CONSTRUCTED WETLAND FOR WASTEWATER TREATMENT

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CONSTRUCTED WETLAND FOR WASTEWATER TREATMENT

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**A project report submitted in partial fulfilment of the
requirements for the award of Bachelor of Chemical
Engineering with Honours**

**Lee Kong Chian Faculty of Engineering and Science
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April 2024

DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

I certify that this project report entitled **"CONSTRUCTED WETLAND FOR WASTEWATER TREATMENT"** was prepared by **LIM CHU YAN** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Chemical Engineering with Honours at Universiti Tunku Abdul Rahman.

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ACKNOWLEDGEMENTS

Upon the effective culmination of this endeavour, I wish to extend my gratitude to all individuals who actively participated. I wish to extend my sincere appreciation to Dr. Ong Ying Hui, my research supervisor, for her immeasurable fortitude, insight, and counsel during the course of this investigation.

Furthermore, I would like to extend my sincere appreciation to my supportive parents and close friends who have assisted and motivated me since the inception of this research endeavour. Without their assistance and support, I would not have undergone the challenges that I encountered during my research.

Lastly, I also appreciated the assistance and guidance by the staff from Department of Laboratory Management and Safety Administration, Encik Muhammad Izhar Bin Mohamad Pauzi and Encik Mohd Hanis Bin Nazli. Their advice and assistances on carpentry are helpful in the experiment.

ABSTRACT

The issue of water pollution in Malaysia is getting serious due to urbanization and outdated traditional WWTP and become a great concern of Malaysians. Traditional WWTPs in Malaysia are inefficient at removing interested pollutants such as ammoniacal nitrogen and chemical oxygen demand (COD) since sewage discharge regulations were only enforced after 2009 and are only relevant to new plants built after that year. The study on vertical flow constructed wetlands (VF CW) was conducted to investigate the impact of plant types, substrate types and operation modes on COD removal efficiency. In this research, a total of 5 sets of CW prototypes were built to study the aforementioned interesting parameters: Control, Set A, Set B, Set C and Set D. The duration of the experiment is 21 days and analytical tests were conducted weekly for three weeks. During the experiment period, the prototypes were watered by synthetic wastewater. The plants that were studied in this experiment are vetiver grass (*Chrysopogon zizanioides*) and spider plants (*Chlorophytum comosum*), while the substrate types are activated carbon and zeolite. After the experiment, which lasted 21 days, it was concluded that the Set D prototype, which was planted with spider plants and used activated carbon as substrate, had the best performance in COD removal among other prototypes. The average COD removal efficiency of Set D is 77.05 %, with a standard deviation of 13.25 %. Interesting findings were found regarding short contact time but significant COD removal in continuous mode for operation modes. The performance of Set D can also be assessed by nitrogen removal. The nitrification and denitrification efficiency of Set D range from 19.09-126.75 % and 20.83-91.23%, respectively. The outstanding nitrification and denitrification performance of Set D indicates the high potential of CW in COD and nitrogen removal. In short, it is recommended that CW be introduced in conventional WWTP to improve pollutant removal due to its effectiveness and sustainability.

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LIST OF SYMBOLS / ABBREVIATIONS

K_{OW}	Octanol-Water Partition Coefficient
Θ_{10}	Ratio Of The Time For 10 % Of The Tracer To Leave The Wetland
λt	Actual Mean Hydraulic Retention Time, s
λp	Time For The Tracer To Reach The Peak Of RTD Curve, s
DOE	Department of Environment
NQWS	National Quality Water Standards
WQI	Water Quality Index
EQA	Environmental Quality Act
BOD	Biochemical Oxygen Demand
AN	Ammoniacal Nitrogen
SS	Suspended Solid
STP	Sewage Treatment Plant
CW	Constructed Wetland
DO	Dissolved Oxygen
PPCP	Pharmaceuticals and Personal Care Product
WWTP	Wastewater Treatment Plants
HLR	Hydraulic Loading Rate
HRT	Hydraulic Retention Time
ASV	Amplicon Sequences Variant
TSS	Total Suspended Solid
TN	Total Nitrogen
COD	Chemical Oxygen Demand
TP	Total Phosphates
ARG	Antibiotic Resistance Genes
OTC	Oxytetracycline
SMZ	Sulfamethoxazole
MP	Microplastic
LCW	Living Constructed Wetland
NW	Natural Wetland
GHG	Greenhouse Gas

LCA	Life Cycle Assessment
UPW	Ultra-Purified Water

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CHAPTER 1

INTRODUCTION

1.1 Water Pollution in Malaysia

In the context of water pollution, surface water pollution, groundwater pollution and marine pollution are severe global issues. This may be due to the global population growth as more populations dynamize the development of the nation in terms of infrastructure, industry and energy, which brings impacts to the environment. Despite the current deceleration in population growth, the global population is anticipated to surpass 9.7 billion by the year 2050 and 10.4 billion by the year 2080, according to estimates (Zarocostas, 2022). The rising demand for fresh water threatens millions of lives worldwide, leading to the vital issue of the water crisis. By 2020, there will be 2 million residents in this world who live without a safe drinking water supply system (United Nations, 2022). The water shortage not only affects the drinking water supply but also has an impact on manufacturing and agriculture. The social economy of the Central Asia country, which is an agricultural product exporter, is affected by the issue of water shortage (Wang, et al., 2022). Thus, a sufficient and stable freshwater supply becomes a challenging issue facing by many regions like Iran, Bali at, Indonesia, North China Region (NCR), which is a crops base and highly resided area, and Monterrey, a metropolitan with 5.4 million residents (Sisto, et al., 2016; Cole, Wardana and Dharmiasih, 2021; Barati, Pour and Sardooei, 2023; Zhou, et al., 2023).

Fortunately, Malaysia does not have serious water crisis issues like other regions. As a tropical country, Malaysia is hot and humid for the whole year, with varied precipitation of 1700 mm to 5800 mm, depending on the location (Malaysian Meteorological Department, 2020). This is due to the reason of Malaysia’s climate is different across the country as different topography like highland, lowland and coastal are found in Malaysia (World Bank Group and Asian Development Bank, 2021). In addition to this, Malaysia has two monsoon seasons each year, namely the Northeast Monsoon, which spans October to March, and the Southwest Monsoon, which occurs from April to September. Most of the precipitation is brought by the Northeast

Monsoon. However, the rapid development of the country and population growth have increased the problem of water pollution, which then may lead to a water crisis issue in the long term. The statement is proved by the study from Academy of Science Malaysia (2015), which stated that water pollution threatens the water security of the nation.

Water pollution is not a current issue, and it is always commensurate with urbanization and modernization (Afroz, et al., 2014). As mentioned previously, Malaysia is a country with high precipitation, and it is estimated that about 566 billion m^3 of water run-off to the river annually. However, it cannot be assured that the large amount of rainfall is enough to fulfil the demand. This is because rapid urbanization and modernization are affecting the quality of water run-off through human activities such as industrial discharge, mining activities, agriculture run-off, and construction activities. As rainwater flows into the urban area, it washes out the surface contaminants that flow into drainage systems and eventually into the river. When the accumulated contamination reaches an adequate amount, it results in the issue of water pollution, which can result in a negative impact on humans and aqualivings. A contaminated river will threaten the water security of Malaysian as 98 % of use water is extracted from surface water sources like rivers and reservoirs (Ahmed, et al., 2014). To govern the environmental quality and pollution control, Environmental Quality Act 1974 is established. Department of Environment (DOE) is empowered by the EQA to enforce environmental standards, issue permits, conduct monitoring and take action against violators. To measure the quality of the water, there are two practices being implemented by DOE: National Quality Water Standards (NQWS) and Water Quality Index (WQI).

Water pollution can be categorized into two groups: point sources and non-point sources. In contrast to non-point sources, point sources exhibit a comparatively straightforward identification process due to the diffuse and scattered nature of non-point sources. From the Environment Quality Report, the point sources such as manufacturing industries, agriculture industries, sewage treatment plants, pig farms and wet markets are focused as pollutants load sources and parameters like ammoniacal nitrogen (AN), biochemical oxygen demand (BOD) and suspended solid (SS) are the interested parameters in the report (Department of Environment, 2020). Among the sources, sewage treatment plants (STPs) are the source with the highest contribution in every parameter. This may be associated with the previous sewage discharge legislation that was established prior to January 1999, wherein there was no specified limit for nutrient discharge. The Sewage Environment Quality Regulations of 2009 have been revised to include phosphorus removal as a mandatory component of the sewage discharge standard. However, it is important to note that this law is only applicable to newly constructed sewage treatment plants that were established after the effective date of the regulation.

1.2 Importance of the Study

Due to the outdated technology, existing STP cannot remove large amounts of AN effectively. Thus, this study is crucial as it investigates the ability of multiple plants in constructed wetlands (CWs) to remove interested pollutants such as AN, phosphorus and BOD from the sewage wastewater. CWs for wastewater treatment are not a new topic in other developed countries like China, USA, Germany and Australia (Vymazal, 2011; Rozema, et al., 2016; Zhang, et al., 2021). Although there are few samples of CWs in Malaysia, such as Putrajaya Wetland Park, Taman Tun Dr Ismail (TTDI) Wetland Park, Kuala Lumpur and Seri Saujana Sewage Treatment Plant, Kedah, the implementation, continuous study and research regarding constructed wetlands in Malaysia seems to be slack and passive.

By implementation of CWs, lesser environmental impacts and high sustainability are always highlighted in other studies. The emission of carbon dioxide, CO_2 can be reduced by half in a CW treatment plant compared with conventional WWTP (Pan, Zhu and Ye, 2011). The presence of green plants in CWs can potentially serve as a carbon sink, leading to a reduction in GHG emissions. Additionally, the reduced energy consumption associated with CWs can indirectly contribute to the mitigation of GHG emissions (de Klein and van der Werf, 2014; Wang, et al., 2018). Apart from solving the problem of water pollution, this study also highlights the ability and eco-friendly impart of CWs, which perhaps the relevant authority in Malaysia can confront the issue directly and proactively.

1.3 Problem Statement

As shown in the previous section, the most significant contributor to water pollution is the STP, which has the initiative to treat sewage wastewater. An analysis of the samples from the STP of Penang, Johor Bahru and Kuala Lumpur showed that the phosphorus concentration in the STP of Penang, nitrite concentration in all interested STPs and the concentration of nitrate in Johor STP are higher than the limit prescribed in Environment Quality (Sewage) Regulation 2009 (Sabeen, et al., 2018). From the research, the reasons that lead to this circumstance are incomprehensive regulations, ineffectual law implementation, outdated technology and public awareness (Ariffin and Sulaiman, 2015).

Excessive AN in the water will have several negative impacts on human beings and the environment. AN, a source of nitrogen, stimulates the growth of algae, known as eutrophication. The life circle of the algae consumes a large amount of dissolved oxygen (DO) and leads to high BOD, eventually leading to an imbalance ecosystem in habitats like lakes and ponds. The study has proven that overconsumption of nitrates may give rise to chronic fatality effects and excessive nitrates also may cause cardiovascular diseases (Erisman, et al., 2013). For babies, the excessive consumption of nitrates will reduce the haemoglobin’s ability to carry oxygen, leading to methemoglobinemia, also known as Blue Baby Syndrome (Choudhary, Muduli and Ray, 2022).

Although Malaysia is a tropical country with satisfactory rainfall, water pollution in the long term, coupled with rapid population growth, makes the supply of sufficient clean drinking water uncertain. The water pollution incidents, like toxic waste illegally dumped into Sungai Kim Kim in Johor, effluent from industries to Sungai Selangor and pollution incidents of Sungai Semenyih, affected more than 300 000 residents from different areas, which also emphasized the water crisis issue and threatened the water security in Malaysia. In 2020, Selangor, one of the urban cities in Malaysia, had a total of 8 times of water disruptions, which is a very concerning situation (Amin, et al., 2022). This not only causes inconvenience to the residents but also causes economic loss, particularly in manufacturing, which has a significant impact on business owners.

1.4 Aim and Objectives

From the introduction and problem statement, as written in previous sections, the main objectives of this study are to build a prototype of CW for wastewater treatment purposes and investigate the efficiency of different plants on the removal rate of pollutants like nitrogen, phosphorus and COD, with the proper design parameters such as hydraulic loading rate, hydraulic retention time and food to microbes ratio. The main objectives are listed below:

i. To construct a prototype of CW for wastewater treatment
ii. To investigate the efficiency of different substrates on pollutant removal rate
iii. To investigate the efficiency of different plants on pollutant removal rate
iv. To investigate the efficiency of different operation modes on pollutant removal rate

1.5 Scope and Limitation of the Study

This study aims to investigate the relationship between the types of substrates used and the efficiency of pollution removal. Furthermore, it is crucial to integrate a comprehensive investigation that assesses the effectiveness of various plant species in the removal of pollutants. One constraint of this research pertains to the influence of substrate mixtures. The scope of this study is restricted as it focuses exclusively on the examination of two specific plant species, namely vetiver grass and spider plant. The study aims to analyse the efficacy of these plants in removing pollutants utilising two distinct substrates, namely zeolite and activated carbon.

CHAPTER 2

LITERATURE REVIEW

2.1 Background and Development of Constructed Wetland

Wetlands offer distinctive and irreplaceable roles that are connected to a variety of ecosystem services crucial for the preservation of biodiversity, the mitigation of climate change, and the well-being of humans (Ferreira, et al., 2023). Wetlands serve as transitional areas that exist between dry land and open water, found along coastlines, around lakes and rivers, or as marshes spread across landscapes. Ecologically, wetlands occupy a middle ground between terrestrial and aquatic ecosystems. Over time, most wetlands either transition into dry land due to lowered water levels, sediment buildup, and plant growth or become submerged due to rising water levels from factors like sea-level rise or climate shifts. Wetlands are frequently interconnected with a variety of ecological communities, making it challenging to establish distinct boundaries between them. The characteristics of wetlands result in a dearth of scientific consensus on their definition. In contrast, attributes that are commonly accepted as shared characteristics comprise the presence of water on a continuous or seasonal basis, specific soil qualities and plants and animal populations that have acclimated to the damp environment (Ferreira, et al., 2023).

The usage of wetlands as wastewater treatment can be retrospect to the time of the ancient Chinese and Egyptians and this culture has been inherited by their inferiors (Brix, 1994). The use of natural wetlands as wastewater treatment was disposal rather than treatment. Before discovering the ability of wetlands to act as a natural filter, people disposed of wastes in the wetlands, just like a discharge of effluents from factories, as it is the most convenient way to eliminate the waste from their place. The continuous and uncontrolled disposal of wastewater into the wetlands has resulted in the destruction of many wetlands. The wetlands can then be drained and transformed into other land use purposes, such as agriculture, commercial and residential. According to Kadlec, Tilton, and Ewel (1979), the utilization of wetlands as a wastewater treatment continued until the late 1970s. At that time, people started to have the acknowledgement of the efficiency of wetlands in wastewater treatment, and the CWs were introduced.

The study and research regarding the CWs can be traced back to 1901 when a patent similar to the concept of CW came out with the purpose of water purifying (Monjeau, 1901). Figure 2.1 illustrates the diagram of the water purifying system. Another documentary about CW was founded in 1904 by Brian Mackney from Australia. In the 1950s, a scientist named Dr. Käthe Seidel observed that the lakeshore bulrush was able to remove nutrients and other inorganic substances from contaminated water. With this observation, she started many experiments regarding the removal efficiency of lakeshore bulrush on bacteria, heavy metals and hydrocarbons during the 1960s. After getting positive results from the lab-scale experiments, the experiments were expanded to a full-scale trial system to treat wastewater from different sources, including industrial wastewater, river water, and sewage wastewater (Brix, 1994). A system known as the Krefeld System is the pioneering work by Dr. Seidel in the development of CW. In Holland, a large-scale treatment system based on Dr. Seidel's ideal was developed to treat the wastewater from a camping site with a maximum capacity of 6000 people (de Jong, 1976). In the mid-1960s, another scientist named Dr. Reinhold Kickuth developed the concept of the Root Zone Method, in which water flows to the rhizosphere of the macrophytes. The studies and works of these two scientists laid a critical foundation for the research and development of constructed wetlands.

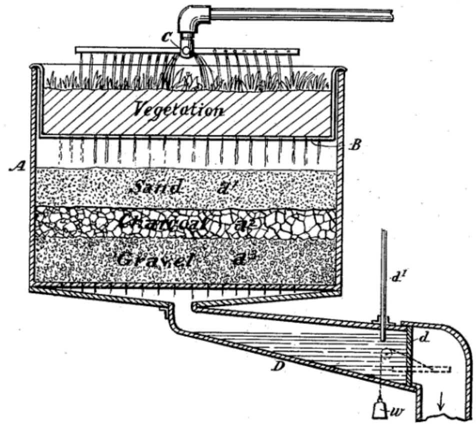

Figure 2.1: The Drawing of the Water Purifying System (Monjeau, 1901).

Constructed wetlands created for wastewater treatment are engineered structures designed to harness the natural processes of wetlands to break down and eliminate pollutants. The systems are constructed under controlled circumstances, providing more regulation and a high degree of control to reduce uncertainty. Unlike natural wetlands, CWs enable the precise configuration of substrate, plant varieties, and flow dynamics in treatment facilities. During the 1980s to 1990s, it can be said that this technology was widespread globally and numerous global conferences, with a particular emphasis on this technology, were convened across Europe, Asia, Australia, and both North and South America (Vymazal, 2022). As shown in Figure 2.2, at the end of the 20th century, the literature research on CW was being focused on by the developed countries at that time, such as the USA, UK, Canada and Germany. Numerous research studies have been conducted concerning various facets of constructed wetlands. These studies have provided valuable information on the design and operation of CW, including hydrological, physical, and biochemical mechanisms. Additionally, an increasing body of scientific literature examines the planning, establishment, and effectiveness of diverse categories of constructed wetlands. Although China was not a developed country during the discussion period, swift urbanization, industrial expansion, and rapid economy raised a series of environmental issues in the local area. The CW, which is relatively energy-saving compared to conventional treatment, has promoted wetland-related studies in China.

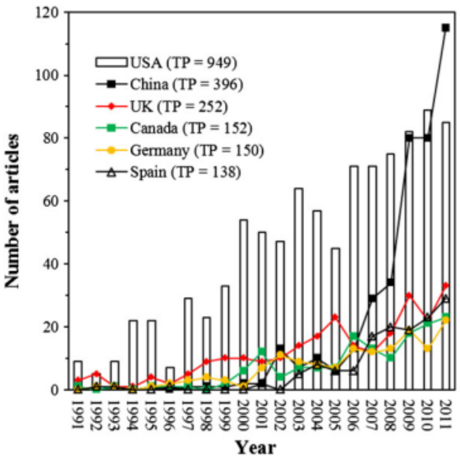

Figure 2.2: The Growth of Publications of the Six Most Productive Countries (Zhi and Ji, 2012).

For decades, since the start of the 21st century, CWs have become one of the most popular wastewater treatment methods. The researchers started to focus on the study of various design and operation conditions of CW to improve the pollutant removal efficiency, such as the selection of plants for enhancing pollutant removal, the efficiency of CW for sewage treatment, the capability of various microbes in pollutant degradation and the efficiency of CW for pharmaceuticals and personal care product (PPCP) removal rate. Apart from that, the research on relevant topics like microbial fuel is also focused on fully utilizing the energy or sources from the CWs. Regrettably, a majority of the research is conducted through limited laboratories and there have been no efforts to incorporate the findings from these experiments into the planning of large-scale implementations. Thus, it can be predicted that the significant challenge in the upcoming years will revolve around effectively translating the outcomes of laboratory experiments to practical applications in full-scale constructed wetland projects.

2.2 Types and Characteristics of Constructed Wetlands

As a qualified treatment wetland, a CW must fulfil three conditions: the existence of macrophytic vegetation, the presence of consistently damp or saturated soil conditions for a specific duration and the inlet of contaminated water with the polluted that needs to be eliminated (Fonder and Headley, 2011). The three characteristics above are commonly accepted for a CW or natural wetland that has wastewater treatment purposes. The classification of CW can be categorized based on three criteria: the hydrology of the CW, the type of growth of the plant and the flow path of the inlet. With those three criteria, CWs are typically categorized into two groups: surface flow CWs and subsurface flow CWs (Vymazal, 2011). The main difference between these two groups of CWs can be noticed in the place of the inlet and outlet of the water. The differences in the water pathways result in various pollutant removal efficiencies as the mechanism applied to treat the pollutants is also different.

2.2.1 Surface Flow Constructed Wetlands

Surface flow CW, sometimes referred to as free water surface CW, usually comprises shallow depression containing soil and other substrate or medium capable of sustaining macrophytes root systems. One of the main design objectives of surface flow CW is to expose sluggish-moving wastewater to responsive biological surfaces (Li, et al., 2018). As can be seen from Figure 2.3, water will flow through the CW above the substrate and flow out from the channel near the water surface. This type of water pathway allows the contaminated water to slowly flow through to maximize the contact time with plants and the substrate, which contains living organisms, such as bacteria. The living microbes then degrade the organic pollutants through bacterial metabolism.

In the surface flow CW, the surface is typically covered with macrophytes with a fraction of more than 50 %. The plants are commonly left untouched as their debris supplies the essential organic carbon that is required for denitrification. The denitrification process can be found within the layer of plant litter. Other than that, the suspended solids are effectively removed through sedimentation by gravity force, which is one of the advantages of surface flow CW. The removal of phosphorus in this type of CW is relatively low due to the limited contact of wastewater with soil particles, compared to the subsurface flow, which has direct contact with soil particles. Other pros of surface flow CW are low capital cost and maintenance cost. However, higher land use is required to achieve the required level of treatment as the low pollutant removal rate. Other than that, the remaining pros and cons of surface water CW are tabulated in Table 2.1.

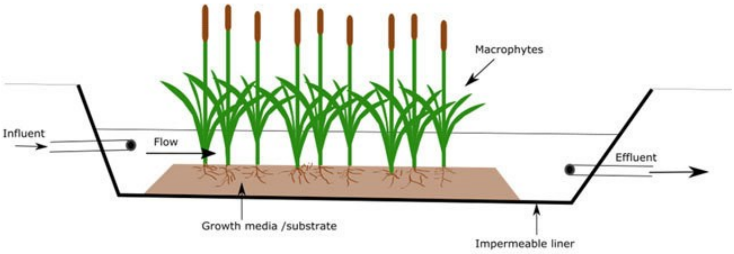

Figure 2.3: The Water Pathway of Surface Flow CW (Fletcher, et al., 2020).

The surface flow CW can be further classified according to the type of plant in the CW: free-floating, floating-leaves, submerged and emergent (Vymazal, 2022). Since the plants are floating on the water surface, the free-floating CW may not require the presence of a substrate for root support. Free-floating species can be found in extensive shapes and environments. Water hyacinth (*Eichhornia crassipes*) and water lettuce (*Pistia stratiotes*), which are examples of large plants with large leaves and roots, are sensitive to temperature and only suitable for tropical and subtropical regions (Brix and Schierup, 1989). Apart from that, species such as *Lemna*, *Spirodela* and *Wolffia* possess a broader geographical distribution due to their ability to endure even in conditions of light frost (Culley and Epps, 1973). Among the types of plants, floating-leaved macrophytes are the least applied in CW due to their low efficiency in pollutant removal and promote the growth of algae (Greenway, 1997). For submerged macrophytes, it is naturally coated with periphyton, which is a community of algae and microorganisms that plays a positive role in purifying pollutants by providing the oxygen needed to oxidize contaminants and by absorbing nutrients (Sutherland and Craggs, 2017). For emergent macrophytes, the most popular plant is *Typha* spp., which requires basins with rooting soil to support it (Vymazal, 2013).

Table 2.1: Pros and Cons of Surface Flow CW (Halverson, 2004).

Advantages	**Disadvantages**
✓ Low capital and operating cost	✗ Lower contaminant removal rate results in more land area required to achieve the required level of treatment
✓ Easier to design than subsurface flow CW and conventional WWTP	✗ Potential for ecological risk or human contact with wastewater flowing on the surface
✓ Have a higher freedom of control	
✓ Prompt more diverse habitat	

2.2.2 Subsurface Flow Constructed Wetland

As it is named, the water pathway of this CW is under the surface of the substrate. Subsurface flow CW can be further divided into two categories: horizontal flow and vertical flow. As observed in Figure 2.4, the water inlet of horizontal flow CW is channelled beneath the plants and flows through the soil medium; eventually, the treated water is collected from the same horizontal level as the influent. For vertical flow, water is channelled from the surface and collected at the bottom, similar to the conventional water purifying system or inversely. The similarity between horizontal and vertical flow is that water flows through the soil medium. For the outlet, water is collected at a similar horizontal level for horizontal flow CW instead of from the bottom of the system in vertical flow CW.

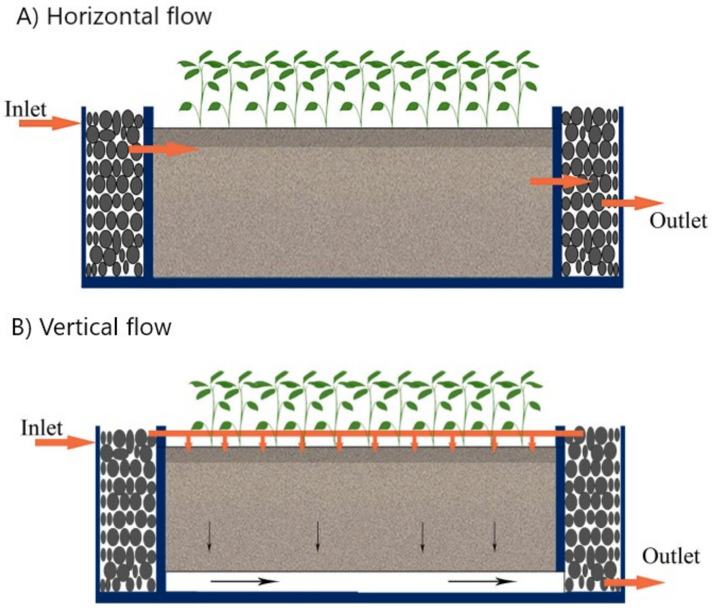

Figure 2.4: Water Pathway of Horizontal Flow CW and Vertical Flow CW (Yang, et al., 2022).

Horizontal flow CW provide an effective pollutant removal system as water will encounter a sequence of aerobic, anoxic, and anaerobic zones when flowing through the soil medium. The contaminants are degraded by aerobic and anaerobic microbes during the residence time. However, aerobic degradation is primarily in the small areas near the roots and rhizomes, where oxygen gas is released (Vymazal and Kröpfelová, 2009). This denotes that the biochemical process that requires oxygen is prohibited due to the anoxic or anaerobic condition. For vertical flow CW, the batch process is promoted to allow air diffusion between batches and ensure the aerobic condition in the filter bed (Vymazal, 2022). Although there are other hydrology designs of vertical flow CW, such as up flow and fill and drain, the down flow, where water flows from top to bottom of the filter bed, is still the most common type of vertical flow CW. Due to the aerobic condition, vertical flow CW is handled on the organic pollutants and suspended solids. However, a high content of suspended solids may cause clogging in both subsurface flow CWs. Table 2.2 succinctly summarizes the advantages and disadvantages of subsurface-constructed wetlands.

Table 2.2: Advantages and Disadvantages of Subsurface CW (Halverson, 2004).

Advantages	**Disadvantages**
✓ High pollutant removal rate than surface flow CW	× Required more land than conventional WWTP
✓ Lower capital and lifetime cost than conventional WWTP	× Expensive to construct than surface flow CW
✓ Minimal ecological risk	× High-suspended solids may cause clogging.
✓ Provides habitat for flora and fauna	

2.3 Mechanism of Constructed Wetlands in Wastewater Treatment

A constructed wetland (CW) comprises various constituents, including water, substrate, plants, plant detritus, invertebrates (particularly the larvae of insects and worms), and microbes (specifically bacteria). When the wastewater enters the system, it is treated with a series of processes. For instance, sedimentation, UV exposure, precipitation, adsorption, microbial degradation, microbial nutrient transformation and so on. As can be observed from Table 2.3, these activities can be categorized into physical, chemical and biological processes (Vymazal, 2011). Obviously, CWs are designed to mimic the natural processes of the wetland ecosystem and these series of processes become the main mechanism that removes pollutants from the contaminated water.

Table 2.3: Summary of Processes in Constructed Wetlands (Jaya and Vigneswaran, 2008).

	Process	Target Pollutant
Biological	Photosynthesis, respiration, fermentation, nitrification, denitrification, microbial activity	Organic waste (COD) Nitrogen Phosphorus
Chemical	Precipitation, adsorption	Organic waste (COD) Phosphorus Heavy metal
Physical	Sedimentation, filtration, adsorption	Organic waste (COD) Suspended solids Heavy metal Pathogens

2.3.1 Biological Process

For biological processes, there are a total of six major processes involved in pollutant removal, which are respiration, photosynthesis, nitrification, denitrification, fermentation and microbial activity (Jaya and Vigneswaran, 2008). One of the most important biological processes is photosynthesis, which generates oxygen for the other biochemical processes. In photosynthesis, carbon dioxide and water are converted into glucose in the presence of sunlight and oxygen is generated as a by-product. The oxygen gas is released adjacent to the rhizosphere of the macrophytes.

Besides that, fermentation in CW plays a role in promoting the growth of microbes. Fermentation is the decomposition process of organic compounds in an anoxic environment, where products like methane, alcohol and fatty acid are generated as waste. However, these compounds are very useful in increasing the growth of microbes. The microbial growth stimulates the formation of biofilm, which acts as a shield to protect the microbes from external stress, such as environmental change, antibiotics and host immune response (Pavlineri, Skoulikidis, and Tsihrintzis, 2017).

With the protective layer, microbes enable the start colony of the CW, which is essential to the following processes: nitrification and denitrification. The nitrification process refers to the process of nitrogen removal from the wastewater by microorganisms in aerobic conditions. Due to the requirement for aerobic conditions, nitrification occurs near the area of the roots of plants and in the biofilm. In contrast, denitrification requires an anaerobic environment, such as the soil medium. The varied environment in CWs has promoted the removal of nitrogen compounds through nitrification and denitrification.

For the microbial ecology, this may start with the plants in CW. Plants uptake the dissolved nutrients and pollutants from the wastewater, transforming them into extra plant biomass; this is known as phytoremediation (Halverson, 2004). When it comes to the end-of-life cycle, the plants eventually decompose and contribute to the accumulation of litter and peat in sediments. Aside from that, the wetland system harbours a diverse array of microorganisms, such as bacteria, fungi, and coagulate colloid material. These microorganisms play a crucial role in stabilizing and eliminating dissolved organic compounds by transforming them into different gases and generating new cellular tissues (Chen, et al., 2020). Other than nitrification and denitrification, microbes are also involved in transforming phosphorus from insoluble to soluble, which can be intake by plants (Feng, et al., 2023).

2.3.2 Chemical Process

In the chemical process, the polarity or the chemical properties of the pollutants become the crucial factor in the removal rate. Numerous mechanisms are engaged in the adsorption of pollutants onto the substrates of constructed wetlands. These mechanisms encompass van der Waals forces, hydrophobic contacts, electrostatic forces, and ion exchange (Zhang, et al., 2023). When the wastewater flows through the filter bed, adsorption may happen in the substrate, the rhizosphere of the plant and the biofilm. One of the useful parameters for measuring the adsorption behaviour of pollutants is the octanol-water partition coefficient, K_{OW}. A chemical with a high K_{OW} value implies that it is more hydrophobic and has a high tendency to adsorb to organic matter. In contrast, a chemical with a low K_{OW} value is preferred hydrophilic and tends to adsorb to the polar surface (Luo, et al, 2014). The general guideline for the probable adsorption characteristics of chemicals is tabulated in Table 2.4. The potential pollutants for this method are heavy metals, pharmaceutical waste and other organic wastes.

Table 2.4: Classification of Adsorption Preference at Different Values of K_{OW} (Luo, et al., 2014).

$\boldsymbol{logK_{OW}}$	**Adsorption preference**
< 2.5	Low potential
$2.5 < logK_{OW} < 4$	Medium potential
> 4	High potential

The precipitation process is always associated with heavy metals, where precipitants include hydroxides, carbonates and sulphides (Yu, et al., 2022). This precipitant is added to increase the pH of the contaminated water, leading to the decrease of the metal ion solubility and eventually forming an insoluble salt. The precipitate, the insoluble ion, becomes an immobilized precipitate, which requires the subsequent physical process. Moreover, nutrients such as phosphorus can also be precipitated by adding ferum (iii) chloride ($FeCl_3$) to form iron phosphate ($FePO_4$), which is another insoluble salt (Gu, et al., 2022). However, the emission of chloride ions has to be aware as it can form a hazardous substance by reacting with other organic compounds.

2.3.3 Physical Process

The physical process is primarily focused on the treatment of suspended solids by sedimentation and filtration. The hydrological dynamics inside the wetland system are characterized by a sheet flow pattern, accompanied by the hydraulic resistance exerted by the vegetation present. The sedimentation of suspended particles is facilitated by low flow velocities and a laminar flow regime. During the sedimentation process, larger particles, including sand, silt, and even larger organic matter, are gradually descended by gravity force and eventually deposited into the sediment layer of the marsh. Coupled with the adsorption of organic matter and suspended solids onto the larger particles, sedimentation not only reduces the turbidity but also contributes to immobilizing other pollutants. The sediment layer then serves as a habitat for various microorganisms that aid in the degradation and transformation of pollutants, contributing to the overall health of the CW (Jaya and Vigneswaran, 2008).

For the subsurface flow CWs, the characteristics of CW enable the sieving out of suspended solids and other pollutants from the flowing influent. The substrate layers, comprising materials such as gravel, sand, and soil, play a crucial role in the filtering mechanism of CWs. As water infiltrates the substrate layers, it experiences a sequence of filtration processes, which is related to the physical adsorption, as shown in Figure 2.5. The substrate layers are intentionally engineered to possess diverse particle sizes, with coarser materials situated at the uppermost layer and finer ones located at the lowermost layer. The variation in particle size within this filter configuration results in a dynamic filtration system that has the ability to effectively capture a diverse array of suspended particles, encompassing both bigger debris and minuscule sediment particles (Fang, et al., 2022).

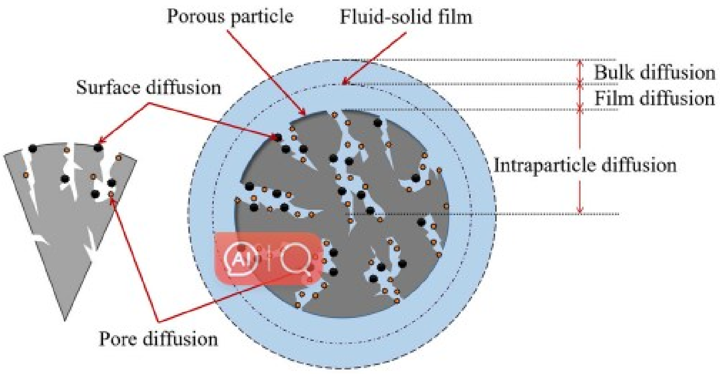

Figure 2.5: Schematic Diagram of Absorption Mechanism (Yang, et al., 2022).

2.4 Comparison between Constructed Wetlands and Conventional WWTP

The comparison between conventional wastewater treatment plants (WWTPs) and CWs offers a thorough investigation of two independent methodologies for tackling a significant issue in contemporary society: the management of wastewater. Although both WWTPs and constructed wetlands CWs have the objective of purifying wastewater prior to its discharge into the environment, they utilize distinct approaches that come with their own respective advantages and limitations.

CWs and conventional WWTPs differ in their treatment mechanisms and processes. In CWs, treatment is primarily achieved through natural processes that leverage the synergy between plants, microorganisms, and the substrate. The extensive root systems and substrate matrix effectively physically filter out suspended materials as water passes through (Halverson, 2004). Nutrients, particularly nitrogen and phosphorus, are removed through a combination of plant uptake, microbial degradation, and adsorption onto the substrate surfaces. Organic contaminants undergo microbial degradation, where microorganisms in the substrate and water column break down complex organic compounds into simpler, less harmful substances. In contrast, conventional WWTPs employ a series of processes that include mechanical, physical, chemical, and biological processes to achieve efficient wastewater treatment. Primary treatment involves physical settling to remove larger suspended solids through screening and sedimentation. Secondary treatment relies on biological processes, such as activated sludge systems or biofilm reactors, to further break down organic matter. While tertiary treatment, which is also known as advanced treatment, often includes chemical processes like coagulation, flocculation, and disinfection. Chemicals like chlorine or UV radiation are used to eliminate pathogens and ensure the quality of the treated effluent (Spellman, 2014).

Moreover, the design of the system also reflects their different working principles. CWs are frequently distinguished by their incorporation of natural components and dependence on ecosystem services. The arrangement of CW optimizes the interactions between water, plants, and substrates, hence facilitating the removal and treatment of pollutants. The substrate, regardless of its composition, such as sand, gravel, or biofilm-covered surfaces, serves as a home for microbial populations that play a role in treatment processes (Pavlineri, Skoulikidis, and Tsihrintzis, 2017). On the other hand, conventional WWTPs involve a series of distinct treatment units that are mechanically and chemically intensive. Grit chambers, screens, aeration tanks, and sedimentation tanks are employed in a sequenced manner to separate solids, promote microbial growth, and remove contaminants. The infrastructure includes energy-intensive components such as pumps for water movement and aeration, which require blowers to provide oxygen to microbial communities (Singh, Carliell-Marquet and Kansal, 2012). CWs have a distinct advantage in terms of lower energy demand due to their reliance on natural processes. Wetland vegetation and microbial communities contribute to treatment without the need for mechanical aeration systems.

As mentioned in the last paragraph, the energy consumption and resource demands of CWs and conventional WWTPs are drastically different. CWs possess a notable benefit in terms of reduced energy use as a result of their dependence on natural processes. Aeration, which is known for its high energy consumption, is not commonly employed in CWs. In contrast, the presence of wetland plants and microbial populations enables treatment processes to occur naturally, eliminating the necessity for mechanical aeration systems. Moreover, the decentralized characteristic of CWs results in a decrease in the energy needed for centralized water conveyance. On the other hand, traditional WWTPs exhibit greater energy requirements. The process of aeration, which is necessary to sustain microbial communities during the secondary treatment phase, constitutes a substantial proportion of the overall energy consumption (Longo, et al., 2016). Pumping, mixing, and chemical dosing activities additionally contribute to the overall energy requirements. Chemical agents, including coagulants, flocculants, and disinfectants, play a crucial role in enhancing the efficiency of WWTPs, hence resulting in heightened utilization of resources.

CWs are recognized for their capacity to integrate seamlessly into pre-existing environments. Engineered ecosystems have the potential to be strategically incorporated into urban, suburban, or rural regions, maximizing land utilization and frequently converting underutilized areas into environmentally advantageous resources. The realistic visual qualities of constructed wetlands have the capacity to augment the aesthetic appeal of their surroundings (Arunbabu, et al., 2015). By providing aesthetically beautiful green areas, community well-being initiatives can effectively stimulate community involvement, encourage recreational pursuits, foster respect for nature, and facilitate educational initiatives even for tourism (Lee and Hsieh, 2016). Conventional WWTPs sometimes necessitate greater land footprints as a result of their centralized characteristics. These facilities include several structures such as treatment units, basins, tanks, and equipment, which combined need a significant amount of space. In order to address potential visual and olfactory concerns, WWTPs are frequently located at a distance from densely inhabited regions. The challenge of incorporating WWTPs into urban environments with minimal visual and olfactory impact highlights the juxtaposition with the inherently attractive aesthetics of CWs.

In short, CWs get rid of pollutants by using the natural abilities of marsh vegetation, substrate, and microbial communities. These methods are easy to use and can be changed to fit many different kinds of landscapes. Due to their low energy use and aesthetic appeal, CWs are able to integrate into communities. On the other hand, standard WWTPs use mechanical and chemical processes, which require more energy and a bigger infrastructure. Even though WWTPs are known for being effective, they do not always look as nice as CWs and can be challenging to implement in a metropolis.

2.5 Study on the Design Parameters

As engineered ecosystems that harness the power of wetland vegetation, substrate materials, and microbial communities, CWs operate within a complex matrix of environmental conditions and design parameters. From hydraulic loading rates to the presence of microbial communities, from vegetation selection to nutrient loading ratios, each factor contributes to the intricate web of physical, chemical, and biological processes that facilitate pollutant removal and water purification.

2.5.1 Hydraulic Loading Rate and Hydraulic Retention Time

The hydraulic loading rate (HLR), representing the volume of wastewater flowing through a CW per unit area, is a pivotal factor in determining treatment efficiency. It plays a crucial role in controlling the contact time between wastewater and treatment components. Apart from the pollutant removal efficiency, HLR also relates to the environment of CW, such as plant growth, oxygen dissolution, wetland moisture and microbial community (Zhang, et al., 2022). An optimal HLR strikes a balance between hydraulic retention time (HRT) and treatment effectiveness.

Generally, insufficient interaction time resulting from high HLR might impede effective pollutant removal, hence diminishing the overall efficacy of the treatment process. In a tidal flow CW, an increase in HLR resulting from an increment of the feeding rate had decreased the nitrogen removal rate from 89.70 % to 55.49 % (Zhang, et al., 2021). It is due to the reason of the residence time within the CW may become inadequate for the proper execution of the diverse treatment process. Thus, it is plausible that contaminates may not have sufficient duration to engage in interactions with the substrate, plants and microorganisms.

With the statement above, it can be summarised that HLR has an inverse relationship with HRT, which indicates the ratio of the volume of the system to the wastewater flow rate. Although both HRT and HLT are important in determining the contact time of wastewater in CW, from the study of Jiang and Chui (2022), the R^2 value for the linear regression model employing the variable of interest, HRT, tends to be greater compared to the R^2 for HLR. This observation suggests that HRT may exhibit greater efficacy in terms of reflecting the efficiency of removal. The longer the HRT, the more effective on pollutant removal. This has been proven by Jiang and Chui (2022), where the BOD removal rate increases by 13.15 % when HRT increases from 8 days to 16 days.

Moreover, HRT also affects the growth of the plants in CW. As high HRT increases the nutrient removal rate at the effluent, the nutrient that stays in CW will be the nutrient supplement for the growth of the plants (Kamilya, 2022). According to the research study of Minakshi, et al. (2022), the high HRT also provides sufficient contact time to the microorganisms to eliminate the contaminants via microbial activity. With the abundant substrate, a longer HRT also enables to facilitate the proliferation and thriving of microbial populations, as the contaminants in the wastewater will be the food sources for microbes.

Other than HLT, HRT may be affected by other factors, such as clogging. Due to the function of a physical filter in CW, clogging may happen as suspended solids will accumulate in the bed of soil in CW. To inspect the clogging issue of CWs, the tracer test may carry out and calculate some important hydraulic parameters, such as θ_{10}, λ_t, and λ_p, which are utilised to characterise short-circuiting, effective volume ratio, and hydrological performance, respectively. Θ_{10}, λ_t , and λ_p represent the proportions of time required for 10% of the tracer to exit the wetland, the average hydraulic retention time, and the time taken for the tracer to reach the peak of the residence time distribution (RTD) curve in relation to the nominal hydraulic retention time, respectively (Yang, 2017).

Apart from that, HLR also has a notable influence on the microbial community. The varied life strategies and ecological roles resulted in diverse reactions between satellite and core taxa in response to changes in HLR, where core taxa are the amplicon sequences variants (ASVs) with an occurrence frequency of more than 60 % is the samples, while the satellite is less than 50% (Mo, et al., 2021; Kan, et al., 2023). The rise in HLR levels led to a reduction in micro eukaryotic community diversity among satellite taxa, whereas core taxa exhibited the opposite trend. This occurrence might be clarified by distinct survival behaviours resulting from the unique traits of core and satellite taxa, which could be linked to the “hunger games” hypothesis, which states that generalist species thrive under the condition of abundant resources, but when resources dwindle, specialists become more competitive (Kan, et al., 2023). Under the conditions of high HLR, a nutrient-rich environment is exposed to core taxa to increase the development of the microbial community. In conditions of increased nutrient availability, the growth of core taxa can lead to significant alterations in the environment due to the production of detrimental metabolites, which in turn suppress the growth of competing species, in this case, satellite taxa (Gralka, et al., 2020). Nevertheless, HLR also declines community diversity when it is increased. The elevated water scouring resulting from increased HLR can render satellite taxa more vulnerable to being eroded from the community, ultimately resulting in a reduction in diversity within the context of CWs (Kan, et al., 2023).

2.5.2 Plant

As mentioned antecedently, plants, macrophytes or vegetation play an essential role in CWs. Aside from the direct uptake of nutrients in wastewater, plants also promote degradation via aeration through their rhizosphere, which is one of the crucial processes in CWs as it provides an aerobic condition for various microbes and stimulates the development of the microbial community. However, different plants may perform differently in terms of pollutant removal efficiency.

From the research of Toscano, et al., (2015), a total of 4 types of emergent plants were investigated regarding their pollutant removal efficiency in horizontal CWs: *Vetiveria zizanioides*, *Miscanthus x giganteus*, *Arundo donax* and *Phragmites australis*. The interested pollutants include total suspended solids (TSS), total phosphates (TP), ammonia, total nitrogen (TN) and chemical oxygen demand (COD). For TSS, *A.* donax has the highest removal rate of 89 %, followed by *P.* australis, with a rate of 88 %. The plant structures, such as stems, roots, and rhizomes, contribute to the enhancement of TSS removal efficiency by slowing water velocity and strengthening the processes of settling and filtration within the root network.

For COD, the removal rate ranges from 53 % to 63 %, where *P.* australis has the best performance among these four plants; thus, it can be deduced that the development of biofilm that is responsible for organic matter degradation is well developed during the experiment period. As horizontal CWs are predominant in an anoxic environment, ammonia oxidation to nitrate is not favourable; thus, it leads to a lower removal rate of ammonia and other nitrogen compounds compared to other pollutants. In between the plants, *P.* australis again has an outstanding accomplishment in the removal of ammonia and other nitrogen pollutants, which is 57 % and 61 %, respectively. For phosphorus removal, a relatively low efficiency was observed for all types of vegetation.

Other than conventional plants, CWs have also witnessed the emergence of attractive plants in their ecosystem. Research has demonstrated that ornamental plants have comparable effectiveness to traditional plants in removing contaminants from CWS (Kotsia, et al., 2020; Stefanatou, et al., 2023). Additionally, aesthetic plants have the added benefit of increasing public acceptance of CWs to a larger degree. In the study of Stefanatou, et al. (2023), the model of vertical flow CWs was constructed while the climbing and ornamental plants were used, which are *Trachelospermum jasminoides*, *Lonicera japonica* and *Callistemon laevis*. All three plants have a remarkable performance on TSS removal, which is around 100 % of removal. Meanwhile for BOD and COD removal, *T.* jasminoides achieved the highest removal rate of as high as 100 %. For the removal of TP, all the CWs in this experiment had a poor performance, which was only up to 34 %, with *T.* jasminoides planted in the vertical flow CW. The effluent of T. jasminoides showed the highest removal rate of TN. With the mentioned achievements of *T.* jasminoides, it can be concluded that *T.* jasminoides is one of the high potential ornamental plants to be employed in CWs. A similar study of ornamental plants was conducted by Kotsia, et al. by using *Pittosporum tobira*, *Polygala myrtifolia* and *Hedera helix* (Ivy) in vertical flow CWs as well. Figure 2.6 shows the removal efficiency of each studied vegetation on respective contaminants. The experiment results from Kotsia, et al. are quite a match to the study of Stefanatou, et al., whereby the plants have a notable outcome in treating TSS, COD and BOD. Among the studied vegetation, *Pittosporum* is excellent in reducing COD, which is as high as 97 % of removal rate. On the other hand, Ivy is good in TSS removal, with a removal rate of about 95 %.

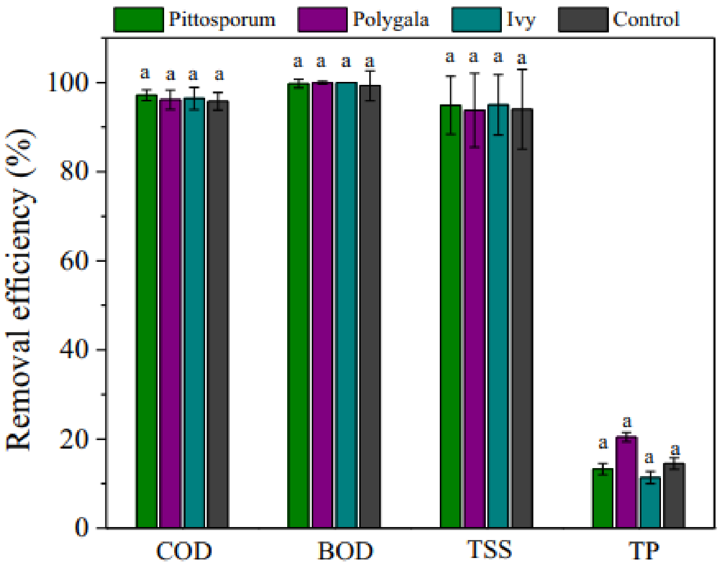

Figure 2.6: Removal Efficiency of Varied Plants on COD, BOD, TSS and TP (Kotsia, et al., 2020).

2.5.3 Substrate

In the context of CWs, substrate pertains to the substance or medium that constitutes the fundamental or underlying structure of the wetland system. Substrates have a significant role in the composition of developed wetland sewage treatment systems, constituting the most substantial portion of the structure of CWs. Substrates take a crucial supportive function within the context of biological treatment methods. Constructed wetlands serve as a means of physical support and transportation for plants and microorganisms. Additionally, the variety of microbial species and the structure of the microbial community are significantly influenced by the different kinds of substrate. Generally, the substrate can be categorized according to its sources: natural substrate, industrial and agriculture by-products and synthetic substrate. However, each type of substrate has a distinctive removal method for pollutants as a result of its distinct physical and chemical properties, which causes variations in the effectiveness of pollutant removal.

Naturally, there are plenty of natural substrates, including zeolites, soil, gravel, limestone and so on. Zeolite, which forms from the reaction between volcanic and ash layers, has a high nitrogen compound adsorption capacity, which is as high as 4500 mg/kg with an influent of 500 mg/L (Cyrus and Reddy, 2011). Based on the study of Lu, et al. (2016), maifanite, which consists of Al_2O_3 and Sio_2, has shown high removal of COD and TN compared with steel slag, limestone and bamboo charcoal, with a removal rate of 81.3 % and 79.2 %, respectively. For soil, the remarkable finding will be its high removal rate of phosphorus at 72.1 %, which then indicates that the soil within the constructed wetland had a significant role in the removal of phosphorus. Gravel, which is generated from the weathering of exposed rock, performs moderately on COD removal at around 65 % and poses a low phosphorus absorption capacity as it mainly consists of SiO_2, which results in a lack of active oxide (Tang, Huang and Scholz, 2009). When discussing limestone, the primary aspect that comes to mind is its calcium (Ca) component. It is hypothesized that the significant presence of calcium in limestone is responsible for its high rate of phosphorus absorption (Mateus, Vaz and Pinho, 2012).

Moreover, the examples of industrial and agriculture by-products are quartz sand, oyster shell and fly ash. Quartz sand, which is the by-product that is generated during the production of quartz stone, poses a moderate COD removal efficiency of 66.86 % from the study of Gao, et al. (2019), but it can be enhanced by increasing its thickness. On the other hand, the oyster shell demonstrates moderate COD removal and significant phosphorus elimination. The study has found that 87.7 % of TP in influent can be removed by oyster shell via absorption (Park and Polprasert, 2008). With the use of swine wastewater, Wang, et al. (2013) claimed that oyster shell has the highest phosphorus absorption among broken brick, volcanic and zeolite. While the fly ash is a suitable substrate that has a great performance in removing COD, TN and TP with a rate of 80 % and more than 70 % for TN and TP (Mao and Zhou, 2005).

Furthermore, the well-known activated carbon and biochar are examples of synthetic substrates used in CWs. The overall performance of activated carbon is said to be poor in removing COD, TN and TP. The removal rate of activated carbon is at a moderate level, but the poor performance in removing TN and TP, which may be linked to its structure that lacks components that contribute to absorption, makes it poor overall efficiency (Dai and Hu, 2017). Compared to activated carbon, biochar is much better at removing COD TN and TP. The study has shown that the removal rate of all three contaminants is over 70 % (Wang, et al., 2020).

In short, every substrate variant possesses a unique mechanism for eliminating contaminants and their removal ability is tabulated in Table 2.5. Generally, the primary mechanisms responsible for the removal of COD are the processes of microbial biodegradation and substrate adsorption. There is a significant correlation between the specific surface area of substrates and the quantity of microorganisms present on the surface. As the specific surface area of substrates increases, the likelihood of adsorbing insoluble COD also increases. The substrates mainly remove N and P through adsorption processes, either physical adsorption or chemical adsorption or both. As with the absorption of COD, the physical adsorption of TN and TP is related to the specific surface area and physical structure of the substrate. Chemical absorption strongly correlates with the chemical composition and inherent properties of the substrate. The adsorption of N typically occurs by an ion exchange process between N and the surface of the substrate. P is typically eliminated from the solution by a precipitation process with calcium (Ca), iron (Fe), and magnesium (Mg) present in the substrate.

Table 2.5: Decontamination Ability of Different Substrates.

Substrate	**Decontamination ability**		
	COD	**TN**	**TP**
Zeolite	High	High	Low
Maifanite	High	High	Medium
Soil	Low	Medium	Medium
Gravel	Medium	Low	Low
Limestone	Medium	Low	High
Quartz sand	Medium	Low	Medium
Oyster shell	Medium	Low	High
Fly ash	High	Medium	Medium
Activated carbon	Medium	Low	Low
Biochar	Medium	Medium	Medium

2.6 Other Pollutants Removal Efficiency of Constructed Wetlands

CWs are multifunctional and ecologically sustainable systems that are specifically engineered to enhance water quality via the utilization of natural processes. CWs have gained recognition for their effectiveness in eliminating traditional pollutants, such as nutrients and organic waste. However, they have also demonstrated potential in mitigating emerging contaminants, including pharmaceuticals, microplastics, and specific biomolecules like antibodies. CWs have the potential to mitigate the presence of toxins through a synergistic interplay of physical, chemical, and biological mechanisms. Nonetheless, the efficacy of the treatment can fluctuate based on various aspects, such as the unique attributes of the contaminant, the configuration of the constructed wetland system, and the precise treatment processes employed.

Antibiotics undergo incomplete metabolism in both humans and animals, resulting in significant quantities of prescribed doses being eliminated through urine and faeces (Binh et al., 2018). Consequently, wastewater serves as a significant pathway for the contamination of antibiotics. Traditional WWTPs are not adequately optimized for the removal of antibiotics, as their design primarily focuses on the elimination of easily biodegradable substances. To investigate the potential of CWs in removing antibiotic resistance genes (ARG), a study was carried out by Tian et al. (2023), specifically oxytetracycline and sulfamethoxazole. In their study, four groups of vertical down-up CWs were constructed and each group will have three parallel experiments with an experiment duration of 77 days: (a) control group, (b) microbial inhibition group, (c) group with no plant but aeration and lastly (d) shading treatment. The schematic diagram of each vertical down-up CW is shown in Figure 2.7. The removal efficiency of COD and TN is as high as 97.8 % and 92.3 %, respectively, at 1 to 10 days. However, the removal rate gradually decreased after the 10th day and remained stable at 84.4 % and 76.6 % after it. For oxytetracycline (OTC) and sulfamethoxazole (SMZ), vertical down-up CWs demonstrated a commendable level of performance in removing OTC and SMZ with a removal rate of 84.3 % and 77.7 %, respectively. Moreover, the calculation of the contribution of each element to antibiotic clearance was based on the principle of conservation of mass. The primary mechanism for the removal of OTC and SMZ was determined to be microbial degradation, accounting for 58.52 % and 65.13 % of the total removal, respectively. Subsequently, photodegradation accounted for 18.47 % and 8.22 %, followed by plant absorption, which contributed 9.01 % and 7.75% respectively. Additionally, substrate adsorption was shown to account for 2.08 % and 1.73 % of the pollutant removal.

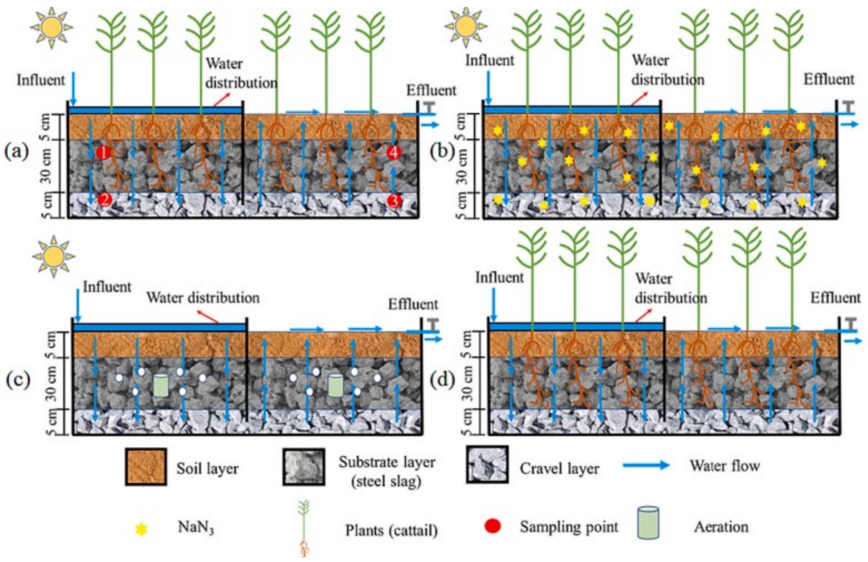

Figure 2.7: Schematic Diagram of Each Group of Vertical Down-up Constructed Wetland.

Similar to antibiotics, the wastewater treatment plant effluents serve as a significant pathway for the introduction of microplastics (MPs) into the aquatic environment, as evidenced by the substantial release of MPs along with wastewater. The study was subsequently undertaken by Rozman, Klun, and Kalčíková (2023) in order to evaluate the effectiveness of MP removal, as well as their distribution and influence on the treatment efficiency of phosphorous, nitrogenous, and carbonaceous materials in a laboratory-constructed wetland (LCW) with a horizontal sub-surface flow. The experiment consisted of four distinct phases. Initially, the plants underwent a process of acclimatization to the controlled laboratory settings. Subsequently, the LCW was utilized for wastewater treatment in the absence of MP. Subsequently, MPs were introduced to the system and prompted an evaluation of the efficacy of the LCW in eliminating MPs, as well as an examination of the influence of MPs on the elimination of carbonaceous, nitrogenous, and phosphorous compounds. Finally, the LCW was dismantled, and a thorough analysis was conducted to investigate the allocation of MPs. Based on the findings, it was seen that a majority of MPs got entangled within the LCW. Furthermore, the analysis revealed that a mere 0.296% and 0.003% of microbeads and fibres, respectively, were observed in the effluent. These results suggest that CWs effectively act as a deterrent, preventing the release of microplastics into the aquatic ecosystem. Rozman, Klun, and Kalčíková (2023) also claimed that the presence of MPs in the wastewater did not affect the removal rate of carbonaceous, nitrogenous, and phosphorous materials.

Other than antibiotics and MPs, the next pollutants that will be discussed are pharmaceutical wastes. Pharmaceutical compounds have been identified in several environmental samples, encompassing sewage, surface water, and groundwater, which are potential drinking water resources. This may relate to the requirements of advanced technology, such as activated carbon and reverse osmosis, to treat the compounds. To prepare an alternative way of pharmaceutical pollutants, a study regarding the efficiency of full-scale hybrid CWs on pharmaceutical compounds was carried out for a duration of 3 years from 2012 (Vystavna, et al., 2017). CWs, in this case, consist of two vertical flow, one horizontal subsurface and one free surface flow. This hybrid CW system had posed a moderate performance with more than 50 % removal in 2012 and 2015. As shown in Figure 2.8, the removal efficiency varied with compounds and duration. The removal rate of propranolol and naproxen was over 80 % in both years studied. Some compounds like caffeine, triclosan and diclofenac were increased to a high removal rate. From Figure 2.8, it can be observed that the removal rate of the interested compound is independent of other variables, which induces a lack of a substantial correlation between the physical and chemical properties of the target compounds and their removal efficiency.

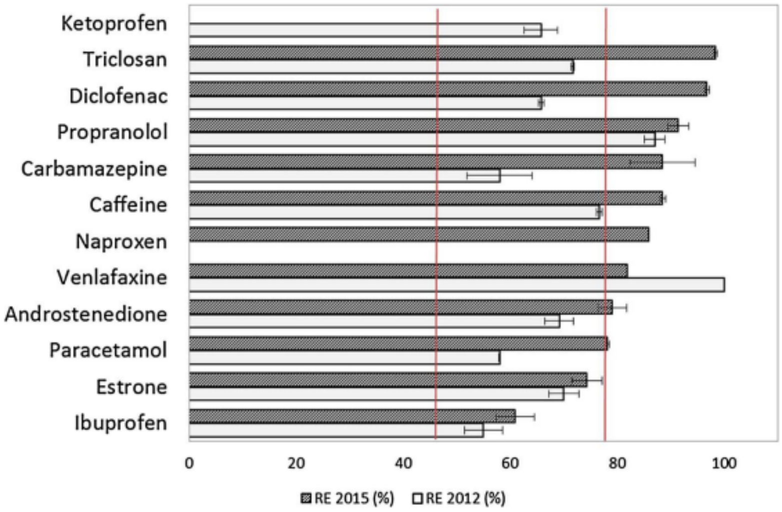

Figure 2.8: Removal Efficiency of Respective Compounds in 2012 and 2015.

2.7 Environmental Impact and Biodiversity of Constructed Wetlands

Within the field of wastewater treatment, there is a significant emphasis on the environmental repercussions and the need to preserve biodiversity, hence promoting the adoption of more sustainable and ecologically balanced approaches. CWs have emerged as a promising solution that combines efficient pollution management with the conservation of natural ecosystems. This following review examines the potential of CWs to act as catalysts for positive change in water quality improvement, habitat establishment, and ecological equilibrium.

To examine the impacts on the ecological environment of CWs, research was carried out to compare the ecological footprint of CWs to a natural wetland (NW), which is adjacent to each other and experiences identical climatic conditions (Zhang, et al., 2022). The emission of greenhouse gases (GHGs) exhibited significant temporal fluctuation in both wetland environments. Notably, there was a substantial release of CH_4 from the CWs, at the range of 0.06 to 1.20 mg/m^{2}h and emissions of CO_2 and N_2O from the natural wetlands at the range of 58.70 to 2087.53 mg/m^{2}h and 0.02 to 3.38 mg/m^{2}h, respectively. It can be implied that the anaerobic conditions in CWs resulting from continuous flooding are likely to lead to increased CH_4 emissions while significantly reducing CO_2 and N_2O emissions. In Figure 2.9, it can be observed that CWs emit around six times more CH_4 than NW but two times and around 12 times less CO_2 and N_2O. Nevertheless, CO_2 produced by the respiration of plants has the potential to be captured through the process of photosynthesis, so establishing a dynamic equilibrium and potentially serving as a reservoir for carbon. Despite the increased emission of CH_4, it effectively enhanced the process of denitrification in its entirety. A significant quantity of N_2O underwent conversion into nitrogen gas, resulting in the inhibition of N_2O emissions.

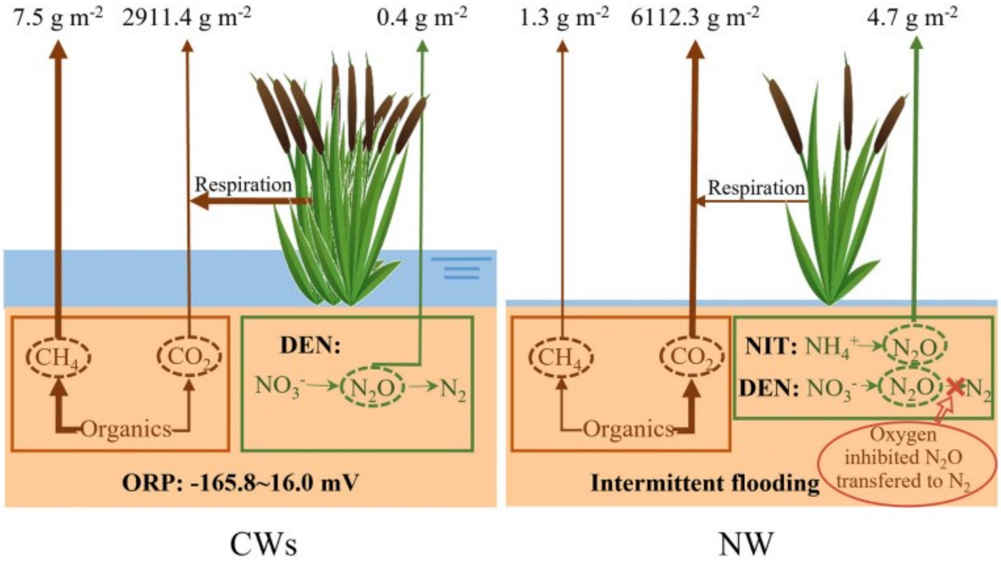

Figure 2.9: Annual GHG Emissions from CWs and NW.

Apart from the comparison between CW and NW, another study was conducted by Carrillo et al. (2023) on the comparison between monoculture and polyculture. In this experiment, a total of six horizontal subsurface flow CWs was constructed, where two were planted with Phragmites australis (Phr), another two were planted with *Schoenoplectus californicus* (Sch), one was planted with *Cyperus papyrus* (Cyp) and last one was planted with *Cyperus papyrus* (Cyp) and *Zantedeschia aethiopica* (Zant). From the result, the polyculture had a greater impact on GHG emissions with the value of 12.2 $kgCO_2eq/m^3$, while the value of monocultures ranged from 1.3 to 8.1 $kgCO_2eq/m^3$. For CH_4 emission, the Cyp/Zant polyculture is 13, 8 and 2 times higher than Phr, Sch, and Cyp, respectively. Based on the findings, it can be posited that the emission of CH4 is influenced by various factors, such as the specific plant species, root type, and composition of bacterial species. The cultivation of polycultures promotes the development of extensive root networks, which in turn give rise to anoxic zones that provide favourable conditions for the proliferation of methanogenic microbes and subsequent emissions of CH_4. Moreover, the outstanding performance of polyculture in phosphorus and nitrogen removal contributed to the reduction of freshwater and marine eutrophication. The implementation of polyculture including Cyp/Zant has resulted in a notable reduction in freshwater eutrophication levels. Specifically, there has been a decrease of 17%, 15%, and 5% in comparison to the monocultures of Phr, Sch, and Cyp, respectively. As for the impact of marine eutrophication, the impact of polycultures was 9 % to 25 % lower than that of monocultures. Figure 2.10 illustrates the normalized result from the life cycle assessment (LCA) of the impact of CW on the environment.

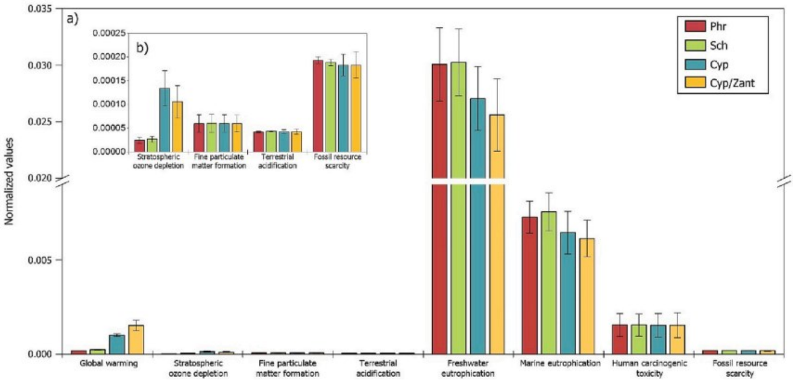

Figure 2.10: Normalization of Interested Impacts of Each Constructed Wetland.

CHAPTER 3

METHODOLOGY AND WORK PLAN

3.1 Flow Chart

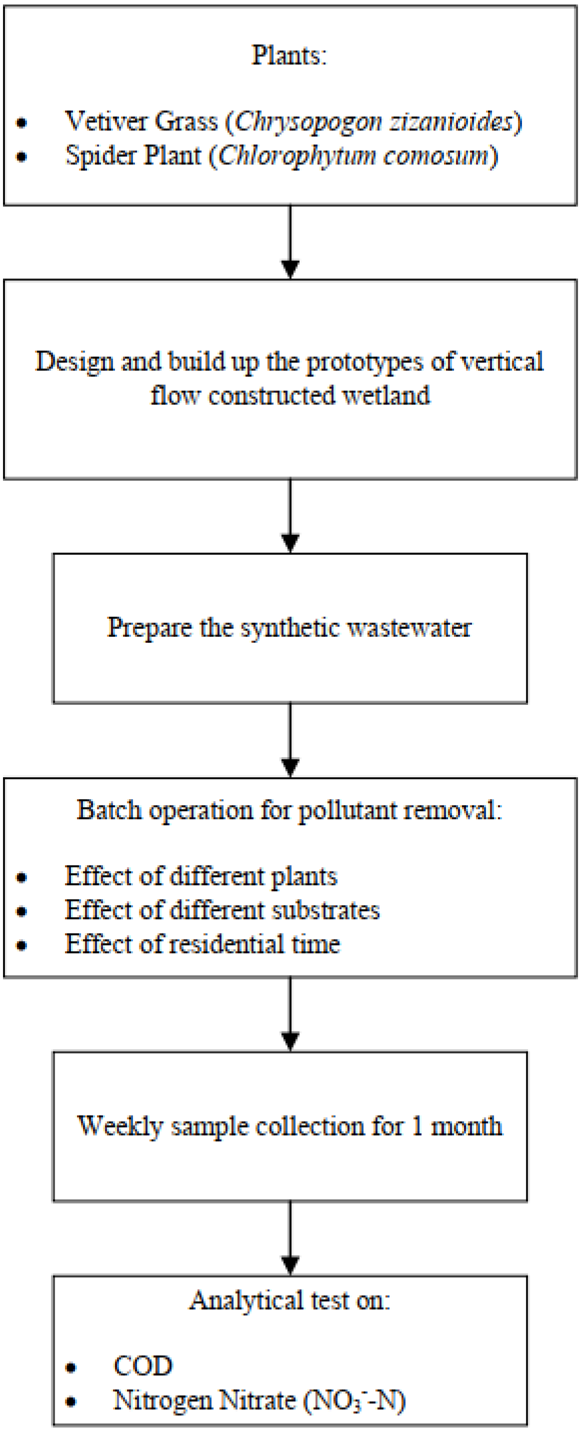

Figure 3.1: Flow Chart of the Work Plan.

3.2 Experiment Set-up

In this experimental study, several preparatory steps must be undertaken prior to executing the experiment. These steps encompassed the cultivation of plants, the design and construction of a prototype, and the preparation of synthetic wastewater.

3.2.1 The Cultivation of Plants

In this experiment, one of the study objectives is to assess the efficacy of different plant species in the removal of pollutants. The selection of vetiver grass (*Chrysopogon zizanioides*) and spider plants (*Chlorophytum comosum*) had been made in order to investigate their potential for contamination removal. Initially, the acquisition of spider plants and vetiver grass was carried out through market transactions. Subsequently, the spider plants and the vetiver grass were sown into different flowerpots. Periodic watering and monitoring activities were conducted to ensure the optimal growth of the plants. The cultivation of these two plants was scheduled to be initiated one week prior to the commencement of the experiment.

3.2.2 Prototypes of Vertical Flow Constructed Wetland

To construct the prototypes of vertical flow CW, a 6-litre mineral water container with a height of 28 cm and an interior diameter of 14 cm was utilised. The container was inverted, and its bottom was removed, but the top of the container, which has a bottleneck with a diameter of 4 cm, remains as the effluent of the system. The uppermost layer of the prototype consists of the plant, while the subsequent layer comprises the soil necessary for the plants to sustain their vitality. The final layer will serve as the substrate for the system. Figure 3.2 displays the schematic diagram of the prototype. In order to mitigate the potential impact of algae growth on the experimental outcomes, the external surface of the prototype was covered with a layer of aluminium foil. This measure aimed to prevent the proliferation of algae, which could lead to an undesirable increase in the COD levels.

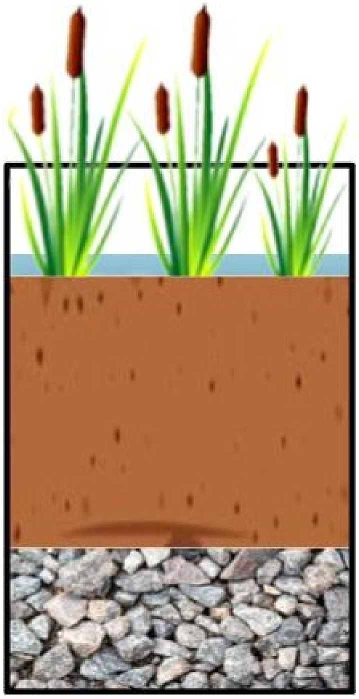

Figure 3.2: Schematic Diagram of the Vertical Flow Constructed Wetland.

3.2.3 The Preparation of Synthetic Wastewater

In this experiment, the source of wastewater was derived from laboratory chemicals. Synthetic wastewater was created by adding tap water with certain concentrations of various compounds and the composition of the compounds is tabulated in Table 3.1. For COD, it is present in the form of glucose, while NH_4Cl is the source of TN. K_2HPO_4 will be the source of phosphate. $MgSO_4{\cdot}7H_2O$, $CaCl_2{\cdot}2H_2O$ and $FeCl_3$ are served as trace elements.

Table 3.1: The Composition of the Wastewater (Chen, et al., 2020).

Chemical Compound	**Chemical Formula**	**Concentration (mg/L)**
Glucose	$C_6H_{12}O_6$	300
Ammonium Chloride	NH_4Cl	48
Potassium Phosphate	K_2HPO_4	12
Magnesium Sulphate Heptahydrate	$MgSO_4{\cdot}7H_2O$	4.5
Calcium Chloride Dihydrate	$CaCl_2{\cdot}2H_2O$	7.3
Ferric Chloride	$FeCl_3$	0.05

The synthetic wastewater was freshly prepared every week. By doing so, the variation in nutrient and organic loading concentrations in wastewater caused by self-degradation or consumption by bacteria entering through exposed air can be avoided. When diluting the stock solution, Equation (3.1) was employed to compute the required extra water volume.

$$C_1V_1 = C_2V_2 \tag{3.1}$$

where,

C_1	=	Concentration of stock solution, mg/L
V_1	=	Volume of stock solution, L
C_2	=	Concentration of diluted solution, mg/L
V_1	=	Volume of diluted solution, L

Sample Calculation

To ease the calculation, the generated synthetic wastewater is 1 L. For one week, the total required wastewater volume for five prototypes will be 49 L.

$$C_1 = \frac{300 \times 49}{1} = 14700\frac{mg}{L}$$

$$C_1V_1 = C_2V_2$$

$$14700(0.1) = 300V_2$$

$$V_2 = 4.9\ L$$

From the calculation above, 100 mL of stock solution can be diluted to 4.9 L. To flood the prototype, 1.4 L of wastewater is required for each prototype. Thus, 7 L of wastewater is required for one day, which means that 200 mL of stock solution is needed.

$$Water\ required\ for\ dilution = 4.9(2) - 0.2 = 9.6\ L$$

9.6 L of tap water is required to dilute 200 mL of stock solution to the desired concentration.

3.3 Design of Experiment

In this experimental study, a total of four vertical flow CW prototypes were constructed. Sets A and B were constructed by combining vetiver grass with various substrates. Sets C and D were created by combining chive plants with various substrates. The design parameters for each set of prototypes are summarized in Table 3.2. One of the purposes of this study is to examine the impact of substrates on pollutant removal, which can be completed by comparing among prototypes. Besides that, a "control" prototype was created solely with soil to compare the situation of a natural environment and a constructed wetland.

Table 3.2: Design Parameters of Each Prototype.

Design Parameters	Set A	Set B	Set C	Set D	Control
Duration			One month		
Vetiver Grass	✓	✓			
Spider Plant			✓	✓	
Soil	✓	✓	✓	✓	✓
Zeolite	✓		✓		
Activated Carbon		✓		✓	

3.4 Analytical Method

In order to assess the effectiveness of vertical flow CW in treating water, the influent and effluent water quality was evaluated by quantifying the concentrations of COD and the concentration of nitrate nitrogen (NO_3^--N). The HACH DR 3900 spectrophotometer was employed as a tool to measure the concentration of COD and $NO3^-$-N parameters.

Figure 3.3: HARCH DR 3900 Spectrophotometer.

3.4.1 Analysis of COD

Method 8000 of the HACH DR 3900 spectrophotometer, which is the reactor digestion method, was implemented to measure the concentration of COD. This method can be further divided based on the concentration of COD. In this instance, a low-range COD concentration of 3 to 150 mg/L was chosen.

In this experimental procedure, this COD test can be separated into two steps: digesting and measuring. At first, the sample was subjected to a two-hour heating process at 150 °C in the presence of sulfuric acid and a potent oxidizing agent, namely potassium dichromate. Organic molecules that are capable of being oxidized undergo a reaction in which they reduce the dichromate ion ($Cr_2O_7^{2-}$) to form the green chromic ion (Cr^{3+}). Eventually, the quantity of Cr^{3+} generated was ascertained. However, some things must be considered, such as the COD digestion reagent containing silver and mercury, which will cause chloride interference.

Figure 3.4: Reactor for Heating Process.

3.4.2 Analysis of Nitrate Nitrogen

To identify the concentration of NO_3^--N, the Method of 8039 of the HACH DR 3900 spectrophotometer, which is the cadmium reduction method, was employed. It is good to know that this method is for high-range concentrations of NO_3^--N, which is able to identify the concentration range of 0 to 30 mg/L.

Initially, 10 mL of water sample was poured into the sample cell and a Nitra Ver 5 Nitrate Reagent Powder Pillow was added to the sample cell. The cadmium metal that was present in Nitra Ver 5 Nitrate Reagent Powder Pillow reduced nitrates in the sample water to nitrite. Then, the nitrite ion (NO_2^-) reacted with sulfanilic acid to produce an intermediate product of diazonium salt, which couples with gentisic acid to yield an amber-coloured product. After a 1-minute vigorous shaking followed by a 5-minute reaction time, the sample cell was ready to be measured.

Since this test is enabled to measure the concentration of nitrogen in nitrate ion, further calculation is not required, and the reading measurement can directly be used to compare with initial nitrogen sources.

3.5 Operation of the Experiment

The duration of this experiment will be 21 days. Other than that, the prototypes were placed outdoors but covered. By doing so, it can ensure that the internal conditions of the prototype are not affected by rainwater, and at the same time, it can carry out photosynthesis as usual.

At day 0, 1.4 L of synthetic wastewater was introduced into the prototypes to allow the microorganism community to adapt to the environment and the conditions of synthetic wastewater. With this action, the phenomenon of nutrient shock can be avoided. Moreover, the time required for drainage of the prototypes was also measured at 30 minutes. Thus, the proposed operation time will be 60 minutes for batch and 30 minutes for dripping to mimic the continuous mode. With this, each prototype will have two sampling times: 60 minutes after submerging and 30 minutes after dripping.

Figure 3.5: Setup for Operation.

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, the discussion of the impact of plant types, substrate types and operation modes on COD removal efficiency was conducted. Moreover, the relationship between COD and nitrification was also studied at the following section. Figure 4.1 shows the COD concentration profile of each prototype for the experiment duration of 21 days. Initially, the control prototype was built solely with soil, with the intention of comparing the planted and unplanted CW. However, the soil has a specific permeability and will become more compact after watering. Compared with other prototypes with more significant porosity in the substrate layer, the control prototype possessed a slow flow rate when dripping, leading to a long contact time between the synthetic wastewater and the microbes in the soil. Besides that, the soil used to build the control prototype was a mixture of loamy soil and sand soil, which had an excellent potential for COD removal. Hence, due to these inequitable conditions of the control prototype, the result of the control prototype is unsuitable to compare with the planted prototype. As mentioned in the previous section, several factors will affect the performance of the constructed wetland. To visualize the comparison, other factors are remained constant while discussing one of the factors in the following discussion.

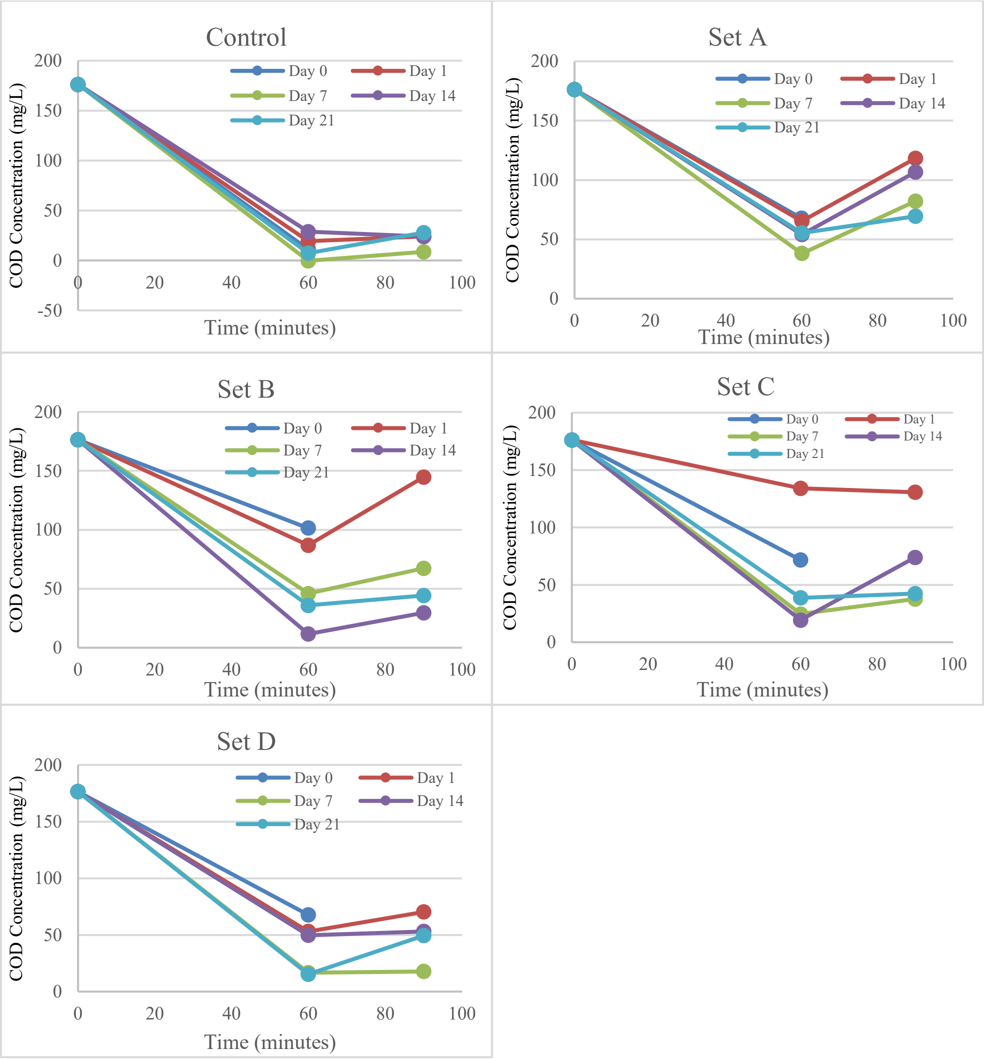

Figure 4.1: Concentration Profile of Each Prototype for 21 Days.

4.1 Establishment of Prototypes

Four major components had to be prepared to build the VF CW prototypes: plants, soil, substrate and the main body of the prototype. In this experiment, a 6 L mineral water bottle was chosen as the main body of the prototype. This is due to the reason that plastic-made water bottles are easy to reshape, and the bottle cap can be further modified to the effluent of the prototype. Besides that, spider plants and loam soil that were rich in biomass were bought from Nursery Yaz San Trading, which is located at Bandar Mahkota Cheras, Selangor. For vetiver grass, it was supplied by Nurseri Melur from Kota Tinggi, Johor. The substrates that were used in this study were purchased from trusted merchandisers through the online shopping platform Shopee.

Starting with the main body of the prototype, 2 cm from the bottom of the water bottle was cut and discarded. After that, the bottle was turned upside down and the bottom of each prototype was filled with the corresponding substrate up to 5 cm from the base, followed by the soil and plants. After filling half of the bottle with soil, the plant was transferred into the bottle and the empty remaining space was filled with soil. For each prototype, the soil was filled up to 2 cm below the top of the bottle. Figure 4.2 illustrates the completed built-up prototypes.

Figure 4.2: VF CW Prototypes.

Other than that, the supports for the prototypes were also made by DIY. The supports are required to ease the moving, transferring and operation throughout the experiment. Initially, woods were collected from the recycling centre. After finishing all the dimension measurements, the supports of the prototype were successfully established with the assistance of the staff of UTAR timber workshop.

Figure 4.3: The Layout of Supports.

4.2 Effect of Plant Types on COD Removal Efficiency

First, the plant types used in constructed wetlands are discussed since they are the primary component of the system. Plant species are essential for the efficiency of constructed wetlands. The selection of plant species greatly affects the efficiency of pollutant removal in these systems. Research from Licata, et al. (2019) has demonstrated that variables like plant species, plant density, and cropping systems can significantly impact the effectiveness of constructed wetlands in wastewater treatment. Hence, choosing the appropriate plant species, as the first step in constructing the wetland, is crucial for enhancing the effectiveness of constructed wetlands in removing pollutants and improving efficiency. To compare the effect of plant types on pollutant removal efficiency, the type of substrate and the residential time are constant. The substrate will be activated carbon and residential time will be 60 minutes in batch mode, as the overall performance of the prototypes under these two conditions is outstanding.

In this instance, Set B and Set D are used to study the impact of different plants on COD removal. From Figure 4.4, it can be seen that Set B had a lower removal rate of 42.53 % at the starting point. Nevertheless, it was gradually increasing to the highest rate of 93.38 % on day 14. For Set D, it achieved a removal rate of 61.63 % on day 0 and reached its peak of 91.30 % on day 21.

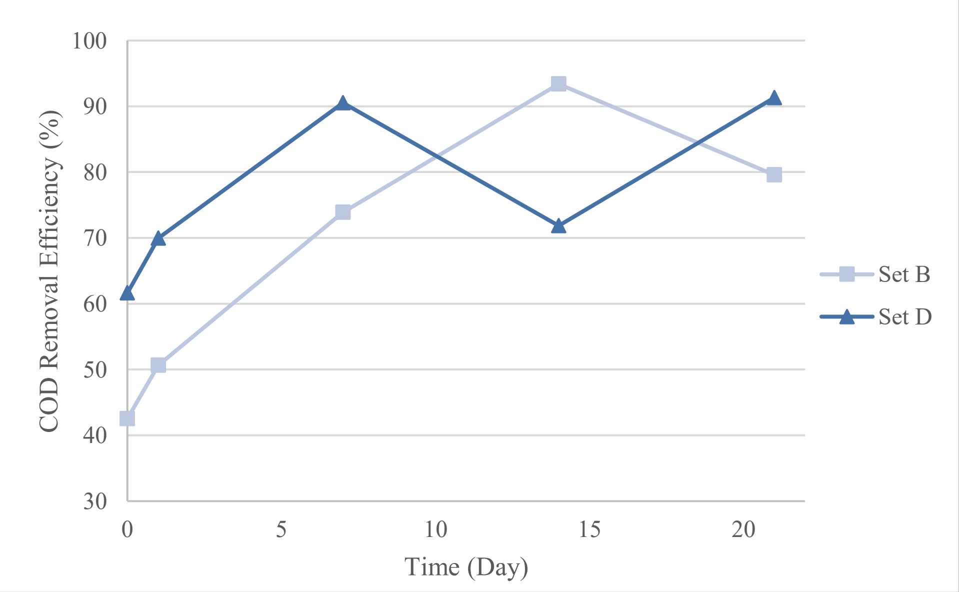

Figure 4.4: Effect of Plant Types on COD Removal.

Meanwhile, it is difficult or unfair to claim that neither prototype has the best performance based solely on their respective removal efficiency statistics. Hence, further processing of the data is required to give a better understanding to compare these two plants in terms of their COD removal capability. In this circumstance, the standard deviation of the removal efficiency of each set of prototypes is calculated with Equation (4.1) and the relevant data is tabulated in Table 4.1.

$$\sigma = \sqrt{\frac{\sum(X_i - \mu)^2}{N}} \tag{4.1}$$

where,

σ = Standard deviation

X_i = The value in the data distribution

μ = The population mean

N = The number of Observations

Taking Set B as a sample calculation, the calculation shall start with the mean and be followed by the standard deviation in Equation (4.1).

$$\mu = \frac{\sum X_i}{N} = \frac{61.63 + 69.94 + 90.55 + 71.83 + 91.30}{5} = 77.11$$

$$\sigma = \sqrt{\frac{\sum(X_i - \mu)^2}{N}}$$

$$= \sqrt{\frac{(61.63-77.11)^2+(69.94-77.11)^2+(90.55-77.11)^2+(71.83-77.11)^2+(91.30-77.11)^2}{5}}$$

$$= 13.2383$$

Table 4.1: COD Statistic of Set B and Set D.

Prototype	**COD (mg/L)**						
	Day 0	**Day1**	**Day 7**	**Day 14**	**Day 21**	**μ**	**σ**
Set B	42.53	50.66	73.91	93.38	79.58	68.02	20.99
Set D	61.63	69.94	90.55	71.83	91.3	77.11	13.24

Mean is a statistical indicator that shows the average value of the data distribution and helps contextualise the data point. In this circumstance, a high value of the mean is pursued as high COD removal efficiency indicates good performance in a particular prototype. Moreover, the standard deviation is used to measure how the value in data distribution deviates from its mean value. In this case, a low standard deviation is sought. This is because a lower standard deviation implies a small range of values, which denotes that the prototype has a stable performance. Considering these two points, Set D, which planted with spider plant, has a better performance in COD removal compared to Set B. Set D has a higher mean value of 77.11 and a lower standard deviation of 13.24, which fulfil two criteria mentioned above.

The higher COD removal rate in set D can be correlated to the root of the spider plant. As can be observed from Figure 4.5, spider plants have dense and fibrous roots that provide a significant surface area for the attachment and growth of microbes. The greater surface area facilitates improved colonisation by microorganisms, which enhances the breakdown of organic pollutants in the rhizosphere. The rhizosphere is a small area of soil affected by root secretions and microorganisms. Spider plants secrete organic compounds known as root exudates into the rhizosphere. Root exudates act as a nutrient supply for a varied group of microorganisms, such as bacteria and fungi, that can break down and process organic contaminants found in the wastewater (Enagbonma, et al., 2023).

Other than that, the activation of rhizospheric microbial metabolism during the electrochemical exchange of spider plants can further aid in COD removal. The prototype itself served the purpose of COD removal and electricity generation simultaneously. The plant’s root system in this prototype acted as a bioanode, supporting the development of microbial communities that can effectively break down organic pollutants (Tou, et al., 2019). Electrical currents produced during electrochemical exchange stimulated the release of root exudates, acting as a carbon source for microbes and boosting their metabolic activity (Korenblum, Massalha and Aharoni, 2022). The interdependent connection among Chlorophytum comosum, rhizospheric microbes, and electrochemical processes results in enhanced COD removal. In a short word, the large surface area for microbes’ communities and the activation of rhizospheric microbial metabolism during electrochemical exchange at Set D has shown good potential in COD removal.

Figure 4.5: The Root Structure of Spider Plant.

4.3 Effect of Substrate on COD Removal Efficiency

After deciding the plant type, the next study will focus on the substrate. A substrate is a substance in a wetland that supports the growth of plants and microbes, assisting in wastewater treatment. The substrate is essential for providing physical support and serving as a carrier for the plants and microorganisms in the biological treatment process in the created wetland. It is a crucial element that enhances the effectiveness of pollution removal in artificial wetlands by promoting the growth of vegetation and microorganisms that aid in wastewater treatment. In this section, Set C and Set D are used to investigate the impact of substrate on COD abatement efficiency.

As can be observed from Figure 4.6, both prototypes, Set C and Set D, have a similar starting point of around the removal rate of 59.36 % and 61.63 %, respectively. However, the removal rate of Set C drastically dropped to 24 %, which has a decrement of more than 50 %. After that, the removal efficiency of Set C was skyrocketing and achieved its maximum at day 14 with a removal rate of 89.04 %. This enormous depletion and augmentation of COD removal rate correlate much to nitrification and denitrification, which will be further discussed in the following section. For Set D, it increased steadily and hit its maximum on day 14 with a removal rate of 91.30 %.

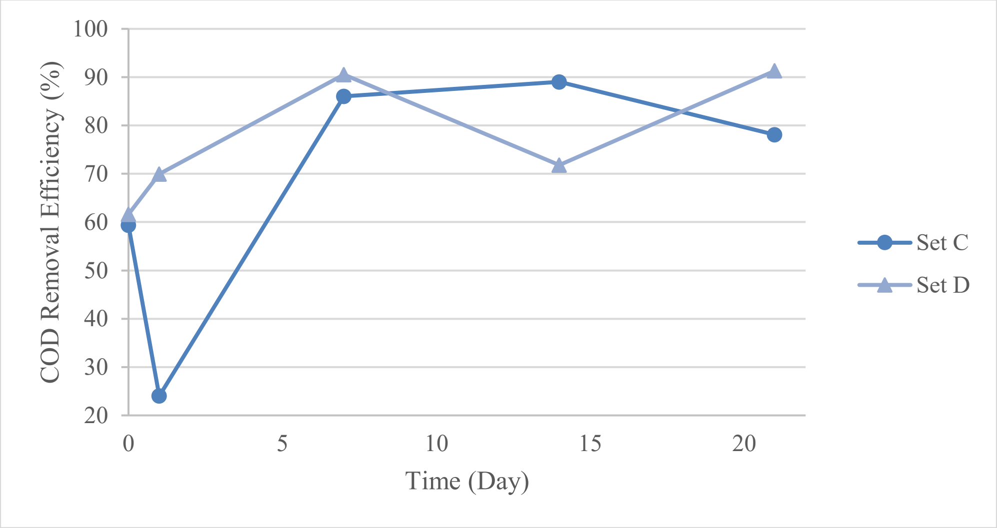

Figure 4.6: Effect of Substrate Types on COD Removal Efficiency.

Similar to the previous section, the mean and standard deviation of the removal rate of each prototype are computed and tabulated in Table 4.2. From Table 4.2, it is suggested that Set D with activated carbon as the substrate, is not only more effective in COD removal but also more consistent in its performance, whereby the mean value is 12.7 % higher than Set C and the stability is as high as double of Set C. The result from this experiment is also aligned with the study from Malekmohammadi, Mirbagheri and Ehteshami (2016), whereby the conclusion that activated carbon is the best adsorbent for COD removal among silica and zeolite was suggested.

Table 4.2: COD Statistic of Set C and Set D.

Prototype	**COD (mg/L)**						
	Day 0	**Day1**	**Day 7**	**Day 14**	**Day 21**	μ	σ
Set C	59.36	24.01	86.01	89.04	78.07	67.30	26.81
Set D	61.63	69.94	90.55	71.83	91.3	77.11	13.24

The distinctive performance between activated carbon and zeolite in COD removal can be explained from several perspectives. In terms of surface area, activated carbon generally has a higher surface area than zeolite, ranging from 500 to 1700 m^2/g (Jiang, et al., 2019). The activated carbon's huge surface area is a result of its porous nature, which offers many adsorption sites. Zeolites have a consistent and orderly pore structure, which may reduce their surface area but enhance their ability to adsorb molecules selectively. From the perspective of structure, activated carbon has a diverse pore structure that includes micropores, mesopores, and macropores, enabling it to adsorb molecules of various sizes (Alves, et al., 2021). Meanwhile, zeolites possess a crystalline structure that results in a consistent pore structure, impacting their ability to interact with specific molecules selectively. Zeolites exhibit selectivity by utilising ion exchange and molecular sieve mechanisms to adsorb certain cations and organic molecules (Tasić, Bogdanović and Antonijević, 2019).

The adsorption capacity and mechanism are often influenced by the surface area and structure. Discrepancies in surface area and structure create a distinction between activated carbon and zeolite. Activated carbon possesses a high adsorption capability for organic and inorganic compounds because of its extensive surface area and intricate pore structure (Alves, et al., 2021). It has the ability to absorb a variety of pollutants, which makes it very efficient in treating wastewater. On the other hand, zeolites also possess a notable adsorption capacity, particularly for specific ions and compounds. The adsorption capacity of natural zeolites is more optimal when the chemical formula has a binary structure, with the central axis being a binary compound (Montaño and Montaño, 2023). From the conception of the adsorption mechanism, activated carbon mostly adsorbs pollutants through physical adsorption, where molecules are attracted to the carbon’s surface by Van der Waals forces and electrostatic forces (Jiang, et al., 2019). Chemical adsorption may take place when molecules create chemical connections with surface functional groups, such as carbonyl, carboxyl, lactone, and phenolic hydroxyl groups (Cai, et al., 2019). Zeolites remove pollutants by utilizing ion exchange and molecular sieving processes. Ion exchange is the process of swapping cations within the zeolite structure with cations in the nearby solution, whilst molecular sieving enables the preferential adsorption of molecules according to their size and shape (Vasconcelos, et al., 2023). In a short word, activated carbon is more versatile and effective in adsorbing a wide range of contaminants due to its surface area and pore structure, while zeolites offer selectivity and efficiency for specific contaminants; thus, zeolites have a poorer performance in terms of COD removal.

4.4 Effect of Operation Mode on COD Removal Efficiency

As mentioned in Section 3.5, there are a total of two sampling times during this experiment: the first hour after submerging and half an hour after dripping. This section focuses on the investigation between contact time and COD removal. Contact time and HRT are interconnected but separate concepts in the realm of CW used for treating wastewater. Contact time and HRT are connected but not always interchangeable due to the intricate flow patterns in wetlands, where water may travel different courses and spend varying amounts of time in different zones. Contact time refers to the unique interaction between water and treatment medium, whereas HRT offers a general measure of water residence duration in the system. As discussed in the previous section, Set D has the best performance among other prototypes, it will be used in the following discussion section.

From Figure 4.1, there is a general trend that the COD concentration in the continuous mode is higher than in batch mode. As mentioned previously, there was a test run of the experiment to let the microbe community adapt to the environment on day 0 to avoid nutrient shock during the following experiment duration; thus, the second sampling was not provided at that moment. From Figure 4.7, the difference between batch and continuous modes was as high as 20 % on day 21. This phenomenon may correlate with the contact time between the synthetic wastewater and the treatment media, such as the rhizosphere zone and substrate layer.

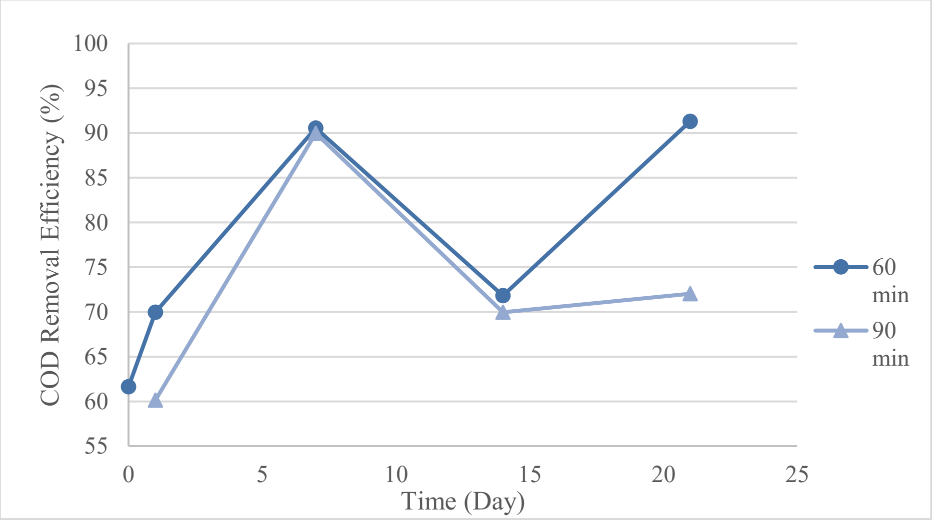

Figure 4.7: Effect of Operation Mode on COD Removal Efficiency.

When the synthetic wastewater was first put into the prototype, it travelled through the plant, the rhizosphere zone, and the soil. Eventually, it arrived at the bottom of the prototype, which is filled with substrate, activated carbon in this instance. After that, the prototype was gradually filled with the synthetic wastewater until it was completely inundated, and the medium was completely submerged for a period of one hour. For the synthetic wastewater that was initially introduced into the prototype, a suitable amount of contact time was provided for the biodegradation or adsorption process to take place during this one hour of immersing the prototype. This is due to the fact that the water that was initially introduced will eventually first reach the rhizosphere zone or the bottom of the prototype, whereby both of them are regions where the pollutants are treated. It was the only place for the remaining synthetic wastewater to remain in the top portion of the prototype because of the accumulation of synthetic wastewater in the rhizosphere zone and at the bottom of the prototype.

The synthetic wastewater that had not been treated was only given the opportunity to come into contact with the treatment medium once the dripping process has begun. Following the fact that the second sampling cut-off time occurs 30 minutes after the commencement of the dripping process and the majority of the water is drained at that moment, it is presumed that the water at the top surface requires 30 minutes to flow through the prototype. In other words, the top surface water only comes into touch with the treatment medium for a length of time that is shorter than 30 minutes.

The performance in the continuous mode is prominent as a short contact time can achieve a significant of COD removal. Table 4.3 shows the statistics of COD removal rate difference between batch mode and continuous mode. The COD removal rate difference between these two operation modes has a mean of 7.89 with a standard deviation of 8.62. The result from this experiment is similar to Abdelhakeem, Aboulroos, and Kamel (2016) and Zhang, et al. (2012), which have a high similarity in terms of geography location and climate with this experiment. To improve the COD removal rate in continuous mode, a series of CW treatments is suggested by Herrera-Melián, et al. (2018). In the study of Herrera-Melián, et al. (2018), there were a total of 3 CWs in the experiment: one horizontal flow CW and two vertical flow CWs. The influent first passed through the horizontal flow CW, followed by the series of two vertical flow CW. The combination of hybrid and series of CW can achieve the COD removal rate as high as 84 %.

Table 4.3: COD Removal Rate Difference Between Batch Mode and Continuous Mode.

COD Difference (mg/L)					
Day1	**Day 7**	**Day 14**	**Day 21**	μ	σ
9.83	0.57	1.89	19.28	7.89	8.62

4.5 Nitrogen Removal in Constructed Wetland

Nitrogen removal involves the process of nitrification and denitrification. In this experiment, ammonium chloride (NH_4Cl) is the source of nitrogen. After adding to the water, NH_4Cl will dissolve to produce ammonium ions (NH_4^+) and chloride ions (Cl^-). After that, the NH_4^+ ion will undergo a series of reactions of nitrification and denitrification, as shown in Equation (4.2) and (4.3), respectively.

$$NH_4^+ \rightarrow NO_2^- \leftrightarrow NO_3^- \tag{4.2}$$

$$NO_3^- \leftrightarrow NO_2^- \leftrightarrow NO \rightarrow N_2O \rightarrow N_2 \tag{4.3}$$

When the nitrification process is carried out under aerobic conditions, the NH_4^+ ion undergoes dissociation, resulting in the formation of nitrite ion (NO_2^-), an intermediate product that is unstable and susceptible to oxidation. Then, NO_2^- ion will be converted into nitrate ion (NO_3^-) with the presence of oxygen in the water. This is due to the fact that nitrate ions are more stable and soluble in water. After this, the ensuing denitrification process, which takes place in anaerobic conditions, will convert the NO_3^- ion to NO_2^- ion once more. Moving on, the denitrification process will be followed by the conversion to nitric oxide (NO) and nitrous oxide (N_2O). Eventually, the nitrous oxide is transformed into nitrogen gas (N_2), which is inert and harmless to the surrounding environment.

Instead of directly measuring the concentration of ammonium ions, the removal of nitrogen by the CW prototype is divided into two parts: nitrification and denitrification efficiency. With this, the concentration of nitrogen can be understood better and provides more insight finding. The nitrification efficiency can be computed by comparing the concentration of nitrogen in NH_4Cl and NO_3^-. The concentration of nitrogen in NH_4Cl can be calculated with Equation (4.4), while the concentration of nitrogen in nitrate ion can be obtained from an analytical test, as stated in Section 3.4.2. From the result of two samplings on each day, the highest concentration of nitrogen in nitrate is chosen to represent the peak of nitrification on a particular day. Meanwhile, the denitrification efficiency can be determined by comparing the nitrification efficiency on that particular day. The difference between the highest and lowest concentrations of nitrogen in nitrate on a particular day is used to measure the extent of denitrification. The efficiency of nitrification and denitrification can be computed with Equation (4.5) and (4.6), respectively. Another thing to highlight is that the values for calculations are extracted from Appendix B.

As mentioned previously, prototype Set D has the best performance in COD removal, and it can also be employed to explain nitrogen removal in the following section. Figure 4.8 shows the nitrification, denitrification and COD removal efficiency of each day, while Figure 4.7 illustrates the overall concentration profile of COD and nitrate ions.

$$N_{NH_4Cl} = \frac{MW_N}{MW_{NH_4Cl}} \times C_{NH_4Cl} \tag{4.4}$$

$$Nitrification\ Efficiency\ (\%) = \frac{N_{NO_3^-}}{N_{NH_4Cl}} \times 100\ \% \tag{4.5}$$

$$Denitrification\ Efficiency\ (\%) = \frac{N_{NO_3^-\,Highest} - N_{NO_3^-\,Lowest}}{N_{NO_3^-\,Highest}} \times 100\ \% \tag{4.6}$$

<u>Sample Calculation</u>

From Table 3.1, the concentration of ammonium chloride is 48 mg/L.

$$N_{NH_4Cl} = \frac{MW_N}{MW_{NH_4Cl}} \times C_{NH_4Cl} = \frac{14.01}{53.49} \times 48 = 12.57 \frac{mg}{L}$$

From Appendix B, on day 1, the highest and lowest nitrogen concentrations in nitrate are 2.4 and 1.9 mg/L, respectively.

$$\begin{aligned} Nitrification\ Efficiency\ (\%) &= \frac{N_{NO_3^-}}{N_{NH_4Cl}} \times 100\ \% \\ &= \frac{2.4}{12.57} \times 100\ \% \\ &= 19.09\ \% \end{aligned}$$

$$\begin{aligned} Denitrification\ Efficiency\ (\%) &= \frac{N_{NO_3^-\,Highest} - N_{NO_3^-\,Lowest}}{N_{NO_3^-\,Highest}} \times 100\ \% \\ &= \frac{2.4 - 1.9}{2.4} \times 100\ \% \\ &= 20.83\ \% \end{aligned}$$

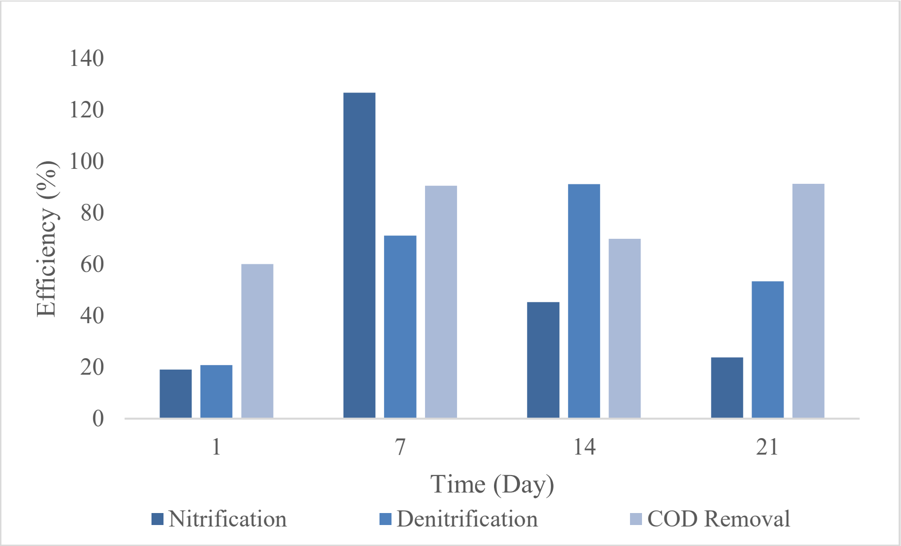

Figure 4.8: Nitrification, Denitrification and COD Removal Efficiency.

As shown in Figure 4.8, the nitrification efficiency ranges from 19.09 % to 126.75 %. The nitrification efficiency of over 100 % advocates that the nitrogen content in synthetic wastewater does not solely consist of ammonium chloride. The potential nitrogen content is suspected to originate from the tapping water when diluting the concentrated synthetic wastewater. On the other hand, the denitrification efficiency has a starting point of 20.83 % and gradually increased to its peak of 91.23 % on day 14. Considering the findings, it is possible to infer that the CW have a significant capacity for nitrogen elimination.

As depicted in Figure 4.9, an overall trend of nitrate concentration was increased when COD concentration decreased. This situation could be attributable to nitrifying bacteria being outcompeted by the heterotrophs over oxygen. As mentioned previously, the nitrification process is an aerobic reaction which requires oxygen by nitrifying bacteria to oxidize ammonium ions to nitrate ions. From Paśmionka, et al. (2022) and Achak, Barka and Lamy (2023), that the nitrification activity was diminished when the COD loading got larger. At high organic pollutant loading circumstances, the heterotroph bacteria will rapidly consume the dissolved oxygen available to degrade the organic pollutants under the biodegradation process. Under the scenario of limited dissolved oxygen, the nitrifying bacteria are frequently beaten by the heterotrophic microorganisms and result in low nitrification efficiency. A similar finding is proposed by Kan, et al. (2023), whereby generalist species flourish in environments with plentiful resources, but specialists become more competitive as resources become scarce. To put it concisely, the nitrification activity of nitrifiers decreases as organic input increases due to competition for oxygen and space with heterotrophs. Hence, it can be expected that the nitrification process will initiate at the low COD location, such as at the bottom of the prototype. The decreasing trend between day 7 and day 14 advocated the denitrification process with the presence of denitrifying bacteria in CW. It is suggested that anaerobic place such as the bottom of the prototype provides a suitable environment for the growth of denitrifying bacteria. As the absent of oxygen, the denitrifying bacteria will use nitrate as an alternative electron acceptor for respiration. Thus, the existence of aerobic and anaerobic conditions in CW has allowed the simultaneous processing of nitrification and denitrification.

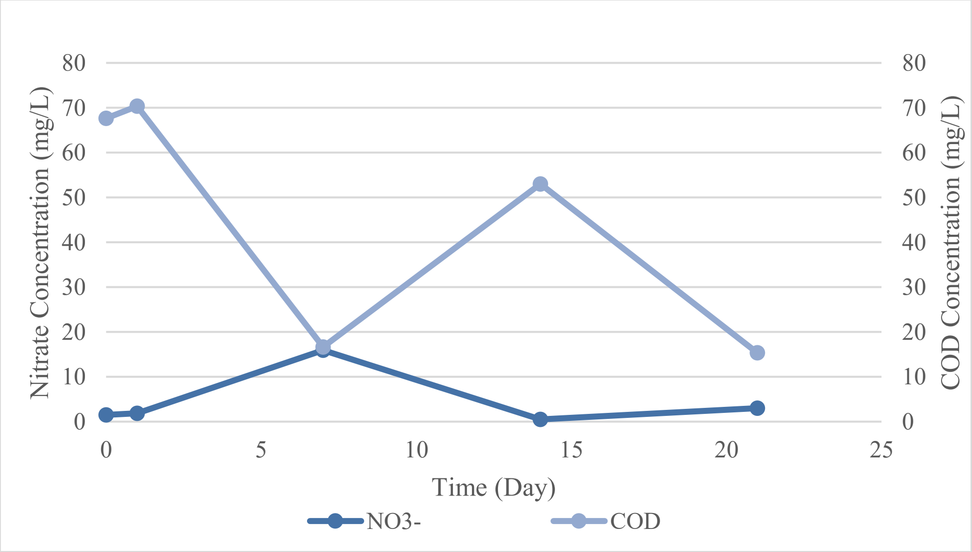

Figure 4.9: Overall Concentration Profile of Nitrate and COD.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this study, the impact of plant types, substrate types and operation modes were investigated through prototypes of the VF CW.

Based on the COD removal efficiency, spider plants (*Chlorophytum comosum*) have a better performance compared to vetiver grass (*Chrysopogon zizanioides*), with an average removal rate of 77.11 % and a standard deviation of 13.24 %. The outstanding performance of spider plants can be related to their dense and fibrous root structure, which provides a large surface area for the attachment and growth of microbes. The electrochemical exchange of spider plants further stimulates the release of root exudates, boosting the metabolic activity of microorganisms. From this statement, the presence of exoelectrogens in the prototype can also be deduced.

Furthermore, a diverse pore structure, high surface area and high absorption capability make activated carbon perform better in COD removal. Meanwhile, zeolite, which exhibits high selectivity by ion exchange process, has a poorer performance in COD removal. In terms of operation mode, batch mode performs slightly better than continuous mode. The interesting finding is that the result from the continuous mode is significant. This is because the average difference in COD removal rate between batch and continuous mode is just 7.89 %, but the contact time for continuous mode is 50 % less than that of batch mode. Moreover, the nitrification and denitrification efficiency range from 19.09 % to 126.75 % and 20.83 % to 91.2 %, respectively. The happening of these two processes induces the CW to be composed of two different environments: an aerobic zone for nitrifying bacteria and an anaerobic zone for denitrifying bacteria.

Overall, the planned objectives were achieved. The outstanding performance of organic pollutant removal of CW suggests it could be included in the existing WWTP in Malaysia to give a better and cleaner water supply to Malaysian.

5.2 Recommendations for Future Work

The experiment was successfully conducted in accordance with the predetermined objectives and scopes. However, further recommendations are proposed to enhance future research endeavors for a greater level of result.

1. The experiment duration must be extended to assess the stability of CW in wastewater treatment over time, mirroring real-world demands. It allows for the observation of long-term performance, microbial community dynamics, and the impact of seasonal variations on treatment efficiency.
2. To achieve a comprehensive understanding of CWs' operating conditions in wastewater treatment, the investigating on parameters such as pH, temperature, HRT and HLR must be caried out. These factors directly impact the efficiency and performance of CW systems, providing valuable insights for their optimization and effective long-term operation.
3. To enhance relevance and applicability of the research to existing WWTP, it is recommended to investigate additional pollutants like phosphorus, PPCP and heavy metals. Understanding the removal efficiency of these pollutants in constructed wetlands can help integrate CW systems into existing WWTPs more effectively, improving overall treatment performance.
4. Characteristics test of the substrate, such as SEM, is suggested to conducted as it provides valuable insights into how its morphology impacts pollutant removal. By studying the substrate's physical and chemical properties, such as porosity, surface area, and nutrient content, researchers can better understand its role in enhancing pollutant removal efficiency.
5. Further study focusing on the continuous mode of operation is crucial as it simulates real-world scenarios where constructed wetlands need to handle large volumes of wastewater continuously. This approach would provide valuable insights into the long-term performance, stability, and scalability of

constructed wetlands for practical applications in wastewater treatment.

6. Focusing future studies on constructed wetlands planted with a mix of plants and using a mix of substrates could provide valuable insights into enhancing pollutant removal efficiency. This approach may mimic natural wetland ecosystems more closely and offer improved treatment performance for various types of wastewaters.

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APPENDICES

Appendix A: Effluent COD Concentration of Each Prototype

		Control	**Set A**	**Set B**	**Set C**	**Set D**
Day 0	Sampling 1	11	101.33	67.67	71.67	67.67
Day 1	Sampling 1	19.33	65.33	87.00	134.00	53.00
	Sampling 2	24.00	118.33	144.67	130.67	70.33
Day 7	Sampling 1	-0.33	38.00	46.00	24.67	16.67
	Sampling 2	8.67	82.00	67.33	37.67	17.67
Day 14	Sampling 1	29.00	54.00	11.67	19.33	49.67
	Sampling 2	24.00	106.67	29.67	74.00	53.00
Day 21	Sampling 1	7.33	55.33	36.00	38.67	15.33
	Sampling 2	28.00	69.33	42.33	44.33	49.33

Appendix B: Effluent NH_3^--N Concentration of Set D Prototype

		Control	**Set D**
Day 0	Sampling 1	46.2	1.5
Day 1	Sampling 1	10.2	1.9
	Sampling 2	10.8	2.4
Day 7	Sampling 1	1.2	15.933
	Sampling 2	1.4	4.6
Day 14	Sampling 1	0.4	0.5
	Sampling 2	0.3	5.7
Day 21	Sampling 1	0.6	3
	Sampling 2	0.8	1.4