Saph Pani

Enhancement of Natural Water Systems and Treatment Methods for Safe and Sustainable Water Supply in India

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Report on strategies for enhancement of constructed wetlands and other natural treatment systems

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Authors	Dinesh Kumar and Shyam R. Asolekar [Section 1 to Section 5 of the Report] Priyanie Amerasinghe (IWMI), Shakeel Ahmed (CSIR-NGRI), Alexandre Boisson (BRGM), Mahesh Jampani (IWMI), Sahebrao Sonkamble (CSIR-NGRI) and Marina Alazard (BRGM) [Section 6 of the Report]
Reviewer	Dr. Saroj Kumar Sharma (UNESCO – IHE)
Contact for queries	Name: Prof Shyam R. Asolekar Phone:+91 022 2576 7876 Centre for Environmental Science and Engineering, Indian Institute of Technology, Bombay Powai, Mumbai-400076, INDIA. Phone: 91-22-25767851/52 Fax: 91-22-25764650 Email: asolekar@iitb.ac.in
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Abbreviations and acronyms

Abbreviation	Description	Dimension
BOD_5	Biochemical Oxygen Demand (5 day basis)	$mg.L^{-1}$
DO	Dissolved Oxygen	$mg.L^{-1}$
WHO	World Health Organization	
USEPA	United States Environmental Protection Agency	
MoEF	Ministry of Environment and Forests	
CPCB	Central Pollution Control Board	
CW	Constructed Wetland	
VF CWs	Vertical Flow Constructed Wetlands	
AP	Anaerobic Pond	
DP	Duckweed Pond	
FC	Faecal Coliform	MPN/100 mL
MP	Maturation Pond	
PP	Polishing Pond	
FP	Facultative Pond	
WHP	Water Hyacinth Pond	
HRT	Hydrolic Retention Time	
KT	Karnal Technology	
MLD	Million Liters per Day	
NTSs	Natural Treatment Systems	
RTD	Research Training and Development	
SFA	Sewage Feed Aquaculture	
SS	Suspended Solids	
STP	Sewage Treatment Plant	
SF	Sub-surface Flow	
TN	Total Nitrogen	$mg.L^{-1}$
NH_4^+ -N	Ammonia Nitrogen	$mg.L^{-1}$
NO_3^- -N	Nitrate Nitrogen	$mg.L^{-1}$
TP	Total Phosphorus	$mg.L^{-1}$
TSS	Total Suspended Solid	$mg.L^{-1}$

Abbreviation	Description	Dimension
WSP	Waste Stabilization Pond	
UASB	Up-flow Anaerobic Sludge Blanket	
F0	Filter media sand unplanted reactor	
FP (1, 2 & 3)	Filter media sand three different planted reactors	
J0	Juhu Beach sand unplanted reactor	
JP (1, 2 & 3)	Juhu Beach sand three different planted reactors	
M0	Crushed aggregate unplanted reactor	
MP (1, 2 & 3)	Crushed aggregate three different planted reactors	

1 The context and overview

Rampant growth in human population, unchecked exploitation of natural resources and urbanization have resulted in the generation of huge amounts of liquid and solid wastes. Generation of liquid wastes occurs predominantly due to domestic sewage. Indeed, safe, economic and effective treatment of sewage is one of the most challenging problems faced worldwide. Inadequate water supply and poor water quality have been provoking serious contemporary concerns for many municipalities, industries, agriculture as well as environment. India is facing a grave crisis with respect to water (in urban as well as rural areas) supplied for potable, domestic, agricultural, and industrial purposes while the available water resources are getting polluted due to disposal of partially treated and untreated domestic and industrial effluents. Although, the number of wastewater treatment plants has increased over the years in urban India, this increase is not adequate to keep pace with the escalating generation of wastewater. A large volume of wastewater continues to be discharged into natural watercourses leading to pollution of the coastal zones and drinking water reservoirs in India. About 38,254 MLD of sewage is generated from Class I and Class II towns, whereas the corresponding available treatment capacity is only 12000 MLD, indicating a large gap between sewage generation and treatment capacity in India (CPCB, 2009). Discharge of this untreated sewage into water courses both surface and ground waters is primarily responsible for water pollution in India.

1.1 Pollution of water bodies: the Indian context

Disposal of untreated or partially treated effluents into rivers and lakes, and runoff from urban and agricultural areas are the two main reasons responsible for deterioration of our drinking water resources.In India, hardly 10% of the sewage generated is treated effectively, while the rest of the sewage finds its way into the natural ecosystems, and can be accounted for large-scale pollution of rivers and ground waters. In addition, excessive withdrawal of water for agricultural and municipal utilities as well as use of rivers and lakes for religious and social practices, and perpetual droughts limits the capacity of natural water courses for dilution of wastes (Asolekar, 2002).

CPCB (2009) also reported the unsatisfactory operation and maintenance of existing treatment plants and sewage pumping stations; effluents of nearly 39% of treatment plants do not conform to the general standards prescribed under the Environmental (Protection) laws for discharge into streams. Moreover, in a number of cities, the existing treatment capacity remains underutilized while a lot of sewage is discharged without any treatment (CPCB, 2009).

Out of total sewage generated in all Class-I cities and Class-II towns of India, 93% is contributed by Class-I cities only. There are 35 metropolitan cities (with population more than 10 Lac) from where 15,644 MLD of sewage is generated. The existing treatment capacity in metropolitan cities is 8,040 MLD, which is 51% of total sewage generated. The sewage generated in class-I cities was estimated to be 35,558 MLD and treatment capacity exists for only 11,553 MLD in these cities, *i.e.*, only 32% of wastewater is being disposed after treatment, whereas the rest goes untreated. The generated sewage in class-II towns was estimated as 2,696 MLD and only 233 MLD treatment capacities exists in these cities which shows that only 8% of wastewater is being disposed after treatment.

1.2 Appropriateness of treatment technologies

Conventional mechanized wastewater treatment plants, involving primary and secondary treatment systems require large capital investments, and demand high operation and maintenance costs and hence do not seem to work effectively in India. Besides that mechanized treatment options do not consider the value of recovering organic waste resources and do not promote "front-end" recycling of treated water. On the other hand, natural systems for wastewater treatment work on the natural principles and usually require nominal operation and maintenance costs. Natural systems can also give the quality of water comparable to the effluents from highly mechanized and energy intensive treatment systems but the duration of the treatment would not be acceptable as treatment processes based on natural mechanisms are relatively slow. Large land area requirement is the second major constraint in adoption and advocacy of natural treatment systems. It is meaningful to give a clear sketch of the adequacy and candidature of treatment systems.Several features can characterize an appropriate wastewater treatment technology:

- The technology should be low-cost and have minimum possible mechanization, which reduces the risk of malfunction,
- The technology should be simple to operate, locally manufactured (at least constructed) as well as labor intensive (rather than power intensive),
- The technology should not rely upon expensive chemical inputs, such as chlorine for tertiary pathogen reductions to meet quality guidelines, and should be able to recover and reuse the resources as far as possible, and
- The technology should be capable of being incrementally upgraded as user demand or quality standards and treatment guidelines increase (Chaturvedi and Asolekar, 2002a).

Furthermore standardized engineering designs and performance control tools for such systems are urgently needed to ensure the sustainability and productivity of the system. Therefore, “appropriate” wastewater treatment technologies are required to enable communities to own, operate, and maintain the process equipment and the technology for wastewater management and, at the same time, offer ecological, environmental and societal benefits. In the last two decades several attempts have been made to develop alternative and appropriate systems for wastewater treatment with a major focus on reduction of the use of non-renewable resources (Geber and Björklund, 2002).

1.3 The need of the hour

Communities are thirsty for potable as well as process waters. In fact, for communities living in slums, getting even 10 litres of water per person per day has not been feasible. There is an escalating demand of water for domestic, agriculture, as well as industrial purposes on one hand and constant deterioration in the quality of available water due to disposal of domestic and industrial effluents on the other hand. The conventional mechanized wastewater treatment systems turn out to be rather expensive in terms of installation as well as operation and maintenance (O&M) costs. It is argued here that the newer solutions should be such that the peri-urban and small communities should be able to own and operate their wastewater treatment systems. Interestingly, in the recent past, communities have been accepting natural treatment systems (NTSs) that are capable of providing adequate treatment to wastewaters in conjunction with supplementing fish and nutrition to the food baskets of the fishing communities engaged in managing the systems, as well as generating adequate water for irrigation of farms and agro-forests. Above all, the engineered NTSs blend well with the agricultural, peri-urban, and rural ecosystems.

In the context of fulfillment of the demand of improving sanitation as well as execution of wastewater treatment systems, the Indian government has installed thousands of systems across the country. Also, after identifying the pulse of Indian community as well as opportunities of using favorable environmental conditions, many NTSs have been implemented in last four decades. Previously, the wastewater treatment systems were implemented to cope up with the regulatory standards prescribed by the regulatory authorities including Central Pollution Control Board (CPCB) as well as the State Pollution Control Boards (SPCBs). However, as the time progressed, India has faced the problem of shortage of water for various purposes and alternate search for reuse of treated water came into picture. Therefore, communities have started to look for systems that are simple in O&M, and also give the required quality of treated water with minimum possible input of energy and manpower.

1.4 Natural Treatment Systems: appropriate systems for wastewater treatment and reuse

A class of sewage treatment technologies that mimic natural processes such as interaction of soil-microorganisms with pollutants as well as interaction of plants and other life forms in natural settings with pollutants in wastewaters are called as Natural Treatment Systems (NTSs). It is well known that the engineered natural wastewater treatment systems including river banks, wet-zones and their modified versions such as constructed wetlands (CWs), waste stabilization ponds, sewage-fed aquaculture ponds, duckweed ponds or algal bacterial systems are known to render quite effective environmental services by treating biodegradable carbonaceous matter and by separating suspended loads of particulates. However, it should be noted that, among these wastewater treatment systems not all are particularly effective in removing nitrogen and phosphorus. In spite of their limitations, NTSs have attracted attention of environmental engineers and scientists by the virtue their abilities of treating sewages and wastewaters at phenomenally low O&M costs. They have been favourably looked upon in the third world countries, especially because of their low energy requirement.

The NTSs typically fill the gap in the sense that they need relatively low O&M costs and far low energy to run them when compared with conventional primary, secondary treatment alternatives such as activated sludge process, trickling filter or extended aeration system.

With this specific motivation, several NTSs have been proposed to be investigated thoroughly in *Saph Pani* Project by IITB team.

The CWs are most prone to engineering adaptation and modular applications and that is why these natural treatment technologies have been chosen as the theme technology for the current research project at IIT Bombay. Specifically, a pilot-scale sewage treatment plant (*Research Station*) based on CWs has been commissioned at IIT Bombay campus. The treated effluent generated from various modules of CWs will then be subjected to the membrane processing units in the laboratory set-up and investigation of possibilities of combining CWs with advanced tertiary treatment unit will be undertaken - which is the main focus in our present research.

1.5 Practices of natural treatment systems in India

There are different types of NTSs available and the most practiced in India include: Constructed Wetlands (CWs), Hyacinth and Duckweed Ponds (DPs), Karnal Technology (KTs) for on-land disposal of wastewater, Fish Ponds, Waste Stabilization Ponds (WSPs), Polishing Ponds (PPs), Oxidation Ponds and Lagoons and, Algal-bacterial Ponds.All wastewater treatment systems based on NTSs have been designed and operated in order to meet the regulatory standards prescribed by CPCB, New Delhi for reuse or discharge into the water body. The major reuses of treated domestic wastewaters from NTSs in India are irrigation of agricultural fields and gardens. Another substantial use has been for disposing into sewage-fed aqua-culture ponds. In most of the cases, the treated effluent from NTSs is directly reused in agriculture or disposed into nearby river.

It was found that PPs is the most commonly practiced NTSs in India, which contribute to nearly 53% of total wastewater treated by the means of NTSs (total load serviced by NTSs is around 1838 MLD).One of the impressive features of PPs is its versatility. For example, several PPs have been employed for municipal as well as industrial wastewater treatment all over India after UASB units for improving the quality of treated effluents by means of the anaerobic biological reactor. WSPs are also equally practiced and they account for nearly 45% of total wastewater treated by means of NTSs in India. However, KTs for on-land disposal of wastewater, engineered CWs as well as DPs were found to cater lower amount of wastewater as compared with total load serviced by NTSs, but their number are significant – which is the direct indication that these treatment technologies (KTs, CWs and DPs) are used as decentralised wastewater treatment systems. Therefore, the NTSs including KTs, CWs and DPs, which are at present treating relatively lower amount of wastewater, may play a significant role in development of proper wastewater management and treatment in India where low-density communities and varying site conditions prevails.

1.6 Scope and objective of the deliverable D3.3

The deliverable D3.3 titled “Report on strategies for enhancement of constructed wetlands and other natural treatment systems” is scheduled to be submitted at the end of M30 (*i.e.* before 1st April, 2014).The main objective of this particular study was “to identify strategies for enhancement of constructed wetlands and other natural treatment systems for treatment of wastewater and water reuse". This objective has been addressed from the beginning of the project by performing the respective sub-tasks listed under Tasks 3.1 and 3.2 – which are elaborated further in this report. Based on the achieved first milestone *i.e.* completion of detailed survey of existing CWs and other NTSs, the strategies for enhancement of constructed wetlands systems in particular and other natural treatment systems in general have been identified and reported. It would be useful to recall the contents and focus of Tasks 3.1 and 3.2 as elaborated in DOW as follows:

Task 3.1: Assessment of the potential of existing CWs and other NTSs for wastewater treatment and reuse across India

The overall aim of this task was to perform a survey of existing CWs and other NTSs across India and selection of engineered CWs and NTSs with special reuse potential and social relevance. Based on the national survey and assessment of CWs and other NTSs a few case studies were selected for further in-depth evaluation. The different sub-tasks performed for completion of Task 3.1 were as follows-

Sub-Task 3.1.1: A national survey of engineered CWs and other NTSs physical, geographical and social aspects as well as performance capacity of the engineered CWs and other NTSs has been compiled.

Sub-Task 3.1.2: Classification of CWs and other NTSs with an emphasis on reuse and/or social relevance

Based on the survey results, all systems have been classified and a few case studies been selected for further investigation. This selection was based on type, quantity, and special features of reuse of treated wastewater.

Sub-Task 3.1.3:In-depth evaluation of selected case studies

Selected case studies from sub-task 3.1.2 have been evaluated in detail for their reuse potential and other special functions. Integrated assessments linking health, environment, society, and institutions have been dealt with WP6.

Task 3.2: Identification of strategies for enhancement of the potential of shortlisted CWs and other NTSs

This task was aimed at identifying strategies for the enhancements of CWs and other NTSs. Concepts for performing this task was to improve their potential for treating wastewater to achieve reuse standards.

Sub-Task 3.2.1: Estimation of design parameters from existing plants (IITB)

A detailed study on design of CWs and other NTSs of selected existing plants were carried out to estimate the design parameters. It was essential to study how a particular wastewater treatment plant is designed and how it is being operated under the realistic situations and associated performance of the plant.

Based on these data, design parameters for the treatment systems were decided.

Sub-Task 3.2.2: Elaboration of possible ways to improve the treatment systems through incorporation of advanced mechanized as well as natural treatment technologies.

Under this task improvement options for NTSs such as CWs were elaborated in the following areas:

- Improving operational stability (e.g. reducing the clogging propensity) through incorporation of advanced pre-treatment mechanized treatment technologies.
- Selection of an ideally suited plant system and timing of harvesting periods
- Selection of an ideally suited filter media for CW systems for reducing the clogging propensity as well as to improve operational stability and performance
- Optimal arrangement of flow paths
- Improving operational reliability with varying feed water qualities

The dependency on operational procedures and maintenance of the alternative systems were taken into account. Optimal conditions were determined based on an India-wide review of good practice examples as identified in Task 3.1. These parameters were determined for alternative uses such as:

- Providing water resources or grey water supplies to communities after appropriate disinfection
- Providing process water for industry

1.7 Organization of the report

During preparation of this report, efforts have been made to articulate the strategies for enhancement of CWs and other NTSs for treatment of wastewater and water reuse by capturing the existing experiences with NTSs for wastewater treatment in India. In section 1, efforts have been made to articulate the context and overview of NTSs under which different aspects related with the imminent challenges and the present need of wastewater treatment and management in India, followed by the scope and objectives of deliverable D3.3 have been discussed. Section 2 covers the methodology adopted for development of strategies for performance enhancement of NTSs based on field experiences and focused research at IIT Bombay Campus. Section 3 summarizes the prevailing design practices for NTSs as well as estimation of design constants based on the performance of existing NTSs. In section 4, the elaboration of possible ways to improve the treatment systems through incorporation of advanced mechanized as well as natural treatment technologies has been given. The development of strategies for enhancement of performance of CWs through a focused research at IIT Bombay Campus has been presented in section 5. The section 6 summarises the findings of Musi River case study as natural treatment system for wastewater treatment and reuse. The last section *i.e.* section 7 covers the summary of the report.

2 Identification of strategies for enhancement of the potential of shortlisted CWs and other NTSs

This section summarizes the methodology adopted for identification and development of strategies for enhancement of the performance of CWs and other NTSs for wastewater treatment and reuse. A summary of recent focused research carried out at IITB has also been included. The focused research at IITB was a part of the buildup goal of development of strategies for enhancement of CWs and other NTSs.

2.1 Methodology adopted for development of strategies

The methodology for development of strategies was focused on CWs and other NTSs for wastewater treatment and reuse. The literature review presented in *Saph Pani* D3.1 (2013) suggests the possible methods of NTSs apart from CWs, including Water Hyacinth Ponds (WHPs), Duckweed Ponds (DPs), Lemna Ponds, Fish Ponds, Waste Stabilization Ponds (WSPs), Oxidation Ponds, Lagoons, Algal-bacterial Ponds, Polishing Ponds (PP), Karnal Technology (KT), *etc*. During the earlier study, the most practiced NTSs were reviewed and a questionnaire was developed for the collecting data from the field during the visit to the wastewater treatment plant based on the natural process. The questionnaire was developed after a broad discussion with experts, along with the inputs of WP3 partners as well as other partners of the *Saph Pani* Project.

2.1.1. Phase I assessment (rapid assessment of NTSs)

In the next step, a tentative list of currently operated NTSs across India was made with the help of various water and wastewater practitioners as well as governing and regulatory bodies, including state pollution control boards, public health engineering departments of different states, and water and sewerage boards. Among the operated engineered NTSs across India, the prospective sites were selected for rapid assessment. During the rapid assessment, on-site data related with technical, physical, geographical as well as social aspects of the engineered CWs and other NTSs were collected. The secondary data were collected by interviewing the operating staff of the respective STPs as well as by utilizing the literature, log books, and progress reports supplied by the respective personnel.

At the same time, the personal views of the operating staff of the respective STPs related to the following focused queries were also recorded:

- past record performance of STP for their consistency in achieving the design goals as well as in meeting the regulatory limits for discharge or reuse of treated wastewater for various applications,
- common issues faced by the operating authorities since commissioning and operation and maintenance in the current settings,
- assessment of the design of the treatment system as well as their flow regime,
- assessment of the treatment units involved in the treatment train,
- day-to-day and seasonal variations in the performance of the system and the influencing factors including climate, system design *etc*.,
- the common troubleshooting occurrences in day-to-day operation of the treatment system,
- any specific need for the improvement in their operation,
- any social issues faced by the plant operators for operation and maintenance of the systems,
- any nuisance due to the system in past and its cause,

- Socio-economic benefits of the treatment system to the nearby community *etc*.

To arrive at the common conclusions based on the rapid assessment results, the pictures of all different treatment units installed and surrounding location/community were also taken from various viewpoints which helped during discussion with experts for making proficient opinion in development of strategies for enhancement of the performance of NTSs. At the completion of first phase of the assessment of NTSs, 41 locations were visited (depicted in **Figure 2.1**) and the various aspects were discussed among the experts for making the common opinions on the defined goals. The outcomes of the rapid assessment survey results have been summarized as follows which eventually helped in arriving at the common conclusion.

- Gap between sewage generation and treatment capacity for class I cities and class II towns,
- regulatory concerns of wastewater treatment, reuse and disposal
- Indian practices for using NTSs,
- various agencies involved for establishing as well as O&M of NTSs,
- generalized treatment train adopted for wastewater treatment at various types of NTSs,
- hydraulic loading, compliance status and overall performance for wastewater treatment,
- integrated practices of wastewater treatment, aquaculture production and post-treatment to treated wastewaters and,
- summary of the available post-treatment and reuse of the wastewater effluents from CWs and other NTSs in India

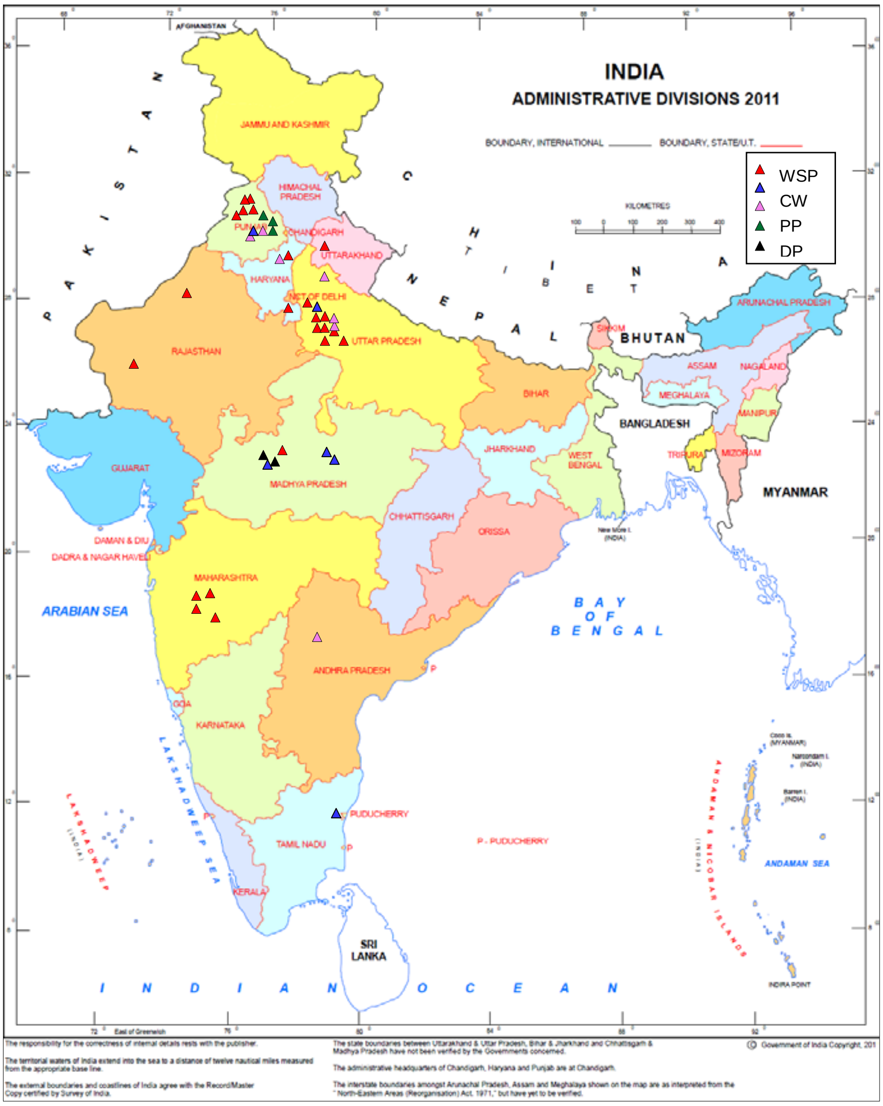


Figure 2.1: Locations of NTSs visited across India during the field visits

2.1.2. Phase II assessment (in-depth evaluation of selected NTSs)

After the completion of the rapid assessment of NTSs across India, representative sites were selected for in-depth assessment during the second phase. The primary aim of selection of prospective sites of NTSs for in-depth evaluation was to investigate if these systems are the most appropriate and representative systems so that the experiences may be replicated in any part of India or world. Although numerous sites of CWs and other NTSs are available in India, only engineered ones were selected for this study so that the treatment process and governing equations can be simulated at any other location if the treatment system gives overall better pollutant removal efficiency with relevance to recycle and reuse of treated wastewater. During the in-depth evaluation of NTSs, the treatment plants were studied with a special emphasis on the reuse potential of treated wastewater and an integrated assessment of STPs, linking health, environment, society, and institutions, was carried out.

The prospective sites selected for in-depth evaluation have been depicted in **Plate 2.1** and in **Table 2.1**.

1: 14.5 MLD, Waste stabilisation pond, Mathura

2: 50 KLD, Constructed wetland, Agra

3:14 MLD Polishing pond, Agra

4: 0.5 MLD Duckweed pond, Ludhiana

5: 8 MLD Sewage fed aquaculture, Karnal

Plate 2.1: Selected NTSs for in-depth evaluation studies

Table 2.1: NTSs selected for in-depth evaluation

Sr. No.	Name of NTSs	Location (State)	Organizations Involved in Assessing the NTSs
1	14.5 MLD, Waste stabilisation pond	Mathura (Utter Pradesh)	IITB, CEMDS
2	50 KLD, Constructed wetland	Agra, (Utter Pradesh)	IITB, CEMDS
3	14 MLD Polishing pond	Agra, (Utter Pradesh)	IITB
4	0.5 MLD Duckweed pond	Ludhiana, (Punjab)	IITB, CEMDS
5	8 MLD Sewage fed aquaculture	Karnal, (Haryana)	IITB

2.1.3. Phase III assessment (performance evaluation and estimation of design constants of selected NTSs)

In third phase, five NTSs based on various treatment technologies were selected and wastewater samples were collected to assess the quality of raw and treated effluents. The detailed study on design of selected CWs and other NTSs was carried out to estimate the design parameters. It is essential to study how a particular plant is designed and how it is being operated in association with the observed plant performance. Based on these data, design parameters for the treatment systems along with rational approaches for design have been proposed.

2.2 Development of strategies for enhancement of the potential of shortlisted CWs and other NTSs

Based on the extensive India-wide field visits to CWs and other NTSs, the strategies have been shortlisted. The aim for the identification of these strategies was to enhance the performance of CWs and other NTSs. The basic concept was to improve their potential for treating wastewater in order to achieve reuse standards. The strategies were identified after a broad discussion among the experts on various aspects of NTSs. Also, the on-going research findings on enhancement of the performance of NTSs around the world have been included.

2.3 Focused research on CW for development of strategies for performance enhancement

For the development of strategies especially for CWs, a focused research has been conducted for its enhancement. The key issues impairing the system performance identified during the field research have been addressed and development strategies have been formulated. The following key points have been decided for the focused research on CWs for its enhancement:

- Selection of an appropriate plant system for better removal of pollutants
- Feasibility study for the use of alternate porous media to improve the nutrient removal performance of CW systems
- Assessment of CW plant biomass for various applications
- Study on removal of nutrients and carbonaceous pollutants from sewage using CW

3 Design practices and associated performance of NTSs

This task was aimed at identifying strategies for the performance enhancement of CWs and other NTSs with a focus to improve their potential for treating wastewater to achieve reuse standards. In order to achieve this task, two major sub-tasks namely, estimation of design parameters from existing plants and elaboration of possible ways to improve the treatment systems were studied. There are many factors that may affect the performance of the NTSs, therefore several approaches have been given for designing.

The important approaches used for designing of NTSs have taken into account before estimation of design parameters from existing plants. The aim of this activity was to assess the performance of the selected NTSs based wastewater treatment plants with reference to their design based on theory versus operation under practical conditions.

3.1 Design and performance of waste stabilization ponds

The various approaches for design of WSPs that have been adopted so far can be characterized as follows:

<u>Approach 1</u>: based on loading rate and residence time,

<u>Approach 2</u>: based on empirical design equations, and

<u>Approach 3</u>: based on modelling of hydrodynamics as well as biological and chemical reaction kinetics.

"Approach 1" based on loading rate and residence time for the process design of pond systems has been very commonly used throughout the world. For example, in New Zealand, a figure of 84kg BOD/ha.day, *as cited in* Shilton (2001), has been routinely used for facultative pond design regardless of the marked differences in environmental conditions throughout the country. "Approach 2", the design based on the empirical equations and regression coefficients, attempts to account for numerous variables that may have influence on pond performance, but they still treat the ponds as a 'black box'. This approach, too, does not give attention to mechanisms of reactions and changes (Shilton, 2001). Furthermore, it is questionable how applicable it would be to different ponds because an equation derived from regression of particular data will give of best fit for that data only. In the context of hydraulics, for example, such equation would again be incapable of differentiating between different pond shapes, inlet designs etc. Thus, these two approaches have been reported to be debatable when they are applied to different locations (Finney and Middlebrooks, 1980 *as cited in* Shilton, 2001).

The design based on the bio-reactor theory (*i.e.* “Approach 3”, listed above) has received greater attention from engineering scientists and technologists around the world (Arceivala and Asolekar, 2006; Metcalf and Eddy, 2003; Mara and Pearson, 1998; Mara, 1997). Mara and Pearson (1998) proposed the use of ideal Continuous flow Stirred Tank Reactor (CSTR) model for design of pond systems. A number of researchers opposed the application of ideal CSTR model because the typical ponds have far larger lengths and breadths when compared with their depths. The approach of Wehner and Wilhem (1956) for degradation of substrate “S” with pseudo first order degradation kinetics using a plug-flow idealization of the reactor was recommended. Based on the observations from several ponds and after considering their non-idealities, Chaturvedi (2008) pointed out that ponds should be designed to achieve minimum possible scouring and re-suspension of benthic sediments by maintaining laminar flow regime in the ponds in conjunction with the design conditions to minimize short-circuiting and non-ideal flows. Consequently, channels, manifolds, weirs, splitter boxes, or a network of nozzles or pipes devised with a series of openings separated by appropriate distance have been suggested for introduction of wastewater into the ponds rather than a single point inlet. Furthermore, it was also recognized that a careful decision-making is required to adopt adequate depth of pond and Reynolds Number so as to ensure mixing and desirable flow of bulk liquid in axial direction. Thus, an algorithm for design of pond systems, giving consideration to the aforementioned points was proposed to achieve a superior quality of water suitable for a variety of uses and at the same time minimize capital and operating costs of the pond.

According to Arceivala and Asolekar (2007) the size of a pond may be determined from the viewpoint of substrate removal rate at the prevailing temperature beside oxygen utilization and the higher of the two values should be used so that desired performance is obtained. In the presence of oxygen, aerobic bacteria produce CO_2 from organic carbon, nitrates from organic nitrogen, phosphates from organic phosphorus, and sulphate from organic sulphur.

Practically the dispersed flow conditions prevail in the treatment ponds, *i.e.*, each element of the incoming flow resides in the treatment pond for a different period of time. Such a condition is also called intermixing flow and lies between the two established ideal flow conditions, namely, plug flow and completely mixed flow. Thus, dispersed flow is a non-ideal case and can, in fact, be used in practice to describe the flow condition in most large reactor like lagoon and ponds.

Using Fick`s second law but replacing the diffusion coefficient therein by a dispersion coefficient, D, the concentration is given as:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

C = concentration of substance, mass/volume

D = axial or longitudinal dispersion coefficient (= L^2/t),

X = distance L in the direction of the main flow, Taking a steady state differentials balance at any cross-section in a reactor.Levenspiel (1962) obtained the following general equation for any reactant following nth order kinetics:

$$D\frac{\partial^2 c}{\partial x^2} - U\frac{\partial C}{\partial t} - KC^n = 0$$

U= mean flow velocity along reactor L/t,

L = the length of axial travel in reactor

K= removal rate constant, per unit time

n= order of the reaction

Equation (2) was solved for first order kinetics by Wehner and Wilhen (1956) with regard to chemical engineering processes, but has found increasing applications in designing of wastewater treatment processes. For reactions other than that of first-order, only a numerical solution is possible. Fortunately, in wastewater treatment, most processes of interest involving removal of organic substrate are of the first-order type and can be represented with the following equation:

$$\frac{S}{So} = \frac{4ae^{1/2d}}{(1+a)^2.e^{a/2d} - (1-a)^2.e^{-a/2d}}$$

where a = $\sqrt{1 + 4k_p t.d}$

d = D/UL= Dispersion number (dimensionless)

D= Dispersion coefficient, m^2/hour

U = Flow velocity, m/hour

L = Length of flow, m

S_o and S= initial and final substrate concentrations (mass/vol.) respectively.

This method gives a more realistic value of K_p (substrate removal rate per unit time) since it takes into account the actual flow pattern (and, therefore, the actual residence time of fluid elements in the pond) rather than assumed ideal flow patterns. Moreover, as substrate removal is assumed to follow first-order kinetics, the removal rate also depends on the initial substrate concentration in the pond. The K_p value, in case of facultative units, is also a composite value, the result of partially aerobic and partially anaerobic activity. A comprehensive description of the laboratory study carried out for determining K_p values can be found in Arceivala (1980).

Analyzing pond data for domestic sewage from USA, Canada, Thailand, India, and elsewhere, after taking actual dispersion condition and loading into account, Arceivala (1981) gives the following equation:

K_p(20 ºC) = 0.132 log (BOD_U load) − 0.169

In practical, K_p values at 20 ºC are found to vary, in most cases, from 0.10 to 0.15 depending on the ultimate BOD load in the pond as indicated in **Table 3.1**(Arceivala, 1981).If during designing, the pond load (BOD_U) is not known, it would be safe to assume the BOD_U load to be equal to oxygen co-produced by algae, kg/ha/day.

Table 3.1: Reported K_p values at different organic loading rates

BODu Load kg/ha-day	K_p (20 ^oC) Per Day
100	0.10
200	013
300	0.15

Source: Arceivala (1981)

In the design procedure used by Asolekar and Langote (2004), the K_p values were found to be similar, *i.e.*, they varied from 0.13 to 0.20 per day at 25^0 C, the lower value being applicable to facultative ponds with a depth of 2.5 m or more and the higher value to aerobic ponds with a depth less than 2.5 m. However, the effect of pond loading on the $K_{p,}$ values has not been taken into account by them.

If the average temperature in the pond is expected to be less than 20 ^0C, the K_p value obtained from a particular pond load should be corrected for temperature using

K_p (T ºC) = K_p (20 ºC) $(1.035)^{T-20}$

The detention time required for any desired efficiency and flow pattern is determined using the Wehner-Wilhem equation as indicated:

- determination of substrate removal efficiency using the dispersed flow model
- determination of substrate removal efficiency under different types of mixing conditions using the dispersed flow model

It should be noted that the mixing condition in a pond has a considerable effect on the detention time requirement for a given efficiency. For instance, a pond of only half the size would be required if the flow pattern is plug flow rather than complete mixing. The use of dispersed flow models gives the designer an opportunity to choose the flow pattern to be adopted based on the objective of treatment.

The equal-size cells-in series model has often been used with success in case of domestic or municipal wastewater as two or three cells in series usually gives an overall D/UL value of around 0.2 to 0.7.However in other cases, unequal-sized cells may be advantageous to use, where the first cell is designed to be larger than the following cells, thereby promoting well mixed condition in the first cell, with the flow pattern shifting towards plug flow in the following cells. This flexibility has an added advantage especially when dealing with certain industrial effluents or in case of uneven terrain.

If completely-mixed flow regime is desired in a pond, the pond should either be more squarish in layout with just a single inlet or the same volume can be split into two or three cells in series with incremental feed.

Chaturvedi (2008) proposed an algorithm for rational design of pond systems, which was developed using the models based on dispersed flow regime in pond and describes the conservation of substrate in conjunction with the process of biodegradation as well as die-off of pathogenic organisms. The proposed model was calibrated to yield rate constants for organic biodegradation (k) and bacterial die-off (k_b) using field data, physico-chemical parameters, as well as overall oxygen mass transfer coefficient (K_L).Rate constants estimated during calibration of the models along with primary inlet data from fields were used to validate the models. The outlet concentrations thus estimated were found comparable with the actual primary data collected from field. The calibrated and validated rate constants were also used as a diagnostic tool to assess the performance of any other comparable sewage treatment plants.

Estimation of parameters for waste stabilization pond using the field data: Efforts were made to estimate rate constants (for processes like oxygen transfer, organic biodegradation, and bacterial die-off) by collecting primary and secondary data from field and using the algorithm developed by Chaturvedi (2008). It is important to note that although the proposed model is capable of stipulating 99.9% removal of faecal coliforms and achieves the effluent BOD_5 to less than 10 mg/L, these features were disabled in calibration mode (parameter estimation). Thus, the model was used to estimate system parameters biodegradation rate constant (k) and bacterial die-off rate constant (k_b) by inputting actual inlet and outlet data from pond system *viz.* pond systems at Karnal, Haryana in India.

Parameter estimation for STP at Kathal Road, Karnal, Haryana

Location ID: India_HR_1_WSP

The WSP of capacity 8 MLD is performing satisfactorily in achieving design norms of treated effluent. At this STP, facultative and maturation ponds are being utilized for pisciculture. Sometimes, fish-kills have been reported in the facultative pond due to high organic loading. In the situation of fish killing, plant operators are using lime to precipitate suspended particulate matter in the facultative pond. The pisciculture activities in WSP treatment units during sewage treatment are generating the revenue of about INR 10 Lakh per year. The treated effluent is directly used in irrigation without performing any disinfection process, as there are no means available for microbial decontamination at the treatment site.

Input data:

1. Wastewater flow :8.01 MLD
2. Inlet BOD_5 :78 mg/L
3. Outlet BOD_5 :12 mg/L
4. Temperature :25 °C
5. TDS :1000 mg/L
6. Dimension of AP ((L W) xh) : 6336m^2 x 4m
7. Dimension of FP ((L W) xh) : 67324m^2 x 1.25m
8. Dimension of MP ((L W) xh) : 67324m^2 x 1.25m
9. System Properties:

Property	**at 25 ºC**
[a] μ (kg/m s)	0.893×10^{-3}

[b]	ρ (kg/m^3)	997
[c]	C_A*(kg/m^3) for pure water	9.08 x 10^{-3}
[d]	C_A*(kg/m^3) for wastewater having salinity 1000 ppm	8.19 x 10^{-3}

μ = viscosity of the wastewater; ρ = mass density of wastewater; C_A*= Interfacial saturation concentration of oxygen in water governed by the Henry's law (*i.e.* solubility of oxygen in wastewater)

The input data and system properties were used in estimation of overall oxygen mass transfer coefficient (K_L) as well as rate constants for substrate biodegradation (k) and bacterial die-off (k_b) for the STP at Karnal in Haryana were estimated by using the approach proposed by Chaturvedi (2008).

Estimation of overall oxygen mass transfer coefficient (K_L): As the wastewater received at the inlet of STP at Karnal have greater amount of sullage and negligible amount of sewage, K_L value for this system comes around 1.08 x 10^{-5} m/s.

Estimation of biodegradation rate constant (k) and bacterial die-off constant (k_b): The stepwise calculations as suggested by Chaturvedi (2008) were used for parameter estimation at STP at Karnal. Finally, constants for the substrate biodegradation rate (k) and bacterial die-off rate were estimated (the values of K_L, k, and k_b). The biodegradation rate constant (k) for the STP at Karnal at various locations were estimated to be 0.293 – 0.386 d^{-1} in anaerobic ponds, 0.077-0.099 d^{-1} in facultative ponds, and 0.34 d^{-1} in maturation pond while bacterial die off rate constant (k_b) for the STP at Karnal at various locations was found to be 32.5 d^{-1} in anaerobic ponds, 0.01 d^{-1} in facultative ponds, and 0.45 d^{-1} in maturation pond.

3.2 Design and performance of CWs

Batchelor and Loots (1995) have given some process design norms for CWs with subsurface flow in South Africa as shown in **Table 3.2**. These norms cannot be applied directly to warm climate country like India without adjustment.

For the design of macrophytes beds with horizontal flow, two important aspects of design have to be kept in mind. These are, 1) organic removal parameter, and 2) hydraulic flow consideration which are described below:

Table 3.2: Process design norms for subsurface flow wetlands for treating raw domestic wastewaters in India

Parameters	Typical values	
	European Literature	Recommended for India
Area requirement, m^2/person	2.0-5.0	1.0-2.0
BOD_5 loading rate, g/m^2-day	7.5-12.0	17.5-35.0
Detention time ,days	2-7	2-3
Hydraulic loading rate, mm/day	(Must not exceed hydraulic conductivity of bed)	
Depth of bed, meters	-	0.6-0.9
Porosity of bed, % (typical)	-	30-40
1st Order reaction constant, K_T/day	-	0.17-0.18
Evapotranspiration losses, mm/day	10-15	>15

(Adapted from Arceivala and Asolekar, 2006)

Design for organic removal: BOD removal has been approximated by first order, plug flow kinetics. On the basis of the European design and operation guidelines for these systems, Green and Upton (1944) gave the following based on first order kinetics, which has also been used at Severn Trent, UK, for design of constructed reed beds for polishing wastewater treated effluents from small communities:

$$C_t = C_0 e^{-kt}$$

Since t is a function of bed area, we can also write

$$A = \frac{Q(InC_o\_InC_t)}{K_{BOD}}$$

In which

A = Bed area (m^2)

Q = Average flow (m^3/day)

C_o = Inlet BOD_5 (mg/l)

C_t= Outlet BOD_5 (mg/l)

K_{BOD} = BOD_5 reaction constant (day^{-1})

Hydraulic considerations in design: The dimensions of the reed bed can be derived from the following two assumptions by applying Darcy`s Law:

Hydraulic gradient is equivalent to a slope of 5 percent. Hydraulic conductivity will stabilize at around 1×10^{-3} m/sec (86.4 m/day) as the reed bed is fully established. Values as high as 500 m/day have been recorded in India.

The formula is:

$$A = \frac{Q}{K_f(\frac{dH}{dS}) \times 86{,}400}$$

Where

A_C = Cross-sectional area of the bed (m^2)

Q = Average flow (m^3/day)

K_f = Hydraulic conductivity (m/sec)

dH/dS = Slope (m/m)

Estimation of design parameters from existing plant based on CW: For estimation of design parameters from existing CW based STP (Location ID: India_UP_10_CW), the decentralised wastewater treatment system at Kachpura slum, Agra, India was selected. This treatment plant was established under Cross-cutting Agra Program (CAP) for low-income communities for treatment of domestic wastewater, with the aim to improve the sanitation conditions in the slum areas. The system was installed in year 2002 with financial assistance from Water Trust UK and London Metropolitan University, and technical support from Vijay Vigyan foundation. The capital cost for establishing the system was of INR 10-11 lakhs and per year operation and maintenance cost was around INR 70,000. The system treats approximately 50 KLD of the total wastewater which it receives from 5 clusters of slums through a common drain. The remaining untreated wastewater flows through parallel drain into the major drain that connects to the River Yamuna.

The system comprises of screen chamber which prevents the solid waste from entering into the system. The wastewater then enters into a three-chambered septic tank. After primary treatment, it goes to nine-chambered baffled anaerobic reactor filled with gravels. After primary treatment, the wastewater goes to planted filter bed for root zone treatment. The bed has been filled with three different types of filter media (white river pebbles, red stones and gravels) and planted with *Canna indica*. The performance of the system happens to be satisfactory in terms of pollution removal. The treatment system is being properly operated and maintained by local people appointed for O&M. The local community of Kachpura without any disinfection reuses the treated wastewater for horticulture and irrigation purpose.

The various design parameters estimated from existing wastewater treatment plant operated at Kachpura slum, Agra, India are depicted in **Table 3.3**.

Table 3.3: Estimation of design parameters for CW based STP

Parameters	Typical values	
	Design Value	Performance Value
Area requirement, m^2/person	1.0-2.0	--
BOD_5 loading rate, g/m^2-day	17.5-35.0	38
Detention time ,days	2-3	2-3
Depth of bed, meters	0.6-0.9	1
Porosity of bed, % (typical)	30-40	30-40
1^{st} Order reaction constant, K_T/day	0.17-0.18	0.33
Evapotranspiration losses, mm/day	>15	>15

3.3 Design and performance of polishing pond

The design of facultative/polishing ponds focuses on BOD removal. Mara (1997) described how the design of facultative ponds is currently based on rational and empirical approaches. The empirical design approach is based on correlating performance data of existing WSPs. The rational design approach models the ponds performance by using kinetic theories of biochemical reactions in association with the hydraulic flow regime.

Estimation of design parameters from existing plant based on UASB-PP:For estimation of design parameters from existing UASB-PP based STP (Location ID:India_UP_3_PP), of capacity 14 MLD at Jaganpur, Dayal Bag, Agra was established under Yamuna Action Plan II, for treating domestic wastewater of Agra city. The PP was installed after UASB unit for upgrading quality of secondary treated effluent. The STP is performing satisfactorily in achieving design norms of treated effluent. The treated effluent from PP is disinfected before it is discharged into the Yamuna River.

The various design parameters estimated from existing wastewater treatment plant operated at Jaganpur, Dayal Bag, Agra, India are depicted in **Table 3.4**.

Table 3.4:Estimation of design parameters for polishing pond

Parameters	Typical values	
	Design Value	Performance Value
HRT (days)	1	2
Surface loading rate (Kg/ha/day)	122.9	61.46
Organic matter removal efficiency (%)	57	64
Pathogen removal (%)	--	89

<u>Design and performance of duckweed pond</u>: Yield of duckweed biomass to give the desired fish production for marketing. Where the objectives have to be met, the duckweed pond size has to be calculated separately for both purposes and the larger of the two should be adopted. The detention time required to give the desired effluent quality is still estimated on a thumb-rule basis, based on a few measured values of BOD, TSS and TKN at different detention times in laboratory and field studies.

4 Elaboration of possible ways to improve the treatment systems through incorporation of advanced mechanized as well as natural treatment technologies

Under this task, improvement options for NTSs were elaborated in the following areas:

- Improving operational stability (e.g. reducing the clogging propensity) through incorporation of advanced pre-treatment mechanized treatment technologies.
- Selection of an ideally suited plant system and timing of harvesting periods
- Optimal arrangement of flow paths.
- Improving operational reliability with varying feed water qualities

Optimal conditions were determined based on a country-wide review of best practice examples based on the applicability of treated effluent for alternative uses such as providing water resources or grey water supplies to communities after appropriate disinfection, providing process water for industry, *etc*. as completed in task 3.1, as well as the utilisation of NTSs as a pre-treatment option before an advanced water reclamation system, which will be investigated in the pilot study (task 3.4). Some of the important factors that should be considered while deciding upon a strategy to improve the treatment efficiency of NTSs include rate, extent and variability of wastewater reaching the system, climate changes, population changes, pattern of urban and industrial development, changes in agricultural practices, soil erosion and sedimentation, scope of construction activities in nearby areas, nutrient loading, *etc*. The elaboration of possible ways to improve the efficiency of NTSs comprises of the most common and best practices that have been employed at the existing NTS based wastewater treatment plants to enhance their performance with regard to their specific objective in the treatment train.

Moreover, the specific objectives of the “Report on recommendations for enhancement of constructed wetlands, D3.4 Report”, which will be submitted in month 36 are also in progress.

4.1 Waste stabilization ponds

Various kinds of ponds and lagoons have been employed to treat wastewater as a part of NTSs. Lagoons are water bodies confined within natural boundaries while ponds are manmade and shallow. These water bodies are classified based on different ubiquitous conditions in the system as aerobic, anaerobic or facultative. Facultative ponds have two zones of treatment within a system: aerobic on the surface and anaerobic at the bottom.

Facultative ponds are commonly employed in both the systems *i.e.* stabilization pond as well as oxidation pond. Existing stabilization or oxidation pond can be upgraded to facultative pond by decreasing surface BOD loading rate or increasing detention time or both. In case of wastewater coming from cities, a large amount of sand, grit and other inert material might be present, which makes cleaning of ponds imperative. WSPs commonly involve series of anaerobic, facultative and aerobic ponds. The cell first in order is called primary cell and generally consists of two parallel cells to avoid overloading.

The best operation of WSPs is achieved when complete pond is utilized regardless of cell number. The optimum total nitrogen level to produce maximum algal biomass is about 100mg/l (RIRDC, 2003). Short-circuiting is a condition when no water movement happens in a portion of pond. It may be caused because of faulty design of inlet and outlet piping or excess growth of weeds (USEPA, 1977).

For aerobic ponds, the primary cell should be maintained at high *p*H and adequate DO, which can be verified by deep green colour of water. The minimum DO maintained should be 1mg/L. The surface of water should be free of weed plants and oil. This can be checked by wave action on the water surface during windy conditions. This facilitates mixing of water and dissolution of oxygen from the atmosphere in to the water body. Dikes should be planted with grass and kept well mowed to avoid soil erosion and insect problems. Mechanical equipments involved in the system should be well maintained and lubricated at regular intervals. In case of anaerobic ponds, surface of water should be covered with a dense scum mat to avoid oxygen transfer and odour problems. The pH should be maintained near 7 to maintain proper bacterial balance.

4.2 Oxidation ponds

These are the generally employed as polishing ponds to improve quality of treated water from UASB unit. This system also consists of series of ponds but influent is treated water unlike stabilization ponds. It serves as a secondary treatment option. The depth of ponds is shallow in the range 0.5 to 1 meter to provide good natural aeration. In case of UASB polishing pond the purpose is to remove pathogens as well as decrease the oxygen demand of influent. The strategy of improvement is same as aerobic ponds discussed in section 4.1.

4.3 Duckweed ponds

In DPs, thin mat of duckweed grows at the surface of water which maintains anaerobic conditions in the pond. Mkandawire and Dudel (2005) reported that growth of duckweed was restricted above 34^{0}C and also *p*H sensitive. Also, it avoids dissolution of oxygen from atmosphere, traps odour in the system, and prevents breeding of mosquito and growth of algae. Commonly encountered problems in DPs include accumulation of sludge, floating matter and grit in the pond. These problems can be avoided by installing primary sedimentation tank in the system. The roots of duckweed plants are small in size and play no direct role in removal of pollutants especially nutrients. Mechanism of removal is mainly same as in case of conventional wastewater treatment system. The system works under slow current water and gets adversely affected in case of momentarily high flow or flooding

(Oron *et al.* 1988). This can be avoided by construction of equalization or collection tank in the beginning. Short-circuiting is another problem faced by DPs and invariably in most of the pond based system. This can be solved upto a major extent by proper designing like multiple inlet and outlet system. The doubling time of duckweed plant is 4 days under optimum conditions and grows vigorously (Harvey and Fox, 1973). Also, death and decay of plant leads to increase in total suspended solids especially during autumn conditions (Zirschky and Reed, 1988). Therefore, regular harvesting is required to maintain appropriate conditions for wastewater treatment. The anaerobic conditions of the pond system make it necessary to perform aeration of DPs effluent (Zirschky and Reed, 1988). This can also be a solution to the problem of low nitrogen removal in DPs as nitrification is poor (Bonomo *et al.,* 1997). Schumacher and Seoulov (2002) reported that the algae can take up ammonia while Bonomo *et al.* (1997) reported adsorption of other forms of nitrogen on the surface of algae. Caicedo (2005) suggested introduction of algal zones in DPs can increase removal of nitrogen from the wastewater due to increase nitrification activity by photosynthetic release of oxygen by algae.

4.4 Hyacinth ponds

Water hyacinth is fast growing perennial aquatic macrophyte and prolific free floating aquatic weed. Water hyacinth efficiently removes the heavy metals and other pollutants with high reproduction rate, efficiency and tolerance to ecological factors (Gupta *et al.,* 2012). Macrophytes like water hyacinth aid in the removal of nutrients by biomass uptake and also increase the sedimentation of pollutants (Schulz *et al.*, 2003). Appreciable removal of inorganic nitrogen and phosphorus has been reported when water hyacinth was employed in nutrient or metal-rich wastewaters (Lu *et al.*, 2009). Some parameters that affect growth of plant include pH, temperature, salinity and solar radiation (Gupta *et al.,* 2012). Maximum biomass yield occurs during summer (Reddy *et al.,* 1983) with optimum temperature being 28 – 30ºC (Gupta *et al.,* 2012), where the temperature above 33ºC is inhibitory (Center *et al.*, 2002). Low temperature of -3ºC for 12 hours destroys leaves of plant where as temperature of -5ºC for 48 hours destroys complete plant (USEPA, 1988). Stephenson *et al.* (1980) reported that at temperature between 0.5 to -5ºC, the plant can sustain for 24 hours only but at temperature -6 to -7ºC the plant would die. Also, it was concluded that plants will not grow in areas with average winter temperature below 1 ºC. Therefore, water hyacinth pond system is not suitable for areas with cold temperature (Clough *et al.*, 1987). The growth is also disturbed by low humidity of 15 - 40% (Allen *et al.*, 1997). The plant can tolerate *p*H range of 4 - 10 (Gendy *et al.,* 2007) whereas optimum range is between 5.5 - 7 (Lu *et. al.*, 2009). Reddy *et al.* (1991) reported that minimum concentration of N and P required for survival of water hyacinth is 5.5 and 1.05 mg/L where maximum growth occurred when nitrogen, phosphorus and potassium concentration was 20, 3 and 52 ppm, respectively. The ratio of nutrients plays a more important role than the concentration of nutrients. Maximum growth was found at N/P ratio of 3.6 (Ekholm, 2008). Delgado *et al.* (1994) have reported that water hyacinth prefers ammonium over nitrate as the main N source. That proves that water hyacinth pond can be installed after UASB treatment as a polishing step to remove ammonia nitrogen. The overall phosphorus requirement of plant is less as compared to total nitrogen (Reddy *et al.*, 1990). Many authors have reported that transpiration loss from open surface was greater than from vegetated surface (Allen *et al.*, 1992; Glenn *et al.*, 1995) but it has been found by few researchers that evapotranspiration loss from water hyacinth is 3-10 times as compared to open surface (Gopal 1987; FNI,1987). According to Valipour *et al.* (2011) and Atkinson and Smith (1983), water hyacinth cannot tolerate salinity above 2 ppm whereas Haller *et al.*(1974) reported that it can tolerate salinity upto 2500 mg/kg of body weight. Water hyacinth can convert alkaline *p*H into neutral (Dipu *et al.*, 2011). The concentration of nitrate should not be very high as reported by Ayyasamy *et al.* (2009) as it will lead to lower removal of nitrate by plants due to increase in osmotic pressure. Nitrate removal is also affected by presence of other nutrients like phosphate and sulphates (Ayyasamy *et al.*, 2009).

4.5 Constructed wetlands

CWs are generally used as a polishing step in western countries. In the current study, CWs are suggested as secondary treatment unit, which means higher loading rate of pollutants as compared to polishing stage. This resulted in significant increase in land requirement for satisfactory treatment. Two types of wetlands are commonly employed, 1) Surface flow wetlands, which incorporate ponds in combination with aquatic plants and macrophytes, 2) Sub surface flow wetlands, which involve use of gravel matrix with macrophytes. Latter is considered as a high rate treatment plant and is used widely in Europe for nitrogen removal.

CWs are designed on the principle of holding or slowing down the passage of water through a wetland, while physical, biological or chemical processes occurring in the system transform, remove or store the pollutants. With longer residence time, treatment efficiency improves. The overloading of the CWs both in terms of hydraulic and pollutant are the main limitations. The seasonal variability of rainfall may lead to huge flow whereas drought and high temperatures may decrease volume of flow to the wetland. The commonly encountered problems in CWs include clogging of media, re-suspension of suspended particles, lower removal of phosphate, short-circuiting, variable pathogen removal, effect of temperature fluctuation on removal efficiency. For enhancement of complete system, some additions and modifications are needed as discussed below:

<u>Primary treatment</u>: Under primary treatment, sedimentation tank should be installed to remove readily settleable and suspended solids. Screens and bars are also required to removal floating material. Properly functioning sedimentation can considerably reduce the BOD, COD and TSS load on secondary treatment. Due to rapid urbanization, inert material from construction activities comes along with domestic wastewater, which needs to be removed during primary treatment. The readily settable solids like grit, sand and fine stones settled at the bottom of sedimentation tank makes de-silting of tank imperative.

<u>Secondary treatment</u>: In CWs, plants play various roles by performing number of functions concurrently. Contact between plant and water should be made maximum by the use of large reed bed to remove dispersive colloids. The organic flocculants and bio-film sorption aids in this removal process. Macrophytes should not be invasive in nature like *Phragmites australis* and should not be feed for pests and rodents. Short-circuiting can lead to stagnant

pockets in the system with low dissolved oxygen and anaerobic conditions. Under low DO conditions, phosphorus is released from the sediments. The design considerations should allow mixing of water within wetland. The removal of pollutants largely depends on operational conditions of the CW. Well-controlled systems have shown appreciable removal of nitrogen, adequate availability of oxygen and carbon source as food source for microbe. Therefore, organic loading rate and flow rate of wastewater should be controlled and kept invariable. The *p*H of influent and effluent wastewater should be controlled, as low pH may cause mobilization of metals in the media as well as receiving water body or land. Some wetlands have large open water areas near the outlet, which may facilitate growth of suspended biomass like algae, and plankton hence increases suspended solids. The final effluent should pass through aquatic plants as filtration process. There should be stagnancy of water at the outlet to prevent growth of larvae. By-pass line should be provided to main adequate water to the system to avoid flooding as well as drying of plants. The parameters including BOD, nitrogen, phosphorus, total suspended solids, heavy metals, bacteria (total coliform or fecal coliforms) should be regularly monitored to keep a check on quality of water in case of domestic wastewater.

Tertiary treatment: Effluent of CW carries pathogens and nutrients like phosphate above acceptable level. This can be removed by adding tertiary treatment system for removal of phosphate like lime precipitation, use of alum or iron salts. Biological phosphorus removal system may not work properly with CWs due to low BOD, which is required by microbes as food source. However, if some amount of wastewater is by-passed from primary treatment to biological phosphorus removal, the system may sustain. For removal of pathogen large number of options are available which includes conventional methods like disinfection by chlorination or slow sand filters. Recent techniques may also be applied like UV disinfection or microfiltration however; economics needs to be looked into while deciding final technology. Some combinations are not viable like use of iron salts for removal of phosphate with UV disinfection.

4.6 Sewage-fed aquaculture

Ecology of the SFA system is same as of WSPs. The only addition to the later is a new kind of biological system: the fishes. The use of organic residues in aquaculture is best discussed with awareness of the following facts about aquatic biology: (i) Limitations to biological production in fresh, brackish, or ocean waters are predominantly dissolved nutrients and/or food as well as shelter or substrate. Seasonality and intensity of the input of solar energy are also important. (ii) In aquaculture (and incidentally in fisheries), what is eventually to be harvested has to be contained or concentrated.

Among these inputs, nutrients and/or food can be supplied, at least in part, by organic materials or residues. As aquaculture practices increase in magnitude and hasten the flow of materials and energy through the systems, compared to natural conditions, it stands to reason that fertilization wastes can, under certain conditions, save both monetary and caloric inputs. Likewise, judicious use of agricultural or organic industrial wastes as feed materials can lower the cost of growing aquatic animals.

Table 4.1: Different types of products obtained from sewage-fed aquaculture

Category	Listed examples
Edible Plants	High-protein algae (*Spirulina*) Water spinach (*Ipomoea*) Water chestnuts (*Eleocharis dulcis, Cyperus esculentes*) Water nuts (*Trapa, alternanthera*) Hydroponic vegetables and herbs (*Capsicum,* basil, lettuce)
Edible animals	Mussels Prawns (*Macrobrachium*) Crayfish (*Procambarus* clarkii*, Astacus, Cherax*) Fish (Carp-species, Tilapia*, Clarias, Channa striata, Micropterus salmoides*)
Animal feeds	Phytoplankton (*Microcystis, Scenedesmus, Selenastrum Anacystis, Phacus, Closterium)* High-protein floating plants (*Lemna, Azolla, Wolffia*) Zooplankton (*Asplanchna, Filina, Keratella, Brachionus, Moina, Daphnia, Cyclops*) Fish-Feeds (*Earthworms*)
Raw material	Fibers for furniture, baskets (*Eichhornia*) Cellulose for paper (*Typha*) Isolation material (*Typha*) Fertilizer (algae suspension, plant biomass) Renewable energy sources
Luxury products	Pearls (*Hyriopsis*, *Cristaria*) Ornamental plants (*Eichhornia*, *Nuphar*) Ornamental fish (Koi - *Cyprinus carpio*)

Source: Junge (2001)

Anaerobic conditions are the prevalent due to sedimentation of organic detritus at the bottom. This also leads to foul odour and release of other obnoxious gases. Bottom grazer and omnivorous fishes can be a solution to this problem as they directly consumer organic detritus and help in maintaining aerobic conditions by bio-turbation activity (Jana, 1998). Some of the ideal fish species for sewage fed aquaculture include *Indian carp, Israeli Carp, Silver Carp, Bighead Carp, Grass Carp, Common Carp, Hybrid Buffalo, Catfish, Largemouth Bass, Tilapia, Freshwater Prawn* etc (Schroeder, 1975; Moar *et al.*, 1977; Ghosh *et al.*, 1985). *Tilapia* can tolerate low DO, high ammonia and wide range of salinity. Similarly, a type of cat fish called *Clarias batrachus* is suitable for many conditions (Jana, 1998). Sewage fed aquaculture has been found unhealthy by many researchers due to bioaccumulation of heavy metals and other pollutants into four trophic levels of food chain. However, study in Egypt concluded that fish reared in the treated effluent is suitable for human consumption (Easa *et al.* 1995).High BOD and nutrient are a major cause of concern. Establishment of duckweed pond system or anaerobic pond can help in reducing the BOD and nutrient toxicity on aquaculture.

Aquaculture ponds serve as facultative ponds for sewage treatment. Optimal stocking is highly variable and depends upon bio-geographical, cultural and economic conditions. Some of the limiting factors of aquaculture include limited growth rate of organisms, deficient knowledge of conditions controlling aquatic community, presence of pollutants like heavy metals and contamination of industrial effluent. Various kind of products can be obtained by sewage fed aquaculture as shown in **Table 4.1** adapted from Junge (2001). Many studies suggest that aquaculture system with 2-3 ponds is sufficient to reduce pathogens to very low level. Above 90% removal was shown for total coliforms, faecal coliforms, *Salmonella sp*. and faecal *streptococci*. Also, few plants like *Phragmites, Scirpus* have been shown to kill pathogen indicators like *E. coli* and *Salmonella* by root secretions (Soeder, 1981).

5 Development of strategies for enhancement of performance of CWs: a focused research at IITB

Saeed and Sun (2012) defined CWs as an engineered wetlands that have saturated or unsaturated substrates, emergent / floating / submerging vegetation and large varieties of microbial communities that are purposely built for water pollution control. In India, there are only 50-60 units majorly concentrated in Tamil Nadu (Arceivala and Asolekar, 2007). Based water flow regime during the treatment in bed media, CW has been classified in different type (e.g. horizontals flow CW and vertical flow CW). Extensive demands for improved water quality for various purposes, especially for industrial applications, drinking water etc pose a driving force for the implementation of advanced wastewater treatment techniques. Since the beginning of civilization mankind has continued to exploit the nature and natural resources for their basic needs and prosperity. In the global developmental chase of human being lead to the overexploitation of natural resources that leads to the introduction of lethal contaminants into our contagious environment and the situation has become an agenda for discussion among professionals from all arena including academics, politics, and researchers.

5.1 Study on removal of nutrients and carbonaceous pollutants from sewage using CWs

This research was aimed at investigating different media for creation of porous bed in experimental CW reactors *viz*. crushed aggregate, generally used dual media filter sand and Juhu Beach sand. There were four experimental CW reactors for each media type (one unplanted and three planted reactors) resulting into a total of twelve experimental CW reactors. The wetland plant species used in this project work was *Cana indica* (common reed). Natural raw sewage from sump tank station was used for the experiments.

Inlet concentrations of 5-day Biochemical Oxygen Demand (BOD_5), Chemical Oxygen Demand (COD), Ammonia Nitrogen (NH_3-N) and Ortho Phosphate (PO_4^{3-}) were determined during the experimental cycles. Effluents from different experimental CW reactors were analyzed at intervals of 24, 48 and 72 hr, respectively, during each experimental cycle. Removal efficiencies for pollutants in different experimental CW reactors were analyzed and the role of vegetation and associated media on pollutant removals were investigated. It was observed that PO_4^{3-} removal was relatively high in crushed aggregate reactors when compared with the others media, in which maximum removal of ~95% was observed. Ammonia removal was good in Juhu Beach sand (reached 100% removal efficiency within 24 hr of experimental cycle). The overall ammonia nitrogen removal efficiency in crushed aggregate was in the range of 90% to 100%. The COD removal efficiency in all the reactors decreased with increasing inlet COD concentrations. Maximum COD removal of 70% was observed in crushed aggregate reactors, followed by Juhu Beach sand reactors (45%) and filter sand reactors (30%).

The D_{60}/D_{10} for Juhu Beach sand was smaller when compared with the crushed aggregate and filter sand. Juhu Beach sand showed sufficient porosity but very less hydraulic conductivity owing to its lower D_{60}/D_{10} value. Visual observations of wet media suggested that the crushed aggregate and filter sand had desirable draining properties. However, Juhu Beach sand found to retain water and hence was deemed unsuitable in CWs.

Removal of phosphate and ammonia could also be achieved in experimental CW reactors. Thus the role of media plays an important role in providing workable hydraulic conditions in the porous rhizosphere zone in CWs as well as provides suitable chemical and microbiological niche for harboring root-zone and micro-organisms.

5.1.1 Potential of wetland plants for removal of pollutants from the wastewater

Plants play an important role in HF CWs, therefore appropriate selection of plant species is a must do process in design considerations (Faulwetter *et al*., 2009). Aquatic plants like *Typha latifolia*, *Eichhornia crassipes*, *Ipomea* sp., *Lemna minor*, *Polygonum* sp, *Alternanthera philoxeroides*, and *Phragmites* sp. have vital significance in bioremediation. These are being used in water quality assessment and also for fast removal of pollutants from contaminated sites.There are species like *Carex rostrata*, *Phragmites australis*, *Typha angustifolia*, *Typha latifolia*, which can grow under field conditions in pH as low as 2 to 4.4 (Rogers, 2002). Some plant species like *Typha latifolia*, *Glyceria fluitans* and *Phragmites australis* tend to have an inherent tolerance to metals in wastewater while other plant species can develop evolutionary tolerance over a period of time (Prasad, 2001).

For VF CWs systems, plant selection is less critical as the oxygen input is enhanced by the intermittent surface application. Plantation of species according to Indian conditions can be selected from the list as per Arceivala and Asolekar (2007).

- *Phragmites australis* (reed)
- *Phragmites karka* (reed)

- *Cana indica* (reed)
- *Arundo donax* (mediteranean reed)
- *Typha latifolia* (cattail)
- *Typha angustifolia* (cattail)
- *Juncus* (bulrush)
- *Iris pseudacorus*
- *Schoenoplectus lacustris* (bulrush)

Planting is done from supporting boards to avoid compaction of the filter media. Initially the plants are kept well watered (but not flooded).During the first growth period a sufficient supply of nutrients is required. Plantation of reeds in CWs is done in the following way (CPCB, 2003):

- Reeds can be planted as rhizomes, seedlings or planted clumps.
- Clumps can be planted during all seasons (2 / m^2).
- Rhizomes grow best when planted in Pre-Monsoon (4 - 6/ m^2).
- Seedlings should be planted in Pre-Monsoon (3 - 5/ m^2).

Research is being carried out to find out hyper-accumulators which are tolerant as well as have the ability to accumulate heavy metals in them (Boominathan and Doran, 2003). In addition to natural breeding selection, new transgenic plants are being developed by recombinant DNA technology (Singh and Tripathy, 2007). Important factors which influence the uptake of organic pollutants by the plants include the compounds' physicochemical characteristics such as the octanol–water partition coefficient (log K_{ow}), dissociation constant (pK_a), concentration, *etc*. (Wenzel *et al*., 1999). According to Trapp and Karlson (2001) compounds with a log K_{ow} between 0.5 and 3 are taken up best by plants.

The efficiency of different CWs varies based on the local climatic conditions, plant species used, media employed, *etc*. The CWs show appreciable removal of nitrates and ammonia while the phosphate removal remains an issue. CWs show high BOD and suspended solids removal. Phosphorus remains in 3 dominant forms, namely orthophosphate, polyphosphate or condensed phosphate and organic phosphate. Orthophosphate remains in various forms while predominant form depends on *p*H conditions. At a typical pH of wastewater, most common form is HPO_4^{2-} (USEPA, 2008).In raw sewage there are substantial amounts of all three principal forms of phosphorus.

Decomposition of organic phosphate leads to formation or orthophosphate ions. During determination of phosphate concentration in wastewater, polyphosphates and organic phosphates are digested with acid in the presence of strong oxidizing agent to form orthophosphates which later from colored complex and determined calorimetrically. Phosphorus removal has been variable in CWs because the media used in CWs have been selected based on local availability and particle size to reduce the clogging without consideration for their capacity of phosphorus removal (Yang *et al.,* 2001).

CWs have high buffering capacity and their removal efficiency depends on temperature, hydraulic retention time (HRT), organic loading rate, *etc*. (Rousseau *et al.,* 2008). For effluent polishing purpose, effluent nitrogen of 3mg/L or less is achievable with submerged flow at influent nitrogen concentration upto 16 mg/L and hydraulic loading rate upto 300 m^3 ha^{-1} day^{-1} (Bavor *et al.,* 1995). At low phosphorus concentration, typical removal efficiency can range from 60 to 90% and effluent concentration of 1mg/L or lower can be achieved (Rousseau *et al.,* 2008). However, Margaret and Wooley (1999) reported that effluent phosphorus concentration exceeds influent when plant is operated for a long time. This is due to "aging phenomenon'' of wetland in which media become saturated with adsorption and precipitation of effluent pollutant (USEPA, 1988).

Phosphate uptake capacity of macrophytes is also limited as shown in the **Table 5.1** (Brix, 1994). Horizontal sub-surface flow constructed wetlands (HSF CWs) usually do not remove high amount of phosphorus from wastewater due to lack of suitable conditions (Luanaigh *et al.,* 2010; Kem and Idler, 1999). HSF CWs are designed for removal for organic matter and suspended solids (Vymazal, 2002).Removal of phosphorus in HSF CWs is not temperature dependent (Vymazal, 2007). Biological influences on phosphorus removal which happens to be temperature dependent are relatively unimportant (Vymazal, 2009). HSFs CWs are not designed for removal of phosphorus by macrophytes uptake through subsequent harvesting. In order to maintain high hydraulic conductivity necessary for subsurface flow, highly porous media is being used in HSFs CWs.

Table 5.1:Nutrient uptake capacities of macrophytes used in constructed wetland systems

Macrophyte Name	Uptake capabilities (Kg/h/yr)	
	Nitrogen	Phosphorus
Cyperus papyrus	1100	50
Phragmites australis	2500	120
Typha latifolia	1000	180
Eicchornia crassipes	2400	350
Pistia stratiodes	900	40
Potamageton pectinus	500	40
Ceratophylum demersum	100	10

Source:Brix (1994)

Commonly used filter material in CWs includes pea gravel, crushed rock, *etc*. that do not usually contain adequate concentration of calcium, iron or aluminium which may be the critical key composition for phosphorus removal. The decomposing litter matter may also acts as a source of phosphate pool for storage (Babatunde *et al.,* 2008). The litter formed by decomposing matter remains on vegetated bed surface while wastewater flows from beneath the surface, hence no contact and thus no contribution in removal of phosphorus. Field experience suggests that the amount of phosphorus which could be removed by harvesting accounts only for small percentage of total phosphorus removed in the vegetated beds (USEPA, 2008).The amount of phosphorus removed remains usually <10% and in most of the cases <5% (Gottschall *et al.*, 2007). **Table 5.2** shows the removal efficiencies for pollutants and changes in parameters with variable HRT in Indian conditions.

Table 5.2: Wastewater quality parameters and their removal rates in CWs treatment

HRT (Days)	*p*H	TKN (mg/L)	BOD (mg/L)	SS (mg/L)	P (mg/L)	Removal rate (mg/m^2/day)			
						TKN	BOD	SS	P
0	7.5	34.6	180	350	11.3	-	-	-	-
1	6.9	33.7	149	345	11.3	0.25	8.61	1.39	0
2	6.9	32.7	94.3	310	11	0.26	11.90	5.56	0.04
3	6.8	32.3	79.9	217.5	9.97	0.21	9.27	12.27	0.12
4	6.8	25.3	62.4	154.8	9.85	0.65	8.17	13.56	0.10
5	6.8	16.7	35.3	86.54	9.86	0.99	8.04	14.64	0.08
6	6.7	12.2	32.4	55.36	8.69	1.03	6.83	13.64	0.12
7	6.7	11.6	31.5	32.5	8.24	0.91	5.89	12.60	0.12

Source: Adapted from Sonavane *et al.* (2007)

Table 5.3 shows the list countries apart from India where CW systems are in operation and there efficiency for removal of pollutants in various regions of the world. As it is evident from the above Table 5.3 the treated effluent coming-out from CWs contains high amount of phosphorus which need to be removed before discharging to natural water bodies or for any high end applications. The most possible options for phosphorus removal are chemical, biological, physical or combination of all of these. The subsequent sections discuss the options available in the form of technology or processes followed by the strategy shortlisted for best fit technology.

Table 5.3: Efficiencies of CWs for pollutant removal

Country	Area (m^2)	Flow ($m^3\ d^{-1}$)	BOD_5 In Out	TSS In Out	TP In Out	TN In Out	NH_4-N In Out	FC In Out	Reference
UK	328	87	5.8 1.1	9.7 3.8	- -	- -	0.67 0.24	- -	CWA (2006)
UK	825	306	8.5 2.3	17.7 3.8	- -	- -	5.5 0.44	- -	CWA (2006)
USA	2035	14.9	9.4 1.0	72 3.5	6.6 0.45	52 9.9	10.5 2.7	5.3 1.0	Watson (1990)
Jamaica	90	0.9	27 13	57 13	9.6 0.4	40 1.6	5.8 0.4	5.6 2.2	Stewart (2005)
Lithuania	3780	180-400	51 7.8	30.6 12.2	11.2 9.6	9.4 7.4	- -	- -	Gasiunas and Strusevičius (2003)
Italy	96	6	81 7.2	55 18	5.7 1.8	72 25	- -	6.5 2.5	Pucciet *al.* (2004)
Denmark	2640	103	115 6.0	158 6.4	4.8 4.8	22.5 16.8	17.3 12.5		Kadlecet *al.*(2000)
UK	612	30	189 18.5	135 19	- -	- -	65.5 42.3	- -	CWA (2006)

Table 5.3…Continue

Belgium	895	23.3	232 6.0	196 9.0	12.4 4.0	81 29	- -	- -	VMM (2006)
Denmark	437	8.1	330 16	392 10	21 14.3	74.5 43.3	- -	- -	Schierup *et al.* (1990)
UK	168	10	390 25	116 21	- -	- -	63.2 15.7	- -	CWA (2006)
Croatia	360	40	427 56	171 32	13.2 5.9	152 80	- -	6.2 3.0	Shalabi (2004)
Spain	229	5.8	513 67	304 33	14.5 10.9	110 53	84 48.7	- -	Sardon*et al.*(2006)
Brazil	450	6.6	979 19	224 104	- -	- -	49 16	- -	Philippi *et al*. (2006)

Source: Adapted from Vymazal (2009)

5.1.2 Selection of an ideally suited plant systems for CW

The presence of macrophytes is one of the most conspicuous features of wetlands and their presence distinguishes constructed wetlands from unplanted soil filters or lagoons. The macrophytes growing in CWs have several properties in relation to the treatment process that make them an essential component of the design. However, only several roles of macrophytes apply to CWs with horizontal subsurface flow (HF CWs). The plants used in HF CWs designed for treatment should therefore: (1) be tolerant of high organic and nutrient loadings, (2) have rich belowground organs (i.e. roots and rhizomes) in order to provide substrate for attached bacteria and oxygenation (even very limited) of areas adjacent to roots and rhizomes and (3) have high aboveground biomass for winter insulation in cold and temperate regions and for nutrient removal via harvesting. The comparison of treatment efficiency of vegetated HF CWs and unplanted filters is not unanimous but most studies have shown that systems with plants achieve higher treatment efficiency. The vegetation has mostly a positive effect, i.e. supports higher treatment efficiency, for organics and nutrients like nitrogen and phosphorus. By far the most frequently used plant around the globe is *Phragmites australis* (Common reed).Species of the genera *Typha* (*latifolia, angustifolia, domingensis, orientalis and glauca*) and *Scirpus* (e.g. *lacustris, validus, californicus and acutus*), *Canna indiaca* are other commonly used species. In many countries, and especially in the tropics and subtropics, local plants including ornamental species are used for HF CWs.

Nationalize survey of CWs in India as well as available literature indicate that three macrophyte species namely, *Phragmites karka, Typha latifolia* and *Canna indiaca* are the successfully established CWs systems for treatment of different types of wastewaters. The pictures of the most commonly used plant species in CWs for treatment of wastewater in India are shown in **Plate 5.1**.

Phragmites: By far, the most commonly used plant for HF constructed wetlands is *Phragmites australis* (Cav.) is a perennial and flood-tolerant Stems are rigid with hollow internodes with the range in shoot height from less than 0.5 m to giant forms about 8 m tall from the marshes of the Danube delta and Tigris and Euphrates Rivers. Common reed is a cosmopolitan grass occurring as a dominant component in the freshwater, brackish and in some cases also marine littoral communities almost all over the world. Its distribution is widespread throughout Europe, Africa, Asia, Australia and North America between 10 and 70 latitude (Hawke and Jose, 1996).

Typha latifolia: Typha spp. (Cattails) (Typhaceae) is erect rhizomatous perennial plants with joint less stems grow in water logging areas. The plants are generally up to 3 m tall with an extensive branching horizontal rhizome system. The leaves are flat or slightly rounded on the back, in their basal parts spongy (Sainty and Jacobs, 2003). Cattail species is commonly found inhabiting shallow bays, irrigation ditches, lakes, ponds, rivers and both brackish and fresh water marshes. The most important Typha species found in wetlands are *T. latifolia L*. (Common cattail, Broadleaved cattail), *T. angustifolia L*. (Narrow-leaved cattail), *T. domingensis Pers*. (Southern cattail, Santo Domingo cattail), *T. glauca Godr*. (Blue cattail) and *T. orientalis C*. Presl (Broadleaf cumbungi, Raupo). Cattail is very often used in constructed wetlands with free water surface (Kadlec and Wallace, 2008) but it is probably the second most commonly used plant for horizontal flow constructed wetlands (HF CWs) for various types of wastewater around the world.

Phragmites australis (Common reed) planted at site code; India_RJ_3_CW

Free floating constructed wetland of *Phragmites karka* installed at Vikram university, Ujjain, MP

Canna indica planted at site code; India_UP_5_CW

Natural wetland of *Typhalatifolia* grown in, Ujjain, MP

Plate 5.1: Most commonly used plant species in constructed wetland for wastewater treatment in India

<u>*Canna indica*</u>*:* is a species of the Canna genus, belonging to the family *Cannaceae*, a native of the Caribbean and tropical Americas that is also widely cultivated as a garden plant. In India, *Canna indica* are also being used an ornamental plant in house-hold as well as in community gardens. It is a perennial growing from 0.5m to 2.5m, depending on the variety. It is hardy to zone 10 and is frost tender. The flowers are hermaphrodite. This plant species is being at many locations for phytoremediation activities for treatment of wastewater in India.

5.1.3 Performance of CWs for removal pollutants from wastewater treatment

Although plants are a major component of wetlands, relatively little is known about their effects on the processes responsible for wastewater treatment. A greater understanding of plants' influences would allow designers to select appropriate plant species to increase the efficiency of the desired treatment, whether it is organic carbon, nutrient, or heavy metal removal. The most common three mentioned species of wetlands as shown in Plate 5.1, used around the world for treatment of different types of wastewaters. Some facts related with their pollutant performance from the past research have been represented in the table. The results of pollution removal by these species indicates satisfactorily and may be used as effective once for our experiments in achieving the objectives.

<u>Nitrogen removal in CWs</u>: Due to difference in oxygen level saturation inside bed media, formation of aerobic, anoxic and anaerobic zones occurs in CWs. Ammonia–nitrogen removal generally improves with time due to improved oxygen transfer and growth of nitrifiers. Ammonia–nitrogen present in wastewater gets converted into nitrate in aerobic zone of wetland media, whereas anoxic zone contributes to denitrification process (Arceivala and Asolekar, 2007).

It has been determined that increase in plant density in CWs decreases the DO levels of the wastewater by restricting oxygen diffusion (Rai and Munshi, 1979). Therefore, a proper distribution of plants per square meter gives better result on nitrogen removal than highly dense wetland systems. The maximum uptake rate (I_{max}) for NH_4^+–N (623 µmol g^{-1} dry root weight h^{-1}) is higher than that for NO_3^-–N (338 µmol g^{-1} dry root weight h^{-1}) in *Scirpusvalidus*. There is no significant difference in I_{max} of NO_3^-–N and NH_4^+–Nfor *Canna indica*. The I_{max} values for nitrogen removal is higher in *Scirpus validus* than in *Cana indica*. The K_m value is lower in *Canna indica* (385 µmol L^{-1}) as compared to *Scirpus validus* (1908 µmol L^{-1}) (Zhang *et al.*, 2009).

<u>Phosphorous removal in CWs</u>: Phosphorus removal in wetlands takes place due to plant uptake, accretions of wetland soils, microbial immobilization, retention by root bed media and precipitation in the water column (Pant *et al*., 2001). The phosphorus sorption capacity of root bed media increases with accumulation of amorphous and poorly crystalline forms of Al and iron (Fe) whereas in alkaline root bed media, preferential P sorption occurred more on amorphous and poorly crystalline forms of Al than Fe (Pant *et al*., 2001).

Studies also have shown that plant uptake and subsequent harvesting is the only reliable long-term phosphate removal mechanism (Vipat *et al*., 2008). The removal efficiencies in cold climates are generally poor. Relatively higher clay content in the media gives better phosphorus removal but poorer hydraulic conductivity, which creates operational problems (Arceivala and Asolekar, 2007). According to Zhang *et al*. (2009) the maximum uptake rate (I_{max}) for PO_4^{3-} is same for *Canna indica* and *Schoenoplectus validus*, whereas K_m value of C. *indica* (157 µmol L^{-1}) is significantly higher than *S. validus* (60 µmol L^{-1}).

<u>Carbonaceous pollutant degradation in CWs</u>: The presence of rhizosphere, aerobic, anoxic and anaerobic zones in CWs causes the presence of a large number of different strains of

microorganisms and consequently a large variety of biochemical pathways formed for degradation and uptake of pollutants. In case of dispersed settlements, CWs offer a feasible solution for decentralized sewage treatment after adequate pretreatment (Luederitz *et al*., 2001).

Research on common reed sp. have shown that the oxygen transport capacity of these plants is insufficient to ensure aerobic decomposition in rhizosphere and that anoxic and anaerobic decomposition play an important role in HF CWs (Vymazal and Kröpfelová, 2006). The following anaerobic pretreatment systems are especially suitable for small scale CWs for treatment of domestic sewage with high BOD load:

- Multi – compartment septic tank
- Imhoff tank
- Baffle reactor, and
- Biofilm up-flow reactor (CPCB, 2003)

Microbiological removals in constructed wetlands: The removal of pathogens like coliforms, protozoan and helminthes to acceptable range makes CWs a feasible option for recycling of wastewater, especially in decentralized treatment systems (Karathanasis *et al*., 2003). The treated effluent from properly designed CWs is being used safely for gardening within domestic premises, toilet flushing, aquaculture, recharging groundwater *etc*.

The exact role of protozoa, bdellovibrios and bacteriophages in germ reduction in CWs is still largely unknown. The comparison of a pond system with a subsurface flow planted soil filter or CW gave beneficial edge to subsurface flow system, and the findings related to it listed in **Table 5.4**.

Table 5.4: Comparison of the efficiency of a pond and a planted soil filter for wastewater disinfection (elimination efficiency in %)

Microorganism	Lemna pond	Planted soil filter
Giardia cysts	93	83
Cryptosporidium oocysts	91	67
Total coliforms	54	99
Fecal coliforms	59	98
Coliphages	35	94

Source: Thurston *et al*. (1996), Adapted from: Stottmeister *et al*. (2003)

From Table 5.4 it can be said that efficiency of CWs shows fluctuation in terms of pathogen elimination. There were cases of lower pathogen removal compared to that shown in Table 5.4 and in those cases also, the extent of pathogen removal was sufficient to meet standard for agricultural irrigation and aquaculture as defined in WHO guidelines of ≤1000 fecal coliform/100 mL (WHO, 1989) are met (Green *et al.*, 1997). Also, the performance of CW varies with the use of different macrophyte and filter media (depicted in **Table 5.5**).

In a pot experiment, Seidel (1971) found out that helophytes, mainly *Mentha aquatica*, *Alisma plantago* and *J*. *effusus* proved to be especially efficient in removal of *Escherichia coli* upto 99% from wastewater. These findings were largely confirmed by Burger and Weise (1984) again using pot experiments in which 1.2 liters of sand and 5 liters of nutrient solution was used (Stottmeister *et al*., 2003).*Glyceria maxima*, *S*. *lacustris*, *A*. *plantago-aquatica* and *M*. *aquatica* used in pot experiments showed 90% reduction in bacteria after a contact time of 7–11 h and 99% after 16–19 h.

5.1.4 Criterion for selection of media for CWs

The use of media in CWs solely depends upon the type of CWs, prime pollutant to be targeted and plant species used. Various types of root bed media used in CWs include limestone, shale, slag, gravel, and other artificial materials. The use of high sorption capacity media like steel slag and light weight clay aggregates have been used in recent times to enhance phosphate uptake in CWs. In contrast, the fine grained soils show better nitrogen removal through adsorption than the coarse grained soil (Geller *et al*., 1990).

The grain size distribution in CWs media should be verified using soil/sieve analysis and a percolation test should be performed before incorporation of the material in the CW beds (CPCB, 2003).The optimization of the filter or media bed in terms of hydraulic load and microbial biomass growth intensity is therefore the most important factor in designing CWs. Optimum characteristics of CW filter bed media are listed in **Table 5.6**.

Insufficient pre-treatment can cause surface clogging of media in VF systems and clogging in the infiltration area in HF systems. Media containing higher fraction of coarse material let the wastewater flow fast through it and if it contains higher fraction of fine material, clogging and overflow occur in the system. In both the cases, systems give poor treatment efficiency. A remarkable reduction in permeability is observed in media by deposition, sedimentation and bacterial growth. Sand and gravel with rounded grains are considered ideal to use. Media of relatively similar grain size like river sand or sieved materials are used in CWs (CPCB, 2003).

Table 5.5: Performance of existing root zone beds

Plant Type	Bed media	Hydraulic Loading cm/d	Organic loading, g/m2, d	Study time, month	BOD	TSS	NH_3-N	NO_2-N	TN	TP	BOD	TSS	NH_3-N	NO_2-N	TN	TP
Reed	Gravel	11.1	27.8	16	150	94	29	1.9	42	13	54	14	23	1.2	32	12
Reed	Fine Gravel	4	7.5	18	189	243	34	0.3	47.	15	11	6	15	12.6	29	9.6
Reed	Topsoil	1.7	3.2	18	189	243	34	0.3	47	15	15	23	15.3	1.2	18	6
Reed	Gravel	2.7	10.8	15	237	131	43	_	_	_	63	38	36	_	_	_
Reed	Soil/Gravel	4.9	19	20	233	163	34.9	_	_	_	49	24	32.9	_	_	_
Reed	Soil	5.6	8.1	9	87	74	29	_	_	_	16	21	27.5	_	_	_
Typha	Rock	15.9	11.6	19	63	32	_	_	_	_	19	8	_	_	_	_
Typha	Sand/gravel	4.7	12.9	30	140	380	30	_	_	13	17	53	13	_	_	4.2
Typha	Gravel	7.6	14.8	13	148	50	_	_	_	_	33	10	_	_	_	_
Typha	Gravel	18	14.5	12	49	19	_	_	21	_	3.2	1.9	_	_	4	_
Typha	Gravel	4.7	7.3	16	118	57	24.7	0.3	28	_	5.3	3.7	1.5	1	_	_
Reed	Gravel	4.7	7.3	16	118	57	24.7	0.3	28	_	22.2	7.9	5.4	0.1	_	_

(Source: Conley *et al.*, 1991)

Table 5.6: Optimal of characteristics CW media

Name of parameter	Desired value
Permeability (k_f)	≈ 10^{-4} to 10^{-3} m/s for of domestic sewage
Uniformity coefficient (U)	(d_{60} / d_{10}) ≤ 5; (ratio of grain sizes which contain 60% and 10% of the total media)
Effective grain size (d_{10})	should be ≥ 0.2 mm
Content of silt	should be ≤ 5%

Source: CPCB, (2003)

5.1.5 Material and methods used in performing the study

The materials used for the experiments of this study were chosen based on characteristic, availability and suitability for the completion of objectives defined. The methodologies adopted for setting up the experimental units were such that the units resembled actual CWs operating at field scale. Media were tested for parameters based on standard methods (Gee and Bauder, 1986). Sewage sample and treated effluent were tested by standard protocols (APHA, 2005). The materials and method used in this project work were to mimic CWs in a smaller scale known as “Experimental CW Reactors”. The essential materials used in this project work viz. PVC pot or crates, stand for crates, CW media, wetland plant species and raw sewage.

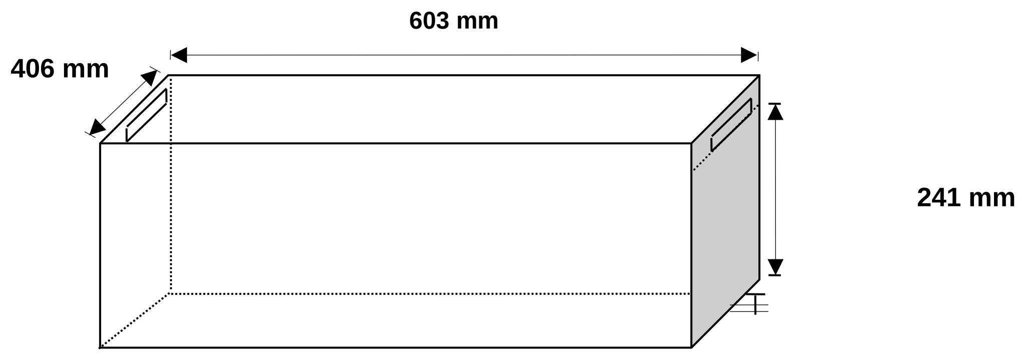


Figure 5.1: Laboratory setup of CW reactor

Poly Vinyl Chloride pots (crates): Experimental CW reactors were set up in crates made up of poly vinyl chloride (PVC). There was a leak proof collection tap in every crate at a height of 6.5 cm and the diameter of the tap was 1.25 cm. The figure and photograph of laboratory setup of CW reactor used during the study are depicted in **Figure 5.1** and **Plate 5.2** respectively.

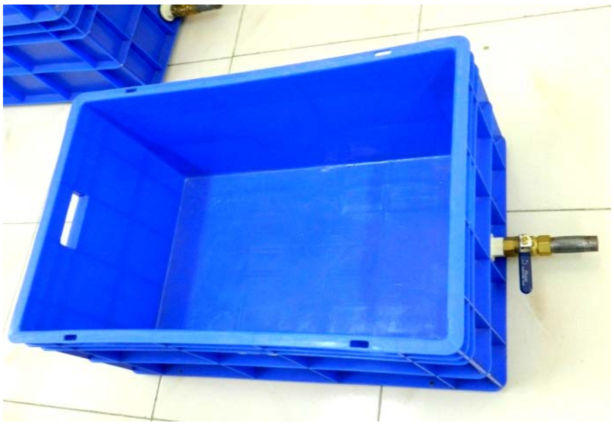
	
1	2

Plate 5.2: Crate used for experimental of constructed wetland reactors

There were total 12 crates of similar shape and size used in this project work. The dimensions of the crates were as follows:

- Length (inner edges) : 0.605 m
- Breadth (inner edges) : 0.405 m
- Height (till holding notch) : 0.235 m
- Area : ≈ 0.245 m^2
- Volume : ≈ 0.0576 m^3

Constructed wetland media: The wetland media characterization in this project work basically emphasized on sieve analysis, porosity, bulk density, pH and ORP. The aim behind determining porosity was to have an estimate of how much sewage could be fed to the media at a particular compaction ratio. Sieve analysis was performed to find out relative hydraulic conductivity among three media used. Bulk density had given the idea of how much media (by weight) was required for the experiment. ORP and pH were determined to find whether the media were acid, basic or neutral, and whether the media were inert or not, which was an essential element to know about phosphate precipitation capacity. Juhu Beach sand was salty and basic. Therefore, washing and proper mixing was given for uniformity. The washed sand was then analyzed for the parameters. There were three different wetland media used in this study. The selection was done on the basis of natural availability and suitability for the experimental setup. The three media used were:

(a) Crushed aggregate – were collected from local retailer. The material is used for concrete production and construction purposes. Crushed aggregate is being prepared by crushing large stones in crusher machines, and different stones have different mineral composition. Therefore, the material collected for experiment was from the same lot so that every replicate of a particular set of experiment can yield similar and comparable results. The local retailers use the code for crushed aggregate as 1,2,3,4, and 5. The crushed aggregate used in this project work was coded 1 by local retailer and the longitudinal length was ranged from 1.5 cm to 2 cm. Crushed aggregate was less spherical and was not analyzed for particle size distribution. The effective porosity was measured by putting it into the crates used in experiment. Effective porosity came out to be 41.48%. Specific gravity was calculated by water displacement method and the value came out to be 2.629 tone/m^3.

The picture of crushed aggregate used is shown in **Plate 5.3**.

Plate 5.3: Crushed aggregate used in project work

(b) Filter Sand – It was the quartz sand usually used in "Dual Media Sand Filters". The sand was collected from local retailer who specifically supplies quartz sand for dual media filters. In retailer terms, the sand purchased was of grain sized. Characterization of filter sand depicts that particle size distribution is preferably good for using it in CW media. Porosity was around 50%, so it can be used for treatment of larger volume of sewage. The pH and OPR values suggest that the filter sand was inert in nature. Bulk density was found to be 1.517. All the values were determined by performing experiments in triplicate and the determined values are shown in **Table 5.7**. The picture of the quartz sand used is shown in **Plate 5.4**.

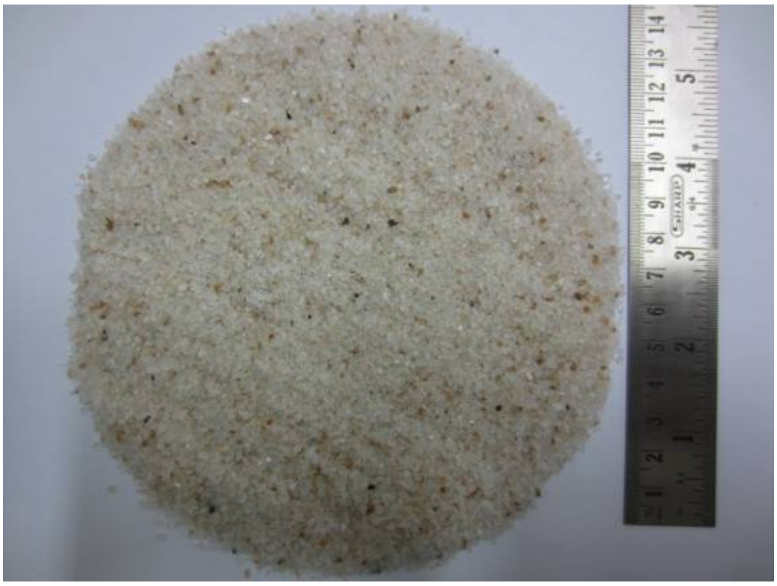


Plate 5.4: Filter (quartz) sand used in project work

(C) Juhu beach sand – was collected from Juhu beach (Juhu Tara Road, Juhu, Mumbai, Maharashtra; 19.1000° N, 72.8167° E) and transported to IIT Bombay campus for the experimental work. The sand was collected by screening it through 2 mm mesh so that larger particles, wrapper waste and twigs can be separated. The particle size distribution of Juhu Beach sand showed that the particles were finer than filter media sand particles. The ratio of d_{60}/d_{10} was towards less preferable regime for using as CW media. Porosity was good for using it for the purpose of CW media but hydraulic conductivity came out to be very less. Prior to washing of sand, salinity and pH was high but after washing, pH became near neutral. The picture of the sand collected is shown in **Plate 5.5**.

Plate 5.5: Juhu beach sand used in project work

Table 5.7: Characteristic of Filter Sand and Juhu Beach Sand Media

Parameters	(D_{60}/D_{10})		Porosity (%)	Bulk Density (tone/m^3)	*pH*	ORP (mV)
Filter Media Sand	3.33		49.5	1.517	6.85	290.27
	D_{60}= 1 mm	D_{10}= 0.3 mm				
Juhu Beach Sand	2		48.33	1.2132	7.12	162.6
	D_{60}= 0.3 mm	D_{10}= 0.15 mm				

CW plant species: The plant species used in this project work was *Canna indica*. This wetland plant species is very common in Indian conditions and can be easily seen in IIT Bombay campus near Powai Lake. The plant seedlings were collected from lake side area of IIT Bombay.

Setting up of experimental CW reactors: There were total of 12 experimental CW reactors setup to carry out this study. The setups were divided in three main groups based on type of media used *viz.* Crushed aggregate, Filter sand and Juhu beach sand (**Table 5.8**). Every group has four experimental CW reactors, one unplanted and three planted reactors.

Table 5.8: Code used in project work for different experimental CW Reactors

Code	Reactor type
M0	Crushed aggregate “**unplanted**” experimental CW reactor
MP1	Crushed aggregate “**planted**” experimental CW reactors
MP2	
MP3	
F0	Dual media filter sand “**unplanted**” experimental CW reactor
FP1	Dual media filter sand “**planted**” experimental CW reactors
FP2	
FP3	
J0	Juhu Beach sand “**unplanted**” experimental CW reactor
JP1	Juhu Beach sand “**planted**” experimental CW reactors
JP2	
JP3	

Raw sewage: Raw sewage was collected from inlet of the sump well station of IIT Bombay. It was taken care that the sewage remains debris free and for that a screen bar was placed before collection of sewage from inlet pipe to the sump well station.

Standard practices and protocols were followed for the experimental setup of CW reactors and for testing various parameters. Methodology for characterizing CW media is adopted from the book Methods of Soil Analysis (Gee and Bauder, 1986).

The experimental CW reactors were placed in the premises of sump well station of IIT Bombay for the convenience in putting sewage (**Plate 5.6**). Sewage was collected from the inlet of sump well right after the screen bar so that debris could be avoided. Proper hygiene was maintained during the operation of experiments so as to avoid pathogen risks. Crates were placed in such a place and manner that seedlings had got sufficient sunlight.

1

2

Plate 5.6: Experimental CW Reactors at sump well station (IIT Bombay)

Media was weighted for every box and then filled up to the height of 0.2 m. The total volume of media put in to each box was ≈ 0.049 m^3. Crushed aggregate was washed to remove dust particles and Juhu Beach sand was washed to remove salinity from it. These media were air dried before weighing and putting into the crates. A particular media for four crates was mixed well before pouring so as to minimize differences if any due to washing. Dual media filter sand was put without washing into the crates. The weights of different media put in their respective boxes were as follows:

- Crushed aggregate : ≈ 105 kg
- Filter sand : ≈ 74.35 kg
- Juhu Beach sand : ≈ 59.5 kg

Plant used in experiment was *Canna indica* and the seedlings were collected from Lake Side area of IIT Bombay. The shoot and root of seedlings were washed and allowed to air dry for 20 minutes prior to weighing. Each seedling were tagged for particular crate and then planted. **Table 5.9** shows the weight and respective crates in which seedlings were placed:

Table 5.9: Initial weight of *Cana indica* seedlings in experimental CW Reactors

Crates	Weight of seedling
M0	Unplanted
MP1	55 g
MP2	8 g
MP3	12 g
F0	Unplanted
FP1	16 g
FP2	12 g
FP3	21 g
J0	Unplanted
JP1	14 g
JP2	33 g
JP3	14 g

Where; M = Crushed aggregates; F = Filter media sand; J = Juhu Beach sand; 0 = unplanted reactor; 1, 2, 3 = Three different planted reactors

Media conditioning and seedling acclimatization: Media used in experimental CW reactors were conditioned first before seedling plantation. For this purpose, sewage from sump well station was put into the crates filled with media for 3 cycles of 2 days retention time. Seedlings were planted in the morning hours for better chance of survival. Acclimatization of seedlings was done for 2 months by putting sewage from sump well station. The raw sewage was used for acclimatization as sewage characterization showed that the sewage was of medium strength. Therefore, sewage was used without dilution.

Operation and HRT: The experimental CW reactors were operated over three different HRTs during the project work viz. 24 hrs, 48 hrs and 72 hrs. Treated wastewater samples were collected for 5 operational cycles for all the three HRTs.

CW media characterization: The three different media used in experiments were characterized before putting into crates. The methods adopted to characterize were taken from Methods of Soil Analysis (Gee and Bauder, 1986).

d_{60}/d_{10}: Filter sand and Juhu Beach sand were passed through standard sieves of pore size (ranging from 0.1 mm to 1 mm).100 gm media sample was passed through the sieve and the volume of sand collected at the bottom of sieve was measured every time. The size of the sieve which allows 10% (i.e. 10 gm) media to pass through is the d_{10} value of that media.

Similarly, d_{60} was determined for both the media. Due to less sphericity of crushed aggregate, it was not subjected to d_{60}/d_{10} value determination.

Porosity of all the three different types of media used were determined in order to found out tentative amount of raw sewage that could be put into experimental CW reactors. For filter sand and Juhu Beach sand, 100 ml of air dried sample was taken into 500 ml measuring cylinder and water was poured up to the level of saturation. The amount of water that was used to fully saturate the media was determined as the porosity of that wetland media. Due to irregular shape of crushed aggregate, 5 liters of media was put into a 5 liter beaker (calibrated from measuring cylinder) and water was poured till its saturation level. The final volume of water required to saturate the air dried media was divided by the volume of media itself and the result gave porosity of crushed aggregate.

Effective Porosity is the actual porosity when the media was put into crates and saturated using raw sewage. The values obtained were slightly different from experimental value due to change in compaction ratio (i.e. area/volume).

Bulk Density of filter sand and Juhu Beach sand was calculated by taking 100 ml air dried sample into 500 ml measuring cylinder and subsequent weighing of the sample on weighing balance.

Specific Gravity of crushed aggregate was determined by water displacement method. Few pieces of crushed aggregate was taken and put into 100 ml measuring cylinder having 50 ml distill water. The rise in volume was noted down and the air dried crushed aggregate was weighed in balance. The ratio of weight to volume gave specific gravity of crushed aggregate.

pH and ORP of media samples were calculated by putting 25 gm sample into 50 ml distill water. The mixture was placed on shaker for 20 min and then allowed to stand still for 5 min. Supernatant was taken out to measure pH and ORP.

Analysis of sewage sample and treated effluent: Sewage sample was collected every time at the start of an experimental cycle. The treated effluent was collected at definite interval based on HRT cycle for example 24 hr HRT cycle, samples were collected at the end of 24 hr and similarly for 48 hr and 72 hr HRT cycles. Samples were collected in 500 ml plastic jars and were kept in cold storage if laboratory testing was not possible at that moment.

All wastewater samples were analyzed in accordance with the Standard Methods for Examination of Water and Wastewater (APHA, 2005). During filed visits of NTSs, physico-chemical and biological analyses were completed in wastewater treatment plant laboratories within 8 h of sample collection. The list of parameters analyzed during field visits of wastewater treatment plant have been summarized in **Table 5.10**. Physico-chemical and biological analysis of wastewater treated by lab scale setup of constructed wetland will begin after the 2 months of its establishment, and continued until the end of second year, so influent and effluent samples will be collected from each bed once a month over an 18 month period of proposed study. Treatment efficiency will be calculated as the per cent removal R for each parameter and was calculated by;

$R = (1 - Ce/Ci)\ 100$

where Ci and Ce are the influent and effluent concentrations in mg/l

Table 5.10: List of parameters selected for wastewater analysis

Sr.No	Name of Parameter	Method/ Instrument
1.	**Physico-chemical Parameters**	
1.1	Temperature (^{0}C)	Celsius Thermometer
1.2	Turbidity (NTU)	NTU Meter
1.3	Total Solids (mg/L)	Gravimetric method (APHA, 2005)
1.4	Total Dissolve Solids (mg/L)	Conductivity meter (APHA, 2005)
1.5	Total Suspended Solids (mg/L)	Gravimetric method (APHA, 2005)
1.6	Volatile Suspended Solids (mg/L)	Muffle furnace &Gravimetric method
2.	**Chemical Parameters**	
2.1	*pH*	*p*H meter
2.2	Conductivity (µS)	Conductivity meter (APHA, 2005)
2.3	Oil and Grease (mg/L)	(APHA, 2005)
2.4	Chloride (mg/L)	Argentometric titration method (APHA, 2005)
2.5	Sulphate (mg/L)	Spectrophotometric (APHA, 2005)
2.6	DO (mg/L)	Titrimetric method (APHA, 2005)
2.7	COD (mg/L)	Closed Reflex method (APHA, 2005)
2.8	BOD (mg/L)	Titrimetric method (APHA, 2005)
2.9	TOC (mg/L)	TOC Analyzer
2.10	Ammonia Nitrogen (mg/L)	Titrimetric method (APHA, 2005)
2.11	Organic Nitrogen (mg/L)	Titrimetric method ((APHA, 2005)
2.12	Nitrate Nitrogen (mg/L)	Spectrophotometric (APHA, 2005)
2.13	Nitrite Nitrogen (mg/L)	Spectrophotometric (APHA, 2005)
2.14	Orthophosphate (mg/L)	Spectrophotometric (APHA, 2005)
2.15	Organic Phosphorus (mg/L)	Spectrophotometric (APHA, 2005)

Table 5.10…Continue

3.	**Biological Parameters**	
3.1	Total Coliform count/100ml	MPN Method (APHA, 2005)
3.2	Fecal Colform Count/100mL	MPN Method (APHA, 2005)
3.3	Fecal Streptococci Count/100mL	MPN Method (APHA, 2005)
3.4	Fecal Enterococci Count/100mL	MPN Method (APHA, 2005)

Parameters subjected to test were BOD_5, COD, NH_3-Nitrogen and Phosphate. The testing protocols were followed from standard methods for analysis of wastewater (APHA, 2005).

$\underline{BOD_5}$:50 ml sample was taken and diluted 20 times with distill water. Initial DO of the diluted sample in BOD bottle was measured and marked on the bottles itself. After a span of 5 days in incubator, final DO was measured. Since the sample was sewage, it was not seeded for BOD testing. The BOD_5 of the particular sample was calculated as follows:

$$BOD_5 = \frac{DO_i - DO_f}{P}$$

Where; DO_i = initial DO; DO_f = final DO; P = dilution factor

COD: 2.5 ml sample was taken into COD tube and 1.5 ml $K_2Cr_2O_7$ was added to it. Then 3.5 ml concentration H_2SO_4 reagent for COD was added slowly to the mixture. The COD tube was then closed tightly with cap and placed in COD digester for 2 hr. After taking out of digester, the mixture was allowed to cool and then ferroin indicator was added. It was titrated with standardized FAS solution. Formula to calculate COD is:

$$\text{COD (mg/L)} = \frac{(A-B) \times N \times 8000}{\text{ml of sample}}$$

Where; A = ml FAS used for blank; B = ml FAS used for sample; N = normality of FAS titrant

$\underline{NH_3\text{-Nitrogen}}$: 100 ml sample was taken into Kjeldahl flask and 25 ml borate buffer was added to it. After maintaining the pH range of 9 – 12, the flask containing sample was put into Kjeldahl unit. The NH_3-Nitrogen was then absorbed into 50 ml boric acid solution. When the final volume of Boric acid solution reached 150 ml, it was titrated with H_2SO_4 solution. NH_3-Nitrogen was calculated by the formula:

$$NH_3\text{-N (mg/L)} = \frac{(B-A) \times N \times 14 \times 1000}{\text{volume of sample}}$$

Where; B = Volume of acid used against sample; A = Volume of acid used against blank; N = Normality of acid

Orthophosphate: Orthophosphate was tested in the sewage and treated effluent by ammonium molybdate test for phosphate. Standard curve was prepared before the test and OD value obtained was fit into the curve to find out PO_4^{3-}concentration in sample.

5.1.6 Removals of nutrients and carbonaceous pollutants from sewage using CW reactor

The three different media (crushed aggregate, filter sand and Juhu Beach sand) used in this project work were characterized before setting up the experimental CW reactors. To characterize media, parameters like (D_{60}/D_{10}) ratio, porosity, bulk density, pH and ORP were analyzed. Sewage and treated effluent from experimental CW reactors were analyzed for BOD_5, COD, PO_4^{3-} and NH_3-N values. BOD_5 values were determined only to characterize sewage samples in terms of BOD_5 to COD ratio which varied from 0.74 to 0.92.

The main natural water body polluting components in sewage are carbonaceous compounds which results into lower DO level and poses threat to aquatic life, phosphate level which results into eutrophication of water bodies, and ammonia nitrogen which causes foul odor and also lowers DO of water bodies. Therefore, these parameters were specifically targeted in this study.

Removal of COD from experimental CW reactors:

Crushed aggregate reactors showed better COD removal among all three reactors. Juhu Beach sand reactors showed more removal of COD compared to filter media sand reactors. The operational time refers in all experiments was of hydraulic retention time. The reactors showed higher efficiency at lower inlet COD concentration. The removal of COD in experimental cycles is shown in **Figure 5.2 (a) – (e)**. The time refer during assessment of the performance of was of the hydraulic retention time that corresponds to reaction time. The values taken for planted reactors in table 4.4 are average of three planted reactors of the respective media.

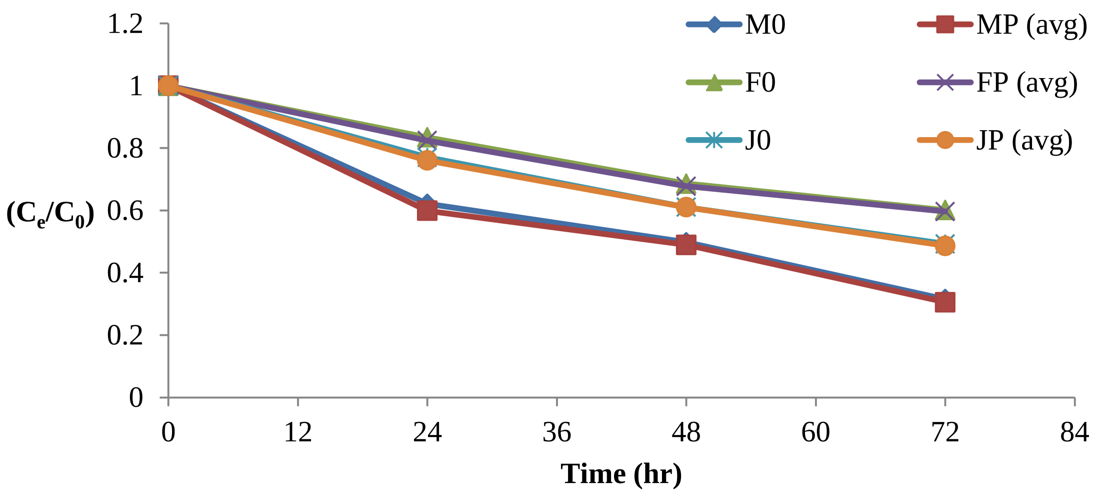


Figure 5.2 (a): Removal of COD by different experimental CW Reactors in experiment 1 (inlet COD concentration 149 mg/L). The time refer during assessment of the performance of was of the hydraulic retention time that corresponds to reaction time

The inlet concentration of COD in experiment 1 was 149 mg/L (comparatively less than other experimental cycles).Removal efficiency was good in crushed aggregate than Juhu Beach and filter media sand reactors. There was no significant difference in removal efficiency between unplanted and planted reactors in experiment 1.

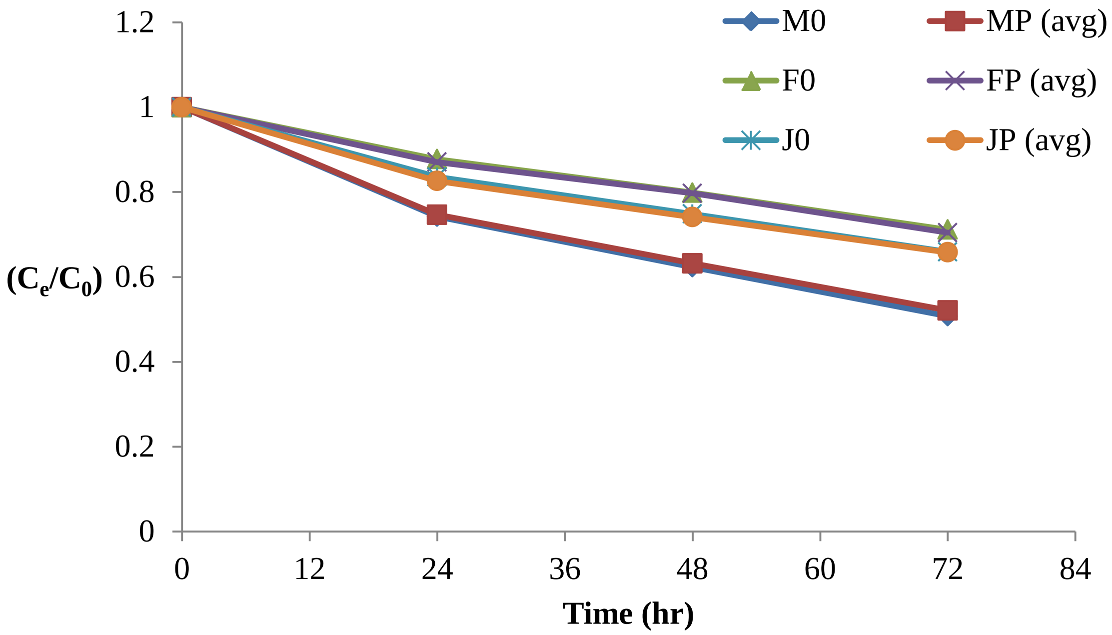


Figure 5.2 (b): Removal of COD by different experimental CW Reactors in experiment 2 (inlet COD concentration 287 mg/L)

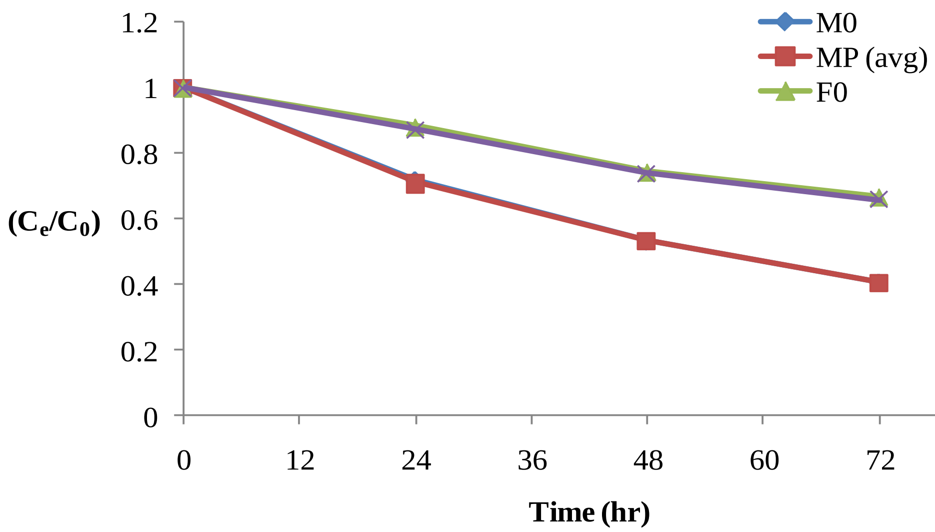


Figure 5.2 (c): Removal of COD by different experimental CW Reactors in experiment 3 (Inlet COD concentration 242 mg/L)

In experiment 2, inlet COD concentration was high and also overall removal by all the reactors showed lower removals. Maximum removal of around 50% was shown by crushed aggregate reactor (a decrement of around 20% than first experimental cycle). Removal efficiency of filter media sand and Juhu Beach sand was almost comparable.

In experiment 3, the removal efficiency of crushed aggregate reactor reached around 60% (an increment of around 10% when compared to experiment 2). There was a slight increment of around 5% in removal efficiency by filter sand media.

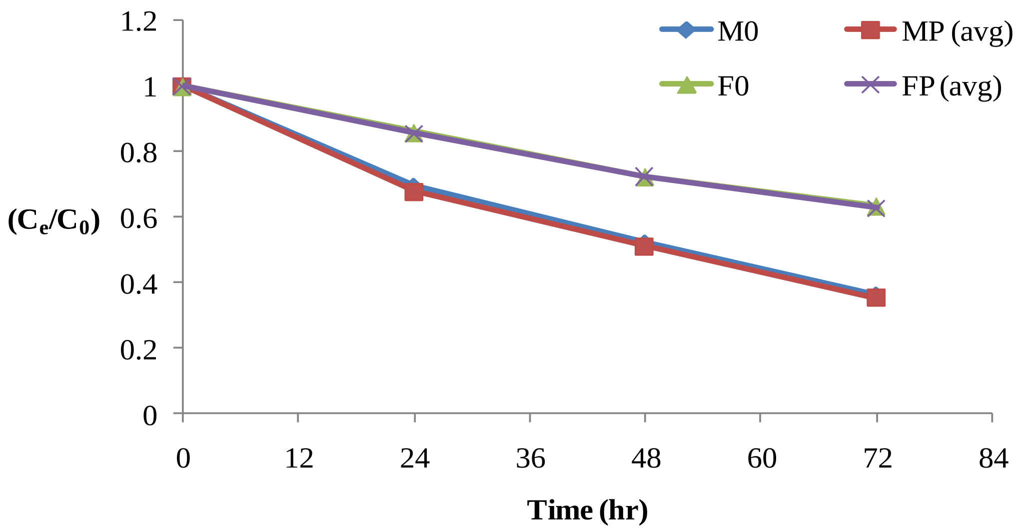


Figure 5.2 (d): Removal of COD by different experimental CW Reactors in experiment 4 (Inlet COD concentration 211 mg/L)

In experiment 4, filter sand did not show any increase in removal efficiency. Crushed aggregate showed an increment of around 5% than that of experiment 3 removal efficiency (total removal of around 70% was reached in experiment 4).

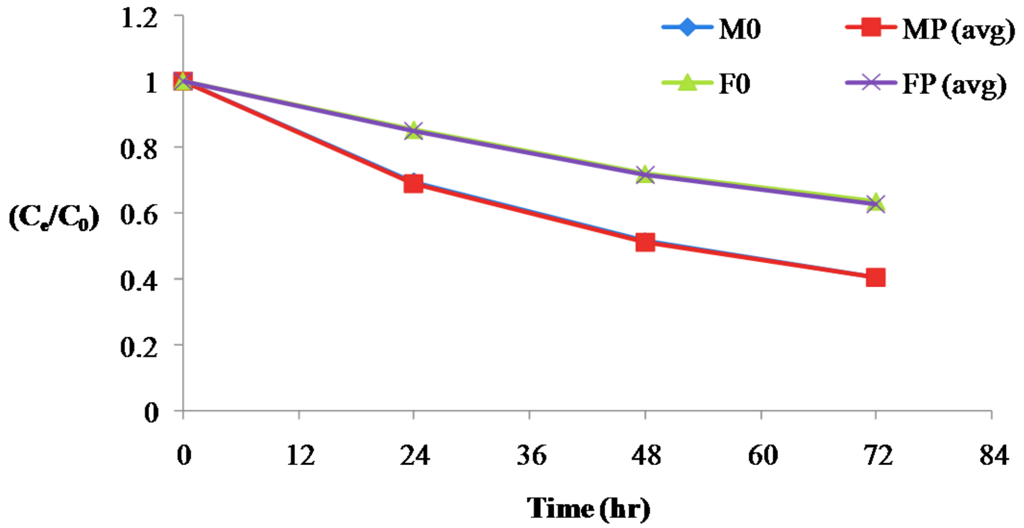


Figure 5.2 (e): Removal of COD by different experimental CW Reactors in experiment 5 (inlet COD concentration 256 mg/L)

In experiment 5, the removal efficiency in both the reactors seemed to show stabilized values. The overall removal in experiment 4 and 5 showed same removal efficiency of ~70% and ~30% in crushed aggregate and filter sand reactors respectively.

The removal of COD at lower strength sewage was found to show higher rate of removal. It was observed that when COD concentration in sewage was high, the rate of removal gets slowed. It shows that removal could be better if low to medium strength sewage is being used to treat by CWs (Zhao *et al*., 2010). The COD concentration in later cycle was in the range of medium strength sewage but the removal was not good. The possible reason behind this would be full drain and flood cycle pattern that was followed for experiments, because full drain results into lesser microbial biomass in the wetland system and system needs higher retention time to treat high COD concentration.

Karathanasis *et al*. (2003) reported that treatment by planted and unplanted system both did not meet the USEPA norms in effluent. The results from this project experiment showed that norms can be achieved when COD concentration was low (Experiment 1. 149 mg/L) but at higher COD concentration the removal was not sufficient for discharge into natural water bodies, thus making compliance with results shown by them.

In COD removal, no significant effect of vegetation was observed. But, prior to experiments it was expected that planted reactors would yield better efficiency than unplanted reactors (Vymazal, 2005).The BOD_5 test confirmed that BOD_5 to COD ratio of sewage varied from ~76% to ~92%. Therefore, the sewage was suitable for overall COD degradation by microbes present in the reactors.

Removal of ammonia nitrogen from experimental CW Reactors: Overall ammonia nitrogen removal was good in crushed aggregate and Juhu Beach sand reactors but filter sand reactor did not show efficient removal. There was a slight improvement in ammonia removal with respect to operation time. Readings were taken at 24 hr, 48 hr and 72 hr of experimental cycle. The percentage removal over the five experimental cycles has been shown in **Figure 5.3 (a) – (e)**.

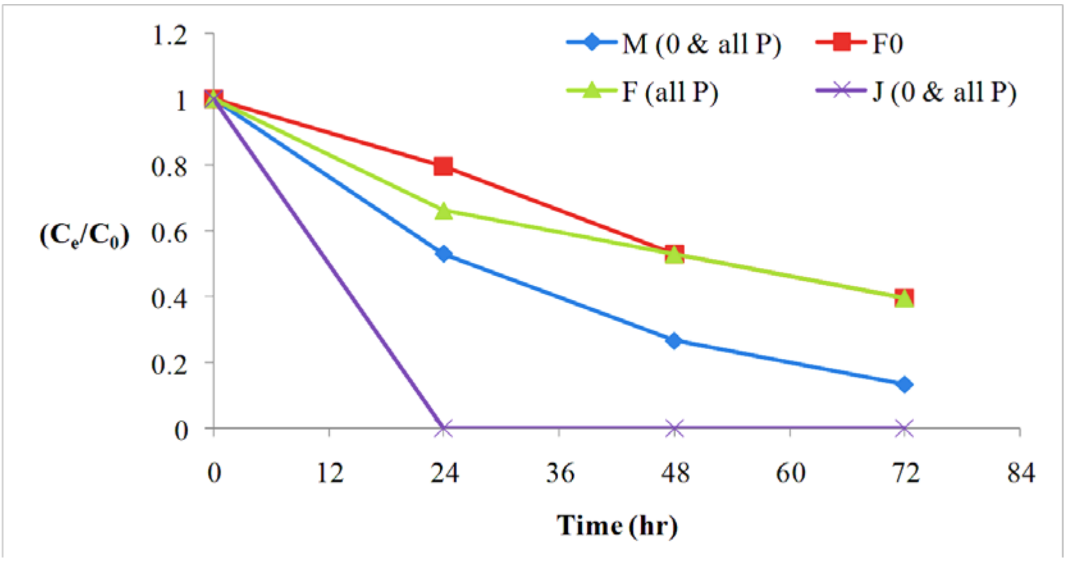


Figure 5.3 (a): Removal of ammonia nitrogen by different experimental CW Reactors in experiment 1 (inlet NH3-N concentration 8.46 mg/L)

Where; M (0 & all P) = Crushed aggregate planted and all three unplanted reactors;F0 = Filter media sand unplanted reactor; F (all P) = Filter media all three planted reactors;J (0 & all P) = Juhu Beach sand unplanted and all three planted reactor value.

The data obtained by Kjeldahl method for ammonia nitrogen determination had same values in almost all sand reactors. The titration point of filter media sand at 24 hr was different for unplanted and planted reactors. Therefore, separate data points in the form of table are not shown for ammonia removal in all the experiments. There was some deviation of data points in further experiments, which can be easily visualized from the Figure 5.3 (b).

The fractional removal of ammonia nitrogen in experiment 1 showed that Juhu Beach sand reactor removed ammonia nitrogen to almost zero within 24 hr of experimental cycle. Removal in crushed aggregate reactor was better than filter media sand reactor.

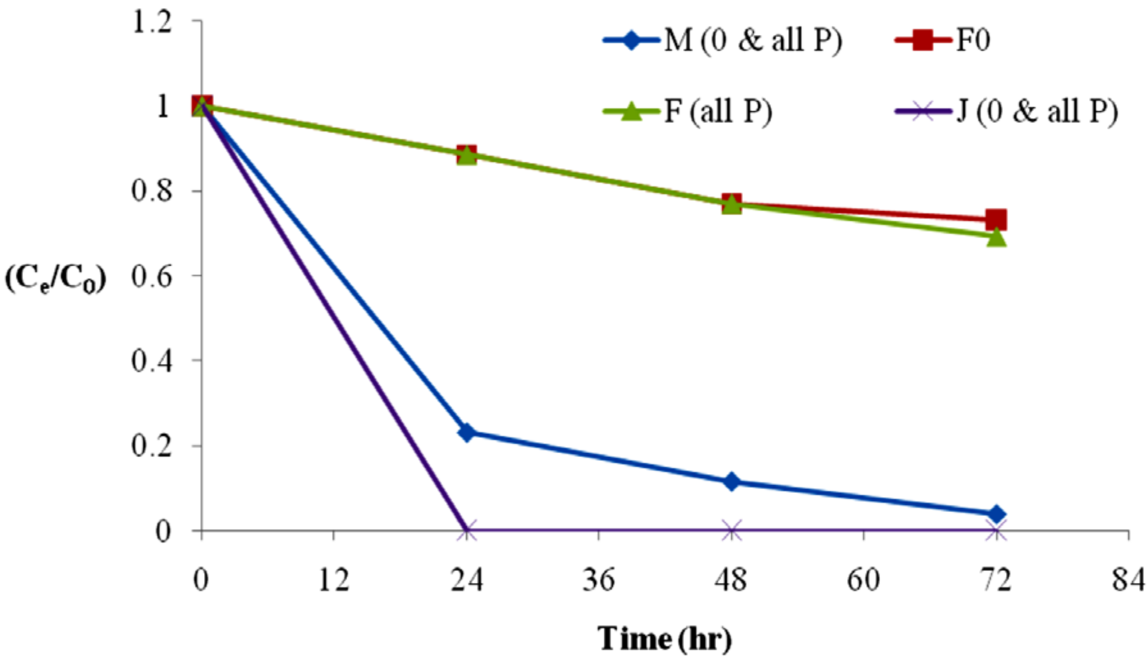


Figure 5.3 (b): Removal of ammonia nitrogen by different experimental CW Reactors in experiment 2 (inlet NH_3-N concentration 14.56 mg/L)

In experiment 2, Juhu Beach sand again showed complete removal of ammonia nitrogen within 24 hr of experimental cycle. But in contrary to experiment 1, filter media sand showed much lesser removal whereas crushed aggregate showed the similar trend in ammonia nitrogen removal as in experiment 1.

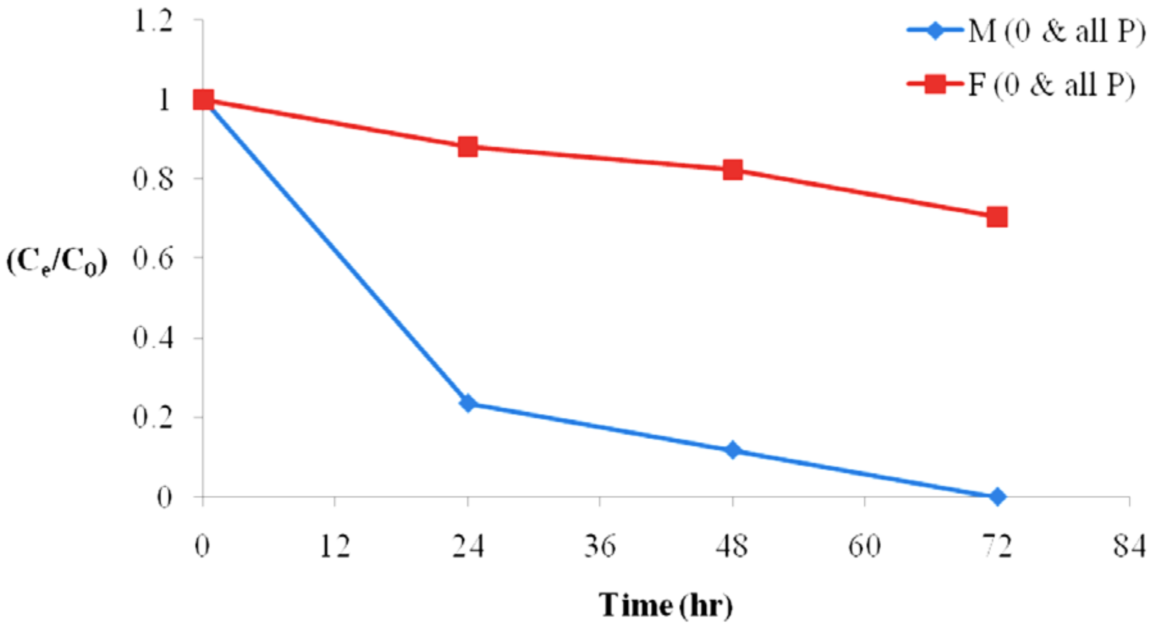


Figure 5.3 (c): Removal of ammonia nitrogen by different experimental CW Reactors in experiment 3 (inlet NH_3-N concentration 9.52 mg/L)

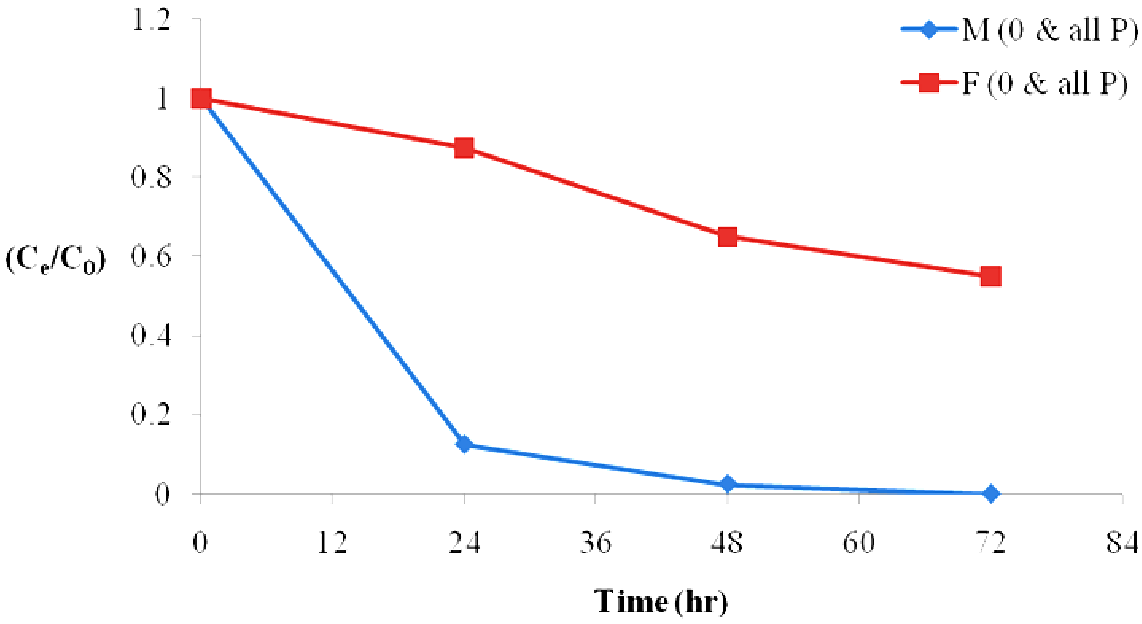


Figure 5.3 (d):Removal of ammonia nitrogen by different experimental CW Reactors in experiment 4 (inlet NH_3-N concentration 11.2 mg/L)

Results obtained in experiment 3, showed similar trend to experiment 2. The removal of ammonia nitrogen in experiment 2 and 3 in filter sand reactor showed around 20% removals even when the inlet concentration varied. The removal efficiency of crushed aggregate showed improvement over time as it had reached almost 100% in the third experimental cycle.

Crushed aggregate showed almost 100% removals in experiment 4. There was almost 20% increment in removal by filter sand reactor (so the overall removal was around 40%). Filter sand showed improvement in removal efficiency as compared to first experimental cycle but the overall removal was still not good enough when compared to its counterpart reactors.

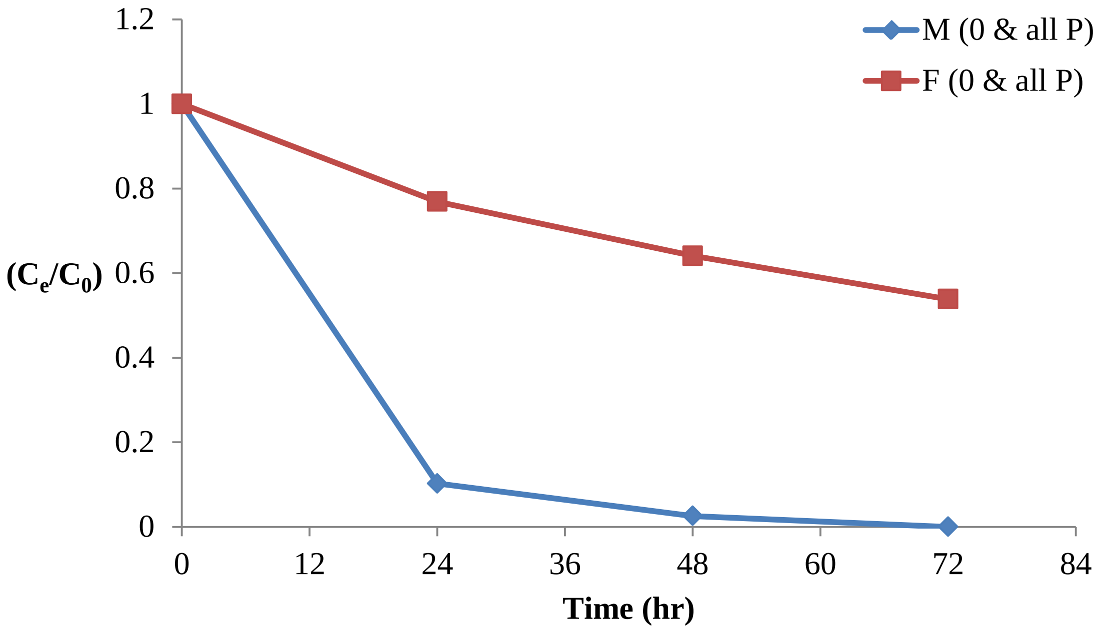


Figure 5.3 (e): Removal of ammonia nitrogen by different experimental CW Reactors in experiment 5 (inlet NH_3-N concentration 10.92 mg/L)

The results in experiment 5 was very much similar to experiment 4 as overall removal in crushed aggregate was almost 100% and in filter sand reactor removal was around 40%. The filter media seemed to show improvement in removal but at lower rate, and also the overall removal was not satisfactory.

As expected, the crushed aggregate gave the higher ammonia removal efficiency and in later experimental cycles, it gave 100% removal (Yang *et al*., 2001). The probable reason behind such good removal of ammonia in crushed aggregate would be large surface area which gives better biofilm growth (Lin *et al*., 2002). Juhu Beach sand also showed good ammonia removal. The possible reason behind ammonia removal in Juhu Beach sand reactor would be adsorption and contribution by nitrification would be less. As finer media particles shows higher sorption capacity due to large surface area (Xu *et al*., 2005). Filter media sand showed very less removal as compared to others. The possible reason behind this would be that the media was inert and the little removal that happened was due to microbial activity.

Lin *et al*. (2002) reported that wastewater with low COD concentration shows greater ammonia removal in shorter retention time. The great ammonia removal of up to ~100% was observed in this study and showed compliance with the work performed earlier as maximum inlet COD concentration was 287 mg/L.

Also in case of ammonia removal, there was no significant difference between planted and unplanted reactors. Gersberg *et al*. (1986) demonstrated that planted systems gave better ammonia removal in CW system but the result obtained from this study is not in compliance to them. The possible reason behind this would be smaller size of plants in reactors.

<u>Removal of phosphate from experimental CW Reactors</u>:

Standard curve for phosphate was prepared by using known concentration of PO_4^{3-} solution (0.2 mg/L to 1.2 mg/L with an interval of 0.2 mg/L) through stannous chloride method. The samples were tested in this range only after proper dilution.

Orthophosphate concentrations were measured during the five experimental cycles at the interval of 24 hours. Samples were stored in cold room if not analyzed instantaneously and analysis was done within 8 hr of sampling. Inlet samples had some suspended particles and hence was allowed to settle down before been tested for phosphate concentration. The readings obtained from three experimental CW reactors are tabulated in fractional removal is shown in **Figure 5.4 (a) – (e)**.

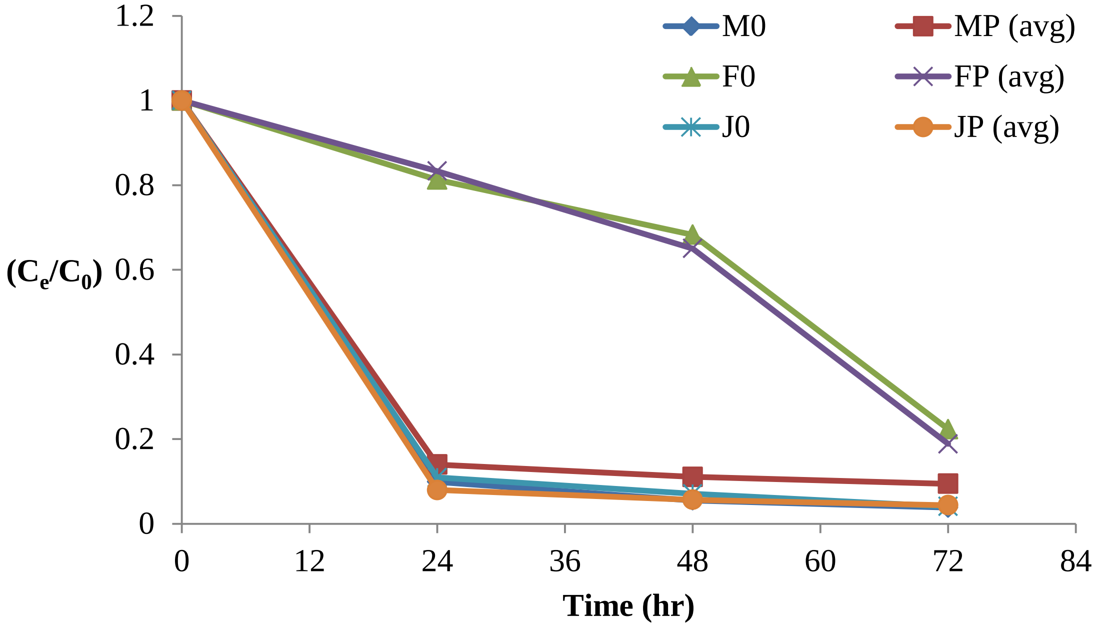


Figure 5.4 (a): Removal of phosphate by different experimental CW Reactors in experiment No. 1

The result in experiment 1 showed that crushed aggregate and Juhu Beach sand removed phosphate to same extent. Maximum removal in crushed aggregate and Juhu Beach sand was observed during the first 24 hours of experiment. Overall removal in filter sand was also comparable but the rate of removal was comparatively very slow.

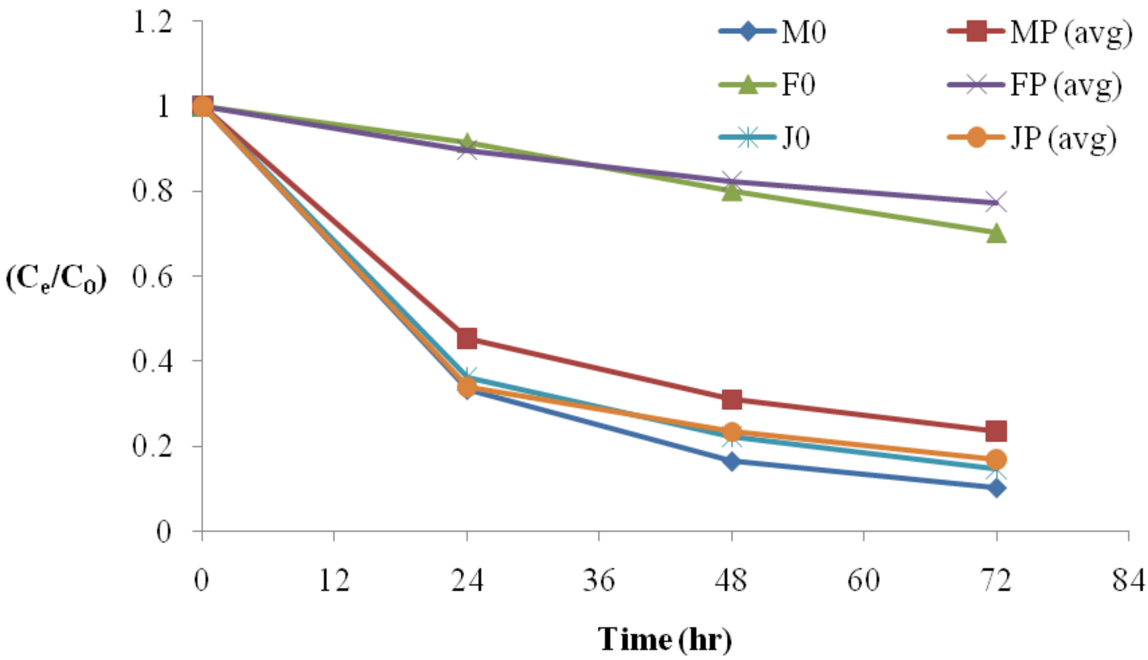


Figure 5.4 (b): Removal of phosphate by different experimental CW Reactors in experiment No. 2

Phosphate removal in experiment 2 showed that the removal was not dependent upon inlet PO_4^{3-} concentration. This might be happens due to the limited uptake potential of phosphorus by the plant system. Rather it was the minimum achievable concentration of phosphate irrespective of inlet concentration.

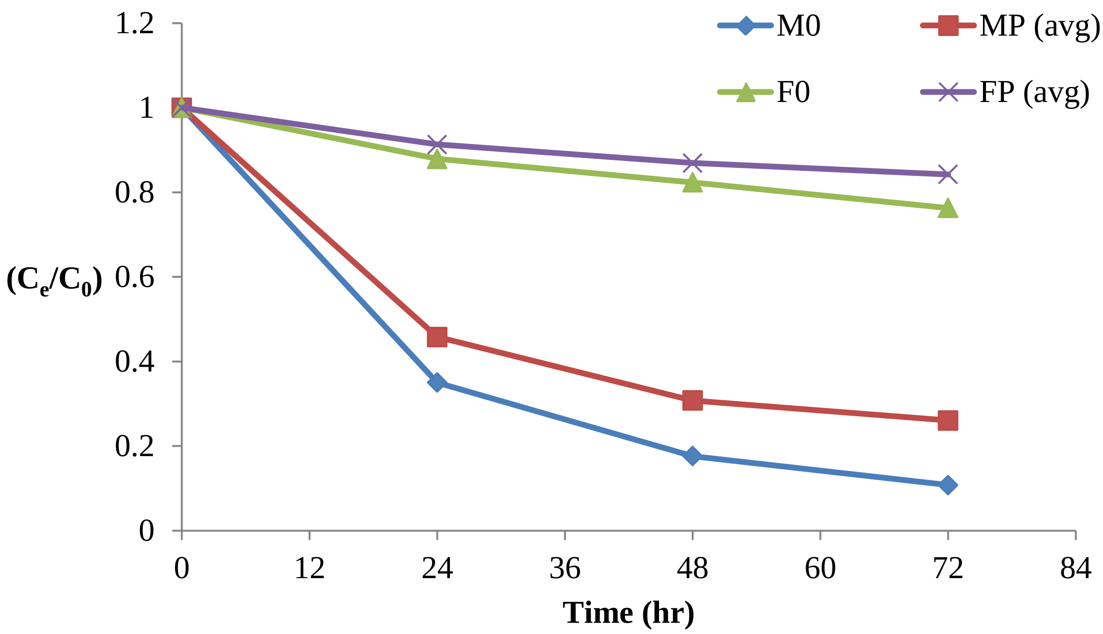


Figure 5.4 (c): Removal of phosphate by different experimental CW Reactors in experiment No. 3

By the time of experiment 3, Juhu Beach sand experimental CW reactors were clogged. So the data comprise of crushed aggregate and filter media sand only. The results showed that overall removal was better in crushed aggregate when inlet concentration phosphate was low.

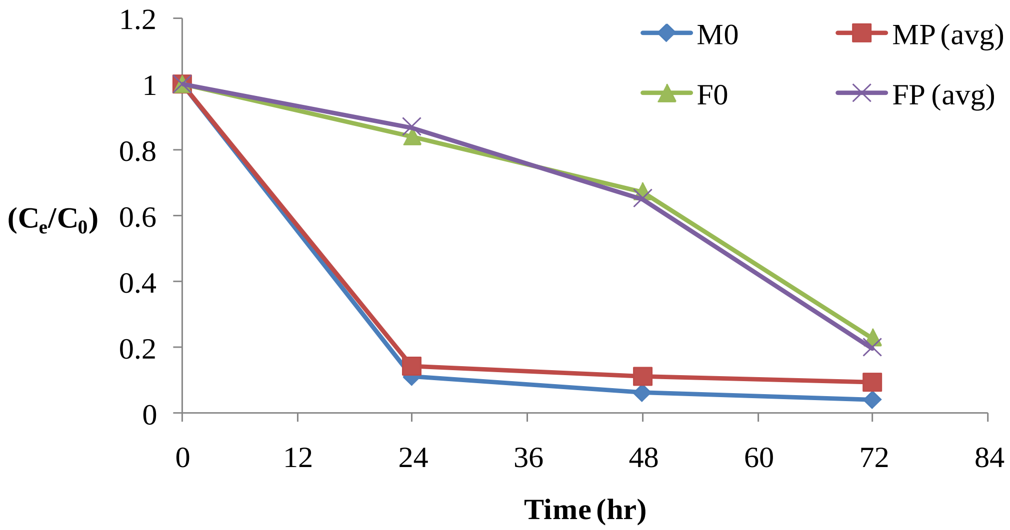


Figure 5.4 (d): Removal of phosphate by different experimental CW Reactors in experiment No. 4

In experiment 4, inlet concentration of phosphate was comparatively high and removal by both the sand reactors was acceptable. But the overall removal of crushed aggregate was again better than filter sand reactor.

In experiment 5, the results showed similarity with the earlier results. The removal comparison over all the experimental cycles did not show much variation and difference between planted and unplanted reactors were negligible.

Prior to start of experiment, it was presumed that crushed aggregate would give better results than Juhu Beach and filter media sand, as practice of using crushed aggregate (also known as gravel, which may vary in size) was already being used in CWs (Vymazal, 2002). The results from the experiments supported the fact that crushed aggregate could be used effectively in CWs. Filter media sand was tested as it contains maximum percentage of SiO_2 (an inert and stable compound). Therefore, the removal could be determined in inert wetland media also. The results of phosphate removal showed that filter media is not as good as other two media used in experiments. The basic idea behind using Juhu beach sand media was to test whether naturally found sand could be used in CW or not. The removal of phosphate by Juhu Beach sand showed that it could remove phosphate up to good extent but reactors could not be used long enough due to clogging. The media removal efficiency shown in this project was from its starting operational phase and it is supposed to be decreased during maturation of media over time (Lin *et al*., 2002).

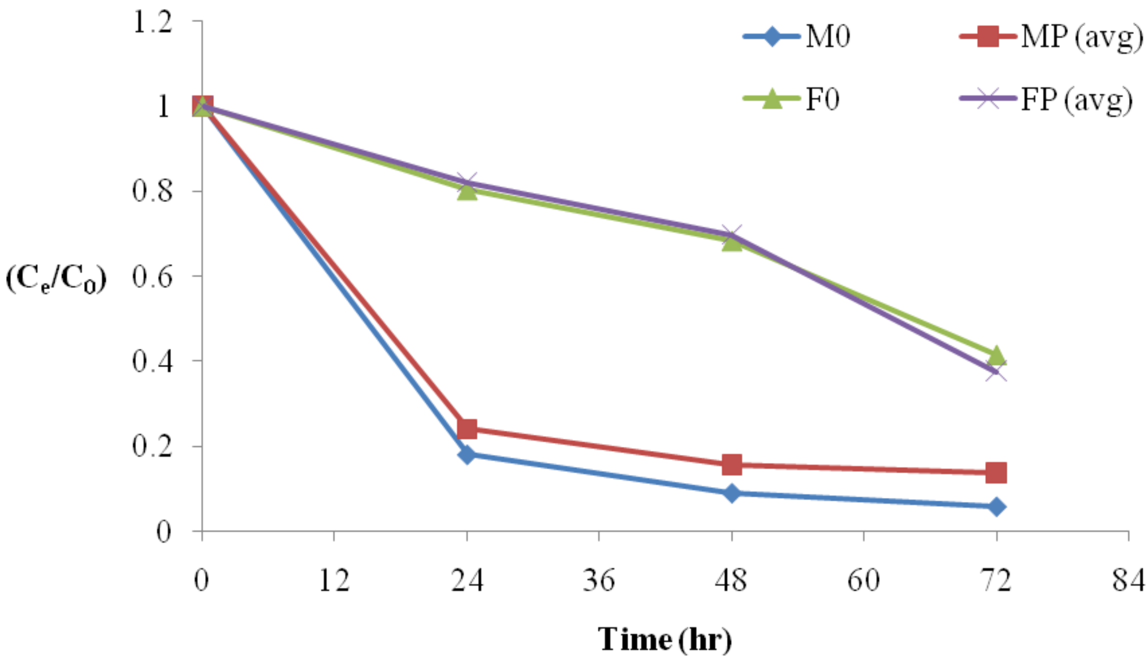


Figure 5.4 (e): Removal of phosphate by different experimental CW Reactors in experiment No. 5

Removal of pollutant in crushed aggregate planted reactors was less compared to unplanted reactor (Vymazal, 2002). The crushed aggregate reactors in this study showed efficient phosphate removal right from the first experimental cycle (when the vegetation was sparse) (Lin *et al*., 2002). Whereas, the removal trend and efficiency (in context of planted and unplanted reactors) in filter media sand and Juhu Beach sand were apparently similar. There was a possibility that phosphate removal may be enhanced during later life cycle of *Canna indica* when it will grow.

5.2 Strategies for selection of available methods for removal of phosphorus from the wastewater

The wastewater treated from NTSs, especially from constructed wetlands(CWs) gives a substantially good quality treated water interims pollution indicator like BOD, COD, TSS and coliforms (Vymazal, 2007). The wastewater from CWs may directly be reuse for non-potable means if some sort of tertiary treatment is given to remove the remaining traces of pollutants like nutrients. Removal of these traces of pollutants from treated water from CWs may accomplish the enhanced potential in reuse. Advanced nutrient removal by applying the physico-chemical or biological methods as well as an appropriate disinfection may produce the safe treated water which can be reused in different purpose. The present study will provide low cost options available for treatment of domestic wastewater using natural treatment methods. The scope of study is restricted to tertiary treatment of secondary treated constructed wetland wastewater.

There are many technologies available for removal of phosphorus from the wastewater. These wide numbers of technologies are based on limited set of principles. These principles have been discussed in the following section which comes under 2 major domains *i.e* chemical and biological removal techniques of phosphorus removal.

5.3 Available methods of phosphorus removal from wastewater

5.3.1 Chemical precipitation:

Orthophosphate ions are the easiest form to be precipitated among all kinds of phosphates (Mainstone and Parr, 2002). The most commonly used ions to precipitate phosphate are the different forms of calcium, aluminium and iron. During the precipitation, the reaction remains fast (Rittman *et al.,* 2011) and solubility of product depends on *p*H of the solution. The mechanism involved is discussed in the simple apparent reactions in the following heading. Apart from the metallic ions, other factors also play the major role in completion of reaction like alkalinity, *p*H, species, concentration, *etc*. The polyphosphates and organic phosphate also get removed either by combination of complex reactions or adsorption to flocks formed during the precipitate reaction.

(a) Alum precipitate

Aluminium reacts with phosphate ions to form aluminium phosphate as follows:

$$Al^{3+} + PO_4^{3} \longrightarrow Al^{3+} + PO_4^{3-}$$

Alum, hydrated aluminium sulphate (Al_2 $(SO_4)_3.14H_2O$), is commonly used as a source of aluminium in wastewater treatment. Molar requirement of Al^{3+} to $PO_4^{3-}$is 1:1.Similarly P : PO_4 is in the molar ratio of 1:1.Hence, stoichiometric relation between Al and P is 1 : 1. Onthe weight basis it can be said that 27gm of Al will react 96 gm of PO_4containing 32 gm of P to form 123gm of $AlPO_4$ sludge. The precipitation reaction proceeds as below:

$$Al_2\,(SO_4)_3.14H_2O + 2\,PO_4^{3-} \longrightarrow AlPO_4 + 3SO_4^{2-} + 14H_2O$$

The sulphate ions released from the addition of alum remains in the solution adding to TDS of the solution. Molecular weight of alum is 594 gm/mole. Above reaction shows that 594 gm of alum reacts with 192 gm of phosphate to give 123gm of $AlPO_4$ sludge carrying 32gm of phosphate. The weight ratio of alum to phosphorus is, therefore, 9.6:1.The alum requirement per gm of phosphorus may also be derived from the Al : P mole ratio using mole ratio of Al : P= 1: 1, therefore weight ratio of Al : P comes out to be 27 : 31 which can also be written as

0.87: 1. Alum contains 9.1% of Al, therefore, alum required per gm of P = 9.6 gm. The solubility of $AlPO_4$ varies with *p*H. It is nearly 0.3 mg/L at *p*H 5, 0.01 mg/L at *p*H 6 and 0.3 mg/L at *p*H 7. Minimum solubility is reported on *p*H 6 (USEPA, 1976). However, a range of *p*H has been suggested for efficient removal of phosphorus *i.e.* 5.5 -6.5.Some removal also occurs above *p*H 6.5. Alum reacts with alkalinity of wastewater and facilitates release of CO_2 hence decreasing concentration of hydroxyl ions (Morse *et al.,* 1998). Both factors results in lowering of *p*H. The extent to which *p*H decreases, depends on alkalinity of wastewater. Higher the alkalinity, lower is the reduction of *p*H by a given aluminium dose. Most wastewater contains sufficient alkalinity to resist drastic change in *p*H. However, in the field applications if *p*H gets reduced too much then *p*H is being maintained by soda ash, sodium hydroxide or lime.

$$Al_2(SO_4)_3.14H_2O + 6HCO_{3-} \longrightarrow 2Al(OH)_3 + 6CO_2 + 14H_2O + 3SO_4^{2-}$$

Table 5.11: Ratios of chemical required for removing phosphorus in different percentages

Phosphorus reduction required	Ratios of Al : P		Ratios of alum : P
	Mole ratio	weight ratio	Weight ratio
75%	1.38:1	1.2:1	13:1
85%	1.72:1	1.5:1	16:1
95%	2.3:1	2.0:1	22:1

Source: USEPA (1976)

However, Bashan and Bashan (2004) mentioned that removal of phosphate from water is not due to formation of $AlPO_4$ as suggested earlier due to formation of aluminium hydroxide phosphate at low *p*H of 3.6.

(b) Sodium aluminate precipitation

Sodium aluminate ($Na_2Al_2O_4$) acts as a source of aluminium ions for precipitation of phosphate. It is present commercially as $Na_2O.Al_2O_3.3H_2O$.It comprises of nearly 24% of Al. Unlike alum, addition of sodium aluminate leads to rise in *p*H during the reaction. Weight ratio of sodium aluminate to P is 3.6: 1 as compared to 9.6 : 1 in case of alum. Following reaction happens in the solution:

$$Na_2O.Al_2O_3 + 2PO_4^{3-} + 4H_2O \longrightarrow 2AlPO_4 + 2NaOH + 6OH^-$$

(c) Iron precipitation

The ferrous and ferric ions can be used in precipitation but both require different sets of *p*H for optimal results. Ferric ions react at *p*H range of 4.5-5 while ferrous performs optimally at pH at range of 7-8 (USEPA, 1976). Ferric ions react in the same manner as aluminium in the molar ratio of 1 : 1. However, due to difference in molecular weights, the weight ratio in which they combine is different. Weight ratio of Fe : P is1.8 : 1. Iron salts, like ferrous sulphate, ferric sulphate, ferric chloride and pickle liquor are present commercially for phosphorus precipitation. Addition of iron salts reduces alkalinity of wastewater by following reaction:

$$FeCl_3 + 3HCO_3^- \longrightarrow Fe(OH)_3 + 3CO_2 + 3Cl^-$$

(d) Lime precipitate

The dissolution reaction of lime with water release calcium ions into the water. These ions react with water in presence of hydroxyl ions to give sparingly soluble precipitate, calcium hydroxyapatite. As typical wastewater *p*H phosphate is present as HPO_4^{2-}.Reaction between calcium and phosphate are as follows:

$$3\,HPO_4^{2-} + 5\,Ca^{2+} + 4OH^- \longrightarrow Ca_5(PO_4)_3OH + 3H_2O$$

When bicarbonate alkalinity of water is low then relatively large amount of lime is consumed. The reaction is *p*H dependent. High-quality removal phosphate is observed at *p*H 9. Lime treatment decreases the total dissolved solids (TDS) content of the water by removal of hardness and alkalinity while mineral addition adds to the TDS (USEPA, 1987). Lime is not used frequently for phosphorus removal due to large amount of sludge generated as it evident from the above reaction. Another reason is operation and maintenance problems associated with the handling, storage, and feeding of lime. The weight ratio of Ca: P is 2.15 : 1. The advantage of using lime over mineral salts is that it leads to removal of TDS by removing hardness and alkalinity while former adds TDS to the solution. Lime treatment can remove turbidity to very low level. Phosphorus removal by metal salts is based on stoichiometry, whereas removal by the lime is based on achieving a target *p*H range. Lime precipitate can be used as fertilizer provided if it is not contaminated with other pollutants (Bashan and Bashan, 2004). In many fertilizer industries, lime is used to remove phosphate and sludge formed is sold to poultry farm as feed supplement. In natural water bodies with high alkalinity and hard water, precipitation of phosphate occurs which settle at the bottom (Rittmann *et al.*, 2011). The advantages and limitations of chemical precipitation by different reactants have been summarized in **Table 5.12.**

Table 5.12: Advantages and limitations of chemical precipitation

Type	Available forms and storage issues	Advantages	Limitations
Aluminium based chemical precipitation			
Aluminium Sulphate (Alum)	Liquid or dry form: Stable at room temperatures in closed containers under normal Near unlimited shelf life, corrosive, dust is irritant	• Most common form of aluminium salt. Has been used to achieve low effluent phosphorus concentration	• May need excess to depress the pH to an optimal operating environment • Alum sludge may be more difficult to thicken and dewater than iron sludge
Sodium Aluminate	Liquid or dry form: Liquid has 2-3 months of shelf-life strong alkali Dry form has 6 month shelf life, non-corrosive, dust is irritant	• Does not consume alkalinity • Appropriate for low alkalinity wastewater or where pH is already low and further depression should be avoided	• Dissolved CO2 or other acidity is needed to avoid pH increase above optimum zone • Performance considered inferior to alum
Polyaluminum Chloride (PACl)	Liquid hydrate form: Corrosive mineral acid. Requires acid resistant materials like PVC, Teflon, rubber, and ceramic materials	• Does not change pH of wastewater • Various formulations (multiple aluminum atoms bonded with chloride) available depending on manufacturer • Can help lower turbidity	• Not compatible with carbon steel, stainless steel, brass or aluminium • Unit cost may be higher

- **Iron based chemical precipitation**

Table 5.12…Continue

Ferric chloride	<u>Liquid</u>: Very corrosive, stains concrete and other material	• More common than ferrous chloride and ferrous sulphate • Has been used to achieve low effluent phosphorus concentrations	• Corrosive and requires special lining • In plants with poor solids capture, it may give slight reddish colour to effluent • Can be an issue if UV disinfection is downstream3
Ferrous Chloride	Available as liquid Slightly less corrosive than Ferric Chloride	• Can be available as a low cost industrial by product	• If industrial by-products, may contain residue of acids or metals • Produces low phosphorus • levels only at high pH
Ferrous sulphate	<u>Dry</u>: Acidic when dissolved Oxidizes in moist air Cakes at storage temp above 20°C	• Can be available as a low cost industrial by product	• If industrial by-products, may have large amounts of impurities, such as free acid • Produces low phosphorus levels only at high pH

Source: USEPA (1987)

5.3.1 Biological removal of phosphorus:

According to Metcalf and Eddy (2011) biological removal of phosphorus is achieved by phosphate accumulating micro-organisms PAOs. The PAOs associated with phosphorus removal belong to various kinds of species. Under aerobic conditions, PAOs take up large amount of phosphate from wastewater and store as polyphosphates. Under anaerobic conditions, polyphosphates are broken down to release energy which is used in taking up easily biodegradable material from the surroundings. This biodegradable material is stored in the form of Polyhydroxyalkanoates (PHAs) most prominent of which is Poly- β-hydroxy-butyrate (PHB). When aerobic conditions return, PHAs are broken to produce energy which is used in taking up phosphates. Acetic acid and propionic acid are the dominant VFAs in domestic wastewater. Research has shown that GAOs do not grow well on propionic relative to PAOs, therefore, the ratio of propionic to acetic acid affects the performance of biological phosphate removal.

Presence of nitrates decreases the efficiency of phosphate removal. Under anaerobic conditions, denitrifiers and PAOs compete for readily biodegradable COD present in the wastewater. This leads to lower release of phosphates by PAOs in anaerobic conditions. These results in lower uptake of phosphates under anaerobic condition. PAOs also face competition from Glycogen Accumulation Organism (GAOs). GAOs compete for substrate but don’t carry out removal of phosphates. The advantages and limitations of biological phosphorus removal have been summarized in **Table 5.13**.

Table 5.14summarize the minimum ratios of substrate to total phosphorus to obtain effluent phosphorus concentrations of less than 1 mg/L. Evaluating the chemical oxygen demand to total phosphorus (COD: TP) and 5 day Biochemical oxygen demand to total phosphorus (BOD_5: TP) ratios provides only a rough approximation of BPR capabilities, but can provide a thumb rule for estimations (USEPA, 1987). Evaluating the ratio of readily biodegradable COD to TP (rbCOD : TP ratio) of the process influent is a more reliable way of assessing the BPR capabilities of wastewater plant and of determining if additional substrate is required to achieve the desired effluent phosphate concentration. Analysis of the rbCOD : TP ratio is superior to analysis of VFA:TP because much of the non VFA rbCOD can be fermented to VFA in the anaerobic zone as long as there is sufficient and favorable temperature conditions. Hence, designers may wrongly predict the need for additional substrate if only VFA: TP ratio is considered.

Table 5.13: Advantages and limitations of biological phosphorus removal

S. No	Advantages	Limitations
1	Sludge generated is large, comparable to generated during conventional Activated sludge systems	In all but phostrip, phosphorus removal performance is controlled by the BOD : TP ratio of wastewater
2	Can be implemented directly at existing plug flow ASP with little or no equipment changes or additions provided that plant has sufficient capacity	Requires highly efficient secondary clarifier performance to achieve 1mg/L total phosphorus
3	Can utilize existing sludge handling equipment for plants retrofitted with biological phosphorus removal process if phosphorus is not solubilized and returned to the plant during sludge handling	Not easily retrofitted into fixed film biological systems
4	Little or no chemicals or chemical handling equipment required except for phostrip process or for effluent polishing	Potential for phosphorus release in sludge handling system, Recycle streams must be low in phosphorus content
5	Phosphorus removal can be accomplished together with ammonia nitrogen or total nitrogen removal at virtually no additional operating cost with some of the processes	Stand by chemical feed equipment may be necessary in case of loss of biological phosphorus removal efficiency.
6	For some of the processes better control of filamentous organisms in the ASP is possible	

Source: USEPA (1987)

Table 5.14: Ratio of substrate to total phosphorus to achieve effluent Phosphorus concentration <1mg/L

Substrate type to total phosphorus	Recommended minimum ratio
COD:TP	40 – 45
BOD:TP	20
rbCOD:TP1	10 – 16
VFA: TP	4 – 16

Source: USEPA, 2008

Where COD = Chemical Oxygen Demand; BOD = Biochemical Oxygen Demand; rbCOD = readily Biodegradable Chemical Oxygen Demand; VFA = Volatile Fatty Acid; TP = Total Phosphorus

<u>Biological phosphorus removal technologies</u>: All biological phosphorus removal technologies are designed to recycle treatment from anaerobic to aerobic conditions to encourage PAOs to grow and uptake phosphorus (USEPA, 2010; Tetreault *et al.,* 2011). This section describes two technologies that have been designed to biologically remove only phosphorus only from wastewater. Most technologies have been designed to remove both nitrogen and phosphorus simultaneously.

(a) Pho-redox (A/O)

The system is similar to conventional activated sludge system with anaerobic zone in the head of aeration basin. Recycle activated sludge (RAS) is pumped back to the anaerobic zone.SRT is being kept low to avoid nitrification. If nitrates are present then anaerobic zone gets divided into anoxic chamber for denitrification followed by anaerobic zone for phosphorus removal. The system is easy to retrofit by creating a baffle in the reactor to create anaerobic zone (Jiang *et al.,* 2004).

(b) Oxidation ditch with anaerobic zone

Oxidation ditches are looped channels that provide continuous circulation of wastewater and biomass. The wastewaters flow around a barrier in the centre. Distance covered remains 1 foot per second or more with long SRTs. The aerators are typically rotating brushes or turbines that move the water as well as transfer oxygen. Therefore, no additional pumping or piping is needed compared to a conventional activated sludge system, which reduces energy costs. The anaerobic zone is most often ahead of the ditch sometimes called as selector.

(c) Phostrip

The process was proposed by Levin in 1965 for the first time. It combines biological and chemical phosphorus removal. It is commonly referred as side stream process because a portion of RAS is diverted remove phosphorus stripping followed by precipitation with lime. In this method, effluent concentration of less than 1mg/L can be achieved. The process has very less dependence on BOD of influent because precipitation of phosphate happens chemically. Lime dose is dependent on alkalinity of wastewater and not on phosphorus concentration unlike alum and iron salts. The Phosphorus stripper tank receives nearly 10-30% of influent flow. The tank also works as gravity sludge thickener with solids retention time of 8-12 hours. Soluble phosphorus gets released in the anaerobic tank. The mechanism involved in release of phosphorus is unknown. It can be in the same way as in anaerobic tank.

In stripper organics released from lysed bacteria can act as source of BOD. Release of soluble phosphorus may be contributed by lysed bacteria or phosphorus removing micro-organisms. Overflow from stripper tank is fed to chemical treatment tank where lime is added for phosphorus removal. Chemical sludge can be removed from this process by 2 different ways. First is by using separate reactor and clarifier. Other is to put lime in the supernatant of stripper tank followed by removal in the primary clarifier. Since the Phostrip performance is related to the performance of stripper and chemical treatment, it can work under broad range of loading as compared for A/O and Modified Bardenpho process.

(d) Modified bardenpho process

It is a combined nitrogen and phosphorus removal system. In this process, first reactor is anaerobic flowed by alternate arrangement of anoxic and aerobic chamber. Influent and RAS are subjected to anaerobic conditions to facilitate release of phosphorus before passing to Bardenpho process. In first anoxic chamber, denitrification occur using BOD of influent as carbon source. About 70% of nitrate nitrogen is removed in this stage. In the first aerobic stage, ammonia is oxidized, phosphorus uptake occurs and BOD is removed. Second anoxic stage provides platform for additional denitrification. The final aerobic tank provides short period of aeration to reduce anaerobic conditions and hence reduce release of phosphorus in secondary clarifier.

(e) UCT Process

This process is modification of Modified Bardenpho Process. It was developed in University of Capetown and so called as UCT Process. In this process, return activated sludge is redirected to anoxic stage instead of anaerobic process in Modified Bardenpho Process. This was developed because earlier studies had shown that biological phosphorus removal gets affected when nitrates are present in anaerobic tank nitrates act as electron acceptor for BOD entering anaerobic chamber. In the absence of nitrates BOD ferment to give organic acids which are used by PAOs to release phosphorus in anaerobic reactor. Due to competition from nitrates efficiency of biological phosphorus removal decreases. In UCT process, return activated sludge goes to anoxic stage for denitrification. This reduce load of nitrates and sludge can then enter anaerobic chamber for better performance: Denitrification also requires external carbon source by heterotrophs thus BOD entering anoxic chamber will also be reduced during denitrification reaction. For wastewater with higher Kjeldahl's Nitrogen: BOD ratio, effect on biological phosphorus removal should be significant.

(f) Modified UCT Process

In this process, one anoxic is provided exclusively for remove nitrates from RAS. Second anoxic zone is made to handle larger quantity of nitrates as mixed liquor is recycled to it from nitrification zone.

Combination of chemical and biological methods: Above mentioned technologies can be combined to obtain desired effluent level. Authors have shown that biological process has lower overall operational cost as compared to chemical process (USEPA, 1998). However, biological removal alone is not reliable and may not achieve high level of phosphorus removal in effluent. **Table 5.15** present removal efficiency of different technologies combined together. The removal is highest when advanced treatment option like ultra-filtration was used along with other biological and physico-chemical method.

Table 5.15: Estimated effluent quality of reference design

Process	BOD mg/L	TSS mg/L	TP mg/L	P removal %
Influent	174	172	7.5	-
Effluent of AS	22	20	5.86	21.8
Effluent of AO	11-20	20	4.12	45.1
Effluent of AAO	11	20	2.95	60.7
Effluent of AAO + Al	10	20	1.00	86.7
Effluent of AAO + M+ T	5-10	5	0.325	95.7
Effluent of AAO + M+ T+ F	5	1	0.145	98.1
Effluent of AAO + M+ T + C	<1	<1	0.10	98.7
Effluent of AAO + M + F + UF	<1	<1	0.05	99.3

(Source: Jiang *et. al,* 2004)

Where, AS = Activated Sludge; M = Metal Salt Addition; AAO = Anaerobic Anoxic Oxic Reactors;T = Tertiary Clarifier; F = Filtration; UF = Ultra-filtration; C = Aluminium Column Absorption

Cost comparison: The cost of technologies varies with size, volume handling and sophistication (Hartman and Cleland, 2007). Total cost reduces with increase in size.

Table 5.16: Cost comparison in different combination of technologies

Process	Flow MGD	Total Capital Cost (2004 $*$10^6$)	Total O&M Cost (2004 $*$10^6$)
AS	1	7.36	0.93
	10	39.53	4.13
	20	65.56	6.84
	50	127.99	13.57
	100	212.28	23.16
AO	1	8.94	1.09
	10	46.89	4.85
	20	77.25	7.98
	50	149.45	15.73
	100	248.29	26.85
AAO	1	9.69	1.17
	10	54.52	5.43
	20	91.68	9.13
	50	182.28	18.29
	100	306.55	31.57
AAO + Al	1	9.76	1.35
	10	54.65	7.1
	20	91.84	12.46
	50	182.54	26.59
	100	306.98	48.17
AAO + Al + T	1	10.12	1.41
	10	56.03	7.5
	20	94.24	13.22
	50	188.58	28.48
	100	318.94	51.96

Table 5.16…Continue

AAO + Al + T + F	1	10.84	1.49
	10	58.72	7.82
	20	100.06	13.88
	50	206.39	30.3
	100	344.41	55.03
AAO +Al + T+ C	1	11.11	1.60
	10	65.88	8.44
	20	112.97	14.91
	50	237.87	32.61
	100	410.95	59.58
AAO +Al + F +UF	1	12.27	1.76
	10	72.79	9.18
	20	113.18	15.62
	50	277.31	36.80
	100	486.18	67.95

Source: Jiang *et al*. (2004)

Where, AS = Activated Sludge; M = Metal Salt Addition; AAO = Anaerobic Anoxic Oxic Reactors;T = Tertiary Clarifier; F = Filtration; UF = Ultra-filtration; C = Aluminium Column Absorption

Table 5.16 shows the comparison between construction and operational costs of different process handling different volumes of wastewater. The table is given for combination of biological and physico-chemical processes. It is evident from the Table 5.16 that operational costs of technologies involving physico-chemical processes are higher than natural biological systems. Main factors contributing to the cost are expensive chemicals, membrane, power requirement, expensive chemical sludge disposal cost, *etc.* (USEPA, 2009).

Cost comparison of phosphorus removal alternatives: This section deals specifically with phosphorus removal technologies keeping nitrogen as constant. The comparison is made on the basis of capital and operation and maintenance cost in plants of different volumes. The cost is given with reference to new plant. In case of retrofitting capital cost will be less because of pre-available infrastructure (Jiang *et al.*, 2005). The cost of installation also depends on desired effluent quality along with scale of operation as shown in **Table 5.17** and **Table5.18**.

Table 5.17: Case 1 - phosphorus removal (effluent total phosphorus = 1 mg/L)

Alternative	Costs	1890 (m^3/d)	18900 (m^3/d)	189200 (m^3/d)
Stage AS with alum addition	Capital $	2,774,000	10,851,000	55,568,000
	O & M. $/yr	218,000	868,000	5,611,000
	Total Present Worth	4,782,000	18,846,000	107,248,000
Phostrip	Capital $	3,801,000	12,602,000	59,073,000
	O & M. $/yr	273,000	744,000	3956,000
	Total Present Worth	6,315,000	19,455,000	95,509,000
A/O (4 hr detention) with effluent filters	Capital $	3,370,000	13,257,000	63,472,000
	O & M. $/yr	227,000	836,000	4,545,000

Source:Jiang *et al*. (2004)

As evident from the Table 5.17 and Table 5.18 per unit cost of treatment decreases with increase in volume of wastewater treated. The cost of treatment decreases with decreasing effluent quality as shown in table below. Trend shows that cost also varies depending upon kind of technology installed. Chemical methods may have lesser O & M cost due to smaller infrastructure.

Table 5.18: Case 2 - phosphorus removal (effluent total phosphorus = 2 mg/L)

Alternative	Costs	1890 (m^3/d)	18900 (m^3/d)	189200 (m^3/d)
1 Stage AS with alum addition	Capital $	2,762,000	10,821,000	55,350,000
	O & M. $/yr	213,000	835,000	5,276,000
	TotalWorth	4,724,000	18,512,000	103,944,000
Phostrip	Capital $	3,801,000	12,602,000	59,073,000
	O & M. $/yr	273,000	744,000	3,956,000
	Total Worth	6,315,000	19,455,000	95,509,000
A/O (4 hr detention) with effluent filters	Capital $	2,813,000	10,819,000	52,314,000
	O & M. $/yr	197,000	692,000	3,820000
	Total Worth	4,627,000	17,193,000	87,498,000

(Source: Jiang *et al*., 2004)

5.3.2 Selecting a phosphorus removal strategy

Approach for selection: There are wide number of technologies available but selection of specific technology depends on end use requirement and need of removal of other pollutants along with phosphorus. All technologies are considered initially and non-applicable technologies are removed step by step. Various other factors are involved before making final selection which is subjective like degree of phosphorus removal required, size of plant, impact on sludge handling, permanent or temporary nature of phosphorus removal requirement, total cost and impact on operation and maintenance.

Information and monitoring data required: Information and monitoring data required for selecting a phosphorus removal system are discussed in the following section. Information required by new plants is different from existing plants. Many times due to stringency of legislation at later stage retrofitting of plants is required. So, to make cost effective selection some prior information/data is required.

New system data requirement: This category majorly requires information like as follows:

- Effluent discharge requirement
- Wastewater characteristics
- Other information like sludge disposal alternative, service area characteristics, plant size and location, available land, facility design lifetime, local availability and cost of chemicals.

Effluent discharge requirement: This is the first step that need to be taken for selection and should be done in detailed manner. Phosphorus limits can be set as either minimum removal percentage, as a specific effluent concentration or on a mass per day basis. Discharge limits of other parameters like BOD_5, TSS, pH, NH_4, and total N should be collected. Removal of parameters like nitrogen has a significant impact on selection of appropriate technology.

Other information: Sludge handling is easier done in rural areas because of land availability. Sludge generation is a major factor deciding choice of phosphorus removal alternative. In many cases options of sludge disposal are limited due to stringent regulations or biased opinion of law makers and public. Chemical alternatives need less space but these processes are expensive to operate. Biological methods are sensitive to temperature and shock loads and require analysis of total treatment requirement including proper selection of BOD removal process. Chemical processes are favourable for short time span while biological processes need high capital cost and are appropriate for long term design period projects.

Existing system requirement (USEPA, 1987): Existing facility poses a few constraints in selection of appropriate technology. Existing systems may give opportunities for cost effective incorporation of some of the available phosphorus removal technologies but at the same time may present severe constraints to the use of others. Important considerations include hydraulic capacity of current plant in order to meet requirement of retrofitting, age and condition of existing plant, possibility of up-gradation or expansion in the near future, biasness of conventional system towards certain specific technology or all. Analysis should proceed in same way by collecting information like type, capacity and efficiency of existing operations in service. Parameters of specific unit operation should be measured which majorly includes Total P, TSS, BOD_5, Total N, NH_4-N. Unused plant capacity if there can be used for expansion should also be taken into consideration.

5.3.3 Selection of phosphorus removal system

The selection procedure followed comprises of 4 steps. At each step applicability of the process is evaluated for given set of conditions using set of matrices. Apparent inappropriate technologies are not considered for the evaluation in the next step of screening. The selected technology is taken for cost effectiveness analysis. The selection process is subjective hence final shortlisted technology may vary from person to person depending on ground conditions.

Step 1: Shortlist whether new plant for phosphorus removal is to be set up or retrofitting is required and whether discharge limit is to be matched only for phosphorus or other pollutants also. This greatly influences selection of technology. In case new plant is needed then all options can be considered whereas in existing facility few options can be completely discarded. **Table 5.19** shows list of technologies showing comparison between phosphorus removal technologies with combination of technologies having potential of simultaneous nitrogen and phosphorus removal. The matrix also includes suspended and attached growth system of biological removal system.

Table 5.19: Matrix showing comparison of technologies for phosphorus and nitrogen removal

Process	P Removal Only			P plus NH_4 or N Removal		
	New Facility	Existing Suspended Growth	Existing Fixed Growth	New Facility	Existing Suspended Growth	Existing Fixed Growth
Phostrip	Y	Y	N	Y	M	Y
Modified Bardenpho	E	E	N	Y	Y	N
A/O	Y	Y	N	Y	M	Y
SBR	Y	Y	N	Y	Y	N
UCT	E	E	N	Y	Y	N
Mod. A.S	Y	Y	N	Y	M	Y
Metal Salt	Y	Y	Y	Y	M	M
1-Stage lime	Y	Y	Y	Y	M	Y
2- Stage lime	Y	Y	Y	Y	M	Y

Source: USEPA (1987)

Y = Applicable, N = Not Applicable, E = May be applicable but exceed treatment requirements; M = may be applicable but N or NH^{4-}removal step require; Y = Applicable where existing fixed film unit can be used for nitrification

Step 2: Apply phosphorus removal process capabilities and determine which processes can meet phosphorus limitations. In case, nitrogen discharge limitation is also there then an additional screening step comprising of nitrogen removal processes need to be added (WDNR, 2009). Additional factors like removal of BOD_5 and suspended solids may lead to acceptance and rejection of a process though they are not mentioned as main factors deciding selection. **Table 5.20** gives matrix of different situation in which different technologies are applicable and achievable effluent levels with different combination of technologies are presented.

Table 5.20: Application criteria matrix: ability of the process to meet effluent phosphorus limitations

0.5 mg/L Effluent TP					1 mg/L Effluent TP				2mg/L Effluent TP			
Process	Alone	w/M.S.	w/F	w/M.S. & F	Alone	w/M.S.	w/F	w/M.S. & F	Alone	w/M.S	w/F	w/M.S. & F
Phostrip	N	N	N	Y	Y	Y	Y	Y	Y	Y	Y	Y
Mode. Bardenpho	N	N	N	Y	M	Y*	M	Y	Y	Y	Y	Y
A/O	N	N	N	Y	M	Y*	M	Y	Y	Y	Y	Y
SBR	N	N	N	Y	M	Y*	M	Y	Y	Y	Y	Y
UCT	N	N	N	Y	M	Y*	M	Y	Y	Y	Y	Y
Mod. A.S	N	N	N	Y	M	Y*	M	Y	Y	Y	Y	Y
Metal Salt	N	-	Y	-	Y*	-	Y	-	Y	-	Y	-
1-Stage Lime	N	N	Y	Y	Y*	M	Y	Y	Y	Y	Y	Y
2- Stage Lime	N	N	Y	Y	Y*	M	Y	Y	Y	-	Y	-

Source: USEPA (1987)

Ability of alternatives (B)-(F) to meet effluent limits alone based on TBOD: TP ratio being above 20

N – Cannot meet effluent limits; M- Marginal for meeting effluent limits; Y – Will meet effluent limits ; Y* - Will meet effluent limits with highly efficient clarification; M.S.- Metal salt addition to secondary clarifier; F- Filtration of secondary clarifier effluent; M.S. & F- metal salt addition to secondary clarifier and secondary clarifier effluent filtration

Table 5.21: Application criteria matrix – ability of process to remove NH_4 or total N

Process	NH_4	TN	NH_4	Total N	NH_4	Total N
Phostrip	NA	NA	Y	N	Y	N
Mod. Bardenpho	NA	NA	Y	Y	Y	Y
A/O	NA	NA	Y	N	Y	-
SBR	NA	NA	Y	Y	Y	Y
UCT	NA	NA	Y	Y	Y	Y
Mod. A.S	NA	NA	Y	N	Y	N
Metal Salt	N	N	N	N	N	N
1-Stage Lime	N	N	N	N	N	N
2- Stage Lime	N	N	N	N	N	N

Source: USEPA (1987)

NA = Not Applicable; Y- Can remove NH_4or total N; N- Need separate process or modification of NH_4 or total N removal

Step 3: This aim of step 3 is to shortlist alternative processes that have potential of meeting the limitations of phosphorus and nitrogen effluent. The purpose is to eliminate the processes unfit for selection. However, if a process has marginal performance then the process should be taken on to next step for screening.

Step 4: This step deals with calculating costs of construction, operation and maintenance and miscellaneous costs for selected alternatives as given in **Table 5.23**. Other factors also considered like site requirements, reliability, environmental impacts and operator skills level required for operations.

Table 5.22: Application criteria matrix – effect of TBOD: TP ratio < 20 on process applicability

Process	0.5 mg/L Effluent TP	1 mg/L effluent TP	2 mg/L Effluent TP
	Application	Application	Application
Phostrip	N/A	L	L
Mod. Bardenpho	N/A	N	M
A/O	N/A	N	M
SBR	N/A	N	M
UCT	N/A	N	M
Mod. A.S	N/A	N	M
Metal Salt	L	L	L
1-Stage Lime	L	L	L
2- Stage Lime	L	L	L

Source: USEPA (1987)

L – No Effect; M- Marginal; May not meet effluent TP limitations w/o metal salt addition; N- Cannot meet phosphorus limits w/o metal salt addition; N/A – Not applicable for effluent; TP limitation shown

Table 5.23: Standard capital cost breakdown

Factor	Component	Estimation Method
Construction cost	Equipment	Technology specific Cost
	Installation	25-55% of equipment Cost
	Piping	31 to 66% of equipment cost
	Instrumentation & Controls	6 to 30% of equipment cost
Indirect cost	Engineering	15% of total construction cost
	Contingency	15% of total construction cost

Source: USEPA (1987)

5.3.4 Plant biomass analysis

The collected plants from the wetlands were weighed before and after drying to find out moisture content. As expected from wetland plants, all the plant species taken were found to contain very high moisture content. This is due to the presence of large air cavities and pore space in the plant tissue to provide buoyancy and high transpiration rate. In most of the cases, stem of wetland plants show higher moisture content as compared to other parts of plant. The possible reason could be the presence of xylem tissue in the stem which facilitates the process rapid transpiration through leafy part and may also holds some amount of water. **Plate 5.7** and **Table 5.24** shows comparison of wet and dry biomass of various wetland plant species assessed.

1: *Canna indica*

2: *Typha latifolia*

3:*Eichhornia crassipens*

4: *Sagittaria latifolia*

5: *Colocasia esculenta*

6: *Colocasia esculenta*

7: *Justicia americana*

8: *Hymenachne amplexicaulis*

Plate 5.7: Selected wetland plant species for biomass analysis

Table 5.24: Comparison of moisture content in different biomass

Canna indica					
Sr. No.	**Plant Part**	**Wet Weight of Biomass (g)**	**Dry Weight of Biomass (g)**	**% of Dry Biomass**	**% of Moisture content**
1	Root	54.56	6.35	11.63	88.37
2	Stem	41.13	2.98	7.246	92.75
3	Leaf	51.13	7.38	14.43	85.57
4	Flower	34.78	3.04	8.728	91.27
5	Total biomass above ground	127.04	13.40	10.54	89.46
6	Total biomass below ground	54.56	6.35	11.63	88.37
Typha latifolia					
Sr. No.	**Plant Part**	**Wet Weight of Biomass (g)**	**Dry Weight of Biomass (g)**	**% of Dry Biomass**	**% of Moisture content**

Table 5.24…Continue

1	Root	34.63	5.71	16.48	83.52
2	Stem	50.00	3.61	7.21	92.77
3	Leaf	50.00	3.59	7.17	92.83
4	Total biomass above ground	84.64	9.31	11.00	89.00
5	Total biomass below ground	34.64	5.71	16.48	83.52
Eichhornia crassipens					
Sr. No.	**Plant Part**	**Wet Weight of Biomass (g)**	**Dry Weight of Biomass (g)**	**% of Dry Biomass**	**% of Moisture content**
1	Root	334.30	23.00	6.88	93.12
2	Stem	359.51	28.73	7.99	92.01
3	Leaf	72.03	20.93	29.06	70.94
4	Total biomass above ground	431.54	49.66	11.07	88.49
5	Total biomass below ground	334.30	23.00	6.88	93.12
Colocasia esculenta					
Sr. No.	**Plant Part**	**Wet Weight of Biomass (g)**	**Dry Weight of Biomass (g)**	**% of Dry Biomass**	**% of Moisture content**
1	Root	951.50	152.40	16.02	83.98
2	Stem	738.90	45.50	6.16	93.84
3	Leaf	139.90	19.90	14.22	85.78
4	Total biomass above ground	878.80	65.40	7.44	92.56
5	Total biomass below ground	951.50	152.40	16.02	83.98

Table 5.24…Continue

Colocasia esculenta-2					
Sr. No.	**Plant Part**	**Wet Weight of Biomass (g)**	**Dry Weight of Biomass (g)**	**% of Dry Biomass**	**% of Moisture content**
1	Root	453.50	62.72	13.93	86.17
2	Stem	368.90	17.47	4.74	95.26
3	Leaf	66.30	16.68	25.16	74.45
4	Total biomass above ground	435.20	34.86	8.01	91.99
5	Total biomass below ground	453.50	62.72	13.93	86.17
Sagittaria latifolia					
Sr. No.	**Plant Part**	**Wet Weight of Biomass (g)**	**Dry Weight of Biomass (g)**	**% of Dry Biomass**	**% of Moisture content**
1	Root	51.50	4.80	9.32	90.68
2	Stem				
3	Leaf	15.00	3.20	21.333	78.67
4	Total biomass above ground	66.50	8.00	12.03	87.97
Justicia americana					
Sr. No.	**Plant Part**	**Wet Weight of Biomass (g)**	**Dry Weight of Biomass (g)**	**% of Dry Biomass**	**% of Moisture content**
1	Root	230.90	34.10	14.77	85.23
2	Stem				
3	Leaf	83.20	17.96	21.59	78.41
4	Total biomass above ground	314.10	52.0	16.58	83.42

Table 5.24…Continue

Hymenachne amplexicaulis					
Sr. No.	**Plant Part**	**Wet Weight of Biomass (g)**	**Dry Weight Biomass (g)**	**% of Dry Biomass**	**% of Moisture content**
1	Root	15.30	9.49	62.00	37.99
2	Stem	81.00	21.83	26.95	73.05
3	Leaf	18.80	13.42	71.38	28.62
4	Total biomass above ground	99.80	35.25	35.33	64.68
5	Total biomass below ground	15.30	9.49	62.00	37.99

5.4 Assessment of plant biomass for application in tertiary treatment of output from constructed wetland aimed at reuse of treated wastewater: a feasibility study

The present section is divided into three major domains which primarily focused on CWs, phosphorus removal as well as biochar and its application for tertiary treatment of wastewater aimed at reuse. The three discussed domains are as follows:

a) Understanding of CWs and associated performance for pollutants removal

b) Biochar for treatment of wastewater

c) Biochar, its preparations, characteristics and application for wastewater treatment

Since, phosphorus remains the limiting factor during the treatment of wastewater with CWs, hence the phosphorus removal strategies have been reviewed in the second part of literature survey. Subsequently in the third domain the use of biochar and magnetic biochar for removal of pollutants has been discussed. The most pronounced solution in the wake of current situation is recycling and reuse of wastewater. The minimum treatment is however necessary to make water fit for reuse purpose. Large number of treatment options is available out of which constructed wetlands are considered economical, social and environmentally viable especially with reference to developing nations where minimum energy and cost is desirable. However, the removal of pollutants especially phosphorus is not appreciable in CW system and needs tertiary treatment depending upon end user requirement. Many technologies are available for their removal at advance treatment level with wide range of efficiency, advantages and limitations. The present study has also reviewed the technological options available for phosphate removal followed by strategy to select an appropriate technology for a given scenario. Cost analysis has also been done for cases when combination of technologies used. The selection strategy reviewed given in the study provides most appropriate technology based on set of information available.

However, the final decision to implement a technology is subjective and depends on various additional factors out of which end user requirement is the most important. During experimental study of assessing biochar and magnetic biochar, high removal of phosphate removal was observed in magnetic *Canna indica* with 60% phosphate removal after stabilisation followed by magnetic biochar samples of water hyacinth stem, water hyacinth leaf, *Typha latifolia*, *Colocasia* (Stem) with removal in the range of 50 – 55% from the standard solution of concentration 50 mg/L PO_4^{3-}. All biochar samples show the Ammonia removal efficiency of 20 – 50 % in the standard solution of concentration of 20 mg/L. In case of nitrate, the nitrate removal found very negligible and few samples showed negative removal *i.e.* leaching of nitrate into the solution. Magnetic biochar pore water showed *p*H in the acidic range where as non-magnetic biochar showed *p*H in the basic range. Presence of nanoparticles in micrometer range pores of biochar. FTIR confirms the presence of oxygen carrying functional group with negative charge on the surface of biochar which plays a crucial role in removal of various pollutants.

5.4.1 Application of biochar for treatment of wastewater

In the present study, carbon rich plant material “Biochar” has been used to perform removal of nutrients (nitrogen and phosphorus) pollutants from CW treated secondary wastewater. Biochar can be defined as the charred organic material which is created with intent to improve soil productivity, means of carbon sequestration, soil nourishment *etc*. The biochar in the present study is prepared from different plants used in CW systems. Biochar is sometimes confused with charcoal. As compared to carbon counterparts like activated charcoal, biochar contains lesser inorganic carbon content and higher fraction of organic carbon. The removal of different kinds of pollutants which includes heavy metals, nutrients, organic chemicals and pathogens using biochar made from different material (Beesley *et al*., 2011). Due to high surface area, it also acts as good adsorbent while high porosity and organic fractions act as host for micro-organism to thrive (Lehmann and Joseph, 2009).

<u>Properties of biochar</u>: Physical properties of biochar vary depending upon the feed material and the processing conditions (Lehmann and Joseph, 2009). The chemical composition of feed material determines physical nature of the biochar. Hemicelluloses begin to degrade in the range of 200ºC – 260ºC, cellulose at 240ºC to 350ºC and lignin at 280ºC to 500ºC (Sjöström, 1993). Abundance of these materials in the feed will determine its reactivity and physical properties to a greater extent. Some processing conditions lead to sintering or ash fusion which further influences biochar physical properties.

Biochar porosity and structure: Biochar is a high carbon porous structure which shows very large variation in structure based on characteristics of raw materials and processing conditions. During the pyrolysis process, volatiles release from the raw material leading to loss of mass and volume is reduced due to shrinkage of material. Few authors have reported the additional factors that could influence structure of biochar like heating rate and pressure conditions during pyrolysis (Antal and Grønli, 2003; Biagini and Tognotti, 2003; Boateng, 2007). Lua *et al*. (2004) discussed the effect like temperature, heating rate, nitrogen flow rate and hold time during processing. He suggested that the pyrolysis temperature has the maximum effect on structure followed by heating rate whereas flow rate and nitrogen residence time has the minimal effect. This claim is further strengthened by work of Zabaniotou *et. al* (2008) where he showed that surface area of biochar made from olive karnel increased with increase in burn-off of carbon, that can happen at higher temperature.

The literature review however suggests that the factors as mentioned by Lua *et al*. (2004) can give variable result with different feedstock. Cracking also plays an important role in structure of biochar. During heating expansion of biomass layer happens. The rate of change of expansion among different layers of biomass leads to formation of cracks. Brown *et. al.* (2006) proposed two major factors governing surface area formed at higher temperature (1000 ºC) as follows:

- Cracks formed at low temperature which are too large and numerous
- High temperature rearrangement of microstructures.
- The biochar majorly composed of following components:
- Organic Fraction which are liquefied volatiles and non-volatile charred biomass
- Inorganic mineral compounds like ash
- Carbonaceous skeleton structure composed of fused aromatic rings

The biochar formed at lower temperatures are amorphous in nature however with increasing high temperature treatment structure starts becoming graphitic with non aligned arrangement of sheets which leaves pores of various sizes in the structure (Lehmann and Joseph, 2009). The pyrolysis of all kinds of biomass gives graphite at temperature of 3500ºC, however in some cases biomass shows graphitization at temperatures below 2000ºC (Setton *et al.*, 2002). Presence of voids in the hexagonal planes contributes to the formation of micropores in the biochar structure (Bourke *et al*., 2007). The oxygen is present at the edges of sheets as a part of different functional groups (Boehm, 1994, 2002).

The biochar formed at low temperatures has lesser porosity due to condensates of volatiles (Pulido- Novicio *et al.*, 2001) and mineral material. The high heating rate leads to cell structure destruction by de-volatilization (Cetin *et al*., 2004) thereby causing low surface area of biochar. In some cases like pistachio-nut feedstock increasing treatment temperature from 500ºC to 800ºC decreased BET surface area due to meltdown of volatiles and deposition in pores. It can be concluded after wide literature survey that there cannot be a thumb rule for proposing porosity and structure of biochar in advance and a thorough analysis has to done before coming to any conclusion.

Immobilisation: Leaching is the normal phenomenon which occurs due to movement of water which relocates the nutrients present in soil. The amount of nutrients lost from the soil due to leaching can be huge. It can as high as 172% of applied calcium (Omoti *et al.*, 1983), 80% of applied nitrogen (Lehman *et al*., 2004) and 136% of applied magnesium (Cahn *et al*., 1993). It is evident that nutrients originally present in the soil also get mobilized (Lehmann and Joseph 2009). Leaching of nutrients not only cause economical loss but also leads to environmental problems like Eutrophication due to leaching of phosphate from agricultural fields to water bodies. Biochar reduces the leaching of nutrients from soil by binding them with different interactions and mechanisms.

Lehmann and Joseph (2009) have mentioned two significant points (i) organic matter amendments increase water retention capacity of soil (ii) movement of water in soil matrix is greatly dependent on pore size *i.e.* macropores with size greater than 80 µm facilitates flow of water and leaching by gravity. Also, the mesopores with size in range of between 30 µm – 80 µm allow movement of water by matrix potential difference and micropores with size less than 30 µm captures water in the capillary space and does not allow movement. Literature survey suggests that pore size of biochar lie in the range of micrometers. This proves that biochar can retain water in the capillaries along with the nutrients dissolved in it even under extreme matric potential like in case of dry sandy soil.

There are many evidences which show that large surface area corresponds to high nutrient adsorption through various kinds of interactions like sorption of hydrophobic as well as hydrophilic molecules on the functional groups of biochar surface (Lehmann and Joseph, 2009). The removal of organic contaminant by sorption to organic matter is explained by dual-mode sorption concept as discussed by Pignatello and Xing (1995). Under this concept, it is assumed that organic matter is composed of 2 different domains (i) non carbonised organic matter, which shows linear and non-competitive absorption or partitioning (Chen *et al*., 2008; Zhou *et al*., 2009) (ii) carbonised organic matter which shows non-linear extensive and competitive surface adsorption (Cornelissen *et al*., 2005). Metals ions form complexes on the surface of biochar hence reducing their bioavailability. Biochar can enhance the soil fertility by retaining fertilizers (Liang *et al*., 2006) and promoting growth of beneficial micro-organisms (Warnock *et al*., 2007). Ability of biochar to immobilise the contaminants can be attributed largely to its high surface and porous structure.

Biological characteristics: Biochar comprises of pores of various sizes which act as host site for various micro-organisms by providing refuge site and protection from desiccation. Also, volatile condensates and mineral of biological origin fulfils the nutritional requirement of micro-organisms (Warnock *et al*, 2007). Biochar with high ash content shows increase in surface area with passing of time as ash will leach out. The biochar particles itself do not act as carbon source to micro-organisms but the residual oil and other compounds adsorbed on the surface act as food source. Sometimes these bio-oils prove to be toxic to microbes as well as plants (Mc Clellan *et al*., 2007). Microbes that grow on the biochar surfaces are those that can produce enzymes to metabolize the substrate. The complex substrate will take more time to metabolize and only restricted type of microbes will be able to metabolize it.

The population growing in the in the fresh biochar will be entirely different form the population inhabiting at the later stage when all the condensates are gone. The carbon source and inorganic nutrients present in the soil get adsorbed to biochar and get metabolized at the later stage. Some amount of biochar also get metabolised with time. The biochar surface also shows cracks in which plants roots can penetrate and which results in net increase in surface area of roots. This penetration is followed by infiltration of micro-organisms near the rhizosphere which results in net increase of biodiversity and can be taken as surrogate measure of capacity to degrade different type of pollutants.

5.4.2 Materials and methods used for assessment of biochar for removal of pollutant from secondary treated wastewater from CW

This section describes in details of the materials and procedures used for various experiments performed during preparation and biochar for its application for removal of pollutants.

Materials: Samples of different types of plants used in constructed wetland were collected and kept in plastic bags for initial storage. Wherever possible, samples were segregated into respective parts like leaf, stem and roots. Metallic trays were used during handling of plant materials. Quartz crucibles were used to prepare biochar in muffle furnace. Volumetric flasks of 50, 100, 250 mL volume were used for conducting experiment according to methods prescribed by APHA (2005). Pestle mortar, ferric chloride hexahydrate, distilled water were used preparation of magnetic biochar. During the preparation of solution of phosphate, nitrate and ammonium, KH_2PO_4, KNO_3, andNH_4Cl were used, respectively.

Methods: There are several methods of preparing biochar as found in literature. Each method of preparation produces peculiar type of biochar with different properties. In the current research, method used for biochar preparation is new and has not been used earlier for material used in this research. However, during preparation of magnetic biochar method used by some authors were used and have been cited in the concerned section.

Preparation of Biochar: The magnetic biochar was prepared according to method described by Chen *et al.* (2011). The segregated plant samples were air dried in sunlight for 4 days to remove the excess moisture. It is followed by drying samples in hot air oven for 24 hours at 105 ºC. The biomass is then pyrolysed in muffle furnace at 500 ºC for 1 hour. The furnace was initially made to heat upto 500 ºC then samples were put and were taken out after 1 hour. The samples were left in ambient air to cool down keeping cover of crucible in place to avoid formation of ash by oxidation. Thesamples then sieved through 0.45 mm standard sieve to avoid fine ash particles in the biochar. After pyrolysis, the samples were crushed using mortar and pestle. The crushed material was then rinsed using distilled water 4-5 times. Then the produced biochar samples were dried and stored for characterization and further use.

Removal studies: During assessment of pollutants, a standard solution of phosphate with 50 mg/l concentrations was prepared. 100 mg of biochar samples were added to 100 ml of standard phosphate solutions and shaken in an orbital shaker during the experiment to minimize mass transfer limitation. The time for reaching the equilibrium was determined by measuring the residual phosphate concentration from 1 minute to 2 hours with the interval of 1 minute for initial 15 minutes followed by 5 minutes for next 45 minutes followed by 15 minutes for next 1 hour. Similarly, nitrate and ammonia solutions of 50 mg/l concentration were prepared to assess the pollutant removal efficiency of biochar. 100 mg of biochar samples was added to 100 ml of each of solution of nitrate and ammonia and shaken in an orbital shaker during the experiment to minimize mass transfer limitation. The time for reaching the equilibrium was determined by measuring the residual concentration periodically up to 2 hours with the interval of 1 minute for initial 15 minutes followed by 5 minutes for next 45 minutes followed by 15 minutes for next 1 hour.

Analytical methods used for characterization of biochar:

(a) Physical properties

Moisture content was estimated by drying the biomass samples in an oven at 105^0C temperature for 24 h (till the mass attained constant value). The dried mass was allowed to cool and weighted. The difference between the initial and final mass of the carbon represents the mass of water in the sample. The parameters, *p*H, conductivity, total dissolved solids for all the samples dried were measured using, HACH, HQ40D instrument.

(b) CHNS elemental analysis

CHNS analyser (LECO CHNS-932) was used for the rapid determination of carbon, hydrogen and nitrogen in the synthesised activated carbon. In the combustion chamber (at a temperature of about 1000^0C), carbon is converted into carbon-dioxide, hydrogen to water; nitrogen to its oxide and sulphur to sulphur-dioxide.

(c) FEG - SEM analysis

The scanning electron microscope (SEM) (LEO-1530VP) images of the biochar samples were obtained to closely observe the material.

(d) FTIR analysis

Fourier Transform Infrared Spectroscopy (FTIR) of the biochar samples was performed in (Bruker IFS 66 vs-1 spectrometer) to identify the functional groups. It was done by linking the different wave numbers obtained to the characteristic infrared frequencies associated with the various functional groups.

5.4.3 Analysis of biochar samples prepared from wetlands plants

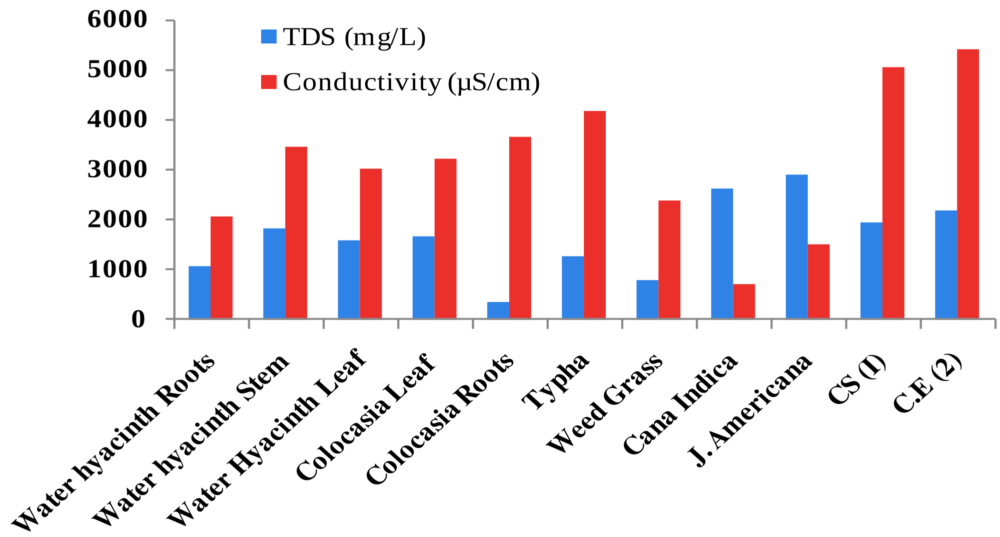
The prepared biochar samples (listed in **Table 5.25**) were analysed for various analysis including *p*H, conductivity, TDS, functional groups, elemental analysis, SEM imaging and FTIR analysis. Similarly, the magnetized biochar samples were also analyzed for the same mentioned parameters. Table 5.27 shows the values of *p*H, conductivity and TDS for different samples.

Table 5.25: Properties of prepared biochar samples

S No.	Sample	TDS (ppm)	*p*H	Conductivity (µS/cm)
1	Water hyacinth (Roots)	1089	10.36	2069
2	Water hyacinth (Stem)	1839	10.59	3460
3	Water hyacinth (Leaf)	1589	10.68	3030
4	*Colocasia* (Leaf)	1659	11.04	3200
5	*Colocasia* (Stem)	1939	10.99	3640
6	*Colocasia* (Roots)	376	10.56	721
7	Hymenachne amplexicaulis	792	9.77	1507
8	*Canna indica* (Leaf)	2630	10.99	5030
9	*Typha latifolia* (Stem)	1269	9.77	2400
10	*Colocasia esculenta* (2)	2185	11.30	4160
11	*J. Americana* (Leaf + Stem)	2910	11.02	5410
12	Magnetic, *Canna indica* (Leaf)	2100	NA	707
13	Magnetic, *Typha latifolia* (Stem)	1980	NA	557
14	Magnetic, *Colocasia* (Leaf)	2700	NA	597
15	Magnetic, *Colocasia* (Stem)	2400	NA	655
16	Magnetic ,Water hyacinth (Stem)	1510	NA	777
17	Magnetic, Water hyacinth (Root)	1700	NA	823

Comparison of various experimental values obtained has shown in **Figure 5.5** and **5.6**.The *p*H of all the non-magnetic biochar samples lies in basic range. The possible reason could be the formation of oxides of magnesium, calcium, potassium and sodium *etc*. present in biochar

(URL1) which dissolved in water release OH^{-} ions. In case of magnetic biochars, *p*H is found lower than 7.This could be due to formation of iron oxide particles which react with water releases net H^{+} into the water.



C.S = *Colocasia esculenta* (Stem); C.E - *Colocasia esculenta* Sample 2

Figure 5.5: Comparison of conductivity and TDS found in different normal biochar samples

The TDS of non-magnetic biochars is lesser than magnetic biochar as obtained from the experiment results.

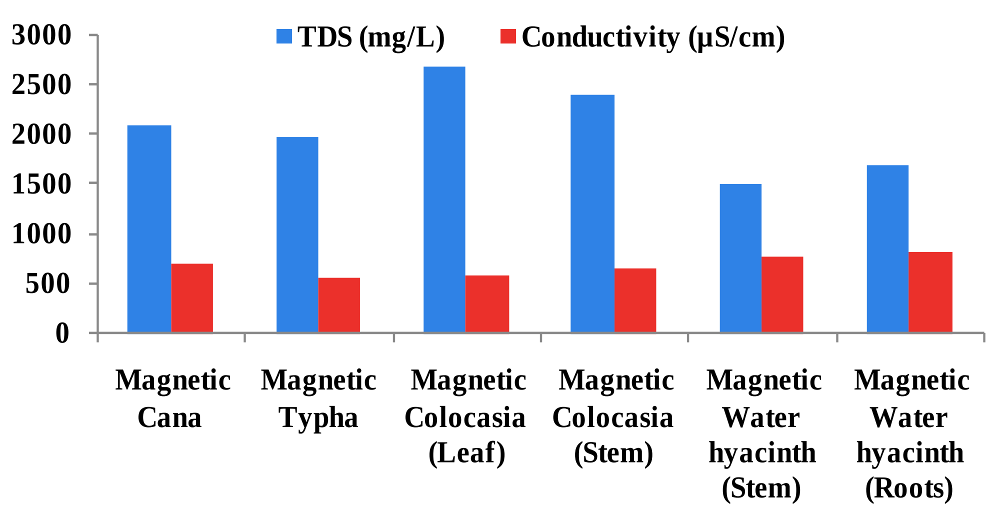


Figure 5.6: Comparison of TDS and conductivity in different magnetic biochar

The use of ferric chloride during preparation of magnetic biochar might have led to addition of TDS into the solution. However, the conductivity of magnetic biochars is low which might be due to the formation of mineral particles as evident from the SEM images of the biochar samples commonly found minerals in biochar include potassium chloride (KCl), quartz (SiO_2), amorphous silica, calcite ($CaCO_3$), hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), calcium phosphates, anhydrite, nitrates, oxides and hydroxides of calcium, magnesium, aluminium, manganese, zinc and iron(Lehmann and Joseph, 2009). Out of all the samples, *Canna indica* and *J. americana* have shown the maximum TDS which was also represented by corresponding maximum conductivity in the respective domains.

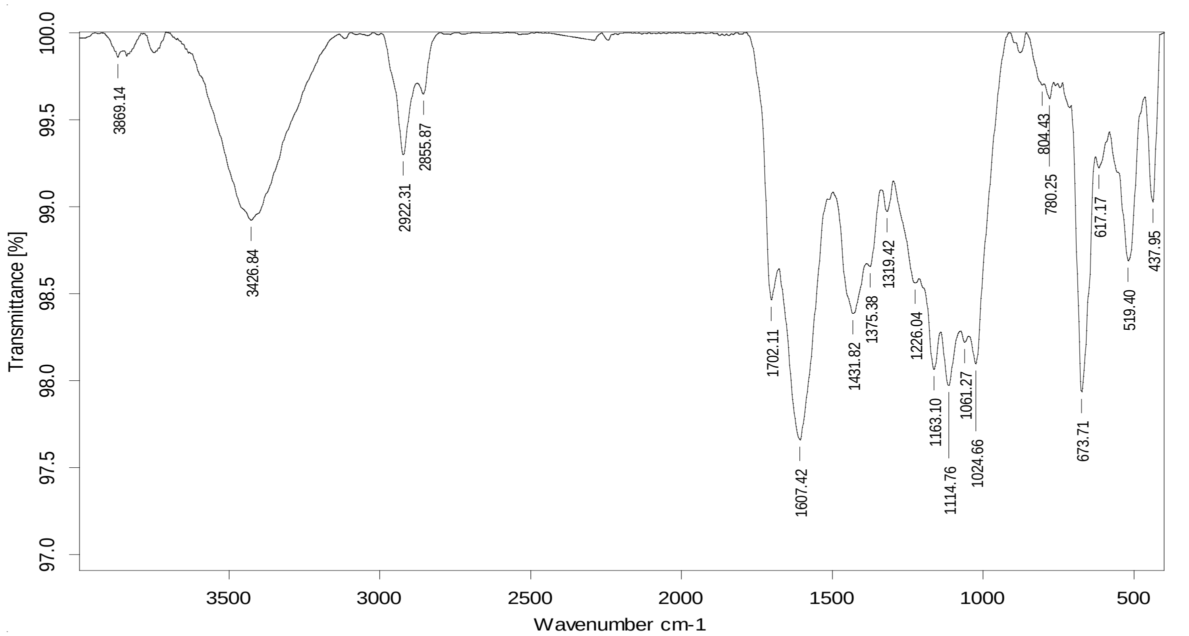
5.4.4 Characterization of biochar samples (FTIR, SEM and Elemental analysis)

Prepared samples were characterized using different analytical instruments to co-relate the performance and verify the hypothesis made before conducting the experiments.

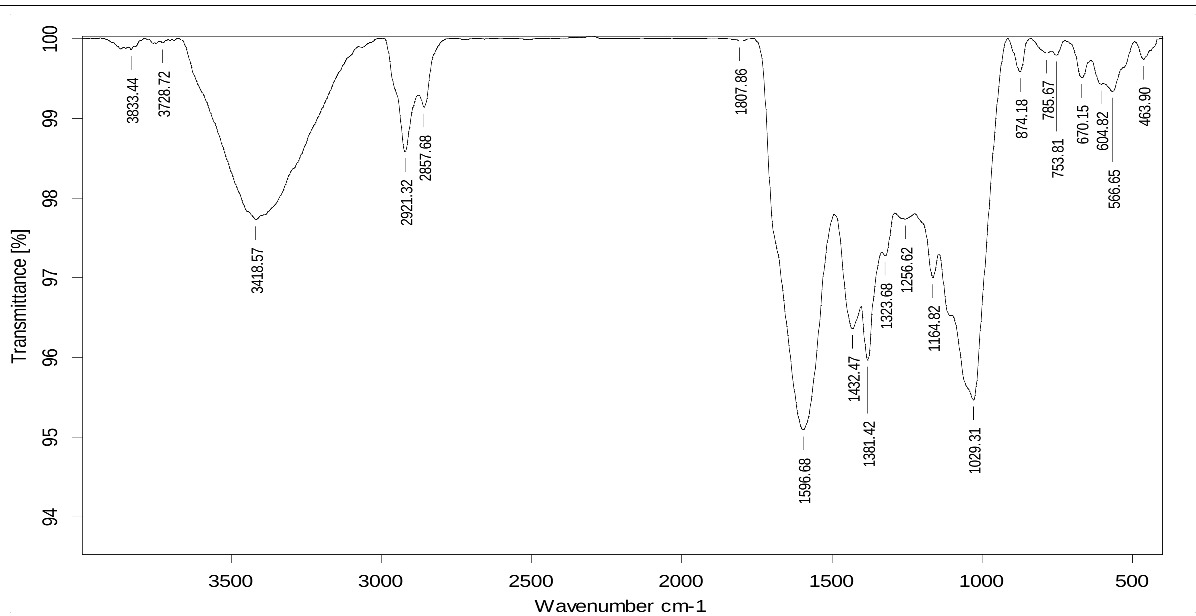
<u>FTIR analysis</u>:

Biochar was produced from pyrolysis of plant biomass which mainly consists of lignocelluloses. The Fourier transform infrared spectroscopy (FTIR) of selected biochar samples (both magnetic and non-magnetic) were carried out which shows the higher removal of phosphate, nitrate and ammonia. The aim of this study was to establish a relation with relative removal of pollutants with different biochar samples that may contain different functional groups – which may be the driving force of pollutant removals. The FTIR were performed for seven biochar samples as follows:

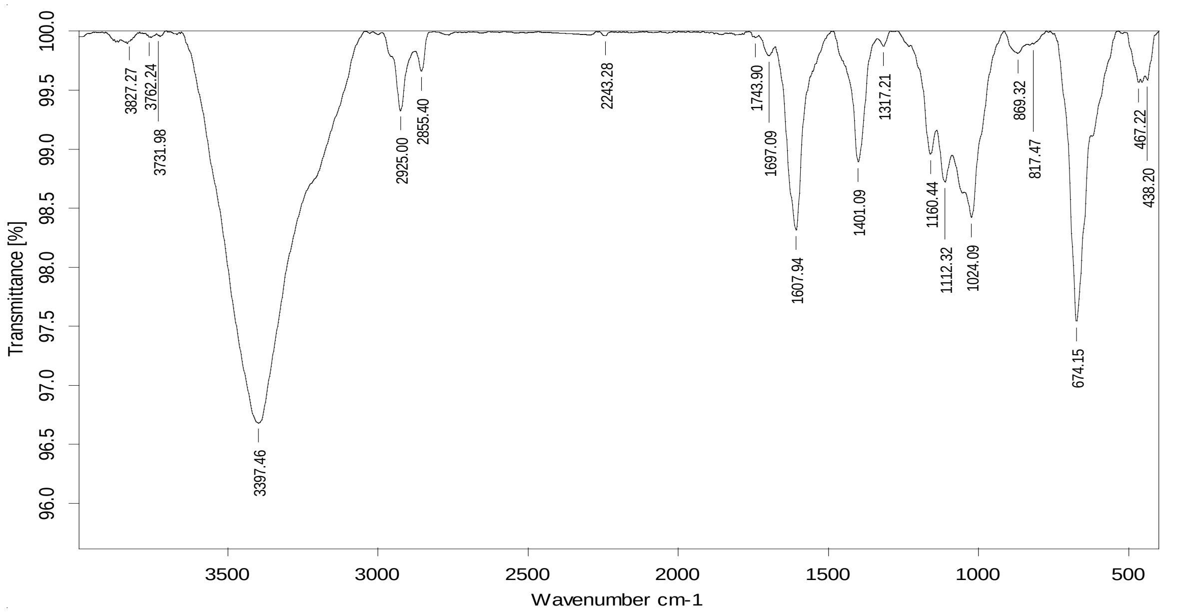
1. Magnetic, *Colocasia* (stem)
2. Magnetic, *Colocasia* (leaf)
3. Magnetic, *Typha latifolia* (stem)
4. Non-magnetic, *Canna Indica* (leaf)
5. Magnetic, *Canna Indica* (leaf)
6. Magnetic, Water hyacinth (leaf)
7. Magnetic, Water hyacinth (stem)



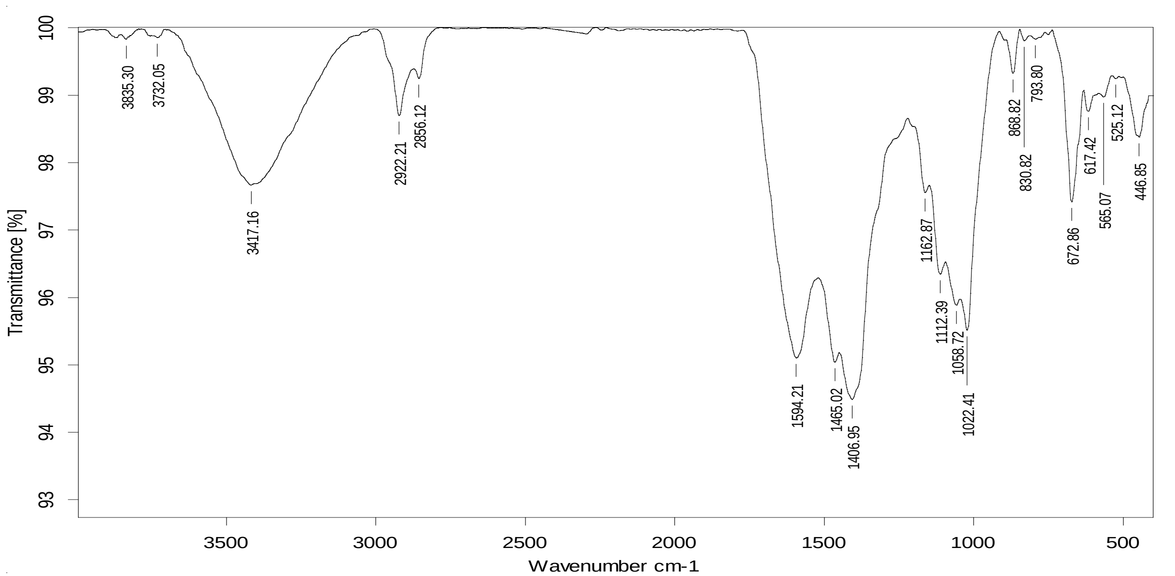
1:Magnetic, *Colocasia* (Stem)



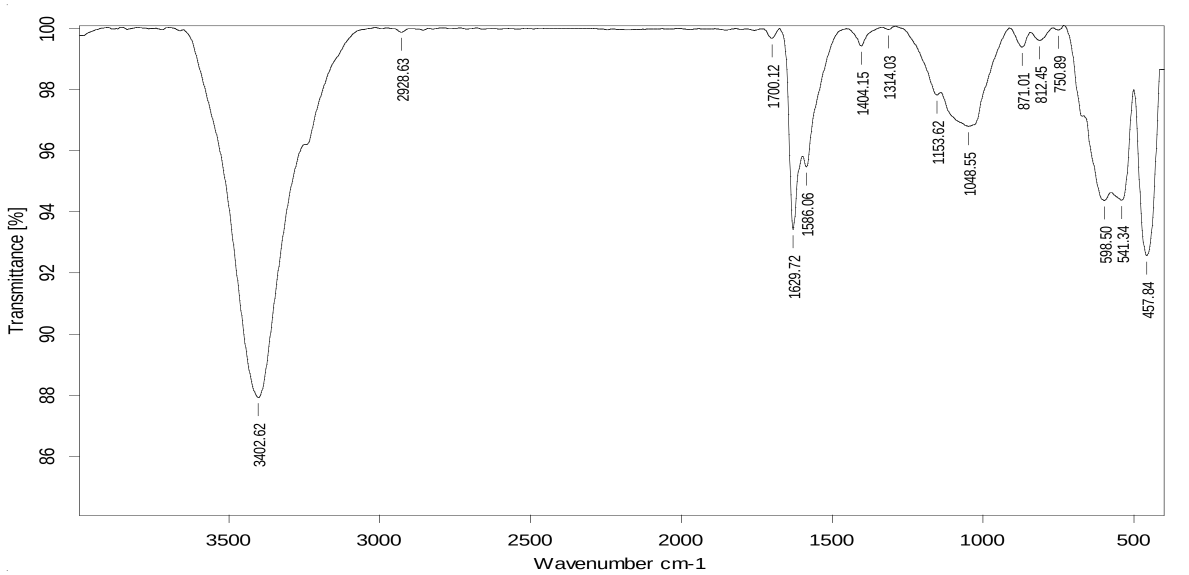
2:Magnetic, *Colocasia* (Leaf)



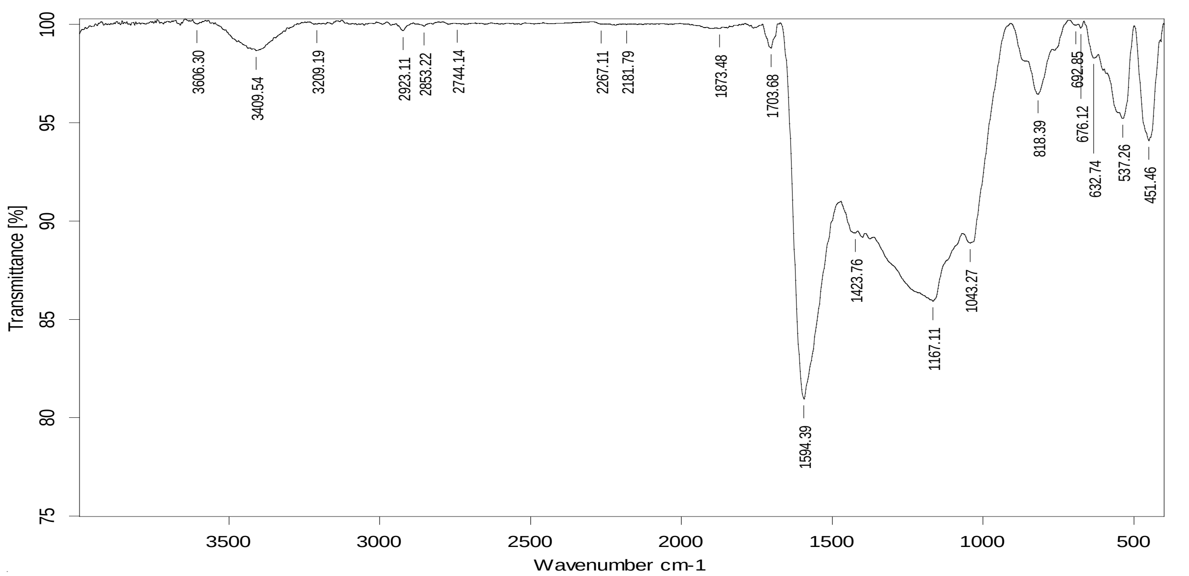
3:*Typha latifolia* (Stem)



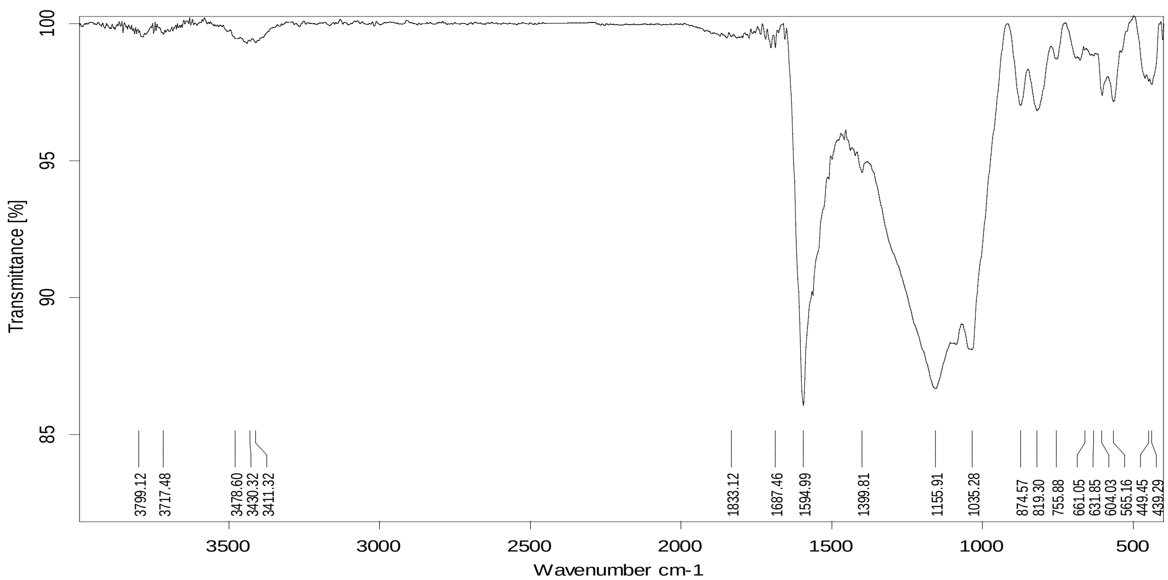
4:Non-magnetic, *Canna Indica* (Leaf)



5:Magnetic, *Canna Indica* (Leaf)



6:Magnetic, Water hyacinth (Leaf)

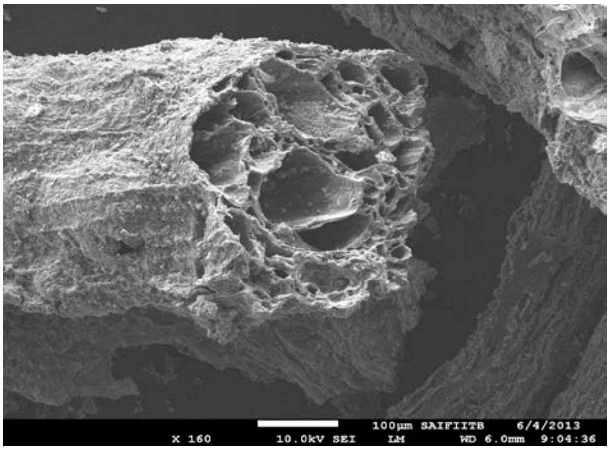


7:Magnetic, Water hyacinth (Stem)

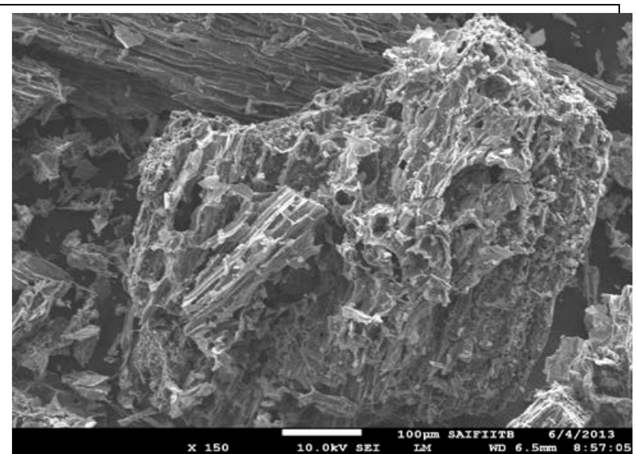
Plate 5.8: FTIR Images (1 to 7) of biochar samples used for pollutants removals

Major functional groups found in biochar samples include, carboxylic, aldehyde, keto, acid chlorides, amino, alkanes bond, ester and alcohol group. These groups provide properties of immobilising positively charge ions onto their surface. In case of magnetic biochar, property of phosphate removal is due to presence of magnetic particles which is not observed in FTIR but evident in SEM images. These functional groups increase cation exchange capacity of the biochar (Lehmann and Joseph, 2009). Due to oxygen containing functional groups, negative charge prevails on the surface of biochar which helps in removal of positive charge contaminants. Brennan *et al*. (2001) reported that presence of hetero-atoms on the surface of biochar results in surface chemical heterogeneity due to difference in electro negativity. Also, the presence of electron donor groups such as OH, NH_2, OR or O (C=O) and electron acceptor group such as (C=O) OH, (C=O) H or NO_2 on the surface of biochar. Biochar reacts with atmospheric oxygen to give functional groups containing oxygen (Bourke *et al*., 2007). Carbon-oxygen bond are also formed from reaction with oxidizing gases like ozone, nitric oxide and CO_2 or reactions with oxidizing solutions (Marsh *et al*., 1997).

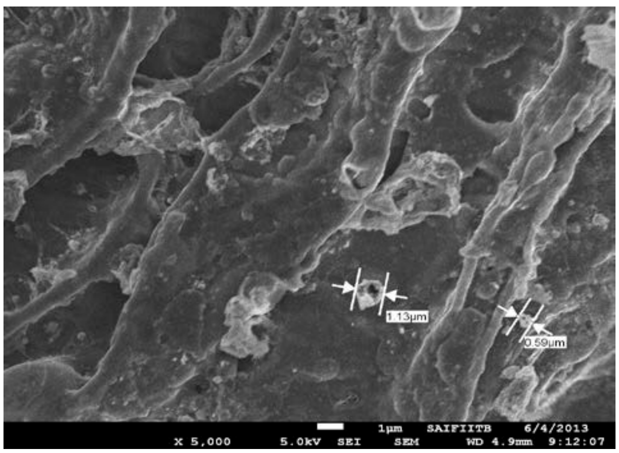
The structure of biochar is porous in nature which was verified from the SEM images as shown in **Images 1 -14**of **Plate 5.8**.



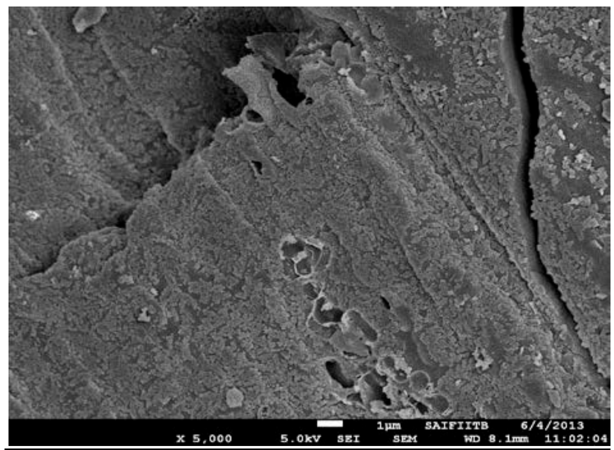
1:Magnetic, *Colocasia* (Leaf)



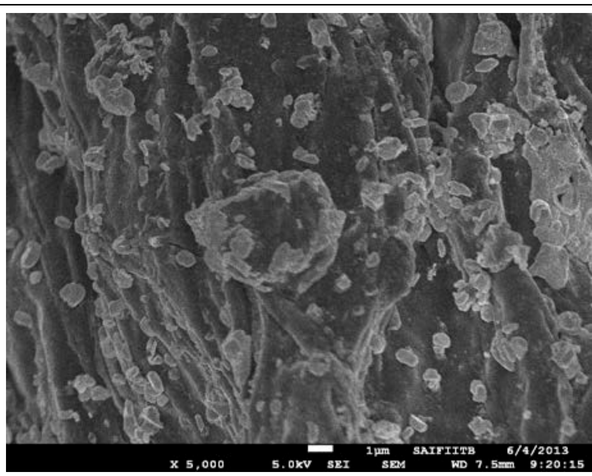
2: Magnetic, *Water Hyacinth* (Stem)



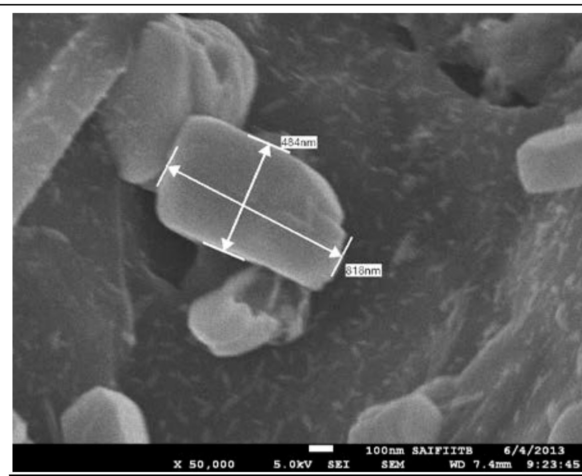
3:Magnetic, *Colocasia* (Leaf)



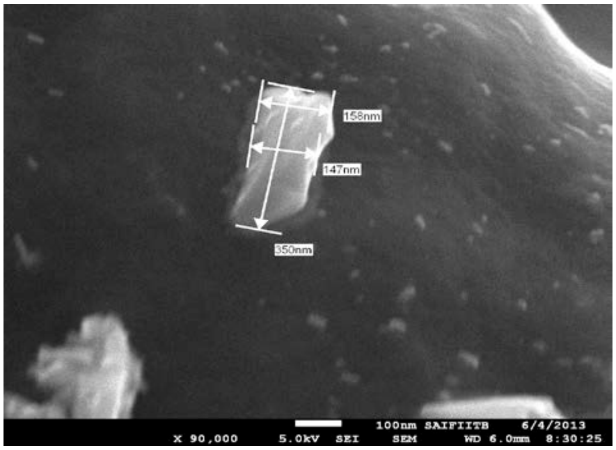
4: Non magnetic, *Colocasia* (Leaf)



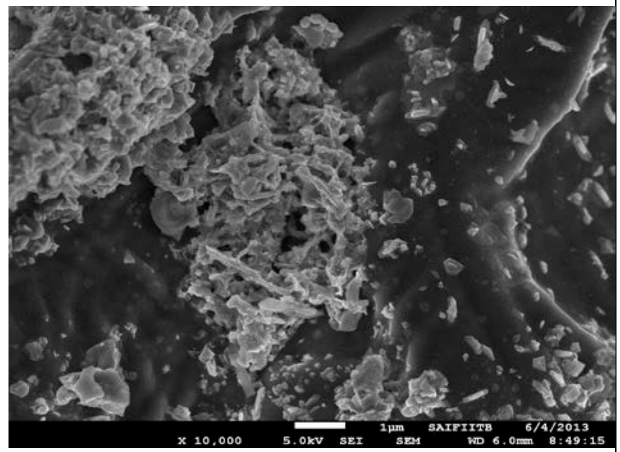
5:Magnetic, *Canna indica*



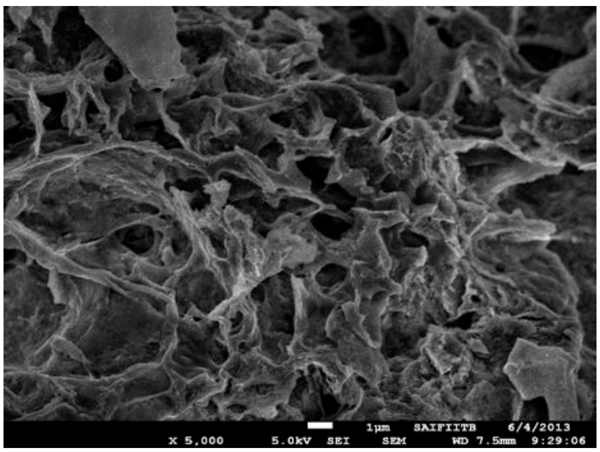
I6: Magnetic, *Canna indica*



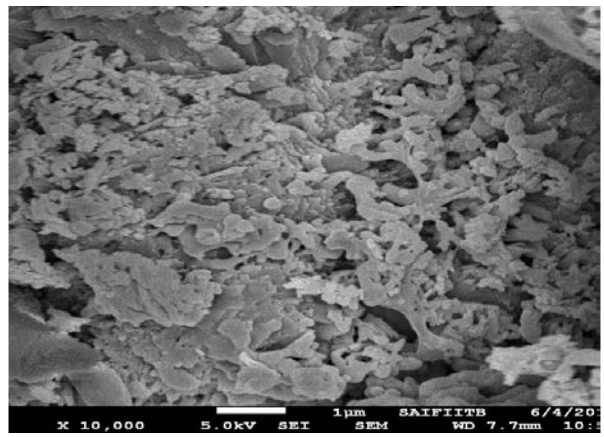
7:Magnetic, Water hyacinth (Leaf)



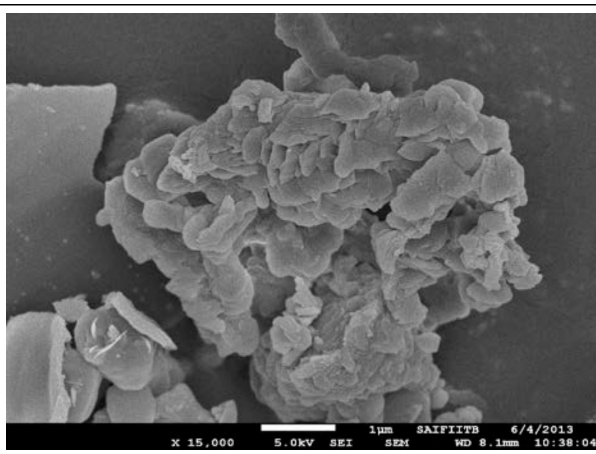
8:Magnetic, Water hyacinth (Leaf)



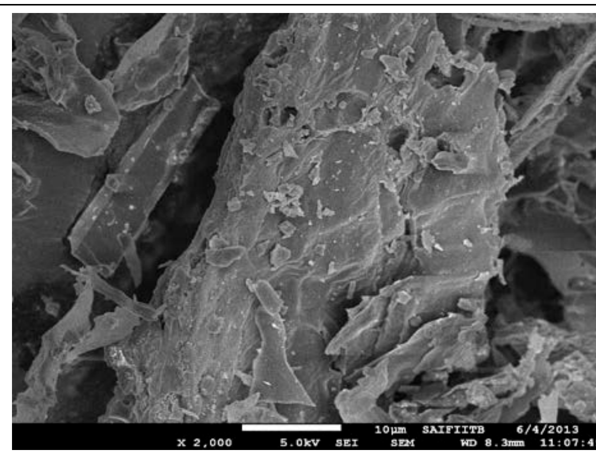
9:Magnetic, *Typha latifolia*



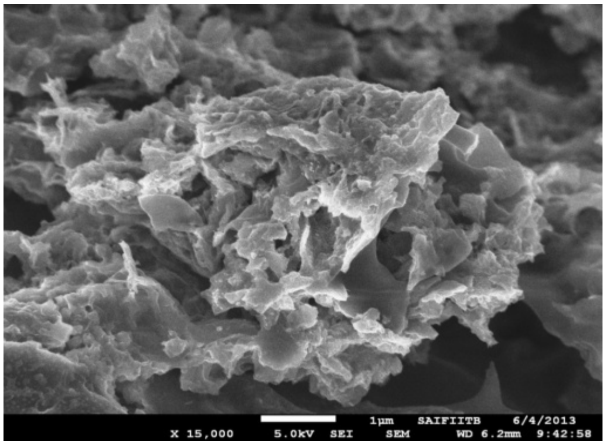
10:Non magnetic Water hyacinth (Stem)



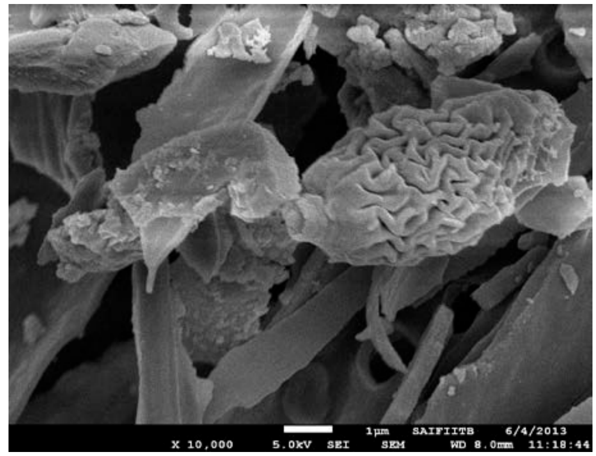
11:Non magnetic *Canna indica* Biochar



12:Non magnetic Water hyacinth (Leaf)



13:Magnetic, *Colocasia* (Stem)



14:*Colocasia* (Stem)

Plate 5.9:SEM Image (1 to 14) of biochar samples used for pollutants removals

Cracks and uneven depressions were also evident from all the SEM images. This unevenness increased the effective surface area for adsorption and precipitation of pollutants. It happens due to uneven expansion and compression of biochar surface. Outer surface expands more than inner surface leading to formation of cracks (Lehmann and Joseph 2009). Morphology depends largely on the treatment temperature and feed biomass. The highly porous structure comprises of mesopores and micropores as evident from images. Different types of minerals were present on the surface of biochar. Amphoteric sites are present on oxide surfaces of biochar surface charge of which varies with solution *p*H (Lehmann and Joseph 2009). Therefore under acidic conditions surface get positive charge whereas under alkaline conditions surface get negatively charge.

Comparison of SEM images from literature shows that the nano particles present on the surface of biochar are mineral particles. In case of magnetic biochar, mineral particles are more evident which might be due to reaction of minerals with iron chloride to form micro and nano level particles (Brennan *et al*., 2001). Image 1 and 2 of plate 5.8 show morphology of magnetic *Colocasia esculenta* leaf and magnetic Water hyacinth stem biochar sample, respectively. However, the same morphology was observed for all the biochar samples possibly due to release of volatiles during preparation of biochar.

Image 3 shows micrometer particles embedded in the matrix. These particles were not present in the non-magnetic biochar samples as evident from Image 4. Presence of nano particles have also been shown in Image 5 and image 6 of plate 5.8. In case of magnetic *Canna indica,* the presence of magnetic nanoparticles was too dense, as depicted in image 5 of plate 5.8. This high density might have led to removal of maximum phosphate by the magnetic *Canna indica* biochar sample. Image 7 and 8 shows size of magnetic nanoparticle present on the surface of magnetic biochar sample of water hyacinth leaf. Image 9 shows morphology of magnetic *Typha* *latifolia* biochar samples while image 10 and 11 of plate 5.8 shows morphology of non-magnetic biochar samples of water hyacinth stem and *Canna indica*. Image 14 shows the depressions develop in the non- magnetic biochar sample of *Colocasia esculenta*stem.

Elemental analysis: Elemental analysis of magnetic biochar samples were done to find out the composition of samples as depicted in **Table5.26**.

Table 5.26: Elemental analysis of different magnetic biochar samples

Sample Name	Carbon	Nitrogen	Hydrogen
Magnetic *Colocasia* Leaf	38.6	2.3	1.8
Magnetic *Colocasia* Stem	32.30	3.4	2.5
Magnetic Water Hyacinth Leaf	38.7	2.2	2.04
Magnetic Water Hyacinth Stem	38.6	2.1	2.1
Magnetic *Typha*	40.275	1.48	2.74
Magnetic *Canna Indica*	39.4	2.2	2.6

It was observed all the samples have almost same amount of carbon in the range of 38 – 40 %. Similarly, nitrogen was observed in the range of 1.5 – 3.5%. Hydrogen though presents in large amount in tissue of plants (Tyagi and Bhatia, 2007) but it gets lost eventually in the form of vapor and volatiles. It can be concluded that variation of carbon, nitrogen and hydrogen depends largely on processing temperature than other factors.

5.4.5 Phosphate removal

The biochar (1g) was used to test the phosphate removal from the prepared 50 ppm standard phosphate solution. The calibration curve was prepared for concentrations in the range of 0 – 2 ppm as shown in **Figure 5.7**.

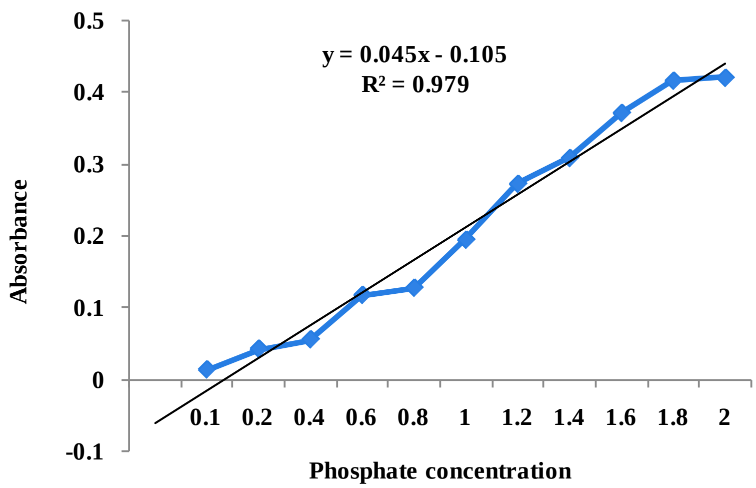


Figure 5.7: Calibration curve used phosphate concentration estimation at 690 nm

In case of non-magnetic biochar, negligible phosphate removal was obtained whereas the magnetic biochar gives the appreciable phosphate removal in range of 10 – 60% as shown in **Table 5.27**. The formation of magnetite particles in the magnetic biochar facilitate in removal of phosphate from the solution (Chen *et al*., 2011). The batch study for assessment of potential of magnetic biochar samples were conducted for 2 hours. Expected result was removal of phosphate with passing time however, when the magnetic biochar was added maximum removal of phosphate observed at 1st minute of duration which indicates the possibility of chemical interaction.

The phosphate leaches out of from the biochar as time progress time after the equilibrium (approximately 30 – 60 min). The maximum removal of phosphate for different biochar samples were achieved during 30 minutes – 60 minutes of incubation time (depicted in **Figure 5.8**).

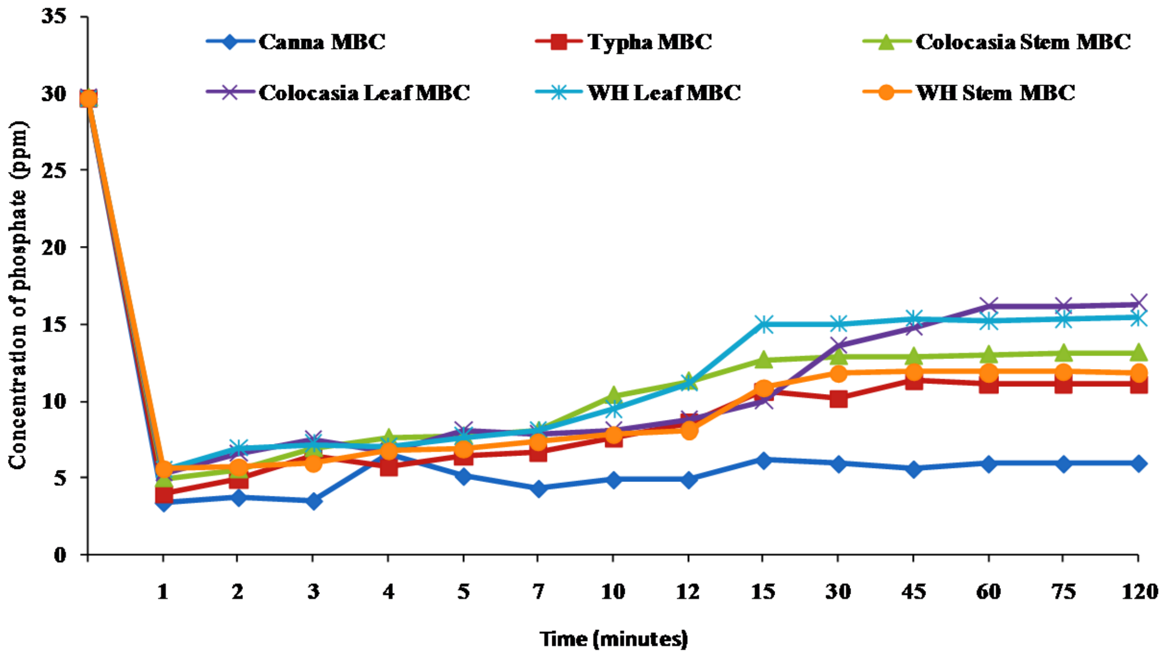


Figure 5.8: Removal of phosphate by different magnetic biochar with respect to time

Where; WH = Water hyacinth; MBC = Magnetic Biochar

The sudden adhesion of phosphate into the magnetic biochar may be due to ionic interaction and surface adsorption however, it was followed by release of phosphate after initial incubation may be due to movement of phosphate molecules from surface to inner voids. Difference in removal of phosphate as shown by different biochar might be due to variation in surface morphology exposing different surface area for phosphate attachment.

Table 5.27: Removal efficiency of phosphate by different biochars

S. No.	Plant Species	Type of Biochar	Phosphate Removal
1	Water hyacinth (Roots)	Non-magnetic / Normal Biochar	Negligible Removal (1 - 4%)
2	Water hyacinth (Stem)		
3	Water hyacinth (Leaf)		
4	*Colocasia esculenta* (Leaf)		

Table 5.27…Continue

5	*Colocasia esculenta* (Roots)		
6	*Typha latifolia* (Stem)		
7	*Hymenachne amplexicaulis* (Leaf)		
8	*Canna Indica* (Leaf)		
9	*J. Americana* (Leaf + Stem)		
10	*Colocasia esculenta* (Roots)		
11	*Canna Indica* (Leaf)	Magnetic Biochar	> 60%
12	*Typha latifolia* (Stem)		~ 50%
13	Water hyacinth (Leaf)		~52%
14	Water hyacinth (Stem)		~ 55%
15	*Colocasia esculenta* (Leaf)		~10%
16	*Colocasia esculenta* (Stem)		~50%

5.4.6 Nitrate removal

The calibration curve was prepared for concentrations in the range of 0 – 10 ppm as shown in **Figure 5.9**.In case of nitrate removal, it was found that many of the biochar samples release nitrate into the solution. The organic part of the biochar contains amino group which get oxidised into nitro group as time passes due to interaction with oxidizing atmosphtere (Lehmann and Joseph, 2009).

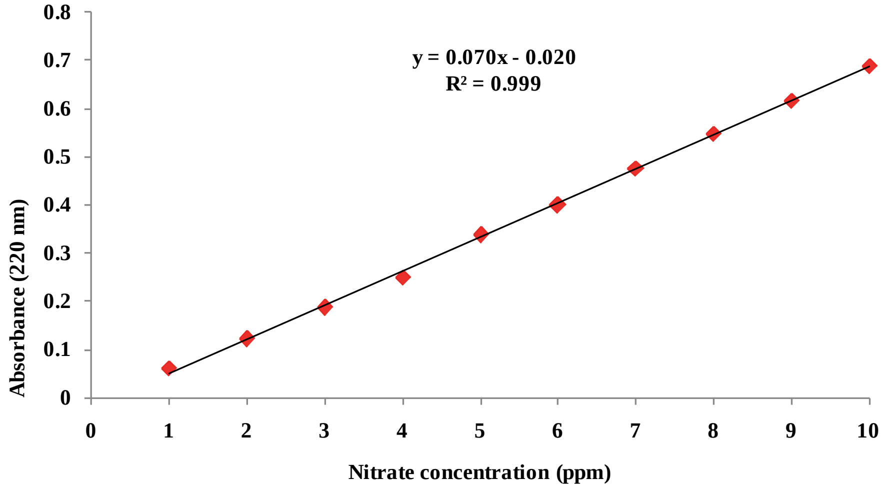


Figure 5.9:Calibration curve of nitrate at 220nm

The same nitrates get leached in to the solution. The results of batch experiments showing the release of nitrate from different biochar samples has been depicted in **Figure 5.10**. The red color columns in Figure 5.10 shows the excess release of nitrates into the solution.

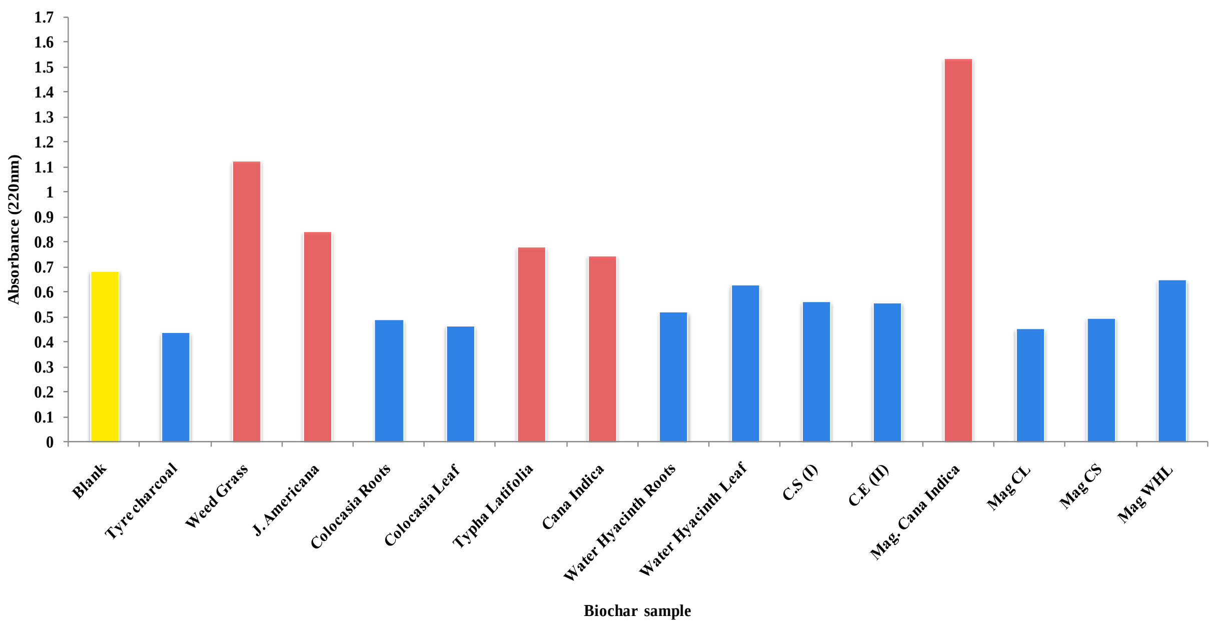


Figure 5.10: Nitrate removal efficiency by different biochar

5.4.7 Removal of ammonia

Similar to nitrate removal studies in batch experiments, ammonia removals from different biochar samples were also studied and the results are depicted in **Figure 5.11**.

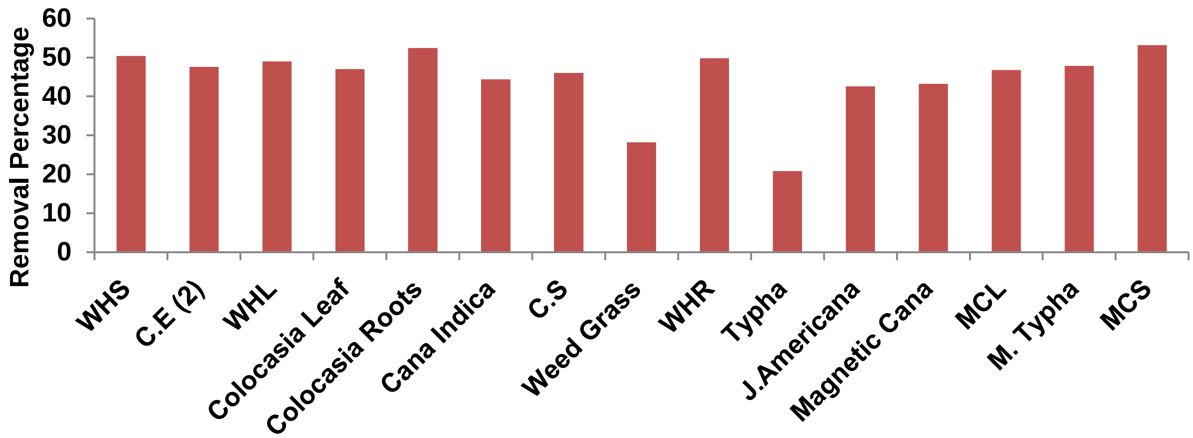


Figure 5.11: Ammonia removal efficiency by different biochar

WHS = Water hyacinth Stem; WHR = Water hyacinth Roots; C.E = *Colocasia esculenta* 2nd sample; C.S = *Colocasia esculenta* Stem; Weed grass = *Hymenachne amplexicaulis*; J. Americana = Justicia *americana*; MCL = Magnetic *Colocasia esculenta* Leaf; M.Typha = Magnetic *Typha latifolia*; MCS = Magnetic *Colocasia* Stem

The maximum removal was shown by magnetic *Colocasia* stem and non-magnetic *Colocasia* roots biochar samples. The probable reason of removal of ammonia by biochar is its adsorption into organic matrix. It was observed that, there were no significant differences for removals ammonia with biochar of magnetic and non-magnetic type. This proves that magnetised biochar has no additional advantage in removal of Ammonia. It can be concluded from the conducted experiments that for ammonia removal both types of biochar samples *i.e*. magnetic as well non magnetic behave in same way.

Ammonia is not a major problem in CWs as sufficient aeration prevails in the media and sufficient removal has been done by plants and microbes (Vymazal, 2002). However, ammonia removal is a misnomer in many cases as it is the conversion of ammonia into nitrates that happen in CWs and it is called as ammonia removal in many research papers (Vymazal, 2007).

6 Natural treatment systems: Musi River case study

A wastewater impacted micro-watershed within the Musi River Basin was assessed for its natural treatment potential. The Kachiwani Singaram micro-watershed (KSMWS), is situated close to the city of Hyderabad, and characterized by typical peri-urban features like rapid economic development, human settlements and agriculture co-existing and interacting offering many livelihood opportunities, especially for the poor. Previous studies have documented changing landscape dynamics (Mahesh *et al.* 2014), hydrogeological and water quality studies (Perrin *et al.,* 2011; Schmitt, 2010; Amerasinghe *et al.,* 2009). This description gives an overview of the characterization and performance assessment of the KSMWS. A more detailed report of the same is found in D3.2.

6.1 Study site and activities

Briefly, the micro-watershed Kachiwani Singaram (KSMWS), is situated in the Musi basin, covers an area of 274 ha, and is 20 km downstream of the city of Hyderabad, Telangana, India (**Figure 6.1**). The climate in the region is semi-arid, with a mean annual rainfall of about 750 mm (June to October) and an annual mean temperature of 25^0C. The daily temperature however, during the summer period can go up to 48^0C. The Musi River, which carries partially treated and untreated wastewater of the city, supports irrigated agriculture in the micro-watershed. Wastewater generation from the city is estimated at over 1000 MLD, making irrigation water available year round (Amerasinghe *et al.*, 2009). The riverbed has a flat topography (mean slope < 1%) (Massuel *et al.*, 2007), and the canal discharge rates were estimated to be less than 2 cubic meters per second, which was highly variable depending on the season (**Figure 6.2**). The area under study comprised areas of irrigated agriculture (wastewater and groundwater), a small reed pond (wetland) in the centre, barren land and built up areas in the northern most region. The major crops grown in the area were paddy rice, paragrass and vegetables. Both canal water and groundwater were used for cultivation. The hamlet of Kachiwani Singaram is close to the eastern border of the delineated micro-watershed.

The following activities were carried out to assess the performance of the natural treatment system/s in the micro-watershed. Land use surveys and ground truthing; Water level monitoring (continuous and piezometric campaigns); Geophysical surveys (Electrical resistivity tomography); Water quality analysis (major ions, trace elements, microbiology and pesticides).

The performance assessment was carried out based on geo-morphology, hydrology and water quality.

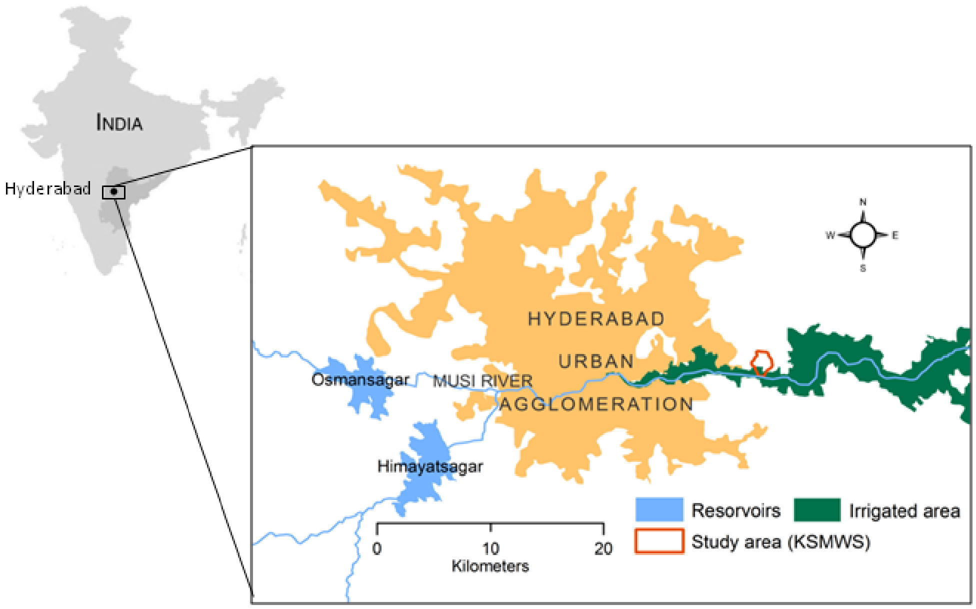


Figure 6.1: The study site – Kachiwani Singaram micro-watershed (KSMWS) in relation to the city of Hyderabad (Modified from Mahesh et al., 2014)

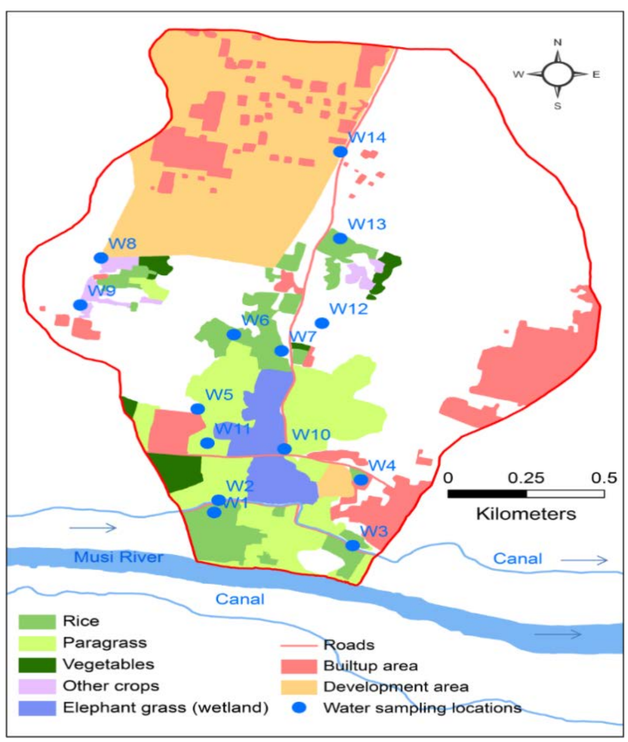


Figure 6.2: The water sampling locations (W1-W14) and land use classification in the micro-water shed

6.2 Materials and Methods[1]

Land use mapping was carried out using high resolution satellite imagery (Google Earth) and existing interpretation from a former study (Amerasinghe *et al.*, 2009). To observe the micro-level spatial land use variability in KSMWS digital globe satellite data (dataset used: January 21st 2012) were used from Google earth and validated with ground truth data, field observations and farmer interviews. The datasets were geo-referenced with UTM projections and WGS 84 data.

Discharge measurements: River and canal discharge measurements were carried out using a simple floatation method, where the time taken for a floating object to travel a fixed distance was measured (**Figure 6.3**). Flow measurements were carried out in the river stretch from A – Nagole and canal stretch KSM 12 -13. Surface flow Modelling was also carried out to see the impact of land use activity associated with urbanization. Surface Modelling based on topography was performed using ArcGIS software. Topography was estimated from the ASTER DEM with 30 m resolution datasets.

Monthly measurements of water levels were carried out in the four monitoring piezometers drilled in 2009 by the BRGM (MU01 = W_1, MU02 = W_5, MU03 = W_8 and MU04 = W_6) (Figure 2). The W_1 well is located at south of the Musi canal in the paddy field and captured a wastewater contaminated shallow unconfined aquifer. W_5 is located 400 m north of Musi Canal and located in a paragrass field irrigated with wastewater. W6 is at 700 m north from Musi Canal, located in a paddy field irrigated with groundwater. Similarly, W8 is 1 km north of the irrigation canal, and positioned at an elevated topography, located in a vegetable farmland irrigated with groundwater.

Automatic level-loggers (Solinst® Levelogger), recording water level and water temperature at a 30 min time step interval were installed in W8 and W6.

Four extended piezometric campaigns over the catchment were carried out in May, June (pre-monsoon), September (monsoon), and October (post-monsoon) of 2010.Through interpolation using inverse distance weighting (IDW), annual (pre / post- monsoon 2010) and inter-annual comparison (post-monsoon 2010 / post-monsoon 2013) maps were computed and further analyzed to highlight particular patterns of the groundwater levels.

Hydrodynamics properties were assessed by conducting hydraulic tests, i.e. pumping test, in the four piezometers (W_1, W_5, W_8 and W_6). Drawdown was monitored during the entire pumping duration (recorded at 1 min interval). The recovery was recorded every minute until the initial water level was reached. These data were used to estimate the hydrodynamic characteristics of the aquifer, using the software WinIsape© developed by BRGM. The Theis method was used for

[1]More details are available in the D3.2 report

interpretation (Theis 1935). A best-fitting procedure led to the computation of the transmissivity parameter.

Variations of water velocity inside the bore well were measured using a flow meter fitted with a propeller. Measurements were made at the point of the casing and up to the base of the hole. Measurements and productive fissures were noted and were correlated with geological observations of cuttings to identify the productive zones.

Geophysical investigations: Electrical resistivity tomography (ERT) was carried out to delineate the deposition of the subsurface lithological layers and saturated thickness (for details see D3.2 report). A total of 17 ERT profiles were carried out at 11 different locations (**Figure 6.4**) to cover all possible stages of weathering processes in the study site. The geology, geomorphological and hydrogeological conditions at each ERT profile was noted.

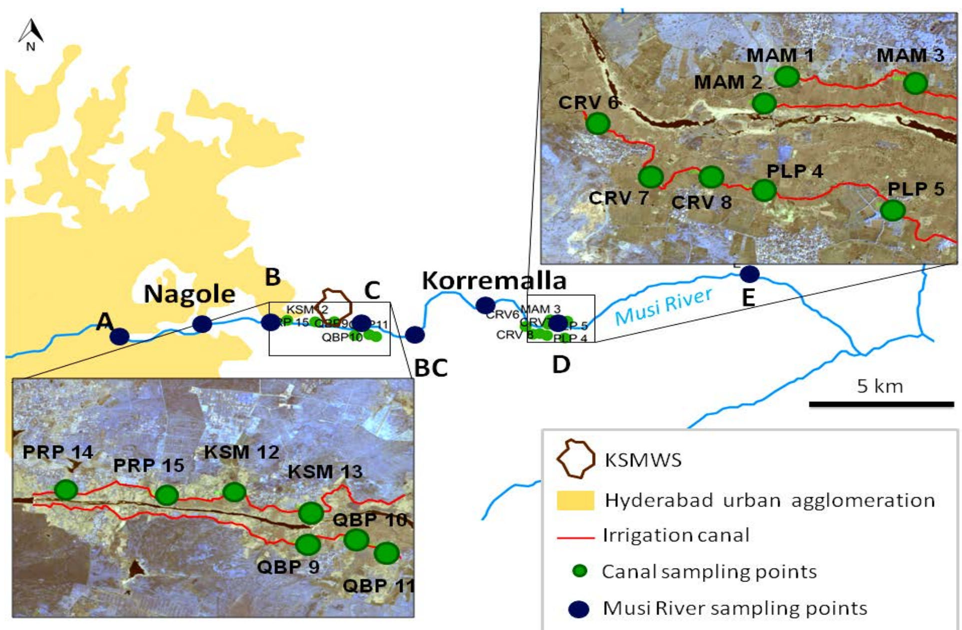


Figure 6.3: Location of the Musi River and associated canal discharge measurement points[2]

[2]River and canal sampling points A, B, C, BC, D and E (2006-2008) and PRP 14 and 15; KSM 12 and 13; QBP 9, 10 and 11; CRV 6, 7 and 8; MAM 1, 2 and 3; PLP 4 and 5 (2007/2008) respectively.

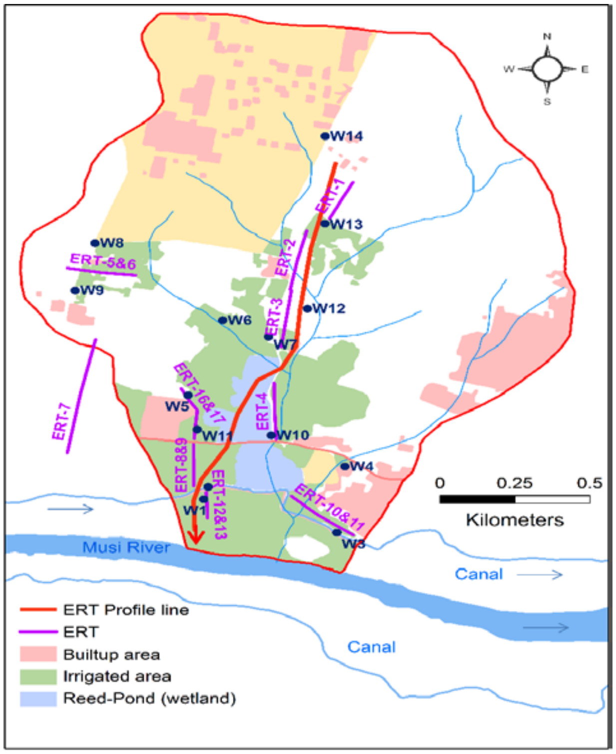


Figure 6.4: Geophysical measurement (ERT) locations in the KSMWS. W1-W14 indicate the water sampling locations

Water quality tests: In 2012, two hydro-chemical water sampling campaigns were carried out in pre monsoon (June) and post monsoon seasons (November) on ground water (n=11), surface water (n=2) and reed pond (wetland) water samples (Figure 2). Groundwater samples were from piezometers (4), tube wells (3 agriculture and 1 domestic wells) and open dug wells (3) (**Table 6.1**). The parameters tested were pH, total dissolved solids, electrical conductivity, carbonates, bicarbonates, calcium and magnesium, sulphate, fluoride, sodium and potassium nitrate, pesticides and pathogenic microbial organisms. Data collected during previous studies were also used for analysis, for example, campaigns carried out in 2010 by Perrin *et al.,* (2011) and in 2006-2008 by Amerasinghe *et al.* (2009).

6.3 Results

The total size of the micro-watershed was 274 ha, of which 49 ha were under irrigated agriculture. Both groundwater and wastewater were used for irrigation and wastewater constituted the highest proportion (74%) of the total. The predominant crops in the area were paragrass (56%), paddy rice (32%) and vegetables (8%). The total area under cultivation had hardly changed over time, though the boundaries had moved more towards the hinterland

(Mahesh et al., 2014). Wastewater was lifted from the irrigation channels under gravity as well as pumps, and little change was observed in the cropping pattern over the years.

Table 6.1: Land-use classification observed in the micro-watershed (year 2012)

Land-use type	Crop type	Area (ha)
Built-up area		**30**
Area under development		**50**
Irrigated land		**49**
	Paragrass	27
	Paddy rice	15
	Vegetables	4
	Other crops	2
Groundwater-irrigated area		**13**
Wastewater-irrigated area		**36**

6.3.1 River and canal discharge:

Over 1000 MLD of city water is discharged into the river, which makes Musi River perennial and useful for the downstream user year round. The greatest users are the farmers living in the banks of the Musi River. Flow rate measurement campaigns carried out showed an increase in irrigation rates during the wet season. However, a direct correlation between the river discharge and rainfall could not be seen as the maximum contribution of the water flow in the river was from urban wastewater **(Figure 6.5** and **Figure 6.6**).

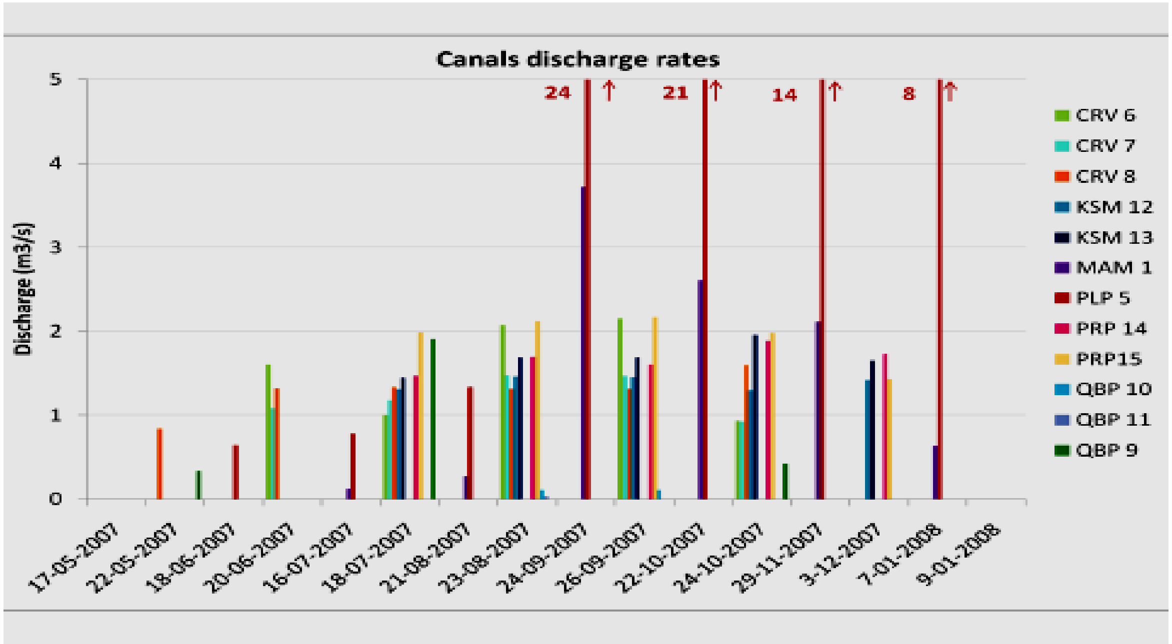


Figure 6.5: Discharge rate measurements in the canals during the years 2007 and 2008 (m3/s)

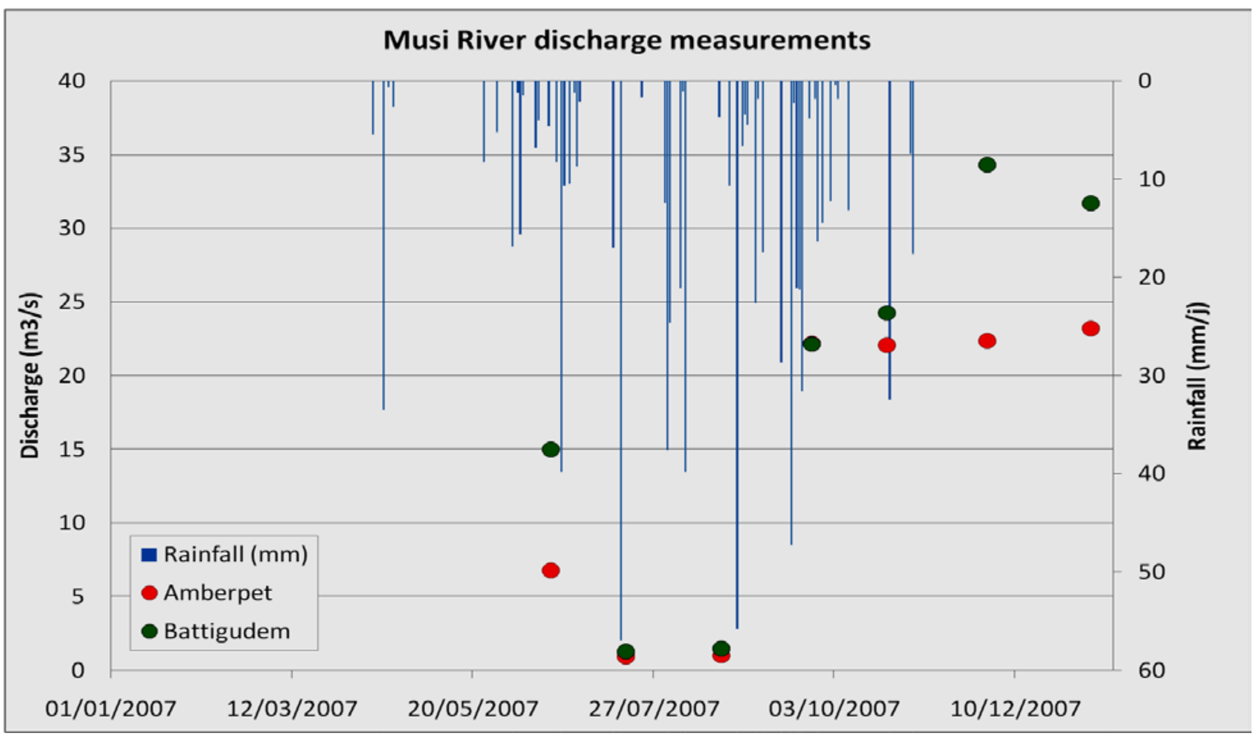


Figure 6.6: Discharge rate (m^3/s) measurements of the Musi River in Amberpet and Battigudem from May 2007 to January 2008 and daily rainfall (mm) in Hyderabad from January 2007 to January 2008

6.3.2 Surface run-off

The natural flow direction was towards the irrigation canal and the Musi River. As in many semi-arid environments, spatial and temporal interactions between surface water and groundwater are complex. The surface water percolation mainly occurred through preferential paths based on the natural topography and underground hydraulic properties.

6.3.3 Geology

The watershed geology was characterized by a basement made of orthogneissic granite also known as "pink granite" with granite, quartz and dolerite intrusions. It was characterized by cm-large feldspars chunks and an important amount of biotite that indicated a generally well-developed weathering profile. The hydrogeological boundaries of the study area encompassed the surface watershed limit and extended northwards to an extensive dolerite dyke. In the western part of the watershed, significant intrusions of leucocratic granites, doleritic material and quartz/pegmatite veins constituted the main observed outcrops. The geomorphologic studies showed that the potential recharge conditions can vary from poor to good from north to south of the micro-watershed (**Figure 6.7** and **Table 6.2**).

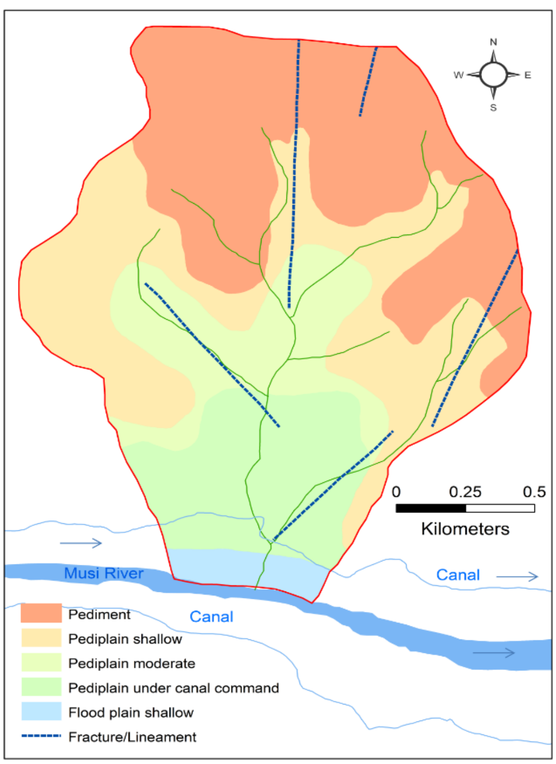


Figure 6.7: Geomorphology of the micro-watershed

Table 6.2: Geomorphic and potential ground water recharge conditions

Geological Sequence	Rock Type	Geomorphic form Landform	Recharge potential recharge conditions
Archean	Granite	Pediment	Poor
	Migmatite	Pediplain shallow	Moderate
	Granite Gneiss	Pediplain under canal command	Good
	Migmatite	Pediplain moderate	Moderate
	Granite	Floodplain shallow	Good

The electrical resistivity of the top soil and weathered zone ranged from 10 to 70 Ω-m (**Figure 6.8**). The maximum thickness of top soil and weathered zone was attained at the wetland point (W10), due to chemical weathering. Here, low resistivity ranged from 10-35 Ω-m and indicated a conductive saturated zone with possible contamination up to 15 m depth from the ground surface. Further, the gentle raise in topographic elevation towards the Musi River, causes thinning of weathered layer up to 4 m depth. The weathered zone was followed by a semi weathered zone with a resistivity range of 100-300 Ω-m. A similar level of thickness was observed in the semi weathered zone which increased from north to south of the watershed. The semi weathered zone was followed by a thin ~1-5 m thick fractured layer (ρ: 350-500 Ω-m) over the basement rock. The electrical resistivity of regolith varied from 30 Ω-m to 350 Ω-m attaining a maximum thickness about 32 m. The bed rock topography indicated a gentle slope towards the south and sudden rise followed by a slope close to the Musi River (Figure 6.8). The electrical resistivity of the rock (massive granite gneiss) ranged from 600 Ω-m to 4000 Ω-m.

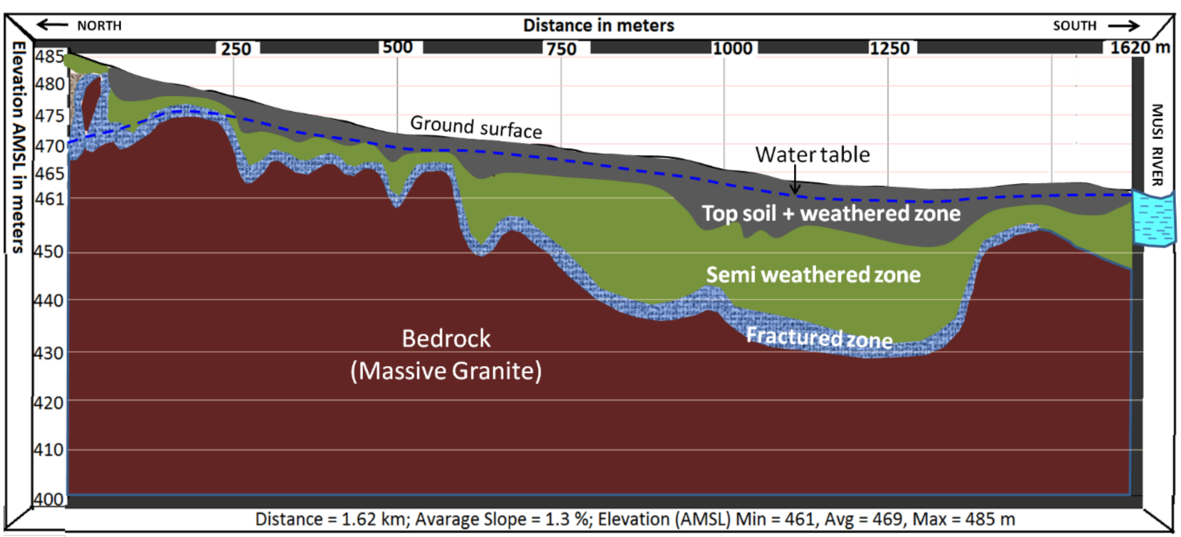


Figure 6.8: Geological cross section with altitude derived from A-A│ERT data of N-S profile at Musi River study area

6.3.4. Aquifer hydrodynamic properties

General groundwater flows were observed from north to south towards the river, following the general topography. The piezometric levels were highly variable in both time and space which was under the influence of the strong heterogeneities of the aquifer and the irrigation activities (**Figure 6.9**). Piezometric levels in W_1 and W_5, close to the canal did not vary significantly during the year and were within 2 m below the ground surface. The water levels in the southern zone were impacted by the river which constitutes a boundary of the aquifer. A significant influence was observed daily or even hourly with irrigation pumping during the pre-monsoon season (May and June). During the monsoon (October and November), the pumping influence was much reduced and a rise in the water table (about 5 meters) was observed in the central part of the study area. The water levels in W_8 and W_6 were strongly influenced by the monsoon recharge that occurs from end of June, which was expected, in these unconfined crystalline aquifers with vertical recharge. The rapid rise of the water levels after each rainfall event indicated the presence of rapid preferential flow paths in the saprolite due to the existence of preserved fractures (rise of groundwater levels in less than one day after a rainfall event). After the monsoon, the decrease in water level was fairly constant in time (dependent of natural flow and pumping) and between the years. These differences show two different hydrodynamic behaviors in the north-south gradient, exhibited by the more constant level in the southern part due to the continuous wastewater irrigation (mainly for paragrass) and a decreasing level in the northern part due to the over exploitation of groundwater (for all types of crops) (**Figure 6.10**).

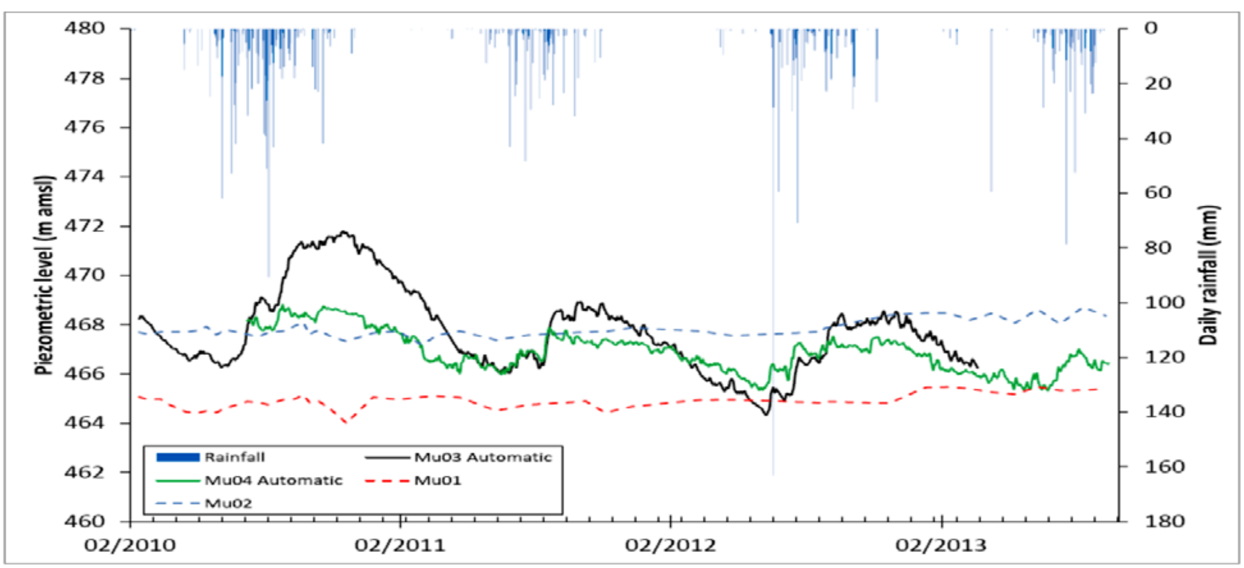


Figure 6.9: Water level evolution in bore wells MU01=W1, MU02 =W5, MU03 = W8 and MU04 = W6

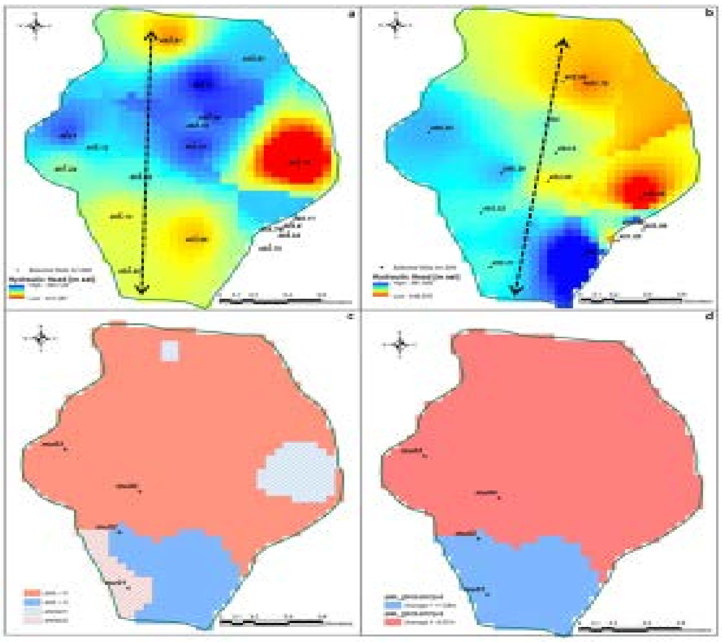


Figure 6.10: Inter-annual comparisons of the spatialized groundwater table grid computed. a) IDW on 03-11-2010 ; b) IDW on 20-09-2013 ; c) Water table fluctuation between 2010 & 2013 ; d) Water table fluctuation modified between 2010 & 2013

The high level of water abstraction for irrigation impacted the groundwater flows, and the pumping frequency was heterogeneous. Since the electricity was free in the state, farmers used the electricity to abstract water maximally and cultivated crops that suited the particular season. During the monsoon season, a general water flow from north to south was observed due to high water levels (in the saprolite). Thus one can expect a contaminant flow to take place in the same direction. However, during the dry season, the water levels in the northern region drops, and the gradient created is reversed allowing the contaminants to move in the south to north direction, aided by the river discharge in the reverse direction. As such, the potential for aquifer contamination is high in this scenario. Also, since the pumping activities are heterogeneous, patchy flow patterns can be expected. Drawdown based on the pumping tests (W_1 and W_6) is reported in **Table 6.3**. These data were used to further analyze the hydrodynamic characteristics of the aquifer using the software WinIsape developed by BRGM. The Theis method was used for interpretation with a best-fitting procedure. The outcome is presented in **Table 6.4**. The permeability values are in the range of the expected permeability on this geological media which usually range between $1{\times}10^{-7}$ m.s^{-1} to $3{\times}10^{-5}$m.s^{-1} (Dewandel *et al.* 2006). The flow meter measurements used at W_1, W_5, W_8, and W_6 yielded the following results.

W_1: productive fissure zone between 7- 8 m below ground surface (bgs).

W_5: productive fissure zone between 10-12.5 m bgs.

W_8: productive fissure zones between 17- 17.5 m bgs, 19- 19.5 m bgs and 20.5- 23 m bgs.

W_6: productive fissure zone between 12-13 m bgs.

Table 6.3: Pumping and recovery times

Piezometer	Pumping duration (min)	Recovery time (min)
W_1	80	42
W_5	55	20
W_8	81	16
W_6	81	29

Table 6.4: Aquifer characteristics

Piezometer	Discharge ($l.s^{-1}$)	EC (µS/cm)	T ($m^2.s^{-1}$)	Max drawdown (m)	K ($m.s^{-1}$)	S [-]
W_1	0.63	1.4 -1.55	$9.9\ 10^{-4}$	0.78	$1.7\ 10^{-5}$	$3.02\ 10^{-4}$
W_5	0.61	1.55 – 1.63	$1.1\ 10^{-3}$	0.59	$3.4\ 10^{-5}$	$3.03\ 10^{-4}$
W_8	0.55	0.95 – 1.15	$3.4\ 10^{-3}$	0.32	$7.4\ 10^{-5}$	$8.9\ 10^{-8}$
W_6	0.18	1.65 – 1.7	-	2.35	-	-

EC = Electrical Conductivity; T = Transmissivity; K = Hydraulic conductivity (K=T/e, with e, aquifer thickness). Storativity values are indicative as tests were carried out in pumping wells (i.e., no observation wells) and during a short period.

Water quality: Pre-monsoon and post-monsoon water samples collected from the micro-watershed (canal water = W_2, W_3 and wetland = W_{10}, 2012) was compared with studies carried out in the same watershed in 2010, and Musi River (source water) in 2006-2008.

In the surface water the pH ranged from 7 to 8.37 in the samples tested, and did not vary much between the pre and post monsoon samples. The electrical conductivity in the canal on the other hand, showed an increasing trend though not significant (1217 – 1490 µS/cm). This was contrary to the general expectation that monsoon will result in the lowering of EC. In the wetland sample (W10) the EC was higher than in the canal reaching 1750 µS/cm during post monsoon period. This could be due to weathering, silicate hydrolyses process and the hydraulic gradient.

Major ions (sodium and chlorides) that contribute to salinity, did not vary significantly in the pre- and post-monsoon samples, however, values were indicative of anthropogenic influences (**Figures 6.11** and **Figure 6.12**). The wetland showed a greater variation in its constituents compared to the canal water.

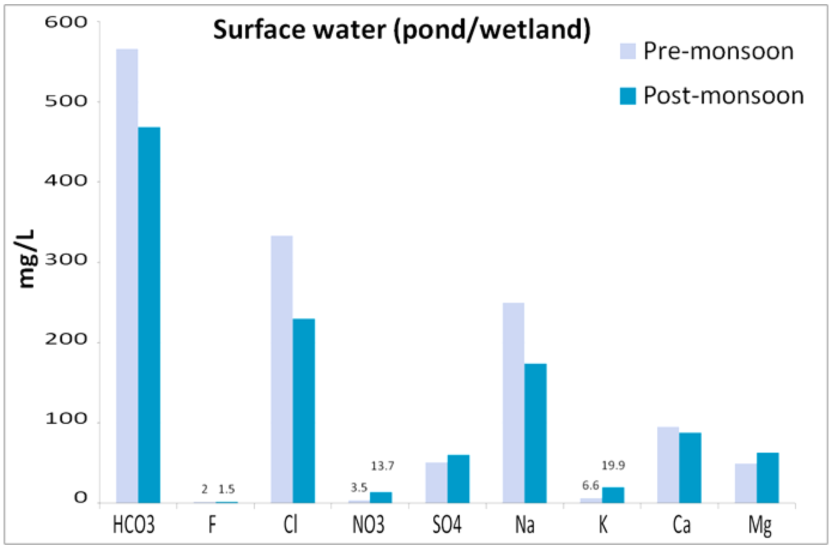


Figure 6.11: Pre-monsoon and post-monsoon major ion concentrations (mg/L) in the surface water samples (W10) in 2012 n = 1

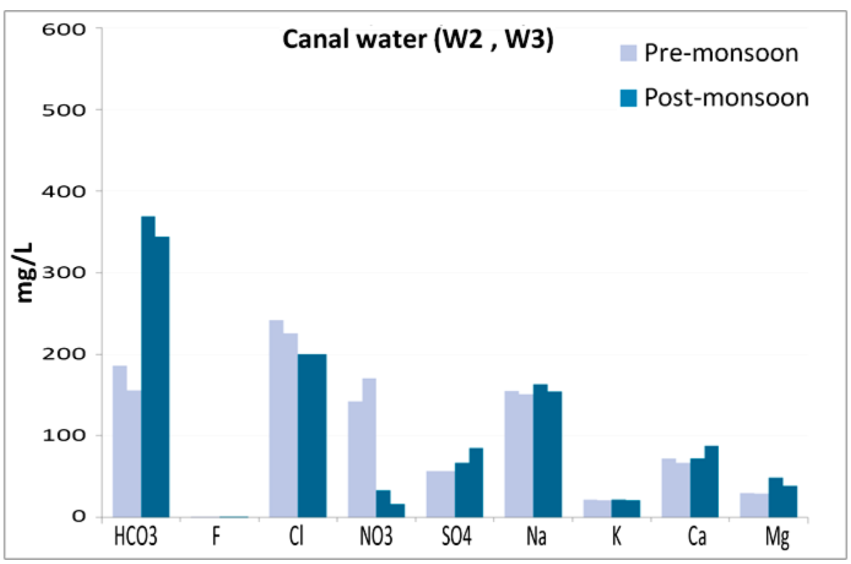


Figure 6.12: Pre-monsoon and post-monsoon major ions contents (mg/L) in the canal water samples (W2 and W3 sampling points) in 2012 n = 1

The canal water samples had variable nitrate concentrations ranging from 0 to greater than 150 mg/L. The high values could be due to the influence of agricultural activities as well as the source water, which carries urban run-off (Figure 12) Nitrate content in the Musi River and wetland (W10) were low (<20 mg/L) probably dueto denitrification process in surface water linked to high organic matter loads (Reeds) (Lofton *et al.* 2007).

6.3.5. Groundwater

Irrigation water quality from bore wells and groundwater wells are depicted in **Figures 6.13** and **Figures 6.14**. The results show a strong spatial variability in groundwater chemistry (i.e. mineralization, long term wastewater irrigation, agriculture practices etc.). Two main poles of EC are visible: one representative of fresh groundwater with EC< 1000 µS/cm, in the north part and one pole with groundwater influenced by canal water return flows with EC>1000 µS/cm in the south part. It is also clear that additional sources of groundwater contamination (e.g. agriculture, sewerage) exist in the study area with localized points showing quite high EC (even higher than 2000 µS/cm). In the areas where the groundwater is impacted by canal water return flows, it should be noted that groundwater EC is higher than raw canal water most likely as a result of re-concentration by evapotranspiration processes. Electrical conductivity in post monsoon 2012 is in general higher than the pre monsoon samples in the southern part of the watershed. This may be due to the increase in $HCO3^{-}$ and Ca^{2+} contents or the strong influence of the wastewater in the canal.

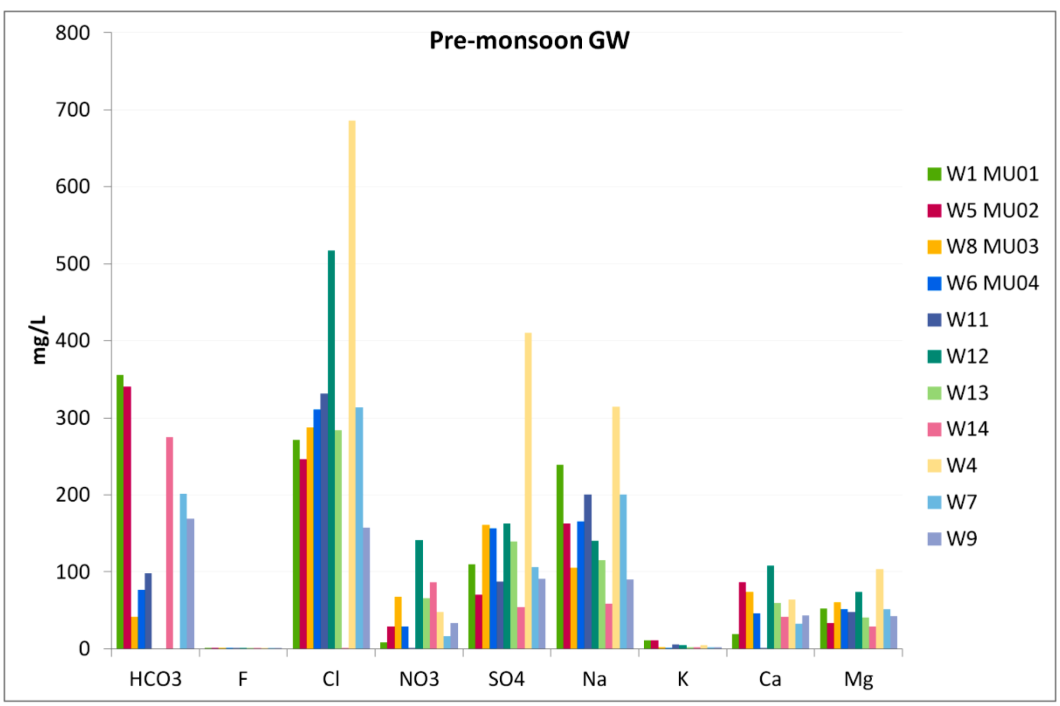


Figure 6.13: Distribution of major ions (mg/L) in all types of wells in the micro-watershed, during the pre-monsoon sampling period (2012) n = 1

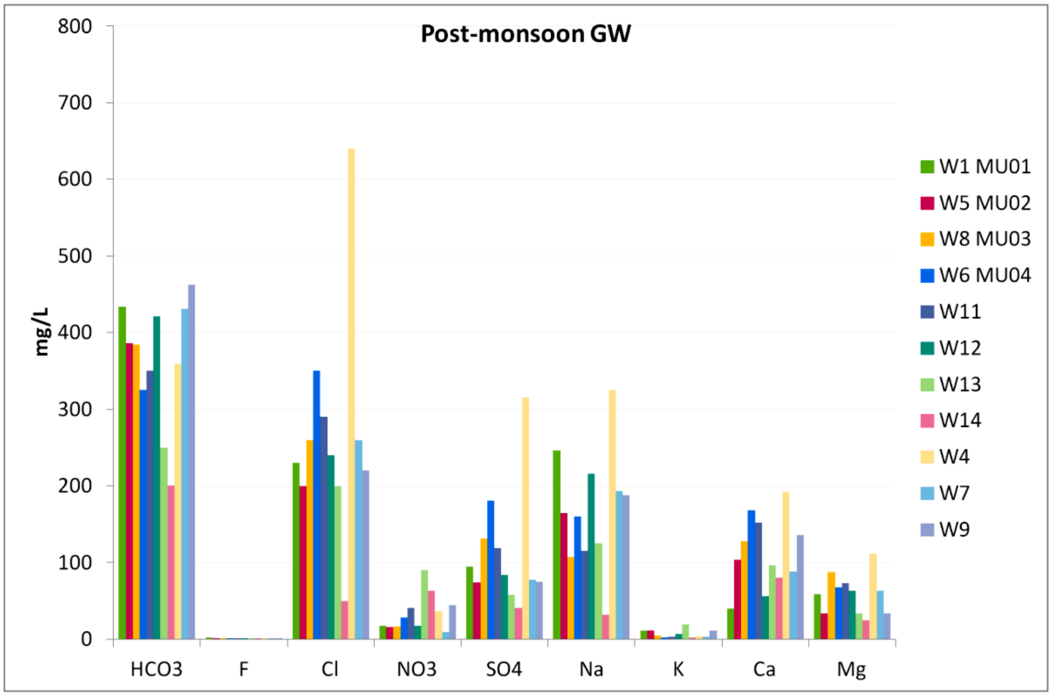


Figure 6.14: Distribution of major ions (mg/L) in all types of wells in the micro-watershed, during the post-monsoon sampling period (2012) n = 1

Chloride, nitrates and sulphate concentrations decreased in the post monsoon samples. This could be due to rainfall flushing out the accumulated ions. Except a slight increase in W_1 in post-monsoon, there is not much variation in the fluoride concentrations in groundwater. The nitrate and fluoride concentrations were above permissible limits for drinking water (50 mg/L and 1.5 mg/L respectively according to the WHO guidelines) (**Figure 6.15** and **Figures 6.16**). Sulphates were reported up to 411 mg/L (W 4).

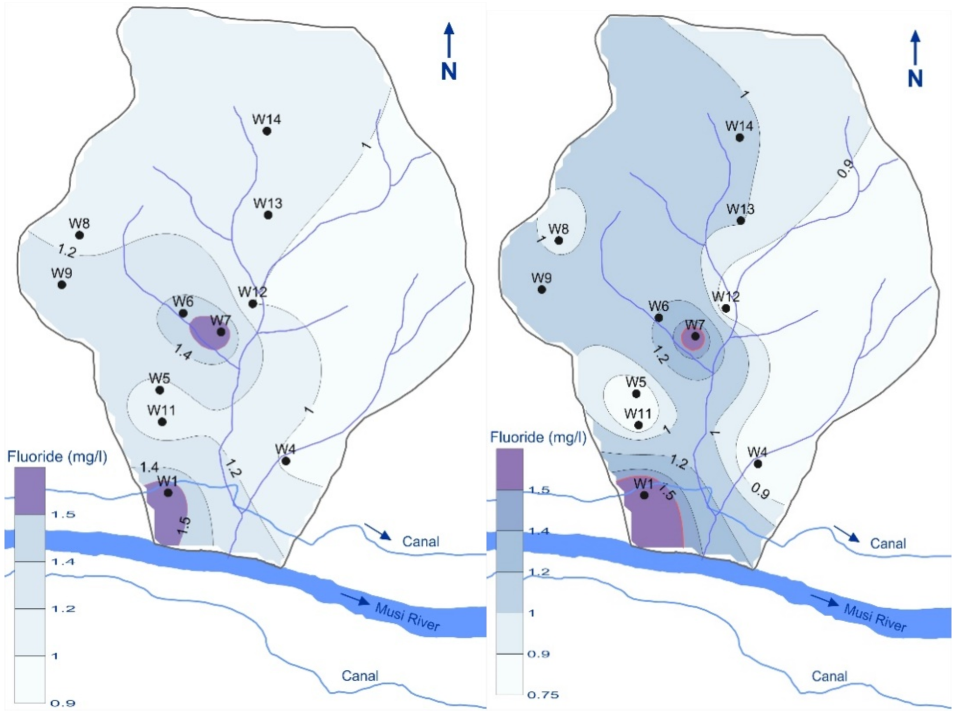


Figure 6.15: Fluoride map pre (left) and post monsoon (right) for the 2012 campaigns

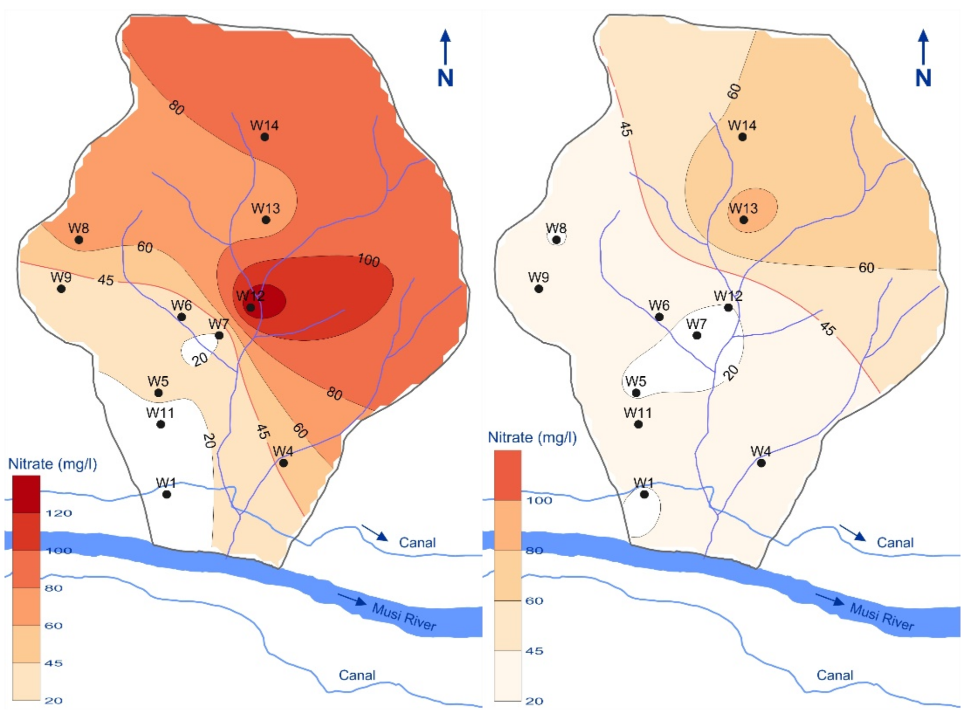


Figure 6.16: Nitrates map pre (left) and post monsoon (right) for the 2012 campaigns

The groundwater in the micro-watershed is influenced by long term waste water irrigation, soil salinity and rainfall. High contents of HCO_3^- ions are due to organic matter mineralization leading to high CO_2 content in the soils. The increased HCO_3^- content in GW, after the monsoon can be due to the runoff processes, which results in high rate of dissolved CO_2, enhancing the mineralization processes. The chlorides do not have lithological origin in this hard rock terrains. It could be due to anthropogenic and/or meteoric origin enhanced by evaporation processes in soils. There was an excess of Na+ was seen in the southern part highlighting the strong cationic exchanges within the clay minerals in the soil. The high concentrations of fluoride are due to water rock interactions enhanced by irrigation return flows (Pettenati *et al.*, 2013). High nitrates and sulphates are due to agricultural practices and wastewater irrigation impact on groundwater. Chemical water facies can be classified using piper diagrams. It shows that temporal variations of major ions due to rainfall are not significant, and anthropogenic activities like wastewater irrigation, application of fertiliser, soil salinity are contributing to the high levels of nitrates and sulphates. The groundwater samples from piezometers (W1, W5, W8 and W6), that were used only for monitoring purposes illustrates the spatial and temporal variability (2010 and 2012) of water quality within the micro catchment:

- W_1=MU01: variability in the chemical facies was not that significant in the monitoring years 2010 and 2012, and was not influenced by the hydrological condition that prevailed. However, of the ions that are considered important for irrigation, sodium, chloride and TDS were at moderate restriction levels.
- W_5=MU02: a strong spatial variability at different depths was observed for EC during 2010. In general, influence of the monsoon period can be regarded as minimal in 2012
- W_8=MU03: variability in EC was observable in 2010, however, no clear trend can be attributed. Effect of the monsoon was minimal in 2012.
- W_6=MU04: variability in the water quality facies indicates that monsoon had little impact.

The monitoring piezometers were positioned in a north-south gradient. Both W_1 and W_5 were situated in areas where wastewater irrigation practice is extensive. The W_8 and W_6 were positioned in the middle and northern part of the watershed where more ground water was in use. Accordingly, looking at the sodium and chloride values, W_1, W_5 and W_8 appear to be influenced by the wastewater irrigation practices. The noteworthy observation is that W6 was not impacted by the wastewater irrigation practices and had different hydrodynamic characteristics. It is clear that the long term wastewater irrigation coupled with clay mineralization would have contributed to the sodium excess. Excessive irrigation return flows, through solute recycling may have led to significant aquifer salinization further exacerbated by the presence of thick clay soils (geophysical study), which favour strong cationic exchanges in this area (Perrin *et al.,* 2011).

6.3.6. Suitability for irrigation

The cations and anions contribute to the overall EC and determine the suitability for irrigation purposes. Anthropogenic origin of ions could be attributed to the high level of EC, and can be related to the agricultural activities as well as the source water. The Musi river chemical quality has been studied for up to a 40 km stretch, and based on data collected in 2007, some parameters indicated that at some points, the river water may not be suitable for irrigation according to FAO guidelines (Ayers and Westcott, 1994). With respect to chlorides, values increased downstream with concentrations even higher than 10 meq/L (350 mg/L), and SAR (sodium adsorption ratio) higher than 9. Within the watershed, the Wilcox diagram for salinity hazard *Vs* sodium hazard falls under C3S1, C3S2 and C4S2 categories, which indicates a high salinity hazard (**Figure 6.17**) and therefore, non-suitability for sustainable irrigation. Even though the salinity of the canal water is very high in the watershed, many farmers continue to use wastewater to irrigate paragrass (*Urochloa mutica*) which is saline tolerant. It is clear that long term wastewater irrigation has impacted the local groundwater quality (increase in salinity), further confirmed by the local inhabitants.

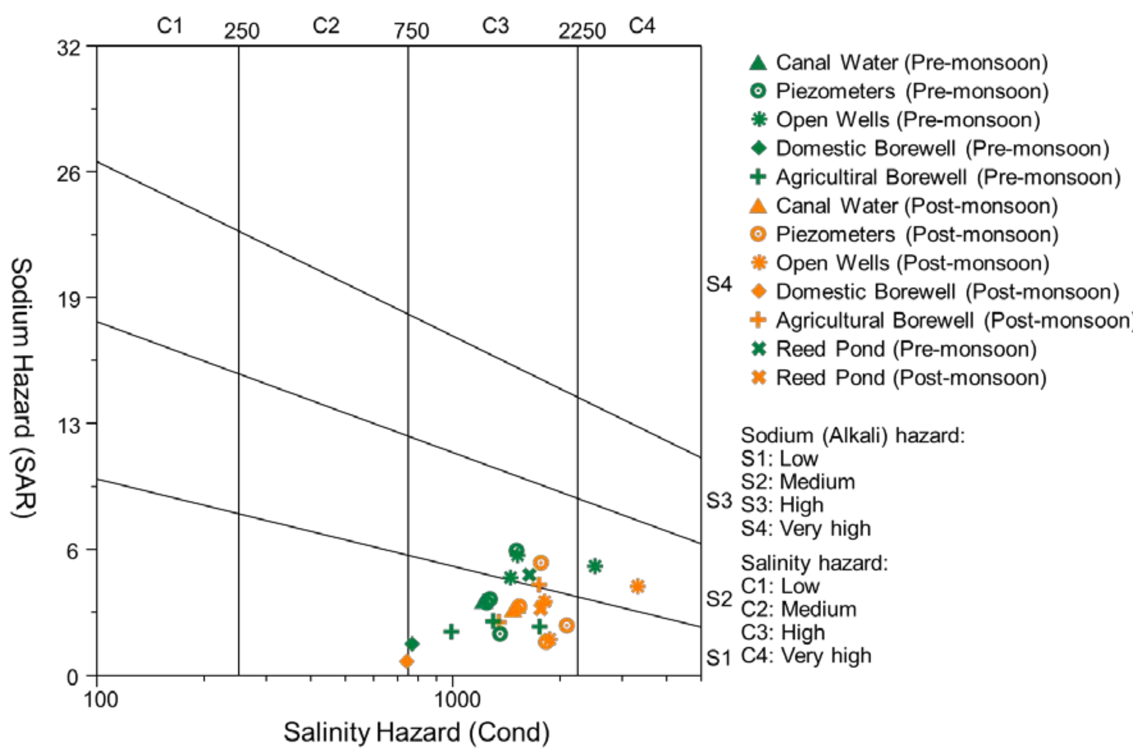


Figure 6.17: Water quality dynamics for the irrigation suitability (Wilcox Diagram) (pre-monsoon and post-monsoon data of 2012)

Pesticides: Of the 14 samples tested, 7 samples (W_1, W_2, W_3, W_5, W_7, W_{10} and W_{14}) showed the presence of pesticides, to levels that were detectable. The pesticides belonged to three families, namely, organochlorine, organophophorus and carbamate. Farmers in the study area are using organochlorine pesticides (OCP's) like butachlor, organophosphorous pesticides like (OPP's) like Malathion and carbamate pesticides like carbofloro nuclon granules.

The pre and post monsoon sampling campaign results show a high temporal variability on the groundwater pesticide contents (0.01 – 0.09 µg/L). W14 had the highest number of pesticide residues in the pre-monsoon period, which was not detected during the post-monsoon sampling. It also raises concerns that it is a domestic bore well, however, not much information is available on the pesticide application in the same area, to make further statements. Atrazine was not a pesticide that was used by the farmers, however, they appeared consistently in some of the wells which is somewhat baffling, and needs further investigation to trace the sources. The presence of pesticides in the canal water can be due to many sources other than the agriculture runoff. However, in this study we did not trace the other sources to make a definitive comment.

The permissible limit for drinking water as per BIS standards (Bureau of Indian Standards) for each pesticide is 0.01 µg/L, and most samples showed values higher than 0.01 µg/L. Even though people are not drinking the water either from the canal or local groundwater wells that were tested, the elevated concentrations of pesticide elements raise a question of ecological sustainability of the environment.

Microbiology: The faecal coliform levels were way below the levels expected in the pre-monsoon period. In the post monsoon period W_2 and W_5 wells recorded faecal coliform levels that were high, >1600 MPN/100 ml and 170 MPN/100 ml respectively. The microbial contamination can be variable depending on the activities of the local area, therefore, reuse in agriculture has to be done only after a proper testing, risk assessment and treatment.

6.3.7. The conceptual model

The KSMWS consists of agriculture, built-up and barren land, and a small wetland. Hydrodynamic monitoring, hydraulic tests, hydro-geophysical surveying, land use data, water chemistry data were utilized to produce the conceptual model for flow and transport at the peri-urban micro-watershed (KSMWS) (**Figure 6.18**). Water budgeting showed that the canal irrigation was the main recharge flux at the basin scale and have a strong impact on groundwater quality. In such hard rock aquifers the saprolite plays a storage role due to its porosity, and the fissured zones provides the transmissive function. When water levels are high, the saprolite layer allows a regional ground water flow. In the study area, the ground water flow was from north to south, towards the Musi River. However, due to intense pumping, water levels decreased in the northern part. The return flows induced a mixing of the groundwater and the canal water pumped for irrigation, in the middle potion of the watershed, and allows ground water recharge as well. Long term wastewater irrigation in the area has resulted in high ground water salinity in the area, while agriculture run-off appears to have contributed to the presence of some anions and cations including pesticides (e.g. nitrates, pesticides). The Musi River on the south, and W1 and W5 share similar hydrogeological conditions with minimal variations in relation to water levels. Thus, the irrigation canal plays only a passive role on the hydrogeology in the southern part of the watershed.

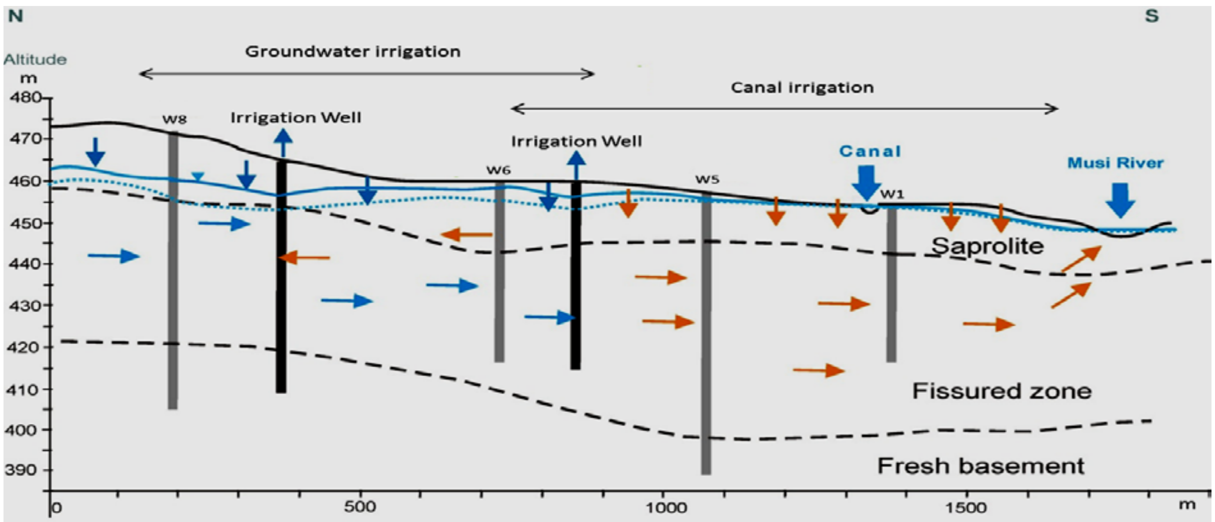


Figure 6.18: Conceptual model of groundwater flow and transport

W8, W6, W5 and W1 are piezometric wells. The irrigation wells are used for agriculture. Dotted blue line – pre-monsoon (June); Blue line – post monsoon (November)

7 Summary

Natural treatment systems are suggested to be the most appropriate technologies for tropical countries such as India (Arceivala and Asolekar 2006). Constructed wetlands are the most developed of the NTSs and many examples for their successful implementation in developing as well developed countries have been reported. Horizontal flow constructed wetlands (HFCW) were evaluated in the countries with tropical climate such as India and Thailand. Removal efficiency of chemical oxygen demand and total suspended solids was satisfactory but poor for other nutrient removal (Juwarkar *et al.*, 1995; Billore *et al.*, 1999; Konnerup 2008). To remove nutrients, a combination of horizontal and vertical CWs or a combination with other technologies is recommended. Modified wetlands have been trialed which used commercially available ornamental plants for treatment which then help produce additional income for the local population (Zurita *et al.*, 2008). Filter bed materials can also be modified to improve treatment (Aslam, 2007; Antinomos, 2007).

In designing of the different kinds of NTSs various approaches have been utilized. These approaches are based on research as well as experience gained during the operation of NTSs around the world. In designing WSPs, dispersed flow, a non-ideal flow regime is assumed with first-order type of organic substrate removal. This method gives the applicable value of substrate removal (K_p) since it takes into account the actual flow pattern (and, therefore, the actual residence time in the pond) rather than assumed ideal flow patterns. In the design procedure used by Asolekar and Langote (2004), the K_p values obtained are similar and they range from 0.13 to 0.20 per day at 25° C, the lower value being applicable to facultative ponds with h>2.5 m and the higher value to aerobic ponds with h<2.5 m. The effect of pond loading on the K_p, values has not been taken into account by them.

In designing HFCWs, two important aspects have been taken into consideration, namely the organic removal parameter, and hydraulic flow consideration assuming first order kinetics. The BOD removal in CWs has been approximated by first order, plug flow kinetics. In hydraulic flow consideration, the dimension of CWs can be derived from the assumptions including hydraulic gradient and hydraulic conductivity in applying Darcy`s Law. In polishing/maturation pond, rational design approach models the ponds performance by using kinetic theories of biochemical reactions in association with the hydraulic flow regime. Duckweed pond sizing depends on whether one or both of the yields of duckweed biomass to give the desired fish production for marketing. The detention time required to give the desired effluent quality is still estimated on a thumb-rule basis, based on a few measured values of BOD, TSS and TKN at different detention times in laboratory and field studies.

During elaboration of possible ways to improve the performance of NTSs, optimal conditions were determined based on a country wide review of good practice examples as identified in Task 3.1 and 3.3 have been included. The parameters were determined for alternative uses such as providing water resources or grey water supplies to communities after appropriate disinfection, providing process water for industry and utilization as pre-treatment before an advanced water reclamation system as investigations are in progress in the pilot study (Task 3.4). The important factors that should be considered while strategizing to improve the treatment efficiency of NTSs include, rate, extent and variability of wastewater reaching the system, climate changes, population changes pattern of urban and industrial development, changes in agricultural practices, soil erosion and sedimentation, scope of construction activities in nearby areas, nutrient loading *etc*.

CWs for treatment of raw sewage can resolve the issue of discharge of untreated sewage into the natural water bodies. CWs are not energy intensive systems and also the O&M cost is quite reasonable when compared to conventional wastewater treatment technologies. Therefore, successful implementation of CWs for sewage treatment in developing countries would bring up the value of their natural capital. Decentralized treatment of wastewater from small communities could result into better water quality in natural water bodies. The research in the field of CWs has brought up its performance and application in wastewater from industries also (for example, paper and pulp wastewater, acid mine drainage and thermal power plant wastewater).

The sustainable wastewater treatment through CWs could be achieved but prior to that there are some few questions which need to be answered first like, i) what is the pollutant removal kinetics prevailing in wetland system? As this is the key to answer how much hydraulic retention time is required for treatment of sewage; ii) does the variation in pollutant concentration in inlet sewage has effect in overall performance? As higher inlet concentration shows different removal kinetics than lower concentration (which can be seen from the results of this project); and iii) what could be the role of wetland media and plant in removal of pollutants? These are the problems still prevailing in the field of CWs for sewage treatment especially when it comes to treatment of sewage from communities at different geographical locations.

To find out the removal of pollutants from sewage and to find out role of wetland media and plants species in pollutant removal, CW rectors were prepared. There were three different media (crushed aggregate, filter media sand and Juhu Beach sand) tested in this project. Each wetland media had four experimental CW reactors, one unplanted and three planted. Raw sewage from sump well station of IIT Bombay was used in experiments. The results were obtained from five experimental cycles at 24 hr, 48 hr and 72 hr. The inlet sewage and treated effluent were analyzed for BOD_5, COD, PO_4^{3-} and NH_3-N.BOD_5 was analyzed only to characterize the sewage and the final results were shown only in terms of COD values. The removal of pollutants varies among different CW media used. However, the effect of vegetation on removal of pollutants does not seem to have much influence as the plants were in the starting phase of their growth cycle. The removal of PO_4^{3-} showed that there was a minimum concentration achieved by each reactor and was independent of varying inlet PO_4^{3-} concentration. Filter sand reactors did not show as promising results as crushed aggregate reactors had shown. Ammonia nitrogen removal was very fast in crushed aggregate and Juhu Beach sand (which showed almost 100% removals) than filter sand.COD removal was good but not sufficient enough for discharge into water bodies (maximum removal of 70% had been observed). It can be concluded from the results that efficiency of COD removal deteriorates with increasing COD concentration in inlet sewage. The practice of full drain and then flooding CW system (which was used in these experiments) might result into lesser removal of COD due to loss of microbial biomass.

The main conclusions from this CW-based focused research by using different types of media are:

- Area is not the issue, shallow depth CW system can be successfully implemented for treatment of medium strength sewage.
- Use of suitable media which can support microbial growth and removal of phosphate is necessary. As filter (quartz) sand media was inert, it did show as promising results as crushed aggregate.
- Natural sand cannot be used without appropriate sorting of particle sizes, otherwise clogging can take place as in case of Juhu Beach sand reactors having fine particle size.

There are many types of technologies available for removal of nutrients present in secondary treated wastewater. In case of CWs, phosphate is a major pollutant remaining in the treated water. Out of many technologies, selection of most appropriate technology was done using series of matrix compiled by extensive literature survey. It was concluded that biological methods of phosphorus removal may not be advisable when constructed wetland is employed at secondary level due to presence of low BOD in the treated water. In case of biological methods for phosphorus removal, sufficient BOD is being required as the carbon source – which may not be fulfill from secondary treated effluent from constructed wetlands. These demands for addition of BOD at the subsequent treatment level which makes the system expensive and non-feasible.

The biomass generated in the CW can be used for further removal of pollutants after conversion into biochar and magnetic biochar. The used biochar can be regenerated using different methods or can be reused as soil nourishment. The structure of biochar is greatly affected by processing conditions and feed material used in the preparation. Biochar comprises of organic matrix of pyrolyzed biomass along with backbone of inorganic carbon like activated carbon but with lesser surface area. In the present study, biochar (non-magnetic / normal biochar) and magnetic biochar were prepared from the various constructed wetland species. The prepared biochar and magnetized biochar were assessed for removal of phosphate, nitrate and ammonia from the wastewater.

Magnetic biochar samples showed high phosphate (ortho-phosphate) removal of 80-90% in first few minutes followed by bleeding out and getting stabilised after 30 – 60 minutes of incubation. Most of biochar samples did not show any appreciable nitrate removal while few even added nitrates into the solution due to leaching from biomass matrix. Both types of magnetic as well as non-magnetic biochar showed appreciable ammonia removal. *p*H of non-magnetic biochar pore water was alkaline while that of magnetic biochar was acidic. The possible reason for basic *p*H was due to formation of oxides of base metals like potassium, calcium, magnesium, sodium *etc*. which dissolve in water to form OH^- ions while in case of magnetic biochar iron oxide is formed which reacts with water to form H^+ ions. It might be due to formation of inorganic minerals contributing to TDS but not to conductivity.

The characteristics of magnetic biochar are quite different from that of non-magnetic biochar. FTIR imaging shows that major functional groups present in biochar are alcohol, aldehydes, ketones, acid chlorides, esters and alkanes. In some cases, ambiguity of functional group was there which may be resolved by studying the structure composition of biomass used during preparation. Elemental analysis of magnetic biochar showed that carbon content of biochar produced at given temperature ranges between 38 – 40 %. SEM images confirmed the presence of highly porous structure and nanoparticles in the magnetic biochar while they are absent in non-magnetic biochar.

Considering the number of elements considered in Musi River case study, SAT may not be a direct solution to improve wastewater quality. It has the potential to work for some elements. Overall, the geophysical studies showed that the deep weathering (potentially inducing high permeability), limited size of the micro-watershed combined with intensive agricultural activities, may not allow the sufficient retention time for removal of contaminants. The return flows may further enhance mineralization releasing fluoride from the rocks. The reed pond might play a role in reducing nitrates from the inflow streams of water, however, it constituted only a small part of the watershed. If soil aquifer treatment and wetlands were to perform to capacity, the retention time will have to be increased to achieve the desired results. Further studies on flow patterns and in-depth analysis of elemental transport across irrigation water, soil retention and plant uptake will have to be studied to fully understand the treatment processes in the site. The wetland site is promising if it can be engineered to increase the retention time for contaminant removal. Such small scale on-site systems have the potential to treat wastewater to a level that can be used for agriculture, provided more studies are conducted to assess the specific risks associated with irrigation practices and the types of crops.

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