NUTRIENT REMOVAL EFFICIENCIES IN A BIORETENTION CELL USING PRE-TREATED COCONUT BY-PRODUCT AS CARBON SOURCE

NUR DIANNA BINTI DINNO

UNIVERSITI SAINS MALAYSIA

2022

SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

NUTRIENT REMOVAL EFFICIENCIES IN A BIORETENTION CELL USING PRE-TREATED COCONUT BY-PRODUCT AS CARBON SOURCE

By

NUR DIANNA BINTI DINNO

Supervisor:

Prof. Hazizan Md. Akil

Co-Supervisor:

Dr Goh Hui Weng

Dissertation submitted in partial fulfilment of the requirements for the degree of

Bachelor of Engineering with Honours

(Materials Engineering)

Universiti Sains Malaysia

August 2022

DECLARATION

I hereby declare that I have conducted and completed the research work, as well as written the dissertation entitled “Nutrient Removal Efficiencies in a Bioretention Cell Using Pre-treated Coconut By-Product as Carbon Source”. I also hereby declare that it has not been previously submitted for the award of any degree or diploma, or other similar title with this for any other examining body or university.

Name of Student: Nur Dianna Binti Dinno Signature:

Date: 17 August 2022

Witnessed by: Signature:

Supervisor: Prof Hazizan Md Akil

Date: 17 August 2022

ACKNOWLEDGEMENT

Alhamdulillah, praise be to Allah SWT, the everlasting source of strength, for the chance to complete this final year project with good faith in Him, and gratification to all of the blessings received throughout the length of this study.

To my supervisors, Prof. Dr Hazizan Md Akil and Dr Goh Hui Weng, thank you for the constant guidance and guidance and motivations that she offered in ensuring that I could learn and grow professionally while under her supervision.

To Dean of School of Materials and Mineral Resources Engineering (SMMRE), thank you for the research facility provided as well as the good environment projected throughout the length of this project. With this, I would like to take this opportunity to thank Encik Rashid, Encik Khairi, Encik Azrul, Puan Haslina, Puan Hasnah from SMMRE as well as Encik Zack, Encik Sufian, and Encik Fitri from REDAC for the technical guidance and lessons given that helped a lot in giving exposure to the nature of the work.

Finally, to my friends, Aisyah, Atiqah, Ju Liyana, Emiellia, and all of my batch classmates, thank you for all the merriments that all of you have offered in making the tough times better, and for always being there with me to face the working challenges. I hope that wherever you find yourself in the future, nothing will ever diminish the vibrant soul that each and every one of you possess.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

$m^{-3}\ s^{-1}$	Discharge flow
mm	Milimeter
mg/L	Miligram per liter
t	Time
°C	Degree Celsius
g	Gram
ml	Mililiter
L	Liter
cm	Centimeter
cm^{-1}	Reciprocal Wavelength
m^2/kg	Square meter per kilogram

LIST OF ABBREVIATIONS

AN	Ammoniacal Nitrogen
BMP	Best Management Practices
BOD	Biological Oxygen Demand
C	Carbon
CHN elemental analyzer	Carbon Hydrogen Nitrogen elemental analyzer
COD	Chemical Oxygen Demand
DSEWPC	Department of Sustainability, Environment, Water, Population, and Communities
FTIR	Fourier Transform Infrared
GI	Green Infrastructure
HCT	Hydraulic Conductivity
KBr	Potassium Bromide
LID	Low Impact Development
MSMA	Manual Saliran Mesra Alam (Urban Storm Water Management)
N_2	Nitrogen gas
NaOH	Sodium Hydroxide
NH_4^+	Ammonium ion
NO_2^-	Nitrite
NO_3^-	Nitrate
O	Oxygen
P	Phosphorus
PO_4^{3-}	Phosphate ion
PSA	Particle Size Analyzer
PVC	Polyvinyl Chloride
RT	Room Temperature
SBTR	Sediment Basin Trash Rack

SEM	Scanning Electron Microscope
Si-OH	Silica Zeolite
SMMRE	School of Materials and Mineral Resources Engineering
SO_4^{2-}	Sulphate
TCH	Treated Coconut Husk
TCS	Treated Coconut Shell
TN	Total Nitrogen
TOC	Total Organic Carbon
TP	Total Phosphorus
TSS	Total Soluble Solid
UCH	Untreated Coconut Husk
UCS	Untreated Coconut Shell
UHI	Urban Heat Island
USEPA	United States Environmental Protection Agency
UV-Vis spectroscopy	Ultraviolet–visible spectroscopy

KECEKAPAN PENYINGKIRAN NUTRIEN DALAM SEL BIORETENSI MENGGUNAKAN PRODUK SAMPINGAN KELAPA YANG TELAH DIPRARAWAT SEBAGAI SUMBER KARBON

ABSTRAK

Dalam kajian ini, kesesuaian penggunaan prarawatan alkali terhadap keluaran sampingan kelapa telah dilaksanakan apabila sabut dan tempurung kelapa dirawat dengan 2M NaOH. Hasil daripada itu, sampel berbentuk serbuk telah dianalisis untuk pemerhatian morfologi, FTIR, PSA dan ujian kualiti air. Melalui pemerhatian morfologi, prarawatan alkali mampu untuk melemahkan struktur hemiselulosa tempurung kelapa. Sementara itu, analisis FTIR menunjukkan bahawa regangan O-H terdapat dalam kesemua sampel prarawatan, menandakan bahawa penurunan lignin telah berlaku, manakala kedua-dua sampel bahan tambah menunjukkan ketiadaan fungsi kumpulan C=O selepas melalui prarawat alkali. Seterusnya, semua sampel menghasilkan taburan saiz zarah yang lebih halus daripada piawaian, dengan nilai terkecil untuk D_{50} adalah TCS, diikuti oleh UCS, UCH dan TCH, masing-masing pada 0.341, 0.357, 0.450, dan 1.37 mm. Kemudian, D_{10} berada pada 0.0723, 0.0732, 0.151 dan 0.736 mm masing-masing untuk UCS, TCS, UCH dan TCH. Jika dibandingkan dengan saiz taburan menurut piawai yang dicadangkan oleh MSMA dan DSEWPC, hanya TCH yang dapat memenuhi kedua-dua julat keperluan yang disyorkan. Ini seterusnya membawa kepada penyingkiran TSS yang teruk, dimana nilai kepekatan TSS dalam efluen melebihi nilai Inlet, menandakan bahawa media penapisan yang digunakan menyumbang kepada pencemaran TSS. Tambahan pula, setiap sampel menunjukkan kepekatan TP yang tinggi dan tidak teratur, bermakna bahawa semua sampel dapat membekalkan ion fosfat (PO_4^{-3}) kepada sistem bioretensi. Hal ini penting kerana ia merupakan antara nutrien utama untuk pertumbuhan pokok. Sebaliknya, pengesanan kepekatan AN yang sangat rendah diperhatikan sepanjang tempoh ujian dengan nilai yang

kurang daripada 4 mg/L, berbanding dengan sampel Inlet yang merekod kepekatan AN tinggi dalam julat 5.2 hingga 11.4 mg/L.

NUTRIENT REMOVAL EFFICIENCIES IN A BIORETENTION CELL USING PRE-TREATED COCONUT BY-PRODUCT AS CARBON SOURCE

ABSTRACT

In this study, the suitability of alkali pre-treatment on coconut by-products were done by subjecting coconut husk and shell to 2M NaOH. The powdered samples were analyzed for morphology observation, FTIR, PSA and water quality test. The morphology observation showed that subjecting the coconut shell to alkali pre-treatment was able to weaken the hemicellulose structure. Meanwhile, the FTIR analysis showed that O-H stretch were present in all pre-treated samples act as indication that lignin breakdown has taken place, while both additive samples showed an absence of C=O functional group after being subjected to alkali pre-treatment. For particle size analysis, all samples resulted in finer than standard particle size distribution, with the smallest value for D_{50} was that of TCS, followed by UCS, UCH and TCH at 0.341, 0.357, 0.450, and 1.37 mm respectively. Then, the D_{10} were found to be at 0.0723, 0.0732, 0.151 and 0.736 mm for UCS, TCS, UCH and TCH respectively. When compared to the suggested recommendation by MSMA and DSEWPC, only TCH were able to fulfill both of the recommended and typical requirement ranges. This in turn, caused poor TSS removal, whereby the TSS concentration exceeded the Inlet value, signifying that the filtering media contributed to the TSS contamination. Furthermore, all sample types showed an irregular and high concentration of TP. This is important as it indicates that all samples were able to provide phosphate ion (PO_4^{-3}) to the bioretention system, which is an important nutrient for the growth of plants. In contrast, significantly low detection of AN concentration was observed throughout the test period with values less than 4 mg/L as compared to the high AN concentration of the Inlet samples within the range 5.2 to 11.4 mg/L.

CHAPTER 1

INTRODUCTION

1.1 Highlight of Study

In a fast-developing cities, the urban design incorporated impervious surfaces in their buildings, pavements, roadways, rooftops, parking lots, and other facilities. These developments have removed vegetations and water storage depressions that would help to uptake runoffs or provide a storage basin respectively. The effect of urban development to the water quality is increasing the pollutants in the stormwater runoffs, due to the components used in the building material.

Not only that, the reduction of vegetations such as trees, tall grasses and bushes has also resulted in lesser natural filtration of stormwater (Davis, 2005). Furthermore, the urban management would usually focus on directing the stormwater runoffs away from public area immediately, not allowing pooling to happen. However, this affects the water quality due to the accumulation of pollutants in the water body, as well as causing stream erosion to happen more commonly.

1.1.1 General Introduction to Bioretention

Bioretention is a type of Best Management Practices (BMPs) and Low Impact Development (LID) that is being utilized for the treatment of stormwater runoff. It is also known as the raingarden, and is usually identified as a shallow depression in the landscape with presence of vegetations (LeFevre *et al.*, 2015). The system functions by incorporating processes such as adsorption, sedimentation, ion exchange, phytoremediation, decomposition, and filtration in order to carry out its purposes. Accordingly, the system's main purposes are to remove surface and groundwater pollutants, reduce peak flow and maintain the groundwater recharge, as well as to provide channel protection (Davis *et al.*, 2009).

Since its initial development, there have been several kinds of bioretention system that were utilized, such as parking lot and highway median, swale-side bioretention, and the landscaped garden (The Prince George's Country, 2009). In general, the bioretention system consisted of filtering media with mulch layer on top, vegetations, underdrain system, gravel layer, inlet and outlet for stormwater runoffs to flow into and out of the system respectively (LeFevre *et al.*, 2015).

As shown in Figure 1.1, the runoff influent will enter the system through the inlet, where it will be pooled at 15-30 cm from the surface of the system. Then, it will infiltrate into typically 0.7-1.0 m of the filtering media, before being collected by the underdrains (Davis et al., 2009).

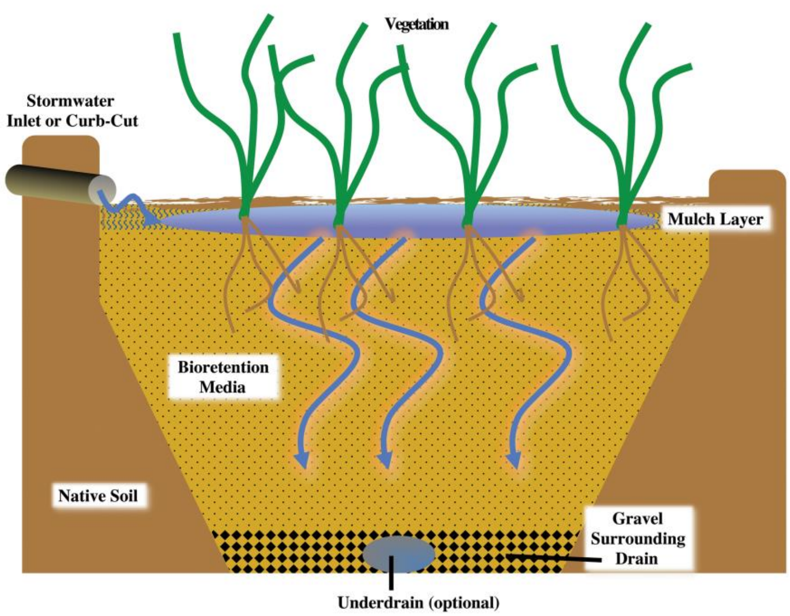

Figure 1.1 Diagram of a typical bioretention system (Retrieved from LeFevre et al., 2015).

Bioretention has been known to effectively reduce the concentration of nutrients such as Total Nitrogen (TN), Total Phosphorus (TP), Total Soluble Solid (TSS), Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), ammonium (NH_4^+), nitrate (NO_3^-) and nitrite (NO_2^-) from the stormwater runoffs (Read *et al.*, 2008a; LeFevre *et al.*, 2015). Not only that, the presence of vegetations in the bioretention system was reported to improve the removal of nitrogen and phosphorus as it served as nutrients for plant growth (Dagenais, Brisson and Fletcher, 2018).

1.1.2 Previous Studies using additives in filtering media

In a bioretention system, the filtering media plays an important role in removing nutrients and fine particulate pollutants. This system uses two filtration methods; biofiltration from the incorporation of vegetations, and media filtration by the application of porous media (MSMA, 2012). According to the Urban Storm Water Management or *Manual Saliran Mesra Alam* (MSMA), a guideline for stormwater management as set by the Government of Malaysia, the engineered soil suitable to be used as planting bed in this country should be loamy sand that have about 10-25% of clay content. Other type of media such as sand, topsoil, and compost have the suggested compositions as shown in Table 1.1.

Table 1.1 Suggested Engineered Soil Composition (Retrieved from MSMA, 2012).

Soil Mixture	*Contents by Volume (%)*
Topsoil	20-25
Medium Sand	50-60
Compost	12-20

However, in recent years, the stormwater runoffs have become heavily polluted due to the increasing human activity, especially from vehicle combustions, agricultural and industrial activities. For instance, poorly managed fecal matter from pets and wildlife animals were found to end up in stormwater runoffs, which usually contains high amount of nitrogen and carbon (McCabe *et al.*, 2021). Hence, improving the MSMA suggested soil composition with the incorporation of carbon source as additives such as pine bark (Tuo *et al.*, 2021), fly ash (Zhang *et al.*, 2008), corn cob, rice straw and rice husk (Tao *et al.*, 2021), and sawdust (Hu *et al.*, 2019), it was found that the additives were able to effectively remove NH_4^+, TN, NO_3^-, NO_4^-, and COD.

1.2 Problem Statement and Objectives

As previously stated, the urban areas in Malaysia are seeing a rapid development in its population along with its economic and industrial growth. Along with this advancement, the quality and quantity of the stormwater runoffs are getting worse. For instance, the high percentage of nutrient concentration in the stormwater may be caused by the escalation of human daily activities in urban areas such as more people using vehicles to commute, more urban agriculture activities, as well as poor municipal drainage system in urban housing areas.

Meanwhile, the increased in the quantity of stormwater is caused by the incorporation of impervious surfaces in most city designs as well as low amount of vegetation in urban landscaping. Eventually, these factors will lead to the deterioration of stormwater quality dues to polluted stormwater and occurrence of eutrophication in the water body. Meanwhile, the increase in stormwater quantity will lead to flash flood events in urban areas.

Hence, the bioretention system, as one of the BMP and LID proposed by MSMA initially in 2001, is a suitable method for urban stormwater management. However, due to the current deteriorating quality of the stormwater runoffs, several improvements to the initially suggested filtering media should be made in order to properly address the problem on hand. The recurring issue relating to the performance of a bioretention system mostly concerns the removal of the nitrogen species. Usually, its removal is assisted by the uptake of vegetations and conversion to nitrogen gas (N_2) by microbial activities.

Despite that, the microbial activities are limited to the availability of carbon sources in the media, which provided glucose for the microorganism to complete the nitrogen cycle. Due to the heavily polluted stormwater runoffs being loaded into the bioretention system, the initial count of carbon source in the media might be insufficient to sustain the microbial activities, which will result in relatively poor reduction in nitrogen concentration of the effluent.

Hence, incorporating additives into the filtering media composition would help to provide the necessary amount of carbon sources for the continuation of the microbial activities. Since design cost will be an issue especially for a large-scale bioretention system, additives derived from agricultural waste is preferable. Therefore, the objectives of this project were as the following:

1. The investigate the suitability of coconut by-products such as its shell and husk to be used as additives in a bioretention filtering media were investigated.
2. To evaluate the role of pre-treatment processes in improving the release of carbon sources from the additives.

1.3 Scope of Work

In this project, all experiments were done within the Universiti Sains Malaysia Engineering Campus vicinity. Chemicals used in pre-treatment of the biomass additives were prepared at the Chemical Laboratory in School of Materials and Mineral Resources Engineering (SMMRE), while the experiment itself was conducted at REDAC's Environmental Laboratory 3, and the column setup and sampling were done at REDAC's workshop.

Figure 1.2 Showing the mini column setup for the water test.

1.3.1 Experimental Procedures

The coconut shells were first subjected to physical pre-treatment in order to reduce its surface area, before it was chemically treated with sodium hydroxide (NaOH). Then, the samples were added into the filtering media composition, and was used to fill up the polyvinyl chloride (PVC) column prepared for the water test. Afterwards, the prepared columns were used to treat USM's sewage water that was collected from the university's oxidation sewer. The collected influent was dosed into the column intermittently in every three hours, where each dosing added 200 ml of influent into the column, totalling up to 1 L per column. The influent was then left to pond for 24 hours. Finally, the effluent samples were collected and tested for several parameters.

1.3.2 Sample Testing

The effluent collected were tested to detect the concentration of AN, TSS, and TP, whereby all the reagents were prepared by REDAC, and the test were done in Environmental Lab 3. Meanwhile, the additive samples were sent to SMMRE for FTIR to learn of its chemical compositions, particle analyzer for its particle size distribution, and was also observed under the Tabletop SEM in order to understand the effect of chemical pre-treatment onto the surface morphology of the additive samples.

1.4 Significance of Study

The findings from this investigation will provide useful information on the suitability of coconut by-product such as its husk and shell to be used as additives in a bioretention filtering media. Not only that, this project also provided information on the effect of alkali pre-treatment on the coconut by-product's performance as filtering media additives, which will provide information on its credibility to release the carbon source from the additives' biomass structure. With this, the information obtained is suitable for future project developments that focus on the treatment of heavily polluted stormwater runoffs.

1.5 Structure of Dissertation

In Chapter 1, brief explanation on the bioretention concept was explained, along with the overview of the research topic. Then, the problem statement and objectives of the research was established and explained. This chapter also provided the highlight on the scope of work done throughout the research period, and the significance of study was also explained.

In Chapter 2, the related topics concerning the subject, such as basic concept and types of the bioretention system available, other parameters that also contributed to the removal of pollutant from the water body were thoroughly discussed. Then, similar studies on the use of plant biomass to provide carbon source to a bioretention system were also analyzed and discussed.

In Chapter 3, the procedures used to carry out the experiment were chronologically laid out. This includes the pre-treatment of the coconut by-product, the mini column setup, the water quality test, as well as the sample preparation for FTIR, morphology by Tabletop SEM, and particle analyzer.

In Chapter 4, the results obtained from all tests conducted such as the water quality test, FTIR, SEM morphology, particle size analyzer were discussed thoroughly, and correlation were made in order to achieve the objectives of the study.

In Chapter 5, all chapters were concluded accordingly, and the achievement of each objective were evaluated. Then, reflections and suggestions on the project were also summarized by the end of this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 The Concept of Bioretention

As a part of the BMP for stormwater management, bioretention system incorporated the use of vegetation and engineered soil media to treat the polluted stormwater runoffs. The system is suitable to be installed in urban cities to help address issues such as flash flood and water shortages, as the system is essentially a depression in the landscape that would allow runoffs to pond on its surface for a designated period. The system also consisted of storage layer and an underdrain system (Jiang *et al.*, 2019).

There are several factors that must be considered before choosing a development site, such as the site conditions, soil type and moisture condition, plant species suitable to be used at the site, suitable drainage condition, and other hydrological factors as well. Although the bioretention system's main purpose is to treat stormwater runoffs, it also functions as a rain garden, which adds diversity to the landscaping design, which was helps to give good community impression as well as add to the environmental benefits (The Prince George's Country, 2009).

In essence, a bioretention site will carry out runoff infiltration and filtration, as well as allowing assisted water uptake and storage due to the presence of vegetation. Through the system's soil media, runoffs will fill up the pore space until the system is pooled to the surface. Afterwards, pooled water will infiltrate into the soil or underdrain, after a certain period of time has passed.

2.1.1 Problems related to urban cities development

Upon the rapid growth of urban cities, it carries along several issues that resulted consequently to the uncontrolled development activities and climate change has caused re-occurring natural disasters such as temperature extreme and flash flood. Major events of flash floods displace many families from their homes, destroying properties and assets, as well as taking lives. In a recent study by Wang, Yu and Cao in 2022, the effects of urban developments, such as the construction of impermeable surfaces and high density of buildings in close vicinity eventually leads to the effect of heavy rainfall.

To further explain, the impermeable surfaces, lack of vegetations and human activities caused these areas to experience urban heat island (UHI) effect, which is a phenomenon on the accumulation of heat (Yang *et al.*, 2016). Several efforts were proposed to control the issue, such as introducing Low Impact Development (LID) and green infrastructure (GI) practices. For example, China's Sponge City projects were developed since 2014, which were expected to control the country's smaller and more frequent runoff events (Jia *et al.*, 2017). LIDs usually require low-cost maintenance in order to ensure the facilities could deliver its peak performance. However, events such as disastrous flash flood that might only happen 10 to 100 years will require high development and maintenance cost to construct (Yang *et al.*, 2016). Accordingly, selection criteria for the LID projects must consider the local climate, especially its hydrograph and rainfall pattern, as well as its socio-economy factors. Other site suitability factors to consider such as the local conditions, soil and groundwater characteristics, space and catchment properties, as well as the site topography (Jia *et al.*, 2013).

It must be noted that the pollutants concentration in the runoffs are characteristic to the site, which will burden construction of the LID projects if manuals with detailed information on the necessary ecological and environmental data is unavailable prior to development.

2.1.2 Effect of stormwater in urban cities

The development of urban cities brings upon impervious surfaces from the constructions of roads, roofs, buildings, and pavements. Due to this, urban cities are becoming more vulnerable to flash flooding events due to increasing number of runoff volumes that are unable to infiltrate into the ground (Shafique, 2016). Furthermore, the impervious surfaces will cause lesser recession time due to quicker runoff flow (Fletcher, Andrieu and Hamel, 2013).

As shown in Figure 2.1, the general storm hydrograph showed that in every rainfall event, the discharge flow (in m^{-3} s^{-1}) will increase from point A to point B, achieving peak discharge that leads to direct runoff in time immediately after the rainfall event. With more impervious surfaces in the city design, quicker runoff flow will result in lesser time needed to achieve normal discharge at point D. With less impervious surfaces, the quick runoff flow, as well as no available storage for water retention, the discharge will overflow and causes flash flood to occur.

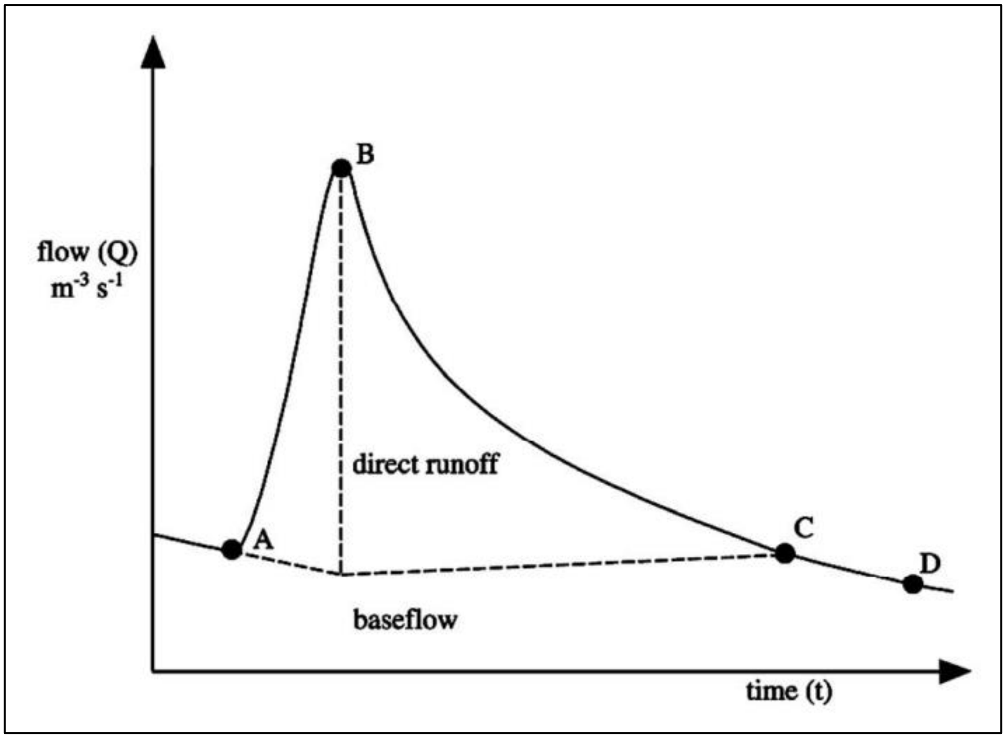

Figure 2.1 General storm hydrograph form (Retrieved from Pizarro-Tapia et al., 2013; Chow et al., 1988).

According to a review by Osman et al., in 2019, stormwater management includes quantity and quality control, whereby, quantitative control is focused to avoid flash flood events. Meanwhile, the quality control is primarily to obtain clean water. The team also reported that the reduction targets for common pollutants in stormwater such as TSS, TN and TP were classified into low, medium and high, as shown in Table 2.1. This classification enables evaluations to be made for quality control.

Table 2.1 The classification of reduction targets for common pollutants in stormwater runoffs (Retrieved from Osman et al., 2019).

Pollutant	***Low***	***Medium***	***High***
TSS	Less than 40% of particulates greater than 0.125 mm retained	40-70% of particulates greater than 0.125 mm retained	>70% of particulates greater than 0.125 mm retained
TN and TP	< 10% reduction	10-40% reduction	>40% reduction

2.2 Critical Processes in a Bioretention System

To further understand on the functions of the bioretention system, the Department of Environmental Resources of The Prince George's County, in their Bioretention Manual summarized that the system is governed by several processes, as shown in Table 2.2.

Table 2.2 Showing the selected major processes taking place in a bioretention system and its functions (Retrieved from (The Prince George's Country, 2009)

Process	***Function***
Infiltration	Downward flow of runoff through the system's soil media, into the in-situ soil.
Interception	The runoff capture by vegetation or soil media.
Settling and Filtration	The separation of particles and suspended solid from the runoff as it passes through the bioretention's surface.
Absorption	Absorption of water into soil by the available vegetation and fungi community.

Evapotranspiration	Loss of water due to evaporation and transpiration.
Assimilation	Pollutants and nutrients uptake from runoff and into plants, and to be used in plant growth.
Adsorption	Attachment of dissolved substance onto a solid surface due to ionic bonding. For example, presence of humus in the soil media will encourage the adsorption of metal and nitrates.
Nitrification	The oxidization of ammonia species into nitrate that is beneficial to plants.
Denitrification	Reduction of nitrate (NO_3) into nitrous oxide (N_2O) and nitrogen gas (N_2) by microorganisms, due to anaerobic condition in the system.

2.3 Selected Nutrient Cycle

Nutrients such as nitrogen and phosphorus coming from fertilizers and biological waste may pollute the stormwater runoff and bring harm to the aquatic life, as well as altering the soil properties. In stormwater runoffs, it was found that it accumulated the highest amount of nitrogen, which may be received from agricultural activities, as well as vehicle emissions (Collins et al., 2010; Osman et al., 2019).

For nitrogen species, the presence of vegetations helped to reduce its concentration in the runoffs, as plants adsorb nitrogen for their growth. However, the nitrogen species tend to leach into the groundwater due to its volatile nature, causing it to easily leach into the groundwater, as it is easily volatized.

Phosphorus on the other hand, is not heavily dependent on plant for its removal from the runoffs but is influenced by percolation through the filtering media (Read *et al.*, 2008). As an addition, the team also speculated that the high nitrogen level in their effluent may be caused by soil leaching that was resulted from high level of nitrogen mineralization in the media, or through increased nitrification.

2.3.1 Nitrogen Cycle

The removal of nitrogen from the ecosystem could be through nitrogen fixation, plant uptake, or even through volatilization. Nitrogen fixation, such as nitrification, converts the nitrogen gas (N_2) from the environment into ammonium ions (NH_4^+) through the decomposition of biomass. The NH_4^+ will then become oxidized into nitrite (NO_2^-), then into nitrate (NO_3^-), which is very soluble and is consumed by vegetations (The Prince George's Country, 2009). The chemical reactions involved in a nitrification process were as follows:

$$2NH_4^+ + 3O_2^- \longrightarrow 2NO_2^- + 2H_2O + 4H^+$$

$$2NO_2^- + O_2 \longrightarrow 2NO_3^-$$

Due to its high solubility, nitrogen takes longer to be removed as compared to other pollutant species, as it exhibited a more complicated biogeochemical process. Nevertheless, it was discovered that its removal was heavily influenced by biological and physical processes, as well as chemical reactions (Osman *et al.*, 2019). Other factors that also contributes to nitrogen removal are the presence of vegetation, the filtering media, hydraulic factor, and the concentration of influent. Meanwhile, denitrification process allows the conversion of the highly soluble nitrate ion into the stable nitrogen gas (N_2) through anaerobic respiration.

$$NO_3^- \longrightarrow NO_2^- \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2$$

$$6CH_2O + 4NO_3^- \longrightarrow 6CO_2 + 2N_2 + 6H_2O$$

2.4 Design Requirements for a Bioretention System

In designing a bioretention system, several design issues associated with the application such as the design objectives (concerning hydrological issues and pollution removals), BMP location guidelines, pre-treatment requirements, treatment processes, surface area sizing, filtering media composition, ponding depth, overflow and underdrain designs, vegetation species selection, problems concerning time of concentration, fate of the accumulated pollutants, and finally the service life maintenance (Davis *et al.*, 2009).

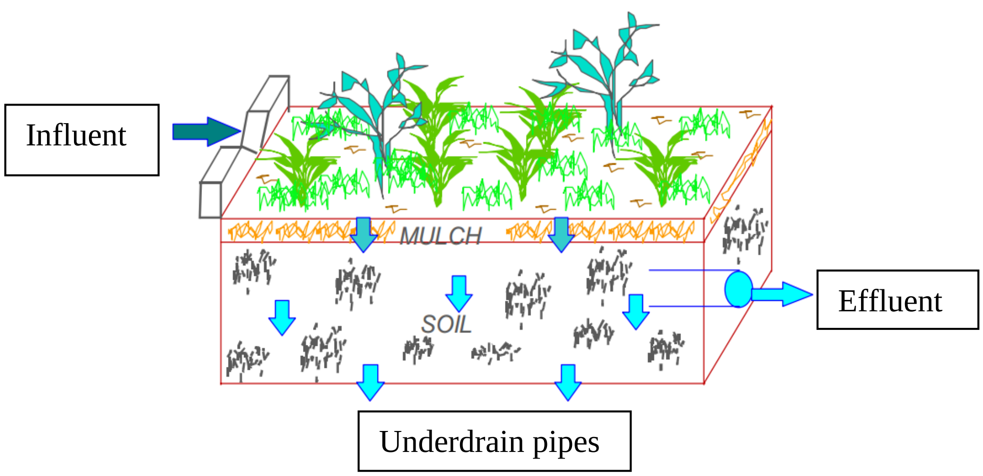

Figure 2.2 Diagram showing the bioretention system (Retrieved from Davis *et al.*, 2009).

2.4.1 Site Criteria

Before designing a bioretention system, the properties of the selected site must be studied so that design issues related to the site could be addressed properly. Some of the criteria to be considered are soil properties, building foundations, underdrains, drainages, groundwater, minimum depth criteria, wooded areas, hydrologic data, as well as the slope and grades of the site (The Prince George's Country, 2009).

2.4.2 Pollutant Removal Capabilities of a Bioretention System

As mentioned previously, the pollutant removal in a bioretention system were governed by several processes such as adsorption, infiltration, and evapotranspiration. Due to this processes, concentration of pollutants such as TSS, TN, TP and heavy metals were successfully reduced. The Table 2.3 below shows the general removal performance of a bioretention system, as provided in MSMA.

Table 2.3 Showing the typical pollutant removal efficiency of an infiltration system (Retrieved from MSMA, 2012).

Pollutant	*Expected Removal (%)*
Litter	>90
TSS	65-99
TN	50-70
TP	40-80
Heavy metals	50-95

2.4.3 Types of Bioretention System

Over the years, there have been several types of bioretention system built on commercial or residential grounds, such as parking lot, highway median, swale-side, and landscaped garden.

Figure 2.3 Showing the bioretention facility installed at a parking lot (Retrieved from Davis et al., 2009).

Figure 2.4 Showing the bioretention landscaped garden (Retrieved from The Prince George's Country, 2009).

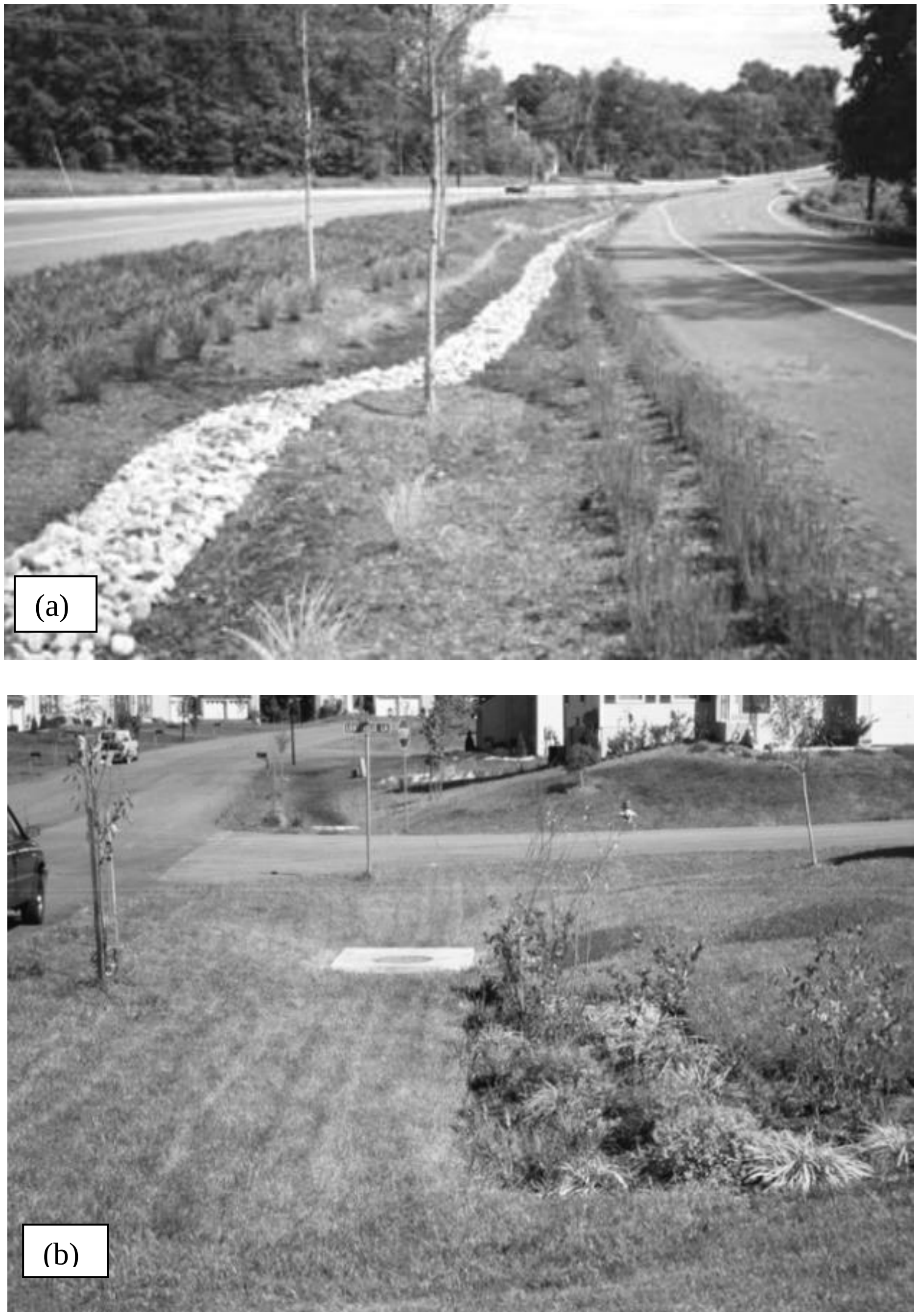

Figure 2.5 (a) Highway median bioretention, and (b) Swale-side bioretention system (Retrieved from The Prince George's Country, 2009).

There was also a dual mode bioretention system that was designed to treat both stormwater and greywater, where it alternates following a seasonal change. Greywaters are wastewater coming from shower, sink, and washing machines. According to Barron et al. in

2020, their dual mode bioretention system received stormwater during rainy seasons, and alternate to greywater during dry seasons. With the help of the selected plant varieties, the team found that the dual-mode system was able to successfully remove pollutants such as phosphorus, nitrogen, heavy metals, and sediments from both water bodies. The researchers also mentioned that for pollutants such as Total Soluble Solid (TSS), Total Organic Carbon (TOC), Biochemical Oxygen Demand (BOD), and heavy metals are more influenced by the filtering media used, even when there is no inclusion of vegetations.

2.5 Importance of a Bioretention System

Over the years, the bioretention system developed has shown its capabilities to reduce the concentration of pollutants in stormwater runoffs. The effluent from the system has improved water quality, especially for nutrients such as TN, TP, TSS, and heavy metals. Other than that, the system also served to provide evaporation and cooling of the UHI effect (Jamei and Tapper, 2018).

Furthermore, the bioretention site could produce reliable performance even after it has achieved maturity (of more than 3 years post-construction). In a study by Spraakman and Drake in 2021, a matured bioretention system located in Southern Ontario, Canada was investigated for its performance by analyzing several properties such as the water retention of soil at different tension, soil porosity and its size distribution, as well as the hydraulic conductivity (HCT) of the site. It was found that after 7-10 years of service under cold climate, only about half of the 22 sites tested required minor maintenance to clear the sedimented inlet (which could be done by removing the top 10 cm of sediments close to the inlet), while only two sites required major maintenance, but it was caused by design flaw, while the rest only required the routine maintenance it was already receiving.

The researchers also found that the presence microbes and insects in the soil, as well as the roots from vegetations helped to regulate the hydrologic capacity of the system (Six *et al.*, 2004), allowing it to maintain peak performance, even after years of service. Not only that, it was also found that the effluent quality improved to becoming more stable after the maturity period (Spraakman *et al.*, 2020).

2.6 Agricultural by-product as low-cost carbon source alternatives

In order to provide the extra carbon source, low-cost alternatives such as agricultural wastes could be incorporated into the bioretention system. Agricultural wastes such as corncob, pine bark, coconut husk, and rice husk contain lignocellulosic materials that when decomposed by microorganisms' activity, will release carbohydrates, which will provide the necessary carbon source to assist the nitrification process (Tuo *et al.*, 2021). Initially, carbon source was provided by the addition of ethanol into the system. The ethanol, which will be used by the nitrifying bacteria, will create an aerobic system, allowing for complete nitrification process to take place (Abdul Aziz, 2019), thus enhancing the removal of nitrogen species from the polluted stormwater.

Although the agricultural waste could be a good alternative, it is difficult to degrade its lignocellulosic structure in order to release its carbon. But subjecting the biomass to chemical pre-treatments will help to alter its construct, allowing for control to the release of carbon. The denitrification rate of woody biomass was found to be strongly influenced by temperature, followed by pH, then the degree of the pre-treatment used (Hu *et al.*, 2019), as well as the dissolved oxygen (DO) concentration.

With this, it was reported that increasing the temperature while reducing the pH value of the system was the optimum environment to achieve improved denitrification rate. In a study by Warneke et al. in 2011 on different carbon substrates used for nitrate removal, it was found that the DO concentration at the inlet decreased due to the presence of denitrifying bacteria activity that causes the inlet to be in anaerobic. The team also found that at higher service temperature, the system showed higher NO_3-N removal rate as compared to systems treated in cold incubation. This was due to the higher replication of nitrite reductase genes at higher temperature, that are responsible in the breaking down of NO_3-N. However, the temperature dependency of the denitrification rate was also found to be influenced by the species of woody biomass used.

As for the degree of pre-treatment, different degrees will subject different levels of damage to the biomass structure, thus influencing the carbon release rate and pattern (Tuo *et al.*, 2021). Usually, the biomass will experience physical degradation through mechanical method such as grinding and cutting prior to chemical treatment. The performance of carbon release will be measured by the Chemical Oxygen Demand (COD) concentration in the leachate produced after the pre-treatment (Tuo *et al.*, 2021). The increase in COD concentration will provide the necessary carbon source needed for denitrification process.

2.7 The breaking down of the lignocellulosic mass

Lignocellulose is composed of mostly cellulose and hemicellulose, followed by lignin, and a small portion of other groups such as proteins and pectins, terpenes, tannins, and acetyl groups, which are distributed throughout the plant structure (Liao *et al.*, 2020). For this case, the cellulose will provide the most carbon source as its structure consisted of polysaccharides that will be broken down and used by the nitrifying bacteria.

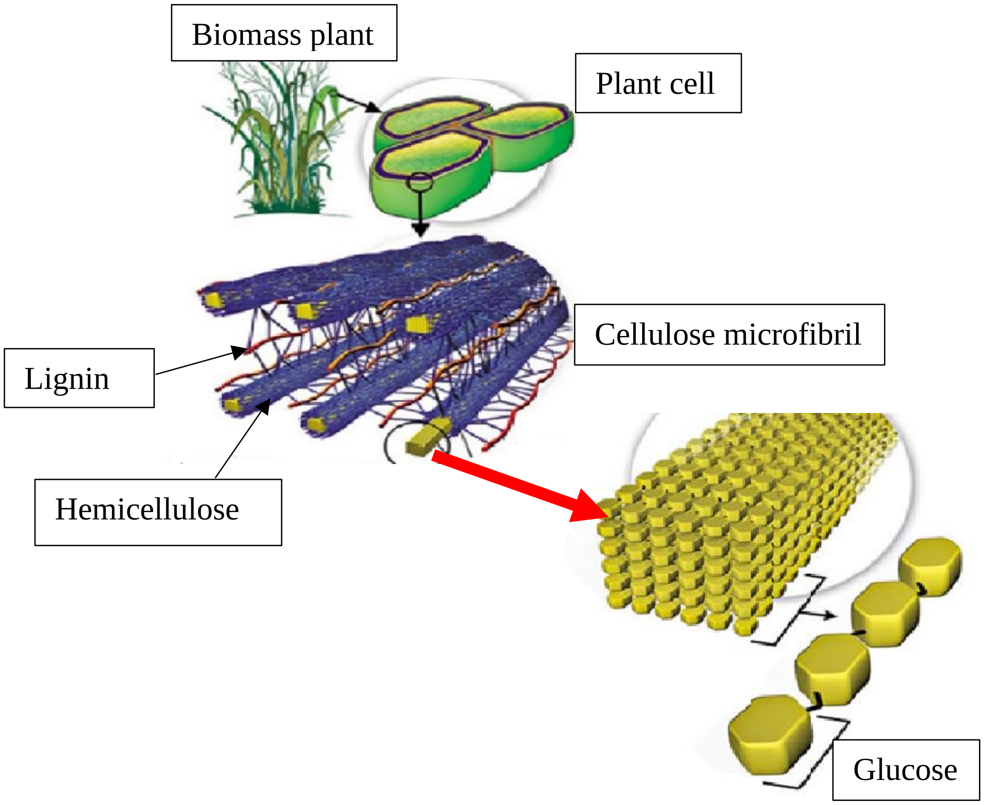

Figure 2.6 Showing the lignocellulosic composition of a plant (Retrieved from Ritter, 2008).

According to Jnawali et al. in 2018, NaOH pre-treatment has been used to treat lignocellulosic biomass to extract the xylan, which is a part of the plant's cell wall. The treatment will cause the biomass to increase its surface area due to swelling, as well as disrupting the lignin structure by reduce the degree of polymerization and separating the lignin from the carbohydrates. Increasing the concentration of NaOH used to treat the biomass will cause more lignin structure to be disrupted, allowing better extraction of the xylan cell.

The team then analyzed the treated coconut husk through FTIR, and found that the xylan cell resides within the wavelength of H-OH, and C-H stretching with strong bonds.

The wavelengths found within this band will mark the presence of xylan cell, indicating that NaOH treatment has taken place. Meanwhile, the detection of lignin in the spectrum will suggest the incomplete digestion of the coconut husk, all of which will be helpful for the FTIR analysis for this project.

2.8 Presence of carbon source in biomass

A study was done in 2018 by Wang and Sarkar, on the pyrolysis behavior of the coconut shell and husk by subjecting the biomass to air drying and physical crushing. The analysis on the biomass composition were done using a CHN analyzer with focus on analysing its cellulose, lignin, and hemicellulose content. It was found that the coconut shell contained the most cellulose, while the husk has more lignin in its structure.

After the breaking down process, the researcher found that the lignocellulosic content of the biomass started to degrade when it was subjected to temperature of 230°C to 400°C, with a major weight loss due to the degradation process. It was also stated that the degradation happens by having the polymeric chains in the biomass broken down, forming CO, CO_2, and other carbonaceous matters. Not only that, but the degradation of lignin also took place at temperature above 400°C and produces high char yield. This indicates that the lignin of a woody is more difficult to decompose than the other cellulosic components.