REFINERY WASTEWATER TREATMENT USING CONSTRUCTED WETLANDS

By

MUHAMMAD MASUD ASLAM

(2001-NUST-MS-PhD-Env-235)

Institute of Environmental Science and Engineering
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A thesis submitted in partial fulfillment of
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This is to certify that the

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MUHAMMAD MASUD ASLAM

has been accepted towards the partial fulfillment

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We hereby recommend that the dissertation prepared under our supervision by **Mr. Muhammad Masud Aslam** Regn No **2001-NUST-MS-PhD-Env-235**, Entitled: **Refinery Wastewater Treatment Using Constructed Wetlands** be accepted as fulfilling in part of Doctor of Philosophy Degree.

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Dedicated

to

Dr. Ali Muhammad Ch.

And my beloved

Parents, sisters, brother

&

Wife

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All praise to Almighty Allah, Who bestowed man with intelligence and knowledge as well as the sight to observe and the mind to think and judge. Peace and blessings of Allah be upon the Holy Prophet, Muhammad (pearl of my eyes), who exhorted his followers to seek knowledge from cradle to grave.

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Abstract

With the regular discharge of large volumes of wastewater containing excessive accretions of organics, suspended solids, and heavy metals by the Pakistani oil refining industry, over a period of years, major damage has been done to the environment The dearth of a wastewater treatment system, and a lack of economically viable and sustainability-oriented solutions have exacerbated the extent of environmental damage that has taken place so far. As the industry in Pakistan has become progressively circumscribed by increased taxation, inconstant as well ever more expensive electrical power supply, and last but not least, stringent environmental laws, there has arisen a strong need for the development of a treatment technology which is sustainable, efficient and cost effective. As most of the research work on wastewater treatment through constructed wetland treatment system, thus far, has been oriented to the disposal of domestic wastewater, it has transpired that little focus has been directed toward research on the tertiary treatment of refinery wastewater. Therefore, the aim of this thesis, has been to address this gap in wastewater technology research by exploring the utility of constructed wetlands as a possible solution for the treatment of wastewater discharged by the oil refining industry thereby enabling the industry to meet its own guidelines as well as comply with those prescribed by Pakistan National Environmental Quality Standards.

Eight constructed wetlands with dimensions of 1.83 m length × 0.85 m width × 1.0 m depth, the aspect ratio (L:W) being 3:4, having a slope of 1 cm/m from inlet to outlet, filled with coarse gravel and coarse sand planted with *Phragmites karka* and *Typha lattifolia* were developed and tested at pilot scale for wastewater COD, BOD and heavy metals removal. Experiments using actual oil refinery wastewaters from the oil refinery (COD range: 256 – 347 $mgL^{-}1$) were used for the experiment at three different hydraulic loading rates of 1.21, 1.44 and $1.71 m^3/m^2/day$.

The results of the experiments showed evidence of significant sedimentation and filtration within wetland cells because of reduction in velocity due to plants and filter material. In general, suspended solid removal efficiency decreased with the increasing hydraulic loading rates but the removal dissolved solids were stable. Some removal was observed at the start up of the system but as the sediments got saturated with dissolved solids exchange, no significant removal was recorded. Significant removal was observed for the chemical and biological oxygen demand at HLR of $1.23m^3/m^2$/day but as the loading increased, it adversely affected the removal efficiency of the wetland system. It was shown that, comparatively, removal was high in wetlands planted with phragmites and filled with coarse gravel. Significant metal removal was observed in case of *Phragmites karka* planted in sand as compared to *Typha lattifolia* planted in gravel. From the experimental work, it was evident that constructed wetlands planted with *Phragmites karka* and coarse sand combined the advantages thus effectively maximizing performance while being cost-effectively superior over other existing natural treatment systems.

List of Abbreviations

ARL	Attock Refinery Limited
BOD	Biological oxygen demand
cm	Centimetre
COD	Chemical oxygen demand
CPP	Cleaner production program
CW	Constructed wetland
EPA	Environmental Protection Agency
FWS	Free water surface
HFCW	Horizontal flow constructed wetland
HFRBs	Horizontal subsurface flow reed beds
HFS	Horizontal flow system
HLR	Hydraulic loading rate
mm	Millimetre
O&G	Oil and grease
PNEQS	Pakistan National Environmental Quality Standards
RP	Reactive phosphorous
SFS	Subsurface flow system
SS	Suspended solids
TDS	Total dissolved solids
TN	Total nitrogen
TSS	Total suspended solids
VFCW	Vertical flow constructed wetland
VFS	Vertical flow system

Chapter 1

Introduction

1.1 BACKGROUND

The oil refining industry is one of Pakistan’s largest industries, operating with approximately 16 oil-refining units. Although it is based throughout Pakistan, yet the larger companies operate primarily in Punjab and Sindh. An oil refinery usually operates with huge amounts of raw materials and a variety of chemicals, and as a result, consumes large quantities of energy and water. In a well-managed facility, more than 99.5% of the incoming material is accounted for in various products the refinery produces and in the fuel used for its functioning, while the remaining finds its way into the environment, most commonly in the form of pollutants (CPP, 1999).

1.2 OIL REFINING AND ENVIRONMENTAL ISSUES

The major environmental concern associated with oil refineries is untreated wastewater which is causing contamination of water sources. Prior to the introduction of wastewater treatment and reuse, it was a common practice to discharge waste into rivers or onto ground surfaces. However, strict environmental legislation has made polluting wastewater treatment a pressing issue. If these industries failed to comply then many of the presently functioning industries will no longer be acceptable. Stringent regulations are being proposed for sensitive areas especially the drinking water abstraction areas and ecosystems (Schories, 2008).

Chemical composition and process used in refinery wastewater determines the type and concentration of pollutants in a given refinery's effluent. Refineries use large amounts of water as a cooling agent as well as in the refining process. This water picks up waste oil and impurities from the refining process. Some impurities, such as heavy metals, sulfide, and phenols, are in the crude oil itself, while others, such as cyanide, dioxins and furans are produced during the refining process (Figure 1.1). All of these chemicals, even at very low concentrations, can be toxic to aquatic life. The main problem associated with oil-polluted wastewater is its suitable disposal. The refinery wastewater poses grave ramifications for the maintenance of biodiversity. It is important to note at this juncture that the reclamation and reuse of such wastewater can also be instrumental in pre-empting the ubiquitous threat of water scarcity particularly in oil-producing arid regions (Zarooni and Elshorbagy, 2006; Szklo and Schaeffer, 2007).

The key contaminants of concern in oil refinery wastewater fall into various categories i.e. COD and BOD, oil and grease and heavy, metals the brief details of which are as follow: -

a. **Organic Pollutants:** Organic pollution is caused due to release of organic compounds in water sources which during decomposition consume oxygen at higher rate than it can be replenished. This consequently, leads to adverse effects on the aquatic environment by creating an anaerobic environment which effects the habitat, especially the fish. Suspended solids present in wastewater are usually partly organic in nature and settle on the waterbed and ultimately decompose aerobically as well as anaerobically, depending on the prevailing conditions. Usually these solids first consume all the dissolved oxygen available and then start decomposing anaerobically. (Llorens *et al.*, 2009, Matamoros *et al.,* 2007 and Sooknah and Wilkie, 2004).

b. **Oil and Grease:** occurrence of oil and grease in the wastewater block the light transmission of receiving water body thereby inhibiting the process of photosynthesis leading to anaerobic conditions. Due to anaerobic conditions sulphide are converted in to forms hydrogen sulphide that is exceedingly malodorous and toxic at high concentrations (Borghei and Hosseini, 2008). These oil and grease contents may find their way into the soil and water due to unintentional leakage. This poses risk to both human health and the environment because of poor biodegradation rate and the presence of hazardous substances.

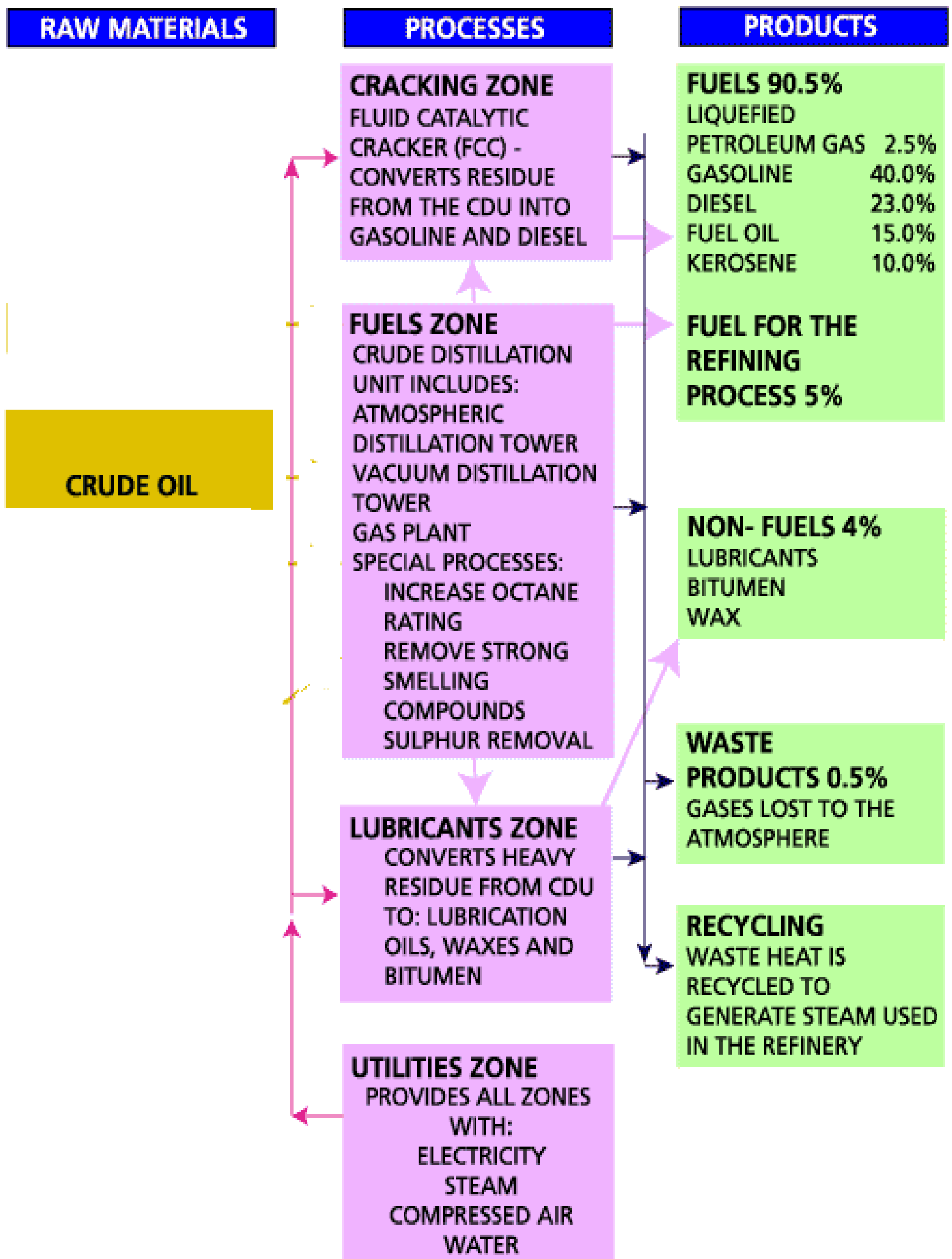

Figure 1.1: Process Flow diagram of manufacturing processes in refinery industry (Source: CPP 1999).

c. **Heavy Metals:** Metals are the main cause of toxicity in industrial pollution and the contamination of ecosystem with heavy metals is a major environmental problem that are produced as a result of oil refining processes (Lee *et al*., 2008). Upon release of untreated wastewater, these are either accumulated in soils or are bio accumulated in the aquatic flora and fuana. Some of these metals are potentially toxic or carcinogenic at sufficient concentrations and can cause serious health hazards if they enter the food chain. For refinery wastewater the disposal of heavy metals (due to their non-degradable nature) requires further safe removal even after wastewater treatment, whereas the utilization of the proposed wetlands would enable the bioaccumulation of heavy metals, thereby reducing the need for further treatment.

1.3 METHODS FOR WASTEWATER TREATMENT

For the sustainability of a healthy environment, treatment of industrial effluents is essential to decrease the threat of downstream water contamination and its uses. Considerable advances have been made in the field of wastewater purification technology, and presently it encompasses a range of low tech as well as high tech solutions. However, in developing countries available wastewater treatment facilities are limited. This is due to a number of reasons, which include costly treatment processes, lack of effective environmental pollution control laws as well as poor implementation of the said laws. A number of conventional and natural treatment systems for wastewater treatment are in use, brief details of which are given below.

1.3.1 Conventional Treatment System

A wide range of treatment methods including stabilization pond systems, septic tanks, activated sludges, trickling filters, anaerobic systems and land application systems are used in developing countries (Canter *et al*., 1982; Von Sperling and Marcos, 1996). The cost of constructing and operating wastewater treatment facilities that accomplish advanced treatment in terms of further BOD_5 or nitrogen removal is high compared to the cost of primary and secondary treatment. The search for an economical approach for polishing effluent and for removing nutrients has caused renewed interest in land application and wetlands application of effluent generated by conventional wastewater treatment facilities.

1.3.2. **Natural Systems: Constructed Wetlands**

Natural systems rely on naturally occurring biological pollutant transformation mechanisms that are facilitated by natural aeration, mixing, solar radiation and storage of potential energy in biomass and soils. The interest in natural systems is based on the conservation of resources in contrast to conventional wastewater treatment processes, which use a lot of energy and chemicals. Among natural treatment systems can be listed oxidation ponds, aerated lagoons, composting and constructed wetlands. However, speaking comparatively, the most successful of such treatment systems, and one, which is in particularly high demand within USA and Canada, is that of constructed wetlands.

Wetlands represent a form of natural treatment system that utilizes the ability of a range of fauna and flora, with a very small input of energy, to remove and stabilise pollutants from water. The U.S. Fish and Wildlife Service (Cowardin *et al*, 1979) describes wetlands as “lands transitional between terrestrial and an aquatic system where the water table is usually at or near the surface or the land is covered by shallow water with attributes at least periodically, like the land supports predominantly hydrophytes; the substrate is predominantly undrained hydric soils; or the substrate is nonsoil (organic matter) with water or covered by shallow water for some time during the growing season each year”.

Wetlands are one of the many types of natural systems that can be used for treatment and pollution control as defined by (U.S. EPA 1993) "a wetland (is) specifically constructed for the purpose of pollution control and waste management, at a location other than existing natural wetlands." Thus, constructed wetlands are the most economical treatment systems due to their low cost of installation and maintenance in optimum climatic conditions.

Constructed wetlands have been described as the "kidneys of the landscape" which filter out pollutants and act as sinks for nutrients by purifying the water through physical (sedimentation, filtration), physico-chemical (adsorption onto plants, soil and organic substrates as well as absorption by flora) and biochemical processes like biochemical degradation, nitrification, denitrification, decomposition and plant uptake (Novotny and Olem, 1994; Mitsch and Gosselink, 1993). At present constructed wetlands treats not only common pollutants but also special parameters such as pharmaceuticals or linear alkylbenzensulfonates generated from oil refineries, chemical factories, pulp and paper production, tannery and textile industries, abattoir, distillery and winery industries (Vymazal, 2009). Therefore, for the purpose of this study, the focus was on a wetland's capacity for pollution control.

1.4. POTENTIAL FOR APPLICATION OF CONSTURCTED WETLANS IN DEVELOPING COUNTRIES

Due to cost effectiveness of constructed wetlands these are widely accepted and are being successfully used for the wastewater treatment over the last decades. In the beginning, constructed wetlands were mainly used for nutrient retention in municipal sewage, storm water and agricultural runoff and later on used for the industrial wastewater treatment (Greenway, 1997: Merlin *et al*., 2002). Due to it being a system that is not only naturally occurring but also cost effective the scope for the application of wetland technology in developing world is enormical. One feasible limiting factor in the use of wetlands for pollution control may be that of land scarcity in dense urban areas; however, constructed wetlands remain suitable for communities and industries having access to vast land areas and natural wetlands. There is limited information on how far wetland technology has evolved in developing countries. In some countries, basic research is being carried out, while in others, the technology has reached pilot and full-scale levels for various applications (Yang *et al.,* 2008).

Research to evaluate the potential of constructed wetlands for wastewater treatment as economical technology has motivated obtaining engineering data as to the biological physico-geochemical constraints. Although there are more than 650 natural and constructed wetland systems in North America and above 5000 subsurface flow constructed wetlands in Europe for wastewater treatment (Kadlec and Knight, 1996: Vymazal, 1998). It is evident that the guidelines for these systems may not be directly transferable to the environment in Pakistan. For instance, aquatic plants suitable for use in European and North American constructed wetlands (CWs) may not be well suited to Pakistan.

1.5 RATIONALE

Keeping in view the damage wrought upon the environment by existing oil refining practices, this study has been designed and implemented to explore the potential of constructed wetlands as a form of pollution containment under the environmental conditions of Pakistan. Theoretically possibility does exist to indigenously develop and use constructed wetland design for refinery wastewater treatment based on local parameters and resources with a concomitant understanding of the biological, hydraulic and chemical processes involved. Since information concerning tropical plant species suitable for sustainable CW development is limited, there is a need to further assess their tolerance to wastewater pollutant levels, their suitability in regional climatic conditions and their functioning under local environment containing refinery wastewater.

1.6. AIMS AND OBJECTIVES

A review of relevant literature reveals that constructed wetlands have a great potential to be used as wastewater polishing facility for refinery wastewater treatment. Previous studies show that it has effectively reduced the chemical oxygen demand (COD), biological oxygen demand (BOD_5), total dissolved solids (TDS) and total suspended solids (TSS) in case of domestic, industrial wastewaters, landfill leachate and paper mill effluent, where it is used as a component and also for full-fledged treatment.

In developing countries like Pakistan, there is a need for research to contribute to the development of cost-effective treatment technologies like constructed wetlands for wastewater treatment, while taking into account various operational parameters. Therefore, to better understand the role of plants and fill materials with different hydraulic loading rates in constructed wetlands for refinery effluent treatment, there is a strong need to explore the treatment's potential and to identify and optimize various operating parameters.

The perceived advantages of Constructed Wetlands (CW) are:

1. Superior organic removal efficiency with lower cost of constructed wetlands;
2. Existing wetlands can be voluntarily iterated;
3. Economical capital cost and low operational & maintenance cost and
4. Achievable discharge standards set by environmental regulatory authorities.

a. **Aim**

The aim of this research is to investigate the possibility of using constructed wetlands for secondary treatment of refinery wastewater by including the appraisal of the role of wetland plants and fill materials in this process. This research project should contribute to improvements in the design and operation of these systems in wastewater treatment applications. Accordingly, it has been investigated the treatment efficiency of surface flow wetlands when fed with a refinery wastewater having similar carbon BOD and heavy metals concentration.

b. **Hypothesis**

Fill materials like coarse gravel and coarse sand are responsible for the filtration and adsorption of heavy metals in wetlands. Furthermore, plants like *Pharagmites karka* and *Typha lattifolia* are likely to be involved in the major processing of wastewater treatment. However, only two plants and fill materials have been studied, since the latter are a highly diverse group whose study would be too complex to include in this research.

c. **Objectives**

The research is structured into two sets of objectives: those related to the parameters involved in the operation of wetlands and those concerning the role of plants and fill materials in the treatment of wastewater. Based on the hypothesis, the fill materials and plants were assumed key players in the treatment of refinery wastewater in five wetlands. Therefore, following are the major objectives of this study:

1. To study the effect of various operating parameters on the removal efficiency of organic matter and heavy metals from refinery wastewater.

1.1 To assess the feasibility of using various locally available reeds i.e. *Phragmites karka* and *Typha latifolia* for treatment of wastewater.

1.2 To assess the treatment efficiency of wetland with coarse sand and coarse gravel as fill material.

1.3 To investigate the treatment response of constructed wetlands to varying degrees of hydraulic loading rates.

2. To develop a standard design applicable to Pakistan environmental conditions that would be custom designed and site specific.

Chapter 2

Review of Literature

2.1. General

The treatment of refinery wastewater through an economical method is a cause for growing concern because of the eco-toxicological effects, mainly caused by the discharge of untreated effluents from processes employing a variety of chemicals. Many “natural systems” have been considered for the purpose of wastewater treatment and interest in such systems is based on the conservation of resources associated with these systems as opposed to the conventional wastewater treatment processes, which are intensive with regard to the use of both energy and chemicals.

Wetlands represent a form of natural treatment system that utilizes the ability of a range of fauna and flora, with a very small input of energy, to remove and stabilise pollutants from water. These systems are particularly appealing for the treatment of wastewaters in developing countries, where economy and simplicity are of paramount importance. Even though the potential for application of wetland technology in the developing world is enormous, the rate of adoption of wetlands technology for wastewater treatment in those countries has been slow (Kivaisi, 2001). Historically the discharge of wastewater to natural wetlands has been carried out for the past one hundred years which is approximately same time frame when sewage collection started. However, it was not until 1952 that these were used in Germany, at the Max Planck Institute in Plon, as a formal means of wastewater treatment by two German scientists, Seidel and Kickuth (Moshiri, 1993). These first constructed wetlands, planted with bulrushes, were used to treat phenolic and dairy wastewater.

This technology spread to the rest of Western hemisphere in 1970s, and it has been used extensively all over the world since the mid-eighties. Nevertheless, constructed wetland systems are still a nascent technology and knowledge and experience of using these are rather limited. For this reason, extensive research needs to be carried out on the mechanisms of removal of different pollutants and on wetland operation under various conditions, so that the secrets within these “black-boxes” can be gradually unfolded (Kadlec and Knight, 1996; Haberl, 1999).

Conventional treatment systems (e.g. activated sludge, trickling filters, rotating biological contactors) although are based on natural biodegradation of pollutants, yet eventually rely on non-renewable energy sources. Natural treatment systems use renewable energy sources (namely solar radiation, kinetic energy of wind, energy of rainwater, surface water and groundwater) and also possess mechanisms of storing potential energy in biomass and soils, which makes these more economical and easier to operate. These are also not sensitive to variations in organic loading of the feed and also provide various secondary benefits (e.g. enhance the habitat, appear aesthetically pleasing), all of which make them attractive treatment alternatives whenever land area is not an obstacle, such as in small communities in developing countries (Pinney *et al.*, 2000; Shutes, 2001; Vymazal, 2002).

Being low-cost and low-technology systems, eco-technological approaches like “Constructed Wetlands” (CWs) are now emerging as potential alternatives or supplementary systems for the treatment of municipal, industrial, agricultural wastewater as well as storm water (Kadlec and Brix, 1995; Cooper *et al.*, 1996). Recently, as a result of transfer of the knowledge, technical collaboration and co-operation by the developed countries, a variety of applications for CW technology for water quality improvement have also been implemented in developing countries like China, Kenya, Mexico, Nepal, Nicaragua, Tanzania, Uganda, India, Morocco, Iran, Thailand, and Egypt (Haberl, 1999). In similarity to other developing countries, there is a great need for simpler, cost effective, more reliable, effective and practical wastewater treatment alternatives in Pakistan.

2.2 Constructed Wetlands

2.2.1. Overview

Constructed wetland are engineered wastewater treatment systems comprising cells filled with porous media and planted with emergent wetland plants such as cattails, bulrushes and reeds. The systems are designed to maximize physical, chemical and biological abilities of natural wetlands to reduce the biochemical oxygen demand (BOD), total suspended solids (TSS), total nitrogen (TN), phosphorus and pathogens, as wastewater flows slowly through the vegetated subsurface. Bioaccumulation, biotransformation and biodegradation of metals are also possible.

The mechanisms of pollutant removal in these systems include both aerobic and anaerobic microbiological conversions, sorption, sedimentation, volatilization and chemical transformations (Kadlec and Knight, 1996). Literature suggests that constructed wetland would be ideal for treatment facility for wastewater because their performance is comparable to conventional wastewater treatment plants.

2.2.2. Types of constructed wetlands

Constructed wetlands are designed to take advantage of many processes that occur in natural wetlands but within a more controlled environment (Hammer, 1989). The basic classification of these natural systems is based on the type of water flow regime, i.e. free water surface, sub-surface horizontal and vertical flow systems.

a. Free Water Surface Systems (FWS)

These systems typically consist of basins or channels, with some sort of subsurface barrier to prevent seepage, soil or another suitable medium to support the emergent vegetation, and of water at a relatively shallow depth flowing through the unit. The shallow water depth, low flow velocity and presence of plant stalks and litter regulate water flow especially in long, narrow channels minimize short circuiting (Ji *et al*., 2007, Brix 1997).

b. **Subsurface Flow Systems (SFS)**

These systems are essentially horizontal trickling filters using rock media. These have the added component of emergent plants with extensive root systems within the media. Systems with sand or soil media are also used. Soil media systems designated as the Root-Zone-Method (RZM) have been developed in West Germany (Vohla *et al.,* 2007, Bigambo and Mayo, 2005, Kaseva, 2004). Wastewater treatment in subsurface flow constructed wetlands with gravel media and emergent macrophytes is carried out via a complex set of chemical, physical and biological reactions (Hammer, 1989; Shutes, 2001).

c. **Horizontal Flow Systems (HFS)**

Subsurface system is also called horizontal flow system (HFS) because wastewater is fed at the inlet and flows horizontally through the bed to the outlet (Garcia *et al*., 2004, Luederitz *et al*., 2001, Mashauri *et al* 2000).

d. **Vertical Flow Systems (VFS)**

These systems are similar to free water surface systems but VFS are fed intermittently and the flow regime is directed vertically through the bed via a network of drainage pipes (Moshiri, 1993; Cooper *et al*., 1996; Kadlec and Knight, 1996; Vymazal *et al*., 1998; Haberl, 1999)..

2.2.3. **Types of fill materials**

a. **Sand**: This is a granular material of fine minerals comprising particles or granules ranging in diameter from 0.06 to 2 millimeters. Sand is commonly divided into five sub-categories based on size, i.e. very fine sand (0.05 - 0.1 mm), fine sand

(0.1 - 0.25 mm), medium sand (0.25 - 0.5 mm), coarse sand (0.5 - 1.0 mm), and very coarse sand (1 - 2 mm). The most common constituent of sand is silica (SiO_2), usually in the form of quartz which, due to chemical inertness and considerable hardness, is resistant to weathering.

Intermittent sand filter may have the potential to treat dairy parlour washings effectively and has been used in the dewatering of swine wastewater to increase settlement of suspended solids (SS) and organic compounds (Vanotti *et al*., 2005) and in the treatment of detergent and milk fat wastewaters (Liu *et al*., 1998, 2000, 2003). As mentioned above, previous experimental work provides important information about the suitability of sand for use as media in constructed wetlands (Arias *et al*., 2001, Piotr *et al.,* 2006 and Healy *et al*., 2006).

b. **Gravel:** Gravel is rock that is at least two millimeters (2mm) in diameter and is mostly in the form of creek rocks which are generally rounded, semi-polished stones, potentially of a wide range of types, which are dredged or scooped from river beds and creek beds. It is also often used as concrete aggregate material (Liang *et al*., 2003, Giraud *et al*., 2001 and Arias *et al*., 2001). Gravels in wetlands provide an attachment surface for the micro organisms and for ion-exchange process thus promotes settling of suspended solids and filtration of larger particles.

2.2.4. **Types of Plants**

Phragmites, *Typha* and *Juncus* are the macrophytes that are widely used within treatment wetlands in Europe and Northern America. The more significant functions of these plants are to enrich their substrate with oxygen to reduce filter erosion and to modify texture as well as hydraulic conductivity of the substrate by root and rhizome growth alongwith the key role of transferring oxygen to the root zone.

The plants provide an attachment surface for the microorganisms in rhizomes and roots alongwith channels for the release of gaseous by-products from the wetland (e.g. H_2S, CH_4). They also provide shading and insulation of the surface; reduce fluid in the wetland through evapotranspiration; and, evidently, allow the creation of open channels for the water to go through (e.g. by disturbing and loosening the media) (Tanner *et al.*, 1998; Kadlec *et al.*, 2000). The microbial communities on plants are the mediators for most of the transformations taking place in wetlands and they also indirectly affect some reactions, by influencing the environmental conditions in a system (e.g. redox potential, pH) (D'Angelo and Reddy, 1999).

a. **Phragmites**

Phragmites australis, the Common Reed is a large perennial grass native to wetland sites throughout temperate and tropical regions of the world. It commonly spreads, up to a square kilometer or more (known as reedbeds) and grows up to 2 - 6 m in height in hot summers and fertile growing conditions. Reeds (*Phragmites communis*) are tall annual grasses with an extensive perennial rhizome. Reeds have been used in Europe in the root-zone method and are the most widespread emergent aquatic plants. Systems utilizing reeds may be more effective in the transfer of oxygen because the rhizomes penetrate vertically, and more deeply than cattails (Neralla *et al.*, 2000, Wood, 1995 and Bastviken *et al*., 2005).

b. **Typha**

Typha latifolia (Broadleaf Cattail, Common Cattail) is a perennial plant of the genus *Typha*, which grows in temperate, subtropical and tropical areas throughout the Northern Hemisphere. Common cattail is usually found in shallower water than narrow leaf cattail, 1.5 to 3 meters high and has 2-4 cm broad leaves. These are ubiquitous in distribution, hardy, capable of thriving under diverse environmental conditions, and easy to propagate and thus represent an ideal plant species for constructed wetlands. They are also capable of producing a large annual biomass and provide a small potential for N and P removal, when harvesting is practised (Sundberg *et al*., 2006, Pantip and Nitisoravut, 2005 and Poach *et al*., 2003).

2.2.5. **Hydraulic Loading Rate**

One of the principal parameters used in wastewater system design is the hydraulic loading rate. The recent criteria for estimation of loading rate are empirical and either based on a percolation test or textural analysis of soil (USEPA 1980). The hydraulic loading rate is also a critical constructed wetland system design parameter that integrates constructed wetland's system hydraulic and treatment performance. Wastewater loading rates are increasingly based on soil physical properties, particularly structures and texture (Gross *et al*., 2007; Tyler and Converse, 1994).

The design criteria for constructed wetlands vary according to the wastewater to be treated and to the treatment objectives. As a result, hydraulic retention times vary greatly amongst wetlands, ranging between 2 and 20 days. In general, shorter retention times can be used when the wetland is going to be used for secondary or even tertiary treatment or when it is used for design objectives other than wastewater treatment (e.g. habitat enhancement). Longer retention times are needed when the organic load of wastewater is high (Pinney *et al*., 2000). Important factors in predicting hydraulic conductivity characteristics are the pore geometry, pore size, shape and continuity of soil pores. The performance and duration of these systems varies according to their design and operating conditions (organic and hydraulic loading rates). However, in general, an average lifetime of 20 years is reported. The observed removal efficiencies in successful systems have been of the order of over

90% for pathogens, 80% or more for organic material and suspended solids and below 60% for nutrients removal (Shutes, 2001).

2.2.6. **Wastewater quality parameters**

a. **Organic contaminants**

Municipal and industrial wastewaters contain variable concentrations of synthetic organic compounds. During 1960 -1970, environmental researchers became aware of the tendency of some organic contaminants to resist removal in conventional wastewater treatment and to persist in the environment for very long periods. A more disturbing observation was that persistent and toxic compounds were found to accumulate in food chains because of the tendency of such compounds to be fat-soluble (Mantovi *et al*., 2003).

A compound can disappear from solution in an aqueous system by means of a number of mechanisms. The mechanisms include: biological, chemical, physical, photochemical alternatives and physicochemical processes such as absorption, sedimentation and evaporative stripping. Biological degradation of easily degraded organic compounds is considered the most important of these. Absorption of trace organics by organic matter and clay particles present in the treatment system is thought to be the primary physicochemical mechanism for removal of refractory compounds in wetlands and aquatic plant systems (Meuleman *et al*., 2003 and Ciria *et al*., 2005).

b. **Suspended Solids**

Industrial influents into wetlands may contain significant quantities of suspended solids depending upon wastewater type. Pond effluent suspended solids are likely to be predominantly algal cells and will be high in organic content. Total suspended solids are both removed and produced by natural wetland processes. The predominant physical mechanisms for suspended solids removal are flocculation, sedimentation, filtration and interception. Whereas suspended solids production within the wetland may occur due to death of invertebrates, fragmentation of detritus from plants, production of plankton and microbes within the water columns or attachment to plant surfaces, and formation of chemical precipitates such as iron sulfide. Water velocities are too low to re-suspend settled particles from bottom sediments or from plant surfaces. Furthermore, fully vegetated wetlands provide excellent stabilization of sediments by virtue of sediment detritus and root mats (Okurut *et al*., 1999, Hench *et al*., 2003 and Al-Omarie and Manar, 2003).

c. **Heavy Metals**

Heavy metals are common environmental pollutants that are produced as the result of industrial, commercial and domestic activities. New pre-treatment standards require some industrial discharges, such as electroplating and metal finishing operations, to limit heavy metal levels to very low residual concentrations. The goal of treatment for heavy metals is to remove the metals from the larger environment and from the food chain, especially the food chain in rivers and ocean waters. The heavy metals are deposited in landfills or wetlands depending on how these are removed (Kjellin *et al*., 2006, Maine *et al*., 2006 and Hadad *et al*., 2006).

Constructed wetlands (SFS) at Santee, California received municipal wastewater which was spiked with the heavy metals such as copper, zinc and cadmium. At hydraulic retention times of 5.5 days, removal efficiencies were 99, 97, and 99 %, respectively and attributed to precipitation-adsorption phenomena. Chemical precipitation is enhanced by wetland metabolism, especially of algal cells which deplete the dissolved CO_2 and raise the pH. Metal removal in constructed wetlands was significant. In one case, metals removal in a water hyacinth system was 85 % for cadmium, 92 % for mercury and 60 % for selenium (Manios *et al*., 2003).

2.2.7. Types of Wastewater

Wetlands are used all over the world to remove organic matter, nutrients, metals, suspended solids and pathogens from domestic wastewaters from both the small and large communities (Barrett *et al*., 2000; Pinney *et al.*, 2000; Vymazal *et al.*, 2000 a; Decamp and Warren, 2001; Koottatep *et al.*, 2002; Stott and William, 2002; Vymazal, 2002). These have also been used as part of a treatment chain, for the management of agricultural and farming runoff (e.g. swine and dairy effluents; Hunt and Poach, 2000) the treatment of industrial wastewaters (e.g. from refineries, electroplating and textile production; (Kadlec *et al.*, 2000), acid mine drainage (Shutes, 2001) and high strength wastewaters (e.g. landfill leachate; Kadlec *et al.*, 2000; Shutes, 2001). With all these unquestionable advantages, wetland creation and restoration is being widely promoted across a wide range of climates and geographical locations.

2.3. Types of Constructed Wetlands Based on Flow Direction

a. Vertical flow constructed wetlands

Since the 1950s, constructed wetlands with different configurations, scales and designs have been used effectively all over the world for the treatment of municipal, industrial and agricultural wastewater, as well as storm water. This is due to their high nutrient capturing capacity, simplicity, low construction operation and maintenance costs, low energy demand, process stability, low excess sludge production, effectiveness and potential for creating biodiversity. The most widely used constructed wetland configurations are the free water surface wetlands (like pond systems) and subsurface flow wetlands (like-filters), where water does not have a free water surface. (Moshiri, 1993; Cooper *et al*., 1996; Kadlec and Knight, 1996; Vymazal *et al*., 1998; Haberl, 1999).

Now a days, vertical flow subsurface constructed wetlands with intermittent feeding are state-of-the-art in Europe due to their advantages over other designs. Vertical flow constructed wetlands have more equal root distribution and water-root contact and fewer problems of bad odor and proliferation of insects since they do not have a free water surface (Haberl *et al.*, 1995; Cooper, 1990). Even though vertical flow constructed wetlands have been mainly used for the removal of carbonaceous oxygen demand, total suspended solids and coliform bacteria, there is growing interest in their use for nitrogen and phosphorus removal as well.

Grey water used for irrigation is becoming more common which is an environmental hazard and poses a serious risk. This necessitates the development of a cost effective, low-tech and easily maintainable treatment system to have a sustainable use of grey water for irrigation. (Gross., *et al*, 2007). For the treatment, a combination of vertical flow constructed wetland with water recycling and trickling filter was developed resulting in the establishment of recycled vertical flow constructed wetland (RVFCW) which facilitates hydraulic parameters and feasibility to assess the environmental effects of treatment through the analysis of soil and plant parameters. The RVFCW was efficient for removing suspended solids and biological oxygen demand, and about 80% of the chemical oxygen demand after 8 h. The resulting treated grey water had no significant negative impact on plants or soil during the study period leading to the conclusion that the RVFCW is a sustainable and potential treatment system for grey water, which can be operated and maintained by unskilled operators.

Korkusuz., *et. al*. (2006) replicated a lab scale study at field level by using blast furnace granulated slag (BFGS) in a vertical subsurface flow constructed wetland (30 m^2), planted with *Phragmite*s *australis.* This was implemented to treat primarily treated domestic wastewater, at a hydraulic rate of 100 mm d^{-1}, intermittently. Results showed that average influent and effluent total phosphorus (TP) concentrations were 6.61 ± 1.78 mg L^{-1} and 3.18 ± 1.82 mg L^{-1}; respectively. It was found that main sites for P-retention were the loosely bounded Ca and P in alkaline conditions (average pH > 7.7) and higher Ca content of soil.

Vertical flow constructed wetlands (VFCWs) proved successful in France where design of VFCWs was based on organic load along with storm water intrusion (Molle *et al*., 2006). Pollutant removal in the pilot and full-scale studies depend on infiltration rate (IR) pressure head profiles which is explained by the hydraulic behaviour of the filter and the role of reeds. Consequently, this resulted in development of new hydraulic limits with accompanying sizing rules and operational recommendations resulting in compliance with the European standards.

Vymazal (2005) has critically reviewed the evolution of constructed wetlands using macrophytes for wastewater treatment. It was reported that horizontal sub-surface flow constructed wetlands (HF CWs) were initiated in the early 1960s and improved under the name Root Zone Method in late 1960s and early 1970s and spread throughout Europe in 1980s and 1990s. However, cohesive soils got clogged quickly because of low hydraulic permeability which were replaced by more porous media such as gravel in late 1980s in the United Kingdom, which is a design feature still in use. Previous studies showed that HF CWs provided high removal of organics and suspended solids but removal of nitrogen was limited by anoxic/anaerobic conditions in filtration beds, which did not allow for ammonia nitrification. In order to improve the treatment efficiency, various types of constructed wetlands were combined resulting in formation of hybrid systems, which most frequently comprised vertical flow (VF) and HF systems arranged in a staged manner.

To meet the treatment requirements for single houses and dwellings in rural areas through constructed wetlands (Brix and Carlos., 2005), the Danish Ministry of Environment have recently been published Guidelines. According to these guidelines surface area of the filter bed is 3.2 m^2/person equivalent and the effective filter depth is 1.0 m. The filter medium must be filter sand with a d_{10} between 0.25 mm, a d_{60} between 1 - 4 mm, and a uniformity coefficient ($U = d_{60}/d_{10}$) less than 3.5. The sewage is to be pulse-loaded on the surface of the bed using pumping and a network of distribution pipes while the mixing of chemicals is done by airlift pump, which also circulates water in the sedimentation tank. The vertical flow constructed wetland system developed on these guidelines proved an economical option and provided efficient treatment of sewage for discharge into the aquatic environment.

In vertical-flow wetlands (VFWs), orthophosphate removal from wastewater occurs successfully through reaction rates of sorption to substratum, biofilm assimilation and macrophytes uptake and P removed by substratum sorption, or non-reactive P (NRP) formation, can be returned as reactive phosphorus (RP) (Lantzke *et al*., 1999). In the upper surface of constructed wetland system, environmental temperature change cause daily mixing while prevailing soil temperature gradients limited below-ground mixing resulting in better treatment efficiency from a planted wetland mainly due to retention times. It is operationally dependent on RP concentration and mixing, and as substratum Fe (III) oxide–hydroxide is prevailing in these systems, the system is made highly efficient by providing additional assimilation for some years.

Two vertical flow constructed wetlands have been used for domestic wastewater treatment at two farmhouses (8 p.e.) mainly for elimination of organic compounds (Laber *et al*., 1997). Two systems, i.e. system A which is a one-stage system while system B has two stages operated in series with the approach that the one-stage system pumped a part of the nitrified effluent from the soil filter back to a settling tank of the influent. An external carbon source (methanol) was used in the system B at water-saturated stage. After undergoing several experimental stages and recirculation ratios with intermittent or continuous feeding it was found that the highest elimination rates were achieved with system B when intermittent loading was done four times a day.

b. **Horizontal flow constructed wetlands**

To check the performance of horizontal subsurface flow reed beds (HFRBs) for the removal of selected contaminants at varying hydraulic loading rates and granular medium sizes, Garcia *et al*., (2004) constructed in a pilot-scale HFRB system comprising four pairs of lined beds of almost equal surface area (54 - 56 m^2 each bed). The beds with longest aspect ratio were made shallower (0.27 m) than the rest (0.5 m) and the sampling was carried out weekly. The results indicated that beds with a water depth of 0.27 m removed 70 - 80 % COD, 70 - 85 % BOD_5 and 40 - 50 % ammonia compared to beds with depth of 0.5 m which removed 60 - 65 % COD, 50 - 60 % BOD_5 and 25 - 30 % ammonia. This higher efficiency was assured due to their lower reducing conditions [average redox potential (E) ranging from −351 to −338 mV] than beds with a depth of 0.5 m (−390 to −358 mV).

Simultaneous variations of temperature and contaminants over the width, length, and depth of horizontal flow reed bed (HFRB) were studied on a system treating wastewater from a housing scheme in four pairs of lined (Garcia *et al*., 2004), parallel beds with areas (54–56 m^2 each bed) and different length-to-width (L:W) ratios and granular medium sizes. The other system treats the domestic wastewater in two parallel beds (187.5 m^2). The results indicated that temperature does not vary across the width, while changes with length and depth remained significant, especially those associated with depth. So it was concluded that vertical temperature gradients were very important in unplanted beds in summer (12 °C/m) but were greatly reduced in planted beds due to shading (3.4 °C/m) while daily variations in temperature gradients did not have a clear effect on the quality of effluents from the HFRBs.

Constructed wetlands have proved successful in treating wastewater. To compare the purification performance of different types of constructed wetlands; horizontal flow wetlands (HFW), and vertical flow wetlands (VFW), including a small horizontal flow wetland (HFW), a sloped HFW, a larger HFW, a stratified vertical flow wetland (VFW) and an unstratified VFW were studied conducted by Luederitz *et al*., (2001). Results showed that both the horizontal flow and vertical flow systems could remove more than 90% of the organic load. The HFWs have an advantage in the long-term removal of P because it bounds to organic substances to a high degree while decentral and semi central natural treatment systems save material (76%) and energy (83%) for their function compared with central technical systems.

Mashauri *et al.,(* 2000) commissioned a horizontal flow constructed wetland for treatment of wastewater effluent at an outlet of the waste stabilization pond to promote the use of constructed wetland for wastewater treatment. Treatment effectiveness indicated high mean removal efficiencies; 80% for suspended solids, 66% for chemical oxygen demand, 91% for faecal coliforms (FC) and 90% for total coliforms (TC) achieved at the low filtration rate. Results showed that with proper design, operation and maintenance, constructed wetland could serve efficient and economical means of upgrading the quality of secondary treated wastewater to an acceptable level.

Constructed wetland was constructed in combination of a sub-surface horizontal flow system planted with *Typha lattifolia*, *Cyperus latifolius, Cyperus papyrus*, *Hydrocotyle, Hydrolysis and Pontederia* for the treatment of restaurant wastewater and a swimming pool resort with recreational facilities (Nyakango and Bruggen, 1999). The main objective was to treat wastewater as well as to provide an aesthetically pleasing and environmentally sensitive landscape with ponds and ornamental plants for recreation. A 0.5 ha constructed wetland was designed for 1,200 population equivalents and results showed high treatment efficiencies for BOD_5, SS, COD, faecal coliforms, Kj-N, NH_4^-N and PO_4 of 98, 85, 96, 99, 90, 92 and 88% removal, respectively. Most of the nitrogen and phosphorus deposited in soil of both the subsurface horizontal flow constructed wetland and the ponds playing the key role of sediments. Besides this, constructed wetland attracted many birds (128 bird species) and amphibians.

c. **Surface flow constructed wetlands**:

In surface flow constructed wetland (SFCW) heavy oil contaminated water from an oilfield was purified during a 3 year field experiment. During the treatment high mean removal efficiencies of 80, 93, 88 and 86 % for COD, oil, BOD and TKN, respectively for reed bed number 1 and 71, 92, 77 and 81% for COD, oil, BOD and TKN, respectively for reed bed were recorded. (Ji *et al*., 2007). The reeds got acclimatized to wastewater during the third year of the system's operation resulting in positive impacts on the reed's growth's parameters. This help to conclusion that reed can be used as a feasible wetland macrophyte for treating wastewater and this SFCW system can function for a long time.

Brix (1997) concluded that the most important functions of the macrophytes in constructed wetlands are the physical effects due to the presence of plants which lead to stabilization of the surface of beds, provide good conditions for physical filtration thus preventing vertical flow systems from clogging and provide a huge surface area for attached microbial growth. Contrary to previous belief, growth of macrophytes does not increase the hydraulic conductivity of a substrate in soil-based subsurface flow constructed wetlands. The metabolism of macrophytes affects treatment processes to a different extent depending on the type of constructed wetland, as plant uptake of nutrients is only of quantitative importance in low-loaded systems (surface flow systems), while macrophytes mediated transfer of oxygen to the rhizosphere by leakage from roots increases aerobic degradation of organic matter and nitrification.

d. **<u>Sub-Surface flow constructed wetlands</u>**

Ji *et al*., (2007) studied the effectiveness of surface flow constructed wetland (SFCW) for treatment of heavy oil-produced water. Results showed that high mean removal efficiencies of 80, 93, 88 and 86% for COD, oil, BOD and TKN were achieved and the effluent quality of the system remained stable. This system proved very successful and it started giving positive impacts on the reed’s health parameters during third year of operation. Therefore this study proved that reed can be used as a feasible wetland macrophyte for treating such wastewater, and this system can treat wastewater for long time.

In order to assess the dynamics of horizontal subsurface constructed wetland (HSSF CW) for carbon (C) accumulation in the filter material and in a specially designed oil-shale ash filter have been studied (Vohla *et al.,* 2007). Resulting concentrations of N, P and C in filter media (coarse sand) in the HSSF beds showed increasing trend of adsorption while increasing outflow concentration of P in the

HSSF CW reflect the possible saturation of filter media with P after 8 years of working. Ash material derived from oil-shale combustion demonstrated very high P removal efficiency and during the first 4 months of the in-situ ash filter experiment, the efficiency of P removal was about 71% that later decreased to 10 - 20%, which might be a sign of saturation or clogging due to quick biofilm development on ash particles. This means that increasing the hydraulic retention time and improving contact time between the material and the wastewater are some of the key factors that can provide effective treatment.

An experiment was carried out in a horizontal subsurface flow constructed wetland planted with *Phragmites mauritianus* and filled with 6 - 25 mm diameter gravel pack (Bigambo and Mayo, 2005) to develop a model for designing. The effects of biofilm biomass activities were studied by removing the effects of plant and gravel bed biofilm in an already calibrated model and by carrying out a re-run of the same. Results indicated that total nitrogen removal was largely influenced by the growth of biofilm on plants than on aggregates. When plant biofilm and suspended biomass were considered, nitrogen removal was 38.1% compared to 25.1% when aggregate-biofilm and suspended biomasses were considered; this was because plants have more surface areas, which are active sites for the effective biofilm activities than the aggregates. Statistical analysis indicated 0.71 gN/m^2 of nitrogen when aggregate-biofilm was considered, but increased to 0.83 gN/m^2 without biofilm.

Performance of three units of a sub-surface horizontal flow constructed wetland (CW) pilot plant was carried out for polishing effluent from the upflow anaerobic sludge blanket (UASB) reactor plant (Kaseva, 2004). Out of the three units, unit B was planted with *Phragmites mauritianus*, unit C with *Typha latifolia* and A was used as a control with no plantation at an average hydraulic retention time of 1.93

days (1.85 in unit A, 1.96 in unit B and 1.99 in unit C) obtained as a ratio of the volume of wastewater in the wetland and the volumetric flow rate of wastewater through the wetland. Better performance for the vegetated units B and C was obtained compared to the control unit A. Nutrients were removed the least in all the units while the COD removal rate was 33.6, 56.3 and 60.7% for units A, B and C, respectively.

It appears that constructed wetlands represent a low-cost alternative for wastewater treatment in developing nations; however, special attention to appropriate design, monitoring and maintenance needs to be given especially as this region is particularly susceptible to wastewater pollution because of its geology and the lack of effective treatment systems. Results of study by Whitney *et al*., (2003) indicated organic matter removal efficiency for the wetland of about 68% while ammonia and nitrate measurements showed that little nitrification had taken place. Oxygen transfer limitations and preferential flow pathways are the likely explanations for the low organic matter removal efficiencies and lack of nitrification.

A subsurface flow wetland wastewater treatment system for a ground-based experimental prototype was established because of distinct advantages i.e. odorlessness, relatively less requirement for labour and lower consumption of energy which assist in purification of water and recycling of atmospheric CO_2 (Nelson *et al*., 2003). Resulting treated water from the wetland system was to be used for irrigation, hence ensuring complete recycling and utilization of nutrients. Since the primary requirements for wetland treatment systems are warm temperatures and lighting, these can eventually be met with the use of in-situ materials, such as gravel. Because this technique requires little machinery and no chemicals, and relies more on natural ecological mechanisms (microbial and plant metabolism), maintenance requirements are minimized, and systems can be expected to have long operating lifetimes.

Assessment of the bacterial population (abundance, biomass and viability) in influents and effluents of four constructed wetlands was carried out to analyze the effect of such biological treatment (Decamp and Warren, 2001). The reduction in bacterial concentration was higher (67%) in the wetland used for secondary treatment than in those used for tertiary treatment (15 - 39%). The proportion of damaged cells was higher in the influent (i.e. settled sewage) of the wetland used for secondary treatment (78%) than in the influents of those wetlands used for tertiary treatment (45–70%). This suggests that the majority of bacteria in the settled sewage died or damaged and that these were removed from the wastewaters more effectively during conventional secondary treatment (in this case, using rotating biological contactors or RBCs). This proves that bulk of bacteria leaving the constructed wetlands was used for tertiary treatment and 50% for the secondary treatment wetland which means they were physically intact and therefore probably viable.

2.4. <u>**Fill Materials in Constructed Wetlands**</u>

Media in the root zone bed could serve many purposes. The first role of the media is physical treatment of the wastewater (Wood, 1995). Filtration and sedimentation of suspended solids and pathogens occurs along with the sorption of phosphorus, and dissolved organics. Smaller media, such as sand, are more effective in sorption and filtration than gravel or rocks owing to its smaller pores sizes and large surface areas. The media does provide a stable surface area for the attachment of microbial biofilms which help accomplish biological treatment of wastewater passing thorough root zone bed. The SF wetlands are commonly referred to as attached growth biofilters (Wood, 1995). The third function of the media is the solid support it gives for wetland plant growth.

Wetland beds have been constructed of many different types of materials. As stated earlier, when considering the appropriate media to use, the available surface area for the attachment of microbial population must be an important consideration. Also of importance is the selection of a medium that has hydraulic conductivity which allows the influent water to remain below surface. By optimizing both factors, there might be a reduction in the treatment efficiency of a system due to a decrease of contact time between the wastewater and biofilm.

Freeman, Jr. (1993) reported that as size of rock increase, the porosity decrease. In order to avoid such conditions, wetland areas must be increased to prolong the contact time between wastewater and microbial communities necessary for adequate biodegradation. In certain cases where the wetland areas were not increased to allow for this reduced contact time, poor treatment performance was recorded.

a. **Gravel**

Gravel filled vertical/reverse-vertical flow constructed wetland system was set up to study its treatment efficiency of polluted lake water (Liang *et al.*, 2003). The numbers of substrate, micro-organisms and the intensity of urease activity in the substrate of the constructed wetland were determined by plate counts and colorimetric analysis, respectively. The results showed there was significant positive correlation ($P < 0.05$) between the number of micro-organism in the gravel substrate and the removal rates of TKN and COD. Meanwhile, there was significant positive correlation ($P<0.05$) between urease activities and removal efficiencies of TKN and negative correlation between urease activities and removal efficiencies of BOD_5 leading to the conclusion that substrate micro-organisms and urease activities played a key role and could be utilized as indicators of wastewater treatment performance in a constructed wetland system.

To check the possible role of fungi present in these ecosystems, a study was carried out in pilot-scale constructed wetlands for treatment of wastewater contaminated by polycyclic aromatic hydrocarbons (PAHs), particularly fluoranthene (Giraud *et al*., 2001). Forty fungal species were isolated from samples (gravel and sediments) from a contaminated and a control wetland. It was found that FA was degraded proficiently by 33 species while only 2 species were able to remove AC over 70%. Further selection of 10 strains of micromycetes was carried out for FA and AC degradation. It was found that all were able to greatly degrade the PAH.

The P-removal properties were evaluated in short-term isotherm batch-experiments mimicking the P-loading conditions in constructed reed bed systems. Sorption of P to the sand medium is a major removal mechanism for P in subsurface flow constructed reed beds (Arias *et al*., 2001). The most important characteristic of sands determining their P-removal capacity was their Ca-contents, which favours precipitation with P as sparingly soluble calcium phosphates particularly at slightly alkaline conditions typical of domestic sewage. In acidic conditions, contents of Fe and Al may be more important as the precipitation reactions with these ions are favoured at lower pH levels. It was found that maximum P-sorption capacities estimated using the Langmuir-isotherm plots did not correlate with the actual amount of P removed, therefore, it does not estimate the P-removal capacities of sands.

Performance evaluation of artificial wetland treatment systems was done in pilot scale artificial wetlands, one planted with *Phragmites australis* and three unplanted and filled with maerl in the laboratory (Gray *et al*., 2000). Results showed variability within and between treatments however, maerl effectively removed total phosphorus (98%) and nitrogen removal was less effective, with the tanks producing ammonium-N. However it was noted that ammonification did decrease in planted tanks over time. But phosphorus removal by maerl was considerably higher than that taking place in gravel bed wetlands and was comparable with the very best figures given for artificial wetlands based on novel substrates such as shales and slags. Maerl has proved its potential as a constructed wetland substrate due to its high phosphorus-adsorbing capacity.

Scirpus lacustris was grown in hydroponic culture and in siliceous gravel to compare these with the efficiency of gravel beds without macrophytes (Soto *et al*., 1999). Results showed that organic carbon removal was not significantly correlated to the presence of *Scirpus lacustris,* while the removal efficiency of phosphorus and nitrogen was improved in the presence of plants, even with extremely low C:N ratios. It was found that *Scirpus lacustris* was responsible for 30% TN and 20% TP removal in summer and that this was due to changes in plant activity while removal efficiencies for nutrients increased 10% from spring to summer. Gravel bed efficiency with macrophytes was significantly higher than those from other treatments, with accomplishment up to 99.9%.

A study was carried out to estimate the accumulated organic matter (OM) after two and five years in a series of four gravel-bed constructed wetlands supplied with different hydraulic loading rates (21, 26, 46 and 72 mm d^{-1}) of farm dairy wastewaters (Tanner *et al*., 1998). At these hydraulic loadings, mean wastewater loadings of particulate OM to the wetlands ranged between 1.7 and 5.8 g m^{-2} d^{-1}. Results showed that mean accumulation of organic matter in the wetlands after five years operation ranged between 6.8 and 14.9 kg m^{-2}, increasing with wastewater loading rate. The organic matter accumulation in wetlands considerably exceeded that contributed by applied wastewaters, with wetland plant derived detritus supplying substantial additional quantities of organic matter. This means that the effective void space of the wetland substrata was markedly changed in the highest loaded wetland, with mean wastewater retention time reduced to 50% of its theoretical value.

For the treatment of domestic wastewater, a sand plant filter was used which combined treatment of faeces in compost toilets and the liquid wastes in a constructed wetland (Schonborn *et al*., 1997). The wastewater of 5.1 population equivalents is treated in a two chambered settling tank followed by an underground vertical flow sand filter and a horizontal flow constructed wetland. Results showed that COD elimination (91 %) and Total-P removal (90 %) were stable over the years; whereas, NH_4^-N and Total-N elimination improved markedly from around 55 to 93% (NH_4^-N) and 80 % (Total-N). In winter, the addition of an easily degradable carbon source to the plant filter in summer resulted in markedly decreased phosphorus retention and a releasing of iron during the experiment.

b. **Sand**

Hydraulic characteristics of constructed wetlands have been evaluated for the subsurface-flow system filled with inhomogeneous gravel cells planted with *Phragmites australis* (Piotr *et al.,* 2006). Bromide and tritium tracers were used to calculate the residence time distributions of wastewaters. A multi flow dispersion model was used assuming that several flow-paths are existing with different hydraulic properties. The same constructed wetlands were developed using the respective parallel combination of analytical solutions of the one-dimensional advection–dispersion equation. The model proved to be successful to fit the experimental tracer breakthrough curves.

In order to compare the sorption capacity of fill materials, like filtralite P and shell sand, constructed wetland substrates have been tested (Adam., 2006). Two columns were filled with filtralite P and one column with shell sand and were loaded with a synthetic P solution, while the second filtralite P column (FLWW) was loaded with secondary wastewater. Average P removal of 92, 91 and 54%, respectively was obtained in the columns for the entire experimental period. The comparison of FLWW and FLPS proved that FLWW kept its high P removal efficiency (91%) throughout experimental period, while the removal efficiency of FLPS decreased after reaching 1 ppm effluent P concentration. Results from both the batch and the column experiment proved that shell sand has a more sustainable P sorption capacity than Filtralite P material, possibly due to the persistent high concentration of Ca in the shell sand.

The most common method for disposal of dairy parlor washings is through land spreading which is labour intensive and also holds the potential for eutrophication (death of biotic organisms due to deficiency of oxygen) of surface and ground waters (Healy *et al*., 2006). While constructed wetlands are commonly used for treatment of secondary municipal wastewaters, intermittent sand filtration may offer comparable treatment performance due to, the substantially higher organic loading rates that may be applied to their surfaces. This study showed that the performance and design criteria of constructed wetlands for the treatment of domestic and agricultural wastewater, and sand filters for the treatment of domestic wastewater have proved successful. It also proposes sand filtration as an alternative treatment mechanism for agricultural wastewater and suggests design guidelines.

Performance of a mixture of river sand and dolomite was evaluated (10:1, w/w) as substrates in vertical-flow constructed wetlands (Prochaska and Zouboulis, 2006). Two duplicate pilot-scale artificial wetlands (total 4 units) were set up, planted with *Phragmites australis* and fed with a synthetic sewage solution, corresponding to medium strength municipal wastewater and these wetlands were fed with two batch (intermittent) operational modes. The wetlands were capable of removing more than 45% of initially applied phosphates, while accumulation at the end of operation period was 6.5 - 18%, as compared with the unused media. The Ca Mehlich-III extractable contents also increased, indicating that the removal of phosphates could be mainly attributed to the sorption of orthophosphate ions onto calcium carbonates. Orthophosphate ions also precipitated with calcium ions as the respective insoluble calcium phosphates.

For the biological performance evaluation of constructed wetlands, samples were taken from the inflow and outflow, rhizosphere, and from the bulk soil at various depths (Vacca *et al*., 2005). Colony-forming units of heterotrophic bacteria and coliforms were analyzed to estimate the removal of bacteria. Analysis indicated that a pronounced decrease in diversity from the inflow to the outflow of treated wastewater took place. The same was seen true for the finger printing of the rhizosphere of plants grown on sand or expanded clay showing that different microbial communities exist depending on the soil type of filters. After sequencing *Pantoea agglomerans*, it was found in nearly all the samples from soil, whereas *Citrobacter species* could not be removed by the horizontal unplanted sand and vertical planted expanded clay filters thereby proving that the community in wetland system was strongly influenced by the filtration process, the filter material and the plants.

The use of a submerged flow constructed wetland (Vega *et al*., 2003) and a sand filter to remove bacterial and viral pathogens from wastewater streams was evaluated by using *Salmonella* species and a bacteriophage tracer was used in conjunction with the conservative bromide tracer. Viral breakthrough numbers in the sand filter and CW were similar to a Spearman Rank correlation of 0.8 ($P<0.05$). In the CW, virus exhibited almost a 3 log reduction, while in the sand filter, viruses exhibited a 2 log reduction; whereas, bacterial tracers did not exhibit similar reductions. The results suggested that microbial removal characteristics of decentralized wastewater treatment systems can vary depending on factors such as adsorption, desorption and inactivation which in turn depend on the design specifics such as filter media characteristics and local climatic conditions.

Four laboratory-scale wetland units planted with cattails (*Typha augustifolia*), were fed with primary-treated sewage and operated at nominal retention times of 0.6–7 days (Lim *et al*., 2001). The influent and effluent BOD/COD and nitrogen concentrations were monitored. The results showed that wetland vegetation did not play an important role in oxygen demand removal but was capable of removing about 22 and 26% of the nitrogen input. Mass balance analysis indicated that less than 1% of copper introduced was taken up by the cattails while speciation patterns in the sand media showed that the exchangeable fraction contributed 30 - 57% and 63 - 80% to the planted and unplanted FWS wetlands, respectively. For SF units, percentages were 52 - 62% and 59 - 67%, respectively leading to the conclusion that copper in the media was potentially remobilizable.

Fill materials play a key role in the phosphorus retention capacity of wetlands and significant results have been achieved with the reduction of phosphorus in wastewater through the use of constructed wetlands (Johansson, 1997). Light Expanded Clay Aggregates (LECA) has been tested in laboratory and field investigations along with P-fractionation experiment which showed promising results. Both experiments, however, showed that only a small amount of the applied phosphate was sorbed by the LECA and amount sorbed was primarily attached to complexes. In a second column experiment Polka, a reactive medium rich in $CaCO_3$, was added to LECA and sand to investigate the P-sorption capacity, which showed a higher P-uptake than that in the previous column experiment.

Organic matter (OM) composition, microbial biomass and microbial activity in a planted gravel-bed wetland receiving cumulative OM loadings over 5 years from farm dairy wastewater (8.2 kg OM m^{-2}) and in-situ plant residues (8.4 kg OM m^{-2}) were investigated by Nguyen, (2000). Organic deposits above and within the gravel stratum were collected from six sites along the wetland channel. Analysis showed that over 90% of organic matter accumulated in the wetland was present as stable organic matter fractions in the form of humic acid, fulvic acid and humin accounting for 63 - 96% of total C in surface deposits and the gravel substratum. Humic compounds were at least 2-fold higher in surface deposits than in deep layers and the top 100 mm of the gravel-bed, suggesting that pore clogging was more prominent in the top layer of the gravel-bed. Microbial respiration rate and microbial biomass significantly correlated with sediment organic matter fractions, indicating that these microbial parameters may be used to calculate changes in the labile and stable fractions of OM build-up in a wetland.

2.5. Role of Plants in Constructed Wetlands:

Plants used in constructed wetland systems are known as emergent hydrophytes and macrophytes. The major portions of these plants (leaves and flowers) emerge above the media surface and are exposed to air, while their roots and rhizomes remain submerged beneath the water and media (Kadlec and Knight, 1996). Three of the commonly used plant species in SF wetlands are bulrush (*Scirpus*), reeds (*Phragmites*) and cattails (*Typha*). Extensive rooting structures of these plant species make them suitable for wastewater treatment. Flowering plants, such as the Yellow Flag Iris, are also utilized to a lesser extent (US EPA, 1993). It has been shown that these species did not grow as vigorously as other plant types under simulated SF wetland conditions (Neralla *et al.*, 2000).

Several of the plant functions are well-established and several others are highly debatable. One role that is beyond debate is the aesthetic appeal that wetland plants provide by covering the wetland bed and by controlling odors. The wetland plants could provide a habitat to many animals, including small mammals and birds. The plant cover also limits the amount of ponding water on the bed surface that serves as a breeding environment for nuisance insects such as gnats and mosquitoes (Wood, 1995). Plant roots and rhizomes provide surface for microbial growth and also help filtration of solids.

A major premise of the root-zone method is that the wetland plants are able to provide oxygen to the heterotrophic bacteria in the rhizosphere thereby allowing aerobic degradation of organic matter and nitrification to occur (Brix, 1987). It cannot be debated that oxygen is transferred from the aboveground parts of plants through airways to roots and rhizomes. Like other aerobic organisms, plants require oxygen for respiration, growth, and protection from phytotoxins in the root zone (Good and Patrick, 1987). Without oxygen, the wetland plants would not be able to survive and grow. Aerated microzones are developed around roots and rhizomes by the leaking of oxygen through these structures (Brix, 1987). These oxidized areas in an otherwise anaerobic environment generally provide conditions in which the aerobic biological transformations could occur. Many design approaches are based on the fact that significant aerobic biodegradation of organic wastes and nitrification take place in these microzones.

It was stated by Hiley *et al.* (1995) that the only situation in which plant roots and rhizomes are likely to leak any significant amount of oxygen into the rhizosphere are ones in which the oxygen demand is relatively low. However, it is very rare to encounter low oxygen demand conditions in constructed wetlands treating wastewater; therefore, from a quantitative perspective, the amount of oxygen provided to the surrounding media by roots and rhizomes are minimal. The respiration and growth of the wetland plants appear to require almost all of the oxygen transported to the root zone (Kadlec and Knight, 1996).

Expectations that saturated organic-rich sediments can be sufficiently aerated by macrophytes are not realistic (Wetzel, 1993). Even if plants were able to leak sufficient amount of oxygen, in most cases roots and rhizomes do not extend throughout the entire depth of the wetland bed. Typical depths of constructed wetland beds range from 0.3 m to 0.6 m, with some reaching depths of 0.84 m (US EPA, 1993). Regardless of the plant species, roots on operational systems seldom reach below 0.3 m.

The oxygen provided to the wetland is taken up through the surface of water (Hiley *et al.,* 1995) and is dominated by air-water-media interfacial transfer (Kadlec and Knight, 1996). The implication of this is that only the very top portions of the wetland bed experience aerobic conditions. The resulting anaerobic conditions throughout the rest of root zone bed and their impact on treatment performance was highly positive.

The second debatable role of plants in SF wetlands is their ability to increase or stabilize the hydraulic conductivity of media. This is of particular importance when utilizing a small sized media such as soil. By disturbing and loosening soil, the growth of plant roots and rhizomes generally increases the porous nature of soil thereby allowing less hindered flow through the rhizosphere (Reed *et al,* 1988). Brix (1987) proposed that regardless of the initial porosity of soil, the root and rhizome growth would, within two to five years, increase the hydraulic conductivity to that of the coarse sand.

a. ***Phragmites***

The effect of detritus originating from different plant species on denitrifying capacity was investigated in intact sediment cores which were collected from wetland basins dominated by *Typha latifolia, Phragmites australis* or *Elodea canadensis* and potential denitrification was measured using the acetylene-inhibition method (Bastviken *et al*., 2005). Analysis showed that cores from stands of *Elodea canadensis* affected more than three times higher denitrification capacity than cores of the other plants. Bacterial abundance per unit dry weight was both the highest and lowest in detritus of *Phragmites australis*; whereas, the C/N ratio was lower in the cores of *Elodea canadensis* which suggested that the submerged plants provided more organic material of high quality to support heterotrophic organisms. It is apparent that denitrifying bacteria were more favoured by *Elodea canadensis* detritus than by detritus from the emergent plant species.

Calheiros *et al*., (2009) evaluated the performance of *Phragmites australis* and *Typha lattifolia* for tannery wastewater treatment by using a two-stage series of horizontal subsurface flow constructed wetland and system was operated at hydraulic retention times of 2, 5 and 7 days. The system provided high removal of organics from wastewater i.e. equal to 88% of biochemical oxygen demand (BOD_5) and 92% of chemical oxygen demand (COD) along with other contaminants, such as nitrogen. Results showed that no significant ($P < 0.05$) differences in treatment performance were created between both the series and on the whole mass removals of up to 1294 kg COD had^{-1} and 529 kg BOD_5 ha^{-1}d^{-1} were achieved for loading range varying from 242 to 1925 kg COD ha^{-1}d^{-1} and from 126 to 900 kg BOD_5 ha^{-1}d^{-1}. The end results revealed that plants were resilient to the conditions imposed, however *Phragmites australis* exceeded *Typha latifolia* in terms of propagation.

Wetland macrophytes (*Phragmites* and/or *Typha*) and granular media with different adsorption capacities were used to assess the treatment efficiency of passive vertical-flow constructed wetland (Scholz and Jing, 2002). Different concentrations of lead (Pb) and copper sulphate were added to the polluted urban stream inflow water to simulate pre-treated mine wastewater and for nitrogen a fertilizer was added to one filter only. Lead, copper and 5-day biochemical oxygen demand (BOD) concentrations were reduced, while an analysis of variance showed that the concentration reductions (mg/L) of lead, copper and BOD were significantly similar to each other. This suggests that there appears no supplementary benefit in using expensive adsorption media like granular activated carbon to increase biomass performance.

An existing free-water-surface constructed wetland system was evaluated for the effect of plant fill ratio on water temperature (Hill and Payton, 2000). Each wetland consisted of two cells in series; one series contained an approximate 10% fill of *Sagittaria lancifolia;* and, second series contained *Phragmites australis* and Scirpus spp. with an approximate 5% fill of plants while the third was un-vegetated and acted as a control. Water temperature was compared between each cell and the results showed that un-vegetated cells had significantly higher temperatures than the vegetated cells. The 10% fill ratio series had significantly higher temperatures than the 5% fill ratio during the winter months while un-vegetated cells were significantly warmer than the vegetated cells and also exhibited greater daily variation in temperature.

Treatment performance of a field-scale horizontal subsurface (SF) constructed wetland was evaluated (Billore *et al.*, 1999). The constructed wetland was planted initially with locally grown grass, *Phragmites* karka planted in a rectangular design at the rate of 3 to 4 plants per m^2 increased to 6157 plants within ten months producing a biomass of 121 tonnes ha^{-1}. Results showed that removal rates of TSS (48%), TKN (36%) and NH_4-N (22%) occurred and after 5 months, removal efficiencies of 78% for NH_4^-N, TSS; 58–65% for P, BOD and TKN were achieved which was attributable to an increase in oxygen level. The study proved that SF system is a very cost-effective treatment technology with removal efficiency above 50% for BOD_5 and NH_4-N.

For the treatment of municipal wastewater, nine pilot wetlands (eight free water surface and one subsurface flow) were constructed by Greenway and Anne (1999) to investigate the performance efficiency of nutrient bioaccumulation in wetland plants. Results showed that biochemical oxygen demand concentrations were reduced by 17 - 89% and suspended solids concentration by 14 - 77% to produce wetland effluent with BOD less than 12 mg L^{-1} and suspended solids less than 22 mg L^{-1}. Submerged (*Ceratophyllum*) and free floating species (duckweed) had the highest tissue nutrient concentration, followed by water lily, aquatic vines and water ferns. It was found that all these species removed nutrients and emergent species had lower nutrient concentrations, while among the aquatic grasses, *Phragmites* had higher nutrient contents than the sedges.

In order to evaluate and compare their biomass production and NPK retention rates in unpolluted and polluted wetlands, a field study was undertaken on *Phragmites* australis, *Typha angustifolia*, *Sparganium erectum and Juncus acutus* (Ennabili *et al*., 1998). The main objective was to identify species with a potential for macrophyte-based wastewater treatment systems. Total biomass values were recorded for *Typha, Phragmites* and *Sparganium* were 56.5, 52.7 and 20.1 t dry weight ha^{-1} $year^{-1}$, respectively along with nitrogen and phosphorus at the rates of 922, 561 and 375 kg N ha^{-1}; and 114, 72.1 and 84.8 kg P ha^{-1}, respectively. It was noted that above ground annual net productivity for *Phragmites* is greater in the Mediterranean climate than the oceanic climate.

To assess the efficiency of a constructed reed bed for domestic wastewater purification under an arid climate, the experimental system was constructed of four beds differing in length (20, 30, 40 and 50 m) and planted with *Phragmites australis* (Mandi *et al*., 1998). Raw wastewater inflow through these beds was horizontal with a flow of 10 L/s. Results showed that the constructed reed beds were efficient in reducing organic load (TSS: 58 - 67%; COD: 48 - 62%) and parasitical load (Helminth eggs: 71 - 95%) in arid climates even with high hydraulic application rate. However, reduction of nutrient concentrations by the four beds is slight (TKN : 23 to 43% ; NH_4 : 18 to 41%). During the periods of extreme heat, (March to August), the reed beds remained more efficient in reducing organic load, nutrients and parasitical load.

Zinc (Zn), lead (Pb) and cadmium (Cd) tolerance in populations of seedlings of *Phragmites* were studied under glasshouse conditions (Ye *et al*., 1997). Few differences were found between the metal-contaminated population and the three ‘clean’ populations when seedlings were grown in 1.0 μg mL^{-1} Zn and 10.0 μg mL^{-1}Pb treatment solutions. However, different populations of seedlings showed similar growth responses, metal uptake and indices of Zn, Pb and Cd tolerance when cultured in the same metal-contaminated media for 89 d. There was insufficient evidence to support the hypothesis that the metal-contaminated population has evolved to a Zn-, Pb- or Cd-tolerant ecotype.

b. ***Typha***

Calheiros *et al*., (2009) studied the bacterial communities' role in treating tannery wastewater under different hydraulic conditions by planting *Typha latifolia* and *Phragmites australis* through bacterial enumeration and denaturating gradient gel electrophoresis (DGGE). It was observed that diverse bacterial communities were found in each system unit that attributes to the type of plant and stage position. Numerical analysis of DGGE profiles also proved high diversity with an even distribution of species while no clear relation was established between the sample collection time, hydraulic loading applied and the bacterial diversity. *Proteobacteria, Firmicutes, Proteobacteria, Sphingobacteria, Actinobacteria* and *Bacteroidetes* were the key isolates extracted from plant roots and substrates which proved effectiveness of the constructed wetlands in removing organic matter.

Chazarenca (2009) studied the effect of plants and artificial aeration on solids accumulation and treatment efficiency as it decreases the longevity but enhances biological activity. Horizontal and vertical sampling was done using solids traps in 12 constructed wetland meso-cosms. Microbial density and activity were evaluated in the biological fraction and it was observed that the plant presence reduced accumulated solids by 26% and sulphide content by 50%. *Typha angustifolia* planted wetlands settled more solids and thus more biological activity due to biofilm than Phragmites australis. It was found that aeration stimulated biofilm development, reduced mineral matter accumulation and triggered biological activity same as in planted beds enabling to reach a total nitrogen removal rate of up to $0.65 gNm^{-2}d^{-1}$.

Constructed wetland treatment system planted with *Schoenoplectus californicus* and *Typha angustifolia* was designed to treat constituents of flue gas desulfurization wastewater having high concentrations of Hg, Se and As (Sundberg *et al*. 2006). Results indicated that Hg, Se and As were enriched in detritus from *Schoenoplectus californicus* and *Typha angustifolia* by factors up to 4600, 26,300, and 15,600, respectively. Being a significant food source for many organisms, element enrichment could make the detritus an even greater source of contaminants to the food chain. Results demonstrated that the natural decomposition of plants produce detritus enriched with Hg, Se and As at levels potentially hazardous to aquatic organisms.

A mathematical model was developed in order to describe the system behaviour and performance of a constructed wetland (CW) planted with cattail (*Typha angustifolia*) and fed with spiked municipal wastewater treatment under salt-affected conditions (Nitisoravut and Pantip, 2005). The rate of biodegradation of organic wastes was modelled using the first-order kinetics while the effect of salt concentration was accounted for by growth inhibition. Experimental data were used to determine constants of the mathematical model. The hydraulic retention time varied from 12 to 120 h, and wastewater conductivity was in the range of 4-32 mS/cm. At specified conditions, the model was found to describe accurately the trend of the experimental data in terms of BOD removal with the Pearson correlation of 0.872.

Denitrification is more desirable than ammonia volatilization for nitrogen removal from constructed wetlands treating animal manure but is limited by the availability of nitrate/nitrite (Poach *et al*., 2003). Constructed wetlands were more efficient at removing total nitrogen from partially nitrified (64 and 78%) than from unaltered wastewater (32 and 68%). However, the *Schoenoplectus*-dominated wetland was more effective than the *Typha-Echinochloa* dominated wetland in removing total (85 vs. 61%) and ammoniacal nitrogen (91 vs. 52%) from both the types of wastewater. A correlation (r^2=33%) between ammonia-nitrogen volatilization and ammoniac nitrogen concentration suggested that partial nitrification reduced ammonia volatilization.

The effects of ammonia concentration (0, 50, 100, 200 and 400 mg/L) on the growth and biomass production of *Juncus effusus, Sagittaria latifolia, Schoenoplectus tabernaemontani, Typha angustifolia,* and *Typha latifolia* were studied on these plants commonly used in constructed wetlands for treating animal waste (Clarke and Andrew., 2002). Interactions between ammonia concentration and water level for *S. tabernaemontani* and *T. latifolia* were evaluated and it was found that ammonia levels in excess of 200 mg/L inhibited growth of *Juncus effusus, Sagittaria latifolia* and *Typha latifolia* and levels in excess of 100 mg/L similarly inhibited growth of *Schoenoplectus tabernaemontani* only.

Four laboratory-scale wetland units with one of each planted with cattails (*Typha augustifolia*) were fed with primary-treated sewage and operated at nominal retention times of 0.6 - 7 days (Lim *et al*., 2001). The influent and effluent BOD, COD and nitrogen concentrations were monitored to assess the performance of wetland units. The results showed that wetland vegetation did not play an important role in oxygen demand removal but were capable of removing about 22 and 26% of the nitrogen input in the FWS and SF wetland units, respectively. Copper speciation patterns in the sand media showed that exchangeable fraction contributed 30 - 57% and 63 - 80% in the planted and unplanted FWS wetlands, respectively showing that huge quantity of copper in the media was potentially remobilizable.

Evaluation has been done to measure the impact of residence time on N removal in constructed wetlands to treat domestic wastewater using gravel-based, SF wetlands planted with *Scirpus cyperinus* and *Typha latifolia* at three residence times of 2.6, 3.9 and 5.9 days (Huang *et al*., 2000). Both the $NH^{+}{}_{4}$ and TKN concentrations in the wetlands decreased exponentially with increased residence time and ranged from 18.1 to 39.0% and from 31.3 to 45.8%, respectively for the KRF site and from 44.4 to 73.4% and from 46.2 to 67.5%, respectively at the PRP site. The NO^{-3} concentrations in the influent and effluent at both the sites were low while temperature dependent rate constants (KT) were effective in predicting $NH^{+}{}_{4}$–N and TKN concentrations as a function of residence time.

Three commonly used free-surface marsh vegetation treatments (*Scirpus and Typha species*) were used in replicated macrocosms to determine nitrate removal rates for treating nitrogen-rich wastewaters (Bachand and Alexander, 1999). Implementation of management and design practices for denitrification may be one method to increase efficiencies, reduce costs and increase reliability. If one plant provides substantially better conditions for denitrification, wetlands designed for denitrification could be smaller and less expensive. Nitrate removal rates between vegetation types were large and differed significantly ($P < 0.001$; cattails = 565 mg N m^{-2} day^{-1}, bulrush = 261 mg N m^{-2} day^{-1} and mixed = 835 mg N m^{-2} day^{-1}). Mass balance calculations demonstrated that bacterial denitrification rather than plant uptake was the main mechanism for nitrate removal.

2.6. Relation of HLR to Removal Efficiency

2.6.1 Hydraulic loading rate

Due to serious concerns regarding the high capital, operational and maintenance costs of municipal wastewater treatment plants, wastewater treatments in constructed wetlands seems to be a viable option (Badkoubi *et al*., 1998). The performance of a pilot-scale subsurface constructed wetland with *Phragmite*s *australis* to treat municipal wastewater has been investigated to achieve an acceptable quality in terms of discharge standards. Experiments were carried out in two cells (15 × 10 mxm) with media size ranging from 4 - 8 mm. Different hydraulic loading rates ranging from 5 to 20 L/min were used. Minimum land requirement was determined as 1–2 m^2/P.E. to reduce COD (86±4%), BOD_5 (90±3%), TSS (89±4%), TN (34±6%), TP (56±5%) and fecal coliform (>99%).

To foster the practical development of constructed wetlands (CWs) for domestic wastewater treatment, vertical subsurface flow constructed wetlands (30 m^2 each) were planted with *Phragmites australis* (Korkusuz *et al*., 2005). The main objective of the research was to quantify the effect of different filter media on the treatment performance. Thus, a gravel-filled wetland and a blast furnace granulated iron slag-filled wetland were operated identically with primarily treated domestic wastewater (3 m^3 d^{-1}) at a hydraulic loading rate of 0.100 m d^{-1}, intermittently. Results showed that average removal efficiencies for the slag and gravel wetland cells were: total suspended solids (63 and 59%), chemical oxygen demand (47 and 44%), NH_{4+}–N (88 and 53%), total nitrogen (44 and 39%), PO_4^{3-}P (44 and 1%) and total phosphorus (45 and 4%).

A pilot-scale horizontal flow constructed wetland (HFCW) system planted with common reed (*Phragmite*s sp.) was constructed to study how hydraulic loading rate (HLR), aspect ratio, water depth, and granular medium affect the fate of several organic matter degradation intermediates namely acetic acid, isovaleric acid, and dimethylsulfide (Huang *et al*., 2005). Statistical analysis showed that the HLR and the water depth were the two major factors that controlled the performance of HFCWs for the target analytes. Results showed that effluents of the shallow water depth contained lower DMS (1.05 - 1.44 μg L^{-1}), acetic acid (7.91 - 10.9 mg L^{-1}) and Isoval (0.11 - 0.15 mg L^{-1}) concentrations than the deeper beds (DMS: 1.68 - 2.40 μgL^{-1}; HAc: 9.29 - 14.4 mg L^{-1} and Isoval: 0.20 - 0.31 mg L^{-1}).

The effects of hydraulic loading rate (HLR), aspect ratio, granular medium size and water depth on the removal of selected contaminants in horizontal subsurface flow constructed wetlands (SSF) were evaluated by Garcia *et al*., (2005). The size of the granular medium of each pair varied from coarse granitic gravel (D_{60} = 10 mm, Cu = 1.6) to small granitic gravel (D_{60} = 3.5 mm, Cu = 1.7). The results indicated that water depth was the determining factor and beds with a water depth of 0.27 m in general removed more chemical oxygen demand and biochemical oxygen demand. The HLR was also a very important factor in controlling the efficiency of the SSF, as fine gravel produced effluents of better quality than those with coarse gravel. The differences in treatment efficiency were low in comparison to the effect of water depth and HLR.

Phosphorus accumulation was investigated in the substrata and surface deposits of pilot-scale gravel-bed constructed wetlands after 2 (planted and unplanted) and 5 (planted only) years of operation (Tanner *et al*., 1999). Four hydraulic loading rates of farm dairy wastewater provided mean cumulative total P (TP) loading from 520 - 2000 g m^{-2}. Mean substratum TP accumulation after 2 years operation ranged from 52 - 100 g m^{-2} in the planted wetlands and from 40 - 51 g m^{-2} in the unplanted wetlands, both showing a general increase with wastewater loading. Wetland TP removal performance, substratum TP accumulation in all the planted wetlands converged at similar values of 115 - 128 g m^{-2} showing 6 - 23% of their cumulative loading.

Nutrient removal is essential for aquaculture wastewater treatment and for this pilot-scale, wastewater treatment system consisting of a free water surface (FWS) and a subsurface flow (SSF) constructed wetlands arranged in series was operated under various hydraulic loading rates (1.8 to 13.5 cm day^{-1}) (Lin *et al*., 2002). Nitrogen removals were excellent, with efficiencies of 86 - 98% for ammonium nitrogen (NH_4–N) and 95 to 98% for total inorganic nitrogen (TIN). Removal efficiencies were affected insignificantly by the hydraulic loading rates; and phosphate removal of 32 to 71% took place with the efficiencies being inversely related to hydraulic loading. The FWS wetland removed most inorganic nitrogen, whereas the SSF wetland removed phosphate at a rate equal to or even greater than the FWS.

Two-stage constructed wetland was built with a settlement tank, a horizontal flow bed as the first stage and a vertical flow bed as the second stage for the treatment of hospital wastewater (Laber *et al*., 1999). The aim was the elimination of organic compounds and to achieve this, different phases of operation were investigated, of which the serial operation with high water level in the horizontal flow bed and low water level in the vertical flow bed showed the best elimination performance. The areal removal rate constants (k-values) turned out very high and for the vertical flow bed kCOD was 0.22 m/d and kNH_4-N was 0.85 m/d^{-1} during serial operation. For kNH_4-N, a strong correlation with the hydraulic loading rate and the COD inlet concentration did exist.

2.6.2. <u>Biological Oxygen Demand</u>

Two horizontal subsurface flow reed beds of 75 m^2 each, treating dairy parlor effluent and domestic sewage (about 6.5 $m^3 day^{-1}$), were set up to determine the efficiency of this system in reducing the polluting load (Mantovi *et al*., 2003). A total suspended solid value of about 0.70 gL^{-1} and chemical oxygen demand (COD) and biological oxygen demand (BOD_5) values of about 1200 and 450 mg L^{-1}, respectively, were characteristic of the influent waters. Removal of suspended solids and organic load remained constantly at levels above 90%. Results demonstrated the use of reed beds as an economical treatment to reduce pollutants in wastewater from rural activities to values acceptable for discharge into surface waters.

To estimate the biological oxygen demand and chemical oxygen demand, constructed wetlands comprising four parallel compartments of 0.25 ha each were established and planted with *Phragmites australis* which were loaded sequentially with sewage from recreational facilities by (Meuleman *et al*., 2003). Annual loading rates were moderate as 16 700 kg COD ha^{-1}, 6700 kg BOD_5 ha^{-1}, 2400 kg N ha^{-1} and 335 kg P ha^{-1}. The removal efficiencies for COD (81%) and BOD_5 (96%) were high; while for nitrogen (30%) and phosphorus (24%) were much lower. Nutrient removal was the result of plant uptake and harvesting, denitrification, sedimentation and accumulation of organic matter in soil. Removal efficiencies for N and P could be increased by harvesting *Phragmites* vegetation in October. This vertical-flow wetland appeared P-saturated after 15 years of operation, owing to which use of sandy sediments with better P-adsorbing capacity is advocated as a critical issue for the design of such systems.

Although different solutions have been proposed to transform plants into compost or feed supplements for animals, yet the biomass potential for fuel production has been neglected (Ciria *et al*., 2005). Therefore, the objectives of this work were focused on studying the suitability of macrophyte *Typha latifolia* produced in a wetland for fuel. The main goals were to assess the role of the macrophyte in the removal of biological oxygen demand (BOD), and to determine the thermo chemical characterization of the biomass produced in order to examine the suitability of the biomass for fuel. The hydraulic application rate was 50 mm day^{-1} and one bed was planted with cattail (*Typha latifolia*) and the other was an unplanted control. With regard to wastewater treatment efficacy, the results obtained agreed with the important role of macrophytes for maintaining the wetlands treatment capability, particularly for systems with high organic matter and ammonia-N content.

Constructed wetlands have emerged as a viable alternative for secondary treatment of domestic wastewater. Investigation on the removal efficiency of biological oxygen demand (BOD) and total suspended solids (TSS) in 12 constructed wetlands treating secondary effluent were undertaken by Karathanasis *et al*., (2003). The wetlands were monoculture systems planted with cattails (*Typha latifolia*) or fescue (*Festuca arundinacea Schreb*.), polyculture systems planted with a variety of flowering plants, and unplanted systems. The vegetated systems showed significantly ($P<0.05$) greater removal efficiencies for BOD (>75%) and TSS (>88%) than that in the unplanted systems (63 and 46%, respectively) throughout the year. Overall, the polyculture systems provided the best and most consistent treatment for all the wastewater parameters and remained least susceptible to seasonal variations.

Constructed wetlands have been used for the past 2 - 4 years to determine their effectiveness from residences at eight locations in improving the quality of septic effluent passing through them (Neralla *et al*., 2000). Results indicate that the organic load, fecal coliform populations, and N and P concentrations of the septic water decreased considerably by passing through wetlands. Constructed wetlands reduced BOD_5 of septic water by 80–90%, which provided for feasible disinfection by chlorination. Decline in populations of fecal coliforms varied but normally, population decreased by 90 - 99%. Chlorination further decreased population of fecal coliforms to less than 2 cfu 100 mL^{-1}.

2.6.3. Total Suspended Solids

Treatment efficiency of constructed wetlands planted with indigenous *Cyperus papyrus* and *Phragmites mauritianus* was investigated for the purification of pre-settled municipal wastewater in tropical environments in concrete lined constructed wetlands (Okurut *et al*., 1999). The results showed that BOD and total suspended solids concentrations in the effluents from both the systems were below 20 mgL^{-1} and 25 mg L^{-1}, respectively, while in the *Cyperus papyrus* systems, removal rates for COD, NH_4^+ and o-PO_4' averaged to 3.75, 1.01 and 0.05 ($gm^{-2}day^{-1}$), respectively. In *Phragmites mauritianus* units, rates were 1.52, 0.97 and 0.068 ($gm^{-2}day^{-1}$), respectively.

For evaluatory purposes, efficacy of constructed wetlands for treatment of domestic wastewater having high suspended solids concentration, was studied in two treatment designs (a mixture of *Typha*, *Scirpus, and Juncus* species; control without vegetation) which were planted into two depths (45 or 60 cm) with pea gravel (Hench *et al*., 2003). Each mesocosm received 19 L/day of primary-treated domestic sewage. Significant ($p < 0.05$) differences between influent and effluent water quality for the vegetated wetlands were observed in TSS, BOD_5, and TKN. Increased DO and reduction in fecal coliform, *Enterococcus, Salmonella, Shigella, Yersinia*, and *Coliphage* populations also were observed in vegetated wetlands.

The use of subsurface flow constructed wetlands for treating domestic wastewater was tested for being a low-cost technology (Al-Omarie and Manar, 2003). Results proved that subsurface flow constructed wetlands were capable of reducing biochemical oxygen demand (BOD), different forms of nitrogen, total suspended solids (TSS), fecal coliform count (FCC) and total coliform count (TCC). There was a strong correlation between BOD_5 removal efficiency and BOD_5 loading. The coefficient of determination (R^2) for the six beds varied from 0.827 for bed number one to 0.608 for bed number four. Total and fecal coliform counts were reduced by one to three logs, since influent was high in total and fecal coliform but even after treatment the counts were still high.

To analyze the purification efficiency of a hybrid constructed wetland (CW), a system consisting of two subsurface flow filter beds using light weight aggregates (LWA), a two-chamber vertical subsurface flow (VSSF) filter bed followed by a horizontal subsurface flow (HSSF) filter bed, with a total area of 432 m^2 (Oovel *et al*., 2006) was established for treatment of wastewater. The analyses showed an outstanding purification effect of the system: for BOD_7 the average purification efficiency was 91%; for total suspended solids (TSS) - 78%, for total P - 89%, for total N - 63% and for NH_4-N - 77%. The average outlet values for the above-listed parameters were 5.5, 7.0, 0.4, 19.2 and 9.1 mg L^{-1}, respectively which meet the standards set by the Water Act of Estonia for wastewater treatment plants. The results show that hybrid CW systems could work efficiently in conditions of changing hydraulic loading and relatively cold climate.

2.6.4. <u>Heavy Metals</u>

Dorman *et al.,* (2009) studied pilot-scale constructed wetland treatment system (CWTS) for treatment of toxicity constituents in ash basin water from coal-burning power plants by precipitation as non-bioavailable sulfides, co-precipitation with iron oxyhydroxides and adsorption onto iron oxides. This system proved successful in reducing the concentrations of Zn, Cr, Hg, As and Se less than USEPA-recommended water quality criteria. Moreover it proved that the removal efficiency was dependent on the influent concentration of the constituent, while the extent of removal was independent of the influent concentration. Results indicated that constructed wetland not only controlled the influent toxicity with regard to survival but also reduced influent toxicity with regard to reproduction resulting control in scale formation and bio-fouling.

Constructed wetlands do have an important role in removing heavy metalsfrom wastewater and run-off water (Kjellin *et al.*, 2006). The efficiency of treatment depends strongly on flow pattern and hydraulic retention time of water. A 2D flow and inert transport model was used. Results from computer simulations and independent measurements of friction losses as well as wetland geometry showed that variations in bottom topography, formed by several deep zones, decreased the variance in water residence time to a small extent. Analyses showed that in the Ekeby treatment wetland, basin shape explained about 10% of variance in the observed residence times, whereas vegetation explained about 60 - 80%. This shows its contribution to the spread of residence times and primarily to the long tail of the observed breakthrough curves.

Nutrient and metal removal of a free water surface constructed wetland was compared with the previous small-scale prototype (Maine *et al.*, 2006). Among numerous locally available macrophyte species, *Eichhornia crassipes* showed a fast growth and it soon became dominant, attaining 80% cover followed by *Typha domingensis* and *Panicum elephantipes* (*elephant panicgrass*), which developed as accompanying species each attained 14 and 4% cover. The wetland removed 86% of Cr and 67% of Ni while Zn concentrations were below 50 μgL^{-1}. The FeS precipitation likely caused the high retention of Fe (95%). The out flowing water was anoxic in most samplings which mean that Cr, Ni and Zn were retained by the macrophytes in the larger wetland and in sediment in the small-scale one.

A pilot-scale wetland was constructed (6 × 3 × 0.4 m) to assess the feasibility of treating wastewater from a tool industry (Hadad *et al*., 2006). The variables measured in the influent were significantly higher than those in the effluent. The TP and metal concentration in sediment at the inlet were significantly higher than those at the outlet. *Typha domingensis* displaced other species and reached positive relative cover rate and biomass greater than those at the undisturbed natural environment. *Typha domingensis* proved highly efficient for the treatment of wastewater. For that reason, it is the most suitable species for the treatment of wastewater of high electrical conductivity and pH enriched with metals, characteristic of many industrial processes.

For the removal of heavy metals, *Typha latifolia* plants were grown in a mixture of sewage sludge compost, commercial compost and perlite (Manios *et al*., 2003). Four groups (A, B, C and D) were irrigated with a solution of different concentrations of Cd, Cu, Ni, Pb and Zn, whereas in the fifth (group M) tap water was used. Over time, groups A, B, C and M presented an increasing concentration of total chlorophyll. In group D (stronger solution), the mean total chlorophyll concentration was reduced from 1080.69 μg/g to 715.14 μg/g fresh weight, a probable evidence of inhibition. However, upon implementation of statistical analysis in the ratios of chlorophyll a and chlorophyll b, there was significant reduction of the ratios in groups D plants, suggesting some increase in chlorophyll hydrolysis due to phyto-accumulation of metals.

A twin-shaped constructed wetland (CW) comprising a vertical flow chamber with *Cyperus alternifolius* followed by a reverse-vertical flow was assessed for decontamination of artificial wastewater polluted by heavy metals (Cheng *et al*., 2002). After application of Cd, Cu, Pb, Zn over 150 days, together with Al and Mn during the final 114 days, analysis showed that lateral roots of *Cyperus alternifolius* absorbed about one-third of the applied Cu and Mn. Lower phyto-accumulation levels were observed for Zn (5%), Cd (6%), Al (13%), and Pb (14%). Contents of Cd, Cu, Mn, and Zn in soil were the highest in top layer, while Al and Pb were evenly distributed through the whole soil column. Therefore, it was concluded that a vertical flow CW with *Cyperus alternifolius* was an effective tool in phytoremediation for treatment of water polluted with heavy metals.

The use of constructed wetlands for the treatment of domestic wastewater is now well-established in the UK (Scholes *et al*., 1998) but their ability to treat urban runoff is relatively untested despite the fact that this application could have important environmental and operational benefits in both the industrial and developing countries. In response to this, constructed wetland treatment systems as established at two selected sites in South-east England, both of which received large volumes of urban runoff. The analysis of plant tissues indicated that the reeds phyto-accumulate trace metals and that metal uptake was the greatest in roots. Sediment metal concentrations were typical of a site receiving urban runoff. At both the sites, the highest sediment concentrations were consistently recorded in samples collected from the settlement tanks.

For the enhancement of transfers and transformations of selected metals (Cu, Pb and Zn) in an aqueous matrix, two pilot-scale wetland cells (6.1 × 30.5 m) were integratively designed and constructed (Hawkins *et al*., 1997). Wetland cells were operated in series or parallel with nominal hydraulic retention times of 24 - 48 h, with water depth of 30 cm: both the wetland cells had hydro soil (45 cm) planted with *Scirpus californicus*. Average inflow concentrations of total recoverable Cu, Pb, and Zn were 22.4, 10.5, and 565.9 μgL^{-1}, respectively. After a 46h HRT, average outflow concentrations of total recoverable Cu, Pb, and Zn were 15, 2.2, and 85.9 $\mu g\ L^{-1}$, resulting in removal of 33, 79 and 85% respectively. These results suggest that constructed wetlands can be effectively used to remove targeted metals from wastewater.

For the removal of chromium from tannery wastewater *Penisetum purpureum*, *Brachiaria decumbens* and *Phragmites australis* were grown hydroponically in experimental gravel beds to determine their potential for the phytoremediation. Synthetic solution of concentration, similar to tannery wastewater was used with the aim of developing an economic secondary treatment to protect the environment (Mant., *et. al.* 2006). All the systems achieved removal efficiencies of 97 - 99.6% within 24 h: *Penisetum purpureum* and *Brachiaria decumbens* removed 78.1and 68.5% respectively. Both the *Penisetum purpureum* and *Brachiaria decumbens* were tolerant to chromium applied, but *Penisetum purpureum* showed the greatest potential because its faster growth and larger biomass achieved a much greater chromium removal over the whole duration of the experiment.

2.7. **Contaminant Removal Phenomenon in Constructed Wetlands**

To control the hygienic hazards of pathogens, removal of bacteria in laboratory-scale model sand filters simulating vertical flow systems of constructed wetlands (CW) was done in sand-filled glass columns and planted with *Juncus effuses* or *Phragmites australis* (Wand *et al*., 2007). Results showed that removal rate was low in columns without plantation while predation by protozoa were found in concentrations up to 104 mL^{-1} in the effluent and proved the main reason for its elimination. Considering the transpiration of plants, higher removal efficiencies were found in the planted variants. Protozoa and *Bdellovibrio* were detected in the domestic wastewater in varying concentrations, suggesting that predation and lysis were the major removal mechanisms.

This study was carried out to investigate manifold processes affecting wastewater treatment in constructed wetlands (CWs). These processes include NH_3 volatilization, nitrification, and microbial uptake (Vymazal., 2006). Removal of total nitrogen in studied types of constructed wetlands varied between 40 and 55% with removal load 250 to 630 g N m^{-} 2 yr^{-1} depending on CWs type and inflow loading. Vertical flow constructed wetlands remove successfully ammonia-N but very limited denitrification took place in these systems. On the other hand, horizontal-flow constructed wetlands provided good conditions for denitrification but the ability of these systems to nitrify ammonia removal very limited. Therefore, various types of constructed wetlands may be combined with each other in order to exploit specific advantages of the individual system. Major phosphorus removal processes seemed sorption, precipitation, plant uptake and soil accretion.

Nitrous oxide (N_2O), dinitrogen (N_2), methane (CH_4), and carbon dioxide (CO_2) fluxes were measured in horizontal and vertical flow constructed wetlands (Teiter and Ulo, 2005). The average values of N_2O, N_2, CH_4 and CO_2 fluxes from the riparian gray alder stand varied from −0.4 to 58 µg N_2O-N m^{-2} h^{-1}, 0.02–17.4 mg N^2-N m^{-2} h^{-1}, 0.1–265 µg CH_4-C m^{-2} h^{-1} and 55–61 mg CO_2-C m^{-2} h^{-1}. In horizontal subsurface flow (HSSF) beds of CWs, average N_2 emission varied from 0.17 to 130 and from 0.33 to 119 mg N^2-N m^{-2} h^{-1} in the vertical subsurface flow (VSSF) beds.

Effluent recirculation was investigated in a vertical flow reed bed system treating an agricultural wastewater (Liang *et al*., 2003). A comparison was made for the efficacy of this system before and after recirculation was adopted. Recirculation considerably improved the removal of BOD_5, COD, suspended solids (SS) and NH_4-N. The most significant improvement was made for NH_4-N, and nitrification of NH_4-N into NO_2 and NO_3 only took place when recirculation was employed. With recirculation, the pH value of wastewater gradually decreased as a result of alkalinity being consumed during the nitrification process: whereas without recirculation, the pH remained virtually unchanged. When recirculation was employed, the ambient temperature did not have a significant influence on the removal of BOD_5 but appeared to affect NH_4-N removal.

Gravel has been used as fill material in anaerobic tests in subsurface flow constructed wetlands for treatment of urban wastewater and to evaluate the anaerobic biodegradability (Davison *et al*., 2006). The reactors for the first type of experiment were glass vials of 45 ml capacity whereas those used for the second type of experiment were of multiple measurements having a capacity of 2.2 ml. The evolution of CO_2 in the headspace of reactors was used as an indicator of anaerobic biodegradation rates which ranged from 0.005 to 0.015 μmol/ml day while CH_4 generation was not detected. In-situ measurement of CO_2 and CH_4 emissions ranged from 0.106 to 0.464 and from 0.039 to 0.107 mmol/m^2 h, respectively.

For the improvement in the nitrification and denitrification process, vertical-flow beds (VFBs) were constructed by improving oxygen balance in the filter, which controls the nitrification (Platzer., 1999). For the full nitrification process, oxygen balance should be positive. For technical wastewater treatment plants pre denitrification is well known. Results showed that resulting return rates up to 200% can be used without hydraulic problems for the VFBs. In case of low C/N ratios, an additional application of HFBs will be used. The design can be carried out using a design of 1 g NO_3-N/m^2d^{-1} achieving a 65% removal in more than 90% of the cases.

2.8. Types of Wastewater being Treated by CW

Vymazal and Kröpfelová (2009) studied effectiveness of constructed wetlands from more than 400 HF CWs from 36 countries around the world mostly for the municipal sewage but nowadays being used for agriculture, industry and landfill leachate wastewater. The survey revealed best performance for BOD_5 and COD in treating municipal wastewater and HF CWs are successfully used for both secondary and tertiary treatment. In terms of hydraulic loading, systems treating agriculture and tertiary municipal wastewaters systems were highly loaded and landfill leachate systems were receiving low load. For both BOD_5 and COD, the highest average loadings were recorded for agricultural wastewaters (541 and 1239 $kgha^{-1}d^{-1}$, respectively) followed by industrial wastewaters (365 and 1212 $kgha^{-1}d^{-1}$, respectively). The statistical regression equations for BOD_5 and COD, inflow/outflow concentrations yielded very loose relationships but much stronger relationships for inflow/outflow COD loadings.

Abu and Dike (2008) studied an oil impacted wetland to replicate and compare natural attenuation processes for remediation. Initially hydrocarbon concentration was 90, 212 mg/kg of sediment but as the system developed the natural attenuation processes of photo oxidation, evaporation, volatilization and biodegradation accounted for 31.9% of the total hydrocarbon removed. Thirteen percent removal was attributed to forced aeration which resulted in 44.9% cumulative hydrocarbon removal. It was found that biodegradation alone accounted for 24.7% removal. The sediment analysis showed that *Pseudomonas, Micrococcus, Flavocterium, Staphylococcus, Serratia, Bacillus, Chromobacterium* and *Alkaligenes* contributed to hydrocarbon assimilation in mesophilic and acidic conditions. This proved the applicability and the electiveness of natural attenuation and forced aeration in the remediation.

For use in single houses, wastewater treatment system was constructed based on the principles of sub-surface flow constructed wetlands by using different types of filter media (Heistad *et al*., 2006). The main purpose was to remove organic matter and facilitate nitrification. The system has shown stable and high removal with average values measured from the outlet of septic tank to the outlet of the upflow filter as 97.0% BOD_7, 30% N, 99.4% P and 70.8% SS. Due to considerable removal of organic mater, nutrients and pathogens, the effluent was not harmful for water and soil ecosystems. These CWs require low maintenance and designed for 5 years while the upflow filter media required regular replacement. After saturation of media with phosphorus, it can be used as fertilizer for plant production. Besides this, constructed wetlands have been used for a variety of wastewaters as mentioned in Table 2.1.

Table 2.1: Removal efficiencies of different types of wastewater being treated by constructed wetlands.

S #	Study	Wastewater type	Pollutant removal efficiency %.						
			BOD	**COD**	**SS**	**N**	**P**	**Cl**	**Fe**
1	Heistad *et al*., 2006	Domestic wastewater	97	-	70	30	99	-	-
2	Bulc *et al*., 1997	Landfill leachate	59	50	-	51	53	35	84
3	Chen *et al*., 2006	Industrial wastewater	89	61	81	56	35	-	-
4	Burgoon *et al*., 1999	Potato wastewater	-	-	-	65	-	-	-
5	Mhlum and Stlnacke, 1999	Abattoir wastewater	75	-	-	60	90	-	-
6	Lin *et al*., 2003	Aquaculture system	24	-	71	90	5	-	-
7	Geary and Moore, 1999	Dairy parlor waters	61	-	-	43	28	-	-

2.9. **Summary**

The review of literature shows that these constructed wetlands had proved successful in developed countries for the domestic wastewater, landfill leachate and processing wastewater treatment by using different reeds. This constructed wetland technology had been established as most economical and self sustainable eco-technology. This type of treatment technology is highly required in developing countries but designs being developed in developed countries cannot be replicated in developing counties as such because these countries have different flora & fauna and climatic conditions. Therefore there is need of research on local plant species and wetland design parameters which can best perform in Pakistan climatic conditions. Therefore for this study local plant specie i.e. *Phragmites karka* which is native of Pakistan had been experimented along with *Typha lattifolia* for the treatment of refinery wastewater. While the operating parameter will be three different hydraulic loading rates to achieve best treatment.

Chapter 3

Materials and Methods

To achieve the research objectives of the this study, pilot scale constructed wetlands were installed at Central Laboratories of the Attock Refinery Limited, Rawalpindi, Pakistan for the operational setup and application of wastewater on these wetlands as per design parameters. For the assessment of the treatment efficiency of PSCWs, testing and chemical analysis were done at the environmental engineering and analytical laboratory, National University of Sciences and Technology, Rawalpindi, Pakistan. Detailed description of the experimental setup, characterization of the wastewater, commissioning of the wetlands, types of plants and fill material used is given in the following sections.

3.1. Experimental setup

The dimensions of the wetland beds were chosen on the basis of BOD loading as reported in literature findings (Hammer *et al.*, 1989; Cooper, 1990; Kadlec *et al.*, 1996; Kadlec., 2000). The basic concept of this design equation is that area of wetland was calculated on the basis of influent BOD and effluent BOD which is to be achieved after treatment.

$$A = \left(\frac{0.0365Q}{k}\right) \ln\left(\frac{C_i - C^*}{C_e - C^*}\right) \qquad 3.1$$

Where

A	required wetland area (ha)
Ce	the outlet concentration (mg L^{-1})
Ci	inlet concentration (mg L^{-1})
C*	background concentration (mg L^{-1})
k	first-order areal rate constant (m yr^{-1})
Q	hydraulic loading rate (m d^{-1})

Based on the design equation 3.1, the constructed wetlands dimensions were 1.83 m length × 0.85 m width × 1.0 m depth. The depth of medium in the bed was

0.30 m, leaving a free depth of 0.70 m. The coarse sand and coarse gravel were used for the beds with particle diameter of 0.010 m and 0.030m, respectively. The volume of the bed filled with media was 0.255 m^3, the aspect ratio (L:W) was 3.4 while all the tanks had a slope of 1cmm^{-1}, from inlet to outlet. Depending on the water quality parameters used to size the CW, constants in the model (C* and k) may be different for FWS and SSHF CWs (Kadlec and Knight, 1996). For example, if using BOD_5 to size a CW, C* = 3.5 + 0.053Ci for a FWS CW or a SSHF CW and k would be 34 and 180 m yr^{-1} for a FWS CW and a SSHF CW, respectively (Kadlec and Knight, 1996).

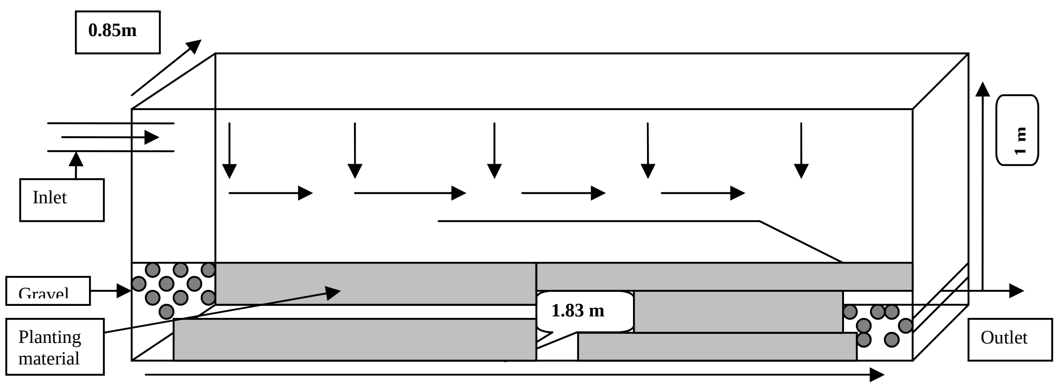

Figure.3.1. A schematic diagram of the pilot-scale wetlands used in this study.

The reactors were fabricated from fibreglass, an inert material and semi transparent material, to avoid reactions between container and the wastewater. There was one inlet and one outlet pipe which was located midway along the reactor width on the respective sides. The inlet pipes were located at a height of 0.85 m from the bottom of the reactor and the outlet pipe, having an internal diameter of 0.015 m, was located at a height of 0.1 m from the bottom. The refinery wastewater was pumped from inlet pipe using a peristaltic pump (VELP Scientifica, Italy) to utilise the bed more effectively. The wastewater in the container was mixed, prior to being pumped into the wetlands.

Taking into account the guidelines for the construction of wetlands (Cooper, 1990), each reactor contained a wire mesh gabion located at the inlet end of reactors in order to facilitate good flow distribution at the inlet. The gabions had 0.050 m length × 0.50 m width × 0.30 m depth and were filled with gravel of 0.020 m nominal size since larger rocks would be too large for the size of the gabion. Baffles were installed in the bed to maintain uniform flow distribution and hence reduce risk of supply of mains water was processed by a valve and the mixture was homogenised.

Figure.3.2. Pumps supplying refinery wastewater to containers.

Figure 3.3. The wastewater application to into constructed wetlands for treatment.

There were two baffles in each reactor, one on each side, located at 0.60m and 1.10m from the inlet point. Two wetland cells were planted with *Phragmites karka* with a density of approximately 4-5 plants per m^2, while the other two were planted with *Typha lattifolia. T*he same was the case for fill materials in that in two wetland cells coarse sand was used as fill material, and the other two were filled with coarse gravel. In total, there were nine batch wetland systems in ready-made vessels and each was batch fed; hence the wastewater was fed to reactors at designed hydraulic loading rates and then effluent was siphoned out to keep the same retention time as for the continuously fed systems.

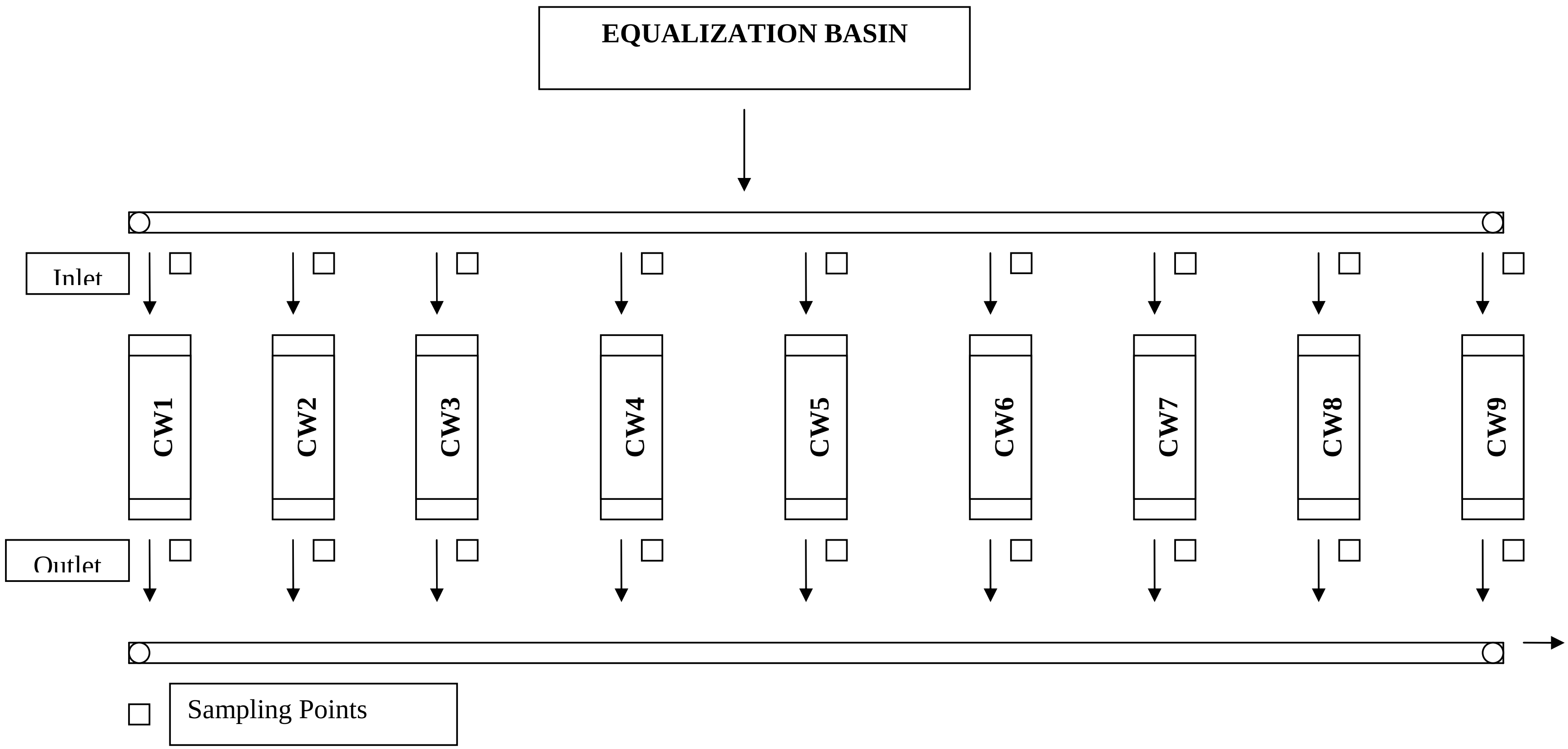

Figure 3.4. Process flow diagram of constructed wetlands for study

3.2. Hydraulic Loading Rate

Based on the review of literature for the current study, these pilot scale constructed wetlands were designed on the basis of BOD loading under which, area and flow rate and hydraulic loading rates were calculated by using equation 3.2 and 3.3 (mentioned as follows in Table 3.1):

$$HRT = V/Q \qquad (3.2)$$

$$HLR = Q/A \qquad (3.3)$$

Table 3.1 Calculation of hydraulic loading rates

HRT	**V**	**Q (m^3/h)**	**HRT (h)**
	0.44	0.125	3.5
	0.44	0.105	4.2
	0.44	0.09	4.9

	Q	**A**	**$m^3m^{-2}h^{-1}$**	**$m^3m^{-2}day^{-1}$**
HLR 1	0.125	1.75	0.07	1.71
HLR 2	0.105	1.75	0.06	1.44
HLR 3	0.09	1.75	0.05	1.23

HRT 3.5	HLR 1	HLR1 =1.71 $m^3m^{-2}day^{-1}$
HRT 4.2	HLR 2	HLR2 =1.44 $m^3m^{-2}day^{-1}$
HRT 4.9	HLR 3	HLR3 =1.23 $m^3m^{-2}day^{-1}$

The wetlands were operated with three different hydraulic loading rates of 1.71 $m^3m^{-2}day^{-1}$, 1.44 $m^3m^{-2}day^{-1}$ and 1.23 $m^3m^{-2}day^{-1}$. In order to establish a microbial community in these wetlands, pilot scale constructed wetlands were seeded with settled sewage and sludge from the refinery drain with effect from Nov 2, 2004 until Dec 24, 2005. At the start of acclimatization period, diluted wastewater was fed to wetlands up till Jan, 2005 in order to acclimatize plants and microbes to refinery wastewater.

Table 3.2. Details of PSCW for plants, fill materials and HLR

Wetland Cell	**Plant**	**Fill material**	**Hydraulic loading rate ($m^3m^{-2}day^{-1}$)**
CW1	*Phragmites karka*	Coarse sand	HLR1 =1.71 (HRT = 3.5 h)
CW2		Coarse gravel	
CW3	*Typha lattifolia*	Coarse sand	
CW4		Coarse gravel	HLR2 =1.44 (HRT = 4.2 h)
CW5	*Phragmites karka*	Coarse sand	
CW6		Coarse gravel	
CW7	*Typha lattifolia*	Coarse sand	HLR3 =1.23 (HRT = 4.9 h)
CW8		Coarse gravel	

3.3. Commissioning of Laboratory Scale Wetlands

The *Phragmites karka and Typha lattifolia* were brought from a pond near Rawalpindi, situated close to the refinery drain. Sterilization of reeds was carried out by immersing the plants in a solution of potassium permanganate ($KMnO_4$) with a concentration of 0.018g $KMnO_4L^{-1}$ for 10 minutes (Dutta., 1977). After transplantation, plants were fed with diluted wastewater to acclimatize them to the particular type of wastewater, characteristics and to growing media. The plants were grown for 2 months (Nov - Dec 2004) in the ARL premises. Initially 50 plants were planted in each replication i.e. in four constructed wetlands and two replications were used at a time.

3.3.1. Fill materials for constructed wetlands

On the basis of the literature review, two fill materials were selected which are coarse gravel and coarse sand, the brief characteristics are given in Table 3.3 and 3.4.

Table 3.3. Characteristics of media in vertical flow constructed wetlands

Characteristic	**Coarse sand**	**Coarse gravel**
Effective size (mm)	2	32
Porosity (%)	32	40
Hydraulic conductivity ($m^3m^{-2}day^{-1}$)	1000	10000

Table 3.4. Chemical characteristics of soil used in constructed wetlands

S#	Contents	Value
1	Organic matter (g/kg)	4.57
2	pH	6.10
3	Total N (g/kg)	0.33
4	Total P (g/kg)	0.14
5	Total K (g/kg)	4.48
6	Total S (g/kg)	0.11
7	Available N (mg/kg)	30.00
8	Available P (mg/kg)	12.70
9	Available K (mg/kg)	74.70

3.3.2. Transplantation of *Phragmites karka* and *Typha lattifolia*

The most commonly used macrophyte in subsurface flow (SSF) wetlands is *Phragmites australis* but *Phragmites karka* was chosen because it is a native specie of Pakistan and *Typha latifolia* was chosen because of its higher biomass yield obtained in a previous study (Solano *et al*., 2004). Young cattail plants (*Typha latifolia*) were collected from natural marshes at the end of October, 2004 and were transplanted on the same day in the respective constructed wetland bed. Each plant, composed of a piece of about 35 cm long rhizome and stem, was established in the bed at a density of four plants per square meter. After planting, all the wetland beds were flooded with fresh water to about 10 cm above the gravel level and plants were allowed to establish in fresh water. Two months later, raw wastewater replaced the fresh water as the influent to these beds. These cattails exhibited a good survival rate, demonstrating a vigorous spread a few weeks after planting to which change was noted after changing the influent. At the end of autumn of 2004, biomass was harvested and a new vegetative cycle began in the following spring of 2005. During the first week of March, plants began to sprout.

3.4. Wastewater Analysis

The wastewater used, which was from the Attock Refinery's main drain, was being diluted with treated water from dissolved air floatation unit (DAF) and from gravity separators. The wastewater was collected on a weekly basis and was analysed for COD, BOD, TDS, TSS, O & G and heavy metals i.e. (Fe^{+2}, Cu^{+2} and Zn^{+2}) prior to its application to pilot scale constructed wetlands as presented in Table 3.1. The wastewater from the refinery has high COD and BOD. The wastewater were analysed in the Environmental Engineering Analytical laboratory of the NUST, using standard methods (APHA, 1998).

3.4.1. Wastewater sample handling

Samples for analysis were usually taken on a weekly basis from the influent (at the inlet pipe to either of the wetlands) and the effluent (at the outlet pipe) of wetlands A, B, C and D. For this test, samples were taken from the inlet and outlet sections of wetlands A and B (see Figure 3.1.).

Between uses in the field, sample bottles were cleaned by the following procedure:

1. Phosphorus-free detergent hand-wash with hot tap water
2. 15 minute soak in 50% HCl
3. Rinse 3X with RO water
4. Rinse 2X with Milli-Q water
5. Air dry

Samples were transported in iced coolers. Upon receipt in the laboratory, each sample was given an unique identification number for unambiguous in-house identification. Trace metals were analyzed using a Perkin Elmer model 5100 Atomic Absorption Spectrophotometer as described in either EPA Method 200.9 or Standard Method 3111, and modified in the Quality Assurance Plan for the Occoquan

Watershed Monitoring Laboratory part III. Metals, TSS, TDS, COD, BOD and O & G were analyzed following the APHA and EPA methods (APHA, 1992; USEPA, 1979).

3.5. Analysis of Sediments and *Phragmites Karka* and *Typha lattifolia*

Since one of the main objectives of this work was to estimate heavy metals removal in constructed wetlands, a carbon content analysis was carried out on the *Phragmites karka* and *Typha lattifolia* in order to evaluate the carbon contents of different plant parts (leaves, stems, rhizomes and roots) during the study period. The weight and water contents variations of different parts of reeds were also studied.

3.5.1. Plant analysis

From each tank, two plants were randomly harvested each month and the harvested plants were rinsed in desorbing solvents and the plants were separated into aerial tissues (stems and leaves) and roots. The separate parts were oven dried at 70–80^{o}C for 48 h in order to determine the dry weights. Three 1 g samples of these oven dried separate tissues were then ashed in a muffle furnace at 550^{o}C for 4 h. The ash was transferred to a 100 mL Pyrex conical flask containing 10 – 15mL of conc. HCl (which was diluted to a 1:1 ratio) and the ash-conc. HCl mixture was heated for 10 min using a steam bath (i.e., until the ash completely dissolved and the mixture turned pale or dull yellow in color). Thereafter, the resulting solution was cooled and filtered into a 100 mL volumetric flask through filter paper. The filtrate was diluted to 100 mLwith distilled water prior to the analysis of Fe.

Simultaneously, sediments including detritus produced by senescing plants were also collected once a week by placing three equal sized Petri dishes at the bottom of each tank. All the sediments were collected by placing an inverted Petri dish on each of the three Petri dishes. The sediment samples were first filtered, and then oven dried at 70 - 80^{o}C for 24 h. Acid digestion was performed using 100mL of distilled water as for the wastewater samples (ASTM D1971-91, 1991). The aciddigested samples were re-filtered and the filtrates were also topped up to 100mL with distilled water prior to analysis.

3.5.2. Processing of coarse gravel and coarse sand

The gravel was sieved to remove any grains with a diameter smaller than 0.0050 m and thoroughly washed, prior to growing the reeds in it. After growing the plants in the gravel for three months, the gravel was sterilised with a solution of 5% sodium hypochlorite for 24 hours. The coarse sand and coarse gravel were sieved to have uniform size compost grains with a diameter of 1-3 mm and 28-35 mm respectively.

3.6. Statistical Analyses

The experimental setup design was 2 Factor Factorial Completely Randomised Design and statistical analysis using a normality test was carried out to assess the interdependence of the variables. For this reason, tests carried out to compare the individual performance of pilot scale were based on two parametric methods, which assume a distribution, for the different data sets. The tests used for the analysis were analysis of variance (MS Excel 2007, Regression analysis). Both methods compare the medians of the data sets, and test if the null hypothesis is true (Sokal and Rholf, 1995).

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Chapter 4
Results and discussion

4.1. CHARACTERIZATION OF REFINERY WASTEWATER

The samples for characterization of refinery wastewater being treated in the constructed wetlands were collected directly from the main drain (Table 4.1). As it underwent primary treatment while flowing through the gravity separators there was a decrease in the suspended and organic load during treatment and average concentrations of some of the pollutants of refinery wastewater were lower than that of the literature values reported by CPP (1999). The COD:BOD_5 ratio of wastewater of refinery was approximately 1.89 which indicated that the refinery wastewater had medium biodegradability and could be classified as "medium strength" wastewater (Tchobanoglous and Burton, 1991).

Since the raw wastewater was generally kept in sedimentation tanks for 2-3 h, total suspended solids (TSS), concentration was reduced almost by 28% after primary treatment, whereas biological oxygen demand (BOD_5) and chemical oxygen demand (COD) concentration was reduced by about 18%. Due to the prevailing aerobic conditions in sedimentation tanks, significant differences in the total dissolved solids concentration before and after the primary treatment could not be noted.

Table 4.1. Characteristics of the refinery wastewater

Parameter (mg L^{-1})	**BOD_5**	**COD**	**TSS**	**TDS**	**Phenols**	**Oil & grease**	**pH**
Average (4 samplings were carried out at different intervals) (n = 6)	135	256	154	1940	6	45	9.7
Minimum	109	165	95	1167	3	24	8.3
Maximum	197	347	154	2850	9	66	10.5
PNEQS*	80	150	150	3500	1	10	7

* Pakistan National Environmental Quality Standards (1997).

There was a fluctuation in the influent concentrations of different parameters hourly, daily, seasonally and periodically raw wastewater received by the sedimentation tank, from which the wastewater was applied to pilot scale constructed wetlands for treatment. Influent concentration of total suspended solid (TSS) (Table 4.1) showed an increase due to the additional inorganic pollutants carried by the surface runoff; whereas dissolved solids concentration of wastewater decreased because of dilution by the storm water. The decrease could also be attributed to shock loads of the refinery sewerage system.

The influent chemical oxygen demand (COD) concentration showed corresponding changes in the concentration of suspended solids, as these values were also affected by the increase of amount of inorganic pollutants. Influent and effluent concentration of wastewater quality parameters was monitored throughout the research period. For calculation of the percent removal efficiencies, average, mean and standard deviation were calculated and discussed in the following sections.

4.2. TREATMENT PERFORMANCE OF CONSTRUCTED WETLANDS

At the start of study, average height of the transplanted plants was 50±5 cm (n = 48) for *Phragmites karka* and *Typha lattifolia*; whereas at the conclusion of the study, the average height of *Phragmites karka* was 110±34 cm and 105±18 cm while that of *Typha lattifolia* was 135±19 cm and 125±26 cm for the coarse sand and coarse gravel wetlands, respectively. The annual average growth rate of *Phragmites karka* plants as 0.21 and 0.25 mm d^{-1}, respectively, while the average growth rate of *Typha lattifolia* was 0.25 and 0.27 mm d^{-1} in the coarse sand and coarse gravel wetlands.

After transplantation, the growth was slow but after the initial stage, the plants were well-acclimatized to the wetlands and did not wither up till the end of the life cycle. The detailed results of the monitoring study (Jan - Dec, 2005) are presented in the following sections for both the coarse sand and coarse gravel in combination with both these *Typha lattifolia* and *Phragmites karka*. Treatment performance has been illustrated against the sampling date versus influent and effluent concentrations of COD, BOD and heavy metals, i.e. Fe^{+2}, Cu^{+2} and $Zn^{+2,}$ in the subsequent sections.

Table: 4.2. Growth of *Phragmites karka* and *Typha lattifolia* with different fill materials using refinery wastewater.

Growth of Macrophyte (in centimeters)

Months	***Phragmites karka***		***Typha lattifolia***	
	Coarse Sand	**Coarse Gravel**	**Coarse Sand**	**Coarse gravel**
Jan, 05	13	15	14	17
Feb, 05	13	17	18	19
Mar, 05	15	18	21	23
Apr, 05	14	12	25	27
May, 05	11	11	19	21
Jun, 05	9	9	17	16
Jul, 05	8	7	9	16
Aug, 05	6	6	3	0
Sep, 05	0	7	0	0
Oct, 05	0	0	0	0
Nov, 05	0	0	0	0
Dec, 05	0	0	0	0
Average monthly growth (cm $month^{-1}$)	7.42	8.50	10.50	11.58
Growth (mm day^{-1}).	0.20	0.20	0.25	0.27

Table: 4.3. Average length of roots and number of leaves of *Phragmites* and *Typha* with different fill materials using refinery wastewater

Parameters	***Phragmites karka***				***Typha lattifolia***			
	Coarse sand		**Coarse gravel**		**Coarse sand**		**Coarse gravel**	
	No of Leaves	**Length of roots (cm)**	**No of Leaves**	**Length of roots (cm)**	**No of Leaves**	**Length of roots (cm)**	**No of Leaves**	**Length of roots (cm)**
Nov, 04	23	12	44	12	7	7	5	6
Dec, 04	31	-	44	-	6	-	7	-
Jan, 05	38	-	63	-	8	-	5	-
Feb, 05	44	19	68	19	7	12	6	13
Mar, 05	55	-	74	-	5	-	6	-
Apr, 05	65	-	81	-	7	-	5	-
May, 05	75	22	87	22	5	17	5	16
Jun, 05	105	-	97	-	7	-	6	-
Jul, 05	123	-	109	-	6	-	5	-
Aug, 05	145	21	114	21	5	22	7	23
Sep, 05	147	-	113	-	7	-	6	-
Oct, 05	143	-	113	-	8	-	5	-
Nov, 05	135	-	108	-	6	-	4	-
Dec, 05	95	22	109	22	7	20	6	21

4.2.1. Performance of *Typha lattifolia* and coarse gravel for treatment

For the performance evaluation of these pilot scales, constructed wetlands were planted with *Typha lattifolia* and filled with coarse gravel along with native soil from the refinery premises. Influent and effluent concentrations of all the designed parameters were measured, which will be discussed in detail in the following sections.

a. Removal of total suspended solids

The efficiency of the suspended solids removal is depicted by its change in the effluent passed through constructed wetland system. Three hydraulic loading rates were applied to compare removal efficiency, while keeping the wetland conditions the same, i.e. all wetland cells were planted with *Typha lattifolia* and filled with coarse gravel as fill material. At hydraulic loading rates of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$ the total suspended solids removal was 16 - 77, 32 - 119 and 32 - 86 mg L^{-1} (62 ± 17 mg L^{-1}) (n = 36), respectively during the monitoring period as mentioned in Table 4.4.

Concentration based total suspended solids removal efficiency of the coarse gravel system varied between 19 - 71 %, 27 - 77% and 33 - 85% at hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$ respectively as presented in Figure 4.1. Statistical analysis shows 89 % variation in the removal efficiency, which is dependent upon *Typha lattifolia* and coarse gravel variables. Coefficient of HLR is 4.91, which indicates that on an average, it increases removal by 4.91 % with every unit increase in HLR. The standard error value is 1.30 which indicates that this coefficient is significant (P = 0.013) and that hydraulic loading rate contributed towards the treatment, although to a minimal extent.

Since the wetlands remained functional at Attock Refinery for one year, the observed total suspended solids removal efficiencies could mostly be related to the processes of sedimentation, filtration, bacterial decomposition and adsorption to the wetland media (Stowell *et al*., 1981). Maximum removal efficiency was observed at hydraulic loading rate of 1.44 $m^3m^{-2}day^{-1}$ during the experimental period, which was consistent up till the start of drying period of plants in constructed wetlands.

During the start-up period of wetlands, the effluent total suspended solids (TSS) concentrations were very low (21 - 51%) but as time passed, total suspended solids effluent values increased up to a maximum of 72 - 85%. Consequently, the variation in the influent and effluent total suspended solids (TSS) values (Table 4.2) could be related to the extensive root system developed by the *Typha* plants in one and a half year old constructed wetlands. This helped in enhancing the total suspended solids

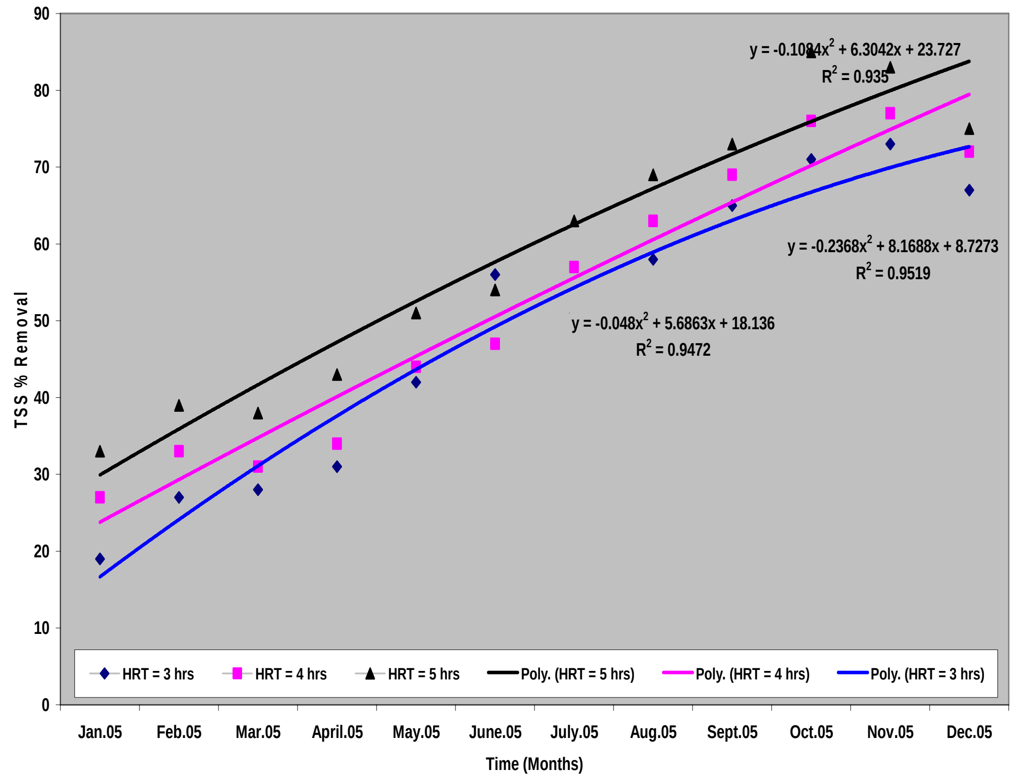

Figure 4.1. Removal (%) age of total suspended solids (Gravel and *Typha lattifolia*)

Table 4.4. Mean values of the quality of influents and effluents (Gravel and *Typha lattifolia*) for total suspended solids

Months	**HLR 1 =1.71 $m^3m^{-2}day^{-1}$**				**HLR 2 =1.44 $m^3m^{-2}day^{-1}$**				**HLR 3 =1.23 $m^3m^{-2}day^{-1}$**			
	Influent (mg/L)		**Effluent (mg/L)**		**Influent (mg/L)**		**Effluent (mg/L)**		**Influent (mg/L)**		**Effluent (mg/L)**	
Jan	85	(±16)	69	(±7)	117	(±6)	85	(±1)	98	(±13)	66	(±4)
Feb	107	(±13)	78	(±9)	126	(±14)	84	(±8)	117	(±14)	71	(±8)
Mar	126	(±6)	91	(±2)	106	(±1)	73	(±2)	97	(±15)	60	(±5)
Apr	135	(±28)	93	(±27)	107	(±0)	71	(±8)	118	(±4)	67	(±5)
May	95	(±31)	55	(±4)	107	(±7)	60	(±1)	124	(±7)	61	(±6)
Jun	139	(±8)	61	(±1)	117	(±6)	62	(±11)	114	(±3)	52	(±6)
Jul	128	(±6)	63	(±9)	109	(±13)	47	(±0)	118	(±16)	44	(±10)
Aug	119	(±11)	50	(±10)	127	(±0)	47	(±5)	95	(±16)	29	(±2)
Sep	104	(±8)	36	(±2)	127	(±6)	39	(±5)	118	(±15)	32	(±12)
Oct	115	(±8)	33	(±0)	135	(±13)	32	(±2)	97	(±7)	15	(±0)
Nov	126	(±6)	34	(±3)	154	(±11)	35	(±2)	87	(±7)	15	(±7)
Dec	118	(±23)	39	(±21)	139	(±16)	39	(±33)	97	(±1)	24	(±29)
Mean	117		57		122		56		107		45	
Stdev	±16		±21		±15		±19		±13		±21	

removal efficiency by providing a larger surface area, reducing the water velocity, and reinforcing settling and filtration in the root network after flowing from coarse gravel (Brix, 1997; Tanner, 2001).

Previous studies examined only some of these factors and monitoring time was significantly shorter (3 - 6 months). The removal efficiency of *Typha lattifolia* and reeds at different hydraulic loading rates was examined by Solano *et al*., (2004) who observed 88% suspended solids removal; Griffin *et al* (1999) found 87% suspended solids removal, Morris and Herbert (1997) found 88% suspended solids removal and Karathanasis *et al*., (2003) observed 88% suspended solids removal.

Abissy and Mandi (1999) found 73% suspended solids removal in the case of coarse gravel, and these results equate with the findings of this study. Greenway (2005) observed 98% suspended solids removal and Plamondon *et al*. (2006) observed 95% suspended solids removal. Significant removal has been achieved for medium strength refinery wastewater, although complex in nature, due to presence of diversified pollutants, but in tertiary treatment, good results have been achieved comparable to those reported in literature.

Therefore, minor differences in suspended solid removal performances at different hydraulic loading rates indicate that the contribution of this macrophyte and fill material to the physical suspended solids removal processes was considerable in the vertical-flow wetland (Tanner *et al*., 1995; Thomas *et al*., 1995). The problem of clogging was not observed during the operation periods in planted filters. This shows that coarse gravel planted with *P. australi*s provided good filtration conditions by preventing the filters from clogging (Brix, 1997).

These results clearly show that the suspended solids removal performance is contributed by *Typha lattifolia*, and show consistency with results reported by

Karathanasis *et al*. (2003), who recorded that the vegetated systems exhibit nearly twice as high removal efficiencies when compared to an unplanted system. Brix (1997) reported that the higher total suspended solids (TSS) removal performances in planted systems could be attributed to larger surface areas, reduced water velocities and reinforced settling and filtration by the coarse gravel and root network.

b. **Removal of total dissolved solids**

Total dissolved solids removal efficiency is specified by the change in its effluent content from the constructed wetland system. By applying three hydraulic loading rates, it was possible to compare this removal efficiency. Treatment achieved at hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$ was 438 - 805, 662–1185 and 696–1406 mg L^{-1} respectively during the study period as shown in Table 4.5.

Concentration based total dissolved solids removal efficiencies of the coarse gravel system varied between 15 - 29% (22±5 %) at hydraulic loading rate of 1.71m^3/m^2/day and 23 - 37 % (28±6 %) at hydraulic loading rate of 1.44m^3/m^2/day and at hydraulic loading rate of 1.23m^3/m^2/day the removal concentration was 26 - 44 % (33±7 %) as presented in Figure 4.2.

During the start-up period of wetlands, total dissolved solids removal concentration was 15 - 26 %, but as time passed, total dissolved solids removal concentration increased up to the value of 29 - 44 %. Statistical analysis shows 96% variation in the removal efficiency, which is dependent upon *Typha lattifolia* and coarse gravel. Coefficient of HLR is 5.625, which indicates that on an average it increases removal by 5.625 % with every one unit increase in HLR. The standard error value is 4.66, which suggests that this coefficient is significant (P = 0.016) and hydraulic loading rate variable increases the percent removal significantly.

Results have shown significant removal of dissolved solids in the present

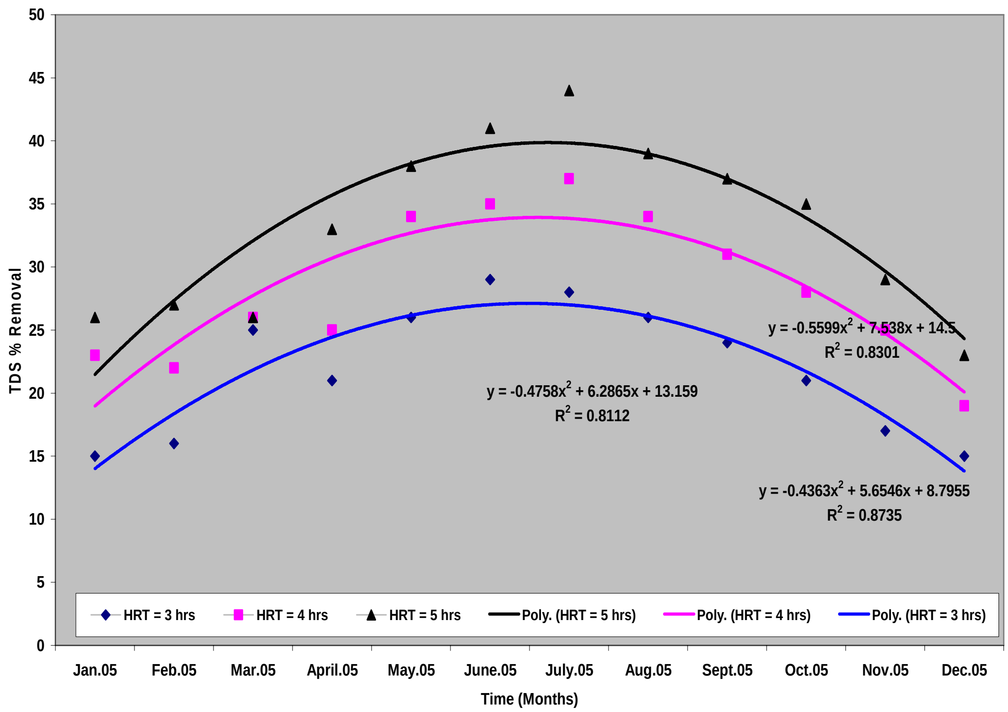

Figure 4.2. Removal (%) age of total dissolved solids (Gravel and *Typha lattifolia*)

Table 4.5. Mean values of the quality of influents and effluents (Gravel and *Typha lattifolia*) for total dissolved solids

Month	HLR 1 =1.71 $m^3m^{-2}day^{-1}$		HLR 2 =1.44 $m^3m^{-2}day^{-1}$		HLR 3 =1.23 $m^3m^{-2}day^{-1}$	
	Influent (mg/L)	**Effluent (mg/L)**	**Influent (mg/L)**	**Effluent (mg/L)**	**Influent (mg/L)**	**Effluent (mg/L)**
Jan	3556 (±581)	3023 (±513)	3155 (±7)	2429 (±17)	2875 (±210)	2128 (±174)
Feb	2735 (±298)	2297 (±50)	3145 (±422)	2453 (±401)	2578 (±132)	1882 (±116)
Mar	3157 (±207)	2368 (±253)	2548 (±665)	1886 (±517)	2765 (±347)	2046 (±96)
Apr	3450 (±407)	2726 (±423)	3488 (±214)	2616 (±363)	3256 (±303)	2182 (±73)
May	2875 (±212)	2128 (±212)	3185 (±143)	2102 (±70)	3684 (±523)	2284 (±386)
Jun	2575 (±213)	1828 (±171)	3387 (±798)	2202 (±551)	2945 (±177)	1738 (±37)
Jul	2876 (±274)	2071 (±162)	2258 (±853)	1423 (±611)	3195 (±288)	1789 (±63)
Aug	2488 (±71)	1841 (±89)	3465 (±77)	2287 (±20)	2788 (±101)	1701 (±24)
Sep	2588 (±511)	1967 (±349)	3356 (±327)	2316 (±164)	2645 (±554)	1666 (±397)
Oct	1865 (±785)	1473 (±704)	2894 (±272)	2084 (±265)	3428 (±469)	2228 (±187)
Nov	2975 (±276)	2469 (±192)	3278 (±207)	2459 (±29)	2765 (±7)	1963 (±112)
Dec	2585 (±687)	2197 (±584)	2985 (±120)	2418 (±8)	2755 (±85)	2121 (±4)
Mean	2810	2199	3095	2223	2973	1977
Stdev	±455	±419	±375	±322	±342	±218

study, and low level of removal could be attributed to absorption, sedimentation and filtration process, which is actually the removal of heavy metals from the dissolved portion. Generally, throughout the monitoring period, average effluent dissolved solids concentration of systems remained below the National Environmental Quality Standards of Pakistan CPP (1999), which is 3500 mg L^{-1} for treated domestic wastewater.

c. **Removal of chemical oxygen demand**

The efficiency of organic pollutant removal is indicated by the change in chemical oxygen demand of the effluent in our pilot scale vertical flow constructed wetland systems, three different hydraulic loading rates were tested to compare removal efficiency, while keeping the wetland conditions the same. At hydraulic loading rate of 1.71, 1.44, 1.23 $m^3m^{-2}day^{-1}$, the chemical oxygen demand removal was 45–189, 61–215 and 88–226 mg L^{-1}, respectively during the monitoring period as shown in Table 4.6.

Chemical oxygen demand removal efficiencies of the coarse gravel system varied between 16 - 58 % (32±13 %) at hydraulic loading rate of 1.71 $m^3m^{-2}day^{-1}$, 21 - 65 % (43±17 %) at hydraulic loading rate of 1.44 $m^3m^{-2}day^{-1}$ and 34 - 74 % (53±15%) at hydraulic loading rate of 1.23 $m^3m^{-2}day^{-1}$ as presented in Figure 4.3 respectively. Statistical analysis shows 90% variation in the removal efficiency, while the coefficient of HLR is 10.375, which indicates that on average, it increases removal by 10.375% with every one unit increase in HLR. The standard error value is 3.40, which indicates that this coefficient is significant (P = 0.017), and hydraulic loading rate variable is significant in increasing the percentage removal.

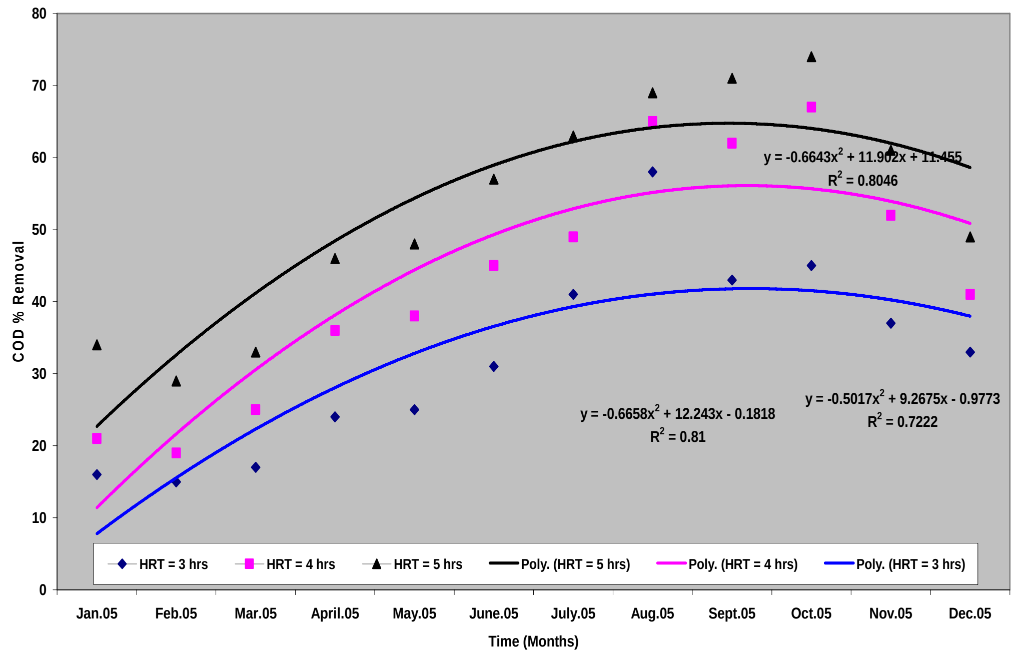

Figure 4.3. Removal (%) age of chemical oxygen demand (Gravel and *Typha lattifolia*)

Table 4.6. Mean values of the quality of influents and effluents (Gravel and *Typha lattifolia*) for chemical oxygen demand

Months	**HLR 1 =1.71 $m^3m^{-2}day^{-1}$**		**HLR 2 =1.44 $m^3m^{-2}day^{-1}$**		**HLR 3 =1.23 $m^3m^{-2}day^{-1}$**	
	Influent (mg/L)	**Effluent (mg/L)**	**Influent (mg/L)**	**Effluent (mg/L)**	**Influent (mg/L)**	**Effluent (mg/L)**
Jan	341 (±30)	286 (±23)	309 (±7)	244 (±10)	327 (±16)	216 (±1)
Feb	298 (±9)	253 (±12)	319 (±11)	258 (±21)	305 (±6)	217 (±12)
Mar	285 (±21)	237 (±2)	304 (±1)	228 (±23)	297 (±1)	199 (±28)
Apr	315 (±7)	239 (±3)	306 (±1)	196 (±5)	296 (±13)	160 (±2.8)
May	325 (±3)	244 (±16)	304 (±3)	188 (±13)	315 (±1)	164 (±20)
Jun	321 (±1)	221 (±22)	308 (±2)	169 (±10)	316 (±16)	136 (±19)
Jul	322 (±3)	190 (±38)	305 (±9)	156 (±31)	294 (±1)	109 (±12)
Aug	326 (±13)	137 (±27)	318 (±25)	111 (±3)	295 (±7)	91 (±2)
Sep	307 (±6)	175 (±8)	282 (±28)	107 (±1)	305 (±1)	88 (±6)
Oct	298 (±11)	164 (±24)	321 (±11)	106 (±29)	306 (±14)	80 (±34)
Nov	314 (±13)	198 (±0)	306 (±1)	147 (±25)	326 (±6)	127 (±24)
Dec	296 (±32)	198 (±62)	308 (±1)	182 (±44)	317 (±7)	162 (±38)
Mean	312	212	308	174	308	146
Stdev	±16	±43	±10	±52	±12	±49

As the wetlands remained functional at Attock Refinery for one year, the observed chemical oxygen demand removal efficiencies could be related mostly to quiescent conditions by deposition and filtration, under which organic compounds had undergone both aerobic and anaerobic degradation by the heterotrophic micro-organisms in the wetland systems arising from the oxygen concentration in the bed (IWA, 2000). The present study shows that at hydraulic loading rate of $1.77 m^3/m^2/day$, removal efficiency was 100 mg L^{-1}, at $1.44 m^3/m^2/day$, the removal was 133 mg L^{-1} and at $1.23 m^3/m^2/day$, the removal was 163 mg L^{-1}. During the start-up period of wetlands, chemical oxygen demand removal concentration was 16 - 34 % but as time passed, chemical oxygen demand removal concentration increased up to the value of 58 - 74 %.

In wetland systems, treatment efficiency of the constructed wetlands for the removal of organics is, generally, highly dependent on the oxygen concentration in the bed which is provided by diffusion and oxygen leakage from the macrophytes roots into rhizosphere. (Vymazal *et al*., 1998; IWA, 2000).

Nevertheless, all the studies showed that plants played a significant role in aeration process to facilitate the biodegradation process. This could be explained by the low organic content of the wastewater applied to wetlands, which probably did not clog pores of substrates with settled organics. The similar chemical oxygen demand treatment trend at all the hydraulic loading rates of wetlands could also be related to sufficient oxygen diffusion into wetland cells. Chemical oxygen demand removal at three different hydraulic loading rates could be attributed to the biological degradation, as well as due to plant contribution to aeration process, since one and half year old wetlands had established an extensive plant root network during the operation period.

It can be stated that when low loading rate was applied, the effluent had more retention time in the wetland resulting in better removal efficiency, which means that the chemical oxygen demand removal in both the wetlands was mainly due to biological degradation and adsorption or absorption of heavy metals to sediments as the one-year old wetlands of refinery might not have established an extensive plant root network during the operation period.

Excellent chemical oxygen demand removal was achieved by an optimum of physical and microbial mechanisms in the CWs. The SFCW system has two important features which make wetlands efficient at removing chemical oxygen demand under heavy loads. Firstly, owing to the physical separation mechanism, organic solids could settle out and retained in the wetland cell for a longer time, thereby allowing improved hydrolysis of organic solids for biodegradation to proceed easily. Further, coarse gravel media placed inside the wetland cell allow accumulation of immense amounts of attached bacteria, which can be very helpful in rapidly catalyzing chemical reactions to affect the treatment.

As such, the limitation of oxygen supply can be avoided, and maintaining anaerobic conditions inside the wetland cell provides the advantage of low sludge production, which largely prevents the wetland being clogged by biomass. Previous studies examined only some of these factors and monitoring time was significantly shorter (3 - 6 months). Drizo *et al*. (2000), Gray *et al*. (2000), Huang *et al*. (2000) and He and Mankin (2002) examined the effect of plants. The effect of porous media size and type was examined by He and Mankin (2002). Huang *et al*. (2000) examined the effect of hydraulic loading rate on chemical oxygen demand removal efficiencies. After treatment at these constructed wetlands, effluent chemical oxygen demand was around 104 mg L^{-1}, which is well below the limit for effluent discharge concentration set by the Pakistan National Environmental Quality Standards (CPP 1999).

d. **Removal of biological oxygen demand**

The efficiency of organic pollutant removal is indicated by a change in biological oxygen demand of the effluent released after treatment from the constructed wetland systems. Three different hydraulic loading rates were applied on CWs to compare removal efficiency, while keeping the wetland conditions constant. At hydraulic loading rate of 1.77, 1.44 and 1.23 $m^3m^{-2}day^{-1}$, the biological oxygen demand removal was 19 - 66, 32 - 105 and 36 - 92 mg L^{-1}, respectively during the monitoring period as shown in Table 4.7.

The biological oxygen demand removal efficiencies of the coarse gravel system varied between 15 - 51 % (33 ± 13%) at hydraulic loading rate of 1.77 $m^3m^{-2}day^{-1}$, 27 – 68 % (44 ± 16 %) at hydraulic loading rate of 1.41 $m^3m^{-2}day^{-1}$ and 33-78 % (55 ± 17 %) at hydraulic loading rate of 1.23 $m^3m^{-2}day^{-1}$, as presented in Figure 4.4. Statistical analysis shows 90% variation in the removal efficiency, which is dependent upon these variables. Coefficient of HLR is 10.375 indicated that on average it increased removal by 10.375% with every one unit increase in HLR. The standard error value is 3.40, which indicates that this coefficient is significant (P = 0.014) and that the hydraulic loading rate variable is significant in increasing the BOD removal.

During the start-up, biological oxygen demand removal was 51%, but as time passed it increased up to 85%. During one-year functional period at ARL, observed biological oxygen demand removal efficiencies could be related mostly to quiescent conditions by deposition and filtration. Organic compounds degraded both aerobically and anaerobically by the heterotrophic microorganisms depending on the oxygen

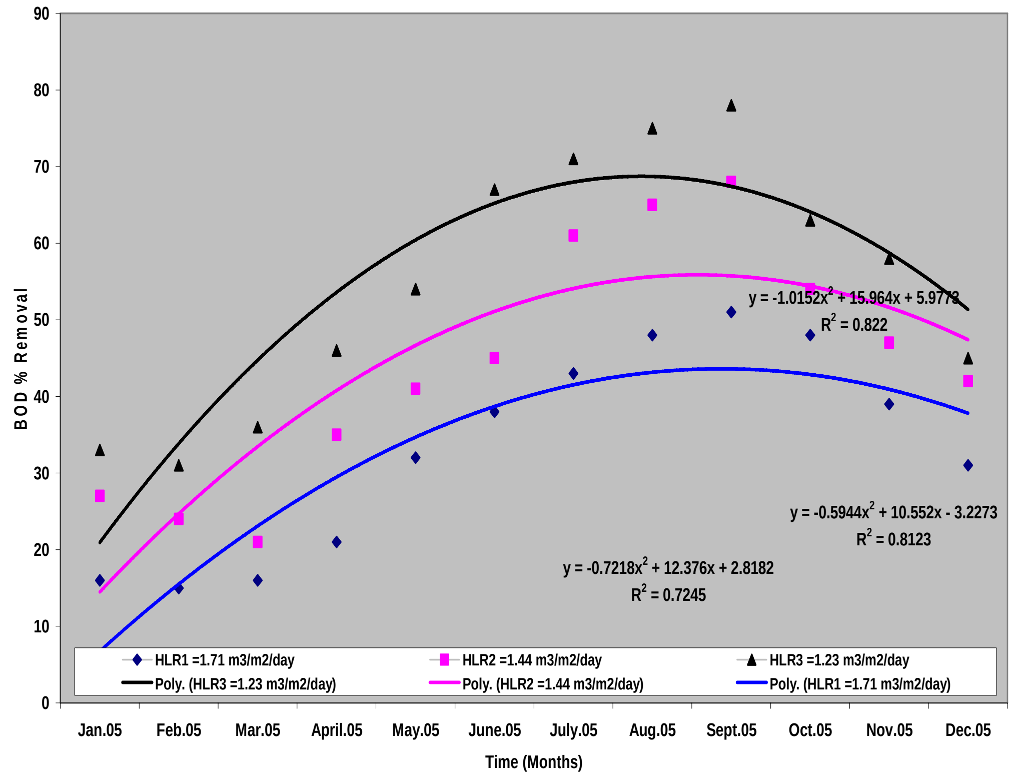

Figure 4.4. Removal (%) age of biological oxygen demand (Gravel and *Typha lattifolia*)

Table 4.7. Mean values of the quality of influents and effluents (Gravel and *Typha lattifolia*) for biological oxygen demand

Months	HLR 1 =1.71 $m^3m^{-2}day^{-1}$		HLR 2 =1.44 $m^3m^{-2}day^{-1}$		HLR 3 =1.23 $m^3m^{-2}day^{-1}$	
	Influent (mg/L)	**Effluent (mg/L)**	**Influent (mg/L)**	**Effluent (mg/L)**	**Influent (mg/L)**	**Effluent (mg/L)**
Jan	128 (±3)	108 (±1)	118 (±4)	86 (±6)	109 (±0)	73 (±2)
Feb	124 (±0)	105 (±1)	124 (±0)	94 (±3)	109 (±6)	75 (±0)
Mar	124 (±18)	104 (±19)	124 (±2)	98 (±14)	117 (±7)	75 (±12)
Apr	98 (±19)	77 (±5)	121 (±95)	79 (±51)	107 (±105)	58 (±42)
May	125 (±6)	85 (±1)	256 (±91)	151 (±57)	256 (±83)	118 (±51)
Jun	134 (±6)	83 (±8)	127 (±1)	70 (±14)	138 (±12)	46 (±7)
Jul	125 (±1)	71 (±4)	128 (±8)	50 (±6)	121 (±9)	35 (±6)
Aug	127 (±1)	66 (±3)	117 (±14)	41 (±2)	108 (±5)	27 (±1)
Sep	125 (±8)	61 (±7)	137 (±20)	44 (±4)	115 (±7)	25 (±15)
Oct	137 (±7)	71 (±4)	109 (±6)	50 (±9)	125 (±11)	46 (±0)
Nov	127 (±1)	77 (±7)	118 (±2)	63 (±5)	109 (±8)	46 (±6)
Dec	126 (±1)	87 (±15)	121 (±2)	70 (±11)	98 (±8)	54 (±14)
Mean	125	83	133	75	126	56
Stdev	±10	±16	±39	±31	±42	±26

concentration in the bed (IWA, 2000).

The present study shows that at hydraulic loading rate of $1.77m^3/m^2$/day, the removal efficiency was 42 mg L^{-1} at loading rate of $1.44m^3/m^2$/day, the removal was 59 mg L^{-1} and at $1.23m^3/m^2$/day loading rate, the removal was 70 mg L^{-1}. Treatment of effluent containing BOD using constructed wetlands is accomplished through several physical, chemical and biological processes. Removal of BOD_5 in wetlands is dominantly through aerobic microbial degradation, sedimentation and filtration processes (Watson *et al*., 1989). According to the wetland design, the oxygen required for aerobic degradation could be supplied by diffusion, convection and oxygen leakage from the macrophyte roots into the rhizosphere (Moshiri, 1993). Thus, treatment efficiency of the constructed wetlands for the removal of organics is, generally, highly dependent on the oxygen concentration in the bed. In our studies significant BOD reduction shows that aerobic conditions were prevailing which facilitated greater removal efficiency.

The biological oxygen demand removal in wetland hydrosoils is carried by the oxidation of organic matter, which provides energy for microbial metabolic processes and can be synthesized or incorporated into cell mass (Manahan, 1994). The organic matter present in effluent provides a substrate for aerobic microbial metabolism. The function, therefore, of constructed wetlands is to encourage contact of microorganisms with its substrate, resulting in conversion of organic matter to CO_2, biomass and water (Portier and Palmer, 1989). Thus, the design rationale for this system was that by utilizing *Phragmites* and coarse sandy hydrosoil combination to create an oxygen-rich rhizosphere and consequently aerobic microbial degradation of BOD would be enhanced.

The main objective of the present study is the examination of effect of HLRs, *Typha lattifolia* and coarse gravel on removal efficiencies of organic matter (BOD), through continuous monitoring of controlled parallel experiments. Previous studies examined only some of these factors and monitoring time was significantly shorter (3 - 6 months). Drizo *et al*. (2000), Gray *et al*. (2000), Huang *et al*. (2000) and He and Mankin (2002) examined the effect of plants. In addition, the effect of porous media size and type was examined by He and Mankin (2002) and that of hydraulic loading rate was examined by Huang *et al*. (2000).

Another possible reason for the relatively low effluent biological oxygen demand concentration seems due to proper spacing in plants or plant density, which resulted in extra aeration and oxidation of organic load (Thomas *et al*., 1995). The decay of plant debris within the wetland also contributed to organic loading. These results suggest that the water treatment potential of the so developed (i.e. matured) biofilm substrate could help improve the biological oxygen demand removal (Scholz and Xu, 2002; Scholz, 2006). It is generally accepted that the mature root system enhances the capacity of transporting oxygen to substrates and provides a large surface area for microorganisms to grow (Cooper *et al*., 1996; Scholz, 2006).

Thus, it can be concluded that the biological oxygen demand removal in the wetlands was mainly due to biological degradation and establishment of bio-film during the one-year old wetlands operation period. The average effluent biological oxygen demand concentration was around 68 mg L^{-1}, which is significantly below the limit set by the National Environmental Quality Standards of Pakistan's CPP (1999).

e. <u>Removal of oil and grease</u>

The efficiency of pilot scale vertical flow constructed wetland systems is also indicated by the reduction in oil and grease concentration with different hydraulic loading rates. At hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$, oil and grease removal was 10 - 20, 14 - 22 and 14 - 28 mg L^{-1}, respectively during the monitoring period as shown in Table 4.8.

Oil and grease removal efficiencies of the coarse gravel system varied between 22 - 31 % (26±2 %) at hydraulic loading rate of 1.71 $m^3m^{-2}day^{-1}$, 25 - 39 % (34±4 %) at 1.41 $m^3m^{-2}day^{-1}$ and at HLR of 1.23 $m^3m^{-2}day^{-1}$, the removal was 34 - 44 % (39±3 %) as presented in Figure 4.5. At the start-up period of the wetlands, oil and grease removal was 19 - 28%. During the year long functional period at Attock Refinery, the observed oil and grease removal efficiencies could be related mostly to quiescent conditions but with the system maturation and stabilization, the removal concentration increased up to 24 - 51 %.

The present study shows that at hydraulic loading rate of 1.77 $m^3m^{-2}day^{-1}$, the removal efficiency was 13 mg L^{-1}, at HLR of 1.44 $m^3m^{-2}day^{-1}$, the removal was 15 mg L^{-1} and at HLR of 1.23 $m^3m^{-2}day^{-1}$, the removal was 20 mg L^{-1}. Statistical analysis shows 99% variation in the removal efficiency, which is dependent upon coarse gravel and *Typha lattifolia*. Coefficient of HLR is 6.54, which indicates that on average it increases removal by 6.54 %, with every unit increase in HLR. The standard error calculated value is 9.92, which is significant (P = 0.013) and hydraulic loading rate variable is significant in increasing the percentage removal. Treatment of effluents containing oil and grease using constructed wetlands is accomplished through several physical, chemical, and biological processes (Watson *et al.*, 1989). In the wetland systems, oil and grease removal is due to filtration and degradation of oil and grease, both aerobically and anaerobically by the heterotrophic microorganisms in wetland systems. In line with the wetland design, the oxygen required for aerobic degradation

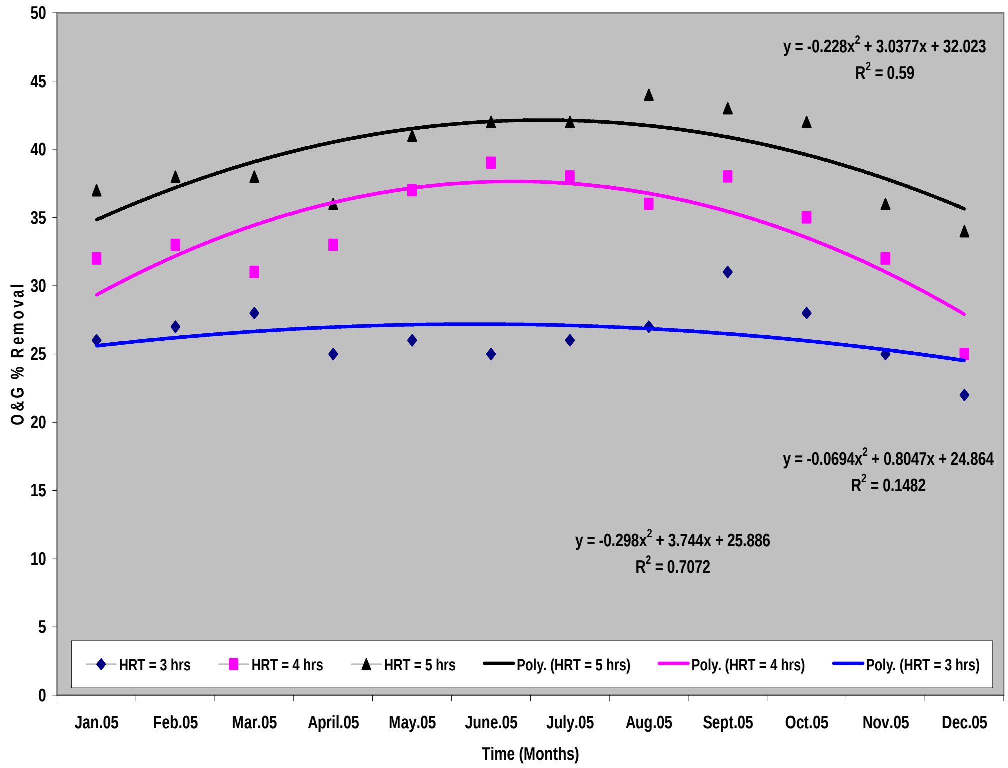

Figure 4.5. Removal (%) age of oil and grease (Gravel and *Typha lattifolia*)

Table 4.8. Mean values of the quality of influents and effluents (Gravel and *Typha lattifolia*) for oil and grease

Months	HLR 1 =1.71 $m^3m^{-2}day^{-1}$		HLR 2 =1.44 $m^3m^{-2}day^{-1}$		HLR 3 =1.23 $m^3m^{-2}day^{-1}$	
	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)
Jan	45 (±16)	33 (±11)	57 (±1)	39 (±0)	39 (±8)	25 (±5)
Feb	67 (±4)	49 (±3)	58 (±6)	39 (±4)	51 (±1)	32 (±1)
Mar	73 (±11)	53 (±6)	49 (±4)	34 (±4)	53 (±8)	33 (±5)
Apr	58 (±14)	44 (±11)	43 (±11)	29 (±5)	41 (±7)	26 (±3)
May	38 (±0)	28 (±0)	58 (±5)	37 (±4)	51 (±3)	30 (±2)
Jun	38 (±13)	29 (±9)	51 (±11)	31 (±6)	47 (±2)	27 (±1)
Jul	56 (±6)	41 (±5)	36 (±1)	22 (±0)	44 (±13)	26 (±7)
Aug	47 (±3)	34 (±3)	35 (±0)	22 (±0)	63 (±4)	35 (±2)
Sep	43 (±1)	30 (±2)	35 (±5)	22 (±2)	57 (±3)	32 (±2)
Oct	45 (±4)	32 (±2)	28 (±14)	18 (±10)	61 (±11)	35 (±5)
Nov	39 (±13)	29 (±11)	48 (±1)	33 (±1)	45 (±1)	29 (±0)
Dec	58 (±9)	45 (±8)	46 (±8)	35 (±3)	43 (±3)	28 (±3)
Mean Stdev	51 ±12	37 ±9	45 ±10	30 ±7	50 ±8	30 ±7

could be supplied by diffusion, convection and oxygen leakage from the macrophyte roots into the rhizosphere (Moshiri, 1993).

Our results indicated that CW system could remove oil and grease effectively. Plants in the wetland have a natural mechanism for pumping air via their root systems. The root rhizosphere would help an oxygen-rich environment, which supports a range of aerobic bacteria like *Pseudomonas, Staphylococcus, Bacillus* and *Alkaligenes* (Brix, 1994). Furthermore, a range of anoxic and anaerobic microbial processes occur within wetlands (Reddy and Patrick, 1984). These biological processes do promote the degradation of mineral oil. Oil and grease in wetlands are also subjected to physical processes such as evaporation, leaching, sorption on to soil particles and sedimentation, which can also elevate removal efficiency (Mashauri *et al*., 2000). It should be pointed out that seasonal variation of outlet oil and grease concentration may be due to variations in temperature, biomass of reed, and the types and quantities of micro-organisms, which need to be studied further.

f. <u>Removal of Iron, Copper and Zinc</u>

The efficiency of inorganic pollutant removal is indicated by the change in concentrations of the effluent upon passing through any constructed wetland systems. At hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$ the Fe removal was 0.72 - 2.33, 32 - 119 and 1.17 - 2.08 mg L^{-1}, the copper removal was 0.58 - 3.05, 1.19 – 3.2 and 1.57 - 4.38 mg L^{-1} and the zinc removal was 0.40 - 2.77, 0.68 - 2.24 and 0.89 - 2.68 mg L^{-1} respectively during the monitoring period as shown in Table 4.9.

Iron removal efficiencies of the coarse gravel system varied between 21 - 51% (35±11%), 26 - 67% (45±16%) and 33 - 75% (52±16%), 18 - 61% (33±13%), 27 - 77% (51±26%) and 29 -73% (45±13%) for copper and 21 - 58% (37±13%), 25 - 63% (42±14%) and 31 - 69% (48±13%) for zinc at hydraulic loading rate of 1.71, 1.44 and

1.23 $m^3m^{-2}day^{-1}$, respectively as shown in Figure 4.6, 4.7 and 4.8. During the start-up period of wetlands, the heavy metal removal was low but as time passed, treatment efficiency increased. During the wetlands functional period of one year at Attock Refinery for one year, the observed heavy metal removal efficiencies could be related mostly to quiescent conditions by deposition and filtration.

For iron, statistical analysis shows 89% variation in the removal efficiency, which is dependent upon coarse gravel and *Typha lattifolia*. Coefficient of HLR is 4.91, which indicates that it increases removal by 4.91% with every unit increase in HLR. The standard error value is 1.30 which indicates that effect of this coefficient is highly significant (P = 0.013) and that the hydraulic loading rate variable acts significantly for increasing the Fe removal. For copper the statistical analysis demonstrates 90% variation in the removal efficiency which is dependent upon coarse gravel and *Typha lattifolia*. Coefficient of HLR is 6.33, which indicates that it increases removal by 6.33 % with every unit increase in HLR. The standard error value is 2.34, which is significant and hydraulic loading rate variable non significantly increased Cu removal.

Statistical analysis for zinc shows 89% variation in the removal efficiency, which is dependent upon coarse gravel and *Typha lattifolia*. Coefficient of HLR is 4.91, which indicates that it increases removal by 4.91% with every unit increase in HLR. The standard error value is 1.30 which indicates that effect of this coefficient is highly significant (P = 0.015) and that the hydraulic loading rate variable acts significantly for increasing the Fe removal. For copper the statistical analysis demonstrates 90% variation in the removal efficiency which is dependent upon coarse gravel and *Typha lattifolia*. Coefficient of HLR is 6.33, which indicates that it increases removal by 6.33 % with every unit increase in HLR. The standard error

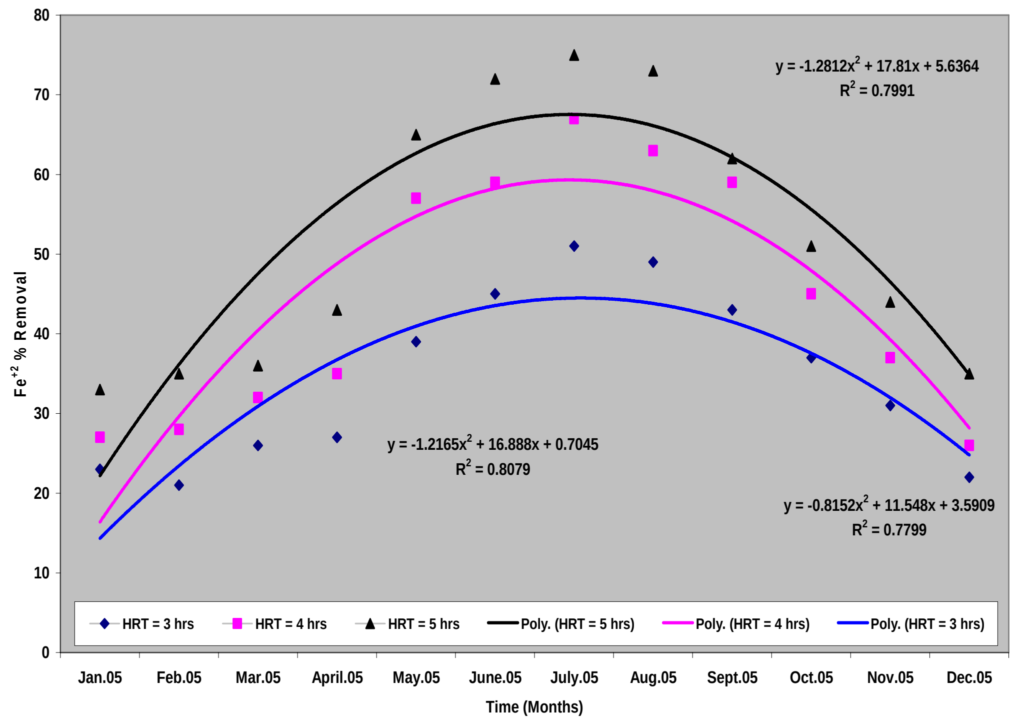

Figure 4.6. Removal (%) age of iron (Gravel and *Typha lattifolia*)

Table 4.9. Treatment performance values for iron, copper and zinc in influent and effluent (Gravel and *Typha lattifolia*)

Plant	***Fill Material***	***Heavy Metal***	***Statistical Results***	***HLR 1*** ***1.71 $m^3m^{-2}day^{-1}$***	***HLR 2*** ***1.44 $m^3m^{-2}day^{-1}$***	***HLR 3*** ***1.23 $m^3m^{-2}day^{-1}$***
Typha lattifolia	*Coarse gravel*	*Iron*	*Max*	*51*	*27*	*33*
			Min	*21*	*67*	*75*
			Mean	*35*	*45*	*52*
			Stdev	*11*	*16*	*16*
		Copper	*Max*	*61*	*69*	*73*
			Min	*18*	*23*	*29*
			Mean	*33*	*40*	*45*
			Stdev	*13*	*14*	*13*
		Zinc	*Max*	*58*	*63*	*69*
			Min	*21*	*25*	*31*
			Mean	*37*	*42*	*48*
			Stdev	*13*	*14*	*13*

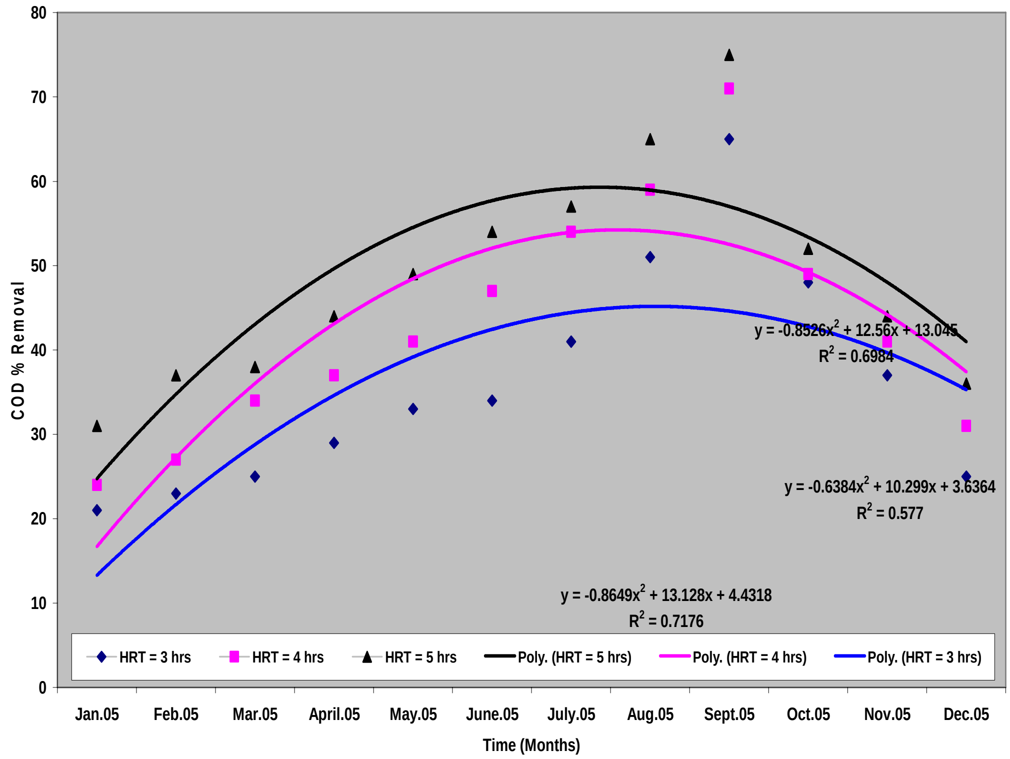

Figure 4.7. Removal (%) age of copper (Gravel and *Typha lattifolia*)

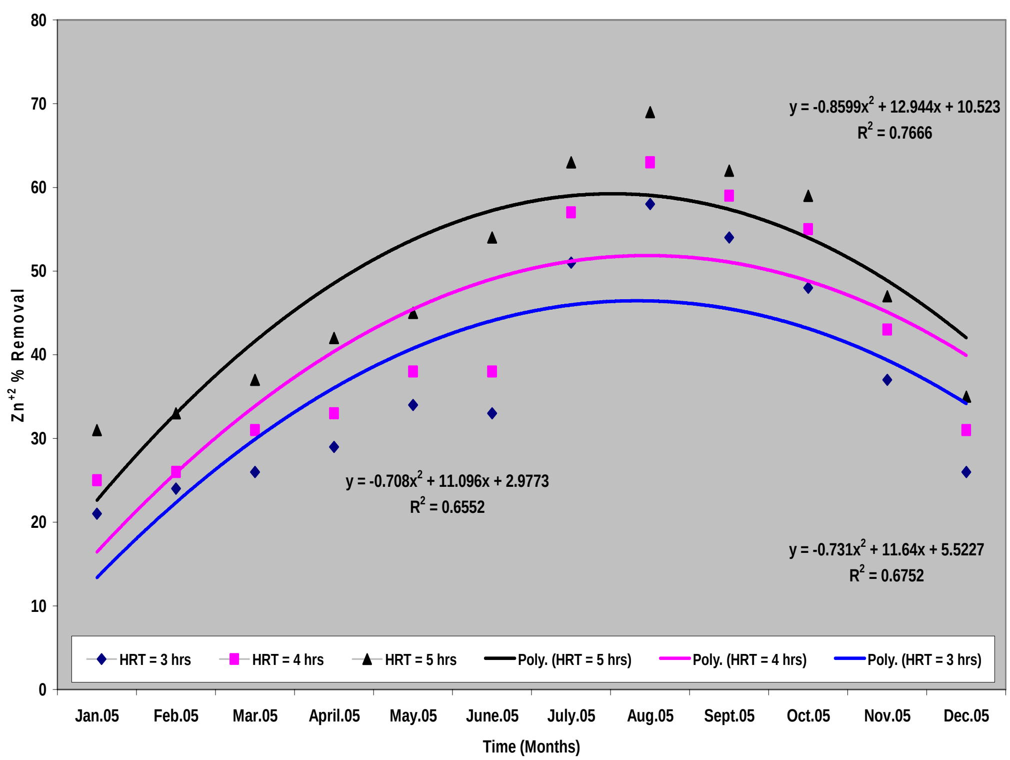

Figure 4.8. Removal (%) age of zinc (Gravel and *Typha lattifolia*)

value is 2.34, which is significant (P = 0.016) and hydraulic loading rate variable non significantly increased Cu removal. Statistical analysis for zinc illustrates 91% variation in the removal efficiency which is dependent upon coarse gravel and *Typha lattifolia*. Coefficient of HLR is 5.66, which indicates that on the average, it increases removal by 5.66%, with every unit increase in HLR. The standard error value is 2.14, which is significant and hydraulic loading rate variable is significant for increasing the Zn removal.

In constructed wetlands, both substrate interactions and wetland plant species have the capacity to remove heavy metals from contaminated water (Matagi *et al*., 1998; Scholz, 2006; Sherrard *et al*., 2004). The role of plants through plant uptake, reduction of water flow, and plant-induced chemical changes in the rhizosphere could increase the storage capacity of sediments. Since wetland plant species have great capacity to accumulate and translocate metals (Greger and Kautsky, 1993; Rai *et al*., 1995; Wolterbeek and van der Meer, 2002), the metal removal can be greatly enhanced by the selection of plant species suitable to the growth environments (Lewander *et al*., 1996).

Nevertheless, these facts justify that any direct involvement of bacteria in the oxidation of Fe_{2+} and subsequent precipitation was insignificant in this study. Basically our results implied that the average pH of Fe-rich industrial wastewaters and the pH of the pipe-borne water added to the constructed wetlands (i.e., prior to introducing the wastewaters) is conducive for Fe removal through chemical precipitation, provided DO levels are higher than 3 - 4 mg/L for the abiotic oxidation of Fe_{2+} to occur (van der Meer, 2002).

The coarse gravel used as a substrate component in this experiment was highly contaminated with heavy metals (Annex A), which, however, did not have a significant impact in any way on the development and growth of the *Typha latifolia* plants. There was a significant increase in the Fe concentration in plants which correlated with the metals in the wastewater and with the metals in the substrate. There was some what retarded plant growth recorded in the plants and in the same plants larger heavy metals concentrations were recorded (Annex A). This toxicity was significantly correlated with the wastewater.

Previous studies examined only some of these factors for shorter timings (3 - 6 months). Lim *et al*., (2001), Scholz and Xu (2002), Maehlum (1995), Dunbabin and Bowmer (1992) and Dunbabin *et al*., (1988) examined the effect of plant on metal removal. During the application of wastewater in constructed wetlands, a milky-white, cloudy appearance was noticed in the wastewater surfaces in all the set-ups suggests formation of Fe rich colloidal (precipitates). Generally precipitation of Fe occurs, following the atmospheric- (abiotic) and bacterial mediated oxidation. Mostly *Thiobacillus ferrooxidans* and bacteria of the genera *Sphaerotilus, Metallogenium* and *Crenothrix* help transform Fe^{2+} to Fe^{3+} (Groudeva *et al*., 2001; Vymazal, 2003).

It can be argued that deposition of this superficial plaque is due to oxygen moving towards the rhizosphere, with formation of copper oxyhydroxides (Peverley *et al*., 1995). Such plaque causes precipitation of metals such as copper, iron and zinc upon itself and also function as a physical and chemical barrier against penetration and translocation within into roots of other plants (Batty *et al*., 2002). This mechanism could protect plants from accumulation of toxic metals. A comparison between plants from the coarse sand and coarse gravel based CWs did not show significant differences in these metal distribution among tissues.

In conclusion, it is safe to suggest that there was no evidence of incompatibility in the use of coarse gravel and *Typha lattifolia* plants in wetlands treating metaliferus wastewater. Copper, iron and zinc contents are evaluated in *Typha lattifolia* tissues at the end of the first year of growth. Such plaque would cause precipitation of metals such as copper, iron and zinc upon itself, also functioning as a physical and chemical barrier against penetration and translocation into the roots of other plants (Batty *et al*., 2002).

4.3.2 Performance of Coarse Gravel and *Phragmites karka* for Treatment

For the performance evaluation of these pilot scales, constructed wetlands were planted with *Phragmites karka* and filled with coarse gravel along with native soil from the refinery premises. Influent and effluent concentration of all the design parameters have been measured, which has been discussed in detail in the following sections.

a. Removal of Total Suspended Solids

The assessment of efficiency of organic pollutant removal is indicated by the change in total suspended solids of the effluent treated through the constructed wetland systems. Three different hydraulic loading rates were applied to obtain maximum removal efficiency. At hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$, total suspended solids removal was 20 - 92 mg L^{-1}, (n = 36), 33–119 mg L^{-1} (66 ± 30 mg L^{-1}) and 34 - 86.1 mg L^{-1} (62 ± 17 mg L^{-1}), respectively during the monitoring period as shown in Table 4.10. Total suspended solids removal efficiencies of the coarse gravel system varied between 14 - 73 % (47±20 %) at hydraulic loading rate of 1.71 $m^3m^{-2}day^{-1}$, 28 - 77 % (52±18 %), at hydraulic loading rate of 1.44 $m^3m^{-2}day^{-1}$ and 35 - 85 % (59±18 %) at hydraulic loading rate of 1.23 $m^3m^{-2}day^{-1}$ as presented in Figure 4.9.

During the start-up period of wetlands, total suspended solids removal was 7-18 % but as time passed, total suspended solids removal increased up to 35 - 85 %.

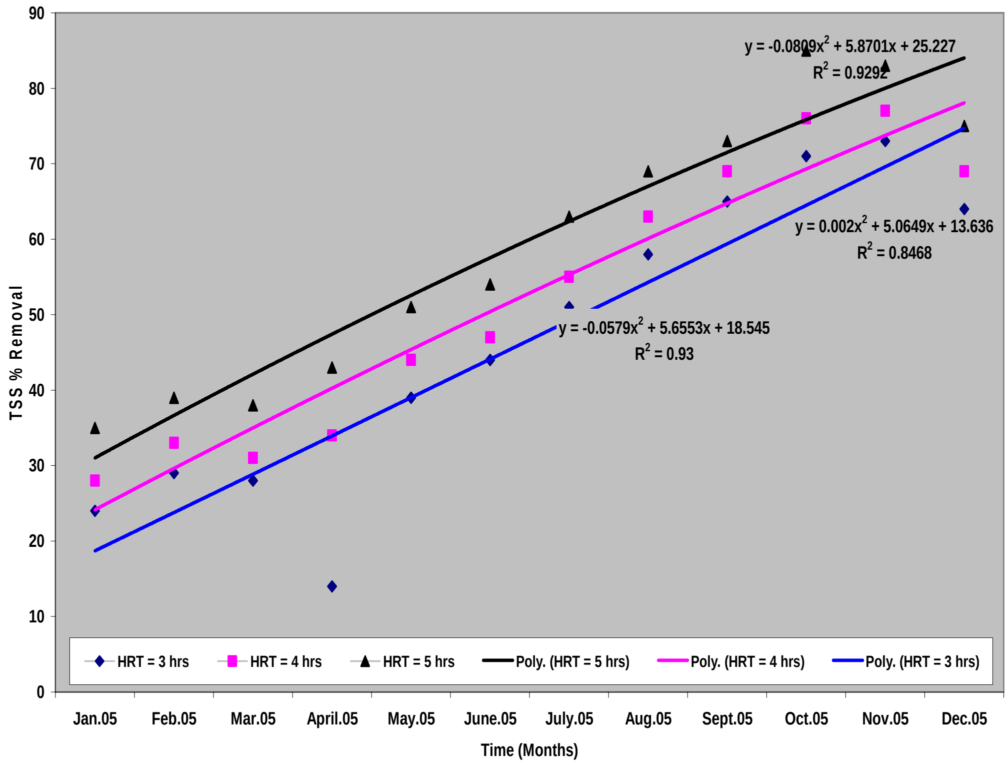

Figure 4.9. Removal (%) age of total suspended solids (Gravel and *Phragmites karka*)

Table 4.10. Mean values of the quality of influents and effluents (Gravel and *Phragmites karka*) for total suspended solids

Parameters	HLR 1 =1.71 $m^3m^{-2}day^{-1}$		HLR 2 =1.44 $m^3m^{-2}day^{-1}$		HLR 3 =1.23 $m^3m^{-2}day^{-1}$	
	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)
Jan	85 (±16)	65 8)	117 (±6)	84 (±0)	98 (±13)	64 (±5)
Feb	107 (±13)	76 10)	126 (±14)	84 (±8)	117 (±14)	71 (±8)
Mar	126 (±6)	91 (±18)	106 (±1)	73 (±2)	97 (±15)	60 (±5)
Apr	135 (±28)	116 (±41)	107 (±0)	71 (±8)	118 (±4)	67 (±5)
May	95 (±31)	58 (±14)	107 (±7)	60 (±1)	124 (±7)	61 (±6)
Jun	139 (±8)	78 (±11)	117 (±6)	62 (±9)	114 (±3)	52 (±6)
Jul	128 (±6)	63 (±9)	109 (±13)	49 (±1)	118 (±16)	44 (±10)
Aug	119 (±11)	50 (±10)	127 (±0)	47 (±5)	95 (±16)	29 (±2)
Sep	104 (±8)	36 (±2)	127 (±6)	39 (±5)	118 (±15)	32 (±12)
Oct	115 (±8)	33 (±0)	135 (±13)	32 (±2)	97 (±7)	15 (±0)
Nov	126 (±6)	34 (±6)	154 (±11)	35 (±5)	87 (±7)	15 (±7)
Dec	118 (±23)	42 (±16)	139 (±16)	43 (±29)	97 (±1)	24 (±28)
Mean	116	62	123	57	107	45
Stdev	±17	±25	±15	±18	±13	±21

unit increase in HLR. The standard error value is 3.40 which is significant and that the hydraulic loading rate variable is significant (P = 0.013) for increasing the removal.

Total suspended solids (TSS), removal was high which indicates that, the removal of TSS is almost entirely due to physical processes rather than biological Suspended solids in effluent at the outlet of constructed wetlands are a function of the treatment system and weather conditions among others. Statistical analysis shows 90% variation in the removal efficiency, which is dependent upon coarse gravel and *Phragmites karka*. Coefficient of HLR is 10.375, which indicates that on an average it increases the removal by 10.375% with every process.

This accords with some of the results obtained by Lee *et al*. (2004), Hill and Payton (2000) and Manios *et al*. (2000) but contrasts with results obtained by Stober *et al*. (1997), Mandi *et al*. (1998) and Jing *et al*. (2001). According to Armstrong *et al*., (1992), oxygen transport takes place during winter when the plants are dead by a 'venturi' mechanism through the open-ended culms. These earlier finding suggest that microorganisms present in plant root are playing an important role in the process. Differences between studies again may be due to influent type and characteristics, size and shape of the pilot unit and operating conditions. Nevertheless, all the studies show that plants played significant role in aeration process to facilitate the biodegradation process of TSS.

A one and half year old constructed wetland planted with *Phragmites karka* developed an extensive root system, which improved the total suspended solids removal efficiency by providing a larger surface area, reducing the water velocity and reinforcing settling and filtration (Brix, 1997). Since the wetlands at the refinery functioned for one year, the observed total suspended solids removal efficiencies of the coarse gravel system could be related mostly to the processes of sedimentation, and filtration by the wetland media (Stowell *et al*., 1981). During the operation period, surface overflow did not take place in either of the wetlands at the refinery, which might be due to the low organic content of the raw wastewater, efficient pre-treatment of suspended solids by 28% before entering the wetlands and low plant litter production and accumulation. For the monitoring period, total suspended solids removal efficiencies of the coarse gravel system increased gradually and the performances of coarse gravel system showed gradual improvement with the maturation of the system.

Previous studies examined only some of these factors for shorter duration (3 - 6 months). The effect of *Phragmites karka* at different hydraulic loading rate was examined during the course of different studies: Korkusuz *et al*., (2005), observed 59% reduction, Kimwaga *et al*., (2004) observed 89% reduction, Hench *et al*., (2003) noted 73% reduction, Billore *et al*., (1999) recorded 48% reduction, Saidam *et al* (1995) found 60% removal efficiency in suspended solids in constructed wetlands filled with coarse gravel and planted with *Phragmites karka* and our results are similar to these findings. Bolton and Greenway (1999) observed 98% suspended solids removal and Plamondon *et al*., (2006), observed 95% suspended solids removal after passing effluents through CW.

Therefore, it could be stated that differences in size, compositions and porosities of substrates of the coarse gravel system have shown significant effects on the total suspended solids removal of wetlands, which have received pre-treated wastewater with suspended solids concentration (85±38 mg L^{-1}). Generally, throughout the monitoring period, average effluent total suspended solids concentration of the coarse gravel system was below the National Environmental

Quality Standards of Pakistan CPP (1999), which is 150 mg L^{-1} for treated domestic wastewater.

b. Removal of Total Dissolved Solids

The efficiency of organic pollutant removal is indicated by the change in total dissolved solids of the effluent treated through the constructed wetland systems, by applying three different hydraulic loading rates to compare removal efficiency. At the hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$, the total dissolved solids removal was 438-719 mg L^{-1}, 694–1282 mg L^{-1} and 722–1438 mg L^{-1} respectively, during the monitoring period as shown in Table 4.11.

Total dissolved solids removal efficiencies of the coarse gravel system varied between 15–26% (21±5 %) at hydraulic loading rate of 1.71 $m^3m^{-2}day^{-1}$, 22–37 % (29±6 %), at hydraulic loading rate of 1.44 $m^3m^{-2}day^{-1}$ and 27-45 % (34±8 %) at hydraulic loading rate of 1.23 $m^3m^{-2}day^{-1}$ respectively as presented in Figure 4.10. During the start-up period of the wetlands, the total dissolved solids removal concentration was 7 - 18 % but as time passed, total dissolved solids removal concentration increased up to value of 45%. During the start-up period of the wetlands, the total dissolved solids removal concentration was 15 - 26 %, but as time passed, total dissolved solids removal concentration increased up to value of 29 - 44 %.

Statistical analysis shows 95% variation in removal efficiency and co-efficient of HLR is 5.95 which indicates that on average it increases the removal by 5.95 %, with every unit increase in HLR. The standard error value is 4.78, which indicates that this coefficient is significant (P = 0.013) and that the hydraulic loading rate variable is significant in increasing the percentage removal. Results have shown significant removal of dissolved solids in the present study and

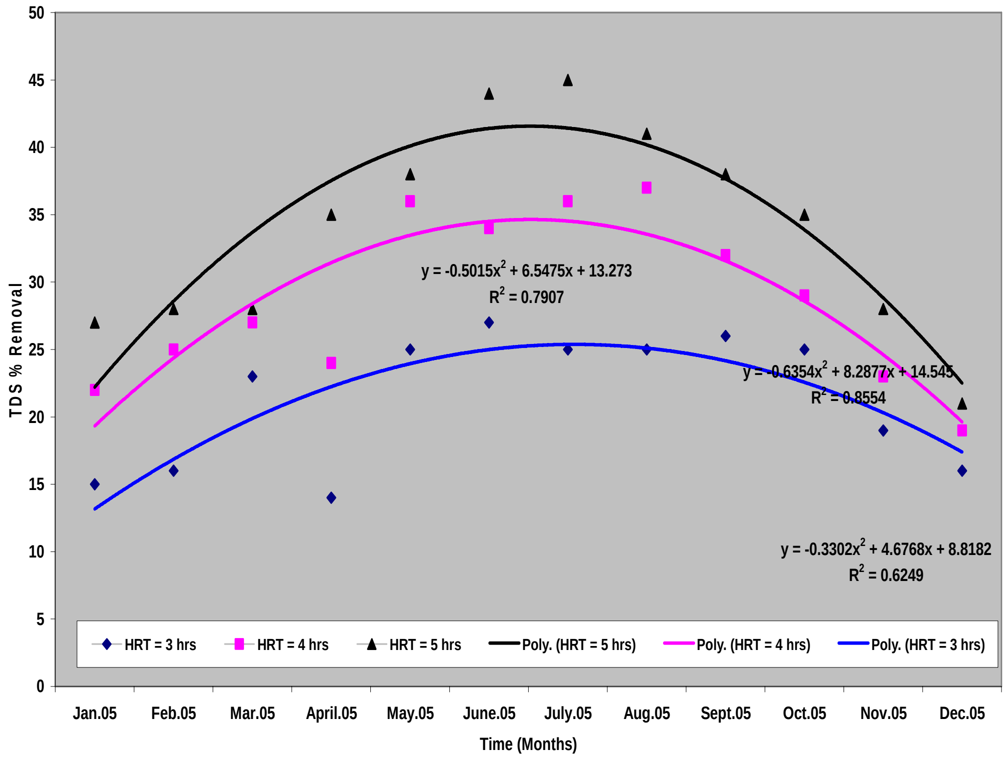

Figure 4.10. Removal (%) age of total dissolved solids (Gravel and *Phragmites karka*)

Table 4.11. Mean values of the quality of influents and effluents (Gravel and *Phragmites karka*) for total dissolved solids

Months	HLR 1 =1.71 $m^3m^{-2}day^{-1}$				HLR 2 =1.44 $m^3m^{-2}day^{-1}$				HLR 3 =1.23 $m^3m^{-2}day^{-1}$			
	Influent (mg/L)		Effluent (mg/L)		Influent (mg/L)		Effluent (mg/L)		Influent (mg/L)		Effluent (mg/L)	
Jan	3556	(±581)	3023	(±513)	3155	(±7)	2461	(±72)	2875	(±210)	2099	(±172)
Feb	2735	(±298)	2297	(±94)	3145	(±422)	2359	(±353)	2578	(±132)	1856	(±95)
Mar	3157	(±207)	2431	(±379)	2548	(±665)	1860	(±559)	2765	(±347)	1991	(±89)
Apr	3450	(±407)	2967	(±573)	3488	(±214)	2651	(±433)	3256	(±303)	2116	(±119)
May	2875	(±212)	2156	(±196)	3185	(±143)	2038	(±139)	3684	(±523)	2284	(±449)
Jun	2575	(±213)	1880	(±196)	3387	(±798)	2235	(±559)	2945	(±177)	1649	(±76)
Jul	2876	(±274)	2157	(±206)	2258	(±853)	1445	(±522)	3195	(±288)	1757	(±79)
Aug	2488	(±71)	1866	(±35)	3465	(±77)	2183	(±70)	2788	(±101)	1645	(±4)
Sep	2588	(±511)	1915	(±365)	3356	(±327)	2282	(±161)	2645	(±554)	1640	(±416)
Oct	1865	(±785)	1399	(±715)	2894	(±272)	2055	(±332)	3428	(±469)	2228	(±168)
Nov	2975	(±276)	2410	(±169)	3278	(±207)	2524	(±75)	2765	(±7)	1991	(±131)
Dec	2585	(±687)	2171	(±602)	2985	(±120)	2418	(±30)	2755	(±85)	2176	(±55)
Mean	2810		2223		3095		2209		2973		1953	
Stdev	±455		±458		±375		±329		±342		±237	

low level of removal is attributed to absorption, sedimentation and filtration process, which is actually the removal of heavy metals from the dissolved portion and discussed in detail in heavy metals removal section.

c. Removal of Chemical Oxygen Demand

The efficiency of organic pollutant removal is indicated by the change in chemical oxygen demand of the effluent treated through the constructed wetland systems planted with *Phragmites karka* and coarse gravel being used as fill material with native soil of refinery. Three different hydraulic loading rates were applied to obtain maximum removal efficiency, while keeping the wetland conditions same i.e. all wetland cells were planted with *Phragmites karka* and filled with coarse gravel as fill material. At hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$, the chemical oxygen demand removal was 42 - 189, 62 - 186 and 88 - 223 mg L^{-1} respectively, during the monitoring period as shown in Table 4.12.

Chemical oxygen demand removal efficiencies of the coarse gravel system varied between 913–58 % (33±16 %) at hydraulic loading rate of 1.71 $m^3m^{-2}day^{-1}$, 20 - 63 % (42 ± 16 %) at hydraulic loading rate of 1.44 $m^3m^{-2}day^{-1}$ and 27 - 73 % (52±17%) at hydraulic loading rate of 1.23 $m^3m^{-2}day^{-1}$ respectively as presented in Figure 4.11. During the start-up period of the wetlands, the chemical oxygen demand removal concentration was 9 -15 %, but as time passed, chemical oxygen demand removal concentration increased up to the value of 27 - 73 %. Statistical analysis shows 88% variation in the removal efficiency, which is dependent upon coarse gravel and *Phragmites karka*. Coefficient of HLR is 9.04, which indicates that on average it increases removal by 9.04% with every unit increase in HLR. The standard error value is 2.78 which indicates that this coefficient is significant (P = 0.017) and that the hydraulic loading rate variable is significant for increasing the removal.

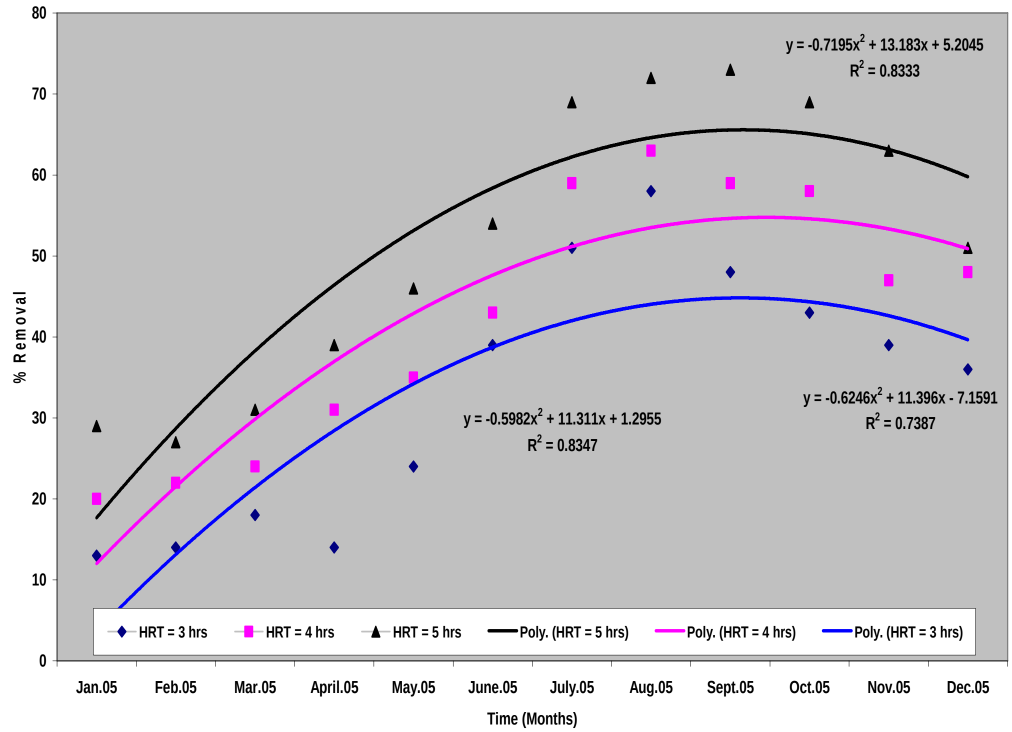

Figure 4.11. Removal (%) age of chemical oxygen demand (Gravel and *Phragmites karka*)

Table 4.12. Mean values of the quality of influents and effluents (Gravel and *Phragmites karka*) for chemical oxygen demand

Months	HLR 1 =1.71 $m^3m^{-2}day^{-1}$		HLR 2 =1.44 $m^3m^{-2}day^{-1}$		HLR 3 =1.23 $m^3m^{-2}day^{-1}$	
	Influent (mg/L)	**Effluent (mg/L)**	**Influent (mg/L)**	**Effluent (mg/L)**	**Influent (mg/L)**	**Effluent (mg/L)**
Jan	341 (±30)	297 (±29)	309 (±7)	247 (±1)	327 (±16)	232 (±7)
Feb	298 (±9)	256 (±16)	319 (±11)	249 (±13)	305 (±6)	223 (±13)
Mar	285 (±21)	234 (±26)	304 (±1)	231 (±14)	297 (±1)	205 (±17)
Apr	315 (±7)	271 (±17)	306 (±1)	211 (±10)	296 (±13)	181 (±7)
May	325 (±3)	247 (±36)	304 (±3)	198 (±16)	315 (±1)	170 (±17)
Jun	321 (±1)	196 (±27)	308 (±2)	176 (±36)	316 (±52)	145 (±50)
Jul	322 (±3)	158 (±15)	305 (±9)	125 (±5)	243 (±37)	75 (±5)
Aug	326 (±13)	137 (±16)	318 (±25)	118 (±1)	295 (±7)	83 (±0)
Sep	307 (±6)	160 (±7)	282 (±28)	116 (±14)	305 (±1)	82 (±9)
Oct	298 (±11)	170 (±15)	321 (±11)	135 (±19)	306 (±14)	95 (±18)
Nov	314 (±13)	192 (±1)	306 (±1)	162 (±1)	326 (±6)	121 (±25)
Dec	296 (±32)	189 (±76)	308 (±1)	160 (±62)	317 (±7)	155 (±54)
Mean	312	209	308	177	304	147
Stdev	±16	±51	±10	±49	±22	±56

Wetlands composed of substrates-vegetables-micro-organisms have a complicated mechanism of purification (Ji *et al*., 2002). Brix (1994) and House *et al*., (1999) showed that substrate filtration, plant sorption, substrate adsorption and the settling process in a wetland removed suspended chemical oxygen demand in wastewater. However, in our present study the produced water flowed through the surface of the substrate, which resulted in filtration, adsorption, sorption that had significant impact on chemical oxygen demand removal. Thus, the last three processes played an important role in suspended chemical oxygen demand removal. It is aerobic oxidation that plays an important role in removal of soluble chemical oxygen demand (Kadlec., 2000).

As the wetlands were designed on BOD loading, the oxygen required for aerobic degradation can be supplied by oxygen leakage from the macrophyte roots into the rhizosphere. A significant portion of oxygen needed to support aerobic degradation processes in wetlands is obtained through lacuna translocation from the atmosphere to the rhizosphere by rooted aquatic macrophytes (Reddy *et al*., 1989; Brix, 1993; Reddy *et al*., 1990).

Nevertheless, all studies show that the *Phragmites karka* in combination with coarse gravel, played a significant role in aeration process to facilitate the biodegradation process. The first-rate chemical oxygen demand removal was accomplished by good cooperation between physical and microbial mechanisms. This means constructed wetlands have proved successful in removing chemical oxygen demand due to the physical separation mechanism, during which organic solids settled down, and due to coarse gravel media which allowed the accumulation of immense amounts of attached bacteria, which were very helpful in rapidly catalyzing chemical reactions.

The smooth functioning of constructed wetlands can be explained by the low organic content of the wastewater applied to the wetlands, which probably has not clogged the pores of the substrates with settled organics. The similar chemical oxygen demand treatment trend of the wetlands could also be related to sufficient oxygen diffusion into the wetland cells. This proves that that the chemical oxygen demand removal in the wetlands were mainly due to the biological degradation and secondarily due to adsorption or absorption of heavy metals to sediments as the one-year old wetlands of refinery had established an extensive plant root network during the operation period.

The treatment efficiency of *Phragmites karka* along with coarse gravel as fill material at different hydraulic loading rates has been studied and Chen *et al*., (2006) observed 89% reduction in chemical oxygen demand, Korkusuz *et al*., (2005) noted 44% reduction, Garcia *et al*., (2004) recorded 75% reduction, Ayaz and Lutfi (2001) distinguished 90% reduction, Kern and Idler (1999) detected 80% reduction, Tanner *et al* (1999) observed 70% reduction and Rivera *et al*., (1997) marked 87% reduction. Average effluent chemical oxygen demand concentrations at three hydraulic loading rates were around a value of 104 mg L^{-1}, which is well below the limit chemical oxygen demand effluent discharge concentration set by the National Environmental Quality Standards of Pakistan's CPP (1999).

d. <u>Removal of biological oxygen demand</u>

The efficiency of organic pollutant removal is indicated by the change in biological oxygen demand of the effluent treated through the constructed wetland systems and three different hydraulic loading rates were applied to achieve maximum removal efficiency. At hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$, biological oxygen demand removal was 24 - 71, 21 - 95 and 32 - 89 mg L^{-1} respectively during the monitoring period as shown in Table 4.13.

Concentration based biological oxygen demand removal efficiencies of the coarse gravel system varied between 14 – 57 % (35 ± 15%) at hydraulic loading rate of 1.71 $m^3m^{-2}day^{-1}$, 23 – 69 % (45 ± 16 %) at hydraulic loading rate of 1.71 $m^3m^{-2}day^{-1}$ and 29 - 77 % (55 ± 17 %) at hydraulic loading rate of 1.71 $m^3m^{-2}day^{-1}$ respectively as presented in Figure 4.12. During the start-up period of the wetlands, the biological oxygen demand removal concentration was 14% but as time passed, the removal concentration increased up to the value of 77%. Statistical analysis shows 90% variation in the removal efficiency, which is dependent upon these variables. Coefficient of HLR is 9.79, which indicates that on average it increases removal by 9.79%, with every unit increase in HLR. The standard error value is 3.15, which is significant (P = 0.014) and that the hydraulic loading rate variable acts significantly in increasing the removal.

The effluent concentrations were affected by the fluctuations of the influent BOD concentrations. The similar biological oxygen demand treatment trend of both wetlands could also be related to sufficient oxygen diffusion into the wetland cells. It can also be stated that the biological oxygen demand removal in both the wetlands was primarily due to the biological degradation and secondarily due to establishment of bio-film since the one-year old wetlands might not have become established during the operation period. Both average effluent biological oxygen demand concentrations were around a value of 68 mg L^{-1}, which is well below the limit of biological oxygen demand effluent discharge concentration prescribed by the national environmental quality standards of Pakistan CPP (1999).

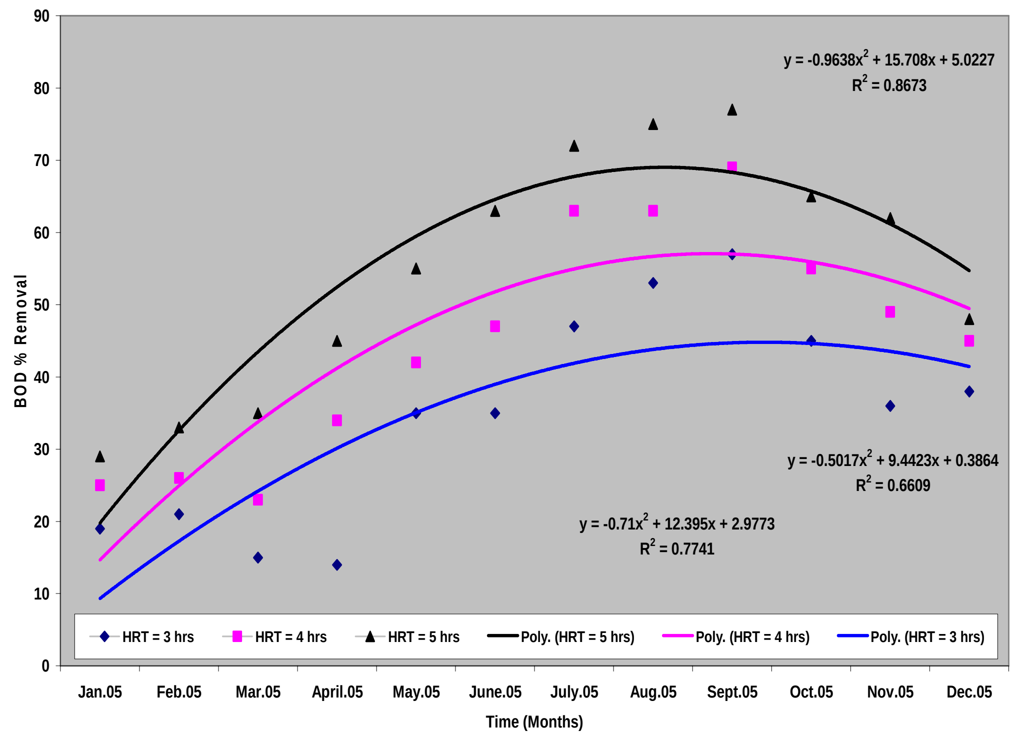

Figure 4.12. Removal (%) age of biological oxygen demand (Gravel and *Phragmites karka*)

Table 4.13. Mean values of the quality of influents and effluents (Gravel and *Phragmites karka*) for biological oxygen demand.

Months	HLR 1 =1.71 $m^3m^{-2}day^{-1}$				HLR 2 =1.44 $m^3m^{-2}day^{-1}$				HLR 3 =1.23 $m^3m^{-2}day^{-1}$			
	Influent (mg/L)		Effluent (mg/L)		Influent (mg/L)		Effluent (mg/L)		Influent (mg/L)		Effluent (mg/L)	
Jan	128	(±6)	104	(±7)	85	(±28)	63	(±20)	109	(±0)	77	(±3)
Feb	119	(±12)	94	(±15)	124	(±20)	92	(±13)	109	(±6)	73	(±2)
Mar	136	(±27)	116	(±22)	95	(±18)	74	(±4)	117	(±7)	76	(±12)
Apr	98	(±19)	84	(±2)	121	(±11)	80	(±13)	107	(±5)	59	(±5)
May	125	(±6)	81	(±4)	106	(±27)	61	(±18)	114	(±17)	51	(±0)
Jun	134	(±6)	87	(±15)	67	(±43)	36	(±8)	138	(±12)	51	(±12)
Jul	125	(±1)	66	(±5)	128	(±8)	47	(±3)	121	(±9)	34	(±5)
Aug	127	(±1)	60	(±4)	117	(±14)	43	(±1)	108	(±5)	27	(±0)
Sep	125	(±8)	54	(±15)	137	(±20)	42	(±5)	115	(±7)	26	(±12)
Oct	137	(±7)	75	(±4)	109	(±6)	49	(±8)	125	(±11)	44	(±2)
Nov	127	(±1)	81	(±2)	118	(±2)	60	(±5)	109	(±8)	41	(±7)
Dec	126	(±1)	78	(±18)	121	(±26)	67	(±2)	98	(±8)	51	(±19)
Mean	126		82		111		60		114		60	
Stdev	±10		±15		±20		±17		±10		±18	

The biological oxygen demand removal in wetland hydrosoils is carried out by the oxidation of organic matter, which provides energy for microbial metabolic processes and can be synthesized or incorporated into cell mass. The organic matter present in effluents provides a substrate for aerobic microbial metabolism. The objective, therefore of constructed wetlands is to encourage contact of micro-organisms with this substrate, resulting in conversion of organic matter to CO_2, biomass, and water (Portier and Palmer, 1989). Thus, the design rationale for this system was that with the utilization of *Phragmites karka and* coarse sand hydrosoil combination to encourage an oxygen-rich rhizosphere, aerobic microbial degradation of biological oxygen demand would be enhanced.

Previous studies examined only some of these factors for shorter timings (3 - 6 months). The effect of different hydraulic loading rates on treatment efficiency of constructed wetlands filled with coarse gravel and planted with *Phragmites karka* has been studied by Akratos and Tsihrintzis (2007) who observed 89% reduction; whereas, Chen *et al* (2006) observed 81% reduction, Billore *et al*., (1999) recorded 58-65% reduction, Tanner *et al*., (1995) noticed 50 - 80% reduction, Williams *et al*., (1995) and Chick and Mitchell (1995) detected significant reductions.

Our results are consistent with many other studies of wetlands used for wastewater treatment (Bucksteeg, 1987; Bahlo and Wach, 1990; Cooper and Findlater, 1990; Hammer, 1989; Reddy and Smith, 1987; Kadlec and Knight, 1996; Tanner *et al*., 2002; Merlin *et al*., 2002). Data on wetlands in North America, Europe and Australia indicated removal efficiency rates of 80 - 99% in most cases. Several authors suggest that the high removal efficiencies of COD and BOD_5 are due to chemical oxidation, mineralization (both aerobic and anaerobic) and sedimentation (Kadlec and Knight, 1996; Merlin *et al*., 2002).

e. Removal of Oil and Grease

The efficiency of organic pollutant removal is indicated by the change in oil and grease of the effluent from the constructed wetland systems by using three different hydraulic loading rates to ascertain the maximum impact on removal efficiency. At hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$ the oil and grease removal was 11 – 15, 16 – 26 and 14 – 27 mg L^{-1} (20 ± 4 mg L^{-1}), respectively during the monitoring period as shown in Table 4.14.

Oil and grease removal efficiencies of the coarse gravel system varied between 18–34 % (29±6 %) at hydraulic loading rate of 1.71 $m^3m^{-2}day^{-1}$, 28–45 % (35±6 %) at hydraulic loading rate of 1.44 $m^3m^{-2}day^{-1}$ and 35-44 % (40±5 %) at hydraulic loading rate of 1.23 $m^3m^{-2}day^{-1}$ respectively as presented in Figure 4.13. During the start-up period of wetlands, oil and grease removal concentration was 19 - 28% but as time passed, the removal concentration increased up to value of 24 - 51 %. Statistical analysis shows 97 % variation in the removal efficiency, which is dependent *Phragmites karka* and coarse sand. Coefficient of HLR is 5.04, which indicates that on average it increases removal by 5.04 %, with every unit increase in HLR. The standard error value is 4.57, which is significant (P = 0.011) and that the hydraulic loading rate variable is significant for increasing the removal.

In the wetland systems, initially the oil and grease removal was very low but as plants established, they increased the aeration thus contributing towards the formation of the bio-film. This resulted in the rapid aeration and suspension of oil and grease layer on the surface. Removal of oil and grease from refinery wastewater is accomplished through several physical, chemical and biological processes which are facilitated by the aerobic microbial degradation and sedimentation/filtration processes (Watson *et al.*, 1989).

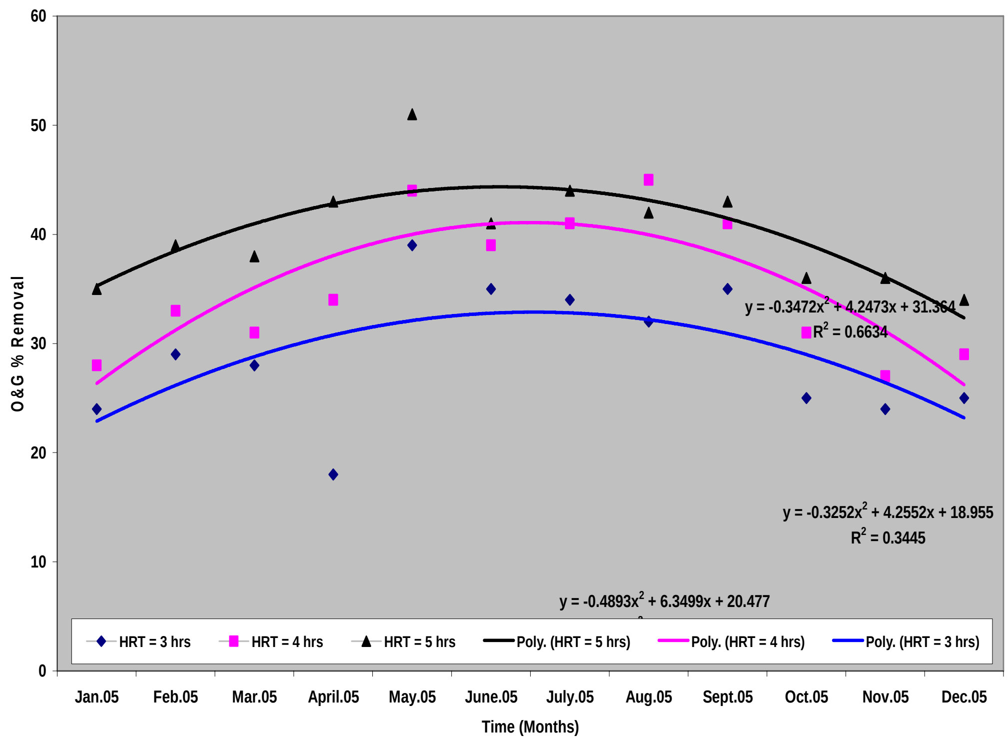

Figure 4.13. Removal (%) age of oil and grease (Gravel and *Phragmites karka*)

Table 4.14. Mean values of the quality of influents and effluents (Gravel and *Phragmites karka*) for oil and grease

Months	HLR 1 =1.71 $m^3m^{-2}day^{-1}$		HLR 2 =1.44 $m^3m^{-2}day^{-1}$		HLR 3 =1.23 $m^3m^{-2}day^{-1}$	
	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)
Jan	45 (±16)	34 (±9)	57 (±1)	41 (±2)	39 (±8)	25 (±4)
Feb	67 (±4)	48 (±4)	58 (±6)	39 (±4)	51 (±1)	31 (±1)
Mar	73 (±11)	53 (±4)	49 (±4)	34 (±4)	53 (±8)	33 (±7)
Apr	58 (±14)	48 (±17)	43 (±11)	28 (±3)	41 (±7)	23 (±1)
May	38 (±0)	23 (±1)	58 (±5)	32 (±1)	51 (±3)	25 (±2)
Jun	38 (±13)	25 (±9)	51 (±11)	31 (±7)	47 (±2)	28 (±2)
Jul	56 (±6)	37 (±4)	36 (±1)	21 (±1)	44 (±13)	25 (±8)
Aug	47 (±3)	32 (±3)	35 (±0)	19 (±1)	63 (±4)	37 (±3)
Sep	43 (±1)	28 (±4)	35 (±5)	21 (±1)	57 (±3)	32 (±5)
Oct	45 (±4)	34 (±3)	28 (±14)	19 (±11)	61 (±11)	39 (±7)
Nov	39 (±13)	30 (±10)	48 (±1)	35 (±2)	45 (±1)	29 (±0)
Dec	58 (±9)	44 (±7)	46 (±8)	33 (±6)	43 (±3)	28 (±2)
Mean	51	36	45	30	50	30
Stdev	±12	±10	±10	±8	±8	±5

The results show that constructed wetland system could remove oil and grease effectively. Plants in the wetland have a natural mechanism for pumping air via their root systems. The root area provides an oxygen-rich environment which supports a range of aerobic bacteria (Brix, 1994). Furthermore, a range of anoxic and anaerobic microbial processes occurs within wetlands (Reddy and Patrick, 1984). These biological processes promote the degradation of mineral oil. Oil and grease in wetlands are also subjected to physical processes such as evaporation, leaching, sorption of soil particles and sedimentation, which can also ensure a high removal efficiency of oil and grease (Mashauri *et al.*, 2000). It should be pointed out that seasonal variation of outlet oil and grease concentrations may be due to biomass of *Phragmites karka* and types and quantities of micro-organisms which need to be studied further.

f. <u>Removal of Iron, Copper and Zinc</u>

The performance of iron removal is specified by the change in Fe of the effluent processed through the constructed wetland systems and to estimate these, three different hydraulic loading rates were applied to compare removal efficiency while keeping the wetland conditions same. At hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$ the iron removal was 0.45 – 2.09 mg L^{-1} (n = 36), 0.83 – 1.86 mg L^{-1}, the copper removal was 0.69 - 2.59 (n = 36), 0.88 - 3.13 and 1.80 - 4.14 mg L^{-1} and zinc removal was 0.36 – 2.29, 0.68 – 2.21 and 0.97 – 2.93 mg L^{-1} respectively shown in Table 4.15.

Fe removal efficiencies of the coarse gravel system at hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$ varied between 13 - 44% (30±10%), 23 - 59% (39±13%) and 28 - 71% (48±16%), for copper 21 - 51% (35±11%), 26 - 67% (45±16%) and 33 - 75% (52±16%) and for zinc 19 - 58% (35±13%), 25 - 64%

(41±12%) and 32 - 69% (47±12%) respectively as presented in Figure 4.14, 4.15 and 4.16.

Statistical analysis for iron removal shows 90% variation in the removal efficiency which is dependent upon coarse gravel and *Phragmites karka*. Coefficient of HLR is 5.45, which indicates that on average it increases removal by 5.45 %, with every unit increase in HLR. The standard error value is 1.49 which is significant (P = 0.016) and that the loading rate variable is significant for increasing the percentage removal. For copper statistical analysis shows 92% variation in the removal efficiency, this is dependent upon Phragmites karka and coarse gravel. Coefficient of HLR is 4.91 which indicate that on average it increases removal by 4.91 % with every unit increase in HLR. The standard error value is 1.95 which is significant (P = 0.015) and hydraulic loading rate variable is significant in increasing the removal.

For zinc statistical analysis shows 93% variation in the removal efficiency, which is dependent upon *Phragmites karka* and coarse gravel. Coefficient of HLR is 5.125, which indicates that on average it increases removal by 5.125 % with every unit increase in HLR. The standard error value is 2.14 which is significant (P = 0.013) and that the hydraulic loading rate variable is significant for increasing the percentage removal.

Usually accumulation of a given metal is a function of uptake capacity and intracellular binding sites. In a multi-cellular organism, the situation is complicated by tissue and cell-specific differences, and also by intracellular transport. The processes that are assumed to be influencing metal accumulation rates in plants are: mobilization and uptake from the soil, compartmentalization and sequestration within the root, efficiency of xylem loading and in their apoplastic system. Fe oxides appear as reddish coating on wetland roots.

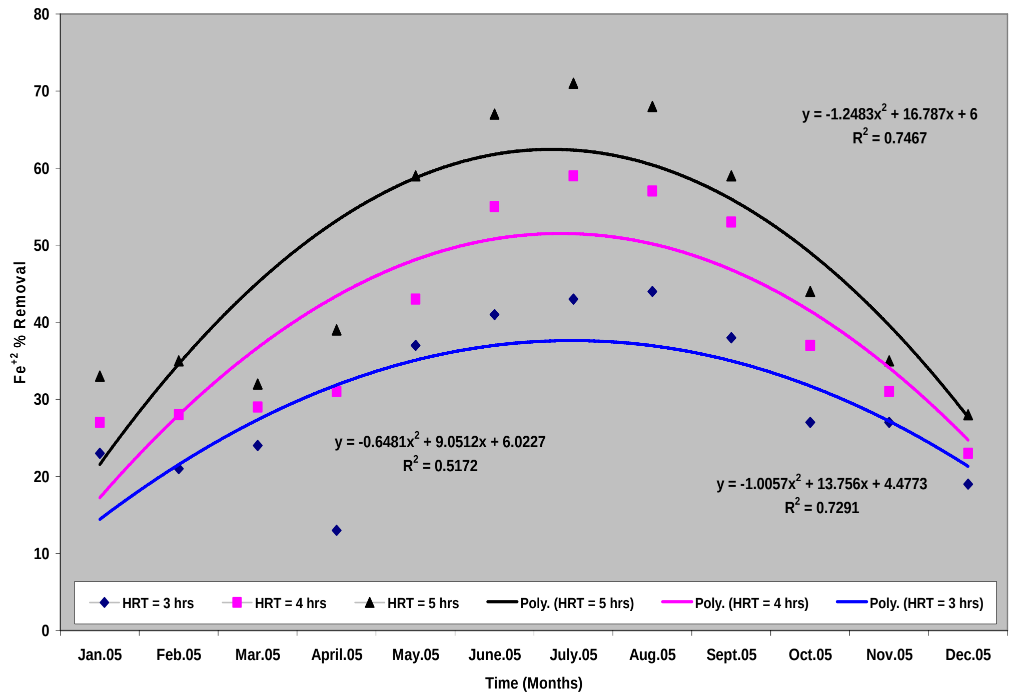

Figure 4.14. Removal (%) age of iron (Gravel and *Phragmites karka*) for Iron.

Table 4.15. Treatment performance values for iron, copper and zinc influents and effluents (Gravel and *Phragmites karka*)

Plant	***Fill Material***	***Heavy Metal***	***Statistical Results***	***HLR 1*** ***1.71 $m^3m^{-2}day^{-1}$***	***HLR 2*** ***1.44 $m^3m^{-2}day^{-1}$***	***HLR 3*** ***1.23 $m^3m^{-2}day^{-1}$***
Phragmites karka	*Coarse gravel*	*Iron*	*Max*	*21*	*59*	*71*
			Min	*44*	*27*	*32*
			Mean	*31*	*39*	*48*
			Stdev	*9*	*13*	*16*
		Copper	*Max*	*57*	*63*	*69*
			Min	*22*	*25*	*32*
			Mean	*39*	*43*	*49*
			Stdev	*14*	*13*	*13*
		Zinc	*Max*	*58*	*64*	*69*
			Min	*19*	*25*	*32*
			Mean	*36*	*41*	*47*
			Stdev	*16*	*12*	*12*

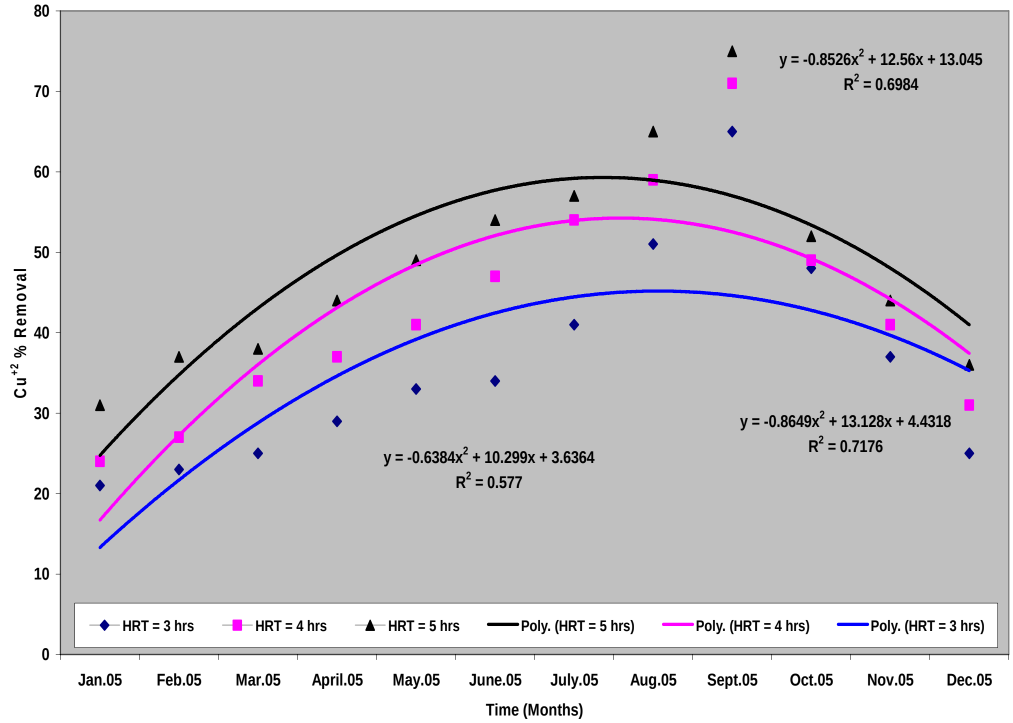

Figure 4.15. Removal (%) age of copper (Gravel and *Phragmites karka*)

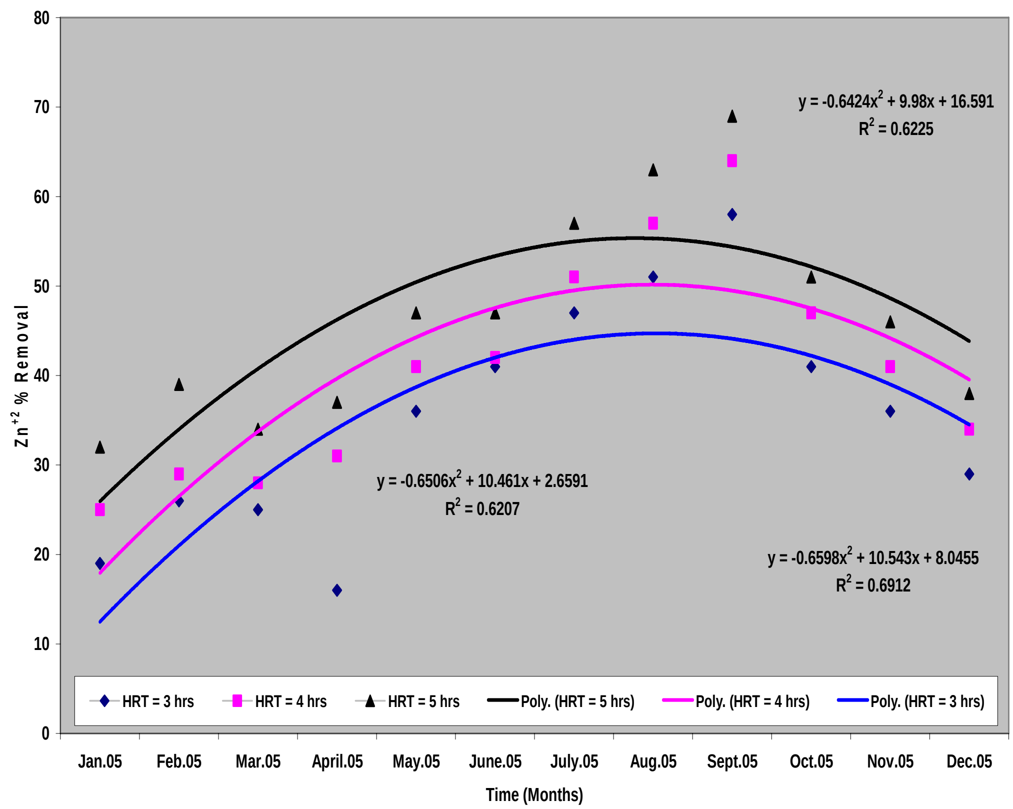

Figure 4.16. Removal (%) age of zinc (Gravel and *Phragmites karka*)

In this context, Crowder (1991) points out that radial oxygen loss could precipitate oxides of metals in soil and sediments. Generally speaking, accumulation of a given metal is a function of uptake capacity and intracellular binding sites. In a multi-cellular organism, the situation is complicated by tissue and cell-specific differences, and also by intracellular transport (Clemens *et al*., 2002). The processes that are assumed to be influencing metal accumulation rates in plants are: mobilization and uptake from the soil, compartmentalization and sequestration within the root, efficiency of xylem loading and in their apoplastic system. Fe oxides appear as reddish coating on wetland roots; both types of oxide can scavenge other metallic ions, including Cu and Zn (Lee *et al*., 1978), Cd (Rozema *et al*., 1985) or Cu (St-Cyr and Crowder, 1989). The iron plaques do not generally impede metal uptake by wetland plants, but decrease their toxic effect (Greipsson, 1989).

Removal of heavy metals in constructed wetlands planted with *Phragmites* and filled with coarse gravel as fill material has been studied by Scholz and Xu (2002), Osterkamp *et al*., 1999, Maehlum (1995) and Dunbabin and Bowner (1992), and overall removal of 75 - 90% has been observed. In this study, it was observed that some of the Zn-rich colloidal formed after chemical precipitation were adsorbed by the fine *Phragmites* root hairs, possibly for solubilization and subsequent assimilation through the secretion of organic acids. This observed adsorption of Zn-rich colloidals may have been due to the fact that the surfaces of the fine root hairs of water hyacinth not only provide extraordinarily large surface areas with high affinity chemical receptors, but also are specifically evolved with pH-dependent charged sites for the effective adsorption of Fe (Matagi *et al*., 1998; Meagher, 2000; Soltan and Rashed, 2003). Our findings are consistent with the previous results and the difference in minimum and maximum removal is due to the study of four factors at a time.

4.3.3. Study of the coarse sand and *Typha lattifolia* for treatment

For the performance evaluation of these pilot scales, constructed wetlands were planted with *Typha lattifolia* and filled with coarse sand along with native soil from the refinery premises. Influent and effluent concentrations of all the design parameters were measured, and have been discussed in detail in the following sections.

a. Removal of Total Suspended Solids

For the assessment of higher removal efficiency of the constructed wetland systems, three different hydraulic loading rates were applied to compare removal efficiency. At hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$, the total suspended solids removal was 21 - 92 (n = 36), 33 – 119 and 35 - 86 mg L^{-1} respectively during the monitoring period as shown in Table 4.16.

Total suspended solids removal efficiencies of the coarse gravel system varied between 24 - 73 % (48±18 %) at hydraulic loading rate of 1.71 $m^3m^{-2}day^{-1}$, 33 - 86 % (52±18 %), at hydraulic loading rate of 1.44 $m^3m^{-2}day^{-1}$ and 35 - 85 % (59±18 %) at hydraulic loading rate of 1.23 $m^3m^{-2}day^{-1}$ respectively as presented in Figure 4.17. At the start up, total suspended solids removal concentration was 7 - 17 %, but as time passed, total suspended solids removal concentration increased up to the value of 35-85 %. Statistical analysis shows 90 % variation in the removal efficiency which is dependent upon *Typha lattifolia* and coarse sand. Coefficient of HLR is 5.45, which indicates that on average it increases removal by 5.45 % with every unit increase.

The standard error value is 1.49, which indicates that this is significant (P = 0.016) and that hydraulic loading rate variable is increasing the percentage removal significantly. Constructed wetland system planted with *Typha lattifolia,* having an extensive root

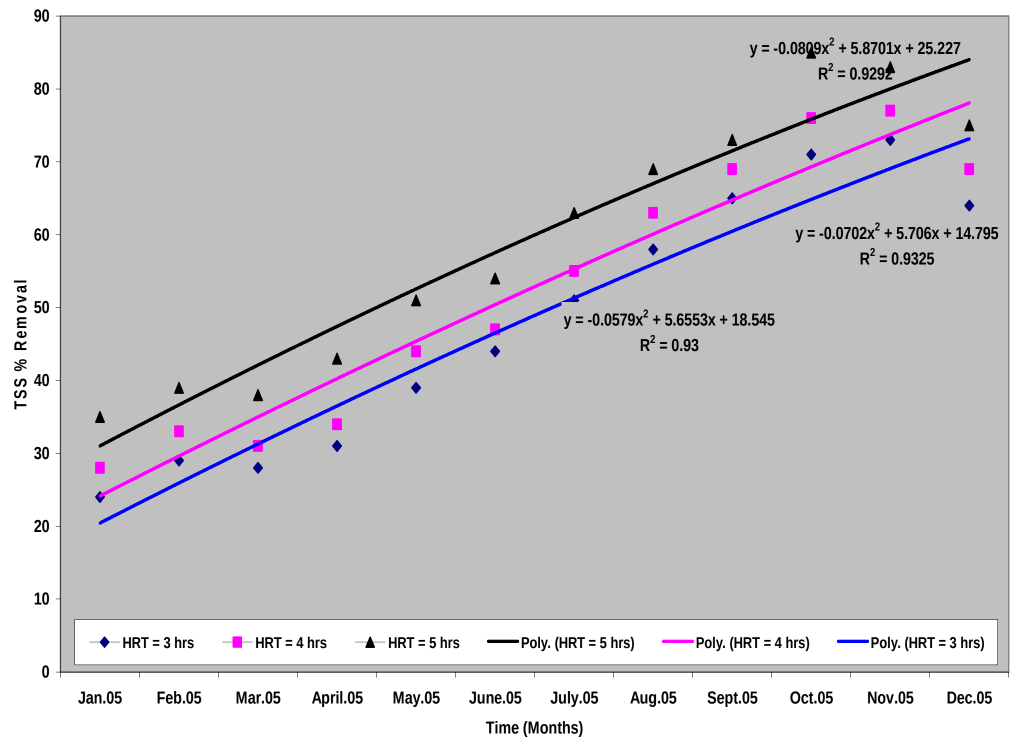

Figure 4.17. Removal (%) age of total suspended solids (Sand and *Typha lattifolia*)

Table 4.16. Mean values of the quality of influents and effluents (Sand and *Typha lattifolia*) for total suspended solids

Months	**HLR 1 =1.71 $m^3m^{-2}day^{-1}$**				**HLR 2 =1.44 $m^3m^{-2}day^{-1}$**				**HLR 3 =1.23 $m^3m^{-2}day^{-1}$**			
	Influent (mg/L)		**Effluent (mg/L)**		**Influent (mg/L)**		**Effluent (mg/L)**		**Influent (mg/L)**		**Effluent (mg/L)**	
Jan	85	(±16)	65	(±8)	117	(±6)	84	(±0)	98	(±13)	64	(±5)
Feb	107	(±13)	76	(±10)	126	(±14)	84	(±8)	117	(±14)	71	(±8)
Mar	126	(±6)	91	(±2)	106	(±1)	73	(±2)	97	(±15)	60	(±5)
Apr	135	(±28)	93	(±25)	107	(±0)	71	(±8)	118	(±4)	67	(±5)
May	95	(±31)	58	(±14)	107	(±7)	60	(±1)	124	(±7)	61	(±6)
Jun	139	(±8)	78	(±11)	117	(±6)	62	(±9)	114	(±3)	52	(±6)
Jul	128	(±0)	63	(±6)	109	(±0)	49	(±6)	118	(±0)	44	(±5)
Aug	128	(±17)	54	(±12)	109	(±13)	40	(±1)	118	(±0)	37	(±3)
Sep	104	(±8)	36	(±2)	127	(±6)	39	(±5)	118	(±15)	32	(±12)
Oct	115	(±8)	33	(±0)	135	(±13)	32	(±2)	97	(±7)	15	(±0)
Nov	126	(±6)	34	(±6)	154	(±11)	35	(±5)	87	(±7)	15	(±7)
Dec	118	(±23)	42	(±16)	139	(±16)	43	(±29)	97	(±1)	24	(±28)
Mean	117		60		121		56		109		64	
Stdev	±16		±21		±15		±19		±12		±18	

system can improve the total suspended solids removal efficiency by providing a larger surface area, reducing the water velocity and reinforcing settling and filtration in the root network (Brix, 1997). Since the wetlands of refinery have operated for one year, the observed total suspended solids removal efficiencies of the coarse gravel system could be related mostly to the processes of sedimentation, filtration, bacterial decomposition and adsorption to the wetland media (Stowell *et al*., 1981).

For the monitoring period, concentration-based total suspended solids removal efficiencies of the coarse gravel system varied between 48 - 73 % and 39 - 58 %, respectively showing gradual improvement in efficiency as the system developed. Slight variation in removal efficiencies again may be due to influent type and characteristics, size and shape of the pilot unit and operating conditions. Nevertheless, all studies show that the plants played a significant role in aeration process to facilitate the biodegradation process. The main purification processes for the removal of suspended solids are sedimentation and filtration (Vymazal *et al*., 1998).

Previous studies examined only some of these factors for shorter timings (3 - 6 months). The effect of hydraulic loading rate on the removal efficiency of suspended solids in constructed wetland with coarse sand as fill material, and planted with *Typha lattifolia* has been examined by the Abissy and Mandi (1999) and they observed 73% reduction; Schulz, (2003) observed 96% reduction in wetlands which were filled with coarse sand as fill material and planted with emergent macrophytes; Gearheart (1999) also had similar observations regarding the suspended solids reduction. *Typha lattifolia* contribution in suspended solids removal in constructed wetland has been observed by Belmont *et al*., (2004) who observed 80% removal efficiency; in this regard, Karathanasis *et al*., (2003) observed 88% removal efficiency, Abissy and Mandi (1999) noted 73% reduction in suspended solids and

Perdomo *et al*., (1999) recorded 95% reduction in suspended solids. Similar conclusions have been reached by Ciria *et al*., (2005), Solano *et al*., (2004), Hench *et al*., (2003), Burgoon *et al*., (1999).

Therefore, it could be stated that at low hydraulic loading rates better results are due to prolonged retention time for sedimentation and filtration process which have shown significant effects on the total suspended solids removal performances of the wetlands, which have received pre-treated wastewater with suspended solids concentrations (218±41 mgL^{-1}). Generally, throughout the monitoring period, average effluent total suspended solids concentration of the coarse gravel system was below the National Environmental Quality Standards of Pakistan CPP (1999) which is 150 mgL^{-1} for treated industrial wastewater.

b. <u>Removal of Total Dissolved Solids</u>

For the assessment of the removal efficiency by constructed wetland systems, three different three different hydraulic loading rates were applied. At hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$, the total dissolved solids removal was 429 - 805, 757-1247 and 661–1374 mg L^{-1} respectively during the monitoring period as shown in Table 4.17.

Concentration based total dissolved solids removal efficiencies of the coarse gravel system varied between 17 – 28% (24±5 %) at hydraulic loading rate of 1.71 $m^3m^{-2}day^{-1}$, 24 – 39 % (31±6 %), at hydraulic loading rate of 1.44 $m^3m^{-2}day^{-1}$ and 29-46 % (36±7 %) at hydraulic loading rate of 1.23 $m^3m^{-2}day^{-1}$ respectively as presented in Figure 4.18. During the start-up period of the wetlands, the total dissolved solids removal concentration was 8 - 21 %, but as time went on, total dissolved solids removal concentration increased up to the value of 85%.

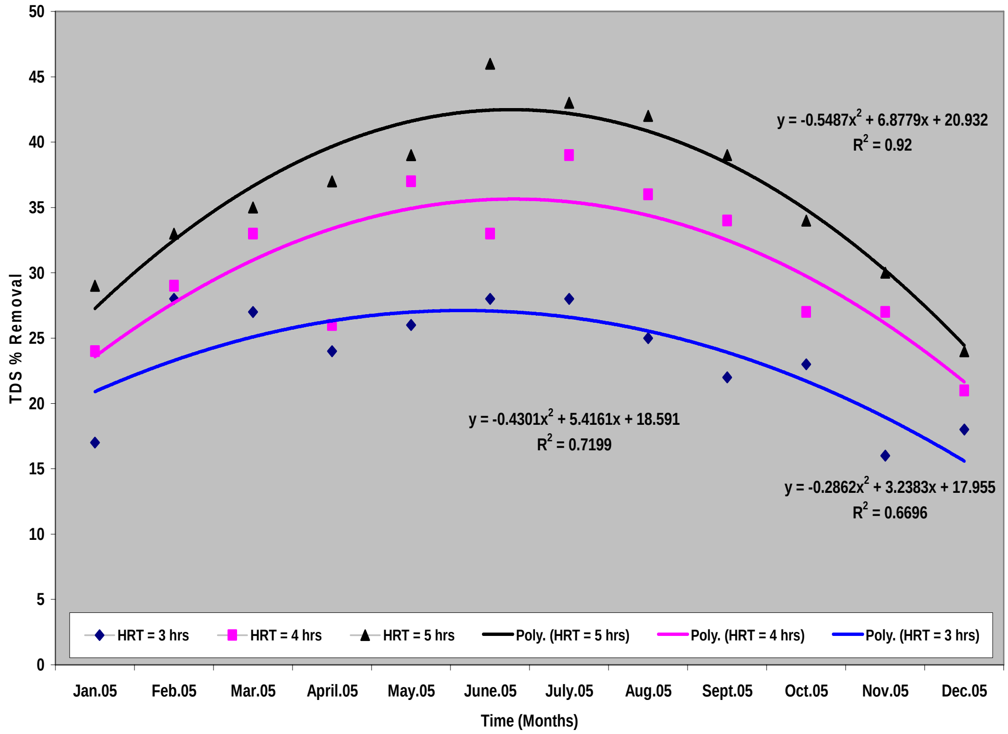

Figure 4.18. Removal (%) age of total dissolved solids (Sand and *Typha lattifolia*)

Table 4.17. Mean values of the quality of influents and effluents (Sand and *Typha lattifolia*) for total dissolved solids

Months	HLR 1 =1.71 $m^3m^{-2}day^{-1}$				HLR 2 =1.44 $m^3m^{-2}day^{-1}$				HLR 3 =1.23 $m^3m^{-2}day^{-1}$			
	Influent (mg/L)		Effluent (mg/L)		Influent (mg/L)		Effluent (mg/L)		Influent (mg/L)		Effluent (mg/L)	
Jan	3556	(±581)	2951	(±695)	3155	(±7)	2398	(±117)	2875	(±210)	2041	(±222)
Feb	2735	(±298)	1969	(±237)	3145	(±422)	2233	(±372)	2578	(±132)	1727	(±49)
Mar	3157	(±207)	2305	(±224)	2548	(±665)	1707	(±618)	2765	(±347)	1797	(±180)
Apr	3450	(±407)	2622	(±350)	3488	(±214)	2581	(±406.3)	3256	(±303)	2051	(±139)
May	2875	(±212)	2128	(±193)	3185	(±143)	2007	(±186)	3684	(±523)	2247	(±465)
Jun	2575	(±213)	1854	(±153)	3387	(±798)	2269	(±631)	2945	(±177)	1590	(±163)
Jul	2876	(±274)	2071	(±145)	2258	(±853)	1377	(±594)	3195	(±288)	1821	(±144)
Aug	2488	(±71)	1866	(±108)	3465	(±77)	2218	(±2)	2788	(±101)	1617	(±3)
Sep	2588	(±511)	2019	(±412)	3356	(±327)	2215	(±72)	2645	(±554)	1613	(±459)
Oct	1865	(±785)	1436	(±752)	2894	(±272)	2113	(±198)	3428	(±469)	2262	(±231)
Nov	2975	(±276)	2499	(±268)	3278	(±207)	2393	(±25)	2765	(±7)	1936	(±112)
Dec	2585	(±687)	2120	(±588)	2985	(±120)	2358	(±28)	2755	(±85)	2094	(±37)
Mean	2810		2153		3095		2156		2973		1900	
Stdev	±455		±398		±375		±330		±342		±241	

Statistical analysis shows 97% variation in the removal efficiency which is dependent upon *Typha lattifolia* and coarse sand. Coefficient of HLR is 6.20, which indicates that on average it increases removal by 6.20 % with every unit increase in HLR. The standard error value is 5.56 which is significant (P = 0.013) and that the hydraulic loading rate variable is significant for increasing the percentage removal. Results have shown significant removal of dissolved solids in the present study and removal is attributed to absorption, sedimentation and filtration process.

c. <u>Removal of Chemical Oxygen Demand</u>

The efficiency of organic pollutant removal is indicated by change in chemical oxygen demand of the effluent from the constructed wetland systems, by applying three different hydraulic loading rates to compare removal efficiency. At hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$, the chemical oxygen demand removal was 72 - 189, 96 - 219 and 124 - 235 mg L^{-1} (187 ± 36 mg L^{-1}) respectively during the monitoring period as shown in Table 4.18.

Chemical oxygen demand removal efficiencies of the coarse gravel system varied between 21 - 58 % (39±11 %) at hydraulic loading rate of 1.71 $m^3m^{-2}day^{-1}$, 31 - 69 % (49±13 %), at hydraulic loading rate of 1.44 $m^3m^{-2}day^{-1}$ and 38 - 77 % (61±12%) at hydraulic loading rate of 1.23 $m^3m^{-2}day^{-1}$ respectively as presented in Figure 4.19. During the start-up period of the wetlands, the chemical oxygen demand removal concentration was 9 - 15 % but as time passed, the removal concentration increased up to the value of 38 - 77 %. Statistical analysis shows 95 % variation in the removal efficiency, which is dependent upon sand and *Typha lattifolia*. Coefficient of HLR is 10.75, which indicates that on average it increases removal by 10.75 %, with every unit increase in HLR. The standard error value is 4.50 which is significant (P = 0.011) and that

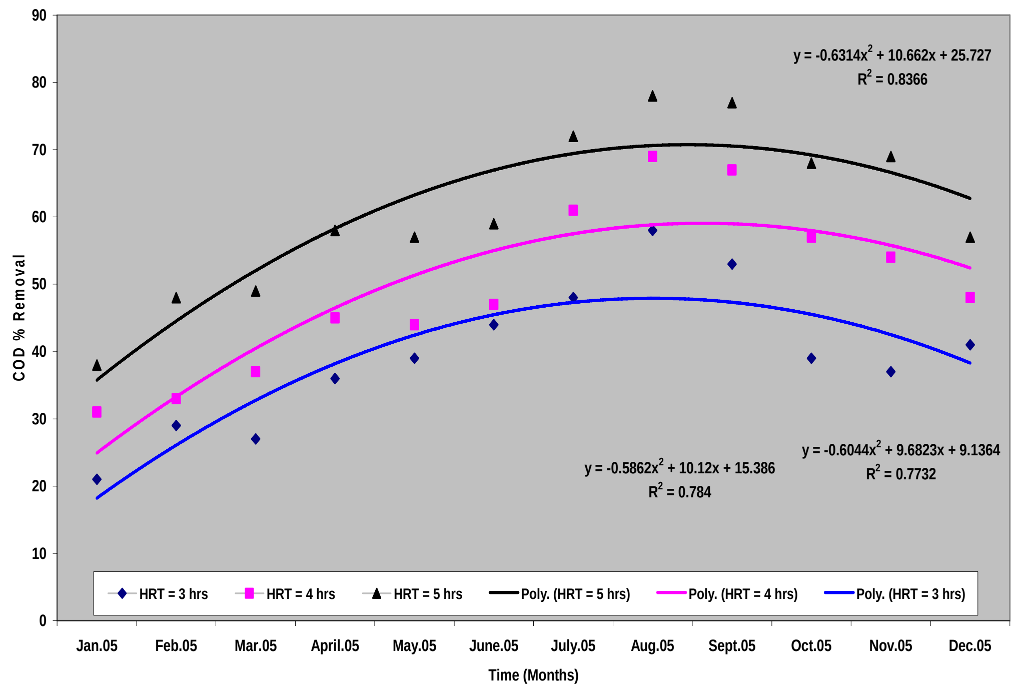

Figure 4.19. Removal (%) age of chemical oxygen demand (Sand and *Typha lattifolia*)

Table 4.18. Mean values of the quality of influents and effluents (Sand and *Typha lattifolia*) for chemical oxygen demand

Months	HLR 1 =1.71 $m^3m^{-2}day^{-1}$				HLR 2 =1.44 $m^3m^{-2}day^{-1}$				HLR 3 =1.23 $m^3m^{-2}day^{-1}$			
	Influent (mg/L)		Effluent (mg/L)		Influent (mg/L)		Effluent (mg/L)		Influent (mg/L)		Effluent (mg/L)	
Jan	341	(±30)	269	(±41)	309	(±7)	213	(±0)	327	(±16)	203	(±31)
Feb	298	(±9)	212	(±2)	319	(±11)	214	(±16)	305	(±6)	159	(±5)
Mar	285	(±21)	208	(±5)	304	(±1)	192	(±16)	297	(±1)	151	(±19)
Apr	315	(±7)	202	(±2)	306	(±1)	168	(±1)	296	(±13)	124	(±8)
May	325	(±3)	198	(±13)	304	(±3)	170	(±5)	315	(±1)	135	(±4)
Jun	321	(±1)	180	(±9)	308	(±2)	163	(±31)	316	(±16)	130	(±33)
Jul	322	(±3)	167	(±22)	305	(±9)	119	(±14)	294	(±1)	82	(±12)
Aug	326	(±13)	137	(±5)	318	(±25)	99	(±4)	295	(±7)	65	(±4)
Sep	307	(±6)	144	(±27)	282	(±28)	93	(±32)	305	(±1)	70	(±20)
Oct	298	(±11)	182	(±11)	321	(±11)	138	(±2)	306	(±14)	98	(±2)
Nov	314	(±13)	198	(±16)	306	(±1)	141	(±14)	326	(±6)	101	(±25)
Dec	296	(±32)	175	(±67)	308	(±1)	160	(±38)	317	(±7)	136	(±47)
Mean	312		189		308		156		308		121	
Stdev	±16		±34		±10		±40		±12		±40	

hydraulic loading rate variable is a significant factor for increasing percentage removal.

Removal of chemical oxygen demand of the wetland under study showed high removal percentages and these results are seen to be consistent with many other studies of wetlands used for wastewater treatment (Bucksteeg, 1987; Bahlo and Wach, 1990; Cooper and Findlater, 1990; Hammer, 1989; Reddy and Smith, 1987; Kadlec and Knight, 1996; Tanner *et al*., 2002; Merlin *et al*., 2002). Several authors suggest that the high removal efficiencies of chemical oxygen demand and BOD_5 are due to chemical oxidation, mineralization (both aerobic and anaerobic) and sedimentation (Kadlec and Knight, 1996; Merlin *et al*., 2002).

The similar chemical oxygen demand treatment trend of these wetlands could also be related to sufficient oxygen diffusion into the wetland cells. It can be further stated that chemical oxygen demand removal in both wetlands was primarily due to biological degradation and adsorption or absorption of heavy metals to sediments. Both average effluent chemical oxygen demand concentrations were around 104 mgL^{-1}, which is significantly below the limit chemical oxygen demand effluent discharge concentration according to the national environmental quality standards of Pakistan CPP (1999).

The oxygen for aerobic degradation could be supplied by oxygen transport from the macrophyte roots into the rhizosphere which means the removal of organics is highly dependent on the oxygen concentration in the bed and the characteristics of the filled medium (Vymazal *et al*., 1998; IWA, 2000). While significant is obtained through lacuna translocation by rooted aquatic macrophytes (Brix, 1993; Moorhead and Reddy *et al*., 1990).

Efficiency of the constructed wetlands planted with *Typha lattifolia* and filled with coarse sand for the removal of chemical oxygen demand was examined by Abissy and Mandi (1999) who found 91% removal efficiency, Calheiros *et al*., (2007) observed 41 - 73% removal efficiency, Chen *et al*., (2006) noted 61% removal efficiency, Masbough *et al*., (2005) recorded 50% removal efficiency and Ansola *et al*., (2003) detected 89% removal efficiency. Similar findings have been reported by Lim *et al*., (2001), Stein *et al.,* (2006), Ciria *et al*., (2005).

d. <u>Removal of Biological Oxygen Demand</u>

The efficiency of organic pollutant removal is indicated by the change in biological oxygen demand of the effluent from constructed wetland systems planted with *Typha lattifolia* and filled with coarse sand along with native refinery soil. Three different hydraulic loading rates were applied on constructed wetlands to compare removal efficiency keeping the wetland conditions same i.e. all wetland cells were planted with *Typha lattifolia* and filled with coarse sand as fill material. At hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$, the biological oxygen demand removal was 31 – 90, 33 – 105 and 38 – 92 mg L^{-1} respectively, during the monitoring period as shown in Table 4.19.

Biological oxygen demand removal efficiencies of the coarse gravel system varied between 24 – 71 % (44 ± 15%) at hydraulic loading rate of 1.71 $m^3m^{-2}day^{-1}$, 28 – 77 % (51 ± 16 %) at hydraulic loading rate of 1.44 $m^3m^{-2}day^{-1}$ and 35 - 85 % (58 ± 17 %) at hydraulic loading rate of 1.23 $m^3m^{-2}day^{-1}$ respectively as presented in Figure 4.20. During the start-up period of the wetlands, the biological oxygen demand removal concentration was 51% but as time passed, biological oxygen demand removal concentration increased up to the value of 85%. Statistical analysis shows 92 % variation in the removal efficiency, which is dependent upon *Typha lattifolia* and

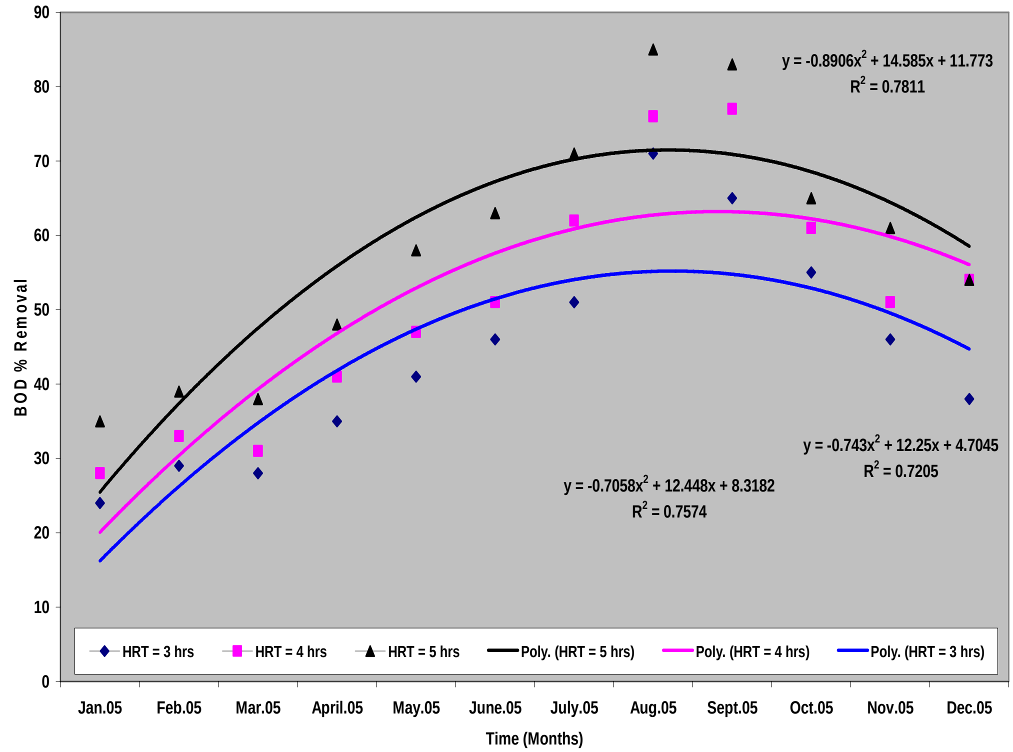

Figure 4.20. Removal (%) age of biological oxygen demand (Sand and *Typha lattifolia*)

Table 4.19. Mean values of the quality of influents and effluents (Sand and *Typha lattifolia*) for biological oxygen demand

Months	**HLR 1 =1.71 $m^3m^{-2}day^{-1}$**				**HLR 2 =1.44 $m^3m^{-2}day^{-1}$**				**HLR 3 =1.23 $m^3m^{-2}day^{-1}$**			
	Influent (mg/L)		**Effluent (mg/L)**		**Influent (mg/L)**		**Effluent (mg/L)**		**Influent (mg/L)**		**Effluent (mg/L)**	
Jan	128	(±6)	97	(±9)	118	(±4)	85	(±1)	109	(±0)	71	(±3)
Feb	119	(±12)	84	(±9)	124	(±0)	83	(±2)	109	(±6)	66	(±4)
Mar	136	(±27)	98	(±24)	124	(±2)	86	(±10)	117	(±7)	73	(±12)
Apr	98	(±19)	64	(±7)	121	(±11)	71	(±11)	107	(±5)	56	(±5)
May	125	(±6)	74	(±1)	106	(±15)	56	(±4)	114	(±17)	48	(±2)
Jun	134	(±6)	72	(±8)	127	(±1)	62	(±10)	138	(±12)	51	(±11)
Jul	125	(±1)	61	(±17)	128	(±8)	49	(±15)	121	(±9)	35	(±13)
Aug	127	(±1)	37	(±5)	117	(±14)	28	(±2)	108	(±5)	16	(±2)
Sep	125	(±8)	44	(±13)	137	(±20)	32	(±8)	115	(±7)	20	(±17)
Oct	137	(±7)	62	(±5)	109	(±6)	43	(±11)	125	(±11)	44	(±1)
Nov	127	(±1)	69	(±7)	118	(±2)	58	(±2)	109	(±8)	43	(±2)
Dec	126	(±1)	78	(±14)	121	(±2)	56	(±21)	98	(±8)	45	(±18)
Mean	125		70		121		60		114		47	
Stdev	±11		±19		±8		±20		±10		±18	

coarse sand. Coefficient of HLR is 7.125, which indicates that on average it increases removal by 7.125 % with every unit increase in HLR. The standard error value is 2.23 which is highly significant ($P = 0.017$) and that hydraulic loading rate plays an important role for increasing the percentage removal.

Initially, in the wetland systems biological oxygen demand removal was very low but as the plants became established they increased the aeration thus contributing towards the formation of the biofilm. This resulted in the rapid degradation of organic compounds both aerobically and anaerobically by the heterotrophic microorganisms in the wetland systems. Removal of BOD_5 in wetlands is primarily by aerobic microbial degradation and sedimentation/filtration processes (Watson *et al*., 1989).

Thus, treatment efficiency of the constructed wetlands for the removal of organics is, generally highly dependent on the oxygen concentration in the bed. According to the wetland design, the oxygen required for aerobic degradation can be supplied by diffusion, convection and oxygen leakage from the macrophyte roots into the rhizosphere (Moshiri, 1993).

Effluent concentrations were affected by the fluctuations of the influent BOD concentrations which could be related to sufficient oxygen diffusion into the wetland cells. Moreover biological oxygen demand removal in both the wetlands were primarily due to the biological degradation as the one-year old wetlands of refinery might not have become established during the operation period. Average effluent biological oxygen demand concentrations were around of 68 mg L^{-1} which is well below the limit of biological oxygen demand effluent discharge concentration set by the national environmental quality standards of Pakistan CPP (1999).

Several authors (Kadlec and Knight, 1996; Merlin *et al*., 2002) suggest that the high removal efficiencies of biological oxygen demand are due to chemical oxidation, mineralization and sedimentation. The biological oxygen demand removal in wetland hydrosoils is achieved by the oxidation of the organic matter, which provides energy for microbial metabolic processes and can be synthesized or incorporated into cell mass. The organic matter present in effluents provides a substrate for aerobic microbial metabolism. The momentum, therefore, of constructed wetlands is to encourage contact of microorganisms with this substrate, resulting in conversion of organic matter to CO_2, biomass, and water (Portier and Palmer, 1989).

Efficiency of the constructed wetlands planted with *Typha lattifolia* and filled with coarse sand as fill material for the removal of biological oxygen demand have been examined by Chen *et al*., (2006) recoreded 89% removal, Masbough *et al*., (2005) detected 60% removal, Others, Karathanasis *et al*., (2003) observed 75% removal and Perdomo *et al*., (1999) noticed 80% removal. The Scholz and Xu (2002), Lim *et al*., (2001), Stewart *et al*., (2004) and Ciria *et al*., (2005) have reported similar findings.

e. <u>Removal of Oil and Grease</u>

The pollutant removal efficiency is indicated by the change in oil and grease effluent from the passed through constructed wetland systems at three different hydraulic loading rates to maximum treatment efficiency. At hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$, oil and grease removal was 11 - 16 mg L^{-1}, 16 - 23 and 18 - 28 mg L^{-1} (19 ± 5 mg L^{-1}) respectively during the monitoring period as shown in Table 4.20.

Oil and grease removal efficiencies of the coarse gravel system varied between 24 - 27 % (25±2 %) at hydraulic loading rate of 1.71 $m^3m^{-2}day^{-1}$, 29 - 41 % (33±6 %), at hydraulic loading rate of 1.44 $m^3m^{-2}day^{-1}$ and 36 - 44 % (38±5 %) at hydraulic loading rate of 1.23 $m^3m^{-2}day^{-1}$ respectively as presented in Figure 4.21.

During the start-up period of wetlands, the oil and grease removal concentration was 17 - 24% but as time passed, the removal concentration increased up to 36 - 44 %. Statistical analysis shows 98% variation in the removal efficiency, which is dependent upon *Typha lattifolia* and coarse sand. Coefficient of HLR is 6.54, which indicates that on average it increases removal by 6.54 % with every unit increase in HLR. The standard error value is 7.41, which indicates that this coefficient is significant ($P = 0.015$) and that the hydraulic rate variable is active for increasing removal.

Initially, oil and grease removal was very low but with the establishment of plants, aeration increase thus contributing towards the development of bio-film. Treatment of effluents containing oil and grease using constructed wetlands is accomplished through aerobic microbial degradation and sedimentation/filtration processes (Watson *et al*., 1989). This resulted in the rapid degradation of the organic compounds both aerobically and anaerobically by the heterotrophic microorganisms in the wetland systems. The results show that constructed wetland system could remove oil and grease effectively due to natural mechanism for pumping air via their root systems. The root area provided an oxygen-rich environment which supports a range of aerobic bacteria (Brix, 1994). Furthermore, a range of anoxic and anaerobic microbial processes occur within wetlands (Reddy and Patrick, 1984).

These biological processes promote the degradation of oil and grease contents by subjecting them to physical processes such as evaporation, leaching, sorption of soil particles, and sedimentation, which can also ensure a high removal efficiency of mineral oil (Mashauri *et al*., 2000).

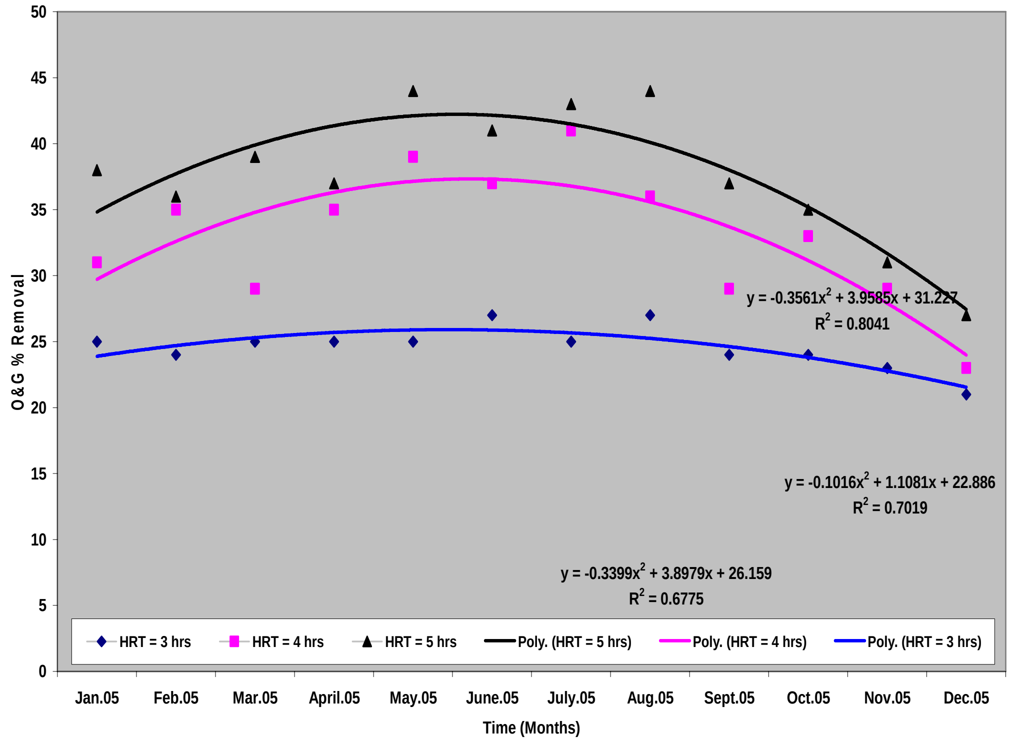

Figure 4.21. Removal (%) age of oil and grease (Sand and *Typha lattifolia*)

Table 4.20. Mean values of the quality of influents and effluents (Sand and *Typha lattifolia*) for oil and grease

Months	HLR 1 =1.71 $m^3m^{-2}day^{-1}$		HLR 2 =1.44 $m^3m^{-2}day^{-1}$		HLR 3 =1.23 $m^3m^{-2}day^{-1}$	
	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)
Jan	45 (±16)	34 (±12)	57 (±1)	39 (±1)	39 (±8)	24 (±6)
Feb	67 (±4)	51 (±3)	58 (±6)	38 (±2)	51 (±1)	33 (±0)
Mar	73 (±11)	55 (±8)	49 (±4)	35 (±5)	53 (±8)	32 (±5)
Apr	58 (±14)	44 (±11)	43 (±11)	28 (±5)	41 (±7)	26 (±2)
May	38 (±0)	29 (±1)	58 (±5)	35 (±2)	51 (±3)	29 (±1)
Jun	38 (±13)	28 (±10)	51 (±11)	32 (±8)	47 (±2)	28 (±2)
Jul	56 (±6)	42 (±5)	36 (±0)	21 (±2)	44 (±13)	25 (±7)
Aug	47 (±3)	34 (±1)	37 (±21)	23 (±8)	63 (±4)	35 (±0)
Sep	43 (±1)	33 (±1)	67 (±28)	35 (±11)	57 (±3)	36 (±3)
Oct	45 (±4)	34 (±3)	28 (±14)	19 (±11)	61 (±11)	40 (±6)
Nov	39 (±13)	30 (±11)	48 (±1)	34 (±1)	45 (±1)	31 (±0)
Dec	58 (±9)	46 (±9)	46 (±8)	35 (±3)	43 (±3)	31 (±5)
Mean	51	38	48	31	50	31
Stdev	±12	±9	±11	±7	±8	±5

f. Removal of Iron, Copper and Zinc

The efficiency of organic pollutant removal is indicated by the change in iron of the effluent from the constructed wetland systems by applying three different hydraulic loading rates to achieve high treatment efficiency. At hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$, the iron removal was 1.0 - 2.48, 0.76 - 2.27 and 1 - 2.33 mg L^{-1}, the copper removal was 2.5 - 4.8, 1.48 - 5.23 and 1.75 - 3.48 mg L^{-1} and the zinc removal was 0.46 - 2.82, 0.76 - 2.27 and 0.94 - 2.93 mg L^{-1} (1.91 ± 0.75 mg L^{-1}) respectively during the monitoring period as shown in Table 4.21. Iron removal efficiencies of the coarse sand system at hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$,varied between 23 - 53 % (36±11 %), 28 - 64 % (43±12 %) and 36 - 76 % (55±16 %) for iron, 24 - 27 % (25±2 %), 29 - 41 % (33±6 %) and 36 - 44 % (38±5 %) for copper and 24 - 59 % (38±12 %), 28 - 64 % (43±12 %) and 33-73 % (50±14 %) for zinc respectively as presented in Figure 4.22, 4.23 and 4.24.

Statistical analysis for iron shows 90% variation in the removal efficiency, which is dependent *Typha lattifolia* and coarse sand. Coefficient of HLR is 5.45 which indicates that on average it increases removal by 5.45 %, with every unit increase. Standard error value is 3.40 which indicates that this is significant (P = 0.011) and that hydraulic loading rate variable increases removal significantly. Statistical analysis for copper exhibits 91% variation in removal efficiency which is dependent upon *Typha lattifolia* and coarse sand. Coefficient of HLR is 6.125, which indicates that on average it increases the removal by 6.125 % with every unit increase in HLR. The standard error value is 2.32, which indicates that this is significant (P = 0.015) and that the hydraulic loading rate variable increases the removal significantly. Statistical analysis for zinc shows 92% variation in the removal efficiency which is dependent upon *Typha lattifolia* and coarse sand. Coefficient of HLR is 5.83 which

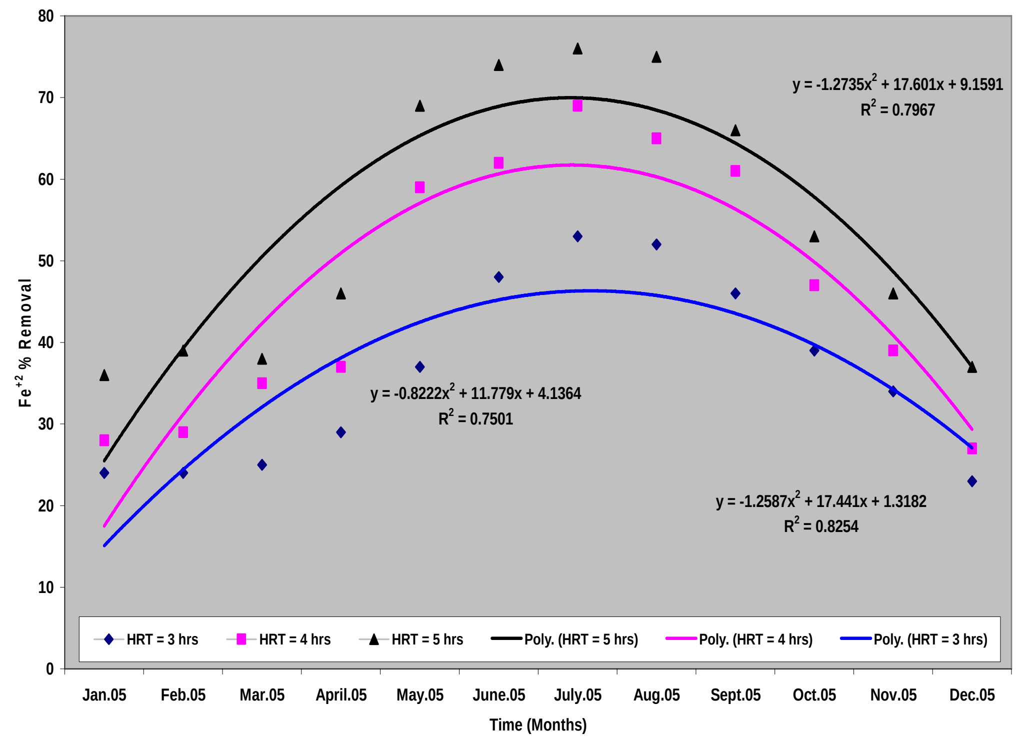

Figure 4.22. Removal (%) age of iron (Sand and *Typha lattifolia*)

Table 4.21. Treatment performance values for iron, copper and zinc influents and effluents (Sand and *Typha lattifolia*)

Plant	***Fill Material***	***Heavy Metal***	***Statistical Results***	***HLR 1*** ***1.71 $m^3m^{-2}day^{-1}$***	***HLR 2*** ***1.44 $m^3m^{-2}day^{-1}$***	***HLR 3*** ***1.23 $m^3m^{-2}day^{-1}$***
Typha lattifolia	*Coarse sand*	*Iron*	*Max*	*53*	*69*	*76*
			Min	*24*	*28*	*36*
			Mean	*36*	*47*	*55*
			Stdev	*12*	*16*	*16*
		Copper	*Max*	*65*	*71*	*75*
			Min	*21*	*24*	*31*
			Mean	*36*	*43*	*49*
			Stdev	*18*	*14*	*13*
		Zinc	*Max*	*59*	*64*	*73*
			Min	*24*	*28*	*33*
			Mean	*38*	*43*	*50*
			Stdev	*14*	*12*	*14*

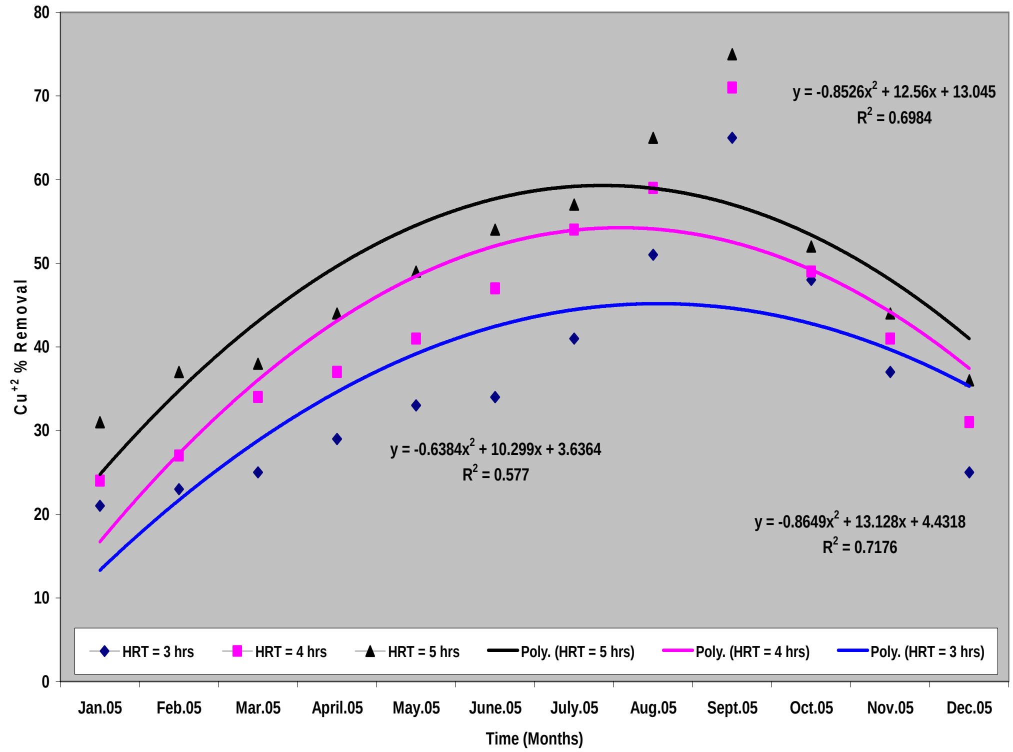

Figure 4.23. Removal (%) age of copper (Sand and *Typha lattifolia*)

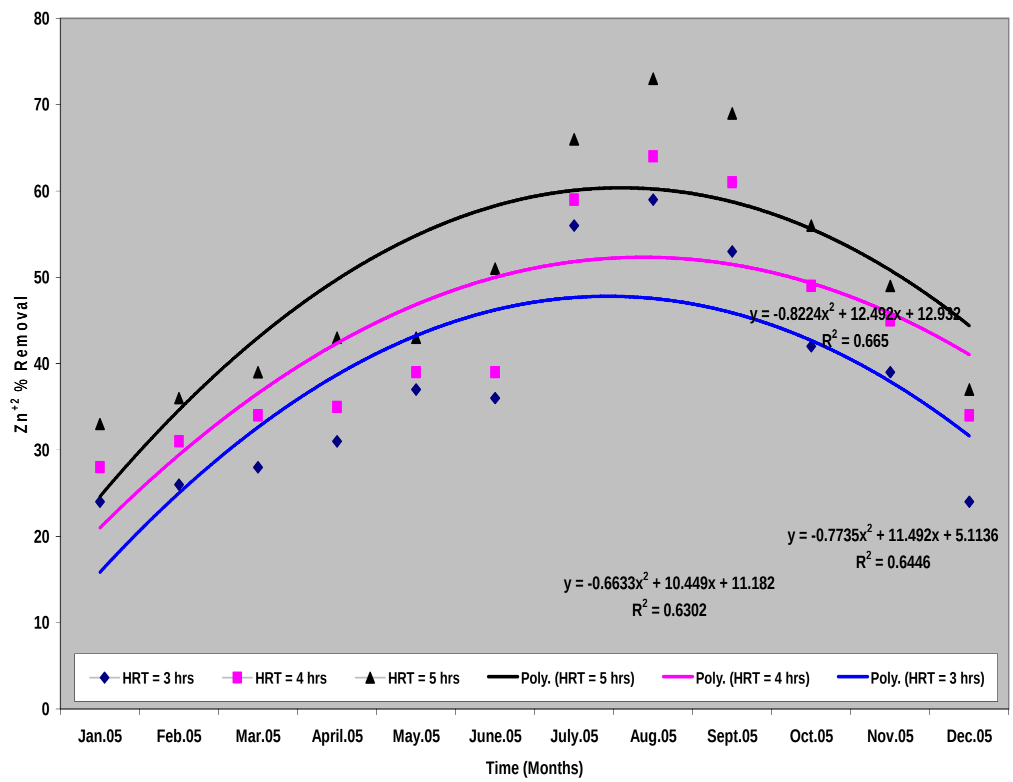

Figure 4.24. Removal (%) age of zinc (Sand and *Typha lattifolia*)

indicates that on average it increases the removal by 5.83 %, with every unit increase in HLR. The standard error value is 2.25 which indicate that this is significant (P = 0.016) and that the hydraulic loading rate variable has positive effect for removal significantly.

Accumulation of a metal is a function of uptake capacity and intracellular binding sites. Factors which influence these are metal accumulation rates in plants, for example: mobilization and uptake from the soil, compartmentalization and sequestration within the root, efficiency of xylem loading and transport, distribution between metal sinks in the aerial parts, sequestration and storage in leaf cells. At every level, concentration and affinities of chelating molecules and the presence and selectivity of transport activities, affect metal accumulation rates (Clemens *et al*., 2002). A fundamental aspect of transition metals is that during their passage through plant, only minute proportions, if any, are present as “free” hydrated ions, and that any movement within the cell involves exchange reactions between ligands (Clemens *et al*., 2002; Outten and O'Halloran, 2001).

Comparison of the removal efficiency while keeping the wetland conditions same i.e. all wetland cells were planted with *Typha lattifolia* and filled with coarse sand as fill material has been studied extensively (Maine *et al*., (2006), Demirezen and Ahmet (2006), Jacob (2004), Lim *et al*., (2003), Sistani *et al*., (1999) and Scholes *et al.*, (1998). The coarse gravel used as a substrate component in this experiment was partially saturated with heavy metals which, however did not significantly impact the development and growth of the *Typha lattifolia* plants. Some inhibition was recorded in the growth in the plants irrigated with the stronger of the watering solutions. In the same plants, larger heavy metals concentrations were also recorded. This toxicity was significantly correlated with the wastewater application pattern and substrate.

In conclusion, it is safe to suggest that there was no evidence of incompatibility in the use of coarse sand and *Typha lattifolia* plants in wetlands treating metaliferus wastewater. Copper, iron and zinc contents were evaluated in *Typha lattifolia* tissues at the end of the first year of growth which showed that the plaque had caused precipitation of metals such as copper, iron and zinc upon itself while also functioning as a physical and chemical barrier against penetration and translocation within the root of other plants (Batty *et al*., 2002). This study shows that removal efficiencies varied during the long-term monitoring campaign and being strongly dependent on influent concentrations and hydraulic loading rates (Kadlec and Knight, 1996). However, other authors have also reported high removal efficiencies of metals in constructed wetlands designed for domestic wastewater treatment.

4.3.4. Study of the Coarse Sand and *Phragmites karka* for Treatment

For the performance evaluation of these pilot scales, constructed wetlands planted with *Phragmites karka* and filled with coarse sand along with soil from the refinery premises were considered. Influent and effluent concentrations of the design parameters were measured which have been discussed in detail in the following sections:

a. Removal of Total Suspended Solids

The efficiency of pollutant removal is indicated by the change in total suspended solids of the effluent from constructed wetland systems by applying three different hydraulic loading rates to compare removal efficiency. At hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$, the total suspended solids removal was 20 - 92, 33 – 119 and 34 - 86 mg L^{-1} respectively during the monitoring period as shown in Table 4.22.

Total suspended solids removal efficiencies of the coarse sand system varied between 24 - 73 % (48±18 %) at 1.71 $m^3m^{-2}day^{-1}$, 28 - 77 % (52±18 %) at hydraulic loading rate of 1.44 $m^3m^{-2}day^{-1}$ and 35 - 85 % (59±18 %) at hydraulic loading rate of 1.23 $m^3m^{-2}day^{-1}$ respectively as presented in Figure 4.25. During the start-up period of the wetlands, the total suspended solids removal concentration was 7 - 17 % but as time went on, total suspended solids removal concentration increased up to 35 - 85 %. Statistical analysis showed 80 % variation in the removal efficiency which is dependent upon coarse sand and *Phragmites karka*. Coefficient of HLR is 12.95, which indicates that on average it increases removal by 12.95 %, with every unit increase in HLR. The standard error value is 16.97, which indicates that this is highly significant (P = 0.010) and that the hydraulic loading rate variable increases removal significantly.

Since the wetlands was operational at refinery for one year, observed total suspended solids removal efficiencies of the coarse sand system could be related mostly to the processes of sedimentation, filtration, bacterial decomposition and adsorption to media (Stowell *et al*., 1981). During operation period, no surface overflow was observed that is due to the low organic content of the raw wastewater and efficient pre-treatment of suspended solids by 28% before entering the wetlands.

For the monitoring period, the concentration-based total suspended solids removal efficiencies of the coarse gravel system varied between 48 - 73 % and 39 - 58 %, respectively. Total suspended solids treatment performances of the coarse sand system showed gradual improvement in the efficiency as the system matured. Therefore, it could be stated that the differences in the size, compositions and porosities of the substrates of the coarse sand system have shown significant effects on the total suspended solids removal performance of the wetlands, which have

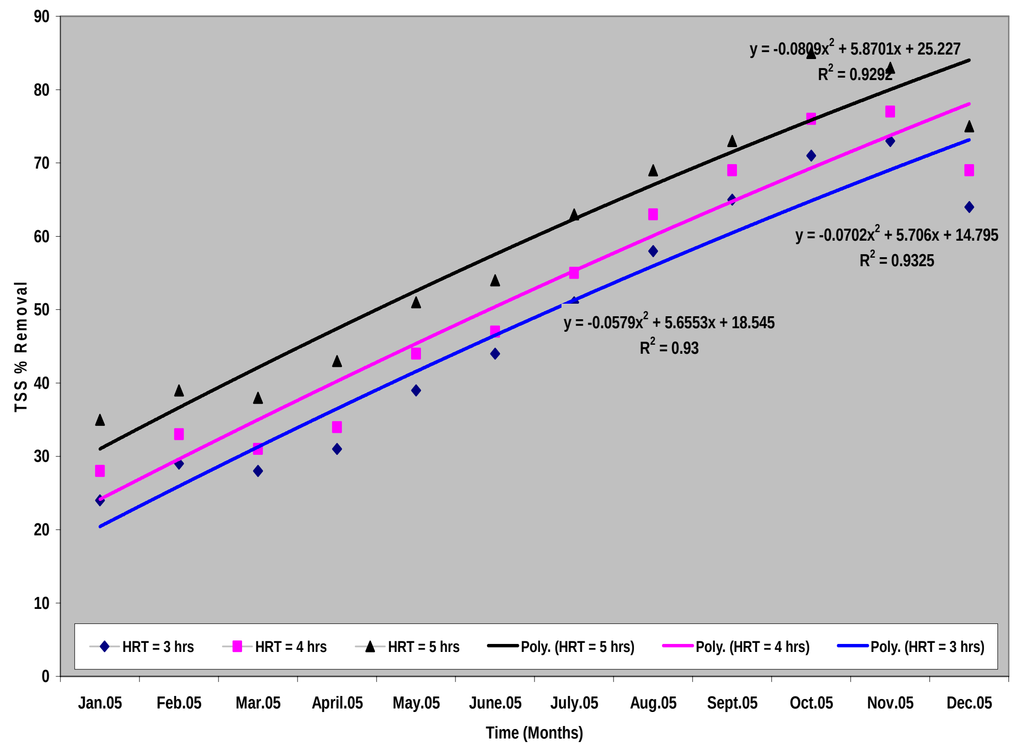

Figure 4.25. Removal (%) age of total suspended solids (Sand and *Phragmites karka*)

Table 4.22. Mean values of the quality of influents and effluents (Sand and *Phragmites karka*) for total suspended solids

Months	**HLR 1 =1.71 $m^3m^{-2}day^{-1}$**				**HLR 2 =1.44 $m^3m^{-2}day^{-1}$**				**HLR 3 =1.23 $m^3m^{-2}day^{-1}$**			
	Influent (mg/L)		**Effluent (mg/L)**		**Influent (mg/L)**		**Effluent (mg/L)**		**Influent (mg/L)**		**Effluent (mg/L)**	
Jan	85	(±16)	65	(±8)	117	(±6)	84	(±0)	98	(±13)	64	(±5)
Feb	107	(±13)	76	(±10)	126	(±14)	84	(±8)	117	(±14)	71	(±8)
Mar	126	(±6)	91	(±2)	106	(±1)	73	(±2)	97	(±15)	60	(±5)
Apr	135	(±28)	93	(±25)	107	(±0)	71	(±8)	118	(±4)	67	(±5)
May	95	(±31)	58	(±14)	107	(±7)	60	(±1)	124	(±7)	61	(±6)
Jun	139	(±8)	78	(±11)	117	(±6)	62	(±9)	114	(±3)	52	(±6)
Jul	128	(±0)	63	(±6)	109	(±0)	49	(±6)	118	(±0)	44	(±5)
Aug	128	(±17)	54	(±12)	109	(±13)	40	(±1)	118	(±0)	37	(±3)
Sep	104	(±8)	36	(±2)	127	(±6)	39	(±5)	118	(±15)	32	(±12)
Oct	115	(±8)	33	(±0)	135	(±13)	32	(±2)	97	(±7)	15	(±0)
Nov	126	(±6)	34	(±6)	154	(±11)	35	(±5)	87	(±7)	15	(±7)
Dec	118	(±23)	42	(±16)	139	(±16)	43	(±29)	97	(±1)	24	(±28)
Mean	117		60		121		56		109		45	
Stdev	±16		±21		±15		±19		±12		±20	

received pre-treated wastewater with suspended solids concentrations (218±41 mg L^{-1}). Previous studies examined only some of these factors and monitoring time was shorter (3 - 6 months). The effect of reeds at different hydraulic loading rates was examined by Korkusuz *et al*., (2005) who observed 59% reduction, Kimwaga *et al*., (2004) found 89% reduction, Hench *et al*., (2003) discovered 73% reduction, and Billore *et al*., (1999) detected 48% reduction. In constructed wetlands planted with *Phragmites karka*, Saidam *et al* (1995) found 60% removal efficiency in suspended solids and the results were similar to the findings of our study. However, Bolton and Greenway and Anne (1999) observed 98% suspended solids removal and Plamondon *et al*., (2006) observed 95% suspended solids removal.

Generally, throughout the monitoring period, average effluent total suspended solids concentration of the coarse gravel system was below the national environmental quality standards of Pakistan CPP (1999), which is 150 mg L^{-1} for treated domestic wastewater.

b. <u>Removal of Total Dissolved Solids</u>

The efficiency of pilot scale vertical flow constructed wetland systems is indicated by the change in total dissolved solids of the effluent and to ascertain best efficiency point at three different hydraulic loading rates. At hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$, total dissolved solids removal was 565 - 1007, 746 - 1421 and 805 - 1438 mg L^{-1} (1138 ± 246 mg L^{-1}) respectively during the monitoring period as shown in Table 4.23.

Total dissolved solids removal efficiencies within the coarse sand system varied between 18 - 35% (26±6 %) at hydraulic loading rate of 1.71 $m^3m^{-2}day^{-1}$, 24 - 42 % (34±6 %) at hydraulic loading rate of 1.44 $m^3m^{-2}day^{-1}$ and 28 - 45% (38±6 %) at hydraulic loading rate of 1.23 $m^3m^{-2}day^{-1}$ respectively as presented in Figure 4.26.

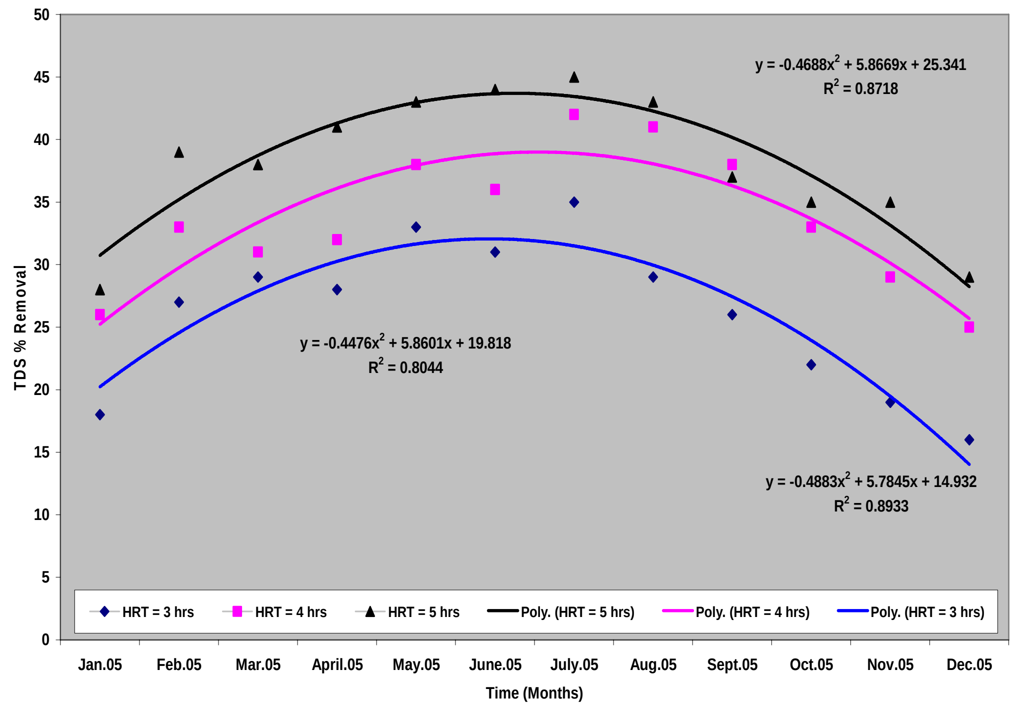

Figure 4.26. Removal (%) age of total dissolved solids (Sand and *Phragmites karka*)

Table 4.23. Mean values of the quality of influents and effluents (Sand and *Phragmites karka*) for total dissolved solids

Months	HLR 1 =1.71 $m^3m^{-2}day^{-1}$				HLR 2 =1.44 $m^3m^{-2}day^{-1}$				HLR 3 =1.23 $m^3m^{-2}day^{-1}$			
	Influent (mg/L)		Effluent (mg/L)		Influent (mg/L)		Effluent (mg/L)		Influent (mg/L)		Effluent (mg/L)	
Jan	3556	(±581)	2916	(±650)	3155	(±7)	2335	(±161)	2875	(±210)	2070	(±352)
Feb	2735	(±298)	1997	(±173)	3145	(±422)	2107	(±247)	2578	(±132)	1573	(±100)
Mar	3157	(±207)	2241	(±171)	2548	(±665)	1758	(±434)	2765	(±347)	1714	(±146)
Apr	3450	(±407)	2484	(±394)	3488	(±214)	2372	(±281)	3256	(±303)	1921	(±126)
May	2875	(±212)	1926	(±106)	3185	(±143)	1975	(±136)	3684	(±523)	2100	(±319)
Jun	2575	(±213)	1777	(±66)	3387	(±798)	2168	(±607)	2945	(±177)	1649	(±76.4)
Jul	2876	(±274)	1869	(±73)	2258	(±853)	1310	(±520)	3195	(±288)	1757	(±119)
Aug	2488	(±71)	1766	(±105)	3465	(±77)	2044	(±26)	2788	(±101)	1589	(±55)
Sep	2588	(±511)	1915	(±326)	3356	(±327)	2081	(±100)	2645	(±554)	1666	(±397)
Oct	1865	(±785)	1455	(±675)	2894	(±272)	1939	(±275)	3428	(±469)	2228	(±305)
Nov	2975	(±276)	2410	(±169)	3278	(±207)	2327	(±63)	2765	(±7)	1797	(±112)
Dec	2585	(±687)	2171	(±526)	2985	(±120)	2239	(±68)	2755	(±85)	1956	(±81)
Mean	2810		2077		3095		2055		2973		1835	
Stdev	±455		±392		±375		±297		±342		±217	

During the start-up period of wetlands, TDS removal concentration was 11 - 18 % but with passage of time, total dissolved solids removal increased up to the value of 45%. Statistical analysis shows 96% variation in the removal efficiency, which is dependent *Phragmites karka* and coarse sand. Coefficient of HLR is 8.06, which indicates that on average it increases removal by 8.06 % with every unit increase in HLR. The standard error value is 33.58, which is significant ($P = 0.018$) and that the hydraulic loading rate variable is significant for increasing removal. Results had shown significant removal of dissolved solids in our study while low level of removal is attributed to absorption, sedimentation and filtration process which is actually the elimination of heavy metals from the dissolved portion and which is discussed in detail in the section dealing with the removal of heavy metals.

c. <u>Removal of Chemical Oxygen Demand</u>

The efficiency of organic pollutant removal is indicated by the change in chemical oxygen demand of the effluent treated through constructed wetland systems, planted with *Phragmites karka* and coarse sand being used as fill material with native refinery soil. Three different hydraulic loading rates were applied on constructed wetlands to compare removal efficiency, while keeping the wetland conditions same i.e. all wetland cells were planted with *Phragmites karka* and filled with coarse sand as fill material. At hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$, the chemical oxygen demand removal was 80 - 164, 87 - 219 and 114 - 241 mg L^{-1} respectively during the monitoring period as shown in Table 4.24.

Chemical oxygen demand removal efficiencies of the coarse gravel system varied between 24 - 59 % (40±12 %) at hydraulic loading rate of 1.71 $m^3m^{-2}day^{-1}$, 28 - 69 % (51±14 %) at hydraulic loading rate of 1.44 $m^3m^{-2}day^{-1}$ and 35 - 79 % (59±15%) at hydraulic loading rate of 1.23 $m^3m^{-2}day^{-1}$ respectively as presented in

Figure 4.27. During the start-up period of wetlands, chemical oxygen demand removal concentration was 9 - 16 % but as time passed, chemical oxygen demand removal concentration increased up to the value of 35 - 79%.

Statistical analysis showed 93% variation in the removal efficiency, which is dependent upon *Phragmites karka* and coarse sand. Coefficient of HLR is 12.35, which indicates that on average it increases removal by 12.35%, with every unit increase in HLR. The standard error value is 22 which indicates that this coefficient is highly significant (P = 0.010) and that hydraulic loading rate variable increases removal significantly.

Mass budgets of COD of wetlands under study showed high removal percentages. Our results are consistent with many other studies of wetlands used for wastewater treatment (Bucksteeg, 1987; Bahlo and Wach, 1990; Cooper and Findlater, 1990; Hammer, 1989; Reddy and Smith, 1987; Kadlec and Knight, 1996; Tanner *et al*., 2002; Merlin *et al*., 2002). Several authors suggest that the high removal efficiencies of COD are due to chemical oxidation, mineralization (both aerobic and anaerobic) and sedimentation (Kadlec and Knight, 1996; Merlin *et al*., 2002). The chemical oxygen demand treatment trend reflected in both wetlands could be related to sufficient oxygen diffusion into the wetland cells and it is attributed to biological degradation and adsorption or absorption of heavy metals to sediments. Because the wetlands of refinery had established an extensive plant root network during the operation period.

The treatment efficiency of *Phragmites karka* along with coarse sand as fill material at different hydraulic loading rates had been studied and 89% reduction (Chen *et al*: 2006) and 44% reduction (Korkusuz *et al*: 2005) in chemical oxygen demand respectively has been observed. A range of reduction percentages, consisting

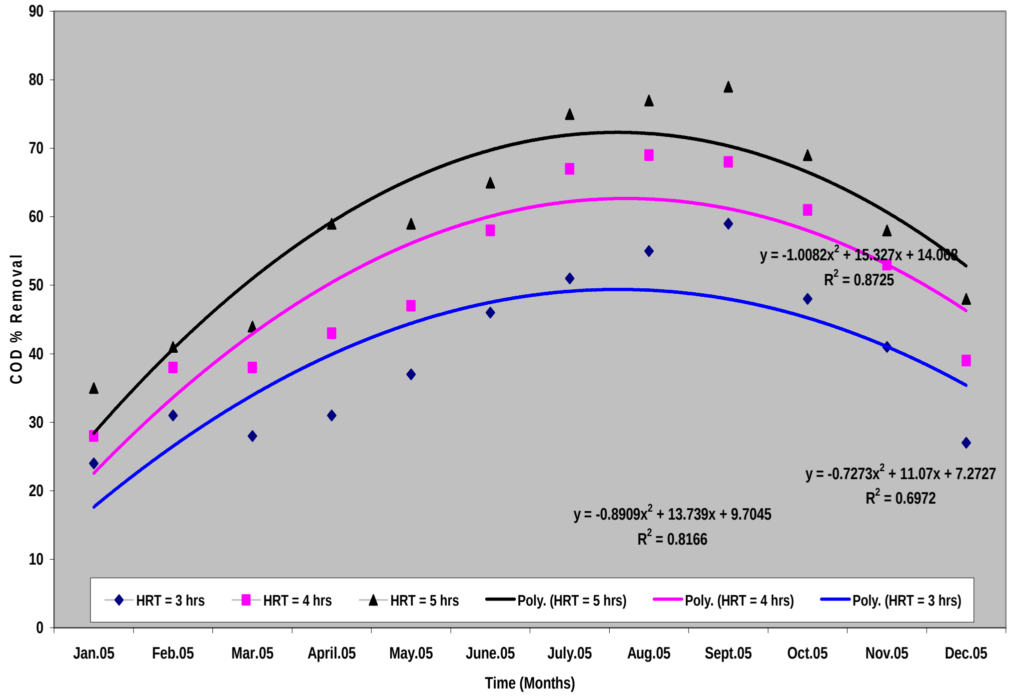

Figure 4.27. Removal (%) age of chemical oxygen demand (Sand and *Phragmites karka*)

Table 4.24. Mean values of the quality of influents and effluents (Sand and *Phragmites karka*) for chemical oxygen demand

Months	HLR 1 =1.71 $m^3m^{-2}day^{-1}$				HLR 2 =1.44 $m^3m^{-2}day^{-1}$				HLR 3 =1.23 $m^3m^{-2}day^{-1}$			
	Influent (mg/L)		**Effluent (mg/L)**		**Influent (mg/L)**		**Effluent (mg/L)**		**Influent (mg/L)**		**Effluent (mg/L)**	
Jan	341	(±30)	259	(±38)	309	(±7)	222	(±17)	327	(±16)	213	(±23)
Feb	298	(±9)	206	(±0)	319	(±11)	198	(±7)	305	(±6)	180	(±10)
Mar	285	(±21)	205	(±9)	304	(±1)	188	(±10)	297	(±1)	166	(±32)
Apr	315	(±7)	217	(±9)	306	(±1)	174	(±9)	296	(±13)	121	(±6)
May	325	(±3)	205	(±22)	304	(±3)	161	(±22)	315	(±1)	129	(±13)
Jun	321	(±1)	173	(±11)	308	(±2)	129	(±20)	316	(±16)	111	(±26)
Jul	322	(±3)	158	(±8)	305	(±9)	101	(±1)	294	(±1)	74	(±4)
Aug	326	(±13)	147	(±15)	318	(±25)	99	(±6)	295	(±7)	68	(±3)
Sep	307	(±6)	126	(±21)	282	(±28)	90	(±25)	305	(±1)	64	(±22)
Oct	298	(±11)	155	(±21)	321	(±11)	125	(±13)	306	(±14)	95	(±30)
Nov	314	(±13)	185	(±22)	306	(±1)	144	(±31)	326	(±6)	137	(±20)
Dec	296	(±32)	216	(±30)	308	(±1)	188	(±24)	317	(±7)	165	(±34)
Mean	312		188		307		152		308		127	
Stdev	±16		±37		±10		±44		±12		±48	

of 75% reduction (Garcia *et al:* 2004), 90% reduction (Ayaz and Lutfi: 2001), 80% reduction (Kern and Idler:1999), 70% reduction (Tanner *et al* :1999) and 87% reduction (Rivera *et al*:1997), in chemical oxygen demand had been recorded which are similar to findings of our study. Average effluent chemical oxygen demand treatment achieved was around a value of 104 mg L^{-1}, which is well below the limit chemical oxygen demand effluent discharge concentration according to the national environmental quality standards of Pakistan CPP (1999).

d. <u>Removal of Biological Oxygen Demand</u>

The efficiency of organic pollutant removal is indicated by the change in biological oxygen demand of the effluent, from constructed wetland systems planted with *Phragmites karka* and coarse sand as fill material along with refinery soil. Three different hydraulic loading rates were applied on CWs to compare removal efficiency, while keeping wetland conditions same i.e. all wetland cells were planted with *Phragmites karka* and filled with coarse sand as fill material. At hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$, the biological oxygen demand removal was 31 - 81, 33 - 95 and 38 - 90 mg L^{-1} (66 ± 19 mg L^{-1}) respectively during the monitoring period as shown in Table 4.25.

Biological oxygen demand removal efficiencies of the coarse gravel system varied between 24 - 65 % (45 ± 14%) at hydraulic loading rate of 1.71 $m^3m^{-2}day^{-1}$, 28 - 69 % (49 ± 15 %) at hydraulic loading rate of 1.44 $m^3m^{-2}day^{-1}$ and 35-79 % (58 ± 15 %) at hydraulic loading rate of 1.23 $m^3m^{-2}day^{-1}$ respectively as indicated in Figure 4.28. During the start-up period of wetlands, biological oxygen demand removal concentration was 24% but as time passed, biological oxygen demand removal concentration increased up to the value of 79%.

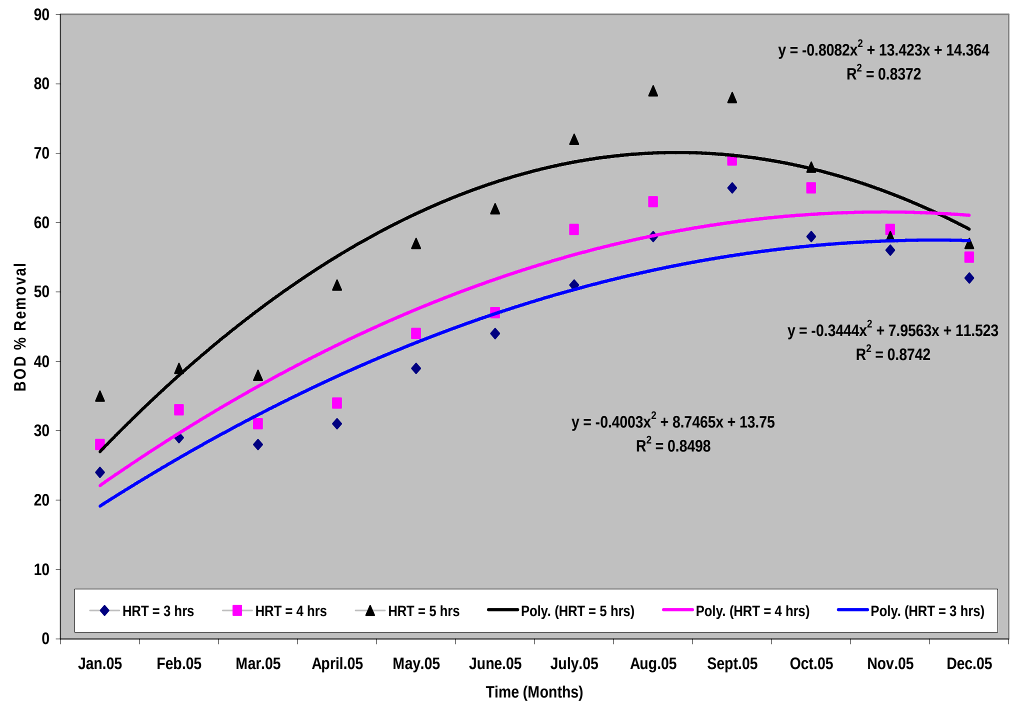

Figure 4.28. Removal (%) age of biological oxygen demand (Sand and *Phragmites karka*)

Table 4.25. Mean values of the quality of influents and effluents (Sand and *Phragmites karka*) for biological oxygen demand

Months	HLR 1 =1.71 $m^3m^{-2}day^{-1}$				HLR 2 =1.44 $m^3m^{-2}day^{-1}$				HLR 3 =1.23 $m^3m^{-2}day^{-1}$			
	Influent (mg/L)		Effluent (mg/L)		Influent (mg/L)		Effluent (mg/L)		Influent (mg/L)		Effluent (mg/L)	
Jan	128	(±6)	97	(±9)	118	(±4)	85	(±1)	109	(±0)	71	(±3)
Feb	119	(±12)	84	(±9)	124	(±0)	83	(±2)	109	(±6)	66	(±4)
Mar	136	(±27)	98	(±21)	124	(±2)	86	(±4)	117	(±7)	73	(±14)
Apr	98	(±19)	68	(±6)	121	(±11)	80	(±14)	107	(±5)	52	(±2)
May	125	(±6)	76	(±1)	106	(±15)	59	(±6)	114	(±17)	49	(±2)
Jun	134	(±6)	75	(±10)	127	(±1)	67	(±10)	138	(±12)	52	(±13)
Jul	125	(±1)	61	(±6)	128	(±8)	52	(±6)	121	(±9)	34	(±8)
Aug	127	(±1)	53	(±7)	117	(±14)	43	(±1)	108	(±5)	23	(±2)
Sep	125	(±8)	44	(±10)	137	(±20)	42	(±3)	115	(±7)	25	(±10)
Oct	137	(±7)	58	(±1)	109	(±6)	38	(±7)	125	(±11)	40	(±4)
Nov	127	(±1)	56	(±3)	118	(±2)	48	(±4)	109	(±8)	46	(±3)
Dec	126	(±1)	60	(±3)	121	(±2)	54	(±4)	98	(±8)	42	(±3)
Mean	115		61		111		55		105		42	
Stdev	±11		±16		±9		±17		±11		±15	

Statistical analysis shows 92 % variation in the removal efficiency, which is dependent *Phragmites karka* and coarse sand. Coefficient of HLR is 12.371, which indicates that on average it increases removal by 12.371 % with every unit increase in HLR. The standard error value is 20.1 which is highly significant (P = 0.016) and that hydraulic loading rate is significant for increasing the removal.

Previous studies examined only some of these factors for shorter timings (3 - 6 months). The effect of different hydraulic loading rates on treatment efficiency of constructed wetlands filled with coarse sand planted with *Phragmites karka* has been noted in a number of studies and the following percentages of reduction have been observed: 89% reduction (Akratos and Tsihrintzis, 2007), 81% reduction (Chen *et al.,* 2006), 58 - 65% reduction (Billore *et al*., 1999) and 50 - 80% reduction (Tanner *et al.,*1995), Williams *et al*., (1995), Chick and Mitchell (1995) also observed significant reductions. The biological oxygen demand removal in wetland hydrosoils is carried out by the oxidation of the organic matter which provides energy for microbial, metabolic processes and which can be synthesized or incorporated into cell mass.

The organic matter present in effluents provides a substrate for aerobic microbial metabolism. The purpose, therefore, of constructed wetlands is to encourage contact of microorganisms with this substrate, resulting in conversion of organic matter to CO_2, biomass, and water (Portier and Palmer, 1989). Thus, the design rationale for *Phragmites karka and* coarse sandy hydro-soil combination facilitated to encourage an oxygen-rich rhizosphere resulting in aerobic microbial degradation of biological oxygen demand enhancement.

In the wetland systems, initially, the biological oxygen demand removal was very low, but as the plants became established, they increased the aeration thus contributing towards the formation of the bio-film. This resulted in the rapid degradation of the organic compounds, both aerobically and anaerobically. Thus, treatment efficiency of the constructed wetlands for the removal of organics is, generally, highly dependent on the oxygen concentration in the bed. Uptake of organic matter by the macrophyte is negligible compared to biological degradation (Watson *et al*., 1989).

Treatment of chemical oxygen demand and BOD_5 of the wetland under study showed high removal percentages. These results are consistent with many other studies of wetlands used for wastewater treatment (Bucksteeg, 1987; Bahlo and Wach, 1990; Cooper and Findlater, 1990; Hammer, 1989; Reddy and Smith, 1987; Kadlec and Knight, 1996; Tanner *et al*., 2002; Merlin *et al*., 2002). A number of studies (Kadlec and Knight, 1996; Merlin *et al*., 2002) suggest that the high removal efficiencies of BOD_5 are due to chemical oxidation, mineralization (both aerobic and anaerobic) and sedimentation and are similar to our studies findings. Average effluent biological oxygen demand achieved were around 68 mg L^{-1}, which is well below the limit biological oxygen demand effluent discharge concentration according to the National Environmental Quality Standards of Pakistan CPP (1999).

e. <u>Removal of Oil and Grease</u>

The efficiency of organic pollutant removal is indicated by the change in oil and grease of the effluent from constructed wetland systems planted with *Phragmites karka* and filled with coarse sand. Three different hydraulic loading rates were applied on constructed wetlands to compare the removal efficiency, while keeping the wetland conditions same i.e. all wetland cells were planted with *Phragmites karka* and filled with coarse sand as fill material. At hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$, the oil and grease removal was 12 - 16, 16 – 24 and 12 - 37 mg L^{-1} (22 ± 7 mg L^{-1}) respectively during the monitoring period as shown in Table 4.26.

Oil and grease removal efficiencies of the coarse sand system varied between 24 - 29% (26±3%) at hydraulic loading rate of 1.71 $m^3m^{-2}day^{-1}$, 23 - 42 % (35±6 %) at hydraulic loading rate of 1.44 $m^3m^{-2}day^{-1}$ and 27 - 59 % (43±9 %) at hydraulic loading rate of 1.23 $m^3m^{-2}day^{-1}$ respectively as indicated in Figure 4.29. During the start-up period of wetlands, oil and grease removal was 17 - 22% but as time passed, the removal concentration increased up to the value of 27 - 59 %. Statistical analysis showed 96 % variation in the removal efficiency, which is dependent upon *Phragmites karka* and coarse sand. Coefficient of HLR is 8.7 which indicate that on average it increases removal by 8.7 % with every unit increase in HLR. The standard error value is 32.76 which is significant ($P = 0.015$) and that the hydraulic loading rate variable is significant for increasing the percentage removal.

Treatment of effluents containing oil and grease using constructed wetlands is accomplished through several physical, chemical, and biological processes and it is primarily by aerobic microbial degradation and sedimentation/filtration processes (Watson *et al*., 1989). According to the wetland design, the oxygen required for aerobic degradation can be supplied by diffusion, convection and oxygen leakage from the macrophyte roots into the rhizosphere (Moshiri, 1993). The results indicated that this CW system removed oil and grease effectively because of natural mechanism for pumping air via their root systems. The root area provides an oxygen-rich environment, which supports a range of aerobic bacteria (Brix, 1994).

Furthermore, a range of anoxic and anaerobic microbial processes occur within wetlands (Reddy and Patrick, 1984). These biological processes promote the degradation of oil and grease. Moreover it is also subjected to physical processes such as evaporation, leaching, sorption of soil particles, and sedimentation (Mashauri *et al*., 2000) which resulted in high removal efficiency.

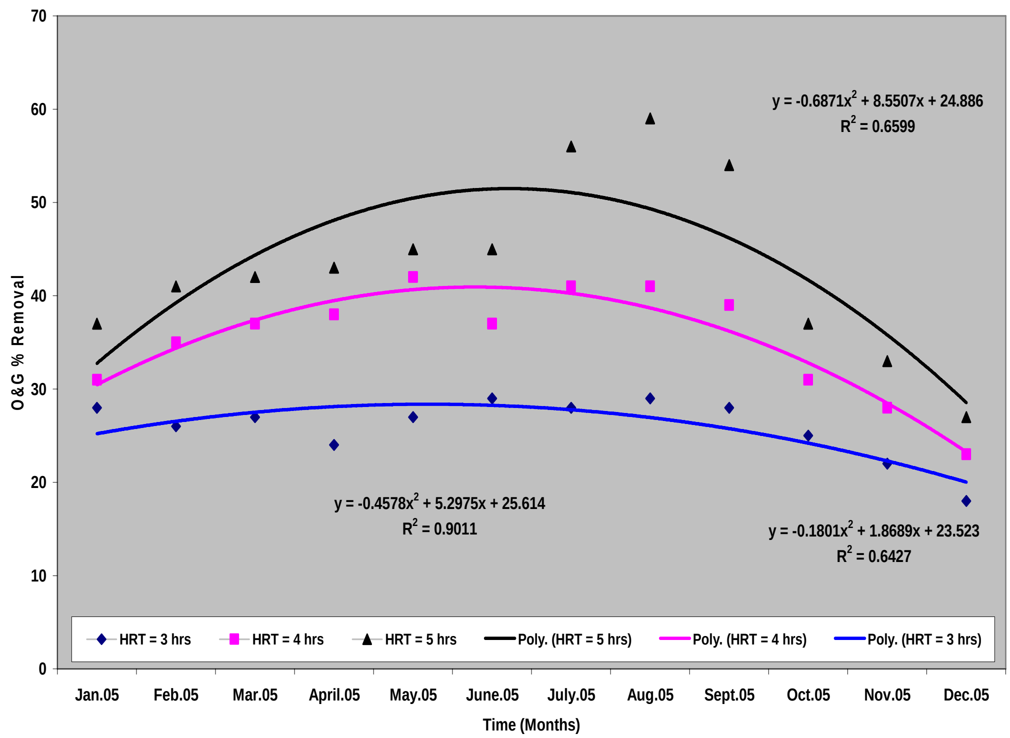

Figure 4.29. Removal (%) age of oil and grease (Sand and *Phragmites karka*)

Table 4.26. Mean values of the quality of influents and effluents (Sand and *Phragmites karka*) for oil and grease

Months	HLR 1 =1.71 $m^3m^{-2}day^{-1}$		HLR 2 =1.44 $m^3m^{-2}day^{-1}$		HLR 3 =1.23 $m^3m^{-2}day^{-1}$	
	Influent (mg/L)	**Effluent (mg/L)**	**Influent (mg/L)**	**Effluent (mg/L)**	**Influent (mg/L)**	**Effluent (mg/L)**
Jan	45 (±16)	32 (±12)	57 (±1)	39 (±1)	39 (±8)	25 (±4)
Feb	67 (±4)	50 (±3)	58 (±6)	38 (±5)	51 (±1)	30 (±0)
Mar	73 (±11)	53 (±7)	49 (±4)	31 (±3)	53 (±8)	31 (±5)
Apr	58 (±14)	44 (±12)	43 (±11)	27 (±5)	41 (±7)	23 (±3)
May	38 (±0)	28 (±1)	58 (±5)	34 (±1)	51 (±3)	28 (±2)
Jun	38 (±13)	27 (±9)	51 (±11)	32 (±8)	47 (±2)	26 (±5)
Jul	56 (±6)	40 (±5)	36 (±1)	21 (±0)	44 (±13)	19 (±5)
Aug	47 (±3)	33 (±2)	35 (±0)	21 (±0)	63 (±4)	26 (±0)
Sep	43 (±1)	31 (±2)	35 (±5)	21 (±1)	57 (±3)	26 (±9)
Oct	45 (±4)	34 (±2)	28 (±14)	19 (±11)	61 (±11)	38 (±6)
Nov	39 (±13)	30 (±12)	48 (±1)	35 (±1)	45 (±1)	30 (±1)
Dec	58 (±9)	48 (±11)	46 (±8)	35 (±3)	43 (±3)	31 (±5)
Mean	51	38	45	29	50	28
Stdev	±12	±9	±10	±7	±8	±5

f. **Removal of Iron, Copper and Zinc**

The efficiency of inorganic pollutant removal is indicated by the change in iron of the effluent treated through the constructed wetland systems by applying three different hydraulic loading rates to achieve high treatment efficiency. At hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$ the iron removal was 0.62 - 2.19, 0.6 – 1.95 and 1.01–2.17 mg L^{-1} (1.64 ± 0.49 mg L^{-1}), the copper removal was 0.7 – 3.25, 1 – 3 and 2 – 4.38 mg L^{-1} (2.64 ± 0.67 mg L^{-1}) and zinc removal was 0.46 - 2.77, 1 - 3 and 1.09 - 3.47 mg L^{-1} (2.23 ± 0.83 mg L^{-1}) respectively during the monitoring period as shown in Table 4.27. Iron removal efficiencies of the coarse gravel system at hydraulic loading rate of 1.71, 1.44 and 1.23 $m^3m^{-2}day^{-1}$varied between 19 - 46 % (33±10 %), 21 - 62 % (41±15 %) and 29 - 73 % (49±17 %) for iron, 65 % (43±13 %), 28–69 % (47±14 %) and 35 - 73 % (53±13 %) for copper and 24 - 71 % (48±18 %), 28 - 77 % (47±14 %) and 35 - 85 % (59±18 %) for zinc respectively as presented in Figure 4.30, 4.31 and 4.32.

Statistical analysis shows 89% variation in the removal efficiency for iron, which is dependent upon *Phragmites karka* and coarse sand. Coefficient of HLR is 12.95 which indicates that on average it increases removal by 12.95 % with every unit increase in HLR. The standard error value is 16.97 which is significant (P = 0.016) and that the hydraulic loading rate variable is significant in increasing removal. In case of copper 92% variation in removal efficiency is observed and the coefficient of HLR is 11.6, which indicates that on average it increases removal by 11.6 %, with every unit increase. The standard error value is 20.2, which indicates that coefficient is significant (P = 0.014) and that the hydraulic loading rate variable increases percentage removal to a great extent. For zinc 89% variation was observed which is dependent upon *Phragmites karka* and coarse sand. Coefficient of HLR is

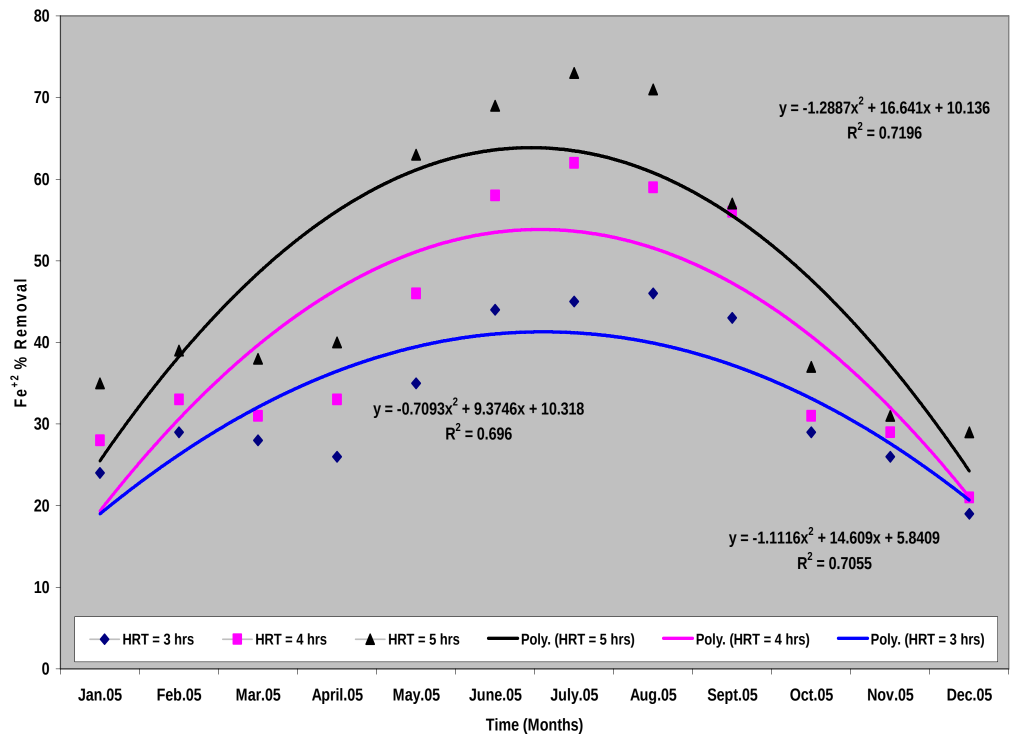

Figure 4.30. Removal (%) age of iron (Sand and *Phragmites karka*)

Table 4.27. Treatment performance values for iron, copper and zinc influents and effluents (Sand and *Phragmites karka*)

Plant	***Fill Material***	***Heavy Metal***	***Statistical Results***	***HLR 1*** ***1.71 $m^3m^{-2}day^{-1}$***	***HLR 2*** ***1.44 $m^3m^{-2}day^{-1}$***	***HLR 3*** ***1.23 $m^3m^{-2}day^{-1}$***
Phragmites karka	*Coarse sand*	*Iron*	*Max*	*46*	*62*	*73*
			Min	*24*	*28*	*35*
			Mean	*33*	*41*	*49*
			Stdev	*9*	*15*	*17*
		Copper	*Max*	*65*	*69*	*73*
			Min	*24*	*28*	*35*
			Mean	*43*	*47*	*53*
			Stdev	*13*	*14*	*13*
		Zinc	*Max*	*73*	*77*	*85*
			Min	*24*	*28*	*35*
			Mean	*48*	*52*	*59*
			Stdev	*18*	*18*	*18*

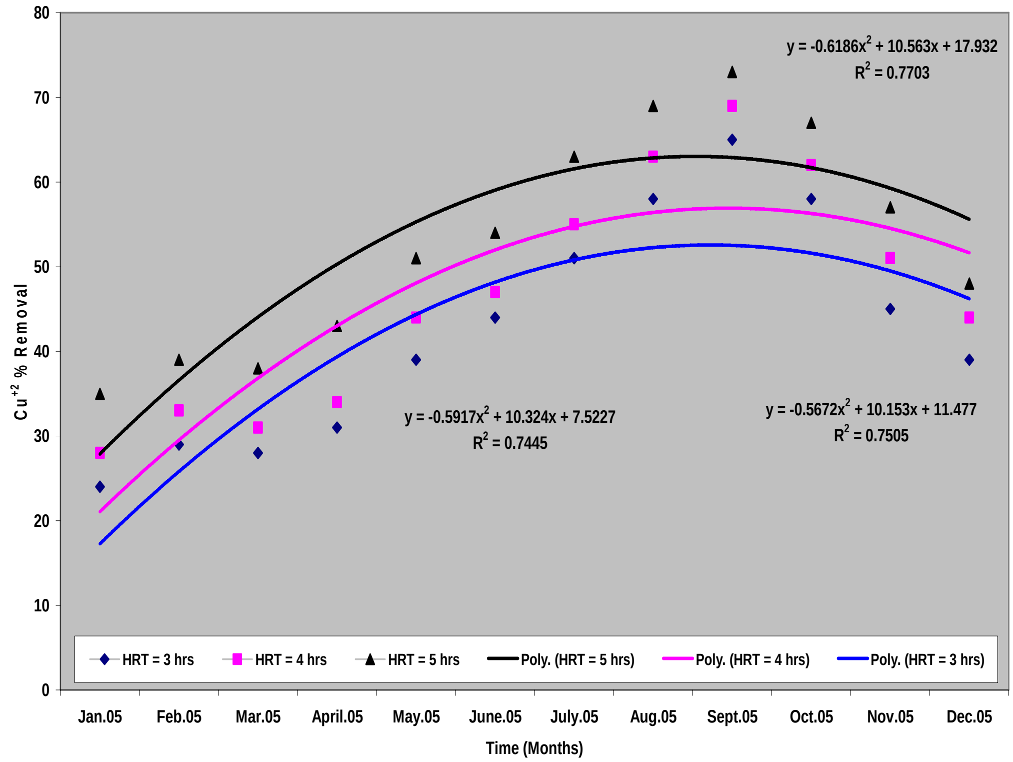

Figure 4.31. Removal (%) age of copper (Sand and *Phragmites karka*)

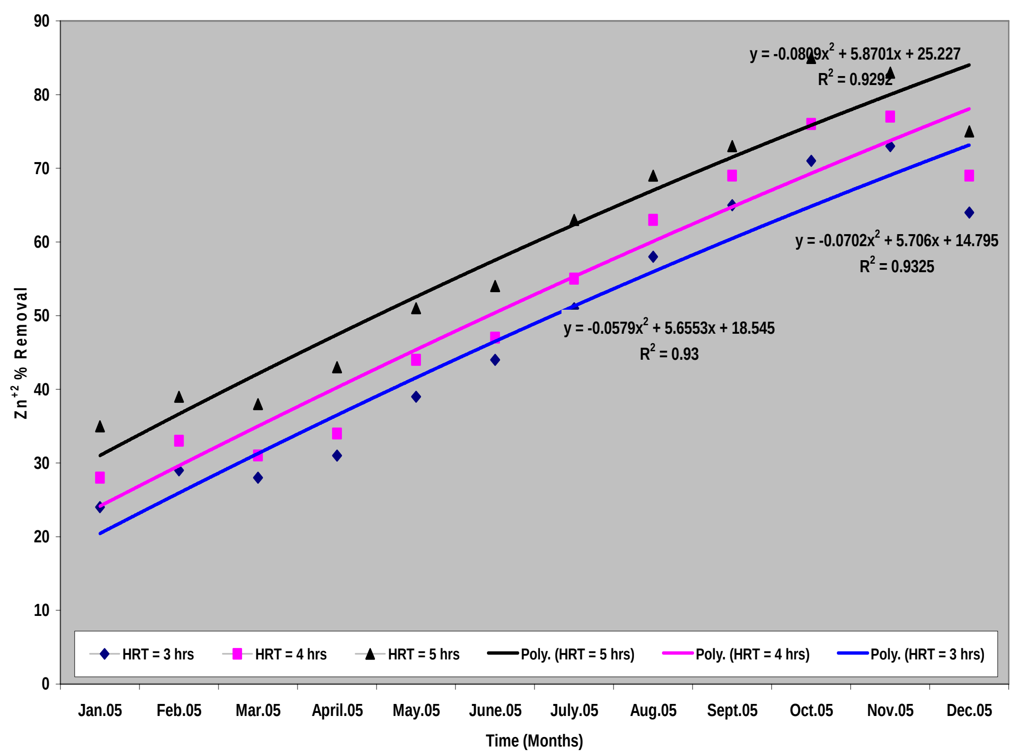

Figure 4.32. Removal (%) age of zinc (Sand and *Phragmites karka*)

12.95 which indicate that on average it increases the removal by 12.95 %, with every unit increase in HLR. The standard error value is 3.40 which is significant ($P = 0.011$) and that the hydraulic loading rate variable is significant for increasing removal.

During the application of wastewater in constructed wetlands, a reddish appearance was noticed in the wastewater surfaces in all set-ups, suggesting the formation of Fe rich colloids (precipitates). Generally precipitation of Fe, Cu and Zn occurred following the atmospheric (abiotic) and bacterial mediated oxidation (mediated by *Thiobacillus ferrooxidans* and bacteria of the genera *Sphaerotilus, Metallogenium* and *Crenothrix* etc.) of Fe_2^+ to Fe_3^+ (Groudeva *et al*., 2001; Vymazal, 1995). Basically our results implied that the average pH of Fe-rich industrial wastewaters and the pH of the pipe-borne water added to the constructed wetlands (i.e., prior to introducing the wastewaters), is conducive for Fe removal to occur through chemical precipitation (provided DO levels are higher than 3 - 4 mg/L for the abiotic oxidation of Fe_2^+ to take place).

The determination of the efficiency of heavy metal removal from the effluent from wetlands having the characteristics of those developed in this study have been studied by a number of researchers (Vymazal *et al* (2007), Batty and Younger (2004), Southichak *et al*., (2006), Ali *et al*., (2004), Baldantoni *et al*., (2004), Windham *et al*., (2003) and Cymerman and Kempers (2001). Results of this study are on par with these studies, except for comparative removals which occurred when the hydraulic loading was being varied which resulted in fluctuation in the removal of the heavy metals.

4.4. **STANDARD DESIGN FOR PAKISTAN ENVIRONMENTAL CONDITOINS**

Based on the treatment performance of the pilot scale constructed wetlands which were planted with *Phragmites karka* and *Typha lattifolia* in native soil and filled with coarse gravel and coarse sand as fill materials, it has been found that the best treatment performance was obtained with coarse gravel planted with *Typha lattifolia* at hydraulic loading rate of $1.44 m^3/m^2/day$. Average daily wastewater generation rate from the refinery is 1200 – 1450 m^3/day and a 15 year system life based on the findings of this study. Cost estimates are based primarily on data compiled during the pilot scale study at ARL and additional cost data were obtained from PHED standard engineering cost reference manuals (Means 1992). Costs are presented in year 2006 and are considered estimates with an accuracy of plus 25 percent and minus 15 percent.

4.4.1. Economic Analysis

On the basis of the treatment results, cost estimates for using vertical flow constructed wetland system was calculated to treat refinery wastewater. The baseline circumstances used for developing this cost estimate was a 1400 m^3 flow rate, the total flow from the Attock Refinery Limited and a 15 year system life. The baseline costs were adjusted for hydraulic loading rate of 1.44 $m^3m^{-2}day^{-1}$ to develop cost estimate and are based primarily on data compiled during the pilot scale study at ARL. Costs were presented in year 2006 and are considered estimates with an accuracy of plus 25 percent and minus 15 percent.

4.4.2. Basis of Economic Analysis

A number of factors affect the costs of treating refinery wastewater with constructed wetland system. These factors include treatment objectives, geo-physical site conditions, hydraulic loading rate, types of plants and type and concentration of contaminants. It was assumed that constructed wetland system will treat contaminated refinery wastewater continuously, 24 hours per day, 7 days per week with an average treatment efficiency of 85 %. Further assumptions about constructed wetlands treatment for each case include the following:

a. A hydraulic loading rate of 1.44 $m^3m^{-2}day^{-1}$ is recommended for satisfactory treatment efficiency.

b. A porosity of 50 percent is assumed for the substrate material.

c. Substrate material will require removal and replacement once every 15 years.

d. The spent substrate will be dewatered on site, some portion of it would be recycled while rest will be incinerated and disposed off at ARL incinerator and landfill.

e. This analysis assumes that PNEQS standards are most appropriate and the attainment of these standards depends on the affected organisms, receiving waters and volume of refinery wastewater.

f. The site will allow for gravity flow of the refinery wastewater through the wetland.

g. Access roads exist at the site.

h. Utilities, such as electricity and telephone lines are available on site.

i. The treatment goal for the site will be to achieve PNEQS.

j. One influent water sample and two effluent water samples will be collected monthly and two composite substrate samples will be collected quarterly to monitor system performance.

k. One full time associate supervisor will be required to inspect the system, collect all required samples, and conduct minor maintenance and repairs.

4.4.3. Cost Components

Cost data associated with the constructed wetland system technology had been categorized into the following categories:

a. Wetland Construction

b. Capital equipment

c. Startup

d. Consumables and supplies;

e. Utilities;

f. Analytical services;

g. Operational cost

h. Repair and maintenance

a. **Wetland construction**

These include land costs, site preparation, site clearing, earthwork, liner, gravel media, plants, inlet and outlet structures, fencing, miscellaneous piping, etc. The gravel media and the clay liner installation are the most critical ones. This analysis assumes a total area of about 0.62 acres to accommodate the wetland area. Site preparation and excavation include clearing the site of brush and trees, excavation of the wetland cell, grading the cell and construction of the earthen berms system design. Adequate land area exist at the site and that only some modifications/development would be required for wetland construction. This also involves transporting all construction equipment and materials to the site.

b. **Capital equipment**

Capital costs take account of the equipment which include flow meters, motor pumps, valves equipment for wastewater sampling, concrete vaults or sumps, weirs and other miscellaneous materials.

c. **Startup**

Startup requirements are minimal for a wetland system. System startup involves introducing flow to the wetland with frequent inspections to verify proper hydraulic operation. Operators are assumed to be trained in health and safety procedures. Therefore training costs are not incurred as a direct startup cost. The only costs directly related to system startup are labor costs associated with more frequent system inspection.

d. **Consumable and supplies**

The only consumables and supplies used during wetland operations are disposable overalls, gloves and boot covers. The treatment system operator will wear these accessories when required by health and safety plans during system operation. Based on the assumed labor required above and an additional 22 days for miscellaneous O&M.

e. **Utilities**

Utilities used by the wetland system are negligible. The wetland system requires no utilities for operation. The only utility required is for electricity for lights in the storage building and for charging monitoring equipment. For the analysis, utility costs are assumed to be zero because these are available on site.

f. **Analytical services**

Analytical costs associated with a wetland system include laboratory analysis, data analysis, quality assurance/quality control and reporting. For each case, this analysis assumes that one influent sample and two effluent samples will be collected once a month and that two substrates sample will be collected quarterly. The substrate samples will be analyzed for total metals. Influent and effluent samples will be analyzed for chemical oxygen demand, biological oxygen demand, total suspended solids, total dissolved solids and oil & grease.

g. **Operational cost**

Operational costs include a part time technician to sample, operate and maintain the system. Once the system is functioning, it is assumed to operate

Table 4.28: Cost estimate for the constructed wetland system at ARL

S#	Items	Units	Unit cost	Total cost
1	**Wetland construction**			
1.1	Land cost			2000000
1.2	Site preparation	1	35000	35000
1.3	Site clearing	1	12000	12000
1.4	Earthwork	1	25000	25000
1.5	Geosynthetic liner	0.62 acers	350000	350000
1.6	Coarse gravel media	235cb ft	235000	235000
1.7	Plants	1	8500	8500
1.8	Inlet and outlet structures	2	8500	17000
1.9	Piping and networking	2200	60	132000
2	**Capital Equipment**			
2.1	Flow meters	6	5500	33000
2.2	Motor pumps	2	25000	50000
2.3	Valves	18	850	15300
2.4	Water sampling equipments	1	7500	7500
2.5	Weirs	2	12500	25000
3	**Startup**			
3.1	Labor	32.5	500	16250
4	**Consumable and supplies**			
4.1	Personal protective equipment	25	2300	57500
4.2	Labor	22	500	11000
5	**Utilities**			
6	**Analytical services**			
6.1	Labortary analysis	5	4500	22500
6.2	Data analysis/reporting	12	15000	180000
7	**Operational cost**			
7.1	Technician	12	12000	144000
7.2	Repair and maintenance	1	25000	25000
	Grand total			**3401550**

continuously at the design flow rate. One technician will monitor the system on a weekly basis. Weekly monitoring will require several hours 2 – 3 times per week to check flow rate and overall system operation. Sampling is assumed to be conducted once a month and will require two technicians for 2 hours which equate to 260 hours annually.

h. **Repair and maintenance**

Annual repair and maintenance costs are expected to be minimal and the major maintenance cost will be removal and replacement of the substrate every 5 years.

Table 4.28. Cost estimate of the pilot scale constructed wetland at ARL.

5 Conclusions

1. **Hydraulic loading rate**: hydraulic loading rate of 1.23m^3/m^2/day has been found effective in chemical and biological oxygen removal efficiencies in the constructed treatment wetlands while significant removal has been achieved at 1.44m^3/m^2/day.

2. ***Phragmites karka***: the high removal effectiveness of *phragmites karka* and *typha lattifolia*, has been observed in terms of suspended solids, chemical oxygen demand; whereas, biological oxygen demand removal in wetlands planted with typha while high metal removal efficiencies have been observed in wetland cells planted with phragmites australis. These were comparable to values found in the literature. The direct role of the plants is to increase aeration in facilitating the oxidation process and in reducing the flow velocity by providing more retention time thus increasing the contacts with fill materials. This has also helped in facilitating the adsorption process thereby resulting in high removal efficiencies.

3. **Fill material**: The maximum removal efficiencies have been observed for suspended solids and chemical and biological oxygen demand in wetland cells filled with sand and native soil, while comparatively lower removal efficiencies have been observed in case of wetlands cells filled with gravel and native soil. Similarly comparatively high removal efficiencies have been observed in wetland cells filled with coarse sand as compared to wetland cells filled with coarse gravel and native soil. The measurement of the COD & BOD reduction rates produced results that were comparable to others found in the literature for marine and freshwater environments. However, they were found to underestimate the actual potential of *Phragmies karka* which has shown good results.

4. **Recycled Water for Fire Fighting Reservoir**: Attock Refinery Limited is generating 1800 m^3 of wastewater per day and by applying this design of constructed wetland this treated recycled water can be used for fire fighting reservoir and gardening.

Overall, the wetland proved successful in removing major refinery wastewater quality parameters, except in the case of total dissolved solids and oil and grease. The plants appear to offer some advantage in terms of COD and heavy metals removal.

Future Recommendations

1. Detailed analysis of plants and sediments need to be done to devise eco friendly disposal of accumulated heavy metals.
2. Multi stage constructed wetland system should be checked for treatment of industrial wastewater.
3. Role of micro-organism needs to be checked in the accumulation of heavy metals.

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Annex A

Metals concenteration in effluent, sediments and plants in constructed wetlands

Plant	Fill material	Heavy Metal	Statistical analysis	Analysis tenures 28-Mar-2005	30-Jun-2005	29-Sep-2005	24-Dec-2005
Typha lattifolia	Coarse Gravel	Iron	Effluent	3983	3090	3097	3240
			Sediments	19	45	78	125
			Plants	BDL	13	42	76
		Copper	Effluent	4667	4133	4833	5390
			Sediments	13	39	69	113
			Plants	BDL	11	36	53
		Zinc	Effluent	3157	4150	3883	850
			Sediments	14	32	71	132
			Plants	BDL	8	35	69
Phragmites karka	Coarse Gravel	Iron	Effluent	3983	3090	3097	3240
			Sediments	18	41	86	141
			Plants	BDL	17	47	89
		Copper	Effluent	4667	4133	4833	5390
			Sediments	9	34	64	89
			Plants	BDL	11	29	47
		Zinc	Effluent	3157	4150	3883	850
			Sediments	14	41	81	117
			Plants	BDL	16	46	74
Typha lattifolia	Coarse sand	Iron	Effluent	3983	3090	3097	3240
			Sediments	10	31	69	116
			Plants	3	14	33	54
		Copper	Effluent	4667	4133	4833	5390
			Sediments	19	39	74	129
			Plants	BDL	14	41	71
		Zinc	Effluent	3157	4150	3883	850
			Sediments	16	37	76	121
			Plants	BDL	14	32	51
Phragmites karka	Coarse sand	Iron	Effluent	3983	3090	3097	3240
			Sediments	13	41	84	145
			Plants	5	20	36	63
		Copper	Effluent	4667	4133	4833	5390
			Sediments	19	35	76	122
			Plants	BDL	12	34	62
		Zinc	Effluent	3157	4150	3883	850
			Sediments	14	30	68	116
			Plants	BDL	17	29	63

Effluent concenterations in µg/L
Sediment and plant concenterations in µg/Kg
BDL = below detectable limits

Annex B

Climatic data during research period

S#	Months	Temperature (^{0}C)	Precipitation (mm)
1	Jan, 05	11	18
2	Feb, 05	18	15
3	Mar, 05	27	8
4	Apr, 05	32	3
5	May, 05	37	8
6	Jun, 05	41	3
7	Jul, 05	39	18
8	Aug, 05	25	33
9	Sep, 05	15	28
10	Oct, 05	11	27
11	Nov, 05	8	32
12	Dec, 05	8	26