Hybrid System Up-Flow Constructed Wetland Integrated with Microbial Fuel Cell for Simultaneous Wastewater Treatment and Bioelectricity Generation

by

OON YOONG LING
(1441211448)

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LIST OF ABBREVIATIONS

AO7	Acid Orange 7
AR18	Acid Red 18
ABRX3	Reactive brilliant red X-3-B
B	Boron
CE	Coulombic efficiency
CO_2	Carbon dioxide
COD	Chemical oxygen demand
CR	Congo Red
CW	Constructed wetland
CW-MFC	Constructed wetland integrated with microbial fuel cell
DO	Dissolved oxygen
e^-	Electron
GC-MS	Gas chromatograph-mass spectrometer
GAC	Granular activated carbon
H^+	Proton
HF	Horizontal flow
HPLC	High-performance liquid chromatography
HRT	Hydraulic retention time
HSSF	Horizontal subsurface flow
MB	Methylene Blue
MO	Methyl Orange
MFC	Microbial fuel cell
NA	Naphthionic acid
NB	Nitrobenzene
NER	Normalised energy recovery
ORP	Oxidation reduction potential
RO	Research objective
SA	Sulfanilic acid
SMX	Sulfamethoxazole
SSF	Subsurface flow
TC	Tetracycline
TN	Total nitrogen
UFCW-MFC	Up-flow constructed wetland integrated with microbial fuel cell
UV-Vis	Ultraviolet-Visible
VF	Vertical flow

LIST OF SYMBOLS

%	Percent
b	Number of electrons donated per mole of acetate
°C	Degree Celsius
Ω	Ohm
C_{eff}	COD concentration of effluent
C_{inf}	COD concentration of influent
cm	Centimetre
cm^2	Square centimetre
C_x	Quantity of removed organic matter at sampling point
F	Faraday’s constant
g/L	Gram per litre
I	Current
L	Litre
L/mg/h	Litre per milligram per hour
M	Molecular mass
mg/L	Milligram per litre
mg/L/h	Milligram per litre per hour
mL/min	Millilitre per minute
mm	Millimetre
mL	Millilitre
mWh/m^3	Milliwatt hour per cubic meter
mWh/kg COD	Milliwatt hour per COD kilogram
P	Power
Q	Flow rate
R^2	Correlation coefficient
Q_{eff}	Volume of effluent
Q_{inf}	Volume of influent
V	Voltage

Sistem Hibrid Paya Tiruan Aliran Atas Bersepadu dengan Sel Bahan Api Mikrob untuk Rawatan Air Sisa dan Penjanaan Bioelektrik Serentak

ABSTRAK

Pencemaran alam sekitar terutamanya pencemaran air dan krisis tenaga adalah dua cabaran besar yang dihadapi oleh dunia kita pada masa kini. Fenomena ini telah mendorong penerokaan teknologi rawatan air sisa yang lestari untuk menangani kedua-dua cabaran. Penyelidikan tesis ini bertujuan untuk membangunkan sistem hibrid, yang merupakan gabungan paya tiruan aliran atas dengan bahan api mikrobial (UFCW-MFC) untuk rawatan air sisa dan penjanaan bioelektrik secara serentak. Objektif utama kajian ini adalah untuk mengkaji kebolehlaksanaan, prestasi dari segi rawatan air sisa dan penjanaan bioelektrik, peranan tumbuhan paya, prinsip kerja dan mekanisme dalam UFCW-MFC. Enam reaktor hibrid telah dibina untuk sesiri kajian sistematik. Kecerunan redoks dalam reaktor sesuai untuk proses pengoksidaan dan pengurangan dan ia juga diperlukan oleh MFC untuk anod anaerob dan katod aerobik. Penyelidikan ini menunjuk bahawa sistem litar tertutup meningkatkan penguraian bahan organik, denitrifikasi dan pengingkiran warna dan ini juga menunjukkan bahawa integrasi MFC ke CW dapat mencapai kecekapan rawatan yang lebih tinggi daripada sistem CW dan MFC yang tunggal. Selain itu, tumbuhan mendorong penjanaan bioelektrik berbanding sistem tiada tumbuhan. Tumbuhan mengangkut oksigen ke rantau katod melalui proses fotosintesis. Peningkatan kepekatan natrium klorida meningkatkan kekonduksian dan justeru meningkatkan penjanaan kuasa. Selain itu, kajian menunjukkan bahawa pengudaraan mempengaruhi prestasi kuasa lebih daripada kekonduksian elektrolit. Pengudaraan secara berjeda pada kadar 600 mL/min adalah optimum untuk penyingkiran tuntutan oksigen, nutrien dan pemulihan tenaga. Pengangkutan elektron di UFCW-MFC dalam keadaan kehadiran pelbagai penerima elektron (anod, pewarna azo dan nitrat) telah dikaji. Kehadiran pelbagai pencemar yang merupakan penerima elektron di rantau anod, bersaing untuk elektron dan penerima elektron yang paling effectif adalah nitrat, diikuti dengan pewarna azo dan anod. Selain itu, pengaruh struktur molekul azo pewarna pada kadar penyingkiran warna dan penjanaan bioelektrik dikaji dengan menggunakan *Acid Red 18* (AR18), *Acid Orange 7* (AO7) dan *Congo Red* (CR). Kadar penyahwarnaan tertinggi diperolehi oleh AR18 (96%), diikuti dengan AO7 (67%) dan CR (60%). Kuasa pengeluaran juga mengikuti tren tersebut. Kadar penyahwarnaan yang lebih tinggi dalam AR18 adalah disebabkan oleh *tautomerisme*, bilangan ikatan azo yang rendah, kumpulan penarikan elektron yang lebih tinggi dan kedudukan elektron yang mengeluarkan substituen kumpulan pada posisi *para* kepada ikatan azo. Tambahan pula, lintasan penguraian pewarna azo dicadangkan dan dijelaskan berdasarkan produk perantara pewarna masing-masing yang dikenalpasti melalui analisis spektrofotometer UV-Vis, kromatografi cecair prestasi tinggi dan spectrometer massa kromatografi gas. Keputusan menunjukkan bahawa pewarna-pewarna diurai di kawasan anod anaerobik dan perantaraan pewarna dimenaralisasikan di rantau katod aerobik kepada produk yang kurang berbahaya atau tidak toksik.

Hybrid System Up-Flow Constructed Wetland Integrated with Microbial Fuel Cell for Simultaneous Wastewater Treatment and Bioelectricity Generation

ABSTRACT

Environmental pollution, particularly water pollution and energy crisis, are two significant challenges that our world is facing nowadays. This phenomenon has driven the exploration of sustainable wastewater treatment technology to address both challenges hand in hand. This thesis aimed to develop a hybrid system, which is up-flow constructed wetland integrated with microbial fuel cell (UFCW-MFC) for simultaneous wastewater treatment and bioelectricity generation. The main objectives of the study were to investigate the feasibility, performance in terms of wastewater treatment and bioelectricity generation, the role of wetland plant, working principle and mechanism in UFCW-MFC. Six hybrid reactors were developed for a series of systematic study. Redox gradient present along the wetland bed was suitable for oxidation and reduction processes, and at the same time, they are needed by MFC as anaerobic anode and aerobic cathode. The present study revealed that the closed circuit system enhanced the organic matter degradation, denitrification and decolourisation, which inferred that the integration of CW into MFC can achieve higher treatment efficiency than CW and MFC standalone system. Besides that, the presence of plant achieved more promising result in bioelectricity generation compared to plant-free system. Wetland plant significantly contributed oxygen to the cathodic region through photosynthesis process. The increased sodium chloride concentration increased the conductivity and subsequently improved power generation. Furthermore, the study showed that aeration influenced power performance more than the electrolyte conductivity. The intermittent aeration at the rate of 600 mL/min found to be optimum for COD, nutrient removal and energy recovery. The fate of electron transport in UFCW-MFC in the presence of multiple electron acceptors (anode, azo dye and nitrate) was investigated. The presence of various pollutants, which are electron acceptor in anodic region, competed for electron and the most favourable electron acceptor in the study was nitrate, followed by azo dye and anode. Moreover, the influence of azo dye molecular structure on decolourisation rate and bioelectricity generation was investigated by using Acid Red 18 (AR18), Acid Orange 7 (AO7) and Congo Red (CR). The highest decolourisation rate was obtained from AR18 (96%), followed by AO7 (67%) and CR (60%). The power output also followed such trend. The higher decolourisation rate in AR18 was due to tautomerism, lower number of azo bond, more electron withdrawing groups and the position of electron withdrawing group substituent at *para* position to azo bond. Moreover, the degradation pathways of azo dyes were proposed and elucidated based on the respective dye intermediate products identified through UV-Vis spectrophotometry, high-performance liquid chromatography and gas chromatograph–mass spectrometer analyses. The results indicated that the dyes were decolourised at the anaerobic anodic region, and dye intermediates were further mineralized at the aerobic cathodic region to less harmful or non-toxic products.

CHAPTER 1 : INTRODUCTION

1.1 Research Background

According to the United Nation World Population Prospects 2017, the world population is projected to reach 8.6 billion in 2030 (UN-DESA, 2017). As the world population grows the demands for both water and energy rises faster than ever (Olsson, 2012). Water and energy are inevitably related. In order to tackle water issues, energy is required to treat wastewater and to transport water. While to generate electrical energy, a considerable amount of water is needed. Energy, water and environmental sustainability are interconnected and are important not only to the economy but to the health and wellbeing of all humankind (Olsson, 2015). Currently, more than 80 % of global energy consumption comes from fossil fuels (IEA, 2018).

In recent years, the use of fossil fuels, especially oil and gas, has accelerated, and this triggers a global energy crisis. Another problem of using fossil fuels is the emissions of greenhouse gasses, which is closely linked to climate change and global warming. Renewable bioenergy is regarded as one of the approaches to alleviate the current global warming crisis. Apart from the ever-increasing of energy demand and depletion of fossil fuel, rapid urbanisation and intensified industrialisation have also contributed to the increasing waste generation. A massive quantity of waste and wastewater is continuously being produced from various domestic and industrial activities, and the volume has increased over time as a result of rapid and sustained development (Venkata Mohan, 2014).

The global crisis such as fossil fuels depletion, environmental deterioration, water and other resource scarcities have been the driving force for sustainable treatment and utilisation of wastewater (Gude, 2016). In view of the above issues, biological processes are preferred to treat waste because of their simple, cost-effective, and environmental-friendly nature. Besides that, current wastewater treatment systems design and operation has transformed from removing the pollutants to recovering resources and minimising energy consumption and maximising the energy recovery.

Among biological treatment technologies, constructed wetlands (CWs) appear to be an attractive, clean and green technology alternative for wastewater treatment. CWs is also known as treatment wetlands that have been designed to utilise the natural processes involving wetland soils, vegetation, and microbes for wastewater treatment (Vymazal, 2014). CWs are designed and constructed to mimic and obtain the benefit of the physical, chemical, and biological processes occurring in natural wetlands. In 1952, the ability of wetland plants to treat wastewater was first demonstrated by Dr Käthe Seidel at the Max Planck Institute in Plon, Germany. In 1967, the first free water surface CW was built in the Netherland, and later the first subsurface flow CW was built for municipal wastewater treatment in Liebenburg-Othfresen, Germany in 1974 (Vymazal, 2019). The low external energy requirement, low construction, maintenance cost and easy operation of CW have led to an increase in its popularity. Traditionally, CWs have been used for sewage treatment, but since the late 1989s, CWs have significantly expanded its application to a variety of wastewater such as agriculture wastewater, landfill leachate, industrial wastewater, stormwater runoff, domestic wastewater and et cetera (Vymazal, 2009; Bakhshoodeh, Alavi, Majlesi, & Paydary, 2017; Vymazal, 2014; Lucas, Earl, & Babatunde, 2014; Mburu et al., 2013). Over the years, CWs have been further improved to enhance the treatment performance as CW can also be seen as a passive system that presents some limitations to meet the requirement of the effluent quality. The design and operational strategies that have been introduced to the system are plant selection, pre-treatment, pH adjustment, effluent recirculation, additional of organic carbon source, artificial aeration, bio-augmentation and wetland integration (H. Wu et al., 2015; Wu, Kuschk, Brix, Vymazal, & Dong, 2014).

Recently, microbial fuel cell (MFC) has garnered extensive attention as a promising technology to achieve sustainable wastewater treatment and renewable energy production. MFC is an emerging technology that utilises wastewater as fuel for electrical current generation through microbial catabolism process. The concept of MFC can be traced back in 1911, where Michael C. Potter demonstrated that electricity generation could achieve with the decomposition of organic by using *Escherichia coli* culture (Potter, 1911). The recent energy crisis and increasing awareness of global warming have shed light on this technology again. MFC offers an interesting solution to solve energy and water issues. Generally, MFC consists of anode and cathode, which placed in the anaerobic compartment and aerobic compartment, respectively. MFCs have been used to treat various type of wastewater, ranging from domestic, agriculture, industrial wastewater (Pandey et al., 2016). However, there were some critical reviews concerning the scaling up for practical application in terms of the technical and economic viability of this technology (Li, Yu, & He, 2014).

The concept of harvesting energy from waste has gained massive global attention as it can address the global environmental issue with a more sustainable approach. The exploration of sustainable wastewater treatment technology has driven the integration of MFC into CW. The first novel design of CW-MFC was demonstrated by Yadav, Dash, Mohanty, Abbassi, & Mishra (2012) for simultaneous dye removal and electricity generation. CW-MFC was constructed based on the similarity traits of both technologies. The primary motivation of such integration is both CW and MFC systems consist of anaerobic and aerobic regions, where oxidation and reduction processes occurred, respectively. The incorporation of MFC into CW was commenced to improve the treatment performance of CW (Yadav et al., 2012; Srivastava, Yadav, & Mishra, 2015). The rationale of this integration is to provide extra electron acceptor in the form of conductive material (anode electrode) in the anaerobic region of the CWs to stimulate the anaerobic reaction (Yadav et al., 2012). Such hybrid system has been gaining tremendous interest due to its ability in enhancing the performance of CW and the potential of bioenergy recovery from MFC (Xu, Zhao, Doherty, Hu, & Hao, 2016; Fang, Song, Yu, & Li, 2016; Oon et al., 2016).

Treatment of nutrient and azo dyes containing wastewater are important as the discharge of these contaminants will cause serious environmental problem. Dyes have been broadly utilised in various industries such as textile, cosmetics, food, plastic and paper printing (Pandey, Singh, & Iyengar, 2007). Among synthetic dyes, azo dyes are the most extensively used and versatile class of dyes, which contribute to more than 50% of the production of the dye worldwide annually (Solanki, Subramanian, & Basu, 2013). The dyes containing azo group are highly stable owing to the complexity of aromatic structure as well as the covalent azo bonds. During the dying process, a considerable quantity of azo dye lost in the wastewater and the discharge of azo dye-containing waste effluent without appropriate treatment is highly undesirable as it would pose a severe threat to the ecosystem and human health (Fatima, Farooq, Lindström, & Saeed, 2017; Solanki, Subramanian, & Basu, 2013). Due to the refractory nature of the azo dye, complete degradation of azo dye is always a challenge. Generally, the decolourisation of azo dye was accomplished anaerobically; however, the colourless aromatic amine formations resist further degradation under anaerobic environment. Therefore, sequential anaerobic and aerobic process strategy has been proposed for more effective biodegradation process (Van Der Zee & Villaverde, 2005). The adaptation of sequential anaerobic-aerobic process in constructed wetlands was demonstrated by Ong, Uchiyama, Inadama, Ishida, & Yamagiwa (2010) for recalcitrant pollutant azo dye treatment. Now, the potential of CW-MFC for dye remediation is worth exploring (Fang, Cheng, Wang, Cao, & Li, 2017; Oon et al., 2018).

1.2 Problem Statement

Constructed wetland (CW) and microbial fuel cell (MFC) are two potent technologies that could address the water pollution and energy shortage issues; however, there are some limitations in the conventional CW and MFC standalone system. CWs are widely used, and they have emerged as one of the sustainable technologies for wastewater treatment, including domestic, industrial, urban and agriculture (Srivastava et al., 2015). Nevertheless, the treatment process of CW in the anaerobic condition is relatively slow. Bioelectrochemical systems research has soared extensively as an emerging sustainable technology for simultaneous wastewater treatment and electricity production (Bajracharya et al., 2016), but MFC standalone systems are rarely tested in field level and still face some challenges for real-world application. A more effective synergy hybrid technology is needed to overcome the shortcomings of the mentioned technologies.

The study of Białowiec, Davies, Albuquerque, & Randerson, (2012) showed that wetland plant could affect the redox potential of the subsurface flow CW, while Vymazal, (2011) reported that the oxygen released from the root is arguably limited in horizontal CW. The wastewater treatment performance in CW with the presence of the wetland plant has been ambiguous. Despite wetland plant being part of the significant components in CW; the assessment on wetland plant in CW-MFC studies is still limited, and the role of the plant on power generation remained the least explored topic.

Dissolved oxygen is one of the primary factors that can directly influence the efficiency of pollutant removal in CW. CWs, which mostly consist of anoxic and anaerobic wetland bed, exhibit a limited capacity for ammonia removal. The lack of aerobic condition in the CW system should be addressed appropriately to enhance the efficiency of the treatment system. Apart from that, from the perspective of MFC, oxygen is used as the terminal electron acceptor for bioelectricity production. Nevertheless, artificial aeration in a treatment system can be energy intensive. Therefore providing optimum airflow rate is vital to achieve the optimum treatment performance and avoid energy wastage over the excess supply.

Wastewater from textile processing and dye-stuff manufacture industries is known to contain a considerable amount of salts in azo dye residues, and nitrate is usually presented in saline textile wastewater as it is a common salt species added to the dye bath to enhance dye fixation (Carliell, Barclay, Shaw, Wheatley, & Buckley, 1998).

The azo dye degradation in nitrate-rich condition has not been explored in CW-MFC. The interaction between multiple contaminants in the hybrid system has not been studied. Interestingly, azo dye, nitrate and anode co-exist as electron acceptors in CW-MFC, and the simultaneous decolourisation, denitrification and bioelectricity generation within CW-MF can be rather complicated and not well understood. The electron transfer pathway in the anodic region is worth exploring as it could influence the performance of CW-MFC.

Due to the refractory nature of the azo dye, the mechanism of azo dye degradation is still a topic of discussion as complete degradation in a single system is always a challenge~~.~~ Hitherto, studies on the dye degradation mechanism involved in CW-MFC is limited, and the degradation pathway is not well understood. Furthermore, since CW-MFC development is still in its infancy, there is also a notable gap in the literature regarding the long term effectiveness of CW-MFC in treating different pollutants.

1.3 Research Objectives

The main objective of this research was to design and evaluate the performance of the innovative CW-MFC hybrid system for wastewater treatment enhancement and energy recovery. This research reveals the synergetic relationship between CW and MFC towards the improvement of wastewater treatment performance as well as the mechanisms involved in CW-MFC.

The specific research objectives to realise the main aim of this research are as follows:

(i) To develop a hybrid system CW-MFC for effective wastewater treatment and energy recovery.

(ii) To evaluate the performance of organic and inorganic pollutant removal and bioelectricity generation via various operating parameters studies (effect of organic loading rate, effect of circuit connection, effect of aeration, effect of dye concentration, effect of salinity).

(iii) To investigate the role of wetland plant in CW-MFC on wastewater treatment and bioelectricity generation performances.

(iv) To evaluate the degradation of azo dye and the fate of electron transport in CW-MFC in the presence of multiple electron acceptors (anode, azo dye and nitrate).

(v) To investigate the influence of azo dyes' molecular structures (azo bond, functional groups and its position) on decolourisation rate and bioenergy recovery performances and explore the degradation mechanism and pathways of azo dyes in CW-MFC.

1.4 Research Scope

A hybrid system was developed by integrating MFC into CW for enhanced wastewater treatment and bioelectricity generation. The research is divided into five major scopes.

The first scope is about design and fabrication of CW-MFC reactor, where electrodes are embedded into CW and feasibility of such hybrid system was tested for simultaneous organic and nutrient-containing wastewater treatment and bioelectricity production. Evaluation on denitrification, nitrification and organic matter removal efficiency corroborate wastewater treatment capabilities, and bioelectricity production performance were carried out. The performance of CW-MFC was compared with previous literature on CW reactor of similar dimension, design and configuration to corroborate the effectiveness of the hybrid system.

The second scope of the research mainly focuses on the investigation of the effect of electrode spacing, the effect of organic loading rates, the effect of circuit connection on the performance of organic pollutant removal and electricity generation. The overall performance between the closed circuit and open circuit system were compared and put into perspective. The morphology of granular activated carbon electrodes was observed by using a scanning electron microscope (SEM).

The third scope of this study is the evaluation of the role of wetland plants and the effect of supplementary aeration on CW-MFC performance. A control reactor was constructed in order to compare the performance between the planted CW-MFC and plant-free system. Two types of wetland macrophytes, *Typha latifolia* and *Elodea nuttallii* were used as the model of wetland plant. The efficiency between *Typha Latifolia* and *Elodea nuttallii* in treatment performance and bioelectricity generation were compared. The role of wetland plant was also evaluated when azo dye was employed in the system. In addition, the correlation between dissolved oxygen, wastewater treatment and energy recovery was further investigated with a variation of aeration rates. The optimum aeration rate obtained could provide a reference on efficient aeration to optimise the wastewater treatment and energy recovery in a cost-effective manner.

The forth scope of this study is about the degradation of azo dye in high saline and nitrate conditions. The influence of such conditions on energy recovery and wastewater treatment performance was investigated via a series of studies for a total of 463 days. The effects of azo dye, salinity and nitrate on wetland plant were examined, and the wastewater treatment and energy recovery performances were evaluated in comparison with the plant-free control system. Furthermore, the correlation of electron transfer in azo dye reduction, denitrification and bioelectricity generation in the up-flow constructed wetland–microbial fuel cell (UFCW-MFC) were explored.

Lastly, in the fifth scope of this research, the evaluation on the effectiveness of hybrid system CW-MFC, standalone system CW, MFC and bioreactor on wastewater treatment efficiency was carried out by circuit connection modes approach (open circuit and closed circuit) as well as the presence and absence of wetland plant in the system. The effect of azo dye molecular structure on decolourisation rate and bioenergy recovery was further investigated. Azo dye of different molecular structure (number of azo bond, number of functional group and its position), Acid Red 18, Acid Orange 7 and Congo Red were used in the investigation. The kinetic studies on decolourisation of the three azo dyes were conducted. The correlation between the decolourisation rate and bioenergy recovery of three different molecular azo dyes was further investigated. The degradation mechanism was further elucidated, and the degradation pathways of the three azo dyes were proposed based on azo dyes reduced intermediates identification via ultraviolet-visible spectrophotometry (UV-Vis), gas chromatography-mass spectroscopy (GC-MS) and high-performance liquid chromatography (HPLC) analyses.

CHAPTER 2 : LITERATURE REVIEW

2.1 Constructed Wetland

Constructed wetlands (CWs), which are also known as treatment wetlands are human-made wetland that use natural processes, including physical and biological processes to treat wastewater. The synonyms of constructed wetland include human-made, engineered and artificial wetland (Vymazal, 2019). CWs are engineered to take the advantages of natural wetland to treat wastewater in a more controlled environment (Vymazal, 2018). The applications of CWs for wastewater treatment are promising, and many successful wetland treatments have been reported since 1960s. Up to now, there are many types of CWs in operation in the world and they can be categorised by three significant criteria as follows: hydrology (surface flow and subsurface flow), flow regime (horizontal and vertical), and type of vegetation or macrophytes (emergent, submerged, free-floating) (Figure 2.1). According to the Wetland International Malaysia Organisation, CWs are becoming popular in Malaysia for the environmental benefit such as treatment and storage of stormwater, urban runoffs and agriculture effluents as well as their aesthetic benefits.

2.1.1 Classification and Characteristic of CW

2.1.1.1 Surface Flow CW

Surface flow (SF) constructed wetland (CW) or also known as free water surface flow (FWSF) CWs, typically consist of a shallow basin made of soil or another medium to support the root system of plant and a water regulator structure that retains a low depth of water (Vymazal, 2018) (Figure 2.2 A). FWSF CWs are similar to natural wetlands, they are biological treatment system which requires a large area of land, and because of that, it also attracts a variety of wildlife.

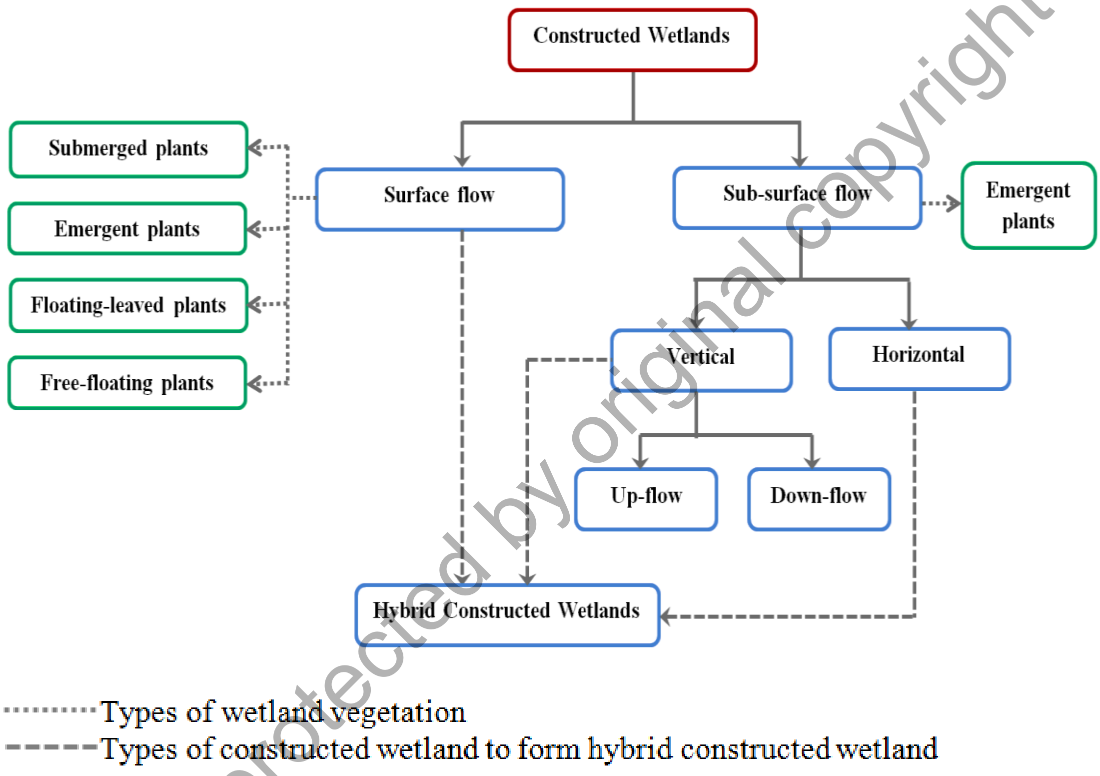

Figure 2.1: Classification of constructed wetland for wastewater treatment

The vital treatment process, such as the degradation of organic matter, mainly relies on the attached and suspended microbial. Algae and cyanobacteria growing in the water are the primary oxygen source for those reactions. Surface flow CW possesses a higher ability to deal with pulse flows and water levels changing. The removal of suspended solids and organics in all SF CWs are considerably high; however, the removal of nutrients is rather modest. SF CWs provide both aerobic and anaerobic regions that are suitable for nitrification and denitrification processes; nevertheless, complete nitrification and denitrification could not occur (Vymazal, 2018). The capital cost of construction and operation for surface flow CW are relatively lower and cost competitive.

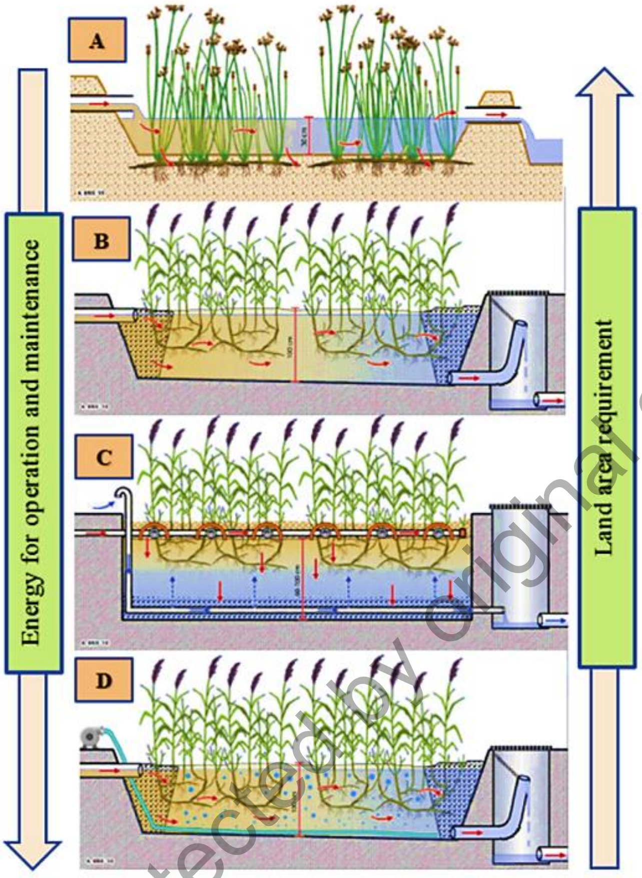

Figure 2.2: Types of constructed wetland and their characteristic. A: FWSF; B: HSSF CWs; C: VF CWs; D: Aerated CWs
Source: S. Wu et al. (2015)

2.1.1.2 Subsurface Flow CW

In subsurface flow (SSF) constructed wetland, wastewater flows through the root system and substrate, (H. Wu et al., 2015). Based on the direction of wastewater flow, SSF CW can be further categorised to horizontal subsurface flow (HSSF) (Figure 2.2 B) and vertical flow (VF) (Figure 2.2 C) CWs. The wastewater in HF CW flow horizontally underneath the surface and usually not exposed to the public. HF CWs are normally sealed to avoid uncontrolled water seepages into groundwater. In terms of land use and size wise, they are typically smaller than free water surface CW. As for VF CWs, there are several variations in feeding operation, i.e. down-flow and up-flow. One of the significant aspects of VF CWs design is to offer an adequate surface for the transfer of oxygen and sufficient bacteria to grow (Vymazal, 2019). Vertical flow constructed wetlands are considered more efficient as less area is needed in comparison to horizontal flow constructed wetlands. Besides that, the high capacity for oxygen transfer in VF CWs can contribute to higher ammonium oxidation. Nevertheless, wastewater that designed to flow against gravity, water pump is required, and air pump may be needed to aerate the wetland bed (S. Wu et al., 2015). VF CWs were constructed during the 1960s; however, it did not develop as fast as HSSF CWs, due to higher operation and maintenance requirements (Vymazal, 2019). Nevertheless, this VF CWs revived when the demand for nitrogen removal, especially ammonia nitrogen, increased in the 1990s.

2.1.1.3 Hybrid CW

Hybrid constructed wetland is the combination of various types of CW to accomplish greater treatment efficacy, especially for nitrogen (Vymazal, 2013). Horizontal flow CWs mostly consist of anoxic or anaerobic region, which are the ideal environments for denitrification process; meanwhile, nitrification is restricted by the limited dissolved oxygen in the wetland bed and lead to low ammonia removal. In contrast, vertical flow constructed wetlands, which are intermittently fed and consist of more aerobic environment, provide appropriate conditions for nitrification but inhibited denitrification process from occurring (Vymazal, 2007). Therefore, the idea of hybrid

CWs by combining various CW systems is moulded and implemented since they can complement each other.

Generally, hybrid CW design consists of two stages of several parallel CWs in series, such as VF-HF CWs, HF-VF CWs, HF-FWS CWs and FWS-HF CWs. The most common hybrid system is a VF-HF combination. Hybrid CWs are mostly used in Europe and Asia and (Vymazal, 2013). Furthermore, the multi-stage CWs that comprised of more than three stages CWs were used (Kadlec & Wallace, 2009). The first hybrid concept CW was developed as early as during the 1960s in Germany and consisted of a series of VF beds, followed by a series of HF beds (Vymazal & Kröpfelová, 2015). The finding of Vymazal & Kröpfelová (2015) proved that multistage hybrid constructed wetland was feasible for municipal sewage treatment. The system was capable of removing organics, suspended solids and nitrogen efficiently. The aerobic vertical flow stage provided a high degree of nitrification (removal rate of 4.17 g NH_4-N m^{-2} d^{-1}), while the remaining anaerobic stages offered suitable conditions for denitrification (removal rates of 0.83 g N-NO_3 $m^{-2}d^{-1}$ and 0.47 g N-NO_3 $m^{-2}d^{-1}$, respectively). Recently, hybrid CWs are gaining more popularity as the additional stage and type of CW are one of the most efficient solutions to improve the shortcoming of a single system and increase the treatment capability.

2.1.2 Strategies to Intensify CW Performance

2.1.2.1 Selection of Wetland Plant

Wetland plant is one of the four major components in constructed wetlands (CWs). A CW cannot be considered as treatment wetland if it does not contain any wetland vegetation. Macrophytes can influence the removal efficacy and contribute to the CW in several ways such as physical effects of roots include filtering, flow velocity reduction, improved sedimentation, decreased resuspension, and even the distribution of water and prevention of clogging. Besides that, the root and rhizomes are the significant base for microorganisms, where microorganisms are considered key drivers in the treatment process (Shelef, Gross, & Rachmilevitch, 2013).

Although more than 150 macrophyte species have been used in CWs worldwide, only a limited number of these plant species are frequently planted in CWs for real application (Vymazal, 2013). *Phragmites australis* is the most frequently used plant globally (Vymazal, 2011; Brix, 1997). Other commonly used species are *Phalaris arundinacea* (reed canarygrass), *Glyceria maxima* (sweet mannagrass) or various cattails (Typha latifolia, *Typha angustifolia*) in Europe, *Cyperus papyrus* (papyrus) in Africa, *Typha domingensis* in South America and *Scirpus spp.* (bulrush) in North America (Vymazal, 2019). Besides that, many other local plants have been used. Submerged plant like *Elodea nuttalli* can commonly found in the local wetland. As an ever-green submerged macrophyte, it possesses high potential to withstand cold weather and purify eutrophic water (Chang et al., 2006). Vymazal, (2011) compared the treatment efficiency of vegetated horizontal flow CWs and non-planted filters, and the findings were not unanimous. However, most studies (20 out of 22 reports) showed positive treatment efficiency with the presence of plant.

Generally, the selection of wetland plant should be focused on the target of the research, the tolerance of plant towards the contaminants in wastewater. Saldanha Vogelmann, Oladele Awe, & Prevedello (2016) suggests that plant selection can be carried out based on several criteria as follows: (i) good natural adaptation to the local climate, (ii) rapid growth and high biomass production, (iii) nutrient absorption capacity, (iv) adaptation and ease of propagation, (v) good root development, and (vi) oxygen transfer capacity to the roots by creating aerobic environment.

One of the roles for wetland vegetation in the constructed wetland is plant-mediated oxygen transfer. Wießner, Kuschk, Kästner, & Stottmeister (2002) found that the highest oxygen release rates were obtained from *Typha latifolia* (1.41mgh^{-1} plant^{-1}), followed by *Phragmites australis* (1.0 mgh^{-1} plant^{-1}), *Juncus effusus* (0.69 mgh^{-1} plant^{-1}), and *Iris pseudacorus* (0.34 mgh^{-1} plant^{-1}). The study of Bezbaruah & Zhang (2004) showed that wetland plant releases a certain amount of oxygen from root system to the immediate environment; however, the oxygen transfer might not be sufficient for the oxidative degradation of domestic wastewater organics. Oxygenation and carbon release from the root has been reported to influence the redox potential, and microbial activity of the subsurface flow CWs (Faulwetter et al., 2009; Wu, Zhang, Austin, Dong, & Pang, 2011). The result often suggests that the rate of oxygen transfer from the wetland plant root to rhizosphere may not be adequate to fulfil the oxygen demand of the wastewater completely. However, Akratos & Tsihrintzis, (2007) demonstrated that the organic matter removals as a function of the plant species grown in the CWs, where species with more vigorous root systems can improve the efficiency of organic matter removal. The plant-mediated oxygen transfer may alter the microbial community within the wetland bed and subsequently influence the treatment processes (Dan, Quang, Chiem, & Brix, 2011). From the literature, the role of wetland plant is one of the most highly debated topics in constructed wetland.

2.1.2.2 Artificial Aeration

The treatment efficiency of traditional CWs, particularly in horizontal subsurface flow often compromised as a result of limited oxygen transfer capabilities. Such a scenario was even more apparent in industrial wastewater effluent. Aerobic environments are important for the removal of nitrogenous and carbonaceous compounds in subsurface flow CW. The main mechanisms for oxygen transfer in subsurface flow treatment wetlands are atmospheric diffusion, plant-mediated oxygen transfer, and oxygen transfer at the water–biofilm interface (Nivala et al., 2013). Artificial or forced aeration in CW wastewater treatment was originally developed by Wallace (2001). Mechanical aeration of subsurface flow wetlands is introduced by using air distribution pipes installed at the bottom of the wetland bed has also been utilised as a method to improve oxygen transfer in treatment wetland (Figure 2.2 D). This includes aeration of horizontal subsurface flow wetlands (Maltais-Landry, Maranger, & Brisson, 2009; Ouellet-Plamondon, Chazarenc, Comeau, & Brisson, 2006) and saturated vertical flow wetlands (Wallace & Liner, 2011).

In recent years, wetland designs target at improving oxygen transfer at the water–biofilm interface and include modifications such as artificial aeration. An aerated up-flow CW for treating nutrient-containing wastewater was investigated by Ong, Uchiyama, Inadama, Ishida, & Yamagiwa (2010). The anaerobic condition of the upper wetland bed not only stimulated the oxidation of organic matter but also aided nitrification and improved ammonium removal efficiencies up to 98 % (Ong et al., 2010). Nevertheless, the nitrate concentration above aeration points significantly increased along with the decrease in ammonium concentration through nitrification. The higher nitrate concentration in the effluent could be a downside of the system. In order to remove ammonium and nitrate simultaneously, the supply of aeration must be strategically controlled through intermittent aeration at the upper wetland bed to stimulate nitrification and denitrification processes simultaneously (Ong, Uchiyama, Inadama, & Yamagiwa, 2009; Ong et al., 2010).

The influence of forced aeration and plants on the removal of nutrients and phenolic compounds in coffee processing wastewater in CWs was evaluated by Rossmann, de Matos, Abreu, e Silva, & Borges (2012). It is worth noting that artificial aeration does not compensate the absence of plants, which inferred that the role of plants goes beyond the transferring oxygen to the medium, plant especially the root system allows the development of a more dynamic and diverse microbial community (Rossmann et al., 2012). Later, cascade aeration was suggested as an alternative to artificial aeration as a result of low implementation and maintenance costs as well as the simple operation of CWs, especially in mountainous regions, for coffee plantation and production (Rossmann, Matos, Abreu, Silva, & Borges, 2013). Apart from that, Uggetti et al. (2016) demonstrated that intermittent aeration was the most efficient solution to improve wastewater treatment efficiency than continuously forced aeration regime in three pilot-scale constructed wetland. Additionally, intermittent aeration was a more energy-efficient strategy compared to a fully aerated system.

Providing aeration to traditional CW is becoming more popular as it is an effective strategy to intensify the treatment performance of wetland. The use of water and air pumps could result in smaller area requirements and better treatment performance; inevitably, it also comes at the cost of energy inputs. Meanwhile, some researcher justified that the energy inputs to CWs can overcome oxygen transfer limitations to meet advanced treatment standards (Wu et al., 2014). As the treatment wetland technology advances, the method and strategies to intensify the treatment performance should also expand (Nivala et al., 2013).

2.1.2.3 Wetlands Integration

The integration of different types of CWs was well reported, and they were primarily targeting to intensify the removal of organic matter and nitrogen from typical municipal and domestic sewage. Nevertheless, the integration of different CWs for the treatment of industrial effluent such as azo dyes is earnestly lacking. As for azo dye removal, although the cleavage of the azo bond in dye compounds removes the visible colour problem in anaerobic systems such as horizontal flow CWs, the aromatic amines in the effluent remain a problem (Pandey et al., 2007). The sequential anaerobic-aerobic treatment in a vertical up-flow CW with artificial aeration was developed for efficient colour removal and complete organic matter degradation. The intensified CW system also capable of mineralising intermediate products (Ong et al., 2009, 2010).

Consequently, a design with partially aerated CW at the final stage is proposed for biodegradation of azo dye.

Besides that, aerobic–anaerobic baffled subsurface flow CW, which integrates up-flow and down-flow sequentially was developed to treat azo dye-containing wastewater (Tee, Lim, Seng, Mohd Nawi, & Adnan, 2015; Lehl et al., 2017). Similarly, the concept of baffled CWs design was to develop sequential aerobic, and anoxic/anaerobic conditions within the same wetland bed, hence overcoming the shortcomings of the hybrid system which require a relatively large land area as well as a recycling system for wastewater treatment under oxidation and reduction conditions repeatedly. Tee et al. (2015) revealed that the removal efficiency of azo dye Acid Red 7 in planted baffled CW was 27, 37 and 39 % higher than a conventional horizontal subsurface CW at hydraulic retention time, 5, 3, and 2 days, respectively. The longer hydraulic path of the baffled CW system permitted more contact between wastewater and microbes, rhizomes and micro-aerobic region and subsequently enhanced the azo dye removal kinetics.

2.1.3 Overview of CW and Their Relationship with Energy and Land Requirement

The relationship between traditional passive CW and modern intensified CW in terms of energy consumption level, operation and maintenance as well as land area requirement was well-illustrated in Figure 2.2. If an equal treatment performance is targeted, free water surface flow CWs require the least energy for operation and maintenance, but the largest land area. Otherwise, the intensified CWs such as aerated

CWs, which require additional energy input would lead to higher costs for operation and maintenance of the facility, but also certainly occupied a smaller land area (S. Wu et al., 2015). In consideration for long term result, the option of relatively higher initial cost that could be counterbalanced by the reduction in operation and maintenance cost can also be adopted (Kadlec & Wallace, 2009). As a result, the decision on CW facility for treatment of industrial effluents can be justified based on the potential of the criteria aforementioned.

2.1.4 Incorporation of CW with Other Treatment Processes

Due to the advantages of cost-effective and simple-operation, constructed wetlands (CWs) have been comprehensively studied and extensively employed in numerous wastewater treatments. Nowadays, there are more stringent discharge standards to decrease environmental deterioration. As a result, CW systems operating as standalone technologies are in some cases may not be able to meet the requirements of these new guidelines despite the enhancements in design, improved operational strategies and the use of intensified systems. Such phenomenon serves a driving force behind the emergence of treatment systems integrating CWs with other treatment technologies to achieve improved treatment efficiency or extended treatment goals.

A novel treatment process of CWs incorporated with photocatalytic oxidation was proposed by Li, Gulyas, Jahn, Gajurel, & Otterpohl (2004) for greywater treatment in suburban and remote areas without a sewer system. Besides that, CW also has been combined with an ultrasound system to control the growth of algae in a closed-loop fish farm (Krivograd Klemenčič & Griessler Bulc, 2013). The combined effect of ultrasound and CW treatment vividly reduced the algae biomass and pollutants and, subsequently, the fish growth rate was significantly higher than the control farm. Furthermore, CWs were coupled with conventional treatment processes to treat high salinity tannery wastewater (Calheiros et al., 2012). In comparison with other biological treatment processes, CWs with salt-tolerant plant species have a higher capability to treat saline wastewater (Lefebvre & Moletta, 2006). In addition, CW also has been integrated with microbial fuel cell (MFC) for wastewater treatment and bioelectricity generation (Yadav et al., 2012). Both CW and MFC system involved biological process, and it is worth noting that such a system could achieve energy recovery from wastewater. Combining CWs with energy recovery technology device like MFC seems encouraging since the hybrid system is capable of generating renewable energy while offsetting the use of fossil fuels for the conventional treatment process. The latter system, CW combined with MFC, is of great interest and will be further discussed in detail in section 2.3.

The innovative integration of CWs with other treatment technologies have been proposed to stimulate organic and nutrient removal, eliminate recalcitrant contaminants, recover energy, and other special goals from the published literature. The combined or integrated treatment systems could present a novel alternative to tackle the shortcomings of the standalone system while simultaneously stabilising or even improving their existing functions (Liu, Zhao, Doherty, Hu, & Hao, 2015). Generally, they may be appealing for treating some particular wastewater such as industrial effluent. Overall, the combinations or incorporations of CWs with other wastewater treatment processes achieved a dual-win performance and also opened a new path for a more extensive application of CWs. Therefore, the inclusion of CWs into the system