The Hong Kong Polytechnic University

Department of Civil and Structural Engineering

Novel Vegetated Sequencing Batch Biofilm Reactor for Treating Suburban Domestic Wastewater

Chan Shing Yan

A thesis submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy

August 2006

Declaration

I hereby declare that this thesis entitled "Novel vegetated Sequencing Batch Biofilm Reactor for Treating Suburban Domestic Wastewater" is original and has not been accepted for the award of any other degree or diploma. It does not contain any material, partly or wholly, published or written by others, except those references quoted in the text.

CHAN Shing Yan

Acknowledgement

This research study has been financially supported by The Hong Kong Polytechnic University, which is thankfully acknowledged. I am also grateful for the award of the research studentship and tuition scholarship offered by the University.

I sincerely acknowledge my chief supervisor, Prof. Chua Hong, Civil and Structural Engineering Department, The Hong Kong Polytechnic University, who has provided me valuable guidance, comments and suggestions throughout my research study.

I am grateful to Prof. Cui Li Hua, College of Resources and Environment Sciences, The South China Agricultural University, for his guidance of the on-site experimental work at the South China Agricultural University, Guangzhou. My thanks also go to the students, especially Miss Lin Yu, at the South China Agricultural University for their assistances and warm hospitality.

I would also like to thank my colleagues, Chris Tsang and Hua Feng Lin, who have contributed fruitful discussions on many computational and technical problems during my study. I am very thankful to Mr. W.S. Lam for his kindness and technical support in the laboratory.

Publications

S.Y. Chan, H. Chua, L.H. Cui and Y.F. Tsang. Ammonia nitrogen removal from domestic wastewater using sequencing batch biofilm reactor. Biochemical Engineering Journal (accepted).

S.Y. Chan, H. Chua, Y.F. Tsang and Y.J. Wang. Performance study of vegetated sequencing batch coal slag bed treating domestic wastewater in suburban area. Ecological Engineering (submitted).

S.Y. Chan, H. Chua, L.H. Cui and S.N. Sin (2005) Domestic wastewater treatment in tidal-flow vertical flow cinder bed with *Cyperus alternifolius*. *Proceeding of 8th International Conference of the Aquatic Ecosystem Health and Management Society.* Restoration and Remediation of Aquatic Ecosystems: *Tools, Techniques and Mechanism.* November 27th – 30th, 2005. Nanjing-Hangzhou, China.

Abstract

Common small-scale domestic wastewater treatment systems such as waste stabilization ponds, lagoons and constructed wetlands are limited to usages in rural areas with small wastewater flows due to their large land requirements and relatively low pollutant treatment efficiencies. Though constructed wetland has gained most popularity among the various biological wastewater treatment methods with its successful applications in small communities worldwide, its large footprint and long retention time restrict it from serving beyond the rural areas to the suburban areas with larger wastewater flows, in where conventional municipal treatment facilities are too costly to be installed.

In this study, a practical and affordable wastewater treatment system serving small community in suburban areas was studied. The principal of the system studied capitalizes on the pollutant removal mechanisms of the soil-plant-microbial interactions of constructed wetlands. The short comings of conventional constructed wetland were attempted to be eliminated by optimizing the operating conditions for equivalent treatment efficiency. The system studied is a vegetated sequencing batch biofilm reactor integrated with the rhythmical movement of wastewater and air like that of a sequencing batch reactor. The controlling factors of pollutant removals being studied included plant, contact time, rhythmical movement of air/wastewater, dissolved oxygen and temperature. Nutrients in the domestic wastewater, which cause environmental nuisance like eutrophication, was targeted to be gotten rid of by the process.

Bench experiments were designed and carried out on the medium, namely coal slag and the plant, namely *Cyperus alternifolius* in the system. Two parallel systems were set up in both laboratory-scale and pilot-scale. The data from the lab-scale experiments were used to establish the nutrient mass balances and to understand the conversion efficiencies of pollutants through different removal mechanisms. Adsorption and microbial degradation dominated in the removal processes at different stages of operation for different pollutants while plant uptake played a minor role. The planted systems in the laboratory-scale experiment showed enhanced ammonia nitrogen removal over the unplanted system. With the longest contact time being tested in the pilot system, the treatment systems achieved around 60 % removal efficiency for carbonaceous matters. The removals of ammonia nitrogen and phosphorus were about 50 and 40 %, respectively, while the removal of total suspended solids was approaching 80 %.

Multivariate regression, first-order kinetics and mass balance models were developed for the prediction of effluent concentration of ammonia nitrogen. The sensitivities of the controlling factors in the mass balance model, including influent ammonia nitrogen concentration, contact time, temperature and dissolved oxygen, were analysed. With the in-depth understandings of the effects of operating conditions on the system performance, contour plots were prepared from the ammonia nitrogen removal predictive model under two temperature ranges of temperate climate. The required contact time for achieving any desired levels of removal efficiencies could be predicted under different influent concentrations.

Treating the domestic wastewater from small community, specifically in suburban areas, the system was found to be cost-effective compared to the conventional activated sludge processes and constructed wetlands, for equivalent treatment efficiencies.

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Nomenclatures

BOD_5	5-day biochemical oxygen demand
COD	Chemical oxygen demand
CT	Contact time
DO	Dissolved oxygen level
HRT	Hydraulic retention time
K_m	Half saturation constant of plant uptake of ammonia nitrogen
K_o	Half saturation constant of DO
K_s	Substrate affinity constant
N	Nitrogen
NH_3-N	Ammonia nitrogen
NH_3-N_{in}	Concentration of ammonia nitrogen in influent
NH_3-N_{out}	Concentration of ammonia nitrogen in effluent
NO_2^-	Nitrite
NO_3^-	Nitrate
P	Phosphorus
Q	Flow rate
r_A	Rate of NH_3-N removal
r_g	Growth rate of nitrifier
S	NH_3-N concentration
S_x	Sensitivity
t	Time
T	Temperature
TKN	Total Kjeldahl Nitrogen

TP	Total phosphorus
TSS	Total suspended solids
V	Reactor volume
VSBBR	Vegetated sequencing batch biofilm reactor
X_p	Plant biomass concentration
$Y_{x/s}$	Yield coefficient of nitrifier
$Y_{x/s(p)}$	Yield coefficient of plant
δx	Relative change in the value of parameter
δY	Relative change of output
θ	Temperature coefficient
μ	Rate coefficient
μ_{20}	Value of μ at 20 °C
μ_{max}	Maximum specific growth rate
χ	Biomass concentration

Chapter 1: Introduction

1.1 Background

1.1.1 Small scale wastewater treatment systems

In most cities in industrialized and developed countries, centralized wastewater treatment plants collectively purify the municipal sewage for the sake of community hygiene. An extensive network of trunk sewers is built to convey the city's wastewater into it. While developing countries use decentralized treatment plant to minimize the costs of trunk sewage and expenditure on pumping. Some small-scale onsite wastewater treatment facilities include waste stabilization ponds, wastewater storage and treatment reservoirs, upflow anaerobic sludge blanket reactors, biofilter, aerated lagoon, oxidation ditches and constructed wetlands are often installed in those developing countries or the rural areas in the developed countries. The re-use of untreated wastewater for crop irrigation or for fishpond fertilization is also a common practice, especially in water-short areas.

The demands of proper wastewater treatment facilities are substantial in the fast developing country like China. Currently, the total amount of wastewater discharge in China is 43.95 billion tons, exceeding the environmental capacity of the region by 82 percent. In the seven major river systems in China, 40.9 percent of the water is not suitable for drinking by humans or livestock. Seventy-five percent of the lakes are polluted so as to produce various degrees of eutrophication (Ministry of Construction, PRC, 2006). The conflicts between man and water environment in China have never been as intense as they are today.

1.1.2 Existing problems and needs for this study

1.1.2.1 Wastewater treatment status in rural areas

In recent years there have been significant advances in the design of wastewater treatment systems having improved performance and operational dependability. This progress has been driven by the need of wastewater discharges to meet ever increasingly stringent effluent discharge standards in many urban areas. Common large-scale wastewater treatment facilities such as activated sludge process and sequencing batch reactor are adopted to treat the municipal wastewater in many modern cities, but these systems are only cost-effective to treat huge amount of wastewater for large population because the construction cost, operating and maintenance fee are comparatively high and the required technical skills are sophisticated.

Without proper sewage collection system or treatment system, inhabitants of rural areas usually discharge their untreated domestic wastewater to the neighbouring natural environment. The pollution status is severe especially in China because most of its populations live with their agricultural work and scatter on the rural land far away from the centralized sewage treatment network. According to the Statistics Yearbook of China 2000, the size of population in rural areas is the double of that in urban areas (National Bureau of Statistics of China, 2000). Inadequate treatment of domestic wastewater in the rural areas could contribute to serious non-point source of pollution of surface waters and contaminate groundwater supplies. Since untreated domestic wastewater causes damage to the environment and to human health, it should be treated to reduce water pollution and consequent damage to aquatic biota, as well as to reduce the transmission of diseases.

1.1.2.2 Wastewater treatment demand in suburban areas

Apart from the small communities in rural areas, the individual lots and the growing populations in suburban areas are also facing the difficulties of treating their domestic wastewater properly and constructing and operation of municipal-wide wastewater treatment systems. Suburban area is defined as the interface between developed urban areas and undeveloped rural areas. Although locating at the boundary of the urban cities, suburban sewer's connection to the existing municipal system is still proved to be cost prohibitive. Moreover, the advanced and costly wastewater treatment facilities used in city cores are not the proper solutions for small-scale wastewater demands in these suburban areas. Without sufficient governmental or municipal financial support, wastewater treatment systems with low cost and easy operation mode are instead an alternative for economic and energy-saving considerations in these areas. The demand of efficient onsite wastewater treatment systems in these suburban areas is even pressing than in rural areas because of the growing population pressure inside it and its proximity to the urban cores. Alternatives or modifications of the conventional on-site wastewater treatment systems are needed to provide solution to the expanding water pollution problems in the suburban areas.

When sustainability is considered in relation to domestic wastewater treatment in developing countries or suburban areas, the systems or the technologies have to be simple of operation and maintenance, with low cost in terms of capital and operation and maintenance, with low energy usage, with low or preferably zero use of chemicals. Some onsite biological treatments like constructed wetlands have relatively low construction and operating costs, provide an economic treatment solution to untreated small flows, and are available to isolated or rural locations without the need for electricity, but land area is prerequisite. Wastewater treatment facilities in rural areas should take maximal advantage of their land availability and hence constructed wetland can play the role. However, land availability in suburban areas is not as adequate as in rural areas. At the boundary of developing zone of urban area, land supply in suburban area is under increasing pressure from the rapid urban development, and so conventional constructed wetland can not be the long-term solution of wastewater treatment demands.

The choice of treatment technologies that is selected for a particular application is determined by the treatment objectives of the facility, the system investigated in this study has to be capable for organic and nutrient removals as it is designed for domestic wastewater treatment in suburban areas. In this study, an economic wastewater treatment system treating domestic wastewater from small community in suburban areas was studied and its operating conditions and removal efficiencies were optimized. Existing treatment technologies were attempted to be modified so as to broaden their capabilities and improve their performances, so the low-cost constructed wetland treatment technology formed the basis of modifications for the studied system. The principal of the studied system was capitalized on the pollutant removal mechanisms of the soil-plant-microbial interactions of constructed wetlands. The rhythmical movement of wastewater in conventional sequencing batch reactor for enhanced pollutant removals was taken as reference. Large land requirement and long retention time was attempted to be eliminated by optimizing the operating conditions in the system for enhanced treatment efficiency. Nutrients in the domestic wastewater, which cause environmental nuisance like eutrophication, were targeted to be get rid of by the process design.

1.2 Goals and objectives

1.2.1 Goals

The study aimed to design and build an ecological engineered wastewater treatment, named as “vegetated sequencing batch biofilm reactor”. The system is practical and affordable wastewater treatment system for the suburban populated areas. The research outcomes were useful in developing predictive engineering design model to cope with difference levels of the domestic wastewater treatment demands. The technology developed under this study will be transferred into wide-ranging engineering applications.

1.2.2 Objectives

The objectives of the current study were:

1. To study the properties of the selected plants and the selected adsorbing medium for the vegetated sequencing batch biofilm reactor;
2. To study the performance of the vegetated sequencing batch biofilm reactor for secondary domestic wastewater treatment;
3. To investigate the importance of different purifying mechanisms of nutrient contents in the system;

4. To examine the effects of plants and different contact time on the pollutant removal efficiencies;
5. To develop predictive model using data-driven multivariate statistical methods, first-order kinetics and mass balance for ammonia nitrogen removal;
6. To predict the removal capacities of the system under different contact times and loads of sewage and so as to adapt different sewage treatment demands;
7. To compare the cost-effectiveness of the system to the conventional biological domestic wastewater treatment systems.

1.2.3 Significances of study

The vegetated sequencing batch biofilm reactor was designated for secondary domestic wastewater treatment. One of the served locations is the suburban populated area in China where is out of the coverage of the municipal sewage treatment network. Domestic wastewater from those areas is usually discharged directly to the natural environment nearby without any pre-treatment. Without adequate financial supports and community resources from the central government, local governmental units in those suburban areas are unlikely to build large-scale and costly conventional sewage treatment plants, as a consequence the studied system with low cost and effective pollutant removal capacity is in demand.

In cities with highly developed infrastructural sewage system, the system studied still has wide range of applications. Since the system is designed for domestic sewage, some private residential areas that are distant from urban core could adopt the studied system into their sewage treatment facilities. The operator could be benefited by the low costs of the system. The outlying islands with growing population could also install the system for maintaining local public hygiene without disrupting the natural landscape due to the construction of large-scale sewage treatment plant. Some individual sewage spots like the public toilets in country parks, and the patrol stations in the border, all require a simple, cost-effective and environment-friendly technology that does more than a septic tank.

There is a lack of operating data for the optimization of such wastewater treatment systems. More data from lab-scale to pilot-scale studies are needed to evaluate how these systems work in the real environment and to enable more rational design parameters to be developed to optimize the design equations.

1.3 Scope of work

Chapter 1 explains the background of the study and provides an introduction to the current status and needs of small scale biological wastewater treatment system in the suburban areas. This chapter also outlines the goals, objectives and significance of the study.

Chapter 2 presents a review of the development of biological treatment technologies for domestic wastewater. A comprehensive literature review was done on the developments and principles of biological wastewater treatments in both urban and rural areas. Common small scale wastewater treatment systems were introduced, with focus on the low cost constructed wetland wastewater treatment technology. The main components of a constructed wetland including hydrology, adsorbing media, plant and microorganisms were considered for the selection of appropriate plant and adsorbing medium in the experiments. The removal mechanisms of pollutants including organic matter, nitrogen, phosphorus and suspended solids in constructed wetland were discussed.

This chapter also brings out the limitations of the current constructed wetland technology especially in nitrogen removal and suggest the integration of rhythmical operation pattern from sequencing batch reactor. The modelling of biological treatment kinetics was also reviewed with regard to microbial reactions and plant uptake kinetics.

Chapter 3 provides an account of the materials and methods of the study as well as the study approach. The details of bench experiments investigating the selected adsorbing medium and the selected plants were given. The design and operating conditions of both laboratory-scale and pilot-scale systems were demonstrated. The analytical procedures and the statistical processing of data were illustrated.

In **Chapter 4**, the findings of bench experiments about coal slag and *Cyperus alternifolis* were shown. The performance data of the laboratory-scale and pilot-scale systems were analyzed and presented. The effects of plants, contact time and rhythmical movement of air/wastewater, loadings, dissolved oxygen and temperature on the removal efficiencies of carbonaceous matter and nutrients proved by statistical tools were discussed. The roles of the main pollutant removal mechanisms were justified.

In **Chapter 5**, predictions of ammonia nitrogen removal were derived from multiple regression model, first-order kinetics model and mass balance model. The overall system capacity of nutrient removals was predicted under different contact times for various sewage loads. In addition, economic analysis of the cost-effectiveness of the system was done with comparison to other similar systems in **Chapter 6**.

Finally, **Chapter 7** provides a summary of results and conclusions of the study, as well as the possible future work.

Chapter 2: Literature Review

2.1 Development of biological wastewater treatment systems

Most of the biological processes used for wastewater treatment are derived from processes occurring in nature. The biological treatment unit operations of a wastewater treatment system form what is called the secondary treatment system. The principal processes used for the biological treatment of wastewater can be classified with respect to the metabolic functions of microorganisms as aerobic processes, anaerobic processes, anoxic processes, facultative processes, and combined processes (Crites and Tchobanoglous, 1998). The individual processes are also further subdivided, depending on whether treatment is accomplished in suspended-growth systems and attached-growth systems (Spellman, 1997). Effective treatment in any biological treatment process depends on the ability to maintain the treatment microorganisms in a satisfactory or optimal physiological state to allow their metabolic well being (Yu *et al.*, 2006).

2.1.1 Aerobic and anaerobic treatment processes

In aerobic microbiological processes oxygen consuming bacteria metabolize dissolved organic compounds and convert them into carbon dioxide and settleable solids. The rate of an aerobic process is often limited by the rate of which oxygen can be dissolved in wastewater. The oxygen transfer rate is often the critical parameter limiting the operation of aerobic waste treatment systems. Energy for aeration is a major operating cost for such systems.

Anaerobic treatment processes are based on microbial biodegradation of organic wastes in the absence of oxygen. Mineralization processes of organic compounds are interactively carried out by fermentative, acetogen and methanogen bacteria. The digestion occurs in four distinct steps: the first step is hydrolysis in which complex organic matter is decomposed into simple soluble organic molecules using water to split the chemical bonds between the substances. The second step is fermentation or acidogenesis in which chemical decomposition of carbohydrates by enzymes, bacteria, yeasts, or molds in the absence of oxygen are carried out. The third step is acetogenesis in which the fermentation products are converted into acetate, hydrogen and carbon dioxide by so-called acetogenic bacteria (Stronach *et al.*, 1986). The last step is methanogenesis, methane (CH_4)

is formed from acetate and hydrogen/carbon dioxide by methanogenic bacteria (Gerardi, 2003).

2.1.2 Suspended and attached growth treatment processes

Biological treatment systems are also classified as suspended or attached growth according to the ways of existence of microorganisms. In attached growth systems - such as rock filters - the biomass grows on media and the sewage passes over its surface. In suspended growth systems - such as activated sludge - the biomass is well mixed with the sewage. Typically, attached growth systems require smaller footprints than for an equivalent suspended growth system; however, suspended growth systems are more able to cope with shocks in biological loadings and provide higher removal rates for BOD and suspended solids than attached growth systems.

The common attached-growth processes are trickling filter, rotating biological contactor, and fixed-film nitrification reactor (Metcalf and Eddy, 1991). The mechanisms involved in the immobilization of pollutants in the soil component of an attached-growth bed system include biological oxidation and mineralization, nitrification and denitrification, adsorption on ion exchange sites, binding to organic matter, precipitation into insoluble compounds, complexation or chelation, and incorporation into lattice structures.

Suspended growth treatment systems freely suspend microorganisms in water. Suspended growth technologies include conventional activated sludge treatment systems that use various process modes, ranging from conventional, extended aeration, contact stabilization, sequencing batch, and single sludge. Among which oxidation ditches and sequencing batch reactor seem to be the most popular treatment technologies being used in small-sized wastewater treatment plants (Eckenfelder and Grau, 1998).

The activated sludge process was developed in England in 1914 by Ardern and Lockett (Metcalf & Eddy, 1991). The activated sludge process is a suspended growth system comprising a mass of microorganisms constantly supplied with organic matter and oxygen. The microorganisms grow in flocs, and these flocs are responsible for the transformation of the organic material into new bacteria, carbon dioxide and water (Horan, 1990). The relatively high population of microorganisms (biomass) being maintained by recycling settled biomass back to the treatment process.

Later on, conventional activated sludge process was modified to increase the microbial biomass being maintained. An inert support medium is added to enhance performance and increase the capacity of the aeration tank. The inert medium fixes and supports additional biomass on its surface for biodegradation, and such system is called as fixed film activated sludge system. In a fixed film activated sludge system, a fixed film of biomass attaches and grows on the inert medium to augment the suspended microbial population, providing more biomass to feed on wastewater constituents. Advantages include increased active microbial mass per unit volume, enhanced potential for nitrification, reduced suspended solid loading to the clarifier.

2.2 Common treatment systems of domestic wastewater

Domestic wastewater is mainly composed of organic matters, nutrients and suspended solid. Table 2.1 shows the typical composition of untreated domestic wastewater. For the treatment of domestic wastewater, the removals of organic matters and nutrients are usually of most concerns. The types of wastewater treatment systems being utilized is a matter of consideration based on the targeted pollutants to be eliminated, the volume of domestic water and hence the

Table 2.1 Typical composition of untreated domestic wastewater

Contaminants	Range	Typical
BOD (mg/L)	110-400	210
COD (mg/L)	250-1000	500
NH_3-N (mg/L)	12-50	22
TP (mg/L)	4-15	7
TSS (mg/L)	100-350	210

(Metcalf and Eddy, 1991)

size of user population, the local financial budget and the geographical characteristics. The choice of cost-effective treatment technologies is thus divergent in urban areas and rural areas.

2.2.1 Urban areas

In highly developed cities, domestic wastewater is treated to different acceptable levels for environmental and hygienic safety of the community according to the required and lawful discharge standards. Primary, secondary and tertiary wastewater treatment units are installed accordingly in a single operation or in a combination to reduce the pollutants in wastewater. Without sufficient land, the systems used in urban areas are designed as high rate systems which are able to treat a much larger quantity of wastewater in a much smaller footprint.

2.2.1.1 Activated sludge process

Conventional activated sludge system is used for large populations. It is widely used throughout the world for the treatment of municipal and industrial wastewaters. Bacteria constitute the majority of microorganisms present in activated sludge. The activated sludge process is a wastewater treatment method in which the carbonaceous organic matter of wastewater provides an energy source for the production of new cells for a mixed population of microorganisms in an aquatic aerobic environment. The microbes convert carbon into cell tissue and oxidized end products that include carbon dioxide and water. In addition, a limited number of microorganisms may exist in activated sludge that obtain energy by oxidizing ammonia nitrogen to nitrate nitrogen in the process known as nitrification. The activated sludge process is effective to degrade most of the pollutants in the domestic wastewater through the biological processes. However, it consumes considerable quantities of electrical energy for system aeration. The suspended microbial floc is complicated to maintain and the required operating conditions involves expertise to operate. Sludge produced from the process needs further treatment for disposal. The construction and operating costs are high compared to other conventional biological process. The cost-effectiveness of the system is subject to the size of user’s population.

2.2.1.2 Sequencing batch reactor

A sequencing batch reactor (SBR) is a fill-and-draw activated sludge treatment system with the unit processes identical to conventional activated-sludge systems. It is also commonly used in most modern cities for various wastewater treatment demands. A SBR is a single tank that serves both as a biological reactor and settler in a temporal sequence (Artan *et al.*, 2002; Wilderer *et al.*, 2001). There are five common steps that are carried out in sequence during the operation of SBR systems, they are: 1) fill, 2) react, 3) settle, 4) draw and 5) idle (Metcalf and Eddy, 1991; Smith and Wilderer, 1987). The major differences between SBR and conventional continuous-flow, activated sludge system is that the SBR tank carries out the functions of equalization aeration and sedimentation in a time sequence rather than in the conventional space sequence of continuous-flow systems (Okada and Sudo, 1986). Foaming occurs in conventional activated sludge process can also be eliminated the sequencing flow of wastewater.

SBR has proven to be a viable alternative to continuous-flow systems in carbon and nutrient removal from domestic and industrial wastewaters (Irvine and Ketchum, 1988; Artan *et al.*, 1996; Wilderer *et al.*, 2001; Keller *et al.*, 1997).

Obaja *et al.*, (2003) proved that SBR are very flexible tool that particularly suitable for the treatment of piggery wastewater with high organic matter, nitrogen and phosphorus contents.

The SBR technology, despite its simplicity as a batch reactor, offers a great flexibility of operation where the sequence of successive phases can be adjusted to sustain any desired combination of growth conditions for different biochemical processes (Irvine *et al.*, 1997; Morgenroth and Wilderer, 1998). Targeting to nitrogen removal, it is crucial to optimize the order and duration of these various phase in order to lead to a complete nitrification of ammonia ions and a total denitrification of the nitrate ions produced (Casellas *et al.*, 2002). Although SBR design for conventional parameters is well understood (Orhon and Arton, 1994), the operation of such sophisticated system required skilled personnel. Similar to activated sludge process, the SBR process is costly for its operation and maintenance.

2.2.2 Rural areas

Wastewater treatment facilities in rural areas should take maximal advantage of their land availability. Besides, most wastewater treatment systems in rural areas are characterized by low capital investment and operation cost. Common treatment methods of domestic wastewater in rural areas include waste stabilization pond, wastewater storage and treatment reservoir, upflow anaerobic sludge blanket reactor, biofilter, aerated lagoon, oxidation ditches and constructed wetland (Mara, 2003).

Waste stabilization ponds are large shallow basins enclosed by earth embankments in which raw wastewater is treated by entirely natural processes involving both algae and bacteria. It is simple to construct and cost the least for both capital and operation and maintenance costs. Removal efficiencies of BOD, ammonia nitrogen and suspended solids can be designed to achieve over 90% (Mara, 2003). Waste stabilization ponds are also particular efficient in removing excreted pathogen. However, the rate of oxidation is slow and longer hydraulic retention times are needed than in other wastewater treatment systems such as in activated sludge processes. The requirement of using such system is sufficient land and favourable temperature. Because the surface required for waste stabilization ponds is large and can be a limiting factor together with the necessary tightness of the underlying soil (Vymazal *et al.*, 1998).

Wastewater storage and treatment reservoir enable the whole year's treated wastewater to be used for crop irrigation during the irrigation season. It maximizes the potential of wastewater re-use for crop production. However, long retention time and formation of odour are the short-comings of the system.

Upflow anaerobic sludge blanket reactors are reinforced-concrete structures, with a short hydraulic retention time of around 6-12 hours. It is a high-rate anaerobic wastewater treatment unit. The wastewater is distributed evenly across the base of reactor, it then flows upwards through the sludge layer. This ensures intimate contact between the wastewater and the anaerobic bacteria in the sludge blanket. Extra energy is required for upflow movement of wastewater and operating cost is relatively higher.

Lagoons sometimes are called as oxidation ditches, are direct modification of conventional activated sludge process. They are activated sludge units operated without sludge return. Floating aerator is used to supply the necessary oxygen and mixing power. BOD removals above 90% are achieved at short retention times (2-6 days) (Mara, 2003). However, aerated lagoons are not particularly effective in removing faecal bacteria. The advantages of lagoons include low capital costs, minimum operations and skill are needed, sludge withdrawal and disposal are needed at 10-20 year intervals, as well as the compatibility with land and aquatic treatment processes (Crites and Tchobanoglous, 1998). However, large land area is required and high concentration of algae may be generated in lagoons.

Lagoon, on the other hand, can operate without aeration, is called as anaerobic lagoon. Anaerobic lagoon are loaded to such an extent that anaerobic conditions exist throughout the liquid volume. The biological process is the same as that occurring in anaerobic digestion tanks, being primarily organic acid formation followed by methane fermentation (Eckenfelder, 1989). The depth of anaerobic ponds is selected to give a minimum surface area/volume ratio. Nonetheless, lagoons often do not provide effluents that meet regulatory standards established by authorities (Vanier and Dahab, 2001).

Biofilter (also called trickling filter, percolating filters and bacteria beds) produces high quality effluents without requiring large land areas or consuming vast quantities of electricity. Wastewater is distributed mechanically over the rock medium and it percolates down through the medium to be collected in an underdrain system. Pollutants are oxidized by the microbial film developed on the surface of the rock in the biofilter. Its pollutant removal principle is similar to that of constructed wetland except the presence of vegetations.

Constructed wetland gains most popularity of its application in wastewater treatment among most other biological wastewater treatment systems with its low cost and simplicity. This technology has been applied successfully in treating domestic sewage from single residence house to small community. They are effectively used for the treatment of landfill leachate, petroleum discharge, and some chemical manufacturing wastewaters. The use of wetland retention basins for storm water runoff also has become relatively commonplace.

Over 1000 treatment wetland systems are in operation worldwide (Kadlec, 1994a). The use of constructed wetland for wastewater treatment dates back to the early 1900s (Kadlec and Knight, 1996). The purifying technology of constructed wetland has been widely investigated and used in many countries. It is a mode of ecological sewage treatment with low investment and operating costs. The treatment of small community wastewater using subsurface flow constructed wetlands is of growing interest since it is an affordable and operable technology.

Wetlands are defined by the presence of standing water (either at the surface or in the root zone), unique wetland soils, and vegetation adapted to water saturated conditions (Mitsch and Gosselink, 1993). The two basic types of constructed wetland treatment systems include surface flow (SF) wetlands, and subsurface (SSF) wetland. The surface-flow wetland consists of an open water area, emergent vegetation, soil to support vegetation, and a subsurface barrier to prevent seepage. The subsurface wetland typically uses a bed of sand or gravel as the adsorbing medium for the growth of rooted wetland plants. Wastewater flows through the bed substrate, where it contacts a mixture of facultative microbes living in association with the adsorbing medium and plant roots.

A common type of constructed wetland system for wastewater treatment is reed (*Phragmites Communis*) bed system. Reed beds consist of a sand bed with dense reed vegetations and an underdrain system. It utilizes the root system of vegetation to aerate and degrade biological solids. Evapotranspiration also occurs through the reeds which assist in dewatering. The reeds hollow stalks maintain aerobic conditions within the dewatered sludge and prevent anaerobic conditions which cause odors (Hammer, 1989). The reed system produces dry and degraded materials that must be removed approximately every 10 years. The advantages of a reed bed system are low operation costs and maintenance requirements. The disadvantages of a reed bed system are the land requirements, annual harvest of the vegetative materials and the potential trace concentrations of heavy metals in the biosolids that can prevent beneficial reuse of the biosolids residue. Extra caution must be taken with reed beds to prevent odors.

The use of constructed wetlands can offer higher degree of process control while allowing for the development of generally applicable design and cost criteria for a given and desired level of wastewater (Gersberg *et al.*, 1984). Mara (2003) suggested that comparing most waste stabilization ponds with constructed wetland, constructed wetland should be considered for use when specific maximum effluent ammonia concentration is desired, due to the nitrogen removal ability of plants. Constructed wetland, which is specifically effective for nutrient removals in wastewater in small community, is a good candidate for system modification to satisfy the domestic wastewater treatment demand in sub-urban areas in this study.

The disadvantages of constructed wetland systems are that they occupy relatively large areas of land and thus tend to be used to serve a small population (The Chartered Institution of Water and Environmental Management, 2000), and long retention time is needed for achieving acceptable effluent quality.

2.3 Constructed wetland for wastewater treatment

2.3.1 Main components in constructed wetland

The successful use of constructed wetlands for the improvement of water quality depends upon four principal components with the processes, namely hydrology, adsorbing medium, plant and presence of certain microbial association (Martin and Johnson, 1995). The rates of movement of a chemical between these major components, together with the rates of accumulation of that chemical within them, could form the basis for rational design.

2.3.1.1 Hydrology

The flow of wastewater through a microbiological reactor can be either complete mixing or plug flow, or a pattern in between, named as dispersed flow. The influent to ideal complete mixing reactor is completely and instantaneously mixed with the reactor contents, as a result of intense mixing, uniform in composition throughout (Mara, 2003). In contrast, the content of a plug flow reactor flow through the reactor in an orderly fashion characterised by the complete absence of longitudinal mixing. The wastewater is like being placed in watertight “packets” which then travel along the length of reactor. As there is no intermixing, every element in the reactor experiences treatment for the same amount of time, namely the theoretical retention time (Horan, 1990). Both complete mixing and plug flow are ideal conditions while dispersed flow describes the real situations in between. Another special case of wastewater flow is that, when there is no inflow or outflow from the container or vessel in which the reaction is occurring, such a container is known as a batch reactor (Metcalf and Eddy, 1991).

Beside the flow pattern, the source of water, velocity, volume, renewal rate, and frequency of inundation influence the chemical and physical properties of adsorbing medium which, in turn, influence species diversity and abundance, primary productivity, organic deposition and flux, and nutrient cycling in bed systems (Livingston, 1989). Moreover, water depth and frequency of flooding or its periodicity are important in determining the plant species appropriate to a constructed wetland system (Allen *et al.*, 1989).

2.3.1.2 Adsorbing medium

The criteria for choosing suitable adsorbing medium for wastewater treatment bed includes inertness, ease to gather biofilm on themselves, reluctance to be carried over from the bed, etc. Jenssen *et al.*, (1997) also emphasized that the hydraulics should always be considered first for the selection of adsorbing medium in bed system, because the hydraulic properties of the soil/porous media to be used will determine the minimum size of the system. However, to enhance the pollutant removal ability of any filter bed system, what's more crucial is the consideration of medium's adsorption capacity of nutrients from the wastewater.

In more technical speaking, roles of adsorbing medium in subsurface-flow wetlands include physical separation of particles, providing attachment sites for microbial growth, adsorbing surfaces for rooted emergent macrophytes, allowing chemical ion interchange between wastewater and ion-rich mineral components in the support medium (Nutall *et al.*, 1997). Adsorbing medium in the gravel-based treatment system is the place where most chemical transformations take place. Oxic metabolism occurs in a thin oxygenated surface layer, while in deeper layers anaerobic and anoxic processes take place. On the other hand, phosphorus removal in constructed wetland is also largely contributed by adsorption and retention in wetland soils by interaction of redox potential, pH, Fe, Al and Ca minerals (Richardson and Craft, 1993). Retention of nitrogen in the soil through the process of cation exchange, whereby the ammonium ion is weakly bound to soil particles by electrostatic attraction. Most soil profiles are negatively charged, so the corresponding retention of nitrate is rare.

Adsorption is the process of collecting soluble substances that are in solution on a suitable interface (Metcalf and Eddy, 1991). Only the liquid-solid interface adsorption process for wastewater treatment was concerned in this study. Adsorption by the filter material is one of the important and major physic-chemical processes in wastewater treatment. It can treat the hardly biodegradable contaminants in wastewater such as phosphorus. During the adsorption process, surface area of the porous cavities on the adsorbing medium provides large area for the process. The impurities diffuse into the pores within the particles and attach onto the internal surfaces by weak electrostatic forces called 'Van Der Waals' forces. The major adsorbents in the wastewater treatment beds used nowadays include materials such as quartz sand, zeolite, polypropylene pellets, fine coke particles, small pieces of synthetic plastic foam, and porous ceramics or activated carbon, etc (Iwai and Kitao, 1994).

High content of Ca in the adsorbing medium will, because of the relatively high pH of domestic sewage, favours precipitation reactions with Ca in the medium.

In situations where the wastewater to be treated is more acidic, the contents of Fe and Al may be more important as the precipitation reactions with these ions are favoured at low pH (Stumm and Morgan, 1981). Furthermore, Brix *et al.*, (2001) examined 13 different sands and found that the most important characteristic of the sands determine the phosphorus sorption capacity is the calcium content. Selection a medium with high adsorption capacity to pollutant is critical to obtain sustainable pollutant removals. To understand the adsorption capacity of an adsorbing medium, laboratory-scale batch experiments or “Isotherms” tests have to be carried out. Knowledge of adsorption process will provide a better understanding of the dynamics of using the adsorbing medium in the purification application. Freundlich Isotherm and Langmuir Isotherm are the two common models to describe and understand the adsorption characteristics of adsorbing medium (Al Duri, 1996).

Freundlich Isotherm

Freundlich isotherm is a model based on an empirical relationship, which is particularly appropriate when low concentration of adsorbent is present. This model describes mathematically the relationship between the amount of impurities adsorbed at equilibrium and the impurity concentration. If substrate fits the Freundlich model, it means the adsorption mechanism of the substrate is multi-layer adsorption. Sorbent was adsorbed from layer to layer (Metcalf and Eddy, 1991). The equation of this model is usually written as follow:

Freundlich model: $qe = kCe^{1/n}$

where,

qe = Amount of solute adsorbed per unit weight of adsorbent,

Ce = Residual equilibrium concentration,

K = Freundlich adsorption coefficient,

n = Coefficient related to the change in residual solution concentration.

This equation also can be expressed in linear form by taking logarithmic plot of qe versus Ce. It yields a straight line. The equation is:

$$\log qe = \log K + 1/n \log Ce$$

Langmuir Isotherm

Langmuir model is based on theoretical development. It is assumed that the solute is adsorbed as a monomolecular layer at the surface of the adsorbent. It is most often used adsorption isotherm, being given by the relationship:

Langmuir model:

$$q_e = \frac{KC_e q_{\max}}{(1 + KC_e)}$$

where,

qe = Amount of solute adsorbed per unit weight of adsorbent,

Ce = Residual equilibrium concentration,

q_{max} = Theoretical maximum of solute adsorbed per unit weight of adsorbent,

K = Constant related to the energy of adsorption.

In order to find the values of constants, K and q_{max}, the model can be expressed as a linear equation:

$$\frac{1}{q_e} = \frac{1}{Kq_{\max} C_e} + \frac{1}{q_{\max}}$$

The biggest advantage in applying the Langmuir model for sorption studies was that it enabled the calculation of theoretical phosphorous sorption maximum for the adsorbing medium (Xu *et al.*, 2006).

2.3.1.3 Plant

To select the appropriate plant species for wastewater treatment purpose in gravel-based system, it is important to consider whether the plants can remediate the contaminants to below action levels and whether they can do so on a reasonable time frame. Plants can withstand fluctuations in flow and shock loadings are recommended. Allen *et al.*, (1989) stated some general criteria for the selection of plants in wetland system. Plants selected should,

1. be active vegetative colonizers with spreading rhizome systems;

2. have considerable biomass or stem densities to achieve maximum translocation of water and assimilation of nutrients;

3. have maximum surface area for microbial populations;

4. have efficient oxygen transport into the anaerobic root zone to facilitate oxidation of reduced toxic metals and support a large rhizosphere; and

Nutrient uptake capacity

Nitrogen and phosphorus are essential elements for the growth of plants. Plant uptake is regard as a direct way to remove nitrogen and phosphorus. Ammonia and ammonium removals by plant uptake are more rapid with growing plants than mature plants (Koottatep *et al.*, 1997; Reed *et al.*, 2001). Ammonia removal will reach steady-state once plant density reaches maximum and the cycle of plant growth and death equalizes. Harvesting of vegetation is practiced to maintain hydraulic capacity and promote active growth (Hoffmann, 1997). It is also done to enhance nutrient removal by growth of new plant tissues. On the other hand, substantial quantities of nitrate can be produced in the rhizosphere of wetland plants through nitrification and taken up by the roots under field conditions. The rate of nitrate uptake can be comparable with those of ammonia nitrogen (Kirk and Kronzucker, 2005). However, it is controversy that the amount of nitrogen and phosphorus removed by uptake is not significant comparing to other removal mechanisms.

Oxygen transferral

Apart from direct plant uptake, plants also facilitate the pollutant removal processes by possible oxygen release from the root zone to the surrounding adsorbing medium. Oxygen diffusion to root tip is one of the physiological characteristics that permit wetland plant species to exist in flooded conditions (Michaud & Richardson, 1989). Oxygen transport varied significantly in the emergent wetland macrophytes. The emergent common reed (*Phragmites australis*), bulrush (*Typha* spp.) and clubrush (*Schoenoplectus* spp.) are morphologically adapted to grow in a water-saturated support medium because of large internal air spaces which transport oxygen from the leaves downwards to the root system. Moreover, the high ammonia nitrogen removal efficiencies shown by bulrush and reed beds are attributed to the ability of these plants to translocate oxygen from the shoots to the roots. The oxidized rhizosphere so formed stimulates sequential nitrification-denitrification (Gersberg *et al.,* 1986).

However, some scholars held the opposite view on the ability of plants of transferring oxygen to root ozone to enhance pollutant degradation in soil or wastewater. Oxygen release from roots into the rhizosphere (according to Platzer, 1998, less than $5g/m^2.d$) is low compared to the oxygen demand for degradation of organic matter and nitrification, and to the amount of oxygen brought into the system via convection and diffusion. Oxygen release from roots can therefore often be neglected especially in subsurface vertical flow constructed wetlands with intermittent loading (Langergraber, 2005).

Area for microbial attachment

Additional surface area for microbial attachment is also provided by plant in wetland systems. Some plants exude enzymes that are capable of transforming organic contaminants into simpler molecules, used directly by the plants for growth, a process known as phytodegradation (Brimblecombe *et al.*, 2004). In some plants, degradation of contaminants occurs when root exudates (e.g. simple sugars, alcohols and acids) stimulate proliferation of microbial communities in the soil around the root (rhizosphere). This is known as rhizo-enhanced degradation. Roots also de-aggregate the soil matrix, allowing aeration and promoting biodegradation (East Texas Plant Materials Center, 2004).

Table 2.2 Common wetland plants in Guangdong

Plant names	**Literature**
Phragmites australis	Tylova-Munzarova *et al*., (2005)
Glyceria maxima	Tylova-Munzarova *et al*., (2005)
Vetiveria zizanioides	Liao (2000)
Calla palustris L.	Liao (2000)
Polygonum hydropiper L.	Liao (2000)
Saururus chinensis (Lour.) Baill	Liao (2000)
Cyperus alternifolius	Liao (2000)
Pennisetum purpureum Schumach	Liao (2000)
Alocasia macrorrhiza	Liao (2000)
Cyperus exaltatus Retz	Liao (2000)
Polygonum lapathifolium L.	Liao (2000)
Juncellus serotinus	Liao (2000)
Ranunculus cantoniensis	Liao (2000)
Scirpus trianulatus Roxb	Liao (2000)
Canna indica L.	Liao (2000)

To sum up, not all the submerged plants or floating plants are suitable for wastewater treatment. As mentioned before, only plants with rapid and relatively constant growth rate, ease of propagation, capacity to absorb or transform pollutants, tolerance of hyper-eutrophic conditions and ease of harvesting can facilitate pollutant removals in constructed wetland system (Mitchell, 1978). Last but not least, climatic and geographic adaptations of the plants are one of the vital considerations for plant selection in designing wastewater treatment systems.

Since the treatment system in this study was designed and tested in Guangdong areas. The common wetland plants in Guangdong areas were considered and are listed in Table 2.2. Most of them actually are used in various wastewater treatment systems world-wide.

Apart from the criteria mentioned before, the predicted depth of plant root penetration has been proposed as a rational basis for determining the appropriate depth of vegetated filter bed treatment systems (Reed *et al*., 1995). Table 2.3 lists the general root depths of some common wetland plants used for wastewater treatment. The longest root length of 300 cm was observed in *Vetiveria zizanioides* (Department of Natural Resources, Mines and Water, Queensland, 2006). The rhizomatous roots of *Phragmites australis* can penetrate to a depth of 40-60 cm (Scholz and Xu, 2002). Sundaravadivel and Vigneswaran (2001) mentioned that the average depth of rhizhosphere for common reed and most other commonly used aquatic macrophytes is 60 cm. *Typha latifolia* is not likely to extend roots down to a depth of >30 cm (Mitsch and Gosselink, 2000). Besides *Phragmites australis*, *Cyperus* species are commonly used in constructed wetlands (Cheng *et al*., 2002; Okurut *et al*., 1999). Liu *et al*., (2004) found that *Cyperus alternifolius* could grow well in phytoremediation system and extend its

Table 2.3 The root depths of common wetland plants.

Plant species	**Root depth (cm)**	**Literatures**
Schoenoplectus spp.	76	Nutall *et al.*, (1997)
Phragmites australis	60	Börner *et al.*, (1998)
Juncus effuses	60	Nutall *et al.*, (1997)
Carex spp.	60	Nutall *et al.*, (1997)
Typha spp.	30	Nutall *et al.*, (1997)
Cyperus alternifolius	200	Liao (2000)
Vetiveria zizanioides	300	Department of Natural Resources, Mines and Water, Queensland (2006)

roots to 200-cm depth. The highest pollutant removal rates (TN, COD and TP) were also demonstrated in *Cyperus alternifolius* compare to *Coleus blumei* and *Jasminum sambac*. It is because *Cyperus alternifolius* and *Vetiveria zizanioides* are both common wetland plants used for wastewater treatment in Guangdong areas, and they are both reported as pollutant tolerated and possessing long root systems. So these two plant species were the good candidates to be employed in the treatment system of this study.

2.3.1.4 Microorganisms

A wide variety of microorganisms are found in wastewaters including: viruses, bacteria, fungi, protozoa and nematodes. These organisms occur in very large numbers, in particular the bacteria for which total counts in the range 1-38 x 10^6

are routinely recorded (Horan, 1990). As mentioned before, most biological processes used for wastewater treatment are derived from processes occurring in nature. Biological treatment process consists of controlling the environment required for optimum growth of the microorganisms involved.

Microbiological processes within wetlands are expected to be similar to those in biological filters like sand filters (Hammer, 1989). Partitioning at interfaces results in sorption of organic materials to form conditioning films, which act as concentrated energy substrate for microbes associated with the surface. These formations of biofilm and bioaggregates favor metabolic interactions, maintenance of refugee, and other enhancement to adaptation, survival, and reproduction of microorganisms (Lawrence *et al.*, 2002; Atlas and Bartha, 1993).

Attached microbial communities colonize all wetted surfaces in aquatic ecosystems (Wetzel, 2001). They form biofilm on the surfaces of adsorbing medium and the plant roots. And biofilm is the place, where most microbiological degradations of pollutant take place in gravel bed system. A biofilm forms when multilayers of bacteria, algae and fungi plus microfauna embedded in a polymer matrix develop at a surface or as mobile biofilms or aggregates (Lawrence *et al.*, 2002). The plant roots and the substrate in biofiltration systems provide a large surface area, which would certainly encourage the development of biofilm at the surface-water interface (Larsen and Greenway, 2004). The rhizosphere of the planted bed is characterized by increased concentrations of heterotrophic bacteria, diatoms, testate amoeba, and other microorganisms (Hattorit and Hottorit, 1973). Vegetation introduced into filter bed system is believed to increase and diversify the microorganisms existing in rooted bed for wastewater treatment purposes.

2.3.2 Removal mechanisms of pollutants

2.3.2.1 Organic matters

Organic matter in wastewater exists in forms of particulate or soluble organics. Particulate organics are mainly removed by filtration and deposition in the adsorbing medium of attached growth system. The biodegradable organics are mainly removed by facultative and anaerobic microbial degradations on surfaces of vegetation root zones and adsorbing medium.

On the other hand, oxygen levels play an important role in degrading the organic matters. With sufficient provision of oxygen, organic matter can be degraded aerobically. The heterotrophic bacteria consume oxygen and release carbon dioxide throughout the aerobic degradation process. And if the oxygen level is not sufficient for heterotrophic bacteria to carry out aerobic processes, the facultative or the obligate anaerobic heterotrophic bacteria will take the roles.

To understand the existing levels of organic matters in the environment, oxygen demands to degrade the organic matters are measured. The three types of oxygen demands commonly used are Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC). BOD is a determination involves the measurement of the dissolved oxygen used by microorganisms in the biochemical oxidation of organic matters. The COD test is used to measure the contents of organic matters, the oxygen equivalent of the organic matter that can be oxidized is measured by using a strong chemical oxidizing agent in an acidic medium. TOC is the measurement of the organic carbon that can be oxidized to carbon dioxide in the presence of a catalyst.

2.3.2.2 Nitrogen

Nitrogen in wastewater and natural environment exists in different forms. Organic forms of nitrogen are mainly urea, amino acid, amines and inorganic forms are ammonium (NH_4^+), nitrate (NO_3^-) and nitrite (NO_2^-). Analysis of nitrogen contents for wastewater treatment also includes the measurement of Total Nitrogen (TN) and Total Kjeldahl Nitrogen (TKN). TKN is the sum of organic nitrogen and ammonia nitrogen while TN is the sum of TKN and NO_3^- plus NO_2^-. Nitrates are highly soluble compounds which can be removed by plant uptake and biological conversion to nitrogen gas. In wetlands, conversion to nitrogen gas by micro-organisms is the main process of removal, where the nitrogen is released into the atmosphere. Nitrite-nitrogen is negatively charged and not adsorbed on soil particles. Thus nitrite-nitrogen remains in the soil solution and can be leached below the root zone and percolate into groundwater (Epstein, 2003).

Major pathways for nitrogen removal in wetlands include mineralization of organic nitrogen, ammonia volatilization, assimilation into biomass, adsorption of ammonium onto the adsorbing medium, and microbial transformations (including nitrification followed by denitrification) (Reddy and Patrick, 1984).

Mineralization is a biological transformation of organic nitrogen to ammonia which occur both in aerobic and anaerobic conditions. **Ammonia volatilization** is the removal of nitrogen via the form of gaseous ammonia to the atmosphere from the system. **Assimilation into biomass** mostly refers to plant uptake and transformation of nitrate into stable organic compounds in plant living tissues. **Adsorption** of ammonium is a process of cation process, however, this removal process is not sustainable as the active sites for adsorption are quickly saturated (Vymazal *et al*., 1998). Ammonia nitrogen is converted to nitrite and nitrate by autotrophic microorganisms in aerobic environment in nitrification. The nitrite and nitrate then provide an alternative electron-acceptor site for bacterial respiration in an anaerobic environment in denitrification, and results in the formation of gaseous nitrogen.

Nitrification

Nitrification of ammonia to nitrate consumes oxygen and biocarbonate ion and releases water and carbonic acid in addition to biomass and nitrate. Nitrification is a principal transformation mechanism that reduces the concentration of ammonia-nitrogen in the treatment system by converting ammonia to nitrates. The oxidation number of nitrogen changes from the -III to the +V through chemical combination with oxygen (Quinlan, 1984; Focht and Verstraete, 1977). It is a two-step microbial process (Reddy and Patrick, 1984). The first step of nitrification, oxidizing ammonia-N(-III) to nitrite-N(+III), is mediated primarily by autotrophic nitrifying bacteria, *Nitrosomonas spp* or nitrite formers. The second step, oxidizing nitrite-N(+III) to nitrate-N(+V), is performed by another nitrifying bacteria species called *Nitrobacter* or nitrate formers. Both steps prefer to proceed under aerobic conditions. Some of the ammonia-nitrogen (NH_3-N) is incorporated into cell mass. The chemical equations of two steps are shown as follows:

Step 1 : $NH_4^+ + 3/2\ O_2 \rightarrow NO_2^- + H_2O + 2H^+$

Step 2 : $NO_2^- + 1/2O_2 \rightarrow NO_3^-$

Vymazal (1985) summarizes that nitrification is influenced by temperature, pH value, alkalinity of the water, inorganic C source, microbial population, and concentrations of ammonium-N and dissolved oxygen. The growth of nitrifying bacteria (autotrophic) is very slow and far more sensitive to growing conditions such as temperature and shock loadings than the heterotrophic bacteria (Tallec *et al*., 1997).

Denitrification

Denitrification is the biological reduction of NO_2^- or NO_3^+ to gaseous forms of nitrogen, usually N_2 and N_2O. Denitrification is generally carried out by facultative heterotrophic bacteria oxidizing carbon substrate as an energy source under the absence of oxygen (Cho *et al*., 2004; Sedlak, 1991). Anaerobes responsible for denitrification are common soil bacteria or fungi, or various wastewater-borne bacteria, the yield of which is a little smaller than that of aerobic bacteria.

Precisely, some nitrate-nitrogen may be reduced to ammonia-nitrogen and assimilated into cell mass, but the bulk of the nitrate-nitrogen is removed from wastewater via dissimilatory metabolism, ultimately to nitrogen gas (N_2). The first stage is dissimilatory nitrate reduction which reverses the nitrification process and converts nitrate (NO_3^-) back to nitrite (NO_2^-). The second stage of denitrification converts nitrite to nitric oxide (NO), nitrous oxide (N_2O) and finally nitrogen gas (N_2) – all of these last three products are gases then can be released into the atmosphere, although denitrifying organisms and an organic carbon source are required (Sedlak, 1991). The carbon requirements may be provided by internal sources, such as wastewater to be denitrified must contain sufficient carbon (organic matter) to provide the energy source for the conversion of nitrate to nitrogen gas by the bacteria. Or the carbon requirements may be provided by an external source, like addition of methanol. The growth of heterotrophic bacteria under anoxic conditions may be limited by the availability of either the carbon required for cell synthesis, or nitrate as the electron acceptor. Unlike, nitrification, however, there do not appear to be specialized organisms responsible for the process, and the two steps are not necessarily performed by two separate organisms. The change of the form of nitrogen in denitrification is shown as follows:

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

The chemical mechanism of denitrification is:

$2NO_3^-$ + organic matter $\rightarrow NO_2^- \rightarrow N_2\uparrow + CO_2$ + H2O

In fact, the conditions for denitrification, an anaerobic (anoxic) environment containing a carbon source, are easily met in most constructed wetland system, but the oxidizing conditions necessary for formation of nitrate are often limited (Brix and Schierup, 1990), hence, nitrification restrains the rate of denitrification.

2.3.2.3 Phosphorus

Because of noxious algal blooms that occur in surface waters, there has been much interest in controlling the amount of phosphorous compounds that enter surface waters from domestic and industrial waste discharges and natural runoff (Metcalf and Eddy, 1991). Apart from nitrogen removal, phosphorus removal is usually another main objective of domestic wastewater treatments.

Phosphorus removal in constructed wetland occurs mainly as a consequence of adsorption, complexation, and precipitation with aluminium, iron, calcium and clay minerals in the sediments (Brix, 1993). Most soils have rather high capacities to retain phosphorus; these are determined by the net effect of physical, chemical and microbial processes involved in phosphorus transformations (Sundblad and Wittgren, 1997). Studies of the removal of phosphorus by constructed wetland have been carried out in many countries (Kadlec and Knight, 1996; Mann, 1997). A more comprehensive of understanding is that the immobility of phosphorous occurred through substrate adsorption, chemical precipitation, bacterial action, plant uptake and incorporation into organic matters.

Arias *et al.*, (2001) studied the phenomenon of total phosphorus removal in subsurface flow constructed wetlands and concluded that the major pollutant removal mechanism was the sorption onto filter media. It is well documented that phosphorous adsorption and retention in fresh-water wetland soil is controlled by interaction of redox potential, pH, Fe, Al and Ca minerals, and the amount of native soil phosphorus (Richardson and Craft, 1993). It is stated that Fe-and Al-rich mineral soils generally have a high capacity for phosphate adsorption and precipitation (Jennsen, 1997; Bucksteeg, 1990). Brix *et al.*, (2001) documented that the most important characteristics of the media determining P-sorption capacity was their Ca-contents.

Besides adsorption, removal of phosphorous can be achieved biologically, the biological alternative has a number of significant advantages such as considerably lower operating costs, less sludge production and no chemical contamination in the sludge (Keller, *et al*., 2001). Phosphorus in the environment cycles between organic and inorganic forms. Orthophosphate (PO_4^{3-}) is the only form of phosphorus that is used readily by most plants and microorganisms.

Basic principles of biological P removal:

1. Certain microorganisms, when subjected to anaerobic conditions, assimilate and store fermentation products produced by other facultative bacteria. These microorganisms derive energy for this assimilation from stored polyphosphates, which are hydrolyzed to liberate energy. The free phosphorus that results from the hydrolysis is released to the mixed liquor.
2. The same organisms, when subsequently exposed to aerobic conditions, consume both phosphorous (which is used for cell synthesis and stored as polyphosphate) and oxygen to metabolize the previously stored substrate for energy production and cell synthesis. The organisms take up the phosphorous in excess, to remedy their former phosphorous starved conditions. They take in more phosphorous than they previously released. The phosphorous is removed form the wastewater stream by wasting of excess sludge generated in the treatment process.

However, biological phosphorus removal by microorganisms did not play an important role in constructed wetland since there is no sludge removal or active control of aerobic and anaerobic conditions in the system. The only sustainable biological removal mechanism for phosphorus is plant uptake and the subsequent harvesting (Lantzke *et al.,* 1998). For long-term removal of phosphorous by subsurface flow wetlands no well founded dimensioning proposal could be found in the literature, nonetheless many publications show very high performance of phosphorous removal by planted or unplanted soil filters in the first year of operation (Rustige and Platzer, 2001).

2.3.2.4 Suspended solids

The removal mechanisms for suspended solids in the wetland treatment system essentially fall under two processes: the first is essentially sedimentation where the suspended solids ultimately settle to the bottom. Retention time and contact with plant materials enhance this process; the second important process is adsorption. Adsorption of suspended solids also aids in the reduction process, many chemical constituents tend to attach or adsorb onto solids (Martin and Johnson, 1995). Physical settling and entrapment of solids occur in the pore spaces or interstices between the soil particles, gravel or rock in the constructed

Table 2.4 The main removal mechanisms of organic matters, nitrogen, phosphorus and suspended solids in constructed wetlands.

Wastewater constituent	**Removal mechanisms**
Organic matter	- Microbial degradation (aerobic and anaerobic) - Sedimentation (accumulation on sediment surface)
Nitrogen	- Ammonification followed by microbial nitrification and denitrification - Plant uptake - Assimilation by biomass - Ammonia volatilization
Phosphorus	- Soil sorption (adsorption-precipitation reactions with Al, Fe, Ca, clay and mineral in soil) - Sedimentation
Suspended solids	- Sedimentation - Filtration - Microbial degradation

(From Brix, 1993)

wetland support medium, there is also some removals by microbial decomposition in the support medium under both aerobic and anaerobic conditions (Nutall *et al.*, 1997). Most of the removal of suspended solids occurs within the first few metre of inlet and this is caused by filtering and trapping ability of particles in the support medium of subsurface-flow system (Nutall *et al.*, 1997). A subsurface-flow gravel-bed system is more efficient at promoting sedimentation and separation of particles than surface-flow bed system.

To conclude, the dominant removal mechanisms of main wastewater constituents in constructed wetland are summarized in Table 2.4.

2.3.3 Limitations and modifications of constructed wetlands

The subsurface flow constructed wetland can be divided into horizontal flow and vertical flow. The applications of horizontal flow wetland to sewage treatment have been widely studied, while the understanding of vertical flow is comparatively low. **Horizontal flow constructed wetlands** are effective in removing biochemical oxygen demand (BOD) and total suspended solids (TSS), but most systems have been relatively ineffective in removing ammonia nitrogen (Watson and Danzig, 1993). They are usually applied to tertiary treatment because of their limited oxygen transport ability (Sun *et al*., 1999).**Vertical flow constructed wetlands** have smaller foot-print than the horizontal flow system, like the requirement of land. Vertical-flow systems have been promoted for the ammonification of nitrogen, and oxidation of ammonia nitrogen to nitrite and nitrate thus providing a fully nitrified effluent, low in both biochemical oxygen demand and suspended solids (Nutall *et al.*, 1997). Under the fact that vertical flow bed provides aerobic environment but not anaerobic one, it has a higher rate of nitrification but a relative low rate of denitrification. Moreover, BOD removal is more efficient in vertical down-flow wetlands than horizontal-flow systems.

Hence, subsurface-flow constructed wetland treatment system typically results in satisfactory organics removals. However, the removal of nutrients, particularly nitrogen, is often weak and typically less than desired, though the removal of ammonia nitrogen has been enhanced in vertical flow bed than in horizontal flow bed. In fact, the complete removal of nitrogen from a wastewater requires that both nitrification and denitrification occur, as denitrification cannot proceed without the presence of nitrate. The two reactions appear to have fundamentally opposite environmental requirements, particularly with respect to oxygen (Horan, 1990). Classical constructed wetlands are not capable to provide both requirements simultaneously. In addition, constructed wetlands' application to wastewater treatment constraints to areas with sufficient lands, and so is not flexible to adapt different geographical situations and various wastewater demands. Other means of the operation technology have to be integrated into the constructed wetland system to overcome its shortcomings. The conventional constructed wetland technology has to be modified before it could be applied to wastewater treatment in suburban areas. In other wastewater treatment systems like the sequencing batch reactor, nitrification and denitrification could be achieved in a single reactor. By providing spatial or temporal zones within the reactor where aerators are switched off, and only mixing occurs, anoxic conditions are quickly established and denitrification will occur in a sequencing batch reactor. Sequencing batch reactor technology also possesses its advantages of small land requirement.

Latest modification of vertical flow constructed wetland raised by the western scholars is the integration of tidal flow rhythms into the operation cycles. Tidal flow reed bed emerged in recent years as a novel system in that the bed matrix is rhythmically filled with wastewater then drained (Green *et al*., 1997 & Sun *et al*., 1999). Vertical flow systems with intermittent dosing which use sand as the main layer represent the latest generation of subsurface flow constructed wetlands and are state of the art for this technology for wastewater treatment in Europe (Vymazal *et al*., 1998). Currently, there have been a number of systems which combine fixed-film processes with sequencing batch reactors and some with sequenced fixed-film processes (Dowing and Cooper, 1998). The concept of rhythmical flow operation in constructed wetland is similar to that of the conventional sequencing batch reactor (SBR). The sequencing “fill” and “draw” actions on the water flow alter the air content of the system, and as a result improve the pollutant removal efficiency of the system. When wastewater is filling into the soil bed, biochemical reaction take place to degrade the pollutants in the wastewater. After the soil bed has been fully soaked for a period of time, water is then drawn out from the system and air is simultaneously sucked back to the soil bed. It is found that at the time when water is drawn out from the system, oxygen is consumed at the highest rate. So fresh air enters the system during the “draw” phase is the main source of oxygen for pollutant removal reactions. By alternating in and out action of wastewater and air, the system can achieve the highest rates of oxygen transferal and consumption, have the most diversified microbiological, chemical and physical reactions for removing pollutants, as a result highly enhance the efficiency of the treatment system. However, the research or technical reports about this technology can be scarcely found, and the optimal operational conditions for this type of sewage treatment system are still not well known. In spite of a large number of theoretical and empirical investigations already carried out concerning similar kinds of bed system, a specific design approach has not yet been established.

2.4 Modelling of biological treatment kinetics

The reactions which occur in a wastewater treatment process may be considered as a change in concentration of a substance or an organism. Physical, chemical and biological processes induce these changes, which can often be modelled using simple reaction rate theory. The aims of system modelling are to optimize the design and operation of the treatment facility and to predict the treatment performance. The earliest modelling of wetland was published in the mid 1970s (Mitsch, 1983). The number of models of more different kinds of operations has steadily increased.

The derivation of mathematical models which can accurately describe and predict the events occurring during a wastewater treatment process, required the selection of suitable equations to describe both the hydraulic regime within the reactor and also the growth of microorganisms on organic and inorganic substrate (Horan, 1990). The purpose of reaction kinetics in biological treatment processes is to develop microorganism and substrate balances and to predict the effluent microorganisms and substrate concentrations. Novák *et al*., (1997) developed a mathematical model that describes volume changes and simultaneously the biodegradation kinetics.

On the other hand, selection of reaction-rate expression for the fate processes is also important for accurate prediction of wetland treatment performance. The selection is based on 1) information obtained from the literature, 2) experience with the design and operation of similar system or 3) data derived from pilot plant studies (Crites and Tchobanoglous, 1998). Wynn and Liehr (2001) stated that in current wastewater wetland design models, reactions are lumped into zero- or first-order black-box kinetics models and plug flow hydraulics are used (Kadlec and Knight, 1996).

2.4.1 Microbial reaction kinetics

The simplest technique for modelling substrate removal in wastewater reactors is to observe the rate at which substrate is removed with time and to define this by means of a simple rate-removal constant (zero, first or second order). Mostly the Monod model for microbial growth on rate-limiting substrate is utilized (Horan, 1990). The Monod model differs from the classical growth model in the last half century in the way that it introduces the concept of growth-controlling substrate. It described microbial growth rate as a function of substrate availability and the requirements of the specific organisms. Monod's model relates the growth rate to the concentration of a single growth-controlling substrate via two parameters, the maximum growth rate ($\mu_{\max}$) and the substrate affinity constant (K_s),

→ $$\mu = \frac{\mu_{\max}(NH_3{-}N)}{K_s + (NH_3{-}N)} \qquad \text{(Monod equation)}$$

where,

μ is the growth rate (d^{-1}),

$(NH_3\text{-}N)$ is the concentration of ammonia nitrogen (mg/L),

$\mu_{\max}$ is maximum specific growth rate (d^{-1}),

K_s is substrate affinity constant (mg/L).

2.4.2 Plant uptake kinetics

Elements are taken up by vegetation at a rate that is a Michaelis-Menten function of element concentration and is proportional to the surface area of vegetation that is active in uptake of that element (Rastetter and Shaver, 1992). Vegetative uptake of ammonia and nitrate can be described by Michaelis-Menten kinetics or zero-order kinetics (Kadlec and Knight, 1996; Martin and Reddy, 1997).

Michaelis-Menten kinetics:

$$\frac{dS}{dt} = \frac{k_m S}{k_m + S}$$

where,

S is the substrate concentration (mg/L),

k_m is the Michaelis-Menten constant (mg/L).

Some relevant literatures on plant uptake kinetics were studied. Romero *et al.*, (1999) has studied the interactive effects of nitrogen and phosphorus on growth and nutrient uptake kinetics by *Phragmites australis* by Michaelis-Menten kinetics. Later on, Bijlsma and Lambers (2000) presented a whole-plant model of carbon and nitrogen metabolism and aimed at comparing the growth performance of plant species in a range of environments with respect to irradiance and availability of nitrate and ammonium. Recently, Verkroost and Wassen (2005) have developed a model that quantified the nitrogen allocation and its relationship to plant nitrogen concentration in nitrogen-limited plant growth. Extensive considerations of the kinetics and energetic of both nitrate and ammonia nitrogen have been carried out for the understandings of nitrogen for the growth of plants.

Chapter 3: Materials and Methods

3.1 Study Approach

The study aimed to understand the pollutant removal mechanisms and to optimize the operating conditions of a vegetated sequencing batch biofilm reactor for domestic sewage treatment, and to form a database from the optimal values of the controlled variables that can be modified to adapt different domestic sewage treatment demands. Both planted and unplanted coal slag beds were established in laboratory-scale and pilot-scale. The flow chart in Fig. 3.1 shows the study approach of this study.

The selection of plant species and adsorbing medium in the filter bed were based on the comprehensive literature reviews and the bench experiments. Some bench experiments were done for the basic understandings of the selected adsorbing medium and plants in the system. Hydroponics experiments with three levels of organic strengths were used to test the plant tolerances to pollutant concentrations and plant growth conditions. The final combination of supporting medium and plant formed the basis of the system configurations.

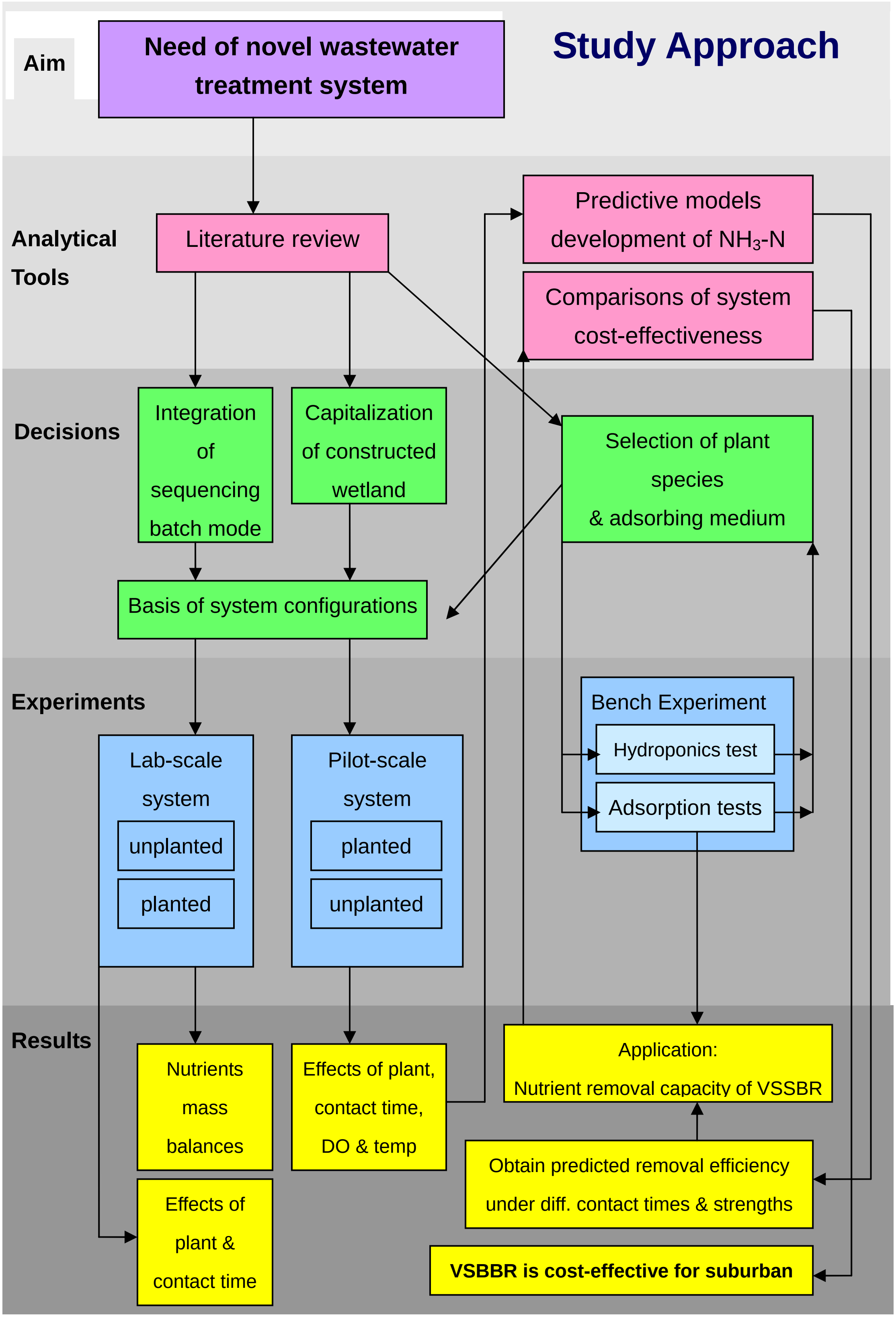


Fig. 3.1 Flow chart showing the study approach.

Both laboratory-scale and pilot-scale reactors were set up with similar system configurations. The operation of the pilot-scale experiment was targeted to scale up that of the lab-scale experiment. The contact time and hence the rhythmical (tidal-flow) movement of air/water was tested for its optimal value. The organic strength from the local wastewater discharge was tested as the influent concentration in the pilot-scale experiment. The most appropriate operational strategy has been identified by comparing pollutant removal efficiencies with different contact times. Engineering design details that play a determinant role to maximize the efficiency of the system were carefully studied.

The lab-scale experiment with both planted and unplanted (control) systems were set up to test the pollutant removal efficiencies of the reactor in a controlled environment. The data from the lab-scale experiment were used to formulate the nutrients mass balances and to understand the conversion efficiencies of different pollutants through different removal mechanisms. The optimal operational conditions in the pilot-scale experiment also took the real case fluctuations into considerations. The effects of plant, contact time, dissolved oxygen and the seasonal variations were particularly examined in the pilot-scale experiment.

Since the system was designed to treat domestic sewage in suburban areas, in where discharge of nutrients including nitrogen and phosphorus always lead to the problem of eutrophication, so the elimination of nitrogen and phosphorus is prior to the system design process. Predictive model was generated specific to the removal of ammonia nitrogen in this study while adsorption isotherm study was also done to understand the removal of phosphorus by such coal slag bed system. The findings and the model being generated from the pilot-scale experiment were used to predict the system performance under different pollutant strengths and for different treatment demands. Contour plots with a set of suitable operating combinations of contact time and organic strengths were determined to get desirable removal efficiencies of pollutant.

3.1.1 Conceptual details of the system studied

Under the fact that wastewater treatment facilities in rural areas should take maximal advantage of their land availabilities and hence constructed wetland can play the role. However, land availability in suburban areas is not as adequate as in rural areas. At the boundary of developing zone of urban area, land supply in suburban area is under increasing pressure from the rapid urban development, and so conventional constructed wetland can not be the long-term solution of wastewater treatment demands. Modification of existing constructed wetland technology has to be made to adopt the wastewater treatment demands in suburban areas.

In this study, a low cost wastewater treatment system treating small community in suburban areas was developed and its operating conditions and removal efficiencies were optimized. Small community in this study was defined as the population equivalent (p.e.) of 500-10,000 (Tsagarakis *et al.*, 2003). The low-cost constructed wetland treatment technology formed the basis of the studied system. The principal of the studied system is capitalized on the pollutant removal mechanisms of the soil-plant-microbe interaction of constructed wetlands. Large land requirement was attempted to be eliminated by optimizing the operating conditions in the system for equivalent treatment efficiency. On the other hand, no matter constructed wetlands or biofilter beds need to be rested periodically to allow breakdown of accumulated organic matter. It is because resting of beds allows air to get into the bed to aerate and reduce the likelihood of anoxia. Drying of beds is occasionally required to enhance performance. The process design of the studied system has integrated the resting of bed in a single bed as a time sequence.

Subsurface flow wetlands are designed to provide contact between water, roots and adsorbing media. This type of system is variously called underground, gravel bed, or rock bed wetland, or rock bed filter (Kadlec and Watson, 1993). As the studied system adopted the periodic feeding frequency like that of sequencing batch reactor, and plant is present in it to provide functional and aesthetic values, it was named as vegetated sequencing batch biofilm reactor in this study. Other way of saying, the studied system is vegetated gravel beds, somewhat similar to a traditional percolating filter but planted with emergent vegetations.

The vegetated sequencing batch biofilm reactor actively utilizes the natural behaviour of plant, soil and microbes. It is a self-contained, artificially biological system which capitalizes on the purifying nature of vertical flow constructed wetland. A symbiotic relationship of plant, soil and soil microbes are established in the system to remove pollutants from wastewater. Microbiological, chemical and physical processes naturally occurring in wastewater treatment are optimized by the sequencing batch modes to obtain the highest pollutant removal efficiency. The basic removal processes for pollutants include biological conversion, sedimentation, chemical precipitation, and adsorption (Tchobanoglous, 1997). Pollutants are adsorbed in the soil bed and decomposed by the soil microbes. The biological activity is contributed by numerous microbes and living organisms exist in the soil be which contains clay minerals and organic substances. When the soil contacts with wastewater pollutants such as nitrogen compounds and phosphorous compounds, there follows a process of adsorption onto the soil particle surface, dissolution by soil water and absorption and decomposition by soil microbes, the micro-organisms use organic pollutants as a food source, breaking down a wide range of organic chemicals. These chemical are not simply stored in the soil, but are actually degraded into harmless components, resulting in purification of the wastewater. Other contaminants, such as metals, are transformed from their toxic, mobile state and fixed in the soil via complex chemical reactions. Moreover, the plants are supposed to transfer atmospheric oxygen down through their roots in order to survive, allowing extraordinary microbial species to flourish. The plants also provide additional pollutant absorption functions to the system.

3.2 Bench experiments

3.2.1 Adsorbing medium

The characteristics of adsorbing medium influence the design of fixed-film bioreactor like constructed wetland. Coal slag from one of the power plants in Guangzhou was used as the adsorbing medium in this study. Some physical-chemical studies were carried out on the coal slag to understand the resulting hydraulic properties and adsorption properties of the vegetated sequencing batch biofilm reactor. Since physical adsorption is the one of the major removal mechanisms of pollutants from wastewater passing through attached-growth system. High adsorption capacity of a material to pollutant would imply its fitness to be the adsorbing media in the system. It is because the adsorbing medium in the system is the place where most chemical transformations take place. To investigate the adsorption capacity of coal slag, batch equilibrium adsorption isotherm experiments were performed on the two main nutrients in domestic wastewater, nitrogen and phosphorus.

3.2.1.1 Physio-chemical studies

Size Distribution of coal slag

The particle size distribution was analyzed by sieve analysis. The standard sieve sizes used in the experiment were 20mm, 10mm, 5mm, 2.36mm, 1.18mm, 600μm, 425μm, 300μm, 150μm, 75μm and pan (with mesh opening). The size distribution was plotted on the semi-log scale chart. The D_{10}, D_{60} and the uniformity of the particle size distribution were calculated.

Porosity

Porosity is the ratio of the volume of voids to the total volume of the filter media (Craig, 1997). The amount of water needed to saturate a known volume of medium was used to determine the porosity. (i.e. Put coal slag into a 1-litre container fully, then fill water until the coal slag saturates. The ratio of the volume of water being filled to the volume of container is regarded as porosity).

Surface observation by Scanning Electron Microscope

Surface of the adsorbing medium is the place where biofilm forms. Porous surface favours microbial attachment and provides larger area for physical adsorption sites. Hence, the surface characteristic of coal slag was observed under Scanning Electron Microscope (SEM). The principal of the microscopy is basically a small probe of electrons that move rapidly across a soil surface. The back-scatter of these electrons gives the three-dimensional effect and thus in situ analyses of roots and soil organisms are possible (Paul and Clark, 1988).

Before observed under SEM, small pieces of coal slag were fixed with the fixative of 4% paraformaldehyde in 0.1 M PBS (phosphate buffer saline). Then the coal slag was dehydrated in a sequence with different concentrations of 30%, 50%, 70%, 90% & 100% of ethanol for 20 mins to 30 mins in each concentration. A drying agent - hexamethyldisilazane was used to soak the coal slag to replace the ethanol (Dykstra and Reuss, 2003). Then the coal slag were poured onto filter paper in fumehood and mounted onto aluminium holder by carbon tape. The whole aluminium holder with coal slag was then coated with gold by BAL-TEC SCD 050 Sputter coater. The surface characteristic was then observed under Philips XL 30 Esem-FEG Environmental Scanning Electron Microscope.

3.2.1.2 Adsorption tests

Adsorption experiments were carried out to understand the transferals of pollutant compounds between solid (adsorbing medium) and liquid (wastewater) phases in soil medium. Adsorption isotherms are simply relations between the moles of sorbate adsorbed per unit mass of sorbent and the concentration of sorbate remaining in solution at equilibrium at a constant condition. Experimental determination of an isotherm was accomplished by mixing a known amount of adsorbent with a given volume of liquid of known initial sorbate concentration. The adsorption process was described by the use of Langmuir or Freundlich expression. Langmuir and Freundlich equations were fitted to the bench experimental adsorption data using least squares parameter estimation method.

Phosphorus adsorption test

The physical size distribution of the samples being tested must be consistent because particle size affects the rate of adsorption. In this bench study, the size fractions of the coal slag chosen for adsorption isotherm experiment ranged from 1.18 mm to 475 μm. Approximately 5g of coal slag were placed in 200-ml flasks, 100 ml deionized water spiked with NaH_2PO_4 to give one of the 15 levels of phosphorus concentrations (0, 2.5, 3.66, 5, 10, 20, 40, 60, 80, 160, 240, 320 and 360, 480 and 540 mg P/L) was added to the flasks (Brix *et al.*, 2001). The flasks were sealed with parafilm and were agitated in an electrical shaker at 200 rpm for 24 hours at temperature of 25℃. The supernatant from each flask was centrifuged at 4000 rpm for 10 mins before filtration. The filtrate was then analysed for the concentration of total phosphorus.

Ammonia nitrogen adsorption test

The size fractions of the coal slag chosen for adsorption isotherm experiment ranged from 1.18mm to 475μm. Approximately 5g of coal slag was placed in each 200-ml flask. Nine levels of ammonia-nitrogen concentrations chosen for the adsorption isotherm experiment were 0.5, 1, 2, 10, 50, 100, 200, 500 and 1000 mg/L. The flasks containing 100 ml of ammonia nitrogen solution with various concentrations were sealed with parafilm and were agitated in an electrical shaker at 2000 rpm for 24 hours. The supernatant from each flask was centrifuged at 4000 rpm for 10 mins before filtration. The filtrate was then analysed for the concentration of ammonia nitrogen.

3.3.2 Plant selection

3.3.2.1 Growth rate and pollutant tolerance tests

Hydroponics experiment was done to test the growth rates and the pollutant tolerance abilities of the two plant species selected from literature reviews. One of the reason of selecting *Cyperus alternifolius* and *Vetiver zizanioides* as the candidate plants in the vegetated sequencing batch biofilm reactor is their long root lengths. Plant with long root would be an advantage in the pilot-scale system with 1.5 m in depth. Hydroponics cultures were maintained in three plastic boxes with the dimensions of 40 cm in length, 30 cm in width and 15 cm in height. Young plants of 2-week old bought from local flower market were used in the experiment. Three individual plants of each species were supported by floating foam board inside the box with the root parts submerged (Total 6 plants in each box). Municipal wastewater from Tai Po wastewater treatment plant, Hong Kong was used in the cultures. Dilutions of the wastewater were made to get three organic strengths for the test.

The ranges of organic strengths with various pollutant concentrations are shown in Table 3. 1. The wastewater in plastic boxes was replaced every 3-4 days. The cultures were subject to sufficient direct and indirect variable natural day-light and artificial light. The air temperature range was between 18.9 and 22.5℃ throughout the experiment. After one-month culturing period, the biometric characteristics of the two plant species were compared and the plant species with better growing performance was employed in both laboratory-scale and pilot-scale systems for wastewater treatments. The biometric characteristics being investigated included the increments of shoot length and root length, fresh weight increment before and after the experiment. Dry weight proportions of

Table 3.1 Pollutant concentrations of the three strengths of wastewater (mg/L)

Parameters	LOW	MEDIUM	HIGH
BOD_5	29.29 ± 9.86	60.64 ± 16.50	115.87 ± 38.64
COD	105.16 ± 38.44	214.81 ± 52.59	484.83 ± 83.10
TSS	39.44 ± 8.55	69.00 ± 12.94	125.67 ± 22.63
TKN	10.821 ± 3.719	14.952 ± 4.643	26.072 ± 6.579
NH_3-N	11.53 ± 2.29	21.1 ± 2.86	44.09 ± 5.26
NO_3^--N	4.4 ± 0.83	7.4 ± 1.21	15.5 ± 2.30
TP	3.48 ± 0.89	7.57 ± 2.89	15.38 ± 4.12

Concentration values are given as averages (mg/L) ± standard deviation (mg/L).

nitrogen and phosphorus contents in the two plant species were also determined.

3.3 Laboratory scale system performance study

3.3.1 Process designs

The main objective of the laboratory-scale experiment was to examine the compatibility of growing the selected plants in the selected adsorbing medium for domestic wastewater treatment. Another objective was to investigate the nutrient balance of the whole system within the study period.

After selecting the adsorbing medium and the plant for the soil-plant-microbe interactive system, treatment process was designed to investigate the performance of such combination for domestic wastewater treatment. To imitate the operation of the on-site treatment system, two laboratory-scale bed systems were set up. Ten young plants of *Cyperus alternifolis* was planted into one of the systems with their initial fresh weights being recorded. Coal slag filled up the tanks of 15 cm in height, 40 cm in length and 30 cm in width. The effluent point was at the bottom of one side of the tank. 5 cm of gravel layer was placed at the bottom of the tank to prevent washing out of coal slag from the outlet. The empty tank volume was 18 L. Municipal wastewater from Tai Po wastewater treatment plant, Hong Kong, was used as the raw influent to the systems. Dilution of wastewater was made to obtain the pollutant concentrations equivalent to the low strength of wastewater being used in the hydroponics experiment.

3.3.2 Operating conditions

The analysis commenced when the plants have been established in the bed for 3 weeks with regular watering. The two beds of coal slag (one with plants and one without) were placed in the laboratory, which were subject to sufficient direct and indirect variable natural day-light and artificial light. The air temperature range was between 18.9 and 22.5 ℃ throughout the experiment.

The laboratory-scale experiment started in November 2003. Three-month start-up period from November 2003 to February 2004 was allocated to allow extensive plant root development and establishment of biofilm on the coal slag. Wastewater was fed into the system intermittently. Build up of biofilm on coal slag surface was verified by observation of coal slag under SEM.

After completion of the start-up stage, the operating stage of the laboratory-scale experiment began in March 2004. The operation of the laboratory-scale was the preliminary test of the pilot-scale experiment. The operating cycle of the laboratory-scale experiment involved “fill” phase, “react” phase, “draw” phase and “idle” phase, among which the “fill” phase was fixed at 4 hours due to the limitation of onsite pump facilities in the pilot system in Guangzhou. Operation of the laboratory experiment was attempted to imitate that of pilot experiment as much as possible. The flow rate of the pump was fixed at 4.5 L/hour. The “draw” phase was 2 hours in the laboratory-scale system because it was found that 2 hours were needed for the pilot system to release effluent completely by gravity.

The pollutant removal capacity of the laboratory system was examined with contact time of 18 hours and 0 hour after the “fill” phase of 4 hours. Every contact time was tested for a 2-month period. The treated wastewater was drained into the laboratory-scale bed systems by peristaltic pump on Monday, Wednesday and Friday of each operational week. In other words the systems were roughly filled with wastewater every two days. The two contact times were chosen in the lab-scale test because 18 hours and 0 hour were the maximum and the minimum durations based on the on-site operating conditions of the pilot system with a cycle of 24 hours a day. With a “fill” phase of 4 hours and a “draw” phase of 2 hours in the pilot systems, the resulting maximum hours of “react” phase within 24 hours is 18 hours.

The schedule of the system operation is summarized in Table 3.1. Apart from the studying the nutrient mass balance in the system, the findings from the laboratory-scale experiment on one hand could give some hints for the preparation of the pilot-scale experiment, and on the other hand could be used in comparison with the performance of the real case pilot-scale systems.

Table 3.2 Operating schedule of the laboratory-scale systems

Stage	**Duration**	**Contact time**
Start-up	Nov 03- Feb 04	
Operation	Mar - Apr 04	18 hours
	May - Jun 04	0 hours

3.3.3 Sampling and analytical details

Influent and effluent were collected from the laboratory-scale systems for the calculations of pollutant removal efficiency. Parameters being analyzed were COD, BOD_5, NH_3-N, NO_3-N, TKN, TP and TSS in the wastewater.

Plant heights and root lengths were determined following the procedures outlined by Hendry and Grime (1993). Samples of above-ground biomass of plant were taken at the end of Feb 04 (after start-up stage) and at the end of Apr 04 (after 18-hour operation period) for N and P analyses. The total nutrient input and retention in the systems were monitored. These nutrient analyses were used together with biomass measurement to estimate nutrient pools in vegetations.

Nutrients retained on the adsorbing medium and accumulated in plant contents were measured as follows: either coal slag samples or plant samples were freeze-dried and ground into fine power form for measurements of nitrogen and phosphorus contents.

For total phosphorus analysis, about 0.250g (± 0.001g) of ground samples were weighted into a pre-washed digestion tube added with 3.5 g potassium persulfate. 50 ml deionized water was added to wet the sample. 10 ml of concentrated H_2SO_4 was added into each tube and vortex (~ scale 6). The tubes were then placed in the aluminium heating block and heated for 30 mins at 200ºC. The digestion was continued for 2 hrs at 370ºC. Cooling to room temperature, the solution was poured into centrifuge tube and centrifuged for 4000 rpm for 10 mins. The pH of the supernatants was adjusted to 8.2 by adding 40% NaOH. The level of total phosphorus was measured by Acid Persulfate Digestion Method (USEPA accepted for reporting wastewater analysis).

For total nitrogen analysis, 0.250g (± 0.001g) of dry ground samples were weighted into digestion tubes. 50 ml of deionized water was added to each tube to wet the samples. 3.5 g K_2SO_4-catalyst mixture and 10.0 ml of concentrated H_2SO_4 were added into each tube. The digestion tubes were placed in the aluminium heating block and heated for 30 mins at 200°C. Then the digestion was continued for 2 hrs at 370°C. After the digestion, the tubes were placed at room temperature for cooling. Afterwards, 50 ml of ammonia free deionized water was added into each tube. 25 ml of receiving solution and 10 drops of bromocresol green methyl red mixed indicator were filled in an Erlenmeyer flask. The flask was placed in the receiving position in the steam distilling unit. The distilling unit automatically added 50 ml of dilution water and 50 ml of 40% NaOH and performed the distillation process. The resulting solution in the Erlenmeyer flask was titrated with standard H_2SO_4 (0.02 N acid).

Mass balance of nitrogen and phosphorus were calculated by the comparison of total nutrient inputs and outputs for the system, the total nutrient retained in the adsorbing medium, the total nutrient uptake by plant and the estimation of total nutrient biodegraded by microorganisms in the designated period. The different pollutant removal mechanisms contributed by different components of the systems and the system equilibrium could be understood. The concentration of total nitrogen was obtained by summing up the concentrations of NH_3-N and NO^-_3. For the calculation of nutrient balance, the concentration of TKN (mean of influent = 15.67 ± 0.63 mg/L) was assumed to be equal to the concentration of

NH_3-N (mean of influent = 14.61 ± 4.68 mg/L) in this study after comparing the measured values of the two parameters.

3.4 Pilot scale system performance study

3.4.1 System specifications

The pilot-scale experiment was carried out onsite in the South China Agricultural University, Guangzhou, People's Republic of China. Start-up stage of the system began in November 2004. About four months from November 2004 to April 2005 was allocated to allow plant growth and establishment of biofilm on the coal slag in the start-up period. Establishment of biofilm was confirmed by the observation by SEM, as well as reflected by steady pollutant removal efficiencies.

The pilot systems in parallel were constructed near a pond in the campus of the South China Agricultural University. Before the installation of the studied systems, the pond has been receiving the domestic sewage without any treatment from about 800 households in the campus for many years. The pond water was stinky and turbid. During the study period, the domestic sewage collected from the local sewer in the campus, instead of discharging into the pond directly, was drained to a sedimentation tank before entering the pilot treatment systems (Fig. 3.2). This pretreatment is to reduce the level of suspended solids in the influent and it was intended to defer the replacement of adsorbing medium in the system due to possible clogging.

Each pilot system was made of concrete with the dimensions of 5.0 m in length, 3.0 m in width and 1.8 m in depth (Fig. 3.3). The depth of the system was similar to that of constructed wetland with a range of 1.5 m to 2.0 m (Hammer, 1989). The empty bed volume of each system is 27 m^3 with an effective volume of 13.6 m^3. 50-100 mm stone were placed around the influent distributor and the effluent collector pipes to reduce the potential of clogging. The wastewater fell into the inlet zone from the tap, and then passed through the perforated partition into the bed matrix.

Fig. 3.2 Sedimentation tank

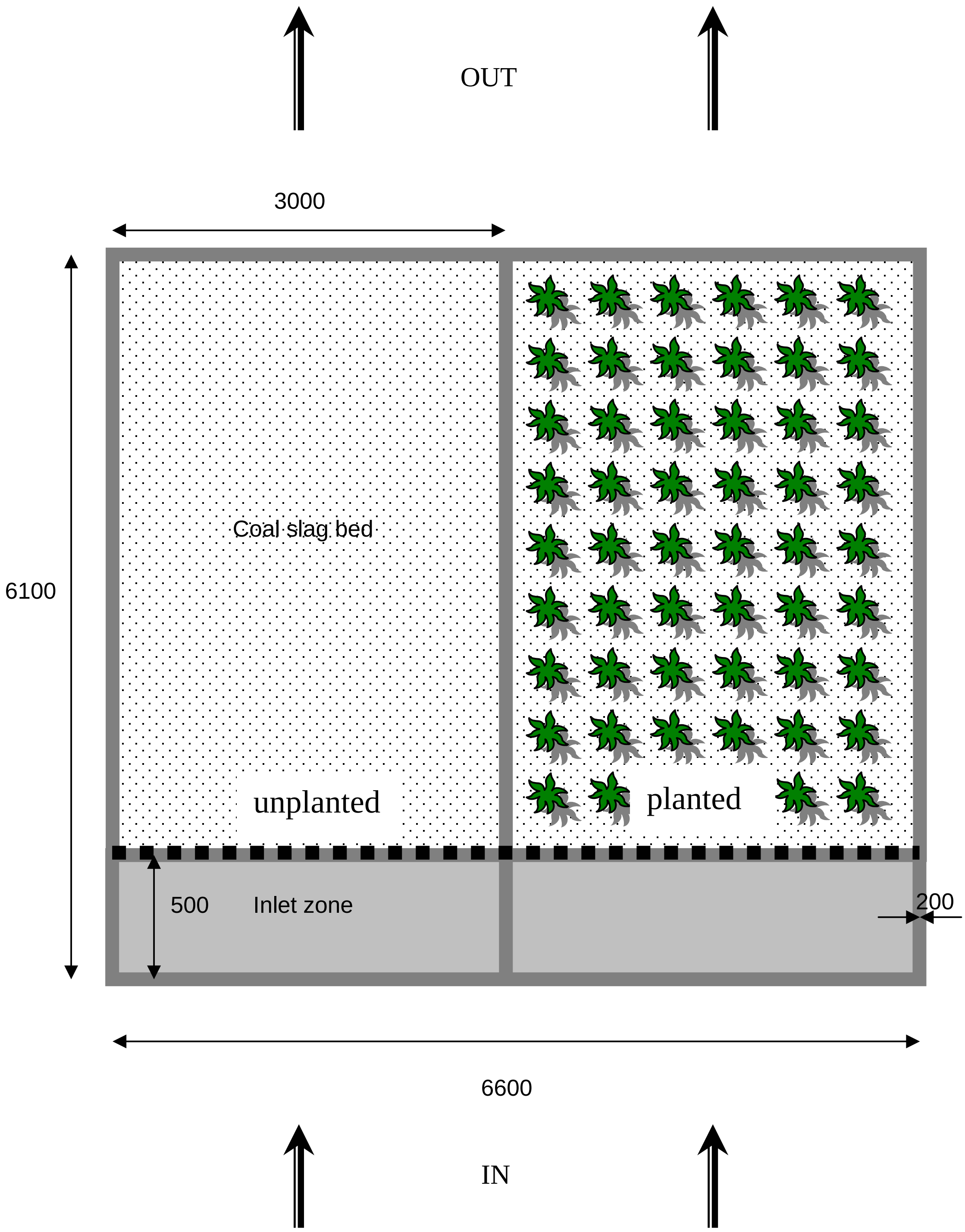


Fig. 3.3 Top view of the parallel pilot systems

The outlet valves of the systems were at the bottom of the systems on the other side (Fig. 3.4).

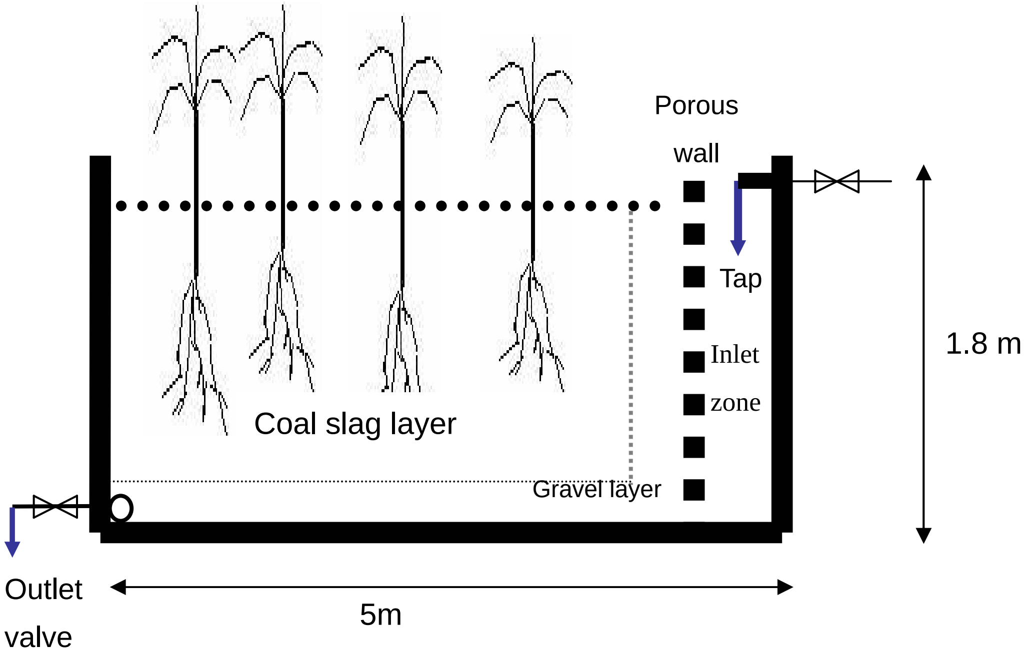


Fig. 3.4 Side view of the pilot system

Fig. 3.5 shows the schematic flow of the pilot-scale systems. To study the effect of plantings to the system performance, the selected plant species - *Cyperus alternifolius* was planted into one of the parallel systems with a density of 3-4 plant/m^2 (Figs. 3.6 a & b). Adequate spaces have to be reserved for the spreading of above-ground parts and the plant root system in the bed matrix. Clumps of whole plant of *Cyperus alternifolius* of one-month old were transplanted into the coal slag bed and regularly watered before the start-up of the system. Sufficient water must be provided until the plants become established.

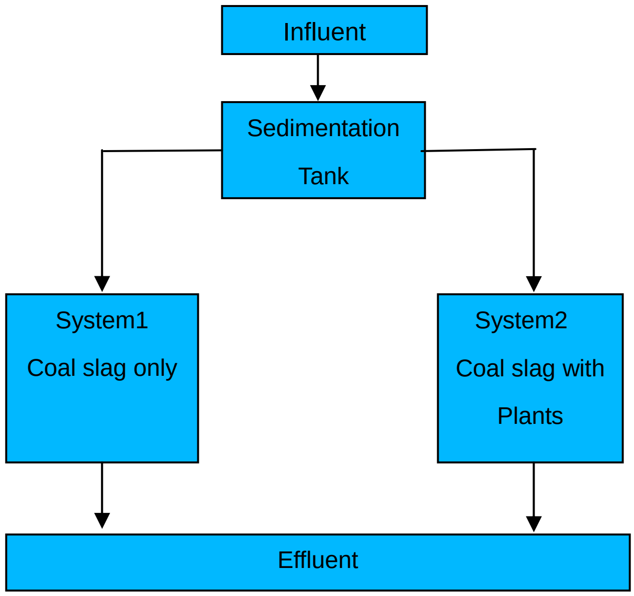


Fig. 3.5 Schematic flow of the pilot-scale systems

3.4.2 Operating conditions

The systems were fed with wastewater regularly in the start-up stage started in November 2004 and ended in April 2005. The systems were then operated with different contact times from May 2005 to March 2006. The domestic wastewater was drained into the vegetated sequencing batch biofilm reactor about every 2 days. Due to the power limitation of the pump system onsite, wastewater was fed into the systems in a period of 4 hours after passing through the sedimentation tank. Nevertheless, this “fill” phase could allow certain level of aeration to the wastewater and let the biochemical pollutant removal processes began

a)

b)

Figs. 3.6 (a & b) Photo of pilot-scale system with young plants introduced at the start-up stage (a). Photo of pilot-scale system without plant (b).

when the systems have not been fully filled (unsaturated) with wastewater. In sequencing batch reactor, the optimum length of aeration period and aeration-stopping period must be determined empirically. Similarly, the optimal length of contact time, which alters the aerobic conditions and pollutant removal efficiency inside the sequencing batch biofilm reactor, has to be investigated through experiment. Five contact times including 18 hours, 12 hours, 6 hours, 3 hours and 0 hours were investigated as the duration of "react" phase in the systems. Each system was fed with 13.6 m^3 wastewater with a cycle of 48 hours approximately. The resulting hydraulic loading was at a rate of about 0.45 m / d based on the system surface area of 15 m^2. Similar to a sequencing batch reactor, the operation period of the system studied was divided into several stages. The detail and duration of each stage on 24-hour basis in this experiment are shown in Table 3.3. The effect of duration of idle phase was attenuated by the resting of bed for 24 hours in between each operating cycle.

Seasonal variation was considered as the pilot scale experiment was carried out outdoor. The five contact times were tested for their pollutant removal effects in both warm and cold seasons. With reference to the sub-tropical climate in the South China, seasonal climate is distinct in different months. Taking the weather

Table 3.3 Descriptions and durations of different operating stages

Phase	Descriptions	Duration (hrs)				
Fill	The wastewater was fed from the sedimentation tank to the two reactors in parallel. The wastewater was slightly aerated when it fell into the inlet zone from the tap opening.	4	4	4	4	4
React	Pollutant removal processes took place and varied in different durations of this phase	18	12	6	3	0
Draw	The effluent of system was drawn out from the system through the outlet valve at the bottom of the tank by gravity	2	2	2	2	2
Idle	The main function of idle phase was to enhance decomposition of accumulated organic matters on coal slag	0	6	12	15	18
	Total	24				

report of Guangzhou in 2004 as reference (Table 3.4), May to September having mean temperature (daily minimum) from 22.7 ℃ to 25.3 ℃ were classified as warm periods in this experiment while November to March having mean temperature (daily minimum) from 9.8 ℃ to 19.1 ℃ were classified as cool periods. As a result, the five contact times were operated in both warm period and cool period with each period lasted for one month. The operating schedule of the pilot-scale system performance is shown in Table 3.5.

Table 3.4 Annual air temperature of Guangzhou in 2004

Month	**Mean air temperature**	
	Daily minimum	Daily maximum
Jan	9.8	18.3
Feb	11.3	18.4
Mar	14.9	21.6
Apr	19.1	25.5
May	22.7	29.4
Jun	24.5	31.3
Jul	25.3	32.7
Aug	25.2	32.6
Sept	23.7	31.4
Oct	20.5	28.6
Nov	15.7	24.4
Dec	11.1	20.5

Sources: World Meteorological Organization (World weather information service).

Table 3.5 Schedule of pilot-scale system performance study

Stage	**Season**	**Duration**	**Contact time**
Start-up		Nov 04- Apr 05	
Operation	***Warm***	May 05	18 hours
		Jun 05	12 hours
		Jul 05	6 hours
		Aug 05	3 hours
		Sept 05	0 hours
	Cool	Nov 05	18 hours
		Dec 05	12 hours
		Jan 06	6 hours
		Feb 06	3 hours
		Mar 06	0 hours

3.4.3 Sampling and analytical details

3.4.3.1 Wastewater samples

Wastewater samples were collected 2-3 times per week in the whole pilot study period (November 04 to March 06). Wastewater samples were collected at the inflow and outflow from each tank. Composition of influent usually varied diurnally, consequently, composite influent samples were collected to have a representative water sample. Likewise, composite samples of effluent were collected to ensure the accuracy of the grab samples. The effluent was drawn out from the systems through the outlet valve at the bottom of the tank by gravity. Parameters being analyzed in the pilot-scale experiment were chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), ammonia nitrogen (NH_3-N), total phosphorous (TP), total suspended solids (TSS) and volatile suspended solid (VSS).

3.4.3.2 Plant samples

Plants were harvested three times in the study period. The first harvesting was done right after the start-up stage in Apr 05. Fig. 3.7 shows the *Cyperus alternifolius* in the system before harvesting. The second harvesting was done after the completion of operation in warm period from May 05 to September 05.

Fig. 3.7 *Cyperus alternifolius* in the system

The final harvesting of plants was carried out at the end of the operation in cool period from Nov 05 to Mar 06. Samples of above-ground biomass of plant were taken for fresh weight and dry weight measurements, as well as for nitrogen and phosphorus contents analysis.

3.5 Experimental procedure and statistical data analysis

3.5.1 Wastewater analysis

Analyses of COD, BOD_5, NH_3-N, TKN, NO_3^-, TP, TSS and VSS were performed following the Standard Methods (APHA, 1998). Temperature and pH of wastewater were recorded onsite with triplicate measurements.

3.5.2 Plant samples analysis

In order to examine nitrogen and phosphorus contents in the plants, leaves and shoots of *Cyperus alternifolius* were freeze-dried and ground into fine power form before weighting with balance.

3.5.2.1 Phosphorus

About 0.250 g (± 0.001g) of ground samples were weighted into a pre-washed digestion tubes added with 3.5 g potassium persulfate. 50 ml of deionized water was added to wet the sample. 10.0 ml of concentrated H_2SO_4 was added into each tube and vortex (~ scale 6). The tubes were then placed in the aluminium heating block and heated for 30 mins at 200ºC. The digestion was continued for 2 hrs at 370ºC. Cooling to room temperature, the solution was poured into centrifuge tube and centrifuged for 4000 rpm for 10 mins. The pH of the supernatants were adjusted to 8.2 by adding 40% NaOH. The level of total phosphorus was measured by Acid Persulfate Digestion Method (USEPA accepted for reporting wastewater analysis).

3.5.2.2 Nitrogen

About 0.25g of dry ground samples were weighted into digestion tubes. 50 ml of deionized water was added to each tube to wet the samples. 3.5 g K_2SO_4-catalyst mixture and 10.0 ml of concentrated H_2SO_4 were added into each tube. The digestion tubes were placed in the aluminium heating block and heated for 30 mins at 200°C. Then the digestion was continued for 2 hrs at 370°C. After the digestion, the tubes were placed at room temperature for cooling. Afterwards, 50 ml of ammonia free deionized water was added into each tube. 25 ml of receiving solution and 10 drops of bromocresol green methyl red mixed Indicator were filled in an Erlenmeyer flask. The flask was placed in the receiving position in the steam distilling unit. The distilling unit automatically added 50 ml of dilution water and 50 ml of 40% NaOH and performed the distillation process. The resulting solution in the Erlenmeyer flask was titrated with standard H_2SO_4 (0.02 N acid).

3.5.3 Dissolved oxygen

Dissolved oxygen (D.O) levels at different depths of the pilot systems were measured using a portable D.O. meter (YSI Model no. 51). The D.O. levels at the depths of 40 cm, 80 cm and 120 cm were determined at three sampling points of the filter beds (Fig. 3.8). Some hollow stainless steel pipes with length of 50cm, 100 cm and 150 cm were inserted near the inlet, in the middle and near the outlet of the coal slag beds (Fig. 3.9), to allow the D.O. meter probes to measure the D.O. levels inside the bed systems.

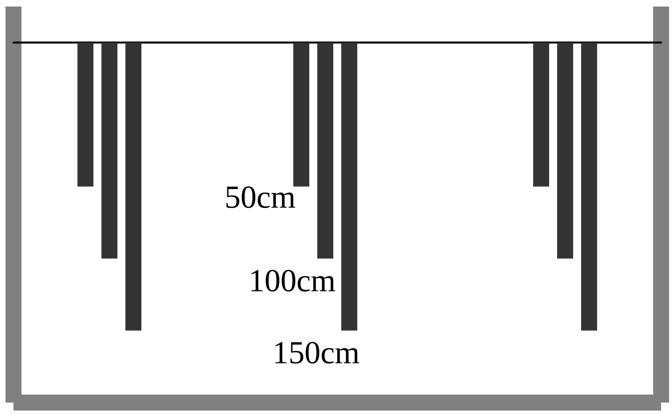


Fig. 3.8 Depths of hollow pipes for D.O. measurement (side view).

3.5.4 Calculations

Removal efficiency of the system was expressed in concentration percentage removal rate. Percentage removal is based on inlet and outlet concentrations. In the laboratory-scale experiment, the nutrient balance was calculated by the mass flux using the influent and effluent volumes as well as influent and effluent concentrations, the mass adsorbed on the coal slag and the mass retained in the plant contents. The total mass of pollutants removed by adsorption on adsorbing

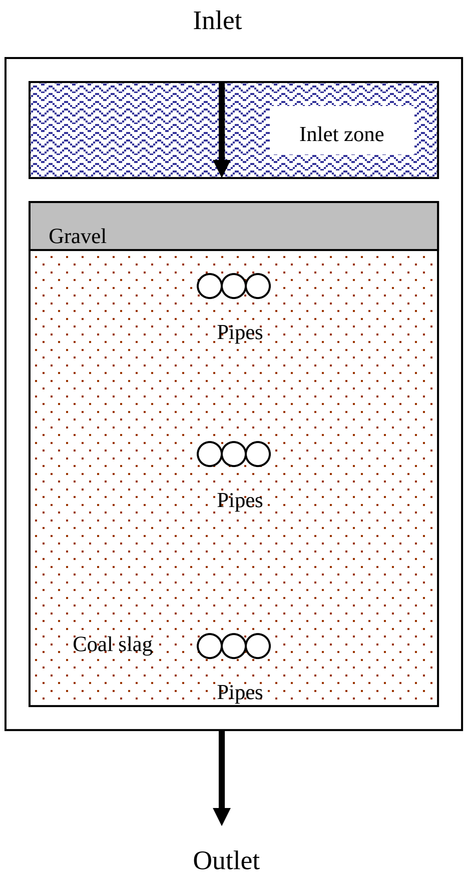


Fig. 3.9 Locations of pipes for D.O. measurement (Top view).

medium was calculated by the mass of pollutant (mg) found on certain mass of adsorbing medium (g), by measuring the density and the volume of adsorbing medium in the system, the total mass of pollutants retained by adsorption in the system was known. In the pilot-scale experiment, the total mass retained in the systems in the study period was calculated by sum up the differences between influent concentrations and effluent concentrations in all operations, with consideration of the volume of wastewater.

3.5.5 Statistical analysis

The performance data collected from both laboratory-scale and pilot-scale experiments were analyzed using statistical data analysis. Comparisons of the differences of pollutant removal efficiencies were performed using analysis of variance (ANOVA) and the significance level is 5 %. The relationships between the removals of the pollutants and the controlling factors were established by multiple regressions. Statistical and mathematical software being used were SPSS 10.0, Datafit 8.0 Okadale and Igor Pro 5.03.

3.6 Modelling of nitrogen transformations

Three models using different analytical approaches for ammonia nitrogen transformation were developed based on actual performance data from the pilot-scale experiment, the most appropriate and explaining model, which in turn, was use to replicate and predict the system performance.

Firstly, multiple regression model was used to predict the effluent concentrations of the pollutants. The degree to which two or more predictors (independent variables) are related to the dependent variable is expressed in the multiple correlation coefficient R, which is the square root of R^2. Multivariate analysis provides a simultaneous analysis of multiple independent and dependent variables (Tabachnick and Fidell, 1989). Secondly, first-order kinetics of the transformation process was generated to model the removal of ammonia nitrogen as it is often used to describe the pollutant removal kinetics in constructed wetland based systems (Liu *et al.*, 2005).

Lastly, a mass balance model was developed based on the ammonia nitrogen transformation by microorganisms and uptake by plants. The effects of temperature, dissolved oxygen and contact time were taken into account. The decomposition and ammonification rates are linked to microbial energy requirements, the carbon to nitrogen ratio (C/N) of the organic matter, the growth rate of microbes (Reddy and D'Angelo, 1997). Monod kinetics was employed to describe the microbial growth rate as a function of adsorbing mediums availability and the requirement of the specific organisms (Wynn and Liehr, 2001; Halling-Sørensen and Nielsen, 1996; Kovárová-Kovar and Egli, 1998). Vegetative uptake of pollutant was represented with Michaelis-Menten kinetics (Romero *et al*., 1999; Marcus-Wyner and Rains 1982; Wang *et al*., 1993; Hanson 1977; Kirk and Kronzucker, 2005).

Model was developed based on ammonia nitrogen removal only because ammonia nitrogen is one of the most dominant elements in domestic wastewater. And the rhythmical operation of the sequencing batch biofilm reactor was to enhance the oxygen supply in the coal slag bed, and hence the degradation of ammonia nitrogen by nitrification was supposed to be improved. The other major pollutants in domestic wastewater like carbonaceous matter and phosphorus were not modelled. It was because the mass balance calculations of carbonaceous matters were not feasible because the uptake of carbon dioxide by plant could not be quantified in this experiment. Also, no equation for phosphorus mass balance was done as sources and sinks of phosphorus is mainly dependent on adsorption and desorption, and the mass balance model describes only the steady state conditions where equilibrium is reached between the ion exchange processes and the biological processes.

Chapter 4: Experimental Results

4.1 Plant-substrate-microbe interaction

4.1.1 Coal slag as the adsorbing media

The selection of adsorbing media is often a central question when implementing gravel-based wastewater treatment system, and it is important because of its major cost implication. Locally available filter materials are usually utilized for on site wastewater treatment system. The uses of industrial wastes and by-products in wastewater treatment could fulfill the need of economically viable industrial and wastewater treatment processes for protection of the environment and public health. Coal slag, which is the waste residue from burning coal for electricity generation in Guangdong areas (Cui *et al*., 2003), was employed as adsorbing media in this study.

The basic physio-chemical properties of coal slag are listed in Table 4.1. The porosity of coal slag was found to be 0.5. The porosity describes how densely the material is packed. It is the proportion of the non-solid volume to the total volume of material. The porosity of the adsorbing medium is an important factor

Table 4.1 Physio-chemical properties of coal slag

Parameters	**Values**
pH	6.22 ± 0.06
Porosity	0.5 ± 0.17
Density	1.818 ± 0.425 kg/L
D_{10}	0.31mm
D_{60}	9 mm
$K_{60}= D_{60}/D_{10}$	29
Surface area	3.541 ± 0.689 m^2/g
Average pore diameter	6.14 nm
Metal contents favour P adsorption	Al = 15721.513 mg/kg Ca = 7294.792 mg/kg Fe = 12645.736 mg/kg

affecting the hydraulic conductivity of the system. The medium with a higher porosity will typically have a higher hydraulic conductivity. Coal slag typically is composed of 504 g/kg SiO_2, 278 g/kg Al_2O_3, 68.8 g/kg FeO + Fe_2O_3, 31.4 g/kg CaO, 8.6 g/kg MgO, 0.6 g/kg MnO_2, 12.4 g/kg K_2O and 4.3 g/kg Na_2O (Yuan *et al*., 1998). The coal slag used in this study was found to be composed of 15721.513 mg/kg of Al, 7294.792 mg/kg of Ca and 12645.736 mg/kg of Fe by ICP-AES analysis (ICP-AES, Perkin-Elmer Optima 3300 DV) after extraction. The high levels of Al, Ca and Fe contents imply that coal slag has high potential to be a good substrate in wastewater treatment system with regard to phosphorus removal (Grüneberg and Kern, 2001; Comeau *et al*.., 2001). Other phosphorus-sorbing substrates include shale (Drizo *et al.*, 1999), lightweight aggregates (Zhu *et al.*, 1997), wollastonite (Brooks, *et al.*, 2000), and opoka (Johansson, 1999) have been suggested as common wetland filter substrates.

4.1.1.1 Size Distribution of Coal Slag

The overall result of sieve analysis of coal slag is shown in Table 4.2 and the size distribution curve is shown in Fig. 4.1. The dominant sizes of particle are the coarse ones with diameter between 2.36 mm-10 mm. For the bulk of support medium, coarse medium with diameter of 5-15mm is preferred. The value of D_{10} was 0.31 mm and that of D_{60} was 9 mm, with the uniformity coefficient $K_{60}= D_{60}/D_{10}$ of 29. D_{10} and D_{60} are the grain sizes that are 10% and 60 % respectively, finer by weight. The size distribution is represented by the uniformity coefficient, which enables to see how well graded the coal slag is. The lower the uniformity coefficient, the more even the particles size distribution is. Since the uniform coefficient of the coal slag was comparatively low, clogging problem of coal slag was less likely to occur.

Table 4.2 Overall result of sieve analysis

B.S. Sieve Size	Total weight = 3427.1g		
	Retained (g)	Retained %	Passing %
20mm			100
10mm	1287.1	37.55653	62.44347
5mm	503.6	14.69464	47.74883
2.36mm	436	12.72213	35.0267
1.18mm	331.8	9.681655	25.34504
600µm	277.7	8.103061	17.24198
425µm	147.9	4.315602	12.92638
300µm	127.6	3.723265	9.203116
150µm	153.5	4.479006	4.724111
75µm	96.2	2.807038	1.917073
PAN	55.8	1.628199	0.288874

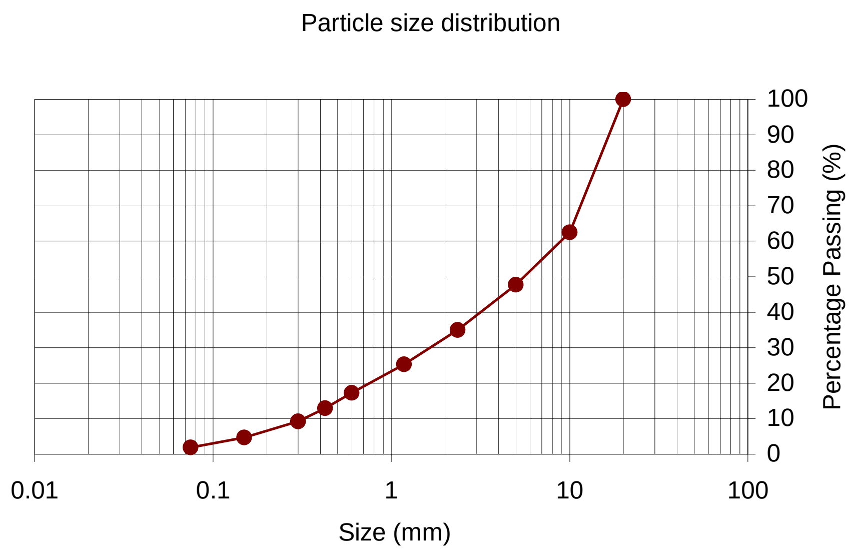
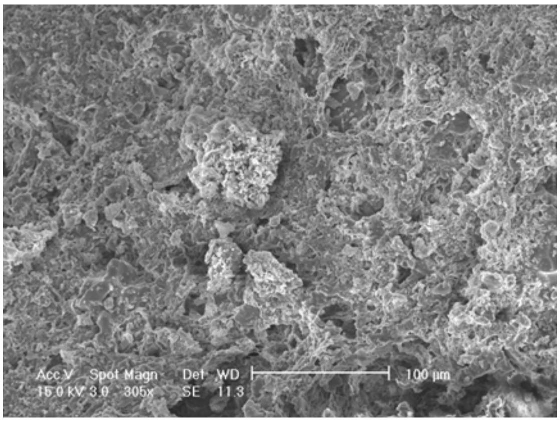


Fig. 4.1 Size distribution curve of coal slag

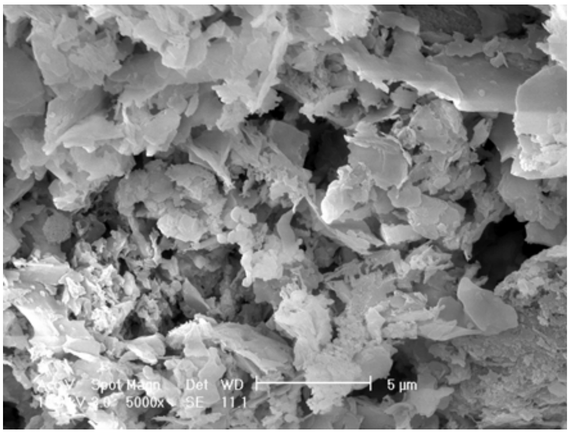
4.1.1.2 Observation of coal slag under SEM

In principal, any porous solid may be an adsorbent. Common natural adsorbents are fly ash, bone char, sawdust, charcoal, peat and lignite (Al Duri, 1996). Figs. 4.2(a-c) show the texture of coal slag examined under SEM with different magnifications. Porous surface provides large number of adsorption sites compared with plane structure. The SEM pictures confirmed that porous structure of coal slag and it provides large number of adsorption sites for pollutant removal.

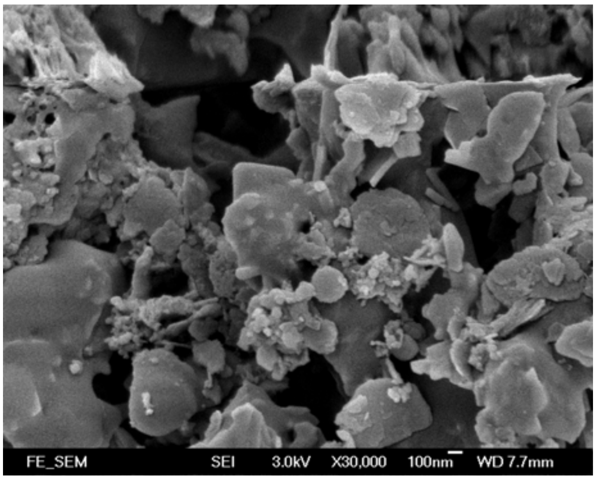
The first step of the adsorption process involves migration or diffusion of the impurities into the porous cavities with the coal slag particles. Once inside the pore structure, the impurity molecules are attracted to the internal pore surfaces by weak electrostatic forces known as van der Waals' force. This physical adsorption of impurity molecules onto the internal surface of the pore structure is the most common type of adsorption and is reversible. But in some cases, the adsorbed material may interact with active sites on the carbon pore surfaces and form chemical bonds with the surface. This process is called chemisorption and is considered irreversible.



a)



b)



c)

Figs. 4.2 (a-c) Surface structure of coal slag under different magnifications.

4.1.1.3 Adsorption of phosphorus and nitrogen

In a batch treatment process, adsorption of impurities from a liquid is essentially an equilibrium phenomenon. Results from laboratory isotherm tests conducted at equilibrium would correlate directly with full scale plant process performance. The results obtained from the tests could be used to predict the maximum adsorption capacity of adsorbing medium for specific pollutants. In this study, Langmuir and Freundlich equations were fitted to the bench experimental adsorption data using least squares parameter estimation method.

Freundlich isotherm: $qe = kCe^{1/n}$

where,

qe = Amount of solute adsorbed per unit weight of adsorbent,

Ce = Residual equilibrium concentration,

K = Freundlich adsorption coefficient,

n = Coefficient related to the change in residual solution concentration.

This equation also can be expressed in linear form by taking logarithmic plot of qe versus Ce. It yields a straight line. The equation is:

$$log\ qe = log\ K + 1/n\ logCe$$

And,

Langmuir Isotherm

$$q_e = \frac{KC_e q_{\max}}{(1 + KC_e)}$$

where,

qe = Amount of solute adsorbed per unit weight of adsorbent,

Ce = Residual equilibrium concentration,

q_{max} = Theoretical maximum of solute adsorbed per unit weight of adsorbent,

K = Constant related to the energy of adsorption.

In order to find the values of constants, K and q_{max}, the model can be expressed as a linear equation:

$$\frac{1}{q_e} = \frac{1}{Kq_{\max}C_e} + \frac{1}{q_{\max}}$$

The biggest advantage in applying the Langmuir model for sorption studies was that it enabled the calculation of theoretical phosphorous sorption maximum for the adsorbing medium (Xu *et al.*, 2006).

The Langmuir and Freundlich equations were fitted to the experimental adsorption data using least squares estimation method. As the plot for the Freundlich isotherm is not a linear relation, use of Freundlich adsorption isotherm is inappropriate. The experimental data and isotherms fitted to Langmuir equations are shown in Fig. 4.3 & Fig. 4.4, and the values of K and q_{max} together with the corresponding determination coefficients (R^2) are listed in Table 4.3. Good fits of the Langmuir equation to the experimental data of total phosphorus and ammonia nitrogen were obtained (R^2>0.97). Apparent phosphorus adsorption capacity of coal slag was estimated using the linear form of the Langmuir equation. The maximum adsorption capacities, evaluated from fits of Langmuir isotherm to the experimental data were 1.369 mg P /g for phosphorus and 0.071 mg NH_3-N/g for ammonia nitrogen. If best results are obtained with the Freundlich isotherm, it can interpret that the number of sorption sites are not limited, and the adsorption capacity depends on the initial concentration of sorbate in the solution (López *et al.*, 1998). But it is not the case

Table 4.3 Summary of isotherm constants for adsorption of phosphorus and ammonia nitrogen at temp of 25 ℃.

Sorbate	Langmuir		
	q_{max} (mg/g)	K	R^2
P	1.369	0.161	0.979
N	0.071	0.129	0.971

for coal slag in this study. Freundlich isotherm equation did not fit the adsorption characteristic of coal slag in this study.

Since the isotherm tests determined the adsorption constants and maximum capacity of coal slag, the results could be used to compare the performance of different adsorbing media and to identify the cost-effective ones. Table 4.4 lists out the coefficients of Freundlich and Langmuir adsorption isotherms of phosphorus by various adsorbing media from literatures. These coefficients reveal how well the adsorbing media perform relative to each other. Relative to phosphorus adsorption, coal slag was empirically found to have a higher maximum adsorption capacity than sand, bentonite, vermiculite, quartz sand and diatomaceous earth.

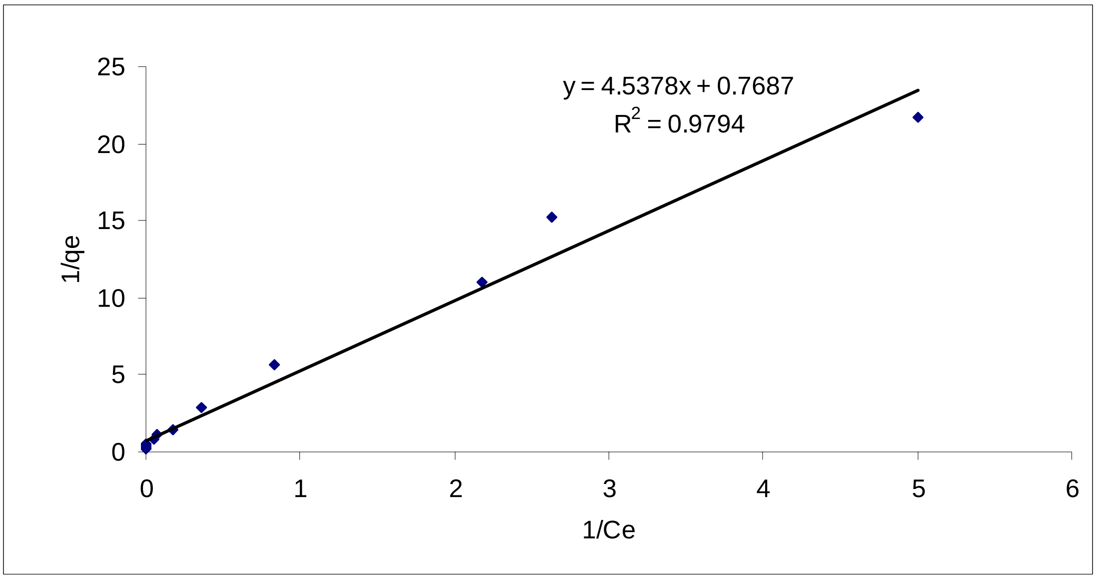


Fig. 4.3 Phosphorus adsorption data fitted to Langmuir equation

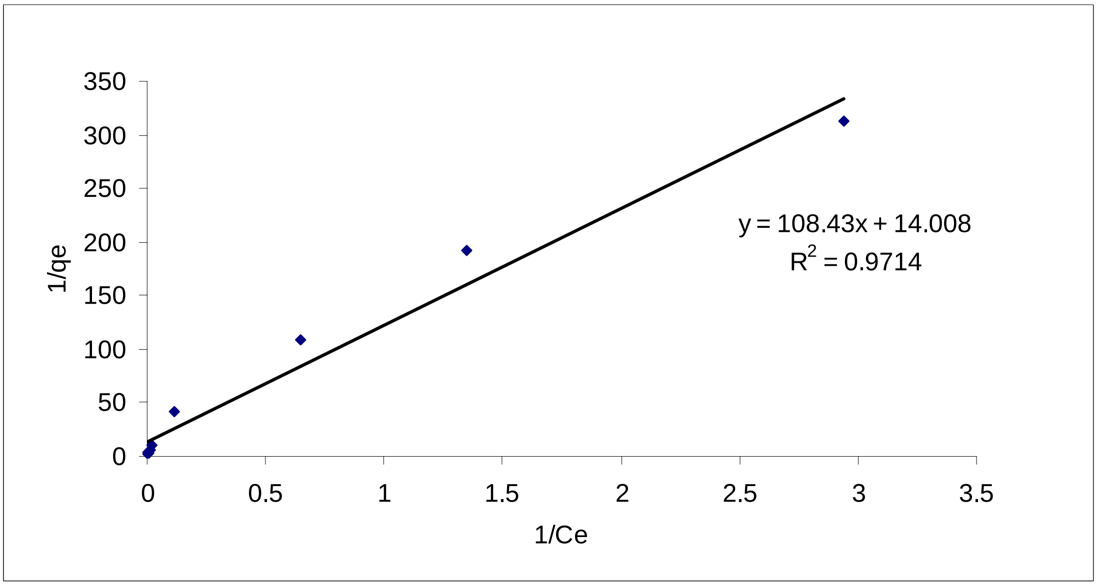


Fig. 4.4 Ammonia nitrogen adsorption data fitted to Langmuir equation

Table 4.4 Coefficients of Freundlich and Langmuir adsorption isotherms for various adsorbing medium

	Freundlich Isotherm			Langmuir Isotherm		
Material	**R^2**	**K**	**n**	**R^2**	**K**	**q_{max} (g P kg^{-1})**
Calcite (Brix *et al.*, 2001)	0.960	1.14815	0.978	7E-06	8.1E-05	14286
Marble (Brix *et al.*, 2001)	0.983	0.11455	1.139	0.179	0.00532	17.73
Darup (Brix *et al.*, 2001)	0.953	0.04791	1.018	-	-	-
LECA (Brix *et al.*, 2001)	0.871	0.02328	1.607	0.0156	0.00052	8.045
Diatomceous earth (Brix *et al.*, 2001)	0.885	0.11179	3.218	0.70	0.0181	0.899
Quartz Sand (Brix *et al.*, 2001)	0.997	0.01545	2.148	0.995	0.0095	0.292
Vermiculite (Brix *et al.*, 2001)	0.883	0.02278	3.248	0.94	0.256	0.109
Bentonite (Xu *et al.*, 2006)	-	-	-	-	0.107	0.930
Sand (Zhu *et al.*, 1997)	-	-	-	-	-	0.439-0.443
Slags (Sakadevan and Bavor,1998)	-	-	-	-	-	1.430-44.200
Sands (Stuanes, 1984)	-	-	-	-	-	0.084-0.850
Coal slag	**-**	**-**	**-**	**0.979**	**0.161**	**1.369**

Adsorbed ammonia is available for uptake by vegetation and microorganisms or for conversion to nitrate nitrogen through biological nitrification under aerobic conditions. Different to phosphorus removal, ammonia nitrogen degradation is much more dependent on biological processes instead of physical adsorption. Nritrification, instead, is the main process for the elimination of ammonia nitrogen. Ammonia adsorption capacity of natural systems is finite and are quickly saturated, nitrification is necessary to release adsorbed ammonia and thereby regenerate adsorption sites (Metcalf & Eddy, 1991; Vymazal *et al.*, 1998).

4.1.2 *Cyperus alternifolius & Vetiver zizanioides*

Two wetland plant species (*Cyperus alternifolius* & *Vetiver zizanioides*) were selected to be examined for their fitness to treat domestic wastewater in the vegetated sequencing batch biofilm reactor in this study. Apart from their prevalent occurrences in Guangdong area, as well as their tolerances to flooding and wastewater pollutants, *Cyperus alternifolius* & *Vetiver zizanioides* were selected among other wetland plant species to be examined in this study because of their long root lengths and extensive rhizomes. Since the depth of plant root penetration, and thus potential for oxygen release, has been proposed as a rational basis for determining the appropriate depth of subsurface treatment wetlands (Reed *et al.*, 1995). The long root system of the two selected species allows the dimension of bed system to be vertically extended and ensure the hypothetic enhancement of plant root system to pollutant degradation even in the deeper zones in the sequencing batch biofilm reactor.

Cyperus alternifolius (Umbrella grass) is a perennial herb, which grows in humid areas or swampland. Umbrella grass grows fast with strong root system. Its productivity is high and can form a good landscape. It has strong underground root and erect aerial stem, with hollow core construction and without branching. It is monoecious with bisexual flower. The blooming stage is from June to July and the maturing stage is from September to October. Umbrella grass can be easily multiplied by seed, plant division or cutting. *Cyperus* spp. has been used successfully in small-scale gravel-bed constructed wetlands in Australia and New Zealand. As identified by Hocking (1985), the attributes that make *Cyperus* spp. a potentially useful plant for constructed wetlands include: year-round growth in warm temperate regions (withstanding moderate frosts), tolerance of hyper-eutrophic conditions and salinity, ease of propagation, and apparent lack of serious weed potential. It is also able to tolerate a wide range of soil moisture conditions. Moreover, Cheng *et al.*, (2002) summarized that *Cyperus alternifolius* has a great potential for heavy metal phytoremediation, especially for Cu, as well as for Mn and Zn.

Vetiver zizanioides is native to South and South-East Asia. It is non-invasive. *Vetiver* spp. can be grown in areas with an annual rainfall greater than 450-500 mm. It is adaptable to a wide range of soil and climatic conditions. Zheng *et al*., (1998) has proved that *Vetiver* spp. is powerful to remove nitrogen and phosphorous from eutrophic water bodies. *Vetiver* spp. also tolerates very high levels of aluminium, manganese, and a range of heavy metals in soil (Department of Natural Resources, Mines and Water, Queensland, 2006). Due to its extensive and deep root system, it is very tolerant to drought. The dense spongy root system that binds the soil together to a depth up to 3m.

4.1.2.1 Growth rates and pollutant tolerances

The growth performances of both species in the hydroponics experiment ere summarized in Table 4.5. The three strengths (strong, medium and weak) of wastewater used in the hydroponics experiment were obtained by diluting water into the raw wastewater. The concentrations of pollutants in medium strength wastewater were doubled than that in low strength wastewater, while the concentrations of pollutants in high strength wastewater were doubled than that in medium strength wastewater.

Table 4.5 Growth performances of the two plants in the hydroponics experiment.

	Strength	***Cyperus alternifolius***	***Vetiver zizanioides***
Nitrogen content (mg/g)	*Low*	0.633 ± 0.041	0.730 ± 0.036
	Medium	0.749 ± 0.047	0.802 ±0.056
	High	0.831 ± 0.071	0.796 ± 0.022
Phosphorus content (mg/g)	*Low*	0.173 ± 0.013	0.176 ± 0.011
	Medium	0.179 ± 0.004	0.182 ± 0.010
	High	0.212 ± 0.014	0.164 ± 0.017
Height increment (cm/month)	*Low*	39.53 ± 2.25	20.80 ± 3.16
	Medium	38.10 ± 1.90	19.57 ± 2.72
	High	36.07 ± 3.82	17.47 ± 2.91
Root length increment (cm/month)	*Low*	7.77 ± 0.57	4.93 ± 0.57
	Medium	8.03 ± 0.31	4.67 ± 0.85
	High	7.70 ± 0.50	5.07 ± 1.15
Fresh weight increment (g/ plant/month)	*Low*	59.67 ± 3.06	45.67 ± 4.04
	Medium	62.67 ± 2.31	50.00 ± 7.55
	High	60.33 ± 8.74	45.67 ± 6.66

After 1-month growth in wastewater, both *Cyperus alternifolius* and *Vetiver zizanioides* showed high tolerances to sewage loads even in the high strength wastewater. The nitrogen and phosphorus contents of *Cyperus alternifolius* and *Vetiver zizanioides* showed similar concentrations in their tissues regardless of the organic strengths of the wastewater. The concentration of ammonia nitrogen was 11.53 ± 2.29 mg/L in low strength wastewater and was 44.09 ± 5.26 mg/L in high strength wastewater, *Cyperus alternifolius* accumulated a rising concentration of nitrogen in its tissue of 0.633 ± 0.041 mg/g developed from low strength wastewater and 0.831 ± 0.071 mg/g developed from high strength wastewater. The nitrogen content *of Cyperus alternifolius* showed a direct proportional relationship to the loadings of wastewater.

Cyperus alternifolius demonstrated a more active growth than *Vetiver zizanioides* did from their biometric characteristics. Both the shoots and the roots of *Cyperus alternifolius* grew faster than that of *Vetiver zizanioides.* The increments of shoot heights, root lengths and fresh weights were all higher in *Cyperus alternifolius*. Referring to Table 4.6, the maximum uptake rate of ammonium nitrogen by *Vetiver* spp. is 40 μmol $NH_4^+ g^{-1}$ root dry wt. h^{-1}, which is comparable to those of other wetland plant species commonly used in wastewater treatment, such as *Phragmite* spp. *and Typha* spp. .Although the relative uptake rate of *Cyperus* spp. is lacking, it is predicted that *Cyperus* spp. could have comparable rates of nutrient uptake because the growth performance and the pollutant tolerance of *Cyperus alternifolis* were both better than *Vetiver zizanioides* in this study.

Concluding the growth performances of the two species in the hydroponics experiment, *Cyperus alternifolius* showed fast-growing and more competitive

Table 4.6 Maximum uptake rate of ammonium nitrogen of various wetland plants.

Plant species	Maximum uptake rate of ammonium nitrogen ($\mu mol\ NH_4^+ g^{-1}$ *root dry wt.* h^{-1})	
Phragmite australis	50	(Romero *et al*., 1999)
Glyceria maxima	65	(Tylova-Munzarova *et al*., 2005)
Glycine max L.	76	(Marcus-Wyner and Rains, 1982)
Laminaria spp.	2	(Costa Braga and Yoneshigue-Valentine, 1996)
Typha latifolia L.	30.9	(Brix *et al*., 2002)
Vetiveria spp.	40.5	(Xia *et al*., 1994)

metabolic patterns than *Vetiver zizanioides* did. In addition, considering the appearances of the two plant species, *Cyperus alternifolius* form a better landscape with its umbrella like structure, so it has been chosen to employ in the vegetated sequencing batch biofilm reactor in this study.

4.2 Laboratory-scale systems performances

The main objective of the laboratory-scale performance study was to investigate the compatibility of growing the selected plant in the selected adsorbing medium for domestic wastewater treatment. *Cyperus alternifolius* was planted into the coal slag bed in the laboratory-scale system. Another objective of the laboratory-scale experiment was to investigate the nutrients flux of the whole system and the roles of different pollutant removal mechanisms.

4.2.1 Treatment performances

Since the pollutant concentrations in the low strength wastewater used in the hydroponics experiment were similar to that of the onsite pilot experiment, so the low strength wastewater was used again in the laboratory-scale operation to test the system performance. The influent characteristics are listed in Table 4.7. In this study, approximate 3 months were taken for the start-up of the system and the equilibrium state was reflected by the stable pollutant removal performance in Mar 2004 (Fig. 4.5). Regardless of slight fluctuation of influent concentrations of ammonia nitrogen, the effluent concentrations from the system were maintained at a narrow range of 10.5 to 13.4 mg/L in the operation in Apr 2004. The hydraulic loading rate of the system was 0.45 $m^3 / m^2 \cdot d$.

As mentioned in Chapter 3, contact time is the duration of wastewater staying in the system after the system has been saturated with wastewater by a 4-hour “fill” phase. Contact time of 0 hour represented the situation in which wastewater was drawn out from the system immediately after 4-hour “fill” phase. Certain levels of pollutant removal were observed even under 0-hour contact time because the removal processes actually have started taking place once wastewater was filled in the system and have continued in the 4-hour “fill” phase.

Table 4.7 Influent characteristics of the laboratory-scale experiment (n = 40).

Parameter	**Mean**	**Standard Deviation**
pH	7.34	0.35
Sewage Temp (℃)	19.11	2.16
BOD_5 (mg/L)	29.36	9.64
COD (mg/L)	103.5	26.05
NH_3–N (mg/L)	14.61	4.68
TKN (mg/L)	15.67	0.63
Nitrate (mg/L)	3.73	1.28
Total phosphorus (mg/L)	4.61	1.71
TSS (mg/L)	43.56	11.43
DO (mg/L)	1.59	1.24

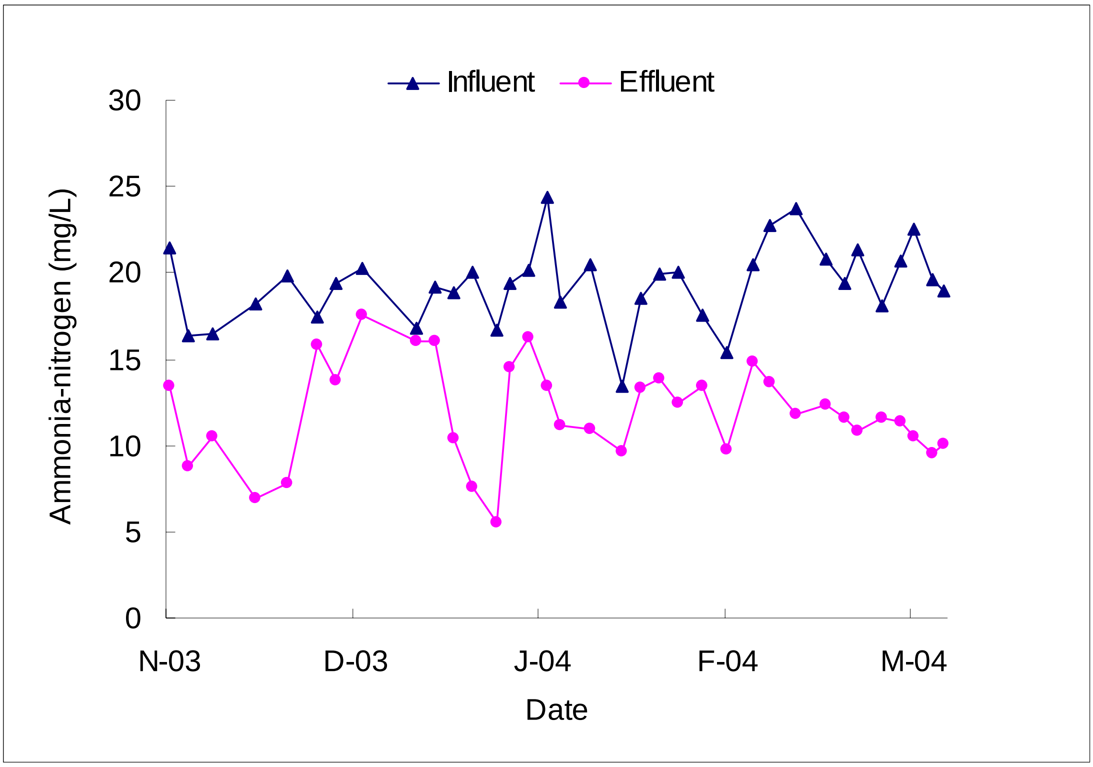


Fig. 4.5 Start-up period of laboratory-scale system (reflected by ammonia nitrogen concentrations)

Table 4.8 *p*-values of different pollutant removal efficiencies between planted and unplanted system.

	BOD_5	**COD**	**NH_3 - N**	**TP**	**TSS**
18	0.639	0.473	**0.011**	0.139	0.267
0	0.773	0.073	0.242	0.088	0.204

One-way ANOVA was carried out to examine the effects of plants on the pollutant removal efficiencies of the treatment process. Table 4.8 shows the *p*-values of different pollutant removal efficiencies between planted and unplanted system with 18-hour and 0-hour contact time. Corresponding to an observed value of a test statistic, the p-value is the lowest level of significance at which the null hypothesis could have been rejected. The null hypothesis would have rejected usually at the actual specified level of significance $\alpha = 0.05$ (Freund and Simon, 1992). The null hypothesis adopted here is that the removal efficiencies of planted system equals to that of unplanted system. With 0-hour contact time, no significant differences were found between the planted and the unplanted systems for all pollutant removal efficiencies (*p*-values >0.05). Under 18-hour contact time, all pollutant removal efficiencies between planted and unplanted systems were not significantly different except ammonia nitrogen removal efficiencies. Ammonia nitrogen removed by planted and unplanted systems significantly differed from each other with a *p*-value = 0.011 < 0.05. The means of ammonia nitrogen removal in the planted and the unplanted systems were 42.34 ± 7.98 % and 35.26 8.73 % respectively. Planted system had the enhanced level of ammonia nitrogen with the presence of *Cyperus alternifolius*. Direct uptake of ammonia nitrogen by the plants may contribute to enhanced removal efficiency. Oxygen transferal by plants might also facilitate aerobic pollutant degradation process in the rooted bed matrix.

4.2.1.1 Organic matters

There was no significant difference between the carbonaceous matters removal in the planted and the unplanted systems at laboratory-scale (*p*-value > 0.05). The means of BOD_5 removal efficiencies of the planted and the unplanted systems operating with 18-hour contact time were 67.66 ± 13.14 % and 65.87 ± 10.64 % respectively, while operating with 0-hour contact time were 22.62 ± 11.74 % and 23.76 ± 18.02 % respectively (Fig. 4.6). The means of COD removal efficiencies of the planted and the unplanted system operating with 18-hour contact time were 68.52 ± 14.87 % and 61.91 ± 18.91 % respectively, while operating with 0-hour contact time were 20.25 ± 13.18 % and 14.19 ± 6.44 % respectively (Fig. 4.7). Carbonaceous matters have an average of around 60 % removal with

18-hour contact time and around 20 % removal with 0-hour contact time. Settleable organics are rapidly removed in wetland systems under quiescent conditions by deposition and filtration (Vymazal *et al.*, 1998). Organic compounds are mainly degraded aerobically and anaerobically by microorganisms. Cooper *et al*., (1996) stated that uptake of organic matters by macrophytes in wetland system is negligible compared to biological degradation. The amount of organic matters taken by plants was not significant compared to the microbial degradation by heterotrophic bacteria, so there was no significant difference of organic matters removal between the planted and the unplanted systems. The adsorption of organic compounds in the systems also played a less important role compared to the biological degradation.

4.2.1.2 Nitrogen

A number of studies have proven that the major removal mechanisms of nitrogen in most wetland systems are microbial nitrification and denitrification. Ammonia nitrogen is oxidized biologically to nitrate with nitrite as an intermediate in the reaction sequence in nitrification. Nitrate is then reduced by heterotrophic bacteria into gaseous nitrogen in denitrification. Comparison of ammonia nitrogen removal performance for planted and unplanted systems with 18-hour

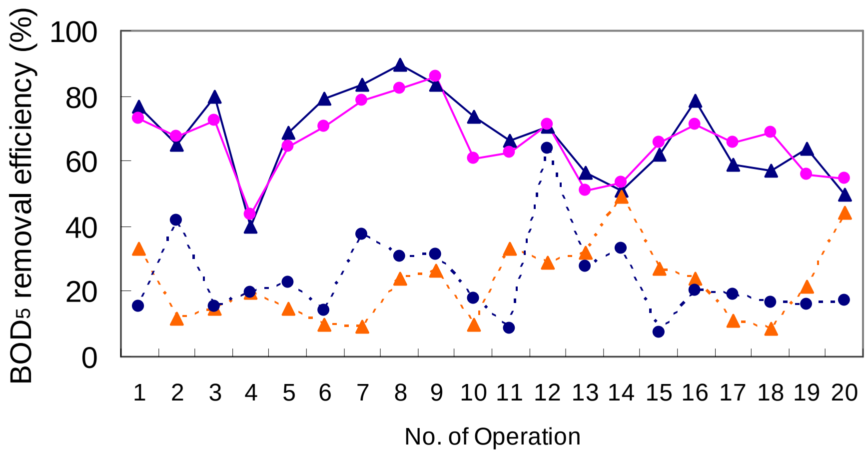


Fig. 4.6 BOD_5 removal efficiency in laboratory-scale system.

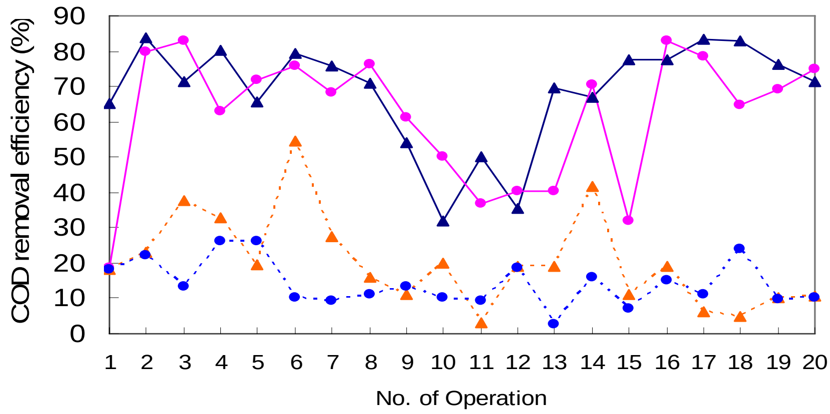


Fig. 4.7 COD removal efficiency in laboratory-scale system.

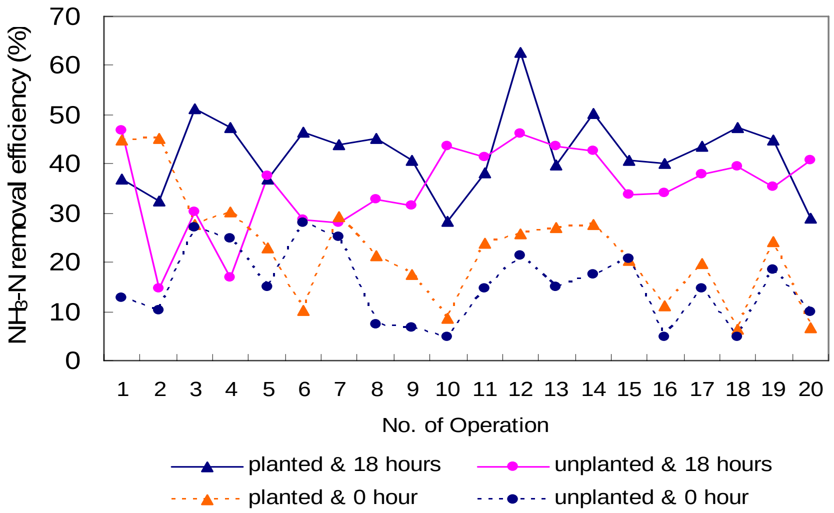


Fig. 4.8 NH_3-N removal efficiency in laboratory-scale system.

and 0-hour contact time is shown in Fig. 4.8. The means of NH_3-N removal efficiencies of the planted and the unplanted systems with 18-hour contact time were 42.34 ± 7.98 % and 35.26 ± 8.73 % respectively, while with 0-hour contact time were 22.56 ± 10.81 % and 15.19 ± 7.56 % respectively. The removal of ammonia nitrogen was significantly different in the planted and the unplanted systems with 18-hour contact time (p-value < 0.05). The *Cyperus alternifolius* was found to be effective to enhance ammonia removal from the wastewater in the laboratory-scale systems. Gersberg *et al*., (1986) compared the ammonia nitrogen removal of three different vegetated beds, and reported that the mean effluent ammonia concentrations were significantly lower than that of unvegetated bed. The high ammonia nitrogen removal efficiencies shown by the bulrush and reed beds were attributed to the ability of these plants to translocate oxygen from the shoots to the roots, The oxidized rhizosphere so formed stimulates sequential nitrification-denitrification. *Cyperus alternifolius* in the laboratory-scale system contributed to the improved ammonia nitrogen reduction in the planted system by either direct uptake or oxygen translocation to root zones.

Nonetheless, Green *et al*., (1997) stated that nitrogen compounds removal in wetlands system is governed mainly by microbial nitrification and denitrification, whilst other mechanisms such as plant uptake and ammonia volatilisation are generally of less importance. Ammonia nitrogen is oxidized to nitrate in a two-step nitrification process. In the first step, aerobic bacteria like *Nitrosomonas,* which depend on the oxidation of ammonia for the generation of energy for growth, converts the ammonium to nitrite. In the second step, facultative bacteria like *Nitrobacter,* oxidizes nitrite to nitrate by using organic compounds and nitrite, for the generation of energy for growth. In addition, physical adsorption also contributes to ammonia removal until all the adsorption sites are saturated (Reed *et al*., 2001).

In-depth investigation of nitrogen conversion occurred in the sequencing batch biofilm reactors were carried out in the laboratory-scale system operation with 18-hour contact time. Table 4.9 shows the changes in nitrogen contents in the sequencing batch biofilm reactors. The temperature inside the systems was 18.1 ± 1.2 °C. The dissolve oxygen concentration was 1.51 ± 0.54 mg/L at the beginning and 1.04 ± 0.46 mg/L at the end of the 18-hour contact time. As nitrification is facilitated with D.O. level of 2-3 mg/L while denitrification is facilitated with D.O. level < 0.5 mg/L. (Taylor and Bishop, 1989). Nitrification

Table 4.9 Nitrogen forms in the planted and unplanted systems of the laboratory-scale experiment (18-hour contact time).

	In		**Out**	
	Planted	**Unplanted**	**Planted**	**Unplanted**
TKN (mg/L)	15.67	15.67	8.87	10.29
NH_3 – N (mg/L)	14.61	14.61	7.31	9.26
NO_3 – N (mg/L)	3.73	3.73	4.02	4.24
TN (mg/L)	19.4	19.4	12.89	14.53

was favoured to a larger extent than denitrification in the vegetated sequencing batch biofilm reactor in the laboratory-scale experiment. The removal of Kjeldhal nitrogen was over 30% in the unplanted system and over 40% in the planted system, so implying high level of ammonification of the organic nitrogen took place. The ammonia nitrogen concentration reduced in a percentage similar to the reduction of Kjeldhal nitrogen. The enhanced removal percentage in the planted system might due to the facilitation of nitrification process by oxygen transferral from the plant root system. Direct uptake of ammonia nitrogen of *Cyperus alternifolius* was also possible. Nitrate formation occurred from the nitrification process. The initial nitrate concentration is 3.73 mg/L while the effluent nitrate concentration were 4.02 mg/L in planted system and 4.24 mg/L in unplanted system. The higher increment of nitrate in the unplanted system could be explained as, the *Cyperus alternifolius* has consumed the nitrate and resulted in a lower level of nitrate in the effluent in the planted system.

According to Kadlec and Knight (1996), concentrations of nitrite in treatment wetlands are typically very low in comparison to concentrations of nitrate and ammonia nitrogen. Analysis of nitrite was conducted for few times in August and September of 2005 and the results were consistent with the literature. Concentrations of nitrite in the raw sewage were in the range of 0.010–0.244 mg/L.

The total nitrogen removal in the sequencing batch biofilm reactor of the laboratory-scale experiment, apart from possible plant uptakes of ammonia nitrogen and nitrate, could attribute to certain level of denitrification taking place under anaerobic conditions, and eliminating the total nitrogen from the systems. Spieles and Mitsch (2000) emphasized that the total nitrogen retention can become highly variable with loading changes. As noted by Craft (1997), early nitrogen retention in constructed wetlands is a result of assimilation to organic matter, and denitrification will not be a significant contributor until appreciable organic matter accumulates. However, complementary investigation has not been done to study the extent of denitrification process in this study.

4.2.1.3 Phosphorus

Phosphorus is typically present in wastewater as orthophosphate, polyphosphate and organic phosphorus. The means of total phosphorus removal efficiencies of the planted and the unplanted systems operating with 18-hour contact time were 36.57 ± 11.37 % and 40.99 ± 6.45 % respectively, while those operating with 0-hour contact time were 41.05 ± 9.34 % and 46.66 ± 10.87 % respectively (Fig. 4.9). The removals of total phosphorus were not significantly different between the planted and the unplanted systems (p-value > 0.05). The effect of plant uptake of phosphorus was not reflected by the parallel systems comparison in this study.

On the other hand, the increase of contact time from 0 hour to 18 hours did not alter much about the total phosphorus removal. The reason was that the removal of phosphorus mainly relied on physical adsorption, complexation and precipitation (Watson *et al.*, 1989), which are different from biological degradation, not a time-dependent process. The removal rate of total phosphorus is basically a function of the degree of adsorption of ion to the soil matrix. The high concentrations of aluminium, iron and calcium of coal slag provide an enormous potential for the system to serve as phosphorus sinks. However, phosphorous adsorption sites can be blocked by a biofilm coating on the soil particles. Application of low-BOD water may slow down the biofilm

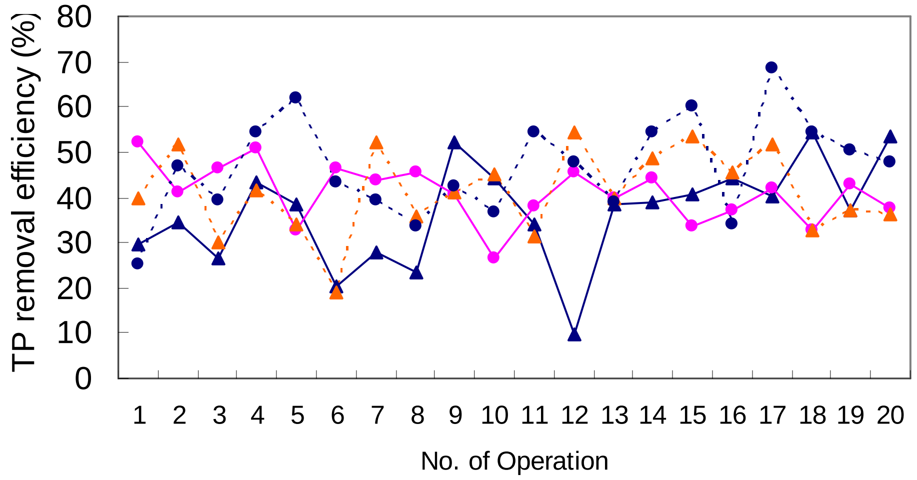


Fig. 4.9 TP removal efficiency in laboratory-scale system.

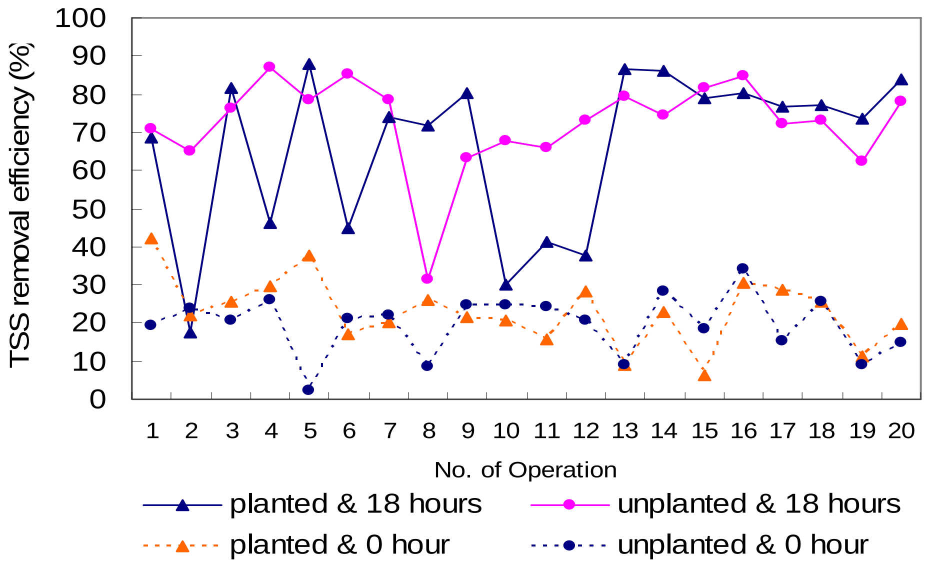


Fig. 4.10 TSS removal efficiency in laboratory-scale system.

production. P removal therefore can be enhanced by efficient aerobic pre-treatment.

Hylander and Simán (2001) reported that phosphorus adsorbed to blast furnace slag that had been used for wastewater treatment, was readily available to plants. So phosphorus adsorbed on coal slag is still available for plant uptake. On the other hand, Greenway and Woolley (1999) mentioned that the only sustainable removal mechanisms for phosphorus in wetland systems are plant uptake and retention by adsorbing medium. Since phosphorus is retained within the system, its ultimate removal from the wetland system is achieved by harvesting plants and replacing the saturated filter media. However, Brix (1997) argued that the amount of phosphorus can be removed by harvesting plants usually constitutes only a small fraction of the amount of phosphorus loaded into the system with the sewage.

4.2.1.4 Total suspended solids

The means of total suspended solids removal efficiencies of the planted and the unplanted systems operating with 18-hour contact time were 66.26 ± 21.46 % and 72.46 ± 12.11 % respectively, while those operating with 0-hour contact time were 22.99 ± 8.93 % and 19.58 ± 7.75 % respectively (Fig. 4.10). Tanner (2001) mentioned that removal of suspended solids, which is primarily a physical process of settling and retention, is very similar for planted and unplanted beds. The major processes responsible for removal of settleable suspended solid are sedimentation and filtration and the plants do not play a determinant role in it. To conclude, the planted systems in the laboratory-scale experiment showed enhanced ammonia nitrogen removal, but there was no significant difference between the planted system and the unplanted system in carbonaceous matter and phosphorus removals.

4.2.2 Removal mechanisms

Mass balance is helpful in identifying potential nutrient sources and sinks and determining effective ways to remove nutrients in wetland treatment system. Considerable debates still exist as to how the reactions between pollutants, substratum, plants and microorganisms occur and to what extent, with many conflicting opinions (Hofmann, 1997). Major fluxes and pools for nitrogen and phosphorus in the start-up stage and in the 18-hour operating stages were investigated. Taking the average of total nitrogen and total phosphorus in the influent and the effluent, the mass input and output of nitrogen and phosphorus in the laboratory system was calculated (Appendix I.). With the concentrations of nitrogen and phosphorus in plant tissues as well as that adsorbed on coal slag surface, the mass balance of nitrogen and phosphorus contributed by plant uptake, physical adsorption on adsorbing medium and microbial degradation were estimated. Table 4.10 and Table 4.11 illustrate the proportions of nitrogen and phosphorus removals by different mechanisms during the start-up stage and during the operating stage of 18-hour contact time respectively.

During the start-up stage from Nov 2003 to Feb 2004, adsorption contributed over 60% of nitrogen removal and phosphorus removal. The high proportion of removal by adsorption was due to the availability of adsorption sites on the adsorbing medium at the start-up stage. Apart from the foremost phosphorus removal, media adsorption contributes to ammonia removal until all the adsorption sites are saturated (Reed *et al.*, 2001). Another reason for the high proportion of removal by adsorption was that the biofilm has not been well established at the start-up stage of the experiment. Microorganisms, in turn play a minor role in nutrient degradation at the start-up stage.

Table 4.10 Proportions of N and P removals by various mechanisms to the total removals in the laboratory-scale system during start-up stage.

	Nitrogen (g)	Percentage of removal	Phosphorus (g)	Percentage of removal
In	4.365		1.843	
Out	2.738		1.073	
Removal	1.627		0.770	
Adsorption	1.080	66.38 %	0.524	68.05 %
Vegetative biomass	0.229	14.07 %	0.039	5.1 %
Microbial processing	0.318	19.55%	0.207	26.89 %

Table 4.11 Proportions of N and P removals by various mechanisms to the total removals in the laboratory-scale system from Mar 04 – Apr 04 (18 hours contact time).

	Nitrogen (g)	Percentage of removal	Phosphorus (g)	Percentage of removal
In	3.492		1.474	
Out	2.191		0.859	
Removal	1.301		0.615	
Adsorption	0.262	20.14 %	0.425	69.11 %
Vegetative biomass	0.140	10.76 %	0.029	4.72 %
Microbial processing	0.899	69.10 %	0.161	26.18 %

The same set of mass balance analysis was carried out again during the operation period with 18-hour contact time after the start-up stage. Since the establishment of biofilm was confirmed by SEM observations and the re-generative pollutant removal function of microorganisms was reflected by the steady pollutant removal efficiency of the system, it could be predicted that microbial removal of nitrogen and phosphorus by biofilm would play a bigger role among the different removal mechanisms in this stage. As expected, the percentage of nitrogen removal by adsorption decreased while the percentage of removal by microbial processes increased. The percentage of nitrogen removal by microbial processes increased from 19.55 % in the start-up stage to 69.10 % in the operating stage. As the removal of phosphorus mainly relies on physical adsorption, the percentage of phosphorus removal by physical adsorption was remained at 68.05 % in the start-up stage and 69.11 % in the operating stage.

For nitrogen removal, adsorption process dominated at the early usage of the filter beds in pollutant removal because biofilm has not built up adequately to carry out microbial degradation. After the establishment of biofilm after start-up stage, the overall removal mechanism would then no longer depend on the limiting physical adsorption, but the microbial activities which were sustainable under favouring operating conditions. Nevertheless, the importance of adsorption process could not be neglected because phosphorus, relying mainly on adsorption, instead of microbial process, for its removal in attached-growth system. To optimize the overall pollutant removal capacity of a filter bed system, the choice of adsorbing medium with high adsorption capacity is always critical to the effectiveness of wastewater treatment system.

Since the proportion of removal due to microbial processing was calculated only by subtracting the total removal by the proportion of removal due to adsorption and vegetative uptake, the contribution of microbial processing should be less than the calculated value, because the fraction of removal of ammonia nitrogen that could not be accounted for was also represented in it.

4.3 Pilot scale system performances

4.3.1 Overall performance

Similar to the laboratory-scale system, start-up period was allocated to let the pilot system to reach a steady state before the real operation for treating wastewater. After reaching the equilibrium, the pollutant removal capacity of system was contributed not only by the limiting physical adsorption capacity, but also by the regenerative degradation ability of microorganisms and the uptake of plants. In the start-up period, extensive root zones of plant and biofilm were allowed to establish inside the sequencing batch biofilm reactor. Zhao *et al.*, (2004) allowed a reed bed system to develop during a 3-month start-up period when colonies of microorganisms were primarily established. In this study, approximate 4-5 months were spent for the start-up of the pilot-scale vegetated sequencing batch biofilm reactor and the equilibrium state was reflected by stable pollutant removal efficiencies in May 2005 (Fig. 4.11). The effluent concentrations of ammonia nitrogen fluctuated from November 2004 - April 2005 and did not go steady until May 2005. Regardless of slight fluctuation of influent concentrations from 36.1 to 24.5 mg/L, the effluent concentrations of ammonia nitrogen from the system were maintained at a narrow range of 11.7 to 15.4 mg/L in the operation in May 2005. Figs. 4.12 shows the biofilm established on the surface of the coal slag in the pilot-scale system under SEM.

The effective volume of the pilot-scale system was 13.6 m^3 and the hydraulic loading was 0.45 $m^3/m^2 \cdot d$. Except the nitrogen contents, physical, chemical and biological characteristics of the domestic wastewater being used onsite belong to weak level of untreated domestic wastewater, according to the classification of Metcalf and Eddy (1991) shown in Table 4.12. With the mean concentration

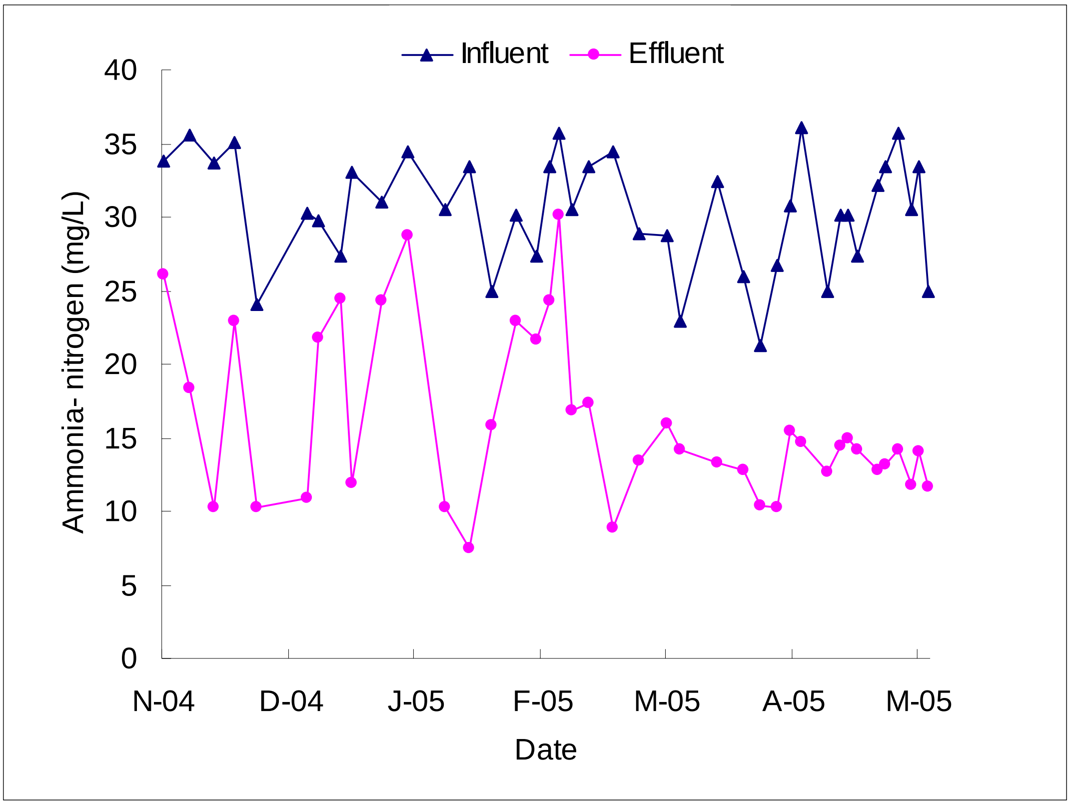
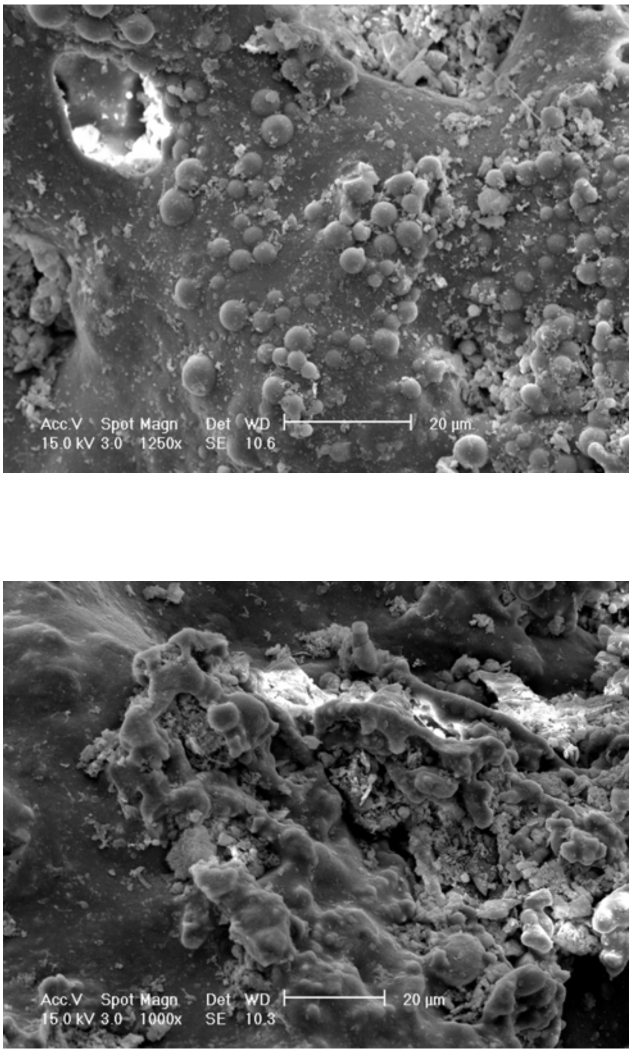


Fig. 4.11 Start-up period of the pilot-scale system (reflected by ammonia nitrogen concentrations)



Figs. 4.12 Biofilm formed on the surface of coal slag

Table 4.12 Classifications of untreated domestic wastewater

	Concentration (mg/L)		
Contaminants	**Weak**	**Medium**	**Strong**
TSS	100	220	350
BOD_5	110	220	400
COD	250	500	1000
NH_3–N	12	25	50
Nitrate	0	0	0
Total phosphorus	4	8	15

(Metcalf and Eddy, 1991)

Table 4.13 Influent characteristics of pilot-scale experiment (May 2005-March 2006) (n = 100)

Parameter	**Mean**	**Standard Deviation**
pH	7.21	0.27
Sewage Temp (℃)	20.47	4.16
BOD_5 (mg/L)	27.59	12.98
COD (mg/L)	80.82	31.52
NH_3–N (mg/L)	32.71	8.37
TKN (mg/L)	35.56	9.69
Nitrate (mg/L)	4.85	4.56
TP (mg/L)	2.61	0.99
TSS (mg/L)	23.26	8.73
DO (mg/L)	1.40	1.04

of ammonia nitrogen of 32.71 mg/L, the wastewater was regarded as having a medium strength of ammonia nitrogen content. The mean concentrations and standard deviations of the influent water quality parameters are presented in Table 4.13.

Ammonia nitrogen comprised nearly 90% of TKN in the raw wastewater onsite. Nitrate concentration in the influent was having an average concentration of 4.85 ± 4.65 mg/L. Total phosphorus was not high in the influent with an average of 2.61 ± 0.99 mg/L. TSS in the domestic wastewater was composed of over 90 % of VSS, the wastewater contained very small amount of fixed solids. For simplicity, only TSS was analyzed for removal efficiency in this study.

Most microorganisms exhibit a pH value at which growth is maximal. This is generally between pH 6.5 to 7.5, at value below 5.0 and in excess of 8.5, growth is frequently inhibited (Stronach *et al.*, 1986). The mean of pH in the system was 7.27 ± 0.27 and so the pH in the system was not the inhibitory factors for the pollutant degradation processes. The BOD/COD ratio of the influent is 0.34. Other water quality parameters were within the typical range of a small community wastewater system (Davis and Cornwell, 1991).

In an attached growth treatment system, there is competition for attachment sites between nitrifying bacteria and heterotrophic bacteria responsible for carbon oxidation. The nitrifying bacteria will be competing with the heterotrophic bacteria for their oxygen supply. Nitrification is impeded until biochemical oxygen demand levels are reduced to approximately the same level as ammonia nitrogen (Metcalf and Eddy, 1991). The availability of oxygen within a filter is a function of the BOD concentration, and the heterotrophic bacteria will outgrow the nitrifiers when BOD is readily available. Horan (1990) stated that a soluble BOD_5 of as low as 20 mg/L is required before sufficient oxygen is available to permit nitrification. The mean of BOD_5 of the influent was 27.59 mg/L in this study, the competition of oxygen for nitrifiers from heterotrophic bacteria was assumed to be not high. According to Mecalf and Eddy (1991), the nitrifier fraction is about 0.21 - 0.35 when BOD_5 /TKN ratio is about 0.5 - 1. The nitrifier fraction in the influent of this study was some value in between 0.21 – 0.35 because BOD_5 /TKN ratio of the wastewater was about 0.78. As the BOD_5 /TKN ratio was less than 3 in the raw sewage, the nitrification process could be classified as a separate-stage, not a combined carbon oxidation and nitrification process (Metcalf and Eddy, 1991).

On the other hand, wastewater flows and loads vary throughout the day in real case on site operation. Daily variation of wastewater loads to the on site pilot-scale system is shown in Fig. 4.13. However, no obvious diurnal pattern was found from the pollutant concentrations in the influent in this study.

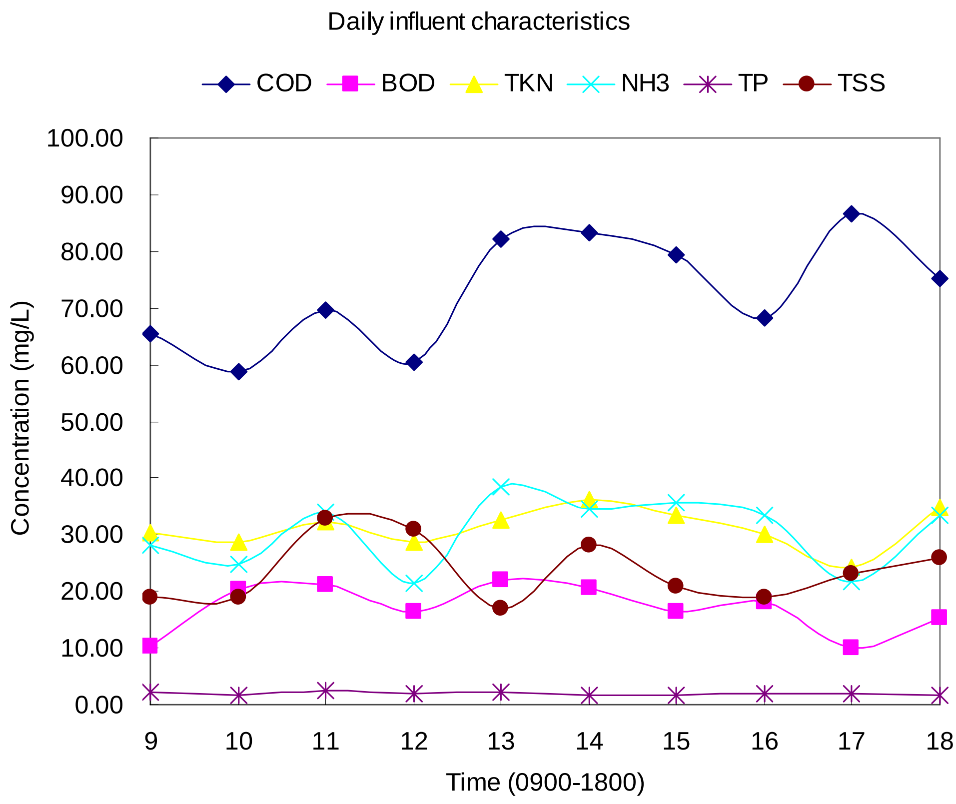


Fig. 4.13 Daily influent characteristics of the pilot experiment.

As mentioned in the previous chapter, the minimum daily air temperatures from May to Oct 2004 were all above 20℃ with a range from 20.5 ℃ to 25.3 ℃ while that from Nov to Apr 2004 were all below 20℃ with a range of 9.8 ℃ to 19.1 ℃. So in this study, the twelve months in 2005 were broadly divided into two categories, namely "cool" and "warm" periods to study the pilot-scale system performance. This classification of study period was found to be appropriate by referring to the temperature of the influent measured in 2005-2006 during the study period (Fig. 4.14). The sewage temperature from May to Oct 05 was ranged from 19.5 ℃ to 26.1 ℃ while that from Nov 05 to Apr 06 was ranged from 13.9 ℃ to 18.9 ℃. The mean sewage temperature in warm period was 23.82 ± 2.81 ℃ and that in cool period was 17.12 ± 1.80 ℃. The overall average sewage temperature throughout the year was 20.47 ± 4.16 ℃.

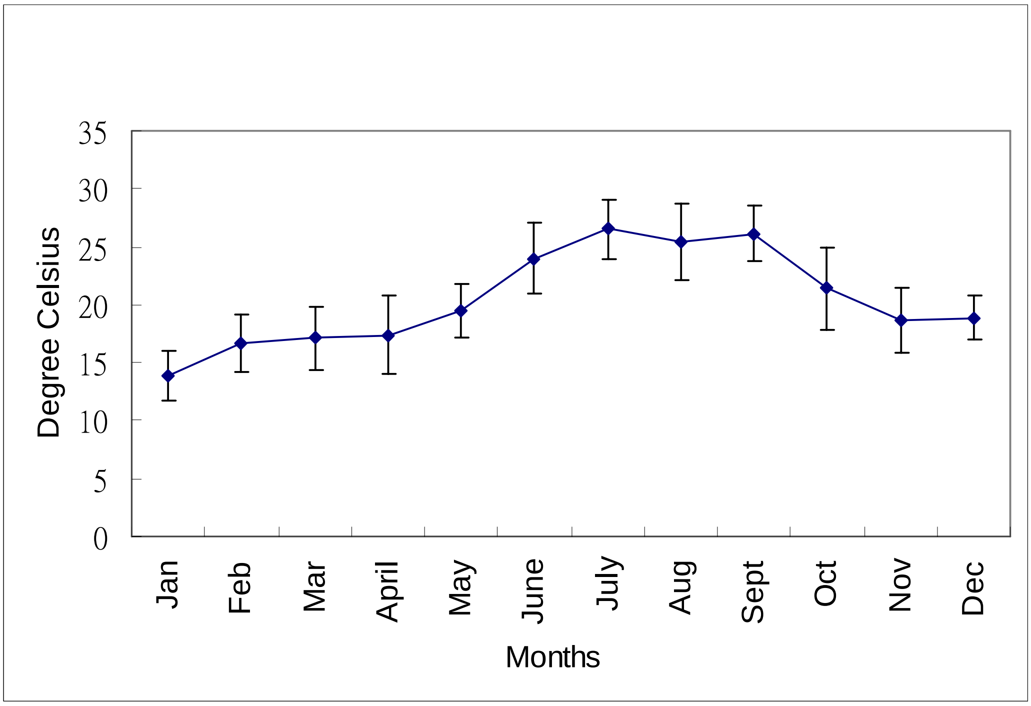


Fig. 4.14 Monthly temperature of influent in 2005-06

In general, the wastewater treatment of vegetated sequencing batch biofilm reactor discharged effluent with pollutant concentrations of $BOD_5 < 20$ mg/L, COD < 60mg/L, NH_3-N < 25 mg/L, TP < 3 mg/L and TSS < 20mg/L (Table 4.14). Average removal efficiencies of BOD_5, COD, NH_3-N, TP and TSS in domestic wastewater were reported as at the maximal of 59.72 %, 63.58 %, 50.51 %, 37.89 % and 78.82 %, respectively with 18-hour contact time, and at the minimal of 29.72 %, 25.96 %, 21.9 %, 23.42 % and 23.25 %, respectively with 0-hour contact time (Figs. 4.15 - 4.19).

4.3.2 Controlling factors

The effects of plants and contact time to the performance of the systems were reflected by the removal efficiencies of different pollutants. The rhythmical movement of the wastewater in the system allowed the operating environment to change in a temporal sequence. The dissolved oxygen available in the bed matrix and the seasonal variations of operating conditions were investigated.

4.3.2.1 Effects of plant

In this part of study, the effects of plant to the pollutant removal efficiency of a sequencing batch biofilm system were presented. Since any increase in microbial population due to the vegetation was difficult to measure, any enhancement of pollutant removal would have to base on empirical observations. Instead of doing tedious in-depth microscopic investigation, side by side system comparison was done to examine the influences of plant to pollutant degradation efficiencies.

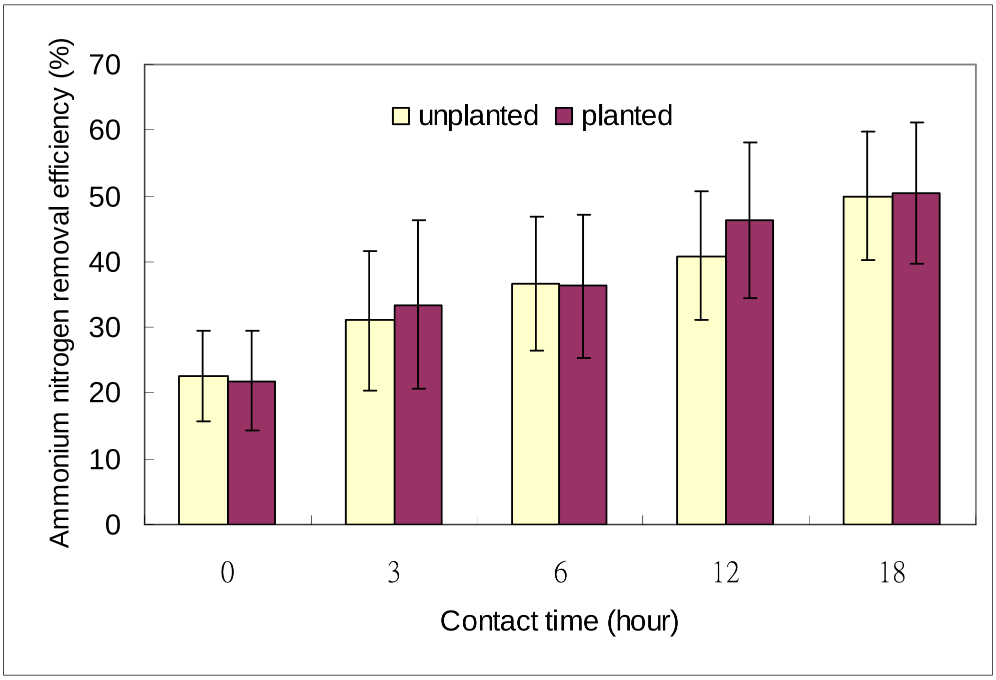


Fig. 4.15 NH_3-N removal efficiency in the planted and the unplanted systems with different contact times in the pilot experiment

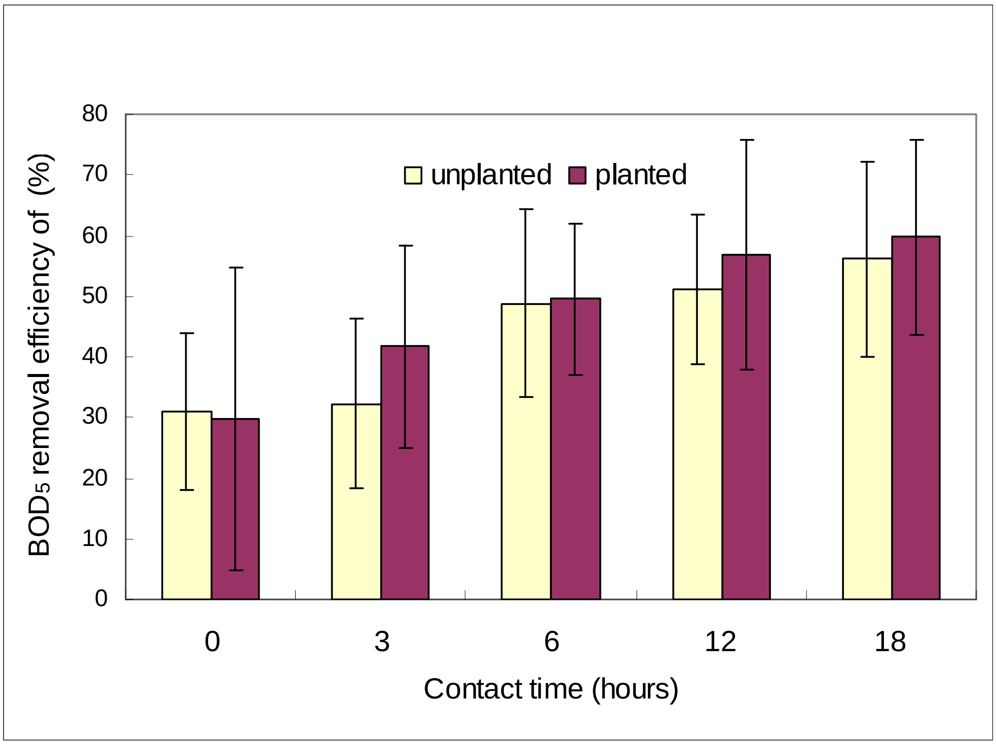


Fig. 4.16 BOD_5 removal efficiency in the planted and the unplanted systems with different contact times in the pilot experiment

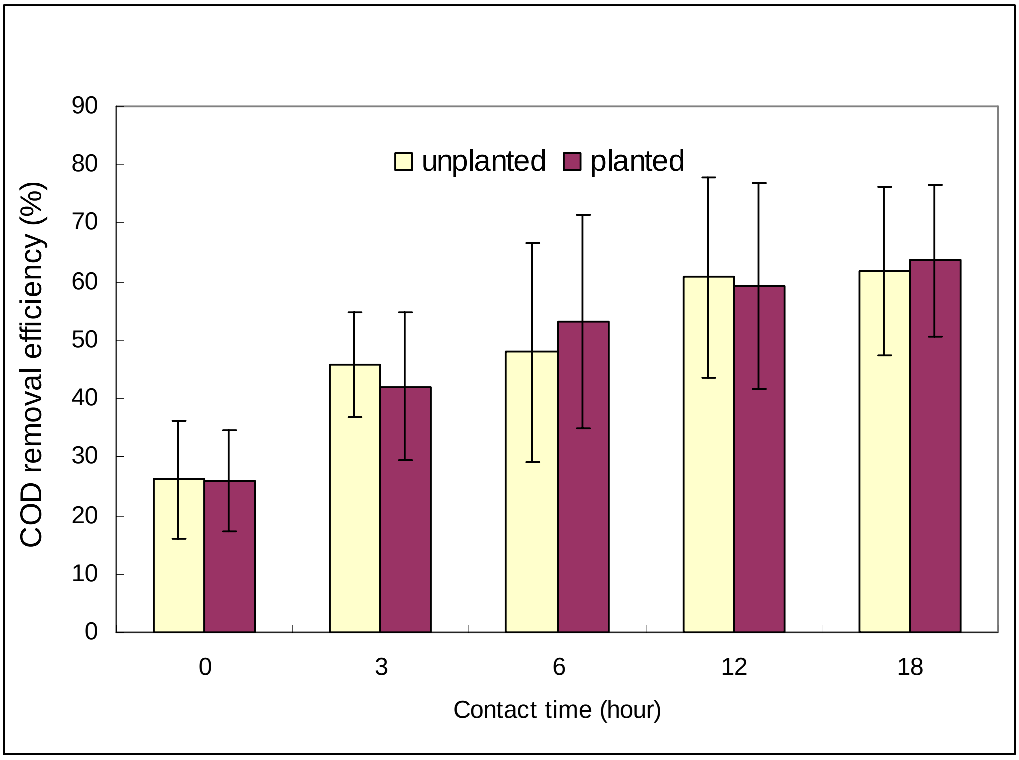


Fig. 4.17 COD removal efficiency in the planted and the unplanted systems with different contact times in the pilot experiment

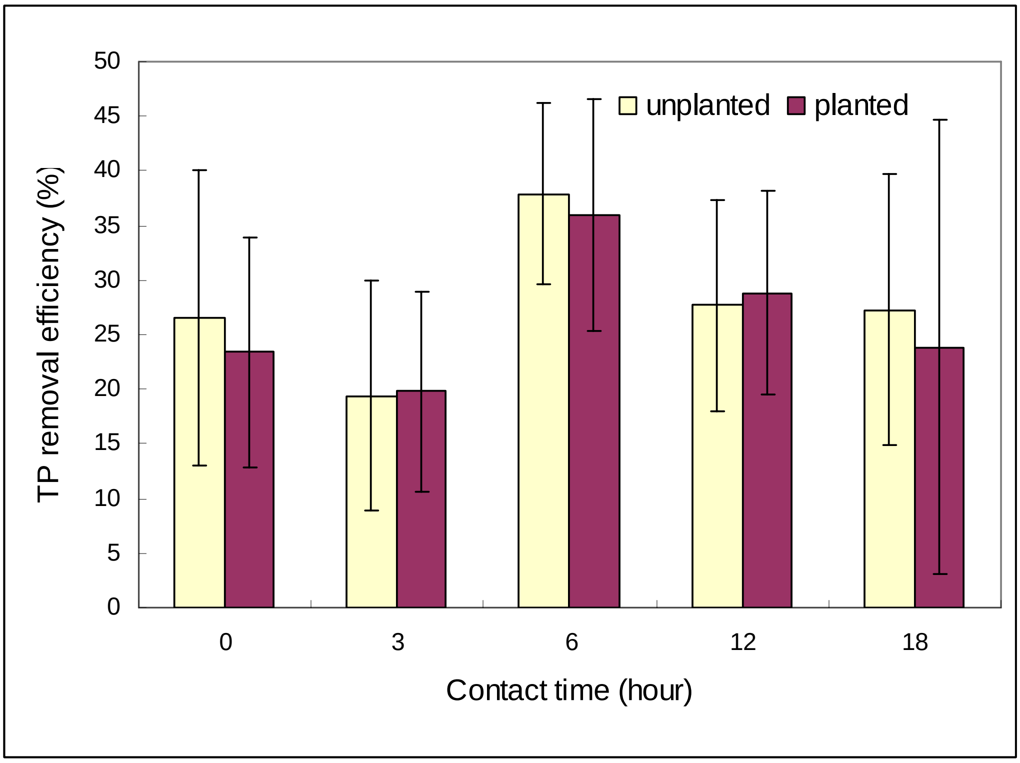


Fig. 4.18 TP removal efficiency in the planted and the unplanted systems with different contact times in the pilot experiment

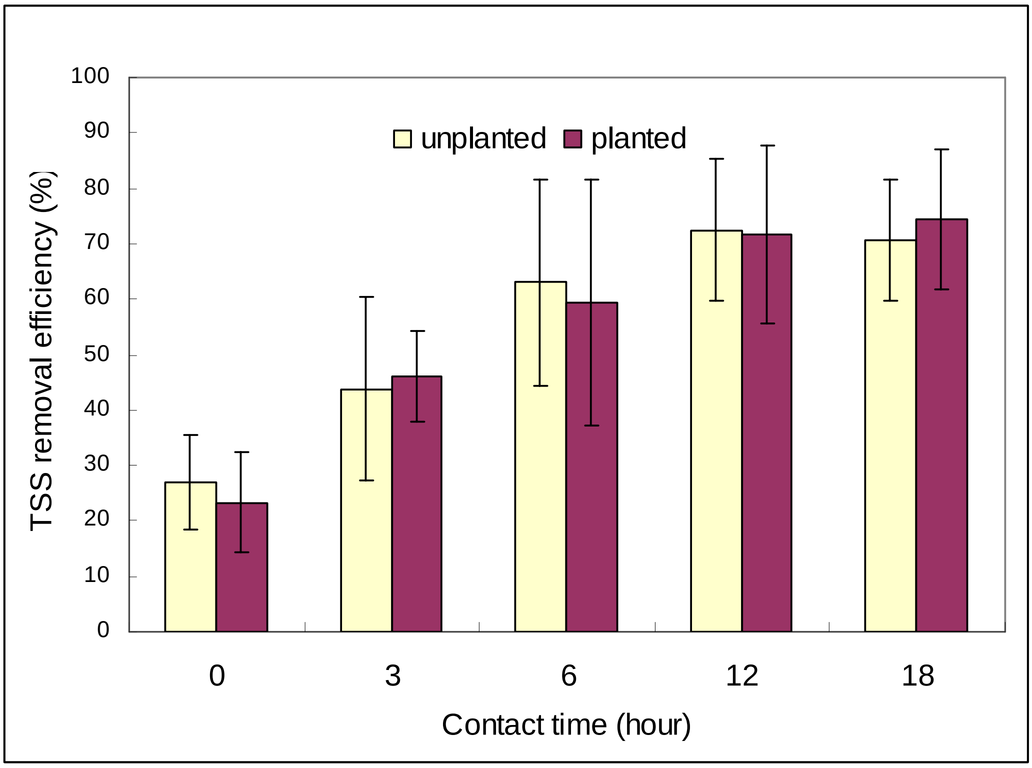


Fig. 4.19 TSS removal efficiency in the planted and the unplanted systems with different contact times in the pilot experiment

Table 4.14 Effluent concentrations (mg/L) from different contact times in pilot-scale experiment.

	Effluent concentration from sequencing batch biofilm reactor				
Hours	0	3	6	12	18
BOD_5	21.28 ± 5.94	18.76 ± 6.10	13.37 ± 4.54	11.23 ± 6.44	10.83 ± 5.35
COD	63.79 ± 17.05	49.74 ± 17.41	45.47 ± 20.89	29.92 ± 14.22	26.90 ± 9.87
NH_3 -N	28.84 ± 4.38	22.94 ± 6.30	22.65 ± 6.57	16.21 ± 6.70	14.60 ± 5.78
TP	2.16 ± 0.45	1.96 ± 0.29	2.16 ± 0.77	1.18 ± 0.20	1.80 ± 0.41
TSS	15.88 ± 4.89	15.08 ± 5.51	9.70 ± 6.07	5.25 ± 2.62	5.83 ± 2.95

Effects of plant to the overall pollutant removal efficiencies were compared in the performance of the side by side pilot-scale treatment systems. The planted and the unplanted systems were operated under identical operating conditions. The effects of plant to the removal efficiencies of BOD_5, COD, NH_3-N, TP and TSS were analysed using one-way ANOVA at a significance level of 0.05 (Table 4.15). The pollutant removal efficiencies of the two systems were very similar and there were no significant differences between two systems for all the parameters (all p-values > 0.05) in this pilot-scale study.

Plant uptakes and oxygen transferals

There has been a controversial review over the function of vegetation in wetlands

Table 4.15 *p*-values of one-way ANOVA between the planted and the unplanted systems on various pollutant removal efficiencies in pilot experiment.

	BOD_5	**COD**	**NH_3-N**	**TP**	**TSS**
18	0.488	0.687	0.866	0.538	0.303
12	0.292	0.786	0.121	0.719	0.867
6	0.873	0.423	0.918	0.607	0.570
3	0.072	0.378	0.518	0.916	0.565
0	0.863	0.946	0.771	0.451	0.238

and fixed bed systems (Armstrong *et al.*, 1990; Tanner, 2001; Brix, 1994). Many early studies reported greater reductions in the concentration of particular contaminants in planted than in unplanted gravel-beds (Tanner, 2001). Gersberg *et al.*, (1986) compared the ammonia nitrogen removal of three different vegetated beds, and reported that the mean effluent ammonia concentrations were significantly lower than that of unvegetated bed. The high ammonia nitrogen removal efficiencies shown by the bulrush and reed beds were attributed to the ability of these plants to translocate oxygen from the shoots to the roots. The oxidized rhizosphere so formed stimulates sequential nitrification-denitrification. Increased rates of BOD removal and ammonia oxidation from wastewaters and elevated dissolved oxygen concentrations have been recorded in the root-zone of wetland plants (Dunbabin *et al.*, 1988; Reddy *et al.*, 1989). Dissolved oxygen level in rootzone of planted system is supposed to be higher due to oxygen transferal from shoot to root, and increased oxygen levels would facilitate pollutant degradation process.

However, there has been controversy about how much of oxygen is actually released into the root-zone from internal spaces of plant by diffusion and convective flows. Although some plants are able to transport oxygen from leaves downwards to the root system, the critical question is whether the amount of oxygen from the plant roots available to the microbes can support a significant oxidation of organic pollutants and ammonia. Brown and Reed (1994) compared the high oxygen demand of municipal wastewater in terms of both the degradation of organ matters and nitrification, and concluded that the amount of available oxygen from plants is probably insignificant. Hiley (1994) also reported that macrophyte vegetation has no significant contribution of oxygen to the process of treating BOD in constructed wetland. In this study, the findings in the pilot-scale system were coherent to the views that plant itself does not uptake significant levels of pollutant from the wastewater or the transferal of oxygen from plant shoots to roots does not influence the aerobic removal processes in the filter bed. *Cyperus alternifolius* used in this study did not contribute to any significant effects on pollutant removal by neither direct uptakes nor oxygen transferal because confirming by statistical analysis, the removal efficiencies of both the planted and the unplanted systems were not significantly different in the pilot-scale experiment.

Apart from the controversy of influencing the oxygen levels available in filter bed, plants are found to provide additional support for the biomass and act as physical filters for the solids. Plant can reduce the tendency of the medium to clog with solids (The Chartered Institution of Water and Environmental Management, 2000). Higher densities and activities of nitrifiers have been recorded in biofilms associated with wetland plant roots and rhizomes than in the gravel media (Williams *et al*., 1994). In contrast, Larsen and Greenway (2004) found that there was no significant difference between biofilm growth on gravel surfaces with and without plants. However, this argument was not proved in this study without in-depth microscopic investigation.

Nutrients accumulation in plant tissues

On the other hand, the *Cyperus alternifolius* in the sequencing batch biofilm reactor was harvested for nitrogen and phosphorus contents measurements. One was done after the completion of operation in warm period from May 05 to September 05. Another was carried out at the end of the operation in cool period

Table 4.16 Nutrient levels of plant tissues in pilot-scale system.

	Warm		Cool	
Growth rate (wet-base) (kg/m^2/month)	1.54		1.25	
Growth rate (dry-base) (kg/m^2/month)	0.36		0.31	
	Leaf	**Stem**	**Leaf**	**Stem**
Total Nitrogen (mg/g)	13.2	9.8	7.5	5.4
Total Phosphorus (mg/g)	3.5	2.4	2.9	1.5

from Nov 05 to Mar 06. The fresh weight production rate of *Cyperus alternifolius* was 1.54 $kg/m^2 \cdot$month in warm period and 1.25 $kg/m^2 \cdot$month in cool period. The nitrogen and phosphorus accumulated in warm period were higher than that in cool period regardless of plant parts. Higher metabolic rates and growth of plants were supported by higher temperature in warm period, hence more active uptake of nutrients took place.

Since plant parts often show changes in nutrient contents during various stages of existence, nitrogen and phosphorus contents in stems and leaves of *Cyperus alternifolius* were analysed separately. The plant nutrient contents in stem and leaves accumulated in warm period and cool period were compared in Table 4.16. During the warmer seasons, the plant grew faster and had sufficient sunlight, both nitrogen and phosphorus contents accumulated in *Cyperus alternifolius* were higher in warm periods than that in cool periods. Moreover, different parts of a plant may have large variations in nitrogen content in different seasons (Kühl and Kohl, 1993). In the case of *Cyperus alternifolius*, the leaves contained higher concentration of both N and P than the stems. Tanner (1996) reported the tissue nitrogen concentration in *Cyperus involucratus* were 15.5 mg/g. This finding is comparable to the nitrogen concentration of 13.2 mg/g in *Cyperus alternifolius* grew up in the system with warm climate in this study.

Compare to the data from hydroponics experiment, *Cyperus alternifolius* accumulated higher concentration of nutrients in the pilot scale system operation. The differences were due to the fact that pilot-scale system was functioning with real-case operating conditions, outdoor environment provided sufficient sunlight and temperature for plant growths. The pilot sequencing batch biofilm reactor offered a more diversified nutritious and microbial soil environment in the sequencing batch biofilm reactor such as through the existence of rhizosphere in the root zone of plant. The rhizosphere is the zone of soil surrounding the root, is a dynamic region governed by complex interactions between plants and the organisms that are in close association with the roots. The composition and pattern of root exudates affect the microbial diversity around it. There is a symbiosis relationship between the plants and the microorganisms in the rhizosphere. Moreover, the *Cyperus alternifolius* being harvested in the pilot-scale system was also in bigger size and more mature after about 5-month growth in the pilot system, and hence the nutrient concentrations were calculated basing on larger biomass.

Plant harvesting

Kadlec (1994b) found that harvesting *Phragmites australis* shoots twice during the growing season increased the total amount of biomass, as well as removal of plant-accumulated nitrogen and phosphorus from wastewater. Nevertheless, some scholars argued that the total amount of nutrients that can be removed by harvesting is generally insignificant compared to the loadings with wastewater (Bachard and Horne, 2000; Tanner, 2001). Moreover, they also argued that the uptake of organic matters by plants is negligible compared to biological degradation by microorganisms (Watson *et al*., 1989; Cooper *et al*., 1996).

On the other hand, plant decay in the system results in an increase of the nutrient loads within the water layer on the top of the filter media. Regular harvesting of plant and clearance of wilted and fallen plant parts at appropriate time are necessary not only to enhance the plant uptake by stimulation of new growth of plant tissues, but also to avoid the return of nutrient load by plant decays.

Although planting has not been completely proved in all literatures as vital to remove pollutants attached-growth system, dense bed of emergent wetland plants are undoubtedly play a major role in enhancing habitat values, aesthetic and perceived naturalness. Plant is always an essential component of any wetland-based wastewater treatment system.

4.3.2.2 Effects of contact time and rhythmical operation

Contact time is a key design and operating variable for the sequencing batch feed filter bed because treatments for any biologically based process are time-dependent. Longer contact time will facilitate the degradation of the pollutants, but it will also reduce the treatment capacity of the constructed wetland. The critical task is to optimize the contact time for the best achievement of removal efficiency.

Under the fact that the effect of *Cyperus alternifolius* was proved to be insignificant by statistical analysis, the analysis of the effects of contact time on pilot system performance was done on the whole set of data regardless of planted or unplanted systems.

Correlations to contact time

Fig. 4.20 shows the whole picture of pollutant removals with the five selected durations of contact time. The Pearson correlation coefficients of contact time with removals of BOD_5, COD, NH_3-N, TP, and TSS were 0.601, 0.511, 0.665, 0.070 and 0.690 respectively. The Pearson correlation coefficient is a summary of the strength of the linear association between the variables. If the variables tend to go up and down together, the correlation coefficient will be positive. BOD_5, COD, NH_3 and TSS associated positively with the contact time, they gave increasing trends of removal with the increases of length of contact time. Removals of BOD_5, COD, NH_3-N and TSS showed similar levels of correlation to contact time with removal of COD displaying a slightly lower correlation. Bavor *et al.*, (1989) found that removal of BOD_5 displaying a slightly higher correlation to contact time than removal of TOC did in all gravel-based systems. His findings were similar to this study, with removal of BOD_5 showing a higher correlation to contact time than other carbonaceous parameters. As BOD_5 is the measurement of the amount of oxygen consumed by microorganisms in decomposing organic matter in wastewater, and it increases with the extension of time for microbial actions.

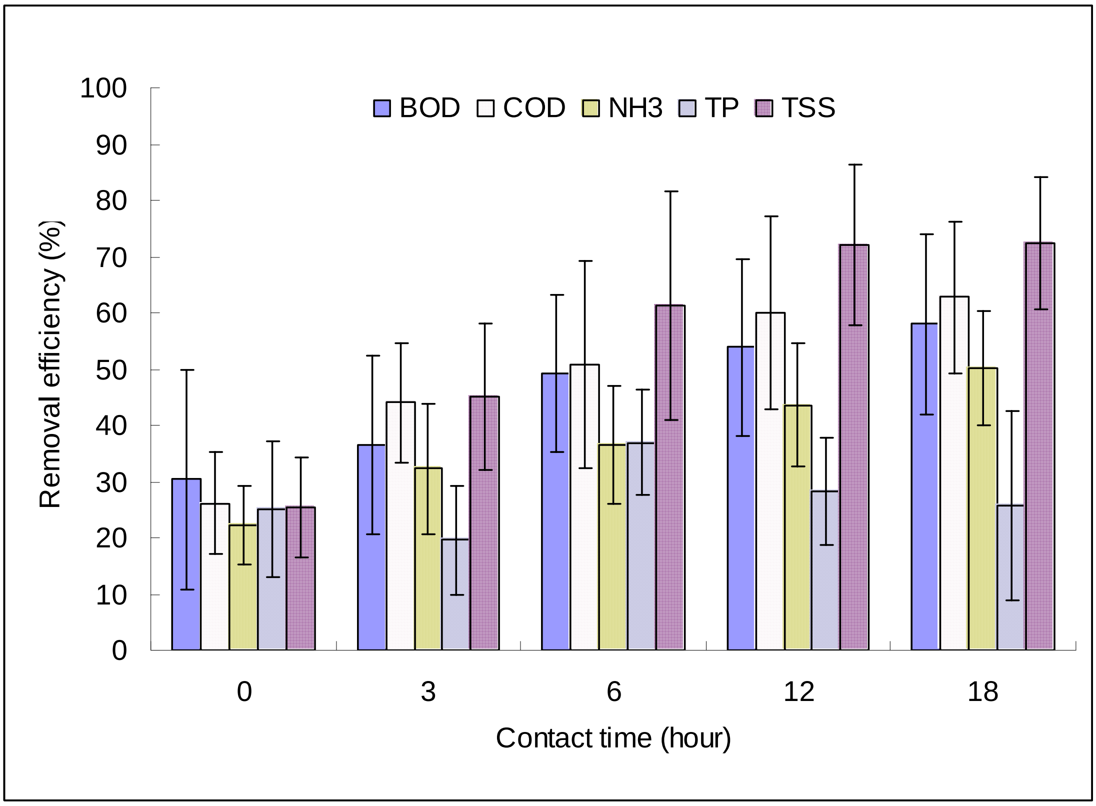


Fig. 4.20 Effects of contact time on different pollutant removal efficiencies in the pilot-scale system.

Contact time has a direct influence on the removal of ammonia nitrogen through the biological process nitrification. Van Benthum *et al*., (1997) studied the relationship between biofilm growth and hydraulic retention time. They concluded that the optimum time range for the development of the nitrifying biofilm was from 3 to 12 hours, much longer than the time required for heterotrophic ones. Hence, longer reaction time was favourable to maximize the removal efficiency of ammonia nitrogen removal, and hence the nitrification process.

The removal mechanisms for TSS in the wetland treatment system essentially include sedimentation where the suspended solids ultimately settle to the bottom, retention time and contact with plant materials enhance this process. Removal of TSS also showed a high correlation to the contact time in the vegetated sequencing batch biofilm reactor in this study. Besides facilitate sedimentation, the long contact time promoted more complete biodegradation because high proportion of the TSS in the domestic wastewater being used onsite were volatile suspended solid, which were readily biodegradable. The extension of time definitely facilitated the reduction of the organic contents in the suspended solids by microorganisms.

In contrast, removal of TP showed a relatively low correlation to the contact time in this study. This phenomenon further confirmed the TP removal in the sequencing batch biofilm reactor was less dependent on biological degradations, and it was in fact time-independent.

Rustige and Platzer (2001) concluded that a retention time of 16-24 hours in overland surface-flow system is sufficient for high performance in the treatment of secondary to tertiary level effluent. Compared to surface-flow system, the sub-surface flow sequencing batch biofilm reactor required less retention time in the treatment of secondary level effluent, eighteen hours or less were needed to treat the domestic wastewater into effluent with concentrations of BOD_5 < 20 mg/L, COD < 60mg/L, NH_3-N < 25 mg/L, TP < 3 mg/L and TSS < 20mg/L.

Rhythmical movement of air and wastewater

Different flow bed systems are distinguished by variation of the frequency of saturation and inundation of water. The sequencing batch biofilm reactor was a gravel-based bed system integrated with the periodic feeding frequency like that of a sequencing batch reactor. The idea is to improve the pollutant removal effectiveness of bed system by tackling with its deficiencies. The air drawn into sequencing batch beds during the “draw” phase was used as an oxygen source to remove the pollutants. The oxygen transport and consumption rate in the beds could be greatly improved by the rhythmical water and air movement in the bed matrix (Sun *et al*., 1999). These alternating phase of “feed” and “rest” are fundamental to control the growth of the attached biomass on the adsorbing medium, to maintain aerobic conditions within the filter bed and to mineralize the organic deposits. Besides the removal of nitrogen, Miller and Wolf (1975) have shown that P adsorption capacity of vertical filtration bed can be regenerated if the system is allowed to rest and dry. In other words, intermittent loadings are feasible to optimize P removal.

Clogging is most likely to occur in gravel-bed system after prolong operation with high strength wastewater. A COD load of less than 20g COD $m^{-2}d^{-1}$ prevents adsorbing medium clogging (Langergraber, 2005). The parameters of adsorbing medium related to clogging, include grain size, filtration rate and organic substance in the adsorbing medium. Clogging was not observed in the sequencing batch biofilm reactors after almost one-and-a-half year operation with comparatively low strength of domestic wastewater. Clogging of the gravel pore spaces over a 5-year wetland operation was probably due to the accumulation of refractory (stable) organic solids, particularly in the top 100 mm of the gravel bed (Nguyen, 2001). Green *et al*., (1997) pointed out that clogging in wetlands could be prevented by rest (drying) periods. The rhythmical feeding mode of wastewater to the sequencing batch biofilm reactor in this study can delay the occurrence of clogging and even the replacement of adsorbing medium. Furthermore, the grain size distribution analysed in section 4.1.1.1 also confirmed that the coal slag in the bed system would not clog easily.

4.3.2.3 Dissolved oxygen

Dissolved oxygen (D.O.) has a mean value of 1.4 ± 1.04 mg/L in the influent of the pilot-scale system. The D.O. of influent was found to be increased after entering the sequencing batch biofilm reactors because air from the pore of the coal slag bed was dissolved into the wastewater. The down flow of influent from the tap opening in the inlet zone also provided aeration effects. The D.O. levels right after the 4-hour "fill" phase, at which the sequencing batch biofilm reactors were just saturated with wastewater, were 1.98 ± 0.86 mg/L and 2.10 ± 1.18 mg/L in the unplanted and the planted systems respectively. However, according to one-way ANOVA test (n=10), there was no significant difference between the D.O. levels in the planted and the unplanted system (p-value > 0.05). It seemed that the presence of plant roots did not contribute to any rising in D.O. in the planted system. On the other hand, the D.O. was found to have a decreasing trend along the depth of the filter bed (Fig. 4.21). The deeper the zone, the lower the D.O. level was. The figure shows the D.O. levels at different depths right after the bed systems have been saturated with wastewater after 4-hour "fill" phase. As the tanks were filled up with wastewater gradually from the bottom to the top, the D.O. in the wastewater was depleted earlier in the deeper zone. The consumption of oxygen by microorganisms occurred once the wastewater entered the sequencing batch biofilm reactor. As a result, a spatial distribution of oxygen levels was found at different depths of the vertical coal slag bed with the current wastewater filling mode.

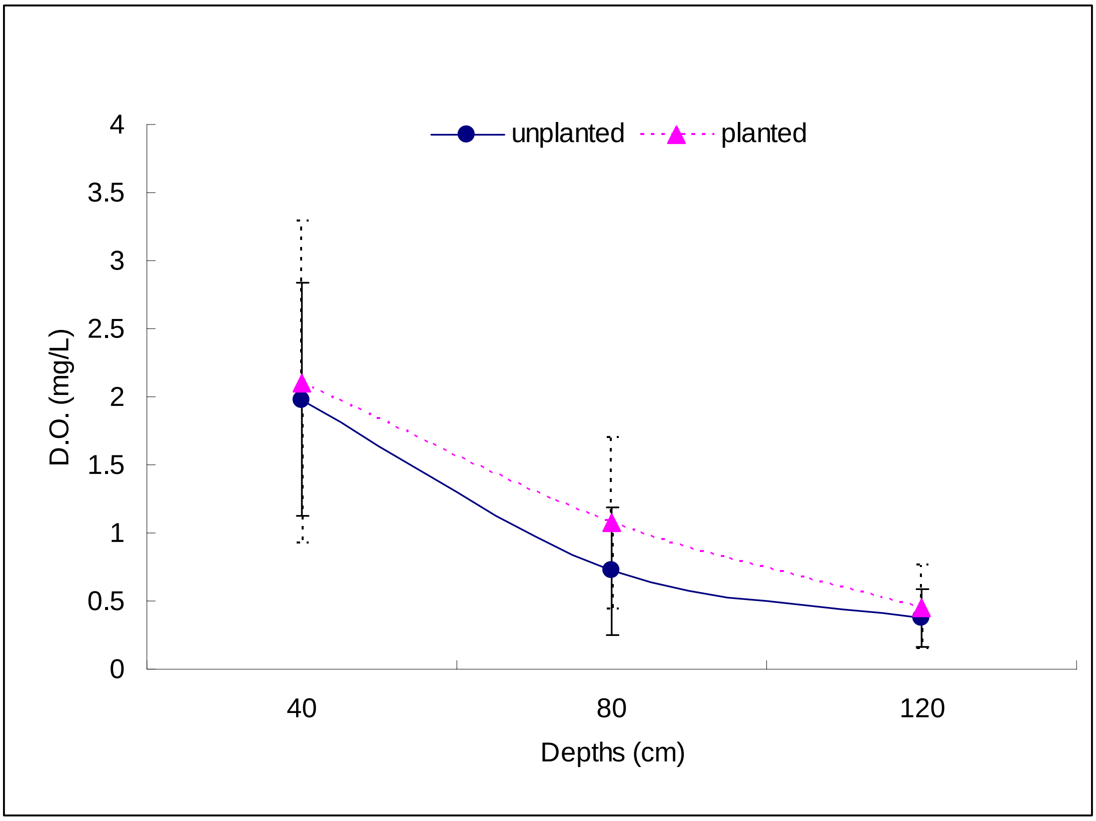


Fig. 4.21 D.O. levels in different depths of planted and unplanted systems

Dissolved oxygen is one of the potentially critical variables in terms of pollutant removal efficiency. It is the primary control variable which is critical for aerobic metabolism. Different pollutant removal processes are favoured in specific ranges of dissolved oxygen concentrations. Carbonaceous BOD removal is favoured with D.O. level of 1-2 mg/L, nitrification is facilitated with D.O. level of 2-3 mg/L while denitrification is facilitated with D.O. level < 0.5 mg/L. And nitrification took place in all locations where D.O. levels were higher than the critical threshold of 0.5 mg/L (Taylor and Bishop, 1989). With the oxygen levels usually over 0.5 mg/L in the sequencing batch biofilm reactor, nitrification was favoured to convert ammonia nitrogen into nitrate. Table 4.17 shows the forms of nitrogen presented in the influent and the effluent after 18 hours contact time in the pilot-scale systems. The reduction of NH_3-N by nitrification was favoured by the D.O. levels with the average values over 0.5 mg/L. However, the total nitrogen removal by nitrification must be followed by denitrification. Conventionally, the rhythmical fill and draw of operation allowed the alternation of aerobic and anaerobic conditions for diversified biochemical reactions to take place in the conventional sequencing batch reactors. Total nitrogen can be removed using a single reactor with intermittent aeration by which nitrification and denitrification are practiced one after the other (Iwai and Kitao, 1994). Reddy and Patrick (1984) have shown that alternating submerged and dry conditions are important for the extent of nitrogen losses through denitrification from soils. The conditions for denitrification in the sequencing batch biofilm reactor could be fulfilling with longer contact time, after which the reactor was saturated with wastewater with D.O. levels dropped to below 0.5 mg/L, especially in the deeper zone of the reactor. From Table 4.17, the reduction of TN concentration reflected the possible removal of nitrogen from the system by denitrification. However, uptake of NH_3-N and NO_3–N by plants would also contribute to the reduction of TN. Further in situ measurements of the coal slag matrices have to be done to make the distinction between the actual rate of nitrification and denitrification, so that the main biochemical mechanisms for TN removal could be identified.

To summarize, D.O. levels can be altered through changes in system design. During the “draw” phase, air is drawn into the sequencing batch biofilm reactor actively when treated effluent is drawn out from the system through the outlet at the bottom. Moreover, during the “idle” phase, resting of beds allow air to get into the bed to aerate and reduce the likelihood of anoxia. Drying of beds is occasionally required to enhance performance. Intensified oxygen flux into bed matrices is highly desirable in the treatment of high strength wastewaters, as a large amount of oxygen is required by aerobic microbes to decompose organic pollutants and by nitrifying bacteria to convert ammonia into nitrite and nitrate.

Table 4.17 Nitrogen forms in the planted and the unplanted systems of the pilot-scale experiment (18-hour contact time).

	In	Out	
		Planted	**Unplanted**
TKN (mg/L)	34.44	17.76	16.61
NH_3 – N (mg/L)	33.32	14.19	15.11
NO_3 – N (mg/L)	4.45	8.93	9.12
TN (mg/L)	38.89	26.69	25.73

Last but not least, availability of D.O. determines not only the system operation, but also the basic system configurations. Jenssen *et al*., (1997) suggested that in order to optimize the conditions for plant uptake and the micro-organisms in the root zone of the constructed wetland system, a shallow system should be chosen (depth < 60cm). However, a deeper system promises the occurrence of anaerobic/anoxic conditions when it is fully saturated with wastewater for a period of time. D.O. level is, in fact, a major consideration for deciding the dimension of such vegetated sequencing batch biofilm reactor.

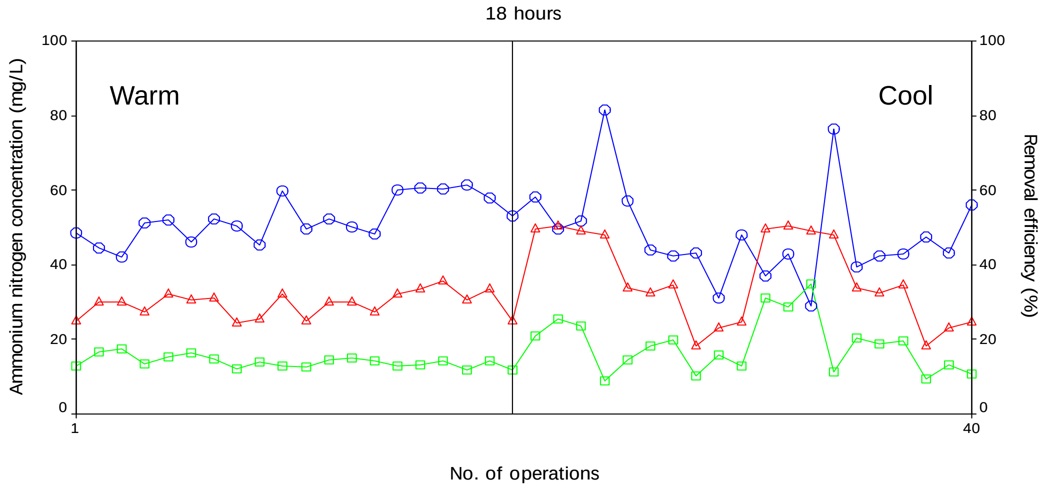
4.3.2.4 Seasonal variations of system performance

Constructed wetlands have been shown to provide sufficient domestic wastewater treatment efficiencies in temperate climates (Vanier and Dahab, 2001). Operating with the temperate climates in Guangdong areas, the sequencing batch biofilm reactor was capable to purify the domestic wastewater efficiently. Yet, seasonal variations have an influence on filtration performance (Hammer, 1989; Jing *et al*., 2001). Since the effect of plants was proved to be insignificant in the previous session, the analysis of seasonal effect on performance was done on the whole set of data regardless of planted or unplanted systems. Table 4.18 shows the *p*-values of one-way ANOVA for the system performances in warm and cool periods.

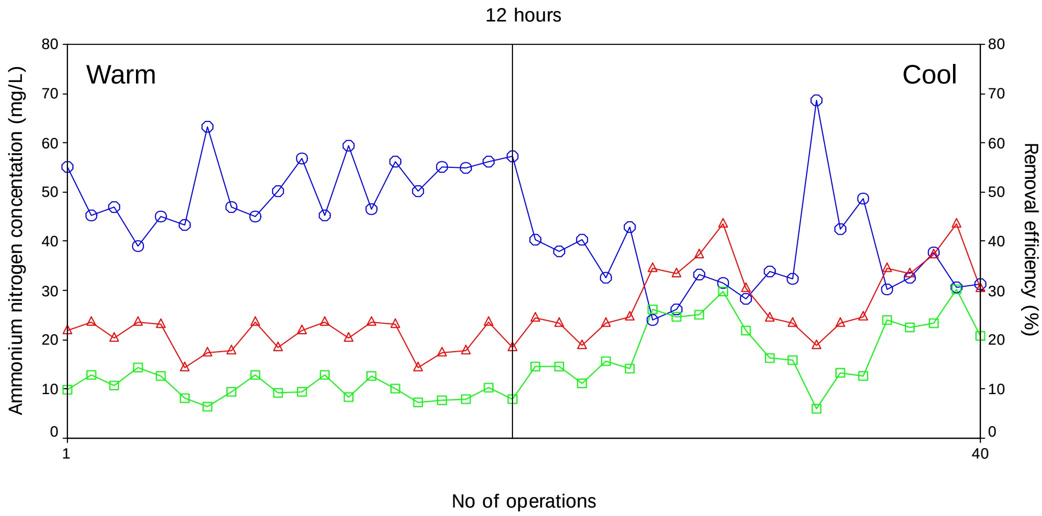
Analysis of the removal efficiencies of COD, TP and TSS with respect to warm and cool periods indicates that temperature appeared to have negligible treatment effects (Figs. 4.22-26). Except under contact time of 18 hours, the removal efficiencies of ammonia nitrogen in warm and cool seasons showed significant differences under contact time of 0, 3, 6 and 12 hours (p-values < 0.05). It implied that the temperature had determinant effects on the removal of ammonia nitrogen in the vegetated sequencing batch biofilm reactors. Water temperature has a strong effect on the growth rate of nitrifying bacteria. Numerous researchers have documented that nitrification episodes are more common during the warmer months (Watson and Danzig, 1993; Williams, 1994; Taylor and Bishop, 1989). Most strains of nitrifiers grow optimally at temperatures between 25 and 30 °C (Watson *et al.*, 1981) but nitrification has occurred over a wide range of temperatures (8-26 °C) (Kirmeyer *et al.*, 1995).

Distinct seasonal patterns of influent concentration, effluent concentration and removal efficiency of ammonia nitrogen existed especially in operations with long contact time such as 18, 12 and 6 hours (Figs. 4. 22). The ammonia nitrogen concentrations in the influent and effluent, as well as the removal efficiency, displayed more stable trends in the warm period than in the cool period. This phenomenon was also correlated to the effects of temperature on nitrification process. Higher temperature in warm periods favoured the biological processes and boost up the process rates while the lower temperature in cool periods inhibited the process rates to certain levels, and hence stable performances were not ensured.

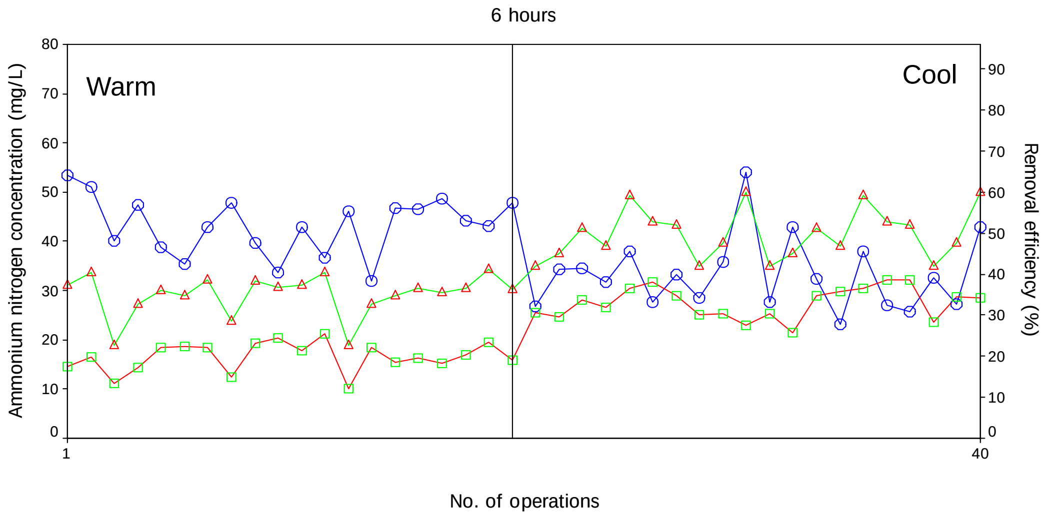
Evaluating Fig. 4.23, removal efficiencies of BOD_5 appeared to be temperature-dependent with significant different values with 3-hour and 6-hour contact time. As one of the most general controlling factors for physicochemical and biological processes is temperature, it has been suggested that the colder temperature in cool period could slow down BOD_5 destruction (Vanier and Dahab, 2001). In contrast, higher temperature enhanced the endogenous respiration of microbes to degrade the organic matters. Note that the higher temperatures gave enhanced BOD_5 removal during the operations with 3-hour and 6-hour contact times, the significant effects of temperature on organic matters degradation were observed in short contact times but not the longer contact times with 12 or 18 hours. It could be assumed that the effects of temperature hence were attenuated by the effects of contact time. This implied that among the several controlling factors of pollutant degradation processes, contact time might have a bigger magnitude to control the rate of degradations of organic matters than temperature did. The importance of different controlling factors (independent variables) have to be further verified by sensitivity analysis during the model development in session 4.4.


18 hours
Warm
Cool
Ammonium nitrogen concentration (mg/L)
Removal efficiency (%)
No. of operations

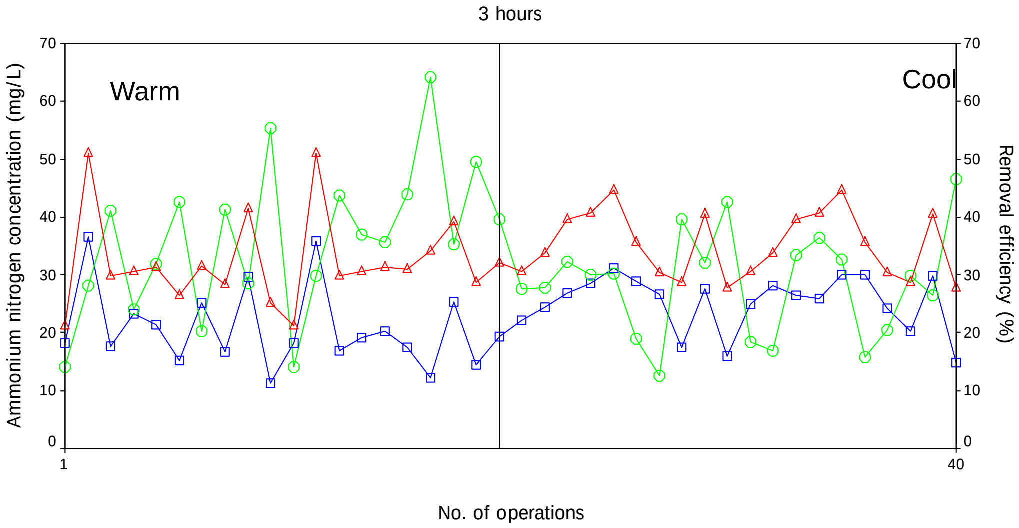
a)


12 hours
Warm
Cool
Ammonium nitrogen concentation (mg/L)
Removal efficiency (%)
No of operations

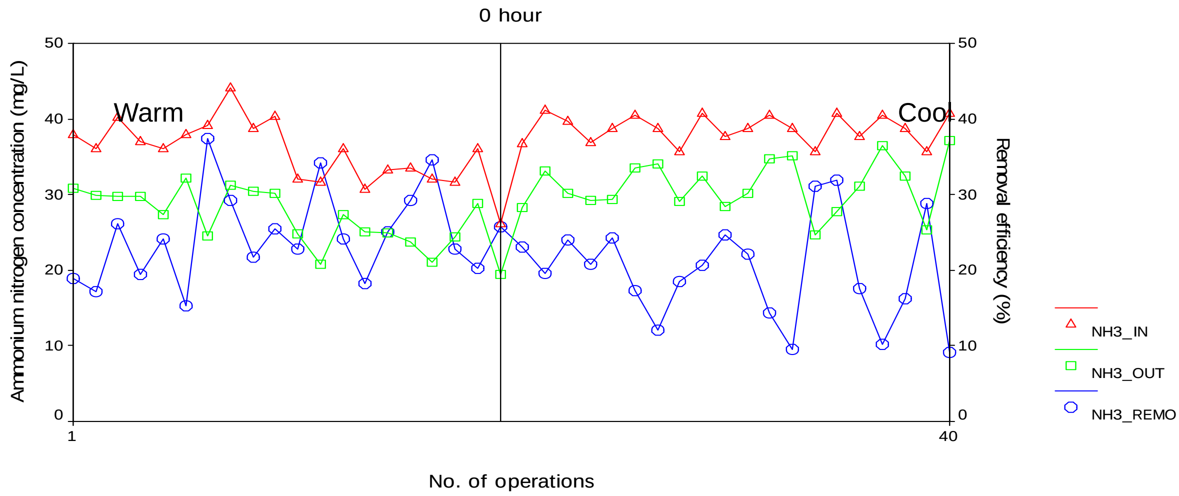
b)


6 hours
Warm
Cool
Ammonium nitrogen concentration (mg/L)
Removal efficiency (%)
No. of operations

c)

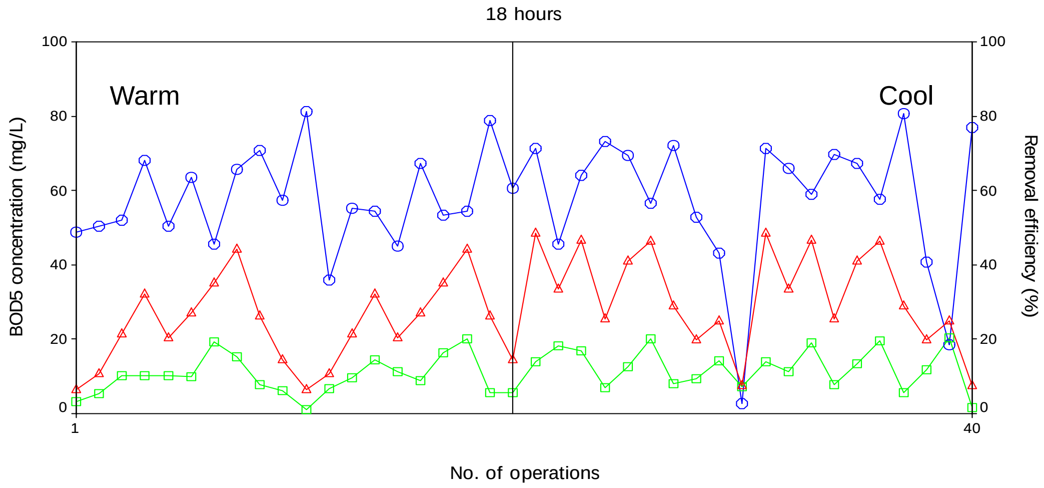


d)



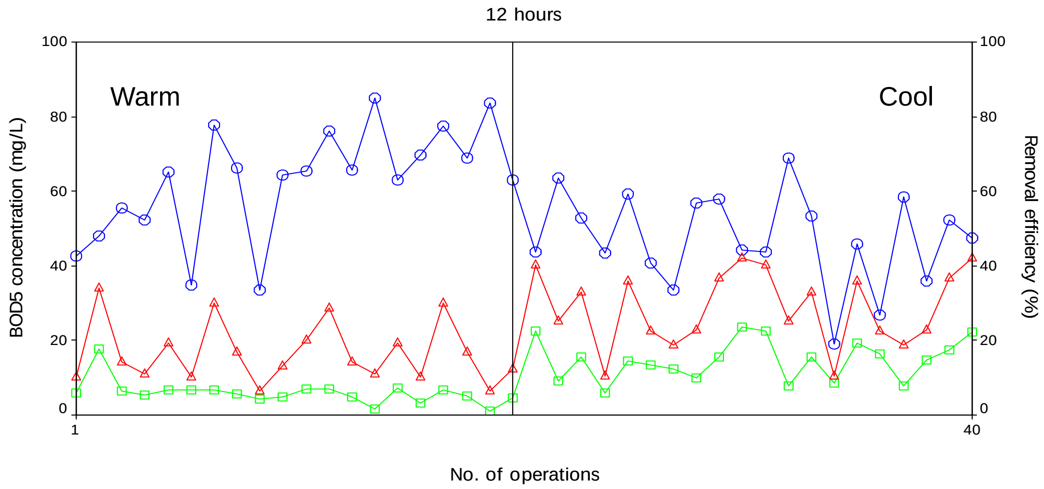
e)

Figs. 4.22 (a-e) Treatments of ammonia nitrogen in warm and cool periods



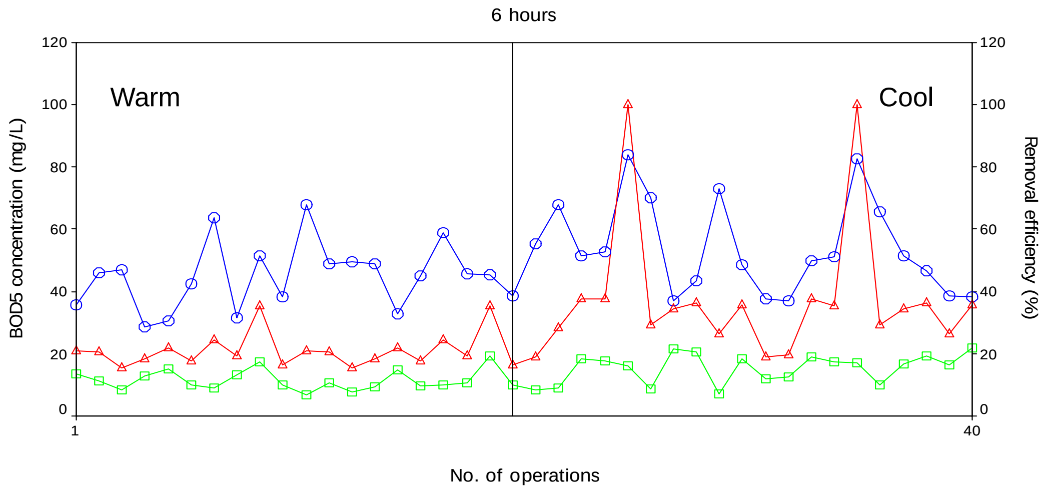
18 hours
Warm
Cool
BOD5 concentration (mg/L)
Removal efficiency (%)
No. of operations

a)



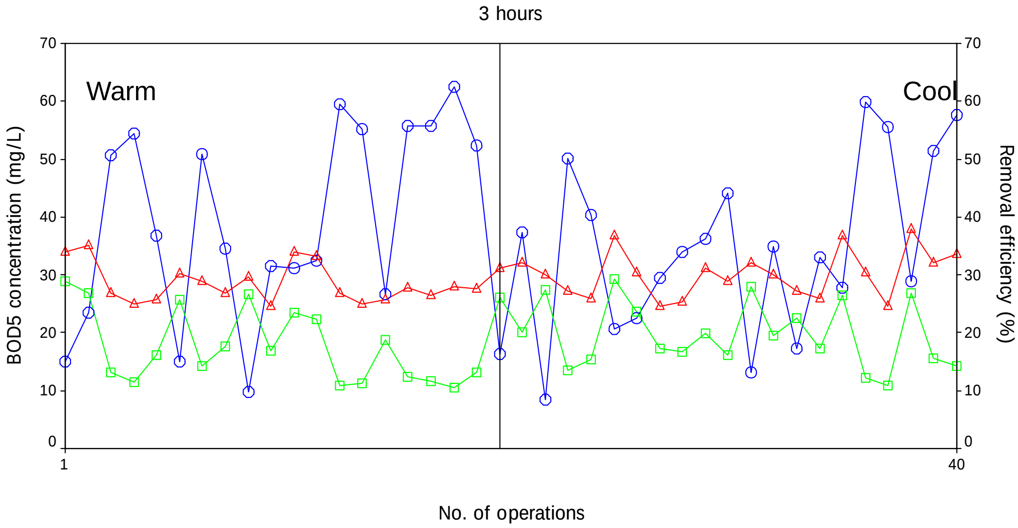
12 hours
Warm
Cool
BOD5 concentration (mg/L)
Removal efficiency (%)
No. of operations

b)

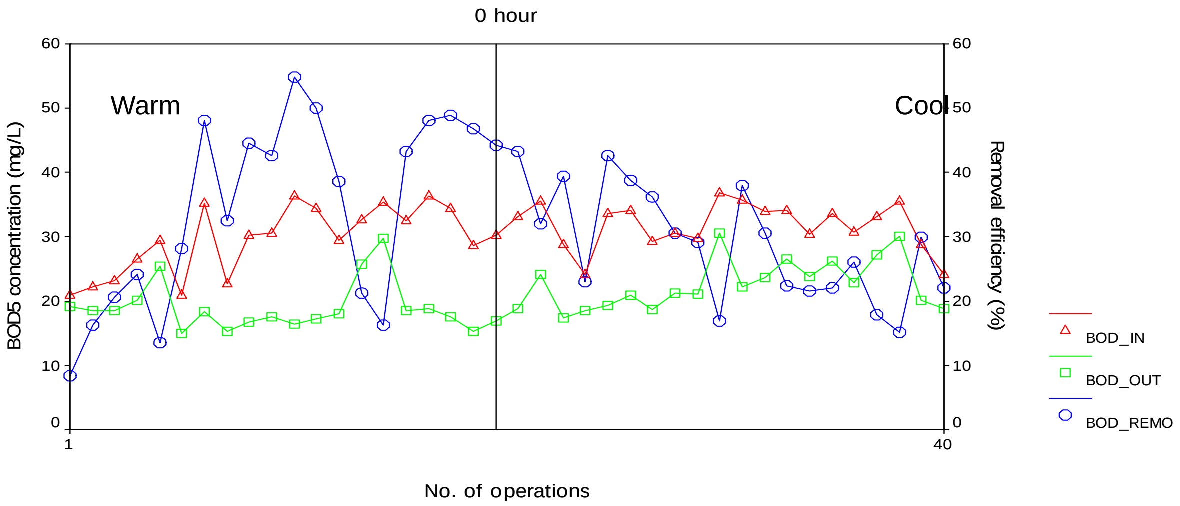


6 hours
Warm
Cool
BOD5 concentration (mg/L)
Removal efficiency (%)
No. of operations

c)

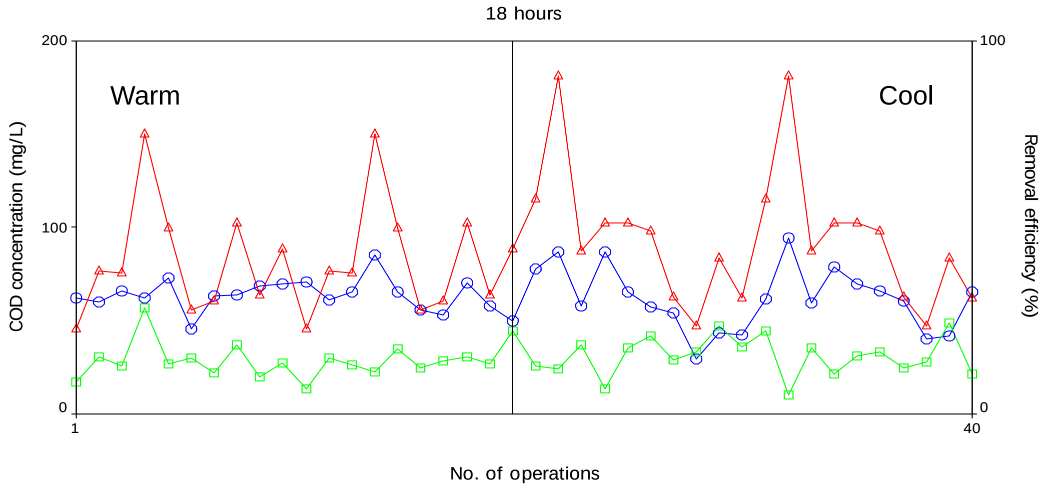


d)

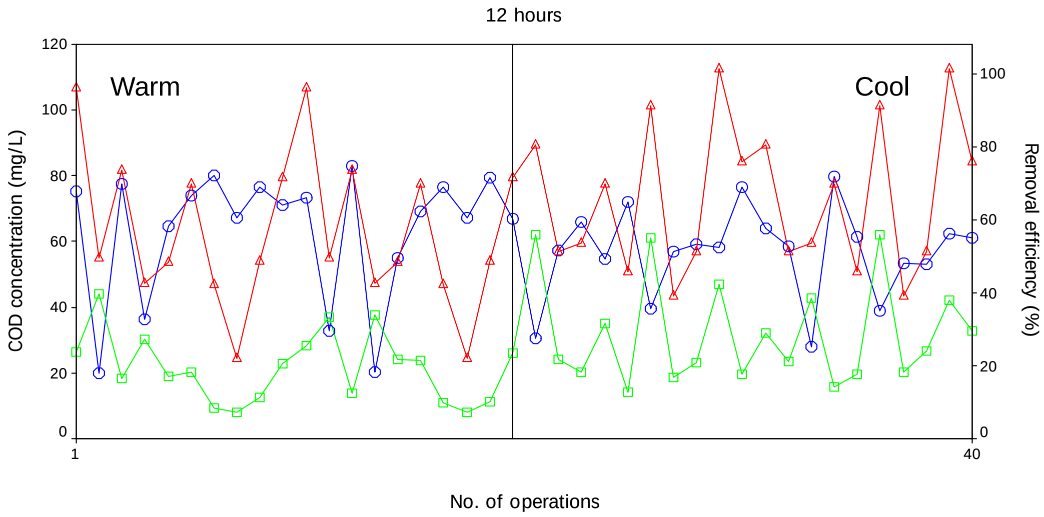


e)

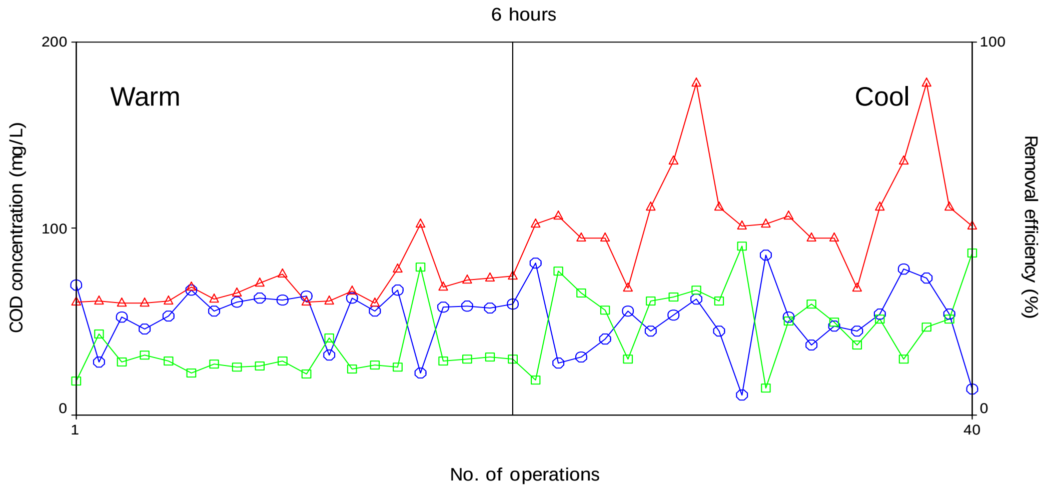
Figs. 4.23 (a-e) Treatments of BOD_5 in warm and cool periods


18 hours
Warm
Cool
COD concentration (mg/L)
Removal efficiency (%)
No. of operations
200
100
0
1
40

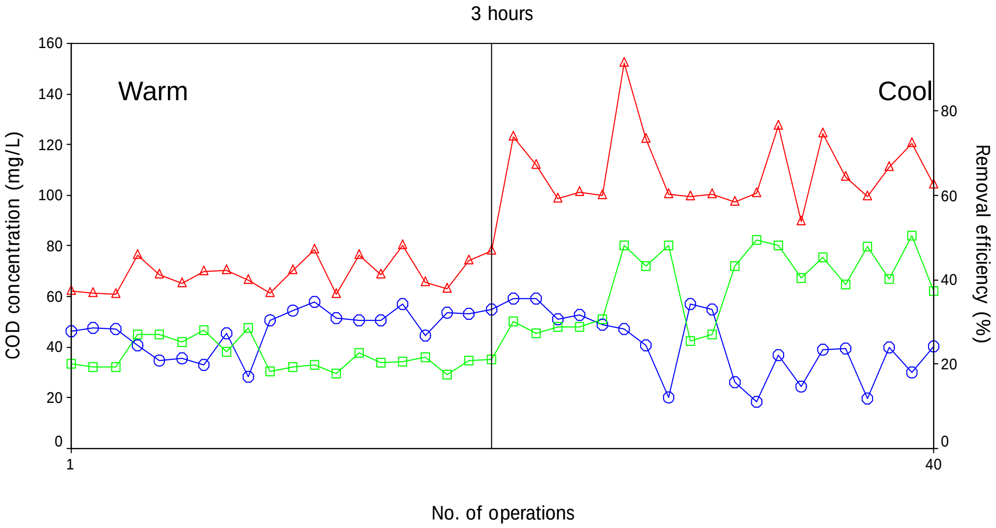
a)


12 hours
Warm
Cool
COD concentration (mg/L)
Removal efficiency (%)
No. of operations
120
100
80
60
40
20
0
1
40

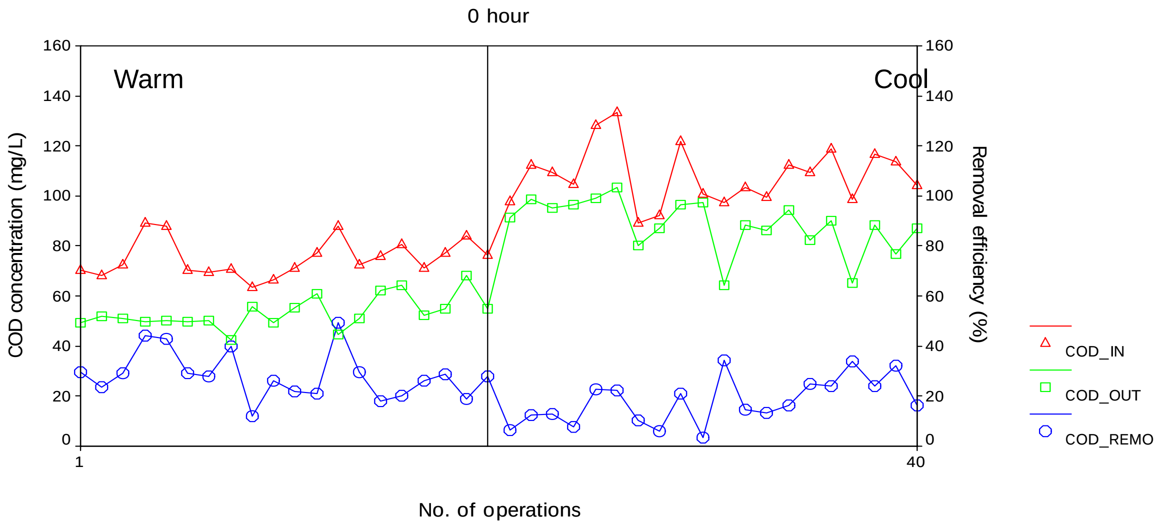
b)


6 hours
Warm
Cool
COD concentration (mg/L)
Removal efficiency (%)
No. of operations
200
100
0
1
40

c)

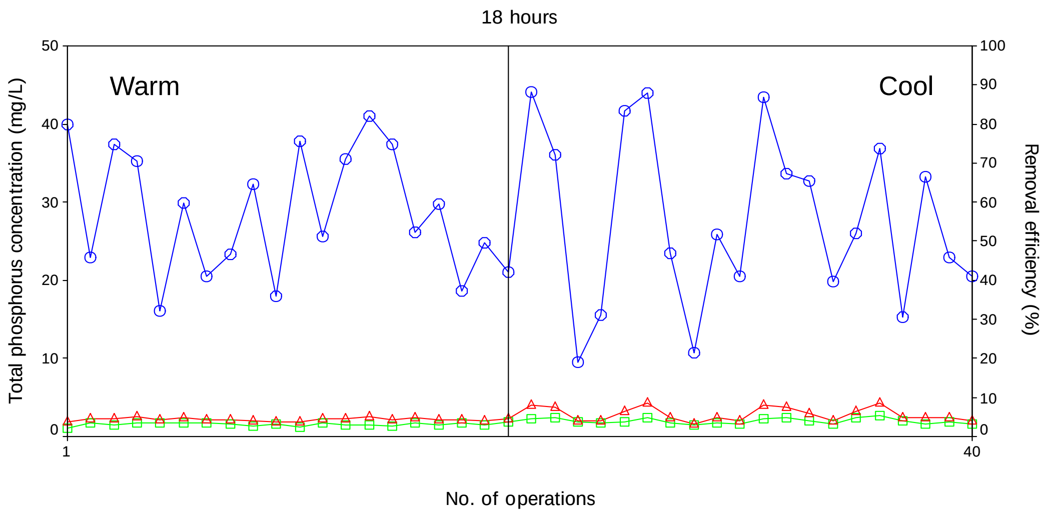


d)

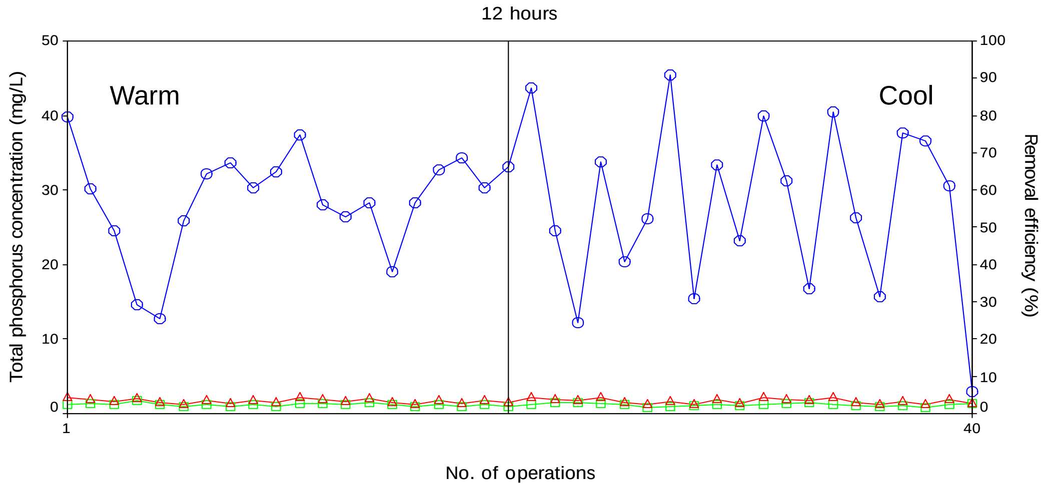


e)

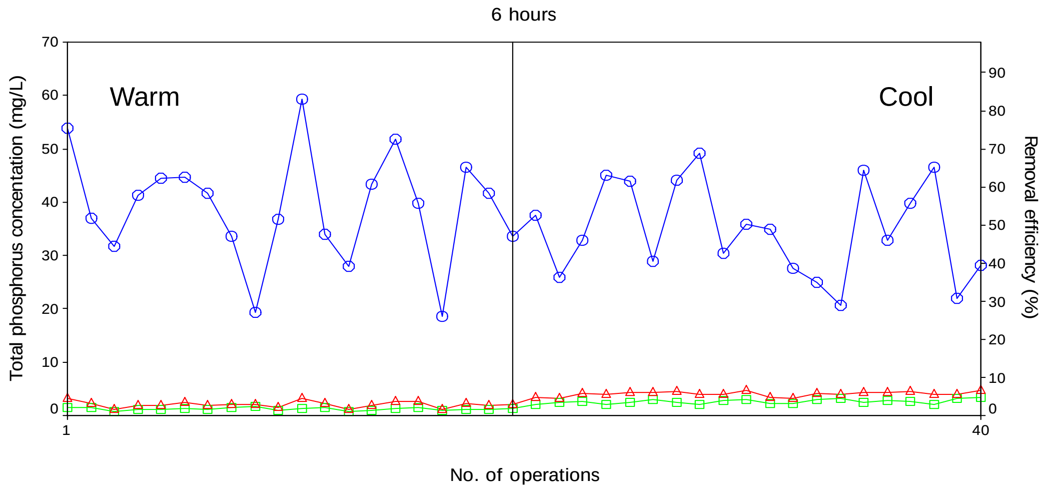
Figs. 4.24 (a-e) Treatments of COD in warm and cool periods


18 hours
Warm
Cool
Total phosphorus concentration (mg/L)
Removal efficiency (%)
No. of operations

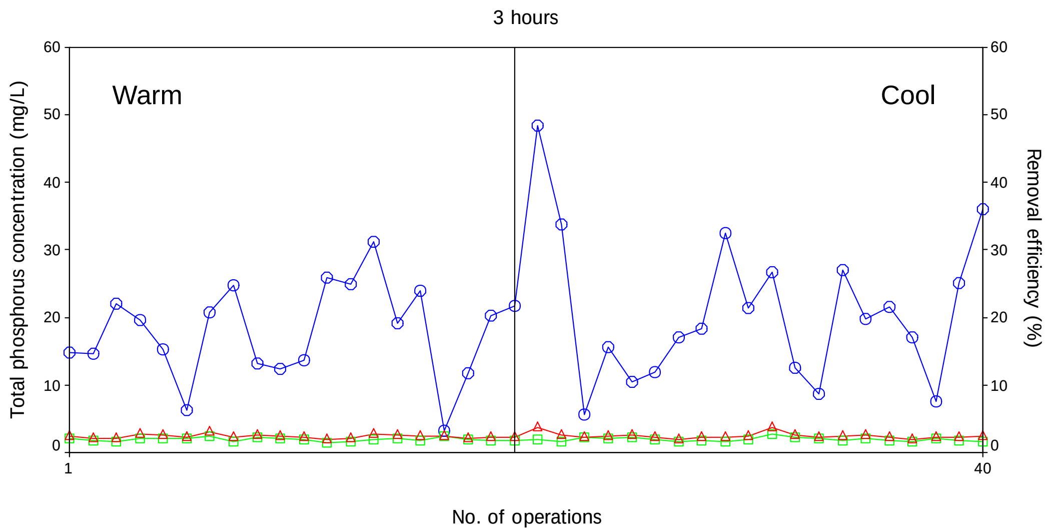
a)


12 hours
Warm
Cool
Total phosphorus concentration (mg/L)
Removal efficiency (%)
No. of operations

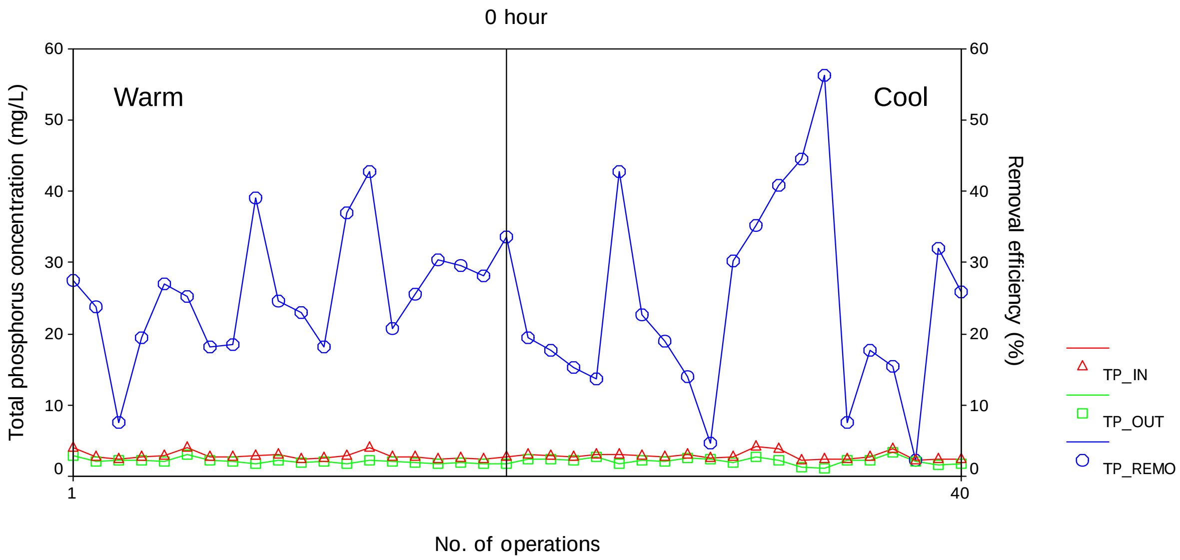
b)


6 hours
Warm
Cool
Total phosphorus concentration (mg/L)
Removal efficiency (%)
No. of operations

c)

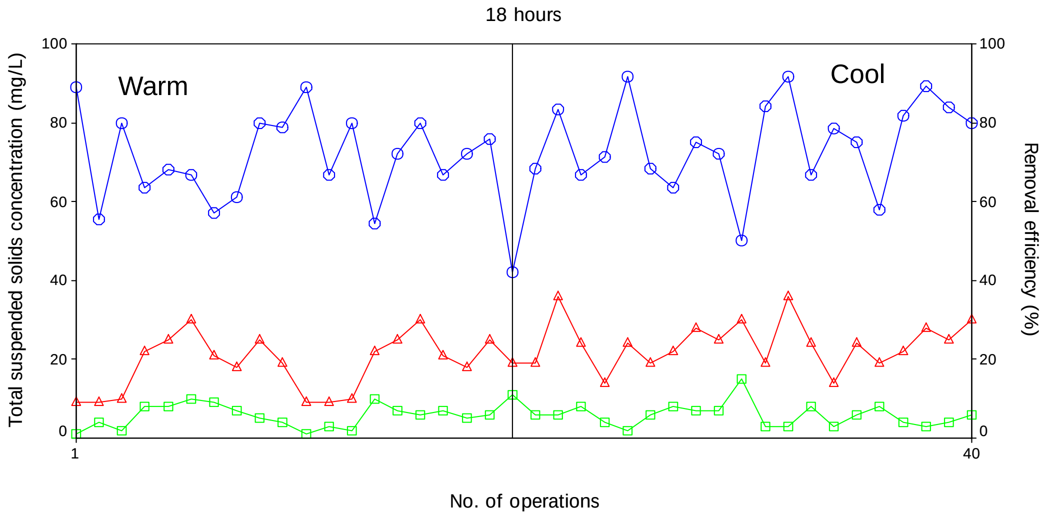


d)

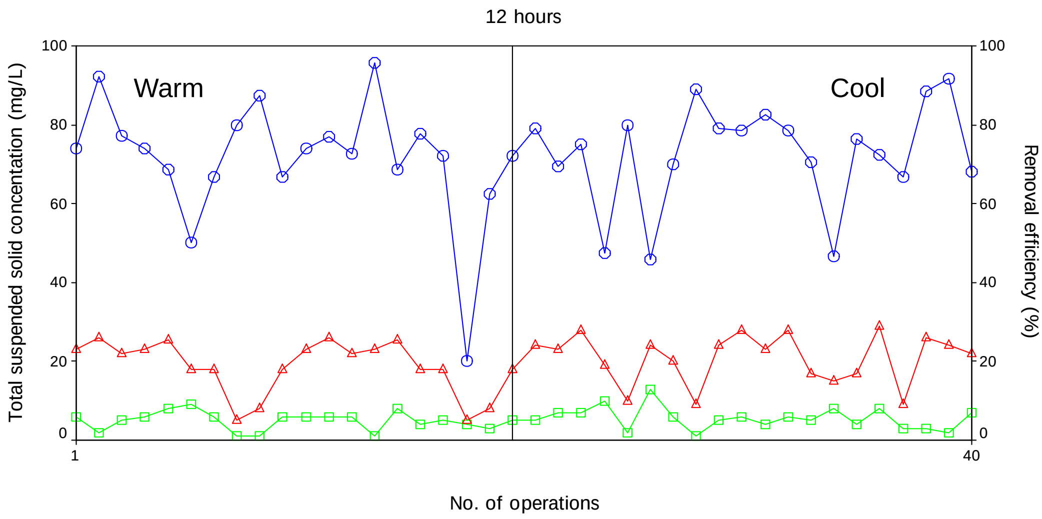


e)

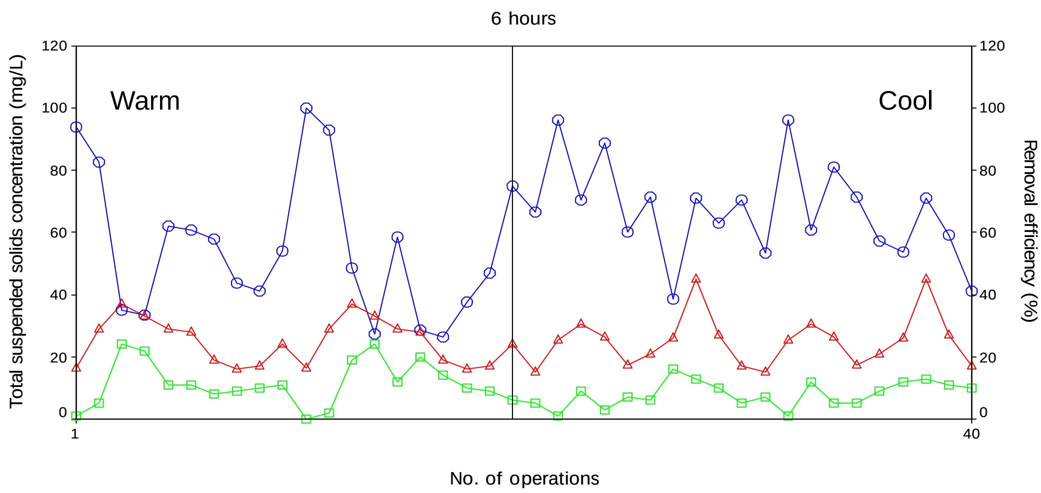
Figs. 4.25 (a-e) Treatments of TP in warm and cool periods


18 hours
Warm
Cool
Total suspended solids concentration (mg/L)
Removal efficiency (%)
No. of operations
100
80
60
40
20
0
1
40

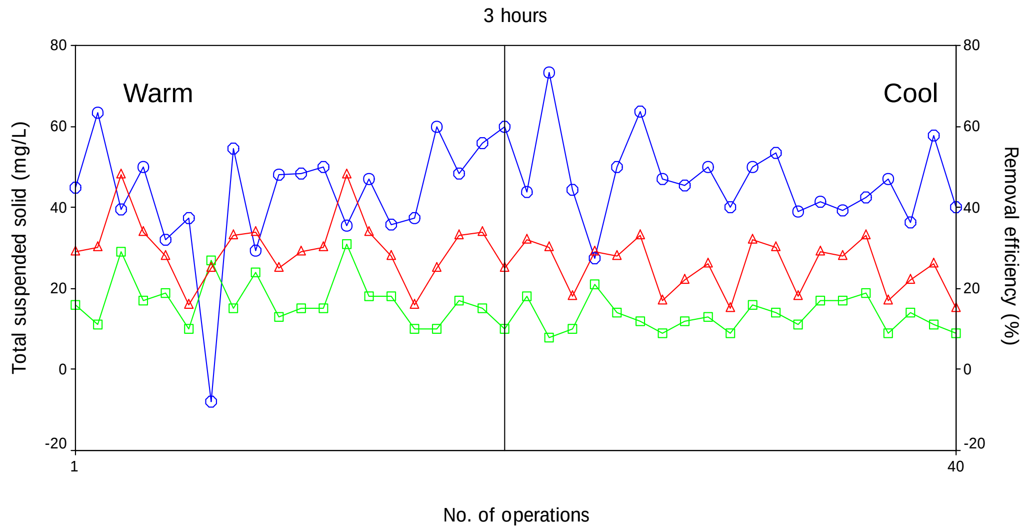
a)


12 hours
Warm
Cool
Total suspended solid concentration (mg/L)
Removal efficiency (%)
No. of operations
100
80
60
40
20
0
1
40

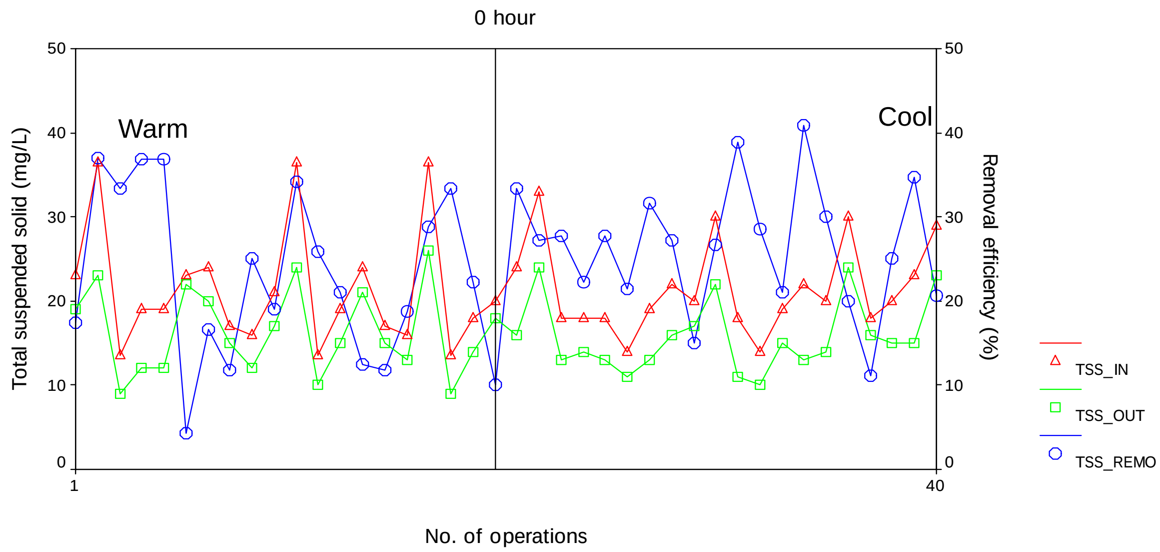
b)


6 hours
Warm
Cool
Total suspended solids concentration (mg/L)
Removal efficiency (%)
No. of operations
120
100
80
60
40
20
0
1
40

c)



d)



e)

Figs. 4.26 (a-e) Treatments of TSS in warm and cool periods

Table 4.18 *p*-values of different pollutant removal efficiencies in warm and cool periods.

	0	3	6	12	18
NH_3-N	**0.023**	**0.040**	**0.048**	**0.000**	0.209
BOD_5	0.917	0.317	**0.034**	**0.005**	0.994
COD	0.290	0.337	0.710	0.219	0.737
TP	0.688	0.372	0.137	0.771	0.248
TSS	0.205	0.458	0.067	0.775	0.758

4.3.3 Comparison with laboratory scale system

Fig. 4.27 and Fig. 4.28 allow the comparison between the performances of laboratory-scale systems and pilot-scale systems. In the operation with 18-hour contact time (Fig. 4.27), the laboratory-scale system could well intimate the performance of pilot-scale system. The discrepancies of BOD_5, COD and TSS removal efficiencies were less than 10 % between the laboratory-scale performance and the pilot-scale performance. In the operation with 0-hour contact time (Fig. 4.28), the discrepancies of BOD_5, COD, NH_3-N and TSS removal efficiencies were generally less than 20 % between the laboratory-scale performance and the pilot-scale performance.

To conclude the comparison between the laboratory-scale system and the pilot-scale system, the performance of laboratory-scale system was closer to that of pilot-scale system with longer contact time. The main divergence of the results of laboratory-scale and pilot-scale systems was the effect of plant to the pollutant removal efficiencies. *Cyperus alternifolius* was regarded as effective to remove ammonia nitrogen in the laboratory-scale experiment, but not in the pilot-scale experiment.

Although the nutrient balance study evident that *Cyperus alternifoilus* played a role in removing nutrient from the system by direct plant uptake, direct nutrient uptake by plants was insignificant comparing to the nutrient levels in the wastewater. Although the planted system in laboratory-scale experiment demonstrated an enhanced level of ammonia nitrogen removal with 18-hour contact time, plant effects may be exaggerated in the smaller-scale experimental studies, where high edge to volume ratios result in ramification of rhizomes and roots at the edges of the container and elevated shoot densities and plant biomass (Tanner, 1994). Another explanation to the high proportion of pollutant removal by plant in laboratory-scale system is that a higher plant biomass to microbial biomass ratio existed in the laboratory-scale system. The ratio was 17.44 in laboratory-scale system while it was only 1.96 in the pilot-scale system. The extremely high plant biomass to microbial biomass ratio in the fundamental study in laboratory-scale actually was not practical in real-case operation.

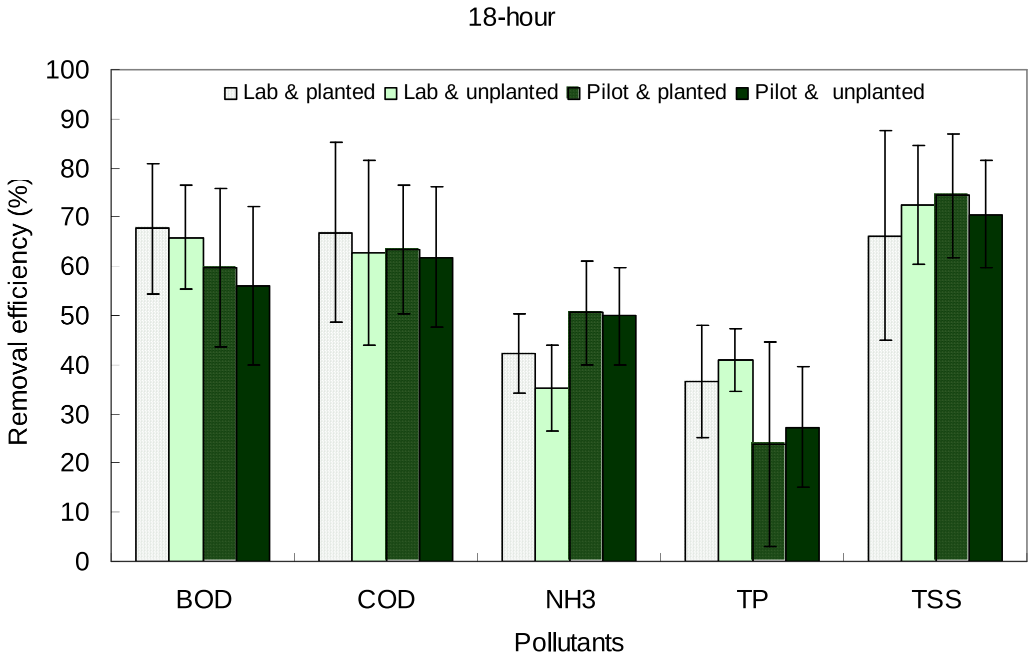


Fig. 4.27 Comparison of removal efficiencies of different pollutants in laboratory-scale and pilot-scale experiments in 18-hour contact time.

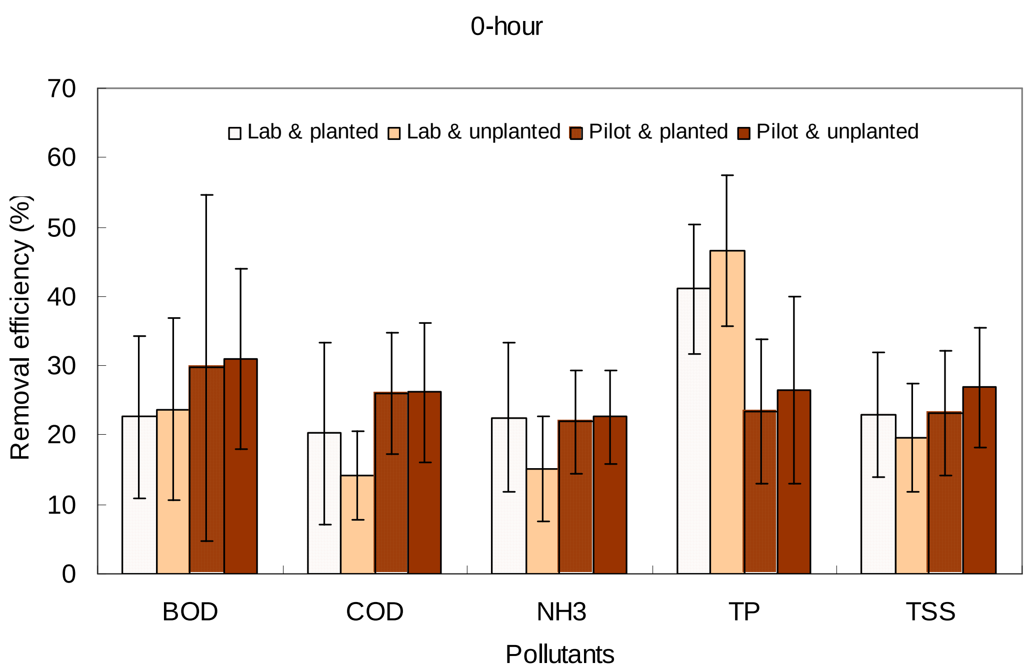


Fig. 4.28 Comparison of removal efficiencies of different pollutants in laboratory-scale and pilot-scale experiments in 0-hour contact time.

Chapter 5: Predictive Model Development

Ammonia nitrogen was chosen to be studied in this model development because nutrients (nitrogen and phosphorus), which are always the wastewater treatment concerns, discharge to the natural environment causes such environmental problems as eutrophication. Moreover, subsurface-flow constructed wetland systems treatment typically results in satisfactory organic removal while the removal of nutrients, particularly nitrogen, is often weak and typically less than desired. So focus has to be made on the efficient removal of nutrients during the wastewater treatment design process. Referring to the findings of this present study, the concentrations of BOD_5, COD, TP and TSS, with the exception of $NH_3 - N$, in the treated effluent from sequencing batch biofilm reactor, could satisfy the Class 2 discharging standards in China (State Environmental Protection Administration of China, 2002) (Details were discussed in section 6.1.1), so attention has to be particularly paid on nitrogen removal when deciding the optimal contact time for achieving certain treatment efficiency. As phosphorus removal in the coal slag packed-bed system, which is dependent on physical adsorption, has a limited capacity. Different from ammonia nitrogen removal, phosphorus removal in the coal slag packed-bed did not reach a steady state condition where equilibrium was reached between the ion exchange processes and the biological process. Thus, ammonia nitrogen then became the pollutant to be studied in the model developments.

Transformations, such as nitrification and denitrification were linked directly to microbial growth. Currently, constructed wetland-type treatment systems are generally considered to be attached-growth biological reactors and designed based on the assumptions of first-order removal kinetics of ammonia nitrogen removal (Liu *et al.*, 2005; Cooper and Findlater, 1990; Reed *et al.*, 1995). Mathematical models were developed to describe ammonia nitrogen degradation in the vegetated sequencing batch biofilm reactor based on the system performance data collected during the study. Three analytical approaches including multivariate regression, first-order kinetics and mass balance analysis were used to formulate the models and predict the system removal efficiency.

According to the onsite operation, it took 4 hours to fill up the system with wastewater. Degradations of pollutant in the bed matrix has started as early as in the 4-hour "fill" phase, and the degradation continued even in the 2-hour "draw" phase, so on average, an extra of three hours were added to the contact time

(CT+3) for all model developments and analysis. Throughout the three model developments, it was assumed that pH value has no inhibitory effect on the degradation process as the measured pH in the system operation was always around 7.

5.1 Multivariate regression model

Since the system performance was influenced by many factors, such as climate conditions, hydraulics, vegetation, water quality, oxygen level, microbiology, influent concentrations, etc.. Statistical analysis was attempted for the purpose of finding the latent factors that may affect and control the system operation. The relationships between the removals of pollutants and the controlling factors can be established by the data-driven technique - multivariate regressions. The elimination of ammonia nitrogen is mainly dependent on nitrification, which is governed by the growth of chemoautotrophic nitrifying bacteria, depends on the pH, temperature, concentration of ammonia nitrogen in the influent and the dissolved oxygen level. On the other hand, the availability of oxygen within the system is a function of BOD, the heterotrophic bacteria will outgrow the nitrifiers when BOD is readily available (Horan, 1990). So BOD is also a governing factor of nitrification. Although pH is an important factor affecting nitrification, there was no significant pH inhibition in the VSBBR Thus, the elimination of ammonia nitrogen in the system is then the function of several factors as follows,

$$(NH_3\text{-}N)_{out} = f\ ((NH_3 - N)_{in}, CT, DO, Temp, BOD_{in}) \qquad \text{(Eq.5.1)}$$

The data was evaluated by least-squares method using SPSS 10.0. The sum of the squares of the residuals between the measured and predicted ammonia nitrogen was calculated. The combination of the multivariate regression model was adjusted by adding or removing factors until a least-squares condition was reached. The process was done by trial-and-error using SPSS 10.0. The best-fit multivariate regression model with the highest value of R^2 generated by SPSS 10.0 for predicting NH_3-N concentration in effluent is as follows,

$$(NH_3\text{-}N)_{out} = 3.685 + 0.623(NH_3\text{-}N)_{in} - 0.484\ (CT+3) + 0.228\ DO \qquad \text{(Eq.5.2)}$$

$$R^2 = 0.74$$

where,

$(NH_3\text{-}N)_{out}$ is the effluent conc. (mg/L),

$(NH_3\text{-}N)_{in}$ is the influent conc. (mg/L), *CT* is the contact time (hours),

DO is the dissolved oxygen concentration (mg/L).

The regression model was further simplified as,

$$(NH_3\text{-}N)_{out} = 2.233 + 0.623(NH_3\text{-}N)_{in} - 0.484\ CT + 0.228\ DO \qquad \text{(Eq.5.3)}$$

The coefficients in the equation indicated the relative rate of change that each parameter effects on $(NH_3\text{-}N)_{out}$. The model showed that the $(NH_3\text{-}N)_{out}$ was proportional to $(NH_3\text{-}N)_{in}$ and dissolved oxygen, but negatively proportional to contact time. The temperature and BOD concentration did not significantly affect the nitrification process from the result of regression analysis of the pilot-scale data. On the other hand, the degree to which independent variables were related to the dependent variable was expressed in the multiple correlation coefficient, which is the square of R. The R^2 of the obtained multiple regression model was 0.74. The value of R^2 can be interpreted as a measure of the maximum correlation that is attainable between the dependent variable and any linear combination of the predictor variables (Johnson, 1998).

Figs. 5.1 show the fitness of the measured effluent concentrations with the predicted effluent concentrations in both planted and unplanted systems from the multivariate regression model. It can be seen that the model generally predicted the variability of the ammonia nitrogen in the effluent, with the correlation between the measured ammonia nitrogen and the predicted ammonia nitrogen effluent concentrations of 0.74 in planted system and 0.75 in unplanted system.

The multivariate regression model was used for modeling the relationship between the controlling factors using a linear equation. Linear regression assumes the best estimate of the response is a linear function. This statistical tool was simple and did not fully reflect all the main controlling factors in the nitrification process occurring in the studied system, including temperature and BOD concentrations. Since the relationship between the controlling factors in the treatment system being analyzed might not be linear, nonlinear analytical techniques were then used to obtain a more accurate model in the next session.

5.2 First-order kinetics model

The growth of the nitrifying bacteria is expressed as a first-order reaction of maximum growth rate and concentration of organisms (Halling-Sørensen and

Nielsen, 1996). Kadlec (1994b) described that first-order kinetics in wetland system are deterministic, meaning that the kinetics purport to represent the wetland output concentrations in response to influent concentration. This first order relationship was tested against the controlling factors to the concentration of ammonia nitrogen in the effluent. A first-order reaction depends on the concentration of only one reactant. Other reactants can be present, but each will be zero-order. The first-order rate kinetics is as follows,

First-order rate kinetics: $\frac{dS}{dt} = -kS$ (Eq.5.4)

Rate of utilization = -k (S) (Eq.5.5)

where,

k is the reaction rate coefficient (1/h)

S is the concentration of reactant (mg/L)

Substituting the first-order reaction to the ammonia nitrogen removal:

Rate of ammonia nitrogen removal = -k ($(NH_3\text{-}N)_{in}$) (Eq.5.6)

where,

k is the reaction rate coefficient (1/h),

$(NH_3\text{-}N)_{in}$ is the influent conc. (mg/L).

The best-fit reactant and factor in the first order kinetics model was selected and evaluated until a least-squares condition was reached. The process was done by trial-and-error approach using Datafit 8.0 Okadale. The first-order kinetics model generated by Datafit 8.0 Okadale is as follows,

$$(NH_3 - N)_{out} = (0.6867(NH_3 - N)_{in})e^{-0.0243(CT+2)} \quad \text{(Eq.5.7)}$$

$R^2 = 0.79$

where,

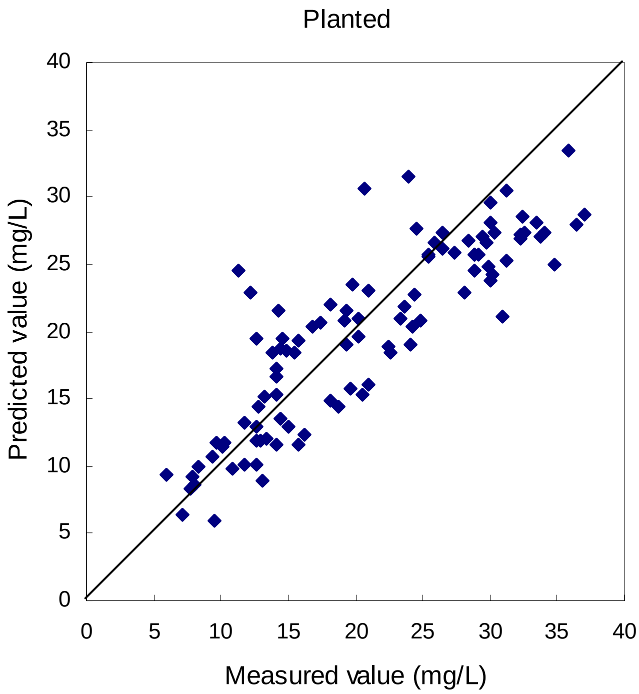
$(NH_3\text{-}N)_{out}$ is the effluent conc. (mg/L),

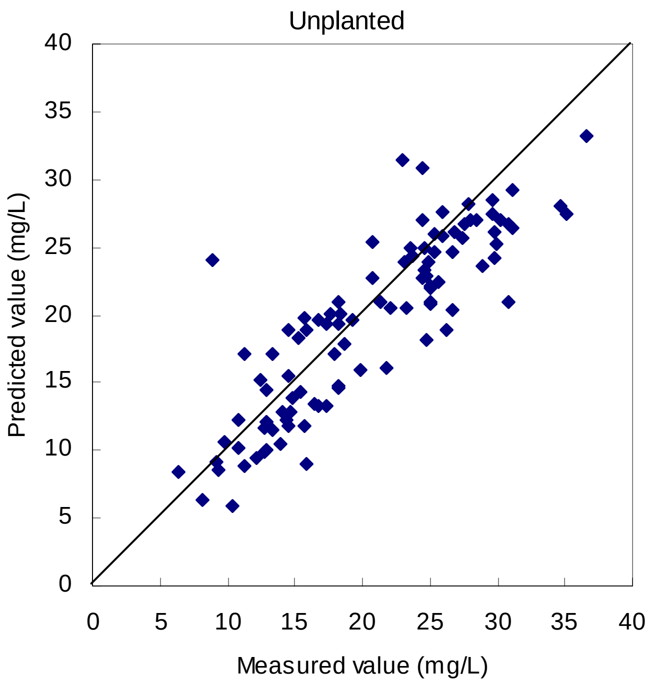
$(NH_3\text{-}N)_{in}$ is the influent conc. (mg/L),

CT is the contact time (hour).

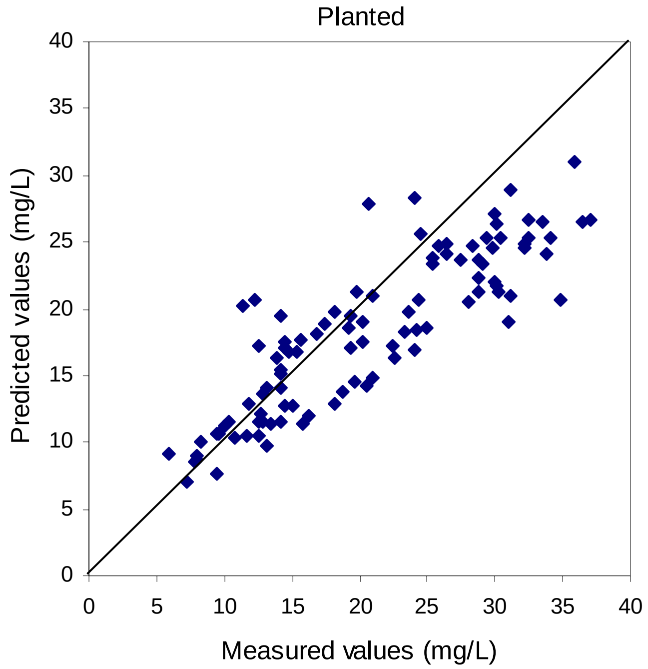
The model showed that $(NH_3\text{-}N)_{out}$ was proportional to $(NH_3\text{-}N)_{in}$, and exponential to contact time. The R^2 was 0.79 and the first-order kinetics model showed a higher correlation than the multivariate regression, although other controlling factors including temperature, D.O. and BOD were not yet embraced in this first-order kinetics model.

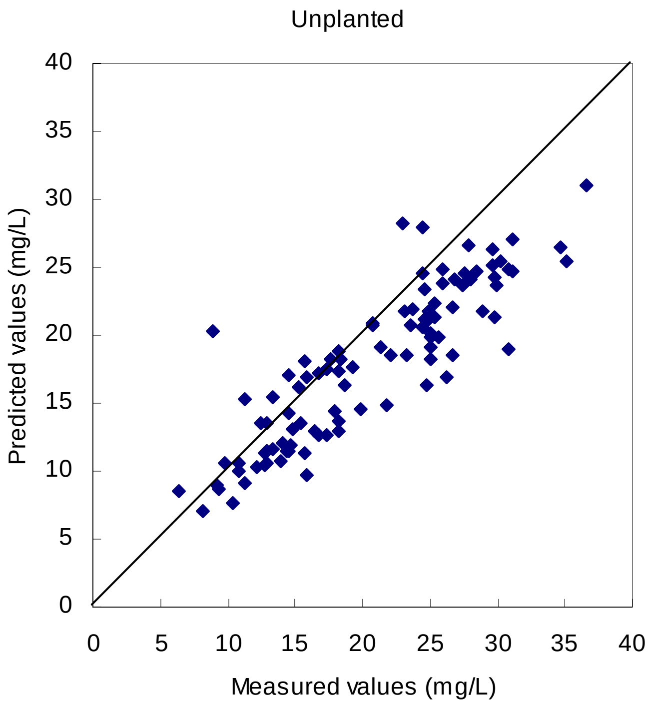
Figs. 5.2 show the fitness of the measured effluent concentrations with the predicted effluent concentrations of ammonia nitrogen from the first-order kinetics model. The R^2 values showing the correlations between the measured and the predicted ammonia nitrogen effluent concentrations were 0.75 in planted system and 0.78 in unplanted system. They showed the certainty that the correlation was not due to randomness of the data.





Figs. 5.1 show the fitness of the measured effluent concentrations with the predicted effluent concentrations from multivariate regression model.





Figs. 5.2 show the fitness of the measured effluent concentrations with the predicted effluent concentrations from the first-order kinetics model.

5.3 Mass balance model

Both multivariate regression and first-order kinetics models are empirical model that derived that input-output data, and both of them utilized a “black box” approach to predict the ammonia nitrogen removal in the system. Both models focused on the overall performance of a system and the major removal mechanisms were not taken into account. So the multivariate regression or the first-order removal kinetics might not adequately describe removal performance. Improved model was developed through examination of removal data in the analysis using mass balance of increased complexity.

A mass balance (also called a material balance) is an accounting of material entering and leaving a system. Fundamental to the balance is the conservation of mass principle. And the conservation of mass is the fundamental basis for all modeling analysis. The conservation of mass principle involves the accounting of the mass of any water quality constituent in a stationary volume of fixed dimensions called a control volume (Crites and Tchobanoglous, 1998). The first step to prepare a mass balance is to define the system boundary so that all the flow of mass into and out of the system boundary can be identified.

A mass balance analysis was employed in studying ammonia nitrogen degradation (nitrification) in the vegetated sequencing batch biofilm system. A mass balance model was developed in order to simulate and investigate the nitrification observed in the vegetated sequencing batch biofilm reactor for the removal of ammonia nitrogen from domestic wastewater. The following basic assumptions were made during the model development and were valid for the present state of model:

1. No equation for adsorption and desorption was included in the model because the model described only the steady state conditions where an equilibrium was reached between the ion exchange processes and the biological process.

2. The sequencing batch biofilm reactor system was regarded as a batch system. There is no inflow or outflow from the container or vessel in which the reaction is occurring. Flow rate (Q) equals to zero (Metcalf and Eddy, 1991).

While the growth of the nitrifying bacteria is expressed as a first-order reaction of maximum growth rate and concentration of organisms, the maximum growth rate is converted to actual growth rate by assuming Monod dependency of the process on the substrate concentration (Halling-Sørensen and Nielsen, 1996). Microbial growth kinetics, i.e., the relationship between the specific growth rate of a microbial population and the substrate concentration. And Monod's model relates the growth rate to the concentration of a single growth-controlling substrate via two parameters, the maximum specific growth rate (μ_{max}) and the substrate affinity constant (K_s),

$$\rightarrow \qquad \mu = \frac{\mu_{\max} \cdot (NH_3 - N)}{K_s + (NH_3 - N)} \qquad \text{(Eq.5.8)}$$

where,

μ is the growth rate (h^{-1}),

$\mu_{\max}$ is maximum specific growth rate (h^{-1}),

$(NH_3\text{-}N)$ is the concentration of ammonia nitrogen (mg/L),

K_s is substrate affinity constant (mg/L).

The Monod equation relates the growth rate of microorganism (nitrifier) to the concentration of a single growth-controlling substrate (NH_3-N). In a batch-growth culture system, a portion of substrate is converted to new cells. And the growth rate of nitrifier (r_g) is related to the rate of NH_3-N utilization (r_A) with a yield coefficient ($Y_{x/s}$). $Y_{x/s}$ is defined as the ration of mass of cell formed to the mass of substrate consumed, measured during any finite period of logarithmic growth (Metcalf and Eddy, 1991). In addition, the yield coefficient ($Y_{x/s\,(p)}$) was also applied to the plant uptake of ammonia nitrogen.

Rate of growth of nitrifier:

$$r_g = \frac{dx}{dt} = \mu(x) \qquad \text{(Eq.5.9)}$$

where,

r_g is the growth rate of nitrifier (mg/L·h),

μ is the growth rate (h^{-1}),

χ is the biomass concentration (mg/L),

t is the time (h).

Rate of substrate utilization (NH_3-N):

$$r_A = \frac{dS}{dt} \qquad \text{(Eq.5.10)}$$

$$r_A = \frac{d(NH_3{}^{-}N)}{dt} \qquad \text{(Eq.5.11)}$$

where,

r_A is the rate of NH_3-N removal (mg/L·h),

S is the NH_3-N concentration (mg/L),

t is the time (h).

And,

Rate of growth of nitrifier = -Yield coefficient · Rate of substrate utilization (NH_3-N)

$$\frac{dx}{dt} = -Y_{x/s}\frac{dS}{dt} \qquad \text{(Eq.5.12)}$$

$$\mu(\chi) = -Y_{x/s}(r_A) \qquad \text{(Eq.5.13)}$$

Putting Eq. 5.8 into Eq. 5.13,

$$\frac{\mu_{\max}(NH_3{}^{-}N)}{K_s + (NH_3{}^{-}N)}(\chi) = -Y_{x/s}(r_A) \qquad \text{(Eq.5.14)}$$

$$r_A = -\frac{1}{Y_{x/s}}\frac{\mu_{\max}(NH_3{}^{-}N)}{K_s + (NH_3{}^{-}N)}(\chi) \qquad \text{(Eq.5.15)}$$

where,

$Y_{x/s}$ is the yield coefficient $\left(\dfrac{mg\ biomass}{mg\ subtrate}\right)$

On the other hand, the ammonia nitrogen balance of the vegetated sequencing batch biofilm system can be summarized as follows,

Rate of accumulation of mass of NH_3-N in the system	=	Mass flow of NH_3-N into the system	-	Mass flow of NH_3-N out of the system	-	Rate of utilization of NH_3-N by the reaction.

$$\rightarrow \qquad V\frac{d(NH_3{}^-N)}{dt} = Q(NH_3{}^-N)_{in} - Q(NH_3{}^-N)_{out} - r_A V$$

(Eq.5.16)

where,

V is the reactor volume (L),

Q is the flow rate (L/h),

$(NH_3{}^-N)_{out}$ is the ammonia nitrogen concentration of effluent (mg/L),

$(NH_3{}^-N)_{in}$ is the ammonia nitrogen concentration of influent (mg/L),

$(NH_3{}^-N)$ is the ammonia nitrogen concentration (mg/L),

r_A is the rate of substrate utilization (mg/L · h).

As the nitrifying bacteria are energetically inefficient, their growth is very slow and in addition they are sensitive to a wide range of environmental conditions. The growth rate of *Nitromonas* bacteria has been shown to respond to substrate concentration and dissolved oxygen concentration according to Monod-type function, and ammonia uptake kinetics by plant were studied using Michaelis-Menten equation (Marcus-Wyner and Rains, 1982; Tylova-Munzarova *et al.*, 2005). Moreover, in section 4.3.2.4, seasonal variation of temperature was proved to have significant effect on the removal of ammonia nitrogen. The *Van't Hoff-Arrhenius* equation provides a generalized estimate of temperature effects on biological reaction rates (Metcalf and Eddy, 1991).

Van't Hoff-Arrhenius equation:

$$\mu = \mu_{20}\theta^{T-20} \quad \text{(Eq.5.17)}$$

where,

μ is the rate coefficient (h^{-1}),

μ_{20} is the value of μ at 20 °C (h^{-1}),

θ is the temperature coefficient (dimensionless),

T is the temperature (°C).

Temperature variations have to be considered in the mass balance model for its effect on the biological process (nitrification), so the nitrogen mass balance model based on the nitrification by nitrifier and plant uptake for the removal of ammonia nitrogen from wastewater was modified as follows,

Integrating Eq. 5.15 and Eq. 5.17 into Eq. 5.16,

$$V\frac{d(NH_3{-}N)}{dt} = Q(NH_3{-}N)_{in} - Q(NH_3{-}N)_{out} - V\Big(\frac{1}{Y_{x/s}}\underbrace{\frac{\mu_{max}(NH_3{-}N)}{K_s + (NH_3{-}N)}(\chi)\Big)\Big(\frac{DO}{K_o + DO}\Big)\theta^{T-20}}_{\text{(Nitrification)}} - V\Big(\underbrace{\frac{1}{Y_{x/s(p)}}\frac{\mu_{max(p)}(NH_3{-}N)}{K_m + (NH_3{-}N)}\Big)(\chi_p)}_{\text{(Plant uptake)}}$$

(Eq.5.18)

where,

V is the reactor volume (L),

Q is the flow rate (L/h),

$(NH_3{-}N)_{out}$ is the ammonia nitrogen concentration of effluent (mg/L),

$(NH_3{-}N)_{in}$ is the ammonia nitrogen concentration of influent (mg/L),

$(NH_3{-}N)$ is the ammonia nitrogen concentration (mg/L),

μ_{max} is maximum specific growth rate of nitrifier(h^{-1}),

K_s is the half saturation constant of nitrification (mg/L),

$\mu_{max(p)}$ is maximum specific growth rate of plant (h^{-1}),

K_m is the half saturation constant of plant uptake of ammonia nitrogen (mg/L),

$Y_{x/s}$ is the yield coefficient of nitrifier $(\frac{mg\ biomass}{mg\ subtrate})$

$Y_{x/s(p)}$ is the yield coefficient of plant $(\frac{mg\ biomass}{mg\ subtrate})$

K_o is the half saturation constant of DO (mg/L),

θ is the temperature coefficient (dimensionless),

DO is the dissolved oxygen level (mg/L),

X_p is the plant biomass concentration (mg/L).

And for batch reactor,

$\rightarrow$ $Q = 0$, (Metcalf and Eddy, 1991) (Eq.5.19)

&

$\rightarrow$ V is constant. (Eq.5.20)

And,

$$\frac{d(NH_3{}^-N)}{dt} = \frac{\Delta(NH_3{}^-N)}{\Delta t} = \frac{(NH_3{}^-N)_{in} - (NH_3{}^-N)_{out}}{HRT} \quad \text{(Eq.5.21)}$$

Put Eq. 5.21 into Eq. 5.18, the model was modified as follows,

$\rightarrow \quad (NH_3{-}N)_{out} =$

$$(NH_3{-}N)_{in} - HRT\left(\frac{1}{Y_{x/s}}\frac{\mu_{\max}(NH_3{-}N)}{K_s+(NH_3{-}N)}(\chi)\right)\left(\frac{DO}{K_o+DO}\right)\theta^{T-20} - \left(\frac{1}{Y_{x/s(p)}}\frac{\mu_{\max(p)}(NH_3{-}N)}{K_m+(NH_3{-}N)}(\chi_p)\right)HRT$$

(Eq.5.22)

where,

$(NH_3{-}N)_{out}$ is the ammonia nitrogen concentration of effluent (mg/L),

$(NH_3{-}N)_{in}$ is the ammonia nitrogen concentration of influent (mg/L),

$(NH_3{-}N)$ is the ammonia nitrogen concentration (mg/L),

$\mu_{\max}$ is maximum specific growth rate of nitrifier(h^{-1}),

K_s is the half saturation constant of nitrification (mg/L),

K_o is the half saturation constant of DO (mg/L),

$\mu_{\max(p)}$ is maximum specific growth rate of plant (h^{-1}),

K_m is the half saturation constant of plant uptake of ammonia nitrogen (mg/L),

$Y_{x/s}$ is the yield coefficient of nitrifier $\left(\frac{mg\ biomass}{mg\ subtrate}\right)$

$Y_{x/s(p)}$ is the yield coefficient of plant $\left(\frac{mg\ biomass}{mg\ subtrate}\right)$

K_o is the half saturation constant of DO (mg/L),

θ is the temperature coefficient (dimensionless), *DO* is the dissolved oxygen level (mg/L),

HRT is the effective contact time (h) (equals to CT+3).

The final valid model obtained using Datafit 8.0 Okadale is shown in Eq. 5.23 and the relative coefficients are also shown in Eq. 5.24,

$$(NH_3{}^-N)_{out} = (NH_3{}^-N)_{in} - (CT+2)\left(\frac{1}{Y_{x/s}}\frac{\mu_{\max}(NH_3{}^-N)}{K_s + (NH_3{}^-N)}(\chi)\right)\left(\frac{DO}{K_o + DO}\right)\theta^{(T-20)}$$

(Eq.5.23)

$$(NH_3{}^-N)_{out} = (NH_3{}^-N)_{in} + (CT+2)(-1.067)\left(\frac{(NH_3{}^-N)}{8.947 + (NH_3{}^-N)}\right)\left(\frac{DO}{0.026 + DO}\right)1.032^{(T-20)}$$

(Eq.5.24)

$R^2 = 0.92$

CT in the final mass balance model is the contact time (duration of "react" phase), as mentioned before, an extra two hours were added to describe the reaction took place in the 4-hour "fill" phase and one extra hour was added to describe the reaction continued in the 2-hour "draw" phase (*HRT = CT + 3*). The final mass balance model told that the most important factors affecting growth rate of nitrifier were substrate concentration in the influent, contact time, dissolved oxygen and temperature. The effect of plant uptake was not included in the final mass balance model, and this was agreed to the result from one-way ANOVA that plant did not significantly influence the pollutant removals in the pilot system. The model development found that the plant uptake function represented by Michaelis-Menten equation was not significant in the ammonia nitrogen degradation process in the vegetated sequencing batch biofilm reactor. On the other hand, the correlation (R^2) of the mass balance model was 0.92, which was the highest among the three types of models being tested. Mass balance approach is able to determine the sources and sinks of nitrogen in the wetland system, and allow the understandings of the types of removal mechanisms involved as well as their significance. As a result, in order to increase the removal of ammonia nitrogen, factors including influent concentration, contact time, dissolved oxygen and temperature have to be considered in priority.

Table 5.1 Coefficients of nitrification in the mass balance model (R^2 = 0.92).

Coefficients	μ_{max}	K_s	K_o	θ
Value in the model	0.0064 d^{-1}	8.947 mg/L	0.026 mg/L	1.032
Typical value	0.008 d^{-1}[*]	1.3 mg/L[**]	0.2 mg/L[***]	1.04[***]

[*]Charley *at al*., 1980

[**] Downing, 1966

[***]Metcalf and Eddy, 1991

By comparing Eq. 5.23 and Eq. 5.24, and

$$1.067 \text{ mg/L}\cdot\text{h} = \left(\frac{\mu_{max} \cdot \chi}{Y_{x/s}}\right) \qquad \text{(Eq.5.25)}$$

As,

χ = 800 (mg/L), (Halling-Sørensen and Nielsen, 1996)

and

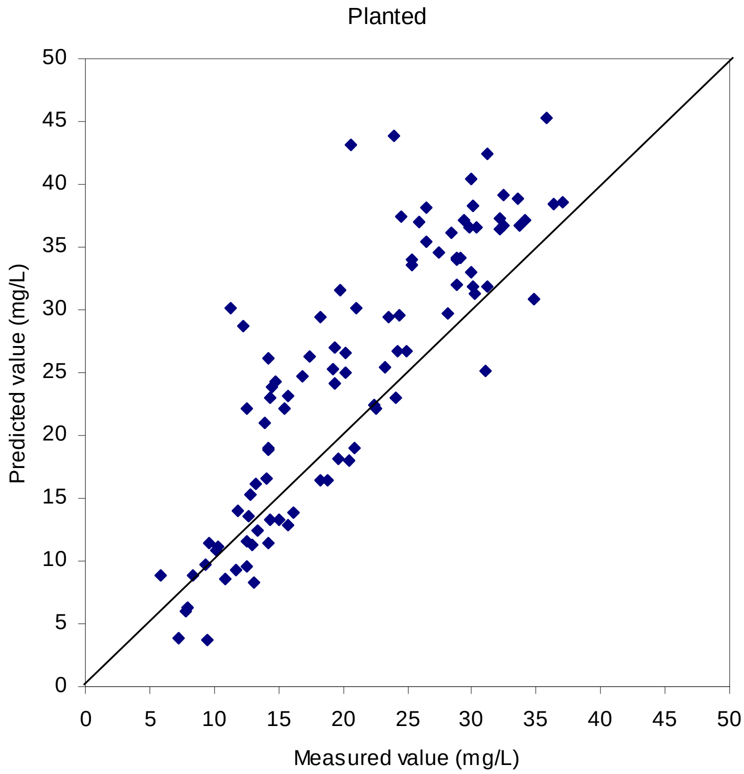
$Y_{x/s}$= 0.2, (Metcalf and Eddy, 1991)

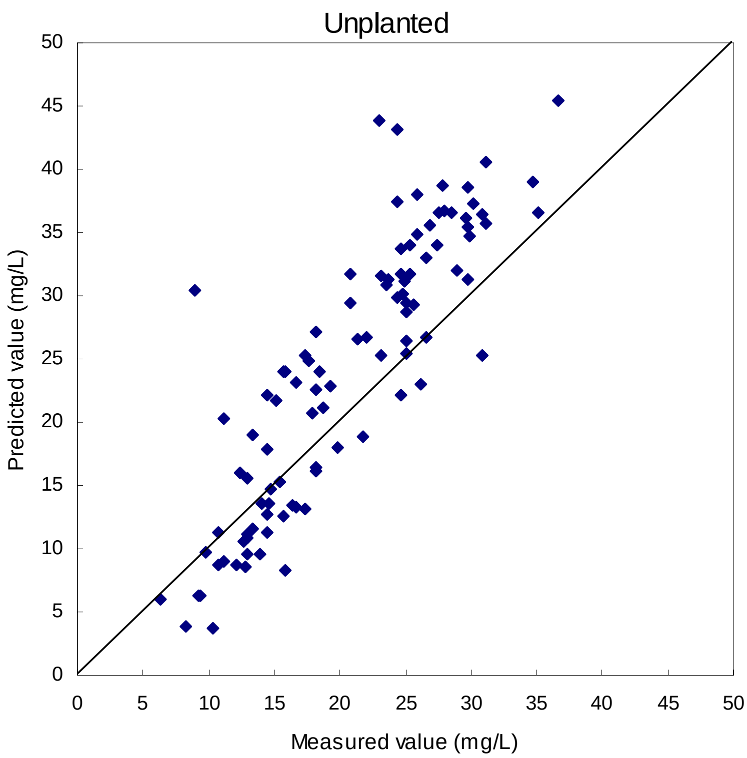
so,

μ_{max} = 0.0064 d^{-1}

Table 5.1 showed the typical kinetics coefficient of the nitrification process with the comparison of the values obtained from the mass balance model. The biomass of a fixed bed reactor (χ) from another literature is 800 (mg/L) (Halling-Sørensen and Nielsen, 1996) and the typical value of $Y_{x/s}$ in nitrification process is 0.2 in pure culture (Metcalf and Eddy, 1991). The calculated value of μ_{max} was 0.0064 d^{-1} (Eq. 5.25). The value was comparable to the μ_{max} of nitrification with value of 0.008 d^{-1} from literature (Charley *et al.*, 1980).

Figs. 5.3 show the fitness of the measured effluent concentration with the predicted effluent concentration from the mass balance model in both planted and unplanted systems. The R^2 values were 0.75 in planted system and 0.76 in unplanted system. This suggested that a reasonable good agreement was observed between measured and predicted values demonstrating that the mass balance model structure chosen is capable of simulating the ammonia nitrogen removal process in the system. With the increased complexity and the number of factors involved in the mass balance model, the R^2 values were still comparable to those in the other two models. The coefficients of correlation of the predicted and the measured values of $NH_3\text{-}N_{out}$ in the three types of models were all above 0.7. The findings were as good as those in other similar modelling study using data from pilot-scale experiment with the range of R^2 value from 0.7-0.8 (Senzia *et al.*, 2002).





Figs. 5.3 show the fitness of the measured effluent concentrations with the predicted effluent concentrations from the mass balance model.

5.4 Sensitivity analysis

A sensitivity analysis is the process of varying model input parameters over a reasonable range (range of uncertainty in values of model parameters) and observing the relative change in model response. This is carried out by examining the relative change in model output (Y) divided by the relative change in the value of the parameter (x) (Peijl & Verhoeven, 1999),

.

$$Sx = \frac{\delta Y / Y}{\delta x / x} \qquad \text{(Eq.5.26)}$$

where,

S_x is the sensitivity,

δY is the relative change of output,

δx is the relative change in the value of parameter.

In this study, the sensitivity of the ammonia nitrogen mass balance model was tested using the four parameters which were found to be important in the model development process. The four variables used as a measure of model output (Y) were influent ammonia nitrogen concentration ($NH_3\text{-}N$)$_{in}$, contact time (CT), temperature (T) and dissolved oxygen (DO). The model output in this study was the concentration of ammonia nitrogen in the effluent. The size of the changes of the parameter values was chosen proportionally to the value of the parameter and was also depended on the possible range of the parameter. A 1% perturbation is a good practical choice (Saltelli *et al*., 2000). Changes of +1% and -1% of the assigned values were tested for the sensitivities of the parameters in this study. Table 5.2 summarizes the results of the sensitivity analysis.

Except the concentration of ammonia nitrogen in influent showing a positive relationship with the model output, contact time, temperature and dissolved oxygen were all showing a negative relationship with the model output. And these findings matched with the real situations of ammonia nitrogen removal in the sequencing batch biofilm reactor. The higher the value of S_x, the more sensitive a model is to changes in that parameter (Jørgensen, 1988). The sensitivity of the influent ammonia nitrogen concentration was the largest with +1.323 (+1%) and +1.322 (-1%), so the model was the most sensitive to it. The contact time and temperature were showing similar S_x values, with contact time having a large value than temperature, but the model was less sensitive to these two parameters than to the influent ammonia nitrogen concentration. The S_x value of contact time was bigger than that of temperature, it confirmed the assumption discussed in section 4.3.2.4, that the effects of temperature on pollutant removal

Table 5.2 Results of sensitivity analysis

Parameters	Units	Assigned range	Assigned value	perturbation	S_x
Ammonia nitrogen concentration ($(NH_3\text{-}N)_{in}$)	mg/L	14.45-51	32.73	+1%	1.323(+)
				-1%	1.322(+)
				Average	1.323(+)
Contact time (CT)	hours	0-18	9	+1%	0.336(-)
				-1%	0.336(-)
				Average	0.336(-)
Temperature(T)	°C	14.47-28.61	21.54	+1%	0.280(-)
				-1%	0.278(-)
				Average	0.279(-)
Dissolved oxygen (DO)	mg/L	0.2-3.28	1.74	+1%	0.006(-)
				-1%	0.006(-)
				Average	0.006(-)

(+) indicates a positive relation between the changes in the parameters and the change in the model output. (-) indicates an inverse relation between the changes in the parameters and the change in the model output.

would be attenuated by the effects of contact time. Among the controlling factors to the degradation processes, contact time have a bigger magnitude than temperature to control the rate of degradations of pollutants. Lastly, the model was the least sensitive to dissolve oxygen as the S_x value was only about 0.006 (±1%).

Chapter 6: Optimization and System Capacity

6.1 System capacity of nutrient removals

6.1.1 Discharge standards

Discharge standard of pollutants for municipal wastewater treatment plant in the People's Republic of China divides into three classes (1, 2 & 3) (Table 6.1). Class 1a discharge standard is applied to the effluent discharging to water areas for recycling and landscaping usages or those rivers and lakes with low dilution capacity. Class 1b discharge standard is applied to the effluent discharging to surface water zone III (Environmental quality standard for surface water - GB3838, 2002), enclosed or semi-enclosed waters like some marine areas II (Sea water quality standard - GB3097, 1997), lake and reservoirs. Class 2 discharge standard is applied to the effluent discharging to surface water zone IV & V (Environmental quality standard for surface water - GB3838, 2002) and marine areas III & IV (Sea water quality standard - GB3097, 1997). Class 3 discharge standard is applied to the effluent from the wastewater treatment plant in the towns out of the drainage control basin or the water resource protection areas. In these areas, wastewater treatments are carried out to the standards according to the local financial budget and water pollution control requirements.

Table 6.1 Comparisons of discharge standards of secondary wastewater treatment plant in China with the effluent qualities of the vegetated sequencing batch biofilm reactor (All units in mg/L).

	Effluent concentration from sequencing batch biofilm reactor (mg/L)					**Standard 1a**	**Standard 1b**	**Standard 2**	**Standard 3**
Hour	0	3	6	12	18				
BOD_5	21.28	18.76	13.37	11.23	10.83	10	20	30	60
COD	63.79	49.74	45.47	29.92	26.90	50	60	100	120
NH_3-N	28.84	22.94	22.65	16.21	14.60	5	8	25	-
TP	2.16	1.96	2.16	1.18	1.80	0.5	1	3	5
TSS	15.88	15.08	9.70	5.25	5.83	10	20	30	50

Discharge standard of pollutants for municipal wastewater treatment plant (GB 18918-2002), State Environmental Protection Administration of China.

The effluent from the sequencing batch biofilm reactor generally fulfilled the requirement of Class 2 discharge standard of pollutants for municipal wastewater treatment plant in the People's Republic of China. In general, the treatment system satisfied the discharge standards of $BOD_5 < 20$ mg/L, COD < 60mg/L, NH_3-N < 25 mg/L, TP < 3 mg/L and TSS < 20mg/L. The concentrations of pollutants including organic matters, ammonia nitrogen and total phosphorus were safe and lawful to be discharged after being treated by the sequencing batch biofilm reactor.

6.1.2 Phosphorus removal capacity

As mentioned in previous chapter, the means of TP in the influent were 2.6046 ± 0.9938 mg/L and 2.6198 ± 0.9989 mg/L in the unplanted and the planted systems respectively. After treating by the sequencing batch biofilm reactor, the means of TP in the effluent were 1.7856 ± 0.5835 mg/L and 1.8236 ± 0.6714 mg/L in the unplanted and the planted systems respectively. Using these means of influent and effluent of TP, the total mass of phosphorus retained in the systems were calculated (Appendix II). In the whole pilot study, the total mass of phosphorus removed by the planted system and the unplanted system were 1.516 kg and 1.558 kg respectively.

In Guangdong, the concentration of total phosphorus in treated wastewater discharging from municipal wastewater treatment plant is not supposed to exceed 3 mg/L under Class 2 wastewater discharge standard of the country. The treatment capacity of sequencing batch biofilm reactor fulfils this wastewater treatment demand with a range of mean effluent concentration of total phosphorus from 1.17 ± 0.20 mg/L (min.) to 2.16 ± 0.77 mg/L (max.).

Since the expected lifetime of the coal slag bed in the sequencing batch biofilm reactor can be estimated by multiplying the P sorption maximum capacity with the total mass of the coal slag bed. If the maximum adsorption capacity is 1.369 g P kg^{-1}, and the volume of the coal slag bed is $13.6m^3$ with the coal slag density as 1.818kg/L, the predicted amount of phosphorus could be adsorbed is 67.20 kg.

The field adsorption capacity was estimated to be 50% of the capacity measured with batch experiments (Drizo *et al.*, 2002) due to the presence of solids and organic matter in the inlet wastewater in the field test. The other reason for the discrepancy was suggested by Ádám *et al.*, (2006) that the inlet concentration of phosphorus is lower in full-scale system than in bench experiment. Moreover, the loading of real wastewater and thus enhance the potential development of biofilm, something which may reduce the adsorption capacity of the material compared to the bench experiment. As a result, the predicted value of phosphorus adsorbed by the coal slag in the pilot system was multiplied by 50%, equals to 33.6 kg of phosphorus.

On the other hand, taking the average value from the data in the pilot experiment, the removal of phosphorus in every operation was equal to 10880 mg (0.8 mg/L x 13.6 m^3). Then under the current operating conditions and loadings to the system, the system could remove 3.97 kg (10880 mg x 365 days) in one year. Basing on a daily operation, the life span of system for phosphorus removal by adsorption is about 8 years (33.6 kg ÷ 3.97 kg/year). In the other way of saying, knowing that one person produces about 1.5 g P/day (equals 547.5 g /year) (Holtan *et al*., 1988), about 7437 kg of coal slag is needed for one person over 8 years for phosphorus removal.

6.1.3 Nitrogen removal capacity

In Guangdong, the concentration of ammonia nitrogen in treated wastewater discharging from municipal wastewater treatment plant is not supposed to exceed 25 mg/L under Class 2 wastewater discharge standard of the country. Except with a contact time of 0-hour, at which the mean effluent was 28.84 ± 4.38 mg/L, the treatment capacities of the sequencing batch biofilm reactor with all other contact time fulfilled this wastewater treatment demand with a range of mean effluent concentration of ammonia nitrogen from 14.60 ± 6.70 mg/L (min.) to 22.94 ± 6.30 mg/L (max.).

Under the fact that BOD_5, COD, TP and TSS, with the exception of $NH_3 – N$, in the treated effluent from the sequencing batch biofilm reactor fulfilled the Class

2 discharging standards, attention has to be paid on ammonia nitrogen removal when deciding the optimal contact time for achieving certain treatment efficiency in the sequencing batch biofilm reactor.

Contour plots were prepared from the ammonia nitrogen removal predictive model. Since the temperature had determinant effects on the removal of ammonia nitrogen and it has been proved in the previous session. The predictions of treatment efficiencies were done for two temperature ranges, with regard to application in areas with temperate climate. Fig. 6.1 shows the predicted removal efficiencies of ammonia nitrogen at sewage temperature below 20°C. Fig. 6.2 shows the predicted removal efficiency of ammonia nitrogen at sewage temperature above 20°C. The required contact time for achieving desired levels of removal efficiencies were predicted under different influent concentrations.

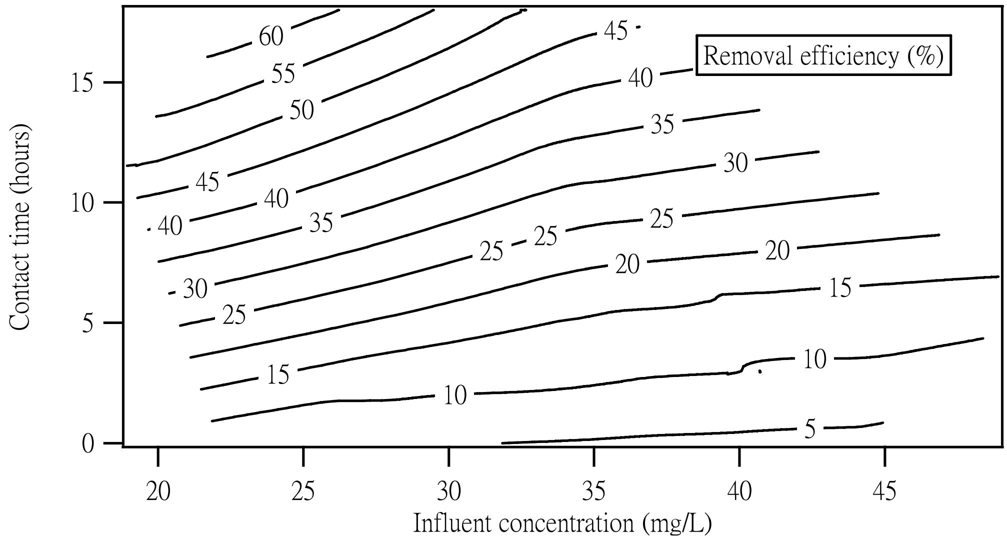


Fig. 6.1 Contour plot for ammonia nitrogen removal prediction at sewage temperature in a range of 9.8 ˚C < T < 20 ˚C.

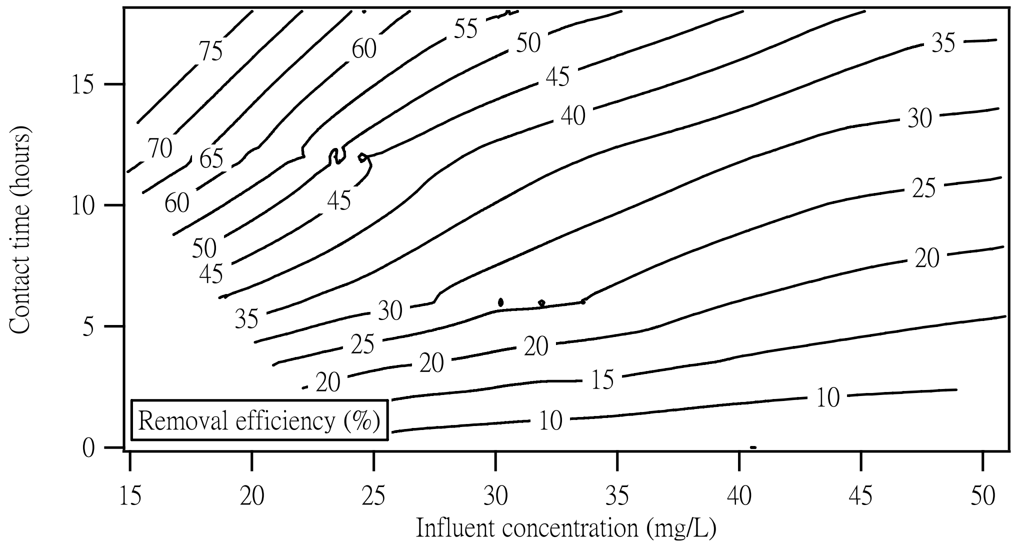


Fig. 6.2 Contour plot for ammonia nitrogen removal prediction at sewage temperature in a range of 20.0 ˚C ≦ T < 35˚C.

6.2 Cost-benefit analysis of the treatment systems

The principal wastewater treatment problems faced by small communities are related to stringent discharge standards, limited finances, high operation and maintenance costs, as well as lack of skilled operators. Increased awareness and concern over the quality of the water environment have led many authorities to pass stringent regulations and guidelines on the discharge of wastewater into the natural environment even in remote areas. Failure to comply with such regulations can result in the levy of high fines. Cost-effectiveness of wastewater management strategy in the suburban areas, on one hand is necessary to upgrade the pollutant efficiency of treatment system for better effluent quality, but on the other hand is necessary not to increase the financial burden on the limiting budgets in the remote areas.

It is generally agreed that constructed wetland systems require lower construction and operating costs. The vegetated sequencing batch biofilm reactor is the modification of the conventional low-cost constructed wetland. It is targeted to get rid of the limiting factor of large land requirement of constructed wetland by temporal sequence of operation in a single reactor. It is expected to be more cost-effective than the constructed wetland in treating wastewater. Serving the small community in the suburban areas, the vegetated sequencing batch biofilm reactor must be also economically competitive compared to the advanced activated sludge process commonly used by large populations in urban area.

6.2.1 Comparison of general design feature

Table 6.2 illustrates the major design features of conventional activated sludge treatment process and conventional constructed wetland with comparison to the vegetated sequencing batch biofilm reactor. The required land area, cost of construction, operation and maintenance, energy consumption and technical expertise are the major parameters of the total cost that need to be taken into account in a cost-benefit analysis.

The main criteria for the design of wetlands and other land treatments is the size requirement, and it closely related to the specified pollutant reductions need to be accomplished. The local geographic conditions are also the limiting factor for the size of wetlands. The amount of land required for treatment process is of primary importance in locations where land is scarce or expensive. In addition, energy for aeration is the major operating cost for most wastewater treatment systems. The energy requirements of constructed wetland are only about 25 to 30 percent of that required for an activated sludge (aeration) system (California Questa Engineering Corporation, 2005) because no specific aeration is needed for conventional constructed wetland. Energy in constructed wetland and the sequencing batch biofilm reactor are comparatively low. The main energy consumptions come from the pumping facilities. Moreover, sophisticated technology and expertise are required in the activated sludge process but not in the other two treatment methods.

Comparing to the highly efficient activated sludge process, neither the constructed wetland nor the vegetated sequencing batch biofilm reactor could compete with it in the treatment of large flow municipal wastewater demands. However, due to the sophistication of the activated sludge process, the required costs and expertise are high. Though it is an efficient wastewater treatment method, its cost-effectiveness can only be achieved when it is applied on the usage of large populations in urban areas. In contrast, the constructed wetland and the vegetated sequencing batch biofilm reactor are more suitable for the wastewater treatment demands in small communities in rural or suburban areas.

Table 6.2 Comparisons of design features of conventional activated sludge treatment process and conventional constructed wetland with the vegetated sequencing batch biofilm reactor.

	Activated sludge	**Constructed wetland**	**Vegetated sequencing batch biofilm reactor**
Land area	Requires little land area	Requires large area	Minimal land requirements in terms of treatment capacity
Cost	High cost of construction, high cost of operation and maintenance	Low operation and maintenance requirements and costs	Low operation and maintenance requirements and costs
Energy	High energy requirement especially for aeration	Low energy requirement	Low energy requirement
Technical personnel	Requires technically skilled manpower for operation and maintenance	Requires low-skilled manpower for operation and maintenance	Requires low-skilled manpower for operation and maintenance
Need for vegetation	No	Yes	Yes
Oxygen supply	Pressurized air	Air Aerobic/anaerobic	Air
Application	Urban areas for regional-scale treatment	Small communities in rural area for local-scale domestic wastewater treatment	Small communities in suburban area for local-scale domestic wastewater treatment

(UNEP, 1997)

6.2.2 Comparison of treatment performance

Treatment performances and capacities are criteria to justify the choice of wastewater treatment systems. Table 6.3 summarizes the treatment performance of typical activated sludge treatment process and conventional constructed wetland with the vegetated sequencing batch biofilm reactor, specific to ammonia nitrogen removal. The comparisons were based on a treatment capacity for 500-10,000 p.e. of domestic wastewater, with effluent quality meeting the general discharge limits of secondary treatment, defined as BOD_5 and TSS concentrations of less than 20mg/L (Tsagarakis *et al.*, 2003 and UNEP, 1997). The performance data of conventional activated sludge process and constructed wetland shown in Table 6.3 was based on the well recognized values from literatures (Metcalf and Eddy, 1991) and the real case operation of a constructed wetland treating 500 tonnes domestic wastewater daily in Beijing (Gao and Ma, 2006).

The activated sludge process requires only several hours for efficient treatment while other common biological treatment processes such as natural vegetated lagoons, require at least 6-7 days for treatment of primary and secondary wastewater (Nutall *et al.*, 1997). And the conventional constructed wetland

Table 6.3 Quantitative performance comparisons of conventional activated sludge treatment process and conventional constructed wetland with the vegetated sequencing batch biofilm reactor for domestic wastewater treatment

	Conventional activated sludge process[1]	**Conventional constructed wetland**[2, 3]	**Vegetated sequencing batch biofilm reactor**
HRT	4-8 hours	4-15 days	10-18 hours
Hydraulic loading rate (m^3 / m^2·d)	30-50	0.014-0.047	0.45
Ammonia nitrogen removal	50-60%	40-50%	40-50%

[1]Metcalf and Eddy, 1991
[2]Tsagarakis *et al*., 2003
[3]Gao and Ma, 2006

usually requires 4-15 days for similar treatment targets (Tsagarakis *et al*., 2003). Compare to vegetated lagoon and constructed wetland, the vegetated sequencing batch biofilm reactor in this study requires only several hours (within 24 hours) to decrease the pollutants concentrations to discharge levels. The hydraulic loading rate of sequencing batch biofilm reactor was also higher than that of conventional constructed wetland to achieve similar ammonia nitrogen levels in the effluent.

6.2.3 Comparison of cost

The optimization of treatment systems relate to performances and costs of operation. The construction cost of the conventional activated sludge process shown in Table 6.4 came from the construction cost of a secondary wastewater treatment plant in Shanghai treating municipal wastewater (Yang *et al.*, 2004); while the operation cost of conventional activated sludge process was quoted from the case of a municipal wastewater treatment plant in Beijing (Yang *et al*., 2004). And the construction and operation costs of the conventional constructed wetland were calculated from the real case operation of a constructed wetland in Shandong in 1997 (Gao and Ma, 2006). The calculation of the construction cost and the expenditure on electricity consumption of the sequencing batch biofilm reactor is shown in Appendix III.

The construction cost of activated sludge process is the highest among the three treatment methods due to the more advanced and sophisticated components of the reactor. Although the construction cost of the sequencing batch biofilm reactor is higher than that of constructed wetland, the low operating cost of the sequencing batch biofilm reactor with enhanced pollutant removal efficiency could sustain a more economical wastewater treatment process. On the other

Table 6.4 Cost comparisons of conventional activated sludge treatment process and conventional constructed wetland with the vegetated sequencing batch biofilm reactor for domestic wastewater treatment (RMB/m^3).

	Conventional activated sludge process[1] (RMB/m^3)	**Conventional constructed wetland**[2] (RMB/m^3)	**Vegetated sequencing batch biofilm reactor*** (RMB/m^3)
Construction	782	196	256
Operation			
Electricity	0.38	0.08	0.09
Manpower	0.15	0.04	0.01
Chemicals	0.06	-	-
E & M maintenance	0.20	0.03	0.03
Total	0.79	0.15	0.13

[1] Yang *et al*., (2004)

[2] Gao and Ma (2006)

*Appendix III

hand, the electricity consumption by activated sludge process is about 4 times of that by constructed wetland and the sequencing batch biofilm reactor. The high electricity utilization of activated sludge process is owing to the more complex mechanical operations and aeration device in the reactor for sludge maintenance and return.

Similarly, the cost of manpower to operate the activated sludge process is the highest because skilful personnel and expertise are required. The expenditure on manpower of the sequencing batch biofilm reactor was lower than that of the constructed wetland because of the reduction of total land area requiring duties such as maintenance, harvesting or clearance of decaying plant materials. And the E & M maintenance costs would be similar in the two natural systems with similar electrical and mechanical installations.

To summarize, about 45-55% of the total operating cost of conventional activated sludge wastewater treatment plant usually is spent for electricity consumption. And about 30% of the total operating cost is spent for manpower while about 15-25% of that is spent for E & M maintenance and other miscellaneous costs (Bao and Wang, 1992). Though slight difference of budget breakdown may exist between individual treatment plant using similar treatment technology and the values shown in Table 6.4 may not give the exact financial situations of every treatment plant, the big disparity of costs for activated sludge process, constructed wetland and the sequencing batch biofilm reactor gives the general idea of the cost-effectiveness of each technology.

With comparable costs, skills and manpower, the benefit of using the vegetated sequencing batch biofilm reactor are the shortening of retention time and decrease of land requirement for equivalent pollutant removal efficiency, when compared to conventional constructed wetland, for domestic wastewater treatment purposes. On the other hand, the benefits of using the vegetated sequencing batch biofilm reactor are the low cost and the low skill requirements, when compared to conventional activated sludge process. With the advantages of ease of operation, low costs, desirable treatment efficiency and aesthetic value, the vegetated sequencing batch biofilm reactor is proposed to be an alternative for onsite domestic wastewater treatment in suburban areas.

Chapter 7: Conclusions

7.1 Summary

1. The sequencing batch biofilm treatment system demonstrated effective removals of carbonaceous matters, ammonia nitrogen and total phosphorus with regard to the state discharge standard of the People's Republic of China. In general, the treatment system satisfied the discharge standards with effluent concentrations of BOD_5 < 20 mg/L, COD < 60mg/L, NH_3-N < 25 mg/L, TP < 3 mg/L and TSS < 20mg/L. The average removal efficiencies of BOD_5, COD, NH_3-N, TP and TSS were reported as at the maximal of 59.72 %, 63.58 %, 50.51 %, 37.89 % and 78.82 %, respectively with 18-hour contact time, and at the minimal of 29.72 %, 25.96 %, 21.9 %, 23.42 % and 23.25 %, respectively with 0-hour contact time.

2. *Cyperus alternifolius* showed satisfying growth and survival in the operation of sequencing batch biofilm reactor. It served as a good component in the soil-plant-microbial interactive system. The coal slag selected to be the adsorbing media also was provided fulfilling removal

capacity of pollutant through physical adsorption. It performed well in providing hydraulic conductivity in the system and no clogging was observed throughout the experimental process. Significant of phosphorus removal was observed by adsorption on the coal slag.

3. The pollutant removal mechanism at the early stage of system operation was dominated by physical adsorption. When biofilm has been build up in the bed matrix after start-up stage, microbial degradation instead took a bigger role as the main removal mechanism for nitrogen removal, when compared to plant uptake and adsorption. Adsorption was found to be effective mechanism for phosphorus removal throughout the operation. Plant uptake contributes to insignificant portion of nutrient removal comparing to the overall removal efficiency of the system.

4. The effects of several controlling factors to ammonia nitrogen removal including influent concentration, contact time, temperature and dissolved oxygen were analysed by statistical analysis, model development and sensitivity analysis. To predict the effluent concentration of ammonia nitrogen, the influent concentration of ammonia nitrogen was the most

determinant factor, with contact time and temperature being the next. And dissolved oxygen shows the less influence to the reduction of ammonia nitrogen.

5. The process design procedure of vegetated sequencing batch biofilm reactor treating domestic wastewater has identified the off-balance of equilibrium of soil-plant-microbial interaction, the mass loading to the operating system, the contact time required for carbonaceous, nitrogen and phosphorus removals and the limiting effluent requirements for pollutants. Operating with rhythmical feeding of wastewater, the plant-soil-microbial interaction with *Cyperus alternifolius* and coal slag were proved to be effective to treat domestic wastewater. It required smaller foot-print than the conventional constructed wetland, and was more cost-effective than conventional activated sludge process for applications in suburban areas. The use of vegetated sequencing batch biofilm reactor is an alternative method for effective wastewater treatment in suburban areas.

7.2 Future work

Further optimizations of operating conditions can be done to enhance the performance of the vegetated sequencing batch biofilm reactor:

1. The selected plant species did not demonstrate a pollutant removal performance as good as the selected adsorbing medium did. Alternative plant species or mixed plant species can be introduced to further optimize the system performance possibly by diversifying the biochemical pollutant degradation processes.
2. Apart from the duration of contact time, the length of each operating cycle could be varied up and down from the current basis.
3. As sustainable removal of phosphorus can be only obtained by plant harvesting or replacement of adsorbing medium in a gravel-base system, under the fact that the coal slag was found to be have a relative long life span for phosphorus adsorption, the system performance can be further optimized by increasing the frequency of plant harvesting.
4. In the current study, the microbial community build up in the system was come from the natural strains of microorganisms in the raw wastewater. The

removal of pollutants is feasible to be enhanced by bioaugmentation. Bioaugmentation is the introduction of novel metabolic functions into a microbial community, e.g. in a soil or wastewater environment, thereby establishing or enhancing the biodegradation of recalcitrant compounds (Bathe *et al.*, 2004).

5. Further modifications and monitoring of the operating conditions are needed if the system is applied in full-scale operation. Variations in influent strength of different sources of domestic wastewater may influence the system capacity and removal efficiency predicted in this study.

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Appendix I

Nitrogen and phosphorus balance in laboratory-scale experiments

<u>1. Total nitrogen balance in laboratory-scale system</u>

Nov 03 – Feb 04 (Start-up stage)

Average concentration of nitrogen in influent = 19.4 mg/L
Average concentration of nitrogen in effluent = 12.17 mg/L
Volume of wastewater per operation: 9 Litres
No. of time of operation from Nov 03 – Feb 04: 25 times
Concentration of nitrogen in plant: 4.6 mg/g
Dry mass of plant: 49.87 g

→ Total nitrogen input from Nov 03 – Feb 04:
19.4 mg/L x 9 L x 25 = 4.365 g

→ Total nitrogen output from Nov 03- Feb 04:
12.17 mg/L x 9L x 25 = 2.738 g

→ Total nitrogen retained from Nov 03 – Feb 04:
(4.365 – 2.738) g = 1.627 g

→ Total nitrogen uptake by plant:
4.6 mg N/g x dry mass of plant = 4.6 mg N/g x 49.87 g
= 0.229 g

→ Total nitrogen adsorbed by coal slag:
Nitrogen concentration on coal slag x density of coal slag x volume of coal slag
= 0.033 mg N /g x 1.818 kg/L x 18 L = 1.080 g

→ Total estimated nitrogen removed by microbial process:
= (1.627 – 0.229 – 1.080) g
= 0.318 g

2. Total phosphorus balance in laboratory-scale system

Nov 03 – Feb 04 (start-up stage)

Average concentration of phosphorus in influent = 8.19 mg/L
Average concentration of phosphorus in effluent = 4.77 mg/L
Volume of wastewater per operation: 9 Litres
No. of time of operation from Nov 03 – Feb 04: 25 times
Concentration of phosphorus in plant: 0.78 mg/g
Dry mass of plant: 49.87 g

→ Total phosphorus input from Nov 03 – Apr 04:
8.19 mg/L x 9 L x 25 = 1.843 g

→ Total phosphorus output from Nov 03- Apr 04:
4.77 mg/L x 9L x 25 = 1.073 g

→ Total phosphorus retained from Nov 03 – Apr 04:
(1.843 – 1.073) g = 0.77 g

Total phosphorus uptake by plant:
→ 0.78 g P/kg x dry mass of plant = 0.78 g P/kg x 49.87 g
= 0.039 g

→ Total phosphorus adsorbed by coal slag:
Phosphorus concentration on coal slag x density of coal slag x volume of coal slag
0.016 mg P /g x 1.818 kg/L x 18 L = 0.524 g

→ Total estimated phosphorus removed by microbial process:
= (0.77 - 0.039 – 0.524) g = 0.207 g

<u>3. Total nitrogen balance in laboratory-scale system</u>

Mar 04 – Apr 04 (operating stage)

Average concentration of nitrogen in influent = 19.4 mg/L
Average concentration of nitrogen in effluent = 12.17 mg/L
Volume of wastewater per operation: 9 Litres
No. of time of operation from Mar 04 – Apr 04: 20 times
Concentration of nitrogen in plant: 3.8 mg/g
Dry mass of plant: 36.87 g

→ Total nitrogen input from Mar 03 – Apr 04:
19.4 mg/L x 9 L x 20 = 3.492 g

→ Total nitrogen output from Mar 03 – Apr 04:
12.17 mg/L x 9L x 20 = 2.191 g

→ Total nitrogen retained from Mar 03 – Apr 04:
(3.492 – 2.191) g = 1.301 g

→ Total nitrogen uptake by plant:
3.8 mg N/g x dry mass of plant = 3.8 mg N/g x 36.87 g
= 0.140 g

→ Total nitrogen adsorbed by coal slag:
(Nitrogen concentration on coal slag at the end of Apr 04- Nitrogen concentration on coal slag at the end of Feb 04) x density of coal slag x volume of coal slag
(0.041-0.033) mg N /g x 1.818 kg/L x 18 L
=0.262 g

→ Total estimated nitrogen removed by microbial process:
= (1.301 – 0.140 – 0.262) g
= 0.899 g

<u>4. Total phosphorus balance in laboratory-scale system</u>

Mar 04 – Apr 04 (operating stage)

Average concentration of phosphorus in influent = 8.19 mg/L
Average concentration of phosphorus in effluent = 4.77 mg/L
Volume of wastewater per operation: 9 Litres
No. of time of operation from Mar 03 – Apr 04: 20 times
Concentration of phosphorus in plant: 0.86 mg/g
Dry mass of plant: 36.87 g

→ Total phosphorus input from Mar 03 – Apr 04:
8.19 mg/L x 9 L x 20 = 1.474 g

→ Total phosphorus output from Mar 03 – Apr 04:
4.77 mg/L x 9L x 20 = 0.859 g

→ Total phosphorus retained from Mar 03 – Apr 04:
(1.474 – 0.859) g = 0.615 g

→ Total phosphorus uptake by plant:
0.86 g P/kg x dry mass of plant = 0.78 g P/kg x 36.87 g
= 0.029 g

→ Total phosphorus adsorbed by coal slag:
(Phosphorus concentration on coal slag at the end of Apr 04 - Phosphorus concentration on coal slag at the end of Feb 04) x density of coal slag x volume of coal slag
= (0.029-0.016) mg P /g x 1.818 kg/L x 18 L
= 0.425 g

→ Total estimated phosphorus removed by microbial process:
= (0.615 - 0.029 – 0.425) g = 0.161 g

Appendix II

Total mass of phosphorus retained in the pilot system in the current study

Mass of TP retained in the pilot system

From start-up period (Nov 04 – Apr 05, 40 times) & operation period (May 05 –Mar 06, 100 times)

Planted system:

(Mean of TP_{in} – Mean of TP_{out}) mg/L x (40 +100) times x effective volume (m^3)

= (2.6198-1.8236)mg/L x 140 x (13.6 x 1000)L

= 1.516 kg

Unplanted system:

(Mean of TP_{in} – Mean of TP_{out}) mg/L x (40 +100) times x effective volume(m^3)

= (2.604-1.7856) mg/L x 140 x (13.6 x 1000)L

= 1.558 kg

Appendix III

Costs of the sequencing batch biofilm reactor

Construction cost:

RMB 5000 / 13.6 m^3

=RMB 368

And based on:

Power of the pump: 1kw

Duration of pumping: 4 hours

Electricity cost per unit: RMB 1/kw·h

Volume of wastewater pumped: 45 m^3 (3 systems)

Electricity expenditure:

1kw x 4 hours x RMB 1/kw·h ÷ 45 m^3

= 0.09 RMB/ m^3