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Research Report

Fate of Cadmium in Wastewater Effluents Treated in Constructed Wetland

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Research results are the researcher's sole responsibility.

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บทคัดย่อ

การวิจัยครั้งนี้ เป็นการศึกษาประสิทธิภาพในการบำบัดแคดเมียม ของพื้นที่ชุ่มน้ำประดิษฐ์แบบไหลบนพื้นผิวและไหลใต้ดิน โดยมีสภาพแวดล้อมที่ต่างๆกัน และเปรียบเทียบประสิทธิภาพของพื้นที่ชุ่มน้ำประดิษฐ์แบบไหลบนพื้นผิว สำหรับน้ำเสียสังเคราะห์ชุมชนและอุตสาหกรรม โดยใช้พืชสองชนิดและค่าความเข้มข้นของแคดเมียมที่แตกต่างกัน การศึกษาแบ่งเป็นสองส่วน คือ ส่วนที่หนึ่งประกอบด้วยบ่อทดลอง 4 บ่อสำหรับพื้นที่ชุ่มน้ำประดิษฐ์แบบไหลบนพื้นผิวและไหลใต้ดินตลอดการทดลอง 4 ช่วงเวลา ทั้งสองระบบปลูกธูปฤาษี (*Typha angustifolia.*) และน้ำเสียที่ใช้คือน้ำเสียสังเคราะห์ชุมชนผสมด้วยแคดเมียมที่ความเข้มข้นต่างๆ คือ 1, 5, 10, และ 20 มิลลิกรัมต่อลิตร ค่า S-COD, TKN, TP, TSS, VSS และแคดเมียมของน้ำเข้าและน้ำออกได้ทำการวิเคราะห์ตลอดการทดลอง ปริมาณแคดเมียมในดินทำการวิเคราะห์เมื่อจบการทดลองในแต่ละช่วงเวลา ส่วนปริมาณแคดเมียมในพืชจะทำการวิเคราะห์เมื่อสิ้นสุดการทดลอง ประสิทธิภาพในการบำบัด S-COD ของพื้นที่ชุ่มน้ำประดิษฐ์ทั้งสองระบบอยู่ในช่วง 78-92% ที่ระยะเวลาเก็บกัก 5.5 วัน ประสิทธิภาพในการบำบัด TKN, TP, TSS และ VSS อยู่ในช่วง 64-91%, 62-90%, 68-91% และ 50-84% ตามลำดับ ค่าเฉลี่ยของแคดเมียมในน้ำออกมีค่าระหว่าง 0.02-0.16 มิลลิกรัมต่อลิตร ประสิทธิภาพในการบำบัดแคดเมียมมีค่า 98.6-99.4% และ 99.3-99.9% สำหรับพื้นที่ชุ่มน้ำประดิษฐ์แบบไหลบนพื้นผิวและไหลใต้ดิน ตามลำดับ พื้นที่ชุ่มน้ำประดิษฐ์แบบไหลใต้ดินมีประสิทธิภาพในการบำบัดมลภาวะต่างๆ ได้ดีกว่าพื้นที่ชุ่มน้ำประดิษฐ์แบบไหลบนพื้นผิวเพียงเล็กน้อย แต่ประสิทธิภาพในการบำบัดแคดเมียมของทั้งสองระบบไม่แตกต่างกัน ในส่วนที่สองประกอบด้วยบ่อทดลอง 5 บ่อ ที่ปลูกกกกลม (*Cyperus corymbosus* Rottb.) ในพื้นที่ชุ่มน้ำประดิษฐ์แบบไหลบนพื้นผิว น้ำเสียสังเคราะห์อุตสาหกรรมผสมด้วยแคดเมียมที่ความเข้มข้นต่างๆ คือ 5, 10, 25, และ 50 มิลลิกรัมต่อลิตร ถูกปล่อยเข้าสู่ระบบตลอดการทดลอง 3 ช่วงเวลา ที่ระยะเวลาเก็บกักที่ 5, 7 และ 10 วัน ค่า S-COD และแคดเมียมของน้ำเข้าและน้ำออก รวมทั้งในดินและพืช ได้ทำการวิเคราะห์ตลอดการทดลอง ประสิทธิภาพในการบำบัด S-COD อยู่ในช่วง 72-91% ค่าเฉลี่ยของแคดเมียมในน้ำออกมีค่าระหว่าง 0.17-12.73 มิลลิกรัมต่อลิตร ประสิทธิภาพในการบำบัดแคดเมียมมีค่าระหว่าง 75-97% แคดเมียมมีปริมาณการสะสมในดิน 56-76% และในพืช 14-23% ของปริมาณแคดเมียมทั้งหมดในน้ำเข้า ปริมาณการสะสมแคดเมียมในดินและพืช มีค่าเพิ่มขึ้นตามปริมาณของแคดเมียมในน้ำเข้าของแต่ละช่วงเวลาของการทดลอง ระยะเวลาเก็บกักที่เหมาะสมในการบำบัดแคดเมียมคือ 10 วัน

จากการเปรียบเทียบพื้นที่ชุ่มน้ำประดิษฐ์แบบไหลบนพื้นผิว สำหรับบำบัดน้ำเสียสังเคราะห์ชุมชนและอุตสาหกรรมผสมด้วยแคดเมียมความเข้มข้น 5 และ 10 มิลลิกรัมต่อลิตร ที่ปลูก

ธูปฤาษีและกกกลม ที่ระยะเวลาเก็บกักที่ 5.5 และ 5 วัน ตามลำดับ พบว่าประสิทธิภาพในการบำบัด S-COD ที่ความเข้มข้นแคดเมียม 5 และ 10 มิลลิกรัมต่อลิตร มีค่า 86.9% และ 85.5% สำหรับบ่อที่ปลูกธูปฤาษี และ 75.5% และ 73.9% สำหรับบ่อที่ปลูกกกกลม ประสิทธิภาพในการบำบัดแคดเมียมมีค่า 99.5% และ 99.4% สำหรับบ่อที่ปลูกธูปฤาษี และ 81.9% และ 80.8% สำหรับบ่อที่ปลูกกกกลม ที่ค่าความเข้มข้นแคดเมียม 5 และ 10 มิลลิกรัมต่อลิตร ตามลำดับ ประสิทธิภาพในการบำบัด S-COD และแคดเมียมของพืชทั้งสองที่ค่าความเข้มข้นแคดเมียม 5 และ 10 มิลลิกรัมต่อลิตรมีค่าแตกต่างกันเล็กน้อย พบว่าพื้นที่ชุ่มน้ำประดิษฐ์แบบไหลบนพื้นผิวมีประสิทธิภาพในการบำบัดแคดเมียมสูงทั้งน้ำเสียสังเคราะห์ชุมชนและอุตสาหกรรม บ่อที่ปลูกธูปฤาษี(น้ำเสียสังเคราะห์ชุมชน) มีประสิทธิภาพสูงกว่าบ่อที่ปลูกด้วยกกกลม(น้ำเสียสังเคราะห์อุตสาหกรรม)

Abstract

This study was conducted to investigate the cadmium removal in the free water surface (FWS) and subsurface flow (SF) constructed wetland systems under different environmental conditions and to compare the performance of FWS for domestic and industrial wastewaters using two different plants and at different cadmium loadings. The investigations were done in two parts. Part 1: Two simultaneous experiments were carried out in four laboratory scale units for the FWS and SF wetland systems during the four runs. Cattail plants (*Typha angustifolia.*) were used in the constructed wetland units. The synthetic domestic wastewater mixed with cadmium concentrations of 1, 5, 10, and 20 mg/L was fed to the wetland units. Concentrations of some monitored parameters, soluble chemical oxygen demand (S-COD), total kjeldahl nitrogen (TKN), total phosphorus (TP), total suspended solid (TSS), volatile suspended solid (VSS), as well as Cd were determined in the influent and effluent at frequent intervals during the four runs. The cadmium content in the soil were determined at the end of each run, while in plants, it was only measured at the end of the fourth run. Removal efficiencies of the S-COD were found to be in the range of 78-92% for two wetland systems at HRT 5.5 days. The removal efficiencies for TKN, TP, TSS, and VSS were in the range of 64-91%, 62-90%, 68-91%, and 50-84%, respectively. The mean effluent cadmium concentrations varied between 0.02-0.16 mg/L. Cadmium removal efficiencies were 98.6-99.4% in FWS, and 99.3-99.9% in the SF wetland systems. The subsurface flow wetland showed slightly better performance than the free water surface wetland in terms of various pollutants' removal. However, the two systems had the similar performance in the cadmium removal. Part 2: Four simultaneous experiments were carried out in five laboratory scale units for FWS wetland system. Bulrush plants (*Cyperus corymbosus* Rottb.) were used in the constructed wetland units. A synthetic wastewater resembling a typical industrial wastewater mixed with cadmium concentrations of 5, 10, 25 and 50 mg/L was fed to the wetland units during the three experimental runs. Concentrations of S-COD, and cadmium concentrations in influent and effluent, as well as in soil and plants were determined at frequent intervals during the experimental run. The performance of the FWS constructed wetland system was evaluated for three hydraulic retention times (HRT) 5, 7 and 10 days. Removal efficiencies of S-COD were found to be in the range of 72-91% during the experimental period. The mean effluent cadmium concentrations varied between 0.17-12.73 mg/L. The overall average cadmium removal efficiency during the

three runs ranged between 75-97%. Most of the cadmium was accumulated in soils (56-76% of total influent cadmium). Of the total cadmium uptakes, about 14 to 23% of the total cadmium intake was accumulated in bulrush plants. The accumulation in soil and in plants increased with influent loading during each run. The optimum HRT for efficient Cd removal from wastewater appears to be 10 days.

The FWS constructed wetlands for synthetic domestic and industrial wastewater mixed with Cd concentrations of 5 and 10 mg/L was compared for cattail and bulrush plants at HRT 5.5 and 5 days, respectively. Mean S-COD removal efficiencies for influent cadmium concentrations of 5 and 10 mg/L were 86.9% and 85.5% for wetland with cattail plants and 75.5% and 73.9% for wetland with bulrush plants. The average Cd removal efficiencies were 99.5% and 99.4% for FWS wetland system with cattail plants and 81.9% and 80.8% for FWS wetland system with bulrush plants at influent cadmium concentrations of 5 and 10 mg/L, respectively. Mean S-COD and Cd removal efficiencies were only slightly different for the two wetland systems with two different plants at influent cadmium concentrations of 5 and 10 mg/L. High removal efficiencies were observed for synthetic domestic and industrial wastewater and were higher in the FWS constructed wetlands with cattail plants (synthetic domestic wastewater) as compared to the wetlands with bulrush plants (synthetic industrial wastewater).

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List of Symbols and Abbreviations

HRT	=	Hydraulic retention time
L	=	Basin length
W	=	Basin width
D	=	Depth of basin
n	=	Porosity of the bed, as a decimal fraction
Q	=	Average flow through the unit
d_m	=	Media depth
d_w	=	Water depth from media surface
D	=	Axial dispersion coefficient characterizing the degree of back mixing during flow
u	=	Flow velocity
L_l	=	Length of fluid travel path from influent to effluent
d	=	Dispersion number
AAS	=	Atomic adsorption spectrometry
FWS	=	Free water surface system
SF	=	Subsurface flow systems
ppm	=	Part per million
COD	=	Chemical oxygen demand
TSS	=	Total suspended solid
VSS	=	Volatile suspended solid
TKN	=	Total kjeldahl nitrogen
TP	=	Total phosphorus
DO	=	Dissolved oxygen
Cd	=	Cadmium
g	=	Gram
mg	=	Milligram
mL	=	Milliliter
mg/L	=	Milligram/Liter
m	=	Meter
cm	=	Centimeter

Chapter I

Introduction

1.1 Introduction

Through mining, industrial activities and fossil fuels combustion, people each year, spew thousands of tons of metallic pollutants in to air and water. Toxic metal pollution is not only a problem for exposed workers, but is one of the global problems that concern us (Delgado et al., 1993). Many industries including electroplating, foundries, electronics, mining, smelting, tanning, photo processing, pulp and paper and metal finishing can be a significant source of wastewater containing heavy metal pollutants such as nickel (Ni), cadmium (Cd), chromium (Cr), zinc (Zn), copper (Cu), iron (Fe), and mercury (Hg), etc. Heavy metals are ubiquitous environmental pollutants that arise from a variety of industrial, commercial, and domestic activities. Furthermore, studies show that heavy metals can be found in municipal sewage treatment plants receiving little or no industrial discharge (Gersberg et al., 1984). Heavy metals constitute a serious form of pollution since they do not degrade as organic pollutants do (Delgado et al., 1993). Heavy metals concentrate in the food chains and they can accumulate poison to plants, animals and human. Especially, cadmium is an environmental pollutant that accumulates in the body and has biological half-life of greater than 10 years in humans (Khosraviani et al., 1998). Therefore, these pollutants must be removed in the effective way before the effluents are discharged from the wastewater treatment plants to the receiving water bodies. Industrial effluent standards of some heavy metal parameters under Ministry of Science, Technology and Environment (MOSTE) in Thailand: Ni < 1 mg/L, Cd < 0.03 mg/L, Cr^{6+} < 0.25 mg/L, Cr^{3+} < 0.75 mg/L, Zn < 5 mg/L, Cu < 2 mg/L, Hg < 0.005 mg/L, respectively.

There are many techniques available for the removal of heavy metals from wastewater such as chemical precipitation, reverse osmosis, electrolysis, and ion exchange but these methods require high capital, operation and maintenance costs. The new alternative for improving effluent wastewater containing heavy metal is wetlands. Wetlands are one of the least expensive treatment systems that require minimum energy and technology, and no chemicals are necessary. Wetland treatment systems use either the natural wetlands or constructed wetlands for treatment of wastewater. Wetlands have been used as convenient wastewater discharge sites for more 100 years in some regions. When monitoring was initiated at some of the existing wetland discharges, an

awareness of the water purification potential of wetlands began to emerge. Significant advances have since been made in the engineering knowledge of creating constructed wetlands that can closely imitate the specialized treatment functions that occur in the natural wetland ecosystems. Among the natural treatment systems, the many advantages such as simplicity of design, and lower costs of installation, operation, and maintenance offered by constructed wetlands make them an appropriate alternative for both developed and developing countries.

Many varieties of wetland plant species are tolerant of high concentrations of heavy metals, perhaps because of the protective effect of the iron plaque, which can develop around the roots. Hence, wetlands can be designed and built for heavy metals removals. In fact, many constructed wetlands specifically built for heavy metal removal are in operation in Australia (Vigneswaran and Sundaravadivel and 2001).

1.2 Research objectives

The main objectives of this study were:

1. To investigate the fate of cadmium in wastewater effluents in constructed wetland systems under different environmental conditions.
2. To compare the efficiency of cadmium removal through laboratory scale experiments in free water surface (FWS) and subsurface flow (SF) wetland systems using cattail plants and bulrush plants.
3. To compare the performance of FWS for the treatment of domestic and industrial wastewaters using two different plants and at different cadmium loadings.

1.3 Scope and limitations of study

In order to achieve first two objectives, following work was conducted:

1. Two simultaneous experiments were carried out in four laboratory scale units for the two wetland systems during the four runs.
2. Cattail plants (*Typha angustifolia.*) were used in the constructed wetland units.
3. A synthetic wastewater resembling a typical domestic wastewater was prepared in the laboratory. The synthetic wastewater mixed with cadmium concentrations of 1, 5, 10, and 20 mg/L was fed to the wetland units during four experimental runs.

4. Concentrations of some monitored parameters, soluble chemical oxygen demand (S-COD), total kjeldahl nitrogen (TKN), total phosphorus (TP), total suspended solid (TSS), volatile suspended solid (VSS), as well as Cd were determined in the influent and effluent at frequent intervals during the four runs. The cadmium content in the soil were determined at the end of each run, while in plants, it was only measured at the end of the fourth run.
5. Performance of free water surface (FWS) and subsurface flow (SF) wetland systems were evaluated and compared for different cadmium loadings.

In order to achieve the third objective, following work was done:

1. Four simultaneous experiments were carried out in five laboratory scale units for FWS wetland system.
2. Bulrush plants (*Cyperus corymbosus* Rottb.) were used in the constructed wetland units.
3. A synthetic wastewater resembling a typical industrial wastewater was prepared in the laboratory. The synthetic wastewater mixed with cadmium concentrations of 5, 10, 25 and 50 mg/L was fed to the wetland units during the three experimental runs.
4. Concentrations of some monitored parameters, soluble chemical oxygen demand (S-COD), and heavy metals concentrations in influent and effluent, as well as in soil and plants were determined at frequent intervals during the experimental run.
5. Performance of free water surface (FWS) for the treatment of domestic and industrial wastewater were evaluated and compared for two different plants and at different cadmium loadings.

Chapter II

Literature Review

2.1 Characteristics of cadmium (Cd)

Cadmium is a rare element and is derived exclusively from zinc ores. It is most often found in combination with other elements, such as oxygen (cadmium oxide), chlorine (cadmium chloride), or sulfer (cadmium sulfide). The mineral greenokite, CdS, is widely dispersed but is of no chemical value. Pure cadmium (Cd), a soft, silver-white metal, is quite ductile. It is not attacked in dry air but is slowly oxidized forming protective film of oxide and carbonate in moist air. The main physical properties of cadmium are reported in Table 2.1 (Townshend, 1995).

Table 2.1 Some physical properties of cadmium

Atomic Weight	112.41
Atomic Number	48
Oxidation State	2
Melting Point (S.T.P)	320.9 $^{\circ}$C
Boiling Point (S.T.P)	765 $\pm$ 2 $^{\circ}$C
Density (20°C)	8.65 g/cm^3

2.2 Sources of cadmium (Cd)

Cadmium (Cd) can be found in electrodeposited and dipped coatings on metals, bearing and low-melting alloys, brazing alloys, fire protection systems, nickel-cadmium storage batteries, power transmission wire, and TV phosphorescence. Cadmium is also used as the basis of pigments in ceramic glazes, machinery enamels, fungicide photography and lithography, selenium rectifiers, electrodes for cadmium-vapor lamps, and photoelectric cell. Cadmium may enter water as a result of industrial discharges or the deterioration of galvanized pipe. Mining industries provide precious and semiprecious minerals including iron, gold, silver, tin, cadmium and nickel to the wastewater discharges. Electroplating is the electrochemical process of applying metal coatings

to metallic objects for corrosion protection and for decorative finishing. Cadmium is one of heavy metals that are the pollutants from this process (Metcalf & Eddy, 1991). Cadmium is also used in the manufacture of photovoltaic devices such as photometers and solar cells and for the automatic control of camera apertures (Mcketta, 1993).

2.3 Harmful effects of cadmium (Cd) and its compounds

The harmful effects of cadmium to humans and environment include: it is flammable in powder form, toxic by inhalation of dust or fume, and is a carcinogen. Soluble compounds of cadmium are highly toxic. Long term-concentrates in the liver, kidneys, pancreas, and thyroid cause hypertension (Metcalf & Eddy, 1991). Short-term health effects include a flu-like illness with chills, headache, aching and/or fever. High exposures can cause rapid and serve lung damage, with shortness of breath, chest pain, cough and a buildup of fluid in the lungs. High exposure to cadmium may cause nausea, salivation, vomiting cramps, and diarrhea (National Safety Council, 2000). The famous "itai-itai" or "ouch-ouch" bone disease of the Japanese in Toyama Inlet was the result of chronic exposure to Cd waste. The disease furthers progress to borne weakness that results in multiple stress fractures in the back and legs (Buzzi, 1992). For this result, the World Health Organization has recommended a maximum intake of 0.4-0.5 mg/week (Wase, 1997). The main target organs for cadmium are the kidney and liver, with critical effects occurring when a content of 200 μg Cd/g (wet weight) is reached in the kidney cortex (O'Neill, 1993).

2.4 Wetlands

Wetlands are areas that are inundated or saturated soil by surface or groundwater at a frequency or duration sufficient to maintain saturated conditions and growth of related vegetation (Polprasert, 1996). Wetlands occur in a wide range of physical settings at the interface of terrestrial and aquatic ecosystems. The natural wetlands are referred to as marshes, swamps, bogs, cypress domes and strands, etc. Constructed wetlands are planned systems designed and constructed to employ wetland vegetation to assist in treating wastewater in a more controlled environment than occurs in natural wetlands. The many advantages of constructed wetlands include site location flexibility, optimal size for anticipated waste load, potential to treat more wastewater in smaller areas than with in natural wetlands, less rigorous preapplication treatment (Bastian et al., 1989). Two types of constructed wetland systems have been developed for wastewater treatment:

1. Free Water Surface System (FWS) consists of parallel basins or channels with relatively impermeable bottom. Soil or suitable media and rock layers to support the emergent vegetation, and water flowing velocity over the top of the soil media and through wetland vegetation in shallow basins or channels. The water depth is maintained at 0.1-0.6 m above the soil surface. Cattails, bulrushes, and various sedges are emergent plants used commonly in free water surface wetlands (Figure 2.1).
2. Subsurface Flow Systems (SF) is called 'root zone', 'rock bed filter' or 'reed beds', consists of channels or trenches with impermeable bottom and soil and rock layers to support the emergent vegetation but the water depth is maintained at or below the soil surface (Figure 2.2) (Polprasert, 1996).

Aquatic plants that use in wetlands may be divided into several forms. Three types of aquatic plants are the major and typical component of the wetlands system.

1. Floating type: there are two subtypes of floating aquatic.
   - Floating unattached plants: the roots hang in the water and are not attached to the soil. The leaves and stems are above the water for receiving sunlight directly. The submerged roots and stems are good habitat for bacteria responsible for waste stabilization. The floating plants such as water hyacinth, duckweed, and water lettuce.
   - Floating attached plants: they have their leaves floating on the water surface, but their roots are anchored in the sediment such as water lilies (Polprasert, 1996).

2. Submerge type: plants that grow below the water surface are called submerged. Submerged species can only grow where there is sufficient light and they may be adversely affected by turbidity and excessive populations of planktonic algae, which decrease the penetration of light into the water. Many submerged plants are known such as hydrilla and water milfoil (Polprasert et al., 1986).

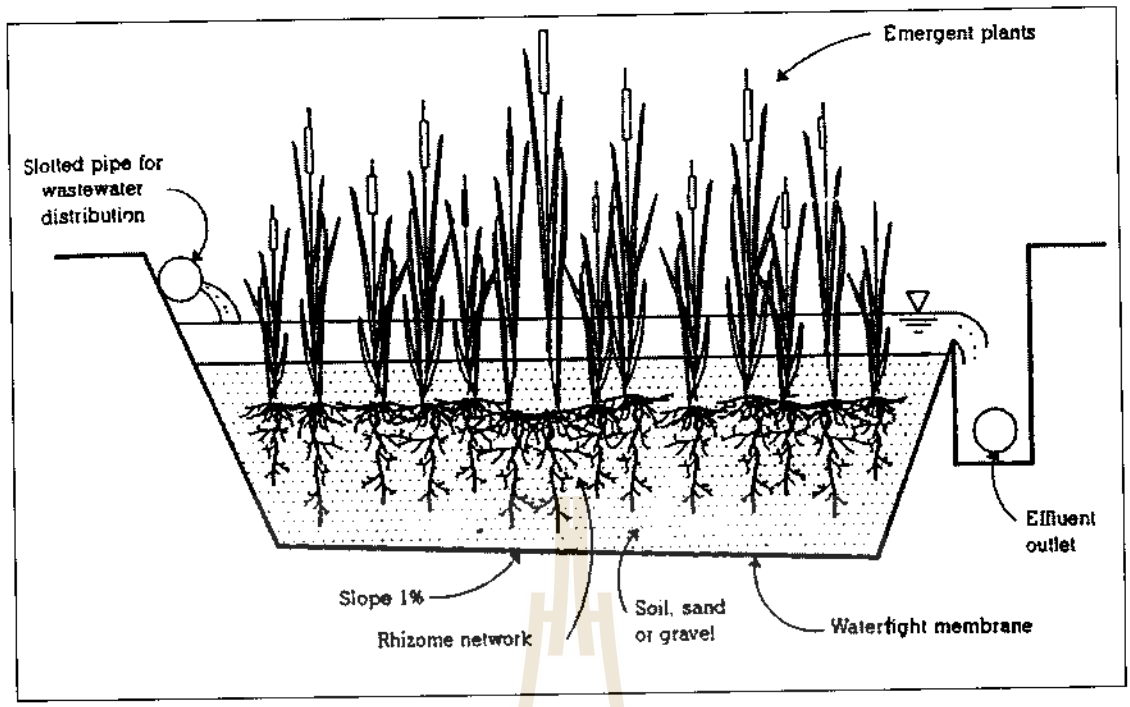


Figure 2.1 Free water surface wetland system (FWS)

(Source Lim and Polprasert, 1996)

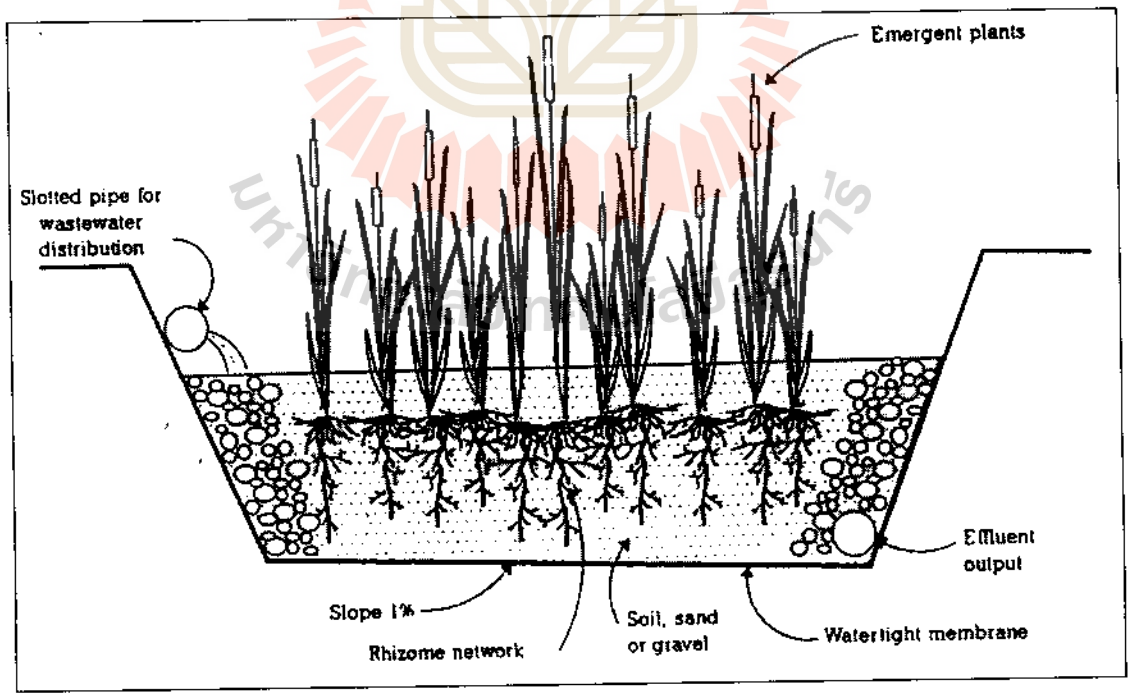


Figure 2.2 Subsurface flow wetland system (SF)

(Source Lim and Polprasert, 1996)

3. Emergent type: they produce aerial stems and leaves, and an extensive root and rhizome system. They have the capability to grow in a wide range of substrate and in rapid or extensive fluctuations in water level occur. Emergent types in wetlands system include cattails, bulrushes and reeds.

Wetlands have a high rate of biological activity; they can transform of the common pollutants into harmless byproducts or essential nutrients that can be used for additional biological productivity. These transformations are accomplished by virtue of the wetland's land area, with its inherent natural environment energies of sun, wind, soil, plants, and animals. These pollutant transformations can be obtained for the relatively low cost of earthwork, piping, pumping, and a few concentrate structures (Kadlec and Knight, 1996).

2.5 Pollutant removal mechanisms

Many monitoring and studies for constructed wetlands have shown the significant removal of organic matter (BOD), suspended solids (SS), nutrients (N and P), and pathogens. In wetlands treatment processes, the pollutants are removed from wastewater through a combination of physical, chemical, and biological processes including sedimentation, precipitation, and adsorption to soil particles, assimilation by the plant tissue, and microbial transformations.

2.5.1 Organic matter removal

BOD removal is due to microbial growth attached to plant roots, stems, and leaves that are submerged in the wastewater and the quiescent condition is attributed for the removal in free water surface wetland system. In subsurface wetlands system, the major BOD removal mechanism is deposition and filtration. The major oxygen source is the transmission by the emergent plants from atmosphere through the root zone and to leakage of some oxygen to the surrounding sediment. In surface flow wetlands, the major oxygen source for these reactions is reaeration at the water surface.

2.5.2 Solids removal

Suspended soils removal is very effective in both types of constructed wetlands due to the long HRT, shallow depth, and quiescent condition. Colloids are removed by attachment of bacteria, and by collisions (inertial and Brownian) with an adsorption to other solids such as plants, pond bottom, and suspended solids.

2.5.3 Nitrogen removal

Nitrogen is removed by a number of mechanisms such as plant uptake, ammonia volatilization, nitrification, and denitrification. Although plant uptake of nitrogen occurs, only plants can remove a minor fraction. Nitrification/denitrification are the most effective removal of nitrogen. Ammonia is oxidized to nitrate by nitrifying bacteria in aerobic zones, and nitrates are converted to free nitrogen in anoxic zones by denitrifying bacteria. In subsurface flow systems, oxygen required by the nitrifiers is supplied by leakage from plant roots. Oxygen mass transfer limits nitrification in attached growth systems. The factors important to the nitrification process are (1) minimizing carbonaceous oxygen demand, so slower growing nitrifiers can compete with the heterotrophic organisms; (2) maintaining pH within the optimum range of 7 to 8; (3) establishing adequate retention time (at least 5 days based on available data); and (4) limiting toxics (certain heavy metals and organic compounds inhibit nitrifiers) (Watson et al., 1989).

2.5.4 Phosphorus removal

The mechanisms of phosphorus removal are plant uptake, and several chemical adsorption and precipitation reactions (occurring primarily at the sediment/water column interface). A significant clay content and iron, aluminum, and calcium will enhance phosphorus removal (Lim and Polprasert, 1996).

2.5.5 Heavy metals removal

Heavy metals can be removed from wastewater in wetlands system by plant uptake, precipitation as oxides, hydroxides, carbonates, phosphates, and sulfides; and also remove by ion exchange with and adsorption to sedimented clay and organic compounds (Polprasert et al., 1986, Sintumongkolchai, 1996).

The three main wetland processes, which remove heavy metals, are:

- Binding to soils, sediments and particulate matter
- Precipitation as insoluble salts; and
- Uptake by bacteria, algae, and plants

Major proportion of heavy metal removal is accounted to binding processes within wetlands. Because of their positive charge, the heavy metals are readily adsorbed, complexed and bound with suspended particles, which subsequently settle on the substrate. Precipitation of heavy metals as insoluble salts such as carbonates, bicarbonates, sulfides and hydroxides is another process that leads to their long-term removal. These salts forms by the

reaction of heavy metals with other chemicals present in water column are insoluble, and hence precipitate to the bottom to become fixed within the wetland substrate.

2.5.6 Pathogens removal

Bacteria and viruses are removed from the waste stream by: (1) physical processes such as aggregate formation, followed by sedimentation, filtration and adsorption; and (2) actual die-off as a result of prolonged exposure to hostile environmental conditions such as temperature, and unfavorable water chemistry (Phanuwan, 1999, Kadlec and Knight, 1996).

2.6 Removal mechanisms and pathways of heavy metals transformation in constructed wetlands

The mobility of heavy metal pollutants in wetland plants and medium depends on a more or less complex network of interactions between aqueous and heterogeneous chemical reactions as well as particle coagulation and flocculation phenomena. Hydrolysis and dissolved complexation tend to increase the solubility of heavy metals while precipitation and adsorption will delay heavy metals availability and transport as shown in Figure 2.3 (Bourg, 1995).

The most mobile fractions of ions occur at a lower range of pH, which is illustrated in Figure 2.4.

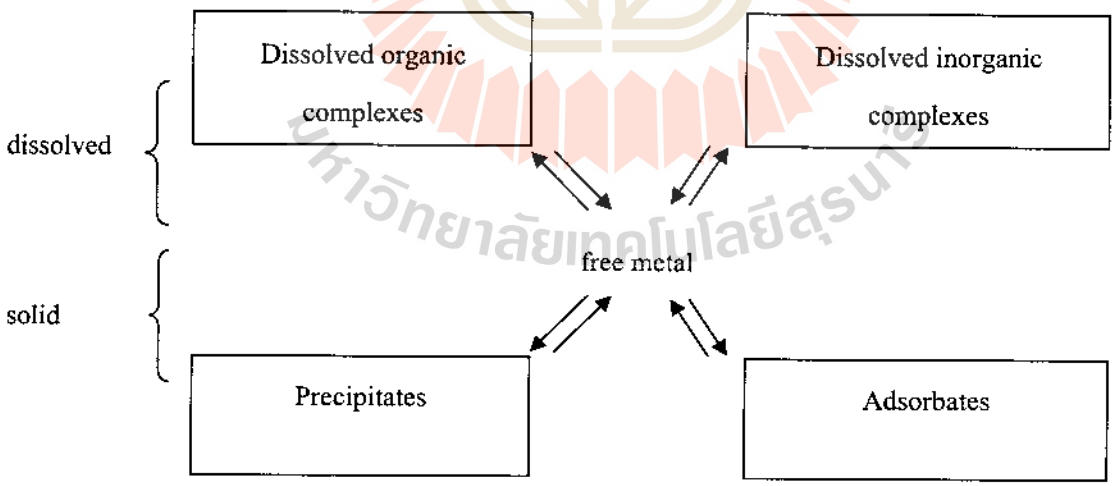


Figure 2.3 Geochemical speciation of heavy metals (all of theses processes are prone to concurrent reactions with other cations, including H^+)

(Source Bourg, 1995)

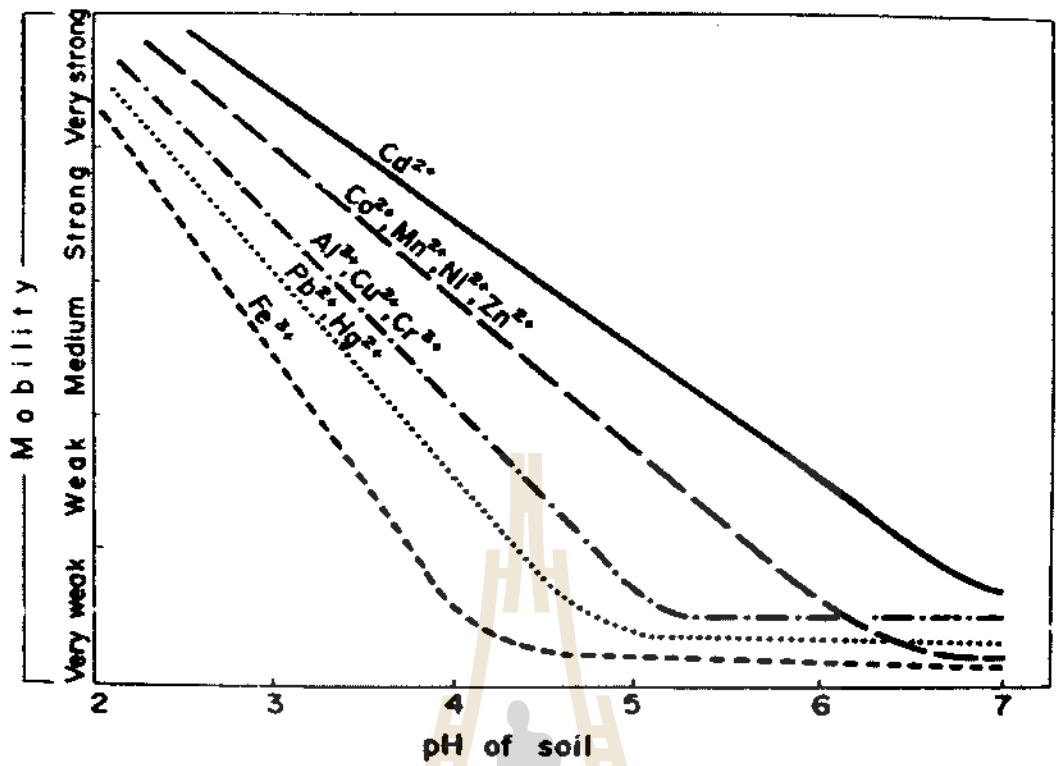


Figure 2.4 Schematic trends in the mobility of some metals as influenced by soil pH (Source Pendis and Pendias, 1992)

The major mechanisms of heavy metals removal in constructed wetlands are:

2.6.1 Plant Uptake

Plants can accumulate heavy metals, in or on their tissues due to their great ability to adapt to variable chemical properties of the environment, thus plants are intermediate reservoirs of heavy metals from soils, and waters. The uptake by roots is the main pathway of heavy metals to plants. Nonmetabolic uptake is the diffusion of ions from the external solution into the root endodermis. Metalbolic uptake requires metabolic energy and takes place against a chemical gradient. Several data support the suggestion that, at the concentration generally present in soil solutions, the adsorption of heavy metals by plant roots is controlled by metabolic processes within roots.

Roots and associated microorganisms are known to produce various organic compounds, which are very effective in releasing the heavy metals from firmly fixed species in soils. The heavy metals most readily available to plants are, in general, those that are adsorbed on clay minerals, while those fixed by oxides and bound onto microorganisms have much less readily

available rate of their uptake by roots than mass-flow and diffusion mechanisms in certain soils. The mechanisms of heavy metals uptake by roots involve several processes:

1. Cation exchange by roots
2. Transport inside cells by cheating agents or other carriers
3. Rhizosphere effects

Cation oxidation states around roots are believed to be of great importance in these processes. Changes in the pH of the root ambient solution may play and especially significant role in the rate of availability of certain heavy metals.

Heavy metals entering plant tissues reactive in metabolic processes, but also can be stored as inactive compounds in cells and on the membranes. In each case, however, they may affect the chemical composition of plants without causing easily visible injury.

2.6.2 Adsorption

The term "adsorption" is commonly used for the process of sorption of chemical elements from solutions by soil particles. Adsorption is thus the kinetic reaction based on thermodynamic equilibrium rules. The forces involved in the adsorption of ionic species at charged surfaces are electrostatic and can be explained by coulomb's law of attraction between unlike charges and repulsion between like charges. Soils are considered as heavy metals' sinks, and for that reason, they play an important role in environmental cycles of these elements. They also have a great ability to fix many species of heavy metals (Pendis and Pendias, 1992). Soil components involved in adsorption of heavy metals are:

1. Oxides (hydrous, amorphic) mainly of iron and manganese and, to much lesser extent, aluminum and silicon
2. Organic matter and biota
3. Carbonates, phosphate, sulfides, and basic salts
4. Clays

Of all these components, clay minerals, hydrated metal oxides, and organic matter are considered to be the most important group in contributing to and competing for adsorption of heavy metals (Pendis and Pendias, 1992).

At metal equilibrium concentrations, either the Langmiur or the Freundlich equations for adsorption isotherms can describe the mechanism of the adsorption by soil particles. Langmiur's Isotherm is normally used in explanation of adsorption mechanism that can be shown in Eq. 2.1 (Sintumongkolchai, 1996).

$$\frac{1}{x/m} = \frac{1}{b} + \frac{1}{abc} \tag{2.1}$$

where; x = mass of heavy metal adsorbed, mg

m = mass of wetland bed media, g

a = constant

b = maximum heavy metal adsorption capacity, mg/g

c = solution concentration at equilibrium

2.6.3 Precipitation

Every soil component is active and affects soil solution ion concentration either by precipitation-dissolution reaction or by ionic interactions with phase surfaces. In the soil aqueous phase organic compounds and water are the most abundant ligands, therefore, hydrolysis and organic complexing are the most common reactions in soil solutions. These reactions are pH sensitive and can be corrected with the size and charge of the cations. Higher ionic potentials usually indicate higher degree of hydration in the solution, resulting an easier precipitation (Pendis and Pendias, 1992). From the basic physical chemistry, it is known that heavy metals precipitate as the result of changes in pH, oxidation and other changes of their chemical composition (Novotny, 1995).

The organic sediments are good cation exchange sites for heavy metals, and hence these are found bound to sediments in preference to the dissolved forms. Further, the anaerobic zones of the wetland-soils can generate sulfide ions which precipitate the insoluble sulfides of heavy metals (Kadlec and Knight, 1996).

2.6.4 Complexation

When heavy metals are added to soils and water (sediments), they undergo complexation with ligands. Ligands are chemical constituents, both organic and inorganic, that combine with the heavy metals in a chemical complex (Novotny, 1995). Organic matter of soils consists of a mixture of plant and animal products in various stages of decomposition and of substances that are synthesized chemically and biological. This complex material, greatly simplified, can be divided into humic and nonhumic substances. The major portion of the organic matter in most soils results from biological decay of the biota residues. The end products of this degradation are humic substances, organic acids of low molecular and high molecular weights, carbohydrates, proteins, peptides, amino acids, lipids, axes, polycyclic aromatic hydrocarbons, and lignin fragments. In addition, the excretion products of roots, composed of a wide variety of simple organic acids, are present in soils.

Presence of compounds that will react with the heavy metals ion and cause its precipitation or adsorption on solids will reduce the toxicity of the heavy metals and makes them less bio-available for organisms. The colloidal and ionic compounds which combine with in a complex with the heavy metal ion are called ligands which include organic acid and humic substances, dissolved sulfides, chloride and OH^- ions.

Hence, the adsorbing and complexing compounds for toxic metals include:

- particulates: sulfides, particulate organic matter, and clays
- dissolved: sulfides, humic compounds, organic acids, chloride ion, hydroxyl ion (Novotny, 1995).

2.7 Previous research work

The heavy metals removal has been studied for a long time. Constructed wetland is biological wastewater treatment that is one effective process to remove heavy metals from wastewater. The uptake of metals by the plant from soils and solutions has been investigated for a variety of species. Most of these studies involve the phytotoxic effects of heavy metals on crop species over a relatively long-term exposure period (30 days) (Delgado et al., 1993). Many researchers have used cattail plants that use to remove heavy metals in wetland systems. Mungur et al. (1997) investigated the removal of some metals by a wetland system. This study complemented the research on the performance of a subsurface flow system treating runoff being carried out by

the Urban Pollution Research Centre, Bounds Green Road, London. The system was planted with *Typha latifolia*, *Phragmites australis*, *Schoenoplectus lacustris* and *Iris pseudacorus*. The wetland system was dosed with various concentrations (1, 5 and 10 mg/l) of Cu, Pb and Zn, respectively. Finally shocked load of metals (concentration 20 mg/l) was introduced to simulate a storm event. In each experiment water samples collected from outlet at timed intervals were analyzed and loadings calculated in order to assess the metal removal efficiency of the system. The removal efficiencies and rates for these different doses ranged from 81.7% to 91.8 % and 36.6 to 372.7 $mg/m^2/d$ for Cu, 75.8% to 95.3% and 30.8 to 387 $mg/m^2/d$ for Pb and 82.8% to 90.4% and 33.6 to 362.1 $mg/m^2/d$ for Zn, respectively.

Heavy metals can also be removed by floating plants in a wetland system. David et al. (1984) studied about cadmium uptake by the water hyacinth. Their results clearly demonstrated that the water hyacinth was able to remove cadmium effectively from solutions over a wide concentration in the sub-ppm range cadmium could be almost completely removed from water with 24 hr. This ability to remove cadmium and, in fact, to survive high exposure concentrations (up to 100 ppm) showed that the water hyacinth could be reasonable alternative to conventional wastewater treatment systems. Concentrations above 100 ppm were acutely toxic to the plants. A biphasic rate of uptake was observed with a fast phase of about 4 hours and a slow phase of at least 72 hours. Stirring the solution enhanced uptake in the fast phase, suggesting that uptake was in part diffusion limited. Increasing the pH from 2 to 5 enhanced the uptake rate.

Gersberg et al. (1984) reported that at the hydraulic application rate of 4.7 cm per day (residence time equal to about 5.5 days) Cu, Zn and Cd removal efficiencies in the wetland units were 99%, 97% and 99% respectively. In their experimental study, the predominant removal mechanisms in the artificial wetlands were attributed to precipitation-adsorption phenomena. Precipitation was enhanced by wetland metabolism, which increased the pH of inflowing acidic waters to near neutrality.

Blake et al. (1987) studied the incorporation of cadmium by water hyacinth. Water hyacinth was grown in plastic tanks for batch system or continuous flow system. Different concentrations of cadmium (0.25, 0.50, 1.00 and 2.00 ppm) were used and toxic effects were obvious at 1.00 ppm concentration. The distribution of metals was followed in the medium and different parts of the plant. As expected, the roots accumulated the major part (73-86%) of the

incorporated cadmium. The removal of cadmium from the solution by the water hyacinth could be predicted by the empirical equation:

$$C_t = C_0\left(1+\frac{t}{a}\right)^n \qquad (2.2)$$

Where, C_t is the cadmium concentration at time t, C_o is the cadmium concentration in solution at time zero, t is the time (hour) and a, n are the constants. From the results, the constants a and n of different cadmium concentrations (0.25, 0.50, 1.00 and 2.00 ppm) were 2.956, 2.213, 6.972, 4.044 for constant a, respectively and -0.698, -0.514, -0.543, -0.281 for constant n, respectively.

Sinha and Chanda (1990) conducted a study to show that cadmium could be removed from water by *Bacopa monnieri*, a common aquatic plant found all over India. Plants showed a capability to accumulate both metals in single and mixed metal treatments. Copper accumulation was stimulated by the presence of Cd whereas Cu inhibited uptake of Cd. The plants showed high concentration factors for both metals. The results suggested the possibility of using this plant for mitigating Cu and Cd pollution in the aquatic environment.

Delgado et al. (1993) conducted a study in green house to determine the phytotoxic effect and uptake capacity of Zn, Cr and Cd by water hyacinth. Results showed that among the three elements tested, Cd was most phytotoxic, showing up some necrosis in the plant when the concentration was greater than 2.5 ppm. In the case of Cr and Zn, the phytotoxicity produced the apperance of chlorosis in the aerial part of the plant. Cr (maximum 9 ppm) caused no reduction of productivity, whereas in the case of Zn the concentration of 9 ppm in solution caused a 30% reduction in the plant weight. It was proved that after 24 days of growth, the heavy metals were totally depleted from the nutritive solution suggesting complete absorption of these metals by the plants.

Shutes et al. (1993) investigated the use of *Typha latifolia* for heavy metal pollution control in urban subsurface wetlands system. Removal of Cd, Cu, Pb and Zn from wastewater was studied in their experiments. The heavy metal uptake patterns of *Typha* plants were more in the roots than leaves. They suggested that the use of a gravel substrate, which would allow adequate root growth but also support high hydraulic loading, might provide a more suitable substrate for

emergent macrophytes with in urban retention basins. Additionally, the subsurface introduction of effluent into the basin through submerged inlets would also maximize the purification potential.

Thayalakumaran (1994) reported the removal efficiencies of heavy metal (Cr and Ni) in subsurface flow systems (SFS) by cattail plants to be more than 99%. The removal mechanisms were mainly precipitation and adsorption. About 15% of these heavy metals were found that be removed by soil adsorption; the extents of heavy metal adsorption decreased along the bed length of the wetland units. Heavy metal accumulation was more in the roots than in the leaves and stem of the cattail plants. The removal efficiency for COD, TSS and TKN were 64, 89 and 85%. The mechanisms for removing COD, TSS and TKN are filtration, flocculation, sedimentation, and biological process also chemical reaction such as nitri-denitrification reaction.

Kananidhinan (1996) studied the efficiency of constructed wetlands to remove chromium in electroplating wastewater with four emergent plants, *Cyperus corymbosus* (bulrush), *Typha angustifolia* (cattail), *Phragmites australias* (reed), and *Eleocharis dulcis* (spikerushes). During experimental period, influent chromium concentrations were in the range of 2.82-20.93 mg/l and the average was 7.61 mg/l. The best efficiency was found in Cyperus, as high as 98.21%, while the efficiencies of Eleocharis, Typha and Phragmites were 95.96%, 95.90%, and 94.87%, respectively. And the lowest efficiency was found in control unit (no plants), 89.13%, which was 9.1% lower than the highest efficiency, Cyperus. Accumulation of chromium in soil and plants were also studied and were found to tend to increase with passage of time. Average accumulation of chromium in soil in each pilot unit was slightly different and the highest mean was 29.16 µg/g dry weight. In plants, Eleocharis dulcis showed the maximum chromium concentration, 397.15 µg/g dry weight, at the end of the experiments, but had the lowest weight per unit. Mass balance showed that more than 90% of total chromium that disappeared from the water was found in the soil.

Sintumongkolchai (1996) observed the removal of cadmium in free water surface (FWS) system with cattail plants to be in the range of 73-98%. The results showed that pH is an important factor, and at pH of 4.26-5.35, Cd removal by plant uptake was 58.83% of total Cd in sand layer, while at pH of 7.42-8.03, Cd uptake by the plants was 35.24% of total Cd. The average removal efficiencies of COD, TSS, TKN and TP were approximately 61.84, 74.18, 85.09 and 77.83%, respectively. The main mechanism of COD removal was biodegradation by the attached and suspended microorganisms. TSS was effectively removed by sedimentation to the wetland beds

and some could be attached to the stems and roots of cattail plants. TKN removal efficiency was high at HRT long. The effects of TP removal relate with snails in wetland units because snails could uptake P and also release P when they died.

Hansen et al (1998) conducted a study on Selenium (Se) removal by constructed wetlands. One environmental friendly way of cleaning up Se from oil refinery effluents was by plant and microbial Se volatilization using constructed wetlands. The results showed that 89% of influent Se was removed in constructed wetlands. Inflow Se concentration of 20-30 μg/l decreased to <5 μg/l in the outflow. Most of the Se was removed by immobilization into sediments and plant tissues where Se concentration reached 5 and 15 mg/kg, respectively. Biological volatilization may have accounted for as much as 10-30% of Se removed. The highest rates of Se volatilization for vegetated sites were 190, 180 and 150 μg of Se/m^2-d for rabbitfoot grass, cattail, and saltmarsh bulrush, respectively.

Scholes et al., (1999) reported the removal of urban pollutants during wet weather by constructed wetlands developed by the Environment Agency for England and Wales. The systems were monitored for a range of determinants including heavy metals, suspended solids and BOD. Initial analysis of the data indicated that during dry weather, removal efficiencies vary greatly. However, during storm events removal efficiencies were higher with mean values of 71% for Zn, 72% for Cd, 69% for Pb, 66% for Cu, 34% for Ni, and 81% for Cr at Dagenham wetland. Mean removal efficiencies of 20% for Cd, 40% for Pb, 36% for Cu, 34% for Ni, and 38% for Cr were observed during storm conditions at the Brentwood wetland, but an overall increase in Zn was measured. Removal of BOD was greater at both sites during storm events with mean removal efficiencies of 24% and 29% at Dagenham and Brentwood, respectively. Suspended solids were reduced on passing through both wetlands during dry weather, but during storm events there was an overall increase.

Treerattanaporn (1999) evaluated efficiency of cadmium removal from wastewater using subsurface flow constructed wetland and cadmium accumulation in wetland at Chulalongkorn University, Bangkok. In addition, cadmium in various parts of the systems, which consisted of varied mediums -sand, sand and soil, and soil, respectively, and also in the plants (*Typha* spp.) was studied. Cd concentration in wastewater was varied at 1, 5, 10, and 20 mg/l. Retention time (HRT) was 5 days, and flow rates were varied at 4, 4.4, and 5 l/d for wetlands with sand, sand and soil, and soil medium, respectively. Constructed wetlands could remove cadmium

from wastewater according to industrial effluent standards in Thailand (< 0.03 mg/l), when $[Cd]_{inf}$ was not more than 5 mg/l. When $[Cd]_{inf}$ increased (10 and 20 mg/l), efficiency in cadmium removal was still more than 99%.

Richer et al. (2002) conducted a study on baseline hydraulic performance of the constructed wetlands subsurface flow system at Heathrow Airport in UK. A constructed wetland treatment system was commissioned by BAA (formerly the British Airports Authority) in order to attenuate airfield runoff contaminated with de-icant and order potentially polluting materials from Heathrow Airport. Airfield runoff containing de-icants has the potential to impose significant oxygen demands on water bodies. The site consists of a number of integrated treatment systems, including a 1ha rafted reed bed canal system and a 2ha subsurface flow gravel reed bed. This research project was concerned with the performance of the subsurface flow reed bed, though attention would be paid in this paper to the operation of the whole system. Prior to the planting of the subsurface flow reed beds, flow-tracing experiments were carried out on the three different types of subsurface beds, so that the baseline performance of the system could be quantified. In association, data regarding the soil organic matter content was also collected prior to the planting of the beds. As expected, soil organic matter content was observed to be negligible within the bed, though a small amount of build up was observed in localized areas on the surface of the beds. This was attributed to the growth of algae in depressions where standing water persisted during the construction phase.

In a similar study, hydraulics of sub-superficial flow constructed wetlands in semi arid climate conditions were investigated in Italy by Ranieri (2002). He reported the evaluation of the hydraulics of two constructed wetland (CWs) plants located in Apulia (South Eastern Italy region characterized by semi arid climate conditions). These fields were planted with *phragmites australis* hydrophytes and were supplied with local secondary wastewater municipal treatment plant effluent. Each plant – Kickuth Root-Zone method based – covers an area of approx. 2,000 m^2. Evapotranspiration phenomen was evaluated with in perforated tubes fixed to the filed bottom and very high values – up to 40 mm/d – were found. Hydraulic conductivity was evaluated by in situ measurements in different field points. Hydraulic gradient and the piezometric curve within the field are also reported.

There have been few more reported research studies on application of constructed wetlands for wastewater treatment conducted in various parts of the world. Meutia (2002)

evaluated the application of subsurface constructed wetland to treat dormitory wastewater in Rural Indonesia. The aim of his research was to examine the capability of constructed wetland to treat dormitory wastewater and to investigate the efficiency of wetland use system in which fish rearing and agriculture were integrated. Dormitory wastewater from bathroom and septic tank flew into the first bed containing gravel and sand planted with mix population of aquatic plants such as *Typha spp.*, Water Spinach (*Pomenus*), Water Hyacinth (*Eichornia crassipes*), etc. Water flew from the bottom of the bed. The outflow was located near the top of the bed. After the first bed, wastewater flew into second bed containing the same substrate with floating plant *Lemna minor* and *Hydrilla*. Treated water then flew into clarifier with three chambers intended to separate the fine sediment and water. Finally, treated water was kept in a pond containing several kinds of fishes such as *Tilapia spp.*, and *Clarias batrachus*. Water from fishpond was used for watering several kinds of vegetables. During first year of operation, several parameters were monitored in order to evaluate the efficiency of the system. The results showed that removal efficiencies based on concentration were found to be BOD_5 15-95%, COD 15-75%, and TOC 34-95%. Total nitrogen (T-N) and phosphorus (T-P) removal varied between 10-73% and 10-40%, respectively. Bacterial pathogen such as total coli and E.coli decreased 14-100% and 68-100%. The results showed that the constructed wetland is capable enough to treat the dormitory wastewater in the integrated system.

Lund (2002) presented the results of his research in designing constructed wetlands for removal of filterable reactive P from storm/groundwater in a Mediterranean climate in the Western Australian city of Perth. Three replicate experimental periods (15 × 5 m), were constructed to present at a 1:1 scale a single cell form a repeating 16 cell design proposed in 1997. Three 5 m zones of each pond were sampled, shallow (0.3 m) vegetated (*Schoenoplectus validus*) inflow and outflow zones and a deeper (1 m), V-shaped central zone. The V-shape was designed to increase hydraulic residence time, control the spread of plants and provide a pool of water to support the plant communities in summer. In 1998/99, inflows and outflow water were intensively sampled and analyzed for FRP. In addition, all major pools of P (plants, interstitial water, sediment) within the ponds, and important P removal processes (benthic flux, uptake by biofilm and *S. validus*) were quantified. A removal efficiency of 5% (1998) and 10% (1999) was obtained for FRP. When scaled to operational size this indicates a removal rate of approximately 40-60% for FRP. Initial uptake was mainly in plant biomass, although the sediment became an increasing important sink.

The highly colored wasters (DOC concentrations of 50 mg/l) were believed responsible for the very low biofilm biomass recorded (<1 g/m^2). This project has demonstrated that constructed wetlands can be effective in this type of the environment, although the high water table does pose particular design challenges.

Chapter III

Material and Methodology

3.1 Experimental site

Laboratory scale experimental set-up was located at a site near the Center for Scientific and Technological Equipment (F5) at the Suranaree University of Technology (SUT) as shown in Figure 3.1.

3.2 Experimental set-ups

Part 1: First experimental set-up consisted of four reactor units designated as R1, R2, R3 and R4 made of zinc plate, with dimension of L×W×D = 2 ×0.5 ×1 m. Details of these units are as follows:

- Reactor R1 was used for the free water surface wetland system, fed with the synthetic domestic wastewater (used as a control unit).
- Reactor R2 was used for the free water surface wetland system, fed with the synthetic domestic wastewater containing known concentrations of the selected heavy metals.
- Reactor R3 was used for the subsurface wetland system, fed with the synthetic domestic wastewater (used as a control unit).
- Reactor R4 was used for the subsurface wetland system, fed with the synthetic domestic wastewater containing known concentrations of the selected heavy metals.

All four units consisted of:

(a) sand (0.1 cm diameter particles) of 10 cm depth at the top.

(b) the medium layer of 25 cm depth with small gravels (1.2-2.5 cm diameter).

(c) large gravels (2.5-5.0 cm diameter) of 25 cm depth at the bottom.

A depth of 30 cm of water was maintained in reactors 1 and 2 as shown in Figure 3.2. For reactors 3 and 4, the flow of wastewater was maintained approximately 15-30 cm below the bed surface as illustrated in Figure 3.3. Cattail plants (*Typha angustifolia.*) were cultured in the wetland beds at approximately 0.15 m intervals.

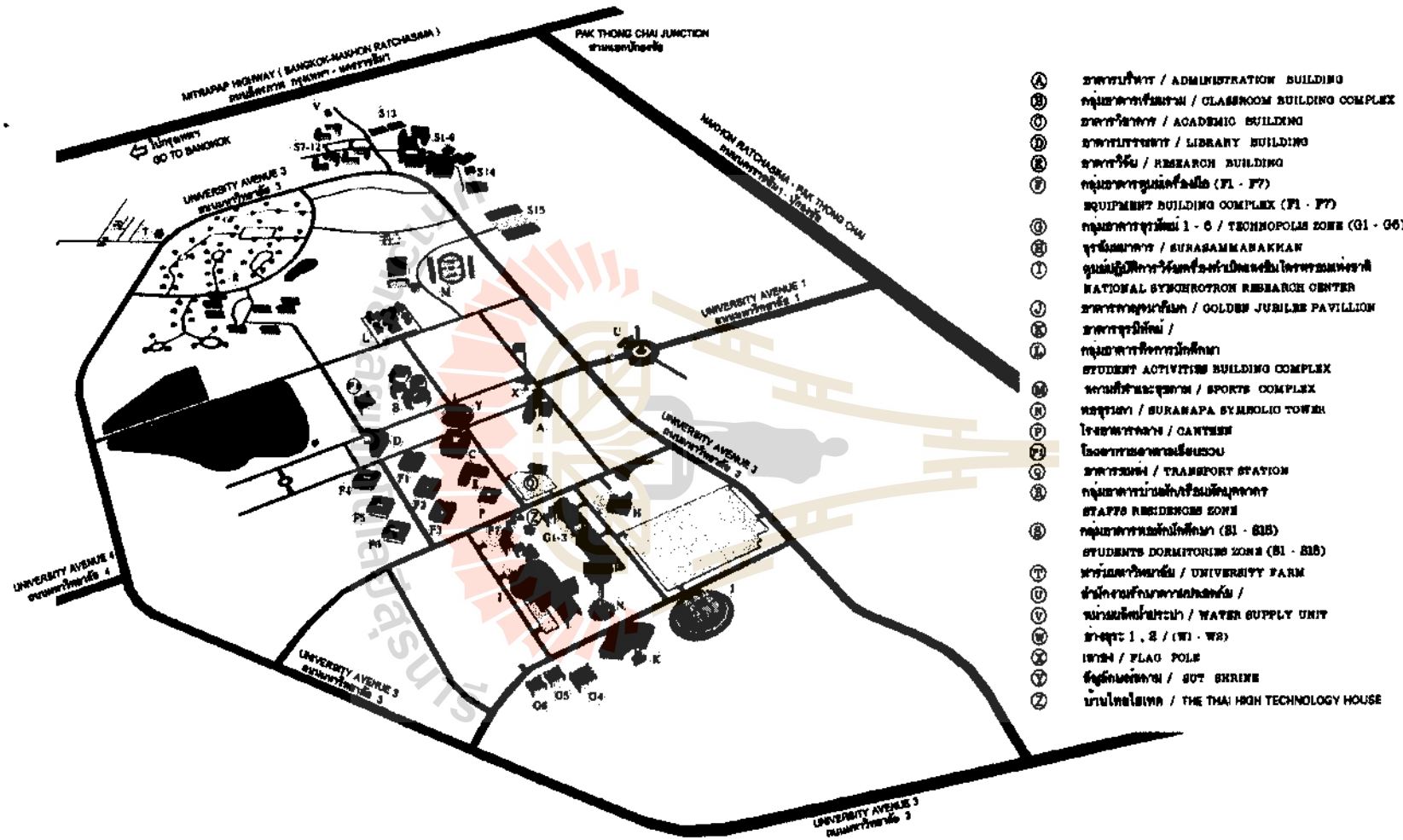
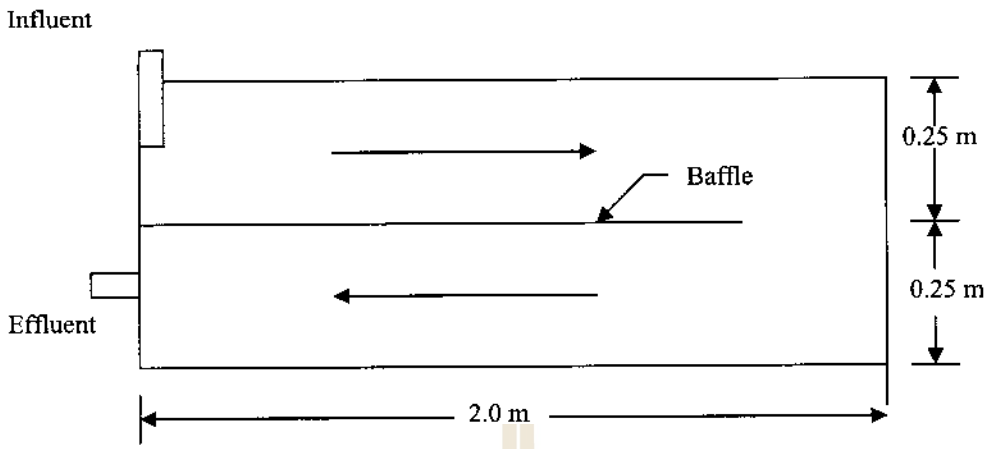
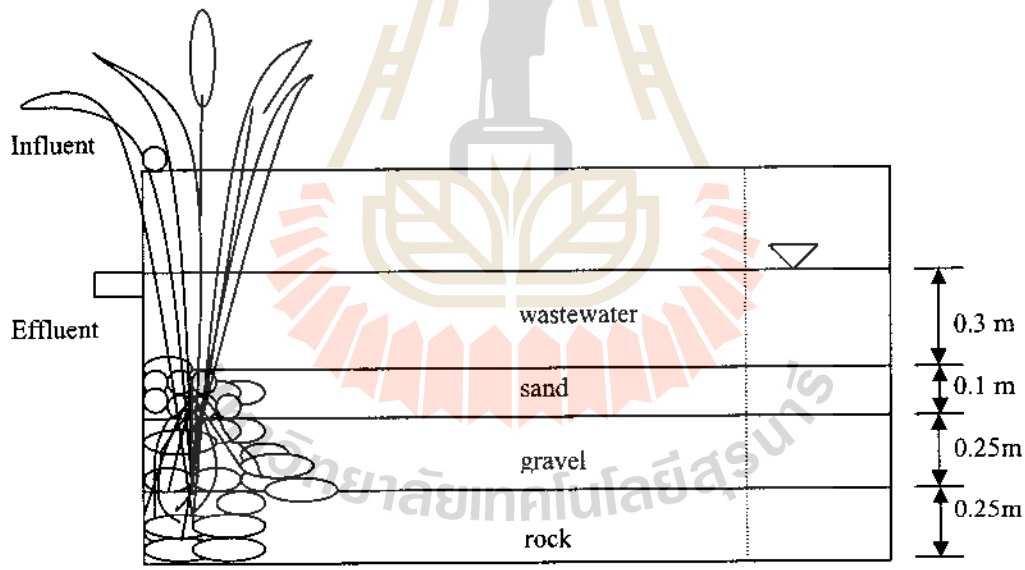


Figure 3.1 Laboratory scale constructed wetland units near the Center for Scientific and Technological Equipments (F5) at SUT

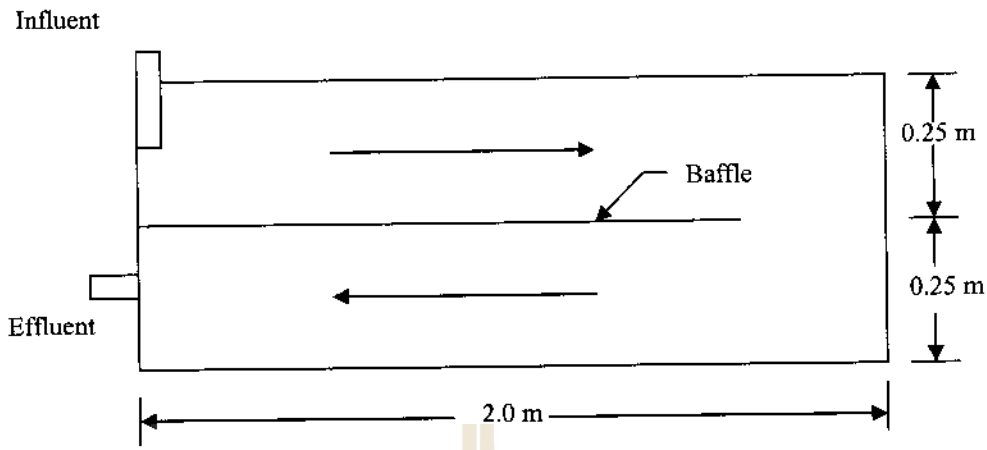


Top View of reactors R1 and R2

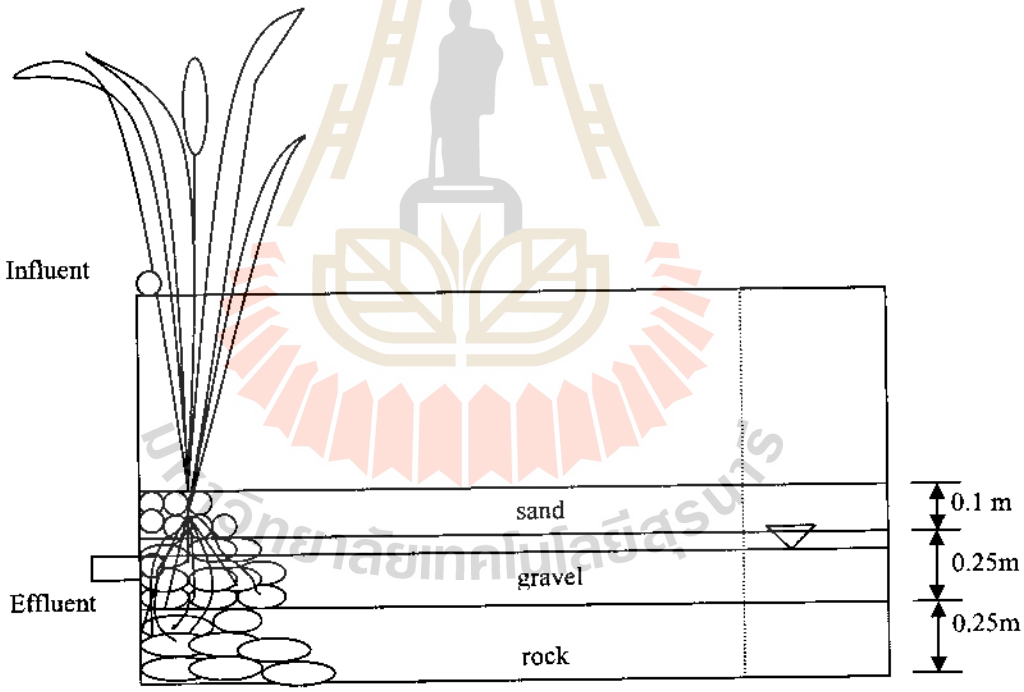


Side View of reactors R1 and R2

Figure 3.2 Reactors R1 and R2 (Free water surface wetland system)-Part 1



Top View of reactors R3 and R4



Side View of reactors R3 and R4

Figure 3.3 Reactors R3 and R4 (Subsurface flow wetland system)-Part 1

Two head tanks (200 L each) were used for feeding the synthetic domestic wastewater to the four constructed wetland units. Head tank no. 1 was used for control reactors R1 & R3. Head tank no. 2 was used for feeding the synthetic wastewater to reactors R2 and R4 after mixing with known concentrations of the heavy metals in a storage/mixing tank. From the head tanks, the influents were fed into the reactors by peristaltic pumps (505S, Watson Marlow). Figure 3.4 shows the four reactor units and head tanks used in Part 1 of this study.

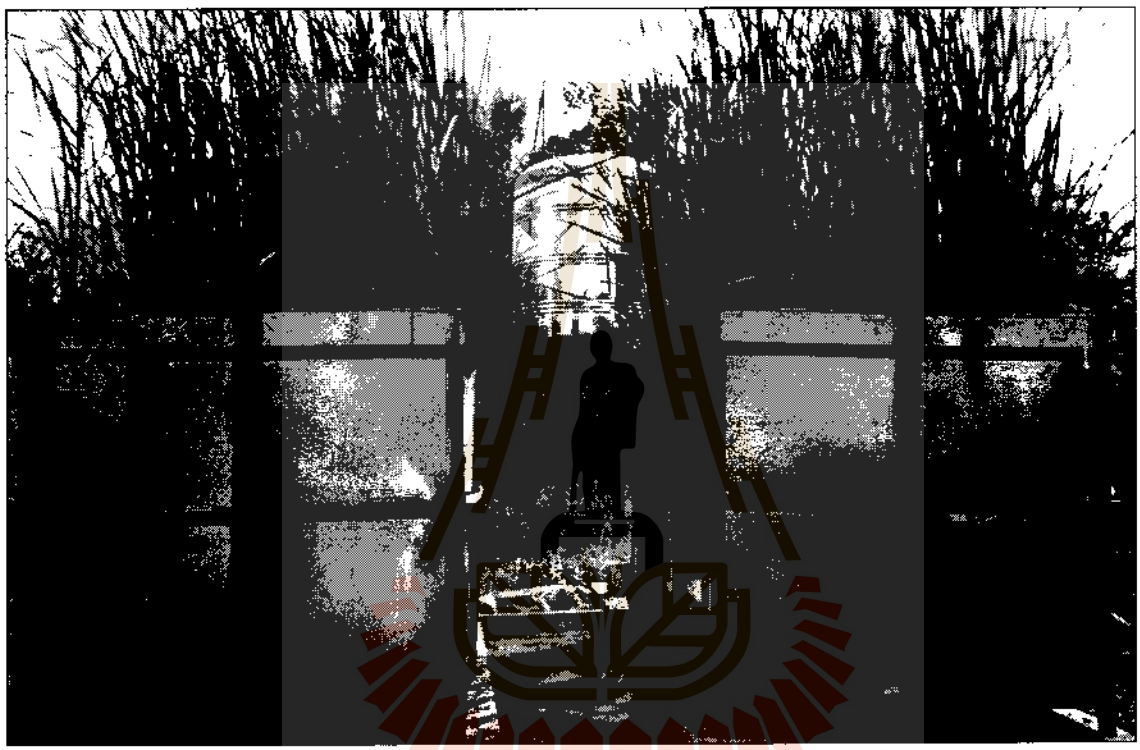


Figure 3.4 Head tanks and four reactors of constructed wetlands-Part 1

Part 2: Second experimental set-up consisted of five reactor units designated as R5, R6, R7, R8 and R9 made of zinc plate, with dimension of L×W×D = 2.5 ×0.25 ×0.85 m. Details of these units are as follows:

- Reactor R5 was used for the free water surface wetland system, fed with the synthetic industrial wastewater (used as a control unit).
- Reactors R6-R9 were used for the free water surface wetland system, fed with the synthetic industrial wastewater having four cadmium concentrations of 5, 10, 25, and 50 mg/L, respectively.

All five units consisted of:

(a) sand and soil mixture with the ratio of 1:3 of 40 cm depth at the top.

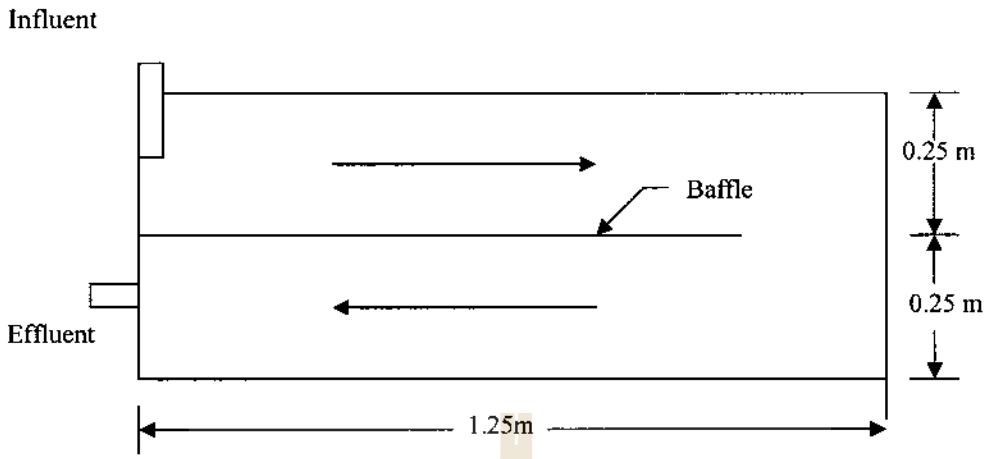
(b) sand (0.1 cm diameter particles) of 20 cm depth at the bottom.

A depth of 15 cm of water was maintained in FWS wetland systems shown in Figure 3.5. Bulrush plants (*Cyperus corymbosus* Rottb.) were cultured in the wetland beds at approximately 0.15 m intervals.

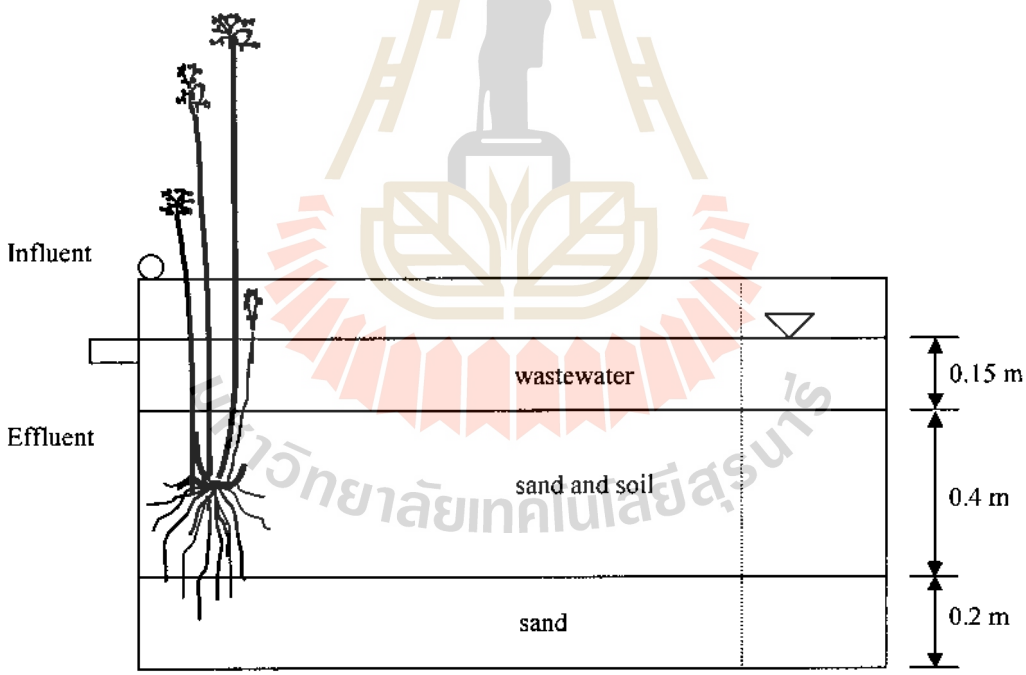
Five head tanks (200 L each) were used for feeding the synthetic industrial wastewater to the five constructed wetland units. Head tank no. 3 was used for control reactor R5. Head tank no. 4-7 were used for feeding the synthetic wastewater to reactors R6-R9 after mixing with known concentrations of the heavy metals in a storage/mixing tank. Five peristaltic pumps (505S, Watson Marlow) were used to feed wastewater to constructed wetland units. Side view of the experimental setup for Part 2 is shown in Figure 3.6.

3.3 Source of wastewater influent to constructed wetland units

Part 1: A synthetic wastewater resembling the domestic sewage was prepared for this study in the laboratory. A 10 ml solution having 15 mg/L $MgSO_4.7H_2O$, 0.5 mg/L $FeSO_4.7H_2O$, 0.5 mg/L $ZnSO_4$, 0.5 mg/L $MnSO_4$ and 2 mg/L $CaCl_2$was mixed with another solution having 131.58 mg/L of glucose, 73.68 mg/L NH_4Cl and 13.15 mg/L KH_2PO_4 (Laboratory Instruction Sheet No. ED082313, 2001). Influents were prepared by mixing the synthetic wastewater with $CdCl_2.H_2O$ at concentrations of 1, 5, 10, and 20 mg/L for each of the four experimental runs designated as Runs 1-4, respectively. Hydraulic retention time (HRT) of 5.5 d was used for the two wetland systems (Gersberg et al., 1984). The designed flow rates (Q) were 90.5 L/d for the FWS and 27 L/d for the SF. The four simultaneous experiments in the wetland units during the four runs were designated as R11, R12, R13, R14; R21, R22, R23, R24; R31, R32, R33, R34; and R41, R42, R43, R44, respectively. The four runs were conducted consecutively by only changing the Cd concentrations in the influent. Each experiment was run for 1.5 months. Influent and effluent points and analyzed for S-COD concentration until steady-state conditions were reached at 40 days. The plans of experimental runs and operating conditions during Part 1 are illustrated in Tables 3.1 and 3.2, respectively.



Top View of reactors R5-R9



Side View of reactors R5-R9

Figure 3.5 Reactors R5-R9 (Free water surface wetland system)-Part 2

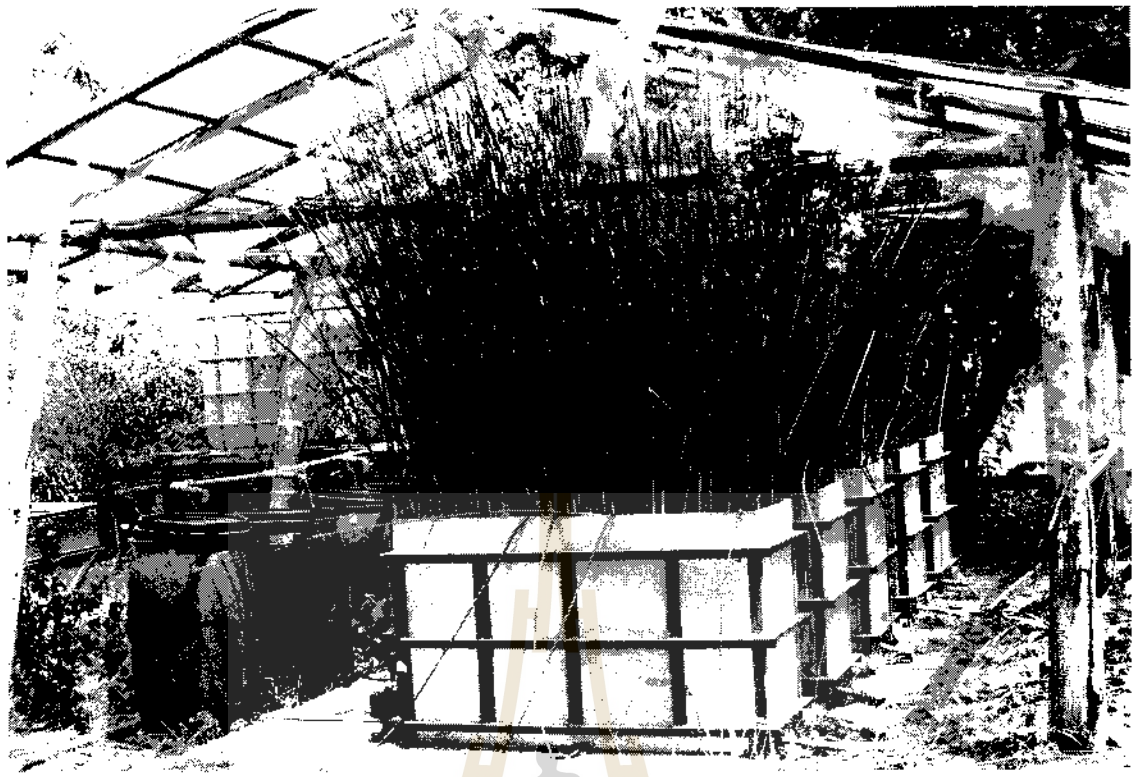


Figure 3.6 Experimental setup of constructed wetlands-Part 2

Table 3.1 Plan of experimental runs (Part 1)

Run	Free Water Surface System		Subsurface Flow System	
	R1	R2	R3	R4
	Cd conc. (mg/L)	Cd conc. (mg/L)	Cd conc. (mg/L)	Cd conc. (mg/L)
Run 1	-	1	-	1
Run 2	-	5	-	5
Run 3	-	10	-	10
Run 4	-	20	-	20

Table 3.2 Plan of operating conditions (Part 1)

Run	Hydraulic Retention Time (HRT) (d)	Flowrate (Q) (L/d)	
		Free Water Surface System	Subsurface Flow System
Run 1	5.5	90.5	27
Run 2	5.5	90.5	27
Run 3	5.5	90.5	27
Run 4	5.5	90.5	27

Part 2: A synthetic wastewater resembling some industrial effluents was prepared in the laboratory having 600-900 mg/L of soluble chemical oxygen demand. A 10 ml solution having 15 g/L $MgSO_4.7H_2O$, 0.5 g/L $FeSO_4.7H_2O$, 0.5 g/L $ZnSO_4.7H_2O$, 0.5 g/L $MnSO_4.3H_2O$ and 2 g/L $CaCl_2$ was mixed with another solution having 93.8 g/L of glucose, 120 g/L NH_4Cl, 160 g/L KH_2PO_4, and 320 g/L K_2HPO_4 (Laboratory Instruction Sheet No. ED082313, 2001). Influents were prepared by mixing the synthetic wastewater with $CdCl_2.H_2O$ at concentrations of 5, 10, 25, and 50 mg/L for each of the four simultaneous experiments during three runs designated as Runs 5-7, respectively. The performance of the wetland system was evaluated for three hydraulic retention times (HRT) 5, 7 and 10 days. The four simultaneous experiments in the wetland units during the three runs were designated as R51, R52, R53, R54, R55; R61, R62, R63, R64, R65; and R71, R72, R73, R74, R75, respectively. The three runs were conducted consecutively by changing the HRT 5, 7 and 10 days, respectively. Each experiment was run for 2 months and 22 days. Influent and effluent points and analyzed for S-COD concentration until steady-state conditions were reached at 50 days. The plans of experimental run and operating condition during Part 2 are summarized in Tables 3.3 and 3.4, respectively.

3.4 Sampling and analysis

The synthetic wastewater was prepared daily to feed to the experimental units. Influent and effluent S-COD concentrations were determined until the steady state conditions reach. Subsequently, the following parameters were analyzed in influent and effluent wastewater samples during first part: pH, DO, S-COD, TSS, TKN and heavy metal concentrations. During second part: pH, DO, S-COD, and heavy metal concentrations. Samples from soil and plants were also analyzed for cadmium accumulations. Cadmium concentrations in the influent, effluent, soil, and plants were analyzed according to the procedures mentioned in the Standard Methods (APHA, AWWA, and WFE, 1995), Chemical Analysis of Ecological Materials (Allen, 1974), and Soil Testing Sorbed Metals (Westerman, 1990), respectively. The details of analysis schedule are shown in Table 3.5 and 3.6.

Table 3.3 Plan of experimental runs (Part 2)

Run	Free Water Surface System				
	R5	R6	R7	R8	R9
	Cd conc. (mg/L)	Cd conc. (mg/L)	Cd conc. (mg/L)	Cd conc. (mg/L)	Cd conc. (mg/L)
Run 5	-	5	10	25	50
Run 6	-	5	10	25	50
Run 7	-	5	10	25	50

Table 3.4 Plan of operating conditions (Part 2)

Run	Hydraulic Retention Time (HRT) (d)	Flowrate (Q) (L/d)
Run 5	5	51.75
Run 6	7	36.96
Run 7	10	25.88

Table 3.5 Plan of sampling and analysis (Part 1)

Parameters	Frequency	Method of Analysis
Cl^-	Beginning of the experiments	Argentometric method
S-COD	3/week	Open Reflux
TSS	3/week	Filtration/Evaporation (103-105°C)
TKN	3/week	Digestion/Distillation
TP	3/week	Digestion with Nitric Acid-Sulfuric Acid
pH	3/week	pH Meter
DO	3/week	DO Meter
Cadmium in wastewater	3/week	Digestion with HNO_3 and use Atomic Adsorption Spectrometry (AAS)
Cadmium in soil	End of each run	Digestion with HNO_3 and use Atomic Adsorption Spectrometry (AAS)
Cadmium in plants	End of the experiments	Digestion with HNO_3, $HClO_4$, H_2SO_4 and use Atomic Adsorption Spectrometry (AAS)

Table 3.6 Plan of sampling and analysis (Part 2)

Parameters	Frequency	Method of Analysis
Cl^-	Beginning of the experiments	Argentometric method
S-COD	2/week	Closed Reflux
pH	2/week	pH Meter
DO	2/week	DO Meter
Cadmium in wastewater	2/week	Digestion with HNO_3 and use Atomic Adsorption Spectrometry (AAS)
Cadmium in soil	2/month and end of each run	Digestion with HNO_3, HCl, H_2O_2 and use Atomic Adsorption Spectrometry (AAS)
Cadmium in plants	2/month and end of each run	Digestion with HNO3, HClO4 and use Atomic Adsorption Spectrometry (AAS)

Chapter IV

Results and Discussion

Part 1

4.1 Tracer study

A solution of NaCl in tap water was used to perform a tracer study for each of the constructed wetlands. The effluent was analyzed for chloride concentration when the flowrates were 83.0 L/h for the FWS and 24.75 L/h for the SF. With equations 4.1-4.6 given below, data of tracer study were used to find out the dispersion number and actual HRT (Levenspiel, 1972). Porosity of the media bed was taken to be 0.33. Raw data of tracer study are given in Tables A.1-A.4 in Appendix A. The values of actual HRT and dispersion number are shown in Table 4.1.

Subsurface flow wetland system

$$HRT = \frac{LWnD}{Q} \quad (4.1)$$

Where

HRT	=	hydraulic retention time, days
L	=	basin length, m
W	=	basin width, m
D	=	depth of basin, m
n	=	porosity of the bed
Q	=	average flow through the unit, m^3/days

Free water surface wetland system

$$HRT = \frac{LW(d_m n + d_w)}{Q} \quad (4.2)$$

Where

HRT	=	hydraulic retention time, days
L	=	basin length, m
W	=	basin width, m
d_m	=	media depth, m
d_w	=	water depth from media surface, m
n	=	void fraction in the media (as a decimal fraction)
Q	=	average flow through the unit, m^3/days

Mean HRT (actual), $$t = \frac{\sum t_i C_i}{\sum C_i} \quad (4.3)$$

Standard Deviation, $$\sigma^2 = \frac{\sum t_i^2 C_i}{\sum C_i} - t^2 \quad (4.4)$$

Then $$\sigma_\theta^2 = \frac{\sigma^2}{t^2} = 2d + 8d^2 \quad (4.5)$$

Table 4.1 Actual hydraulic retention time (HRT) and dispersion numbers of constructed wetlands by tracer study (Part 1)

Reactors	**HRT (days)**	**Actual HRT (days)**	**Dispersion Number**
R1	6.0	5.78	0.14
R2	6.0	5.86	0.14
R3	6.0	5.66	0.13
R4	6.0	5.67	0.12

The flow was characterized using the dispersion number, *d*, defined as (Levenspiel, 1972):

$$d = \frac{D}{uL_1} \quad (4.6)$$

Where, D = the longitudinal or axial dispersion coefficient characterizing the degree of back mixing during flow

u = the flow velocity

L_1 = the length of fluid travel path from influent to effluent

The condition of dispersion number (D/uL_1) can be characterized as follows:

D/uL_1 = 0, is plug flow condition (negligible dispersion)

D/uL_1 = 0.002, is small amount of dispersion

D/uL_1 = 0.025, is intermediate amount of dispersion

D/uL_1 = 0.2, is large amount of dispersion

D/uL_1 = ∞ is mixed flow condition (large dispersion

In view of the low dispersion number (d), the flow characteristic of all of four reactors could be classified as approaching plug flow pattern.

4.2 Influent and effluent concentrations of monitored parameters

During the experimental period (6 months), the DO in the influent was in the range of 0.3-0.5 mg/L. The mean effluent DO concentrations during the four experimental runs varied between 4.4-6 mg/L. The mean ambient, as well as influent and effluent temperatures during the experimental period varied between 25 and 31 °C. The optimum water temperature for growth of cattails is 30 °C. The pH of the prepared synthetic wastewater was in the range of 6.5-6.66, while the pH of synthetic wastewater mixed with different cadmium concentrations varied between 6.46 and 6.57. The mean effluent pH of four experimental runs varied between 6.96 and 7.35. These pH values were favorable for plant growth, as the suitable range for naturally occurring cattails is between 4.7 and 10. At this pH range, precipitation seems to be the predominant mechanism for cadmium removal in wetlands. The effluent pH was higher than the influent pH, effect that could have been a result of plant metabolic activities and cycling of organic substrates associated with the wetland (Haraguchi, 1996; Hutchins and Merrick, 2004).

In wetland systems, microbial degradation plays a dominant role in the removal of soluble/colloidal biodegradable organic matter (BOD or COD) present in wastewater Settable organics are rapidly removed in wetland systems by quiescent conditions, deposition, and filtration. Details of experimental data are showed in Appendix B. Mean S-COD removal efficiencies in the two types of wetland systems were in the range of 78.4 to 92.2% during the experimental period. The overall average removal efficiencies for S-COD, TKN, TP, TSS, and VSS during the four experimental runs in FWS and SF wetland systems are shown in Table 4.2.

The average TKN removal efficiencies during the four experimental runs ranged from 64.7 to 91.3%. The potential rate of nutrient uptake is limited by the growth rate of the plants and the concentration of nutrients in the plant tissues. In view of overall removal of nitrogen from wastewater, plants that have rapid growth rates and capability to attain a high standing crop (biomass per unit area) can influence the rate of removal (Vigneswaran and Sundaravadivel, 2001).

The average phosphorus removal efficiencies were in the range of 61.6-90.5%, and were low in Run 1 and increased in Run 2, 3 and 4 in both wetlands. The high removal efficiencies could be due to the increased adsorption and precipitation in the longer operations.

Table 4.2 Overall average removal efficiencies for S-COD, TKN, TP, TSS and VSS during four experimental runs of Part 1 (Run 1-4)

Parameters	Run 1		Run 2		Run 3		Run 4	
	FWS (%)	SF (%)	FWS (%)	SF (%)	FWS (%)	SF (%)	FWS (%)	SF (%)
S-COD	79	88	87	91	86	92	85	90
TKN	65	85	75	87	84	91	83	88
TP	62	75	80	87	85	90	86	90
TSS	70	80	76	85	81	87	82	91
VSS	51	63	64	69	73	80	74	82

Wetlands are capable of achieving a high efficiency of suspended solids removal from the water column. Settleable solids are removed easily via gravity sedimentation as wetland systems generally have long hydraulic retention times. Nonsettling/colloidal solids are removed via various mechanisms that include: straining (if sand media is used); sedimentation and biodegradation (as a result of bacterial growth); and collisions (inertial and Brownian) with adsorption (van der waals forces) of other solids (plants, soil, sand and gravel media etc.). For SF, gravel media is an important component for the TSS removal. The average TSS removal efficiencies during four experimental runs were in the range of 68.3-90.9%. The average VSS removal efficiencies during four experimental runs were in the range of 50-84%.

From the results of mass removal efficiencies of S-COD, TKN, TP, TSS, and VSS, the statistical analysis was done as shown in Appendix C. There were no significant differences in removal efficiencies between control units and experimental units of both systems. Hence, the various concentrations of cadmium in influent (1, 5, 10 and 20 mg/L) did not affecting the treatment mechanisms for the above parameters in the wetland systems studied.

4.3 Cadmium removal in wastewater

Removal of cadmium in wetlands may occur through a number of processes, including plant uptake and soil adsorption (binding to soil particles). Chemical reactions between substances, especially metals, can lead to their precipitation from the water column as insoluble compounds.

The average cadmium removal efficiencies in the two wetland systems during the four experimental runs are shown in Figure 4.1. Detailed data are given in Appendix B. High removal efficiencies were obtained in both wetland systems and were slightly higher in subsurface flow wetlands as compared to the free water surface wetland system. The average removal efficiencies of FWS wetland during the experimental period ranged between 98.6-99.6%. For SF wetland, the average removal efficiencies were in the range of 99.3-99.9%. For FWS wetland system, the mean effluent concentrations of Cd were 0.02, 0.05, 0.15, and 0.16 mg/L, during Run 1, 2, 3, and 4, respectively. While in SF wetland system, they were 0.01, 0.02, 0.04, and 0.06 mg/L, during Run 1, 2, 3, and 4, respectively.

These results were compared with the industrial effluent standards in Thailand (Ministry of Science, Technology and Environment, 1996). The average effluent concentrations of cadmium during Run 1 and 2 of subsurface flow wetland were below the industrial effluent standards (0.03 mg/L). However, in Run 3, and 4, the average effluent concentrations were higher than 0.03 mg/L. While for free water surface wetland, the average effluent concentrations of cadmium were in general higher than the industrial effluent standards during Run 2, 3 and 4.

For the FWS wetland, the total amounts of influent Cd in each run were 1,957.49, 5,347.69, 13,217.50, and 24,692.40 mg/d for Run 1, 2, 3, and 4, respectively. Cadmium loadings in effluent were 27.21, 28.41, 74.32, and 90.76 mg/d for Run 1, 2, 3, and 4, respectively. These loadings represented 0.5% of the influent cadmium loading. For the SF wetland, cadmium loadings in effluent were 4.13, 4.04, 6.21, and 9.92 mg/d for Run 1, 2, 3, and 4, respectively. These loadings represented 0.18% of the influent cadmium loading.

4.4 Cadmium removal by soil

Wetland soils are potentially effective traps or sinks for metals, due to the relative immobility of most metals in such soils. Cadmium forms nearly insoluble compounds with sulfides under anaerobic conditions in wetland soils.

Soil samples were collected at the end of each run along reactor lengths at distances of 0.5, 1.5, 2.5, and 3.5 m from the inlet, and at depths of 15, and 25 cm of the soil bed. Details are shown in Appendix D. The total accumulation of cadmium in the soil was determined at the end of Run 4. The results showed a high concentration of cadmium at the inlet that decreased along the reactor length for both wetland systems. Concentrations at the depth of 15 cm were higher than at

the depth of 25 cm. This could have been because of a greater adsorption of cadmium in sand (Eriksson, 1988). The total cadmium accumulation in soil in the two wetland systems during four runs is shown in Figure 4.2.

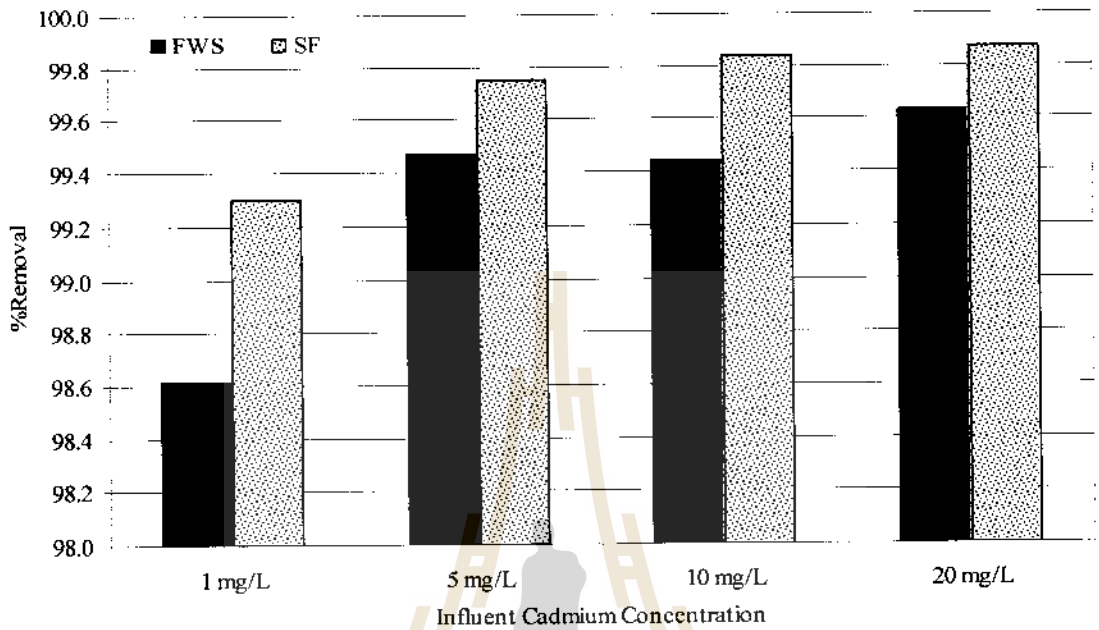


Figure 4.1 Average cadmium removal efficiencies of two wetland systems during four experimental runs of Part 1 (Run 1-4)

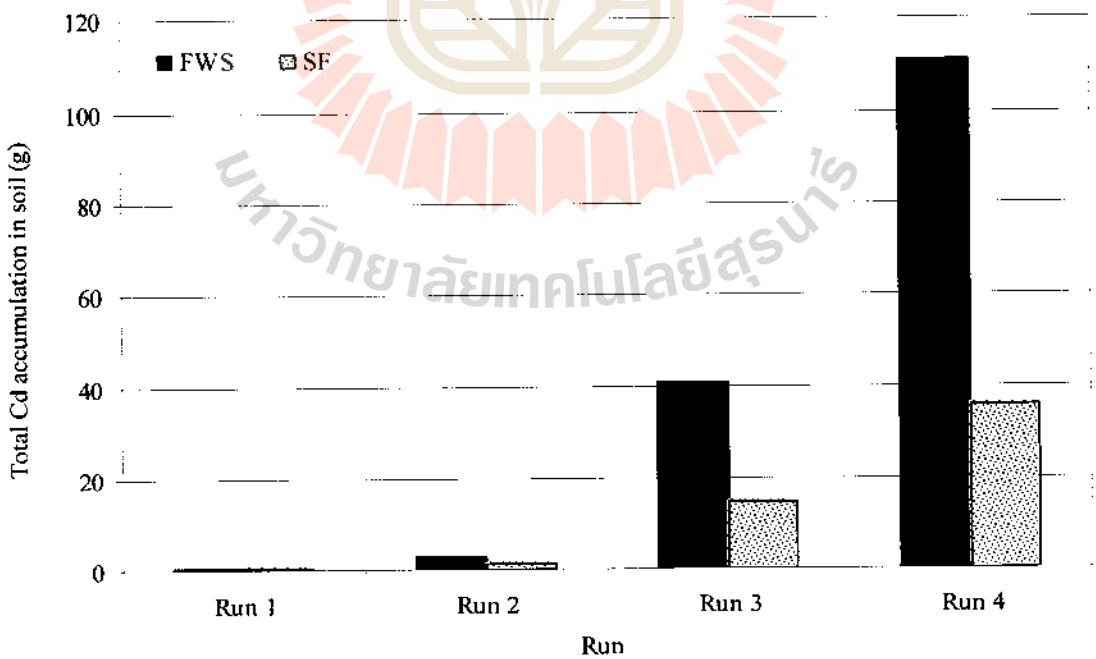


Figure 4.2 Total cadmium accumulation in soil in two wetland systems during four experimental runs of Part 1 (Run 1-4)

4.5 Cadmium removal by plant uptake

Plant uptake rates and tolerance of metals vary considerably among plant species. Some terrestrial plant species are known to be capable of storing high concentrations of metals in roots and other issues. Metals may also tend to accumulate on the root surfaces, rather than being taken up into the plant (Vigneswaran and Sundaravadival, 2001).

Cattail plants could uptake Cd from the roots to stems and leaves issues. At the end of experiments, the cadmium accumulation was determined in each part of plants. Cattail plants were collected along reactor lengths at distances of 0.5, 1.5, 2.5, and 3.5 m from the inlet. Table 4.3 shows the mass density and moisture content of cattail plants in the four reactors at the end of Run 4. Table 4.3 shows that the yield for cattail plants was less for the SF than for the FWS, probably because of a reduced water level in the SF wetland, since the roots were reaching approximately 30 cm from the medium top.

Table 4.3 Mass density and moisture content of the cattail plants in four wetlands units (Part 1)

Reactor	**Wet weight** (kg/m^2)	Moisture (%)
R1	24.0	54.64
R2	19.8	53.49
R3	12.6	48.80
R4	13.0	45.03

The concentration of cadmium accumulated in each section of the plant until the end of Run 4 as shown in Figure 4.3. Raw data is shown in Appendix E. It can be seen that cadmium accumulated in the roots was higher than in the stems and leaves in both wetland systems.

Cadmium accumulation in roots was about 55.2% in the FWS and 61.6% in the SF ith respect to the total accumulation in the whole plant. Cadmium could have been chelated by organic acids and amino acids present in higher concentration in the roots (Thayalakumaran, 1994). Since the cattails were able accumulate up to 3200 ppm in the FWS and 2800 ppm in the SF, these plants can be classified as cadmium hyperaccumulators. However, as the roots accounted for more than 50% of Cd uptake by plants, it is difficult to dispose of these plants after they are used for heavy metals'removal in wetlands.

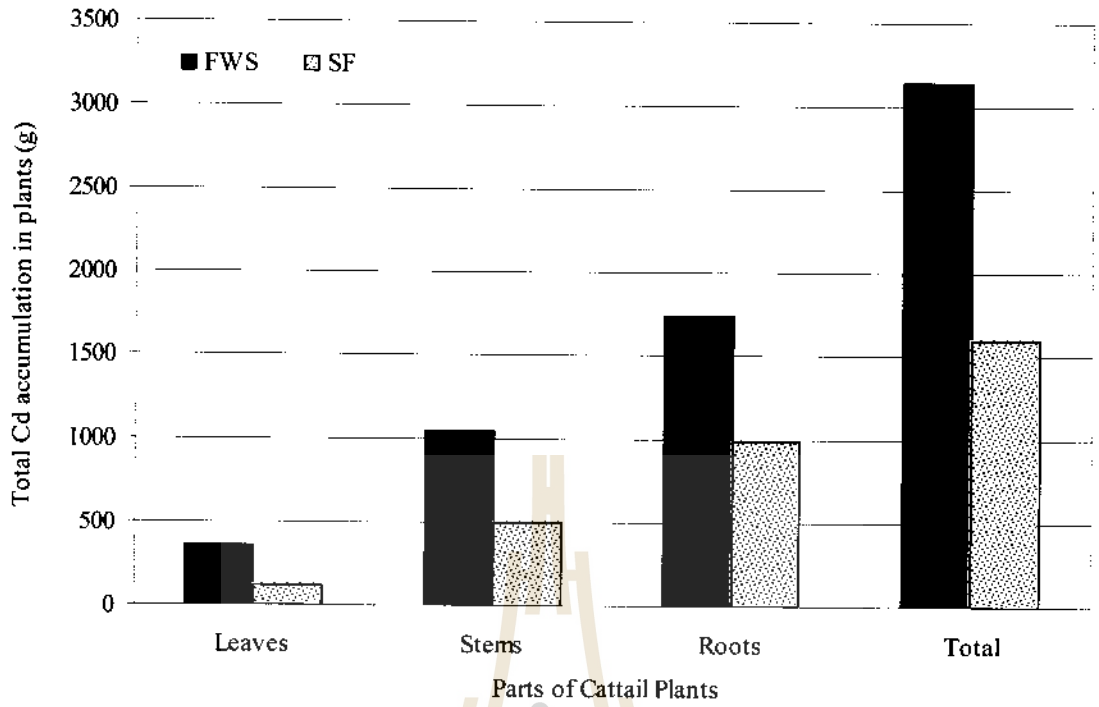


Figure 4.3 Total cadmium in various parts of plants in two wetland systems at the end of run 4 of Part 1

4.6 Mass balance

For removal of cadmium, the overall performance of the wetlands was very good. Both, the soil and plants were the sinks for the accumulation of cadmium. In subsurface flow wetland, cadmium was removed mainly by the media acting as filter beds. The adsorption of cadmium by the media was very effective because of the wastewater flowing through the soil bed. In the FWS, cadmium was not sorbed by to the soil bed as much since the water level was maintained above it. Thus some of the cadmium was not attached to the soil bed. In addition to the soil bed, the stems of cattail plants could also act as a filters for cadmium removal. Chemical precipitation of cadmium could also have occurred in both systems.

Figures 4.4-4.5 show the mass balance for cadmium in each wetland systems. Relative to the total intake, the cadmium present in the effluent was only about 0.5% in the FWS and 0.2% in the SF and the greater accumulation occured in the soil with values of 84.5% for the FWS and 91.3% for the SF. The lost Cd via other sinks (e.g. precipitation) were about 12.5% and 4.5% of total cadmium uptake for FWS and SF system, respectively.

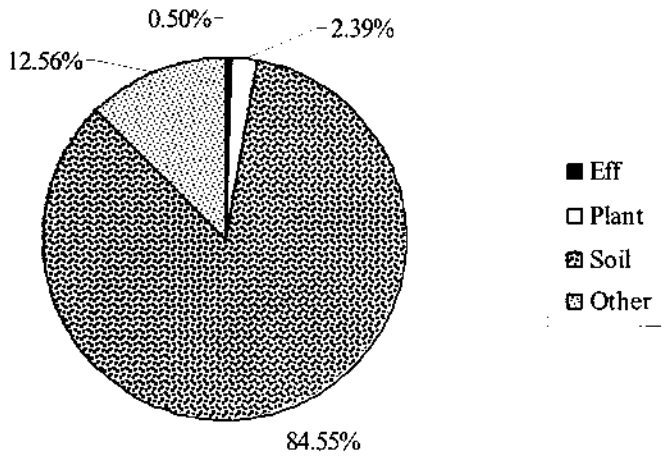


Figure 4.4 Cadmium mass balance in Free water surface wetland system-Part 1

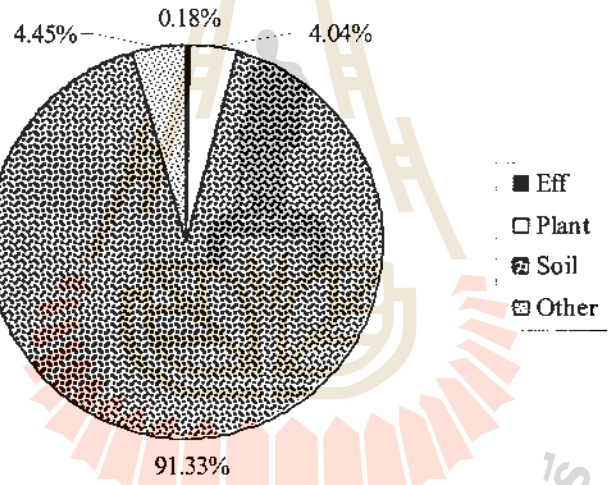


Figure 4.5 Cadmium mass balance in Subsurface flow wetland system-Part1

Part 2

4.7 Tracer study

At the onset of Part 2 of this research, a tracer study was carried out to evaluate the flow pattern in three of the five experimental wetland units. A sodium chloride (NaCl) solution was prepared with tap water at a concentration of 5 g/L and fed into the constructed wetlands. The effluent was analyzed for chloride concentration for the three flowrates used as 51.75 L/d (HRT = 5 days), 36.96 L/d (HRT = 7 days) and 25.88 L/d (HRT = 10 days), respectively. Porosity of the media bed was determined in laboratory (ASTM, 1992) and was found to be 0.44. Chloride (Cl^-)

concentration in the effluent was analyzed at the sampling intervals of 12 hrs during the three HRTs. Raw data of tracer study are given in Tables A.5-A.7 in Appendix A. The values of actual HRT and dispersion number are shown in Table 4.4.

Table 4.4 Actual hydraulic retention time (HRT) and dispersion numbers of constructed wetlands by tracer study (Part 2)

HRT (days)	Actual HRT (days)	Dispersion Number
5	4.78	0.1951
7	6.57	0.1852
10	9.27	0.1855

In view of the moderate dispersion numbers (*d*), the flow characteristics of these constructed wetlands could be classified as approaching plug-flow pattern.

4.8 Influent and effluent concentrations of monitored parameters

During the experimental period (1 year and 6 months), the DO in the influent was in the range of 0-0.3 mg/L. The effluent DO concentrations in the five reactors during three experimental runs varied between 1.6-6.1 mg/L. The ambient, as well as influent and effluent temperatures during the experimental period, varied between 20 and 32 °C. Desirable temperatures for growth of bulrush are 16-27 °C (Reed et al., 1988; USEPA, 1988). The pH of the prepared synthetic wastewater was in the range of 4.2-5.45, while the pH of synthetic wastewater mixed with different cadmium concentrations varied between 4.04 and 5.72. The mean effluent pH during three experimental runs varied between 5.76 and 7.58. Bulrush plants are found to be growing well in a pH range of 4-9 (Reed et al., 1988; USEPA, 1988).

Figure 4.6 shows average removal efficiency of S-COD during three experimental runs. Raw data of S-COD are given in Tables B.5-B.7 in Appendix B. Mean S-COD removal efficiencies in the FWS wetland systems were in the range of 71.58-90.89%. It can be seen in Figure 4.6 that S-COD removal in the wetland units was only slightly affected by the influent Cd concentrations. There was a reduction in S-COD removal with increased influent loading during each run (3.92% in Run 5, 5.12% in Run 6, and 2.76% in Run 7, respectively). With respect to

HRT, the removal increased (15.24% on average) in Run 6 (HRT = 7 days) compared to in Run 5 (HRT = 5 days), but slightly decreased (4.95% on average) in Run 7 (HRT = 10 days). Therefore, 7 days seems to be the optimum HRT for S-COD removal in the FWS wetland systems with bulrush plants in this study.

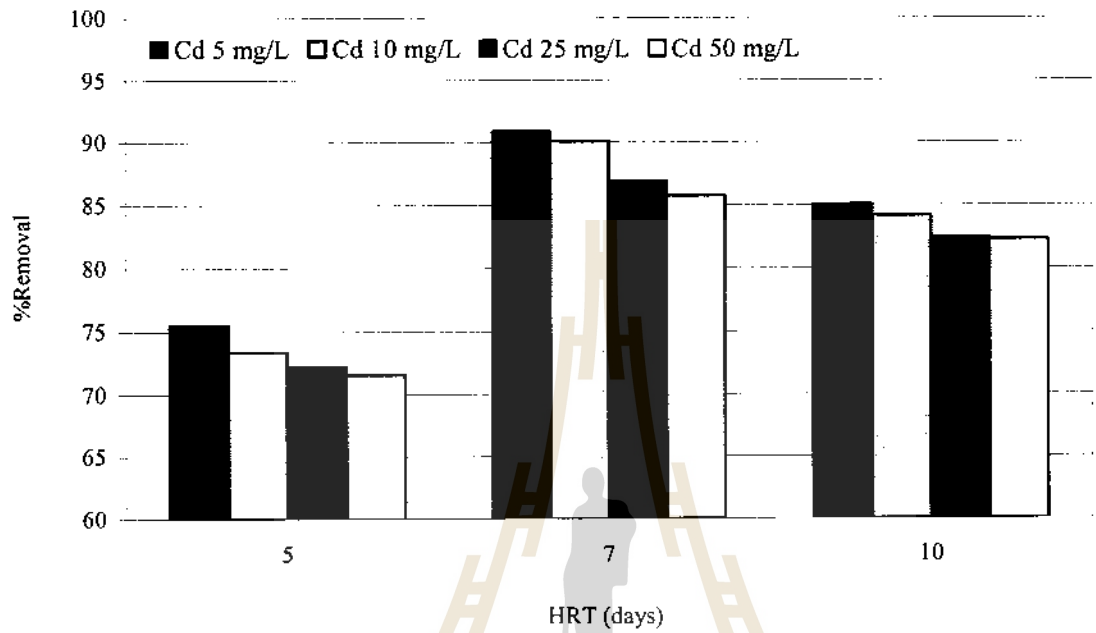


Figure 4.6 Average removal efficiency of S-COD during three experimental runs of Part 2 (Run 5-7)

4.9 Cadmium removal in wastewater

The overall results indicate very effective removal of cadmium in the wetland systems, the detailed data are given in Appendix B. Figure 4.7 shows cadmium removal efficiency of wetland units with four different Cd concentrations in influent during the three experimental runs. The overall average cadmium removal efficiency during the three runs ranged between 75-97% (74.6-81.9% in Run 5 at HRT = 5 days, 82.6-90.8% in Run 6 at HRT = 7 days, and 92.7-96.5% in Run 7 at HRT = 10 days, respectively).

For HRT 5 days, influent and effluent cadmium loadings were 258.8, 517.5, 1,293.8, 2,587.5 mg/d, and 46.6, 99.4, 267.9, 658.5 mg/d, for reactors R6, R7, R8, and R9, respectively. In Run 6, influent and effluent cadmium loadings were 184.8, 369.6, 924, 1,848 mg/d, and 16.7, 38.9, 113.4, 322.3 mg/d, for R6, R7, R8, and R9, respectively. For HRT 10 days, cadmium loadings were 129.4, 258.8, 647, 1,294 mg/d in the influent and 4.5, 10.9, 37.3, 93.9 mg/d in the effluent for R6, R7, R8, and R9, respectively.

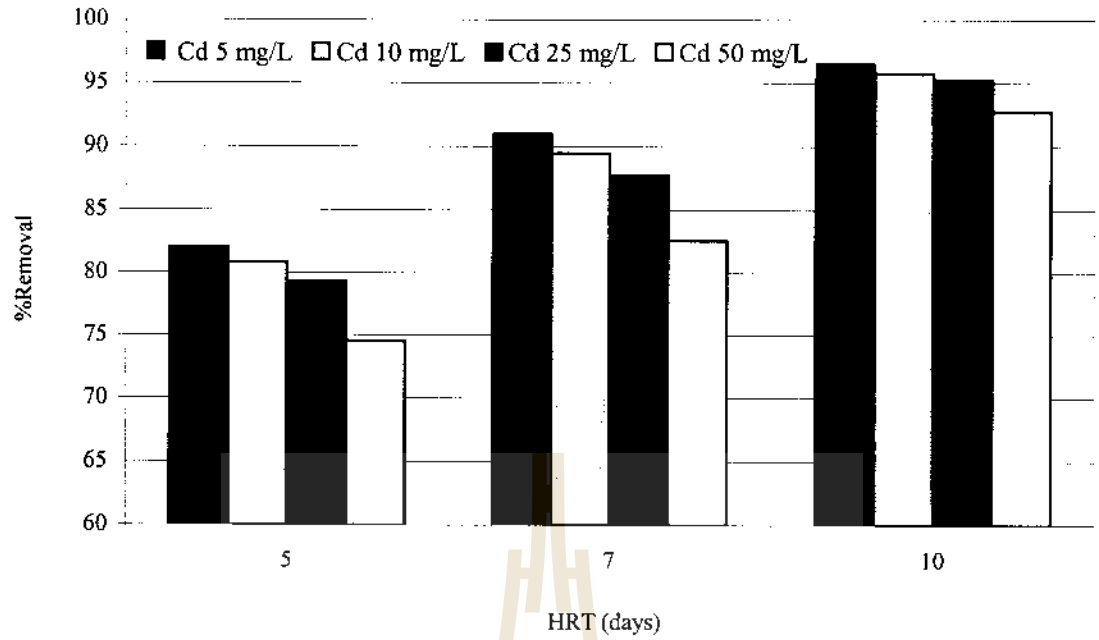


Figure 4.7 Average cadmium removal efficiencies of wetland units during three experimental runs of Part 2 (Run 5-7)

It can be seen in Figure 4.7, that cadmium removal was affected by higher influent loading in each run. Removal decreased with increased loading. However, the removal efficiency for cadmium increased with HRT. Maximum removal occurred at HRT 10 days. Thus, in terms of Cd removal from wastewater in FWS constructed wetlands with bulrush plants, HRT of 10 days seems to be optimum for this study.

4.10 Cadmium removal by soil

Soil samples were collected at the end of each run along reactor lengths at distances of 0.05, 0.65, 1.25, 1.9, and 2.45 m from the inlet, and at depths of 0, 15, 30, and 45 cm from the top of the soil bed. The total accumulation of cadmium in the soils was determined at the end of each run. The results showed a high concentration of cadmium at the inlet that decreased along the reactor length in three experimental runs. Concentrations at the top were higher than at the depth of 15, 30 and 45 cm. The porosity of sand (0.49) being higher than that of the mixture of soils and sands (0.41) could have been the cause of a higher adsorption of cadmium at the top of soil bed. The total cadmium accumulation in soils during three experimental runs is shown in Figure 4.8.

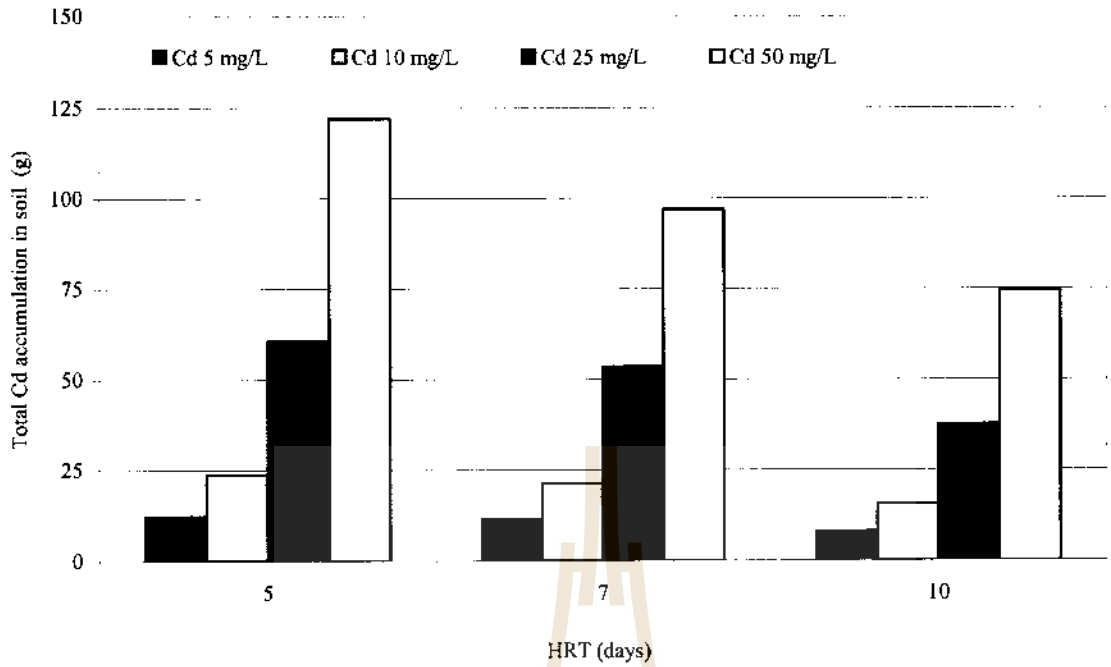


Figure 4.8 Total cadmium accumulation in soil bed in the FWS wetland system during three experimental runs of Part 2 (Run 5-7)

It can be seen in Figure 4.8, that total cadmium accumulation in soil bed increased with influent loading during each run. Also, the accumulation decreased with HRT for all influent concentration.

4.11 Cadmium removal by plant uptake

Bulrush plants were collected at the end of each run along reactor lengths at distances of 0.05, 0.65, 1.25, 1.9, and 2.45 m from the inlet. The cadmium accumulation was determined in each part of plants. Table 4.5 shows the mass density and moisture content of bulrush plants in three experimental runs. It can be seen that the yield for bulrush plants in FWS wetland increased with cadmium concentration during three experimental runs.

Cadmium accumulations in roots and stems of the bulrush plants until the end of each experimental run are shown in Figure 4.9. It can be seen that total Cd accumulation in the stems was higher than in the roots for all four wetland units. It should be also be noted that the cadmium concentration in the roots (mg/g) was found to be higher than in the stems. However, as the dry weight of the roots of bulrushes was only 25% of the stems, the actual mass accumulation of Cd in stems was higher than in the roots.

Table 4.5 Mass density and moisture content of bulrush plants in three experimental runs (Part 2)

Run	Reactors	Wet Weight (kg/m^2)	Moisture (%)
5	R6	45.93	83.97
	R7	47.44	82.66
	R8	53.86	84.75
	R9	71.58	84.88
6	R6	48.15	87.25
	R7	45.29	85.34
	R8	51.72	86.37
	R9	74.54	86.36
7	R6	40.03	87.69
	R7	50.97	87.23
	R8	50.86	85.66
	R9	73.05	86.66

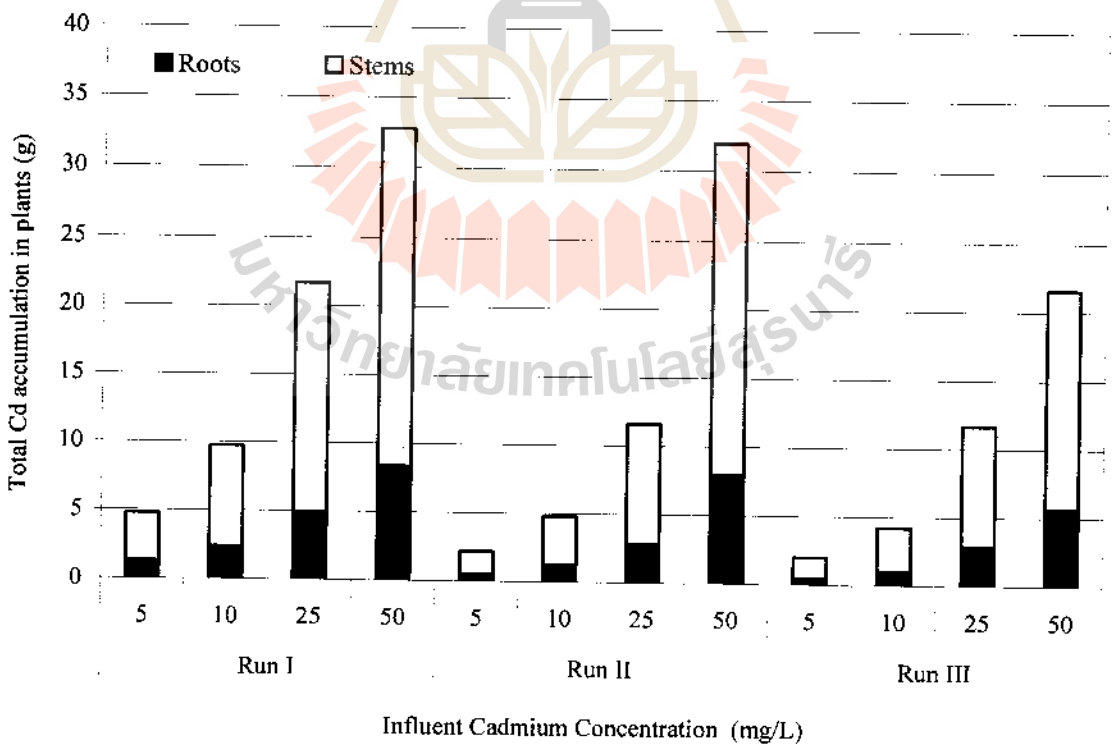


Figure 4.9 Total cadmium accumulation in roots and stems of plants in FWS wetland system at the end of each experimental run in Part 2

It can be seen in Figure 4.9 that, during all the runs cadmium accumulations in stems and roots were higher at high influent loadings. However, the cadmium accumulations in stems and roots at higher HRT (lower loading for each concentration) decreased as compared to those at lower HRT (higher loadings).

4.12 Mass balance

Figure 4.10 shows the mass balance for cadmium during each experimental runs. Relative to the total intake, the cadmium present in the effluents were in the range of 18.1-25.5, 9.1-13.2, and 3.5-7.4% in Run 5, 6, and 7, respectively. The maximum cadmium removal occurred through the accumulation in the soils with mass fraction values of 56.3-57.9, 63.9-74.8, and 69.9-75.5% for HRT = 5 days, 7 days, and 10 days, respectively. The lost Cd via other sinks ranged between 1.5-1.6, 1.7-1.9, and 2.1-2.3% of total cadmium uptake in Run 5, 6, and 7, respectively. Mass fraction of cadmium accumulated in plants ranged between 15.4 and 22.9, 14.4 and 21.1, and 18.9 and 21.9, during Run 5, Run 6, and Run 7, respectively.

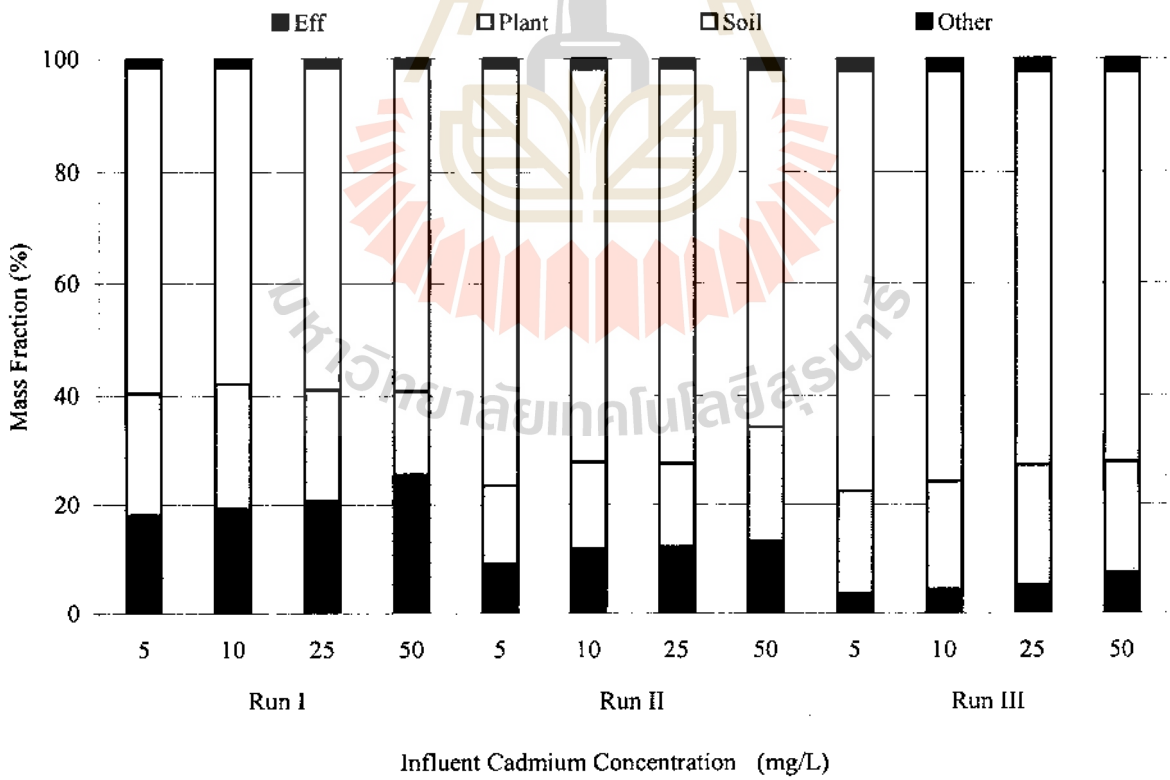


Figure 4.10 Cadmium mass balance in three experimental runs (Part 2)

4.13 Comparison of FWS constructed wetlands under difference environmental conditions

The overall performance of the FWS wetlands in terms of Cd removal was very good. Both, the soils and plants were the sinks for the accumulation of cadmium. Cadmium was sorbed by the soil bed and plant uptake. Chemical precipitation of cadmium could also have occurred in wetland systems. The FWS constructed wetlands for synthetic domestic and industrial wastewater mixed with Cd concentrations of 5 and 10 mg/L was compared for cattail and bulrush plants at HRT 5.5 and 5 days, respectively. Mean S-COD removal efficiencies for influent cadmium concentrations of 5 and 10 mg/L were 86.9% and 85.5% for wetland with cattail plants and 75.5% and 73.9% for wetland with bulrush plants. The average Cd removal efficiencies were 99.5% and 99.4% for FWS wetland system with cattail plants and 81.9% and 80.8% for FWS wetland system with bulrush plants at influent cadmium concentrations of 5 and 10 mg/L, respectively. Mean S-COD and Cd removal efficiencies were only slightly different for the two wetland systems with two different plants at influent cadmium concentrations of 5 and 10 mg/L. High removal efficiencies were observed for synthetic domestic and industrial wastewater and were higher in the FWS constructed wetlands with cattail plants (synthetic domestic wastewater) as compared to the wetlands with bulrush plants (synthetic industrial wastewater).

Chapter V

Conclusions and Recommendations

5.1 Conclusions

Part 1: Treatment performance of free water surface and subsurface constructed wetland systems with cattail plants was investigated by determining removal efficiencies of several monitored parameters including cadmium concentrations in synthetic domestic wastewater. The removal efficiencies of the monitored parameters were not significantly different in the control and experimental reactor units of the two constructed wetlands. For free water surface (FWS) wetland, the overall removal efficiencies ranged between 78-88%, 65-85%, 62-86%, 69-83%, 50-74% for COD, TKN, TP, TSS, and VSS, respectively. The removal efficiencies of these parameters in subsurface flow (SF) wetland were in the range of 88-92%, 85-91%, 74-91%, 78-91%, 62-84%, respectively. Overall cadmium removals of 98.6-99.6% and 99.3-99.9% were achieved for free water surface (FWS) and subsurface flow (SF) wetland, respectively. Most of the cadmium was removed by soil (85-91% of total influent cadmium). Cattail plants could uptake Cd through the roots to stems and leaves' tissues. Of the total cadmium intakes, about 2 to 4% of the total cadmium intake was accumulated in plants. Cattail plants can be classified as heavy metals hyperaccumulators since the concentration of cadmium accumulated in the plant tissue was relatively high. More than 50% of the plant uptake was located in the root tissue.

Part 2: The three FWS constructed wetlands with bulrush plants were used to treat synthetic industrial wastewater with 600-900 mg/L of S-COD. The performance of the wetland system was evaluated for three hydraulic retention times (HRT) 5, 7 and 10 days. The flow characteristics of these constructed wetlands could be classified as approaching plug-flow pattern. The overall average cadmium removal efficiency during the three runs ranged between 75-97% (74.6-81.9% in Run 5 at HRT = 5 days, 82.6-90.8% in Run 6 at HRT = 7 days, and 92.7-96.5% in Run 7 at HRT = 10 days, respectively). Most of the cadmium was accumulated in soils (56-76% of total influent cadmium). Total accumulation of Cd in soil bed was found to be higher in Run 5 (HRT 5 days) and decreased with HRT for all influent concentration. Also, the accumulation increased with influent loading during each run. The cadmium accumulation in soil decreased along the reactor lengths. Cadmium accumulations at the top of soil bed were higher than at the

depth of 15, 30 and 45 cm. The porosity of sand (0.49) being higher than that of the mixture of soils and sands (0.41) could have been the cause of a higher adsorption of cadmium at the top of soil bed. Amount of total Cd uptake by the stems of bulrush plants were higher than roots for all four wetland units fed with synthetic wastewater at different influent loading during the three runs. Of the total cadmium uptakes, about 14 to 23% of the total cadmium intake was accumulated in bulrush plants. During all the runs, cadmium accumulations in stems and roots were higher at high influent loadings. However, the cadmium accumulations in stems and roots at higher HRT (lower loading for each concentration) decreased as compared to those at lower HRT (higher loadings).

The FWS constructed wetlands for synthetic domestic and industrial wastewater mixed with Cd concentrations of 5 and 10 mg/L was compared for cattail and bulrush plants at HRT 5.5 and 5 days, respectively. Mean S-COD removal efficiencies for influent cadmium concentrations of 5 and 10 mg/L were 86.9% and 85.5% for wetland with cattail plants and 75.5% and 73.9% for wetland with bulrush plants. The average Cd removal efficiencies were 99.5% and 99.4% for FWS wetland system with cattail plants and 81.9% and 80.8% for FWS wetland system with bulrush plants at influent cadmium concentrations of 5 and 10 mg/L, respectively. Mean S-COD and Cd removal efficiencies were only slightly different for the two wetland systems with two different plants at influent cadmium concentrations of 5 and 10 mg/L. High removal efficiencies were observed for synthetic domestic and industrial wastewater and were higher in the FWS constructed wetlands with cattail plants (synthetic domestic wastewater) as compared to the wetlands with bulrush plants (synthetic industrial wastewater)

Based on the results of this study, it could be concluded that cadmium at the low concentrations in wastewater may be efficiently removed by using free water surface (FWS) and subsurface flow (SF) wetland systems with cattail plants. The FWS constructed wetland system with bulrush plants may also be effective in cadmium removal from industrial wastewater even at high influent loadings. The optimum HRT for efficient Cd removal from wastewater appears to be 10 days. Thus wetland systems can be used to improve the quality of final effluents from industrial wastewater treatment plants before their disposal into receiving water bodies.

5.2 Recommendations

Based on the results of this study, some recommendations for further research are suggested as follows:

5.2.1 The feasibility study on the reuse/remediation of cattail plants, bulrush plants and soil after the treatment runs in the wetland systems should be conducted in order to avoid public health problems resulting from toxicity of accumulated cadmium in them.

5.2.2 Evaluation of long-term performance of wetlands for treatment of wastewater containing heavy metals, as well as their environmental impact should be investigated.

5.2.3 Since only laboratory-scale data obtained from this study, experiments with full-scale constructed wetlands should be carried out.

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Appendix A

Tracer Study

Table A.1 Data of tracer study of R1

t_i (min)	dt_i	C (mg/L)	C/Co=Ci	$C_i t_i$	$C_i t_i dt_i$	$C_i dt_i$	$t_i^2 Ci\ dti$
20	0	8.82	0.00	0.04	0.00	0.00	0.00
40	20	44.12	0.01	0.35	7.06	0.18	282.37
60	20	70.60	0.01	0.85	16.94	0.28	1,016.64
80	20	167.67	0.03	2.68	53.65	0.67	4,292.35
100	20	220.62	0.04	4.41	88.25	0.88	8,824.80
120	20	255.92	0.05	6.14	122.84	1.02	14,740.99
140	20	264.74	0.05	7.41	148.25	1.06	20,755.62
160	20	317.69	0.06	10.17	203.32	1.27	32,531.46
180	20	397.11	0.08	14.30	285.92	1.59	51,465.46
200	20	423.59	0.08	16.94	338.87	1.69	67,774.40
220	20	450.06	0.09	19.80	396.05	1.80	87,131.62
240	20	529.49	0.11	25.42	508.31	2.12	121,994.50
260	20	661.86	0.13	34.42	688.33	2.65	178,966.94
280	20	529.49	0.11	29.65	593.03	2.12	166,048.06
300	20	458.89	0.09	27.53	550.67	1.84	165,200.40
320	20	432.41	0.09	27.67	553.48	1.73	177,115.14
340	20	264.74	0.05	18.00	360.05	1.06	122,415.78
360	20	238.27	0.05	17.16	343.11	0.95	123,519.17
380	20	185.32	0.04	14.08	281.69	0.74	107,040.83
400	20	176.50	0.04	14.12	282.40	0.71	112,960.00
420	20	167.67	0.03	14.08	281.69	0.67	118,307.95
450	30	132.37	0.03	11.91	357.40	0.79	160,829.55
500	50	132.37	0.03	13.24	661.85	1.32	330,925.00
550	50	88.25	0.02	9.71	485.38	0.88	266,956.25
600	50	79.42	0.02	9.53	476.52	0.79	285,912.00
700	100	61.77	0.01	8.65	864.78	1.24	605,346.00
				SUM	11,226.10	32.35	5,677,327.26

Table A.2 Data of tracer study of R2

t_i (min)	dt_i	C (mg/L)	C/Co=Ci	$C_i t_i$	$C_i t_i dt_i$	$C_i dt_i$	$t_i^2 Ci\ dti$
20	0	8.82	0.00	0.04	0.00	0.00	0.00
40	20	35.30	0.01	0.28	5.65	0.14	225.92
60	20	88.25	0.02	1.06	21.18	0.35	1,270.80
80	20	123.55	0.02	1.98	39.54	0.49	3,162.88
100	20	247.09	0.05	4.94	98.84	0.99	9,883.60
120	20	264.74	0.05	6.35	127.08	1.06	15,249.02
140	20	308.87	0.06	8.65	172.97	1.24	24,215.41
160	20	352.99	0.07	11.30	225.91	1.41	36,146.18
180	20	476.55	0.10	17.16	343.12	1.91	61,760.88
200	20	520.66	0.10	20.83	416.53	2.08	83,305.60
220	20	529.40	0.11	23.29	465.87	2.12	102,491.84
240	20	547.14	0.11	26.26	525.25	2.19	126,061.06
260	20	644.31	0.13	33.50	670.08	2.58	174,221.42
280	20	503.05	0.10	28.17	563.42	2.01	157,756.48
300	20	441.20	0.09	26.47	529.44	1.76	158,832.00
320	20	370.75	0.07	23.73	474.56	1.48	151,859.20
340	20	354.23	0.07	24.09	481.75	1.42	163,795.95
360	20	335.85	0.07	24.18	483.62	1.34	174,104.64
380	20	254.89	0.05	19.37	387.43	1.02	147,224.46
400	20	202.67	0.04	16.21	324.27	0.81	129,708.80
420	20	176.65	0.04	14.84	296.77	0.71	124,644.24
450	30	158.76	0.03	14.29	428.65	0.95	192,893.40
500	50	132.37	0.03	13.24	661.85	1.32	330,925.00
550	50	108.66	0.02	11.95	597.63	1.09	328,696.50
600	50	88.65	0.02	10.64	531.90	0.89	319,140.00
700	100	78.34	0.02	10.97	1,096.76	1.57	767,732.00
				SUM	12,473.85	35.42	6,387,549.28

Table A.3 Data of tracer study of R3

t_i (min)	dt_i	C (mg/L)	C/Co=Ci	$C_i t_i$	$C_i t_i dt_i$	$C_i dt_i$	$t_i^2 Ci\ dti$
20	0	8.82	0.00	0.04	0.00	0.00	0.00
40	20	17.65	0.00	0.14	2.82	0.07	112.96
60	20	70.60	0.01	0.85	16.94	0.28	1,016.64
80	20	97.06	0.02	1.55	31.06	0.39	2,484.74
100	20	132.37	0.03	2.65	52.95	0.53	5,294.80
120	20	176.50	0.04	4.24	84.72	0.71	10,166.40
140	20	308.87	0.06	8.65	172.97	1.24	24,215.41
160	20	335.11	0.07	10.72	214.47	1.34	34,315.26
180	20	397.34	0.08	14.30	286.08	1.59	51,495.26
200	20	441.89	0.09	17.68	353.51	1.77	70,702.40
220	20	529.65	0.11	23.30	466.09	2.12	102,540.24
240	20	547.14	0.11	26.26	525.25	2.19	126,061.06
260	20	635.08	0.13	33.02	660.48	2.54	171,725.63
280	20	555.67	0.11	31.12	622.35	2.22	174,258.11
300	20	476.54	0.10	28.59	571.85	1.91	171,554.40
320	20	450.05	0.09	28.80	576.06	1.80	184,340.48
340	20	405.34	0.08	27.56	551.26	1.62	187,429.22
360	20	397.11	0.08	28.59	571.84	1.59	205,861.82
380	20	361.83	0.07	27.50	549.98	1.45	208,993.01
400	20	326.55	0.07	26.12	522.48	1.31	208,992.00
420	20	220.63	0.04	18.53	370.66	0.88	155,676.53
450	30	132.89	0.03	11.96	358.80	0.80	161,461.35
500	50	105.09	0.02	10.51	525.45	1.05	262,725.00
550	50	88.25	0.02	9.71	485.38	0.88	266,956.25
600	50	70.60	0.01	8.47	423.60	0.71	254,160.00
700	100	52.95	0.01	7.41	741.30	1.06	518,910.00
				SUM	11,379.43	33.62	5,324,174.97

Table A.4 Data of tracer study of R4

t_i (min)	dt_i	C (mg/L)	C/Co=Ci	$C_i t_i$	$C_i t_i dt_i$	$C_i dt_i$	$t_i^2 Ci\ dti$
20	0	8.82	0.00	0.04	0.00	0.00	0.00
40	20	17.65	0.00	0.14	2.82	0.07	112.96
60	20	44.12	0.01	0.53	10.59	0.18	635.33
80	20	61.77	0.01	0.99	19.77	0.25	1,581.31
100	20	132.37	0.03	2.65	52.95	0.53	5,294.80
120	20	202.96	0.04	4.87	97.42	0.81	11,690.50
140	20	264.74	0.05	7.41	148.25	1.06	20,755.62
160	20	300.04	0.06	9.60	192.03	1.20	30,724.10
180	20	317.34	0.06	11.42	228.48	1.27	41,127.26
200	20	370.89	0.07	14.84	296.71	1.48	59,342.40
220	20	432.41	0.09	19.03	380.52	1.73	83,714.58
240	20	555.14	0.11	26.65	532.93	2.22	127,904.26
260	20	653.05	0.13	33.96	679.17	2.61	176,584.72
280	20	520.99	0.10	29.18	583.51	2.08	163,382.46
300	20	476.54	0.10	28.59	571.85	1.91	171,554.40
320	20	450.05	0.09	28.80	576.06	1.80	184,340.48
340	20	361.82	0.07	24.60	492.08	1.45	167,305.57
360	20	291.11	0.06	20.96	419.20	1.16	150,911.42
380	20	264.74	0.05	20.12	402.40	1.06	152,913.82
400	20	202.94	0.04	16.24	324.70	0.81	129,881.60
420	20	176.90	0.04	14.86	297.19	0.71	124,820.64
450	30	123.55	0.02	11.12	333.59	0.74	150,113.25
500	50	105.09	0.02	10.51	525.45	1.05	262,725.00
550	50	79.42	0.02	8.74	436.81	0.79	240,245.50
600	50	61.77	0.01	7.41	370.62	0.62	222,372.00
700	100	44.12	0.01	6.18	617.68	0.88	432,376.00
				SUM	10,145.99	30.24	4,489,109.97

Table A.5 Data of tracer study of HRT = 5 days

t_i (hrs)	dt_i	C (mg/L)	C/Co=Ci	$C_i t_i$	$C_i t_i dt_i$	$C_i dt_i$	t_i^2Ci dti
0	0	5.21	0.00	0.00	0.00	0.00	0.00
12	12	317.84	0.06	0.76	9.15	0.76	109.85
24	12	561.53	0.11	2.70	32.34	1.35	776.26
36	12	489.00	0.10	3.52	42.25	1.17	1,520.99
48	12	410.16	0.08	3.94	47.25	0.98	2,268.02
60	12	361.15	0.07	4.33	52.01	0.87	3,120.34
72	12	315.86	0.06	4.55	54.58	0.76	3,929.80
84	12	297.20	0.06	4.99	59.92	0.71	5,032.90
96	12	254.39	0.05	4.88	58.61	0.61	5,626.70
108	12	198.81	0.04	4.29	51.53	0.48	5,565.41
120	12	186.64	0.04	4.48	53.75	0.45	6,450.28
132	12	173.14	0.03	4.57	54.85	0.42	7,240.30
144	12	148.45	0.03	4.28	51.30	0.36	7,387.82
156	12	125.76	0.03	3.92	47.08	0.30	7,345.19
168	12	118.46	0.02	3.98	47.76	0.28	8,024.20
180	12	101.78	0.02	3.66	43.97	0.24	7,914.41
192	12	96.51	0.02	3.71	44.47	0.23	8,538.59
204	12	92.65	0.02	3.78	45.36	0.22	9,253.73
216	12	82.31	0.02	3.56	42.67	0.20	9,216.61
228	12	71.25	0.01	3.25	38.99	0.17	8,889.26
240	12	70.05	0.01	3.36	40.35	0.17	9,683.71
252	12	69.59	0.01	3.51	42.09	0.17	10,606.18
264	12	67.74	0.01	3.58	42.92	0.16	11,330.90
276	12	66.82	0.01	3.69	44.26	0.16	12,216.19
288	12	64.52	0.01	3.72	44.60	0.15	12,843.71
300	12	57.61	0.01	3.46	41.48	0.14	12,443.76
				SUM	1,414.49	12.33	275,036.17

Table A.6 Data of tracer study of HRT = 7 days

t_i (hrs)	dt_i	C (mg/L)	C/Co=Ci	$C_i t_i$	$C_i t_i dt_i$	$C_i dt_i$	t_i^2Ci dti
0	0	19.54	0.004	0.000	0.000	0.000	0.000
12	12	302.85	0.061	0.727	8.722	0.727	104.665
24	12	575.67	0.115	2.763	33.159	1.382	795.806
36	12	537.52	0.108	3.870	46.442	1.290	1,671.902
48	12	500.02	0.100	4.800	57.602	1.200	2,764.911
60	12	436.48	0.087	5.238	62.853	1.048	3,771.187
72	12	411.57	0.082	5.927	71.119	0.988	5,120.589
84	12	396.26	0.079	6.657	79.886	0.951	6,710.425
96	12	352.23	0.070	6.763	81.154	0.845	7,790.764
108	12	306.67	0.061	6.624	79.489	0.736	8,584.797
120	12	297.51	0.060	7.140	85.683	0.714	10,281.946
132	12	276.51	0.055	7.300	87.598	0.664	11,562.985
144	12	246.42	0.049	7.097	85.163	0.591	12,263.436
156	12	241.80	0.048	7.544	90.530	0.580	14,122.668
168	12	216.29	0.043	7.267	87.208	0.519	14,650.966
180	12	188.35	0.038	6.781	81.367	0.452	14,646.096
192	12	174.89	0.035	6.716	80.589	0.420	15,473.148
204	12	165.18	0.033	6.739	80.872	0.396	16,497.914
216	12	159.14	0.032	6.875	82.498	0.382	17,819.606
228	12	134.43	0.027	6.130	73.560	0.323	16,771.702
240	12	129.04	0.026	6.194	74.327	0.310	17,838.490
252	12	122.59	0.025	6.179	74.142	0.294	18,683.893
264	12	123.51	0.025	6.521	78.256	0.296	20,659.567
276	12	120.74	0.024	6.665	79.978	0.290	22,073.977
288	12	116.13	0.023	6.689	80.269	0.279	23,117.488
300	12	102.77	0.021	6.166	73.994	0.247	22,198.320
				SUM	2,972.119	18.859	770,515.366

Table A.7 Data of tracer study of HRT = 10 days

t_i (hrs)	dt_i	C (mg/L)	C/Co=Ci	$C_i t_i$	$C_i t_i dt_i$	$C_i dt_i$	$t_i^2 Ci\ dti$
0	0	40.34	0.01	0.00	0.00	0.00	0.00
12	12	400.12	0.08	0.96	11.52	0.96	138.28
24	12	605.22	0.12	2.91	34.86	1.45	836.66
36	12	575.39	0.12	4.14	49.71	1.38	1,789.69
48	12	485.17	0.10	4.66	55.89	1.16	2,682.80
60	12	455.12	0.09	5.46	65.54	1.09	3,932.24
72	12	439.74	0.09	6.33	75.99	1.06	5,471.07
84	12	405.10	0.08	6.81	81.67	0.97	6,860.13
96	12	382.01	0.08	7.33	88.02	0.92	8,449.45
108	12	344.87	0.07	7.45	89.39	0.83	9,654.15
120	12	330.12	0.07	7.92	95.07	0.79	11,408.95
132	12	311.50	0.06	8.22	98.68	0.75	13,026.18
144	12	287.95	0.06	8.29	99.52	0.69	14,330.23
156	12	273.44	0.05	8.53	102.38	0.66	15,970.65
168	12	257.23	0.05	8.64	103.72	0.62	17,424.14
180	12	247.51	0.05	8.91	106.92	0.59	19,246.38
192	12	238.75	0.05	9.17	110.02	0.57	21,123.07
204	12	223.81	0.04	9.13	109.58	0.54	22,353.78
216	12	201.63	0.04	8.71	104.52	0.48	22,577.40
228	12	195.11	0.04	8.90	106.76	0.47	24,342.24
240	12	182.81	0.04	8.77	105.30	0.44	25,271.65
252	12	175.14	0.04	8.83	105.92	0.42	26,693.02
264	12	166.67	0.03	8.80	105.60	0.40	27,878.96
276	12	154.10	0.03	8.51	102.08	0.37	28,172.93
288	12	148.29	0.03	8.54	102.50	0.36	29,519.44
300	12	145.15	0.03	8.71	104.51	0.35	31,352.40
				SUM	4,812.88	24.24	1,572,853.80

Appendix B

Data of experiment

Table B.2 Data of COD of Run 2

Frequency	R1			R2			R3			R4		
	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.
1	123.08	22.68	81.57				123.08	18.90	84.64	125.25	20.15	83.91
2	117.20	32.14	72.58				117.20	15.12	87.10	117.20	15.12	87.10
3				100.82	30.77	69.48				111.54	11.54	89.65
4	128.77	22.68	82.39	125.63	36.54	70.91	124.77	19.23	84.59	123.08	23.08	81.25
5	121.15	32.69	73.02	127.88	32.69	74.44	120.84	11.54	90.45			
6	119.23	30.77	74.19									
7				121.15	26.92	77.78	129.78	23.08	82.22			
8	129.77	30.77	76.29	117.20	25.00	78.67	128.77	21.15	83.58	117.20	21.15	81.95
9	125.25	31.44	74.90	120.44	30.48	74.69	128.44	11.43	91.10	116.72	22.47	80.75
10	111.27	25.24	77.32	127.36	32.33	74.62	113.42	24.23	78.64	127.36	25.93	79.64
11	100.56	28.47	71.69	120.88	30.48	74.78	98.81	14.98	84.84	118.29	22.23	81.21
12	120.38	30.25	74.87	122.34	31.24	74.46	120.38	22.63	81.20	122.34	25.41	79.23
Mean	119.67	28.71	75.88	120.41	30.72	74.43	120.549	18.229	84.84	119.89	20.78667	82.74

Table B.4 Data of COD of Run 4

Frequency	R1			R2			R3			R4		
	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.
1	125.69	31.47	74.96	107.20	28.78	73.15	125.69	19.13	84.78	107.20	20.96	80.45
2	113.50	38.03	66.49	96.82	34.33	64.54	113.50	17.98	84.16	96.82	15.78	83.70
3	120.09	45.88	61.80	108.60	43.51	59.94	120.09	26.93	77.58	108.60	23.47	78.39
4	109.39	49.24	54.99	115.65	47.21	59.18	109.39	23.22	78.77	115.65	25.18	78.23
5	98.85	42.51	57.00	95.09	40.62	57.28	98.85	33.64	65.97	95.09	32.52	65.80
6	93.20	36.38	60.97	90.42	38.24	57.71	93.20	31.86	65.82	90.42	29.75	67.10
7	109.43	34.52	68.45	116.98	33.66	71.23	109.43	24.48	77.63	116.98	23.64	79.79
8	90.19	38.03	57.83	99.73	42.97	56.91	90.19	27.44	69.58	99.73	25.08	74.85
9	124.08	35.21	71.62	107.55	35.21	67.26	124.08	25.58	79.38	107.55	24.55	77.17
10	112.80	34.96	69.01	114.77	36.12	68.53	112.80	21.84	80.64	114.77	25.02	78.20
11	107.32	29.62	72.40	106.63	31.48	70.48	107.32	19.75	81.60	106.63	18.04	83.08
12	121.25	25.53	78.94	125.56	28.73	77.12	121.25	22.46	81.48	125.56	19.64	84.36
Mean	111.03	36.14	66.94	107.09	36.06	65.94	111.03	23.85	78.00	107.09	23.37	77.87

Table B.6 Data of COD of Run 6

Frequency	R5			R6			R7			R8			R9		
	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.
1	738	78	89.43	719	62	91.38	801	125	84.39	868	79	90.90	781	41	94.75
2	649	121	81.36	652	241	63.04	698	202	71.06	866	80	90.76	881	99	88.76
3	727	55	92.43	854	145	83.02	891	254	71.49	673	182	72.96	455	109	76.04
4	582	247	57.56	476	176	63.03	564	247	56.21	564	123	78.19	653	247	62.17
5	529	194	63.33	529	159	69.94	547	229	58.14	723	106	85.34	741	106	85.70
6	582	88	84.88	600	123	79.50	653	88	86.52	706	35	95.04	741	53	92.85
7	582	106	81.79	635	71	88.82	653	123	81.16	706	71	89.94	776	35	95.49
8	600	103	82.83	651	154	76.34	668	154	76.95	720	120	83.33	754	86	88.59
9	617	69	88.82	651	86	86.79	668	69	89.67	720	51	92.92	754	86	88.59
10	600	103	82.83	634	120	81.07	651	103	84.18	686	154	77.55	754	120	84.08
11	600	86	85.67	617	69	88.82	668	69	89.67	703	69	90.18	737	69	90.64
12	583	189	67.58	617	51	91.73	668	86	87.13	703	51	92.75	754	34	95.49
Mean	606	86	85.64	636	81	86.90	676	95	85.76	715	69	90.11	751	65	90.89

Table B.8 Data of TKN of Run 1

Frequency	R1			R2			R3			R4		
	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.
1	5.60	3.36	40.00	5.32	3.08	42.11	5.32	2.24	57.89	5.60	2.24	60.00
2	5.04	2.80	44.44	5.04	3.08	38.89	5.32	2.24	57.89	5.32	2.24	57.89
3	5.32	2.80	47.37	5.32	2.80	47.37	5.04	1.68	66.67	5.04	1.68	66.67
4	5.04	1.68	66.67	5.04	2.24	55.56	4.48	1.12	75.00	5.04	1.12	77.78
5	5.04	2.24	55.56				5.32	1.12	78.95	5.04	1.12	77.78
6	5.32	2.24	57.89	5.04	2.80	44.44	5.04	1.68	66.67	5.32	1.68	68.42
7	6.16	2.80	54.55	5.60	2.24	60.00	5.04	1.68	66.67	5.04	1.40	72.22
8	5.32	3.08	42.11	5.60	3.36	40.00	5.32	1.12	78.95	5.60	1.68	70.00
9	5.32	3.08	42.11	5.32	3.08	42.11	6.44	1.40	78.26	5.32	1.40	73.68
10	5.32	2.52	52.63	6.44	2.24	65.22	5.32	1.40	73.68	5.60	1.12	80.00
11	6.44	3.08	52.17	6.16	3.08	50.00	6.16	1.12	81.82	5.60	1.12	80.00
12	5.60	2.80	50.00	5.60	3.08	45.00	5.60	0.84	85.00	6.16	1.40	77.27
Mean	5.44	2.62	51.93	5.41	2.66	50.59	5.32	1.24	76.52	5.31	1.23	76.92

Table B.10 Data of TKN of Run 3

Frequency	R1			R2			R3			R4		
	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.
1	5.44	2.80	48.53	6.16	2.80	54.55	5.60	1.40	75.00	6.16	0.56	90.91
2	5.32	2.24	57.89	6.16	3.08	50.00	5.32	1.68	68.42	6.44	1.12	82.61
3	5.60	3.36	40.00	5.32	2.80	47.37	5.60	1.12	80.00	5.32	1.68	68.42
4	6.16	3.36	45.45	5.44	3.08	43.38	5.60	1.12	80.00	5.44	1.12	79.41
5	5.32	2.80	47.37	5.44	3.36	38.24	5.32	1.96	63.16	5.60	1.12	80.00
6	5.32	2.24	57.89	5.04	2.24	55.56	5.32	2.24	57.89	5.04	1.96	61.11
7	5.44	2.52	53.68	5.32	2.52	52.63	5.44	1.96	63.97	5.32	2.24	57.89
8	5.60	1.40	75.00	5.44	1.40	74.26	5.60	1.68	70.00	5.60	2.24	60.00
9	5.60	1.12	80.00	5.60	1.40	75.00	5.44	0.56	89.71	5.60	0.56	90.00
10	5.32	0.84	84.21	5.32	2.24	57.89	5.04	0.56	88.89	5.44	0.56	89.71
11	5.32	0.56	89.47	5.44	0.56	89.71	5.32	0.56	89.47	5.44	0.56	89.71
12	5.44	0.56	89.71	5.32	0.56	89.47	5.44	0.56	89.71	5.44	0.56	89.71
Mean	5.49	1.87	66.07	5.49	2.05	62.89	5.41	1.23	77.36	5.55	1.14	79.15

Table B.12 Data of TP of Run 1

Frequency	R1			R2			R3			R4		
	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.
1	1.39	1.02	26.62	1.50	1.02	32.00	1.50	0.80	46.67	1.02	0.80	21.57
2	1.44	1.10	23.61	1.50	1.10	26.67	1.39	1.10	20.86	1.10	0.80	27.27
3	1.50	0.96	36.00	1.44	0.96	33.33	1.50	0.96	36.00	1.44	0.80	44.44
4	1.23	0.91	26.02	1.39	0.96	30.94	1.39	0.80	42.45			
5	1.44	0.80	44.44	1.44	0.91	36.81	1.39	0.85	38.85	1.44	0.96	33.33
6	1.39	0.80	42.45	1.39	0.85	38.85	1.44	0.65	54.86	1.39	0.80	42.45
7	1.39	0.75	46.04	1.39	0.85	38.85	1.39	0.65	53.24	1.44	0.65	54.86
8	1.50	0.80	46.67	1.50	0.80	46.67	1.28	0.65	49.22	1.44	0.65	54.86
9	1.28	0.80	37.50	1.28	0.80	37.50	1.34	0.43	67.91	1.39	0.43	69.06
10	1.50	0.85	43.33	1.39	0.80	42.45	1.50	0.43	71.33	1.39	0.43	69.06
11	1.44	0.59	59.03	1.34	0.59	55.97	1.39	0.49	64.75	1.34	0.43	67.91
12	1.39	0.65	53.24	1.50	0.75	50.00	1.44	0.43	70.14	1.44	0.49	65.97
Mean	1.39	0.71	48.58	1.38	0.73	47.26	1.35	0.54	60.28	1.33	0.53	59.89

Table B.14 Data of TP of Run 3

Frequency	R1			R2			R3			R4		
	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.
1	1.44	0.27	81.25	1.71	0.43	74.85	1.50	0.17	88.67	1.71	0.38	77.78
2	1.39	0.33	76.26	1.77	0.49	72.32	1.39	0.27	80.58	1.77	0.27	84.75
3	1.44	0.33	77.08	1.39	0.38	72.66	1.44	0.43	70.14	1.39	0.38	72.66
4	1.50	0.54	64.00	1.44	0.59	59.03	1.50	0.43	71.33	1.02	0.49	51.96
5	1.61	0.65	59.63	1.50	0.65	56.67	1.61	0.59	63.35	1.50	0.43	71.33
6	1.66	0.70	57.83	1.61	0.70	56.52	1.66	0.49	70.48	1.61	0.33	79.50
7	1.50	0.59	60.67	1.71	0.80	53.22	1.44	0.27	81.25	1.61	0.43	73.29
8	1.66	0.59	64.46	1.44	0.80	44.44	1.50	0.27	82.00	1.44	0.27	81.25
9	1.29	0.54	58.14	1.50	0.59	60.67	1.29	0.33	74.42	1.50	0.33	78.00
10	1.34	0.65	51.49	1.50	0.54	64.00	1.34	0.27	79.85	1.44	0.33	77.08
11	1.50	0.54	64.00	1.50	0.54	64.00	1.50	0.33	78.00	1.44	0.27	81.25
12	1.50	0.54	64.00	1.44	0.43	70.14	1.39	0.33	76.26	1.66	0.22	86.75
Mean	1.45	0.51	65.11	1.50	0.57	62.03	1.46	0.35	76.08	1.47	0.33	76.46

Table B.16 Data of TSS of Run 1

Frequency	R1			R2			R3			R4		
	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.
1	84.00	54.00	35.71	80.00	56.00	30.00	76.00	32.00	57.89	86.00	50.00	41.86
2	78.00	56.00	28.21	92.00	74.00	19.57	88.00	44.00	50.00	80.00	52.00	35.00
3				108.00	16.00	85.19	64.00	40.00	37.50	98.00	24.00	75.51
4	56.00	24.00	57.14	64.00	46.00	28.13	78.00	42.00	46.15	62.00	34.00	45.16
5	56.00	28.00	50.00	56.00	44.00	21.43	66.00	32.00	51.52			
6	52.00	20.00	61.54				58.00	20.00	65.52	58.00	20.00	65.52
7	62.00	28.00	54.84	70.00	38.00	45.71	64.00	28.00	56.25	68.00	34.00	50.00
8	74.00	32.00	56.76	56.00	20.00	64.29	66.00	22.00	66.67	64.00	28.00	56.25
9	78.00	38.00	51.28	68.00	32.00	52.94	80.00	30.00	62.50	70.00	26.00	62.86
10	58.00	24.00	58.62				60.00	16.00	73.33	68.00	22.00	67.65
11	50.00	18.00	64.00	56.00	30.00	46.43				72.00	16.00	77.78
12	72.00	46.00	36.11	76.00	38.00	50.00	76.00	32.00	57.89	84.00	38.00	54.76
Mean	74.82	30.47	57.30	83.06	36.12	52.74	78.10	23.50	67.94	75.53	27.06	63.40

Table B.18 Data of TSS of Run 3

Frequency	R1			R2			R3			R4		
	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.
1										122.00	52.00	57.38
2							80.00	28.00	65.00	76.00	32.00	57.89
3	78.00	52.00	33.33	86.00	64.00	25.58	74.00	58.00	21.62	86.00	72.00	16.28
4	52.00	16.00	69.23	104.00	54.00	48.08	56.00	8.00	85.71	112.00	4.00	96.43
5	112.00	44.00	60.71	150.00	52.00	65.33	112.00	46.00	58.93			
6				140.00	48.00	65.71	144.00	20.00	86.11	140.00	28.00	80.00
7	118.00	20.00	83.05				118.00	14.00	88.14	110.00	24.00	78.18
8	76.00	46.00	39.47	118.00	50.00	57.63	82.00	10.00	87.80	124.00	12.00	90.32
9	132.00	36.00	72.73	150.00	28.00	81.33	132.00	52.00	60.61	152.00	52.00	65.79
10				116.00	96.00	17.24				104.00	8.00	92.31
11	110.00	96.00	12.73	90.00	58.00	35.56	110.00	28.00	74.55	94.00	44.00	53.19
12	100.00	20.00	80.00	88.00	68.00	22.73	120.00	34.00	71.67	88.00	22.00	75.00
Mean	100.00	42.44	56.51	110.60	54.20	48.17	104.00	29.27	70.86	106.00	30.00	70.60

Table B.20 Data of Cd of Run 1

Frequency	R1			R2			R3			R4		
	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.
1	0.00	0.00		0.89	0.03	96.11	0.00	0.04		0.95	0.02	98.12
2	0.00	0.00		0.86	0.07	92.39	0.01	0.00		0.97	0.03	97.32
3	0.01	0.00		0.83	0.07	91.47	0.01	0.01		1.02	0.03	97.40
4	0.01	0.01		0.88	0.02	97.35	0.01	0.01		0.97	0.03	97.02
5	0.01	0.00		0.98	0.02	98.25	0.01	0.00		0.90	0.00	100.00
6	0.01	0.01		0.94	0.01	98.67	0.01	0.01		0.87	0.01	98.95
7	0.01	0.01		0.93	0.01	98.68	0.01	0.01		0.84	0.01	99.03
8	0.01	0.00		1.18	0.01	99.15	0.00	0.01		1.09	0.01	99.44
9	0.01	0.01		1.03	0.01	98.85	0.00	0.01		0.95	0.02	98.26
10	0.01	0.00		0.95	0.02	98.06	0.01	0.01		1.03	0.01	99.20
11	0.01	0.00		1.07	0.01	99.27	0.01	0.01		1.04	0.01	99.16
12	0.01	0.00		1.05	0.01	98.85	0.01	0.00		1.07	0.01	99.25
Mean	0.01	0.00		0.95	0.02	98.03	0.01	0.01		0.95	0.01	98.93

Table B.22 Data of Cd of Run 3

Frequency	R1			R2			R3			R4		
	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.
1	0.01	0.01		12.01	0.03	99.79	0.01	0.00		12.01	0.03	99.78
2	0.01	0.01		11.51	0.19	98.35	0.01	0.01		11.51	0.03	99.74
3	0.01	0.01		8.93	0.22	97.58	0.01	0.00		8.93	0.09	99.01
4	0.01	0.01		11.69	0.19	98.35	0.01	0.02		11.69	0.07	99.41
5	0.02	0.02		11.75	0.20	98.32	0.02	0.02		11.75	0.07	99.44
6	0.02	0.00		11.12	0.32	97.16	0.02	0.01		11.12	0.03	99.74
7	0.03	0.01		11.67	0.23	98.04	0.03	0.02		11.67	0.01	99.91
8	0.01	0.02		12.84	0.23	98.22	0.01	0.02		12.84	0.02	99.85
9	0.01	0.00		11.96	0.09	99.21	0.01	0.00		11.96	0.07	99.41
10	0.01	0.00		9.25	0.06	99.35	0.01	0.01		9.25	0.03	99.72
11	0.01	0.00		12.10	0.04	99.70	0.01	0.00		12.10	0.03	99.76
12	0.01	0.00		11.85	0.07	99.37	0.01	0.00		11.85	0.02	99.84
Mean	0.01	0.01		11.30	0.15	98.67	0.01	0.01		11.30	0.04	99.65

Table B.24 Data of Cd of Run 5

Frequency	R5			R6			R7			R8			R9		
	Inf (mg/L)	Eff (mg/L)	%R.E.	Inf (mg/L)	Eff (mg/L)	%R.E.	Inf (mg/L)	Eff (mg/L)	%R.E.	Inf (mg/L)	Eff (mg/L)	%R.E.	Inf (mg/L)	Eff (mg/L)	%R.E.
1	0.133	0.125	6.02	5.300	1.202	77.32	10.300	1.214	88.21	24.650	6.200	74.85	50.200	13.216	73.67
2	0.162	0.149	8.02	6.000	1.125	81.25	9.400	2.105	77.61	25.350	5.800	77.12	52.000	14.280	72.54
3	0.143	0.133	6.99	5.100	0.961	81.15	10.050	1.516	84.92	25.710	4.070	84.17	53.440	15.220	71.52
4	0.267	0.252	5.62	4.820	0.985	79.56	9.650	2.413	74.99	24.390	6.170	74.70	53.460	15.690	70.65
5	0.114	0.101	11.40	5.130	1.200	76.61	9.440	2.227	76.41	24.220	4.590	81.05	47.300	15.190	67.89
6	0.138	0.126	8.70	4.740	1.180	75.11	10.070	3.074	69.47	25.680	5.190	79.79	50.930	14.360	71.80
7	0.125	0.125	0.00	5.000	0.729	85.43	10.620	2.411	77.30	26.140	4.050	84.51	51.000	13.160	74.20
8	0.245	0.243	0.82	4.800	1.110	76.88	10.580	2.657	74.89	25.570	5.920	76.85	47.000	13.423	71.44
9	0.315	0.301	4.44	5.200	0.962	81.50	9.710	2.443	74.84	24.220	4.360	82.00	48.000	14.550	69.69
10	0.194	0.191	1.55	5.110	0.885	82.68	9.630	1.260	86.92	24.010	5.750	76.05	49.000	14.733	69.93
11	0.231	0.226	2.16	4.690	0.744	84.14	9.750	1.734	82.22	24.440	5.946	75.67	47.670	15.950	66.54
12	0.377	0.358	5.04	4.850	1.060	78.14	10.220	1.438	85.93	25.820	4.660	81.95	52.310	14.740	71.82
Mean	0.226	0.217	4.33	5.001	0.961	80.77	9.940	1.909	80.79	25.073	5.177	79.32	50.555	14.498	71.28

Table B.26 Data of Cd of Run 7

Frequency	R5			R6			R7			R8			R9		
	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.	Inf (mg/L)	Eff (mg/L)	% R.E.
1	0.078	0.000	100.000	6.141	0.352	94.267	11.318	0.601	94.687	24.151	1.116	95.377	50.421	1.679	96.670
2	0.000	0.000	0.000	5.849	0.413	92.944	12.637	0.658	94.791	26.666	1.389	94.791	48.186	1.946	95.962
3	0.000	0.000	0.000	5.891	0.343	94.184	11.566	0.557	95.187	24.386	1.299	94.673	51.846	1.992	96.157
4	0.000	0.000	0.000	4.810	0.383	92.031	11.749	0.460	96.087	25.678	1.139	95.564	51.718	1.786	96.546
5	0.000	0.000	0.000	4.769	0.162	96.601	9.437	0.487	94.836	25.223	1.180	95.322	50.623	1.430	97.175
6	0.000	0.000	0.000	4.654	0.284	93.899	10.929	0.400	96.341	26.400	0.927	96.490	49.270	1.330	97.302
7	0.243	0.000	100.000	4.940	0.221	95.518	12.329	0.514	95.835	27.291	1.164	95.735	49.581	1.276	97.427
8	0.431	0.000	100.000	5.136	0.334	93.497	12.678	0.535	95.780	24.965	1.045	95.814	48.589	1.004	97.934
9	0.000	0.000	0.000	5.442	0.293	94.611	9.839	0.456	95.365	24.269	0.933	96.154	52.394	2.149	95.899
10	0.000	0.000	0.000	5.105	0.258	94.942	9.360	0.482	94.851	24.561	0.847	96.551	50.471	2.049	95.941
11	0.000	0.000	0.000	5.308	0.595	88.789	9.336	0.547	94.139	24.607	1.005	95.917	50.337	2.217	95.597
12	0.000	0.018	0.000	5.672	0.645	88.627	10.210	0.515	94.960	25.384	1.096	95.682	51.254	1.129	97.797
Mean	0.055	0.020	24.037	5.104	0.371	92.741	10.895	0.515	95.243	25.370	1.073	95.765	50.219	1.766	96.486

Appendix C

Calculation of coefficient of variation

Table C.1 Coefficient of variation of FWS

Comparison of the average removal efficiencies between control unit and experimental unit of free water surface wetland systems.

Parameters	RUN	Mean	Standard Deviation	Coefficient of variation
COD	1	79.19	1.17	1.47
	2	86.99	0.18	0.21
	3	87.79	0.39	0.44
	4	86.22	0.40	0.47
TKN	1	65.30	0.83	1.27
	2	74.90	1.48	1.98
	3	84.48	1.33	1.57
	4	83.05	1.58	1.91
TP	1	62.33	1.06	1.70
	2	80.18	1.12	1.40
	3	84.60	0.69	0.81
	4	86.00	0.07	0.08
TSS	1	70.23	1.63	2.32
	2	76.22	0.71	0.94
	3	81.14	1.56	1.93
	4	82.24	0.71	0.87
VSS	1	50.86	1.05	2.07
	2	64.02	1.76	2.75
	3	72.51	1.87	2.57
	4	74.05	0.20	0.27

Table C.2 Coefficient of variation of SF

Comparison of the average removal efficiencies between control unit and experimental unit of free subsurface wetland systems.

Parameters	RUN	Mean	Standard Deviation	Coefficient of variation
COD	1	88.09	0.16	0.18
	2	91.35	1.20	1.32
	3	91.79	0.17	0.18
	4	90.02	0.16	0.18
TKN	1	85.23	0.20	0.23
	2	87.25	0.04	0.04
	3	90.69	0.83	0.91
	4	88.39	1.19	1.34
TP	1	74.62	0.52	0.69
	2	86.97	0.02	0.02
	3	89.74	0.44	0.49
	4	89.56	1.29	1.44
TSS	1	79.74	2.45	3.08
	2	84.97	3.04	3.58
	3	86.59	0.39	0.45
	4	90.90	0.75	0.82
VSS	1	62.54	0.56	0.89
	2	69.98	4.21	6.01
	3	79.93	1.04	1.30
	4	81.84	2.62	3.20

Appendix D

Data of soil

Table D.1 Data of cadmium concentration in soil at the depth of 15 cm (Run1)

Reactors	Cadmium concentration along the distance of channel bed (mg/L)			
	0.5 m	1.5 m	2.5 m	3.5 m
R1	0.0008	0.0181	0.0053	0.0087
R2	0.0957	0.0398	0.0303	0.0056
R3	0.0022	0.0169	0.0000	0.0000
R4	0.0782	0.0490	0.0168	0.0113

Table D.2 Data of cadmium concentration in soil at the depth of 25 cm (Run 1)

Reactors	Cadmium concentration along the distance of channel bed (mg/L)			
	0.5 m	1.5 m	2.5 m	3.5 m
R1	0.0092	0.0203	0.0129	0.0248
R2	0.0835	0.0297	0.0177	0.0131
R3	0.0145	0.0077	0.0000	0.0000
R4	0.0640	0.0379	0.0210	0.0143

Table D.3 Data of cadmium in soil at the depth of 15 cm (Run 1)

Reactors	Cadmium along the distance of channel bed (mg/g)			
	0.5 m	1.5 m	2.5 m	3.5 m
R1	0.0000	0.0009	0.0003	0.0004
R2	0.0048	0.0020	0.0015	0.0003
R3	0.0001	0.0008	0.0000	0.0000
R4	0.0039	0.0025	0.0008	0.0006

Table D.4 Data of cadmium in soil at the depth of 25 cm (Run 1)

Reactors	Cadmium along the distance of channel bed (mg/g)			
	0.5 m	1.5 m	2.5 m	3.5 m
R1	0.0005	0.0010	0.0006	0.0012
R2	0.0042	0.0015	0.0009	0.0007
R3	0.0007	0.0004	0.0000	0.0000
R4	0.0032	0.0019	0.0011	0.0007

Table D.5 Data of cadmium concentration in soil at the depth of 15 cm (Run 2)

Reactors	Cadmium concentration along the distance of channel bed (mg/L)			
	0.5 m	1.5 m	2.5 m	3.5 m
R1	0.0019	0.0000	0.0005	0.0000
R2	0.8496	0.3556	0.2328	0.0832
R3	0.0034	0.0143	0.0079	0.0002
R4	0.3056	0.2614	0.1998	0.0446

Table D.6 Data of cadmium concentration in soil at the depth of 25 cm (Run 2)

Reactors	Cadmium concentration along the distance of channel bed (mg/L)			
	0.5 m	1.5 m	2.5 m	3.5 m
R1	0.0190	0.0033	0.0107	0.0041
R2	0.5748	0.3778	0.1894	0.1252
R3	0.0077	0.0000	0.0051	0.0078
R4	0.2581	0.1223	0.0859	0.0725

Table D.7 Data of cadmium in soil at the depth of 15 cm (Run 2)

Reactors	Cadmium along the distance of channel bed (mg/g)			
	0.5 m	1.5 m	2.5 m	3.5 m
R1	0.0001	0.0000	0.0000	0.0000
R2	0.0425	0.0178	0.0116	0.0042
R3	0.0002	0.0007	0.0004	0.0000
R4	0.0153	0.0131	0.0100	0.0022

Table D.8 Data of cadmium in soil at the depth of 25 cm (Run 2)

Reactors	Cadmium along the distance of channel bed (mg/g)			
	0.5 m	1.5 m	2.5 m	3.5 m
R1	0.0010	0.0002	0.0005	0.0002
R2	0.0287	0.0189	0.0095	0.0063
R3	0.0004	0.0000	0.0003	0.0004
R4	0.0129	0.0061	0.0043	0.0036

Table D.9 Data of cadmium concentration in soil at the depth of 15 cm (Run 3)

Reactors	Cadmium concentration along the distance of channel bed (mg/L)			
	0.5 m	1.5 m	2.5 m	3.5 m
R1	0.0088	0.0081	0.0053	0.0048
R2	11.2480	9.4080	0.6910	0.1328
R3	0.0068	0.0050	0.0044	0.0023
R4	4.7440	3.7350	0.3247	0.0588

Table D.10 Data of cadmium concentration in soil at the depth of 25 cm (Run 3)

Reactors	Cadmium concentration along the distance of channel bed (mg/L)			
	0.5 m	1.5 m	2.5 m	3.5 m
R1	0.0077	0.0075	0.0043	0.0040
R2	10.0480	8.3180	0.3706	0.1426
R3	0.0032	0.0030	0.0020	0.0023
R4	3.1380	2.0100	0.3085	0.0553

Table D.11 Data of cadmium in soil at the depth of 15 cm (Run 3)

Reactors	Cadmium along the distance of channel bed (mg/g)			
	0.5 m	1.5 m	2.5 m	3.5 m
R1	0.0004	0.0004	0.0003	0.0002
R2	0.5624	0.4704	0.0346	0.0066
R3	0.0003	0.0003	0.0002	0.0001
R4	0.2372	0.1868	0.0162	0.0029

Table D.12 Data of cadmium in soil at the depth of 25 cm (Run 3)

Reactors	Cadmium along the distance of channel bed (mg/g)			
	0.5 m	1.5 m	2.5 m	3.5 m
R1	0.0004	0.0004	0.0002	0.0002
R2	0.5024	0.4159	0.0185	0.0071
R3	0.0002	0.0002	0.0001	0.0001
R4	0.1569	0.1005	0.0154	0.0028

Table D.13 Data of cadmium concentration in soil at the depth of 15 cm (Run 4)

Reactors	Cadmium concentration along the distance of channel bed (mg/L)			
	0.5 m	1.5 m	2.5 m	3.5 m
R1	0.0129	0.0067	0.0091	0.0054
R2	28.8700	20.9630	5.9220	2.4230
R3	0.0243	0.0161	0.0188	0.0123
R4	10.2000	7.0240	1.5186	0.6580

Table D.14 Data of cadmium concentration in soil at the depth of 25 cm (Run 4)

Reactors	Cadmium concentration along the distance of channel bed (mg/L)			
	0.5 m	1.5 m	2.5 m	3.5 m
R1	0.0103	0.0122	0.0056	0.0099
R2	26.7740	17.8740	5.5829	1.3880
R3	0.0093	0.0077	0.0085	0.0064
R4	8.1870	6.0140	1.6100	0.3827

Table D.15 Data of cadmium in soil at the depth of 15 cm (Run 4)

Reactors	Cadmium along the distance of channel bed (mg/g)			
	0.5 m	1.5 m	2.5 m	3.5 m
R1	0.0006	0.0003	0.0005	0.0003
R2	1.4435	1.0482	0.2961	0.1212
R3	0.0012	0.0008	0.0009	0.0006
R4	0.5100	0.3512	0.0759	0.0329

Table D.16 Data of cadmium in soil at the depth of 25 cm (Run 4)

Reactors	Cadmium along the distance of channel bed (mg/g)			
	0.5 m	1.5 m	2.5 m	3.5 m
R1	0.0005	0.0006	0.0003	0.0005
R2	1.3387	0.8937	0.2791	0.0694
R3	0.0005	0.0004	0.0004	0.0003
R4	0.4094	0.3007	0.0805	0.0191

Table D.17 Total cadmium (g) in soil of free water surface wetland system

Reactors	Cadmium along the distance of channel bed (g)				sum
	0.5 m	1.5 m	2.5 m	3.5 m	
Run 1	181.33	70.33	48.57	18.92	319.15
Run 2	1,441.35	742.13	427.22	210.88	2,821.58
Run 3	21,549.42	17,936.94	1,074.23	278.68	40,839.27
Run 4	56,306.16	39,299.16	11,641.81	3,856.35	111,103.48

Table D.18 Total cadmium (g) in soil of subsurface wetland system

Reactors	Cadmium along the distance of channel bed (g)				sum
	0.5 m	1.5 m	2.5 m	3.5 m	
Run 1	143.89	87.93	38.25	25.90	295.98
Run 2	570.41	388.27	289.10	118.49	1,366.27
Run 3	7,975.80	5,813.37	640.74	115.46	14,545.35
Run 4	18,605.81	13,193.15	3,165.83	1,053.08	36,017.87

Appendix E

Data of plants

Table E.1 Data of cadmium concentration in leaves

Reactors	Cadmium concentration along the distance of channel bed (mg/L)			
	0.5 m	1.5 m	2.5 m	3.5 m
R1	0.0241	0.0239	0.0231	0.0266
R2	2.0840	0.5450	0.1006	0.0660
R3	0.0493	0.0354	0.0337	0.0294
R4	0.6326	0.4479	0.1427	0.2500

Table E.2 Data of cadmium in leaves

Reactors	Cadmium concentration along the distance of channel bed (mg/g)			
	0.5 m	1.5 m	2.5 m	3.5 m
R1	0.0024	0.0024	0.0023	0.0027
R2	0.2084	0.0545	0.0101	0.0066
R3	0.0049	0.0035	0.0034	0.0029
R4	0.0633	0.0448	0.0143	0.0250

Table E.3 Data of cadmium concentration in stems

Reactors	Cadmium concentration along the distance of channel bed (mg/L)			
	0.5 m	1.5 m	2.5 m	3.5 m
R1	0.0387	0.0368	0.0365	0.0379
R2	5.0480	2.0470	0.3760	0.1404
R3	0.0524	0.0480	0.0399	0.0291
R4	4.7200	1.0758	0.4470	0.3795

Table E.4 Data of cadmium in stems

Reactors	Cadmium concentration along the distance of channel bed (mg/g)			
	0.5 m	1.5 m	2.5 m	3.5 m
R1	0.0039	0.0037	0.0037	0.0038
R2	0.5048	0.2047	0.0376	0.0140
R3	0.0052	0.0048	0.0040	0.0029
R4	0.4720	0.1076	0.0447	0.0380

Table E.5 Data of cadmium concentration in roots

Reactors	Cadmium concentration along the distance of channel bed (mg/L)			
	0.5 m	1.5 m	2.5 m	3.5 m
R1	0.0418	0.0451	0.0339	0.0371
R2	24.8700	12.2600	3.0170	1.9680
R3	0.0499	0.0400	0.0286	0.0297
R4	23.3500	10.8000	1.9552	1.4480

Table E.6 Data of cadmium in roots

Reactors	Cadmium concentration along the distance of channel bed (mg/g)			
	0.5 m	1.5 m	2.5 m	3.5 m
R1	0.0042	0.0045	0.0034	0.0037
R2	2.4870	1.2260	0.3017	0.1968
R3	0.0050	0.0040	0.0029	0.0030
R4	2.3350	1.0800	0.1955	0.1448

Table E.7 Calculation the cadmium (g) in cattail plants for free water surface and subsurface wetland

Reactors	Parts	Distance along the soil bed (m)				Total (g)
		0.5	1.5	2.5	3.5	
FWS	Roots	1,024.25	504.92	124.25	81.05	1,734.46
	Stems	694.10	281.46	51.70	19.31	1,046.57
	Leaves	268.21	70.14	12.95	8.49	359.79
SF	Roots	611.30	282.74	51.19	37.91	983.14
	Stems	354.66	80.84	33.59	28.52	497.60
	Leaves	48.93	34.65	11.04	19.34	113.95

Curriculum Vitaes

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WORK EXPERIENCES:

January 1997 – Present	Lecturer of the School of Environmental Engineering, Institute of Engineering, Suranaree University of Technology.
March 1993 – Dec1996	Environmental engineer of Engineering Consultant and Supply Co., Ltd. and Thai-Euro Plastic Industrial Co., Ltd.
July 1991 – Feb 1993	Project coordinator officer of the Asian-Canada Project.
April – June 1991	Process engineer of the Pacific-Thai Electric Wire and Cable Co., Ltd.

RESEARCH WORKS:

1. Application of Dissolved Air Floatation System for Tuna Cannery Industry, 1994.
2. Self-burning Incinerator with Air Pollution Control, 1999.
3. Application of Membrane Bioreactor Systems for Landfill Leachate Treatment, 2004.
4. Application of Chemical Processes for Landfill Leachate Treatment, 2004.

5. Cleaner Technology in A Metal Finishing Industry in Thailand, 2005-2006.
6. A Novel Wastewater Treatment System Using A UASB Reactor and a Downflow Hanging Sponge (DHS) Post Treatment Unit, 2005-2007.

PATENT:

1. "เตาเผาขยะขนาดเล็กประสิทธิภาพสูง" ยื่นคำขอรับสิทธิบัตรเมื่อวันที่ 17 กันยายน 2547 เลขที่คำขอ 093761

PUBLICATION:

1. Wichitsathian, B., Sindhuja, S., Visvanathan, C., and Ahn, K. H., 2004. Landfill Leachate Treatment by Yeast and Bacteria Based Membrane Bioreactors. *Journal of Environmental Science and Health, Part A—Toxic/Hazardous Substances & Environmental Engineering*, 39(9), 2391 – 2404.
2. Wichitsathian, B., Sindhuja, S., Visvanathan, C., and Ahn, K. H., 2004. Landfill Leachate Treatment by Yeast and Bacteria Based Membrane Bioreactors. *The Fourth AIT-KIST International Joint Symposium*, Asian Institute of Technology, Thailand, 20 May.
3. Wichitsathian, B., Sindhuja, S., Visvanathan, C., and Ahn, K. H., 2004. Biokinetic Parameters As an Indicator to Ammonia Toxicity in Leachate Treatment Using Membrane Bioreactors. *Asian Journal of Microbiology Biotechnology Environmental Science*, 6(1), 1-6.
4. บุญชัย วิจิตรเสถียร และ นเรศ เชื้อสุวรรณ, 2548. การบำบัดน้ำเสียจากฟาร์มสุกรในขั้นต้นด้วยวิธีทางเคมีกายภาพ. การสัมมนาการพัฒนากลุ่มงานวิจัยในเครือข่ายอุดมศึกษานครราชสีมา, มหาวิทยาลัยเทคโนโลยีสุรนารี, 24 มิถุนายน 2548.
5. บุญชัย วิจิตรเสถียร และ พัชรินทร์ ราโช, 2548. การศึกษาสถานการณ์และปัญหาในการจัดการขยะติดเชื้อจากโรงพยาบาลในประเทศไทย. การสัมมนาการพัฒนากลุ่มงานวิจัยในเครือข่ายอุดมศึกษานครราชสีมา, มหาวิทยาลัยเทคโนโลยีสุรนารี, 24 มิถุนายน 2548.
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EXTRA CURRICULUM AND SPECIAL TRAINING:

Work Type	Description	Capacity
- Design of wastewater treatment system	- On site system for residential - Prefabricated system for industry - Central treatment system for villages and condominiums	80 – 1,050 m^3/d
	- Treatment plants for textile, frozen food, food, used oil treatment industries, and semi-conductor	30 – 600 m^3/d
- Design of landfill	- Waste management industry	40 tons/d
- Consultant and control of wastewater treatment system	- Frozen food industry	1,000 m^3/d
	- Tapioca starch industry	1,600 m^3/d
	- Hospital	150 m^3/d
- Training	- Hospital wastewater treatment plant	-
- Environmental impact assessment (EIA)	- Condominium	-
- Project	- Self-burning incinerator with air pollution control	-
	- Initial environmental review for industries in Tha-chin river	-
	- Cleaner technology	-
	- Water quality	-

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- Computer modeling of water and wastewater treatment processes
- Solid waste management in Asian countries
- Air pollution control

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D.Tech.Sc.	1995.	Environmental Engineering. Asian Institute of Technology, Bangkok, Thailand.
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OTHER SKILLS:

Languages:	**English:**	Excellent;
	Hindi:	Excellent;
	Thai:	Good speaking abilities;
	French:	Some knowledge.

WORK EXPERIENCE:

October 04 – Sep 05: Visiting Assistant Professor
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January 01 – April 05: Assistant Professor
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Course Taught:

ED24.07: Solid Waste Management *Graduate level*

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503 515: Water Engineering Design *Graduate level*
503 513: Air Pollution Control *Graduate level*
503 504: Atmospheric Environment *Graduate level*
& Dispersion Modeling

Supervising masters and doctoral students' theses research.

Has supervised 8 Masters students.
Currently, supervising 1 doctoral student.

List of Masters Theses Supervised:

1) Domestic Wastewater Treatment Using Rock-bed Filtration Process.
2) Anaerobic Composting of Solid Waste in Batch-Loading Digesters.
3) A Study of Heavy Metals in Bottom Ash From Medical Waste Incinerators in Nakhon Ratchasima Municipality.
4) A Study of the Fate of Cadmium in Wastewater Effluents in Constructed Wetland System.

5) Heat Generation and Temperature Distribution in an Anaerobic Composting process.
6) Removal of Heavy Metals from Wastewater by Adsorption Using Chitosan.
7) Reducing Exhaust Emission from Passenger Cars by Using Three-way Catalytic Converter.
8) Strategies for Municipal Solid Waste Management in Suranaree Military Camp.

Sponsored Research Projects:

1) Principal Investigator: A preliminary study of arsenic contamination in southern Thailand. Funded by National Research Council of Thailand (NRCT)
Baht 182,500 (Oct 2000 – Sept 2001) Completed
2) Principal Investigator: Temperature distribution and heat generation in an aerobic composting process. Funded by National Research Council of Thailand (NRCT)
Baht 210,500 (Oct 2001 – Sept 2002) Completed
3) Principal Investigator: Investigations on the heavy metals' removal from wastewater using constructed wetlands. Funded by National Research Council of Thailand (NRCT)
Baht 815,000 (Oct 2002 – Sept 2005) Ongoing
4) Principal Investigator: A Novel Wastewater Treated System Using A UASB Reactor and A Downflow Hanging Sponge (DHS) Post Treatment Unit. Funded by National Research Council of Thailand (NRCT)
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Royal Golden Jubilee Ph.D. Scholarship Grants – Thailand Research Fund

1) Principal Advisor: Removal of Heavy Metals from Wastewater in Constructed Wetlands.
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Jan 99 – April 99	Guest Lecturer, Suranaree University of Technology for teaching a graduate level course - 503 515: Water Engineering Design.
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Sept 96 - Aug 98	Consultant in a research project "Investigation of Canal Water Quality Improvement by Filtration Through Different Contact Media" funded by Sumitomo Heavy Industries Ltd., Japan under the UNITWIN / UNESCO Chairs Programme, SIIT, Thammasat University.
July 97 - Aug 98	Consultant, Environmental Systems Information Center (ENSIC), Asian Institute of Technology, Bangkok.
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Sep 88 - May 89	Research Associate, Biological & Agricultural Engineering Department, University of Arkansas, Fayetteville, AR, U.S.A.
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PUBLICATIONS:

Theses:

Jindal, Ranjna (1995). Development and modelling of a water treatment system using the rock-bed filtration method. D.Tech.Sc. Dissertation, No. EV-95-2, Asian Institute of Technology, Bangkok, Thailand.

Jindal, Ranjna (1982). A statistical analysis of some sediment components Accumulated in the reservoirs and lakes. M.Sc. Thesis No. EV-82-28, Asian Institute of Technology, Bangkok, Thailand.

Published/Presented:

Jindal, R. and N. Samorkhom (2005). "Investigations on Cadmium removal from Wastewater in Constructed Wetland." *ASCE Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management), Vol. 9, No. 3,* pp. 173-178.

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Jindal, R. and P. Pimpan (2001). "Rock-bed Filtration for Domestic Wastewater Treatment." *Proc. of The Seventh National Convention of Civil Engineers*, Bangkok, Thailand, 18-19 May.

Jindal, R. and P. Ratanamalaya (2001). "Heat Generation and Temperature Distribution in An Aerobic Composting Process." *Proc. of the 8 th Tri-University International Joint Seminar and Symposium*, Chiang Mai, Thailand, 30 October-2 November.

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Papers Accepted / Under Review:

Pimpan, P. and R. Jindal. "Investigations of Cadmium Removal in Laboratory-Scale Constructed Wetlands." Accepted for presentation at *The Eighth International In-Situ and On-Site Bioremediation Symposium*, 6-7 June 2005 in Baltimore, USA.

Professional Contributions:

Have served as a "Reviewer" for the following International and Regional Journals:

1. "Immobilization Technologies" by J.N. Meegoda, A.S. Ezeldin, Hsai-Yang Fang and H.I. Inyang, for the *ASCE Practice Periodical of Hazardous, Toxic, and Radioactive waste Managemnet.*
2. "Efficiency of Arsenic Removal from Soil by *Vetiveria zizanioides* (Linn.) and *Vetiveria nemoralis* (Balansa) A. Camus" by T. Srisatit, T. Kosakul and D. Dhitivara, for the *Science Asia: Journal of the Science Society of Thailand.*

1. "Effect of Temperature Shock on activities of Phosphorus-Accumulating Organisms" by Thongchai Pansawad, Apiradee Doungchai, and Jin Anotai for the *Science Asia: Journal of the Science Society of Thailand.*