium was reduced in the leachate when acacia and willow biomass derived BC was mixed with compost (Agegnehu et al., 2015).

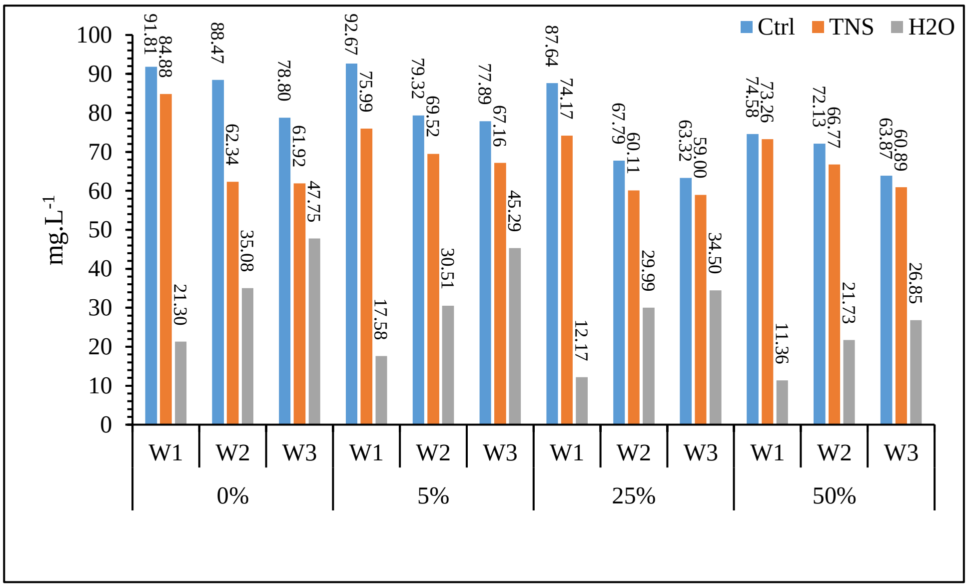


Figure 6.21: Magnesium Changes in the Irrigation Solutions versus BC Ratio

6.2.19 Sulphate Behaviour in Nutrient Solution

Sulphate concentration in the irrigation solution is shown in Figure 6.22. This figure illustrates that SO_4 concentration in the irrigation solutions reduced as BC ratio increased in the media. However, there was less effect on changing irrigation solution on SO_4 concentration than BC ratios. The lowest retention of SO_4 was at 0% BC in the control whereas the lowest was at 50% in the TNS. The results are in line with the other experiments recorded in Chapters 4 and 5. There are limited studies on the effect of BC on SO_4 retention or release in plant substrates (soil or soilless media). Altland and Locke (2017) reported that SO_4 decreased with the addition of 10% (v/v) gasified rice hull BC in their soilless substrate. Waqas et al. (2017) stated that the addition of 10:90 (w/w) hardwood-derived BC to the soybean substrate decreased s SO_4 contents in the soybean media, however, using BC alone as soybean growth media increased SO_4 concentrations.

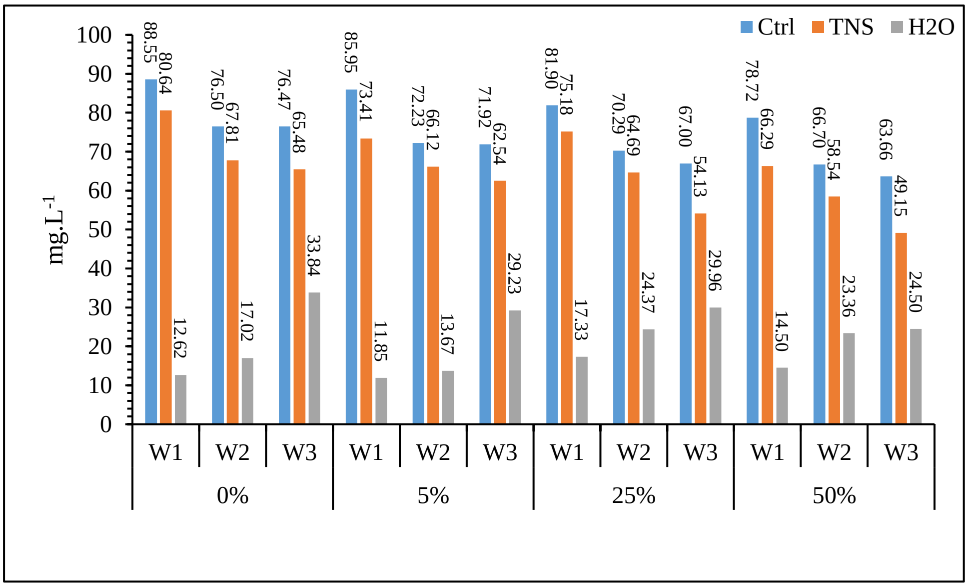


Figure 6.22: Sulphate Changes in the Irrigation Solutions versus BC Ratio

6.3 General Discussion

The results of this study indicate that with relatively low rates of 5-10% BC mixed media, we could alternate tap water with standard nutrient solution to irrigate plants, and save half the cost and impact of high nutrients. Thus, there will be a 50% reduction in fertilisers use, reducing the cost of production and ever more importantly, minimise environmental impact. From the previous studies, it is noted that most soil or hydroponics amendments use BC between 1 - 5% into their growth media. It was demonstrated that mixing BC with growth media produced a better effect on plant productivity than using BC alone or layered as a growth media.

Biochar can affect plant productivity and nutrients in solution in various ways. Increasing yields could be due to a decreases in exchangeable acidity and an increases in water and nutrient use efficiency (Uzoma et al., 2011, Major et al., 2010). Functional groups of CSBC such as amides, aromatics groups, allenes, aldehydes, ketones, amines, and alcohols could be one of the most effective factors in reducing nutrient leachate (Angalaeeswari and Kamaludeen, 2017). Another factor that could be beneficial is microbial populations increased with BC addition (Graber et al., 2010).

Chan et al. (2007) and Lehmann et al. (2003a) suggested that increasing pH value and soil carbon content could reduce some nutrient leachate. Atkinson et al. (2010) stated that the positive effect of BC could be due to influence on nutrient available contents, soil physicochemical properties, and on BC ability to retain nutrients and release them slowly into the solutions.

CHAPTER 7 FIELD EXPERIMENTS:

7.1 Materials and Methods

The experiment was conducted at K Farm, located in Toowoomba (Queensland, Australia) during the 2018 winter season (Figure 7.1). CBS provided by Clearance Water Filters/ Australia was used in this experiment. Rocket plant (*Eruca sativa*) was used to test BC effects on pH, EC, plants and solution nutrients namely NO_3, PO_4, K, Ca, Mg, SO_4 in hydroponics.

Figure 7.1: The Experiment Site

7.2 Media and Biochar Preparation

The peatmoss was soaked in tap water overnight to loosen the bulk for preparing pots media. On the second day, BC was mixed with peatmoss in 4 percentages of 0% control treatment, 5%, 25% and 50% v/v. The seeds were sown manually into the prepared media and then loaded in plastic buckets and placed in a cold room at 16°C for 48 hours until they germinated, plants were then transferred to the hydroponic farm.

7.3 Chemical Parameters

The leaves from each harvested treatment were immediately processed after harvest and they were washed in tap water to remove residuals. The samples were placed in labelled paper bags then placed in the oven at 72 °C for 72 h. Samples were weighed a few times until they reached a constant weight, and then the dry matter weight was recorded. Leaf nutrient content (NO_3, PO_4, K, Ca, Mg, SO_4) was measured in the dry matter. Chlorophyll and photosynthesis were measured one day before harvesting the plants. Leaf area was measured at the end of the test.

Leaf area was measured using leaf area scanner (LI-COR [LI-3100C AREA METER]). Chlorophyll content in the leaves was measured during the last week of the trial using a LEAF CHL PLUS (Novichonok et al., 2016). Five leaves of each treatment were tested. Photosynthesis was measured using a LI-6400XT Portable photosynthesis System following the method reported by Akhtar et al. (2014) but in this study, photosynthesis was measured one time only. Photosynthesis rate was measured for five mature leaves per treatment. These leaves were located in the upper canopy. Photosynthesis was measured between 11:00 am and 02:00 pm. Solution samples were taken three times in the first week and once a week until the end of the experiment to monitor the change in the solution- especially pH and EC- as BC may affect these parameters. The irrigation solutions pH, EC, NO_3, PO_4, K, Ca, Mg, SO_4 were measured where pH and EC measured using a PC2700 from EUTECH INSTRUMENTS. Potassium, Ca, Mg were measured using Atomic Absorption Spectrophotometer AA-7000 (SHIMADZU, Australia); and NO_3, PO_4 and SO_4 were measured using ion chromatography system ICS-2000 following the standard methods described in (Eaton et al., 2005). Plant nutrient content was measured by an external lab at the University of Queensland, Gatton, Australia.

7.4 Statistical Analysis

SPSS13.0 was used to examine single factor analysis of variance (ANOVA). Duncan's multiple comparisons judged handling the differences between the obvious ($p \leq 0.05$). The means of five replicates were used to present the data.

7.5 Results and Discussion

7.5.1 Leaf Area Response to Biochar Addition

Figure 7.2 depicts the impact of BC addition in different ratios on leaf area. The leaf area was significantly affected by BC addition. In general, increasing BC rate in the growth media over 5% decreased leaf area. The decrease in the leaf area was 24% and 28% for 25% and 50% of CSBC, respectively. The 5% CSBC had a positive effect as compared to other rates where leaf area increased by 10%. This is consistent with findings of other researchers. Biederman and Harpole (2013) reported that BC could increase aboveground productivity. Similarly, Song et al. (2014) demonstrated increased garlic plant yield with the use of BC. Another study found that leaf area in pepper and tomato was higher with the addition of 1–5% by weight BC to the media (Graber et al., 2010). There was also a significant increase in leaf area when BC was added to sunflower growth media (Alburquerque et al., 2014a). Puga et al. (2015) observed that BC increased leaf area in maize. The effect of BC on leaf area was also studied by Viger et al. (2015) on lettuce where BC significantly increased leaf area by around 130% compared to treatments without biochar. Viger et al. (2015) also stated that BC increased leaf area of Arabidopsis when combined with fertilizer as compared to using fertilizer alone.

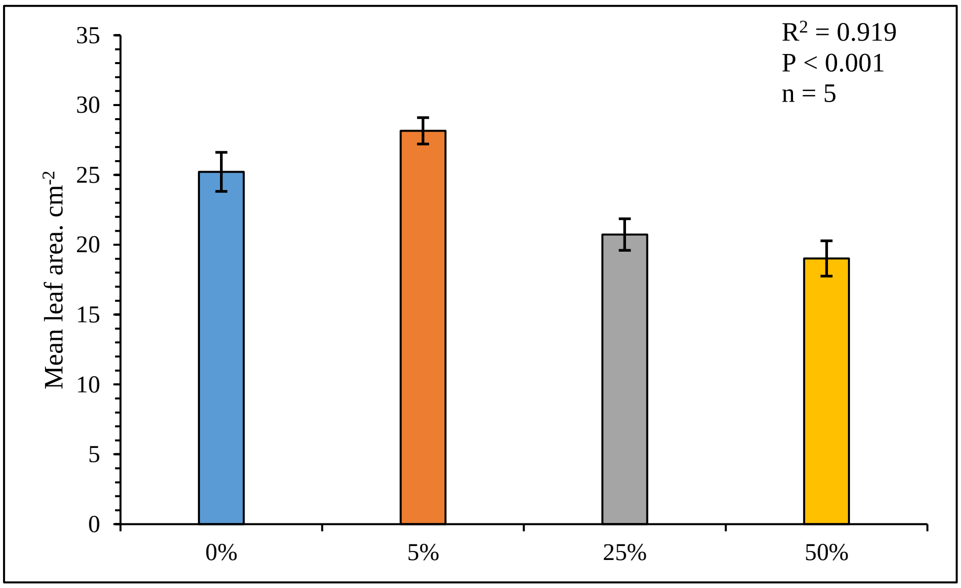


Figure 7.2: Effect of BC Ratios on Plant Leaf Area of Rocket (*E. sativa*)

7.5.2 Plant Height Response to Biochar Addition

Plant height was measured from the media surface to the highest part of the plant. Plant height was significantly affected by the addition of BC to the growth media (Figure 7.3). In general, as the BC increased over 5%, the plant height decreased. There was a 6% increase in plant height with 5% CSBC treated media. In contrast, there was a 45%, and 40% decrease in plant height for those grown on 25% and 50% CSBC treated media, respectively. Similar results were shown by Graber et al. (2010) where a small amount (1-5% by weight) of BC positively enhanced plant height. Puga et al. (2015) also stated that BC increased maize height. Viger et al. (2015) stated that 50 tonnes.ha^{-1} of BC significantly increased plant height by 177% compared to the control treatments which involved the application of fertiliser only without biochar. Biochar with fertiliser have yielded a more beneficial effect on plant height as opposed to treatments without biochar. Compared to the control treatment, the addition of BC to the growth substrates (BC + chicken manure, BC + city waste compost), increased plant height in maize (W. H. Utomo et al., 2012). Another study conducted by Yin et al. (2012) on the effect of BC on soybean showed that BC increased plant height. Alburquerque et al. (2014a) studied the effect of different feedstock based BC on sunflower and demonstrated that it has a significant effect on plant height. Co-composted BC was tested on oat (*Avena sativa* L.) and the results showed an increase in plant height (Schulz et al., 2014). However, some studies showed that plant height was decreased as stated by Schulz and Glaser (2012) when BC was combined with compost.

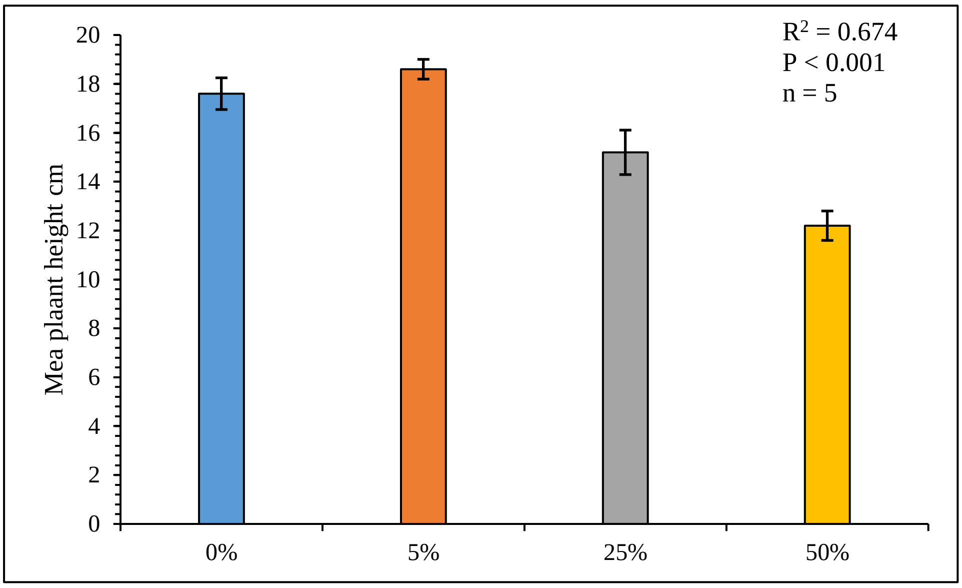


Figure 7.3: Effect of BC Ratios on Plants Height Rocket (*E. sativa*)

7.5.3 Dry Matter Response to Biochar Addition

The dry matter varied, with different BC rates in the growth media as illustrated in Figure 7.4. The lowest dry matter was from plants grown on 50% BC whilst the highest was from those grown using 5% BC. The 5% BC increased dry matter slightly by approximately 4%. There was around 17% reduction of dry matter in the plants grew on 50% BC treated substrate. The increase in the plant dry matter with BC application was reported in the literature. Song et al. (2014) stated that BC increased final dry matter. Biederman and Harpole (2013) found that BC increased plants' green parts and thus increased dry matter. Pepper and tomato growth increased with BC addition which resulted in higher dry biomass (Graber et al., 2010). Other findings by Alburquerque et al. (2014a) to do with sunflower (*Helianthus annuus* L.) growth showed that plant dry biomass increased when BC was added. Dry matter of lettuce (*Lactuca sativa* L.) showed a significant increase from 0.58 in 0 $t.ha^{-1}$ to 1.24 in 50 and 100 $t.ha^{-1}$ (Viger et al., 2015). Song et al. (2014) reported that there was a significant increase in garlic dry mass grown onto BC (produced at 450 °C) amended soil compared to that grown on soil only.

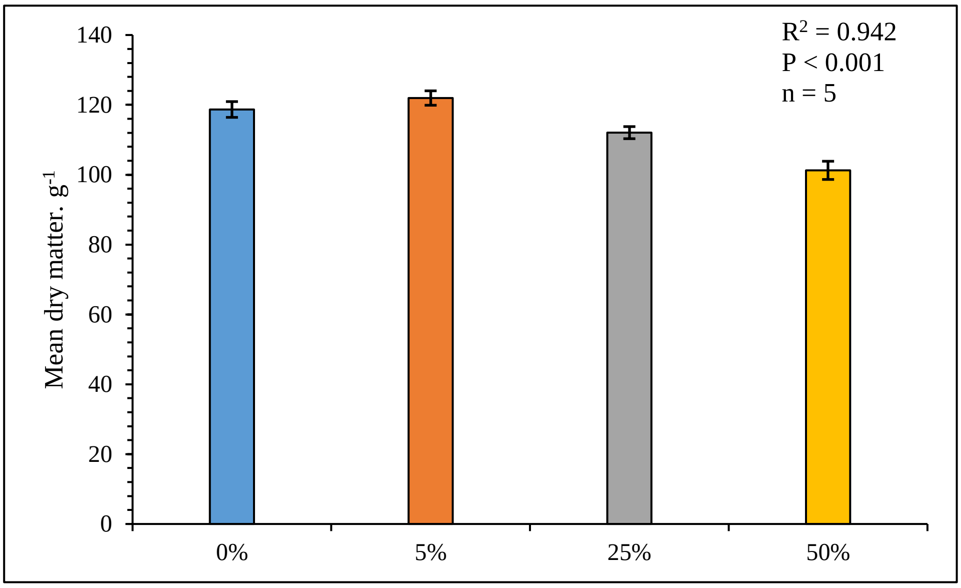


Figure 7.4: Effect of BC Ratios on Plants Dry Matter Rocket (*E. sativa*)

7.5.4 Photosynthesis Trends with Biochar Addition

The influence of BC addition on photosynthesis of the plant is demonstrated in Figure 7.5. In general, statistical analysis revealed that BC effect on photosynthesis was only significant with 5% BC treated media. There is limited studies on the effect of BC on photosynthesis. Graber et al. (2010) who reported that photosynthesis was insignificantly affected by BC treatments.

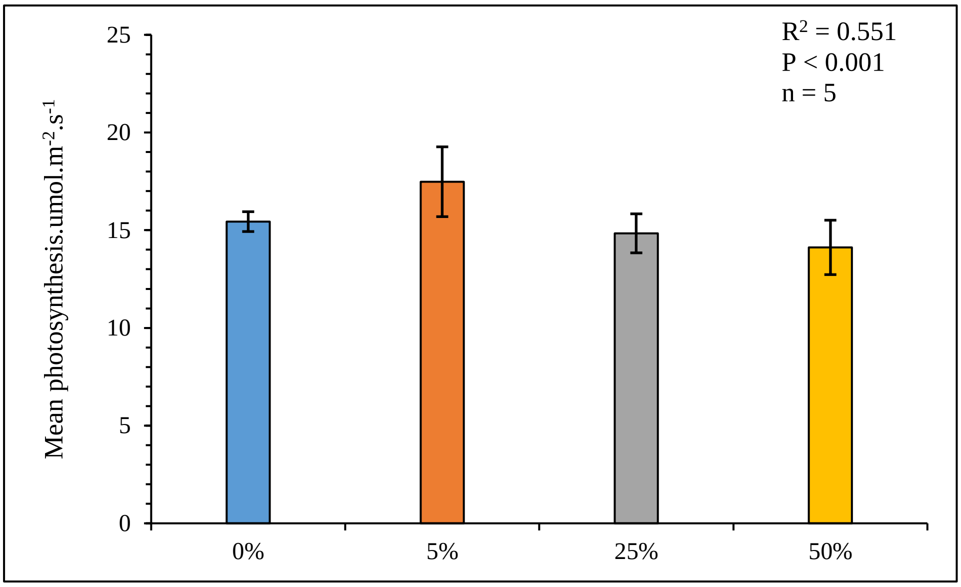


Figure 7.5: Effect of BC Ratios on Photosynthesis Rocket (*E. sativa*)

7.5.5 Chlorophyll Trends with Biochar Addition

Figure 7.6 shows the effect of different BC rates on plant chlorophyll. In general, BC negatively affected chlorophyll content in the plant. The 25% and 50% BC ratios significantly reduced chlorophyll content in the leaves. The reduction was higher in the 50% and 25% BC treated media than the control and 5% BC treatments. The results are in line with Akhtar et al. (2014) and Awad et al. (2017) who demonstrated that chlorophyll decreased significantly with the use of biochar. The reason behind the decrease of chlorophyll could be the reduction of N in the solution as BC significantly decreased N content in the solution. Reducing the N availability to the plants lead to reduce of N content in the plants (Lehmann et al., 2002). Puga et al. (2015) also stated that BC reduced chlorophyll in maize. The reduction of N conjuncture can be confirmed by measuring NO_3 content which will be covered in the following section.

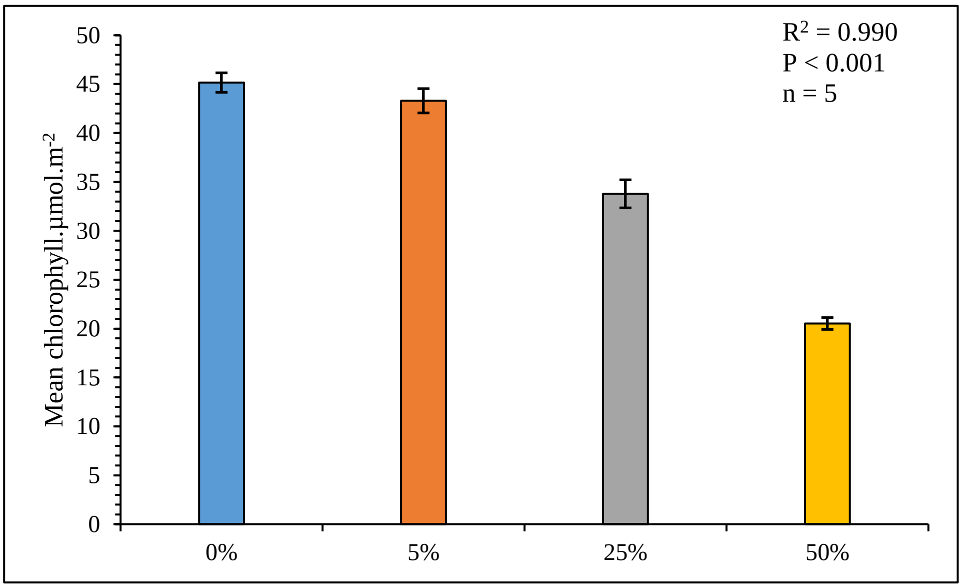


Figure 7.6: Effect of BC Ratios on Chlorophyll Rocket (*E. sativa*)

7.6 Nutrient Content in the Leaves

7.6.1 Nitrate Concentration

Figure 7.7 demonstrates the impact of BC addition on NO_3 content in the plant leaves. Nitrate content in the leaves decreased significantly with the use of BC in the growth media. A higher amount of BC resulted in less NO_3 in the leaves. The NO_3 content was significantly reduced from 22 $g.kg^{-1}$ in the control treatment to 13 $g.kg^{-1}$ in 50% BC treated media. The decrease in NO_3 content had a liner trend. This was the state with the rest of the tests which were done previously (Chapters 4 and 5). The reduction was 57%, 45%, and 12% in the leaves' NO_3 content grown on 50%, 25%, and 5% respectively. The results were consistent with the findings of other studies (Akhtar et al., 2014). The decrease of NO_3 in leaves was due to NO_3 being absorbed on the biochar. Biochar reduced NO_3 concentration in soil applications as stated by Alburquerque et al. (2014b) and Biederman and Harpole (2013) Nitrate concentration was sigificantly reduced when BC was added to plots even with undergoing nitrogen fertiliser application (Adeyemi and Idowu, 2017). Biochar has shown a significant effect on reducing NO_3 in the leachate as well (Dunbabin et al., 2003). Ventura et al. (2013) showed that BC reduced NO_3 concentration in the leachate by 75% compared to the control trearment.

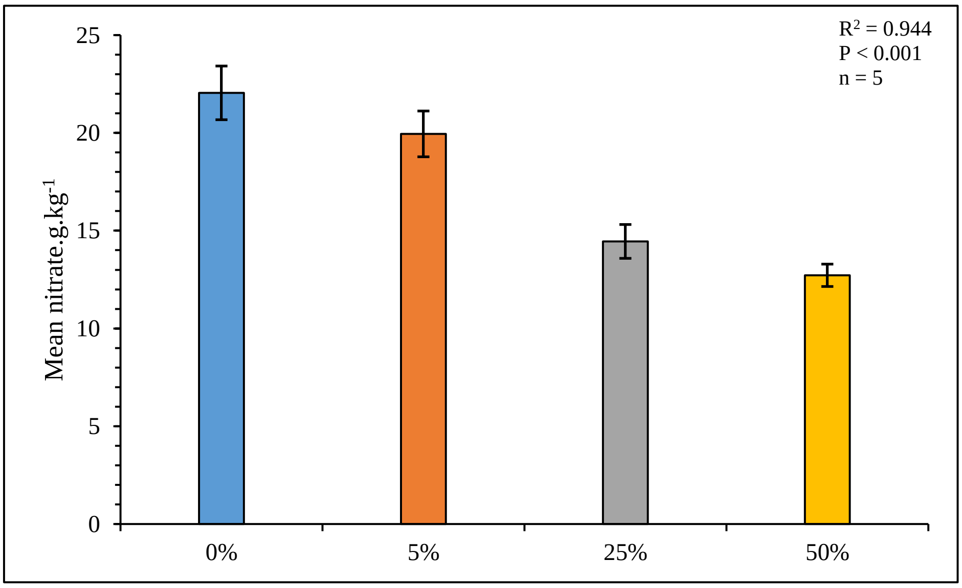


Figure 7.7: Biochar Ratio Effect on Nitrate Content in the Leaves

7.6.2 Phosphate Concentration

Phosphate (PO_4) concentration was slightly affected by BC as shown in Figure 7.8. Plants grown in the control treatments exhibited higher PO_4 levels compared to other treatments. As BC increased more than 25%, the leaves' PO_4 content was decreased further. It seems that there was a retention of PO_4 into BC and that decreased PO_4 concentration in the plants grown on BC treatments. Biochar is one of the most popular absorbers for dissolved PO_4 (Adeyemi and Idowu, 2017). Biochar has shown adsorption capacity of PO_4 between 37-16 mg.-g^{-1} but only when in the presence of Ca ions in the solution (Marshall et al., 2017). As Ca ions were present in the hydroponic solution that was used in this test, PO_4 was adsorbed. Most research on BC effect on PO_4 adsorption stated that BC have no effect or increased PO_4 availability. It is worth mentioning that most of this research conducted on soil application and there are a limited number of reports addressing BC effects on PO_4 in hydroponics. Other have shown that BC can increase PO_4 availability but this could be due to using different types of BC as well as the amount of BC and types of plant (Alburquerque et al., 2014a, Viger et al., 2015).

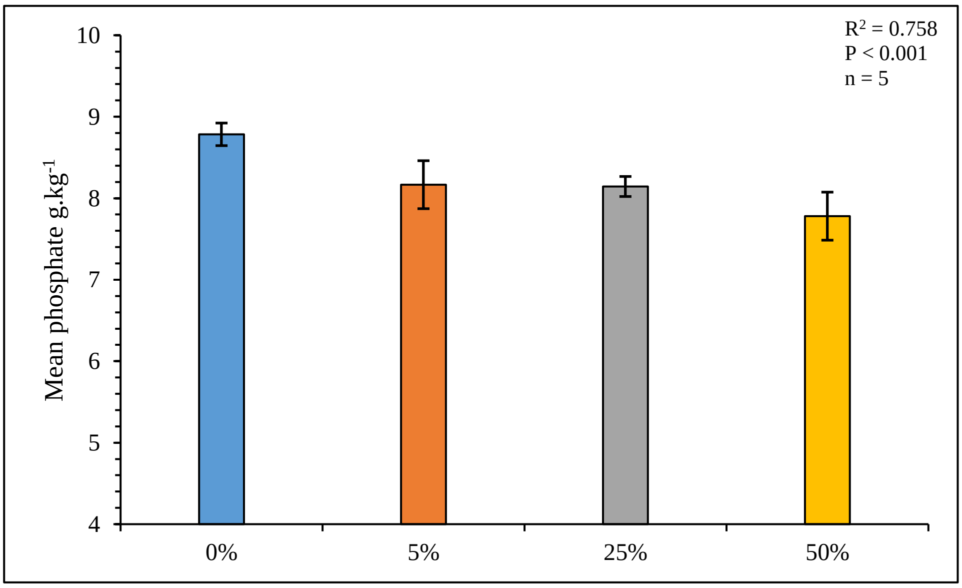


Figure 7.8: Biochar Ratio Effect on Phosphorus Content in the Leaves

7.6.3 Potassium Concentration

Potassium concentration in the leaves increased as BC rate increased in the media (Figure 7.9). The highest concentration of K was in plants grown with 50% BC in the media, whilst the lowest was from the control. Potassium increased from ~52 $g.kg^{-1}$ in the control treatment to ~65 $g.kg^{-1}$ with 50% BC treated media. The addition of biochar significantly affects the concentration of K in the leaves. Biederman and Harpole (2013) found that BC increased K content in plant tissue. These results are in line with what was obtained from the column test in the two previous chapters (Chapters 2 and 3). Potassium was increased when BC was added to the soil (Viger et al., 2015) which in turn could lead to an increase in K concentration in the leaves. The results are in line with Awad et al. (2017) who claimed that BC increased K concentration in the vegetable under study compared to plants in non-BC growth media. Bedussi et al. (2015) proved that biochars from hardwood and softwood increased K in pore water. The increase of K in the soil reflected the increasing K in grain plant tissue (Gaskin et al., 2010).

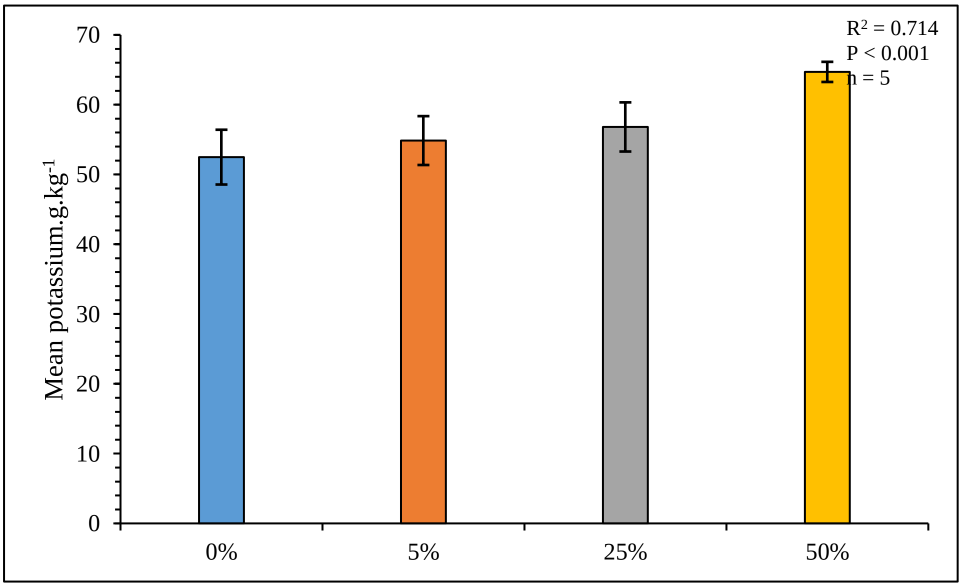


Figure 7.9: Biochar Ratio Effect on Potassium Content in the Leaves

7.6.4 Calcium Concentration

Biochar addition affected Ca concentration in the leaves (Figure 7.10). The highest amount of Ca in the leaves was found with 0% BC in the media whilst the lowest was in plants grown with 50% BC. There was little difference in Ca concentration in plants growing in the control and 5% BC treatments with both ~26-27.5 $g.kg^{-1}$. The highest record of Ca concentration was found in 25% BC ~32 $g.kg^{-1}$. The results were similar to those found in the column test (Chapters 2, and 3). A number of researchers examined BC effects on Ca in hydroponics. Awad et al. (2017) stated that the addition of BC increased Ca concentration in plant tissue. Schulz et al. (2014) also claimed that BC elevated Ca. Our results have shown the opposite i.e. BC reduced Ca in plant tissue. This outcome indicates that further investigation into the effect of BC on Ca concentration in plant tissue of Rocket (*E. sativa*) in hydroponic conditions is needed.

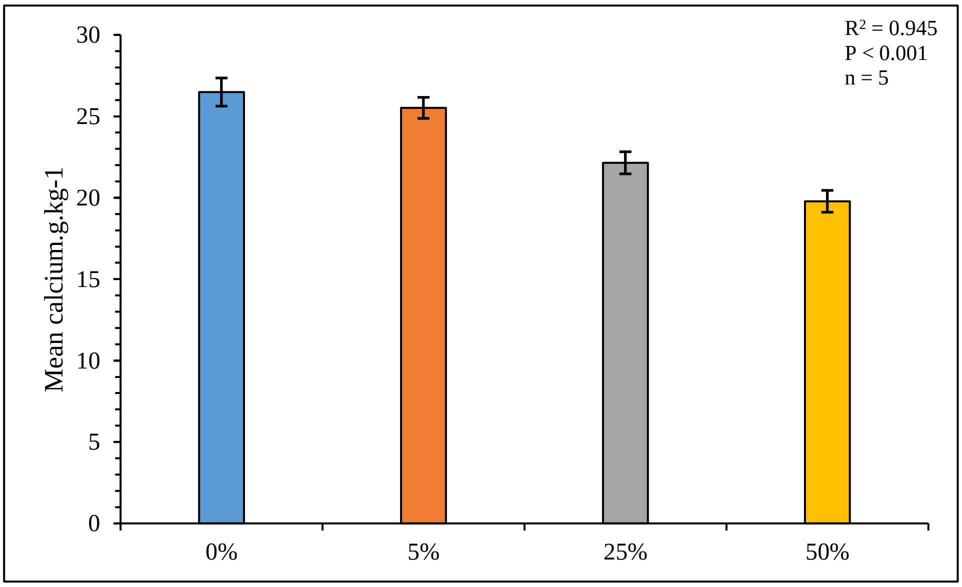


Figure 7.10: Biochar Ratio Effect on Calcium Content in the Leaves

7.6.5 Magnesium Concentration

Magnesium concentration did not significantly change in the leaves with different amount of BC in the media (Figure 7.11). The concentration of Mg was 9-11 $g.kg^{-1}$ in plants growing with different amount of BC in the media. The results were similar to that shown in the column test (Chapter 4, and 5). Awad et al. (2017) stated that BC increased Mg in plants. Different type of vegetables showed different responses to BC addition and the effect of Mg concentration in plants tissue. These vegetable were cabbage, dill, mallow, red lettuce and tatsoi. Magnesium increased in cabbage, dill and tatsoi but decreased in mallow and red lettuce (Awad et al., 2017). Increasing hardwood BC rate led to an increase of Mg concentration in the soil but it did not affect Mg concentration in the fruit (Sorrenti et al., 2016). The results showed that there was no effect of BC on Mg. This could be to the fact that BC contains Mg and therefore there was no active retention and release events.

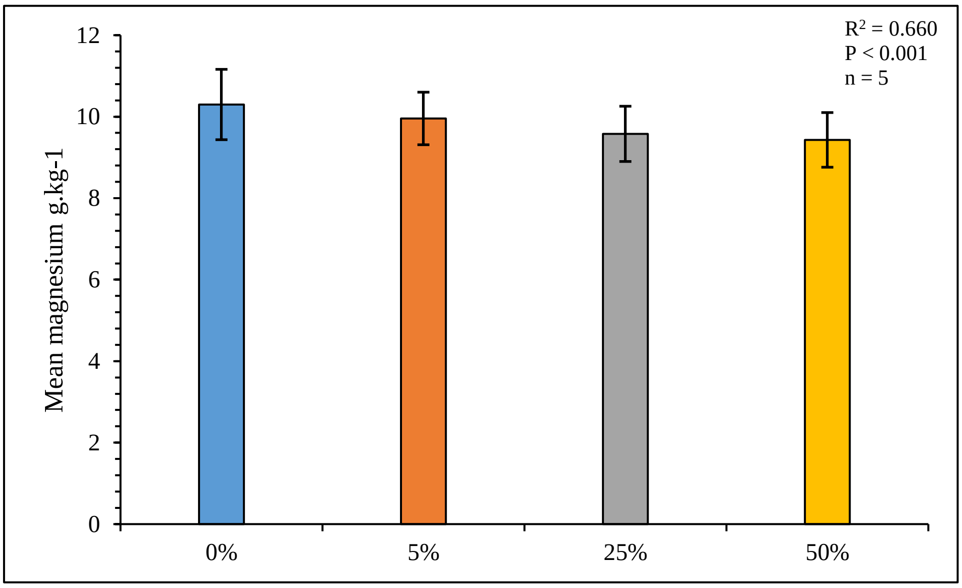


Figure 7.11: Biochar Ratio Effect on Magnesium Content in the Leaves

7.6.6 Sulphate Concentration

There was no significant effect of BC ratios on SO_4 concentrations in the leaves (Figure 7.12). The concentration of SO_4 was ~12-13 g.kg^{-1} in plants grown with 0 - 50% BC media and ~11 g.kg^{-1} in plants grown with 5% BC media. There is plentiful information pertaining to the effect of BC on SO_4 concentration in plant tissues (Borchard et al., 2012b). This study is the first and study that investigated the effect of BC on SO_4 in hydroponics. Kammann et al. (2011) Invested BC effect at (0, 100 and 200 t ha^{-1}) on pseudo-cereal *Chenopodium quinoa* Willd grown in a sandy soil reported that BC increased SO_4 in the plants.

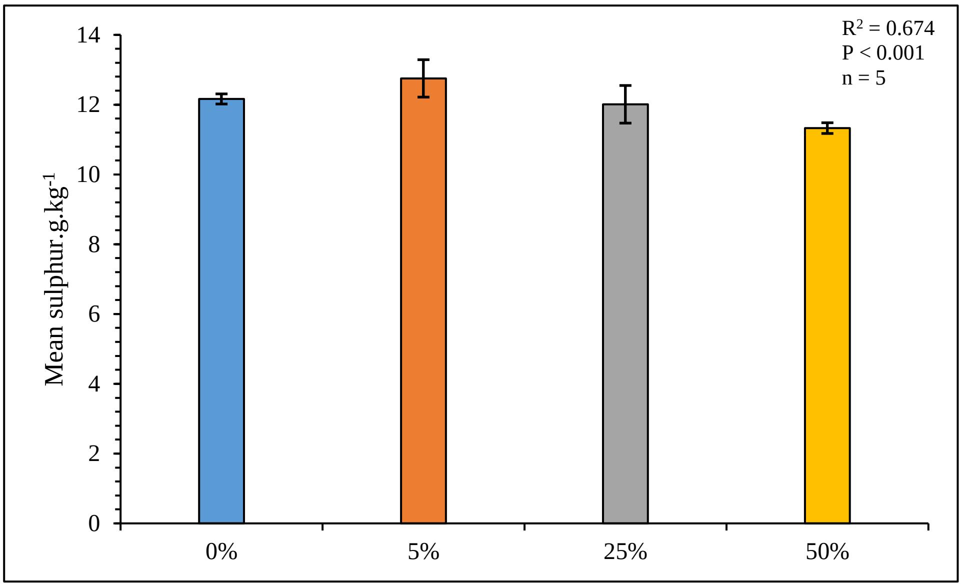


Figure 7.12: Biochar Ratio Effect on Sulphate Content in the Leaves

7.7 General Discussion

This chapter focuses on the most relevant theories to interpret plant productivity data. Most plant parameters were higher with 5% CSBC treated substrate. This could be due to the 5% BC did not adsorb nutrients as much as the other two rates (25% and 50%) of BC which made nutrients become more available in reasonable ranges to the plants. Another reason could be the pH level which was approximately 6.5-6.7 with 5% BC treated media, which suits plants uptake of nutrients. Koehorst et al. (2010) stated that fresh weight was increased with a pH level of 6.5. They also pinpointed that pH level <4.5 and >8.5 significantly reduced plant fresh and dry weight. Another reason could be increased beneficial microbial populations which help with breaking down nutrient and make them more available to plants (Graber et al., 2010).

CHAPTER 8 CONCLUSIONS:

Preliminary tests: from the preliminary tests, it can be seen that biochar type has influence on nutrient retention and release mechanism. Also, washing the sand and BC was better than using them in their raw state. Finally, mixing the sand and BC was better than using BC in a layer into the columns. It is evident that CSBC has the highest nitrate retention, while PSBC and MSBC have somewhat similar reactions toward nitrate recovery. It can be seen generally that the adsorption of nitrate into the three types of BC was high in the first day. It then dropped sharply for PSBC and MSBC the following day, while this drop was less pronounced for CSBC. It is important to point out here that as expected the sand showed only limited adsorption of nitrate throughout the five days of the experiment.

Initial column tests: The application of biochar may lead to better accumulation of macro-nutrient in plant tissue. Which may lead to a healthier plant for consumption.

Second column tests, BC addition to the growth media affected most of the parameters positively. pH was increased as the BC rate increased in the media. In term of EC, BC addition reduces EC level differently. The control treatment released elements more than other treatment while the highest recovery of the elements was from the growth media with 50% BC. Elements retention and release were also affected by BC addition to the media. Nitrate, phosphate, calcium, potassium and sulphate were retained by BC while magnesium did not react to the treatments. According to the findings of this study, it is recommended using ≥25% BC on average of the growth media in hydroponics while ≤25% can be a suitable treatment for water filtration. Bearing in mind that ≥25% of BC in treatment could affect pH level depending on the type of BC, pyrolysis temperature and other pre and post preparation conditions).

Glasshouse experiment: the results of this study support the concept of using nutrient solution alternately with plain water whereby CSBC is mixed with the growth media. The results showed that BC ratios in the growth media affected the plants and the irrigation solution parameters more than changing the irrigation solution. Most of the plant parameters were higher with the addition of 5% BC than the other ratio and the control treatment (0% BC). In contrast, most of the plants' characteristics were negatively affected with ≥ 25% BC. It is important to mention that there are very limited or no study conducted on the effect of BC on sulphate and this can be the basis of further study to into BC effects on sulphate. It is also the first study that monitors BC effect on pH, EC, and the whole plants' macronutrients because there is interaction between these nutrients as well as interactions between the nutrient and pH.

Field experiments: this study investigated the effect of applying CSBC in different rates of 5, 25 and 50% on the growth and nutrient content of Rocket (*E. sativa*). The effective rate of BC was 5%. Beyond that level, BC negatively affected most of the plant parameters under study. Leaf area, dry matter weight, chlorophyll and plant height were all reduced as well as most of plant nutrient content except for K which was higher with an increased amount of biochar. Biochar did not affect Mg and sulphur concentrations in the plants. The release of K from CSBC may be one of the possible mechanisms for improving plant productivity. As there is limited information on the effect of BC on plants grown hydroponically, it is recommended that more focus should be paid to exploring the effect of different types and rates on plant productivity, growth media and nutrient solution in soilless agriculture.

At the end of this project we recommend the following:

1- Utilisation of CSBC ratios between 5% and 25% on different plants and different growth media, especially those media incorporating sand.
2- Investigating different types of BC and amount in hydroponics with different growth media. It is better to use cheap and eco-friendly growth media.
3- Further research into investigating BC effects on other nutrients such as Mn, Fe, Zn, Na, and Cu in hydroponics as these are the other essential elements for plants.
4- Longer term trial to assess the impact of BC rate and type on plant macronutrients and micronutrients in a larger scale hydroponic farm environments (glasshouse).

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APPENDICES

A. Field and Glasshouse Experiments Pictures.

Figure A1: Plants at the 1st Week in the Field

Figure A2: Plants at the 2nd Week in the Field

Figure A3: Plants at the 3rd Week in the Field

Figure A4: Plants at the 4th Week

Figure A5: Plants at the 5th Week

Figure A6: Plants at the 6th Week

Figure A7: Plants at the 7th Week

 **1**	 **2**
 **3**	 **4**

	
5	**6**

Figure 8: 1, 2…6: Show the Preparation of the Hydroponic System

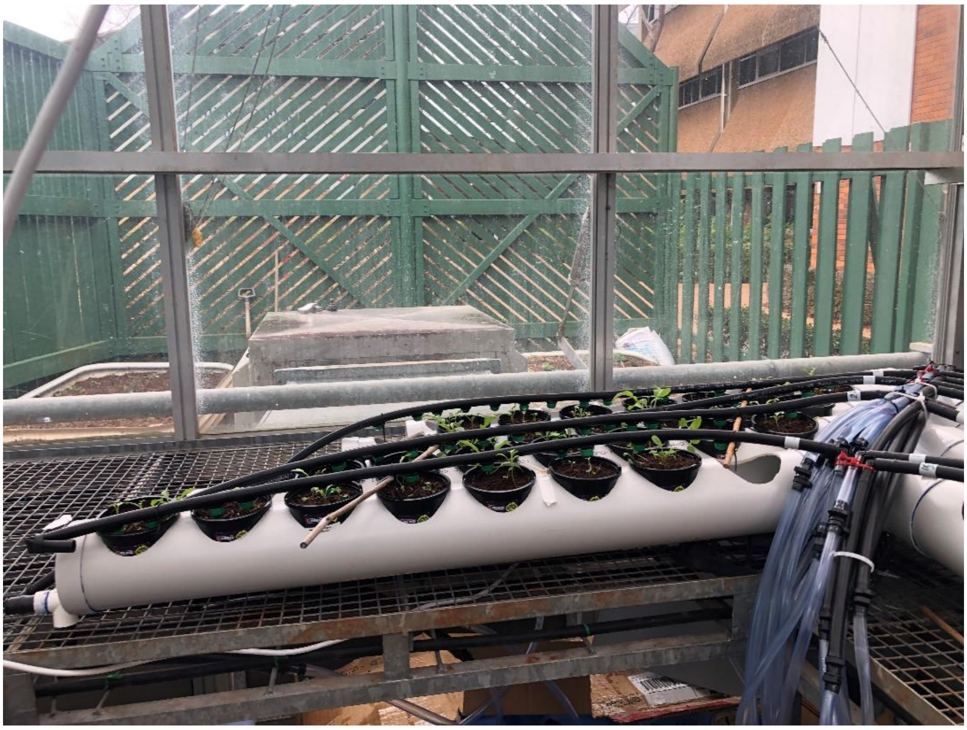

Figure A9: Plants at the 1st Week in the Glasshouse

Figure A10: Plants at the 2nd Week

Figure A11 Plants at the 3rd Week

Figure A12: Plants at the 4th Week

Figure A13: Plants at the 5th Week

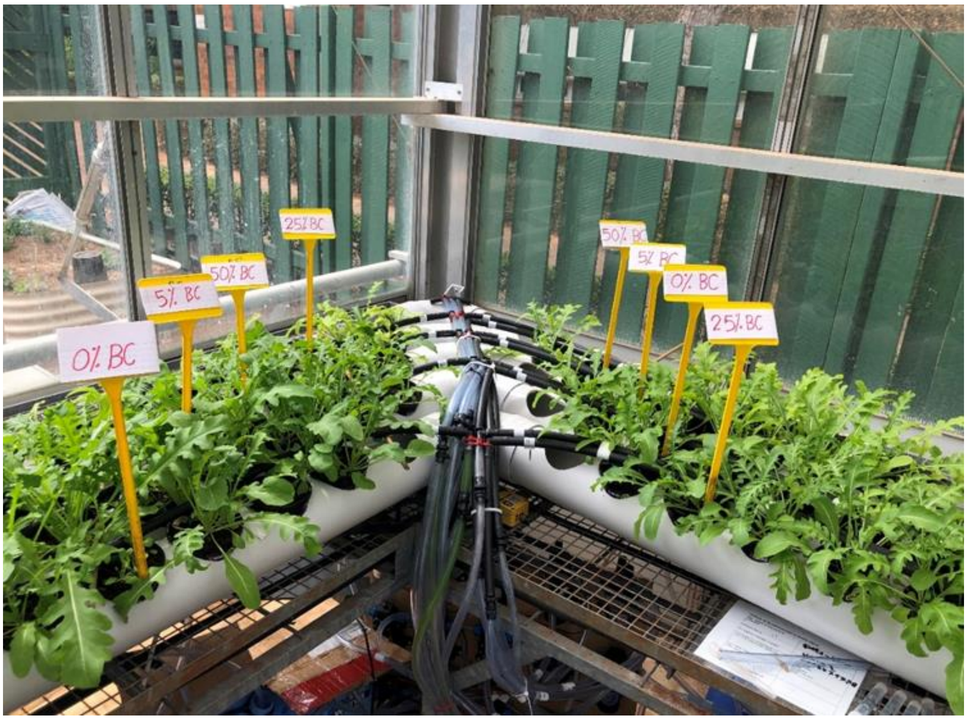

Figure A14: plants at the 6th Week