INTRODUCTION

In many cities, towns, villages and in other places of the world, wastewater from individual houses, small settlements, dwelling units and industries discharges their effluent into the nearby water body and thus indirectly into the environment with only poorly efficient primary treatment system or without any treatment at all which in return often poses a significant threat, danger and damage to the public and environmental health (Gardner *et al*., 1997). In order to limit the groundwater pollution, contamination and eutrophication of surface water bodies such as lakes, ponds and rivers, regulations for the discharge of treated wastewater have become more strict in recent years which makes nutrients such as phosphate and nitrate removal an increasingly common requirement for all small and decentralized wastewater treatment systems (Sasse, 1998; Wallace & Knight, 2006).

In comparison to many conventional and modern wastewater treatment methods and technologies, treatments using the application of wetlands are low cost, relatively simple to operate and can be constructed out of local materials available near the proposed site. Wetlands are the land area that is wet during part or all of the year because of their location in the landscape. Wetlands are also called as swamps, marshes, bogs, fens or sloughs depending upon existing plant and water conditions and on geographic setting. Wetlands are frequently transitional between uplands terrestrial system and continuously or deeply flooded aquatic system. The only thing that differentiates wetlands from other land or water bodies is the presence of characteristic vegetation which is adapted to unique soil which consists of hydric soil and supports the aquatic plants. Wetlands hold seemingly magical properties that make them unique among major ecosystem groups on the earth. Thus, wetlands also play a number of roles in the environment in terms of its protection and diversity, which majorly includes water purification, flood control, and shoreline stability and they are most biologically diverse of all ecosystems, serving as home to a wide range of plant and animal life. Wetlands have an important role in the preservation of environmental quality due to their high capacity for retention and inactivation of harmful substances and for carbon sequestration (Reddy & DeLaune, 2008).

Recent research has also demonstrated that treatment wetlands are not only capable of meeting secondary treatment standards but they can also achieve higher success levels of phosphorus and nitrogen removal through careful design and technology selection (Mitsch, & Gosselink, 2007). Denitrification process, oxidation-reduction reactions, adsorption process over the soil particles, absorption by vegetation and others are some of the processes in the wetlands that removes the pollutants. All these functions depend upon the correct management and preservation of the soil–water–plant system (Reddy & DeLaune, 2008).

The use and application of constructed wetlands (CW) for wastewater treatment has become common practice worldwide not only in developing countries but also in developed countries. A CW is a man made wetland aimed to be used as new or restored habitat for native and migratory wildlife for human discharges such as wastewater, storm water runoff from nearby land area or sewage treatment, for land redemption after mining, refinery, and other ecological disturbances such as required relief for natural areas lost to a development. Wastewater treatment in a constructed wetland takes place as the water passes through the wetland medium in which plant grows and the plant rhizosphere (root zone of the plant). An aerobic thin film is formed around each root hair, as of results of the leakage of oxygen from the rhizomes and roots. Aerobic and anaerobic micro-organisms help in the beak down of organic matter (Choudhary *et al*., 2011). The process of microbial nitrification followed by denitrification releases nitrogen gas into the atmosphere. Phosphorus is co-precipitated along with iron, aluminium and calcium compounds present in the root-bed medium. Suspended solids either filter out as they settle in surface flow wetlands or are manually filtered out by the medium within subsurface flow wetland cells. Harmful bacteria and viruses are decreased by filtration and adsorption on the rock media in subsurface flow wetlands (Choudhary *et al*. 2011).

Ample water is important for most forms of the biological productivity and wetland plants are adapted to take advantage of this abundant supply of water while overcoming the periodic shortage of other essential chemical element such as oxygen. Plant Reed, *Phragmites* is an example of wetland plant which knows how to take the advantage of abundant supply of water and also take up the polluted water and its nutrients from the wetland. *Phragmites* is a recurrent plant with annual cane like stem that develops from an extensive rhizome system and reaches up to 6 m in height (Mal & Narine, 2004). It is abundant in wetlands, which are dynamic ecosystems showcasing great complexity and perform a many benign functions for the environment (Skinner & Zalewski, 1995). Wetlands are generally monopolized by *Phragmites* hence resulting in a change in the ecosystem processes and imposing adverse impacts on the native wildlife. Management methods used to control the invasive populations of *Phragmites* include burning, chemical control, biological control, grazing, mechanical control, drainage and flooding and cutting (*Mal & Narine, 2004*). Plant material derived from cutting can be used as fodder, biological-fuel and or as compost production (Roca-Pérez *et al*., 2009).

Phragmites is known for their hyper accumulating nature in response to the pollution, in a sensitive and very effective manner to the trace metals such as iron and zinc. Hence, they are important for their use in phytoremediation. Studies suggest strong purification and accumulation capabilities of *Phragmites*, particularly for fragment elements. This intense growth is apparently the cause of their resistance to hyper levels of pollution (Kleche *et al.*, 2013). *Phragmites* has also got an application in sewage and domestic waste water treatment.

According to a study carried out by Rezaie and Salehzadeh, performance of *Phragmites* to remove nutrients in domestic effluent which are phosphate in municipal wastewater was investigated. Most of the studies concentrate on the role of different wetlands plants for the removal of heavy metals. Studies on removal of specific nutrients (Phosphorus) are limited since the volume of municipal sewage generated in thickly populated regions is large; wetlands can be providing low-cost option for the waste water treatment particularly in developing nations (Rezaie & Salehzadeh, 2014).

Hence, it is necessary to carry out related studies to understand the distribution of different phosphorus fractions and nitrates in wastewater during the treatment process. This study is designed to meet the following objectives:

- To study the phosphate removal efficiency by *Phragmites* in wastewater.
- To study the various fractions of phosphate in wastewater.

- To study the growth rate of *Phragmites* and factors affecting the same during this study.
- To suggest the efficacy of *Phragmites* for phosphate removal from wastewater.

REVIEW OF LITERATURE

2.1 Phytoremediation

Phyto-remediation is a process in which the term phyto means plant and remedy means to restore or to cure. Thus, phytoremediation refers to the treatment and cure of environmental problems using plants that help in reducing the problem without even excavating the contaminant material and disposing it off elsewhere.

Engineered wetland (EW) phytoremediation system consists of mitigating pollutant concentrations in contaminated soils, water or air, with the help of plant which are able to degrade or eliminate nutrients such as phosphate, poly-aromatic hydrocarbons, landfill leachate, metals and heavy metals, pesticides, solvents, explosives, crude oil and their derivatives, and various other contaminants that contain them (McCutcheon *et al*, 2008) can be constructed artificially as a water management tool, often called as constructed wetland (CW). The largest natural wetlands in the world are the Amazon River basin. A constructed wetland (CW) is an artificial swamp designed and constructed to inculcate the natural processes like wetland vegetation, soils and their associated microbial activities to aid and assist in waste treatment (Richardson, 2001).

Plants in every natural wetland provide a substrate upon which microorganisms can grow as they break down organic materials and uptake nutrients and heavy metals (McCutcheon *et al.*, 2008). There has been alarming increase in the demands of human expansion and resource exploitation in present. Thus, the natural wetland systems in such cases cannot always function efficiently as per requirement, and strict and stringent water quality standards. This may be the factor which led to the rapid development of constructed wetlands (CW) for wastewater treatment.

Efficiency of CWS might be less consistent as compared to conventional treatments due to the environmental changes occurring in different seasons. The biological components are sensitive to shocks caused by toxic chemicals, e.g., ammonia and pesticides. Pollutants or surges in water flow can temporarily hinder the treatment process. Thus Engineered wetland systems (EWSs) are designed to incur for the limitations of CWS in a more controlled way (Davis, 2009). Engineered wetlands (EW) are advanced and semi-passive kind of CWs in which operating conditions are monitored, manipulated and controlled in a more effective manner so that contaminant removal is optimized. With EW many kinds of biological and chemical processing systems, e.g., aerobic and anaerobic bioreactors, limestone drains can be expressed as cells of the system. EW can be used to bridge the gap between active treatment and the passive treatment in CW, ending the need for more engineered treatment methods and technologies (Higgins *et al.*, 2000):

2.2 Wetlands

Wetlands can be broadly classified as:

1) Natural wetland
2) Constructed Wetland

2.2.1 Natural Wetlands

Natural wetlands are saturated with water fully or partially. They receive water from the water table below it or from surface run off. These are the low lying lands in which the water table lies above the ground level making it perennial. Their high potential for filtration and treatment of pollutants have been recognized by environmental engineers and used effectively for the same.

2.2.2 Constructed Wetlands

The constructed wetland systems (CWS) work in highly controlled environments that intend to duplicate the occurrences of soil, flora, and microorganisms in natural wetlands for aid in effluent wastewater treatment. Constructed wetlands (CW) provide a platform to experiment with flow regimes, micro-biotic composition, and flora in order to formulate the most efficient treatment process. Also, it provides the control of hydraulic retention time (HRT) and hydraulic channels (Brix, 1993). The most significant factors of constructed wetlands are the water flow processes amalgamated with the growth of flora. CW systems can be surface flow systems with only free-floating macrophytes, floating-leaved macrophytes, or submerged macrophytes (Vymazal et al, 2008). However, generally free water surface systems are constructed with emergent macrophytes. Constructed wetlands can be used to treat raw sewage, secondary domestic sludge, improve water quality of oxidation pond discharge, storm waters, mining waste, and industrial and agricultural waste effluents.

CW constitutes of numerous rectangular or irregularly-shaped wetland cells connected in series as a cascade which work on the gravitational force and are confined by clay, rock, concrete or other material boundary (http://nature-works.net/; 2014). CW for wastewater treatment may be classified on basis of the flow regimes. Three types of cells may be used in a constructed wetland system (CWS):

1) Surface flow wetland cell

2) Sub-surface flow (SSF) wetlands

3) Hybrid wetlands

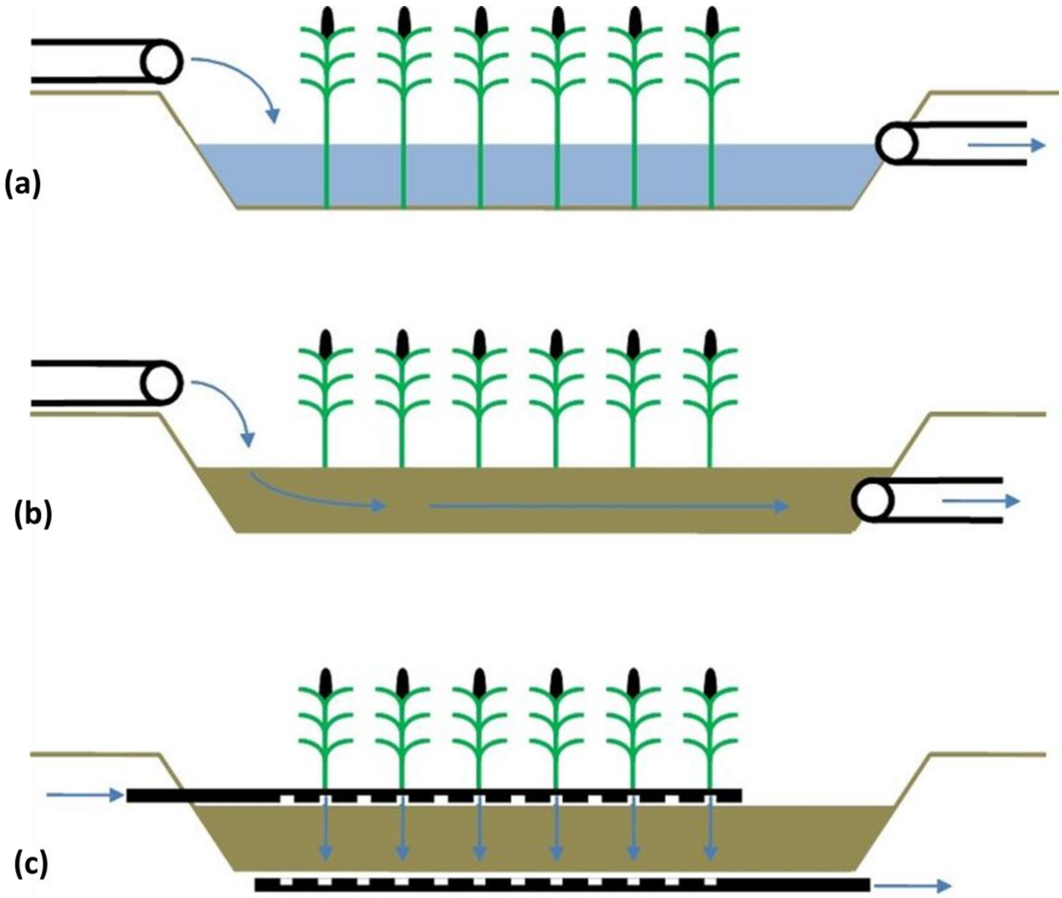

Figure 2.1 Types of flow in a wetland: (a) surface flow wetland, (b) Sub-surface flow wetland, (c) Vertical flow wetland

(Source: http://en.wikipedia.org/wiki/Constructed_wetland)

Surface-flow wetlands

Surface-flow wetlands are the ones in which effluent moves above the soil in a planted marsh or swamp, and hence, can be supported by a wider variety of soil types including bay mud and other silty clays. Use of *Phragmites* is popular in European constructed wetlands, and plants such as cattails (*Typha*), sedges, Water Hyacinth (*Eichhornia crassipes*) and *Pontederia* are used worldwide, although *Typha* and *Phragmites* are highly invasive. These wetlands are engineered and designed to employ use of natural processes in the wetland systems such as wetland vegetation, soils, and their associated microbial activities. It can be further categorized on basis of the life-form of the dominating macrophyte in system as free-floating, floating-leaved, emergent, and submerged macrophytes. CWs with emergent macrophytes are the most commonly used in free water surface (FWS) systems. FWS CW are found worldwide with majority being in Europe. They have been used around the world for various wastewaters treatments including municipal and domestic sewage, wastewaters from livestock operations, industrial wastewaters including those from agro-industry and landfill leachates. Thousands of applications have proved that FWS CWs are viable alternative to conventional treatment technologies (Vymazal, 2005).

Subsurface-flow wetlands

Subsurface-flow wetlands are the ones in which effluent from the household, agricultural, paper mill or mining runoff, tannery or meat processing wastes, or storm drains, or water from other sources to be cleansed, permeate through gravel consisting of generally limestone or volcanic rock lava stone or sand medium in which plants are rooted (Choudhary et al., 2011). Subsurface-flow wetlands can further be classified as horizontal flow (HF) and vertical flow (VF) constructed wetlands. In subsurface-flow systems, the effluent in the packing medium can move either horizontally, parallel to the surface, or vertically, from the planted layer down through the substrate and out. Subsurface horizontal-flow wetlands are less hospitable to mosquitoes breeding as there is no water exposed to the surface. Subsurface-flow systems have the advantage of requiring less land area for water treatment, but are not generally as much suitable for wildlife habitat as are surface-flow constructed wetlands.

Constructed wetlands with horizontal sub-surface flow (HF CWs) have been in use for wastewater treatment since many decades. Most HF CWs have been designed to treat municipal or domestic wastewater. Municipal HF CWs focus not only on common pollutants removal by treatment but also on special parameters such as pharmaceuticals, endocrine disruptive chemicals or linear alkylbenzensulfonates (LAS) which are present in detergents. HF CWs are used to treat many other types of wastewater and thus, have industrial applications too. These include wastewaters from oil refineries, chemical factories, pulp and paper production, tannery and textile industries, distillery and winery industries. In particular, the use of HF CW is becoming very common for treatment of food-processing wastewaters, e.g., production and processing of milk and dairy, cheese, potatoes, sugar, etc. HF constructed wetlands are also successfully used to treat wastewaters from agriculture which is pig and dairy farms, fish farm effluents and various runoff water from agriculture, airports, highway, greenhouses, plant nurseries. HF CWs have also effectively been used to treat landfill leachate. Besides the use as a single unit, HF CWs are also used in combination with other types of constructed wetlands in hybrid systems (Vymazal, 2009)

Hybrid wetlands

These incorporate surface and subsurface flows and are also sometimes called combined systems. Hybrid systems are a combination of different types of constructed wetlands in order to achieve improved treatment efficiencies. Hybrid systems comprise mostly of vertical flow (VF) and the horizontal flow (HF) systems are arranged in a staged manner. Horizontal flow systems can provided with anaerobic conditions because of their limited oxygen transfer capacity. Vertical flow systems do provides aerobic conditions in these systems. In hybrid systems the advantages of the HF and VF systems can be combined to complement processes in each system to produce an effluent low in BOD and nitrogen (Vymazal, 2005).

2.3 Wetland Vegetation

The wetland vegetation can be grouped into four general ecological categories, depending mainly on growth position of the vegetation with respect to water level (Whitley *et al.* 1999). Water level tends to vary in every wetland for different seasons and during the whole year according to climatic conditions and human management. While some wetland plants can tolerate shocks in terms of variations in soil moisture and water level, others demand strict water requirements for their survival. Thus, there are four broad categories of wetland vegetation (Whitley *et al*., 1999):

1) Shoreline Macrophytes
2) Emergent Aquatic Macrophytes
3) Floating-Leaved Aquatic Macrophytes
4) Submerged Aquatic Macrophytes

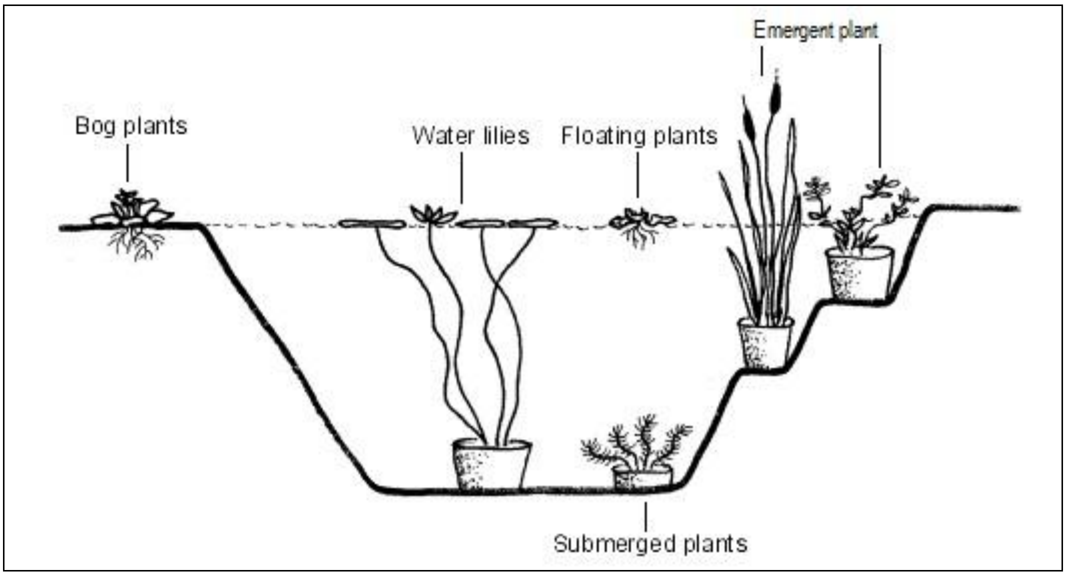

Figure 2.2 Types of wetland vegetation

(Source: http://www.portkellsnurseries.com/images/pond/water_plants_1.gif)

The different types of wetland vegetations are discussed below:

1) Shoreline Macrophytes: these are plants that grow in wet soil along the shorelines of streams, ponds, bog, lakes. These plants grow at or above the level of standing water of the shoreline; some may be rooted in shallow water, e.g., *Equistem, Cephalanthus occidentalis*.

2) Emergent Aquatic Macrophytes: These are those plants whose roots are rooted in soil that is underwater in the organic soil for most of the time. These plants grow up through the water, and hence stems, leaves and flowers emerge out from the water in air above water level. They grow within a water table range of 50 cm below the soil surface to 150 cm or more, e.g., *Typha*, *Canna lily*, *Phragmites*.

3) Floating-Leaved Aquatic Macrophytes: these are those plants whose leaves usually floats on the water surface on which they are growing. Much of the plant body is underwater and may or may not be rooted in the soil below it. Only s small portion of the plants, such as flowers, rises above water level, e.g., Water hyacinth, *Duckweed*.

4) Submerged Aquatic Macrophytes: These are those plants that are that remains underwater with few floating or emergent leaves only. Flowers may emerge briefly in some cases for pollination for reproduction. They have their photosynthetic tissue entirely submerged within the water body, e.g., *Myriophyllum heterophyllum.*

2.3.1 Water hyacinth

General characteristics

Eichhornia crassipes, commonly known as water hyacinth, is floating type aquatic plant which is native to the Amazon basin. It is considered as a problematic invasive species. Water hyacinth it is a perennial hydrophyte. It has broad, thick, glossy leave. It may rise above the surface of the water as much as 1 meter in height. The leaves are 10 to 20 cm across, and float on the water. They have long, spongy and bulbous stalks. The feathery, freely hanging roots are purple-black. Each erect stalk supports a single spike of 8 to 15 conspicuously attractive flowers, mostly lavender to pink in colour with six petals (Sullivan *et al*., 2012).

Reproduction

Water hyacinth is one of the fastest growing plants known; it reproduces primarily by way of runners or stolons, which eventually form daughter plants. Each plant can produce thousands of seeds each year, and these seeds can remain viable for more than 28 years. The common water hyacinth (*Eichhornia crassipes*) are vigorous growers known to double their population in two weeks.

2.3.2 Duckweed

General characteristics

It consists of the smallest and simplest of all flowering plants and are also among the most common plant worldwide. The plant consists of a floating body responsible for photosynthesis, called as a frond, and some species have tiny roots coming below. Duckweeds are incredibly productive and utilized as food for human and feed for domestic animals. They are major food resources for birds, mammals, and fish in wetland environments.

Reproduction

Reproduction is mostly asexual budding, which occurs from a meristem enclosed at the base of the frond. Occasionally three flowers consisting of two stamens and a pistil are produced, by which sexual reproduction occurs. Three flowers are distinct either female or male and which are derived from the spadix in Araceae. Evolution of the duckweed inflorescence remains ambiguous due to the considerable evolutionary reduction of these plants from their earlier relatives.

2.3.3 *Typha*

General characteristics

It comes among the most common wetland plant. It has long and blade like sharp leaves and stiff flower stalks. The mature seed head looks like a sausage. Two varieties are commonly known are Common Cattail (*Typha latifolia*) that grows up to a height of 2.5 m, and Narrow-leafed Cattail (*Typha angustfolia*) that grows up to a height of 1.5 m. *Typha* are normally found in shallow water of pond margins and marshes, but may also be found in any saturated soils from roadside ditches to sinkholes.

Reproduction

The plants are monoecious, with unisexual flowers that develop in dense racemes. The numerous male flowers form a narrow spike at the top of the stem. Large numbers of tiny female flowers form a dense, sausage-shaped spike on the stem below the male spike.

2.3.4 *Canna lily*

General characteristics

Canna or *canna lily,* is a genus of nineteen species of flowering plants. The closest living relations to cannas are the other plant families of the order Zingiberales, that is, the Zingiberaceae (gingers), Musaceae (bananas), Marantaceae, Heliconiaceae, Strelitziaceae, etc. *Canna* is the only genus in the family Cannaceae. The plant has a large tropical and subtropical perennial herb with a rhizomatous rootstock. The broad, flat, leaves place alternatively which is a feature of this plant and grow out of a stem in a long, narrow roll, then unfurl and forms a new leave. The leaves are typically solid green, but brownish, maroon, or even variegated leaves are also found. The flowers are composed of three sepals and three petals that are rarely noticed. They are small and hidden under extravagant stamens. The flowers are typically red, orange, or yellow or any combination of those colours, and are aggregated in inflorescences that are spikes.

Figure 2.3 Wetland plants: (a) Water Hyacinth; (b) Duckweed; (c) *Typha;* (d) *Canna lily*

(Source: http://fullserviceaquatics.com/; http://www.avianaquamiser.com/; http://www.pfaf.org/; http://media.highcountrygardens.com/)

Reproduction

Seeds are produced from sexual reproduction that involves the transfer of pollen from the stamen of the pollen parent onto the stigma of the seed parent. In the case of

Canna, the same plant can usually play the roles of both pollen and seed parents, called as a hermaphrodite.

2.3.5 *Phragmites*

Phragmites, the common reed, is a large perennial grass found in wetlands throughout temperate and tropical regions of the world.

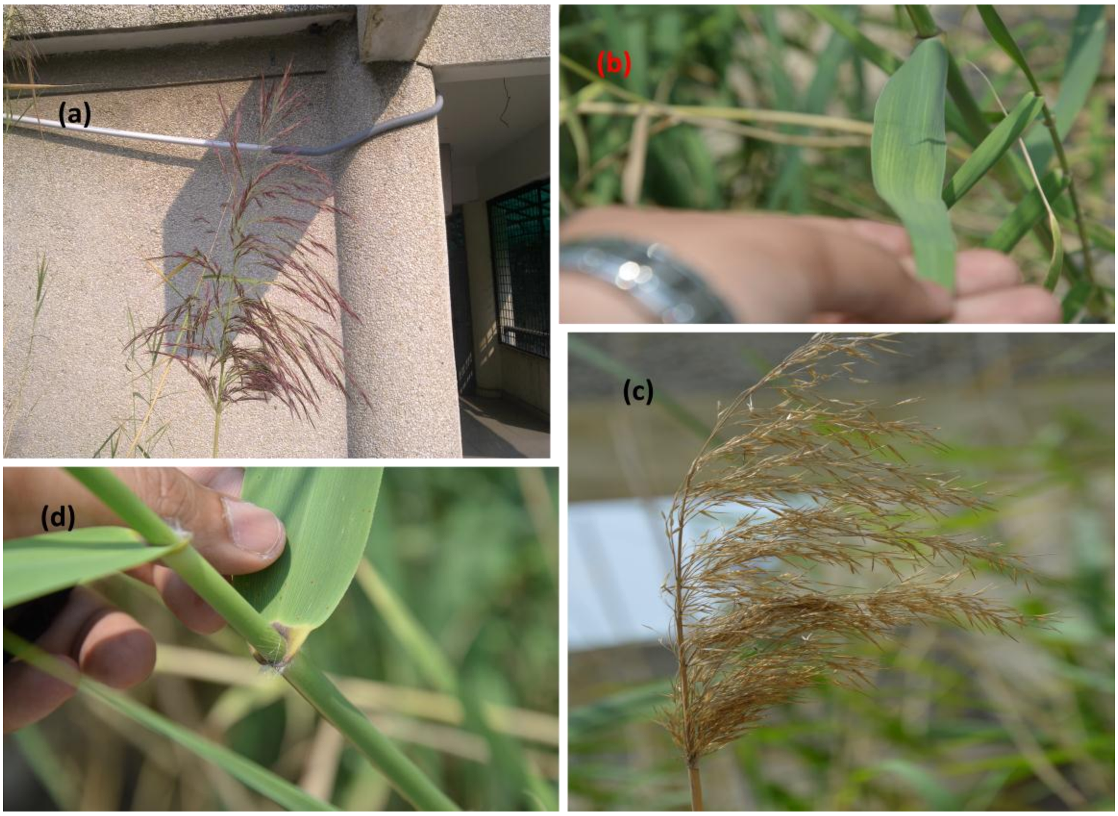

Figure 2.4 *Phragmites* during study: (a) flower; (b) leaves; (c) spikelets; (d) whorl and nodes

General characteristics

Phragmites has the leaves that are long and varies from, 20 to 50 cm and 2 to 3 cm in width. The flowers are produced in late summer in a dense, dark purple panicle, about 20 to 50 cm long. Later, the numerous long, narrow, sharp pointed spikelets appear greyer due to the growth of long, silky hairs.

Taxonomy

The generally accepted botanical name of common reed is *Phragmites australis*. Dozens of other synonyms have been proposed, a few have been widely used. A few of the more important are *Phragmites australis, Phragmites communis, Arundo phragmites, Phragmites vulgaris.*

Subspecies

It has been characterised the morphological distinctions between the introduced and native stands of *Phragmites* in North America. The Eurasian phenotype can be distinguished from the North American phenotype by its shorter ligules of up to 0.9 mm as opposed to over 1.0 mm, shorter glumes of under 3.2 mm against over 3.2 mm and in characteristics. *Phragmites australis* sub-species *americanus,* in North American genotype has been described as a distinct subspecies, subspecies *americanus*, and *Phragmites australis* sub-species *australis*- the Eurasian variety is referred to as subspecies *australis*.

Native and introduced species

Phragmites was commonly considered as an exotic species and often invasive species, introduced from Europe. However, there is evidence of the existence of *Phragmites* as a native plant in North America long before European colonization of the continent. The recent marked expansion of *Phragmites* in North America may be due to the more vigorous, but similar-looking European sub-species *australis*.

Phragmites australis sub species *australis* is causing serious problems for many other North American hydrophyte wetland plants, including the native *Phragmites australis* sub species *americanus*. Gallic acid released by Phragmites is degraded by ultraviolet light to produce mesoxalic acid, effectively hitting susceptible plants and seedlings with two harmful toxins. Phragmites are so difficult to control that one of the most effective methods of eradicating the plant is to burn it over 2-3 seasons. The roots grow so deep and strong that one burn is not enough.

Growth and habitat

Phragmites usually forms extensive stands known as reed beds that may cover a area as much as 1 km^2 or more. If the conditions are suitable it can spread at 5 m or more per year by horizontal runners, which put down roots at regular intervals. It can grow in damp ground, in standing water up to 1 m or so deep, or even as a floating mat. The erect stems can grow to a height of 2 to 6 m, with the tallest plants growing in areas with hot summers and fertile growing conditions. It is a helophyte, especially common in alkaline habitats, and it also tolerate shocks dues to brackish water, and so is often found at the upper edges of estuaries and on other wetlands which are occasionally surrounded by the sea. Common reed is suppressed where it is grazed regularly by livestock. Under these conditions it either grows as small shoots within the grassland sward, or it disappears altogether.

2.4 Removal of Pollutants

As discussed above that phytoremediation process is involved in removal of pollutants from the water body and helps in reducing the degradation of environment. The various mechanisms involved in removal of contaminants in wet lands are discussed below.

2.4.1 Contaminant Removal mechanisms in the Constructed Wetlands

Wetland can effectively remove large quantities of pollutants from point sources which are municipal, industrial and agricultural and non-point sources such as mines, agriculture and urban runoff, including organic matter, suspended solids, trace metals and nutrients. The focus of wastewater treatment through constructed wetlands is to optimize the contact of microbial species with substrate, the final objective being the bioconversion to carbon dioxide, biomass and water. Wetlands are characterized by a range of properties that make them attractive for managing pollutants in water (Bavor & Adcock, 1994). These properties include high plant productivity, large adsorptive capacity of the sediments and roots; high rates of oxidation by micro flora associated with plant biomass, and a large buffering capacity for nutrients and pollutants.

Removal mechanism of Organic compounds

Settle able organics are rapidly removed by wetland systems under low flow conditions by deposition and filtration. Attached and suspended microbial growth is responsible for removal of soluble organics. Organic compounds are degraded aerobically or anaerobically. The oxygen required for aerobic disintegration is supplied directly from the atmosphere by diffusion or oxygen leakage from the macrophytes roots into the rhizosphere. Uptake of organic matter by the macrophytes is negligible compare to biological degradation. Anaerobic degradation of soluble organic matter is governed by aerobic heterotrophic bacteria. The autotrophic group of bacteria which degrades organic compound containing nitrogen under aerobic condition is called nitrifying bacteria. Cooper *et al*., (1996) pointed out that both group consumes organic but the faster metabolic rate of heterotrophs means that they are mainly responsible for the reduction of BOD of the system.

Removal mechanism of Suspended Solids

In case of suspended solids removal process, sedimentation and filtration will play the major role. While the microbial growth in the wetland system helps in removal of colloidal solids. When the growth of vegetation in a particular wetland system is more the removal efficiency of suspended solids and colloidal solids is more.

Removal mechanism of Heavy Metals / Contaminants

Constructed wetlands are wastewater treatment systems that combine biological, chemical, and physical treatment mechanisms for water quality improvement. The mechanisms for water quality improvement in wetlands include adsorption, complexation, chemical precipitation, and plant uptake (Reed *et. al*., 1995). Constructed wetlands have been used extensively for the removal of dissolved metals and metalloids. Although these contaminants are prevalent in mine drainage, they are also found in stormwater, landfill leachate and other sources for which treatment wetlands have been constructed for mines and other applications.

Removal mechanism of Nitrogen

Nitrogen processes in wetland soils constitute Nitrification in aerobic regions, denitrification in anaerobic regions, and release of N_2 and N_2O gases, plant uptake, sedimentation, decomposition, ammonia volatilization and accretion/accumulation of organic nitrogen in peat because of reduction oxidation potential of hydric sediment.

The prominent forms of nitrogen in wetlands which are of high importance to wastewater treatment include organic nitrogen, ammonia, ammonium, nitrate, nitrite, and nitrogen gases. Inorganic forms are essential for plant growth in aquatic systems but if they are scarce, they can limit the plant productivity. Wastewater nitrogen removal is important because of ammonia’s toxicity to aquatic species if discharged into watercourses.

Ammonia Removal

The formation of ammonia (NH_3) occurs because of the mineralisation of organic matter under either anaerobic or aerobic conditions. The ammonium ion (NH_4^+) is the primary form of mineralized nitrogen in most flooded wetland soils. This ion forms when ammonia combines with water. Upon formation, several pathways are available to the ammonium ion. It can be absorbed by plants and algae and converted back into organic matter. At this point, the ammonium ion can be prevented from further oxidation because of the anaerobic nature of wetland soils. Under these conditions the ammonium ion is stable and it is in this form that nitrogen predominates in anaerobic sediments typical of wetlands.

Most wetland soils have a thin aerobic layer at the surface. As an ammonium ion from the anaerobic sediments diffuses upward into this layer it converts to nitrite or nitrified. An increase in the thickness of this aerobic layer results in an increase in nitrification. This diffusion of the ammonium ion sets up a concentration gradient across the aerobic and anaerobic soil layers resulting in further nitrification reactions. Nitrification is the biological conversion of organic and inorganic nitrogenous compounds from a reduced state to a more oxidized state. Nitrification is strictly an aerobic process in which the end product is nitrate (NO_3^-); this process is limited when anaerobic conditions prevail.

Removal mechanism of Phosphorus:

The phosphorus removal is quite different in wetland soils, since there is no mechanism as de-nitrification for phosphorus. Although the processes of plant uptake, sorption, decomposition and long-term storage take place, phosphorus tends to collect in wetlands at a faster rate than nitrogen. Precipitation of phosphate minerals can provide a significant sink to phosphorus in wetlands with large stores or inputs of iron and aluminum (low pH wetlands) or calcium (high-pH wetlands). Although wetlands can remove and store notable amounts of phosphorus, they also potentially release a valuable amount of phosphorus to downstream ecosystems. It is approximated that the long-term elimination rate of the Phosphorus with plants is about $0.05 g/m^2$-day in a constructed wetland (Kapanen, 2008). Phosphorus in wetlands occurs naturally in both organic and inorganic forms. The analytical measurement of biologically active orthophosphates is called as soluble reactive phosphorus. Dissolved organic phosphorus and insoluble forms of organic and inorganic phosphorus are generally not biologically active until transformed into soluble inorganic forms.

The natural scarcity of phosphorus is demonstrated by the explosive growth of algae in water receiving heavy discharges of phosphorus-rich wastes. Phosphorus does not have an atmospheric component, unlike nitrogen, the phosphorus cycle can be characterized as closed. The removal and storage of phosphorus from wastewater can only occur within the constructed wetland itself. Phosphorus may be sequestered within a wetland system by:

1. The binding of phosphorus in organic matter as a result of incorporation into living biomass,
2. Precipitation of insoluble phosphates with ferric iron, calcium, and aluminium found in wetland soils
3. Biomass plants incorporation—phosphorus

Higher plant in wetland system acts as a nutrient storage compartment that absorbs nutrients during the growing season. Generally, plants in nutrient-rich habitats accumulate more nutrients than those in nutrient-poor habitats, a phenomenon referred to as luxury uptake of nutrients. Aquatic vegetation may play an important role in phosphorus removal and, if harvested, extend the life of a system by postponing phosphorus saturation of the sediments. Bernard and Solsky also reported relatively low phosphorus retention, estimating that a sedge (*Carex*) wetland retained 1.9g of phosphorus per square meter of wetland. Bulrushes (*Scirpus*) in a constructed wetland system receiving secondarily treated domestic wastes contained 40.5% of the total phosphorus influent. The remaining 59.0% was found to be stored in the gravel substratum (Bernard and Solsky, 1977).

2.4.2 Role of aquatic mycrophytes in secondary-treated wastewater

Various wetland vegetation like- water hyacinths (*Eichhorina crassipes*), common duckweed (*Lemna minor*), cattail (*Typha*), *Canna lily*, common reed (*Phragmites*) have shown a good result in various studies.

2.4.2.1 BOD, COD, TDS, TSS Removal Efficiency

According to study conducted by Zheng et al, (2014) on the river in Xi'an in China, the overall average COD and BOD removal rate was 72.7% ± 4.5% and 93.4% ±

2.1% respectively when the average surface loading of 0.053 $m^3/(m^2 \cdot day)$ and the bed was planted with *Typha* and *Phragmites* and the substrate was made from the materials available locally.

The study constructed by Shah *et.al*. (2010), potential of water hyachinth (*Eichhorina crassipes*) in treating dye waste water was studied. It was found that the plant was able to remove TDS by 35%, BOD by 42% and COD by 35% for 25% dilution of waste water. For higher dilutions the plant was not able to survive.

2.4.2.2 Removal of Heavy Metal

The study conducted by Snyder (2006), Water Hyacinth was used to remove the arsenic from drinking groundwater of Bangladesh. He found that the plant can remove 300 ppb of arsenic down to 10 ppb.

In another study removal of heavy metals by *Lemna minor* (common duckweed) has been studied by Axtell *et. al.*, (2003). They have found that this plant has a overall efficiency of 76% in lead removal. The average value of removal by *Lemna minor* was 69% at low level of lead and 83% at high concentration level. In the same study Nickel concentration reduced by 82%.Within a span of 4 days, the plant was capable of removing about 75-85% of Cd from 100L of waste water containing 3.0-7.0 mg/l of metal at an optimum pH of 6.5.

2.4.2.3 Removal of Total Nitrogen

According to study conducted by Zheng et al, (2014) on the river in Xi'an in China which consisted of CW with surface and sub surface flow, the overall NH_3-N and total nitrogen (TN) average removal was found to be 54.0% ± 6.3% and 53.9% ± 6.0% respectively, for the average surface loading of 0.053 $m^3/m^2 \cdot day$ when the bed was planted with *Typha* and *Phragmites* and the substrate was made from the materials available locally. Surface-flow cells showed better NH_3-N removal than their TN removal while subsurface-flow cells showed better TN removal than their NH_3-N removal.

2.4.2.4 Removal of Phosphorus

According to study conducted by Zheng et al, (2014), on the river in Xi'an, northwestern China with the CW for treating polluted stream water so that it will be treated before it enters the receiving water body. CW was a combination of surface- and subsurface-flow cells with local gravel, sand or slag as substrates and *Phragmites* and *Typha* as plants. During a one-year operation with an average surface loading of 0.053 $m^3/(m^2 \cdot day)$, total phosphorus (TP) removals was 69.4% ± 4.6%, which brought about an effective improvement of the river water quality. Using local slag as the substrate, phosphorus removal could be much improved. Seasonal variation was also found in the removal of all the pollutants and autumn seemed to be the best season for pollutant removal due to the moderate water temperature and well grown plants in the CW.

2.5 Wetland products

Wetland systems naturally produce an array of vegetation and other ecological products that can harvested for personal and commercial use. The most significant of these is fish which have all or part of their life-cycle occurs within a wetland system.

(a) *Typha, Brachiaria* as fodder

Amongst the well known wetland emergent species, *Brachiaria mutica* grass is extensively used as fodder (Katsenovich et al., 2009). Other wetland grasses such as *Typha*, water hyacinth are also popular as fodder. *Brachiaria ramose* is cultivated in south India (Kimata et al., 2000; Porteres., 1976). Some African species of *Brachiaria* have been introduced into the Americas as pasture grasses and it have been released as commercial cultivars in different tropical countries (Keller-Grein et al., 1996). Currently, the genus *Brachiaria* is the most widely used forage grass. In a study by Tomar *et al.,* (2002), it was observed that higher productivity of green fodder (19.7 to 25.7mg/ha) was monitored in case of grass species like *Brachiaria mutica*, *Panicum maximum,Panicum laevifolium* than other species. The yield was observed to be maximum during July-September period and was low during winter season.

(b) *Phragmites* for composting

Composting is a natural process of recycling. It turns on agricultural waste and other organic materials into a nutrient rich resource enhancing soil fertility and soil quality and brings about increased agricultural productivity, improved soil biodiversity, reduced risks and a better environment (Misra et al., 2003). plant material is a sustainable way to manage its overpopulation in wetlands and to produce fertilizer that can be used not only in conventional but also in alternative farming systems. It can also be used as a handicraft raw material and can be used to produce handcraft products.

(c) *Eichhornia* in composting

In a study by Anushree (2006), uses of *Eichhornia crassipes* for biogas production, composting, fish feed was documented. Better yield of biogas are obtained using mixture of animal waste and water hyacinth. Pretreatment with fungi or chemicals increases the biodegradeability of water hyacinth for sufficient biogas production (Ali et al., 2004)

MATERIALS AND METHODS

3.1 Study Area (Bench- scale CW Cell)

A *Phragmites* based bench-scale constructed wetland (CW) cell was built in laboratory at Delhi Technological University. The system consisted of single cell in working condition. It had the dimensions as 80 cm wide and 110 cm long. The CW cell had the soil substrate packed with gravel-sand mixed gap graded sediments and it consisted of a 35 cm thick layer of soil substrate. The water level was kept at 2 cm above the gravel surface and the volume of water daily applied was 16*l*. *Phragmites* was planted in the cell of dimension 110cm × 80cm × 45cm (l x b x d) and the total volume experimental cell was approximately 400*l*. Also, before starting the study, the wetland system was flushed with water entering from top and exiting from an outlet provided at the bottom of the system.

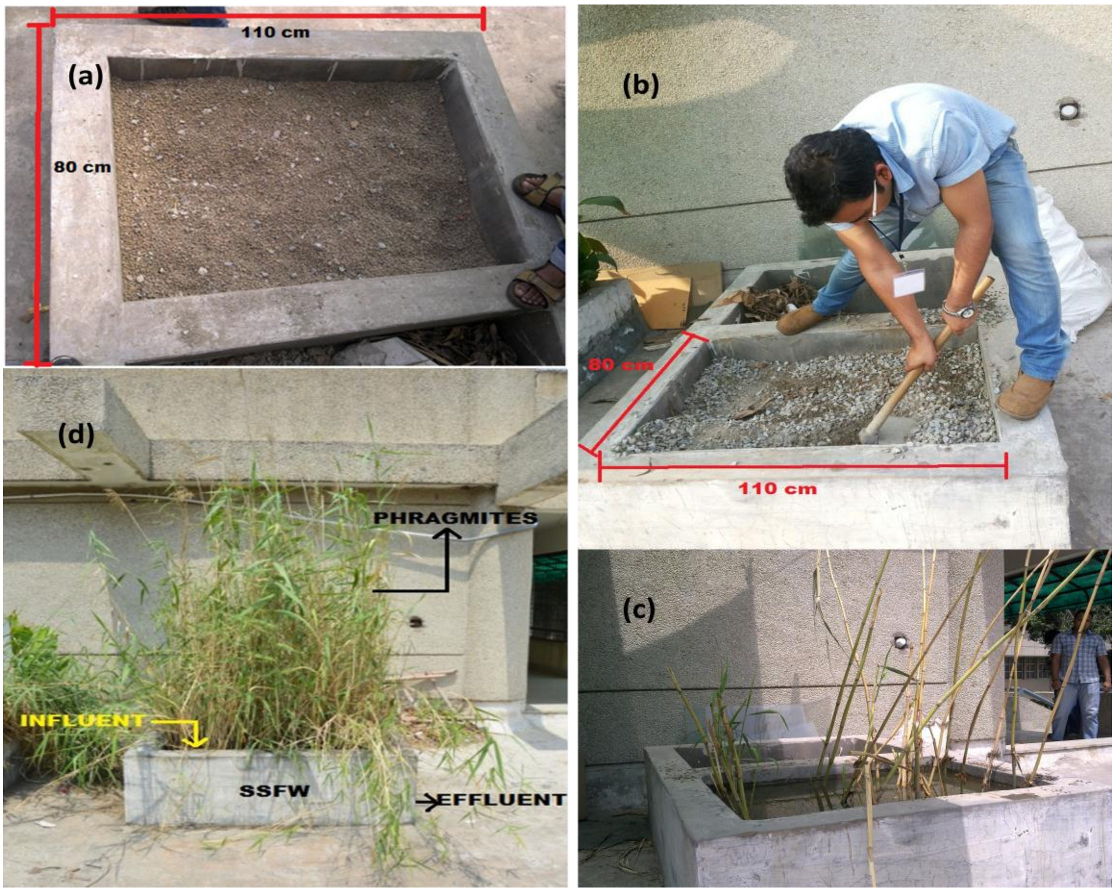

Figure 3.1 CW cell: (a) Unprepared bed; (b) preparation of bed; (c) planted *Phragmites* in CW cell in initial stage; (d) stabilised CW cell used during the study

3.2 Selection of Plants

Phragmites was the plant used during the study and it was planted with 20 numbers of stems in the bed of the CW with a plant density of 22.72plants/m^2 in a grid pattern of 4x5. The plant was uprooted from DTU Campus Lake and planted in the CW cell and with average plant height 106.68 cm. After the experimental period, total stem count was 180 approximate and the height of the plant was approximately 213.44 cm.

3.3 Adaptation of Plant

The plant was planted in the month of April, 2013 after which it received a rainfall and a considerable time was given to the *Phragmites* to adapt in its new habitat and to get stabilised. The system was fed with daily water at the rate of 20 *l*/day. The system was also fed with fertilizers Di-ammonium phosphate (DAP) and urea at the rate of 50 g of each.

3.4 Design of Experiments

The experiments were designed in the following way to achieve the desired objectives:

(i) Preparation of Synthetic Wastewater

The wastewater was synthetically prepared in the laboratory using analytical grade (AG) potassium di-hydrogen orthophosphate salt (KH_2PO_4). The wastewater added had phosphate (PO_4^{3-}-P) in varying concentrations which are 5 mg/l; 10 mg/l and 20 mg/l. Ammonium ions (NH_4^+) were also added to check its reduction or oxidation by nitrification process. Phosphate and ammonium ions are then analysed using the standard methods.

(ii) pH, EC and TDS

pH, electrical conductivity (EC) and total dissolved solids (TDS) were monitored throughout the experiment to comment upon the growth plant and its phosphate removal efficiency. The instrument used for measuring pH was Hanna Instruments make (Italy) (Model number: HI9607) pen type pH meter. For the purpose of measuring EC and TDS, instrument used was Orion make Star A329 model multimeter.

(iii) Effect of Seasons

The study was mainly aimed at monitoring the growth and phosphate removal efficiency of *Phragmites*. Phosphate removal efficiency is determined by the nutrient uptake capacity of the plant and the uptake capacity of the plant depends upon the meteorological conditions since, more is the sunshine hours, more will be the photosynthesis process, more will be the metabolic activities and thus, more will be the uptake of phosphate from the wastewater. For this purpose, different seasons were studied which are autumn, winter, spring and summer season. The effect of rainfall was also considered in the study. The CW cell was constructed over the roof without shade to study the efficacy of plant under natural conditions.

(iv) Effect of Influent Concentration

The water which was fed to the plant had phosphate PO_4^{3-}-P concentration which varied from 5 ppm at the initial stage; followed by 10 ppm; and finally 20 ppm during the period of study. An increasing concentration of phosphate was fed to the plants in order to adapt the plants to high strength waste water with respect to phosphate; and to improve and study the response of *Phragmites* to chemical stress of phosphate and also, to monitor the growth of plant and its phosphate removal efficiency (%). Different concentration of ammonium ions NH_4^+-N were also added in the form of synthetically prepared wastewater when the influent phosphate concentration was 10 mg/l, ammonium ion concentration was 50 mg/l and followed by ammonium ion concentration of 100 mg/l for phosphate concentration of 20mg/l. The ratio of P:N was kept 1:5 for inlet at later stage. The ratio means, for phosphate concentration of 10 mg/l, nitrate concentration was 50 mg/l. The ammonium ions were added to the CW system in order to take care of the nitrogen deficient nitrification conditions.

(v) Redox Conditions

The reduction and oxidation (redox) processes in the CW cell which takes place were monitored using nitrifying conditions and ferric to ferrous ratio in effluent. Ammonium ions (NH_4^+-N) were added to the CW cell from the outside in the form of wastewater and it was analysed for the nitrification process. Due to nitrification, ammonium ion gets converted to nitrite (NO_2^-) and nitrite on its nitrification becomes nitrate (NO_3^-) which shows an oxidation process. Total dissolved iron (TDI) and ferrous (Fe^{2+}) ion was analysed for the effluent and from TDI and ferrous ion concentration, ferric (Fe^{3+}) ions concentration was analysed. The ratio of ferric ion to ferrous ion (Fe^{3+} to Fe^{2+} ratio) tells whether the reaction is reducing or oxidising (redox conditions).

3.5 Analysis: Wastewater Analysis

During the experiment the flow rate had been taken constant and HRT (Hydraulic Retention Time) was 24 hours. Samples of treated water were collected from the wetland cell after every 24 hours (HRT-1 day) for 7 months during the study. The samples were tested for the fractions of Phosphate concentration which are Available Phosphate (AP) and Total Phosphate (TP) using standard method as prescribed by APHA (1997). The concentration of ammonium ions (NH_4^+) and organic nitrogen present in treated waste was determined by Kjeldahl's method.

Figure 3.2 Collection of waste water from the outlet of the CW cell

(a) Characterisation of phosphate

The phosphate is generally considered as the critical nutrient for the growth of algae in water. The enrichment of this nutrients leads to the process of eutrophication. The most important sources of phosphates are the discharge of domestic sewage, detergents and agricultural run-off.

Available Phosphate

Available Phosphate was measured using Ammonium Molybdate- Stannous chloride method (APHA 4500P)

Reagents:

1) Ammonium Molybdate

Take 25 g of ammonium Molybdate and dissolved it in 175 ml of distilled water. In a separate conical flask, add 280 ml of concentrated sulphuric acid H_2SO_4 to 400 ml of distilled water. Mix the two solutions and make the final volume 1*l*.

2) Stannous chloride

Take 2.5 g of stannous chloride and dissolved in 100 ml of Glycerol. Heat the solution with intermittent mixing using a glass rod over a water bath. The mix will become transparent.

3) Preparation of standards

Take 0.143 gm of potassium di-hydrogen orthophosphate and mix in 1*l* of distilled water to obtain 100 ppm of phosphate stock standard solution. Take 10 ml of this solution and make final volume to 100 ml to obtain 10 ppm concentration of phosphate standard solution. Use serial dilution to prepare 10 standards in the range from 0.1 to 1.0 ppm. Take a solution of distilled water to be used as the blank, which has zero phosphate concentration.

Preparation of Standard curve

1) To 10 ml of 0.1 ppm concentration phosphate standard, add 0.4 ml of ammonium molybdate and mix it well.
2) Add 2 drops of stannous chloride to it and mix it well.
3) Let it stand for 5 min, blue colour appears.
4) Note the absorbance at 690 nm and 100% transmittance on a spectrophotometer.
5) Repeat the above step for 0.2ppm, 0.3ppm, 0.4ppm and up to 1ppm.
6) Plot the graph between concentration and absorption. Best fit line was drawn.

7) Absorbance shall be taken after 5 minutes after adding chemicals and before 11 minutes.

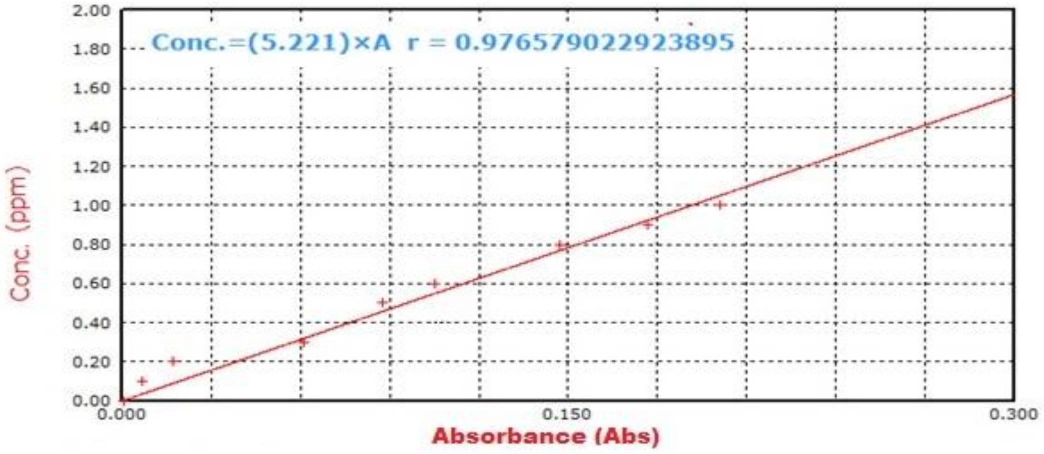

Figure 3.3 Standard curve for phosphate **(Labtronics make Model LT-290 Sprectrophotometer)**

Analysis of available phosphate

1) Take 10 ml of sample, add 0.4 ml of ammonium molybdate and mix it well.
2) Add 2 drops of stannous chloride to it and mix it well.
3) Let it stand for 5 min, blue colour appears.
4) Note the absorbance at 690 nm and 100% transmittance on spectrophotometer.
5) Multiplication of absorbance with graph factor gives the available phosphate concentration of sample.
6) Absorbance shall be taken after 5 minutes after adding chemicals and before 11 minutes.

Total Phosphate

Total Phosphate is extracted by acid digestion using Sulphuric acid (H_2SO_4) - Nitric acid (NHO_3) digestion method. In this study, this fraction of phosphate is determined for wastewater.

Chemicals Required

1) Concentrated Sulphuric Acid (H_2SO_4)
2) Concentrated Nitric Acid (HNO_3)

Apparatus Required

A Micro wave with six digestion units at least.

Extraction of Phosphate (Acid digestion)

The sample collected is taken in the different micro wave digestion units and to every unit, add acids so that the phosphate bound with iron, calcium and aluminium will become unbounded and shall make the total phosphate in the water sample during the study. The acids are added in the ratio of 1:3 (Nitric Acid: Sulphuric Acid)

Analysis of Total Phosphate

1) To 10 ml of sample adds 0.4 ml of conc. H_2SO_4 and to it add 2ml of conc. HNO_3.

2) Keep this solution in the digestion unit and set the microwave for 5-10 minute at low (200KW) level.

3) After completion of digestion add NaOH solution to neutralize the solution. Neutralisation can be seen as pink colour which appears after adding 2 drops of phenolphthalein before adding NaOH solution to the digested samples.

4) To 50 ml of sample, add 2 ml of ammonium molybdate and mix it well.

5) Add 2 drops of stannous chloride to it and mix it well.

6) Let it stand for 5 min, blue colour appears.

7) Note the absorbance at 690 nm and 100% transmittance on spectrophotometer.

8) Multiplication of absorbance with graph factor gives the total phosphate concentration of sample.

9) Absorbance shall be taken after 5 minutes after adding chemicals and before 11 minutes.

(b) Total Kjeldahl’s Nitrogen (TKN)

Ammonia of mineral origin is rare in natural waters. The most important source of ammonia in natural water is the ammonification of organic matter. Sewage is also an important source of ammonia. Occurrence of ammonia can be accepted as the chemical evidence of organic pollution. Total Kjeldahl’s Nitrogen (TKN) process was used to analyse the organic nitrogen as well as ammonia in the waste water sample. It consisted of a micro Kjeldahl unit.

Description of Apparatus:

Micro-TKN apparatus consists of the following units:

Boiler/ Steamer:

It produces the steam with the heat coming from the heating mantle over which it is placed.

Steam Trap:

It traps the excess steam and also collects the waste water during the back wash of the apparatus**.**

Digestion and Distillation Unit:

In this unit, the digestion and the distillation of the sample take place and the distillate goes to the next unit.

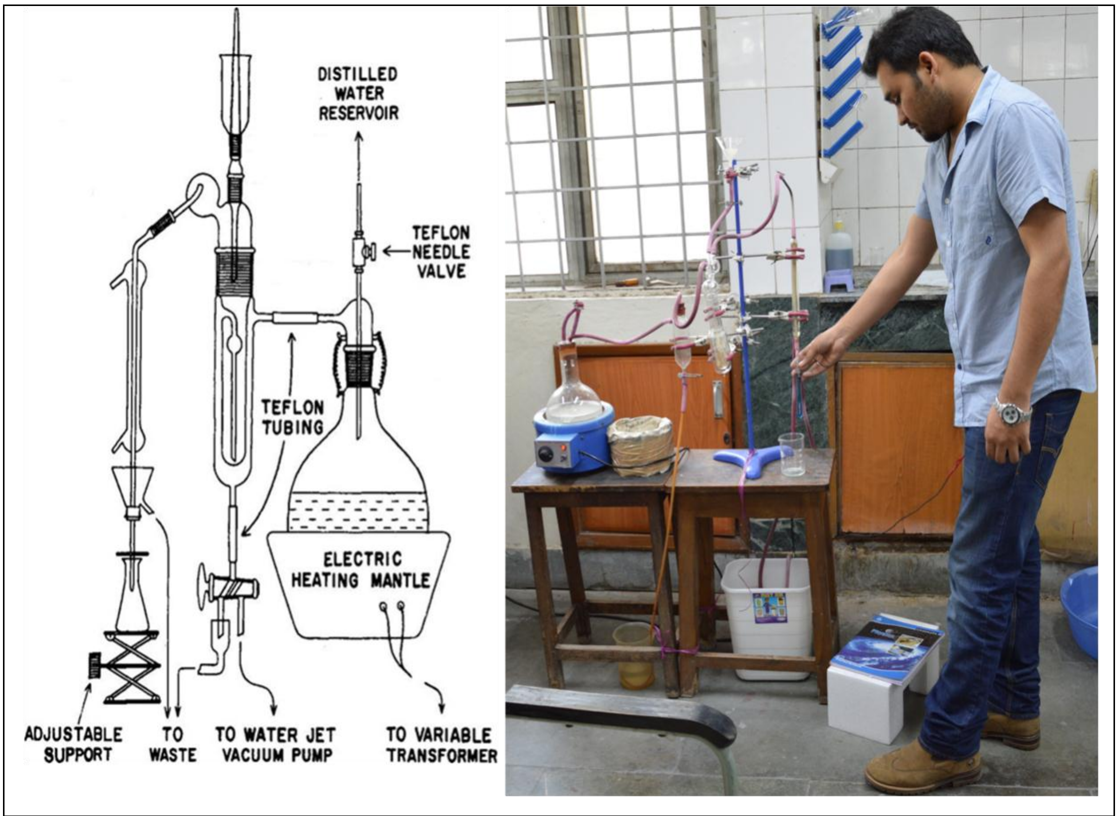

Figure 3.4 Micro Kjeldahl apparatus

Condenser Unit:

It condenses the distillate coming out from the digestion unit and then it is collected and then the sample is titrated against hydrochloric acid.

Preparation of chemicals required:

1) Borax buffer, 4%:

To 100 ml of distilled water, add 4 g of borax $Na_2B_4O_7$ and heat it to mix the crystals well.

2) Boric Acid and Mixed Indicator:

To 100 ml of distilled water, add 4 g of boric acid. To 100 ml of boric acid solution, add 5 ml of mix indicator and mix it well. Mixed indicator is boric acid + mixed alcohol solution of bromocresol green (0.5%) and methyl red (0.1%) in 2:1 ratio. In case solution turns bluish, add drop wise 0.01 N HCl until the colour just turns pink to brown.

3) Titrant:

Use 0.01N HCl for the titration. First make 1 N HCl solution and then dilute it in series.

Analysis of Total Kjeldahl's Nitrogen

1) Start heating the boiler/ steamer to get the steam.

2) Take 10 ml of the sample in a rinsed test tube.

3) To the 10 ml sample, add 1 ml of the borax.

4) In another test tube take 5 ml of the boric acid.

5) The sample and the borax solution are allowed to go inside the distillation and digestion unit of the apparatus only when boiler starts producing steam.

6) In no lapse of time, place the test tube with boric acid at the open end of the condenser unit and make the nitrogen get collected in the test tube. Blue colour will start appearing in the test tube.

7) Now titrate the collected sample until the colour changes from blue to orange.

8) Note the volume of the titrant consumed.

Calculations:

$$\text{TKN (mg/l)} = \frac{\text{(Volume of titrant in ml) x (normality of titrant) x 14 x 1000}}{\text{(Volume of sample taken in ml)}}$$

(c) Iron

Iron is present in` the sediments of the bed of the wetland. The fractions of iron studied here are ferrous and ferric. It was found out using Phenanthroline Method.

Reagents:

Use reagents low in iron. Use iron free distilled water in preparing standards and reagent solutions. Store reagents in the glass stopper bottles. The HCl and ammonium acetate solution are stable for indefinitely if stoppered tightly. The hydroxylamine and phenoanthroline solutions are stable only for few months.

1) Hydrochloric acid:

Concentrated HCl containing less than 0.00005 % iron

2) Hydroxylamine solution:

Dissolve 10 g of hydroxylamine $NH_2OH.HCl$ in 100 ml water.

3) Sodium acetate solution:

Dissolve 200 g of sodium acetate $NaC_2H_3O_2.3H_2O$ in 800 ml water.

4) Phenanthroline solution:

Dissolve 100 mg 1, 10-phenanthroline monohydrate $C_{12}H_8N_2.H_2O$ in 100 ml of water by stirring and heating to 80^oC. Do not boil. Heating is unnecessary if 2 drops of conc. HCl is added to the water. Discard the solution if it darkens.

5) Preparation of standard iron solution

0.0496 g of $FeSO_4.7H_2O$ was mixed in 100 ml of distilled water to get 100 ppm concentration iron solution. 10 ml of this 100 ppm iron standard solution is taken and volume was made up to 100 ml to get final 10 ppm of iron concentration standard solution. Series dilution was done to get the standard solution from range 0.1 ppm to 1 ppm.

Preparation of the Standard Curve:

1) Take 5 ml of the standard solution in a 50 ml volumetric flask.

2) To the 5 ml standard, add 1 ml of hydroxylamine. Shake it well.

3) To the previous solution add 5 ml of the sodium acetate solution and shake it well.

4) To the previous solution add 5 ml phenanthroline solution and mix it well. Red or orange colour will start to develop.

5) Now make the volume of the solution to 50 ml by using distilled water.

6) Wait for 10 minutes.

7) Take the absorbance of the solution at 510 nm wavelength and 100 % transmittance.

8) Repeat the above procedure for the rest of the standards also.

9) Draw the plot between concentration and absorbance. Take the best fit line.

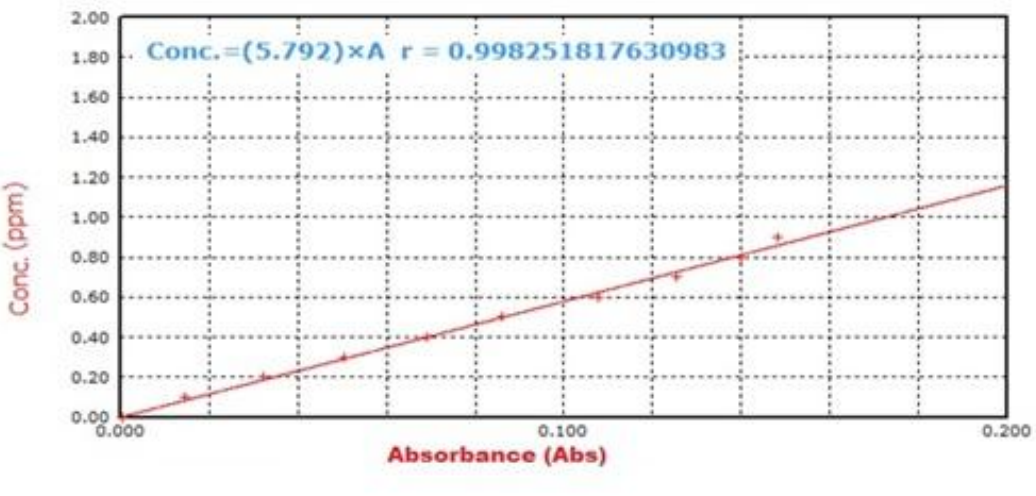

Figure 3.5 Standard curve for iron **(Labtronics make Model LT-290 Sprectrophotometer)**

Analysis of Total Dissolved Iron (TDI)

1) Take 5 ml of the sample solution in a 50 ml volumetric flask.

2) To the 5 ml standard, add 1 ml of hydroxylamine. Shake it well.

3) To the previous solution add 5 ml of the sodium acetate solution and shake it well.

4) To the previous solution add 5 ml phenanthroline solution and mix it well. Red or orange colour will start to develop.

5) Now make the volume of the solution to 50 ml by using distilled water.

6) Wait for 10 minutes.

7) Take the absorbance of the solution at 510 nm wavelength and 100 % transmittance.

8) Multiply graph factor with the absorbance to get the concentration of the total dissolved iron.

Analysis of Ferrous (Fe^{2+}) ions:

1) Take 5 ml of the sample solution in a 50 ml volumetric flask.

2) To the sample solution add 5 ml of the sodium acetate solution and shake it well.

3) To the previous solution add 5 ml phenanthroline solution and mix it well. Red or orange colour will start to develop.

4) Now make the volume of the solution to 50 ml by using distilled water.

5) Wait for 10 minutes.

6) Take the absorbance of the solution at 510 nm wavelength and 100 % transmittance.

7) Multiply graph factor with the absorbance to get the concentration of the ferrous.

Analysis of Ferric (Fe^{3+}) ions:

From the known concentration of TDI and ferrous (Fe^{2+}), concentration of ferric (Fe^{3+}) can be estimated. Ferric concentration is difference in concentration between TDI and ferrous (Fe^{2+}).

RESULTS AND DISCUSSION

The study aims to monitor the removal efficiency of *Phragmites* for phosphate during different seasons, and at different phosphate loading rates. The effect of increasing concentration of phosphate on the removal efficiency, and plant health were also studied. Monitoring of redox conditions in CW cell was also done based on oxidation of ammonium (NH_4^+) ions and ferric to ferrous ratio. During the study, pH, electrical conductivity (EC) and total dissolved solids (TDS) were also monitored regularly to understand any other change in the system. Meteorological parameters were also monitored to study the effect of seasons on removal behaviour. The results so obtained are given below.

4.1 General Observation

As per the general observations for the phosphate removal efficiency, it varies differently for different seasons. It was observed that phosphate removal efficiency was minimum during autumn season, whereas, it was maximum during summer season. It follows the trend as autumn season < winter season < spring season < summer season, having the total phosphate removal efficiency (%) of the order 56.2 < 80.6 < 90.5 < 95.7, respectively. During the study, the efficiency is low in the autumn season because the system was fed with only one type of nutrient which caused excessive loading of phosphates (PO_4^{3-}-P), and deficiency of nitrogen primarily fed into the cell externally. Also, the pH for the treated waste water was almost neutral which means the CW cells makes the water more stable and thus neutral, in terms of its pH. TDS level for the outlet has a significant difference in its concentration at the beginning and at the end of the study and the TDS level ultimately increased. The electrical conductivity (EC) for the outlet also increased during the autumn season and then during the break, it significantly got reduced. After the restart of experiment in winter season, it again increased; and reached its maximum at 5070 µS/cm in summer season. It is noted that EC increased both for inlet and outlet. Ammonium ions added to the CW cell also got converted to nitrates (NO_3^-) owing to nitrification by micro organisms and are subsequently taken up by the plants.

4.2 Ambient Temperature Profile

The ambient temperature profile for the period of almost seven months was studied from the month of October, 2013 to the month of April, 2014. During the period of study, the ambient temperature varied between 2°C to 42°C and the average maximum and minimum temperature during the study were between 13.6°C to 26.8°C, respectively. During the autumn, winter, spring and summer seasons, the minimum and the maximum temperature varied between 9°C to 36°C; 2°C to 28°C; 7°C to 34°C and 17°C to 42°C, respectively. The average ambient temperature for the autumn, winter, spring and summer season was 23.2°C, 14.9°C, 18.9°C and 27.43°C, respectively. The effect of ambient temperature on growth of *Phragmites* and also its phosphate removal efficiency was studied. The average sunshine hours in a day varied between 8 hours to 10 hours during the study. Precipitation in terms of rainfall (mm) was also monitored during the study. Small spells (18 events) of rainfall were observed and the majority of rainfall occurred during the winter season (Annexure I; Fig. 4.1). The rainfall during these events varied from 1 mm to 38 mm.

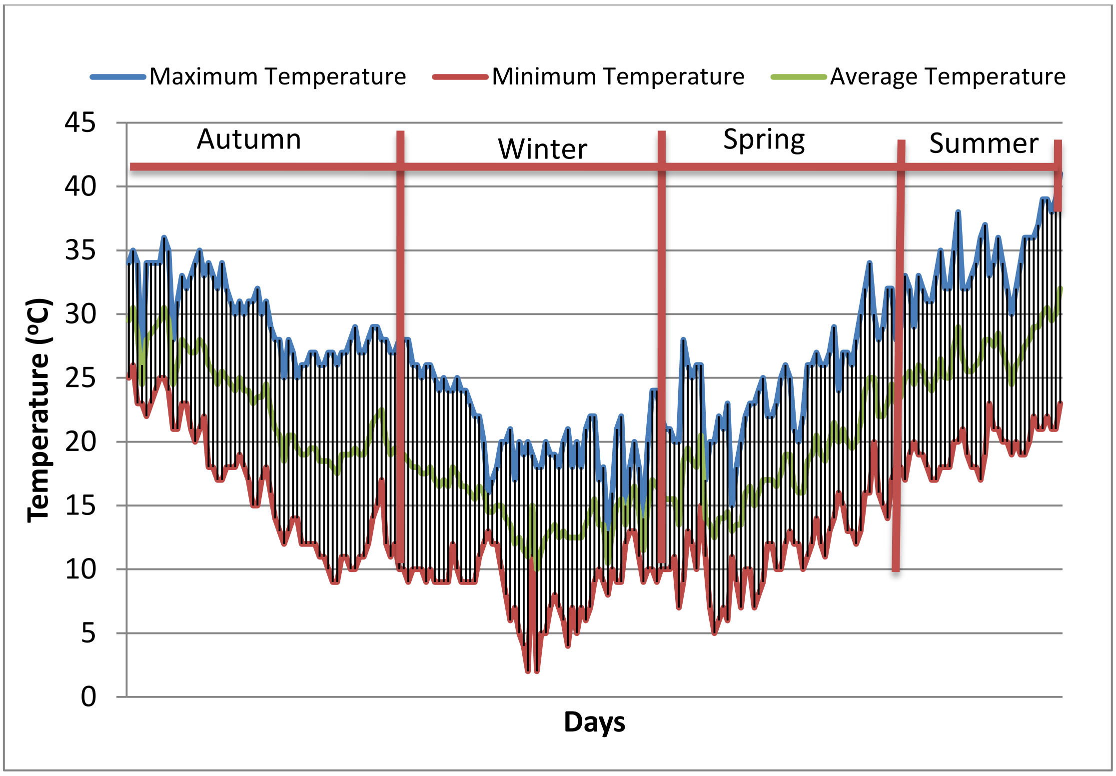

Figure 4.1 Ambient temperature profile during the study (October, 2013 to April, 2014) (Seasons classified as per IMD)

4.3 Sediment Analysis (Sieve Analysis)

The bed of CW cell was packed with the gravel-sandy soil. The packing material used for the preparation of CW cell bed had the specific gravity (S) equal to 2.74 with void ratio (e) of 0.77 and had a bulk density (ρ) of 17.82 kg/m^3. The packing material of CW cell had 39% gravel which retained on 4.75 mm sieve and 59% sand and rest is silt which passed 4.75mm sieve during the analysis (Table 4.1). The packing material duplicates the type of bed usually found in natural wetlands. The gravels with voids forms a porous medium and it helped in easy percolation of influent into the substrate and it made exchange of gases easy at root zone (rhizosphere). Gravels formed the bed so that clogging for the substrate can be avoided. The particle size distribution curve represents a gap graded soil in which intermediate size particles are missing (Fig. 4.2). A gap graded bed provides more hydraulic conductivity and also it helps in better and more efficient removal of nutrients (phosphate) from the wastewater. Similar studies were also done by Vymazal (2005) for the study of nutrient removal through subsurface flow of wastewater (Vymazal, 2005).

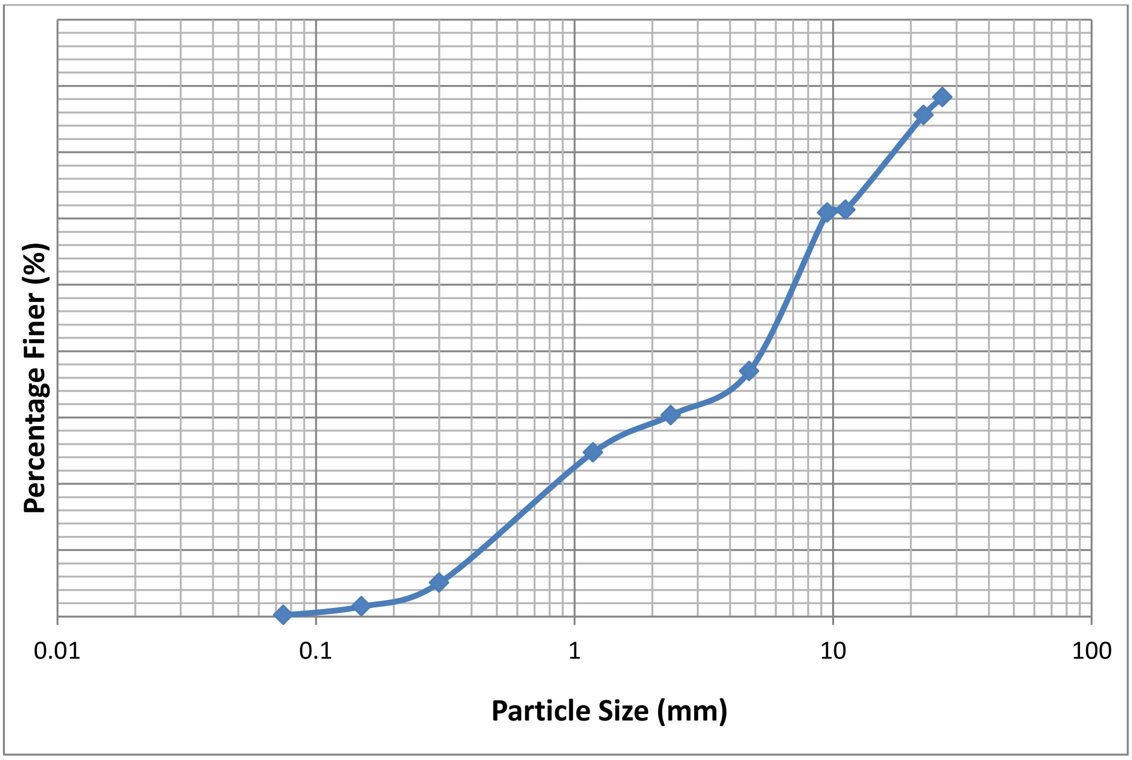

Figure 4.2 Sieve analysis and particle size distribution curve

Table 4.1 Sieve analysis of sediments

Sieve size (mm)	Weight Retained (g)	Percentage Retained	Cumulative Percentage	% Finer
26.5	331.85	21.71	21.71	78.29
22.4	41.52	2.72	24.42	75.58
11.2	218.08	14.26	38.69	61.31
9.5	6.76	0.44	39.13	60.87
4.75	365.28	23.89	63.02	36.98
2.36	101.62	6.65	69.67	30.33
1.18	85.7	5.61	75.27	24.73
0.3	300.84	19.68	94.95	5.05
0.15	54.51	3.57	98.52	1.48
0.075	19.78	1.29	99.81	0.19
Pan	2.9	0.19	100	-
Total	1526.23	100	-	-

4.4 pH, EC and TDS of Wastewater

pH is an important parameter to represent the quality of wastewater. In the present study, the average pH of influent (synthetic wastewater) was slightly alkaline in nature (7.5 to 7.9) because of the addition of KH_2PO_4 and $(NH_4)_2SO_4$. The pH of influent increased with increasing concentration of nutrients. The effluent from CW cell had the average pH of 7.0 at influent concentration of 5 mgP/l. It was observed that the sediments and plants in the wetland system tend to remove the dissolved nutrients and salts to turn the water to almost neutral. At an influent concentration of 10 and 20 mgP/l, the average pH was 7.9, whereas it was 7.2 in the effluent with an insignificant deviation from the mean value (Table 4.6, 4.7, 4.9). The increasing concentration of nutrients had no alteration in the tendency of CW cell to transform wastewater to neutral range. The CW cell acted as a buffering system to maintain the pH to almost neutral range, irrespective of the variation in pH, and therefore, can absorb shocks in respect of pH of influent.

The average electrical conductivity (µS/cm) of influent went on increasing from 671 µS/cm to 933 µS/cm; to 1408 µS/cm with an increasing concentration of phosphate and ammonium ions from 5 mg/l to 10 mg/l and 50 mg/l; and 20 mg/l and 100 mg/l, respectively. The average EC of effluent varied from 2427 µS/cm (at 5 mgP/l) to 1814 µS/cm (at 10 mgP/l), to 3852 µS/cm (at 20 mgP/l). EC was higher in the first set of experiment since flushing of sediments and packing medium of CW cell takes place in the initial stage (Table 4.6, 4.7, 4.9). It went on decreasing in the period from October, 2013 to February, 2014. Kyambadde *et al.*, 2004, gave the similar results for the reduction in EC during their study but for the different plant species. At 10 mgP/l, though the effluent EC increased, a significant decrease in average value of effluent was observed since the wetland had stabilised by the time, and could efficiently remove the nutrients added during the stage. At 20 mg/l of phosphate and 100 mg/l of ammonium ions, the influent loading of the CW cell was high. The excessive load of nutrients resulted in anaerobic conditions (at depths) to dominate over aerobic conditions as reflected by ferric to ferrous ratio less than one during the period. Formation of anaerobic conditions at depths and production of acidic metabolites result in leaching of sediments and the packing media. Similar studies by Jaisi *et al*, (2009) were also resulted in which at surface, conditions were aerobic and Fe^{3+} is present after getting oxidised from ferric. Therefore, there was sharp increase in EC of the effluent during the period. Since EC is regulated by dissolved salts, an increase in TDS concentration was observed as the study progressed. The average TDS increased from 697 mg/l to 865 mg/l; to 1695 mg/l with an increasing concentration of nutrients added (Table 4.6, 4.7, 4.9). An increase in EC and TDS in effluent may be attributed to dissolution of salts from the sediments in lieu of the nutrients removed from the wastewater.

4.5 Nutrient Removal Study

The nutrients present in waste water are taken up by the plants for their metabolic activities. The chemical forms of nutrients present in the water keep transforming depending on the environmental conditions. There occurs bio-chemical transformation of nutrients. Out of the two forms of phosphate studied, available phosphate (AP) was available to the plants and is taken up readily. Ammonium ions fed into the system are converted by microbes by nitrification to form of nitrites (NO_2^-) which are further oxidised to nitrates (NO_3^-) and nitrates (NO_3^-) are taken up by the plants. The effect of environmental conditions (seasons) on growth and removal efficiency of the plant is given below.

4.5.1 Seasonal Variations

Seasonal variations from the month of October, 2013 to April, 2014, were studied for the removal efficiency of the various fractions of phosphate (AP and TP). Later, ammonium ions (NH_4^+) were amended with in varying concentrations to the wetland system; and its change from nitrites (NO_2^-) to nitrates (NO_3^-) was also studied. Various seasons studied during the study were autumn, winter, spring and summer in chronological order. Available and total phosphates are the fractions of phosphate in the study. Waste water was synthetically prepared for inlet and the treated water after a retention period of 24 hours as outlet from the CW cell was analysed. Available and total phosphate are analysed for both inlet and outlet.

Autumn Season

During autumn season, the analysis of waste water was studied and the average was calculated. It was studied from the month of October, 2013 to first week of December, 2013. There was a break till the month of January, 2014 during which it was not studied. During the study, average initial concentration of phosphate (PO_4-P) fed to CW cell was 3.23 mg/l, varying from 2.42 mg/l to 3.56 mg/l (Table 4.2; Fig. 4.3). The fraction of available phosphate in inlet varied from 1.0 mg/l to 1.31 mg/l with an average of 1.1 mg/l. The AP level was considerably reduced in outlet ranging from 0.17 mg/l to 0.89 mg/l with an average of 0.41 mg/l. The concentration of AP in outlet increased in the later stage since the *Phragmites* underwent stress as observed in the form of yellowing of leaves. The average removal efficiency of AP was 63.7%, and varied between 17% to 85.2%. The decrease in removal efficiency by 3 to 4 times may be ascribed to stress on *Phragmites* in later stage. Similar drop in removal efficiency was observed for total phosphate in the later stage. The removal efficiency dropped to ≈ 30% from ≈ 70% (initially). The average removal efficiency of TP was 56.2%, observed to be slightly lower than the removal efficiency of AP (63.7%). The most probable reason could be available phosphate is more readily available to the plants in an unbound form and it was taken up by the plant for its metabolic activities on preference.

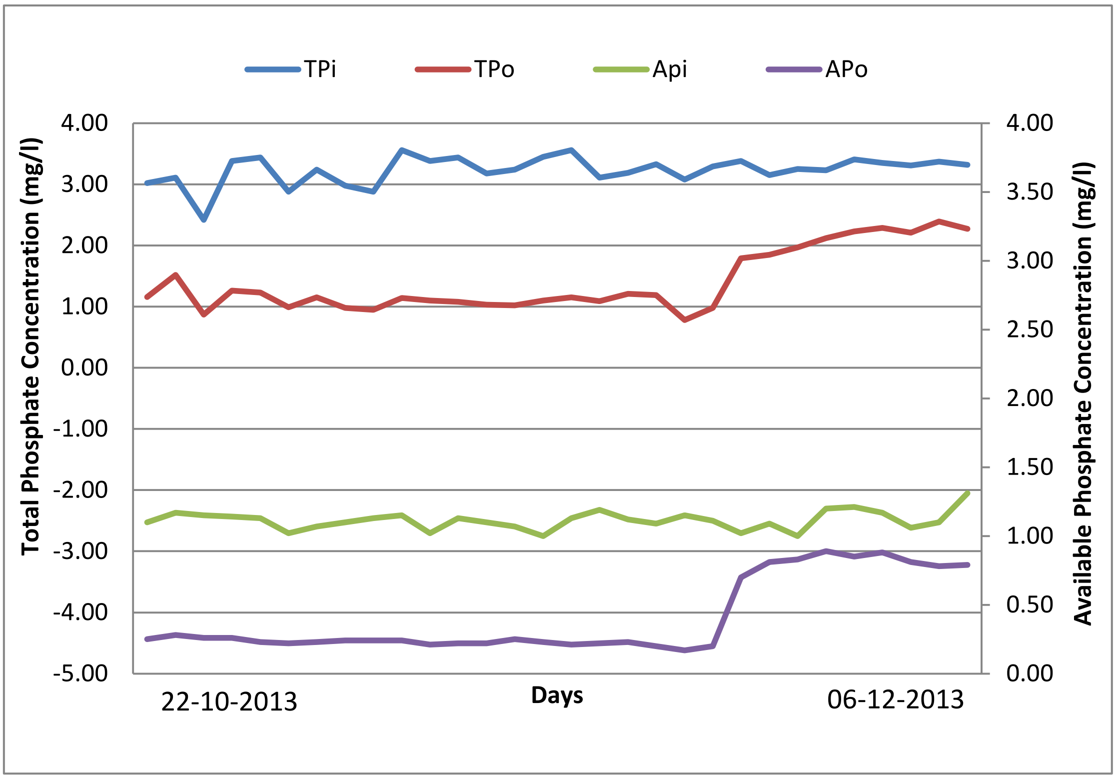

Figure 4.3 Available and total phosphate concentration (mg/l) in influent and effluent during autumn season

The growth of *Phragmites* was stressed in later stage owing to chemical stress on account of deficiency of nitrogen. Since phosphate was added as the only nutrient in synthetic wastewater, nitrogen deficient conditions were created after the period of around 30 days. Initial requirement might be met by the nitrates present in the sediments. The other reason might be the decrease in average ambient temperature from 25.5^{o}C (October) to about 19^{o}C (November) resulting in lower metabolic rates of *Phragmites* at lower temperature on account of onset of transformation of season from autumn to winter. At the same time average sunshine hours reduced resulting in reduced productivity. All these reasons produced a synergistic effect on *Phragmites* in the form of stress.

Table 4.2 Concentration of phosphate PO_4^{3-}-P (mg/l) and its removal efficiency (%) during autumn season

Date (n=30)	**Available Phosphate**			**Total Phosphate**		
	AP_i^* (mg/l)	**AP_o^* (mg/l)**	**Removal Efficiency (%)**	**TP_i^* (mg/l)**	**TP_o^* (mg/l)**	**Removal Efficiency (%)**
22-10-2013	1.10	0.25	77.3	3.02	1.16	46.4
23-10-2013	1.17	0.28	76.1	3.11	1.52	51.1
24-10-2013	1.15	0.26	77.4	2.42	0.87	64.1
25-10-2013	1.14	0.26	77.2	3.38	1.26	62.7
28-10-2013	1.13	0.23	79.7	3.44	1.23	64.2
29-10-2013	1.02	0.22	78.4	2.88	0.99	65.6
30-10-2013	1.07	0.23	78.5	3.24	1.15	64.5
31-10-2013	1.10	0.24	78.2	2.98	0.98	67.1
01-11-2013	1.13	0.24	78.8	2.88	0.95	67.0
04-11-2013	1.15	0.24	79.1	3.56	1.14	68.0
05-11-2013	1.02	0.21	79.4	3.38	1.10	67.5
06-11-2013	1.13	0.22	80.5	3.44	1.08	68.6
07-11-2013	1.10	0.22	80.0	3.18	1.03	67.6
08-11-2013	1.07	0.25	76.6	3.24	1.02	68.5
11-11-2013	1.00	0.23	77.0	3.45	1.10	68.1
12-11-2013	1.13	0.21	81.4	3.56	1.15	67.7
13-11-2013	1.19	0.22	81.2	3.11	1.09	65.0
14-11-2013	1.12	0.23	79.5	3.19	1.21	62.1
15-11-2013	1.09	0.20	81.7	3.33	1.19	64.3
21-11-2013	1.15	0.17	85.2	3.08	0.78	74.7
22-11-2013	1.11	0.20	82.0	3.29	0.98	70.2
25-11-2013	1.02	0.70	31.4	3.38	1.79	47.0
26-11-2013	1.09	0.81	25.7	3.15	1.85	41.3
27-11-2013	1.00	0.83	17.0	3.25	1.97	39.4
28-11-2013	1.20	0.89	25.8	3.23	2.12	34.4
29-11-2013	1.21	0.85	29.8	3.41	2.23	34.6
02-12-2013	1.17	0.88	24.8	3.35	2.29	31.6
03-12-2013	1.06	0.81	23.6	3.31	2.21	33.2

05-12-2013	1.10	0.78	29.1	3.37	2.39	29.1
06-12-2013	1.31	0.79	39.7	3.32	2.27	31.6
Range (min-max)	**1.0-1.31**	**0.17-0.89**	**17.0-85.20**	**2.42-3.56**	**0.78-2.39**	**29.10-74.70**
Mean ±SD	**1.11 ±0.07**	**0.41 ±0.28**	**63.7 ±24.46**	**3.23 ±0.23**	**1.40 ±0.51**	**56.2 ±14.83**

$^{*}AP_i$ = available phosphate at inlet; $^{*}AP_o$ = available phosphate at outlet; $^{*}TP_i$ = available phosphate at inlet; $^{*}TP_o$ = total phosphate at outlet

Winter Season

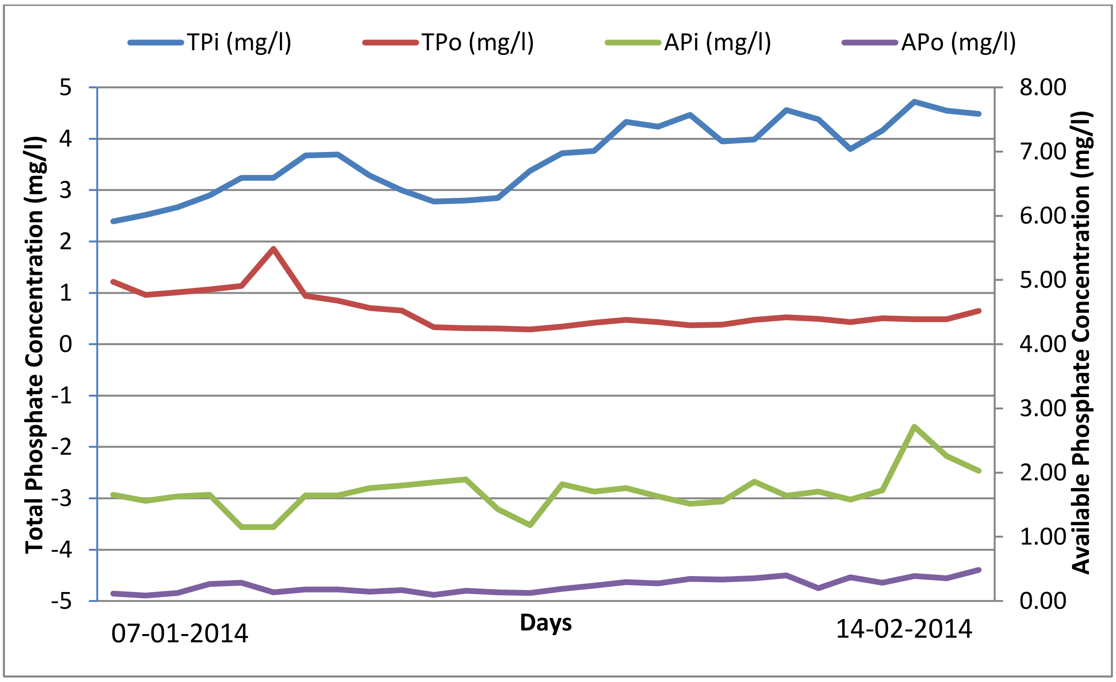

Figure 4.4 Available and total phosphate concentration (mg/l) in influent and effluent during winter season

During winter season from the month of January, 2014 to the month of February, 2014, effect of temperature variation was studied for the removal efficiency of phosphates and growth of *Phragmites*. During this period of study, average initial concentration of phosphate (PO_4^{3-}-P) added was 3.63 mg/l, varying from 2.39 mg/l to 4.72 mg/l in to the CW cell (Table 4.3; Fig. 4.4). The fraction of AP in inlet varied from 1.15 mg/l to 2.71 mg/l with an average of 1.70 mg/l. The fraction of AP in the outlet varied from 0.086 mg/l to 0.486 mg/l with an average of 0.24 mg/l. The average removal efficiency of AP was 85.8 % which varied between 75.2% to 94.8 %. The average removal efficiency of TP was 80.6%, observed to be slightly lower than the removal efficiency of AP (85.8%) and it varied between 49% to 91.7%.

Table 4.3 Concentration of phosphate PO_4^{3-}-P (mg/l) and its removal efficiency (%) during winter season

Date (n=28)	**Available Phosphate**			**Total Phosphate**		
	AP_i^* (mg/l)	**AP_o^* (mg/l)**	**Removal Efficiency (%)**	**TP_i^* (mg/l)**	**TP_o^* (mg/l)**	**Removal Efficiency (%)**
07-01-2014	1.66	0.114	93.1	2.39	1.219	49.0
08-01-2014	1.56	0.086	94.5	2.52	0.962	61.8
09-01-2014	1.63	0.124	92.4	2.67	1.009	62.1
10-01-2014	1.66	0.267	83.9	2.89	1.066	63.2
13-01-2014	1.15	0.286	75.2	3.24	1.133	65.0
15-01-2014	1.15	0.133	88.4	3.24	1.856	42.6
16-01-2014	1.65	0.181	89.0	3.67	0.942	74.4
17-01-2014	1.65	0.181	89.0	3.69	0.847	77.1
20-01-2014	1.76	0.143	91.9	3.28	0.704	78.6
21-01-2014	1.80	0.171	90.5	3.00	0.657	78.1
22-01-2014	1.85	0.095	94.8	2.78	0.333	88.0
23-01-2014	1.89	0.162	91.5	2.80	0.314	88.8
24-01-2014	1.43	0.133	90.7	2.85	0.305	89.3
27-01-2014	1.18	0.124	89.5	3.38	0.286	91.5
28-01-2014	1.82	0.190	89.5	3.72	0.343	90.8
29-01-2014	1.70	0.238	86.0	3.76	0.419	88.9
30-01-2014	1.76	0.295	83.2	4.33	0.475	89.0
31-01-2014	1.63	0.276	83.0	4.24	0.428	89.9
03-02-2014	1.51	0.343	77.4	4.46	0.371	91.7
04-02-2014	1.55	0.333	78.5	3.95	0.381	90.4
05-02-2014	1.86	0.352	81.0	3.99	0.476	88.1
06-02-2014	1.64	0.400	75.6	4.56	0.524	88.5
07-02-2014	1.70	0.200	88.3	4.38	0.495	88.7
10-02-2014	1.58	0.371	76.5	3.80	0.428	88.7
11-02-2014	1.72	0.286	83.4	4.16	0.505	87.9

12-02-2014	2.71	0.390	85.6	4.72	0.486	89.7
13-02-2014	2.26	0.352	84.4	4.55	0.486	89.3
14-02-2014	2.03	0.486	76.1	4.48	0.647	85.6
Range (min-max)	**1.15-2.71**	**0.086-0.486**	**94.80-75.20**	**2.39-4.72**	**0.286-1.856**	**49.0-91.70**
Mean ±SD	**1.70 ±0.31**	**0.24 ±0.11**	**85.8 ±6.09**	**3.63 ±0.71**	**0.65 ±0.36**	**80.6 ±13.73**

$^{*}AP_i$ *= available phosphate at inlet;* $^{*}AP_o$ *= available phosphate at outlet;* $^{*}TP_i$ *= available phosphate at inlet;* $^{*}TP_o$ *= total phosphate at outlet*

The most probable reason could be available phosphate is more readily available to the plants in an unbound form and it was taken up by the plant for its metabolic activities. Also, the average removal rate was increased during the winter season when compared with autumn season. The enhanced removal efficiency during winter season may be attributed to amendments of nitrogen in the form of Di-ammonium phosphate (DAP) and urea during December 7, 2013 to January 6, 2014 at regular interval of ten days to revive the health of *Phragimtes* which had under gone stress during the autumn season.

Spring Season

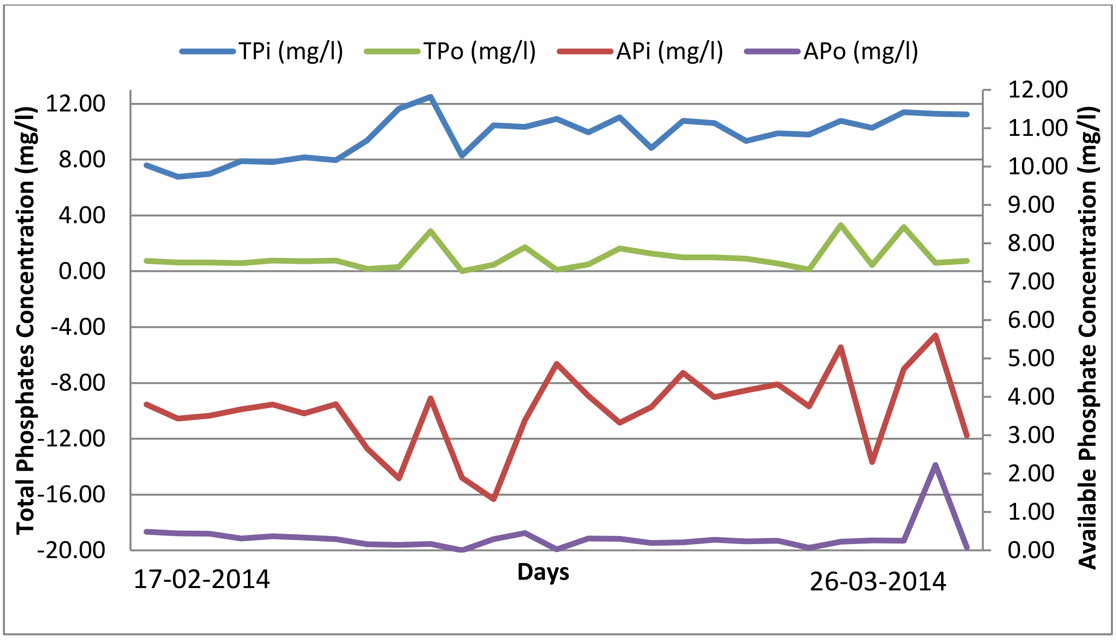

Figure 4.5 Available and total phosphate concentration (mg/l) in influent and effluent during spring season

The spring season was classified as the period from mid-February, 2014 to March, 2014. During autumn and winter season it was observed that nitrogen is required by the plant as external input, or the plant could undergo stress. Therefore, during spring season, ammonium ions were amended to CW cell with the concentration of 50 mg/l in the form of ammonium sulphate ($(NH_4)_2SO_4$), and initial concentration of phosphate was raised to 10 mg/l. The other reason for addition of nitrogen in the form of ammonium ions was to make an indirect inference of nitrifying conditions in CW cell. The difference in inlet and outlet concentration of TKN comments upon nitrification of ammonium ions to nitrates and its uptake up *Phragmites*. Amendment of nitrogen resulted in improved removal of phosphate from wastewater having an average inlet concentration of 9.7 mg/l. The average concentration of phosphate was observed to be 0.95 mg/l ranging from 0.1 mg/l to 3.32 mg/l, resulting in an average removal efficiency of 90.5% as compared to the value of 80.6% during winter season. The improved removal efficiency may be attributed to abundance of nutrients in CW cell. The removal of phosphates from CW cell thus follows first order kinetics. AP in outlet ranged from 0.15 mg/l to 2.23 mg/l with an average of 0.33 mg/l, resulting in an average removal efficiency of 91.2% placed slightly above than that of TP (Table 4.4; Fig. 4.5). Another reason for improved removal rate (176.06mg/m^2-day) may be gradual increase in ambient temperature and average sunshine hours during the spring season. It rose from 16^{o}C to 25.5^{o}C during the period. An increase in temperature results in increased rate of evapotranspiration causing an increased up draft of water from roots to the leaves of Phragmites. Evapotranspiration is, therefore, directly related to the removal efficiency of the plant.

Summer Season

Summer season was classified as the period from last week of March, 2014 to April, 2014 during the study. During this period, nitrogen and phosphorus were amended as ammonium (NH_4^+) and phosphate (PO_4^{3-}) ions at an inlet concentration of 100 mg/l and 20 mg/l, respectively, in influent. The average concentration of total phosphate in inlet was 21.3 mg/l varying from 18.2 mg/l to 23.58 mg/l (Table 4.5; Fig. 4.6). The concentration of TP in outlet ranged from 0.14 to 2.66 mg/l with an average value of 0.88 mg/l, resulting in average removal efficiency of 95.7%. On the other hand,

Table 4.4 Concentration of phosphate PO_4^{3-}-P (mg/l) and its removal efficiency (%) during spring season

Date (n=27)	**Available Phosphate**			**Total Phosphate**		
	AP_i^* (mg/l)	**AP_o^* (mg/l)**	**Removal Efficiency (%)**	**TP_i^* (mg/l)**	**TP_o^* (mg/l)**	**Removal Efficiency (%)**
17-02-2014	3.80	0.49	87.2	7.60	0.74	90.2
18-02-2014	3.44	0.45	87.0	6.76	0.64	90.6
19-02-2014	3.51	0.44	87.5	6.99	0.62	91.1
20-02-2014	3.67	0.31	91.5	7.90	0.58	92.7
21-02-2014	3.80	0.37	90.2	7.82	0.77	90.1
24-02-2014	3.57	0.33	90.7	8.18	0.71	91.3
25-02-2014	3.81	0.30	92.3	7.96	0.76	90.4
26-02-2014	2.65	0.16	94.1	9.38	0.17	98.2
27-02-2014	1.88	0.15	92.2	11.65	0.32	97.3
28-02-2014	3.96	0.17	95.8	12.49	2.88	76.9
03-03-2014	1.90	0.00	100.0	8.29	0.00	100.0
04-03-2014	1.34	0.29	78.2	10.46	0.47	95.5
05-03-2014	3.39	0.45	86.8	10.35	1.74	83.2
06-03-2014	4.86	0.03	99.5	10.91	0.10	99.1
07-03-2014	4.03	0.31	92.4	9.95	0.50	95.0
10-03-2014	3.33	0.30	90.9	11.03	1.63	85.2
11-03-2014	3.73	0.20	94.7	8.84	1.27	85.6
12-03-2014	4.63	0.21	95.4	10.79	0.99	90.9
13-03-2014	4.00	0.28	93.0	10.61	0.99	90.7
14-03-2014	4.17	0.23	94.4	9.33	0.91	90.3
18-03-2014	4.33	0.25	94.2	9.89	0.55	94.4
19-03-2014	3.75	0.07	98.2	9.79	0.13	98.7
20-03-2014	5.29	0.23	95.7	10.79	3.32	69.2
21-03-2014	2.30	0.26	88.8	10.28	0.45	95.6
24-03-2014	4.73	0.25	94.8	11.39	3.17	72.2
25-03-2014	5.60	2.23	60.3	11.28	0.60	94.6
26-03-2014	2.99	0.07	97.6	11.24	0.75	93.3
Range (min-max)	**1.90-5.60**	**0.07-2.23**	**60.30-99.50**	**6.76-12.49**	**0.10-3.32**	**72.20-99.10**
Mean ±SD	**3.65 ±1.01**	**0.33 ±0.40**	**91.2 ±7.73**	**9.70 ±1.55**	**0.95 ±0.88**	**90.5 ±7.67**

$^*AP_i$ = available phosphate at inlet; $^*AP_o$ = available phosphate at outlet; $^*TP_i$ = available phosphate at inlet; $^*TP_o$ = total phosphate at outlet

average concentration of AP in effluent was 0.15 mg/l against the influent concentration of 10.9 mg/l. Removal efficiency varied between 96.3% to ≈ 100% with an average removal efficiency of 98.5% placed significantly above the autumn and winter season. It was slightly above the removal efficiency of TP. An improvement in removal efficiency with an increase in phosphate concentration represents first order kinetics in summer season too. Lightly higher removal efficiency for AP may be attributed to easy bio availability of AP to plants and microbes as compared to inhibited availability of TP. TP is available to wetland vegetation only after its bio conversion to AP being regulated by pH of water and sediments, redox conditions in CW cell, availability of metals like Ca, Mg, Al, and Fe in sediments and wastewater.

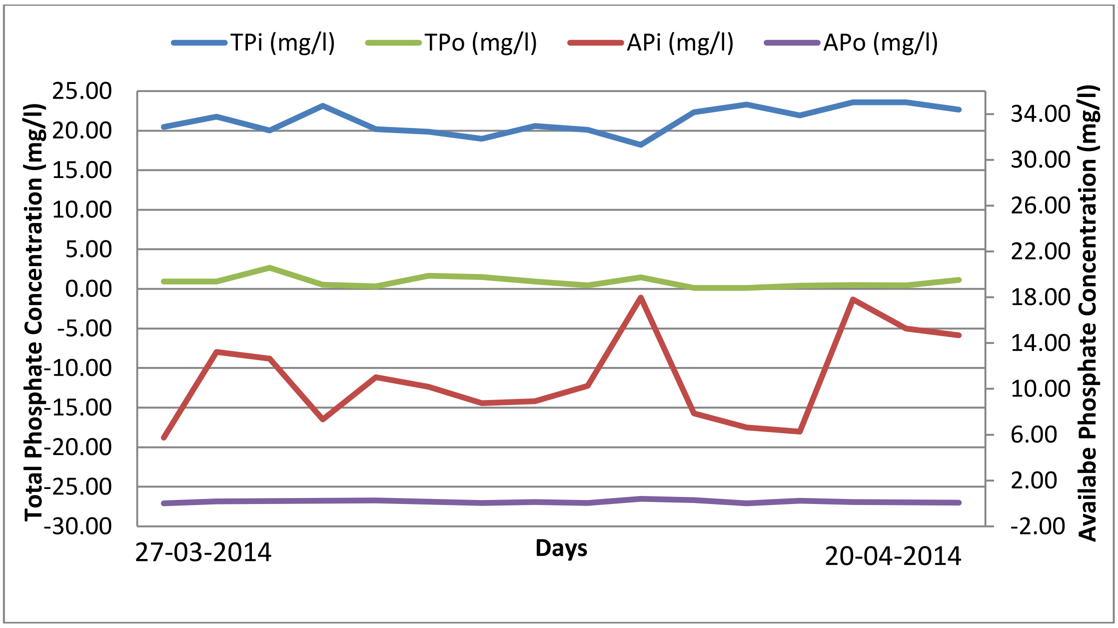

Figure 4.6 Available and total phosphate concentration (mg/l) in influent and effluent during summer season

The removal of phosphate (AP and TP) by Phragmites will chiefly be governed by the environmental conditions, and, therefore, the seasons have an effect over the removal behaviour of plants. Temperature is a significant parameter affecting removal rate for nutrients. Removal efficiency of phosphate was observed to be directly related to temperature since higher the evapotranspiration, more shall be the rate of uptake of water and nutrients from an aquatic system.

Table 4.5 Concentration of phosphate PO_4^{3-}-P (mg/l) and its removal efficiency (%) during summer season

Date (n=16)	**Available Phosphate**			**Total Phosphate**		
	AP_i^* (mg/l)	**AP_o^* (mg/l)**	**Removal Efficiency (%)**	**TP_i^* (mg/l)**	**TP_o^* (mg/l)**	**Removal Efficiency (%)**
27-03-2014	5.74	0.00	100.0	20.49	0.92	95.5
28-03-2014	13.23	0.17	98.7	21.76	0.93	95.7
31-03-2014	12.64	0.20	98.4	20.04	2.66	86.7
01-04-2014	7.34	0.23	96.9	23.14	0.52	97.8
02-04-2014	11.01	0.27	97.6	20.17	0.33	98.4
03-04-2014	10.19	0.14	98.6	19.85	1.65	91.7
04-04-2014	8.77	0.05	99.5	18.96	1.52	92.0
07-04-2014	8.93	0.12	98.7	20.57	0.92	95.5
12-04-2014	10.27	0.05	99.5	20.09	0.44	97.8
13-04-2014	17.98	0.41	97.7	18.20	1.46	92.0
15-04-2014	7.85	0.29	96.3	22.33	0.14	99.4
16-04-2014	6.63	0.00	100.0	23.29	0.14	99.4
17-04-2014	6.26	0.22	96.5	21.93	0.43	98.0
18-04-2014	17.82	0.12	99.3	23.57	0.48	97.9
19-04-2014	15.26	0.11	99.3	23.58	0.47	98.0
20-04-2014	14.69	0.07	99.5	22.66	1.13	95.0
Range (min-max)	**5.74-17.82**	**0.05-0.41**	**93.90-99.50**	**18.20-23.58**	**0.14-2.66**	**86.70-99.40**
Mean ±SD	**10.91 ±3.98**	**0.15 ±0.11**	**98.5 ±1.22**	**21.29 ±1.71**	**0.88 ±0.67**	**95.7 ±3.49**

$^*AP_i$ = available phosphate at inlet; $^*AP_o$ = available phosphate at outlet; $^*TP_i$ = available phosphate at inlet; $^*TP_o$ = total phosphate at outlet

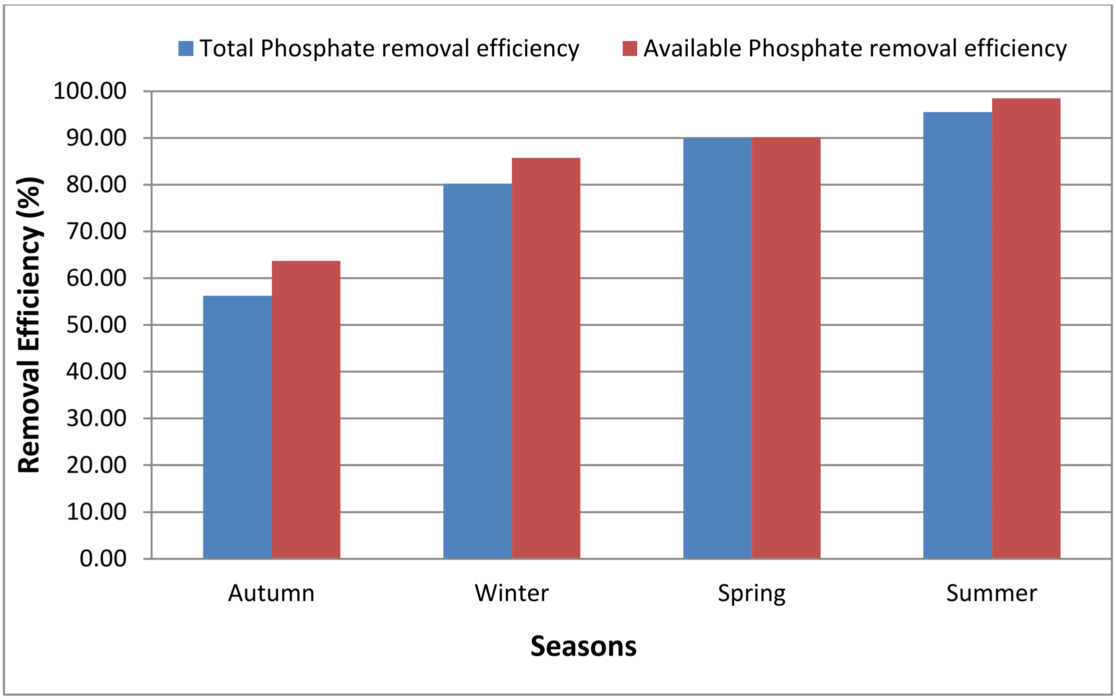

Figure 4.7 Variation in average phosphate removal efficiency (%) of *Phragmites* for different seasons

Similar results were obtained in the present study with the only exception of a sudden drop in late autumn season (Fig. 4.13). The reason may be ascribed to nutrient stress over the plants. It is therefore, necessary to maintain the required supply of nutrients (CNP) in a wetland system. The removal efficiency of AP was placed slightly above the removal efficiency of TP and it increased through the seasons from autumn to summer (Fig. 4.7).

4.5.2 Effect of initial concentration

The effect of initial influent concentration of phosphate on removal efficiency of Phragmites was also investigated to get an insight of adaptability, tolerance and response of the plant to varying chemical shocks of phosphate. The removal efficiency was studied at an initial concentration of 5 mgP/l, raised to 10 mgP/l amended with nitrogen (50 mg/l NH_4^+-N); and finally raised to 20 mgP/l supplemented with nitrogen (ammonium ions at 100 mg/l) with the monitoring of ferric (Fe^{3+}) and Ferrous (Fe^{2+}) ions in the treated wastewater. Phosphate was characterised as AP and TP during the study. Based on the concentration of AP and TP in effluent, removal efficiency (%) and removal rate (mg/m^2-day) were calculated.

The nitrifying conditions in CW cell were monitored on the basis of TKN concentration in influent and effluent. The redox conditions of the CW cell were also monitored on the basis of ferrous and ferric ions concentration in effluent at very high nutrient loading. The results so obtained at varying phosphate loading rates are discussed below.

Available Phosphates (AP) and Total Phosphates (TP)

Available and total phosphate from the synthetically prepared waste water for inlet and treated water after the retention period of 24 hours as outlet from the constructed wetland cell was analysed. Available and total phosphate were analysed for both inlet and outlet. Concentration (mg/l) and removal efficiency (%) of available and total phosphate by the *Phragmites* was analysed during the study and the loading rate (mgP/m^2-day) was also determined for both inlet and outlet.

Removal at 5 mg/l PO_4^{3-}-P Inlet Concentration

The initial loading of phosphate was kept at a moderate value of 5 mg/l. The average inlet concentration was 3.4 mg/l as total phosphate with a deviation of ±0.5 mg/l. The value of average AP in inlet was 1.4 mg/l with a deviation of ±0.4 mg/l against the average concentration of 0.3 mg/l of AP in effluent. The concentration of AP in influent varied from 1.0 mg/l to 2.71 mg/l. Average removal efficiency of 74.4 % was observed for AP as compared to 68.3 % for TP (Table 4.6). Slightly higher removal efficiency of AP is attributed to its easy availability and preferred uptake. The average removal rate of TP was 61.9 mgP/m^2-day as against the initial loading rate of 62.2 mgP/m^2-day. The removal rate of TP was observed to be significantly high at the present loading rate. During the study, a sharp decrease in removal efficiency and rate was observed after a period of one month. The decrease may be attributed to the stressed growth of *Phragmites* in later stage owing to chemical stress on account of deficiency of nitrogen. Since phosphate was added as the only nutrient in synthetic wastewater, nitrogen deficient conditions were created after the period of around 30 days. Initial requirement might be met by the nitrates present in the sediments. The other reason might be the decrease in average ambient temperature from 25.5^{o}C (October) to about 19^{o}C (November) resulting in lower metabolic rates of *Phragmites* at lower temperature on account of onset of transformation of season from autumn to winter.

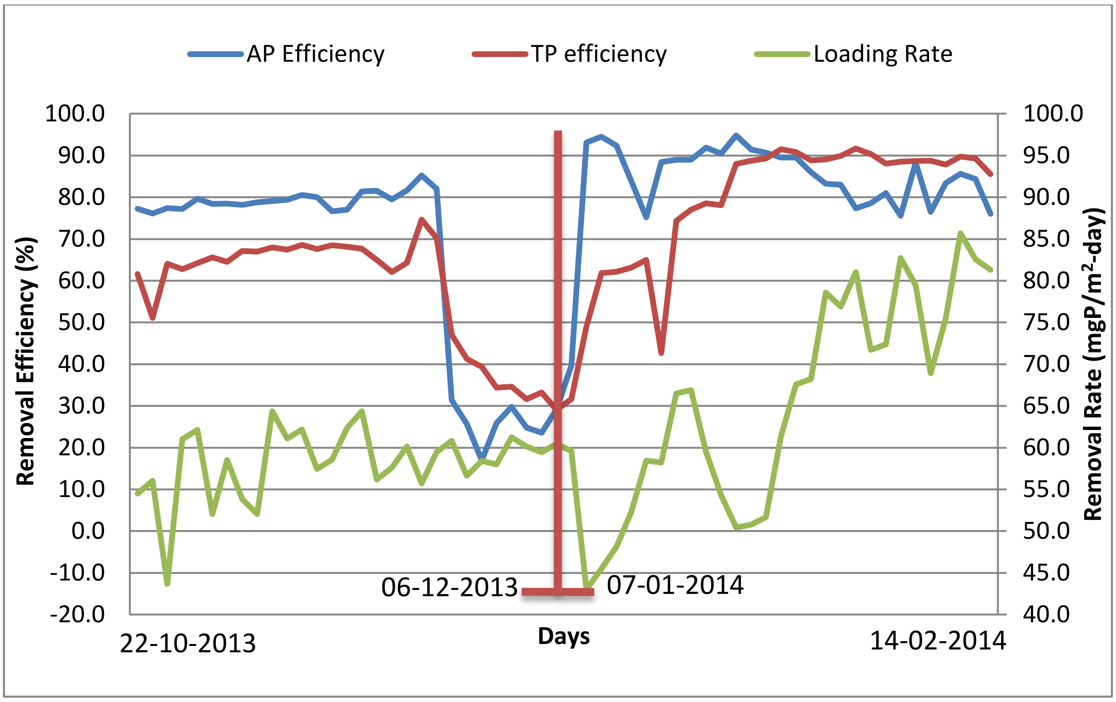

Figure 4.8 AP and TP removal efficiency (%) and removal rate (mgP/m^2-day) for the influent phosphate PO_4^{3-}-P concentration of 5 mg/l

At the same time average sunshine hours reduced resulting in reduced productivity. It had resulted in chlorosis of leaves and onset of drying of stems. During this period (December 07, 2013 to January 06, 2014), efforts were made to revive the health of *Phragmites*, and analysis of phosphate and other characteristics of wastewater remained suspended. In order to revive the plant health, temporary agro-net was removed to facilitate enhanced exposure to sunlight; phosphate was amended with Di-ammonium phosphate (DAP) and urea at regular interval of ten days; and the hydraulic loading was reduced. New leaves and lateral branches generated after a period of around 15 days and the plants had stabilised in a period of about 30 days. Following it the regular analysis as started initially was initiated. Later, it was observed that removal efficiency of AP and TP improved significantly and stabilised at ≈90% for AP and ≈80% for TP (Table 4.6). The removal rate too improved gradually and stabilised at ≈75 mgP/m^2-day in the later stage. The removal efficiency of TP exceeded the removal of AP in later stage owing to removal of TP by sediments. The removal rate increased gradually with slight variations (±10.1 mgP/m^2-day) during the study (Fig. 4.8).

Table 4.6 Removal of PO_4^{3-}-P by *Phragmites* at an initial concentration of 5 mg/l

Date (n=58)	Inlet					Outlet					Removal Efficiency (%)		Loading Rate (mgP/m^2-day)		Removal Rate (mgP/m^2-day)
	pH	TDS (ppm)	EC (µS/cm)	AP (mg/l)	TP (mg/l)	pH	TDS (ppm)	EC (µS/cm)	AP (mg/l)	TP (mg/l)	AP	TP	Inlet	Outlet	
22-10-2013	8.0	211	722	1.1	3.02	8.4	593	2360	0.25	1.16	77.3	61.6	54.9	0.4	54.5
23-10-2013	8.0	210	720	1.17	3.11	8.4	516	2359	0.28	1.52	76.1	51.1	56.5	0.5	56.0
24-10-2013	8.0	219	715	1.15	2.42	8.3	499	2339	0.26	0.87	77.4	64.0	44.0	0.3	43.7
25-10-2013	8.0	221	750	1.14	3.38	7.4	467	2383	0.26	1.26	77.2	62.7	61.5	0.4	61.0
28-10-2013	7.9	229	735	1.13	3.44	7.6	475	2983	0.23	1.23	79.6	64.2	62.5	0.4	62.1
29-10-2013	8.0	222	741	1.02	2.88	7.3	512	2170	0.22	0.99	78.4	65.6	52.4	0.3	52.0
30-10-2013	7.9	245	741	1.07	3.24	7.1	515	3530	0.23	1.15	78.5	64.5	58.9	0.4	58.5
31-10-2013	7.9	235	740	1.1	2.98	7.2	539	3630	0.24	0.98	78.2	67.1	54.2	0.3	53.8
01-11-2013	7.8	224	734	1.13	2.88	7.1	576	3640	0.24	0.95	78.8	67.0	52.4	0.3	52.0
04-11-2013	7.6	213	738	1.15	3.56	7.0	534	3880	0.24	1.14	79.1	68.0	64.7	0.4	64.3
05-11-2013	7.7	238	733	1.02	3.38	7.0	557	3670	0.21	1.1	79.4	67.5	61.5	0.4	61.1
06-11-2013	7.8	216	733	1.13	3.44	6.9	548	3680	0.22	1.08	80.5	68.6	62.5	0.4	62.2
07-11-2013	7.9	247	734	1.1	3.18	7.0	563	3710	0.22	1.03	80.0	67.6	57.8	0.4	57.5
08-11-2013	8.0	239	735	1.07	3.24	7.0	543	3775	0.25	1.02	76.6	68.5	58.9	0.3	58.6
11-11-2013	7.9	220	736	1	3.45	7.0	579	3802	0.23	1.1	77.0	68.1	62.7	0.4	62.4

12-11-2013	7.8	227	738	1.13	3.56	7.0	575	3810	0.21	1.15	81.4	67.7	64.7	0.4	64.3
13-11-2013	7.8	219	740	1.19	3.11	6.9	589	3830	0.22	1.09	81.5	65.0	56.5	0.4	56.2
14-11-2013	7.8	208	740	1.12	3.19	6.9	595	3840	0.23	1.21	79.5	62.1	58.0	0.4	57.6
15-11-2013	7.9	223	741	1.09	3.33	6.9	611	3845	0.2	1.19	81.7	64.3	60.5	0.4	60.1
21-11-2013	7.9	216	698	1.15	3.08	7.2	615	2489	0.17	0.78	85.2	74.7	56.0	0.3	55.7
22-11-2013	7.9	218	720	1.11	3.29	6.9	632	2828	0.2	0.98	82.0	70.2	59.8	0.3	59.5
25-11-2013	8.0	222	715	1.02	3.38	6.9	619	2948	0.7	1.79	31.4	47.0	61.5	0.6	60.8
26-11-2013	7.9	217	723	1.09	3.15	6.9	597	2953	0.81	1.85	25.7	41.3	57.3	0.6	56.6
27-11-2013	7.9	226	730	1	3.25	7.0	587	2889	0.83	1.97	17.0	39.4	59.1	0.7	58.4
28-11-2013	7.9	232	720	1.2	3.23	7.7	616	2513	0.89	2.12	25.8	34.4	58.7	0.7	58.0
29-11-2013	7.9	239	743	1.21	3.41	7.2	633	2705	0.85	2.23	29.8	34.6	62.0	0.8	61.2
02-12-2013	7.9	244	750	1.17	3.35	6.9	678	2448	0.88	2.29	24.8	31.6	60.9	0.8	60.1
03-12-2013	7.9	238	752	1.06	3.31	6.9	658	2307	0.81	2.21	23.6	33.2	60.2	0.8	59.4
05-12-2013	7.9	228	756	1.1	3.37	6.7	667	2334	0.78	2.39	29.1	29.1	61.3	0.8	60.5
06-12-2013	7.9	225	755	1.31	3.32	6.8	643	2350	0.79	2.27	39.7	31.6	60.4	0.8	59.6
07-01-2014	6.7	280	569	1.66	2.39	6.7	898	1831	0.114	1.219	93.1	49.0	43.5	0.4	43.0
08-01-2014	6.8	285	580	1.56	2.52	6.9	935	1908	0.086	0.962	94.5	61.8	45.8	0.3	45.5
09-01-2014	6.8	289	585	1.63	2.67	6.8	887	1809	0.124	1.009	92.4	62.1	48.5	0.3	48.1
10-01-2014	6.9	284	578	1.66	2.89	6.8	862	1759	0.267	1.066	83.9	63.2	52.6	0.4	52.3
13-01-2014	7.1	278	566	1.15	3.24	6.6	863	1957	0.286	1.133	75.2	65.0	58.9	0.4	58.5

15-01-2014	7.2	278	566	1.15	3.24	6.8	882	1799	0.133	1.856	88.4	42.6	58.9	0.6	58.2
16-01-2014	7.4	346	705	1.65	3.67	6.8	1156	2236	0.181	0.942	89.0	74.4	66.8	0.3	66.5
17-01-2014	7.4	351	709	1.65	3.69	6.7	1159	2234	0.181	0.847	89.0	77.1	67.2	0.3	66.9
20-01-2014	7.3	330	701	1.76	3.28	6.8	950	2119	0.143	0.704	91.9	78.6	59.7	0.2	59.5
21-01-2014	7.1	329	690	1.80	3.00	6.9	915	1516	0.171	0.657	90.5	78.1	54.5	0.2	54.3
22-01-2014	6.9	315	696	1.85	2.78	7.0	672	1370	0.095	0.333	94.8	88.0	50.5	0.1	50.4
23-01-2014	6.9	282	574	1.89	2.80	6.8	853	1740	0.162	0.314	91.5	88.8	50.9	0.1	50.8
24-01-2014	7.2	281	573	1.43	2.85	6.7	870	1774	0.133	0.305	90.7	89.3	51.8	0.1	51.7
27-01-2014	6.9	282	574	1.18	3.38	6.8	917	1871	0.124	0.286	89.5	91.5	61.4	0.1	61.3
28-01-2014	6.9	291	569	1.82	3.72	6.8	772	1569	0.190	0.343	89.5	90.8	67.7	0.1	67.6
29-01-2014	6.9	284	580	1.70	3.76	6.7	778	1581	0.238	0.419	86.0	88.9	68.4	0.1	68.2
30-01-2014	7.4	290	591	1.76	4.33	6.9	478	974	0.295	0.475	83.2	89.0	78.8	0.2	78.6
31-01-2014	7.4	296	594	1.63	4.24	7.0	511	1523	0.276	0.428	83.0	89.9	77.0	0.1	76.9
03-02-2014	7.6	290	582	1.51	4.46	6.9	561	1536	0.343	0.371	77.4	91.7	81.2	0.1	81.1
04-02-2014	7.3	298	593	1.55	3.95	6.9	539	1589	0.333	0.381	78.5	90.4	71.8	0.1	71.7
05-02-2014	7.1	279	578	1.86	3.99	6.9	650	1643	0.352	0.476	81.0	88.1	72.5	0.2	72.4
06-02-2014	7.2	293	583	1.64	4.56	6.9	768	1689	0.400	0.524	75.6	88.5	82.9	0.2	82.7
07-02-2014	7.1	299	597	1.70	4.38	6.9	750	1611	0.200	0.495	88.3	88.7	79.6	0.2	79.5
10-02-2014	7.0	280	585	1.58	3.80	6.8	880	1756	0.371	0.428	76.5	88.7	69.1	0.1	68.9
11-02-2014	7.1	287	573	1.72	4.16	6.9	889	1831	0.286	0.505	83.4	87.9	75.6	0.2	75.5

12-02-2014	7.0	292	594	2.71	4.72	7.0	913	1862	0.390	0.486	85.6	89.7	85.9	0.2	85.7
13-02-2014	7.1	293	598	2.26	4.55	7.0	968	1975	0.352	0.486	84.4	89.3	82.7	0.2	82.6
14-02-2014	7.0	278	586	2.03	4.48	7.0	833	1700	0.486	0.647	76.1	85.6	81.5	0.2	81.3
Range (min-max)	**6.7-8.0**	**208-351**	**566-756**	**1.0-2.71**	**2.39-4.72**	**6.6-8.4**	**467-1159**	**974-3380**	**0.086-0.89**	**0.286-2.39**	**17.0-94.8**	**29.1-91.7**	**43.5-85.9**	**0.1-0.8**	**43.0-85.7**
Mean ±SD	**7.5 ±0.43**	**259.2 ±38.42**	**670.6 ±74.59**	**1.4 ±0.36**	**3.4 ±0.55**	**7.0 ±0.38**	**697.2 ±174.42**	**2426.9 ±827.05**	**0.3 ±0.23**	**1.0 ±0.58**	**74.4 ±21.12**	**68.3 ±18.56**	**62.2 ±18.56**	**0.4 ±0.19**	**61.9 ±10.08**

Removal at 10 mg/l PO_4^{3-}-P Inlet Concentration

During this study TP concentration in influent was increased to 10 mg/l representing high strength (Metcalf & Eddy, 1991) wastewater with respect to phosphate. Nitrogen was also amended with the concentration of 50 mg/l as ammonium ions to get an indirect inference of nitrifying conditions.

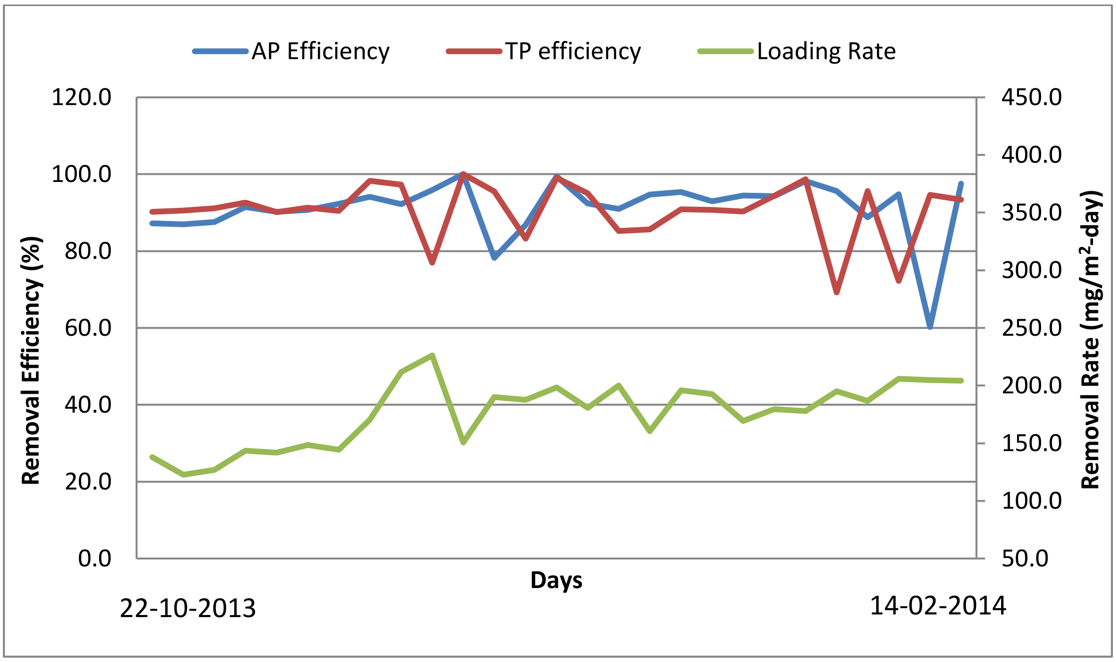

Figure 4.9 AP and TP removal efficiency (%) and removal rate (mgP/m^2-day) for the influent phosphate concentration of 10 mg/l

Nitrifying conditions comment upon/ represent oxidising environment in the CW cell, which in turn comments upon the binding of phosphate with the metal species present in sediments. Addition of ammonium ions also helped nitrifying bacteria stay functional/ active in the aquatic environment. The average concentration of TP in influent was found to be 9.7 mg/l with a deviation of ±1.6 mg/l as against an average concentration of 0.95 mg/l in effluent. It resulted in an average removal efficiency of 91 % for TP. The removal efficiency of AP was almost of the same order with the average influent and effluent concentration of 3.56 mg/l and 0.33 mg/l, respectively (Table 4.7; Fig. 4.9). The average removal rate of phosphate was observed to be 176.1 mg/m^2-day as against the initial phosphate loading of 176.4 mg/m^2-day. The phosphate removal rate of Phragmites was therefore, observed to be substantially high even for high strength wastewater with respect to phosphate.

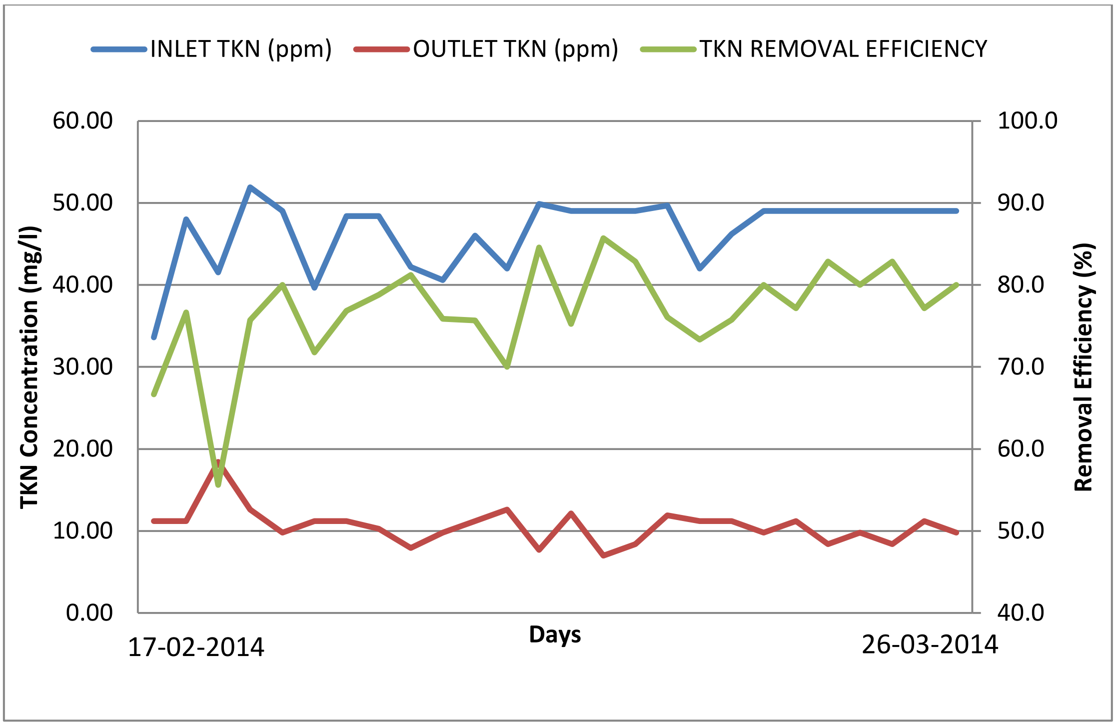

Figure 4.10 TKN concentrations (mg/l) and its removal efficiency (%) for influent concentration of 50 mg/l NH_4^+-N

The possibility of phosphate being removed by sediments was ruled out based on the concentration of TKN in influent and effluent. An average influent concentration of 46.5 mg/l NH_4^+-N was maintained during the period. The average concentration of TKN in effluent was observed to be 10.6 mg/l resulting in average nitrogen removal efficiency of 77% (Table 4.8; Fig. 4.10). This indicates that most of the ammonium ions are converted to nitrates which are subsequently taken up by the plants for growth and metabolism. The removal rate of TKN was observed to be 842 mg/m^2-day as against the influent loading of 846 mg/m^2-day. Since there is significant decrease in NH_4^+/ TKN, oxidising conditions prevailed in the CW cell during the period. Since binding of phosphate with metallic species does not take place under aerobic conditions, and in neutral pH range; most of the removal of phosphate in the present study is by *Phragmites*. In a similar study conducted by Brix *et al.*, (2001), it tells that phosphate do not combine with other metals such as iron. Ferric ions only do forms the bond with phosphate and not the ferrous ions.

Table 4.7 Removal of PO_4^{3-}-P by *Phragmites* at an initial concentration of 10 mg/l

Date (n=27)	**Inlet**					**Outlet**					**REmoval Efficiency (%)**		**Loading Rate (mgP/m^2-day)**		**Removal Rate (mgP/m^2-day)**
	pH	**TDS (ppm)**	**EC (µS/cm)**	**AP (mg/l)**	**TP (mg/l)**	**pH**	**TDS (ppm)**	**EC (µS/cm)**	**AP (mg/l)**	**TP (mg/l)**	**AP**	**TP**	**Inlet**	**Outlet**	
17-02-2014	7.0	428	872	3.80	7.60	7.0	630	1284	0.486	0.743	87.2	90.2	138.1	0.3	137.9
18-02-2014	7.0	444	906	3.44	6.76	6.9	724	1476	0.447	0.638	87.0	90.6	122.9	0.2	122.7
19-02-2014	7.5	431	879	3.51	6.99	6.8	736	1504	0.438	0.619	87.5	91.1	127.0	0.2	126.8
20-02-2014	7.6	391	813	3.67	7.90	6.8	808	1648	0.314	0.581	91.5	92.7	143.7	0.2	143.5
21-02-2014	7.4	452	922	3.80	7.82	6.8	744	1517	0.371	0.771	90.2	90.1	142.1	0.3	141.8
24-02-2014	7.5	365	744	3.57	8.18	6.8	851	1737	0.333	0.714	90.7	91.3	148.7	0.2	148.4
25-02-2014	7.6	363	739	3.81	7.96	6.8	825	1683	0.295	0.762	92.3	90.4	144.7	0.3	144.4
26-02-2014	7.6	366	784	2.65	9.38	6.8	821	1655	0.156	0.165	94.1	98.2	170.5	0.1	170.5
27-02-2014	7.6	370	799	1.88	11.65	6.8	896	1719	0.147	0.316	92.2	97.3	211.8	0.1	211.7
28-02-2014	7.8	396	841	3.96	12.49	7.0	891	1789	0.165	2.880	95.8	76.9	227.1	1.0	226.1
03-03-2014	7.9	404	859	1.90	8.29	6.9	817	1777	0	0.000	100.0	100.0	150.7	0.0	150.7
04-03-2014	8.0	445	897	1.34	10.46	7.1	823	1767	0.291	0.470	78.2	95.5	190.2	0.2	190.0
05-03-2014	8.0	415	899	3.39	10.35	7.2	835	1801	0.449	1.739	86.8	83.2	188.2	0.6	187.6
06-03-2014	8.1	479	910	4.86	10.91	7.2	897	1810	0.026	0.103	99.5	99.1	198.4	0.0	198.3
07-03-2014	8.1	459	914	4.03	9.95	7.4	852	1829	0.306	0.496	92.4	95.0	180.9	0.2	180.7
10-03-2014	8.0	471	961	3.33	11.03	7.4	879	1702	0.302	1.631	90.9	85.2	200.5	0.6	200.0

11-03-2014	8.2	452	921	3.73	8.84	7.5	835	1798	0.197	1.269	94.7	85.6	160.7	0.4	160.3
12-03-2014	8.1	465	951	4.63	10.79	7.6	851	1853	0.213	0.987	95.4	90.9	196.2	0.3	195.8
13-03-2014	8.1	474	965	4.00	10.61	7.6	902	1840	0.28	0.989	93.0	90.7	192.9	0.3	192.6
14-03-2014	8.2	538	1098	4.17	9.33	7.5	944	1911	0.233	0.908	94.4	90.3	169.6	0.3	169.3
18-03-2014	8.2	513	1045	4.33	9.89	7.6	951	2143	0.249	0.554	94.2	94.4	179.8	0.2	179.6
19-03-2014	8.3	505	1020	3.75	9.79	7.6	950	2110	0.068	0.128	98.2	98.7	178.0	0.0	178.0
20-03-2014	8.3	500	1017	5.29	10.79	7.4	978	1937	0.23	3.321	95.7	69.2	196.2	1.1	195.0
21-03-2014	8.2	499	1019	2.30	10.28	7.4	979	1994	0.257	0.452	88.8	95.6	186.9	0.2	186.8
24-03-2014	7.9	499	1020	4.73	11.39	7.5	979	2021	0.248	3.166	94.8	72.2	207.1	1.1	206.0
25-03-2014	7.9	500	1011	5.60	11.28	7.4	976	2277	2.226	0.604	60.3	94.6	205.1	0.2	204.9
26-03-2014	8.0	496	1387	2.99	11.24	7.5	980	2398	0.073	0.748	97.6	93.3	204.4	0.3	204.1
Range (min-max)	**7.0-8.3**	**363-538**	**739-1387**	**1.34-5.60**	**6.76-12.49**	**6.8-7.6**	**630-980**	**1284-2398**	**0.026-2.226**	**0.103-3.321**	**60.3-99.5**	**69.2-99.1**	**122.9-227.1**	**0.1-1.1**	**122.7-226.1**
Mean ±SD	**7.85 ±0.36**	**448.5 ±51.02**	**933.1 ±129.57**	**3.65 ±1.0**	**9.7 ±1.55**	**7.2 ±0.32**	**864.96 ±89.66**	**1814.10 ±242.98**	**.033 ±0.40**	**0.95 ±0.88**	**92.23 ±7.73**	**90.5 ±7.67**	**176.4 ±28.24**	**.033 ±0.301**	**176.06 ±28.12**

Table 4.8 Removal efficiency (%) and removal rate (mg/m^2-day) of TKN at an influent concentration of 50 mg/l NH_4^+-N and 10 mg/l PO_4^{3-}-P

Date (n=26)	TKN			Loading Rate (mg/m^2-day)		Removal Rate (mg/m^2-day)
	Inlet (mg/l)	Outlet (mg/l)	Removal Efficiency (%)	Inlet	Outlet	
18-02-2014	33.60	11.20	66.7	610.9	3.8	607.1
19-02-2014	48.00	11.20	76.7	872.7	3.8	868.9
20-02-2014	41.53	18.44	55.6	755.1	6.3	748.8
21-02-2014	51.90	12.60	75.7	943.6	4.3	939.3
24-02-2014	49.00	9.80	80.0	890.9	3.3	887.6
25-02-2014	39.67	11.20	71.8	721.3	3.8	717.5
26-02-2014	48.40	11.20	76.9	880.0	3.8	876.2
27-02-2014	48.40	10.27	78.8	880.0	3.5	876.5
28-02-2014	42.20	7.93	81.2	767.3	2.7	764.6
03-03-2014	40.60	9.80	75.9	738.2	3.3	734.8
04-03-2014	46.00	11.20	75.7	836.4	3.8	832.5
05-03-2014	42.00	12.60	70.0	763.6	4.3	759.3
06-03-2014	49.87	7.70	84.6	906.7	2.6	904.1
07-03-2014	49.00	12.13	75.2	890.9	4.1	886.8

10-03-2014	49.00	7.00	85.7	890.9	2.4	888.5
11-03-2014	49.00	8.40	82.9	890.9	2.9	888.0
12-03-2014	49.70	11.90	76.1	903.6	4.1	899.6
13-03-2014	42.00	11.20	73.3	763.6	3.8	759.8
14-03-2014	46.20	11.20	75.8	840.0	3.8	836.2
18-03-2014	49.00	9.80	80.0	890.9	3.3	887.6
19-03-2014	49.00	11.20	77.1	890.9	3.8	887.1
20-03-2014	49.00	8.40	82.9	890.9	2.9	888.0
21-03-2014	49.00	9.80	80.0	890.9	3.3	887.6
24-03-2014	49.00	8.40	82.9	890.9	2.9	888.0
25-03-2014	49.00	11.20	77.1	890.9	3.8	887.1
26-03-2014	49.00	9.80	80.0	890.9	3.3	887.6
Range (min-max)	**33.60-51.90**	**1.00-18.44**	**55.6-85.7**	**610.9-943.6**	**2.4-6.3**	**607.1-939.3**
Mean ±SD	**46.50 ±4.29**	**10.59 ±2.29**	**76.86 ±6.19**	**845.50 ±78.06**	**3.61 ±0.76**	**841.9 ±78.28**

Removal at 20 mg/l PO_4^{3-}-P Inlet Concentration

The TP concentration in influent was increased to 20 mg/l representing high strength wastewater (Metcalf & Eddy, 1991) with respect to phosphate. NH_4^+-N was also amended to the CW cell with the concentration of 100 mg/l so as to get an indirect inference of nitrifying conditions at the bed level.

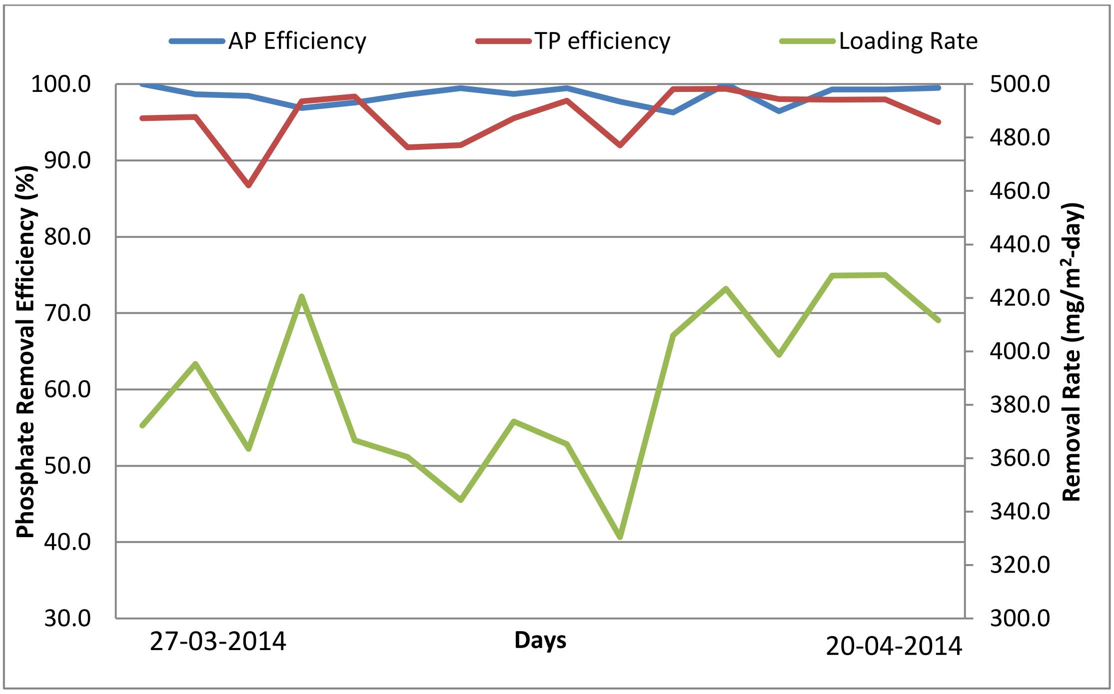

Figure 4.11 AP and TP removal efficiency (%) and removal rate (mgP/m^2-day) for the influent phosphate concentration of 20 mg/l

Nitrifying conditions comment upon/ represent oxidising environment in the CW cell, which in turn comments upon the binding of phosphate with the metal species present in sediments. Addition of ammonium ions also helped nitrifying bacteria to stay functional/ active in the aquatic environment. The average concentration of TP in influent was found to be 21.29 mg/l with a deviation of ±1.71 mg/l as against an average concentration of 0.88 mg/l in effluent with slight deviation of ±6.67 mg/l. It resulted in an average removal efficiency of 95.68% for TP. The removal efficiency of AP was 98.53% which is almost of the same order with the average influent and effluent concentration of 10.91 mg/l and 0.15 mg/l, respectively (Table 4.9; Fig. 4.11). The average removal rate of phosphate was observed to be 386.78 mg/m^2-day as against the initial phosphate loading of 387.08 mg/m^2-day. The phosphate removal rate of Phragmites was, therefore, observed to be substantially high even for high strength wastewater with respect to phosphate.

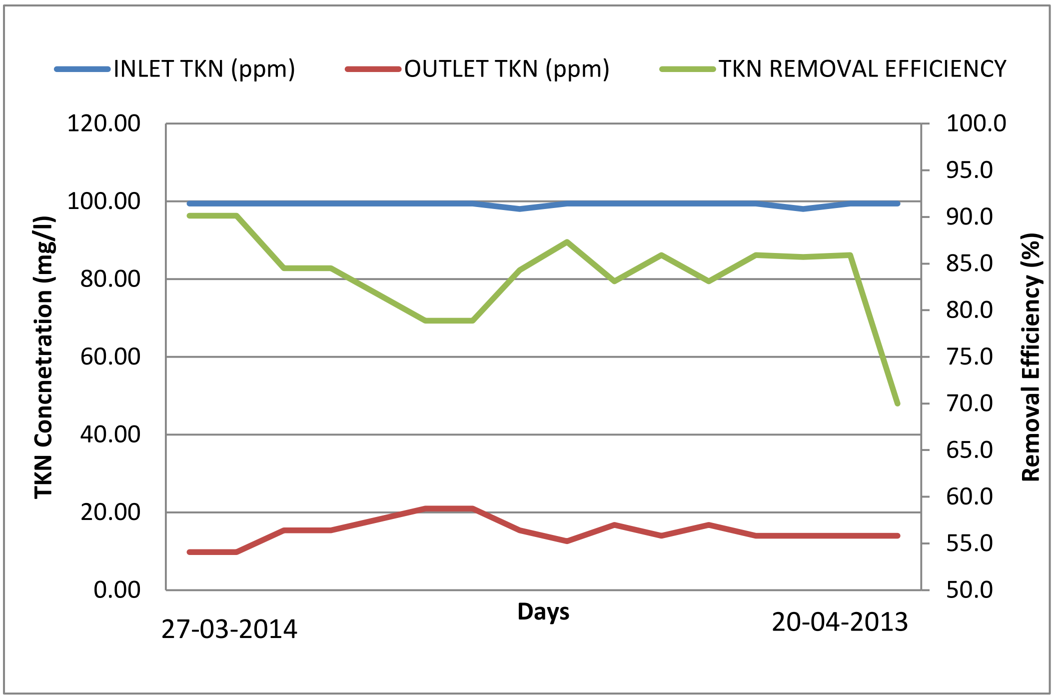

Figure 4.12 TKN concentrations and its removal efficiency (%) for influent concentration of 100 mg/l NH_4^+-N

The possibility of phosphate being removed by sediments can ruled out based on the concentration of TKN in influent and effluent. An average influent concentration of 99.225 mg/l NH_4^+-N was maintained during the period. The average concentration of TKN in effluent was observed to be 15.14 mg/l resulting in average nitrogen removal efficiency of 83.75% with deviation of ±4.87% (Table 4.10; Fig. 4.12). This indicates that most of the ammonium ions are converted to nitrates by its nitrification which is subsequently taken up by the plants for growth and metabolism. The removal rate of TKN was observed to be 1799 mg/m^2-day as against the influent loading of 1804 mg/m^2-day. Since there is significant decrease in NH_4^+/ TKN, oxidising conditions prevailed in the CW cell during the period. Since binding of phosphate with metallic species does not take place under aerobic conditions, and in neutral pH range; most of the removal of phosphate in the present study is by *Phragmites*. In a similar study conducted by Vymazal (2004), it shows that the phosphate do not combine with other metals as such ferrous ions and ferric ions forms the bond with phosphate and thus, the majority of phosphate removal takes by the plant only.

Table 4.9 Removal of PO_4^{3-}-P by *Phragmites* at an initial concentration of 20 mg/l

Date (n=16)	**Inlet**					**Outlet**					**Removal Efficiency (%)**		**Loading Rate (mgP/m^2-day)**		**Removal Rate (mgP/m^2-day)**
	pH	**TDS (ppm)**	**EC (µS/cm)**	**AP (mg/l)**	**TP (mg/l)**	**pH**	**TDS (ppm)**	**EC (µS/cm)**	**AP (mg/l)**	**TP (mg/l)**	**AP**	**TP**	**Inlet**	**Outlet**	
27-03-2014	7.8	680	1395	5.74	20.49	7.3	981	2440	0	0.917	100.0	95.5	372.5	0.3	372.2
28-03-2014	7.8	685	1425	13.23	21.76	7.2	1050	2950	0.174	0.932	98.7	95.7	395.6	0.3	395.2
31-03-2014	7.8	699	1429	12.64	20.04	7.2	1249	3030	0.196	2.659	98.4	86.7	364.4	0.9	363.5
01-04-2014	7.8	658	1383	7.34	23.14	7.2	1150	3250	0.23	0.515	96.9	97.8	420.7	0.2	420.5
02-04-2014	7.8	681	1420	11.01	20.17	7.2	1115	3550	0.267	0.328	97.6	98.4	366.8	0.1	366.7
03-04-2014	7.9	696	1421	10.19	19.85	7.3	1269	3620	0.138	1.645	98.6	91.7	361.0	0.6	360.4
04-04-2014	7.9	680	1389	8.77	18.96	7.2	1339	3789	0.048	1.515	99.5	92.0	344.8	0.5	344.2
07-04-2014	8.0	691	1399	8.93	20.57	7.2	1250	3811	0.116	0.92	98.7	95.5	374.1	0.3	373.8
12-04-2014	7.9	692	1402	10.27	20.09	7.2	1939	3914	0.053	0.435	99.5	97.8	365.3	0.1	365.2
13-04-2014	8.0	687	1388	17.98	18.20	7.3	1780	3999	0.41	1.461	97.7	92.0	330.8	0.5	330.3
15-04-2014	8.2	697	1414	7.85	22.33	7.2	2189	4021	0.29	0.144	96.3	99.4	406.0	0.0	406.0
16-04-2014	7.9	694	1441	6.63	23.29	7.2	2212	4297	0	0.144	100.0	99.4	423.5	0.0	423.4
17-04-2014	7.9	693	1401	6.26	21.93	7.2	2369	4462	0.221	0.429	96.5	98.0	398.7	0.1	398.6
18-04-2014	7.9	699	1403	17.82	23.57	7.2	2355	4537	0.124	0.484	99.3	97.9	428.5	0.2	428.3
19-04-2014	7.9	698	1396	15.26	23.58	7.2	2386	4896	0.105	0.469	99.3	98.0	428.8	0.2	428.6

20-04-2014	7.9	691	1419	14.69	22.66	7.2	2480	5070	0.074	1.128	99.5	95.0	411.9	0.4	411.5
Range (min-max)	**7.8-8.2**	**658-699**	**1383-1441**	**5.74-17.98**	**18.20-23.58**	**7.2-7.3**	**981-2480**	**2440-5070**	**0.048-0.41**	**0.144-2.659**	**96.3-99.5**	**86.7-99.4**	**330.8-428.8**	**0.1-0.9**	**330.3-428.6**
Mean ±SD	**7.9 ±0.103**	**688.81 ±10.51**	**1407.81 ±16.69**	**10.91 ±3.98**	**21.29 ±1.71**	**7.22 ±0.04**	**1694.56 ±567.22**	**3852.25 ±714.75**	**0.15 ±0.11**	**0.88 ±0.67**	**98.53 ±1.21**	**95.68 ±3.49**	**387.08 ±31.1**	**0.30 ±0.23**	**386.78 ±31.24**

Table 4.10 Removal efficiency (%) and removal rate (mg/m^2-day) of TKN at an influent concentration of 100 mg/l NH_4^+-N and 20 mg/l PO_4^{3-}-P

Date (n=16)	TKN			Loading Rate (mg/m^2-day)		Removal Rate (mg/m^2-day)
	Inlet (mg/l)	Outlet (mg/l)	Removal Efficiency (%)	Inlet	Outlet	
27-03-2014	99.40	9.80	90.1	1807.3	3.3	1803.9
28-03-2014	99.40	9.80	90.1	1807.3	3.3	1803.9
31-03-2014	99.40	15.40	84.5	1807.3	5.3	1802.0
01-04-2014	99.40	15.40	84.5	1807.3	5.3	1802.0
02-04-2014	99.40	18.20	81.7	1807.3	6.2	1801.1
03-04-2014	99.40	21.00	78.9	1807.3	7.2	1800.1
04-04-2014	99.40	21.00	78.9	1807.3	7.2	1800.1
07-04-2014	98.00	15.40	84.3	1781.8	5.3	1776.6
12-04-2014	99.40	12.60	87.3	1807.3	4.3	1803.0

13-04-2014	99.40	16.80	83.1	1807.3	5.7	1801.5
15-04-2014	99.40	14.00	85.9	1807.3	4.8	1802.5
16-04-2014	99.40	16.80	83.1	1807.3	5.7	1801.5
17-04-2014	99.40	14.00	85.9	1807.3	4.8	1802.5
18-04-2014	98.00	14.00	85.7	1781.8	4.8	1777.0
19-04-2014	99.40	14.00	85.9	1807.3	4.8	1802.5
20-04-2014	99.40	14.00	70.0	1807.3	4.8	1802.5
Range (min-max)	**98.00-99.40**	**16.80-21.00**	**70.0-90.1**	**1781.8-1807.3**	**3.3-7.2**	**1776.6-1803.9**
Mean ±SD	**99.225 ±0.48**	**15.14 ±3.20**	**83.75 ±4.87**	**1804 ±8.69**	**5.2 ±1.09**	**1798.9 ±8.70**

Table 4.11 Concentration of various iron fractions present in bed sediments

Date (n=22)	**Concentration of iron fractions (mg/l)**		
	Ferrous (Fe^{2+})	**Ferric (Fe^{3+})**	**Ferric/ Ferrous ratio**
18-03-2014	0.238	0.02	0.088
19-03-2014	0.738	0.06	0.082
20-03-2014	0.640	0.05	0.072
21-03-2014	0.464	0.08	0.172
24-03-2014	0.724	0.05	0.065
25-03-2014	0.915	0.02	0.022
26-03-2014	0.583	0.05	0.082
27-03-2014	0.674	0.02	0.025
28-03-2014	1.265	0.09	0.069
31-03-2014	0.914	0.04	0.049
01-04-2014	0.893	0.05	0.059
02-04-2014	0.201	0.01	0.043
03-04-2014	1.376	0.05	0.033
07-04-2014	0.153	0.05	0.342
12-04-2014	4.106	0.08	0.019
13-04-2014	0.303	0.03	0.099
15-04-2014	2.304	0.14	0.060
16-04-2014	2.769	0.02	0.006
17-04-2014	0.167	0.06	0.374
18-04-2014	2.297	0.11	0.047
19-04-2014	3.692	0.10	0.028
20-04-2014	4.069	0.14	0.034
Range (min-max)	**0.153-4.106**	**0.01-0.14**	**0.006-0.374**
Mean ±SD	**1.34 ±1.28**	**0.059 ±0.037**	**0.085 ±0.095**

Iron was also analysed in wetland system which comes into water from wetland sediments. The ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions had the average concentration of 1.34 mg/l and 0.059 mg/l, respectively. The effluent concentration of Fe^{2+} varied from 0.153 mg/l to 4.106 mg/l and on the other hand, concentration of Fe^{3+} varied between

0.01 mg/l to 0.14 mg/l. The ratio of ferric to ferrous (Fe^{3+} to Fe^{2+} ratio) was also calculated and had the average value 0.085 with slight deviation of ±0.095 (Table 4.11). The ratio ranged from 0.006 to 0.374. The ratio had the values less than unity which indicates that most of the iron is present in the form of ferrous (Fe^{2+}) ions and ferric (Fe^{3+}) ions are being converted to ferrous by reduction. This comments upon the existence of aerobic conditions at the surface where oxidation is taking place. At greater depth, anaerobic conditions might be existing. When the anaerobic conditions are present in the CW cell at depths, much more ferrous ion acts as an ATEA and becomes more soluble ferrous iron and releases the phosphorus it had bound to while it was oxidised in the form of ferric. The reactivity of iron and its bonding with phosphate does not exist. Phosphate combines with Ca at $pH \geq 8.5$ (ECS, 1993). The iron being an alternate terminal electron acceptor (ATEA) gets reduced. Iron in the form of ferric (Fe^{3+}) forms the bond with phosphate (PO_4^{3-}) which is no more existed during the anaerobic conditions. This comments that phosphorus is not being removed by iron after forming a bond with the iron. The existence of anaerobic conditions forms the acid. Thus, slightly acidic conditions might have existed at depths (Jaisi *et al*, 2009). The ratio of ferrous to ferric comments on a higher fraction (93%) of ferrous ions out of total iron concentration in the effluent representing dominance of reducing conditions in the CW cell (Kadlec *et al*, 1996).

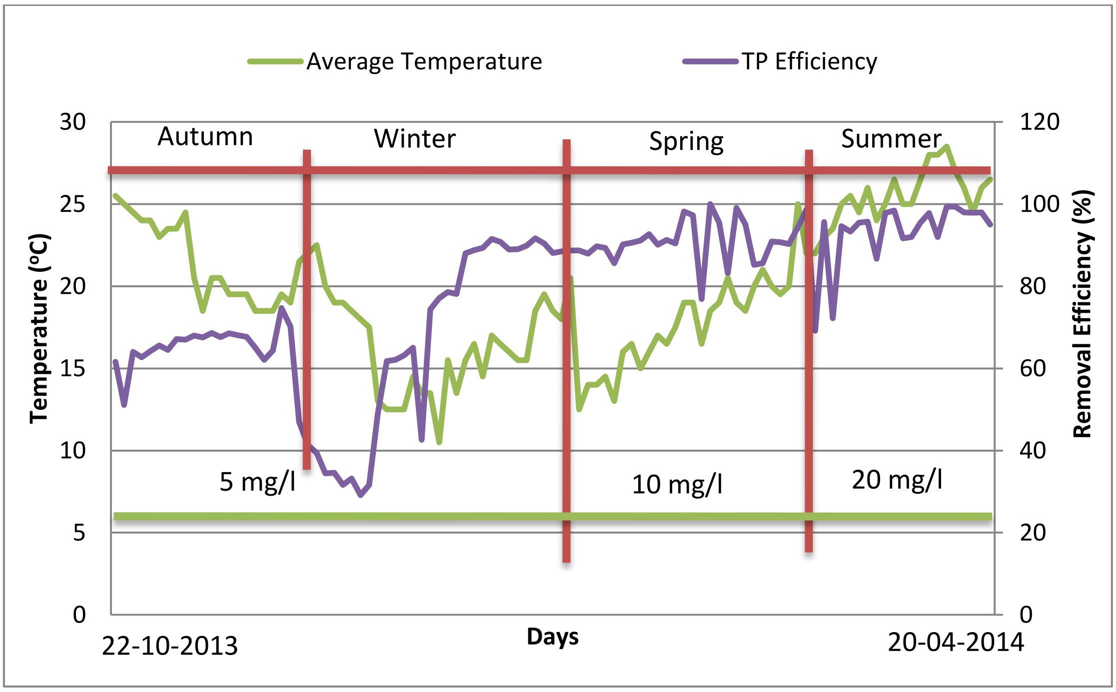

Figure 4.13 Removal efficiency (%) and average ambient temperature (°C) during study

A plot of removal efficiency (%) and average ambient temperature (^{o}C) shows that the removal efficiency depends upon the ambient temperature since the temperature simulate the metabolic activities of plants and thus, its uptake capacity. The evapotranspiration also increases with the increase in ambient temperature and thus, removal efficiency increases (Fig. 4.13). A similar trend can be noticed in terms of initial concentration. The removal efficiency first of all increases for inlet concentration of 5 mgP/l and then a sudden drop in removal efficiency occurs because of the lack of other nutrients. The plant revives after the addition of other nutrients such as DAP and urea. The removal efficiency for 5 mgP/l increases followed by 10 mgP/l and 20 mgP/l along with the rise in ambient temperature.

4.6 Conclusion

Based on the results obtained during the study, following conclusions are be made:

1) *Phragmites* can well adapt to the wetland conditions under tropical Indian environment and can easily absorb the chemical shocks with respect to concentration of influent phosphate. It is important to mention that the influent should be rich in nitrogenous matter since deficiency of nitrogen superimposing with low temperature may exert a stress over the plant, as observed in present study.
2) The *Phragmites*-based CW cell efficiently removes the nutrients (Nitrogen and phosphorus), but an increase in TDS in effluent during treatment may be observed. Therefore, the dissolution of various chemical species from the bed of CW cell is a cause of concern and the regulating factors may be investigated.
3) The removal behaviour of *Phragmites* is largely dependent on the meteorological conditions, and chiefly on temperature and sunshine hours. Temperature regulates the rate of evapotranspiration, *i.e.* higher the temperature, more would be the rate of evapotranspiration resulting in an increased requirement/updraft of water along with nutrients. On the other hand, sunshine hours regulate photosynthetic rate and the productivity. More sunshine hours in summer result in higher productivity and increased up take of nutrients. Therefore, removal efficiency for phosphate followed the trend as

autumn season (56.2%) < winter season (80.6%) < spring season (90.5%) < summer (95.7%) season in the present study.

4) Removal efficiency of *Phragmites* in the present study followed first order kinetics. As the influent concentration increased from 5 mg/l to 20 mg/l, the removal efficiency went on increasing from 68.3% (TP) to 95.68%.
5) The conditions in the CW cell were observed to nitrifying, i.e. oxidation of reduced form of nitrogen (NH_4^+) to nitrate. Removal of TKN from the influent was of the order of 76.86% (50 mgN/l), and 83.75% (100 mgN/l). Since the pH of effluent was around neutral throughout the studies, transformation of NH_4^+ to ammonia gas (NH_3) is ruled out. As the nutrient loading is increased, the conditions changed to reducing (at depths) gradually.
6) Stratification of CW cell with respect to oxygen was observed, and it represented a clinograde oxygen profile. The surface water-sediments micro zone represented aerobic (oxidising condition), whereas at depths, reducing conditions dominated. This resulted in a higher fraction (93%) of ferrous ions out of total iron concentration in the effluent representing dominance of reducing conditions in the CW cell.
7) The major removal of phosphate in the CW cell was by *Phragmites*. Since the conditions were reducing, binding of phosphate to Fe^{2+} ions does not take place, and since the pH was almost neutral throughout the study, binding to Ca is ruled out (takes place at pH ≥ 8.5). Therefore, binding of phosphate to sediments is negligible.

SUMMARY

For the purpose of study, a *Phragmites* based CW cell was developed in a laboratory in DTU having the dimensions 110 cm x 80 cm 45 cm (l x b x h) and its substrate mimicked the bed conditions of that of natural wetlands. The plant for the CW was identified as *Phragmites* which was already present in Lake at DTU, was uprooted and planted in the CW cell during the April, 2013. CW cell was added with the fertilizers Di-ammonium phosphate (DAP) and urea for the stabilisation of the *Phragmites*. When it was found that *Phragmites* has adopted according to its new habitat and stabilised, the study was started. The study was started from October, 2013 to April, 2014, with the aim to check the effect of different seasons and different nutrient influent concentration on the growth and health of *Phragmites* and its nutrient removal efficiency. *Phragmites* was well adapted to the CW under tropical Indian environment and it absorbed the chemical shocks with respect to concentration of influent phosphate. It must be noted that the influent should be rich in nitrogenous matter; otherwise, its deficiency will superimpose with low temperature and may exert a stress over the plant. The *Phragmites*-based CW cell efficiently removed the nutrients (nitrogen and phosphorus), but an increase in TDS in effluent during treatment was observed. Therefore, the dissolution of various chemical species from the bed of CW cell was observed. The removal behaviour of *Phragmites* was largely dependent on the meteorological conditions, and chiefly on temperature and sunshine hours. Temperature regulated the rate of evapotranspiration, *i.e.* higher the temperature, more would be the rate of evapotranspiration resulted in an increased requirement/updraft of water along with nutrients. Also, sunshine hours regulate photosynthesis process and the productivity of plant. More sunshine hours in summer resulted in higher productivity and increased up take of nutrients from the wastewater. Therefore, removal efficiency for phosphate followed the trend as autumn season (56.2%) < winter season (80.6%) < spring season (90.5%) < summer (95.7%) season in the present study for different seasons. Removal efficiency of *Phragmites* in the present study followed first order kinetics. As the influent concentration increased from 5 mg/l to 20 mg/l, the removal efficiency went on increasing from 68.3% (TP) to 95.68% for the effluent. For 5 mg/l, average TP influent and effluent concentrations varied from 3.4mg/l to 1.0 mg/l. For 10 mg/l, average TP concentrations varied from 9.7 mg/l to 0.95 mg/l. For 20 mg/l, average TP concentrations varied from 21.3 mg/l

to 0.88 mg/l The conditions in the CW cell were observed to nitrifying, i.e. oxidation of reduced form of nitrogen (NH_4^+) to nitrate. Removal of TKN from the influent was of the order of 76.86% (50 mgN/l), and 83.75% (100 mgN/l). Since the pH of effluent was around neutral throughout the studies, transformation of NH_4^+ to ammonia gas (NH_3) is ruled out. As the nutrient loading is increased, the conditions changed to reducing (at depths) gradually. Also, the stratification of CW cell with respect to oxygen was observed, and it represented a clinograde oxygen profile. The surface water-sediments micro zone represented aerobic (oxidising condition), whereas at depths, reducing conditions dominated. This resulted in a higher fraction (93%) of ferrous ions out of total iron concentration in the effluent representing dominance of reducing conditions in the CW cell. The ratio of ferric to ferrous is also less than unity and this shows that concentration of ferric is less than ferrous. Ferric makes the bonds with phosphate which is not present in dominance. The major removal of phosphate in the CW cell was by *Phragmites*. Since the conditions were reducing, binding of phosphate to Fe^{2+} ions does not take place, and since the pH was almost neutral throughout the study, binding to Ca is ruled out (takes place at pH > 8.5). Therefore, binding of phosphate to sediments is negligible.

Thus, *Phragmites* proves to be a plant for the CW cell for the removal of pollutants from the wastewater and it provides a very good removal efficiency of secondary wastewater treatment. It is also resistant to the shocks in terms of variation in influent concentration.

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Annexure I

Ambient temperature profile during the study

Date	Maximum Temperature (^{o} C)	Minimum Temperature (^{o} C)	Average Temperature (^{o} C)	Rainfall (mm)
01-10-2013	34	25	29.5	0
02-10-2013	35	26	30.5	0
03-10-2013	34	23	28.5	0
04-10-2013	26	23	24.5	0
05-10-2013	34	22	28	0
06-10-2013	34	23	28.5	0
07-10-2013	34	24	29	0
08-10-2013	34	25	29.5	0
09-10-2013	36	25	30.5	0
10-10-2013	35	24	29.5	0
11-10-2013	28	21	24.5	0
12-10-2013	31	21	26	0
13-10-2013	33	23	28	0
14-10-2013	32	23	27.5	0
15-10-2013	33	21	27	0
16-10-2013	34	20	27	0
17-10-2013	35	21	28	0
18-10-2013	33	22	27.5	0
19-10-2013	34	18	26	0
20-10-2013	33	18	25.5	0
21-10-2013	32	17	24.5	0
22-10-2013	34	17	25.5	0
23-10-2013	32	18	25	0
24-10-2013	31	18	24.5	0
25-10-2013	30	18	24	0
26-10-2013	31	19	25	0
27-10-2013	30	18	24	0
28-10-2013	31	17	24	0
29-10-2013	31	15	23	0
30-10-2013	32	15	23.5	0
31-10-2013	30	17	23.5	0
01-11-2013	31	18	24.5	1
02-11-2013	29	16	22.5	0
03-11-2013	28	14	21	0
04-11-2013	28	13	20.5	0
05-11-2013	25	12	18.5	0
06-11-2013	28	13	20.5	0
07-11-2013	27	14	20.5	0
08-11-2013	25	14	19.5	0

09-11-2013	26	12	19	0
10-11-2013	26	12	19	0
11-11-2013	27	12	19.5	0
12-11-2013	27	12	19.5	0
13-11-2013	26	11	18.5	0
14-11-2013	26	11	18.5	0
15-11-2013	27	10	18.5	0
16-11-2013	27	9	18	0
17-11-2013	26	9	17.5	0
18-11-2013	27	11	19	0
19-11-2013	27	11	19	0
20-11-2013	28	10	19	0
21-11-2013	29	10	19.5	0
22-11-2013	27	11	19	0
23-11-2013	27	11	19	0
24-11-2013	28	12	20	0
25-11-2013	29	14	21.5	0
26-11-2013	29	15	22	0
27-11-2013	28	17	22.5	0
28-11-2013	28	12	20	0
29-11-2013	27	11	19	0
30-11-2013	27	12	19.5	0
01-12-2013	28	10	19	0
02-12-2013	28	10	19	0
03-12-2013	28	9	18.5	0
04-12-2013	26	10	18	0
05-12-2013	26	10	18	0
06-12-2013	25	10	17.5	0
07-12-2013	26	9	17.5	0
08-12-2013	26	10	18	0
09-12-2013	25	9	17	0
10-12-2013	24	9	16.5	0
11-12-2013	25	9	17	0
12-12-2013	24	9	16.5	0
13-12-2013	24	12	18	0
14-12-2013	25	10	17.5	0
15-12-2013	24	9	16.5	0
16-12-2013	24	9	16.5	0
17-12-2013	23	9	16	0
18-12-2013	22	9	15.5	0
19-12-2013	22	11	16.5	0
20-12-2013	20	12	16	0
21-12-2013	16	13	14.5	0
22-12-2013	17	12	14.5	0
23-12-2013	18	12	15	0
24-12-2013	20	10	15	0
25-12-2013	20	8	14	0

26-12-2013	21	6	13.5	0
27-12-2013	17	7	12	0
28-12-2013	20	5	12.5	0
29-12-2013	19	4	11.5	0
30-12-2013	20	2	11	6
31-12-2013	19	11	15	0
01-01-2014	18	2	10	0
02-01-2014	18	5	11.5	0
03-01-2014	20	5	12.5	0
04-01-2014	19	7	13	0
05-01-2014	19	8	13.5	0
06-01-2014	18	7	12.5	0
07-01-2014	20	6	13	0
08-01-2014	21	4	12.5	0
09-01-2014	18	7	12.5	0
10-01-2014	20	5	12.5	0
11-01-2014	18	7	12.5	0
12-01-2014	21	6	13.5	0
13-01-2014	22	7	14.5	0
14-01-2014	22	9	15.5	0
15-01-2014	17	10	13.5	0
16-01-2014	18	9	13.5	0
17-01-2014	13	8	10.5	0
18-01-2014	16	10	13	4
19-01-2014	21	9	15	0
20-01-2014	22	9	15.5	0
21-01-2014	15	12	13.5	5
22-01-2014	18	13	15.5	3
23-01-2014	20	13	16.5	1
24-01-2014	18	11	14.5	0
25-01-2014	14	9	11.5	0
26-01-2014	20	10	15	0
27-01-2014	24	10	17	0
28-01-2014	24	9	16.5	0
29-01-2014	22	10	16	0
30-01-2014	21	10	15.5	0
31-01-2014	21	10	15.5	0
01-02-2014	20	11	15.5	0
02-02-2014	20	7	13.5	0
03-02-2014	28	9	18.5	0
04-02-2014	26	13	19.5	0
05-02-2014	25	12	18.5	0
06-02-2014	26	10	18	0
07-02-2014	26	15	20.5	0
08-02-2014	17	11	14	0
09-02-2014	20	7	13.5	0
10-02-2014	20	5	12.5	0

11-02-2014	22	6	14	0
12-02-2014	21	7	14	0
13-02-2014	23	6	14.5	0
14-02-2014	15	11	13	38
15-02-2014	18	9	13.5	0
16-02-2014	20	7	13.5	0
17-02-2014	22	10	16	0
18-02-2014	23	10	16.5	0
19-02-2014	23	7	15	0
20-02-2014	24	8	16	0
21-02-2014	25	9	17	0
22-02-2014	22	12	17	0
23-02-2014	22	12	17	0
24-02-2014	23	10	16.5	0
25-02-2014	25	10	17.5	0
26-02-2014	26	12	19	0
27-02-2014	25	13	19	0
28-02-2014	21	12	16.5	19
01-03-2014	20	12	16	0
02-03-2014	22	10	16	0
03-03-2014	26	11	18.5	0
04-03-2014	26	12	19	0
05-03-2014	27	14	20.5	4
06-03-2014	26	12	19	0
07-03-2014	26	11	18.5	0
08-03-2014	27	13	20	0
09-03-2014	29	14	21.5	1
10-03-2014	24	16	20	4
11-03-2014	27	15	21	10
12-03-2014	27	13	20	0
13-03-2014	26	13	19.5	0
14-03-2014	28	12	20	0
15-03-2014	30	13	21.5	0
16-03-2014	32	16	24	0
17-03-2014	34	16	25	0
18-03-2014	30	20	25	0
19-03-2014	28	16	22	0
20-03-2014	29	15	22	0
21-03-2014	32	14	23	0
22-03-2014	32	17	24.5	0
23-03-2014	28	18	23	0
24-03-2014	29	18	23.5	1
25-03-2014	33	17	25	0
26-03-2014	32	19	25.5	0
27-03-2014	29	20	24.5	2
28-03-2014	33	19	26	2
29-03-2014	32	19	25.5	0

30-03-2014	31	18	24.5	0
31-03-2014	31	17	24	0
01-04-2014	33	17	25	0
02-04-2014	35	18	26.5	0
03-04-2014	32	18	25	0
04-04-2014	32	18	25	0
05-04-2014	35	20	27.5	0
06-04-2014	38	20	29	0
07-04-2014	32	21	26.5	0
08-04-2014	32	19	25.5	0
09-04-2014	33	18	25.5	0
10-04-2014	34	18	26	0
11-04-2014	36	17	26.5	0
12-04-2014	37	19	28	0
13-04-2014	33	23	28	1
14-04-2014	34	21	27.5	0
15-04-2014	36	21	28.5	0
16-04-2014	34	20	27	2
17-04-2014	32	20	26	0
18-04-2014	30	19	24.5	7
19-04-2014	32	20	26	0
20-04-2014	34	19	26.5	0
21-04-2014	36	19	27.5	0
22-04-2014	36	20	28	0
23-04-2014	36	22	29	0
24-04-2014	37	21	29	0
25-04-2014	39	21	30	0
26-04-2014	39	22	30.5	0
27-04-2014	38	21	29.5	0
28-04-2014	39	21	30	0
29-04-2014	41	23	32	0
30-04-2014	42	23	32.5	0
Range (min-max)	**13-42**	**2-26**	**10-32.5**	**1-38**
Mean ±SD	**26.8 ±5.94**	**13.6 ±5.33**	**20.2 ±5.38**	**0.52 ±3.20**

(Source: http://www.accuweather.com/en/in/india-weather)