CRANFIELD UNIVERSITY

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Constructed Wetlands for Advanced Treatment and Reuse

Centre for Water Sciences
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PhD Thesis

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Abstract

Constructed wetland technology is gaining increasing attention as a low cost-efficient alternative to high-tech treatment systems for treating municipal and industrial wastewaters especially in small communities. However, its application for grey water reuse has been rarely investigated whilst performance for nutrients (N and P) still remains relatively poor.

Pilot scale study was conducted in which three differently configured subsurface constructed wetlands: a horizontal flow reed bed (HFRB), vertical flow reed bed (VFRB) and a novel system - Green Roof Water Recycling System (GROW) were investigated for their suitability and robustness in treating grey water for reuse across a range of influent strengths to represent the limiting conditions observed in the literature. The HFRB and the GROW systems were found to be generally limited to comply with reuse standards especially at high strength. The release of iron from the HFRB media and particulates from the GROW system contributed to the poor turbidity of the final effluent from these systems. Overall, all wetland configurations were able to effectively treat low strength greywater but only the vertical flow system maintained its robustness when high strength greywater was treated. Analysis of the systems reveals this was due to the fact that aerobic metabolism is a more suitable treatment pathway for greywater. Ultimately, the performance of the vertical system was slightly lower but comparable to that of a membrane bioreactor making constructed wetlands a suitable technology for greywater recycling.

Also, Bauxol, Red mud, Bayoxide, Ochre, Filtralite-P, Steel slag, concrete, Zeolite and various form of limestones were investigated for potential removal of soluble reactive phosphorous (SRP) and metals (Cu and Ni) in final sewage effluent for post Constructed Wetland System. P capacities exhibited by the different adsorbents correlated with type of metal (e.g. Fe, Al, Ca) and their cation exchange capacities. Ochre exhibited the best P removal ability with a P capacity of 26 g Kg^{-1} based on a Freundlich isotherm model. The equilibrium sorption capacity of Bauxol^{TM} and Ochre based on a Dubinin-Radushkevich model was found to be 4.1 and 4.9 mg g^{-1} for Cu and Ni unto Bauxol^{TM} respectively and 2.6 and 10.2 mg g^{-1} for Cu and Ni onto Ochre respectively. Kinetic and thermodynamic study revealed a spontaneous and efficient adsorption process via a pseudo-second order mechanism where intra-particle diffusion was shown to be the rate limiting step. An aerobic post constructed wetland system using Ochre as the bed media for large scale applications is suggested.

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TO GOD BE THE GLORY

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Notations and abbreviations

Å	Amstrong
E	Mean free energy
K_f	Freundlich constant
K_l	Langmuir constant
K_P	Intra-particle rate constant
R_L	Adsorption efficiency
q_e	Pseudo-second order equilibrium concentration
q_o	Dubinin-Radushkevich adsorption maximum
1/n	Freundlich coefficient
ANOVA	Analysis of variance
BOD_5	Five day biochemical oxygen demand
BV	Bed volume
CEC	Cation exchange capacity
COD	Chemical oxygen demand
CWs	Constructed wetlands
CWT	Constructed wetland technology
CWS	Constructed wetland systems
DI	Distilled ionised
DO_2	Dissolve oxygen
DOC	Dissolve organic carbon
E_h	Oxidation-reduction potential
EDX	Energy dispersive X-ray spectroscopy

ESEM	Environmental scanning electron microscope
GROW	Green Roof Water Recycling System
HF	Horizontal flow
HFRB	Horizontal flow reed bed
HSSF	Horizontal sub-surface flow
HPI	Hydrophilic organic fraction
HPO	Hydropkobic organic fraction
HPSEC	High performance size exclusion chromatography
HRT	Hydraulic residence time
IWA	International Water Association
K_{BOD}	Biochemical oxygen demand rate constant
MCR	Membrane chemical reactor
MBR	Membrane bioreactor
MW	Molecular weight
NH_4-N	Ammonia-nitrogen
NO_3-N	Nitrate nitrogen
PO_4-P	Phosphate-phosphorous
OTR	Oxygen transfer rate
Q	Flow rate
SF	Surface flow
SRP	Soluble reactive phosphorous
SS	Suspended solids
SSF	Sub-surfaceflow
Std	Standard

TOC	Total organic carbon
TPI	Transphilic organic fraction
TTC	Triphenyl tetrazolium chloride
USEPA	United State Environmental Protection Agency
VF	Vertical flow
VFRB	Vertical flow reed bed
HLR	Hydraulic loading rate
UV	Ultraviolet light
UV_{254}	Ultraviolet at the wavelength of 254nm

List of publications

Journal publications

Frazer-Williams, R., Avery, L., Jeffrey, P., Shirley-Smith, C., Liu, S., and Jefferson, B. (2008). Constructed wetlands for urban grey water recycling." International Journal of Environment and Pollution. Vol. 33, Number 1, 93-109.

Winward, G., Avery, L, M., **Frazer-Williams, R**., Pidou, M., Jeffrey, P. Stephenson, T. and Jefferson, B. (2008). A study of the microbial quality of grey water and an evaluation of treatment technologies for reuse. Ecological engineering.Vol 32, Issue 2, 187-197.

Conference publications

Pidou, M., Memon, F. A., **Frazer-Williams, R**., Jeffrey, P., Stephenson, T. and Jefferson, B. (2007). Technologies for urban water recycling. Proceedings of the 6th IWA conference on Water Rclamation and Reuse for Sustainability, Antwerp, Belgium. 9th-12th October 2007.

Frazer-Williams, **R**., Avery, L., Winward, G., Shirley-Smith, C. and Jefferson, B. (2006). "The Green Roof Water Recycling System - a Constructed wetland for urban grey water recycling." In: Proceedings of 10th International conference on Wetland Systems for Water pollution Control, Lisbon, Portugal. 23 – 29th September 2006.

Avery, L., **Frazer-Williams**, **R**., Winward, G., Shirley-Smith, C. and Jefferson, B. (2006). "The role of constructed wetlands in urban grey water recycling" In Proceedings of 10th International conference on Wetland Systems for Water pollution Control, Lisbon, Portugal. 23 – 29th September 2006.

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Chapter 1 Introduction

1.1 General Iintroduction

The key driving force to develop and implement sustainable water management strategies is to address the issues of available potable water shortage and pollution abatement. Water shortage arises primarily from growing demand for clean water due to increased population, changing lifestyles, diminishing water resources and urbanisation. The UK is amongst 70% of European countries facing water stress issues with a water stress index below 10% (Bixio *et al.*, 2005). To illustrate, rainfall in the densely populated south-east of England is similar to that of water-stressed Mediterranean countries. The water demand in England and Wales has been predicted to rise from 162 to ~203 $l\ h^{-1}d^{-1}$ between the period 1997 to 2024 (CCDeW Report, 2003). The additional impact of climate change on domestic demand, industrial and commerce, and agricultural & horticultural demand could further increase this figure by 1.8%, 2.8% and 20% respectively (CCDeW Report, 2003). The economic water regulator (e.g. OFWAT) has also estimated that between the period 2000 to 2025, the water requirements of water companies could increase by 1000 Ml. d^{-1} due to increase population and water usage. The government's commitment to increase the number of new of housing units from 150,000 to 200,000 over the next decade (ODPM, 2005) is expected to increase pressure on water resources.

Concern over water issues is not only limited to the amount available to meet demand, but also the quality of fresh water (such as river and ground water) which is the source of raw water treated by water companies to meet potble supply. With fresh water representing a small fraction (~3 %) of world water resource (Gleick *et al.*, 2004), the need to control the level of pollutants (e.g. nutrients and heavy metals) entering receiving waters from point sources (e.g. wastewater treatment plants) is of great importance. This has resulted in the imposition of strict compliance discharge limits for effluent from wastewater treatment plants and point source discharges (e.g. the EU Urban Wastewater Treatment Directive). Governments therefore seek to address the pollution of fresh water sources by imposing stricter legislation on discharge criteria, as well as the efficient and appropriate use of potable water as a sustainable water management practice.

Wastewater reuse is one possible response to the challenges of fresh water demand, water shortages and environmental protection. Raw water sources available for recycling include rain water, grey water, and domestic/municipal wastewater. Of these, grey water represents the most profitable in terms of its reliability, availability and raw water quality (Kujawa-Roeleveld and Zeeman, 2006; Dixon *et al.*, 1999). A range of technologies (e.g. biological aerated filters (Laine, 2001), membranes bioreactors (MBR) (Liu *et al.*, 2005), membranes (Ahn *et al.*, 1998), soil filters (Itayama *et al.*, 2004)) have been applied for grey water reuse applications. Any technology selected for any particular application must produce good water quality, be cost effective, suitable to scale and acceptable by the public. Whilst some technologies such as membrane systems have demonstrated the ability to produce high quality treated effluent (Melin *et al.*, 2006), cost, application to scale and the relatively low public perception may limit its application in small communities especially in rural areas. In such communities, simple low-tech and efficient systems may be most appropriate. Constructed wetland systems are relatively simple and are gaining popularity as an effective and low-cost alternative for wastewater treatment especially for villages and small communities where larger high-tech systems are deemed inappropriate. Such systems also have added advantages over conventional treatment systems in that they require relatively low running costs, can be maintained by low skilled personnel, have lower energy requirements and are perceived as a natural treatment system.

Constructed wetland technology has been recognised for its significant contribution in recoverering water from diverse types of wastewater (IWA, 2000; Hofmann, 1996). In isolated cases, treated effluents from constructed wetland treatment systems have been re-circulated to achieve sustainable use of water resources. Therefore, constructed wetlands can be optimised for advanced wastewater treatment for the purpose of urban reuse (e.g. for toilet flushing), especially in areas where water demand is high. However, constructed wetland technology needs to be optimised for nutrients and metals removal to match its ability to remove organics and solids. Constructed wetlands have been widely applied successfully in treating different types of wastewater such as municipal (Cooper *et al*., 1996), storm water (Green and Martin, 1996), industrial wastewater (Abira *et al*., 2005) agricultural wastewater and runoff (Sun *et al*., 1999) and recently refinery effluent (Wallace and Kadlec, 2005). Reported studies of grey water treatment by constructed wetlands are rare and recorded performance for phosphorous and metals removal is relatively poor. Hence performance data that will guide the design and operation of wetland systems in a bid to optimise efficiencies for diverse applications is desirable.

1.2 Research development

The work reported in this thesis integrates three projects within the domain of constructed wetland technology. These include (i) a pilot trial of a 'Green Roof Water Recycling System' -GROW, which arose out of the need to research and develop opportunities for water management within the framework of the Competition Act (Water) 1998; (ii) a pilot trial under Work Package 7 of the EPSRC funded 'Water Cycle for new development' Project, which focuses on contender technologies such as membrane bioreactor, membrane chemical reactor and constructed wetlands; and (iii) a study under the auspices of Severn Trent Water Company Limited, Coventry, UK. which focuses on identifying suitable adsorbent(s) for use as substrates in constructed wetland systems for polishing final effluent from sewage treatment works in order to meet stringent consent limit.

1.3 Aims and objectives

The aims of this thesis are:

(i) To investigate the suitability and robustness of constructed wetlands (CWs) focussing on reliability of performance, technology selection and market opportunity for grey water recycling,

(ii) To determine the appropriate properties of a P adsorbent for use in post CWs.

Based on the above aims, several research objectives identified are:

1. investigate the suitability and robustness of constructed wetland systems treating grey water for urban reuse applications, especially for toilet flushing,

2. assess the level of compliance of the different wetlands to key water quality reuse standards around the world,
3. assess how the test rigs compare with other candidate technologies for grey water treatment and reuse,
4. investigate the influence of configuration type (i.e. horizontal and vertical) on wetland performance and treated water quality,
5. investigate the influence of operational parameters (i.e. influent organic loading and hydraulic loading rate) on wetland treatment performance,
6. investigate the role of oxygen in the aerobic biodegradation of organic matter contained within grey water,
7. investigate how constructed wetlands can be applied as an advance treatment option for polishing final sewage effluents to meet stringent consent limits for phosphorous and metals,
8. investigate the relationship between the cation exchange capacity as well as the type and percent composition (w/w) of metal (e.g. Ca, Fe etc) to the adsorption capacity of the adsorbents,
9. investigate the kinetics and thermodynamics of the adsorption process of P unto the various adsorbents,

It should be noted that although all work reported in this thesis was carried out by Ronnie Frazer-Williams, enumeration of indicator organisms was carried out by Gideon Winward, a colleague PhD researcher working alongside the other on the WaND project.

Chapter 2 Literature review

2.1 A review of constructed wetlands

2.1.1 Introduction

Constructed Wetlands are engineered systems designed to utilize natural processes for water quality improvements. They perform this function by removing contaminants in wastewaters via a combination of physical (filtration, sedimentation), biological (microbial processes, plant uptake) and chemical (precipitation, adsorption) mechanisms (Kadlec and Knight, 1996).

2.1.1.1 Types and configuration of constructed wetlands

Constructed wetlands can be divided into two main types: free water surface (FWS) wetlands also known as surface flow (SF) and subsurface flow (SSF).

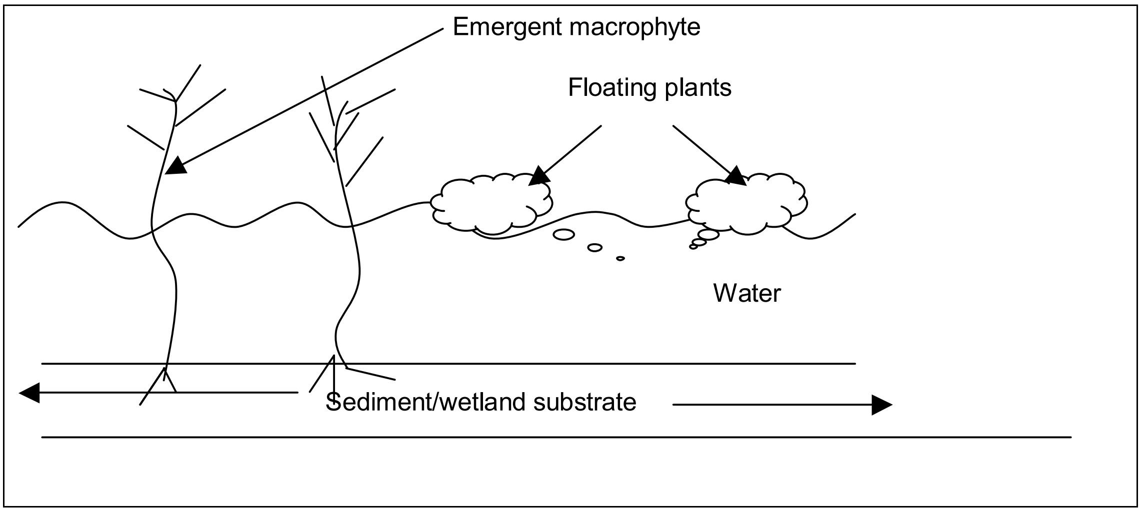


Figure 2.1.1a: Schematic diagram of a free water surface (surface flow) wetland.

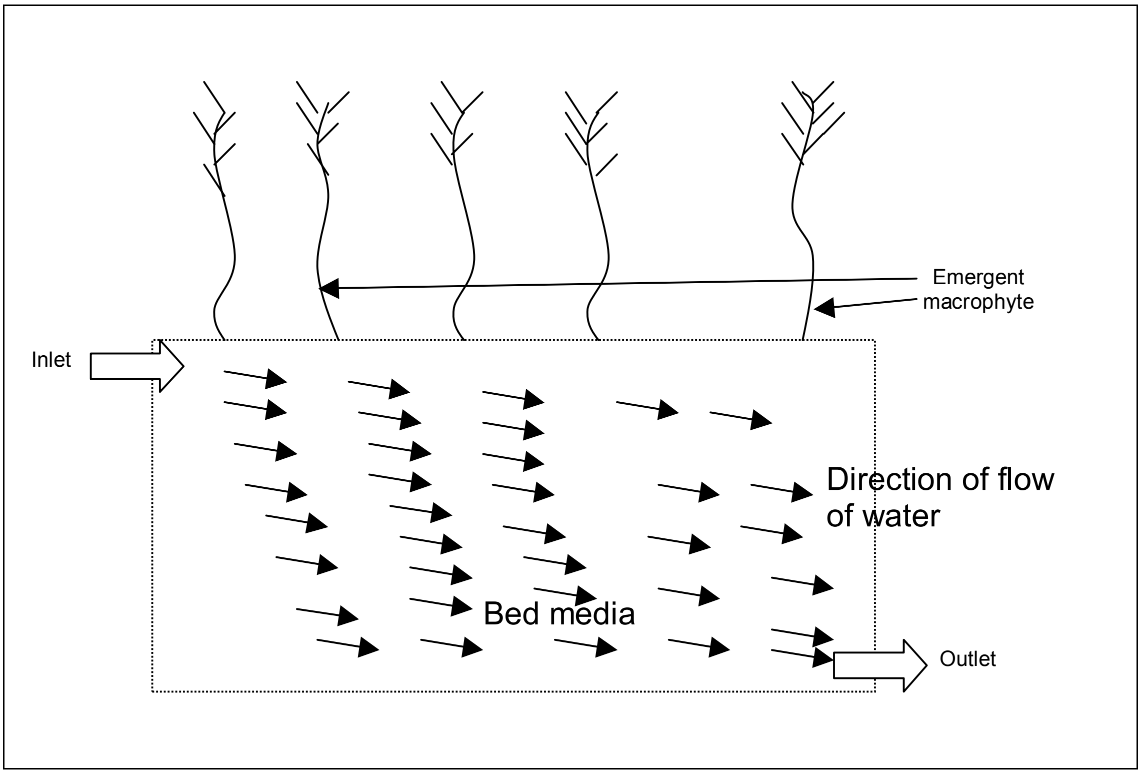


Figure 2.1.1b: Schematic diagram of a horizontal flow sub-surface flow wetland.

- *Surface flow (SF) wetland*

SF wetland technology started in North America in the 1970s as a result of work with natural wetlands systems (IWA, 2000). Surface flow (SF) systems are designed to allow a permanent depth of water to be treated flowing horizontally across the wetland bed surface with landscape similar to a natural wetland (Figure 2.1.1a). The common features of SF wetlands are either a shallow basin of soil or other medium with the water level controlled to ensure that the sediment, leaf litter and soil are always submerged leaving only the stems of plants above the water level; or a treatment wetland that employs a range of macrophytes such as cattail, giant sweet manner grass (*Glyceria maxima*), penny wort (*Hydrocotyle umbellate*) and common reed that form a floating mat. The dimensions of SF wetlands can be quite large and often resemble swamps and marshes with diverse ecology (Gray, 2004).

- *Sub-surface flow (SSF) wetland*

SSF was first described as the root-zone method (RZM) and was established by the work of Siedel and co-workers at the Max Planck Institute in Germany during 1960-80 (IWA, 2000). Since then, uptake of the technology has spread into many European countries and is now used worldwide for treatment of different types of wastewater. In sub-surface flow systems, an excavated basin or impermeable plastic container is filled with porous media such as gravel, sand or soil (Figure 2.1.1b). Wastewater to be treated is encouraged to flow horizontally or vertically through a selected bed medium and root zone. 'Reed bed' is a term used to describe a sub-surface constructed wetland that has been engineered to simulate and optimize natural wetland waste water treatment processes and it is now based on the use of mainly reeds or cattail as the macrophyte. There are several technological variants of RBCW. These include horizontal flow reed bed (HFRB), vertical flow reed bed (VFRB) and hybrid reed bed (HRB).

    - *Horizontal flow (HF) systems*

In horizontal flow systems, water is continuously introduced at the inlet at one end close to the bed surface and flows horizontally through the porous medium. The treated water is removed at the other end with little or no overland flow. The water level is maintained at or slightly below the top of the porous medium. The porous medium supports the emergent aquatic vegetation. The flow of water horizontally through the system is intended to pass through the entire bed medium in a plug-flow; however short-circuiting can occur (Reed *et al.*, 1998; Fisher, 1991). The depth of the bed can range between 0.5-0.8 m and the gravel size is typically between 10-20 mm. A schematic diagram of a typical HFRB is illustrated in Figure 3.1.2.

  - *Vertical flow (VF) systems*

VF systems are characterised as intermittently batch fed where the wastewater percolates down through the bed media. In between batches, the media is not saturated such that air circulates through the voids and refills the bed providing good oxygen transfer and hence the ability to nitrify (Cooper *et al.*, 1996). A schematic diagram of a typical VFRB showing the pipe network on top of bed is illustrated in Figure 3.1.3. VF systems provide efficient removal of organics and suspended solids but provide minimal denitrification. Therefore, ammonia-N is usually only converted to nitrate-N, resulting in an overall low removal of nitrogen compared to HF systems.

- *Hybrid systems*

Hybrid systems originated from the system developed by Seidel at the Max Planck Institute in Krefeld, Germany (Vymazal, 2006). The design comprises two stages of two or more parallel VF beds followed by HF beds in series. Hybrid systems aim to achieve higher removal efficiencies not achievable from using single HF or VF systems in isolation. Such enhancements are most commonly associated with removal of nitrogen. Hybrid systems usually comprises of HF and VF systems in a staggered pattern. In VF-HF hybrid system, the first stage VF provides suitable aerobic conditions for nitrification followed by the second HF stage which provides suitable anoxic-anaerobic condition for denitrification. Whereas in the HF-VF hybrid system the HF removes organics, suspended solids and provide denitrification with further removal of organics, solids and nitrification in the secondary VF stage.

- *Design of reed bed CWs*

The successful use of CW technology for the improvement of water quality depends mainly upon proper design and operational specifications. Table 2.1.1 summarises key design and operational specifications for the efficient performance of HFRB and VFRB. In general, VF systems require less land (1-3 m^2 PE^{-1}) compared to HF systems (5-10 m^2 PE^{-1}). The dimensions of vertical flow systems vary between 1-2 m^2 PE^{-1}; 1 m^2 PE^{-1} for BOD removal only and 2 m^2 PE^{-1} for BOD removal followed by nitrification (Cooper and Green, 1995). Precise area of a reed bed is calculated based on design specifications given in Table 2.1.1.

Table 2.1.1 Key design and operational specifications for HFRB and VFRB

	Subsurface flow	
Parameter	HFRB	VFRB
Flow	Horizontal, continuously	Vertical, intermittent by batch
Bed design equation	$^{*}A_h = Q_d(\ln C_e - C_i)/K_{BOD}$	$**A_1 = 5.25P^{0.35} + 0.9P$ A_2= the area of a second bed, estimated at 50% of A_1
Specific area (m^2 PE^{-1})	5 -10	1 - 2
Recommended organic loading for 3° treatment	***8 – 12g BOD_5 m^2 d^{-1}	****25g COD m^2 d^{-1}
Prevailing condition	Anaerobic	aerobic

*Cooper *et al.*, 1996, **Grant and Griggs, 2001, ***Kadlec and Knight, 1996, ****Platzer, 1999

Where C_e (mg L^{-1}) is effluent concentration, C_i (mg L^{-1}) influent concentration, K (days^{-1}) is a temperature-dependent first order reaction rate constant, A_h (m^2) is the surface area of the bed, and K_{BOD} (m d^{-1}) is the BOD rate constant. A_1 and A_2 are the area of first and second bed in a vertical configuration respectively.

Vegetation

In the UK, reed beds are commonly planted with common reed (*Phragmites australis*) (Cooper and Green, 1995), but elsewhere it has also been used in combination with other species such as Iris (*Iris pseudacorus L.*), cattail (*Typha latifolia L.*) bulrush (*Juncus*), sedge (*Carex*), clubrush (*Schoenoplectus*), and bur-reed (*Sparganium*) (Vymazal 2002). Reeds can be planted as seeds, seedlings, sections of rhizome or as clumps and they can take a minimum of 4 months or up to 3-5 years to mature depending on the method of planting. Cooper and Green (1995) reported that during the initial period of UK experience with reed bed systems, planting using pot-grown seedlings at a density of 4 plants per m^2 gave successful dense stands of reeds whereas planting with rhizome segments with at least one node results in competition and slow development of reeds. Similar observations were reported for the Czech Republic experience (Vymazal, 2002).

- *Liners*

Reed beds are lined to contain the water within the system and to prevent leakage which might cause pollution to ground water. Various types of liners used include puddle clay, high, medium or low density poly ethylene (HDPE, MDPE, and LDPE) and bentonite. HDPE, MDPE and LDPE Liners need to be at least 1mm thick. Liners are protected from puncture by a sand layer or a geo-textile e.g. Fibertex both above and below the liner. In the UK, the HDPE, MDPE, and LDPE liners are used and the most often used has been Monarflex (IWA, 2000).

- *Media*

SSF wetlands have been operated with substrates ranging from fine textured soil to 30 cm fieldstone. Very small particles have very low hydraulic conductivity and can encourage surface flow. Very large gravels have high conductivity but lack the good wetted surface area per unit volume suitable for microbial habitat (IWA, 2000). Hence, as a compromise, a combination of substrates compost has been used depending on the type of water that is being treated and the flow rate required. With regard to VF systems, layers of graded gravel (5-10 mm) topped off with a layer of sand have been used, whilst for HF systems, beds can be filled with 5-10 mm washed gravel except at the inlet and outlets where 50-200 mm rock will be used in gabions (Cooper *et al.*, 1999). Soil and gravel are the most common media of SSF wetlands technology in Europe (IWA, 2000). Gravel substrates have also been used extensively in USA.

2.1.2 Influence of key design parameters on the performance of HSSF systems

CWs have been used in treating wastewater of different characteristics including domestic wastewater (Vymazal, 2002), various types of industrial wastewater (Dotro *et al.*, 2006; Omari *et al.*, 2003; Mays and Edwards, 2001), agricultural wastewater (Tanner *et al.*, 1995) and storm waters (Carleton *et al.*, 2000). Recently, they are used as a hybrid VF-HF system, in conjunction with facultative and stabilization ponds to meet tertiary standards in Norway (Browne and Jenssen, 2005), used in combination with aquatic and soil filters for reclamation of domestic sewage in Chatham County, USA (House *et al.*, 1999) and in treatment train together with a filtering and chlorination unit for public water supply in Brazil (Elias *et al.*, 2001). In all of these applications, CWs have demonstrated consistent high performance in removing organic matter such as BOD, COD (Kadlec, 2003); particulate matter (e.g. suspended solids, turbidity); and pathogenic organisms (Watson *et al.*, 1989) but less effectively for nutrients (N and P compounds) (Vymazal, 2002) (Table 2.1.2).

Table 2.1.2. Typical average removal efficiency of European constructed wetlands in selected countries

Parameter	Average removal efficiency (%)				
	Europe[a]	UK[b*]	Denmark[a]	Czech Republic[c]	Poland[c]
BOD_5	79	72	80	88	89
COD	70	-	66	-	-
TSS	-	80	74	84	-
N_{Tot}	40	-	40	51	-
NH_4-N	30	22	34	-	-
P_{Tot}	47	-	32	42	-

*- data quoted are for Severn Trent 3° Reed beds in UK which comprises the majority of CW data in the UK
[a]-Haberl *et al.*, 1995; [b]- Green *et al.*, 1999; [c]-Vymazal, 1999

The growing potential of this technology coupled with increasingly strict water quality standards demands the need for the optimization of CWs design so that they are capable of meeting discharge and reuse requirements for diverse applications.

In view of above, this review examines assumptions inherent in the basic design models of horizontal configurations in treatment wetlands with the aim to provide further insights on their influence to wetland performances. The VF system was not reviewed because they are recent breed of CW technology with much fewer performance data compared to the HF systems available. To achieve this, the evolution of CW design for pollutant removal in horizontal systems has been reviewed highlighting reasons for the development of newer models. The review focuses on the following:

- The generic Kickuth form equation and its suitability for sizing CW and predicting treatment efficiency,
- The operational and design parameter(s) primarily influencing CW performance.

2.1.2.1 Models of Horizontal subsurface flow systems

The principle of the design for CWs subsurface flow (SSF) systems is based on an assumption of plug flow movement of water through the wetland with first-order reaction kinetics primarily by biological degradation. As an attached biological reactor involving microbes, modelling CWs typically combines biological degradation and system hydraulics. The basic relationship which has been used to simultaneously describe the two components mentioned above is given as:

$$C_e = C_i \exp[-K\tau] \quad \text{..........} \quad 2.1.1$$

Where C_e (mg L^{-1}) is effluent concentration, C_i (mg L^{-1}) influent concentration, K (days^{-1}) is a temperature-dependent first order reaction rate constant and τ (days) is hydraulic residence time. The principle of the design for horizontal flow (HF) SSF systems is based on Equation 1 and is written as:

$$A_h = Q_d \ln(C_e - C_i) / K_{BOD} \quad \ldots\ldots\ldots\ldots 2.1.2$$

Where A_h (m^2) is the surface area of the bed, Q_d ($m^3 \, d^{-1}$) is average flow, C_i (mg L^{-1}) is influent BOD_5, C_e (mg L^{-1}) is effluent BOD_5 and K_{BOD} (m d^{-1}) is the BOD rate constant. Equation (2.1.2) was originally proposed by Professor Kickuth in Germany (Boon, 1985) with K_{BOD} having a value of 0.19 m day^{-1}(IWA, 2000). K is selected based on a 95 percentile BOD removal using Equation (2.1.2). Average K_{BOD} of operational treatment wetlands reported in the literature is presented in Table 2.1.3. The K_{BOD} value varies and this has been reported to be due to the influence or biodegradability of the influent water and the type of media used in the bed (Kadlec, 2000).

Table 2.1.3: Average K_{BOD} of treatment wetland reported for different countries

Country	Treatment application	K (md^{-1})	reference
Denmark	Secondary	0.068	IWA, 2000
Czech	Secondary	0.13	Vymazal, 1998
UK	Secondary	0.06	Cooper *et al.*, 1996
UK	Tertiary	0.31	Cooper *et al*, 1996
USA	Tertiary	0.17	IWA, 2000

Design based on Equation 2.1.2 has generally been used to construct horizontal CWs and predict removal performance for organic matter usually expressed as BOD in constructed wetlands in Europe (Vymazal *et al.*, 1998; Cooper *et al.*, 1996), Australia (Mitchel *et al.*, 1998) and the US (Reed *et al.*, 1998). To date, there has been no published design equation for the construction of horizontal flow systems based on the removal of other pollutants such as microbial indicators, suspended solids, nitrogen and phosphorous other than organics. The removal of these pollutants has been based on Equation 2.1.2 (Neralla *et al.*, 2000; Cooper, 1999) assuming that adequate removal occurs if the design is suitable for BOD.

During the construction of SSF wetlands, bed slope and cross sectional area are selected to encourage plug flow through the bed and avoid flow over the bed surface. Bed slope in the lower range of 1-5% is commonly used whilst the hydraulic gradient for the whole bed is increased by progressively lowering the outlet (Green and Upton, 1994). Bed cross sectional area (also known as aspect ratio-i.e. length: width ratio) for the bed is usually calculated from Darcy's Law given as:

$$A_C = \frac{Q_s}{K_f * (dH / dS)} \qquad \text{.........2.1.3}$$

Where A_C (m^2) is the cross sectional area of the bed, Q_s (m^3 s^{-1}) is average flow, K_f (m s^{-1}) is hydraulic conductivity and dH / dS (m m^{-1}) is the slope of the bed.

Examples of hydraulic conductivity of media of operational treatment wetlands reported in the literature are 10^{-6} m s^{-1} for peat substrate treating landfill leachate (Kinsley *et al.*, 2007) and 1.91×10^{-4} m s^{-1} with a pore volume of 30% for a sand media substrate treating grey water (Shrestha *et al.*, 2001). The slopes of operational CW systems usually range between 1-5%. Examples of slope for HSSF beds from inlet to outlet are: 1% in a gravel bed treating household wastewater (Neralla *et al.*, 2000), 2% for a CW polishing municipal treated effluent (Cameron *et al*., 2003). Steer *et al*., (2002) used a 10cm slope to enhance flow from inlet through the outlet of the bed whilst in a CW polishing sewage effluent, a bed slope of 0.1% was used in the design (Combes and Collett, 1995).

- *Evolution of horizontal flow SSF CW models*
    - *First order models*

An amendment to Equation 2 (Kickuth model) to reflect treatment wetland performance data was developed by Kadlec and Knight (1996). The model commonly referred to as the K-C* model differs from the original Kickuth equation in two ways: Firstly, it is a reversible first-order reaction equation rather than the irreversible equation and secondly it includes a non-zero background concentration. It is believed that an irreversible first-order model does not satisfactorily describe removal of pollutants from treatment wetlands because pollutants in the treated water cannot be reduced to zero due to the subsequent release of pollutants from the wetland into the treated water (Kadlec and Knight, 1996). Thus the non-zero background concentration represents release of pollutants resulting from transformation processes within the sediments and sediment water interactions. These processes are mainly attributed to production of organics from the decomposition of plant litter and other organic materials as well as endogenous autotrophic processes (IWA, 2000; Bavor *et al*., 1988). Background concentrations of BOD lie in the range of 1-10 mg L^{-1} (IWA, 2000). The K-C* model is written as:

$$\ln\left(\frac{C_e - C^*}{C_i - C^*}\right) = \frac{K_v h \varepsilon A}{Q} = -\frac{KA}{Q} \quad \text{..2.1.4}$$

Where: ε (dimensionless) is porosity, h (m) is water depth, K_v (days^{-1}) is volumetric rate constant and C*(mg L^{-1}) is non-zero background BOD$_5$.

Values of K and C* vary from one wetland to another and depend on site-specific factors such as vegetation type and density, strength of influent wastewater, temperature and hydraulic variable (Stein *et al.*, 2007; Kadlec, 2000; Kadkec and Knight, 1996).

The K-C* model does not include a water balance across the wetland. Kadlec (1997) proposed an amended form of the K-C* model (Equation 2.1.5) which incorporates the effects of precipitation and evapotranspiration. Precipitation causes a dilution effect whilst evapotranspiration causes a concentration effect. Thus, both precipitation and evapotranspiration to some extent influences the system hydraulics (Kadlec, 2000).

$$\frac{C_e - C}{C_i - C'} = (1 + [\alpha y / q]^{-(1 + K_A/\alpha)} \quad \text{..2.1.5}$$

Where $C' = C^*\left[\frac{K_A}{K_A + a}\right]$ 2.1.6

α is Precipitation (m d^{-1}) – evapotranspiration (m d^{-1}), q (m yr^{-1}) is hydraulic loading rate, y (m) is fractional distance through wetland (i.e. distance from inlet per length of wetland), a is a constant equal to K for SSF wetland with Dacian flow and other terms carry their meaning as previously defined.

Further development of the model by Shepherd *et al.*, (2001) presented a two parameter time-dependent retardation model for COD removal in a high waste stream. The model is based on the assumption that a high waste stream contains multiple pollutants of variable ease of degradation. As a result, easily degradable substances with faster removal kinetics are gradually replaced with less biodegradable substances with slower removal kinetics. The result is a time dependent constant described as:

$$K_v = \frac{K_o}{(b\tau + 1)} \quad \text{………………………………………………………………..2.1.7}$$

where K_v (days^{-1}) is time dependent rate constant, K_o (days^{-1}) is the initial degradation rate constant, b (days^{-1}) is a time-based retardation coefficient (days^{-1}) and τ (days) is the retention time.

Incorporating Equation 2.1.7 into a simple plug flow model gives a time dependent retardation model (2.1.8):

$$\frac{C}{C_o} = \exp\left[\left(\frac{-K_o}{b}\right)\ln(b\tau + 1)\right] \qquad 2.1.8$$

The model seeks to account for the steady decrease in pollutant concentration with increased treatment time rather than a constant residual (i.e. background) value.

The limitation of first order models for the design of treatment wetlands has been recognised (Kadlec, 2000) because one-parameter, two-parameter and three-parameter versions all attain saturation (i.e. C ≠ 0) with increasing retention time. This effect worsens with a one-parameter model having a greater variability in background concentration (C*). Three parameter models do correct for dispersion of the non-ideal behaviour but cannot correct the degree of treatment influenced by short-circuiting (Kadlec, 2000). Evidently, none of the one, two or three parameter models are independent of operating conditions thus highlighting the importance of wetland hydraulics in improving design models.

- *Monod-type model*

The findings of Mitchell and McNevin (2001) further throw light on the limitations of existing first-order parameter models. They explained the limitation to first order models as due to the fact that biological systems will normally operate under Monod-type kinetics where degradation rates are limited by pollutant availability at relatively low concentration but would reach saturation at relatively high concentrations. Their model identified that most wetlands are operating well below their expected maximum performance partly because they are undersized and estimated that maximum loading for SSF wetlands approximates to 80 kg $ha^{-1}d^{-1}$ for BOD based on USEPA wetland data in North America. The Mitchell and McNevin (2001) proposed Monod model is given as:

$$r = K_{o,v} V \frac{C}{K + C} \quad \text{..........2.1.9}$$

where r is the rate of biological degradation and K is the half saturation constant and C (mg L^{-1}) is pollutant concentration. The contaminant concentration is normalised against the half saturation constant against the total length of the wetland bed Z given as:

$$\frac{dC}{dZ} = -\Omega \frac{C}{1 + C} \quad \text{..........2.1.10}$$

and a normalised removal rate (R_R)given as:

$$R_R = \frac{C_{in} - C_{out}}{\Omega} \quad \text{..........2.1.11}$$

where Z (m) is the length of the wetland bed, Ω indicates the relative effectiveness of the wetland bed and normalizes the maximum possible mass removal on a volumetric basis for a given hydraulic residence time or flow rate. A high value of Ω means that the degradation rate is high compared with the flow rate which leads to better performance.

Although the limitations in the original Kickuth equation for designing and predicting pollutant removal performance have been recognised (Kadlec and Knight, 1996) and various attempts made to address them through the development of models believed to correspond better with wetlands performance (Mitchell and Mcnevin, 2001, Shepherd *et al.*, 2001; Platzer, 1999; Kadkec and Knight, 1996), it is the equation still widely used to design treatment wetland processes (Mitchell and Mcnevin, 2001; IWA, 2000; Kadlec and Knight, 1996). This is because some of these recent models would require very large amount of data for proper calibration (IWA, 2000). In addition it is still uncertain whether detailed models will provide more accurate descriptions of wetland performance in light of the variability displayed by wetland data (Kadlec and Knight, 1996). As the processes involved in CWs is complex and difficult to predict, this technology at present is limited to organic loading guidelines (IWA, 2000).

2.1.2.2 Critical review of horizontal flow systems

To investigate the influence of design and operating conditions on wetlands performance, influent and effluent pollutant concentrations (mg.L^{-1}) and design parameters (flow rates, hydraulic loading and residence times) from 38 published studies were used to create a database. Literature was selected to cover the operational range of 0.01 – 0.10 m d^{-1} hydraulic loading as most treatment wetlands reported in the literature lie within this range (Tanner, 2001; Vymazal, 2001). Operational parameters were adopted as given in literature. When hydraulic loading or residence time was not given, they were calculated from Equations 2.1.12 and

2.1.13. Details of operational and water quality parameters used in this case study are given in Appendix 7.

$$HLR = \frac{Q}{A} \quad \ldots\ldots 2.1.12$$

$$HLR = \frac{\varepsilon h}{\tau} \quad \ldots\ldots 2.1.13$$

Where HLR (m d^{-1}) is hydraulic loading rate, Q (m^3 d^{-1}) is flow rate, A(m^2) is area of bed, ε is porosity of bed media, h(m) is bed depth and τ (d) is residence time. Value of ε (porosity or the fraction of space through which water can flow in the wetland) adopted was 0.75 for SF and 0.4 for SSF (IWA, 2000). Pollutant removal efficiency was calculated as percent mass removal given as:

$$100\frac{m_i - m_o}{m_i} \quad \ldots\ldots 2.1.14$$

Where m_i and m_0 are mass loading of inflow and outflow respectively.

The variables analyzed were influent and effluent loading of the following water quality parameters (BOD, COD, TSS, NH_4-N, NO_3-N, PO_4-P and total coliforms), removal efficiencies according to Equation (11) and HLR. Variables were analyzed by graphical plots with the aid of Microsoft regression equations, Spearman correlation ranking and F statistics.

- *Wetlands performance*
    - *Removal efficiency of pollutants in wetlands*

Results show that the ability of treatment wetlands to remove BOD, COD, TSS and coliforms from influent wastewater is greater (i.e. 73-83%) than for nutrients (30-45%). This result is consistent with the literature. For instance, Vymazal (2007) reported that total nitrogen and phosphorous removal in most CW is low compared to organics and solids and varied between 40-55% for nitrogen removal and 40-60% for phosphorous removal respectively. This is because the processes that affect nitrogen removal in CWs include nitrification and denitrification, and most treatment wetlands (e.g. horizontal or vertical system) cannot achieve high removal of total nitrogen or ammonia and nitrate nitrogen because of their inability to provide oxic conditions for nitrification and anoxic condition for denitrification simultaneously. To illustrate, horizontal systems being saturated and anoxic-anaerobic provide suitable conditions to achieve denitrification (Equation 2.1.1) whilst vertical flow systems being unsaturated and oxic successfully provide the conditions for nitrification (Equation 2.1.2). Thus, horizontal flow systems are limited in nitrification whilst vertical flow systems are limited in denitrification. Denitrification occurs in the presence of available organic substances and can be illustrated by the following equation (Hauck, 1984):

$$6(CH_2O) + 4NO_3^- \rightarrow 6CO_2 + 2N_2 + 6H_2O \text{ ....2.1.1}$$

Nitrification is executed by chemolithotrophic (aerobic) bacteria which are dependent on the oxidation of ammonia for the generation of energy for growth. The overall nitrification process can be represented as (Schmidt *et al.*, 2003, 2001):

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \ldots\ldots 2.1.2$$

Removal of phosphorous in several treatment wetlands has been low because the substrates traditionally employed for municipal/domestic wastewater in treatment wetlands (e.g. sands and gravels) do not have high enough sorption capacity.

Furthermore, most treatment wetlands are effective in removing organics from influent wastewater because they are primarily designed to remove organic matter and solids (Vymazal, 2002). Removals up to 95% can easily be achieved if the systems are not overloaded. The high and comparable removal efficiencies amongst BOD, COD, TSS and coliforms is because significant amount of solids in wastewater is organic in nature, and consequently, reduction of solids corresponds with organic reduction (Neralla *et al.*, 2000; Gopal, 1999).

Evaluation of wetlands overall performance using 1:1 plot in removing pollutants from wastewater revealed that removal efficiency was lower than the expected based on the 95 percentile calculated from the Kickuth equation. Corresponding plots of predicted effluent concentrations based on the 95 percentile versus measured effluent concentrations for all water quality parameters showed data points well below the 1:1

removal line (Figures 2.1.2a to 2.1.9a). The 1:1 removal line represents the 100% efficiency line. Although 100% would not be achieved in a real situation because of subsequent release of organics from the wetland into the effluent waste stream (Kadlec and Knight, 1996), the further the points lie to the right of the 95 percentile removal line indicates the more undersized the wetlands are for the particular application resulting in sub-optimal wetland performance (Mitchell and McNevin, 2001). Although correlation coefficients for all parameters were low indicating that the removal of pollutants were poorly predicted by the first order or Kickuth model, evaluation from the line fitting plots also revealed that measured versus predicted concentrations for BOD, COD, TSS and total coliforms correlated better (r^2 values in the range of 0.24 – 0.32) compared to r^2 values of 0.08 – 0.16 for nutrients (Figure 2.1.2a-2.1.9a). This indicate that the removal of BOD, COD, TSS and total coliforms from wastewater by treatment wetlands were better described and predicted by the models used to design these wetlands. Indeed, it is known that all design equations for pollutant removal and treatment performance in treatment wetlands are based on BOD despite recognising that removal of nutrients from wetlands cannot be adequately described the same way as organics due to different pollutant removal pathways (Kern and Idler, 1999).

Rousseau *et al.*, (2004) in a study of model design of horizontal subsurface wetlands obtained different surface area from different models for treatment wetlands using a single influent and effluent data set. He found that a simple “rule of thumb” model predicts several orders of magnitude of surface area larger than first order (including Kikuth model), regression and retardation models. He further reported large differences between minimum and maximum calculated surface area by each of these models due to parameter uncertainty (i.e. rate constants and background concentrations). Rate constants and background concentrations have been reported to be strongly dependent on hydraulic loading and influent concentration, which consequently renders first order models incapable of acceptable performance design (Kadlec, 2000). Calculation for area based rate constants from collated data in this study ranged from 0.02 to 0.34 $m.d^{-1}$ for domestic/municipal waste water. Despite the extreme of this area based rate constant calculated, the mid range values are comparable to that of the mid-range area-base rate constants in the range of 0.06 to 1.00 reported by Rousseau *et al.*, (2004).

According to first order design models which most wetland designs are based on; K values from treatment wetlands should ideally be within a narrow range. However, such large variations obtained from operational treatment wetlands reflect the impact of wetland age, influent concentration and hydraulic loading (Stein *et al.*, 2007; Kadlec, 2000; Kadlec, 1997). These collective factors are difficult to account for accurately in any model as wetland age varies for any particular wetland and organic matter release from wetlands are influenced by local conditions. Addressing these factors would produce a complex model which would be difficult to calibrate and apply.

- *Influence of operational parameters (hydraulic and influent loading) on pollutant removal*
    - *Organics*

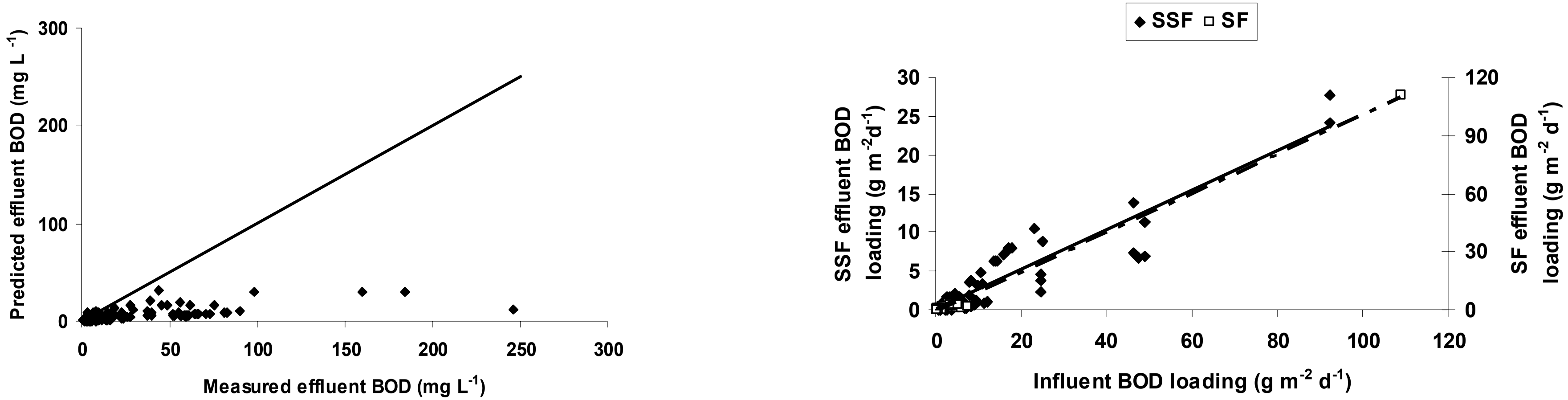
Effluent organic loading (BOD_5 and COD) for both SF and SSF treatment wetlands showed strong positive correlation with influent organic loading (Tables 2.1.4 & 2.1.5, Figure 2.1.2b and 2.1.4b). This indicates that the residual concentration of BOD in the effluent of most treatment wetlands was influenced by the inlet concentration. Vymazal (2002) reported similar findings for 44 horizontal systems in the Czech republic.

Table 2.1.4: Regression summary for the effect of operational parameters on effluent BOD

Parameter	Surface flow	Subsurface flow
Inf vs Eff loading	$y= 1.02x – 1.12, R^2 = 0.99, n = 35$	$y = 0.26x – 0.01, R^2 = 0.86, n = 81$
Inf loading vs % removal	$y= -0.46x + 53.1, R^2 = 0.07, n = 35$	$y = -0.09x + 53.1, R^2 = 0.01, n = 81$
HLR vs % removal	$y= 11.5x +2.34, R^2 = 0.10, n = 35$	$y = 64.4x + 0.43, R^2 = 0.95, n = 81$

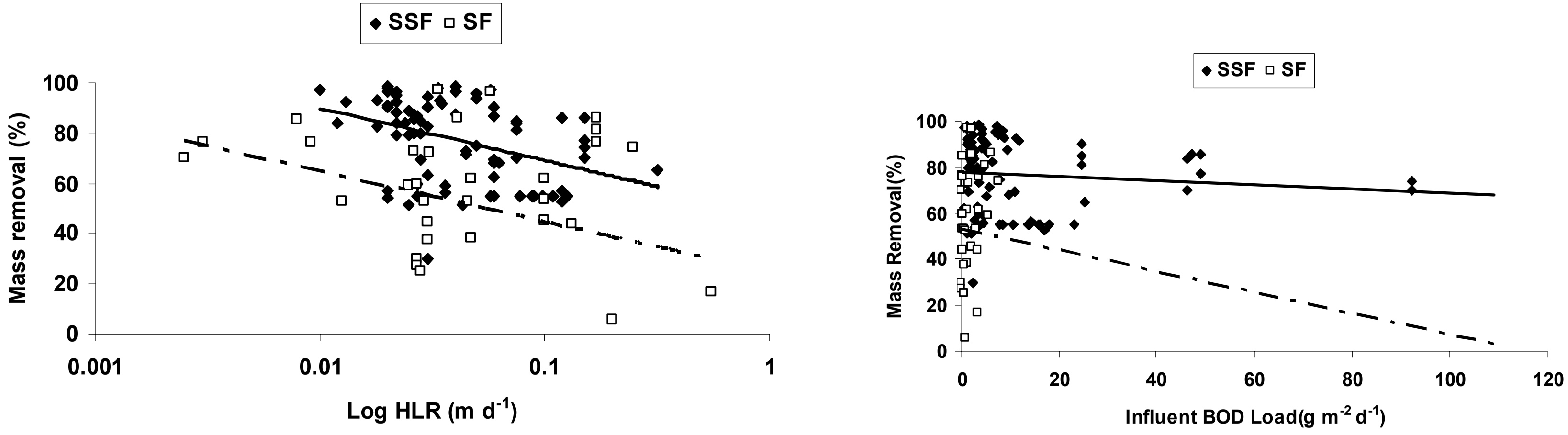
Influent organic loading has been proved to influence wetland performance as reflected in effluent residual organics (IWA, 2000). The explanation is that up to an optimum loading, removal efficiencies increase as loading increases and correlate positively with mass loading rates. To illiustrate, Ghermandi *et al.*, (2007) reviewed 25 tertiary surface flow treatment wetlands and found that in 19 cases, effluent BOD were below 10 mg L^{-1} when the systems were not overloaded in terms of influent organic loading, whereas in 3 cases, effluent exceeded 30 mg L^{-1} of which 2 were caused by higher than recommended influent BOD loading. Results from other operational wetlands for different types of waste water have also exhibited a similar effect of influent loading on effluent residual BOD concentrations (e.g. Langergraber *et al.*, 2007; Noorvee *et al.*, 2005).

The effect of hydraulic loading on effluent organic loading though significant was much weaker ($p<0.05$, Figure 2.1.2c & 2.1.4c). Evaluation of the plots of HLR versus BOD (Figures 2.1.2c and 2.1.3a&b) indicates that removal efficiency of organics decreased with increased HLR. This is consistent with the literature. For instance, Langergraber (*et al*., 2007), da Motta Marques *et al*., (2001), Kern and Idler (1999) Maehlum and Stålnacke



(a) Plot of measured versus predicted values of wetland effluent BOD. Line represent the 100% removal. R^2=0.27, p=0.000, n=116

(b) Influent and effluent BOD loading relationships for SF and SSF wetlands.



(c) The influence of HLR on BOD removal in SSF and SF wetland.

(d) The influence of influent loading on effluent BOD in SSF and SF wetland.

Figure 2.1.2: The influence of operational parameters (HLR & influent loading) on subsurface flow –SSF and surface flow-SF wetland BOD removal. Bold and broken lines represent trend lines for SSF and SF respectively

Table 2.1.5: Regression summary for the effect of operational parameters on effluent COD

Parameter	Surface flow	Subsurface flow
Inf vs Eff loading	$y= 0.24x + 5.82$, $R^2 = 0.81$, n = 23	$y= 0.44x – 2.07$, $R^2 = 0.91$, n = 42
Inf loading vs % removal	$y= 0.03x + 51.6$, $R^2 = 0.08$, n = 23	$y=- 0.10x + 70.2$, $R^2 = 0.07$, n = 42
HLR vs % removal	$y=-7.07x + 60.6$, $R^2 = 0.02$ n = 23	$y= -131.4x + 74.2$, $R^2 = 0.15$, n = 42

(1999) and Geller (1997) reported that organic removal efficiency is improved at lower HLR. Figure 2.1.3 (a and b), showed the effect of gravel and sand/soil substrate on the removal of BOD organics over a range of HLR and influent loading in SSF wetlands. In both substrate types (except gravel for influent loading versus removal), removal efficiency decreases with increased HLR. However, the relationship for gravel substrate is much looser/weaker compared to sand and soil suggesting that the effect of HLR and influent loading on the removal of organic matter is much more pronounced in treatment wetlands having sand or soil substrate. A possible explanation for this is that increased HLR results in increased organic and suspended solids loading. Depending on the nature and loading of solids, increased TSS loading may result in bed surface clogging and soil/sand media are much more susceptible to clogging and surface overflow compared to gravel. Clogging and overflow of a bed usually result in poor effluent quality.

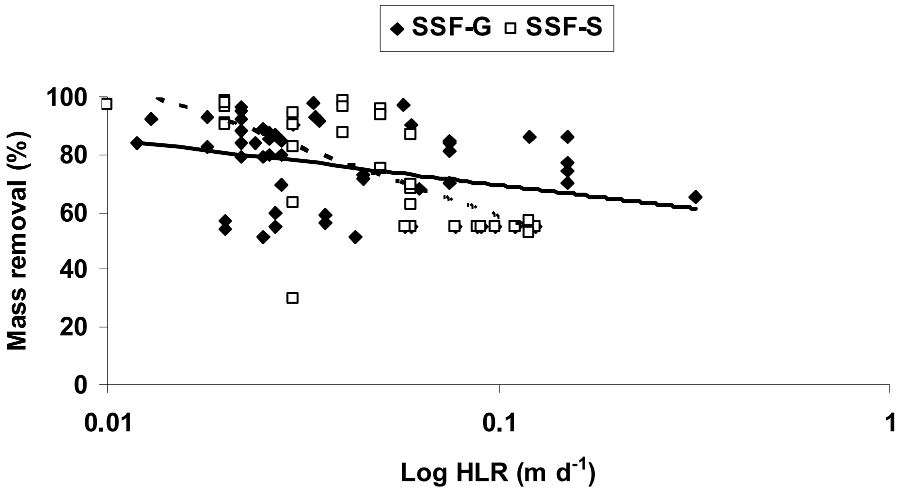


Figure 2.1.3a: Relationship between hydraulic loading rate and substrate type on the removal of organics (BOD) for SSF wetlands. Bold and broken lines represent trend lines for gravel and sand media respectively.

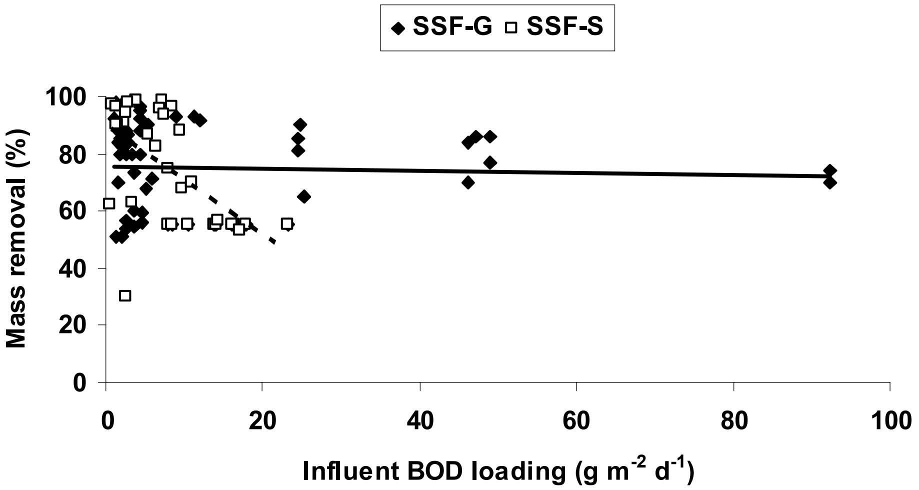
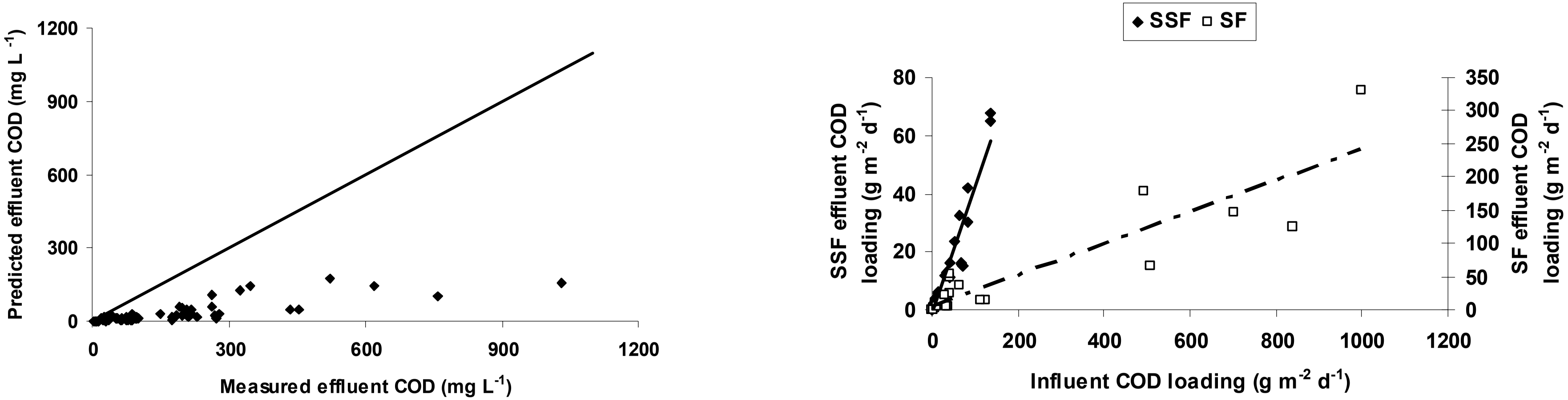
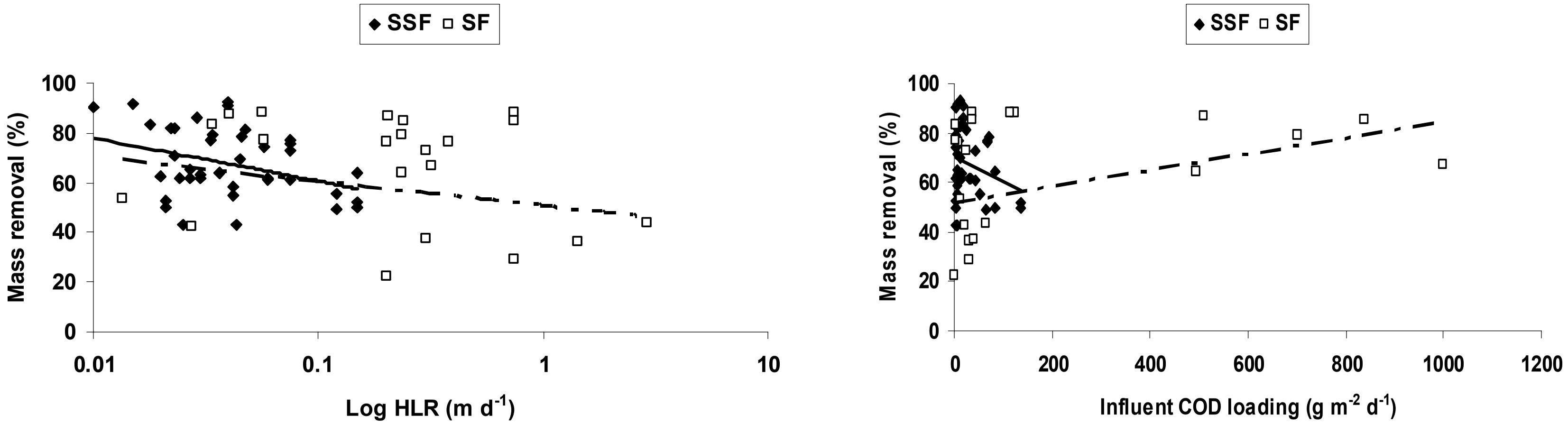


Figure 2.1.3b: Relationship between influent organic loading and substrate type on the removal of organics (BOD) for SSF wetlands. Bold and broken lines represent trend lines for gravel and sand media respectively.



(a) Plot of measured versus predicted values of wetland effluent COD. Line represent the 100% removal $R^2=0.32$, p=0.000, n=81

(b) Influent and effluent COD loading relationships for surface flow-SF and subsurface flow –SSF wetlands.



(c) The influence of HLR on COD removal in SSF and SF wetland.

(d) The influence of influent loading on effluent COD in SSF and SF wetland.

Figure 2.1.4: The influence of operational parameters (HLR & influent loading) on wetland COD removal

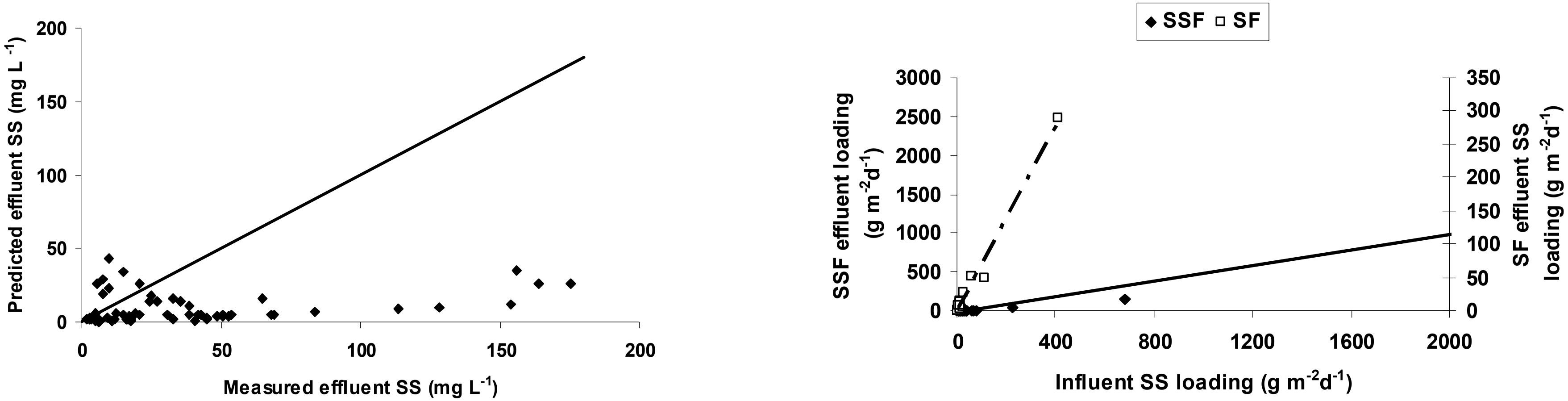
- *Suspended Solids (SS)*

Strong correlations were observed between influent and effluent SS loading for both SF and SSF designs (Figure 2.1.5b). The overall efficiency of SS removal in terms of surface loding averaged 60% for subsurface flow and and 34% for surface flow. The difference in percentage between SF and SSF reflects the removal mechanisms of solids in both wetland types. There is greater contact between the water and the wetland media as water flows through an SSF which encourages filtration compared to SF. Removal of SS correlated weakly with influent load (R^2=0.17) for SSF whilst no relationship was evident between the two for SF. The HLR virtually did not show any effect on SS removal for both systems (Table 2.1.6).

Table 2.1.6: Regression summary for the effect of operational parameters on effluent SS

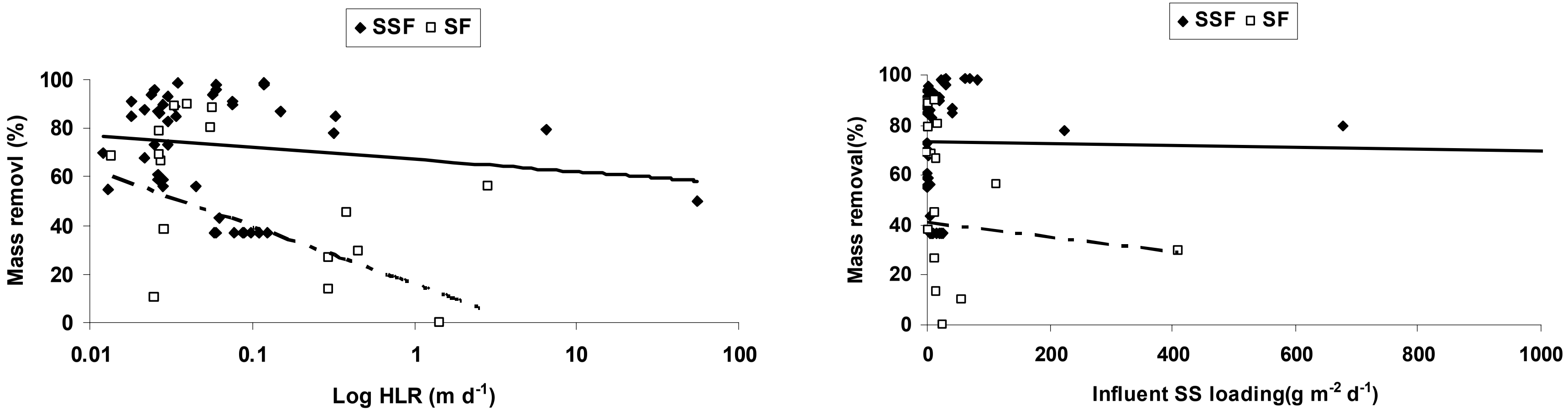
Parameter	**Surface flow**	**Subsurface flow**
Inf vs Eff loading	y= 0.69x – 1.10, R^2 = 0.98, n = 19	y= 0.50x – 10.7, R^2 = 0.99, n = 49
Inf loading vs % removal	y= -0.04x + 40.8, R^2 = 0 , n = 19	y= 0.04x – 64.0, R^2 = 0.17, n = 49
HLR vs % removal	y= -5.82x + 41.2, R^2 = 0.01, n = 19	y= -0.41x + 73.5, R^2 = 0.02, n = 49

The plot of HLR against SS removal shows that for both SF and SSF systems, removal efficiency decreases as HLR increases and that maximum efficiency tends to be achieved within a narrow range of SS (Figure 2.1.5c). These findings are in line with Reddy *et al.*, (2001) who found no relationship between SS removal and SS mass loading in a SF CW whereas Gearheart (1992) reported approximately 75% of TSS removal in the first day retention in his study. Solids removal in treatment wetlands is primarily due to physical processes such as filtration and sedimentation as wastewater passes through the media, much of which can be retained around the inlet bed (Reddy *et al.*, 2001; Cooper *et al.*, 1996). As a result, wetland outlet SS data reflects background concentrations (i.e. C*) and not necessarily wetland dynamics or operational characteristics. SS removal in SSF CW is therefore not strongly sensitive to HLRs (IWA, 2000). The observed removal pattern of solids in wetlands would also mean that an increase in removal rate will not be observed as loading increases as indicative of first order kinetics, but rather will increase at low concentration and tend towards zero order at high concentration as hypothesized by Mitchell and McNevin (2001).



(a) Plot of measured versus predicted values of wetland effluent SS. Line represent the 100% removal R^2=0.24, p=0.031, n=71

(b) Influent and effluent SS loading relationships for surface flow-SF and subsurface flow –SSF wetlands.



(c) The influence of HLR on SS removal in SSF and SF wetland.

(d) The influence of influent loading on effluent SS in SSF and SF wetland.

Figure 2.1.5: The influence of operational parameters (HLR & influent loading) on wetland SS removal

- *Nutrients (NH_4-N, NO_3-N, PO_4-P)*

Influent loading correlated strongly with effluent loading for both NH_4-N and NO_3-N. However, influent loading did not correlate with NH_4-N or NO_3-N mass removal (Tables 2.1.7 & 2.1.8, Figures 2.1.6 & 2.1.7 b & d).

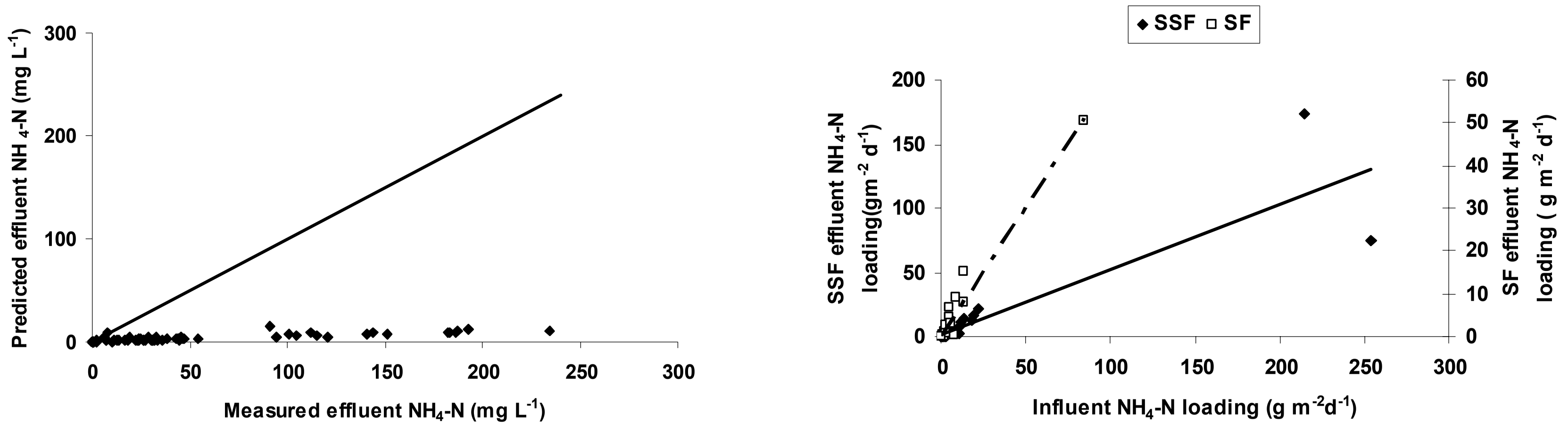
Table 2.1.7: Regression summary for the effect of operational parameters on effluent NH_4-N

Parameter	Surface flow	Subsurface flow
Inf vs Eff loading	$y = 0.60x + 0.07$, $R^2 = 0.95$, n = 23	$y = 0.50x + 1.09$, $R^2 = 0.79$, n = 51
Inf loading vs % removal	$y = 0.04x + 37.1$, $R^2 = 0.5$, n = 23	$y = 0.03x – 36.5$, $R^2 = 0$, n = 51
HLR vs % removal	$y = 0.60x + 0.07$, $R^2 = 0.95$, n = 23	$y = 0.51x + 1.1$, $R^2 = 0.79$, n = 51

Table 2.1.8: Regression summary for the effect of operational parameters on effluent NO_3-N

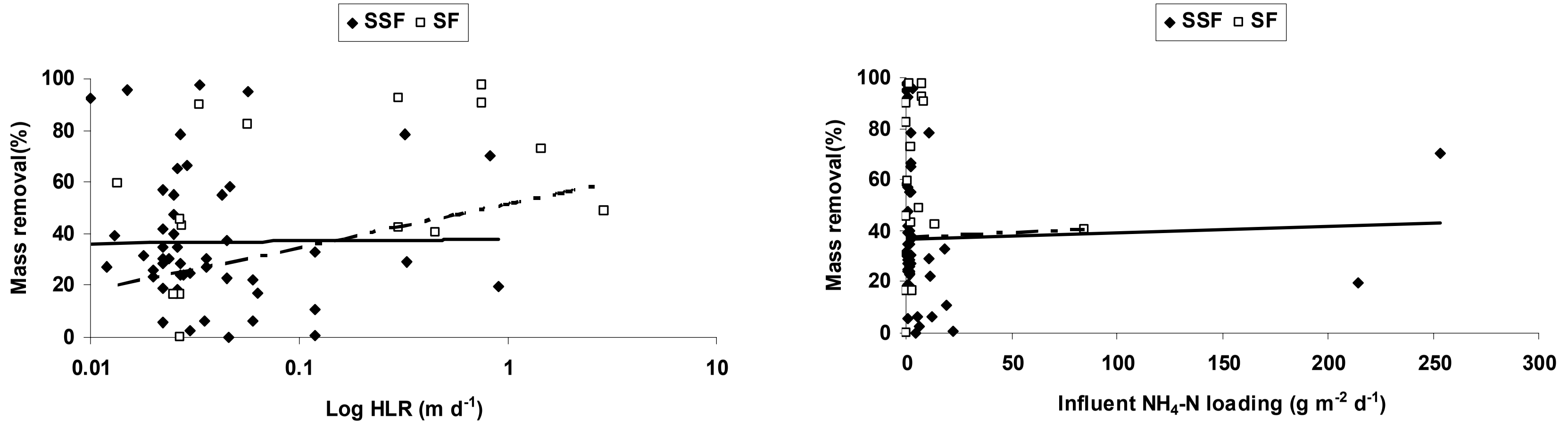
Parameter	Surface flow	Subsurface flow
Inf vs Eff loading	$y = 0.30x + 0.21$, $R^2 = 0.69$, n = 19	$y = 0.80x + 0.07$, $R^2 = 0.37$, n = 14
Inf loading vs % removal	$y = 7.70x – 5.02$, $R^2 = 0.07$, n = 19	$y = 1349x -752.9$, $R^2 = 0.06$, n = 14
HLR vs % removal	$y = -33.3x + 26.3$, $R^2 = 0.05$, n = 19	$y = 3527.6x -781.7$, $R^2 = 0.04$, n = 14

N removal in wetlands undergo complex sequential transformation processes each requiring specific environmental conditions. Operational design for significant nitrogen removal therefore has to ensure oxic conditions for nitrification and anoxic conditions for denitrification. Mass removal of NH_4-N and NO_3-N did not correlate with HLR (Tables 2.1.7 & 2.1.8, Figure 2.1.6 & 2.1.7c) indicating that removal of these nutrients is not influenced by HLR. These observations further indicate the importance of other factors influencing NH_4-N or NO_3-N removal but which are not included in simple regression relationships. Hence reported N removal from treatment wetlands is generally lower than BOD, COD and TSS (Kern and Idler, 1999) and highly variable.



(a) Plot of measured versus predicted values of wetland effluent NH_4-N. Line represent the 100% removal $R^2=0.09$, $p=0.000$, $n=74$

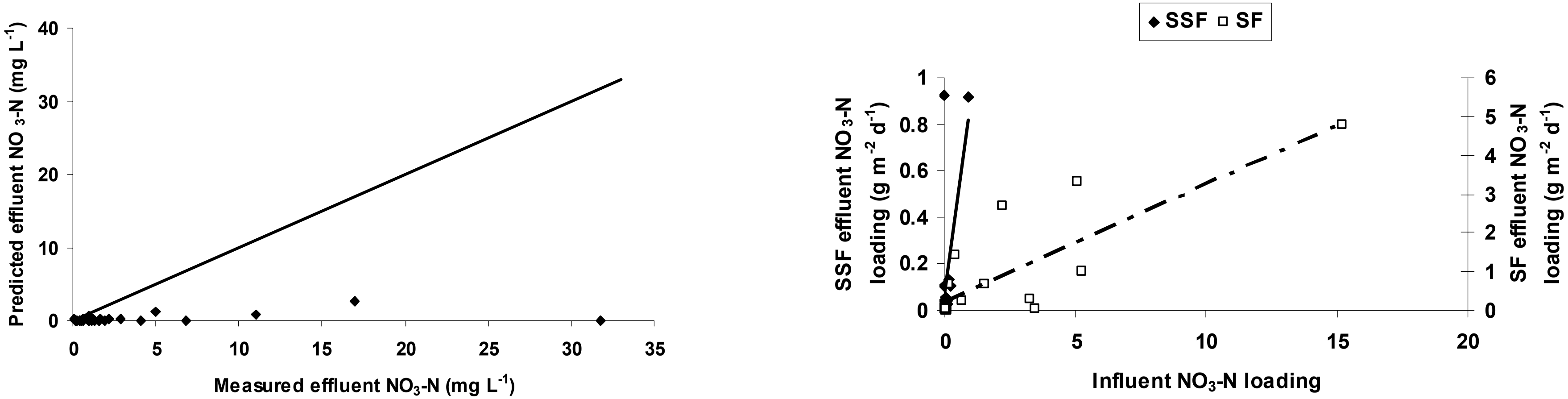
(b) Influent and effluent NH_4-N loading relationships for surface flow-SF and subsurface flow –SSF wetlands.



(c) The influence of HLR on NH_4-N removal in SSF and SF wetland.

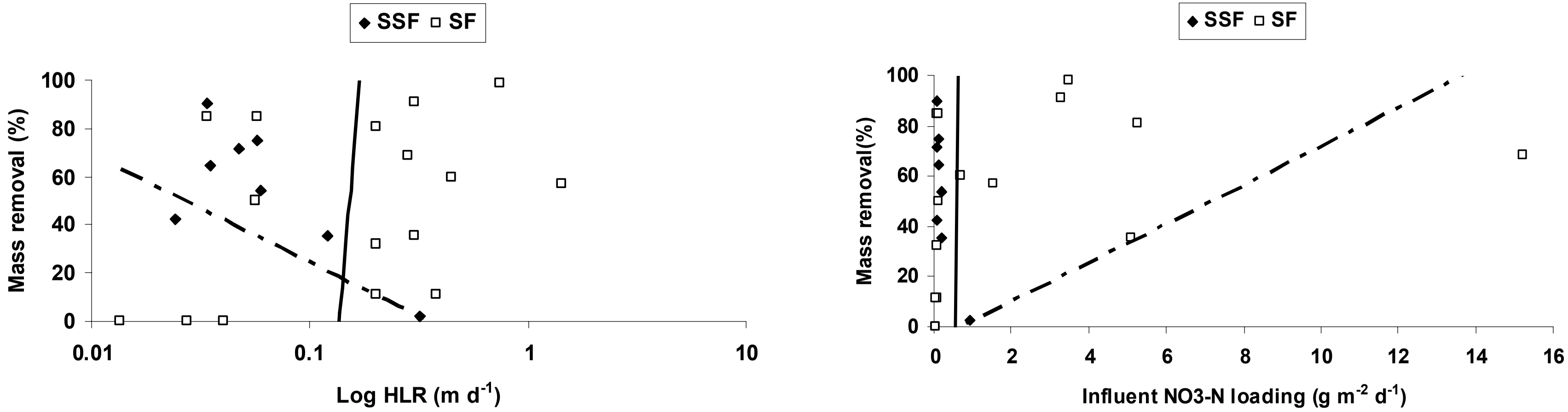
(d) The influence of influent loading on effluent NH_4-N in SSF and SF wetland.

Figure 2.1.6: The influence of operational parameters (HLR & influent loading) on wetland NH_4-N removal. Bold and broken lines represent trend lines for SSF and SF respectively.



(a) **Plot of measured versus predicted values of wetland effluent NO$_3$-N. Line represent the 100% removal** R^2=0.08, p=0.08, n=33

(b) **Influent and effluent NO$_3$-N loading relationships for surface flow-SF and subsurface flow – SSF wetlands.**



(c) **The influence of HLR on NO$_3$-N removal in SSF and SF wetland.**

(d) **The influence of influent loading on effluent NO$_3$-N in SF and SSF wetland**

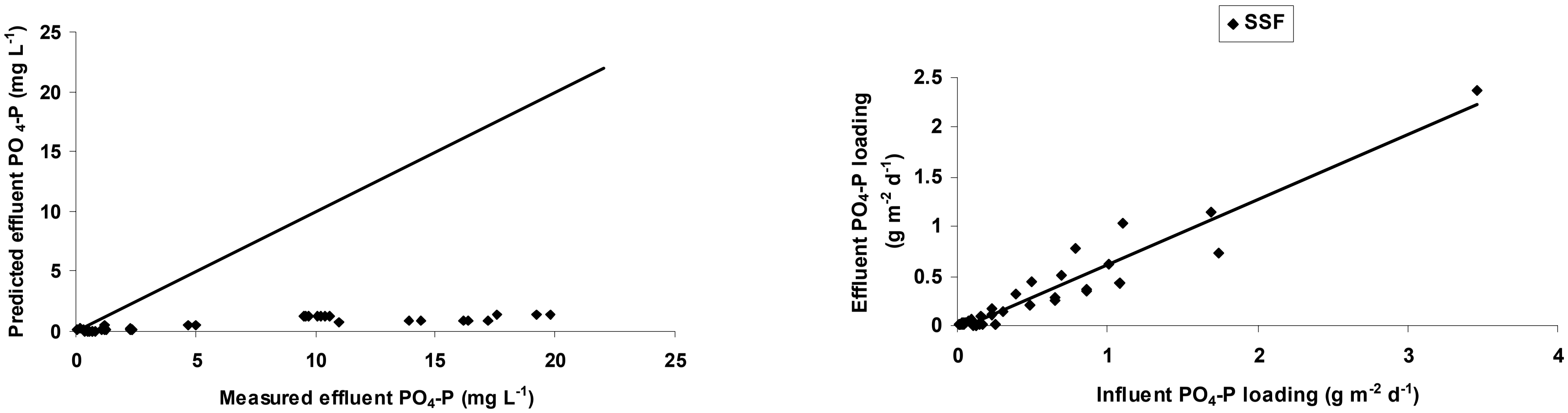
Figure 2.1.7: The influence of operational parameters (HLR & influent loading) on wetland NO$_3$-N removal. Bold and broken lines represent trend lines for SSF and SF respectively.

For phosphate, only the relationship between influent and effluent P loading was significant (Tables 2.1.9, Figure 2.1.8b).

Table 2.1.9: Regression summary for the effect of operational parameters on effluent PO_4-P

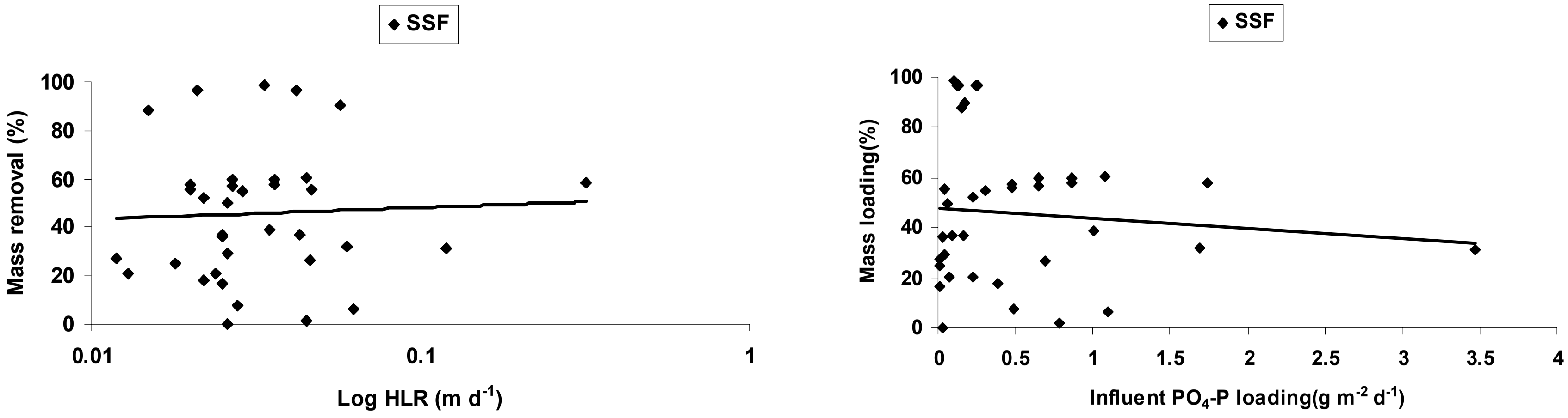
Parameter	Surface flow	Subsurface flow
Inf vs Eff loading	Not investigated	$y= 0.65x - 0.04, R^2 = 0.92, n = 38$
Inf loading vs % removal	Not investigated	$y= -3.93x + 47.7, R^2 = 0.01, n = 38$
HLR vs % removal	Not investigated	$y= 29.1x + 44.5, R^2 = 0, n = 38$

P removal in treatment wetlands is also complex and variable. Removal is dependent mainly on the nature of the bed media which is the major sink for P in wetlands. Generally, P removal involves both biotic (uptake by vegetation, periphyton and microbes; mineralization of plant litter and soil organic phosphorous) and abiotic (sedimentation and burial; adsorption and precipitation; exchanges between soil and overlying water column) processes (Reddy *et al*., 1996). Chick and Mitchell (1995) found that these processes are favoured by longer retention times whilst Sun *et al*., (2003) reported P removal not to be affected by increased contact time since inorganic chemical reactions are normally rapid. The soil/litter compartment is the major long-term storage pool for phosphorous, though some may eventually be released to the water column under less reducing conditions and when sorption sites became saturated/unavailable (Geary and Moore, 1999; Schonerklee *et al*.,1996). Although regression analysis indicates no relationship between inflow P loading and removal efficiency, generally, the plot shows a decrease in removal efficiency with increased loading. Geary and Moore (1999) reported sensitivity of P removal to HLR possibly because of the ability of the substrate to sorb phosphorous.



(a) **Plot of measured versus predicted values of wetland effluent PO4-P Line represent the 100% removal $R^2 = 0.16$, p=0.005, n=38**

(b) **Influent and effluent PO_4-P loading relationships for SSF wetlands.**



(c) **The influence of HLR on PO_4-P removal in SSF wetland.**

(d) **The influence of influent loading on effluent PO_4-P in SSF**

Figure 2.1.8: The influence of operational parameters (HLR & influent loading) on wetland PO_4-P removal.

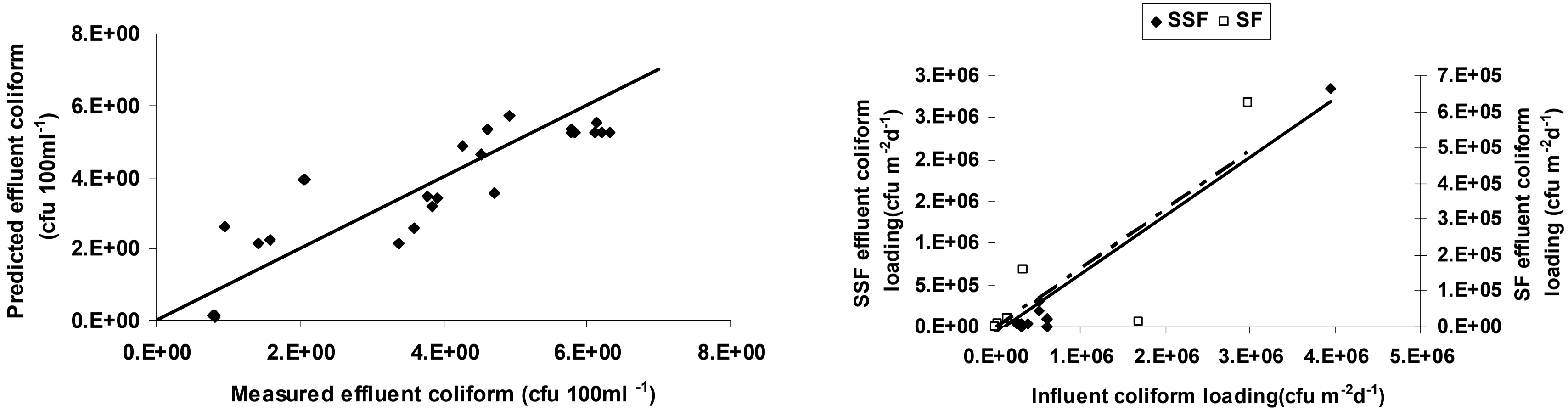
- *Coliforms*

With the exception of influent and effluent loading of coliform counts where strong correlations was evident (Table 2.1.10, Figure 2.1.9b), coliform removal was very weakly correlated to HLR and influent loading for both SF and SSF wetlands (Table 2.1.10, Figures 2.1.9c & d).

Table 2.1.10: Regression summary for the effect of operational parameters on effluent total coliforms

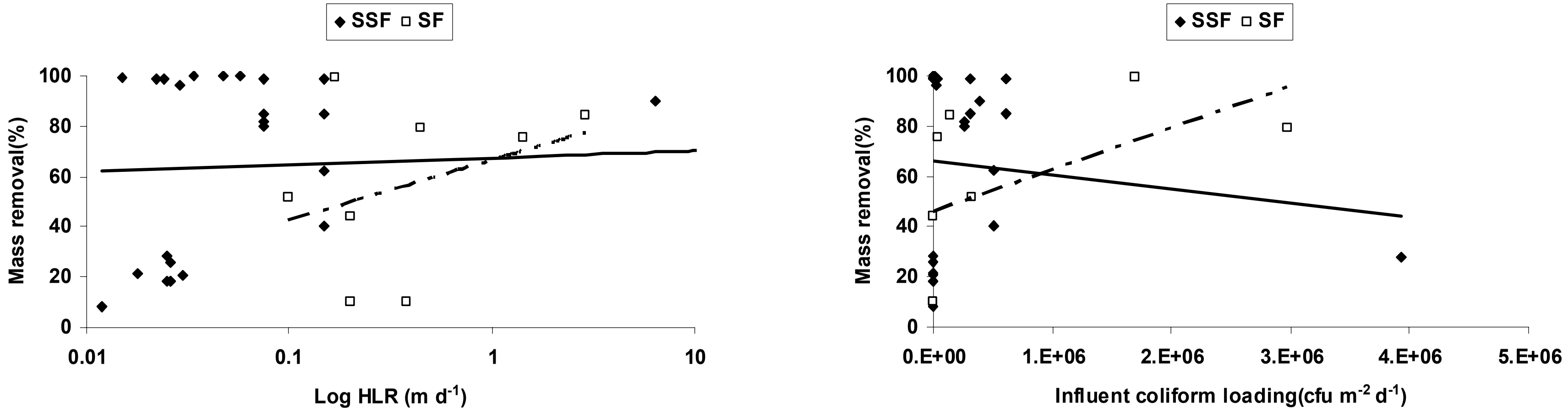
Parameter	Surface flow	Subsurface flow
Inf vs Eff loading	$y= 0.16x – 2489, R^2 = 0.70, n = 35$	$y= 0.70x – 74168, R^2 = 0.95, n = 35$
Inf loading vs % removal	$y= 6.21x – 126.6, R^2 = 0.20, n = 35$	$y= 8.87x +35.63, R^2 = 0.39, n = 35$
HLR vs % removal	$y= 14.1x + 46.4, R^2 = 0.17, n = 35$	$y= -0.62x + 65.7, R^2 = 0.04, n = 35$

High removal of indicator organisms is generally reported for treatment wetlands despite varying influent load and hydraulic loading. For instance, Soto *et al.*, (1998) with an influent count of 7-8 order higher than that in Vymazal *et al.*, (2001) reported removal efficiency of 99.9% and 99.3% respectively. Also, da Motta Marques *et al.*, (2001) reported removal efficiency of 99% coliform removal at HLR of 6.7 cm.d^{-1} compared to 88% at HLR of 13.7 cm.d^{-1}. High removal rates characterised by rapid decline to background concentrations for coliforms in treatment wetlands (IWA, 2000) is indicative of the fact that removal of coliforms from treatment wetlands is not primarily influenced by HLR or influent load. An explanation for this could be due to the combined physical, chemical and biological factors responsible for the removal of microbial indicators from CWs. Physical factors include filtration, sedimentation, and aggregation and ultra-violet ray action. Chemical factors include oxidation, adsorption and exposure to toxins given off by other microorganisms and plants. Biological mechanisms include antibiotics, ingestion by



(a) **Plot of measured versus predicted values of wetland effluent total coliforms. Line represent the 100% removal R^2=0.25, p=0.000, n=33**

(b) **Influent and effluent total coliforms loading relationships for SF and SSF wetlands.**



(c) **The influence of HLR on total coliform removal in SSF and SF wetland.**

(d) **The influence of influent loading on effluent total coliforms in SF and SSF**

Figure 2.1.9: The influence of operational parameters (HLR & influent loading) on wetland total coliform removal.

nematodes or protozoans, lytic bacteria and bacteriophages attacks and natural die-off (Vymazal, 2002).

2.1.2.3 Review findings

Results from this case studied showed that despite high removal efficiency reported for most wetlands, residual concentrations e.g. for BOD are frequently higher than those predicted based on the 95 percentile first-order Kickuth design equation. This observation was attributed to most wetlands being undersized and high hydraulic loading applications implying that sizing and predicting CWs performance cannot be primarily predicted based on Equation 2.1.2 alone. Also correlation results indicate that hydraulic and pollutant loading strongly influence wetland performance for organic removal (BOD, COD). In all cases, removal generally decreases as loading increases. Hydraulic loading was not found to correlate with nutrient removal. This highlights the need to incorporate other operational parameters for the efficient removal of nutrients in wetlands. Overall, it can be concluded that organic removal will be earsier to model in treatment wetlands (e.g. horizontal systems) compared to nutrients because their removal can be influenced primarily by the design parameters (HLR and influent loading) whilst other factors (e.g. aerobic conditions, redox potential, environmental conditions) in addition to HLR and influent loading influence removal of nutrients in treatment wetlands. Because the removal of solids and indicator organisms (coliforms) are not primarily influenced by the key design parameters (HLR and influent loading), it is expected that they will fit into any design model developed.

2.2 Reuse

2.2.1 Background

The primary drivers for implementing water reuse are augmentation of available water supply and pollution abatement. Water shortage arises mainly from rising demand for clean water due to increases in population, changing lifestyle, diminishing water resources, rising economic growth and urbanisation. The implementation of water recycling and reuse offers the opportunity to increase available water supply, reduce potable water demand and reduce environmental impact associated with uncontrolled pollution of water resources.

Of the different sources of water available in urban environments for reuse, grey water reuse represents the most profitable option in terms of its reliability, availability and raw water quality (Kujawa-Roeleveld, 2006; Dixon *et al.*, 1999). For instance, while rain water is cleaner compared to grey water, it's availability is dependent on season. Grey water on the other hand is produced daily through domestic water use such as in bathing, clothes washing, cleaning and cooking. Grey water constitutes a major fraction of domestic waste water, amounting to 70% of the total volume produced (Kujawa-Roeleveld and Zeeman, 2006; Almeida *et al.*, 1999). With about one-third of domestic water consumption used for bathing, showering and hand-washing; and a further third tending to be used for toilet flushing, the reuse of grey water for toilet or urinal flushing could potentially save about a third of potable household water demand with a corresponding decrease in water bills (Diaper *et al.*, 2001; Karpiscak *et al.*, 1990).

Despite being less polluted compared to municipal waste water or black water, grey water contains high enough pollutant loads to cause a health risk if used untreated or not treated adequately. As a result, grey water reuse requires highly efficient and reliable treatment systems.

2.2.2 Standards for reuse

To protect public health and the environment, grey water must be treated to a required standard prior to reuse. However, for practical and economic reasons, the level of treatment depends on the end-use application. For instance, the degree of treatment required for restricted use is different for unrestricted (Table 2.2.1). Countries have developed different approaches to protect public health and the environment which vary from low technology-low cost-controlled risk to high technology-high cost-low risk guidelines (Anderson *et al.*, 2001). Many developed countries have adopted the Quantitative Risk Assessment (QRA) approach which focuses on high technology-high cost-low risk guidelines (Anderson *et al.*, 2001). Examples of the QRA approach are the USEPA and Californian standards. Such approaches usually require state-of-the-art treatment technologies (e.g. Reverse Osmosis, membrane bioreactor) which are often expensive and require skilled personnel to meet the required reuse standards. Less developed countries have adopted the low technology-low cost-controlled risk approach based on economic constraints (Anderson *et al.*, 2001). An example of a low technology-low cost-controlled risk approach is the World health Organization (WHO) standard which is used in many less developed countries especially in Africa and Asia. Low technology-Low cost-controlled risk requires less expensive and more easily managed treatment systems such as constructed wetlands, Stabilization ponds and sand filtration. Examples of a range of standards which encompasses both the high technology-high cost-low risk (e.g. USEPA) and low technology-low cost-controlled risk (WHO) are presented in Table 2.2.1. Evaluation of the standards reveals that reuse standards within the developed world (e.g. Europe) varies with the UK yet to produce a legally binding sub-potable water quality standard. However, the Building Services Research and Information Association (BSRIA, UK) provided published guidelines for grey water and stored rainwater for reuse which includes no detectable Faecal coliforms for 90% samples or 14 for any sample (Lazarova *et al.*, 2003).

Table 2.2.1 Comparison of reuse standards for domestic recycling

Coutry/ Organization	Application	BOD (mg L^{-1})	Turbidity (NTU)	SS (mg L^{-1})	NH_4-N (mg L^{-1})	Residual chlorine (mg L^{-1})	Total coliform (cfu $100ml^{-1}$)	*E. coli* (cfu $100ml^{-1}$)	Faecal coliform (cfu $100ml^{-1}$)
USA, Florida	Toilet flushing	20		5		1		ND	
USA, Texas (Surendran and Wheatley, 1999)	Toilet flushing	5	3						
Israel Gross *et al*., 2007)		10		10					1
Spain canary Islands (USEPA, 2004)		10	2	3					
Italy (Cirelli *et al*., 2007)	Wastewater reuse	<25		<35				<50	
Australia (Queensland, 2003)	Garden watering	20	30				100		
China (Lin *et al*., 2005)	Non portable use	10	10	10	20	0.2		3	
Japan	Toilet flushing		<2			Trace	≤10		
(Lin *et al*., 2005;Tajima,	Landscape		<2			≤4			
2005; Asano *et al*., 1996)	Recreational		<2						
Taiwan (Lin *et al*., 2005)	Non portable use	10				Trace		10	
Costa Rice									<1,000
(Dallas and Ho, 2005)	Restricted use	<40							
WHO	Unrestricted irrigation								<1,000

2.2.3 Characteristics of grey water

Conceptually, grey water should have lower concentrations of the various water quality pollutants compared to black water. This is because grey water usually comprises used water excluding that used for toilet flushing (WC). The exclusion of the toilet waste stream from domestic water means grey water has reduced level of nitrogen, phosphorous, solids and organic matter, but elevated levels of surfactants, oils and salt (Friedler *et al.*, 2004; Eriksson *et al.*, 2002; Günther, 2000). To illustrate, urine and faeces comprises ~90% of nitrogen and ~67% of phosphorous in the human excreta. Thus, their exclusion from grey water means less N and P levels relative to black water. Grey water displays considerable variability in pollutant concentrations and discharge volumes, both between locations and between different users of the same appliances (Friedler and Butler, 1996). The use of house-hold products and individual lifestyles play an important role in influencing the quality of grey water. As a result, the variability of grey water is emphasized at small scales where the activities of one or a few households have proportionally greater impact on grey water quality. Thus, different grey water source have different characteristics (Table 2.2.2). Solids and turbidity in grey water usually range from 113 to 2410 mg L^{-1} and 15.3-240 NTU respectively, and laundry waters are at the upper end of the range reported (Eriksson *et al.*, 2002). In a shower grey water source, Ramon *et al.*, (2004) reported that colloidal particles constitute the dominant fraction (90%) with a mean particle diameter measured as 0.1μm.

Table 2.2.2: Comparison of grey water from different sources

Grey water source	Turbidity (NTU)	SS (mg L^{-1})	BOD (mg L^{-1})	COD (mg L^{-1})	NH_4-N (mg L^{-1})	PO_4-P (mg L^{-1})	Total coliform (cfu $100ml^{-1}$)	*E. coli* (cfu $100ml^{-1}$)	Faecal coliform (cfu $100ml^{-1}$)	References
Shower	29±11	-	59±13	109±33	12±4	1±0.4	-	-	$1.4\times10^5\pm1.1\times10^5$	Merz *et al*., 2007
Shower	23±9	30±11	78±26	170±49	-	-	-	-	-	Ramon *et al*., 2004
Wash basin	102	558	252	433	0.53	-	-	-	-	
Bath, shower & hand basin	101	100	146	451	-	-	7.4×10^3	-	-	Jefferson *et al*., 2004
Hand basin	164	153	155	587			9.4×10^3			Jefferson *et al*., 2004
Domestic grey water	20-120	15-84	10-41	27-102	0.15	-	-	3.8×10^3-5.6×10^3	-	Lin *et al*., 2005
Domestic grey water	103	-	254	-	-	9.6	-	-	7.7×10^7	Dallas and Ho, 2005
Domestic grey water	33	43	59	158	-	-	-	-	-	Friedler *et al*., 2005
University	57	490	96	168	0.8	2.4	5.2×10^6	-	4.8×10^2	Surendran and Wheatley, 1999
Dark	-	-	275-580	471-915	0.6-18.8	-	2×10^{6}-2×10^8	$8\times10^5\pm2\times10^7$	$3\times10^5\pm2\times10^8$	Lazarova, 2001

Organic (e.g. BOD and COD) concentration in grey water reported in the literature ranged from ~10 to >5,000 mg L^{-1}. Concentrations usually fall in the range 76-300 mg L^{-1} BOD for bathroom fractions, 48-472 BOD mg L^{-1} for laundry fractions and 5-1460 BOD mg $L^{-1}$for kitchen fractions. The high organic load emanating from the kitchen reflects the grease, tea, coffee, starch, fats and oils contained with the fraction whilst laundry waters contain soaps, detergents and bleaches (Eriksson *et al.*, 2002). Low molecular size profile of dissolved organics in low load grey water fractions corresponds to low molecular weight, more polar hydrophilic fractions (Jefferson *et al.*, 2004). The specific ultraviolet absorbance (SUVA) which indicates the level of aromaticity of grey water is usually low (Pidou, 2006) compared to surface water (Goslan, 2004) or domestic sewage (Metcalf and Eddy, 2003). Grey water from shower, bathroom sinks are usually deficient in nitrogen and phosphorous. To illustrate, Merz *et al.*, (2007) reported a COD: N: P ratio of 100: 14: 1.5, whilst Jefferson *et al.*, 2004 reported a ratio of 100: 2.9: 0.05 for shower waters respectively. This compares with 100:20: 1 for domestic sewage (Metcalf and Eddy, 2003).

Grey water may contain elevated levels of indicator organisms. Rose *et al.*, (1991) reported total coliform levels varying from 10 and 10^8 cfu $100ml^{-1}$ in baths and showers grey water sources. Grey water emanating from families with young children has been reported to potentially contain high levels of indicator organisms (Lazarova, 2001; Surendrean and Wheatley, 1999).

Based on its pollutant load, grey water can be broadly classified as light or dark grey water (Lazarova *et al.*, 2003). Light grey water comprises used water from shower, bath and hand basins, sinks and is usually less polluted (Friedler *et al.*, 2005). Dark grey water includes used water from laundry facilities, dishwashers and kitchen, and is generally highly polluted. Because individual grey water composition is site specific and depends on user behaviour, no distinct boundary exists between light and dark grey water. Thus there is considerable overlap between light or dark grey highlighting the variability of pollutant load in grey water.

A range of processes recently trialled for grey water treatment are discussed in the literature. These range from simple filtration followed by disinfection to advanced systems such as membrane technology. The selection of appropriate technology for grey water is important considering its variability in raw water quality. Any treatment process for grey water treatment and reuse must be sufficiently robust to maintain effective treatment capable of meeting consent limits under steady and unsteady influent conditions such as inputs of substances not normally associated with grey water (Jefferson *et al.*, 2004). Currently, technology selection for grey water treatment is becoming established and a combination of biological and physical separation process in any technology seems the preferred option (Jefferson *et al.*, 2001). This is because the inclusion of biological process coupled to an efficient physical barrier in the treatment system provides efficient removal of organics, solids and indicator organisms. The Membrane bioreactor (MBR) which combines biological processes and an efficient physical barrier have reportedly produce high water quality (Merz *et al.*, 2007; Melin *et al.*, 2006) better to that produced by other candidate technologies (Table 2.2.3). These and comparable membrane systems find wider use in urban environments where water saving potential is paramount coupled with space constraints. In contrast, there are communities (e.g. rural areas) where land is both affordable and available, and here natural treatment systems such as constructed wetlands seem to be appropriate. Thus, technologies for grey water recycling must produce consistent high effluent quality irrespective of influent load and flow patterns, must be applicable to scale of operation; cost-effective and must be acceptable to the user.

Table 2.2.3: Comparison of performances from different technologies treating grey water

Scheme	BOD (mg L^{-1})	Turbidity (NTU)	SS (mg L^{-1})	NH_4-N (mg L^{-1})	Total coliform (cfu $100ml^{-1}$)	Reference
Sequencing batch reactor + Microfiltration	5	-		0.5		Shin *et al.*, 1998
Sedimentation + Reed bed	5	-	3	-	-	Shrestha *et al.*, 2001
Screening, sedimentation & disinfection	-	17	19	-	-	March *et al.*, 2004
Soil filter	166	-	23	-	-	Itayama *et al.*, 2004
Electrocoagulation + TiO_2	9	3.6	9	0.006	ND	Lin *et al.*, 2005
CW	12.9					Dalls and Ho, 2005
Fluidized bed reactor + UV disinfection	<4	-	-	-	$<10^4$	Nolde, 1999
Screening +membrane bioreactor disinfection+ sedimentation+ anaerobic filter	1	0	13	-	27	Friedel *et al.*, 2004
Membrane bioreactor	2	-	-	-	-	Anderson *et al.*, 2001
Membrane chemical reactor+ TiO_2 + microfiltration	<10	<1				Rivera *et al.*, 2006
Biological aerated filter	4	3	6		2.1×10^4	Laine *et al.*, 2001
Biological reactor+ sand filter + GAC	2	1	-	-	<1	Ward *et al.*, 2000
Anaerobic filter + aerobic filter + sand filter	2.8	1.5	5.1	1.7	-	Surendran and Wheatley, 1998

2.2.4 Previous experiences of grey water treatment using constructed wetland technology

The use of constructed wetland systems for grey water treatment and reuse is relatively recent and rare and results from recent pilot and experimental studies of CWs for grey water treatment gave relatively good treatment performances. In most cases, high removal of organics and solids typical of treatment wetlands (Vymazal, 2007; IWA, 2000) are reported. To illustrate, a vertical flow CW treating grey water of a family of seven gave 98% BOD, 95% COD, 97% TSS and 3-5 logs coliform removal (Shrestha *et al.*, 2001). Li *et al.*, (2003) reported a reduction from 80-94 to ~6 mg L^{-1} TOC using a combined VFRB and TiO_2 at an irradiation time of 6 hours.

In a case study using the locally available macrophyte (*Coix lacryma-jobi*) in reed beds to treat grey water for restricted reuse applications in Monteverde, Costa Rica, Dallas *et al.*, (2004) reported that the final effluent meet the national reuse standard of <40 mg L^{-1} BOD and < 1,000 cfu $100ml^{-1}$. In another study, Dallas and Ho (2005) reported a 3-5 log reduction in faecal coliform and >87% reduction in BOD for influent loadings of 5 and 10 L day^{-1} irrespective of media type (plastic bottle segments versus crushed rock) and planted bed (*Coix lacryma-jobi*) versus unplanted bed. In a study evaluating the effectiveness of *Triglochin huegelii*, an indigenous wetland macrophytes species in Western Australia removing nutrients from domestic grey water, Mars *et al.*, (2003) reported that more nitrate and ammonia removal occurred in the planted systems compared to the unplanted systems whilst only the subsurface system retain significant amount of P irrespective of whether plants were used. Experiences from a study on grey water treatment using a pilot unit comprising of a three-chamber sedimentation tank, a horizontal flow wetland, a sand filter and an artificial pond in the Ecovillage Toarp, Sweden also gave encouraging results with BOD_7, COD and thermostable coliforms being reduced from 165 to <5 mg L^{-1}, 361 to <60 mg L^{-1} and 4-6 logs cfu $100ml^{-1}$ respectively (Fittschen and Niemczynowicz, (1997). Gross *et al*., (2007a) reported a trial study using Recycled Vertical Flow Bioreactor (RVFB) (i.e. a system which recycles the effluent to the influent for a second treatment) to treat synthetic grey water enriched with wastes from a dining hall. They reported that the system produced effluent with *E. coli* concentrations (0.1±0.05 cfu $100ml^{-1}$) that complied with the USEPA water quality criteria for recreational reuse but much higher viable *S. auresis and P aeruginosa* were consistently present (i.e. 1.8 to 4.7 cfu $100ml^{-1}$) in the effluent after 72 hours of treatment period (Gross *et al*., 2007a).

To date, the most probable characteristic of grey water which has been shown to limit its purification by biological treatment is its nutrient deficiency (Jefferson *et al*., 2004, 2001). Gross *et al*., (2007b) carried out a study with nutrient deficient grey water using reed beds planted with the macrophyte *Luctuca sativa*. They reported that although plant growth was retarded, there was no evidence of poor treatment efficiency of the system. A 100% and 80% reduction of BOD and COD organics, 98% total suspended solids and a 3 to 4 log reduction of faecal coliform after 8 hours using a recycled vertical flow constructed wetland (RVFCW) was achieved.

Although there are few recorded performances from studies on grey water treatment by constructed wetlands, there is a paucity of data on the influence of design parameters (influent and hydraulic loading) and configuration type (i.e. vertical and horizontal flow systems) on treatment performance. In addition, the effect of wetland treatment on the distribution of hydrophobicities (i.e. HPO, HPI and TPI fractions of organic matter) in grey water before and after treatment is currently unavailable. Hence performance data from that will provide information on the treatability of grey water as well as the suitability and robustness of the constructed wetland technology is desirable.

2.3 Media for Phosphorous removal in Constructed Wetland Systems

2.3.1 Background

Phosphorous (P) immobilization in constructed wetlands (CW) occurs via adsorption to media, chemical precipitation, uptake by plants and algae and incorporation into organic matter (Kadlec and Knight, 1996). Sorption of P to the wetland media has been recognised as one of the most important removal mechanism in CWs (Faulkner and Richardson 1989). Despite being a sink for P removal, wetland media longevity is limited by their finite P-sorption capacity which decreases rapidly after a short period of time, usually 4 – 5 years (Vymazal, 2004; Kadlec and Knight, 1996). Consequently, the selection of substrate material with high P capacity and appropriate physico-chemical characteristics suitable for use in constructed wetland system (CWS) is important. The substrate material must also be cheap and locally available to reduce costs of construction.

Several studies have been carried out on different adsorbent for their potential use in a CWS (Jahansson and Westholm, 2002). These adsorbents range from natural materials (e.g. minerals, sands, soils, marine sediments and rocks), industrial by-products (e.g. slags) and man-made products (e.g. light weight aggregates-LWA). Results from studies on the sorption capacities of these adsorbents vary widely (Table 2.3.1) as does the physical and chemical composition which together determines the suitability of any adsorbent for use in a CWS.

Table 2.3.1 P capacities of adsorbents

Adsorbent	Adsorbent composition	Scheme	Experimental conditions	Sorption capacity (g Kg^{-1})	Reference
Natural adsorbents					
Zeolite		Batch	Artificial P solution (2.5-40 g P L^{-1})		Drizzo, 1998
Zeolite	Clinoptilite	Batch	Artificial P solution of 0-800 mg P L^{-1}.	2.15	Sakadevan and Bavor, 1998
Alunite	KAl3(SO4)2(OH)6	Batch	Artificial P solution of 0.5-2.5mmol P L^{-1}.		Ozacar, 2003
Bauxite	Mix of Al and Fe-oxides	Batch	20g treated with artificial P solution (2.5-40 g P L^{-1})	0.61	Drizzo *et al*., 1999
		Column	Artificial P solution of 25 g P L^{-1} for 40 days and100 mg P L^{-1} for 30 days	0.35	Drizzo *et al*., 1999
Marl soil	Clay and limestone	Batch	0-5000 mg P L^{-1} Synthetic sewage effluent	1.2	Gray *et al*., 2000
Iron ore	96% Fe_2O_3	Bucket	Dairy farm wastewater	0.14	Gruneberg and Kern, 2001
Feldspar					
Shells	Mussel and Snail shells	Batch	Media treated with artificial P solution 1000 g P L^{-1})	14-27	Roseth, 2000
Industrial by-products					
Blast furnace slag	38-43%CaO, 32-37% SiO_2, 13-16% Al_2O_3	Batch	Artificial P solution of 0-800 mg P L^{-1}.	44.2	Sakadevan and Bavor, 1998
Blast furnace slag	39% CaO, 35% SiO_2	Bucket	Dairy farm wastewater	0.2	Gruneberg and Kern, 2001
Shale	30-60%CaO, 20-50%	HSSF	Wetland effluent	1.9	Vohla *et al*., 2007

Adsorbent	SiO_2 Adsorbent composition	Scheme	Experimental conditions	Sorption capacity g Kg^{-1}	Reference
Electric arc Furnace		Column study	Dairy effluent, 28.5 ±1.6 mg P L^{-1}	1.5	Weber *et al*., 2007
Electric arc Furnace	Major: Fe_2O_3 (36%), CaO(28%), SiO_2(15%)	Pilot unit	Constructed wetland effluent,	2	Chazrenc *et al*., 2007
Man-made products					
LWA(Norwegian with natural additives)	465 mg/g Ca, 147mg/g Al, 93 mg/g Mg and 33 mg/g sample Fe	Batch	Artificial P solution of 0-320 mg P L^{-1}.	3.5	Zhu *et al*., 1997
LWA (Swedish)		Column	Artificial P solution of 200 mg P L^{-1}.	0.29-0.55*	Johansson, 1997
Filtralite		Field	Pre-treated dairy wastewater	34% removal	Hill *et al*., 2000
Filtralite-P^{TM}	Expanded clay(high Ca & Mg)	Box	Artificial P solution of 15 mg P L^{-1}.	8	Ậdảm *et al*., 2006
		Box	Artificial P solution of 15 mg P L^{-1}.	5	
		Column	Artificial P solution of 6 mg P L^{-1}.	4.5	

* = Capacity reported in kg m^{-3}

2.3.2 Influence of adsorbent characteristics on P retention in Constructed Wetlands System (CWS)

The amount of P removed from wastewater is influenced by the metal (e.g. Fe, Al and Ca) content of the adsorbent material (Zhu *et al.*, 1997). These materials contain reactive Fe, Al and Ca hydro(oxide) groups on their surfaces which encourages the precipitation and complexation of the metal phosphates. To illustrate, P removal by slag is believed to occur via the release of Ca^{2+} and OH^{-} resulting in an increase in pH followed by Ca-phosphate precipitates as monetite ($CaHPO_4$) and hydroxyapatite ($Ca_5(PO_4)_3(OH)$) (Baker *et al.*, 1998). Ligand exchange reactions in which phosphate displaces water or hydroxyls from the surface of Fe and Al hydrous oxides to form monodentate and binuclear complexes within the coordination sphere have also been reported in CWS (Faulkner and Richardson, 1989).

The retention of P in CWS is controlled by the prevailing conditions of pH and redox potential within the bed media (Faulkner and Richardson 1989; Richardson, 1985). This is because sorption and desorption of P through Fe, Al and Ca is pH dependent. For instance, in acidic-neutral conditions, P is adsorbed on hydrous oxides of Fe- and Al-phosphates whereas precipitation of insoluble Ca-phosphates occurs at alkaline pH (Qualls and Richardson, 1995). To illustrate, Ca adsorbents dissociate in water to yield an alkaline solution (pH>7). The Ca^{2+} in solution combines with P to form the stable hydroxyapatite complex which has its lowest solubility at pH>9.5 (Tan, 1993). Weber *et al.*, (2007) reported that Ca-phosphates precipitate at pH~10 is the dominant P removal mechanism of Electric arc furnace steel slag adsorbent in CWS. Al adsorbents in solution forms $Al(OH)_3$ which combine with P strongly at pH 6-8 to form insoluble polymeric $Al(OH)_3$. Fe adsorbent reacts with P to form $FeOOH-PO_4$ complexes at an optimum pH of 5-7 (Lijklema, 1977).

Redox potential (E_h) influence P adsorption or desorption in CWS. E_h below +250 mV cause the reduction of Fe^{3+} to Fe^{2+} releasing associated P (Faulker and Richardson, 1989). At reduced redox (e.g. anaerobic) conditions, crystalline Al and Fe minerals are transformed to the amorphous forms. Patrick and Khalid (1974) reported that amorphous Al and Fe hydrous oxides have higher P sorption capacity than their crystalline counterpart due to their larger number of singly-coordinated surface hydroxyl ions.

P removal is also influenced by the adsorptive surface area of the adsorbent (Vymazal *et al.*, 1998). Fine grained materials have larger surface area and consequently exhibit higher sorption capacity relative to a lump/coarse size adsorbent. However, finer materials often have low hydraulic property which leads to surface overflow and consequently decreased contact between sorbet solution and adsorbent in the middle of the bed. Therefore, suitable adsorbent should be sufficiently permeable to allow flow through the bed, prevent surface channelling and overflow (Kadlec and Knight, 1996). P removal is greater in subsurface flow-SSF configuration compared to surface flow-SF configuration (Chapter 2, section 2.1). This is because SSF allows increased contact between sorbate and adsorbent for adsorption which is important in P removal.

Other physical properties of adsorbents which would permit their use in a CWS are bulk density and uniformity coefficient (d_{60}/d_{10}). Bulk density >1 g cm^{-3} and uniformity coefficient >2 are considered suitable (Arias and Brix, 2005). These properties enhance good hydraulic performance of the system and avoid clogging in the beds. Research results from CWS around the world show that sandy materials have a much lower permeability compared to gravel and crushed rock (Vymazal, 2004).

2.3.3 P removal in Constructed Wetland Systems

Treatment wetlands efficiently remove organics and suspended solids from wastewater (Cooper *et al.*, 1999) but do not achieve high removal of P from wastewater (Vymazal, 2004). Data from most operational treatment wetlands show low P removal because the media such as pea gravel and crushed stones often used do not have high P sorption capacity because of inadequate Fe, Ca or Al content (Brix *et al.*, 2001). To illustrate, Vymazal (2004) reported an average removal of P from municipal or domestic wastewater of ~46% in 25 horizontal subsurface flow constructed wetlands using pea gravel or crushed stones as bed media in the Czech Republic. Soils samples collected from three constructed wetlands at the Byron Site in Northern New South Wales, Australia gave a P capacity in the range of 4.2-5.2 g Kg^{-1} (Sakadevan and Bavor, 1998). In comparison, industrial by-products such as blast furnace slag and steel slag from the Australian Steel Mills Limited gave a P sorption capacity of 44.2 g Kg^{-1}. Similarly, a much higher removal (e.g.77%) was recorded from 10 horizontal subsurface CWs in Norway where selective media (such as iron-rich sand, manufactured light-weight ceramic particle aggregate) with high P sorption capacity are used (Mǽehlum and Jensen, 1998). Similarly, test results showed that a Norwegian-manufactured light weight aggregate (LWA) FiltraliteTM (A/S Norsk Leca) has P removal rates of ~95% in subsurface flow constructed wetlands during the first 5 years of operation (Jenssen *et al.*, 1996). Leader *et al.*, (2005) reported a 98% reduction in P from a secondary municipal wastewater in a pilot unit of vertical flow CW which has a co-treatment reactor of iron and lime compared to an 87% from the unit without the co-treatment reactor.

A study on a pilot system combining batch-fed reactors of iron and lime with vertical flow CW mesocosms reduced an influent P level from anaerobic digested dairy wastewater from 7.68 to 5.95 (22%). A pilot CWS comprising of an Electric Arc Furnace (EAF) steel slag added as a post treatment unit to a horizontal subsurface flow CW to reduce P from a dairy farm effluent in Vermont, Canada improved the removal efficiency of the system by 74% (Weber *et al.*, 2007). However, the use of EAF steel slag alone in CW bed media has shown to inhibit macrophyte growth, whilst a combination of slag, granite and limestone of sizes between 2-20mm used as a post polishing unit at the outlet of a 28 m^2 CW treating fish farm supernatant gave more than 75% removal efficiency during the first year of operation (Chazarenc *et al.*, 2007).

A major limitation in the use of limestone and steel slag as bed substrate for P retention in CWS is the elevated pH in the final effluent due to the net release of OH^- from the dissolution of $CaCO_3$. Weber (2006) reported an effluent pH of 11 for the first three weeks which only gradually reduced to 8.0 during the last two months of a trial study from an EAF steel slag unit. Chazarenc *et al*., (2007) reported an increase in pH from 7.1 in the inlet wastewater to 10.3 in the final effluent of an EAF steel slag unit. It is therefore important that if such materials are used for P removal in wastewaters in full scale systems, a pH reducer will be required prior to discharge into receiving waters. Naylor *et al*., (2003) showed that the addition of a post peat unit to the EAF unit could act as a pH reducer in a full scale system.

Materials with small particle size such as sands have lower permeability and can cause surface overflow. Finer adsorbents have also been reported to cause clogging of outlet pipes of such systems (Johansson, 1999; Baker *et al*., 1998). Man-made adsorbents such as Light weight aggregates (LWA) may be expensive to produce.

2.3.4 Adsorption models

The aim of applying adsorption equations to adsorption data is to understand the processes involved in phosphorous (P) adsorption or desorption. In general, two-parameter equations (e.g. Freundlich and Langmuir) are often used compared to three-parameter (e.g. Langmuir-Freundlich) because of the convenience in evaluating two rather than three isotherm parameters. Amongst the various adsorption equations, the Freundlich and Langmuir are the two most commonly used equations.

- *The Freundlich model*

The Freundlich isotherm equation is normally written as:

$$q_e = K_F C^{1/n} \; (n>1)$$

where K and n are Freundlich constants related to adsorption capacity and the intensity of adsorption. Values of n close to 1 indicate that the adsorbent has a large adsorptive capacity at high molecular equilibrium concentration. The linear form of the Freundlich equation for adsorption is given as:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..2.3.1$$

The Freundlich model encompases the heterogeneity of the adsorbent surface as well as the exponential distribution of adsorption sites and adsorption energies.

- *The Langmuir model*

The Langmuir equation was first developed to describe the adsorption of gases by solids. The linear form of the Langmuir equation for adsorption is given as:

$$\frac{C_e}{q_e} = \frac{1}{Q_o K_L} + \frac{C_e}{Q_o} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots...2.3.2$$

where C_e is the concentration of the sorbate in solution at equailibrium (mg L^{-1}), q_e is the mass of molecules adsorbed per unit weight of materials (mg g^{-1}), K_L is a constant related to the binding strength of molecules onto the material (L g^{-1}) and Q_o is the maximum adsorption capacity (mg g^{-1}).

The Langmuir model is governed by the following assumptions (Moore, 1972):

- the solid surface contains a fixed number of adsorption sites;
- each site can only bind one molecule of the adsorbing species;
- the energy of adsorption is the same for all sites and does not depend on the fraction occupied; there is no interaction between adsorbed molecules on adjacent sites.

In addition to the Langmuir and Freundlich models, the Dubinin-Radushkevich (DR), and Temkin equations have also been applied to experimental isotherm sorption data.

The linear form of the Dubinin-Radushkevich (DR) isotherm model is given as:

$$\ln q_e = \ln q_o - K_{DR}\varepsilon^2 \quad \text{...2.3.3}$$

where ε is the Polanyi potential which is related to the equilibrium concentration as follows,

$$\varepsilon = \left[RT \ln\left(1 + \frac{1}{C_e}\right)\right] \quad \text{...2.3.4}$$

where K_{DR} (KJ^2 mol $^{-2}$) is related to the free energy of adsorption and q_o (mg g $^{-1}$) is the Dubinin-Radushkevich isotherm constant related to the degree of sorbate sorption by the adsorbent surface.

The Temkin Isotherm

The Temkin isotherm (Choy *et al*., 1999) is given:

$$q_e = \frac{RT}{b}\ln(AC_e) \text{ ....} 2.3.5$$

A linear form of the Temkin isotherm can be written as:

$$q_e = \frac{RT}{b}\ln A + \frac{RT}{b}\ln C_e \text{ ....} 2.3.6$$

where $B = \frac{RT}{b}$ 2.3.7

A plot of q_e versus ln C_e enables the constants A and B to be determined. A (L g^{-1}) is a constant related to energy of adsorption.

Three parameter (Langmuir-Freundlich and Redlich-Peterson) isotherms

The Langmuir-Freundlich isotherm equation is written as:

$$q_e = K_L q_m C^{\frac{1}{n}} /(1 + K_L C^{\frac{1}{n}}) \text{ ....} 2.3.8$$

where all terms carry their usual meanings. For the Langmuir-Freundlich isotherm, the efficiency of adsorption R_L is modified to:

$$R_L = \frac{1}{(1 + K_L C_o^{1/n})} \text{ ....} 2.3.9$$

and all terms carry their usual meaning.

Efficiency of adsorption

The efficiency of the adsorption process can be investigated by the dimensionless separation term R_L. R_L values are calculated using the equation:

$$R_L = \frac{1}{1 + K_L C_o} \quad \text{..} 2.3.10$$

where C_o is the initial concentration of the sorbate concentration (mg L^{-1}).

The parameter R_L determines the shape of the adsorption isotherm and $0<R_L>1$ indicates a high affinity adsorption.

The free energy of adsorption

The standard free energy change of the adsorption process can be calculated according to the Dubinin-Radushkevich equation given as:

$$E = \frac{1}{\sqrt{2K_{DR}}} \quad \text{..} 2.3.11$$

where E is standard free energy (KJ mol^{-1}) and K_{DR} carry it's usual meaning in Dubinin-Radushkevich equation.

The standard free energy change (ΔG^o) for the adsorption process can also be calculated using the Langmuir constant K_L given as:

$$\ln\left(\frac{1}{K_L}\right) = \frac{\Delta G^o}{RT} \quad \text{...2.3.12}$$

R is a gas constant (8.3145 J mol-1 K^{-1}) and T is temperature in Kelvin.

Column adsorption analysis

Adsorption of sorbate on an adsorbent can also be investigated using column experiments in which process parameters such as effect of influent flow rate, sorbate concentration and bed depth on adsorbent can be assessed. In the adsorption column, the influent containing the sorbate flows through the stationary bed of the adsorbent. As the influent passes through the column, increasing amount of sorbate is adsorbed while the remaining sorbate concentration exits the column. As the experiment progresses, the adsorption zone moves further away from the inlet point towards the exit. When the adsorption zone has moved through the column, the concentration of the adsorbate at the exit equals the inlet concentration. A plot of effluent sorbate concentration as a function of time or volume throughput is known as a breakthrough curve. The characteristic shape of a breakthrough curve depends on bed capacity, influent concentration and flow rate (Ghorai and Pant, 2005).

Evaluation of breakthrough analysis can be assessed using models of Lin and Huang (1999) and Bohart and Adams (1920). The time taken for breakthrough to occur when a sorbate solution travels a column length (bed depth) containing an adsorbent proposed by Bohart and Adams (1920) is given as:

$$\ln\left[\frac{C_o}{C}-1\right]=\ln\left[e^{K_aN_oZ/F}-1\right]-K_aC_ot \quad \text{(2.3.13)}$$

where N_o is the adsorption capacity (mg solute per g adsorbent), K_a is the rate constant in bed depth service time (L (mg h)$^{-1}$) and Z is bed depth/length of column (m). The breakthrough profile in the original equation is given as:

$$\frac{C_t}{C_o}=\frac{e^{K_aC_ot}}{e^{K_aC_ot}+e^{K_aW/F}-1} \quad \text{(2.3.14)}$$

where W is the bed capacity (total weight of sorbate adsorbed).

Lin and Huang (1999) developed equation (2.3.14) for a sorbate concentration flowing through a stationary adsorption column:

$$t=\tau+\frac{1}{k}\ln\left(\frac{p}{1+P}\right) \quad \text{(2.3.15)}$$

For a symmetrical breakthrough plot and at 50% breakthrough (i.e. $C_t/C_o = 0.5$), equation (2.3.15) simplifies to:

$$W_e = C_o F \tau \quad (2.3.16)$$

2.4 Summary of knowledge gaps of Constructed Wetland System for grey water treatment and P removal

To date, there is a paucity of data from constructed wetland systems treating grey water. Consequently, information with regard which type of constructed wetland configuration (i.e. vertical or horizontal) is more suitable for grey water and how the operational and design conditions of the technology influence treatment is unavailable. It is also important to assess its role in grey water reuse and its reliability in performance. Such information would demonstrate where constructed wetland technology fit into an array of existing technology for grey water treatment and reuse and where possible market might exist.

With regard the application of constructed wetland technology for P removal, identifying an adsorbent with high sorption capacity, appropraite physico-chemial properties for use as a wetland substrate and whose effluent pH falls within discharge limit (6-9) is still being sought.

CHAPTER 3 Materials and methods

3.1 Constructed wetlands for grey water recycling

3.1.1 Materials

3.1.1.1 Study site and grey water source

The site for the grey water study was located at the back of Fedden students' family flats at Cranfield University campus (Figure 3.1.1). Influent grey water was sourced from

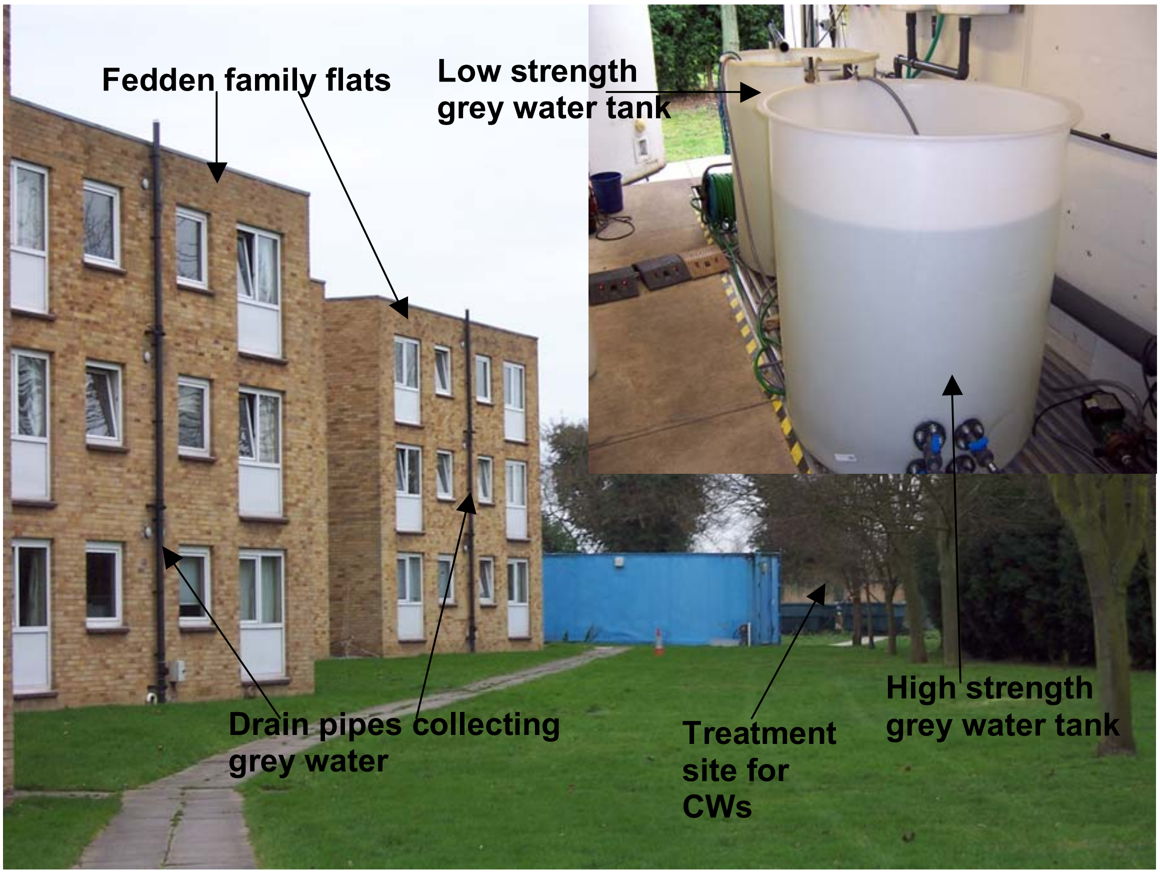


Figure 3.1.1: Grey water collection system showing Fedden family flats, pipe network which channels grey water to holding tanks in container (inset) and study site.

eighteen specially plumbed student flats within the accommodation blocks. Water from baths, showers and bathroom basins drained to a communal sump from which it was pumped underground to two inter-connected holding tanks using a submersible pump with a level control (Figure 3.1.1). Both the sump and the holding tanks had overflow connections to sewer. The holding tanks were mixed using a submersible pump and a recirculation system. The system provided a real grey water source with which any technology could be tested. The grey water was of low organic strength compared to typical values reported in the literature (Table 4.1.2). To enable a medium - high grey water organic strength to be tested, a supplementary dosing system was installed. The high strength supplementary dosing solution was a 10% v/v mixture of Tesco Value shampoo in tap water. The grey water strength was supplemented with shampoo and not laundry detergents or food-based products so as not to change the composition of the grey water but rather to increase the organic concentration. The resulting solution was a high strength feed and not a dark grey water. The high strength supplementary solution and the real low strength grey water were pumped at fixed intervals (10 minutes every three hours) into a second holding tank from which the mixture was pumped to the treatment wetlands. The real grey water is referred to in this study as low strength and the supplemented grey water as high strength.

3.1.1.2 Pilot constructed wetland technologies

The experimental systems consisted of three pilot - scale subsurface constructed wetlands: a horizontal flow reed bed (HFRB), vertical flow reed bed (VFRB) and the Green Roof Water Recycling System 'GROW'.

3.1.1.2.1 Horizontal and vertical flow reed beds

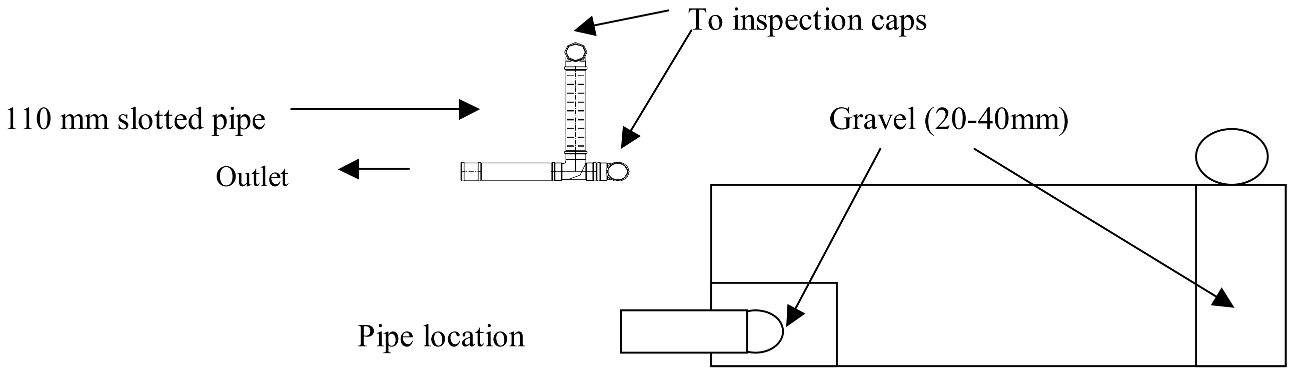


Figure 3.1.2: Schematic diagram of the horizontal flow system showing distribution pipes. Pipes are buried in 20 – 40mm∅ washed gravel mound, followed by sand /compost/soil mix (ratios-65/25/10) to 100mm from top.

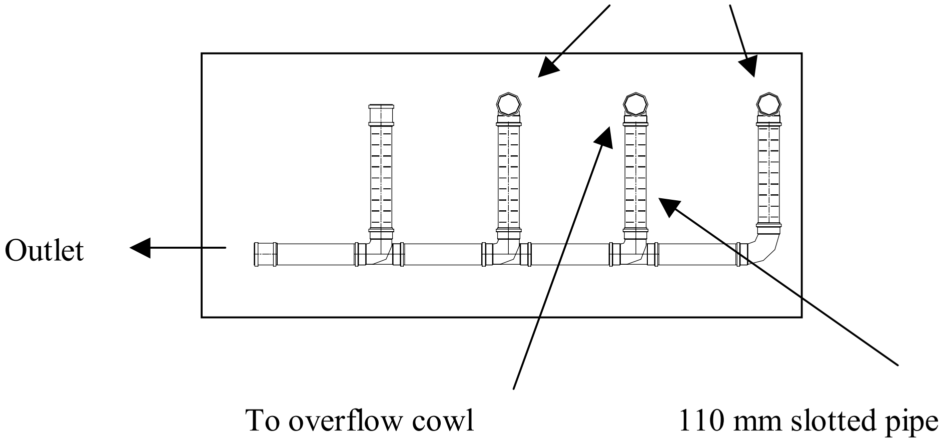


Figure 3.1.3: Vertical flow distribution and collection pipes. Pipes are buried in 150mm (from base) 20 – 40mm∅ washed gravel, followed by ~700mm sand/compost/soil mix (ratios - 65/25/10).

The horizontal flow reed bed (HFRB) and vertical flow reed bed (VFRB) were established in June 2004 at the grey water treatment site, Cranfield University by

Oceans-ESU, Bradford, UK. Both beds comprised a double skinned plastic container (3m × 2m ×1m) and planted with the common reed (*Phragmites australis*) to a depth of 0.7m in a sand: soil: compost medium (ratio 65:25:10) with a coarse gravel (20mm) around the inlet zone for the HFRB and around the outlet (collection) zones for both beds. Since the beds were double skinned, lining was not necessary.

3.1.1.2.2 Green Roof Water Recycling System

The Green Roof Water Recycling System 'GROW' is a patented invention of Water Works, London, UK; patent number GB 2375761 established in June 2004. The GROW system was designed to sit on a pitched roof suitable for use in urban new developments where ground space is limited. However, with a wooden frame, GROW can be used on a flat roof or at ground level.

The test rig (~7m^2) comprised five rows of two troughs (connected in series) and placed onto a tiered wooden framework to represent a sloping roof. The first trough was approximately 1m above the ground and the lowest was 0.7m above ground. Weight is an important design consideration for GROW as it is intended to be located on roof tops with an approximate weight of 50 Kg m^{-2} (WWUK). Hence troughs were filled to approximately 10 cm depth with Optiroc (light-weight expanded clay). Optiroc media was selected for the GROW system due to its light weight. Gravel chippings (10 – 20mm diameter) were used to top the Optiroc to a height of ~16 cm. This was to prevent the Optiroc from floating and blocking weirs within the system. Influent grey water entered the rig *via* an inlet well into the first trough. It then flowed horizontally through the media until reaching a well at the end of the row, whereupon it flowed down a weir to the subsequent row. After passing through each row, the effluent exited the rig *via* an

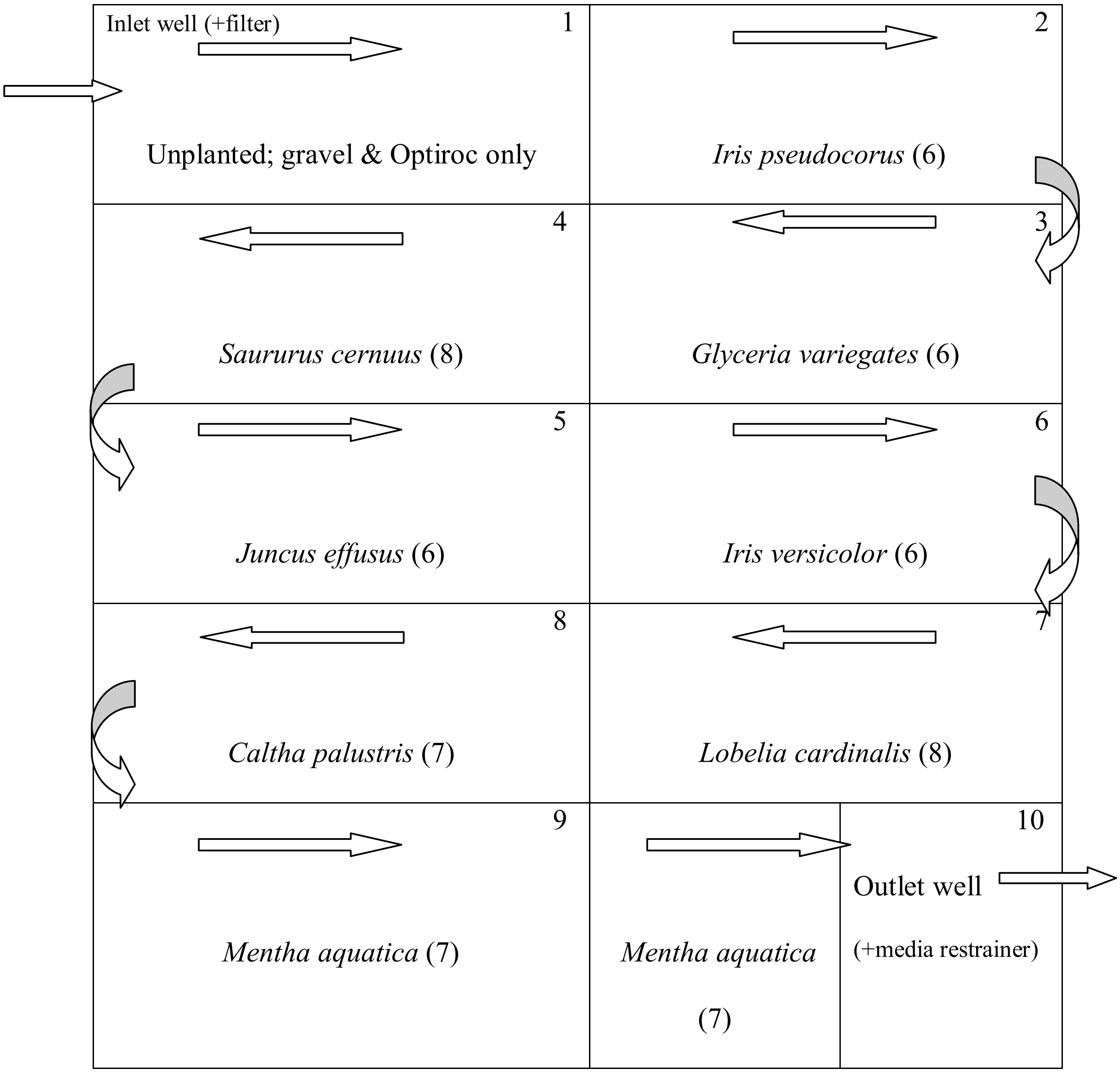


Figure 3.1.4: Schematic diagram of 'GROW'. Arrows indicate direction of flow of grey water through the rig. The numbers in parenthesis refers to the number of plants of each species within troughs.

outflow pipe from the well at the end of the final row. A baffle and a weir within each trough were intended to force the flow through the whole of the media, reducing the potential for short-circuiting. The entire system was covered with a reinforced membrane to prevent entry of rainwater. Aquatic marginal plants, selected for pollutant removal and aesthetic characteristics (WWUK), were inserted into the media (according to Figure 3.1.4) through small slits in the membrane. A removable filter at the inlet of the first trough prevented entry of materials such as hair and other debris that might cause clogging. A coarse mesh (~2 mm) over the outlet hole in trough 10 prevented media from being washed into the effluent pipe. Aeration was provided for one hour each day *via* a porous hose lying at the bottom of each trough.

3.1.3 Methods

3.1.3.1 Monitoring periods

After construction or establishment, constructed wetlands require a few months for vegetation and biofilm establishment, as well as enough time for the development of litter and standing dead compartments (Billore *et al.*, 1999). Hence the first monitoring period covered the start-up of the treatment wetlands at a low hydraulic loading rate (160 $L.d^{-1}$) in order to allow vegetation and microorganisms to acclimatise. During the second period referred to as 'low strength' in this study, the hydraulic load was increased to 480 $L.d^{-1}$. Aproximately 77 L of grey water is produced per person per day in a residence occupied by 2 people (Dixon *et al.*, 1999), thus this provided each constructed wetland with grey water equivalent to that produced by approximately six people. Data from the first period (three months after commissioning) were not incorporated into result analysis as they do not truly reflect wetlands performance but rather system settling-in phase.

3.1.3.2 Operating conditions

- *Hydraulic loading rate*

At start up and for the subsequent three months, all three systems received 160 L d^{-1} grey water applied on a continuous flow basis for HFRB and GROW and supplied as ten batches over 24 hours for the VFRB system. The hydraulic load on each system was increased to 480 l d^{-1} for the monitoring period reported in this study (September 2004 to January 2007). This corresponds to hydraulic loading rates of 0.08 m d^{-1} for the reed beds and 0.07 m d^{-1} for GROW.

- *Hydraulic residence time*

Hydraulic residence time (HRT) for rows and rigs was assessed using lithium (Li) tracer according to the method outlined in Headley and Kadlec (2005). Tracer was added to the influent stream at the inlet well for GROW and with the influent stream for the reed beds. Water samples were collected at hourly intervals from outlet pipe for the reed beds, whilst at weirs at the end of each row for row tracer studies and sampling point after row 5 for the GROW rig. Li concentration in the samples was measured using ICP spectrophotometer. The hydraulic residence times were 2.1 days for both the HFRB and GROW rig and 2 hours per batch for the VFRB.

3.1.3.3 Porosity and hydraulic conductivity

Hydraulic conductivity of used and unused reed bed media was determined by the Falling Head Permeameter whilst that of GROW for the unused gravel and Optiroc was determined by measuring the fraction of pore volume to total volume occupied by gravel and Optiroc in a measuring cylinder.

- *Falling Head Permeameter*

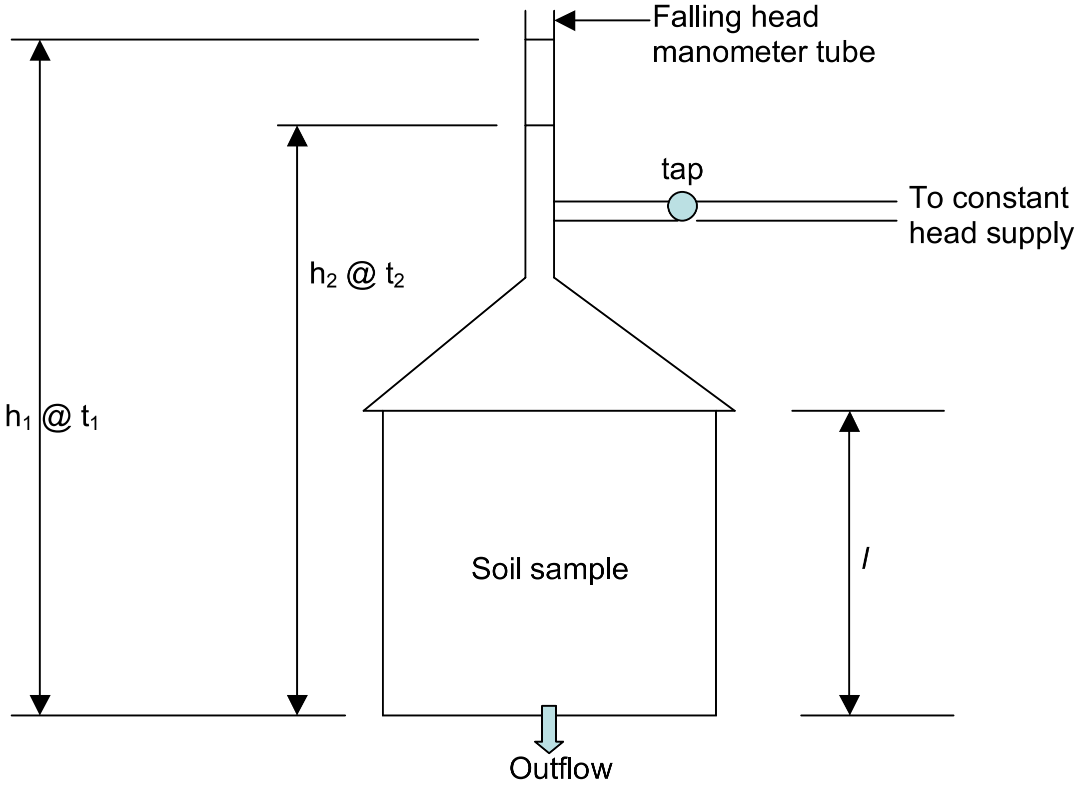


Figure 3.1.5: Schematic diagram of the Falling Head Permeameter

The falling head method measures the permeability of fine textured soils where the rate of flow would be too small to measure with a constant head permeameter. The hydraulic head at the top-gradient end is allowed to decline with time. Undisturbed samples taken at 0.5 cm and 30 cm below bed surface from both reed beds were saturated overnight to remove all air. This was essential as the presence of air will restrict the flow of water and when saturated, flow from the manometer will be equal to flow through the saturated soil sample. The falling head tubes containing water has its lower end attached to the top of the soil core. The rate of fall of water in the manometer tube as the water passes through each soil sample was determined by recording the time taken for the level in the tube to drop 20 cm. All hydraulic determinations were conducted in duplicate. Based on Darcy's law, the discharge through the saturated soil sample is proportional to the difference in hydraulic head between the inlet and outlet as well as the hydraulic conductivity (K) of the bed media given as:

$$Q = KA\frac{\Delta h}{l} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 3.1.1$$

where A (m^2), is the cross sectional area of the soil sample and l (m) is height of soil sample in metres. Equation 3.1.1 on integration yields equation 3.1.2 from which the hydraulic conductivity, K (m s^{-1}) was calculated.

$$K = \left[\frac{al}{A(t_2 - t_1)}\right]\ln\left(\frac{h_1}{h_2}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 3.1.2$$

where a(m^2) is the cross sectional area of the manometer tube, h_1 and h_2 are water height at manometer tube before and after experiment respectively, t_1 and t_2 is the start time and end time (in seconds) taken for the water to drop 20cm down the manometer tube..

3.1.3.4 Sampling for water quality parameters

Influent and effluent water were generally sampled for water quality analysis twice-weekly between 09:00-10:00 hours between July 2004 and September 2005 and thereafter less frequent (once weekly) between October 2005 and March 2006. Following review of the performances of all three CWs, the VFRB was selected for unsteady state studies. Sampling for unsteady state studies was generally carried out weekly till January 2007. The following water quality parameters were monitored throughout the study period: Biological oxygen demand (BOD_5), chemical oxygen demand (COD), suspended solids (SS), turbidity, temperature, pH, dissolved oxygen (DO_2), indicator organisms (total coliforms, *E .coli* and faecal coliforms). Determination of NO_3-N and PO_4-P were also changed from fortnightly to once monthly concurrently. Water samples for other determinations such as fractionation, dissolved organic carbon, and particle size analysis were sampled when necessary. Water samples were collected in previously acid washed PVC containers. Sample bottles for microbial analysis were always sterilised before use. Representative samples of influent were collected at an inlet tap connected to the HFRB. Effluents from all three wetlands were collected at similarly located outlet taps from the respective beds. Samples were generally analysed immediately after collection or stored at 5^{o}C. In no cases were samples analysed after 24 hours.

3.1.3.5. Analytical methods

- *Physical methods*

Temperature was determined in-situ whilst dissolved oxygen was measured immediately after sample collection using a DO analyser/meter using the Jenway 9071 portable dissolve oxygen meter. pH was measured using the Jenway 3540 pH and conductivity meter after calibration of the instrument. Turbidity was measured with HACH 2100N turbidimeter (Camlab Ltd, Cambridge, UK) after being dispersed for 30 seconds in an ultrasonic bath (Scientific Laboratory Suppliers, Hull, UK). Particle sizes of influent grey water and wetland effluents were measured by laser diffraction (Malvern Mastersizer 2000, Malvern UK).

- *Chemical methods*

Biological Oxygen Demand (BOD_5) was measured using the procedure 5 day Biochemical Oxygen Demand from the Standard Methods for Examination of Water and Wastewater (APHA, 1998). Merck cell tests (Merck, VWR International, Poole, UK) were used for the following tests: chemical oxygen demand (COD) (0-150, 25-1500 mg L^{-1}), Ammonia nitrogen (NH_4-N) (0.5-5.0 mg L^{-1}), Nitrate nitrogen (NO_3-N) (0.5-5.0 mg L^{-1}), Phosphate phosphorous (PO_4-P) (0.5-5.0 mg L^{-1}).

  - *Dissolved organic carbon*

Dissolve organic carbon (DOC) was measured as non purgeable organic carbon (NPOC) using a Shimadzu TOC-5000A analyser (Shimadzu, Milton keynes, UK).

  - *Ultraviolet and specific ultraviolet absorbance*

Ultraviolet (UV) absorbance was measured at 254 nm using a Jenway 6505 UV/Vis spectrophotometer (Patterson Scientific Ltd., Luton, UK). Specific Ultra Violet Absorbance, SUVA ($m^{-1}L\ mg^{-1}$) - a measure of relative aromaticity or the contribution of aromatic structures to DOC (Metcalf and Eddy, 2003) was calculated as

$$[(UV\text{-}254/DOC) \times 100] \qquad 3.1.4$$

- *High performance size exclusion chromatography (HPSEC)*

HPSEC was carried out on samples filtered samples using an HPLC (Shimadzu VP Series, Shimadzu, Milton Keynes, UK) with a UV detection set of 254nm.

- *Fractionation of organics*

Distribution of hydrophobicities were obtained based on fractions retained on the XAD-4 and XAD-8 resin as outlined in Malcolm and McCarthy (1992). It involves separating dissolve organic matter present in grey water and constructed wetland effluents into their hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI) components by XAD-8 and XAD-4 resin adsorption techniques. The procedure is categorised in three phases: preparation of the resin, separation of the dissolve organic matter into fractions and determination of organic matter in each fraction using a TOC analyser.

- *Resin preparation*

The cleaning method employed for the resins used in this study was a modified sequential Soxhlet extraction method according to Thurman and Malcolm (1981). Both XAD-8 and XAD-4 resins were separately slurried with 0.1M NaOH (1.5 L) and the fines decanted off. The resin was then stored in methanol for 24 hours after which the resins were Soxhlet extracted for 48 hours each with methanol, acetonitrile and methanol (~1.8 L). Following the sequential Soxhlet extraction, the resins were packed into the fractionation column and rinsed with ultrapure water until the column eluate DOC was <1 mg L^{-1}. The resins were finally rinsed with 250 ml each of 0.1M NaOH, 0.1M HCl and rinsed with DI water before use and in between extractions.

- *Resin fractionation and DOC measurement*

1 litre influent grey water and constructed wetland effluents were filtered through a 0.45 µm glass fibre filter to remove suspended matter (Fujita et al., 1996). The filtrate was acidified to pH 2 using 1M HCl. The acidified filtered sample was put through the XAD-8/XAD-4 column pair. The eluate from both resins contained the hydrophilic fraction. The organic matter retained in the XAD-8 and XAD-4 columns were eluted with 0.1M NaOH. The eluate from the XAD-8 column was the hydrophobic fraction and the XAD-4 the transphilic fraction. The organic content in each fraction was determined by measuring the DOC using a TOC analyser. The resin fractions obtained consisted of HPO, TPI and HPI. The recovery of the DOC was quantified by measuring samples volumes passed through the resin, the volume of fraction produced and the DOC concentration measured by the TOC analyser.

- qualitative identification of iron

About 5 ml aliquot of influent and wetland effluent was treated with aqueous ammonia and caustic alkali to test for the presence of iron. An orange/rusty brown precipitate characteristic of iron confirmed the presence of iron. The concentration of dissolved iron in samples were analysed using an ICP Spectrophotometer.

- *Microbial methods*

Enumeration of total coliforms and *Esherichia coli* (MPN cfu $100ml^{-1}$) was carried out using the method Colilert 18 with quanti-tray 2000 (Idexx, UK) and faecal enterrococci (MPN cfu $100ml^{-1}$) using the Enterolert with quanti-tray 2000 (Idexx, UK).

  - *Determination of microbial activity of constructed wetland media*

Microbial activity of bed media was determined by an enzyme (dehydrogenase) assay. Soil: sand: compost media (for the reed beds) and an aliquot of suspension from gravel and Optiroc shaken in tap water from the GROW rig were incubated with 2, 3, 5-triphenyl tetrazolium chloride for 24 hours at 37°C, followed by extraction and measurement of the formazan formed by the microbes present in the innoculum.

Fresh soil-sand-compost from HFRB and VFRB was sampled along a vertical gradient using a half-inch diameter polyvinyl chloride (PVC) pipe. Sampling was done on three separate occasions and was carried out to obtain samples from much of the bed surface. For 'GROW', 200 ml container full with gravels and Optiroc from troughs were shaken in 10 ml DI water to obtain slurry. 2.5 ml sample of slurry and 2.5g samples of reed bed media pooled by quartering were placed into capped glass tubes for microbial activity investigation and moisture content determination respectively. 1.75 ml of 1% 2, 3, 5-triphenyl tetrazolium chloride (TTC) solution was added to each glass tube followed by 0.5 ml of 3% $CaCO_3$. The contents in the glass tubes were mixed using a vortex mixer for ~45 seconds to obtain a homogenous mixture. Tubes were then placed in test tube rack and completely wrapped with a tin foil to prevent contact with light as TTC is light sensitive. The rack was incubated at 37°C for 24 hours in the dark during which dehydrogenase enzymes convert the TTC to a red coloured substance called Formazan. Formazan is insoluble in water but soluble in methanol. Hence, following the 24 hours incubation period, 25 ml methanol was added to the glass tubes to dissolve the formazan. Tubes were whilmixed to obtain a homogenous mixture of its content and allowed to settle for 1 hour after which a representative 5 ml samples were transferred from the glass tubes using a disposable plastic pipette into a cuvette. The absorbance was read at 485nm. Dehydrogenase activity was calculated according to the equation:

$$Formazan(\mu g^{-1} g^{-1} 24h^{-1}) = \frac{29.54 \times absorbnce \times volume}{dryweight(g)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. \quad 3.1.5$$

3.1.3.6 Maintenance and management

All three wetlands were usually inspected twice weekly. Reeds (*Phragmites australis*) shoots were trimmed down to about 50cm at the end of winter between 2004 and 2007 to remove dead plant stem and to allow the redevelopment of new strands of reeds. Dead leaves on bed surface were always removed to allow air diffuse into the bed. Weeding was done once monthly. Weeding is believed to maintain the hydraulic conductivity of the bed surface. Influent pipes of all three wetlands were flushed once weekly. For GROW, major maintenance included regular (at least fortnightly) cleaning of filter at inlet wells, cut back of proliferated plant shoots and leaves above membrane and trimming of proliferated roots. All influent pipes were lagged during winter to prevent freezing.

3.1.3.7 Statistical analysis

A one-way analysis of variance was performed (Genstat 8th editon, release 8.1. Lawes Agricultural Trust, Rothamsted, UK) to determine differences between influent grey water and effluent from each wetland. Water sample (influent, effluent from HFRB, VFRB and GROW) was incorporated as the factor while each water quality parameter in turn provided the y variate. Data for microbial indicator, turbidity and suspended solids were $\log_{10}$ transformed to meet the assumptions of ANOVA. Fisher's LSD test was used to identify significant differences.

3.2 Reactive barriers for the removal of Phosphorous and metals (Cu and Ni) from 2^o sewage effluent

3.2.1 Materials

3.2.1.1 Sample (adsorbent) preparation

Table 4.2.1 list the different adsorbent investigated in this study for P removal ability. All adsorbent except for Ochre, Red mud and Bauxol were rinsed with deionised (DI) water to remove dust particles, oven dried at 105 °C and cooled in a desiccator prior to their use. Ochre obtained in slurry (moisture content ~ 90%) was oven dried at 105 °C prior to analysis. Red mud was obtained in power. Portion of Red mud was neutralized with sea water to obtain Bauxol according to procedure outlined in McConchie et al., (1999 and references therein). The material formed (Bauxol™ slurry) was filtered using a CF/C filter paper, oven dried at 105 °C, cooled in a desiccator and re-crushed to obtain a fine powder. This material was used in this research as Bauxol^{TM}. Bauxol^{TM} and Ochre, were also used to investigate their ability to remove Cu and Ni from sewage effluent.

3.2.1.2 Analysis of samples

In general, samples for soluble reactive phosphorous (SRP) were analysed using the Merck cell test kit. pH was measured using the Jenway 3540 pH and conductivity meter after calibration of the instrument. Chemical composition and mineralogy were investigated using a scanning electron microscope coupled with energy dispersive X-ray spectroscopy (SEM-EDS, Scanning Electron Microscope XL 30 SFEG, Philips, The Netherlands) and XRD (Powder X-ray diffractometer D5005, Siemens, Germany) tools. Porosity, bulk density and Cation exchange capacity (CEC) of the adsorbents were determined using standard soil science procedure methods (Bascomb, 1964). Surface area was measured using 10 point nitrogen adsorption BET method (using liquid nitrogen bath) on the Gemini Analyser (Micromeritics). Prior to the measurement, the samples were degassed (using N_2) at 100^{o}C overnight using FlowPrep060. Two reference materials: Kaolinite and carbon black and one replicated sample were included in the analysis protocol for quality control purpose. The surface area analysis was performed under the following conditions: 500 mmHg min^{-1} evacuation rate, 760 mmHg. min^{-1} saturation pressure, 5s equilibrium time.

3.2.1.3 Batch isotherms and kinetic experiments

Batch equilibrium isotherms were done by using sewage effluent (typical quality: SRP - 5.3 ± 0.5 mg L^{-1}; COD - 67.5 ± 5.1 mg L^{-1}; pH - 7.3 ± 0.4; SS - 12.0 ± 6.8 mg L^{-1}; turbidity 1.41 ± 0.1 NTU) spiked with phosphate solutions (~1mgP ml^{-1}) to increase the P working range from ~5 to 10 mg L^{-1}. Phosphate solution was prepared by dissolving anhydrous potassium orthophosphate (KH_2PO_4) powders (Fisher Scientific BDH analytical reagent grade) in deionised (DI) water. Known mass of adsorbents were shaken with 100ml aliquots of sewage effluent (range 0- 10 mg L^{-1}) in a 250ml erlenmeyer flask at 150 rpm using an orbital shaker for 24hrs at 20°C. Blanks containing adsorbent in DI water were included in all experiment. At the end of the 24 hr period, the solutions were filtered through GF/C filter. The equilibrium pH of the filtrate was measured and immediately analysed for SRP. Optimum contact time and kinetic studies was determined by shaking a known mass of the adsorbent in sewage effluent (5 mg L^{-1} phosphate) over a given period of time. Aliquots were withdrawn, filtered and determined for SRP.

Batch adsorption studies for Cu and Ni were carried out by agitating in an orbital shaker a suspension of 0.1g sorbent in 100 ml sewage effluent containing known amount of Cu and Ni salts in a 250ml erlenmeyer flask for 24hrs at 150 rpm at 20°C. Both Cu and Ni salts used were of analytical grade. Blanks containing adsorbent in DI water were included in all experiment. At the end of the experimental period (24 and 10hrs for isotherm and kinetic investigation respectively), all samples were filtered through a CF/C filter paper. Cu and Ni concentrations before and after experiment were determined using graphite Furnace Atomic Absorption Spectrophotometer according to standard procedure (APHA, 1998). Kinetic study was determined by shaking a known mass of the adsorbent in sewage effluent over a predetermined (10 hour) period. Aliquots were withdrawn, filtered and determined for Cu and Ni as previously stated.

3.2.1.4 Bed volume experiments

Bed volume experiments were carried out using rectangular trays for steel slag, Ochre and bay oxide and column for Filtralite-P, Bauxol and red mud. Both columns and trays were fed continuously with treated sewage effluent using peristaltic pump (Watson Marlow, Bredel pump, UK). Columns and trays were kept saturated. The columns were fed from the top but with the outlet pipe set at the surface of adsorbent in the column to keep the columns saturated. Flow onto and through the trays was horizontal to mimic horizontal flow in wetlands. The detention times for various bed volume trials were as follows: Ochre - 6 hrs, Bay oxide - 6 hrs, Steel slag 1 and 25hrs, Filtralite-P- 1 hr. Samples from the inflow and outflow trays were taken regularly whilst sampling in the columns were done hourly and later daily or regularly. Samples were analysed for SRP concentration using Merck's cell kit and pH as stated previously.

3.2.1.5 Regeneration experiments

Following adsorption experiments, the spent adsorbents for Ochre and Steel slag were rinsed with DI water and oven dried. Appropriate amount were placed in desorbing reagents (0.05M $NaHCO_3$, HCl , NaOH and NaCl) under static conditions for 24 hours in five batches for Ochre and steel slag until desorption was almost complete. The desorbed phosphate was determined by analysing the desorbing media using the Merck cell kit and ICP analyser. The reusability of the adsorbent following desorption was determined for steel slag bed volume experiments.

3.2.2 Data evaluation

Experimental equilibrium sorption data from both phosphorous (P) and metal (CU and Ni) studies were examined by fitting data on linear plots of two-parameter isotherm models – Freundlich, Langmuir and Dubinin-Radushkevich. Data obtained for P removal from bed volume studies were examined using the models of Bohart and Adam (1920) and Sheng and Huang (1999).

The linear form of the Freundlich equation for adsorption is given as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \text{ .... (3.2.1)}$$

where, q_e (mg.g^{-1}) is the amount of phosphate adsorbed per unit weight, C_e (mg.L^{-1}) is the equilibrium phosphate concentration, K_F (mg.g^{-1}) and 1/n (mg.g^{-1}) are Freundlich constants related to adsorption capacity and adsorption intensity respectively.

The linear form of the Langmuir equation for adsorption is given as:

$$\frac{C_e}{q_e} = \frac{1}{Q_o K_L} + \frac{C_e}{Q_o} \text{ .... (3.2.2)}$$

where, K_L (L g^{-1}) is the Langmuir isotherm adsorption constant related to the enthalpy of adsorption, Q_o (mg.g^{-1}) is the adsorption capacity and C_e (mg. L^{-1}) is the equilibrium concentration.

The linear form of the Dubinin-Radushkevich (DR) isotherm model is given as:

$$\ln q_e = \ln q_o - K_{DR}\varepsilon^2 \quad \text{(3.3.3)}$$

ε is Polanyi potential which is related to the equilibrium concentration as follows,

$$\varepsilon = \left[RT \ln\left(1 + \frac{1}{C_e}\right)\right] \quad \text{(3.2.4)}$$

where K_{DR} (KJ^2 mol $^{-2}$) is related to the free energy of adsorption and q_o is the Dubinin-Radushkevich isotherm constant related to the degree of sorbate sorption by the adsorbent surface.

The efficiency of the adsorption process was investigated by the dimensionless separation constant, R_L (equation 5) to determine the efficiency of phosphate adsorption. R_L values in the range $0<R_L<1$ indicates a high affinity adsorption.

$$R_L = \frac{1}{1 + K_L C_o} \quad \text{(3.2.5)}$$

where C_o ($mg.L^{-1}$) is the initial SRP concentration.

The energy change (E) for the adsorption process was determined from the Dubinin-Radushkevich equation given as:

$$E = \frac{1}{\sqrt{2K_{DR}}} \qquad (3.2.6)$$

Data from P bed volume trials were analysed using models of Lin and Huang (1999) and Bohart and Adams (1920). The time taken for breakthrough to occur when a sorbate solution travels a column length (bed depth) containing an adsorbent proposed by Bohart and Adams (1920) is given as:

$$\ln\left[\frac{C_o}{C} - 1\right] = \ln\left[e^{K_a N_o Z/F} - 1\right] - K_a C_o t \qquad (3.2.7)$$

where N_o is the adsorption capacity (mg solute per g adsorbent), K_a is the rate constant in bed depth service time (L (mg h)$^{-1}$) and Z is bed depth/length of column (m). The breakthrough profile in the original equation is given as:

$$\frac{C_t}{C_o} = \frac{e^{K_a C_o t}}{e^{K_a C_o t} + e^{K_a W/F} - 1} \qquad (3.2.8)$$

where W is the bed capacity (total weight of sorbate adsorbed).

Lin and Huang (1999) developed equation (3.2.9) for a sorbate concentration flowing through a stationary adsorption column:

$$t = \tau + \frac{1}{k}\ln\left(\frac{p}{1+P}\right) \qquad (3.2.9)$$

For a symmetrical breakthrough plot and at 50% breakthrough (i.e.*Ct/Co* = 0.5) Equation (3.2.9) simplifies to:

$$W_e = C_o F\tau \quad \text{.......} \quad (3.2.10)$$

3.2.3 Statistical analysis

One way analysis of variance was performed to test for significant differences at 5% level. Correlation analysis between variables was performed using the Spearman's correlation ranking. The relationship assumed that the P-sorption capacity (dependent variable) was influenced by the CEC or Fe, Al, Si and Ca content (independent variable) of the adsorbents.

CHAPTER 4 *Constructed wetlands for grey water treatment and reuse*

4.1 Results

4.1.1 Influent grey water quality

A summary of the physical, chemical and microbiological parameters of the influent grey water during the monitoring period is presented in Table 4.1.1. Pollutant parameters in influent grey water displayed considerable variability in concentration throughout the monitoring period and this is evident in scatter plots of pollutant parameters (Appendix 4). Such variations are consistent with reported variability of pollutant concentration in grey water within individual sites (Jefferson *et al*., 2004; Lazarova *et al*., 2003; Eriksson *et al*., 2002; Jefferson *et al*., 1999). This is because, domestic grey water quality is site specific and reflects differences in lifestyle of individuals (Ramon *et al*., 2004; Eriksson *et al*., 2002). Variability of grey water pollutant load is emphasised at smaller scales where the activities within one household have a proportionally greater impact on grey water quality. The period covered in this study covers approximately three academic years. Thus, it is possible that change in occupancy between academic years and individual user behaviour of personal products may have contributed to the varying influent concentration during the monitoring period. To illustrate further, BOD and turbidity of low strength influent grey water from the same source averaged 22.3±1.2 mg L^{-1} and 25.6±3.1 NTU in 2004 compared to 16.7±1.0 mg L^{-1} and 15.6±2.3 NTU in 2005 academic season respectively.

With the exception of dissolved oxygen and nutrients, level of pollutants increased considerably from low to high strength when light grey water was dosed with shampoo to increase the organic load so that it was comparable to reported ranges in the literature (Table 4.1.2). The resulting organic strength (155.8±9.3 mg. L^{-1}; COD 475.0±54.9 mg. L^{-1}) corresponds to mid range domestic grey water strength reported in the literature (Eriksson *et al.*, 2002).

Table 4.1.1. Summary of influent grey water quality, Values represent mean ±se except for indicator organisms which is $\log_{10}$ units, n = number of replicate samples.

Parameters		Low strength	High strength
Physical (mg. L^{-1})			
	DO_2	$3.2\pm0.3_{(n=67)}$	$1.8\pm0.3_{(n=22)}$
	Turbidity NTU)	$18.9\pm1.8_{(n=70)}$	$62.9\pm11.7_{(n=28)}$
	Suspended solids	$28.0\pm3.8_{(n=70)}$	$86.7\pm12.5_{(n=27)}$
Chemical(mg. L^{-1})			
	BOD_5	$19.3\pm0.9_{(n=71)}$	$155.8\pm9.3_{(n=25)}$
	COD	$84.4\pm3.8_{(n=40)}$	$475.0\pm54.9_{(n=13)}$
	NO_3-N	$1.5\pm0.2_{(n=20)}$	$1.2\pm0.6_{(n=5)}$
	NH_4-N	$1.7\pm0.4_{(n=20)}$	$0.3\pm0.1_{(n=5)}$
	PO_4-P	$0.7\pm0.1_{(n=20)}$	$0.3\pm0.1_{(n=5)}$
Microbial indicators (cfu 100 ml^{-1})			
	Total coliform	$6.0\pm5.4_{(n=57)}$	$7.7\pm7.3_{(n=16)}$
	E. coli	$3.4\pm2.8_{(n=57)}$	$3.2\pm2.6_{(n=16)}$
	Faecal enterococci	$3.9\pm3.6_{(n=57)}$	$3.1\pm3.0_{(n=16)}$

This resulted in a three-fold increase in turbidity and solids whilst BOD and COD organics increased six and eight-fold respectively (Table 4.1.1). The magnitude of DOC increase was similar to BOD and COD organic. Of the three microbial quality indicators (total coliform, *E. coli* and faecal enterococci) monitored in the influent grey water, only total coliform showed an increased with approximately 2 $\log_{10}$ units compared to the low strength grey water. The concentration of *E. coli* at high strength was similar to low strength whilst faecal enterococci decreased (Table 4.1.1). The 2

$\log_{10}$ increase in the total coliforms may have been due to the presence of the opportunistic pathogen *Pseudomonas aeruginosa* in the influent grey water, which increased in a similar trend to total coliform from low to high strength grey water (Winward, 2007). Winward (2007) showed that total coliforms were suitable indicators for *Pseudomonas aeruginos* in the influent grey water during the study period.

The influent grey water utilized during low strength period (light grey water) was weak in terms of organic strength with mean BOD concentrations of 19.3±0.3 $mg.L^{-1}$. Such concentration lies at the low end of the range for typical grey water strength from similar sources (bath, hand basin and sink) reported in the literature (Table 4.1.2). The very low organic strength of the influent grey water compared to literature values (Table 4.1.2) could be attributed to the lifestyles and water usage of occupants in the Feden flats. The BOD: COD ratio gives an indication of the biodegradability of organics within a particular source water. The BOD: COD ratio of the influent grey water during the monitoring period ranged from 0.21 at low strength to 0.23 at high strength.

Table 4.1.2 Comparison of grey water characteristics

Category	Reference	Grey water source
BOD (mg L^{-1})		
8.7-34	This study (LS)	Hand basin, showers, sinks
225-840	This study (HS)	Hand basin, showers, sinks & dosing shampoo
59	Friedler *et al.*, 2005	Bath, shower and washbasin
42-84	Nolde,1999	Bath, shower
96-181	Al-Jayousi, 2003	Handbasins, showers, sinks
BOD:COD		
0.21-0.23	This study	Hand basin, showers, sinks
0.34-0.35	Jefferson *et al.*, 2004	Hand basin, showers, sinks
0.37	*Friedler *et al.*, 2005	Bath, shower and washbasin from university family flats
0.46	Ramon, 2004	Shower water
0.50-0.91	Merz *et al*, 2007	Shower water
0.3-0.8	Metcalf and Eddy, 2003; Gray, 2004	Domestic sewage
C:N:P		
100:3.3:0.9	This study (LS)	Hand basin, showers, sinks
100:0.3:0.1	This study (HS)	Hand basin, showers, sinks
100:2.3:0.1	Jefferson *et al.*, 2004	Bath
100:2.9:0.1	Jefferson *et al.*, 2004	Shower
100:8.0:0.2	Jefferson *et al.*, 2004	Hand basin
100:20:1	Metcalf and Eddy, 2003	Domestic sewage

* = calculated from average total BOD and COD reported.

Biodegradability of waste waters usually range from 0.3 to 0.8 (Metcalf and Eddy, 2003). Low ratios (e.g. <0.3) are less biodegradable. This implies the biodegradability of the grey water used in this study (e.g. 0.21-0.23<0.3) was low. It was lower than grey water obtained from similar source reported in the literature (Table 4.1.2). The lower value of BOD: COD of the influent grey water suggest that some degradation occurred in the pipework between source and grey water collection tank. Investigation showed that 30% degradation occurred between the collection tank and inlet point of the wetlands. This is demonstrated by a reduction of BOD_5 from 21 to 15 mg.L^{-1} and COD from 136 to 94 mg.L^{-1} when comparing samples from the collection tank to the inlet of the wetlands. This result is in agreement with findings of changes in grey water quality on storage. To illustrate, Dixon *et al*., (2000) showed that storage of grey water can improve its water quality through settling of suspended materials, and aerobic growth and anaerobic release of soluble COD. Gross *et al.,* (2007a) reported that domestic grey water undergo rapid, short – term changes in waste composition in storage. Jefferson *et al*., (1999) reported that grey water follow first order decay kinetics equating to a 50% organic reduction over a four hour period.

The specific ultraviolet absorbance (SUVA) of the grey water throughout the study period was less than 1 $L.mg^{-1}.m^{-1}$. It has been shown that waters with low SUVA (<3 $L.mg^{-1}.m^{-1}$) contain predominantly hydrophilic and low MW materials (Goslan, 2004). The hydrophilic nature of the grey water was confirmed by results obtained from XAD fractionation and HPSEC studies. The Hydrophilic content as revealed by XAD fractionation average 70%. Results of HPSEC corroborate the findings from SUVA and XAD fractionation. The majority of the organic material contained within the grey water had an eluted time of ~10-12 minutes (Figure 4.1.1).

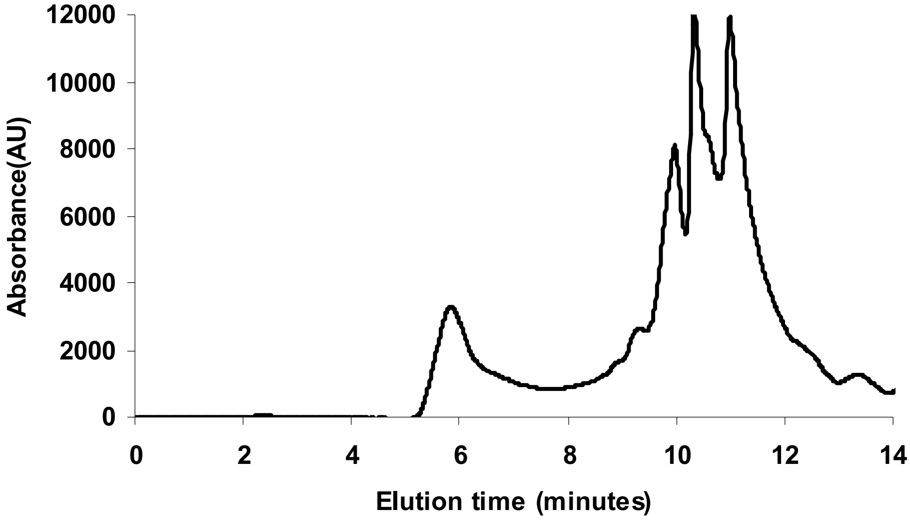


Figure 4.1.1 HPSEC chromatogram of influent grey water at high strength

This elution time has been reported to correspond to smaller MW hydrophilic fractions in contrast to high MW hydrophobic fractions which have a much shorter elution time of ~6 minutes (Fearing *et al.*, 2004). According to reported calibration between elution time of organics through a chromatographic column and MW of dissolved organics of NOM, fractions molecular size of 0.5 – 1 KDa and >5KDa corresponds to an elution time of 10.5 – 10.8 and <8 minutes respectively (Goslan, 2004). In comparison to other grey water sources, Jefferson *et al.*, (2004) reported molecular sizes of >5 KDa, 3-4 KDa and 0.5-1 KDa corresponding to elution times of 6.4-6.7 minutes, 7.6-7.8 minutes and 9.7-9.9 minutes respectively of organic molecules contained in grey water. Elsewhere, a much larger molecular size distribution of organic molecules in grey water has been reported. For, instance, Ramon *et al.*, (2004) reported MW sizes in the range <200 Da to >1μm (~52% = >400 KDa, 30 KDa -200 KDa = ~34%) for organics in shower grey water based on result on COD rejection by filtration at different MWCO ratings. In comparison, typical sizes of natural organic matter (NOM) in wastewater range from 2 to 5 KDa for hydrophobic organics and <2 KDa for hydrophilic organics (Fearing *et al.*, 2004). A 30% HPO content of this grey water source is comparable to a range of 30-40% reported for individual shower water (Pidou, 2006) but less than 40-60% reported for river water (Parsons and Jefferson, 2006; Goslan, 2004).

Nutrient (N and P) concentrations (measured as NH_4-N, NO_3-N and PO_4-P) in influent grey water were low (Table 4.1.1) and consistently below reuse standard (e.g. <10 mg L^{-1} NH_4-N for toilet flushing in China, Ernst *et al.*, 2005) throughout the duration of the study. The low values of N and P in this grey water source is typical of light grey water (grey water emanating from bath, shower, sinks and handbasins with low levels of N and P concentrations) due to the absence of kitchen and laundry wastewaters (Eriksson *et al.*, 2002; Baker, 1998; Shin *et al.*, 1997). The COD: N: P ratio at low and high strength was low, averaging 100:3.3:0.09 and 100:0.3:0.07 respectively. Consequently, in both low and high strength period, C: N were >>10:1 indicating nutrient deficiency. The optimum ratio for biological treatment has been quoted as 100:5:1 (Gray, 2004). Ratios below this value potentially reduce the efficiency of biological processes (Gray, 2004, Jefferson *et al.*, 2004). Indeed, nutrient (N or P) and trace metals (Zn or Cu) additions to light grey water to correct nutrient imbalance have been shown to increase the efficacy of biological systems treating grey water (Jefferson *et al.*, 2001).

The level of physical pollutants (solids and turbidity) contained within the influent grey water was highly variable throughout the monitoring period (Figures 17 & 18, Appendix 4). To illustrate, concentrations of turbidity and solid in the influent grey water range from 3 to 488 NTU and 3-332 mg L^{-1} for turbidity and suspended solids respectively. The mean suspended solid mass loading of 2.24 and 6.96 g m^{-2} d^{-1} at low and high strength respectively are within the range of 1- 10 g m^{-2} d^{-1} suspended solids loads recommended to treat secondary domestic wastewaters under temperate conditions (Kadlec and Knight, 1996). However, care must be taken when applying these "rule of thumb" guidelines as other factors such as the nature of wastewater and substrate effective particle size (e.g. d_{10}) influence treatment performance (Austin *et al.*, 2007). Particle sizes of solids in the influent grey water range from 1 - 900 µm. Particle size in the range of 5-200 µm have been reported for grey water (Ramon *et al.*, 2004). Similarly, Jefferson *et al.*, (2001) reported particle size from different bathroom sources to be in the range of 10-100 µm. This indicates that the influent grey water used in this study occasionally contained larger particles compared to those reported in earlier studies which also reflect the variability in particle size of solids in grey water (Jefferson *et al.*, 2004).

Total coliforms, *E. coli* and faecal enterocci in the low strength grey water averaged 6.0±5.4, 3.4±2.8 and 3.9±3.6 $\log_{10}$ respectively. In the high strength grey water, the concentrations of total coliforms were approximately 2 $\log_{10}$ units greater. Mean concentration for *E. coli* remained fairly constant whilst that of faecal enterocci fairly decreased slightly (Table 4.1.1). In general, mean concentration of total coliform in both low and high strength grey water is at the high end of literature data for grey water from similar sources (bath, shower and sink) of between 3.0 and 3.5 $\log_{10}$ cfu 100ml^{-1} (Eriksson *et al.*, 2003; Nolde, 1999). Rose *et al.*, (1991) reported total coliforms varying between 1 and 8 $\log_{10}$ cfu 100 ml^{-1} of grey water originating from showers and bath. The level of faecal enterococci ($\sim 10^4$) recorded in this study is also at the upper end of literature data. For instance, levels of faecal enterococci as high as 10^5 in grey water usually corresponds to sources emanating from families having younger children (Lazarova, 2003: Lazarova, 2001; Surendran and Wheatley, 1999 Rose *et al.*, 1991).

4.1.2 Wetlands performance

4.1.2.1 Organics

Result of the treatment efficiency of the three constructed wetlands fed with low strength grey water revealed overall removal of BOD_5 of 89%, 95% and 93% for the HFRB, VFRB and GROW respectively. Corresponding residual effluent BOD_5 concentrations were 2±0.1, 1±0.1 and 1.3±0.1 mg.L^{-1} for HFRB, VFRB and GROW respectively (Figure 4.1.2). Comparison of the performance of the different wetland systems revealed no significant difference ($P>0.05$, $n = 71$) between the distribution of effluent concentrations produced from the three technologies (Figure 4.1.2). Comparison of the distributions revealed that all three technologies were capable of robustly treating light grey water. This is evidence by the shape of the cumulative curves presented in Figure 4.1.3.

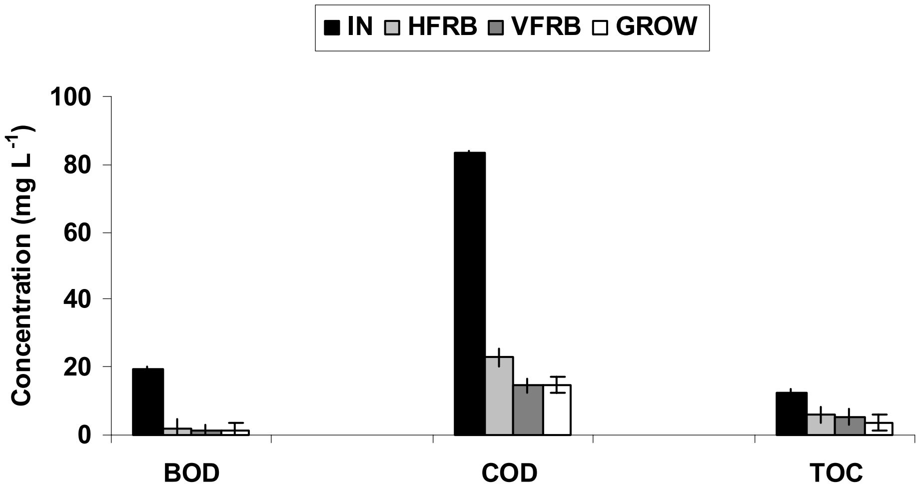


Figure 4.1.2 Performance of the technologies during low strength grey water treatment

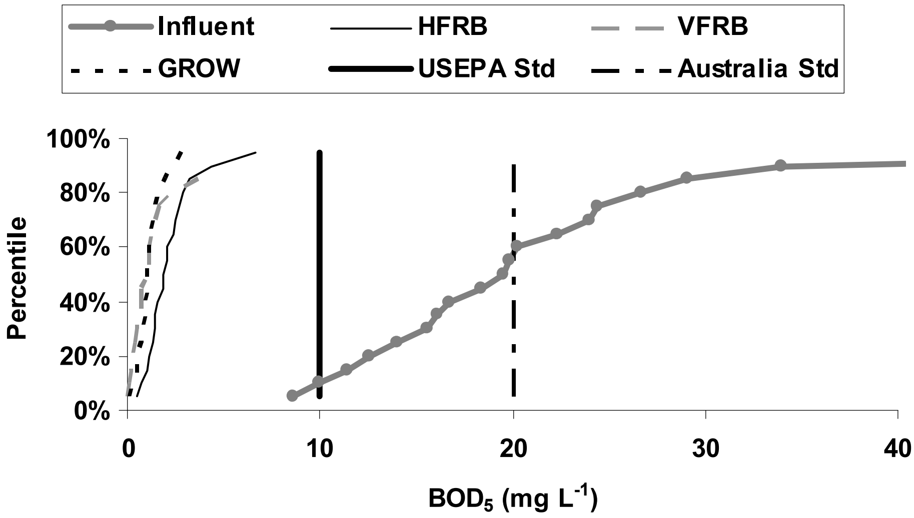


Figure 4.1.3: Percentile curves for the three wetlands removing organics at low strength

The influent grey water was represented by a robustness gradient (i.e. ratio of the change in percentile on the y-axis to the change in cumulative value of the x-axis) of 5 whilst the gradient of the wetlands were 27, 32 and 51 for HFRB, VFRB and

GROW respectively. All treatment robustness curves are characterized by a tail near the maximum observed values indicating what percentage of the performance is most variable. In the current case, the tail occurred for only the top 20% of the data and decayed at a gradient of 4, 4 and 12 for HFRB, VFRB and GROW respectively. The robustness gradient and tailing of robustness curves are indicative of highly robust technologies (Jefferson *et al.*, 2000).

Supplementing the grey water with a bathing shampoo to increase the organic content resulted in influent grey water BOD_5 of 155±9.3 $mg.L^{-1}$ which is towards the high end of previously reported grey water strengths of 90-185 $mg.L^{-1}$ for similar grey water source (Jefferson *et al*, 2004). Thus, the two trial periods represent the range of possible situations that may be encountered. Treated grey water concentrations at high strength were 51±7.5, 4.3±1.3 and 76.2±9.5 $mg.L^{-1}$ with corresponding removal efficiencies of 66%, 97% and 53 % for HFRB, VFRB and GROW respectively (Figure 4.1.4, Table 1 Appendix 4). In contrast to the low strength tests where residual concentrations were not significantly different ($p>0.05$, $n = 71$) from each other,

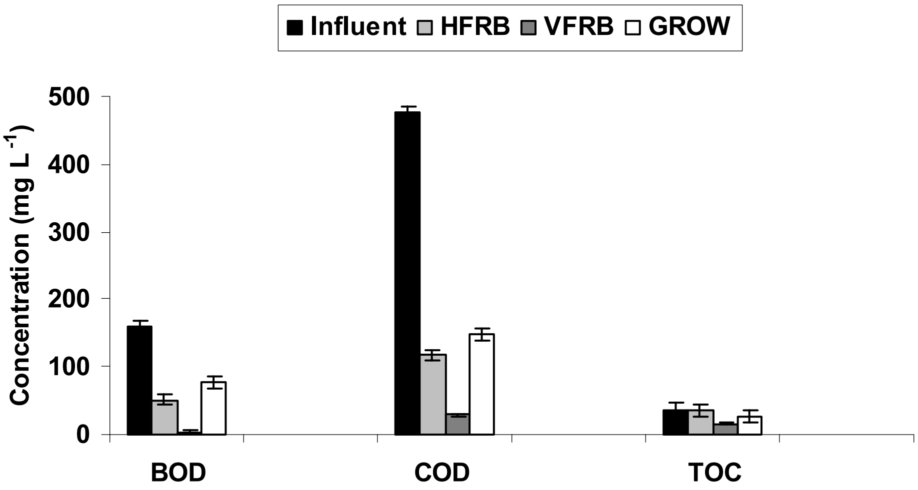


Figure 4.1.4: Performance of the technologies during high strength grey water treatment.

treatment performances at high strength from the three wetlands were found to be highly significant from each other ($p<0.0001$, $n = 25$). There was a notable decrease in the performance of the HFRB and the GROW system when organic load was increased from low to high strength (Figure 4.1.5), therefore a correlation analyses was carried out to investigate the effect of influent grey water on wetland residual concentration. Result showed that concentration of influent grey water correlated strongly with residual organics in wetland effluents, especially for HFRB and GROW (r_s= 0.50, $P<0.001$ for HFRB; r_s = 0.59, $P<0.01$ for GROW, r_s =-0.22, $P<0.001$ for VFRB). In terms of compliance to worldwide standards, the VFRB, HFRB and GROW systems met the USEPA standard of 10 mg.L^{-1} BOD$_5$ on 80%, <10% and <10% respectively of the samples (Figure 4.1.5). Equivalent analysis to the less stringent Australian standard still resulted in very low compliance (~15%) for both

HFRB and GROW whilst compliance for VFRB increased from 80% to 90% (Figure 4.1.5).

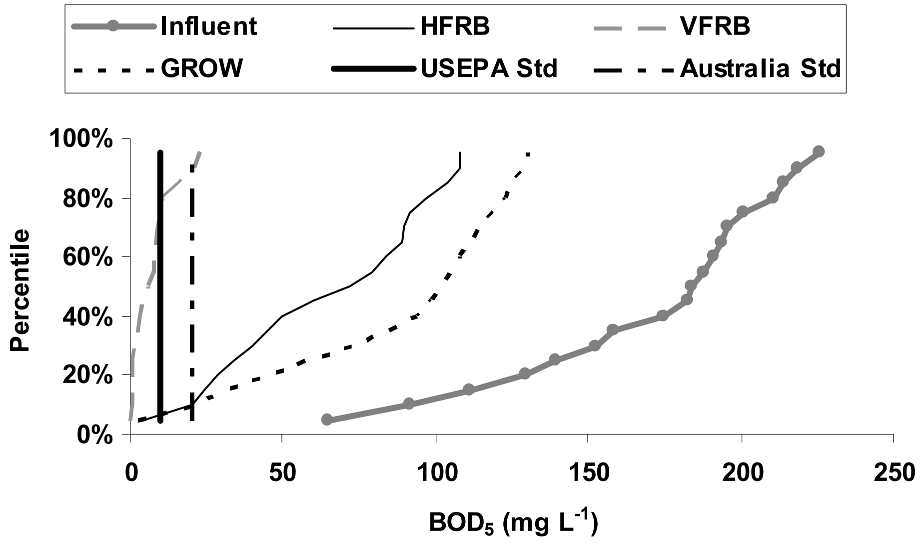


Figure 4.1.5: Cumulative plots for influent grey water and wetlands effluent at high strength.

Compared to the robustness of the three technologies treating the low strength grey water, a much lower robustness was achieved at high strength (Figures 4.1.3 and 4.15). For instance, the response of the robustness curves of both the HFRB and GROW show similar shaped curves to the influent curve. In contrast, the observed resistance to sudden deviation from the y-axis by the VFRB indicates that the VFRB was more robust compared to the HFRB and GROW.

Wetland residual COD concentration at low strength averaged 22.9±2.6 for HFRB, 14.6±2.1 for VFRB and 14.8±2.8 for GROW with corresponding removal efficiencies of 73%, 83% and 83% respectively. Differences in average removal efficiencies were not significant ($p>0.05$, $n = 40$). At high strength, an average influent COD concentration of 475±0 was only significantly reduced by VFRB (mean residual of 29.1±8.2 corresponding to 94% removal). Residual concentrations for the HFRB and GROW averaged 117.5±14.7 and 148.1±20.1 mg L^{-1} corresponding to a removal of 75% and 69% respectively. In contrast to the low strength feed where removal efficiency of COD was lower compared to BOD in all three wetlands, at high strength, removal efficiency of COD was greater than BOD for HFRB and GROW (Table 1, Appendix 4).

The ability of the three wetlands to remove organic matter during low strength and high strength trials was also reflected in the BOD: COD ratio of the treated effluents. The BOD: COD ratios of the wetlands at low strength were 0.095, 0.08 and 0.09 for HFRB, VFRB and GROW respectively. These ratios lie at the top end of a ratio of 0.1-0.3 obtained for final treated effluent (Metcalf and Eddy, 2003). Comparative data in the literature reported a BOD: COD ratio of 0.04 for an MBR unit treating shower water from sports and leisure club (Merz *et al.*, 2007). At high strength, the BOD: COD ratio of the treated effluents for both HFRB and GROW increased to 0.45 and 0.50 respectively. These values fall outside the range of 0.1-0.3 for final treated effluent and mid way the range of 0.3-0.8 for untreated waste water (Metcalf and Eddy, 2003). This indicates deterioration of treatment performance at high strength. The BOD: COD ratio for the VFRB remained low, averaging 0.17. In comparison, Pidou (2006) obtained a BOD: COD ratio of 0.11 and 0.02 for the same grey water source reported in this study using an MCR and MBR respectively in a complementary study.

4.1.2.2 Total dissolved organic carbon and fraction removal

All three CWs efficiently remove DOC at low strength. Residual DOC in wetland effluents averaged 3.8, 45 and 3.3 mg. L^{-1} for HFRB, VFRB and GROW respectively. Differences between residual DOC of the three wetlands were not significant ($p>0.05$, $n = 3$). However, at high strength, significant ($P=0.01$, $n = 8$) differences in treatment performance in removing dissolved organic carbon (DOC) was observed, with an average removal of 57% for VFRB, 3% for HFRB and 26% for GROW. Residual DOC in wetland effluents at high strength averaged 35.5±6.6, 15.3±7.9 and 25.9±7.5 mg. L^{-1} for HFRB, VFRB and GROW respectively. DOC from CW in the range of 2.9 to 10.5 mg. L^{-1} treating lagoon effluent of influent concentration 15-25 mg. L^{-1} has been reported (Pinney *et al.*, 2000). Influent DOC level was found to influence residual DOC in the three wetland effluents. This relationship was explored using linear regression analyses with influent DOC as an independent variable and effluent DOC as the dependent variable. DOC removal from all three CWs correlated significantly and strongly with influent DOC level ($R^2 = 0.94$ for VFRB; 0.82 for HFRB and 0.96 for GROW). Furthermore, the removal of DOC from VFRB generally decreased below 50% at influent DOC concentration of ≥ 40 mg.L^{-1}, whilst minimal removal occurred in HFRB and GROW at influent concentration of ≥ 20 mg.L^{-1}. BOD: TOC ratios of the three wetland effluent averaged 1.46, 0.29 and 2.9 for HFRB, VFRB and GROW respectively. The BOD: TOC ratio for the VFRB is in agreement to values of 0.2 – 0.5 normally observed for final treated effluent. The ratios for HFRB and GROW are well above this range and lie mid way in the range of 1.2 – 2 for untreated waste water (Metcalf and Eddy, 2003).

The result of XAD fractionation of the influent grey water and wetland effluents at low strength revealed that all three CWs removed hydrophilic (HPI) fractions and hydrophobic (HPO) fractions (Figure 4.1.6a and b) with HFRB and GROW exhibiting the most effective removal of the HPI fraction. At high strength when total DOC rose to ~60 mg L^{-1}, all three CWs demonstrated lack of ability to remove the HPI fractions (Figure 4.1.7a and b). The percentage distribution of DOC in wetland effluents were, 46% HPI, 25% TPI and 29% HPO in VFRB; 65% HPI, 16% TPI and 19% HPO in HFRB and 64% HPI, 18% TPI and 18% HPO in GROW effluents. The level of HPI in HFRB and GROW effluents was significantly higher than in VFRB ($p<0.05$, $n = 5$).

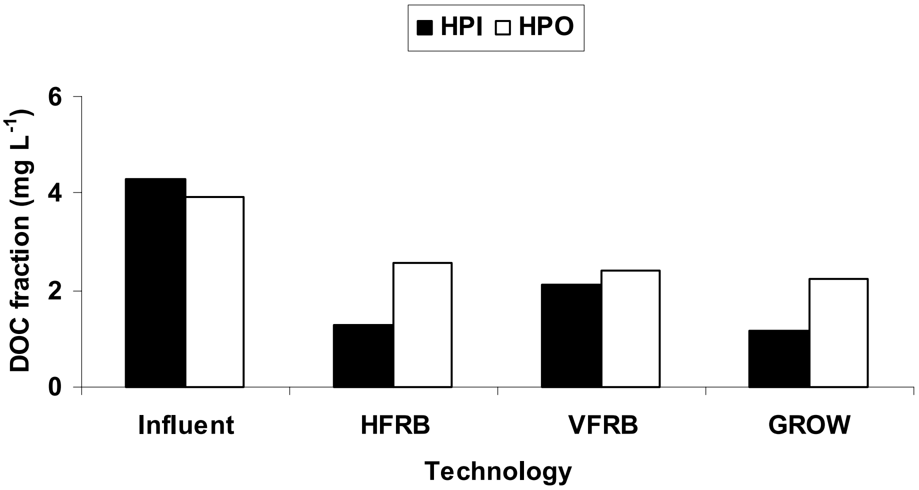


Figure 4.1.6a: Total DOC (mg L^{-1}) in hydrophilic (HPI) and hydrophobic (HPO) fractions in influent and wetland effluents at low strength

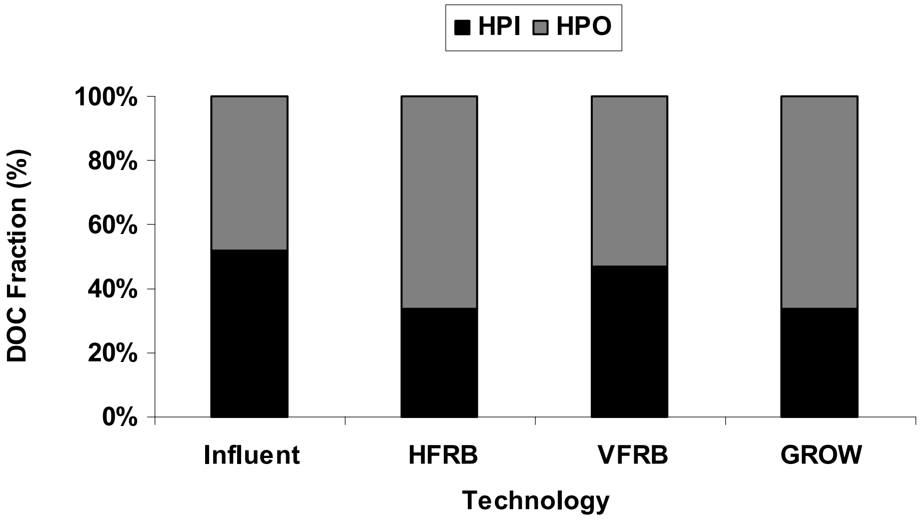


Figure 4.1.6b: Percent DOC in hydrophilic (HPI) and hydrophobic (HPO) fractions in influent and wetland effluents at low strength

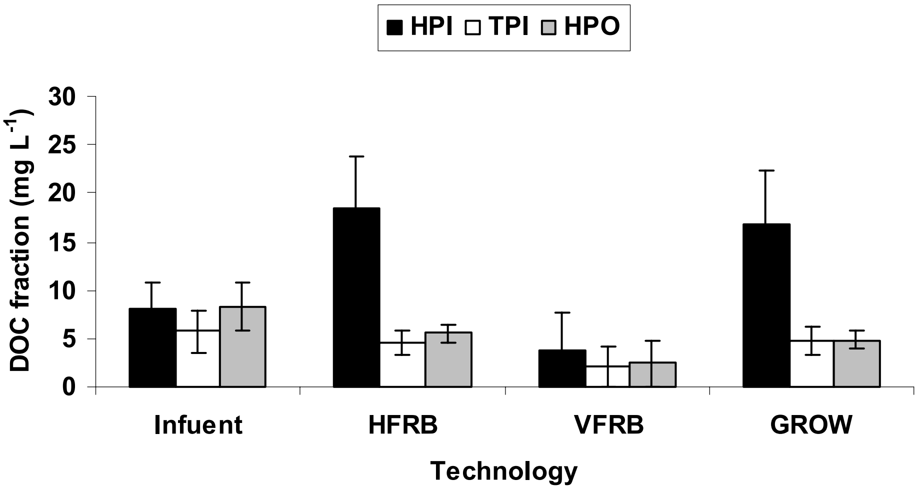


Figure 4.1.7a: Total DOC (mg L^{-1}) in hydrophilic (HPI), transphilic (TPI) and hydrophobic (HPO) fractions in influent and wetland effluents at high strength.

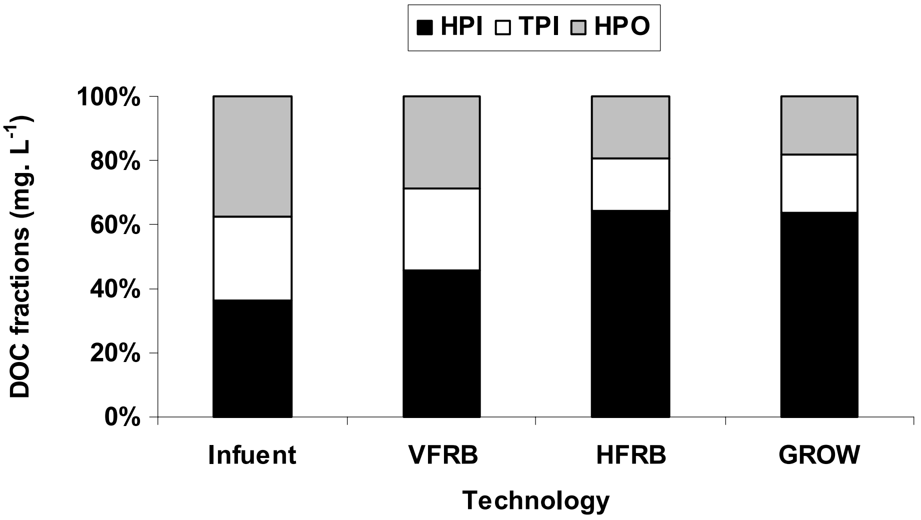


Figure 4.1.7b: Percent DOC in hydrophilic (HPI), transphilic (TPI) and hydrophobic (HPO) fractions in influent and wetland effluents at high strength

Molecular weight profile of the three wetland effluents measured by high performance size exclusion chromatography (HPSEC) with UV detection is presented (Figure 4.1.8). Results of chromatograms revealed that all three wetland effluents contain high proportion of UV absorbing substances. High UV absorbing substances at elution time ~10 minutes corresponds to low MW hydrophilic molecules (Goslan, 2004).

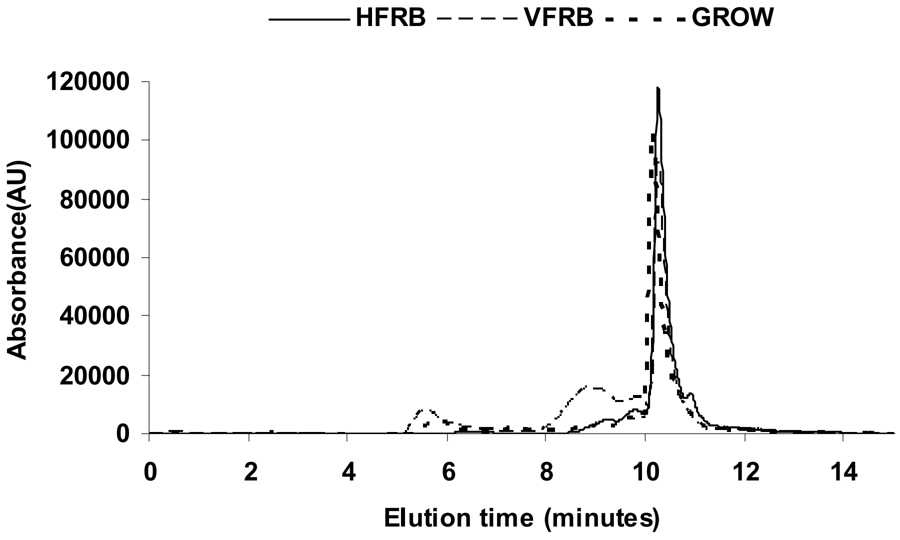


Figure 4.1.8 HPSEC chromatograms of wetland effluents during high strength

Compared to the influent grey water HPSEC chromatogram (Figure 4.1.1), the increase proportion of HPI molecules in all three wetland effluents indicate that transformation occurred as a consequence of wetland treatment. It is possible that the increase in HPI in the wetland effluents may have been derived from the wetlands or transformation from higher MW HPO fractions based on previous studies confirming release of DOC into the effluent waste stream (Barber *et al.*, 2001; Kadlec and Knight, 1996). Comparison between chromatograms of wetland effluents revealed a relatively greater proportion of molecular sizes at elution times 5-6 minutes and ~9 minutes for VFRB compared to HFRB and GROW.

4.1.2.3 Solids and turbidity

Despite the variability of suspended solids load in influent grey water, all three wetlands efficiently removed suspended solids from the influent grey water at low strength. Residual concentrations of the wetlands averaged 7.4±0.9 mg L^{-1} for HFRB, 2.2±0.3 mg L^{-1} for VFRB and 2.8±0.4 mg L^{-1} for GROW. Effluent turbidity for the three wetlands averaged 15.5 NTU for HFRB, 10.6 for VFRB and 0.6 for GROW. Solid to turbidity ratios were 0.47 for HFRB, 0.21 for VFRB and 4.67 for GROW indicating that VFRB was best at removing colloids. In order to characterise the suspended solids present in the grey water and the size range removed by the wetlands, influent and effluent samples were analysed for particle volume distributions using particle size analyser (Figure 4.1.9). Results revealed that the particle sizes from the GROW effluent were below the detection limit (0.02 µm) of the instrument. This therefore explains the high efficiency of the GROW system in removing turbidity as reflected in a mean turbidity of 0.6NTU. The efficiency of GROW in removing turbidity at low strength can be appreciated considering that the turbidity value for drinking water is 0.6 NTU and 1 NTU for MBR permeate (Friedler *et al.*, 2005). GROW was also effective in removing colloidal matter since particle size on random sampling gave no reading below 0.02 µm. The size distribution of the HFRB and VFRB are characterised by d_{50} (median size) of 94.6±4.9µm and 0.2±0µm for HFRB and VFRB respectively (Figure 4.1.9). The sizes of particles contained in the VFRB effluent were generally smaller compared to the HFRB.

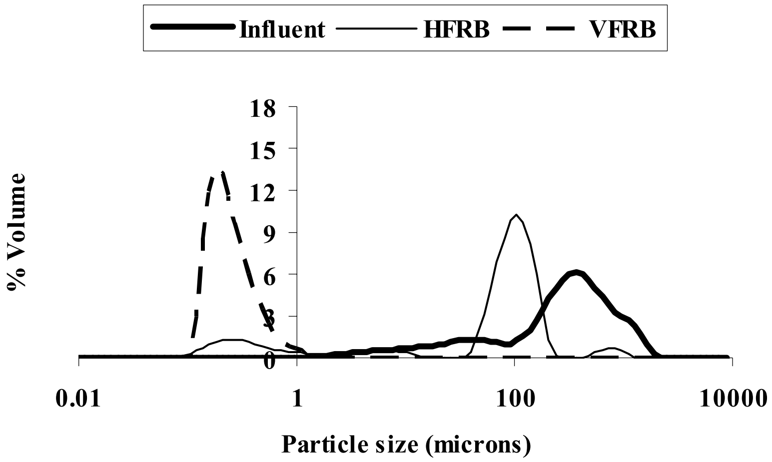


Figure 4.1.9: Particle size distribution of Influent grey water and HFRB and VFRB effluents at low strength.

At high strength, mean residual SS concentration of the three CWs differed significantly ($P<0.001$, n = 27). Corresponding residual solids in the final effluent were 31.1±3.0 mg L^{-1} for HFRB, 9.3±1.2 mg L^{-1} for VFRB and 18.6±1.7 mg L^{-1} for GROW. Turbidity profiles were similar to those of solids at high strength. For both solids and turbidity, residual concentrations in wetland effluents were significantly different from each other ($p<0.05$). Suspended solids to turbidity ratios were 2.66 for HFRB, 4.23 for VFRB and 0.72 for GROW. The low suspended solids to turbidity ratio for GROW is reflected in the range of particle size (<1 to 1000 μm) present in GROW effluent. In the effluent of GROW, three secondary peaks around 10, ~75 and ~500 were evident (Figure 4.1.10). The release of biofilms and particulates as a result of excessive root growth within the troughs of the GROW system contributed to the poor removal efficiency at high strength trial.

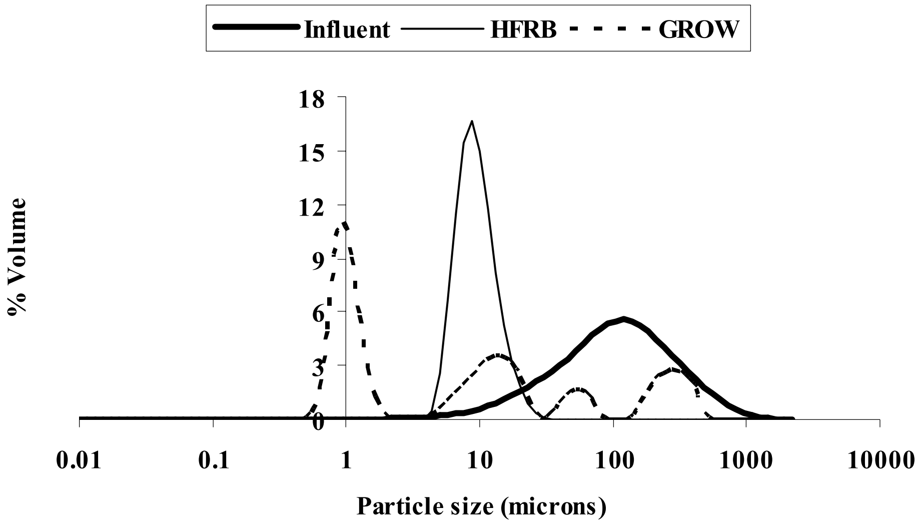


Figure 4.1.10: Particle size distribution of influent grey water and CW effluents at high strength

The relatively high level of solids in the HFRB effluent compared to the VFRB was due to the presence of iron (III) hydroxides in the HFRB effluent. Because the HFRB system was anoxic-anaerobic, dissolved iron leeched out with the effluent which on exposure to air oxidises to form the rusty brown coloured iron (III) hydroxides. This did not happen with the VFRB since the latter was aerobic. The presence of dissolved iron in the HFRB effluent was confirmed qualitatively using aqueous alkali and hydroxide. A pale green gelatinous precipitate with aqueous alkali which remains insoluble in excess was used to confirm qualitatively the presence of iron according to Equations 4.1 and 4.2 below.

$$Fe^{2+}_{(aq)} + 2OH^{-}_{(aq)} \rightarrow Fe(OH)_{2(s)}\text{(Pale green)}\ldots\ldots 4.1$$

$$Fe(OH)_{2(s)} + OH^{-}_{(aq)} \rightarrow Fe(OH)_{3(s)}\text{(Rusty brown)}\ldots\ldots 4.2$$

Following qualitative confirmation of dissolved iron in the HFRB effluent, quantitative determination was carried out. Typical concentrations of total iron in HFRB effluent was 14.5±2.1 mg L^{-1}. Nivala *et al.*, (2007) reported a decrease in performance from 90% to 0% for BOD_5 and NH_4-N removal for a horizontal flow CW treating landfill leachate due to clogging of effluent pipes with iron precipitates as a result of conversion of dissolved iron in leachate with air around the orifices of pipes.

HFRB effluent analysed by particle distribution at low and high strength revealed that the primary peaks occurred at about 100 and 10 µm respectively. The shapes of the turbidity robustness curves revealed that GROW was efficient and robust in removing turbidity at low strength but not at high strength (Figures 4.1.11 and 4.1.12). The robustness curve for GROW was characterised by a tail only at the top 20% of the data at low strength. In contrast, both the HFRB and VFRB systems were unable to effectively remove turbidity from the influent grey water. This was evident by the significant deviation from the y- axis for virtually all the data set (Figure 4.1.11).

Performance at high strength was in contrast to low strength for VFRB and GROW. GROW showed no ability to remove solids and this was evident with the immediate and continuous impact of increase solid concentration at high strength (Figure 4.1.12). The robustness curve of GROW was similar to the influent grey water curve. Reasons for the decreased performance of the GROW system at high strength is discussed in section 4.1.2.7 & 4.1.2.8. In contrast, the VFRB demonstrated increase

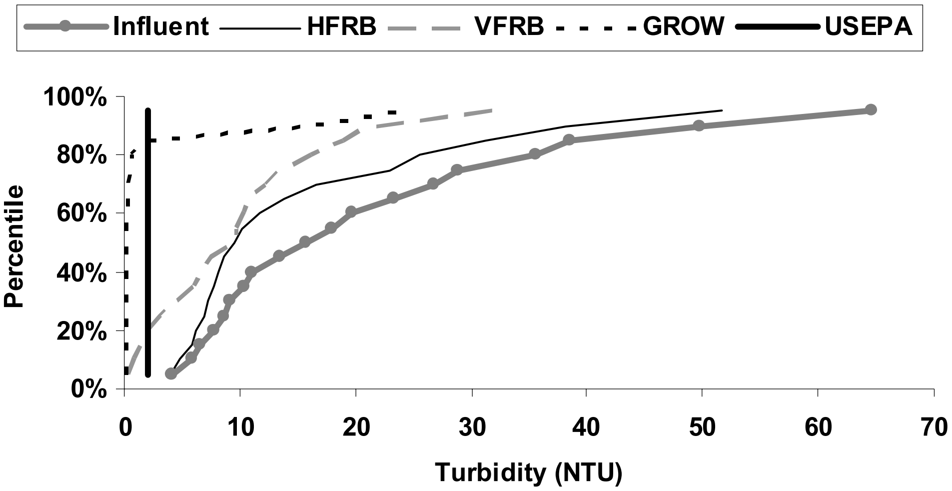


Figure 4.1.11: Percentile plots for HFRB, VFRB and GROW removing turbidity from influent grey water at low strength

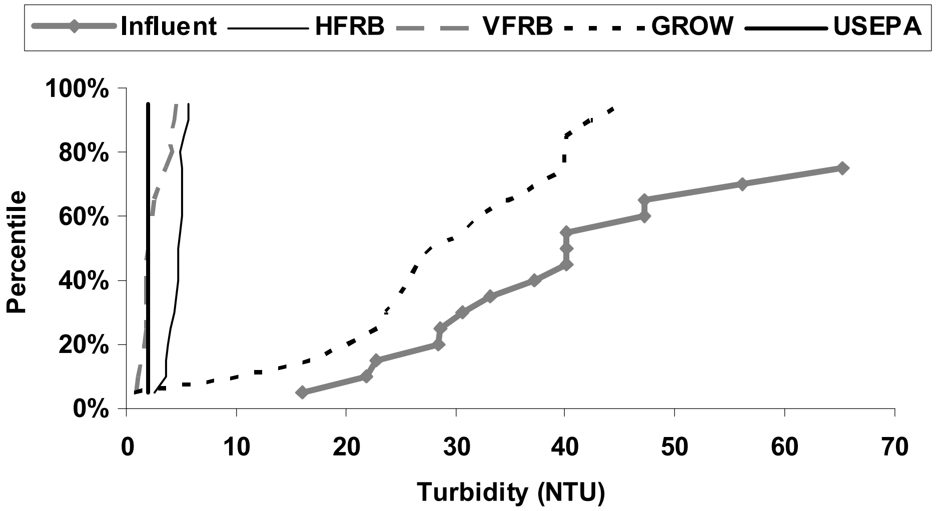


Figure 4.1.12: Percentile plots for HFRB, VFRB and GROW removing turbidity from influent grey water at high strength

performance in removing turbidity from low to high strength (Figure 4.1.11 and 4.1.12). Compliance to the 2 NTU reuse standard of GROW decreased from 80% to 12% whilst that of VFRB increased from 20 to 68%. Turbidity of the HFRB effluent remained poor despite removal of solids because of the presence of colloidal iron (III) phates as previously explained.

4.1.2.4 Indicator organisms

The three CWs demonstrated differences in ability to remove indicator microorganisms from the influent grey water throughout the duration of the study. At low strength, total coliform, *E coli* and faecal enterococci log removal averaged 2.7, 2.1 and 2.1 for HFRB; 4.8, 3.3 and 2.2 for VFRB and 3.8, 2.4 and 2.2 for GROW at low strength. Residual levels of indicator organisms in the three wetland effluents were only significantly different from each other for total coliform. Comparable log removals were recorded for HFRB and VFRB at high strength (3.3, 2.3 and 2.1 log reduction for total coliform, *E coli* and faecal enterococci respectively for HFRB and 3.3, 2.0 and 3.0 log reduction for total coliform, *E coli* and faecal enterococci respectively for VFRB) but GROW demonstrated considerable decreased performance (1.7, 0.6 and 1.8 log reduction for total coliform, *E coli* and faecal enterococci respectively).

The magnitude of log removal recorded in this study is comparable to those reported in the literature. For instance, average total coliform count at low strength is comparable to reported effluent count of 80-740 cfu 100ml^{-1} for horizontal flow CW treating raw sewage in the Czech Republic (Vymazal *et al.*, 2001) as well as a three log removal reported for grey water treatment using a microfiltration membrane (Jefferson *et al.*, 2000). Furthermore, the high removal efficiency at low strength is in agreement with literature data where comparable efficiency has been reported. To illustrate, average total coliform count at low strength is comparable to reported effluent count of 80-740 cfu 100ml^{-1} for horizontal flow CW treating raw sewage in the Czech Republic. Removal at high strength was lower compared to low strength (Table 1, appendix 4), and average residual counts ranging from 2.8×10^4 to 1.3×10^6 cfu 100ml^{-1} are comparatively lower to that reported 3900 cfu 100ml^{-1} for effluent total coliform counts for secondary treatment in England (Stott *et al*., 1996).

Comparison of robustness curves for the three wetlands in removing total coliform, *E coli* and faecal enterococci from the influent grey water over the monitoring period revealed that overall, the VFRB was superior to both the HFRB and GROW (Figure 4.1.13 a, b & c). To illustrate, tailing of the robustness curves was minimal and more gradual in VFRB compared to the HFRB and GROW for all three indicator organisms monitored. Calculated decay gradients of the three wetland technologies removing total coliforms from influent grey water averaged 14, 19 and 14 for VFRB, HFRB and GROW respectively. Gradient for removing *E coli* from influent grey water averaged 22, 40 and 14 for VFRB, HFRB and GROW respectively whilst gradient for removing faecal enterococci averaged 26, 31 and 37 for VFRB, HFRB and GROW respectively.

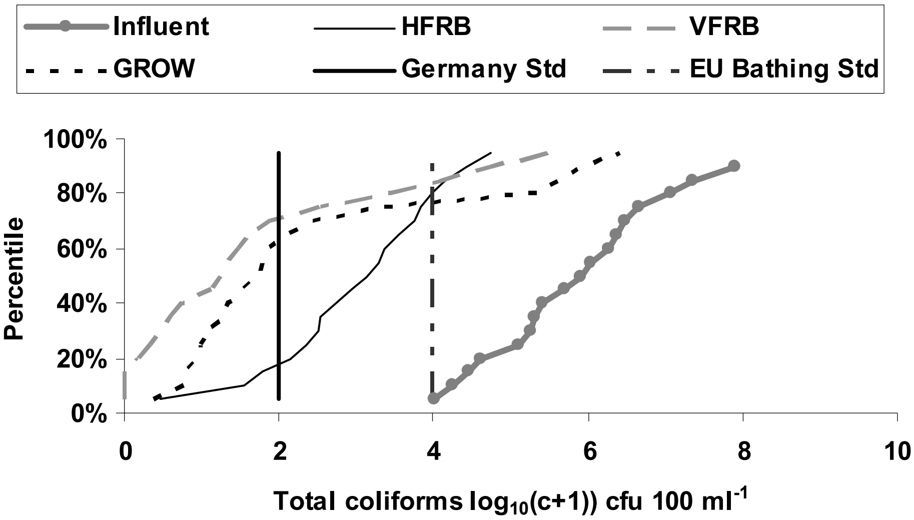


Figure 4.1.13a: Percentile plots of the three constructed wetlands in removing total coliform from influent grey water at high strength.

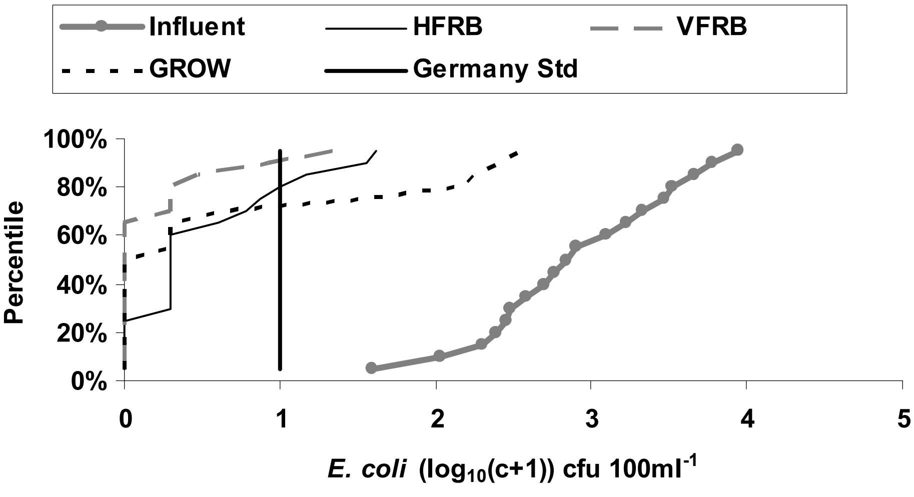


Figure 4.1.13b: Percentile plots of the three constructed wetlands in removing *E. coli* from influent grey water at high strength.

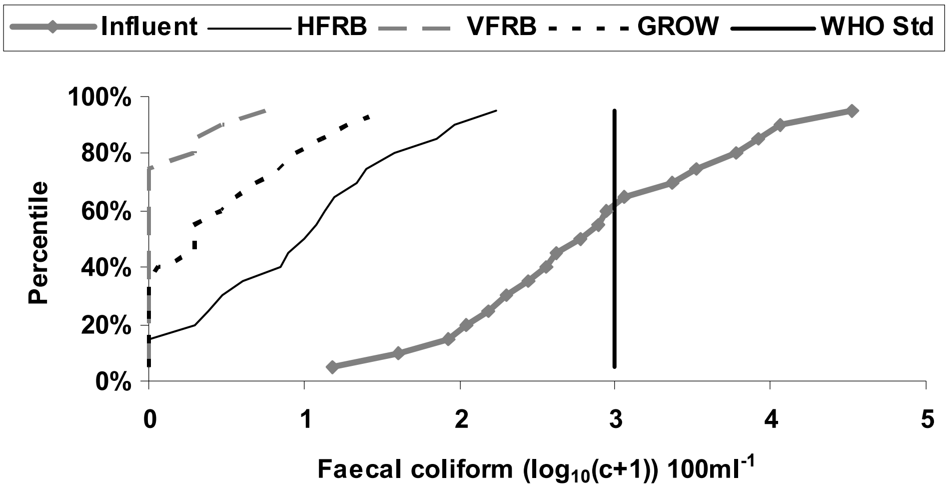


Figure 4.1.13c: Percentile plots of the three constructed wetlands in removing faecal enterococci from influent grey water at high strength.

Result of average microbial activity on bed media at high strength for combined upper and middle sections of the two reed beds was comparable (345.1 μg Formazan cm^{-3} for VFRB and 435.8μg Formazan cm^{-3} for HFRB). Microbial activity for GROW was much lower (1.4 μg Formazan cm^{-3}). It must be noted that whilst the investigation was carried out using soil/sand/compost mixture for the reed beds, that for GROW was obtained from gravel which have a much smaller surface area for microbial attachment compared to the soil/sand/compost mixture. The importance of the results of microbial activity of the two reed beds suggests that the aerobic conditions could have been the major contributing factor of the VFRB in removing organic and indicator organisms more efficiently than the HFRB at high strength.

4.1.2.5 Dissolve oxygen, E_h and pH

At low strength, mean influent dissolved oxygen (3.2±0.2 mg L^{-1}) generally rose during treatment (4.5±0.2, 7.5±0.3 and 7.2±0.3 mg L^{-1} for HFRB, VFRB and GROW respectively). The relatively higher dissolved oxygen concentration for VFRB compared to HFRB reflects the more aerobic conditions which prevail in conventional vertical flow CWs. Mean redox (E_h) measurements for the HFRB and VFRB at 10 cm below the surface were -45 and +245 mV respectively confirming anoxic-anaerobic and aerobic conditions in HFRB and VFRB respectively. At high strength, the mean redox (E_h) measurement for all three wetlands decreased, ranging from +(20 – 100) mV in the VFRB, and -(100 – 250) mV for HFRB and GROW across the bed surfaces for the reed beds and in the gravel and Optiroc media in GROW. Dissolved oxygen decreased correspondingly (Table 4.1.1, Appendix 4). During the entire study period, there was a significant but weak correlation between influent temperature and effluent dissolved oxygen for both the HFRB and VFRB ($P<0001$, $R^2=0.24$ for HFRB and $P=0.0025$, $R^2=0.13$ for VFRB). The correlation for GROW was not significant.

Mean influent pH of 7.3 at low strength was slightly reduced to a mean of 7.0 in both HFRB and VFRB but was unaffected by passage through GROW (effluent pH 7.3). At high strength, mean influent pH of 7.0 increased slightly in GROW (effluent pH 7.2), unchanged in VFRB (effluent pH 7.0) and decreased slightly in HFRB (effluent 6.8). In both periods, effluent pH of the three CWs were not significantly different from each other ($p>0.05$, $n=68$ low strength, $n=20$ high strength).

4.1.2.6 Loading tolerance and unsteady state trials of the VFRB

Due to the inability of the HFRB and GROW systems to cope with the sustained increase in pollutant load at high strength, only the VFRB was used for unsteady state trials to assess its tolerance to variability in organic load. Three hydraulic loads (0.03, 0.06 and 0.08 m d^{-1}) and four organic loading applications of 0.51, 1.52, 6.4 and 12.4 g_{BOD} m^{-2} d^{-1} at steady state conditions were tested on the VFRB treating grey water. Result show that average mass removal of organics were proportional to influent organic mass loading. For instance, mass removal of 1.03, 5.58, 16.5 g m^{-2} d^{-1} and 35.7 equates to an influent mass loading of 2.27, 6.75, 18.59 and 38.0 g m^{-2} d^{-1}. However, effluent COD were sometimes higher at elevated loading rate (Figure 4.1.14, Figure 20 Appendix 4).

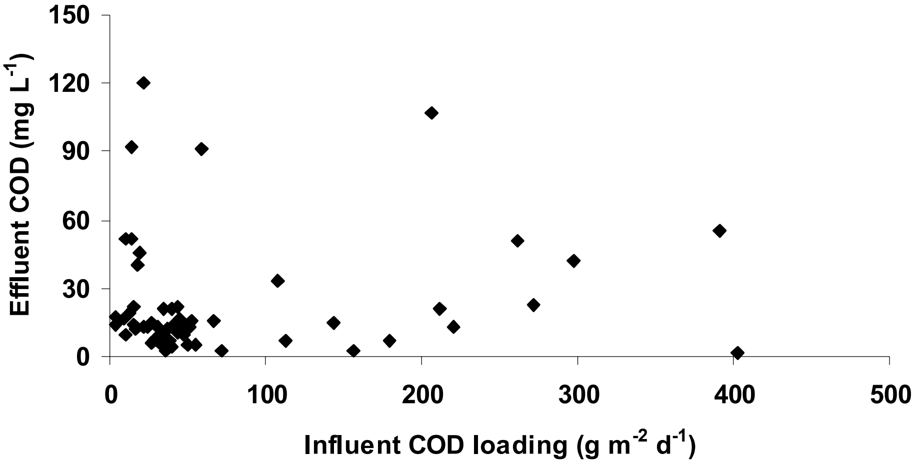


Figure 4.1.14: Effect of influent loading on VFRB residual concentration at four different hydraulic loading

Mass removal of 16.5 g m^{-2} d^{-1} and 35.7 g m^{-2} d^{-1} compares favourably with reported mass removal rates of operational and pilot treatment wetlands in the literature. In this trial, a suspended solid mass removal of 3.44 g m^{-2} d^{-1} and 6.72 g m^{-2} d^{-1} were associated with a COD mass removal of 16.5 g m^{-2} d^{-1} and 35.7 g m^{-2} d^{-1} respectively. This equates to a SS/COD ratio of 4.8 - 5.3. This large ratio may suggest high particulate organics and that the removal of solids resulted in decrease organics. The removals recorded in this trial are comparable to those reported in the literature. For instance, Chazarenc *et al*., (2007) reported a suspended solid mass removal of 7.2 g m^{-2} d^{-1} associated with a COD mass removal of 11.6 g m^{-2} d^{-1} for a wetland treating anaerobic fish farm supernatant.

Results of steady and unsteady state trial using Tesco and Ecover washing-up shampoos (Ecover was chosen to compare a non- toxic washing up liquid (Pidou, 2006) to a bathing shampoo) at steady concentration in the range of 150-200 mg L^{-1} and Tesco shampoo under fluctuating high and low BOD_5 concentration in the range of 100 – 600 mg L^{-1} coupled with 7 days resting between high organic loads is shown in Figure 4.1.15. As demonstrated by the plot, effluent quality failed to meet the USEPA BOD_5 standard of 10 mg L^{-1} whenever influent concentration exceeded 200 mg L^{-1}. Effluent organic concentration was directly influenced by influent organic loading as demonstrated by the loading and removal plot above (Figure 4.1.14).

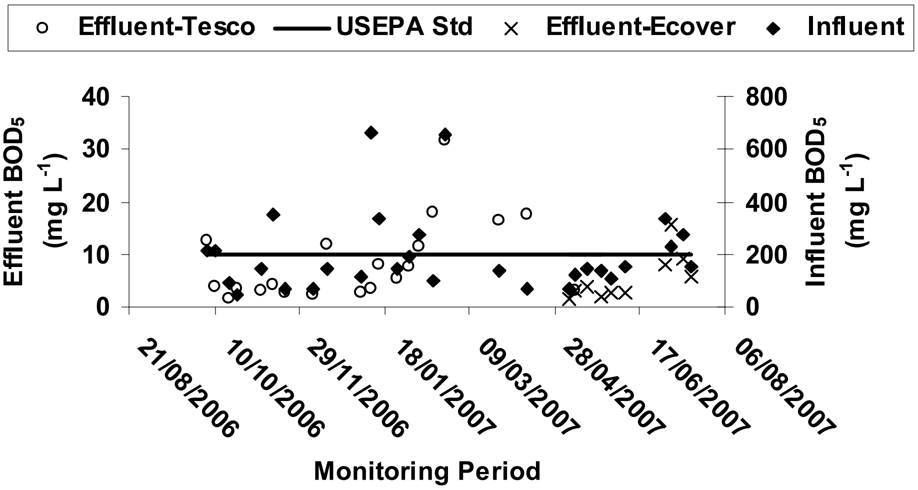


Figure 4.1.15: Performance of VFRB during unsteady state trials at 320 L d^{-1}

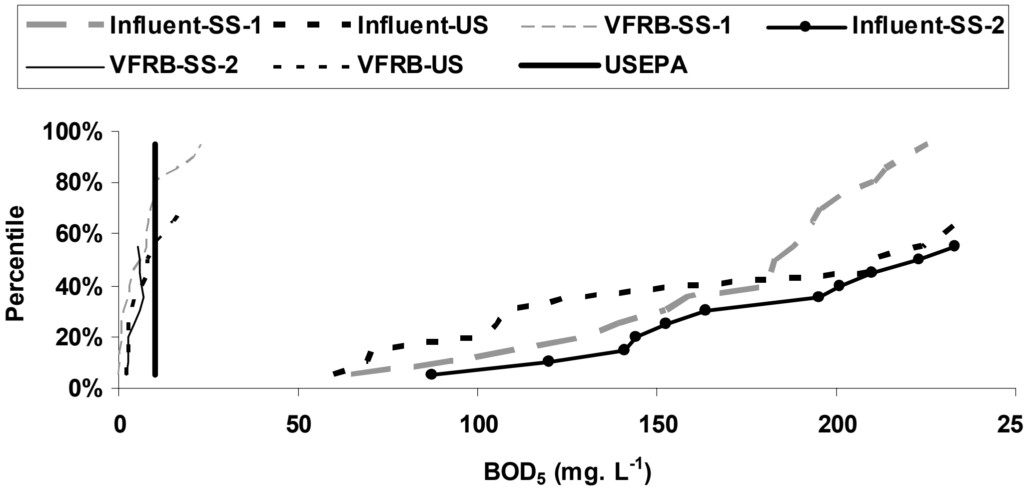


Figure 4.1.16: Percentile plots for VFRB during steady and unsteady states. SS-1, SS-2 and US represent influent at steady state trial 1 and 2 respectively, and US at Unsteady state.

Evaluation of the performance data during unsteady trials gave ~60% compliance at unsteady state compared to ~80% to the USEPA standard for steady state trials (Figure 4.1.16). Both steady state trials for Ecover and Tesco shampoos gave similar result exhibiting robust performance as indicated by non deviation from the y-axis for influent concentration up to 150 mg. L^{-1} followed by effluent BOD exceeding the 10 mg. L^{-1} limit when sustained influent concentration of ≥200 mg. L^{-1} was fed into the bed (Figures 4.1.15 & 4.1.16). Comparison of the robustness curves for the steady and unsteady state runs shows that whilst tailing occurred for the last 20% of the data for the steady state trial, tailing occurred for 50% of the data at unsteady state. This indicates that robust performance is achieved at steady state rather than unsteady state conditions in agreement with findings that CWs are susceptible to loading fluctuations (IWA, 2000).

4.1.2.7 The influence of oxygenation and plant type on the treatment performance of GROW

The main purpose of designing shallow troughs in the GROW system was to ensure oxygen saturation of the bed matrix via diffusion of air from the atmosphere into the bed matrix (WWUK) so as to enhance aerobic microbial degradation (Cooper, 1999). Mean dissolved oxygen concentrations along the treatment path during low and high strength ranged from 5.8 to 7.6 and 0.06 to 0.87 mg L^{-1} respectively. This is corroborated by redox potential (E_h) measurement at low and high strength which averaged ~250mV and ~ -210mV respectively indicating aerobic and anoxic-anaerobic conditions at low and high strength respectively. The measured level of dissolved oxygen at high strength was insufficient to support aerobic microbial degradation (Kadlec and Knight, 1996) and this was reflected in the overall decreased removal efficiency from 93% to 53% from low to high strength respectively. Increased aeration to the GROW troughs from 1 hour to 24 hours daily resulted in improved treatment performance (Figure 4.1.17).

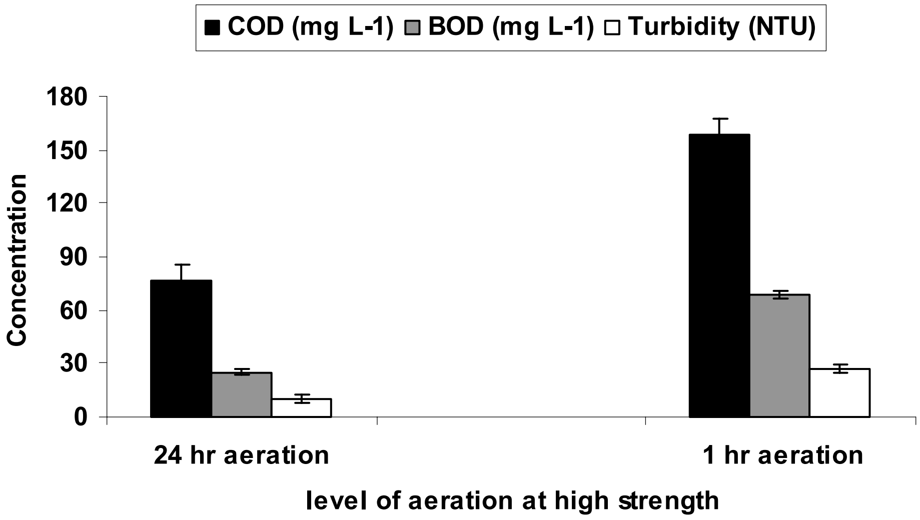


Figure 4.1.17: Level of pollutants in final GROW effluent under two aeration regimes at high strength

Removal efficiency increased from 53% to 86% for BOD_5, 69% to 82% for COD and 59% to 67% turbidity respectively when aeration was increased. Evaluation of the results under the two aeration regimes revealed that the removal efficiency for COD was higher than that for BOD_5 at 1 hour aeration whilst removal efficiency for COD was lower than BOD_5 at 24 hour aeration. Removal efficiencies for COD are usually lower than for BOD_5 for treatment wetlands (Vymzal, 2002) due to the presence of pollutants which are recalcitrant to biological degradation (Gray, 2004). Thus, the removal efficiency trend at 24 hour aeration is in agreement with observations reported in the literature. The higher removal efficiency for COD over BOD_5 at 1 hour aeration suggests decreased microbiological degradation. This is corroborated by the BOD: COD values for both aeration regimes. For instance, BOD: COD ratio at 1 hour and 24 hours aeration averaged 0.48 and 0.37 respectively. This indicates that the effluent at 24 hour aeration contained less biodegradable organic content than effluent at 1 hour aeration. Despite the improved performance of GROW under continuous aeration, residual effluent concentration of 25.4±2.2 of BOD_5 mg L^{-1} from an influent concentration of 117.8±12.3 and a BOD: COD ratio of 0.37 indicates that appreciable organic matter was still present in the final effluent. The value of 0.37 falls outside the range of 0.1 to 0.3 for final effluent (Metcalf and Eddy, 2003).

In addition to insufficient oxygen to support aerobic microbial degradation in the GROW troughs at high strength, another factor which hinders the GROW system's ability at high strength was the increased level of suspended solids due to dislodged biofilms reintroduced into the effluent waste stream. This was due to frequent excessive root growth and bulging sections of plants roots such as *Glyceria, Juncus species* when plants outgrow the toughs. These created channels and short-circuiting within the bed media and sometimes overflow of untreated water (on average once monthly) in some of the troughs. As a result, portions of the grey water did not filter through the media resulting in high amounts of settleable solids in the effluent. Consequently, the level of solids/particle sizes in the effluent stream progressively increased towards the end of the GROW process train rather than exhibiting a decrease (Figure 4.1.18).

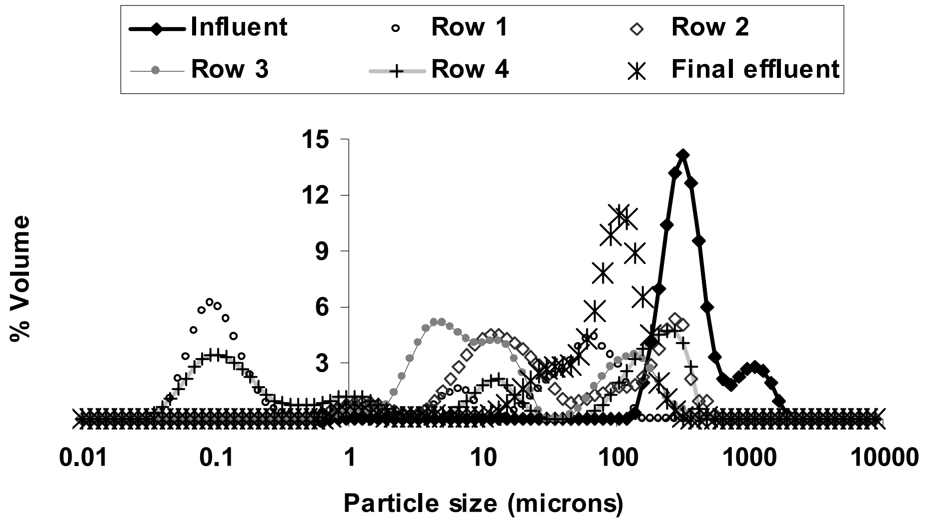


Figure 4.1.18: Distribution of particle size along the treatment path of GROW

The particle size distribution analysis shows an increased proportion of smaller particle size from Row 1 to Row 4. Thus, although larger size particles were removed from the influent grey water, smaller particles were subsequently released into the effluent waste stream. The increased level of larger solids in the final effluent could be due to release of such sizes into the effluent waste stream in Row 5.

Sampling of effluent waste stream in wells of Rows 1 to 5 of the GROW system in order to investigate removal and transformation of pollutants along the treatment path revealed that removal of organics at high greywater strength was limited to Row 1. For instance, 95%, 77% and 70% of the total BOD_5, COD and DOC removal occurred within the first row of GROW (Figure 4.1.19). Similar trends in the removal patterns of organics and solids along the treatment path were observed for indicator organisms (Figure 4.1.20).

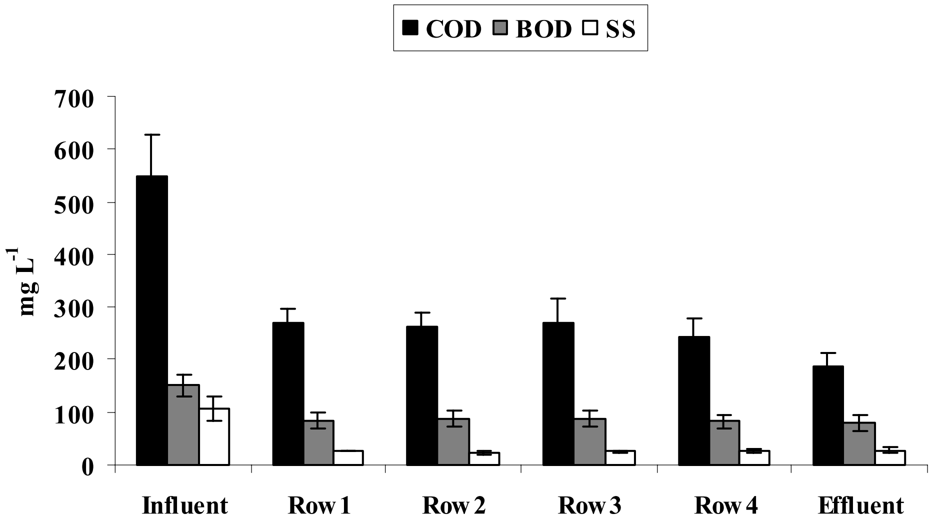


Figure 4.1.19: Concentration of BOD_5, COD and suspended solids along treatment path of GROW.

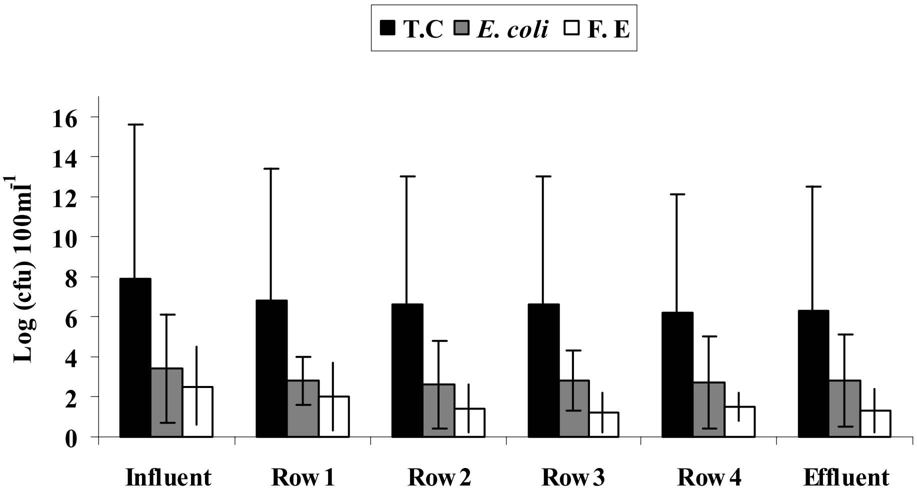


Figure 4.1.20: Total coliform (TC), *E. coli* and Faecal enterococci (F. E) along the treatment path of GROW at high strength

4.1.2.8 Maintenance, management and hydraulic conductivity

The most common maintenance undertaken in both reeds beds during the study period was weeding and flushing of inlet pipes which on average required 1-2 hours per week. Weeding was done by hand. With regards to the HFRB, a common problem encountered during the study period was maintaining the water level just above the bed surface. At high strength, descaling of rusty brown iron(III)hydroxide precipitates along the effluent outlet pipe was done fortnightly. The water level was kept about at bed surface by regularly adjusting the loop end that is attached to the top of the bed. Maintaining the GROW system was more demanding compared to the reed beds. Between the period July 2006 and August 2006, an average maintenance time of ~20 hours was spent on maintenance and management. The time required to maintain GROW can substantially be reduced if certain modifications to the design are made. For instance, using miniature plants instead of larger plants used in full scale wetlands would eliminate or at least significantly reduce extensive root and shoot growth which requires frequent trimming. This would minimise the release of particulates in treated waste stream by bulging and proliferated root growth. It would also minimise flooding in troughs.

The hydraulic conductivity of the unused sand/soil/compost media of the reed beds was measured as 7.53 m d^{-1}. After six months of operation, the hydraulic conductivity of the reed beds were 0.97 and 3.31 m d^{-1} at 5 -15cm below the reed bed surface for HFRB and VFRB respectively and 0.17 m d^{-1} at 30-40 cm down the VFRB. The lower hydraulic conductivity of the used media compared to the unused media could be due to accumulation of organic matter within the pores of the used media. However, it is clear why the hydraulic conductivity of the VFRB was higher than that of the HFRB. The hydraulic conductivity of the VFRB measured after 2 years of operation before the start of the unsteady state trials was 3.24 m d^{-1} at 5 -15cm below the reed bed surface. Consistency of similar hydraulic conductivity over a two year period indicates that the VFRB was not affected by surface clogging which is a common problem encountered by vertical flow systems. Possible reason for unchanged permeability of the VFRB media could be attributed to the regular weeding of schedule.

Discussion

4.2 Constructed wetlands for grey water treatment and reuse

4.2.1 Reclaimed water quality and compliance to world wide standard for reuse

The reuse of treated grey water can substantially reduce demand on potable water. However, adequate treatment is required to ensure that the reclaimed water is safe for public use. All three CWs produced water quality capable of meeting any reuse standard for organics (e.g. BOD_5, COD and DOC) at low strength, though the grey water strength in terms of organic concentration was quite low, at the low end of range reported in the literature (Table 1, Appendix 4) and at a low enough level to comply with less stringent reuse standard without treatment (Table 4.2.1). However, the wetlands did not produce an effluent that would meet consent limits for turbidity and indicator organisms (objectives 1& 2).

Table 4.2.2 lists the overall level of compliance of the three constructed wetlands assessed for grey water reuse during the study. All three CWs exhibited varying degrees of limitation with complying to reuse standards. Compliance was well below 100% level for key water parameters. The VFRB was the only technology to come close to compliance to stringent reuse standards. Both the horizontal configurations (HFRB and GROW) were unable to comply fully (i.e. 100%) with even the least stringent reuse standard (Table 4.2.2) (objective 4). To illustrate, the USEPA requires that the 10 mg L^{-1} BOD_5 standard is consistently met (Asano, 1998). This requirement was almost met by the VFRB (96%) which complied consistently with the less stringent Australian standard of 20 mg L^{-1} BOD_5 (Figure 4.1.3). HFRB and GROW were unable to fully comply with any of the standards. Also, compliance with the USEPA

Table 4.2.1: Comparison of treatment performance of this work with other technologies (objective 3)

Performance										Treatment Scheme	Wastewater type	Reference
BOD_5 (mg L^{-1})		COD (mg L^{-1})		SS (mg L^{-1})		Turbidity (NTU)		Total coliform (cfu 100 ml^{-1})				
Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent			
19.3	2.2	84.4	22.9	28.0	7.4	18.9	15.5	1.1×10^6	1.8×10^3	HFRB	Grey water	This study
19.3	1.1	84.4	14.6	28.0	2.2	18.9	10.6	1.1×10^6	3.6×10^1	VFRB	Grey water	This study
19.3	1.4	84.4	14.8	28.0	2.8	18.9	0.6	1.1×10^6	1.7×10^2	GROW	Grey water	This study
155.8	52.4	475	117.5	86.7	31.1	62.9	11.7	5.6×10^8	2.8×10^4	HFRB	Grey water	This study
155.8	5.1	475	29.1	86.7	9.3	62.9	2.2	5.6×10^8	2.8×10^4	VFRB	Grey water	This study
155.8	73.9	475	148.1	86.7	18.6	62.9	25.8	5.6×10^8	1.3×10^6	GROW	Grey water	This study
466	0.7	839	157	158	3	-	-	-	-	Recycled VFCW	Grey water	Gross *et al.*, 2007a
23	9	55	22	29	9	43.1	3.6	-	-	Electrocoagulation with bipolar Al electrodes	Grey water	Lin *et al.*, 2005
59	4	109	15	-	-	-	-	-	-	Membrane bioreactor	Grey water	Merz *et al.*, 2007
5	5	79	20	-	-	-	-	-	-	Pilot scale Sequencing Batch Reactor and Microfiltration	Grey water	Shin *et al.*, 1998
34	11	70	17	68	9	-	-	-	-	Constructed wetland	Domestic wastewater	Cirelli *et al.*, 2007
										Construed wetland + TiO_2	Grey water	Li *et al.*, 2003
96	11	168	57	490	108	57	66	5.2×10^6	2.4×10^5	Anaerobic roughing flter+combined process aerobic biofilter+active slow filter + standby slow filter	Grey water	Surendran and Wheatley, 1999

Table 4.2.2: Comparison of compliance levels for the three wetlands and an MBR and MCR monitored simultaneously during steady state trials to world wide standards (objectives 1- 3)

			Technologies				
Organization	**Parameter**	**Standard**	**HFRB**	**VFRB**	**GROW**	**MBR**	**MCR**
[1]USEPA	BOD	10	79	96	67	100	100
	Turbidity	2	0	33	75	100	93
[2]BSRIA	Faecal coliforms	nd*	18	61	33	100	100
[3]Japan	Turbidity	2	0	33	75	100	93
	E. coli	nd*	26	56	44	100	100
[4]Israel	BOD	10	79	96	67	100	54
	SS	10	57	92	78	100	100
	Faecal coliforms	1	62	93	70	100	100
[5]Queensland, Australia	BOD	20	79	100	79	100	92
	SS	30	87	100	99	100	100
	Total coliforms	100	15	77	58	100	100
[6]WHO	Faecal coliform	1000	99	100	99	100	100

*: Not detectable

[1]USEPA, [2]Mustow and Grey, 1997, [3]Tajima, 2005, [4]Gross et al., 2007, [5]Queensland, [6]Queensland . MBR and MCR data from Pidou *et al.*, 2007.

standard requires no detectable *E. coli* in 100 ml sample. In this study, *E. coli* was detected in the VFRB, HFRB and GROW 6%, 70% and 40% at low strength and 81%, 56% and 100% at high strength respectively. Based on the robustness plots and experimental data, the chances of the VFRB meeting 100% compliance throughout the monitoring period could have been improved if the maximum influent organic concentration was ~200 mg L^{-1}. For instance, the upper or critical influent organic concentration above which the 10 BOD$_5$ mg L^{-1} consent limit could no longer be met was ~200 mg L^{-1} for VFRB and 60-75 mg L^{-1} for GROW and HFRB respectively (Figures 4.1.3 & 4.1.5).

Comparison of wetlands performance with other contender contender technologies used for grey water reuse purposes showed that membrane technology (e.g. MBRs) and biological aeration filters (BAF) produce consistently lower residuals in organics, turbidity and indicator organisms compared to CWs (Tables 4.2.1). This observation was also evident in this study (Table 4.2.2) (objective 3). Pidou *et al*., (2007) and Melin *et al*., (2006) reported 100% and 95% compliance levels for MBR and BAF respectively for the BOD 10 mg.L^{-1} USEPA reuse standard. The superior turbidity removal demonstrated by MCR and MBR technologies can be explained by the presence of the physical barrier which retains solids/particulates larger than its pore size (e.g. 0.1μm). With this membrane pore size, most solids would be retained as majority of particulate sizes in the grey water fraction used in this study and domestic waste water exceed 0.1μm (this study, Metcalf and Eddy, 2003). In comparison, CW cannot produce similar effluent quality in terms of turbidity compared to MCR and MBR. This is because the media of CW usually consist of coarse gravel or sand with size (e.g. 0.06-4 mm, Langergraber *et al*., 2007; 4-8mm, Masi *et al*., 2007) far larger than membrane pore size (0.1 μm) in MBR, an order of magnitude three or more times pores size for CW compared to MBR. Consequently, small colloidal particles and even microorganisms which can easily be retained by the physical barrier in MCR and MBR processes cannot be retained in CW. Furthermore, 100% removal of indicator organisms in CW cannot be achieved due to natural inputs from the system (Kadlec and Knight, 1996).

In general, the performance of all three CWs was poor compared to the MBR tested simultaneously during the study period, and it must be noted that the influent organic loading of 38.0 g COD m^{-2} d^{-1} fed onto the constructed wetlands at high strength was outside the recommended load of 25 g COD m^{-2} d^{-1} (Platzer, 1999) generally required to produce good effluent quality for the given wetlands. For the MBR system however, the organic loading rate (OLR) applied to the pilot rig equate to 0.98 kg COD m^{-3} d^{-1} which falls within the range (0.26 – 3.2 kg COD m^{-3} d^{-1}) usually reported for MBR systems (Pidou, 2006).

4.2.2 Wetlands performance

4.2.2.1 Organic removal

All three CWs achieved good removal of organics (i.e. BOD_5, COD and DOC) from the influent grey water at low strength. Residual concentrations of 0-7.5 $mg.L^{-1}$ from the three wetlands are comparable to highly efficient grey water treatment achieved by biological and chemical systems reported in the literature. For example, an MBR system treating grey water of strength BOD_5 59 $mg.L^{-1}$ from sports and leisure club produced an effluent of BOD_5 4 $mg.L^{-1}$ (Merz *et al.*, 2007). A treatment system consisting of two reed beds in series planted with *Coix lacryma* followed by a pond and soakaway treating grey water produced an effluent BOD_5 of 1-10 (Dallas *et al.*, 2004). A Rotatory Biological Contactor (RBC) and fluidised-bed reactor treating grey water produced an effluent BOD_5 of less than 5 $mg.L^{-1}$ (Nolde, 1999). A reuse unit consisting of a filtration stage (0.3 mm mesh filter and $1m^2$ surface of filtration), sedimentation and disinfection with sodium hydroclorite gave an effluent COD of 78 $mg.L^{-1}$ (March *et al.*, 2004).

Effluent DOC at low strength for the three wetlands (3.3 - 4.5 $mg.L^{-1}$) fell within the lower end of the range reported in the literature for various technologies. To illustrate, Li *et al.*, (2003) reported 5 $mg.L^{-1}$ in grey water treated effluent using a vertical flow constructed wetland followed by TiO_2 photocatalytic oxidation at an irradiation time of 3 hours. DOC values for the three wetlands effluents were also comparable to limits suggested for DOC in discharge waters for ground water recharge (Jekel and Ernst, 1999). The removal efficiencies (89-97%) of the three CWs in terms of organics at low strength is at the upper end in the range ~70 to >90% achievable in CWs (e.g. Table 2.1 and 2.2).

In contrast to the performance at low strength, a dramatic decrease in performance of the HFRB and GROW in removing organics was evident when a sustained influent concentration of BOD_5 155± $mg.L^{-1}$ was fed to the wetlands at high strength. Residual concentrations for HFRB and GROW were BOD_5 51.0±7.5 $mg.L^{-1}$ and BOD_5 76.2±9.5 $mg.L^{-1}$ respectively. These equates to a removal efficiency of 66% for HFRB and 53% for GROW which are at the lower end of reported efficiencies for BOD removal in CW (e.g. Table 2.1 & 2.2). In contrast, the VFRB exhibited improved performance from 95% to 97% despite the increase in organic strength from 19.3±0.9 $mg.L^{-1}$ to 155.8±9.3 $mg.L^{-1}$. The VFRB was robust and residual concentration in the VFRB effluent at high strength averaged 4.3±1.3 $mg.L^{-1}$.

BOD reduction is related to microbial activity resulting in a decrease in dissolved oxygen in the waste water. BOD is reduced when dissolved oxygen is utilised for respiration and nitrate reduction (Kadlec, 1995). The low efficiency of the HFRB and more especially the GROW system was primarily attributed to insufficient oxygen to support microbial degradation of organics contained in the influent grey water. The HFRB is anaerobic in design and therefore improved performance could only have been achieved by either increasing the size of the bed or limiting the influent organic concentration within the range of 60-75 $mg.L^{-1}$. This range is the upper limit as demonstrated by the HFRB robustness curve before effluent no longer meet the 10 mg L^{-1} consent limit (Figures 4.1.2 & 4.1.5) and is in agreement with experimental data as seen in scatter plot (Figures 19a & b, Appendix 4). The results of residual BOD_5 and dissolved oxygen for the HFRB were however comparable to horizontal flow systems utilised for secondary treatment reported in the literature (e.g Cirelli *et al.*, 2007; Vymazal *et al.*, 1998). This indicates that the influent load of 12.5 g m^{-2} d^{-1} for BOD_5 and 38 g m^{-2} d^{-1} for COD for a surface area of 6 m^2 can be treated to meet secondary treatment limits but not a tertiary limit.

The GROW system showed increased efficiency from 69% to 82% in removing BOD_5 when aeration was increased from 1hour to 24 hours confirming that the performance of GROW in removing organics at high strength was at least partially limited to available oxygen. The decreased performance in BOD_5 and COD removal of the HFRB and GROW was reflected in the BOD: COD ratios of the effluents. The BOD: COD ratios at high strength were 0.45 and 0.50 for HFRB and GROW respectively. This represents about a six-fold increase in BOD: COD ratios for both technologies reflecting a dramatic decrease in effluent quality. In contrast, the BOD: COD ratio for the VFRB effluent remained low at high strength averaging 0.17 which is at the top end of the range 0.1-0-3 for final effluent.

As in BOD_5 and COD, there was significantly higher residual DOC in the effluents of HFRB and GROW compared to that from the VFRB at high strength. The notable difference between these systems at high strength was related to aerobic conditions and flow pattern (objective 6). The HFRB and GROW were both horizontal configurations and anoxic-anaerobic whilst the VFRB was vertical and aerobic. Compared to other studies, effective removal of DOC has been reported for soil aquifer treatment (SAT) of domestic wastewater and secondary effluent (Rauch and Drewes, 2004; Quanrud *et al.*, 2003; Quanrud *et al.*, 2001). SAT and VFRB have similar mode of operation with respect to flow and aerobic conditions. In this type of treatment, the combine active filtration and aerobic microbial degradation as the wastewater percolates through an unsaturated filter material believed to be a biologically active zone (Rauch and Drewes, 2004), may have contributed to significant removals of DOC. The higher residual DOC in the HFRB and GROW compared to the VFRB may be due to wetland derived DOC and reduced biological degradation in the horizontal flow systems. To illustrate, wetlands have been documented to release soluble organics to the effluent waste stream (Pinney *et al.*, 1999; Kadlec and Knight, 1996); and wetlands with shorter HRT experience a lower DOC leaching from plant material compared to wetlands with longer HRT (Pinney *et al.*, 1999). Wetland DOC or organic matter release however depends on wetland age and strength of influent waste water (Pinney *et al.*, 1999; Kadlec and Knight, 1996).

The overall change (i.e. increase or decrease) in the hydrophobic and hydrophilic fractions of the low strength grey water after passing through all three wetlands was minimal. This could be attributed to the low DOC level of the influent grey water and the relatively young age of the beds. A relatively new wetland releases lower DOC to the effluent waste stream compared to a mature wetland (Kadlec and Knight, 1996) and DOC in wetland effluent is dependent on influent level (Pinney *et al.*, 1999). At high strength, the effect was obvious, with a shift towards the more hydrophilic (most polar and lower MW) molecules in final effluents. Larger weight hydrophobic (HPO) fractions were preferentially removed from the influent grey water. This result is consistent with the findings that HPI fractions comprise the largest proportion of secondary effluents (Quanrud *et al.*, 2004; Ma *et al.*, 2001). The decreased removal efficiency of the HPI fraction at high strength could be attributed to a combination of reduced biodegradation, wetland derived HPI and transformation from other fractions contained in the influent grey water. However, conclusive investigations were not carried out to confirm the primary cause of increased HPI in wetland effluents at high strength. Overall, aerobic conditions within the bed matrix influenced the treatment performance of the wetlands in removing organics from the influent grey water (objective 6).

4.2.2.2 Solids and turbidity

Solids and turbidity removal efficiencies for the three wetlands at low and high strength follow the same general trend as organics. This is because particulate organic matter constitutes a significant proportion of solids in wastewater, and consequently, reduction in particulates correlates with BOD reduction (Gopal, 1999). The main mechanism for the removal of solids in CWs is sedimentation and filtration (Vymazal *et al.*, 1998). This was evident in the GROW system. For example, a minimum of 50% of total solids were removed from the influent grey water after passage through the first row of GROW which contains only bed media (gravel and Optiroc). The incorporation of baffles, wells and weirs into the GROW design provided additional barriers and may have created further opportunities for sedimentation of finer particles. Effluent residual solids were higher in HFRB than VFRB and it was concluded that the bed substrate influenced this. To illustrate, the bed substrate was iron rich (e.g. ~1% exchangeable Fe). In aerobic conditions, iron is in the form of Fe^{3+} and in anaerobic conditions Fe^{2+}. Fe^{2+} is soluble in water whilst Fe^{3+} is virtually insoluble in water forming sediments. It was evident during the monitoring period that soluble iron washed out with the effluent from the HFRB which on exposure to air oxidises to form colloidal iron (III) hydroxide as described in Section 4.1.8. This resulted in increased suspended solid content in the HFRB effluent.

Grow successfully removed turbidity at low strength, consistently meeting the 2 NTU standard despite variability in turbidity of influent (Figure 17 Appendix 4). The effluent from the GROW system was even less turbid (mean 0.6±0.1NTU) than that reported (2-5 NTU) for a combined reed bed and pond system (Dallas *et al.*, 2004). It was comparable to effluent turbidity of <1NTU from post-membrane treatment (Al-Jayyousi, 2003) and 0.3-0.4 NTU for MBR treatment (Jefferson *et al.*, 2001). The design of the GROW system may have contributed to turbidity removal performance by sedimentation and filtration. Performance of the VFRB in removing turbidity improved at high strength. Although the HFRB removed turbidity from the influent grey water, its ability to do so was inferior to the VFRB. In addition, turbidity in the HFRB effluent deteriorated as a result of the dissolved iron that was leached out of the HFRB being oxidised to the colloidal iron (III) phosphate.

4.2.2.3 Microbial quality of wetland effluents

The microbial quality of the wetland effluents was much more stable at low strength but showed considerable variability at high strength. The microbial quality of the wetland effluents at low strength is in the range consistent with those reported previously for grey water treatment (e.g. Dallas and Ho, 2005) and domestic wastewater (e.g. Hench *et al.*, 2003). Residual concentrations consistently complied with mandatory EU bathing water directive standards and WHO standards for reuse (<10^4 cfu 100 ml^{-1} total coliforms). However, these reductions were insufficient to meet stringent reuse standard such as USEPA. Therefore, a post treatment disinfection step would be required to meet a stringent consent standard.

Overall, the VFRB was superior to the other two wetlands in removing indicator organisms. This was attributed to the aerobic conditions in the VFRB compared to the anoxic-anaerobic condition in the HFRB. To illustrate, it has been shown that the level of gas saturation in an unsaturated media influences the extent to which indicator organisms are adsorbed, with a preference to adhere to gas-water or gas-solid interfaces (Powelson and Mills, 2001; Wan *et al.*, 1994). With more air in the VFRB compared to the HFRB, this suggests that the presence of air in the VFRB accounted for its higher removal efficiency. Removal rates for all three wetlands decreased at high strength when light grey water was supplemented with an organic- and surfactant-rich shampoo. Organics and surfactants reduce bacterial adsorption in porous media by competing for adsorption sites (Stevik *et al.*, 2004), thus reducing the available surfaces for adsorption (Powelson and Mills, 2001).

4.2.2.4 Nutrients, oxygen, pH, temperature

Influent concentrations of nitrogen (measured as NH_4-N and NO_3-N) and orthophosphate (PO_4-P) were consistently low, frequently below 5 mg. L^{-1} (Figures 21-23, Appendix 2). Nevertheless, denitrification occurred in the HFRB especially during the high strength trial period when the bed was anaerobic. Nitrification was evident in the VFRB throughout the monitoring period because sufficient oxygen was available.

One of the most important removal mechanisms of phosphorous in CWs is chemical precipitation of metal (Ca, Al and Fe) phosphates. In aerobic conditions, iron is in the form of Fe^{3+} and in anaerobic conditions Fe^{2+}. Orthophosphate forms a stable insoluble complex with Fe^{3+} but forms a soluble complex with Fe^{2+}. Since residual levels of dissolved iron were confirmed in the HFRB effluent and not in the VFRB effluent, this implies that leaching of soluble iron(II)phosphate accounted for the higher residual phosphate level in the HFRB effluent.

Dissolve oxygen (DO_2) generally rose after passage through the wetlands at low strength (Appendix 4). DO_2 in the wetland effluents at low strength (4.5±0.2 HFRB, 7.2±0.3 VFRB and 6.9±0.3) fall in the range of ~50% to full saturation. These values are indicative of good effluent quality as they fall within the range of >50% saturation requirement for reuse effluent in Germany (percentage saturation level for reuse is unavailable for the USEPA or Australian standards). At high strength, DO_2 of HFRB and GROW effluent decreased to mean values of 3.3±0.2 and 3.7±0.4 respectively reflecting deterioration in water quality.

Effluent pH did not change significantly ($p>0.05$) on passage through the wetlands. Changes in pH of wetland effluents were always within approximately half to one pH unit. Effluent pH of GROW was comparatively higher than those of HFRB and VFRB, likewise pH of HFRB was generally higher than those of VFRB. This was attributed to the predominant denitrification process which prevails in horizontal flow beds compared to nitrification in vertical flow beds. Denitrification produces alkalinity whilst nitrification decreases alkalinity. However, effluent pH of the three CWs were comparable with effluent reported for other studies (e.g. pH 6-8; Al-

Jayyousi, 2003 and pH 7.5, March *et al.*, 2004) and fall within the range of 6-9 accepted for reuse.

4.2.2.5 Temperature and seasonal trends

Influent temperature was generally higher than the wetland effluents throughout the monitoring period. There was a strong positive correlation between influent and wetland effluent temperatures throughout the monitoring period ($P<0.001$) but no strong correlation between influent or effluent temperature with other water quality parameters. Effluent temperature of the GROW system was as low as $0^{o}C$ and freezing problems were encountered for GROW during the winter periods in 2004, 2005 and 2006. Water in the wells of the GROW system was frequently frozen. No freezing problems were encountered for the HFRB or the VFRB.

Only data collated during the low strength trial were analysed for seasonal trends as this dataset covers a full year. Only temperature and DO_2 showed seasonal trends (Appendix 4). DO_2 was lowest in Autumn and highest in Winter. High DO_2 in winter could generally be attributed to windy conditions. Of the various water quality parameters, seasonal change was only notable for indicator organisms. Seasonal temperature change influenced removal of indicator organisms in the HFRB. Highest removal occurred when temperature increases. Sunlight is one of the mechanisms of coliform reductions in CWs and it is likely that inactivation by UV radiation reached it peak during summer. This is consistent with findings from studies of HFRBs (Karathanasis *et al.*, 2003; Quinoez-Diaz, 2001). No such seasonal change was evident for the VFRB or GROW. The lack of clear seasonal change of key water parameters is in line with findings that sub-surface CW show lack of temperature sensitivity (Bavor *et al.*, 1988).

4.2.2.6 Influence of design and operational conditions on wetlands performance

The constructed wetlands investigated in the current study were designed based hydraulic loading rates of 0.08, 0.07 and 0.08 $m.d^{-1}$ for the HFRB, GROW and the VFRB respectively. These are in line with standard design numbers for such applications (Cooper, 1999) which equate to around 2 $m^2.PE^{-1}$. However, one of the key characteristics of greywater is its variability from one site to another such that technologies must be able to handle a wide range of organic loading rates to be suitable (Pidou *et al.*, 2007). This is especially important as it is not common to pre sample greywater prior to system design as normally the collection system is installed at the same time as the technology. The current testing approach attempts to understand the implications of this for wetland systems by testing at both low and high strength.

At low strength, organic loading to all wetlands averaged 1.5 $g.m^{-2}.d^{-1}$ which equates to a tertiary treatment application in municipal sewage works. Reported loading rates for tertiary treatment HFRB suggests a range between 0.5 and 1 $m^2.PE^{-1}$ (Cooper and Green, 1995; Copper, 1999). This suggests the wetlands tested were below the critical design level and so contained a high level of process redundancy. In comparison, at high strength the loading rate was 12.5 $g.m^{-2}.d^{-1}$ which equates to a secondary treatment level for municipal sewage applications (Kadlec and Knight, 1996). The required design rates for municipal sewage treatment under these conditions for HFRB is 5 $m^2.PE^{-1}$ (Copper, 1999; Cooper and Green, 1995). Similarly, at high strength the design rate for a VFRB is 25 gCOD. m^2 d^{-1} (Paltzer, 1999) which is below the operating level of 38 gCOD. m^2 d^{-1}. As such the tested wetlands were above the limiting design rate at high strength and should be highly challenged.

Analysis of the data generated across the trial indicated that the HFRB and GROW deviated from a high treatment level beyond ~7 gBOD. m^2 d^{-1} whereas the VFRB performance was much better across the higher loading rates (Figure 4.2.1) (objective 5).

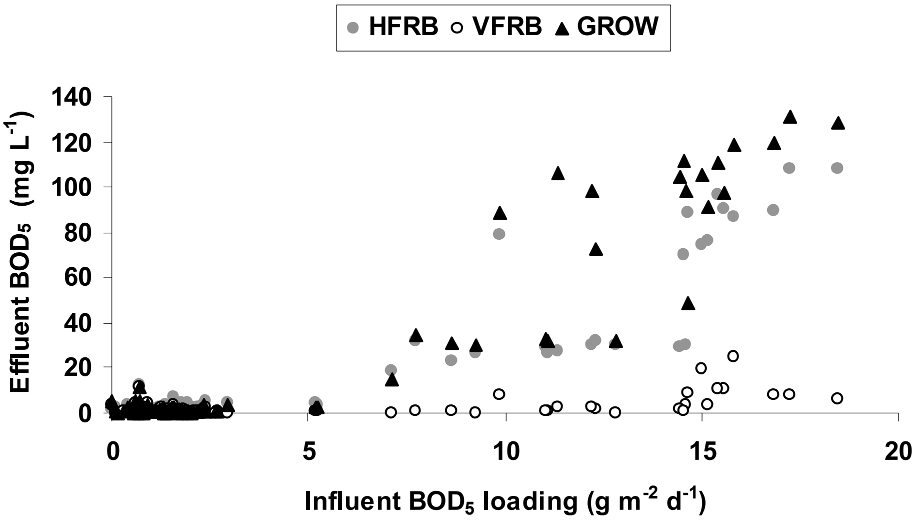


Figure 4.2.1 Effect of influent organic loading on wetlands residual BOD$_5$ concentration.

The data enables an estimate of the design loading rates of wetlands for greywater treatment as ~7 for HFRB and ~14 VRFB gBOD m^{-2} d^{-1}. The findings of the effect of organic loading on the treatment performance of the CWs are consistent with the literature. For example, Langergraber *et al.*, (2007) found that a VFRB receiving pre-treated wastewater plant effluent with an organic loading of 20 g COD m^{-2} d^{-1} met the Austrian effluent standard all year round whilst loadings of 27 g COD m^{-2} d^{-1} and 40 g

COD m^{-2} d^{-1} met effluent standard part of the time and not at all in winter respectively. Similar effects of organic loading on wetlands performance have been reported (Chazarenc *et al.*, 2007; Noorvee *et al.*, 2005).

At the hydraulic loading rate tested in the current trial which equates to an influent BOD of up to 200 $mg.L^{-1}$, results indicate that vertical flow systems are widely applicable for grey water treatment. More detailed analysis of the VFRB indicated that the high effluent BOD concentrations were linked to reduction in the dissolved oxygen concentration (Figure 4.2.2). This suggests that improved performance at high loading rates may be possible with enhanced oxygen transfer as has been shown for sewage applications (Weedon, 2003). Typical minimum oxygen transfer rates in VFRBs are reported to be 28 g O_2 m^{-2} d^{-1} (Cooper, 2005), although it is acknowledged that this varies considerably depending on design and especially hydraulic loading cycles (Platzer, 1999). In the current study at high rate, an estimated OTR of 12 g O_2

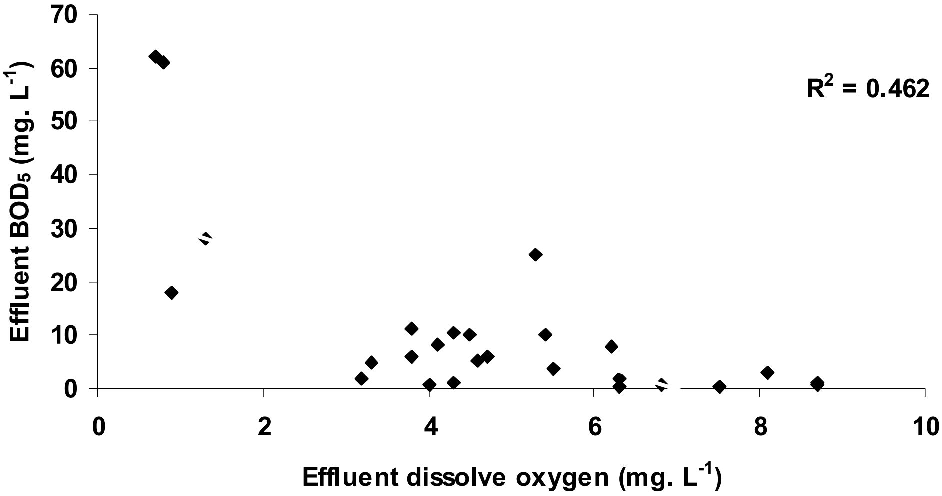


Figure 4.2.2: Relationship between VFRB effluent dissolve oxygen and BOD_5 during high strength period

m^{-2} d^{-1} suggested the bed was operating under an oxygen limited growth environment. This is manifested in a limiting hydraulic or organic loading rate so that the OTR potential of the system is met during the feed/drain cycle. In this study, OTR during the high strength trial of 12 O_2 m^{-2} d^{-1} for the VFRB implies that the bed was operating below this value. As a result, treatment efficiency decreased because the available oxygen was insufficient to support aerobic microbial degradation of organics in the influent grey water. For an operational wetland with fixed bed size and steady influent organic concentration, OTR could only be controlled by reducing the volumetric flow so that the oxygen demand of the total organic load entering the bed is met principally by the aeration potential of the bed via diffusion of air. It is for this reason that organic loading correlates strongly and positively with effluent residual organic concentration. In this study, an upper influent BOD_5 limit of ~200 mg L^{-1} at a flow rate of 320 L d^{-1} would have improved the OTR and increased the chance of consistent compliance with the 10 BOD_5 mg L^{-1} consent limit. This is evident in Figure 4.1.15 where during unsteady state trial, this consent limit was exceeded whenever influent BOD_5 concentration exceeded 200 mg L^{-1} even though flow was reduced from 480 to 320 L d^{-1}. In comparison with the literature, few studies have reported OTR. For instance, Weedon (2003) reported OTR of 28-35 $gO_2.m^{-2}.d^{-1}$ from a VRFB treating domestic wastewater from two neighbouring households.

4.2.2.7 Influence of design and planting regime on GROW's performance

Although high influent organic loading affected the performance of GROW, there appears to be process redundancy within the GROW system. This was exemplified by analysis of organic and solids removal along the pathway of GROW at high strength. Results showed that 95%, 77%, 70% and 94% of the total BOD_5, COD, DOC and SS removal occurred within the first row of the system. Similar results were obtained for all three indicator organisms (total coliform, *E. coli* and faecal indicator organisms) along the treatment path of GROW.

There is still ongoing debate of the importance of plants (macrophytes) for pollutant removal in constructed wetlands (Brix, 1997). In some studies, pollutant removal did not differ significantly between planted and unplanted beds (e.g. da Matta Maeques *et al*., 2001). Other studies have shown that plants play an important role in treatment (e.g. Al-Omari and Fayyad, 2003; de Sousa *et al*., 2003; Mars *et al*., 2003). The primary functions of plants in treatment wetlands are believed to be provision of surface area for microbial degradation, generation of oxygen from roots into the the rhizophere and maintaining hydraulic conductivity (Brix, 1997; Kadlec and Knight, 1996). However, oxygen release from roots is estimated to be low (5 g m^{-2} d^{-1}, Platzer, 1998) compared to the oxygen required (28-30 g m^{-2} d^{-1} Cooper, 2005; Platzer, 1998) for degradation of organic matter and nitrification. Tanner (2001) reported annual removal of 2-8% N and 1.9-5.3% P in treatment wetlands. In the GROW system, one hour per day aeration was provided via the porous pipe and together with a low organic load, results of mean dissolved oxygen from the GROW effluent at low strength and effluent DO_2 during winter months when the plants almost died would suggest that the contribution of the plants were minimal. At high strength, effluent DO_2 level during summer and winter months remained low which could possibly support the above the notion of minimal contribution of plants in providing DO_2.

The plants used in the GROW system were originally selected based on treatment capabilities and/or aesthetic properties (WWUK). *Iris, Juncus and Glyceria* species have been utilised in constructed wetlands for wastewater treatment (e.g. Kadlec and Knight 1996; van Oostrom, 1994). Planting density has become established for more commonly utilised species such as *Phragmites australis* (3-10 plants per m^2) (e.g. Cooper and Green, 1995), however there is little or no information in the literature on appropriate planting densities for the majority of species used in the GROW system.

All the plants used during the trial period proliferated on the feed water during summer, autumn and spring but as expected were reduced mainly to below ground biomass during winter (Appendix 4). Plants generally recovered well after the winter period to produce abundant growth during the second growing season. Shoot growth was intended to be restricted to above ground biomass. However, it became evident that shoots of *Juncus effuses* in Row 3 were proliferating beneath the membranes which resulted in the membrane becoming pushed upwards and shoots encroaching into other rows. Of more significance was the increase in shoot proliferation, bulging rhizomes and increased root densities which fill sections of troughs and causing overflows and short circuiting of water movement in the system. The disturbance generated suspended particulate material and dislodged biolilms formed on the gravel and Optiroc media and plant roots. The obvious effect of this was reflected in very poor effluent quality (e.g. high suspended solids and high residuals in organic, increased coliform counts). Thus, *Iris pseudomonas, Juncus effuses, Glyceria variegates and Caltha palustris* were not appropriate for a wetland trough system such as GROW. Although roots of *Mentha aquatica* were also quite extensive, spreading into wells of rows, there was no evidence that the tiny roots of *Mentha* had any negative effect to the hydraulic flow of water in Rows 9 and 10.

4.2.2.8 Rate constant

The parameters of first order models are referred to as rate constants but in fact depend upon operational and structural characteristics of the wetland (Kadlec 2000; Kadlec, 1997). Design variables such as hydraulic loading and influent loading have been shown to influence the one parameter rate constant- K_{BOD}. Average K_{BOD} for the three wetlands were 1.04, 1.38 and 1.26 (m d^{-1}) for HFRB, VFRB and GROW respectively for the low strength period. These values are much higher than that reported for grey water treatment using a novel recycled vertical flow CW (0.16 m d^{-1}, Gross *et al*., 2007a) but fall within the range of those reported for domestic waste water in horizontal flow treatment wetlands and batch systems (Stein *et al* ., 2007; Rousseau *et al*., 2004; Kadlec, 2000). K_{BOD} at high strength changed with a one-half decrease for both HFRB and GROW whilst that of VFRB doubles. As all other conditions during low and high strength period were unchanged, changes in K_{BOD} can be explained as a result of the increase in organic pollutant concentration. K_{BOD} has been thought to be influenced by the biodegradability of the feed water and the type of media used in the bed (Kadlec, 2000).

4.2.2.9 The influence of clogging and age on the performance of VFRB system

VFRB systems are succeptible to surface clogging which can lead to overflow (Cooper, 2005). This is because influent wastewater is fed into the bed by repeated application on the bed surface. If a wastewater contains high suspended solid concentration with low degradability, then the rate of accumulation will be greater than the rate of degradation. A nett accumulation of solids on the bed surface can lead to poor oxygen transfer from the atmosphere in to the bed matrix causing insufficient oxygen to support microbial degradation. In this study, there was no incident of clogging and surface flooding. This was possibly due to the young age of the bed (i.e. three years of operation after commissioning) and frequent weeding (usually fortnightly). Old VFRB with many years of operation without proper maintenance do encounter problems of surface clogging and flooding. Weeding improves the performance of treatment wetlands (Cooper, 2005; Cooper *et al.*, 2005).

There is a paucity of data relating to the effect of age on the performance of VFRB. However, it is expected that a properly maintained bed will continue to produce good performance within the normal design conditions of hydraulic and influent pollutant loading. A mature bed normally contribute more dissolve organic matter to the effluent waste stream than a relatively young bed due to internal processing within the bed matrix (Pinney *et al.*, 2000; Kadlec and Knight, 1996), but this effect is secondary to the hydraulic and influent loading which primarily influences wetland effluent quality (IWA, 2000; Kadlec and Knight, 1996). Cognisant of this, the results obtained for the VFRB in this study would be expected to be similar if this study had been conducted using a much older (e.g a ten year old VFRB), properly maintained (e.g. weeding, cleaning of effluent pipes, sufficient time between dosing to allow aeration of bed before the next batch of influent dose) and managed bed (i.e. operated within its design limit).

4.2.2.10 Implication of findings of study for reuse

The results of the trials indicate that wetlands are appropriate technologies for greywater treatment. However, typical design approaches are insufficient as they do not reflect the variability of greywater and indicate that hydraulic design could result in underperforming systems. The key result was that even under conditions of excessive loading, the VFRB treated the greywater to a good standard although failed to comply with the USEPA (regarded as one of the most stringent reuse standard) 20% of the time. Irrespective of this, the VFRB was shown to be robust to the needs of greywater treatment and so can be considered a suitable option for consideration. At the current time, the leading technology for greywater recycling is an MBR (Pidou *et al*., 2007) although such technologies are known to suffer from poor public perception in relation to sustainability and environmental concerns. Consequently, the VRFB offer a suitable alternative and offers a different range of perceptive benefits.

In comparison, constructed wetlands are less expensive compared to MBR with respect to investment, energy and operational cost. The major cost in a CW are land acquisition and construction which is estimated to be in the range of 25-250 US\$ ha^{-1} depending on size (Kadlec and Knight, 1996). Costs relating to energy and maintenance are minimal since energy is limited to pumping and some wetlands can even function gravimetrically thus eliminating the need for pumps. Maintenance costs merely involve cleaning of distribution pipes, weed control, plant harvesting, sampling and site inspection. To illustrate, Gross *et al*., (2007) reported expenditure of US\$ 600 constructing a recycled vertical flow constructed wetland for grey water treatment for a household and an annual cost of US\$ 100 for maintenance. In the case of MBR, investment and operational cost are both expensive. Though investment cost can be site specific, specific membrane cost for an MBR is estimated about 30 US\$ m^{-2} (Aquarec reports, 2006). Operational costs in MBR include energy, membrane replacement, personnel, and maintenance. Dallas and Ho (2004) reported total cost (excluding supervision and design) of a reed bed for grey water treatment in Costa Rica to be US\$ 250 per household. In comparison, Brewer *et al.*, 2000 reported an estimated cost of £1,000 (~US\$ 500) for grey water treatment for toilet flushing in Liverpool, UK for three adults using MBR.

In light of the above, the implementation of CW technology would find wider use in villages, rural and small communities and developing countries where land is cheap and available. In contrast, because of its small footprint, niche markets for MBRs would include urban areas where space is limited and saving potential is high.

Chapter 5 ***Reactive barriers for the removal of Phosphorous (P) and metals (Cu and Ni) from sewage effluent***

5.1.1Physico-chemical characteristics of adsorbents

The physico-chemical characteristics of the various adsorbents used to investigate P and metal (Cu and Ni) removal ability from sewage effluent is presented (Table 5.1.1). The Cation exchange capacity (CEC) of the different adsorbents varied widely from 1 to 83 meq $100g^{-1}$ sample. Ochre, Bayoxide, Bauxol and Red mud which are predominantly Fe rich exhibited significantly higher ($p<0.05$) CEC (e.g. 60-80 times greater) than the others which are calcium rich (Table 5.1.1). The mineral content of the adsorbents as revealed by EDX and XRD showed that the limestone and shell adsorbents are primarily composed of calcite, Ochre and Bayoxide composed of geothite, Red mud and Bauxol^{TM} composed of haematite whilst Filtralite-P is composed of silicate minerals (Appendix 5). EDX analysis revealed a w/w% increase in P from unused to used adsorbents as follows, 0 to 0.3% for Filtralite-P, 0 to 1% for Bayoxide and 0.2 to 2.6% for Steel slag. The larger increase for Steel slag compared to Bayoxide and Filtralite-P could be due to the fact that the Steel slag sample was obtained from completed bed volume experiment whilst the other two were samples previously used for batch isotherm experiment. The adsorbents used in the bed volume experiment were in contact with a larger volume of sewage effluent compared to 100ml sewage effluent for isotherm experiment.

Table 5.1.1: Physico-chemical properties of adsorbents

Adsorbent	C.E.C (meq.100g^{-1})	Porosity (%)	Bulk density (g cm^{-3})	Main chemical composition
Ochre	83.00	65-80	0.8	**FeO(OH)***
Bayoxide	76.85	80	0.4	**FeO(OH)**
Bauxol	82.12	N.D	N.D	N.D
Bauxol^{TM}	68.18	N.D	N.D	$\mathbf{Fe_2O_3}$,$CaSiO_3$ Ca_2SiO_4
Red mud	64.90	N.D	N.D	$\mathbf{Fe_2O_3}$,$CaSiO_3$ Ca_2SiO_4
Steel slag	35.35	55	1.53	Ca_2SiO_4, $AlFeO_3$, $CaFeO_3$, $FeCO_3$,
Filtralite-P	72.05	68	0.3	$\mathbf{SiO_2}$, Al_2SiO_5 $FeFe_2O_4$
Zeolite	11.43	55	0.9	$KCa_4Si_8O_{20}(OH).8H_2O$, $Ca(Si_7Al_2)O_{18}.6\ H_2O$
Shell	<1	82	0.4	$CaCO_3$
Carboniferous limestone	~2	52	1.3	$CaMg(CO_3)_2$, $CaCO_3$
Dolomitic limestone	~1	52	1.2	$CaMg(CO_3)_2$
Oolitic limestone	1.54	62	0.9	$CaCO_3$
Dowlow limestone	2.66	55	1.1	$CaCO_3$
Concrete	~1	60	1.0	SiO_2, $CaCO_3$

*From Heal *et al.*, 2005

ND = not determined

N.B. Chemical composition in bold denotes main constituent of mineral from XRD.

Porosity of the adsorbents was comparable but bulk density varied considerably (Table 5.1.1). The specific surface area for most of the adsorbents could not be measured because they were unable to fit into the machine. The specific area of Red mud and Ochre were 11.61±0.02 and 295.28±1.77 m^2 g^{-1} respectively. Particle size of the various adsorbents differed markedly, ranging from <1mm for Red mud and Bauxol^{TM} to ~10mm for portions of Ochre and steel slag.

5.1.2 Phosphorous capacity

Result obtained for P capacity calculated from the Freundlich isotherm of the various adsorbent ranged from 0.01 to 26.5 mg g^{-1}. The results of P removal from sewage effluent by the various adsorbent differed significantly ($p<0.05$) as reflected in the P capacity plot presented (Figure 5.1.1). As P capacities and CEC varied between adsorbents, correlation analyses were carried out to investigate the effect of CEC and type of metal present on adsorbent P removal ability. Results showed that P capacity of the various adsorbents correlated strongly ($P=0.0002$, $R^2 = 0.74$) with the percentage of the dominant element (e.g. Fe, Ca, Al, Si) as well as with CEC of the adsorbent ($P=0.00003$, $R^2 = 0.87$), confirming that P capacity of adsorbent was influenced by type of metal and CEC of adsorbent. Following preliminary screening of the various adsorbents, the following adsorbents (Ochre, Bayoxide, Bauxol, Red mud, Bayoxide, Steel slag and Filtralite-P) were the focus of further investigation for P removal ability. Results of batch isotherm studies for the three adsorption models

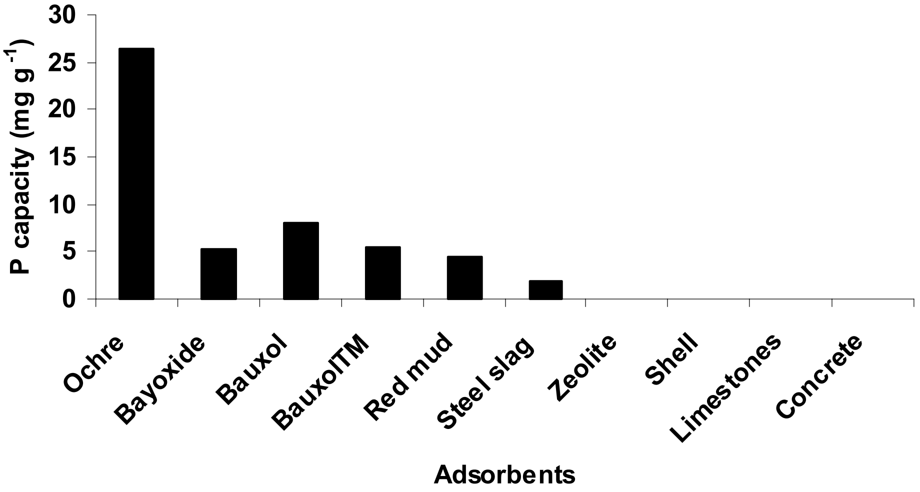


Figure 5.1.1: P capacities of different adsorbents according to Freundlich isotherm at 298K. Value of 0.01 mg g^{-1} represent average measurement for all the limestone adsorbents

((Freundlich, Langmuir and Dubinin-Radushkevich (DR)) used to investigate adsorption characteristics of the various adsorbents is presented (Figure 5.1.2a, b & c).

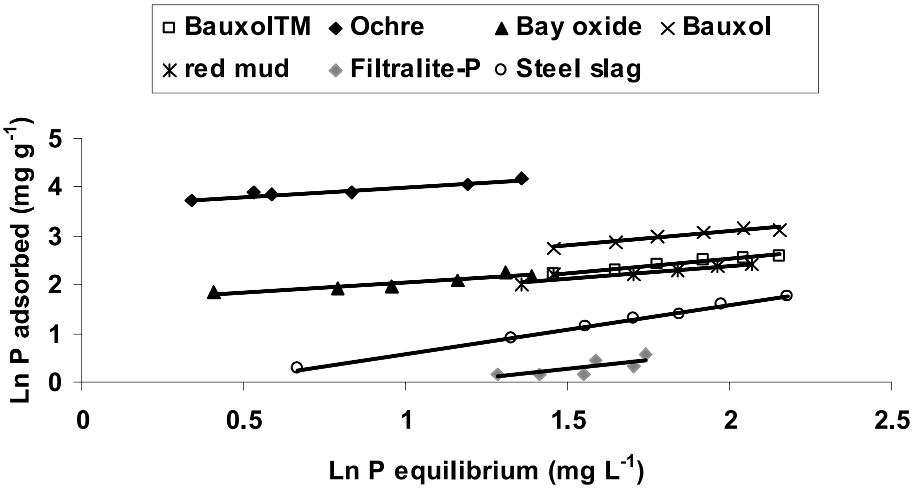


Figure 5.1.2a: Equilibrium Freundlich plot of mean P (n=3) adsorption data for seven adsorbents.

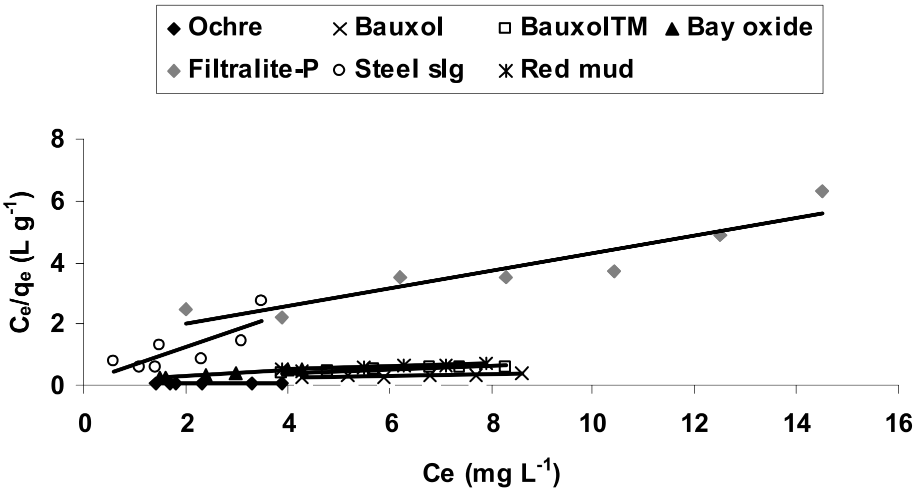


Figure 5.1.2b: Equilibrium Langmuir plot of mean P (n=3) adsorption data for seven adsorbents.

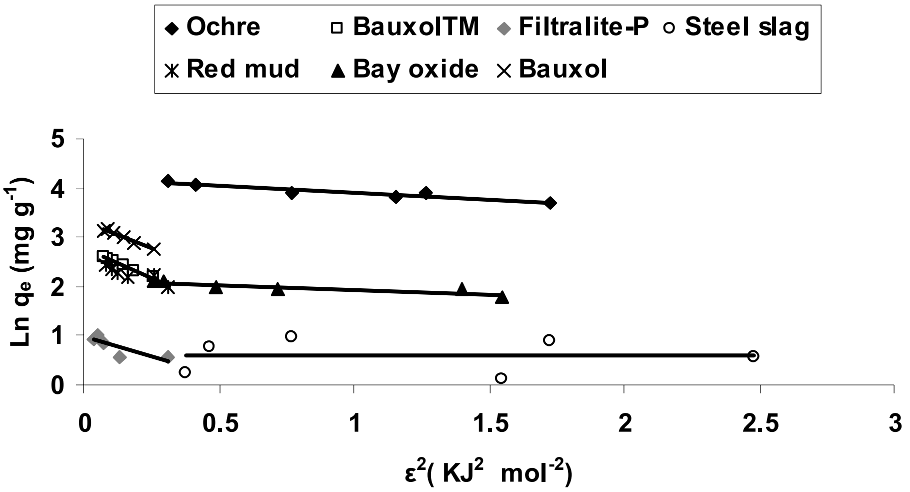


Figure 5.1.2c: Equilibrium Dubinin-Radushkevich plot of mean P (n=3) adsorption data for seven adsorbents.

The slopes and intercepts of plots were used to calculate model parameters. Results of model parameters from the three adsorption models are summarised in Tabe 5.1.2. Values of P capacities of the adsorbents calculated by the three models vary in magnitude but generally consistent in trend (Table 5.1.2). In all three models Ochre exhibited the highest P capacities confirming it to be the best adsorbent amongst those tested for P removal ability.

Table 5.1.2: Summary of model parameters for P removal from sewage effluent by selected adsorbents.

	Freundlich		Langmuir			DR	
Adsorbent	K_F (mg g^{-1})	1/n	Q_o (mg g^{-1})	K_L (L g^{-1})	R_L	q_o (mg g^{-1})	-E (KJ mol^{-1})
Ochre	26.5	0.39	73.6	0.89	0.12	61.1	1.2
Bauxol	8.1	0.64	71.8	0.11	0.52	33.9	0.6
Bauxol^{TM}	5.5	0.45	22.4	0.23	0.34	14.9	0.5
Red mud	4.5	0.41	14.4	0.61	0.16	11.0	0.7
Bay oxide	5.2	0.33	9.6	2.31	0.05	8.2	3.0
Steel slag	1.8	1.17	1.8	6.0	0.03	2.2	1.8
Filtralite-P	2.0	0.99	2.9	0.2	0.33	2.2	1.4

Of the three models, the Freundlich equation seems to provide the best fit to the experimental data. For instance, the P capacity for the Freundlich model averaged 26.5 mg g^{-1}. P capacity from the kinetic experiment averaged 33.4 mg g^{-1}. This observation is in agreement with previous independent reports that the Freundlich adsorption model explains P adsorption better compared to the Langmuir model (e.g. Sanyal *et al.*, 1993; Ratkowsky, 1986). This may be due to the fact that Freundlich model encompasses heterogeneity in adsorption materials surface and accounts for decreased affinity of adsorption with increasing saturation. In comparison, Langmuir model assume constant binding energy during the adsorption process. Based on the fact that most of the adsorbent investigated in this study are heterogeneous in chemical composition and external surface morphology, the Freundlich model seems closer to reality than the Langmuir. In comparison, Arias *et al.*, (2001) found no correlation between P capacities obtained for different sands with actual removal of P from column experiments. Barrow (1978) reported that the Langmuir model seldom applies to complex reactions which involve more than one steps in the adsorption process.

The Freundlich constant $1/n$ is related to the adsorption intensity. The value of $1/n$ for all the adsorbents except Steel slag for Freundlich isotherm are less than unity which is indicative of favourable adsorption. For Ochre, Bayoxide, Bauxol and Red mud, n lies between 2 and 8 indicative. Values within this range indicate that there is a high chance of achieving complete adsorption in the adsorption process (Mckay *et al.*, 1980). The dimensionless separation constant (R_L) of the various adsorbents which describes the efficiency of the adsorption process ranged from 0.03 to 0.52. Values of $R_L < 1$ indicate favourable adsorption process. These results agree with the findings of the Freundlich model. The free energy of the adsorption process (*E*) for the various adsorbents is negative indicative of a spontaneous adsorption process.

5.1.3 Bed volume trials

Bed volume trials were also carried out to (i) confirm P removal ability obtained from initial isotherm studies and (ii) provide insight as to how long the tested media can be used before exceeding the discharge limit of 0.5 mg L^{-1}. Results of average P capacity of the different adsorbents calculated using equations 9, 10 and 12 for bed volume trials are as summarised in Table 5.1.3. Only P capacity for Steel slag and Filtralite-P represents a possible maximum limit as they were conducted to completion and hence were saturated before the end of the study. The high P capacity of Ochre (evident from isotherm and kinetic results) and the relatively low inlet P concentration of 4-7 mg L^{-1} is believed to have contributed to the inability of Ochre to reach saturation within the time of saturation for Steel slag and Filtralite-P. However, bed volume trial of Ochre was conducted until effluent target (0.5 mg P L^{-1}) was exceeded (Figure 5.1.3). Although bed volume trial shows that Filtralite-P, Steel slag and Ochre at 1 hour HRT were unable to meet the 0.5 mg P L^{-1} target, they were capable of removing P from the sewage effluent. Thus, they may not be appropriate for tertiary treatment for this contact time but could be appropriate for secondary treatment.

Table 5.1.3 Comparison of P capacity from Bed volume trials for various adsorbents

Adsorbent	Capacity (mg Kg^{-1})	HRT(hr)	Bed volume
Ochre	4.1×10^3	1	115
Ochre	4.2×10^3	5	700
Steel slag	1.5×10^3	1	1800
Steel slag	3.3×10^3	24	115
Filtralite-P	1.2×10^3	1	250

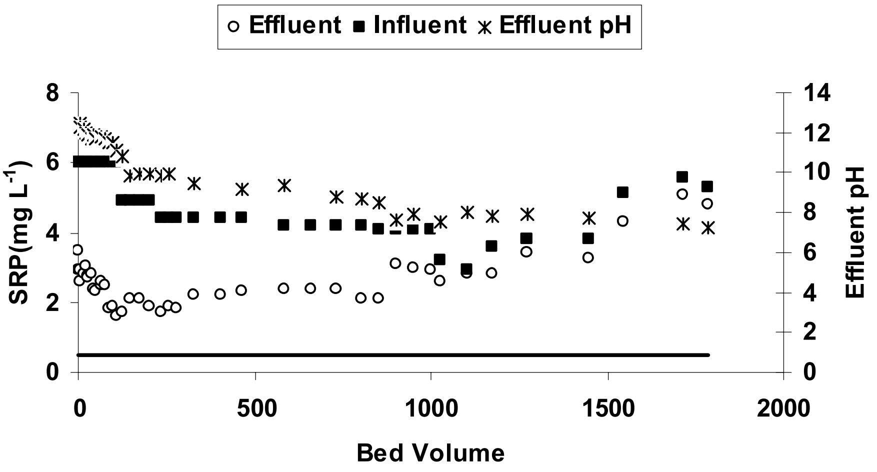


Figure 5.1.3a: Removal of SRP from sewage effluent by fixed bed pilot trial using 10mm Steel slag at 1 hour HRT

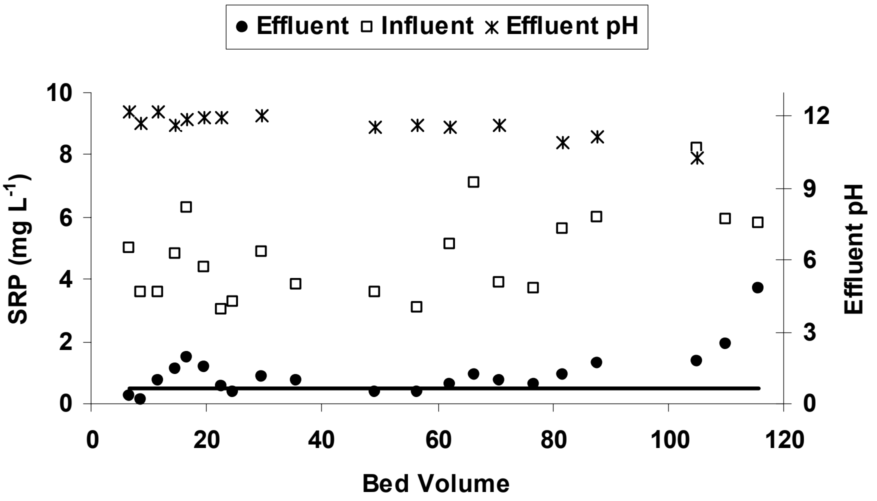


Figure 5.1.3b: Removal of SRP from sewage effluent by fixed bed pilot trial using 10mm Steel slag at 24 hours HRT.

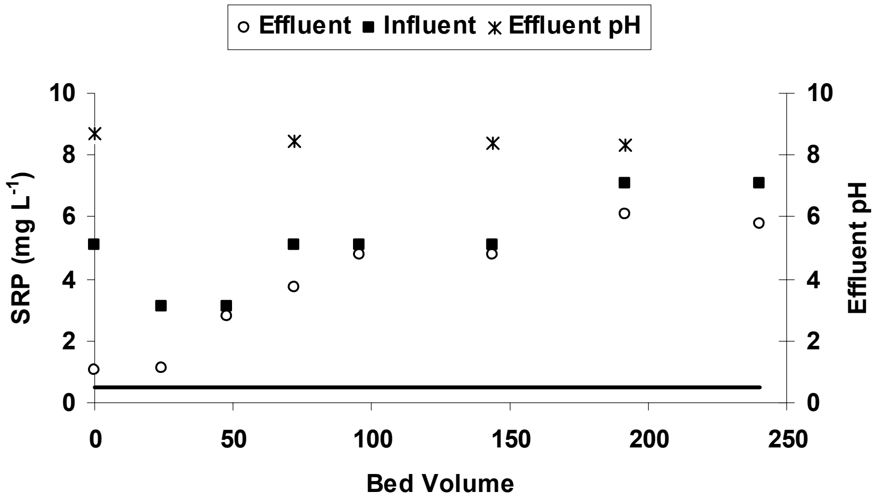


Figure 5.1.3c: Removal of SRP from sewage effluent by fixed bed pilot trial using Filtralite-P at 1hour HRT.

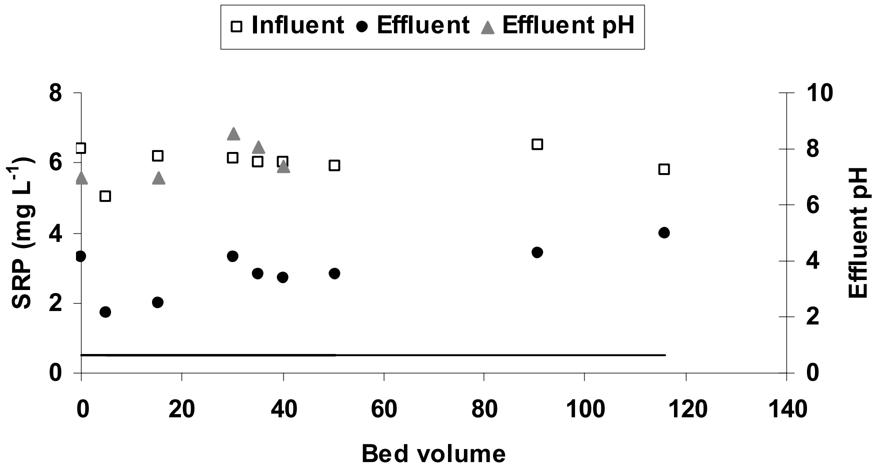


Figure 5.1.3d: Removal of SRP from sewage effluent by fixed bed pilot trial using Ochre at 1 hour HRT.

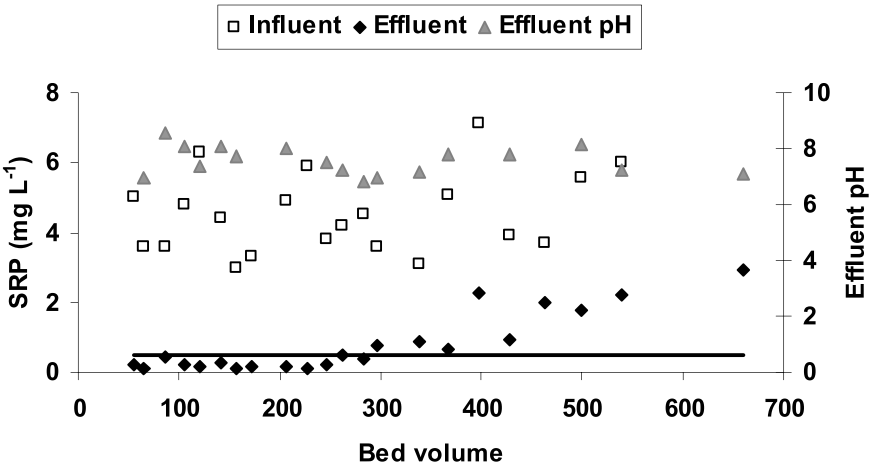


Figure 5.1.3e: Removal of SRP from sewage effluent by fixed bed pilot trial using Ochre at 5 hour HRT.

Despite this, Ochre gave a P capacity higher than Steel slag and Filtralite-P indicative of its superior ability. Also, effluent from Ochre bed volume trial was consistently $\leq$0.5 mg L^{-1} SRP up to a volume throughput of ~250BV compared to Filtralite-P and Steel slag. Filtralite-P was unable to meet the 0.5 mg L^{-1} SRP target whilst this target was met by Steel slag at optimal contact time only up to ~60 bed volume throughput (Figure 5.1.4.).

The shapes of the breakthrough curves of Ochre at 5 hours HRT and Steel slag at 1 hour HRT show distinct pattern. (Figure 5.1.4). In the Steel slag breakthrough curve,

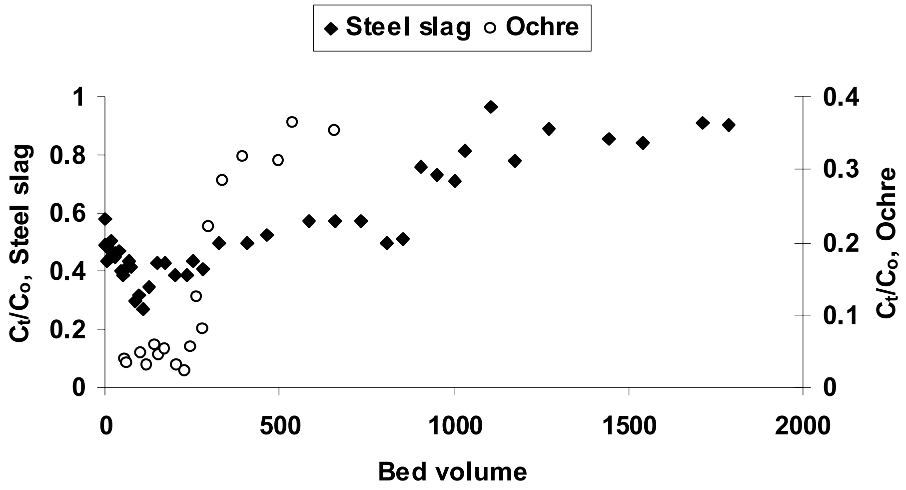


Figure 5.1.4: Breakthrough curves for Ochre at 5 hours HRT and Steel slag at 1 hour HRT

there appears to be no clear mass transfer zone. The curve rises continuously with no break until it reaches the saturation point. In contrast, the curve for Ochre exhibited a distinct mass transfer zone between ~250 to ~500 BV before levelling off at ~ C_t/C_o of 0.35. However, as saturation occurs at $C_t/C_o = 1$, it is possible that Ochre might exhibit another similar shape breakthrough curve between C_t/C_o of 0.5 to 1. Similar shaped breakthrough curve to Steel slag was obtained for the adsorption of fluoride on activated alumina (Ghorai and Pant, 2004). The contrasting shape of the breakthrough curve of Ochre compared to Steel slag may reflect differences in mechanism of adsorption. Surface precipitation, mass transfer and diffusion are well established pathways for P adsorption on adsorbents depending on the type of adsorbent and metal (e.g. Ca, Al, Fe) present. The Steel slag used in this study is predominantly calcium rich although smaller amount of iron (II) carbonate is present (Table 2, appendix 5). Ochre however, is composed almost entirely of geotite (FeOOH). However, the shape of a breakthrough is believed to depend on inlet flow rate, concentration, bed capacity (Ghorai and Pant, 2004).

5.1.4 Kinetics and thermodynamics of the P adsorption process

Graphical plot for the removal of P from sewage effluent over time showed that P removal was characterised by high initial adsorption rate for most of the adsorbents notably for Bay oxide, Bauxol, Bauxol^{TM} and Ochre (Figure 5.1.5).

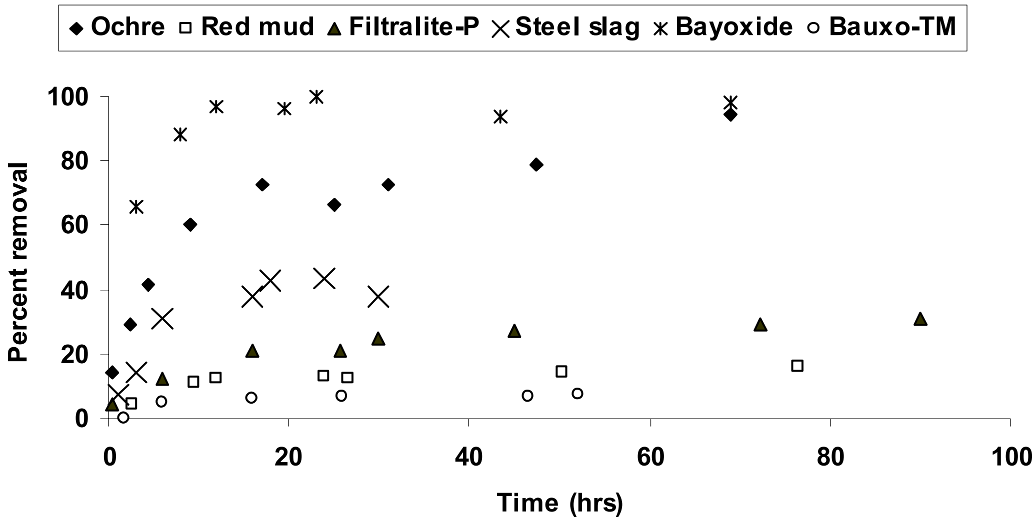


Figure 5.1.5: Adsorption of phosphate from 5 mg. L^{-1} final sewage effluent as a function of time at 298K under dynamic condition.

However, the rate of adsorption varied considerably from 0.0003 to 0.0964 g mg $^{-1}$ hr (Figure 5.1.6; Table 5.1.4). This variation was attributed to varying surface area/particle size of the adsorbent and adsorbent dose (Table 5.1.4). To illustrate, particle size of 10mm for Steel slag resulted in an adsorbent dose of 30 g L^{-1} whilst a particle size of <1mm for Bauxol^{TM} and Red mud resulted in an adsorbent dose of 1-2 g L^{-1}.

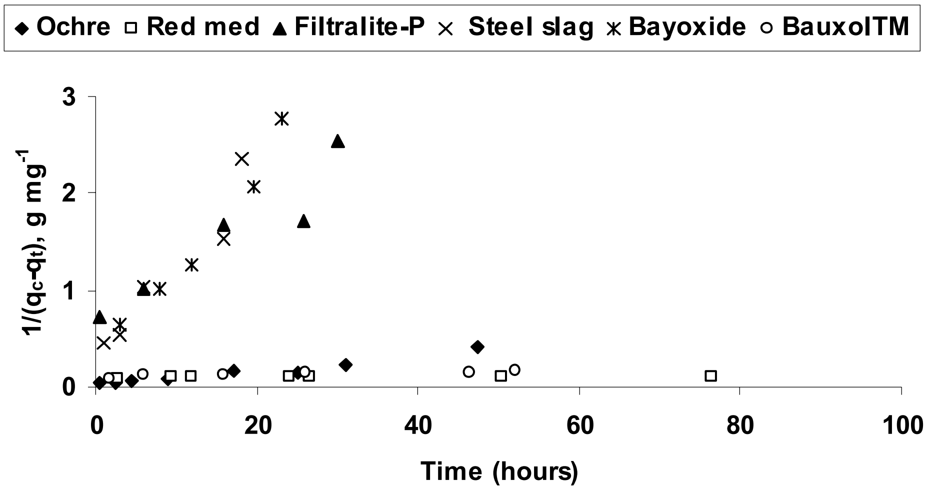


Figure 5.1.6: Pseudo-second order rate plot for the removal of phosphate from 5 mg. L^{-1} final sewage effluent as a function of time at 298K under dynamic condition.

Table 5.1.4: Comparison of pseudo second order rate constant for the removal of P from sewage effluent by different adsorbents

Adsorbent	Adsorbent dose (g L^{-1})	Rate constant (g mg $^{-1}$. hr)	R^2
Red mud	1	0.0003	0.65
Filtralite-P	10	0.0536	0.90
Bauxol^{TM}	2	0.0012	0.64
Steel slag	30	0.0964	0.91
Bay oxide	20	0.0104	0.96
Ochre	1	0.0076	0.95

Kinetic data for P adsorption onto the various adsorbents were fitted to pseudo-first order Lagergren and pseudo-second order to investigate the mechanism of adsorption. The Lagergren first order (calculations not shown) was ruled out because its regression was not significant ($r^2 \leq 0.14$). Hence, P removal by the adsorbents did not follow the Lagergren first order kinetics. The pseudo-second order fitted the experimental data well (Figure 5.1.7, $R^2 \geq 0.95$).

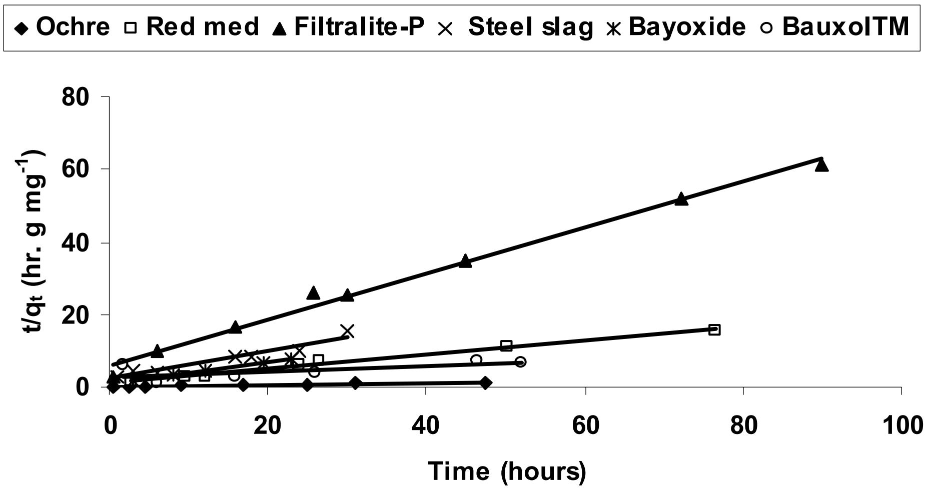


Figure 5.1.7a: Pseudo second order plot for the adsorption of phosphate from sewage effluent onto different adsorbents at 298K under dynamic conditions.

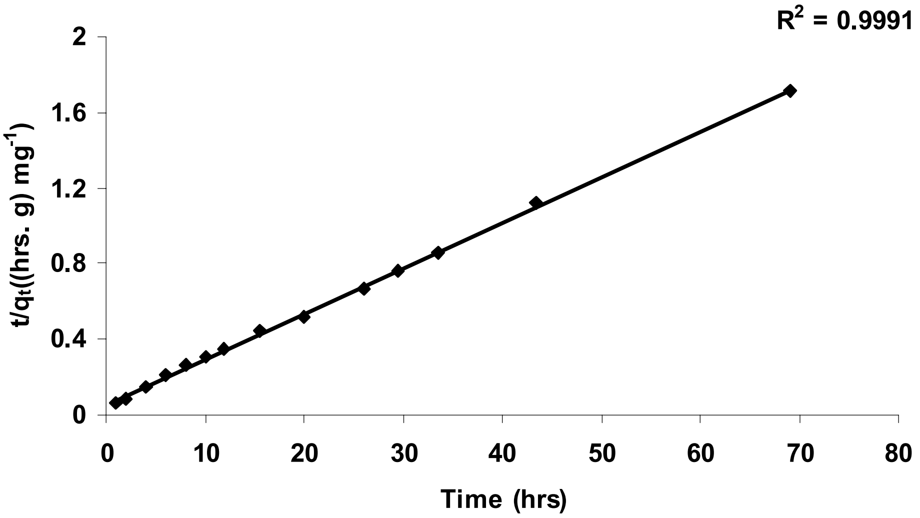


Figure 5.1.7b: Pseudo second order plot for the adsorption of phosphate from sewage effluent unto Ochre at 298K under dynamic conditions.

The calculated equilibrium concentration (q_e) from the pseudo second order model (41.5 mg. g^{-1}) for Ochre was very close to the mean experimental equilibrium value (37.8±1.8 mg. g^{-1}), confirming that adsorption occurred by a Pseudo second-order mechanism. Calculated rate constant from the model plot was 93.2 g. mg. hr $^{-1}$.

The intra-particle model which also is used to further investigate pseudo-second order adsorption kinetics gave a clear understanding of the stages involved during the adsorption of P unto Ochre (Figure 5.1.8b). Intra-particle diffusion plots indicate

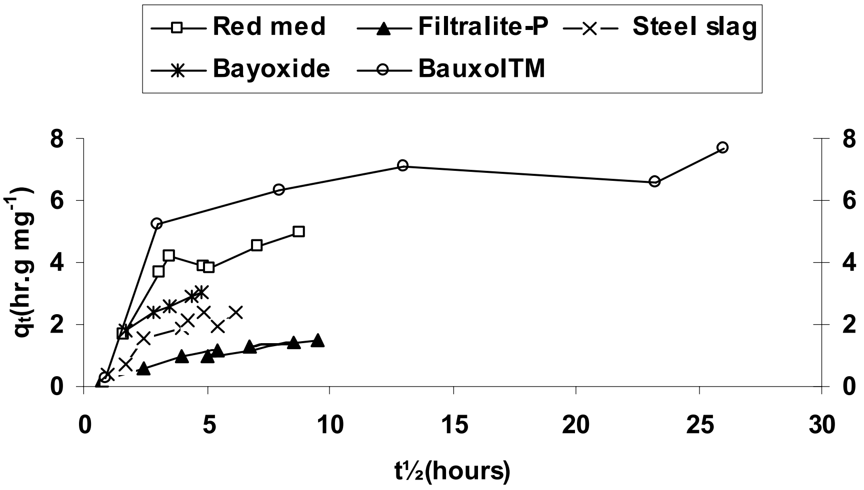


Figure 5.1.8a: Plot of intra-particle diffusion model for adsorption of P onto Ochre at 298K under dynamic conditions

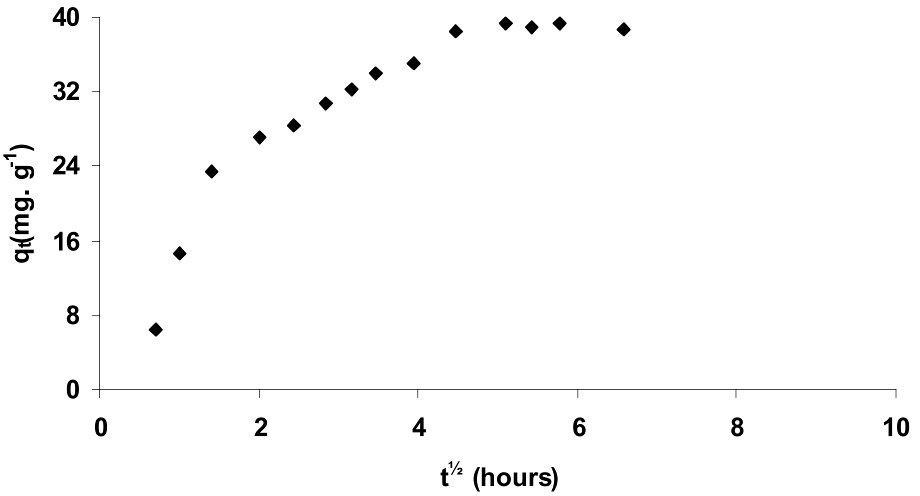


Figure 5.1.8b: Plot of intra-particle diffusion model for adsorption of P onto Ochre at 298K under dynamic conditions

multi-linear phases of three steps for the adsorption process (Annadurai *et al.*, 2002). This is in agreement with the intra-particle diffusion plot of the kinetic data of P adsorption onto Ochre (Figure 5.1.7). The intra-particle plot for Filtralite-P did not show a distinct phase 1, but rather a gradual continuum between phases 1 and 2.

In the intra-particle plot for Ochre, phase 1 was the most rapid (gradient of ~16 mg. g^{-1} $hr^{-½}$) and was completed within 2 hrs. The gradient of phase 2 referred to as the intra-particle rate constant (Kp ~ 5 mg. g^{-1} $hr^{-½}$) was less rapid followed by phase 3, the final equilibrium phase where intra particle diffusion slows down due to very low adsorbate concentration in solution. The first phase of intra-particle mechanism has been reported to be a rapid external surface adsorption or instantaneous adsorption stage, the second is the gradual adsorption where intra particle diffusion is rate-controlled and the third is the final equilibrium phase where intra particle diffusion slows down due to very low adsorbate concentration in solution (Özacar, 2003).

5.1.5 Regeneration studies

Results of P fractions from five sequential extractions using 0.05M NaCl, HCl, $NaHCO_3$ and NaOH under static conditions showed that recovery of P from Ochre was only possible using an alkaline medium (Figure 5.1.7). Recovery of P from Ochre was more effective at pH 12 (more alkaline medium) than pH 9 (Figure 5.1.9). These results support the findings of Zeng *et al.,* (2004) that P adsorption onto goethite (constituent of Ochre) decreases with increasing alkalinity. Desorption test conducted by shaking 10g used Ochre with 100 ml DI water for 24 hours gave only 4 mg P g^{-1} (equivalent of ~2% that released by 0.05M NaOH).

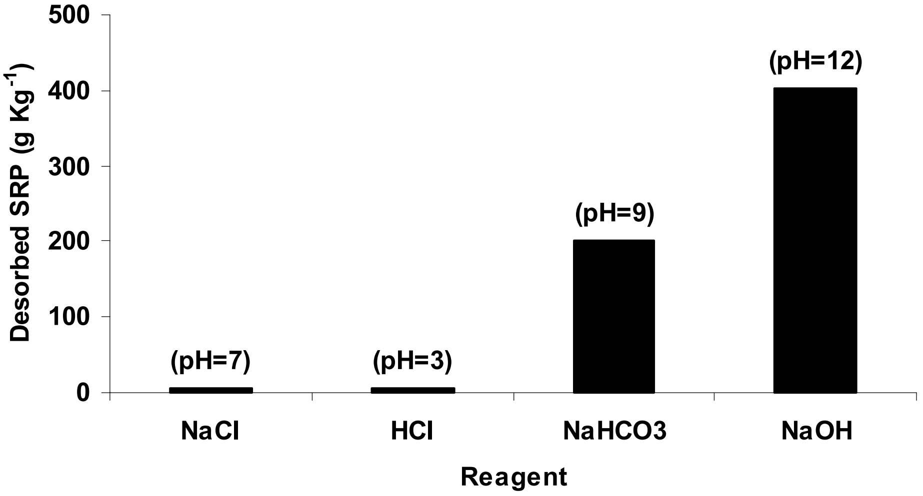


Figure 5.1.9: Regeneration of used Ochre with 0.05M NaCl, HCl, $NaHCO_3$ and NaOH under static conditions for 12 extractions.

5.1.6 Cu and Ni sorption capacity of Ochre and Bauxol™

Result of sorption capacities of Cu and Ni by Ochre and Bauxol™ computed by the Freundlich, DR and Langmuir equations differ in magnitude but are not significantly different from each other (p=0.08, n=3). The parameter coefficients of the three models used to investigate the adsorption process is summarised in Table 5.1.5. Sorption capacities of Ochre and Bauxol™ for Cu are generally comparable whilst that for Ochre generally doubles Bauxol™ for Ni in all three models. Overall, sorption capacities obtained from the Langmuir and DR models are comparable and higher than that of Freundlich. The experimental sorption data for the adsorption of Cu and Ni in sewage effluent by Ochre and Bauxol™ however gave better fit with Freundlich and DR models compared to the Langmuir (Figure 5.1.10 a, b and c). This may be due to the fact that the assumptions of the Langmuir model (i.e. constant binding energy throughout the adsorption process, monolayer adsorption and no interaction between adsorbed molecules on adjacent sites) are incompartible with the heterogeneous chemical composition and physical surface (Appendix 5) of Ochre and

Bauxol™. The Freundlich model however encompasses these adsorbent properties of the adsorbents.

Table 5.1.5: Isotherm parameters for the adsorption of Cu and Ni unto Bauxol™ and Ochre.

		Freundlich		DR		Langmuir		
Adsorbent	Metal	K_f (µg. g^{-1})	1/n	q_o (mg.g^{-1})	-E (KJ mol^{-1})	Q_o (mg. g^{-1})	K_L (L µg^{-1})	R_L
Bauxol™	Cu	36.6	1.23	4.1	0.08	5	0.012	0.84-0.74
Ochre	Cu	38.7	0.98	2.6	0.05	10	0.0035	0.62-0.38
Bauxol™	Ni	31.6	0.79	4.9	0.01	20	0.0006	0.40-0.78
Ochre	Ni	93.3	0.96	10.2	0.04	50	0.0014	0.08-0.39

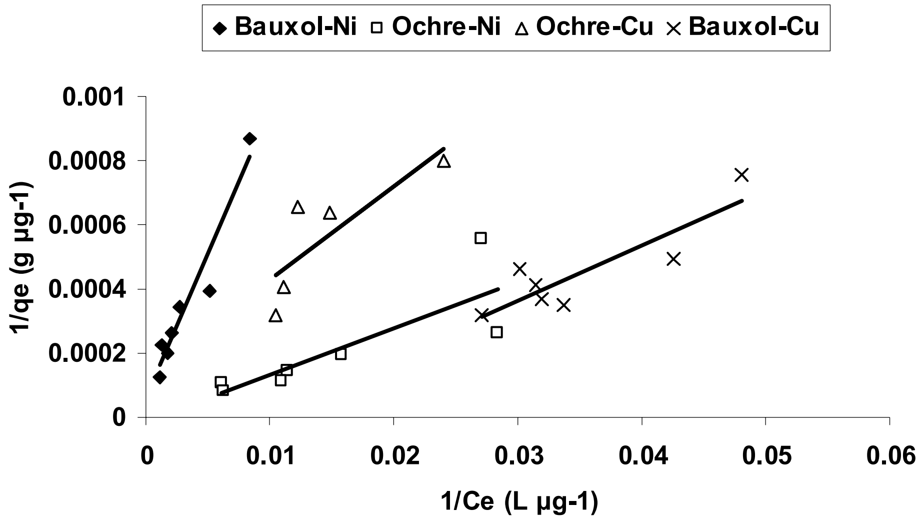


Figure 5.1.10a: Langmuir equilibrium plot for the adsorption of Cu and Ni unto Bauxol™ and Ochre.

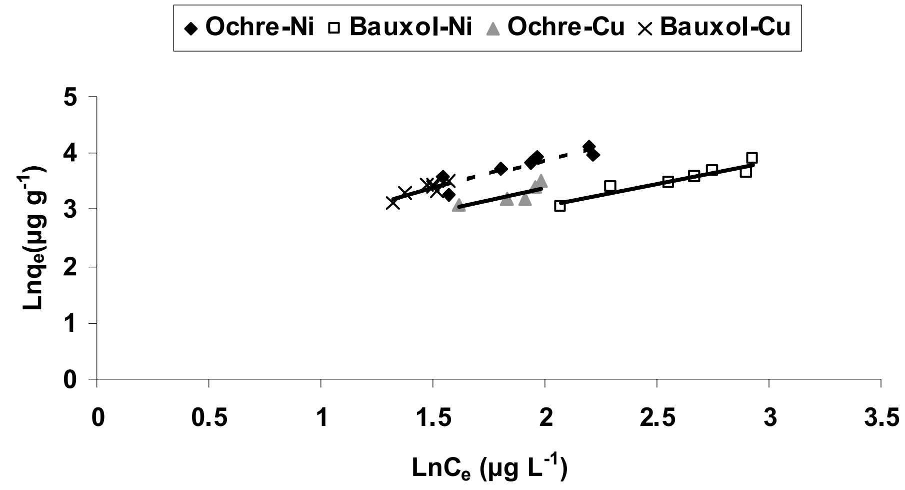


Figure 5.1.10b: Freundlich equilibrium plot for the adsorption of Cu and Ni unto Bauxol^{TM} and Ochre.

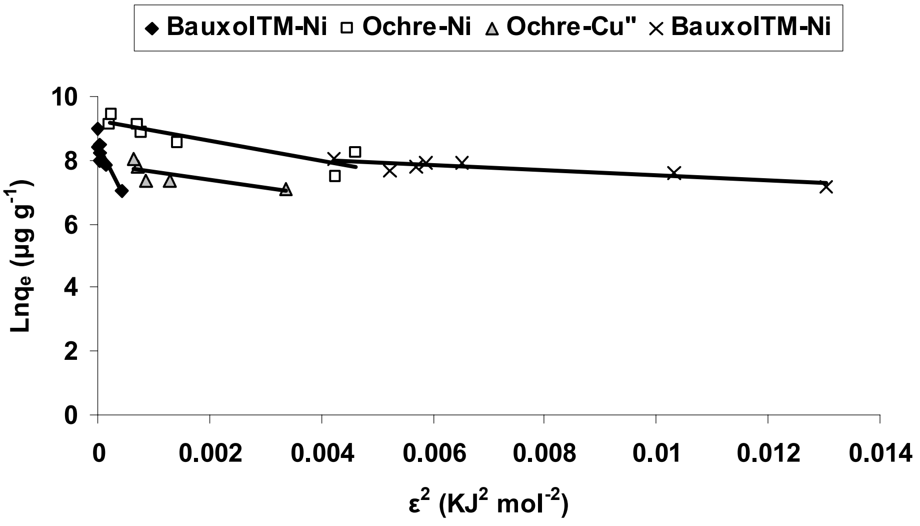


Figure 5.1.10c: Dubinin-Raduskevich equilibrium plot for the adsorption of Cu and Ni unto Bauxol^{TM} and Ochre.

The Freundlich isotherm parameter 1/*n* measures the adsorption intensity of Cu and Ni onto Ochre and Bauxol^{TM}. The 1/*n* values of Cu and Ni onto Ochre and Ni unto Bauxol^{TM} are less than unity. The adsorption of Cu onto Bauxol^{TM} is characterised by a 1/*n* value greater than unity indicative of a convex Freundlich isotherm (Horsfall and Spiff, 2005).

In order to predict the efficiency of the adsorption process, the dimensionless separation constant R_L was determined. The R_L values computed for both Cu and Ni were less than unity (Table 5.1.4) indicative of a favourable adsorption. Furthermore, the mean free energy (*E*) of the adsorption process computed using the DR model was also negative indicative of a spontaneous adsorption process.

5.1.7 Kinetics and thermodynamics of Cu and Ni adsorption by Ochre and Bauxol^{TM}

The removal of Cu and Ni from sewage effluent by Bauxol^{TM} and Ochre was rapid (Figure 5.1.11a & b). Initial removal of Cu and Ni by Bauxol^{TM} and Ochre was not significantly different (p>0.05) from the average removal over the entire 10 hr period.

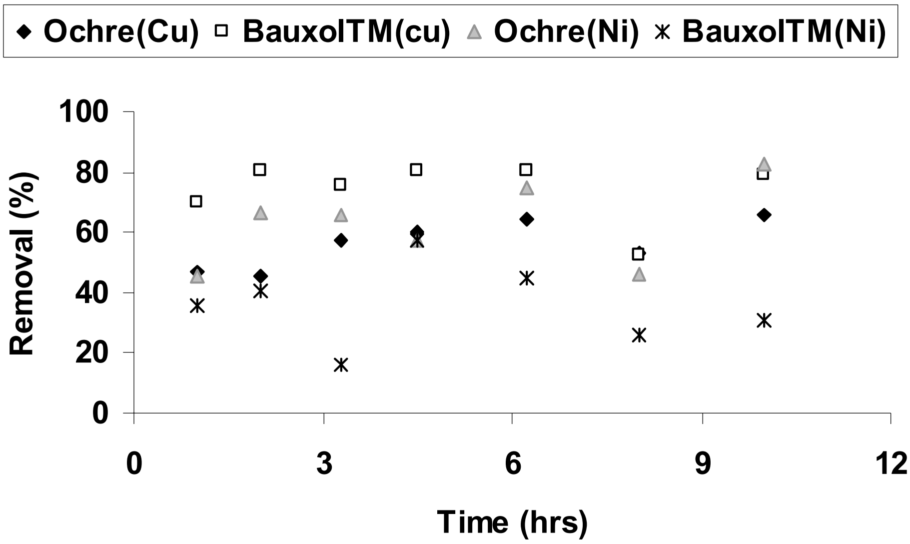


Figure 5.1.11a: Percent removal of Cu and Ni in sewage effluent by Ochre and Bauxol^{TM} under dynamic conditions at 293K.

This implies a short contact time for both adsorbent is adequate for Cu and Ni adsorption from sewage effluent. The short contact time may be due to the high surface affinity that governs transition metals (e.g Cu and Ni) adsorption onto goethite (component of Ochre) Trivedi *et al.*, (2001). Metal adsorption onto goethite is also influenced by the hydration shell of metal (Trivedi *et al.*, 2001).

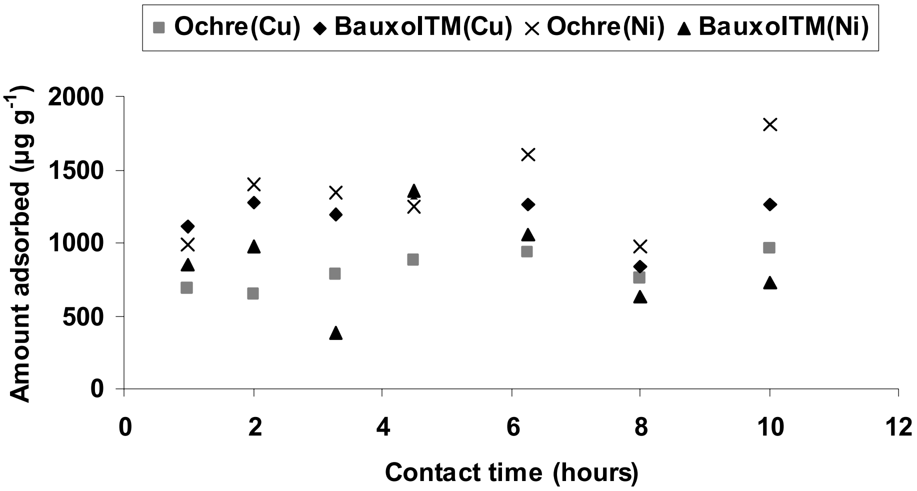


Figure 5.1.11b: Amount of Cu and Ni removed in sewage effluent by Ochre and Bauxol^{TM} under dynamic conditions at 293K.

The amount of Ni adsorbed by Bauxol^{TM} and Ochre over a 10 hour period averaged 852.1 and 1335.3 µg g^{-1} respectively whilst average Cu capacity by Bauxol^{TM} and Ochre were 1172.6 and 799.9 µg g^{-1} over a 10 hour period respectively. The results revealed that Bauxol^{TM} adsorb more Cu than Ni whilst Ochre adsorbed more Ni than Cu. However, these differences were not significant ($p>0.05$, $n=3$). Removal of Cu and Ni Bauxol^{TM} and Ochre was best described by the pseudo second order kinetic model (Figure 5.1.12). However, insufficient data was obtained due to limited time available to investigate further the details of the adsorption mechanism.

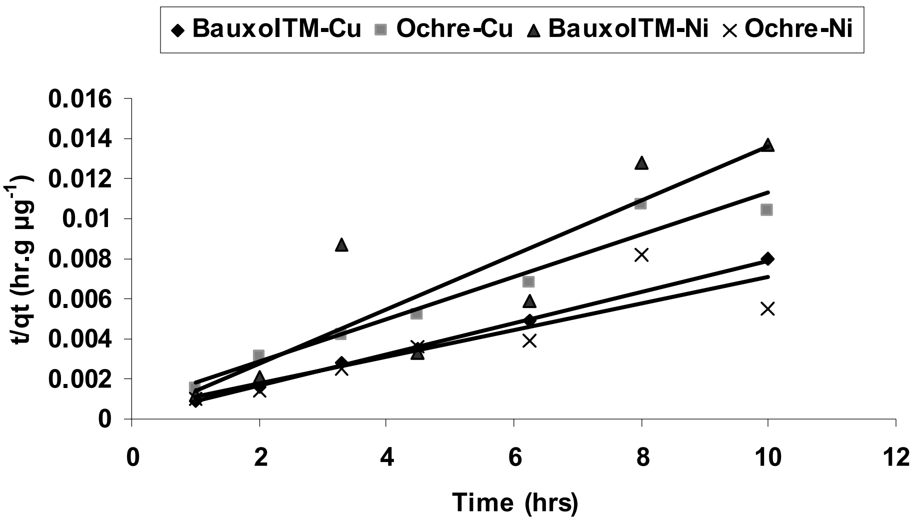


Figure 5.1.12. Pseudo-second order plot for the adsorption of Cu and Ni in sewage effluent by Bauxol^{TM} and Ochre under dynamic conditions at 293K.

Table 5.1.6: Summary of pseudo second order kinetic parameters for the adsorption of Cu and Ni unto Bauxol^{TM} and Ochre under dynamic conditions. Number of replicate for experimental value is 3.

	K (g. µg^{-1} hr^{-1}	q_e (µg .g^{-1}) calculated	q_e (µg .g^{-1}) experimental	r^2
Bauxol^{TM}(Cu)	1.1 ×10^{-2}	1,250	1,117± 142	0.99
Ochre (Cu)	1.7 ×10^{-3}	909	878±65	0.95
Bauxol^{TM}(Ni)	2.0 ×10^{-1}	714	805±132	0.76
Ochre (Ni)	1.2 ×10^{-3}	1,429	1,460±252	0.76

The calculated pseudo-second order model parameters and correlation coefficients are presented in Table 5.1.6. The calculated equilibrium concentration (q_e) from the pseudo second order model was comparable to experimental equilibrium values (Table 4.2.4), confirming that adsorption occurred by a Pseudo second-order mechanism. Result of the thermodynamics governing the adsorption of Cu and Ni removal from sewage effluent by is also summarized in Table 4.2.4. The efficiency of adsorption and spontaneity of the adsorption process as denoted by R$_L$ and E respectively are indicative of high efficient and feasible adsorption.

5.2 Discussion

5.2.1 P capacity of adsorbents

The physical and chemical properties of the adsorbents investigated in this study influenced their adsorption capacities (objective 7). P capacities obtained for the various adsorbents in this study showed that the Fe rich minerals (e.g. Ochre, Bay oxide, Bauxols and Red mud) better removed P from sewage effluent compared to Ca rich adsorbents (e.g. limestones). In comparison, P capacities of 26, 500, 5,200 and 5500-8100 mg Kg^{-1} for Ochre, Bayoxide and Bauxol obtained in this study is comparable to those reported by Heal *et al.*, (2004, 2005) for Ochre, Parfitt *et al.*, (1975) for FeOOH and β-FeOOH, Akhurst *et al.*, (2006) for Bauxol and Lopez *et al.*, (1998) for Red mud. Other reported P capacities of 650-700 mg Kg^{-1} for Shale (Drizzo *et al.*, 1999) and 1390 mg Kg^{-1} for Norwegian light weight aggregate (Zhu *et al.*, 1997) earlier thought to be at the higher end of good P removal adsorbents seems inferior to Ochre. The sorption values for Ochre, Bay oxide, Bauxols and Red mud are orders of magnitude higher than those measured in other wetland substrates (Table 5.2.1) suggesting that the use of these substrates could greatly improve the performance of constructed wetlands for

Table 5.2.1 Comparison of P adsorption capacities of different wetland substrates

Adsorbent	Adsorption capacity (mg P g^{-1})	Source
Gravel	0.03-0.05	Heal *et al.*, 2004
Steel slag	0.38	Heal *et al.*, 2004
Blast furnace slag	0.40-0.45	Heal *et al.*, 2004
Fly ash	0.62	Heal *et al.*, 2004
Shale	0.73	Drizzo *et al.*, 1998
LWA	1.3	Drizzo *et al.*, 1998
Steel slag	1.8	This study
Ochre	26.5	This study
Ochre	26.0	Heal *et al.*, 2005

phosphorous removal. The results are consistent with the expectation that Fe oxyhydroxides are amongst the most effective adsorbents for P removal from solution (Li and Stanforth, 2000).

The P capacities of most of the calcium rich adsorbents suggest that although they are capable of removing a measure of P from wastewater, their capacities are too small if applied in real situation. Furthermore, the results obtained for these absorbents are for batch isotherm studies which are considered an overestimation of real full scale results (Drizzo *et al.*, 2002) because the potential development of biofilm (Drizzo *et al.*, 2002), hydraulic regime, residence time and P concentration (Arias and Brix, 2005) using real wastewater reduce the capacity of adsorbents compared to lab-scale experiments.

As the results obtained in this study were carried out under aerobic conditions, the sorption capacity of Ochre could have been lower if the experiment had been carried out under anaerobic conditions. To illustrate, iron(II)phosphate form in anaerobic condition is less stable compared to iron(III)phosphate form under aerobic condition (i. e. dissociation constant of iron(II)phosphate is 561 KJ mol^{-1} which is far lower than 2956 KJ mol^{-1} for iron(III)phosphate) (Skoog *et al.*, 2003). Consequently, solubilization of iron(II)phosphate can occur far more easily compared to iron(III)phosphate and this could lead to leaching of dissolve phosphate from an anaerobic CWS. Srption isotherm studies are normally carried out in an aerobic environment and therefore literature data for studies carried out in anaerobic environment are unavailable to make comparisons.

5.2.2 Bed volume trials

A residence time of ~5 hours (compared to ~24 hours optimal contact time) for Ochre was able to produce water quality of ≤ 0.5 mgP L^{-1} up to 250BV irrespective of fluctuating influent concentration. In comparison, this effluent quality was only produced using Steel slag at optimal contact time for a limited time (60BV) when influent P does not exceed 4 mg L^{-1}. This implies that the use of Ochre based treatment system would treat larger volume of sewage effluent at shorter time more efficiently compared to Steel slag or other adsorbents with P capacity comparable to Steel slag. In comparison with the literature, Berg *et al.*, (2005) achieved 1900BVs using crushed gas concrete to treat a biological sewage effluent strength ranging from 5-12 mgP L^{-1} to meet a target of 2 mgP L^{-1}. Based on the results of this study which shows that the 0.5 mg L^{-1} target was reached at C_t/C_o ~0.1, 2 mg L^{-1} target could be reached at ~500-1000BV for this Ochre system at ~5 hours. The BV capacity achieved in adsorption experiment is dependent on influent concentration and type of adsorbent used. For instance, Thirunavukkarasu *et al.*, (2003) achieved a BV of 1140 and 3240 for a 5 µg L^{-1} and 10 µg L^{-1} respectively using an influent strength of 500 µg L^{-1} for As(V) removal from waste water using granular ferric hydroxide, whilst Clifford *et al.*, (1999) achieved a BV of 400-800 for a target of 2 µg L^{-1} using an influent strength of 21 µg L^{-1} for As(V) removal from waste water.

Effluent from the Steel slag system was consistently > pH 10 (outside consent discharge limit pH 6-8) compared to a pH ~7 for Ochre. Removal of P from sewage effluent and pH of effluent was strongly correlated (P= 0000, $r^2 = 0.7$). This is because; Ca^{2+} combines with P forming hydroxyapatite with lowest solubility at pH >

9.5 (Stumm and Morgan, 1996; Tan, 1993). Fe however combines with P to form FeOOH-$PO_{4\,(s)}$ complexes, which occurs at optimum pH 5-7 (Lijklema, 1977).

5.2.3 Kinetics and thermodynamics of adsorption

Ochre, Bayoxide, Bauxol, Red mud, Filtralite-P and Steel slag all exhibited high initial P adsorption rate (objective 9). The high removal rate observed for Ochre and Bauxol^{TM} in this study is consistent with the literature. For instance, Akhurst *et al.*, (2006) reported a P reduction of 46% within 24 hours using an adsorbent dose of 4 g Bauxol^{TM} L^{-1}. In this study, a reduction of 42% within 48 hours was achieved using an adsorbent dose of 2g Bauxol^{TM} L^{-1}.

McHaffie *et al.*, (2000) reported a reduction from 5 to <0.01 mg P L^{-1} within 8 minutes whilst a reduction of 4.8 to 1 mg P L^{-1} was obtained in 48 hours in this study. However, a much larger adsorbent dose (volume artificial P solution to mass of Ochre ratio of 10:1) was used in McHaffie *et al.*, (2000) compared to that used in this study volume of sewage solution to mass of Ochre ratio of 1000:1.

The dimensionless separation (R_L) and free energy (E) of the adsorption processes are indicative of favourable and spontaneous adsorption. Favourable adsorption of phosphate unto FeOOH (component of Ochre) and Bauxol^{TM} had also been reported by Zeng *et al.*, (2004) and Akhurst et al., (2006) respectively.

Adsorption of P from sewage effluent onto Ochre proceeded via a pseudo-second order mechanism (objective 9). Three distinct linear adsorption phases consistent with the intra-particle mechanism was evident. The first phase of intra-particle has been reported to be a rapid external surface adsorption, the second is the gradual adsorption where intra-particle diffusion is rate controlled and the third is the final equilibrium phase where intra-particle diffusion slows down due to very low adsorbate concentration in solution (Özacar, 2003; Annadurai *et al.*, 2002). It is proposed that the first phase involves rapid ligand exchange with surface OH^- groups at reactive sites and the formation of a binuclear bridging complex between a phosphate group and two surface Fe atoms followed by a slower penetration of phosphate into the solid matrix via sites and pores (Parfitt, 1989). Similar mechanism has been proposed for phosphate adsorption onto goethite by Hongshao and Stanforth (2001). The second and gradual adsorption where intra-particle diffusion is rate controlled is believed to be the chemical sorption phase in the pseudo-second order mechanism (Ho and McKay, 1999). Hongshao and Stanforth (2001) describe the adsorption of phosphate onto goethite as a two-phase reaction on the adsorbent surface; the first phase being a rapid surface complex formation followed by a gradual surface precipitate on the adsorbed layer. They identified an exchangeable ion phase in the surface precipitate which could describe the third phase of the intra-particle model.

5.2.4 Desorption and regeneration studies

Desorbability is a measure which indicate the degree of P desorption from an adsorbent (He *et al.*, 1999). The low/negligible desorbability of sorbed P on Ochre in water, neutral and acid medium but which increases at high pH (e.g. strong alkali) indicates that the interaction is not easily reversible and that strong chemical bonding occurred during the sorption process. Parfitt (1989) reported that P adsorption unto Ochre becomes more stable with time. Fe precipitates with phosphate under acidic conditions (Arias *et al.*, 2001) and P adsorption unto geothite (FeOOH) decrease with increase alkalinity (Zeng *et al.*, 2004). These findings implies that the use of Ochre as substrate in constructed wetland systems would not readily leach sorbed P or toxic metals while making it possible to regenerate spent Ochre to increase the longevity of the treatment system. This would reduce the cost and disruption associated with frequent excavations and the high volume of material required for reconstruction.

5.2.5 Life expectancy of Ochre, Filtralite-P and Steel slag based CWS

The results obtained from the sorption isotherm and bed volume studies for Ochre and Steel slag can be extrapolated to determine the expected lifetime of a CWs using either Ochre or Steel slag as a substrate. One approach is that of Jensen and Krogstad (2003). They estimated lifetime of CWS by multiplying the maximum sorption capacity with the total mass of filter material. This assumption together with the assumptions that the land area required to treat wastewater from one person is 5m^2 and at a wetland depth of 0.6m (EC/EWPA, 1990), then 3m^2 or 4.5 tonnes of substrate would be needed to treat the effluent from one person. Using this approach, the lifetime estimated by Drizzo *et al.*, (1998), Heal *et al.*, (2005) and for adsorbents investigated in this study is compared in Table 5.2.3.

Table 5.2.2 Comparison of estimated lifetimes according to procedure of Jensen and Krogstad (2003) for 3m^2 area per person

Adsorbent	Lifetime (years)	Source
Shale	7	Drizzo et al., 1998
Steel slag	41	This study
Filtralite-P	12	This study
Ochre	224	Heal et al., 2005
Ochre	271	This study

Although the calculations of the above estimated lifetimes does not take into account the decline in flow rates and chanellization through ill-distributed flow, yet the results clearly indicate considerable longevity in a properly designed CWS with Ochre based system compared to Shale or Steel slag or Filtralite-P. Also, it is well documented in the literature that CWs undergo a sharp decline in ability to remove P from waste water after few years of commissioning. For instance, Wolstenholme and Bayes, (1990) reported a decline after 2 years using pulverised fuel ash, (Mann and Bavor, 1993) reported a decline after 1-2 years using a gravel-based system in Richmond Australia, Maehlum et al., (1995) reported a decline after 2-3 years using LECA, Kadlec and Knight (1996) showed that initial P removal rates from wetland systems in the USA are often in excess of 90% but decline sharply after 4-5 years. This is because P accumulates in substrates until they are saturated. This suggests that the use of adsorbent with high P sorption capacity is essential since substrate accounts for the majority of P immobilized in treatment wetlands (Richard, 1989). This makes Ochre an excellent candidate to increase the longevity of treatment wetlands for diverse applications of P removal.

As treatment wetlands are utilised to achieve a desired discharge target, the actual expected lifetimes presented in Table 5.1.2 would be far less for specific applications such as tertiary treatment. For instance, the Ochre based trial system achieved the 0.5 mg L^{-1} limit up to a volume throughput of ~250 BV although it was still far below the saturation point of the adsorbent. Similarly, the Steel slag system produced the same effluent quality only up to ~60 BV. Hence calculating expected lifetimes using equation 5.2.1 assuming a HFS operating 1.2 m^3 d^{-1} having a volume of 50 m^3 will have an approximate lifetimes of 86 and 7 years respectively.

$$BV = \frac{Q * t}{V} \quad 5.2.1$$

Where BV is bed volume throughput (dimensionless), Q is flow rate (m^3 d^{-1}), time (d) and V is volume (m^3).

The aim of fitting experimental sorption data to an adsorption model is to predict the sorbent capacity and describe the adsorption process. As the ultimate aim of adsorption capacities is for design purposes, it is therefore important that correct isotherm coefficients for the experimental data are established. This was achieved by fitting experimental data to three established and widely used models (Freundlich, Langmuir and Dubinin-Radushkevich) to obtain the best fit. Furthermore, model parameter coefficients and their corresponding thermodynamic outputs collectively provide insight into the adsorbent ability, efficiency and mechanism involved in the adsorption process, thereby providing a complete understanding of adsorption process. Fitting experimental data in this study to the Freundlich, Langmuir and Dubinin-Radushkevich models confirms the above statement. For instance, the adsorption capacities from the three models vary in magnitude, with that from Freundlich much smaller compared to the Langmuir and Dubinin-Radushkevich (Table 4.2.3), but it is the adsorption capacity predicted by the Dubinin-Radushkevich isotherm that came closest to adsorption capacities calculated from equilibrium and rate studies. Furthermore, the Freundlich model also modelled the sorption data better compared to the Langmuir model having greater regression coefficients. This may be because the Freundlich equation is an empirical model which encompasses adsorbent heterogeneity and accounts for decreased affinity of adsorbate with increasing saturation. In comparison, the Langmuir model assumes constant binding energy during adsorption process, monolayer adsorption on an ideal surface. The Freundlich model thus seem closer to reality compared to the Lanmuir model. For instance, ESEM analysis revealed heterogeneous surfaces for Bauxol^{TM} and Ochre which is considered incompatible with ideal localised adsorption without interaction on identical sites for the Langmuir model (Ruthven, 1984).

The Freundlich model allows an evaluation of the adsorption intensity (indicated by $1/n$) of Cu and Ni unto Bauxol^{TM} and Ochre to be assessed. A higher $1/n$ value for Cu compared to Ni for Bauxol^{TM} indicates a preferential adsorption of Cu over Ni. This is reflected in Fig 4.2.8 where removal of Cu is higher than Ni and consistent with the free energy of adsorption computed for the DR model and Langmuir constant related to energy of absorption (Table 4.2.3). A similar finding was reported by Clark *et al.*, (2002). With regards Ochre, $1/n$ value for the adsorption of Cu and Ni by Ochre are comparable and this is exemplified in the rate plot (Figure 4.2.9). The comparable energy change of adsorption for Cu and Ni unto Ochre and $1/n$ value from the Freundlich model indicates that both metals had no inhibitory effect on the adsorption of the other. This observation is consistent with the findings of Balistrieri and Murray (1982) who reported that the presence of Pb, Zn, Cd, PO_4^{3-} and CO_3^{2-} had no inhibitory effect on the adsorption of Cu onto goethite.

Reasons for the preferential adsorption of Cu over Ni for Bauxol^{TM} as oppose to Ochre is not clearly known. In general, preferential adsorption of heavy metals is influenced by the stable oxidation state of the metal in solution and its ionic radii (Richard, 1996; Horsfall and Spiff, 2005). Cu and Ni are both commonly divalent, with similar ionic radii and hydration energies (Cu^{2+}: 0.71Å, -2100 KJ mol^{-1}; Ni $^{2+}$: 0.69 Å, -2105 KJ mol^{-1}), therefore it is unlikely that these parameters influenced their preferential ability to sorb unto Bauxol^{TM}. Adsorption of heavy metals (positive ions) onto solid surfaces (negative surfaces) can be explained in terms of Lewis acid -base or hard and soft acid-base reactions, and Ni and Cu are both borderline Lewis acids (Ralph, 1973). Hence, the preferential adsorption of Cu and Ni unto Bauxol^{TM} could be explained as a consequence of the nature of the heterogeneous chemical composition of Bauxol^{TM} (see Table 5.1.1), the influence of the various elements present in Bauxol^{TM} and surface attractive forces (Pradhan *et al.*, 1999).

The adsorption of Cu in solution by goethite has been reported to take place via inner-sphere complexes mechanism (Peacock and Sherman, 2005). Using sorption isotherm and EXAFS spectra, they showed that Copper(II) absorbs as $(CuO_4H_n)^{n-6}$ and binuclear $(Cu_2O_6H_n)^{n-8}$ complexes forming inner-sphere complexes with iron(hydr)oxide by corner-sharing with two or three edge-sharing $Fe(OH)_6$ polyhedra.

The data in Table 5.1.4 for R_L (adsorption efficiency) and energy change (E) indicate that adsorption of Cu and Ni by Bauxol^{TM} and Ochre is favourable and spontaneous. Kinetic study performed at fixed initial concentration at different time intervals indicate that adsorption of Cu and Ni onto Bauxol^{TM} and Ochre follows pseudo second order reaction kinetics.

Sorption capacities obtained in this study are comparable to a range of values reported for different adsorbents in the literature. For instance, Lopez *et al.*, (1998) reported capacities of 19.7 and 10.9 mg.g^{-1} for Cu and Ni adsorption unto Bauxol^{TM} respectively; Liu *et al.*, (2007) reported a sorption capacity of 25 mg.g^{-1} for Cu unto Bauxol^{TM}; Yavuz et al., (2003), reported sorption capacity of 1.7 and 10.8 mg.g^{-1} for

Cu and Ni unto raw Kaolinite; Brown *et al*., (2000) reported a sorption capacity of 8 $mg.g^{-1}$ for Cu unto Peanut Hull. Although, the findings of this study show that both Bauxol^{TM} and Ochre could effectively be used to remove Cu and Ni from sewage effluent, the size of the adsorbents are unsuitable for use in constructed wetland system due to problems of clogging. Therefore, remaking these samples into appropriate size would be required. These should be followed by durability and sorption capacity tests.

CHAPTER 6 Conclusions and recommendations

Conclusion

The application of constructed wetlands for greywater treatment was shown to be appropriate. Performance at the two ends of the influent strength spectrum revealed that all configurations of wetlands can treat low strength greywater but horizontal systems exhibited more limited scope as the concentration increases (objective 1). The ability of the three wetlands to remove organic matter from the influent grey water was primarily influenced by the influent organic loading (objective 5). Residual concentration of BOD_5, COD and TOC increased as influent organic concentration increases. Overall compliance to the USEPA standard for reuse averaged 96% for the VFRB, 79% for the HFRB and 67% for GROW for BOD_5 and 0% for the HFRB, 33% for the VFRB and 75% for the GROW system for turbidity (objective 2 - 4). Although the VFRB was best overall with no evidence of clogging on the bed surface during the study period, clogging would have resulted in a decreased performance of the VFRB due to poorer diffusion of air into the bed to support aerobic microbial degradation (objective 6). This study reveals that the removal mechanism of key pollutants such as organics, solids and indicator organisms that are present in grey water is similar to those occurring in domestic wastewater in constructed wetland systems.

Both the HFRB and the GROW system removed turbidity from the influent grey water. However, the formation of colloidal ferric phosphate in the HFRB effluent and the release of solids as a result of continued proliferated root growth from larger plants within the troughs of GROW resulted in an overall high turbidity in the final effluent. The use of a bed substrate which does not contain iron would have resulted in a lower turbidity in the final effluent. Improvement of the GROW system could be achieved by the use of miniature wetland plants which will reduce the possibility of proliferated or extensive root growth caused by larger plants in troughs that resulted in the release of biofilms and particulates into the effluent stream. In addition, increased aeration would be required to enable the GROW system to treat higher organic strength grey water.

Overall, the study shows that CW based on vertical configurations are most appropriate for greywater treatment (objective 3). The principle reason for this was shown to be that aerobic degradation pathways are more appropriate and develop more robust solutions. The effluent quality and general robustness of the VFRB was similar but slightly poorer than that of a membrane bioreactor (e.g. 96% compliance to the USEPA BOD standard for reuse for the VFRB compared to 100% compliance for the MBR). Consequently, VFRB offer a suitable alternative to MBR, providing choices with either intensive or extensive solutions that are suitable for greywater recycling (objectives 2 - 3). Overall, constructed wetlands have a place within the range of available technologies for grey water treatment and reuse. In particular, there would be market opportunities in small communities and environment where land is cheap and available.

The use of Ochre, Bauxol, Bauxol^{TM}, Red mud, Bayoxide, Filtralite-P, Steel slag, Concrete, Zeolite and various form of limestones were investigated for potential removal of soluble reactive phosphorous (SRP) and metals (Cu and Ni) in final sewage effluent for post Constructed Wetland System. The type of metal (e.g. Fe, Al, Ca) present in the adsorbents and their cation exchange capacities strongly influenced

P capacities exhibited by the various adsorbents (objective 8). Bauxol, Bauxol^{TM}, Red mud, Bayoxide, Ochre, Filtralite-P, Steel slag were found to have a significantly higher P capacity compared to the limestone adsorbents. Ochre exhibited the best P removal ability with a P capacity of 26 g Kg^{-1} based on a Freundlich isotherm model. Result also showed that the equilibrium sorption capacity of Bauxol^{TM} and Ochre based on a Dubinin-Radushkevich model was 4.1 and 4.9 mg g^{-1} for Cu and Ni unto Bauxol^{TM} respectively and 2.6 and 10.2 mg g^{-1} for Cu and Ni onto Ochre respectively. Thus, they could both be regarded as a low-cost economic adsorbent for toxic metals from sewage effluent. Kinetic and thermodynamic study revealed a spontaneous and efficient adsorption process via a pseudo-second order mechanism where intra-particle diffusion was shown to be the rate limiting step (objective 9).

Cognisant of the fact that the results presented in this study were carried out under aerobic conditions and that iron (III) phosphate/ferric phosphate ($FePO_4$) formed under aerobic conditions is more stable compared to $(Fe)_3(PO_4)_2$ formed under anaerobic condition, the sorption capacity could have been much lower if the study had been carried out under anaerobic conditions. Overall, it may be concluded that Ochre offers a suitable, low-cost and natural means for the removal or polishing of P, Cu and Ni in sewage effluent from wastewater treatment plant and thus could be an alternative to more costly techniques.

With current increasing emphasis on sustainability in terms of protecting and conserving the environment, cost, waste generation and other environmental hazard associated with any treatment process, an Ochre based constructed wetland system is a genuine possibility in the near future. A proposed setup of a treatment system for P removal would be a vertical flow CW followed by an aerobic contact bed using Ochre as the bed substrate (objective 7).

Recommendations for further work

1. Further studies should be carried out to determine more accurately the optimal organic load in relation to surface area (m^2 PE^{-1}) required to treat high strength grey water using the HFRB and GROW treatment wetlands.

2. The effect of very low temperature (winter conditions), influence of phosphate speciation on P removal by Ochre and development of ~10mm Ochre pellet sizes using binding agents containing some Ca and Al substance which would ensure good hydraulic property when used in wetland system should be the focus of future research.

3. Pilot scale work under actual environmental conditions in the field would be required to determine maximum sorption capacity of Bauxol and Ochre for metals and what factors would limit or influence its adsorption.

4. A comparative study on sorption of P onto Ochre under aerobic and aerobic conditions.

Chapter 7 References

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Appendix

Appendix 1: Photos of Constructed wetlands

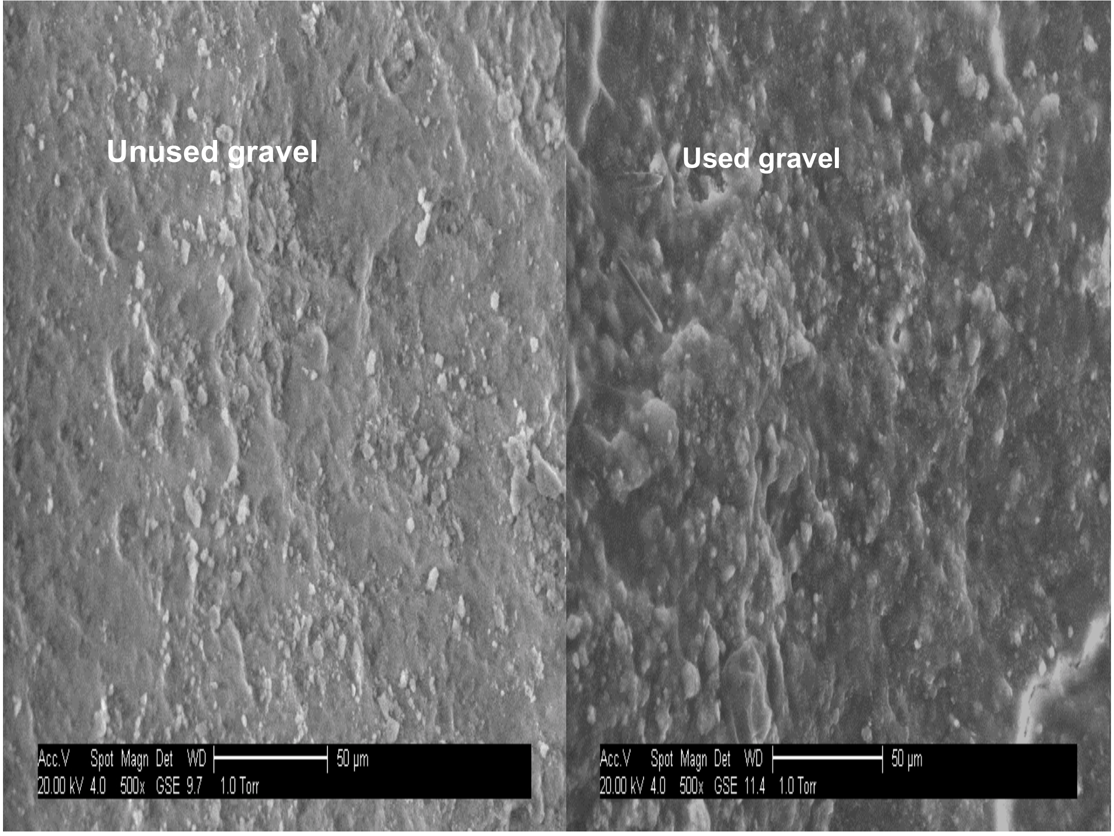
Figure 1: Photo of HFRB

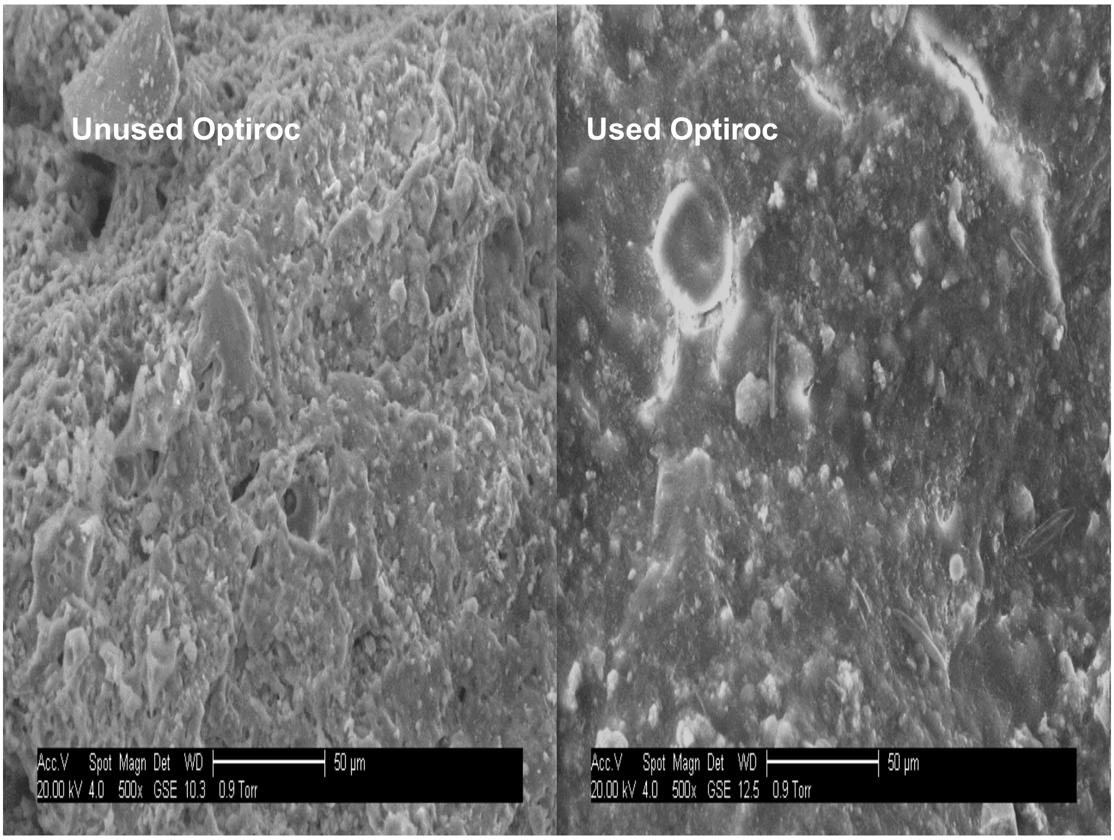
Figure 2: Photo of VFRB

Figure 3: Photo of 'GROW'

Figure 4: Photo of 'GROW' with membrane showing internal features

Appendix 2 Media of GROW





Appendix 3: Tracer response curves of Constructed wetlands and rows of GROW. Vertical lines represent nominal hydraulic residence time.

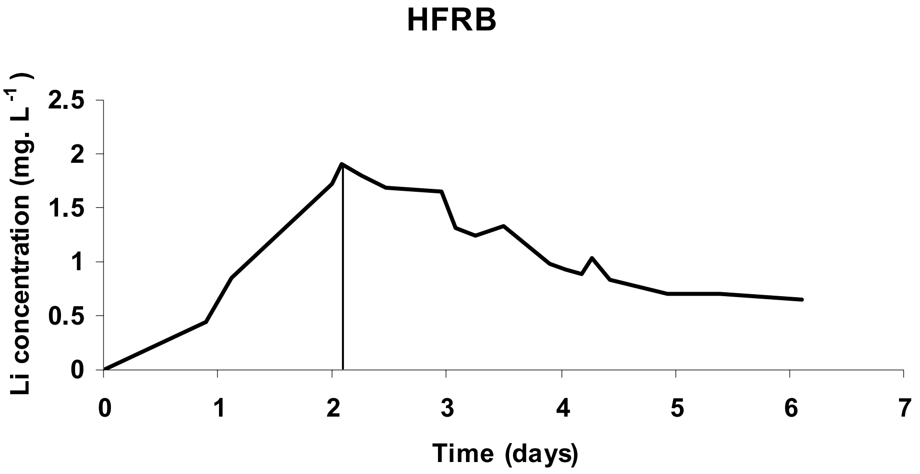


Figure 6: Tracer response curve for HFRB

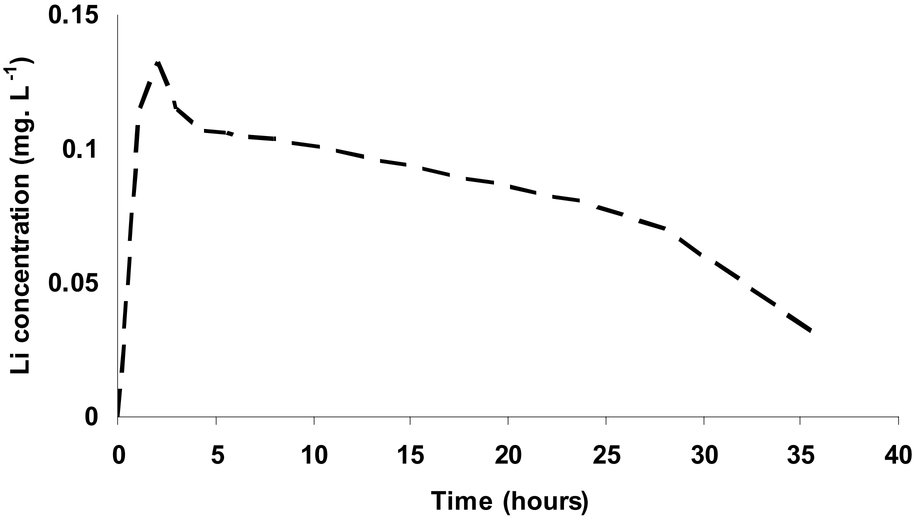


Figure 7: Tracer response curve for VFRB

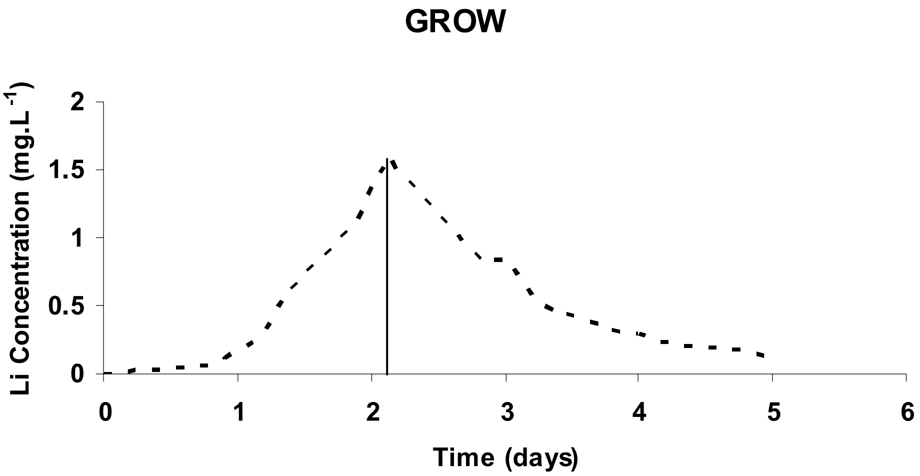


Figure 8: Tracer response curve for GROW rig

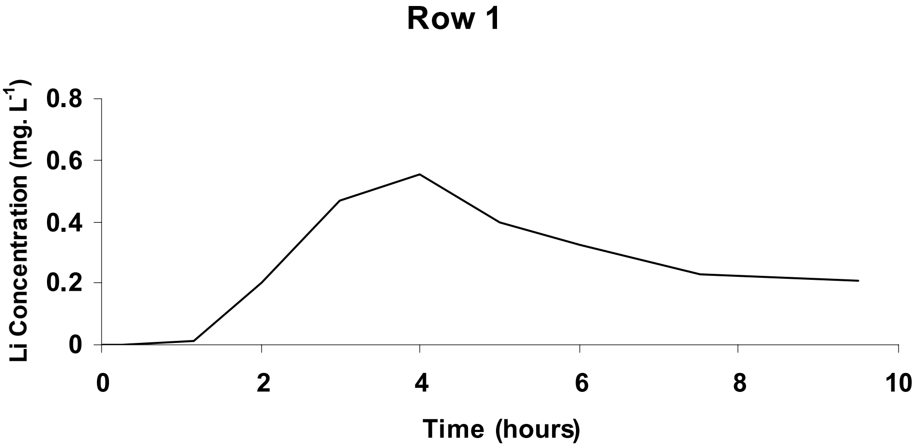


Figure 9: Tracer response curve for Row 1 of GROW

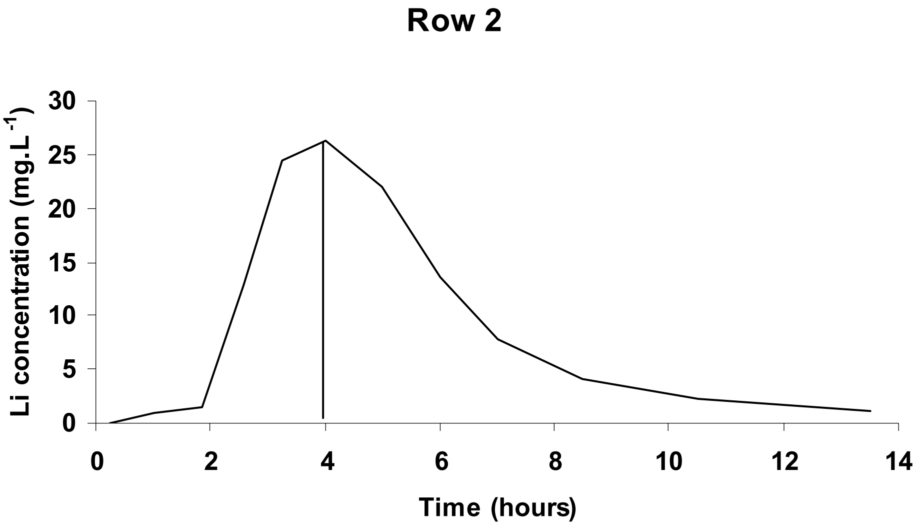


Figure 10: Tracer response curve for Row 2 of GROW

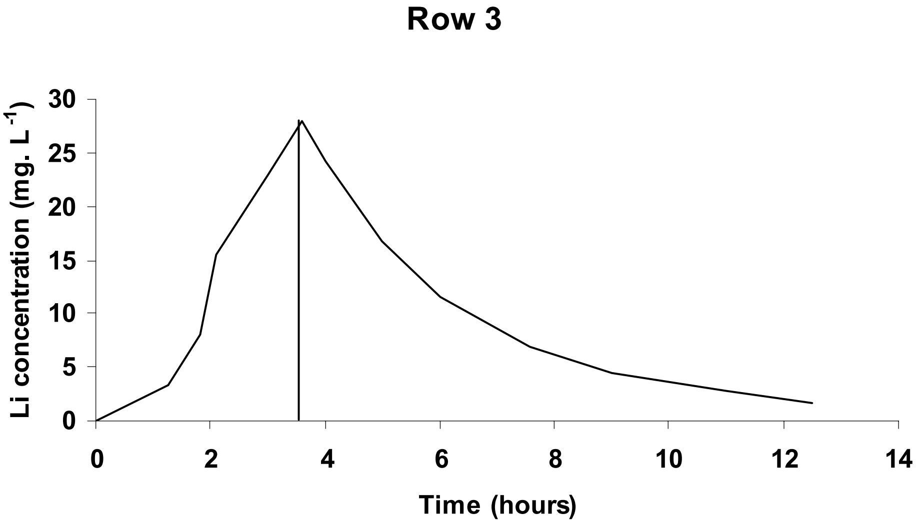


Figure 11: Tracer response curve of Row 3 of GROW

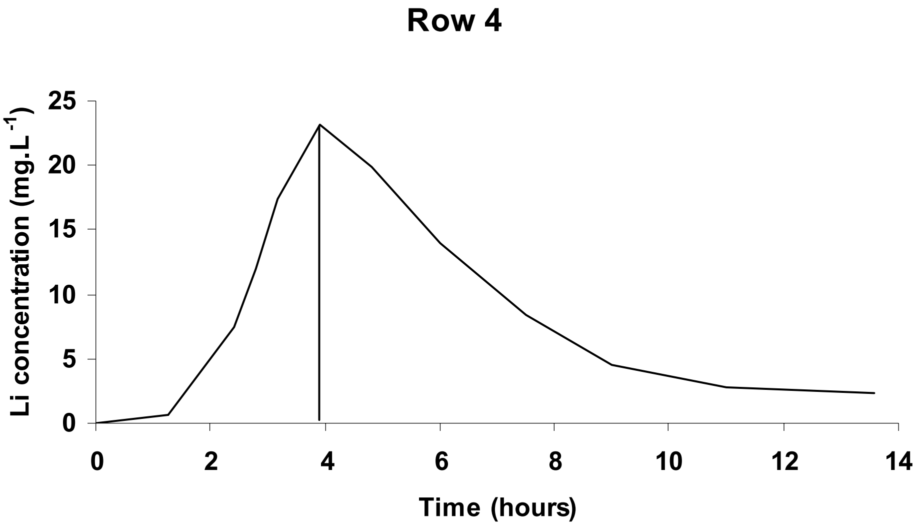


Figure 12: Tracer response curve of Row 4 of GROW

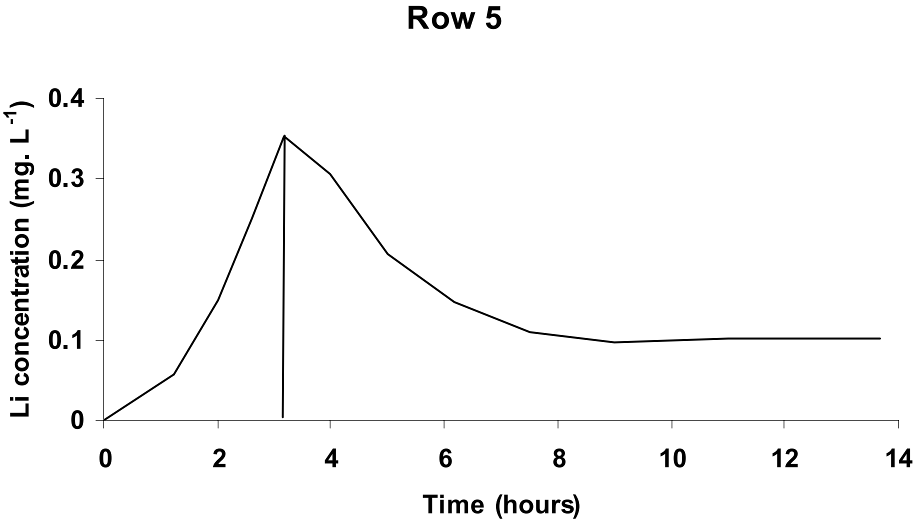


Figure 13: Tracer response curve of Row 5 of GROW

Appendix 4: Influent and constructed wetland effluent parameters over the experimental monitoring period

Table 1: Mean removal efficiency of pollutants (%) and microbial indicators (log reduction) during study

Parameters	HFRB		VFRB		GROW	
	LS	HS	LS	HS	LS	HS
BOD_5	89	66	95	97	93	53
COD	73	75	83	94	83	69
SS	74	64	92	89	90	79
Turbidity	18	82	44	96	97	59
NH_4-N	47	none	93	42	67	38
NO_3-N	34	83	none	50	none	38
PO_4-P	63	none	87	75	06	none
Total coliform	2.7	3.3	4.8	3.3	3.8	1.7
E. coli	2.1	2.3	3.3	2.0	2.4	0.6
Faecal enterococci	2.1	2.2	2.2	3.0	2.2	1.8

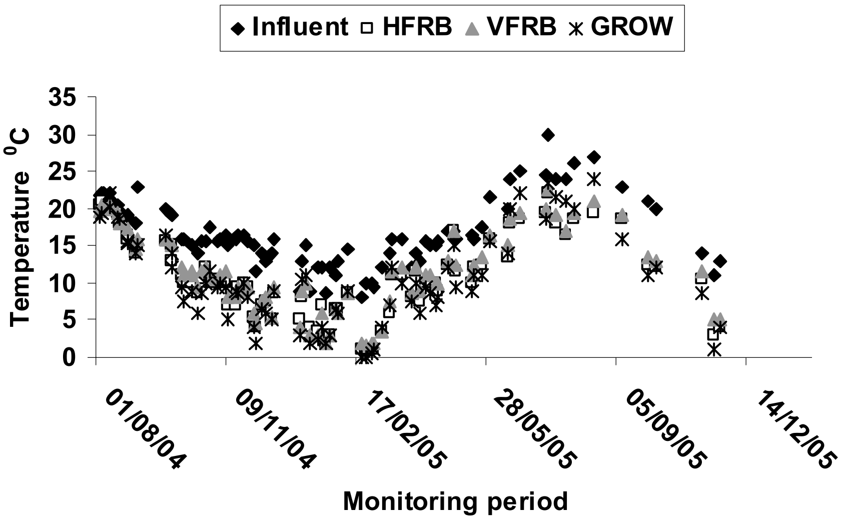


Figure 14: Influent grey water and CW effluent temperature during the monitoring period.

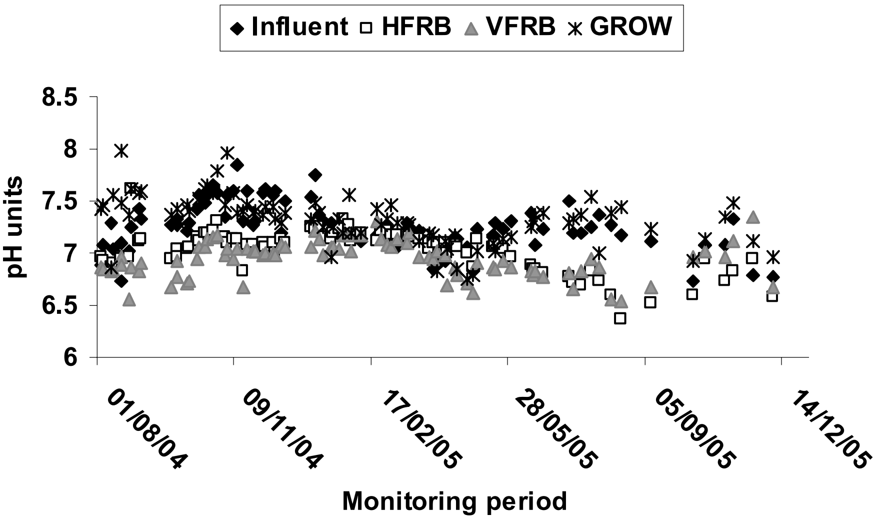


Figure 15: Influent grey water and CW effluent pH during the monitoring period.

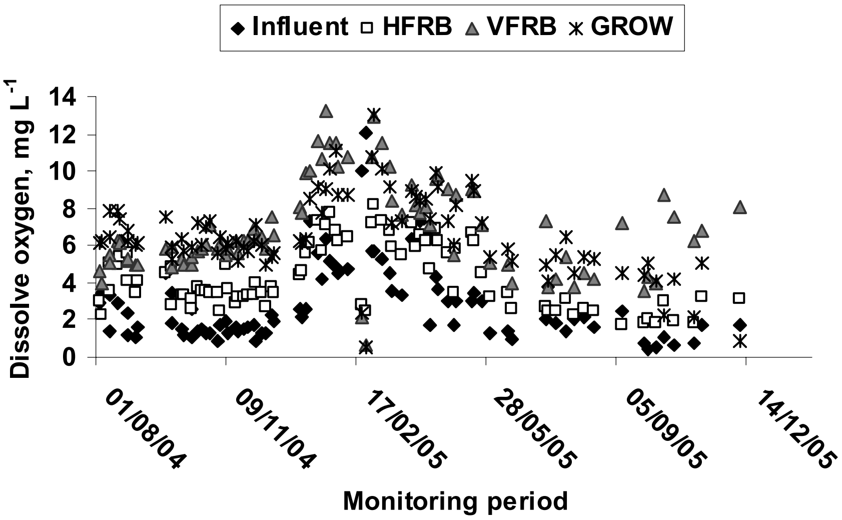


Figure 16: Influent grey water and CW effluent dissolve oxygen during the monitoring period.

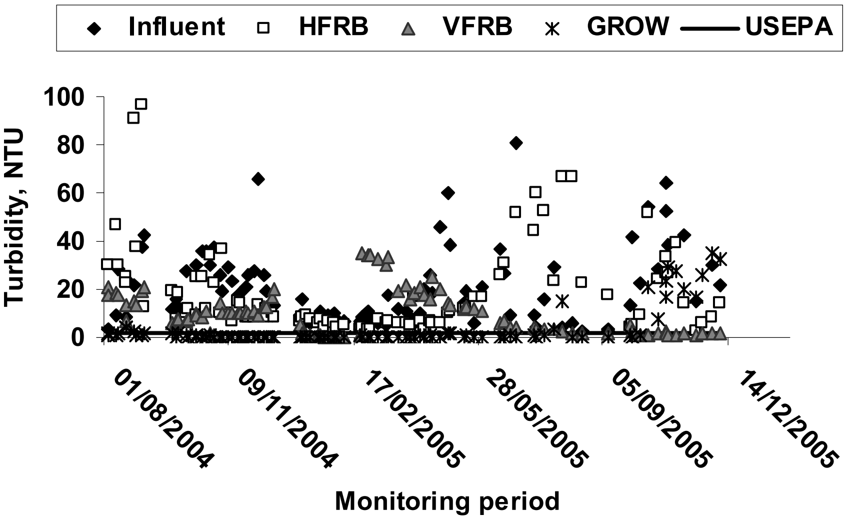


Figure 17: Influent grey water and CW effluent turbidity during the monitoring period.

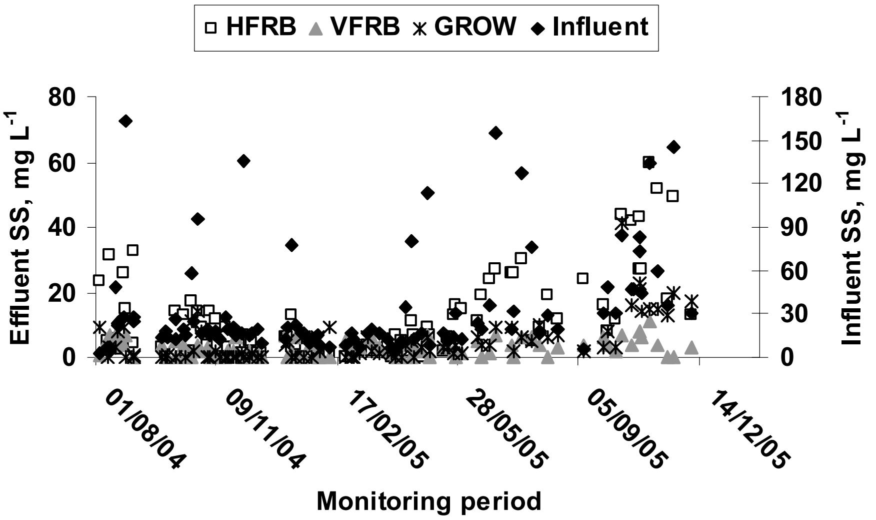


Figure 18: Influent grey water and CW effluent suspended solids during the monitoring period.

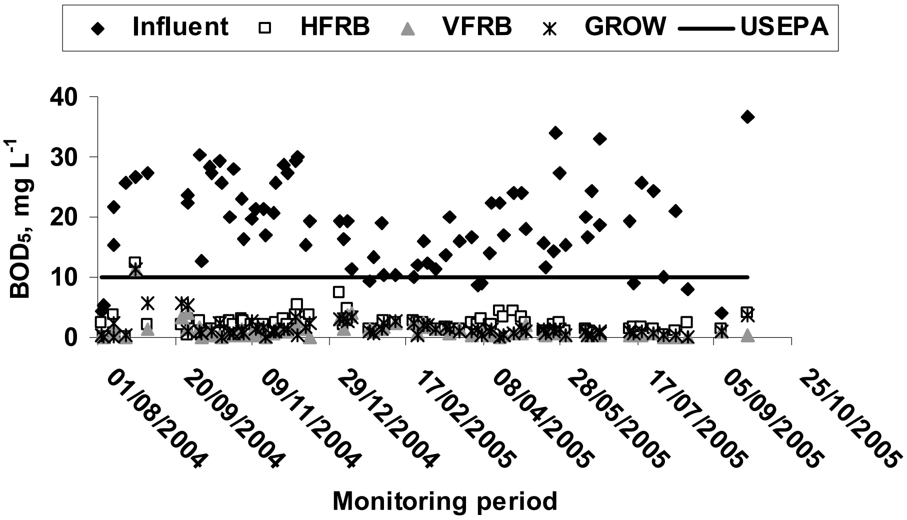


Figure 19a: Influent grey water and CW effluent BOD_5 at low strength during the monitoring period.

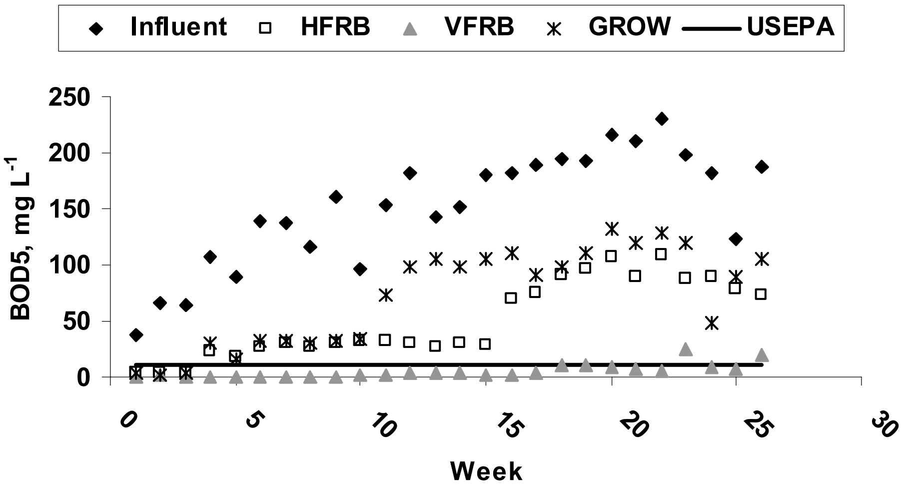


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Figure 19b: Influent grey water and CW effluent BOD_5 at high strength during the monitoring period.

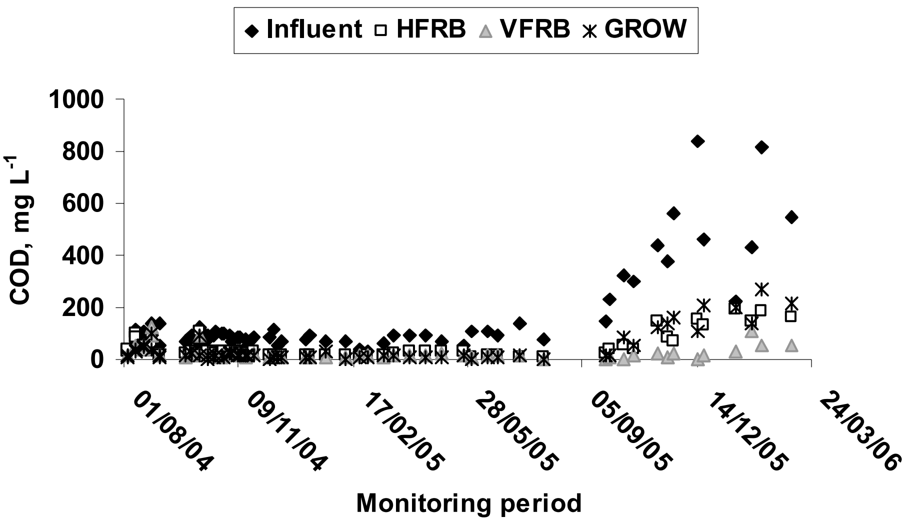

Figure 20: Influent grey water and CW effluent COD during the monitoring period.

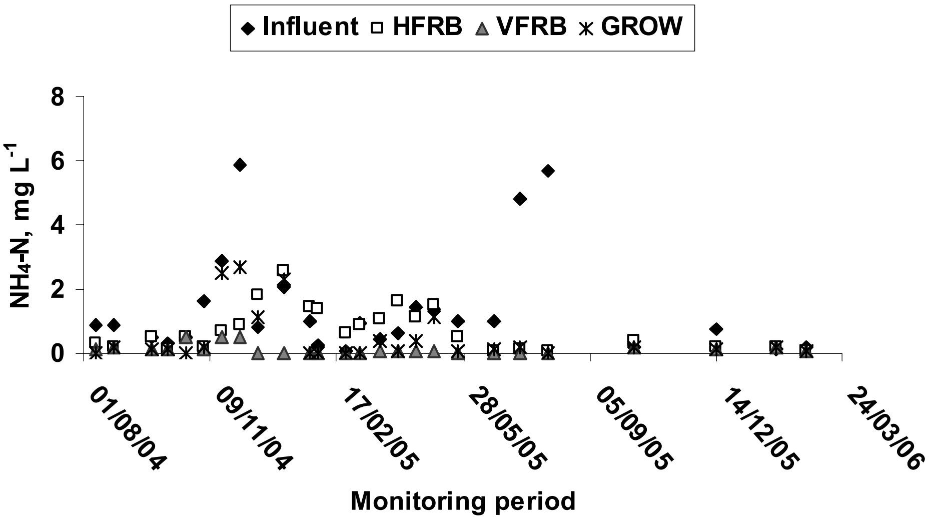

Figure 21: Influent grey water and CW effluent NH4-N during the monitoring period

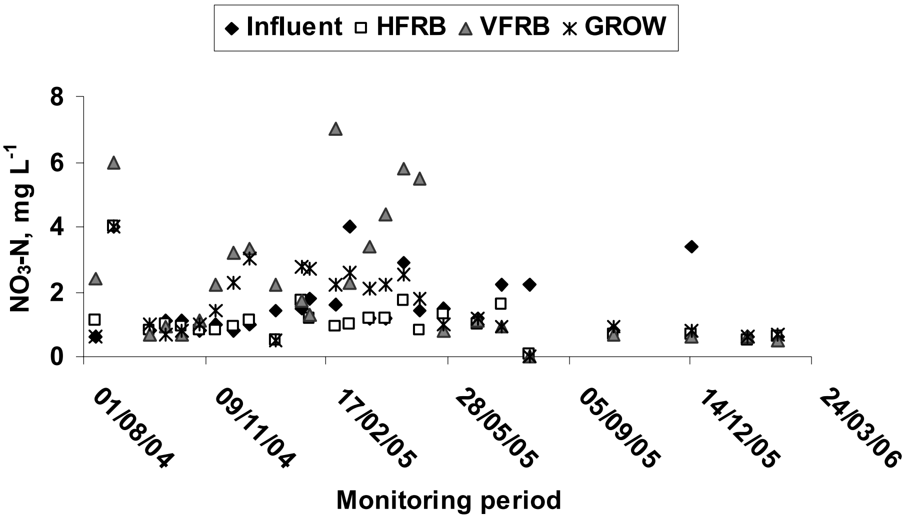

Figure 22: Influent grey water and CW effluent NO_3-N during the monitoring period

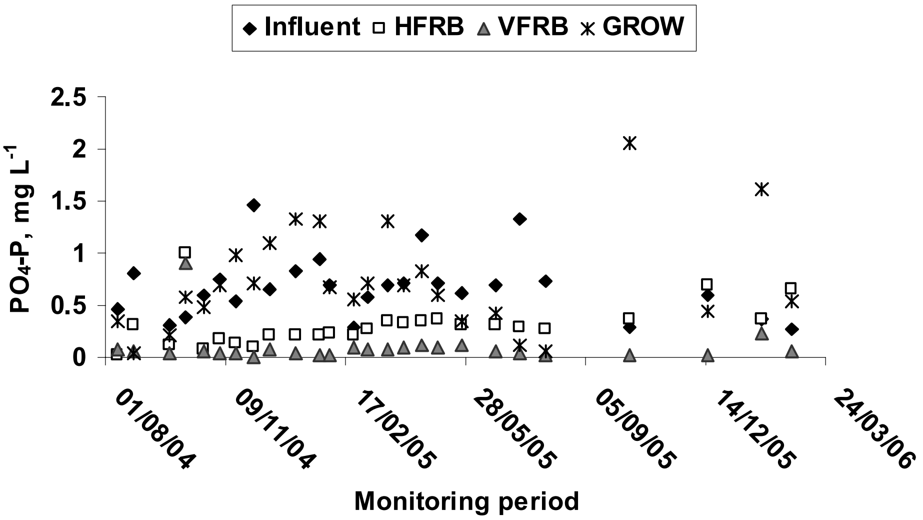

Figure 23: Influent grey water and CW effluent PO_4-P during the monitoring period

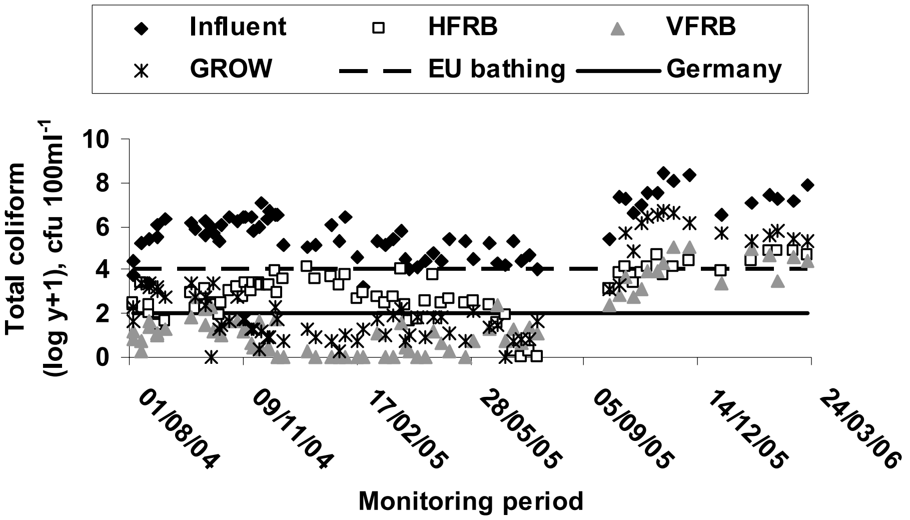

Figure 24a: Influent grey water and CW effluent total coliforms during the monitoring period

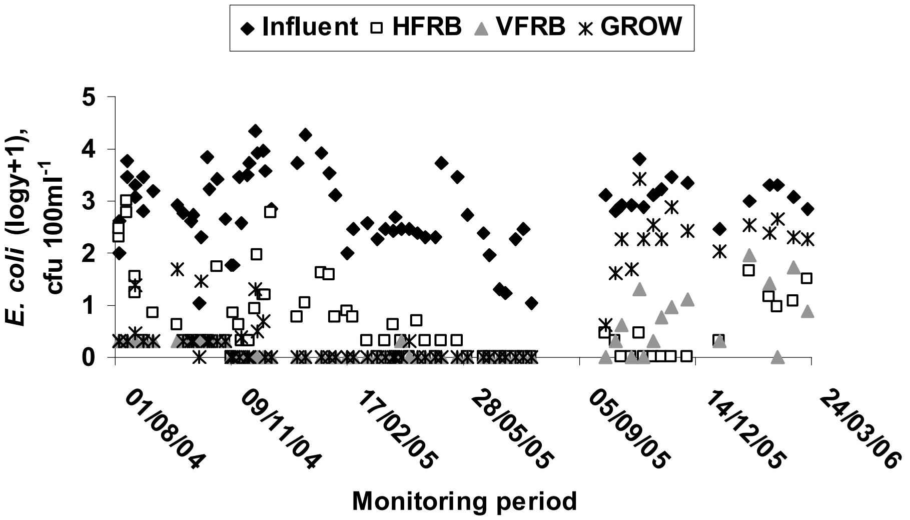

Figure 24b: Influent grey water and CW effluent *E. coli* during the monitoring period

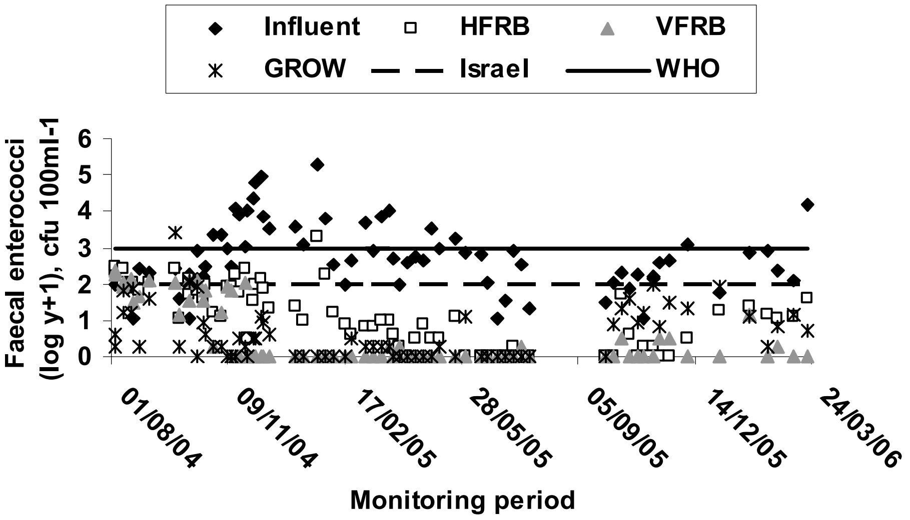

Figure 24c: Influent grey water and CW effluent faecal coliforms during the monitoring period

Appendix 5: EDX and XRD spectra of adsorbents

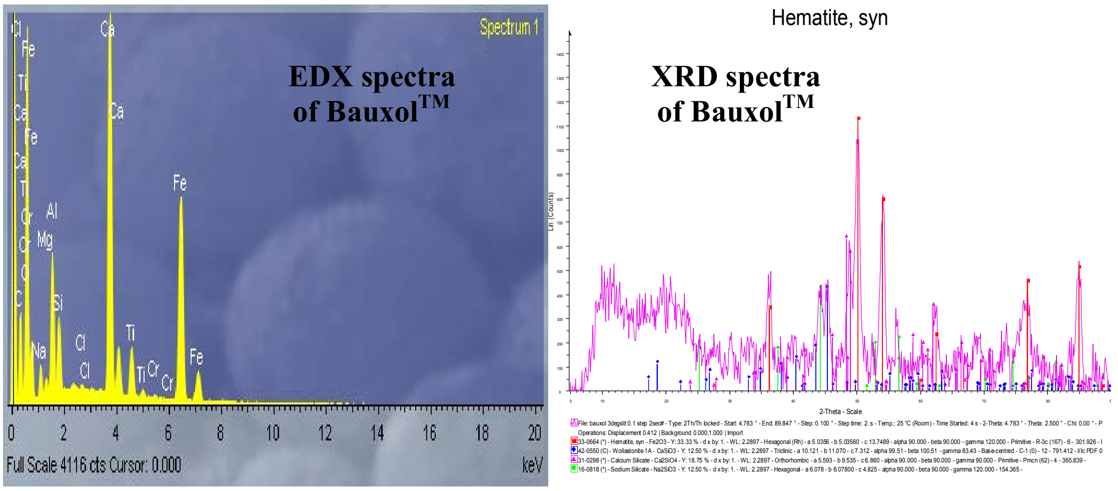

Figure 25: EDX and XRD spectra of Bauxol^{TM}

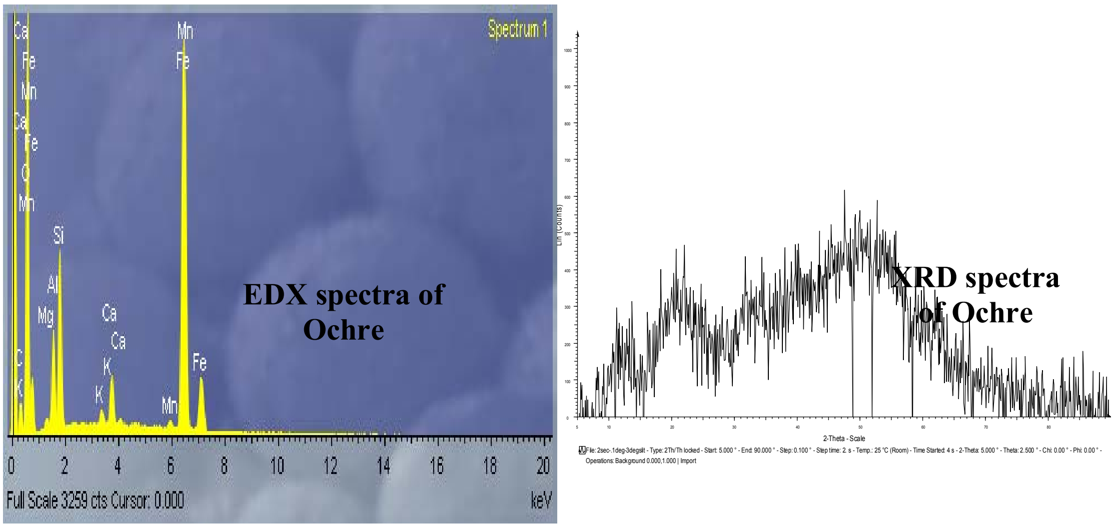

Figure 26: EDX and XRD spectra of Ochre

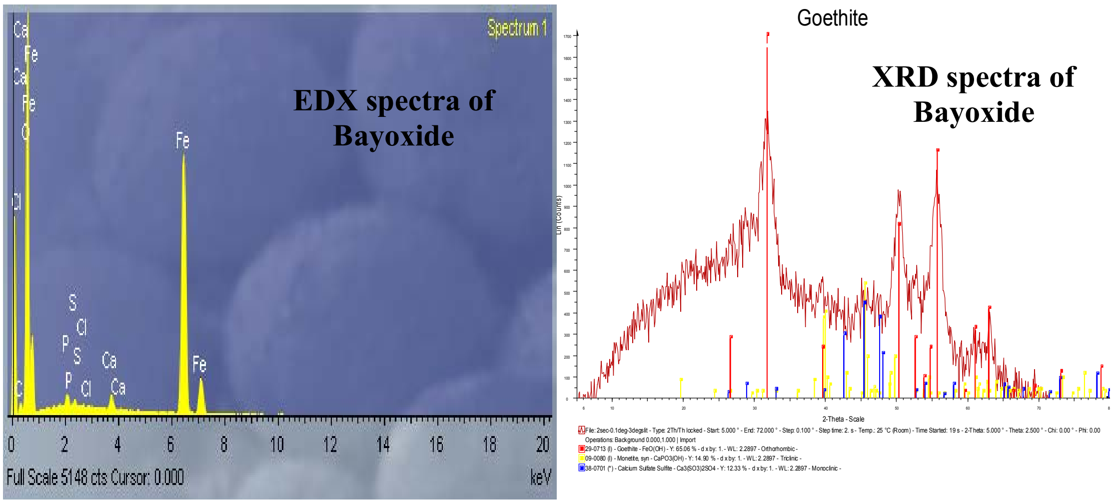

Figure 26: EDX and XRD spectra of Bayoxide

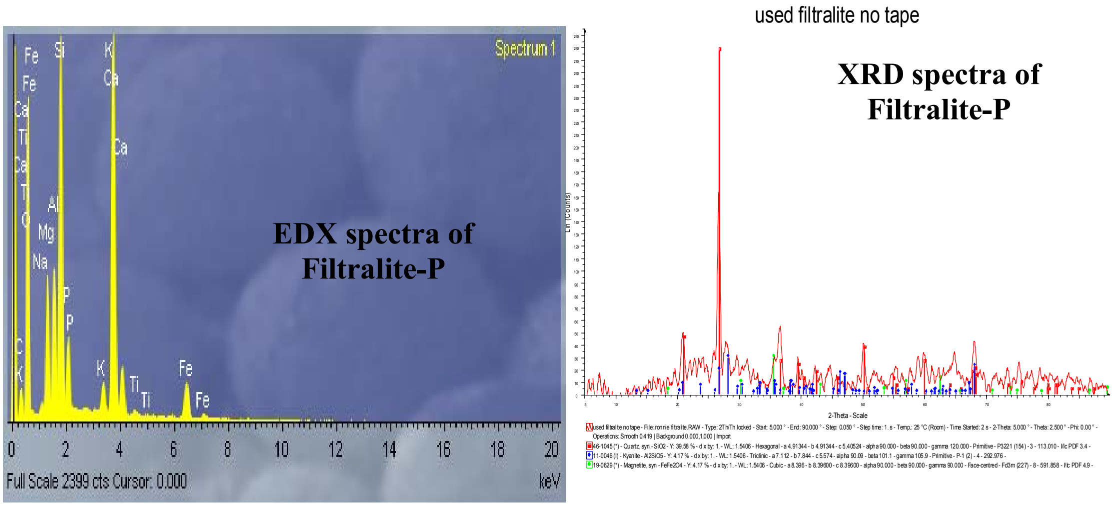

Figure 27: EDX and XRD spectra of Filtralite-P

Appendix 6

Table 2 Composition of adsorbent

Adsorbents	EDX Elemental composition												XRD Chemical composition
	Fe	Ca	Al	Si	Mg	Na	Mn	Ti	K	S	C	O	
Ochre	47	3	1	44	-	-	1	-	-	1	8	37	FeO(OH)*
Bay oxide	55	0.2	-	-	-	0.4	-	-	-	-	4	44	FeO(OH)
Bauxol^{TM}	20	6	5	2	0.3	2	-	3	-	-	18	44	Fe_2O_3,$CaSiO_3$ Ca_2SiO_4
Bauxol	6	19	6	1	1	4	-	2	-	1	-	55	ND
Red mud	15	3	20	2	-	1	-	2	-	-	6	51	Fe_2O_3,$CaSiO_3$ Ca_2SiO_4
Steel slag	5	30	2	2	1	-	1	-	-	-	7	52	Ca_2SiO_4, $FeCO_3$, $CaFeO_3$, $AlFeO_3$,
Filtralite-P	8	3	8	18	3	1	-	-	2	-	4	53	SiO_2, Al_2SiO_5 $FeFe_2O_4$
Zeolite	-	-	-	-	-	-	-	-	-	-	-	-	$KCa_4Si_8O_{20}(OH).8H_2O$, $Ca(Si_7Al_2)O_{18}.6\ H_2O$
Concrete	1	33	1	2	-	-	-	-	-	-	11	53	$CaCO_3$, SiO_2
Dowlow Limestone	-	33	-	-	-	-	-	-	-	-	11	56	$CaCO_3$
Oolitic Limestone	1	16	-	-	10	-	-	-	-	-	11	56	$CaMg(CO_3)_2$
Shell	-	-	-	-	-	-	-	-	-	-	-	-	$Ca_3Si_2O_7$, $CaCO_3$

*- From Heal *et al.*, 2005

Appendix 7

Table 3: Operational and water parameters data of wetlands used for Literature review case study

Q ($m^3 d^{-1}$)	HLR ($m d^{-1}$)	τ (m)	BOD ($mg L^{-1}$)		COD ($mg L^{-1}$)		TSS ($mg L^{-1}$)		NH_4-N ($mg L^{-1}$)		NO_3-N ($mg L^{-1}$)		PO_4-P ($mg L^{-1}$)		TC (cfu 100m L^{-1})		Information	Reference
			In	out	In	out	In	out	In	out	In	out	In	out	In	out		
120	0.024	7.5	116	18.7	167	64.1	53.1	3.3	19.7	14	3.8	2.2	2.9	2.3	1.5×10^6	1.9×10^4	G, SSF	Dahab and Surampalli, 2001
0.16	0.034		38	0.7	47	9.9	31	3.3	4	0.1	2	0.2	3	0.04	1.7×10^5	1.1×10^2	G, SSF	Gonzalez *et al*., 2001
0.25	0.057		38	1.1	47	12	31	1.9	4	0.	2	0.5	3	0.3	1.7×10^5	1.2×1^{62}	G, SSF	Gonzalez *et al*., 2001
3.5	0.088	3.5	157	70.7			108	68									G, SSF	Al-Omari and Fayyad, 2003
2.4	0.06	5	130	58.5			110	69.3									G, SSF	Al-Omari and Fayyad,
3.1	0.78	3.9	135	60.8			77	48.5									G, SSF	Al-Omari and Fayyad,
2.3	0.058	5.2	147	66.2			84	52.9									G, SSF	Al-Omari and Fayyad,
3.9	0.098	3.1	143	64.4			204	128.5									G, SSF	Al-Omari and Fayyad,
4.4	0.11	2.7	163	73.4			133	83.8									G, SSF	Al-Omari and Fayyad,
5	0.125	2.4	185	83.3			180	113.4									G, SSF	Al-Omari and Fayyad,
3.6	0.09	3.3	180	81			81	51.0									G, SSF	Al-Omari and Fayyad,
4.2	0.11	2.9	145	65.3			244	153.7									G, SSF	Al-Omari and Fayyad,
0.86	0.043	7	48.4	23.6	155.2	88.5	133	83.8			0.1	0.4	3.7	2.3			G, SSF	Okurut *et al*., 1999
0.5	0.025	12						113.4			0.1	0.4	3.7	2.3			G, SSF	Okurut *et al*.,1999
0.57	0.025	2.4	74	8			26	7	21	11			0.6	0.5	6.5	5.3	G, SSF	Neraella *et al*., 2000
1.14	0.03	2	177	17					24	18			0.6	0.7	6.7	5.3	G, SSF	Neraella *et al*., 2000
0.85	0.026	2.3	72	9			46	6	84	29			2.2	1.1	6.6	5.4	G, SSF	Neraella *et al*., 2000
0.57	0.012	5.1	120	19			40	12	44	32			1.1	0.8	6.1	5.6	G, SSF	Neraella *et al*., 2000
0.85	0.026	2.3	64	13			28	11	54	44			1.3	1.3	7.3	5.4	G, SSF	Neraella *et al*., 2000
0.85	0.026	2.3	69	10			39	16	49	32			1.7	1.2	6.5	5.3	G, SSF	Neraella *et al*., 2000
0.57	0.025	2.4	126	22			66	6	19	13			0.8	0.6	6.5	5.1	G, SSF	Neraella *et al*., 2000
32.4	0.018	32	625	43.8			62	9.6	63	38			1.1	0.7	7.1	5.1		Nyakango and Van Bruggen, 1999

Table 3 : Contd. 1

Q ($m^3 d^{-1}$)	HLR ($m d^{-1}$)	τ (m)	BOD ($mg L^{-1}$)		COD ($mg L^{-1}$)		TSS ($mg L^{-1}$)		NH_4-N ($mg L^{-1}$)		NO_3-N ($mg L^{-1}$)		PO_4-P ($mg L^{-1}$)		TC (cfu 100m L^{-1})		Information	Reference
			In	out	In	out	In	out	In	out	In	out	In	out	In	out		
0.25	0.013	9.5	82	6.5			95.5	43	40								G, SSF	Tanner *et al.*, 1998
86	0.03	8.9	107	14													G, SSF	Vymazal and Krasa, 2003
0.42	0.022	5.7	82	13.3			95.5	31	40	24			18	14			G, SSF	Tanner *et al.*, 1998
0.53	0.03	4.3	82	12.3			95.5	39	40	26			18	14			G, SSF	Tanner *et al.*, 1998
0.86	0.05	2.9	82	22			95.5	42	40	30			18	16			G, SSF	Tanner *et al.*, 1998
1.2	0.06	2	82	26.4			95.5	54	40	31			18	17			G, SSF	Tanner *et al.*, 1998
1.1	0.02	10	130	56	260	98	28	11	40	33			18	16			G, SSF	Garcia *et al.*, 2004
1.1	0.02	10	130	60	260	97	39	16	61.5	47			24	11			G, SSF	Garcia *et al.*, 2004
1.5	0.3	7.41	130	59	260	100	66	6	61.5	46			24	10			G, SSF	Garcia *et al.*, 2004
1.5	0.3	7.41	130	52	260	91	114	5	61.5	47			24	10			G, SSF	Garcia *et al.*, 2004
1.98	0.04	5.56	130	53	260	94	62	9.6	61.5	44			24	10			G, SSF	Garcia *et al.*, 2004
1.98	0.04	5.56	130	57	260	94	127	19.2	61.5	45			24	10			G, SSF	Garcia *et al.*, 2004
2.48	0.05	2.4	130	37	260	79	95.5	43	61.5	43			24	10			G, SSF	Garcia *et al.*, 2004
13.2	0.32	1.4	78.8	27.5			701	156	61.5	38			24	10			G, SSF	Billore *et al.*, 1999
1.76	0.022	9.1	116	13.9			45.5	5.5									G, SSF	Davidson *et al.*, 1999
2.25	0.028	7.1	117	23.4			125	12.5									G, SSF	Davidson *et al.*, 1999
0.31	0.034	4.5	264	18.5			102	15.3									G, SSF	Davidson *et al.*, 1999
0.1	0.028	5.7	54	16.4			40	17.6									G, SSF	Davidson *et al.*,
	0.022	1.7	194	39.8					38.5	36							G, SSF	Bayley *et al.*, 2003
	0.022	3.5	194	22.7					38.5	31							G, SSF	Bayley *et al.*, 2003
	0.022	5.2	194	14.7					38.5	28							G, SSF	Bayley *et al.*, 2003
	0.022	6.9	194	10					38.5	22							G, SSF	Bayley *et al.*, 2003

Table 3: Contd. 2

Q (m^3 d^{-1})	HLR (m d^{-1})	τ (m)	BOD (mg L^{-1})		COD (mg L^{-1})		TSS (mg L^{-1})		NH_4-N (mg L^{-1})		NO_3-N (mg L^{-1})		PO_4-P (mg L^{-1})		TC (cfu 100m L^{-1})		Information	Reference
			In	out	In	out	In	out	In	out	In	out	In	out	In	out		
	0.022	8.7	194	6.3					38.5	17							G, SSF	Bayley *et al*., 2003
13.2	0.32	1.1	79	27.5					34	7							G, SSF	Billore et al.,
0.12	0.03	8	84	59	484	186	227	39	191				5	2			S, SSF	Kantawanichkul *et al*., 2003
0.24	0.06	4	163	52	512	198	378	8	218	186							S, SSF	Kantawanichkul *et al*., 2003
0.48	0.12	2	120	52	442	197	579	8	158	141							S, SSF	Kantawanichkul *et al*., 2003
0.11	0.03	8	108	40	561	205	356	25	177	182							S, SSF	Kantawanichkul *et al*., 2003
0.23	0.06	4	182	55	554	213	466	10	199	187							S, SSF	Kantawanichkul *et al*., 2003
0.45	0.12	2	142	67	530	289	686	15	151	101							S, SSF	Kantawanichkul *et al*., 2003
13	0.01		73	2													S, SSF	Geller, 1997
	0.04		179	3	288	21											S, SSF	Gschlobi and Stuible, 2000
	0.04		210	8	456	42											S, SSF	Gschlobi and Stuible, 2000
6	0.15	1.5	327	45.8	557	201	272	35.4							4.1×10^6	6.2×10^5	G, SSF	Solano *et al*., 2004
3	0.08	3	327	62.1	557	217	272	27.2							4.1×10^6	6.2×10^5	G, SSF	Solano *et al*., 2004
6	0.15	1.5	327	75.2	557	279	272	25.4							4.1×10^6	4.1×10^4	G, SSF	Solano *et al*., 2004
3	0.08	3	327	49.1	557	150	272	24.5							4.1×10^6	4.1×10^4	G, SSF	Solano *et al*., 2004
6	0.15	1.5	616	185	905	453									3.4×10^6	1.3×10^6	G, SSF	Solano *et al*., 2004
3	0.08	3	616	185	905	217									3.4×10^6	7×10^5	G, SSF	Solano *et al*., 2004
6	0.15	1.5	616	160	905	434									3.4×10^6	2×10^6	G, SSF	Solano *et al*., 2004
3	0.08	3	616	98.6	905	208									3.4×10^6	6.1×10^5	G, SSF	Solano *et al*., 2004
58.6	0.06		90	12	199	55											S, SSF	Geller, 1997

Table 3 : Contd. 3

Q (m^3 d^{-1})	HLR (m d^{-1})	τ (m)	BOD (mg L^{-1})		COD (mg L^{-1})		TSS (mg L^{-1})		NH_4-N (mg L^{-1})		NO_3-N (mg L^{-1})		PO_4-P (mg L^{-1})		TC (cfu 100m L^{-1})		Information	Reference
			In	out	In	Out	In	out	In	out	In	out	In	out	In	out		
15.4	0.02		59	2	143	27											S, SSF	Geller, 1997
17.6	0.02		187	3	349	26											S, SSF	Geller, 1997
16	0.02		111	10	261	53											S, SSF	Geller, 1997
16	0.02		72	7	238	54											S, SSF	Geller, 1997
16	0.02		140	3	300	19											S, SSF	Geller, 1997
30	0.02		211	37	358	96											S, SSF	Geller, 1997
30	0.03		150	9	249	53											S, SSF	Geller, 1997
30	0.05		85	5	202	28											S, SSF	Geller, 1997
30	0.03		42	4	145	24											S, SSF	Geller, 1997
68	0.06		8	3	44	29											S, SSF	Geller, 1997
36.5	0.04		238	29	351	73											S, SSF	Geller, 1997
1.4	0.06	8.5	411	39	1160	190	519	21	185	144	3.7	1.7	28	19			G, SSF	Lee *et al*., 2004
2.96	0.12	4.3	394	56	1160	264	519	6	184	183	1.7	1.1	29	20			G, SSF	Lee *et al*., 2004
0.9	0.04	14.7	343	28	1115	198	873	10	161	151	3.4	1.2	29	18			G, SSF	Lee *et al*., 2004
0.16	0.034		38	1.1	47	7.8	31	3.4									G, SF	Gonzalez *et al*., 2001
0.25	0.06		38	1.2	47	10.9	31	3.6									G, SF	Gonzalez *et al*., 2001
83.5	0.17	2.65																Karpiscak *et al*., 1996
83.5	0.17	2.65																Karpiscak *et al*., 1996
83.5	0.17	2.65																Karpiscak *et al*., 1996
79.2	0.1	6.75																Karpiscak *et al*., 1996
79.2	0.1	6.75																Karpiscak *et al*., 1996
79.2	0.1	6.75																Karpiscak *et al*., 1996

Table 3: Contd. 4

Q ($m^3 d^{-1}$)	HLR ($m d^{-1}$)	τ (m)	BOD ($mg L^{-1}$)		COD ($mg L^{-1}$)		TSS ($mg L^{-1}$)		NH_4-N ($mg L^{-1}$)		NO_3-N ($mg L^{-1}$)		PO_4-P ($mg L^{-1}$)		TC (cfu 100m L^{-1})		Information	Reference
			In	out	In	Out	In	out	In	out	In	out	In	out	In	out		
84.2	0.03	15	3.62	2.54													S, SF	Cameron and Kinsley, 2003
84.2	0.03	15	2.54	1.86													S, SF	Cameron and Kinsley, 2003
42.1	0.03	15	1.9	2.4													S, SF	Cameron and Kinsley, 2003
331.2	0.03	15	12.3	5.8													S, SF	Craig *et al*., 1999
7.5	0.025	12	220	90													S, SF	Geary *et al*., 1999
691	0.38	0.9	7.8	8.2													S, SF	Salati *et al*., 1999
648	0.2	3	7.8	8.2													S, SF	Elias *et al*., 2001
648	0.2	3	4.2	3.93													S, SF	Elias *et al*., 2001
	0.03		29	8													SF	Kadlec, 2003
	0.01		34	5													SF	Kadlec, 2003
	0.013		49	23													SF	Kadlec, 2003
	0.04		50	7													SF	Kadlec, 2003
	0.05		26	10													SF	Kadlec, 2003
	0.05		26	16													SF	Kadlec, 2003
	0.03		20	15													SF	Kadlec, 2003
	0.03		56	15													SF	Kadlec, 2003
	0.003		17	4													SF	Kadlec, 2003
	0.046		19	9													SF	Kadlec, 2003
	0.25		31	8													SF	Kadlec, 2003
	0.009		21	5													SF	Kadlec, 2003
	0.003		27	8													SF	Kadlec, 2003

Table 3: Contd.5

Q ($m^3 d^{-1}$)	HLR ($m d^{-1}$)	τ (m)	BOD ($mg L^{-1}$)		COD ($mg L^{-1}$)		TSS ($mg L^{-1}$)		NH_4-N ($mg L^{-1}$)		NO_3-N ($mg L^{-1}$)		PO_4-P ($mg L^{-1}$)		TC (cfu 100m L^{-1})		Information	Reference
			In	out	In	Out	In	out	In	out	In	out	In	out	In	out		
46.8	0.05		156	39	261	81											S, SSF	Geller, 1997
48.3	0.05		138	6	246	97											S, SSF	Geller, 1997
	0.13		25	14													SF	Kadlec, 2003
	0.03		10	4													SF	Kadlec, 2003
	0.03		16	10													SF	Kadlec, 2003
	0.03		9	5													SF	Kadlec, 2003
	0.55		6	5													SF	Kadlec, 2003
	0.45	4.5	242	246													S, SF	Karpiscak *et al*., 1999
1.95	0.02	12									0.7	6.8	9.9	1.2	3×10^3	26	G	Kern and Idler, 1999
4.06	0.03	15.5									0.6	32	10	5	8.4×10^5	3.3×10^4	G	Kern and Idler, 1999
0.0014	0.021	5											6	0.2			G	Breen, 1997
0.003	0.04	2.5											6	0.2			G	Breen, 1997
0.0014	0.021	5											6	0.2			G	Breen, 1997
0.003	0.04	2.5											6	0.2			G	Breen, 1997
0.23	0.023	10					288.7	83.7									S, SSF	Sousa *et al*., 2003
0.33	0.033	7					288.7	66.4									S, SSF	Sousa *et al*., 2003
0.23	0.023	10					288.7	52									S, SSF	Sousa *et al*., 2003
864	2.2	0.05					309	232										Mandi *et al*., 1998
864	1.44	0.074					309	210										Mandi *et al*., 1998
864	1.	0.1					309	176										Mandi *et al*., 1998
864	0.86	0.15					309	176										Mandi *et al*., 1998

Table 3: Contd.6

Q ($m^3 d^{-1}$)	HLR ($m d^{-1}$)	τ (m)	BOD ($mg L^{-1}$)		COD ($mg L^{-1}$)		TSS ($mg L^{-1}$)		NH_4-N ($mg L^{-1}$)		NO_3-N ($mg L^{-1}$)		PO_4-P ($mg L^{-1}$)		TC (cfu 100m L^{-1})		Information	Reference
			In	out	In	Out	In	out	In	out	In	out	In	out	In	out		
5300	0.24	1.5					3489	523									SF	Burgoon, 2001
5300	0.238	1.5					2950	620									SF	Burgoon, 2001
5300	0.32	1.5					3125	1031									SF	Burgoon, 2001
5300	0.235	1.5					2104	757									SF	Burgoon, 2001
5300	0.21	1.5					2488	323									SF	Burgoon, 2001
0.25	0.8	0.75					50	6									S, SF	Meutia, 2001
0.25	0.8	0.75					48	7.2									S, SF	Meutia, 2001
0.25	0.8	0.75					42	29.8									S, SF	Meutia, 2001
5643	0.06						2218	262									S, SF	Burgoon, 1999
	0.28						144	175									S, SF	Burgoon, 1999
4035	0.04						2838	346									S, SF	Burgoon, 1999
	0.20						200	272									S, SF	Burgoon, 1999
691	0.384	0.9					20.3	4.8									S, SF	Salati *et al.*, 1999
43.2	1.44	5					22	14									S, SF	Salati *et al.*, 1999
86.4	2.9	2.5					23	13									S, SF	Salati *et al.*, 1999
648	0.2	3					20.3	4.8									S, SF	Elias *et al.*, 2001
648	0.2	3					2.9	2.3									S, SF	Elias *et al.*, 2001