BIOCHAR – A MULTI-BENEFICIAL AND COST-EFFECTIVE AMENDMENT TO FINE-GRAINED SOILS TO IMPROVE HYDRAULIC PROPERTIES AND TREAT POLLUTANTS FROM STORMWATER RUNOFF

by

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ABSTRACT

MOHAMMAD KHALID. Biochar – A Multi-Beneficial and Cost-Effective Amendment to Fine-Grained Soils to Improve Hydraulic Properties and Treat Pollutants from Stormwater Runoff. (Under the direction of DR. MARIYA MUNIR)

Stormwater runoff can contain significant amounts of pollutants that can result in adverse impacts on receiving water bodies. Highways are considered a major source of stormwater pollution, and their runoff contains various contaminants, including suspended solids, as well as organic and inorganic pollutants. Moreover, the roadside soil gets compacted over time and can't infiltrate the stormwater through it. The situation becomes worse if it is fine-grained, which results in increased stormwater runoff. This study assessed the ability of biochar, a carbon-rich by-product generated from the pyrolysis of biomass, to remove various contaminants and to enhance the infiltration capacity of a soil-biochar mixture, as well as to understand the effect of chemical modification of biochar on contaminant removal.

For this, commercially available biochar was strategically selected. Lab-scale batch testing was done to find the preliminary estimate of contaminant removal, along with saturated hydraulic conductivity and water retention capacity. Furthermore, from the preliminary results, the bench-scale filtration columns were designed to evaluate the performance of biochar in the long term. Based on specific infiltration capacity, soil biochar column packing was done. The testing has been conducted for nutrient, heavy metal, and indicator bacteria analysis over a year, which includes different weather conditions. The results from saturated hydraulic conductivity show that biochar was able to greatly improve the infiltration capacity, which is attributed to the high porosity of the biochar soil mixture. The data from the column testing shows that biochar has the ability to significantly remove different contaminants. Overall, this study demonstrates that biochar could be efficiently applied with clay soil to improve the soil's hydraulic characteristics as well as to remove pollutants from stormwater runoff.

The first objective of my dissertation is based on saturated and unsaturated hydraulic conductivity. Soil structure and hydraulic properties are adversely affected by construction activities and vehicular traffic that results in reduced infiltration, reduced porosity, and increased stormwater runoff. Biochar offers a promising solution for improving soil structure and stormwater management. This study used two fine-grained soils mixed with nine commercially available biochars at 3% and 6% by weight of the soil. Laboratory tests included index properties, scanning electron microscopy (SEM), saturated hydraulic conductivity (Ksat), and unsaturated hydraulic conductivity (Kunsat) analysis of biochar soil mixture. SEM analysis reveals varied surface structures and pore formations among the biochars, indicating the impact of feedstock and production temperature. Results showed biochar application, especially 6% biochar content, resulted in reduced dry bulk density, increased porosity, and increased K_{sat} & K_{unsat} of biochar soil mixture. Among the biochar types tested, Biochar Now Medium, Biochar Now Small, and Char Bliss were found most effective in increasing K_{sat} for both soils, while certain biochar exhibits no or limited effects. The governing factors were soil type, type of biochar, and application rates. Overall, these findings highlight the importance of biochar amendment for addressing stormwater runoff and infiltration problems in fine-grained soils.

The second objective of my dissertation focuses on the longer-term performance of biochar application. Conventional green infrastructure often fails to effectively treat these pollutants, and biochar is a promising sustainable filter media. This study evaluates the long-term efficacy of ten commercially available biochars, amended into fine-grained soils, for stormwater runoff treatment. Lab studies were conducted to assess contaminant removal efficiencies and to characterize the physicochemical properties of biochar using methylene blue (MB) adsorption, surface morphology analysis, and batch tests. Six top-performing biochars were further selected for one-year column studies with real-world stormwater collected samples. Batch testing results showed additional benefit of up to 60% of target contaminants, with up to 95% removal at low concentrations (25–50 mg/L) of MB. SEM showed porous structures and high surface areas of biochar, which correlate with enhanced adsorption capacity. Column studies found Blue Sky, Char Bliss, and Naked Char biochar consistently performed better than others, where up to 90% removal of nutrients, heavy metals, and indicator bacteria was achieved initially. However, performance declined over time, and 10–30% added benefits were observed over one year due to active site saturation of biochar. Overall, this study shows that biochar can be efficiently used with fine-grained soil as an effective stormwater management practice to treat different contaminants from stormwater runoff. The results of this study provide a critical insight for optimizing biochar-based green infrastructure to mitigate urban stormwater pollution.

The third chapter evaluates the modified and unmodified biochar for the removal of different contaminants from stormwater runoff. The modification of biochar offers various advantages compared to traditional biochar, such as enhanced surface functional groups, higher surface area and porosity, enhanced adsorption properties, and environmental sustainability. This study explores the effectiveness of chemically modified biochar, specifically through acid and alkali treatments, in enhancing the removal of contaminants from stormwater runoff. Laboratory batch and column experiments were conducted to evaluate adsorption kinetics and interactions between pollutants and biochar under varying environmental conditions. Results demonstrate that higher pH of biochar exhibits enhanced adsorption capacities, particularly for heavy metals, total organic carbon, and indicator bacteria for this project. Furthermore, batch and column studies reveal that Naked Char biochar showed significant improvements in contaminant removal rates compared to Char Bliss biochar, especially alkali-modified biochar. These findings highlight the potential of modified biochar as an eco-friendly and cost-effective solution for mitigating different contaminants in stormwater management systems.

Key Words: Biochar; stormwater; saturated and unsaturated hydraulic conductivity; column filtration; contaminants removal.

DEDICATION

To my parents, especially my late father, whose sacrifices and values continue to guide me, and my mother, whose unwavering love and strength have been my foundation. And to my mentors, whose guidance shaped this journey.

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
BET	Brunauer-Emmett-Teller (method for surface area analysis)
BMPs	Best Management Practices
CL	Low Plasticity Clay (soil classification)
D50	Median particle size (50% of particles are smaller than this size)
DI	Deionized (water)
E. coli	Escherichia coli (indicator bacteria)
EDX	Energy Dispersive X-ray Spectroscopy
EPA	Environmental Protection Agency
FRG	Faculty Research Grant
H_2SO_4	Sulfuric Acid
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
IDEXX	A company providing water testing kits (used for bacterial analysis)
KOH	Potassium Hydroxide
Ksat	Saturated Hydraulic Conductivity
Kunsat	Unsaturated Hydraulic Conductivity
LID	Low-Impact Development
MB	Methylene Blue
ML	Low Plasticity Silt (soil classification)
NaOH	Sodium Hydroxide
NC	Naked Char
NCDOT	North Carolina Department of Transportation
PVC	Polyvinyl Chloride (material used in column setup)
PZC	Point of Zero Charge
SEM	Scanning Electron Microscopy
SI	Supplementary Information
SSA	Specific Surface Area
TOC	Total Organic Carbon
TSS	Total Suspended Solids

USCS	Unified Soil Classification System
vG model	van Genuchten model (for soil hydraulic properties)

1 BACKGROUND

1.1 Biochar: a new research paradigm

The increased impervious surface area due to the expansion of urban regions results in potential effects on the water environment. With intensifying climate change and urbanization, non-point source pollution caused by stormwater runoff and flooding is becoming a more and more serious issue that is threatening ecosystem health and water supply in urban areas (Hasan et al., 2021). Stormwater runoff requires a sustainable treatment to mitigate the adverse environmental and public health impacts associated with urbanization and climate change while promoting health and resilient urban environments (Corvalan et al. 2020). The reduced infiltration capacity of roadside soils leads to increased stormwater runoff. Organic and inorganic contaminants like nutrients, pesticides, indicator bacteria, and heavy metals could be found in highway stormwater runoff. Due to the higher risk of contamination, highway runoff could play a critical role in receiving water bodies (Müller et al., 2020).

Biochar is considered a sustainable solution to alter soil hydrological properties, nutrient retention in agricultural fields, and increase crop productivity while balancing a healthy ecosystem (Gámiz et al. 2017; Garg et al. 2020). Biochar is an organic material produced through the thermal processing of biomass in the absence or limited amount of oxygen and is considered highly porous and carbon-rich. Biochar is known to have high porosity, large specific surface area (SSA), high pH value (alkaline), and high nutrient content (Lehmann and Joseph, 2009; Ahmad et al., 2014); thus, proposed as a soil amendment for carbon sequestration, landfill cover material, improving soil fertility, organic pollutants such as polycyclic aromatic hydrocarbon (PAH) from soil, and inorganic pollutants such as heavy metals (Waqas et al., 2015; Wong et al., 2017).

Feedstock type and operating conditions, such as temperature, residence time, and flow rate mainly govern the production of biochar (Meyer et al. 2011). It has been found that temperature alters the pore structure of the biochar (Ganesan et al. 2020). By utilizing biochar in the soil, various physical properties of soil such as pore size distribution, porosity, soil density, soil moisture content, water holding capacity, total porosity, and hydraulic conductivity can be improved (Hardie et al. 2014, Zwieten et al. 2012). Due to the low deterioration rate, biochar can last up to several hundred years for its complete degradation (Castellini et al. 2015). So, biochar amendments to the soil will result in long-term impacts on soil physical health, such as soil structure and saturated hydraulic conductivity (Amoakwah et al. 2017).

Low-impact development (LID) systems are typically used to manage stormwater. This helps in reducing the flooding by improving the filtration system. Commonly used LID systems to reduce runoff are bio-infiltration systems, bioswales, green roofs, and dry/wet ponds (Ekka et al., 2021). The challenge with the single media filter is that different stormwater contaminants may not be efficiently treated (Grebel et al., 2013). Stormwater treatment systems are subjected to intermittent infiltration during different weather conditions. This includes wet and dry weather periods characterized by rainfall duration, intensity, and antecedent drying period that can affect the performance of the filtration system (Li et al., 2012; Mohanty et al., 2014a; Mohanty et al., 2013). Previous studies have suggested that biochar can be effective in removing different contaminants under such complex situations (Nabiul Afrooz and Boehm, 2017; Lau et al., 2017).

1.2 Biochar properties: effect of pyrolysis temperature and feedstock

The properties of biochar, such as surface area, pH, pore structure, and carbon content, are strongly influenced by the feedstock type and production conditions, particularly the pyrolysis process (Tomczyk et al., 2020). Pyrolysis, the most common method of biochar production, involves heating biomass at high temperatures under limited oxygen (Liu et al., 2015). Higher pyrolysis temperatures generally enhance surface area and microporosity due to increased volatile release and internal pore formation (Mohanty et al., 2018). Although pyrolysis was not performed as part of this study, understanding these factors is important in selecting appropriate commercially available biochar with desired physicochemical characteristics. Table 1-1 summarizes the biochar used in this research.

Table 1-1 Summary of biochar with different feedstock and pyrolysis conditions used for this study

Company Name	Product Name	Feedstock	Location	Pyrolysis Temp.
American Biochar Company	Naked Char	Wood (Southern Yellow Pine)	Niles, MI	550 – 900°C
Aries Clean Technologies	Aries Green	Wood Chip	Franklin, TN	400°C
Blue Sky Biochar	Organic Granular Pine Biochar; Organic Micronized Powder Pine Biochar	Wood (Pine)	Thousand Oaks, CA	---
Biochar Now	BN Small, BN Chip, BN Medium	Wood (Pine)	Berthoud, CO Loveland, CO	300 - 700°C
Plantonix	Char Bliss Premium Wood Biochar	Softwood	Ashland, OR	---
Soil Reef LLC	Soil Reef Biochar	Wood	Berwyn, PA	500°C
The Andersons	Biochar DG	Wood	Maumee, Ohio	---
Wakefield Biochar	Wakefield Premium Biochar	Wood (Pine)	Valdosta, GA Columbia, MO	500°C

1.3 Modified biochar for the removal of contaminants

The modification of biochar offers various advantages compared to traditional biochar, which makes it a potential candidate for various environmental applications. Some of the key advantages include increased yield, higher surface area and porosity, improved adsorption and adsorption properties leading to higher contaminants removal, and environmental sustainability (Jeyasubramanian et al., 2021).

Previous studies have shown a higher yield of modified biochar. For example, the study by Suwunwong et al. (2020) found around 25% increased yield through internal modification at a temperature of 500 °C for 2 hours, utilizing a heating rate of 10 °C/min. The modification of biochar processes can be optimized to reduce energy consumption, as demonstrated by microwave pyrolysis, which requires a significantly shorter heating time, approximately ten percent of conventional heating when employing K3PO4 with bentonite (Mohamed et al., 2016). In another study by Song et al. (2020), the incorporation of nano-magnetite in biochar resulted in a notable increase in its adsorption capacity. The modified biochar exhibited a maximum adsorption capacity of 9.92 mg/g, significantly surpassing the 8.03 mg/g observed for the original biochar. Moreover, chemical modification of biochar has been found to significantly enhance its surface area. For instance, the introduction of potassium hydroxide as a modifier increased the surface area of the biochar from 14.4 to 49.1 m^2/g (Wang and Wang 2019). Studies showing enhanced performance of chemical modification of biochar are summarized in Table 1-2. Modified biochar can also serve as a low-cost, sustainable, and environmentally friendly material. The utilization of waste materials as feedstock, combined with the enhanced adsorption capabilities, contaminants immobilization, carbon sequestration potential, and the promotion of green infrastructure, collectively contribute to the environmentally friendly nature of biochar modification (Elkhlifi et al., 2023; Wang et al., 2019).

Table 1-2 Studies showing the effect of chemical modification on pollutant removal from different feedstocks.

Chemical Modification	**Biochar feedstock**	**Production temperature °C**	**Target contaminants**	**Enhancement**	**References**
H_2O_2 modification	Peanut hull	300	Pb^{2+}	Enhanced sorption from 0.88 to 22.82 mg g^{-1}	Xue et al. (2012)
10% H_2SO_4 or 3 M KOH	Rice husk	450–500	Tetracycline	Exhibited better sorption	Liu et al. (2012)
KOH modification	Municipal solid waste	400, 500 and 600	As^{5+}	More than 1.3 times	Jin et al. (2014)
Phosphoric acid-microwave method	Pine tree sawdust	550	Fluoride	Increasing sorption	Guan et al. (2014)
Polyethyleneimine modified	Rice husk	450–500	Cr^{6+}	sorption capacity from 23.09 to 435.7 mg g^{-1}	Ma et al. (2014)

1.4 Research gap

Despite growing interest in the use of biochar for environmental applications, significant research gaps remain regarding its performance in stormwater management systems, especially when integrated with fine-grained soils and subjected to real-world conditions. The following gaps were identified through a comprehensive review and analysis conducted in this study:

- Biochar in fine-grained soils: Limited studies have explored how biochar improves hydraulic properties in compacted clays and silts used for managing stormwater runoff.

- Long-term performance: The durability of biochar's contaminant removal under real-world conditions is not well understood.
- Biochar variability: A lack of comparative data exists on how different biochar types (e.g., feedstock, application rate) affect treatment outcomes.
- Modified biochar efficacy: The potential of chemically modified biochars for multi-contaminant stormwater treatment remains underexplored.

1.5 Objectives of the study

To address the research gaps identified above, this study was designed with the following specific objectives:

- To understand the effect of biochar amendment on the hydraulic conductivity of engineered media.
- To evaluate the long-term performance of biochar amendment to fine-grained soils to treat stormwater runoff.
- To assess biochar modification for enhanced removal of different contaminants from stormwater runoff.

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2 OBJECTIVE 1: TO UNDERSTAND THE EFFECT OF BIOCHAR AMENDMENT ON THE HYDRAULIC CONDUCTIVITY OF ENGINEERED MEDIA. (FUNDED BY: NCDOT)

2.1 Introduction

Biochar is carbon-rich, highly porous organic material produced through the thermal processing of biomass under limited or no oxygen and can be amended with soil to potentially improve soil health and promote plant growth (Brantley et al., 2015; Hornung et al., 2024). Due to its multifunctional characteristics, biochar has the potential for engineered media application, which includes stormwater biofilters, landfill covers, water retention, and infiltration (Ulrich et al., 2015; Mohanty et al., 2018; Boehm et al., 2020). When mixed with soil, it can impact porosity, bulk density, and particle size distribution parameters that directly influence soil hydraulic properties. The functional performance of a biochar–soil mixture is primarily influenced by properties such as porosity, structural arrangement, carbon content, pH, and surface area. (Brewer et al., 2009; Ajayi and Horn, 2017; Faloye et al., 2020; Zhang et al., 2021). This affects the formation of intra- and inter-particle pores within the Biochar soil matrix, which mainly depends on biochar-soil particle size and the amount of compaction (Hardie et al. 2014). The porous nature of biochar results in improved soil structure, which results in enhanced total porosity and water retention capacity (Blanco-Canqui, 2017). A comprehensive review by Blanco-Canqui (2017) reported that biochar amendment typically reduces the bulk density of fine-grained soils by an average of 9.2%, while porosity tends to increase with increasing biochar dosage, with reported average improvements of up to 8.4%.

Biochar feedstock (e.g., softwood, hardwood, sewage sludge, etc.) and production conditions (temperature, oxygen, reactor type, heating time, and rate) govern the properties of biochar (Gaskin et al., 2008; Zimmerman, 2010; Meyer et al., 2011). Various physical properties of soil such as pore size distribution, porosity, soil density, soil moisture content, water holding capacity, carbon sequestration, nutrient retention, contaminant immobilization, and hydraulic conductivity can be improved by using biochar in the soil (Zwieten et al. 2012, Hardie et al. 2014, Nuruddin & Moghal 2024). K_{sat} is a soil hydraulic property used to evaluate soil drainage and water infiltration capacity (Yazdanpanah et al. 2016) and largely depends on soil structure (Zhou et al. 2019). One of the