Addis Ababa University

Institute of Technology (AAiT)

School of Graduate Studies

Chemical Engineering Department

Environmental Engineering Stream

Evaluation of the Performance of Constructed Wetland System for the Treatment of Brewery Wastewater

kenatu Angassa

June, 2011

Addis Ababa University

Institute of Technology (AAiT)

School of Graduate Studies
Chemical Engineering Department

Evaluation of the Performance of Constructed Wetland System for the Treatment of Brewery Wastewater

A Thesis Submitted to the School of Graduate Studies of Addis Ababa University Institute of Technology in Partial Fulfillment of

Requirements for the Degree of Masters of Science in Chemical

Engineering (Environmental Engineering)

By: Kenatu Angassa Wakuma

Advisor: Dr.Ing Birhanu Assefa

Addis Ababa, Ethiopia

June, 2011

Evaluation of the Performance of Constructed Wetland System for the Treatment of Brewery Wastewater

By

Kenatu Angassa Wakuma

Approved by Board of Examiners:

Name	Signature	Date
________________	_______________	_________________
(Chairman)		
Dr. Ing, Birhanu Assefa	__________________	________________
(Advisor)		
___________________	__________________	_______________
(Internal Examiner)		
___________________	__________________	_________________
(External Examiner)		

DECLARATION

I, the undersigned, declare that this thesis entitled "Evaluation of the Performance of Constructed Wetland System for the Treatment of Brewery Wastewater" is my original work, and it has not been presented in this and any other person for an award of degree in this or other University, all sources of materials used in this thesis work have been duly acknowledged.

Name: Kenatu Angassa Wakuma

Signature: ____________________

Place Addis Ababa, Ethiopia

Date of Submission: June, 2011

This thesis has been submitted for examination with my approval as University Advisor.

Name Dr.Ing Birhanu Assefa

Signature __________________

Acknowledgments

I am ever grateful to God, the Creator and the Guardian, and to whom I owe my very existence, who makes everything to happen for good, for giving me the strength, patience and endurance throughout my graduate study as well as for providing me the opportunity to be a man of academics.

I would like to express my sincere gratitude and appreciation to my research advisor Dr.Ing. Birhanu Assefa, his technical support, guidance, kindness and encouragement starting from title selection, final proposal formulation and proposal implementation throughout this study.

My special gratitude goes to Prof. Sileshi Nemomissa for providing financial support, advice and encouragement from starting my education up to the fulfillment of this research paper. I really appreciate the effort and time he had spent which eventually enabled me to complete my graduate study.

I warmly acknowledge and thank to Prof. Masresha Fetene, Prof. Esermu Kelbessa, Dr.Seyuome Leta, Dr. Tadesse W/mairam the Manger of Environment and Coffee Forest Forum (ECFF) and my brother Benti for their providing financial support to my educational and research work paper.

I also would like to acknowledge St. George Beer Factory for allowing me to use the brewery effluent throughout my research work and to its staffs Ato Esayas, Ato Chala and Ato Kebana, for providing me materials, their comments and suggestions. Next, I am also thankful to JIJE LABOGLASS PLC Laboratory and all the technicians.

Also my sincere appreciation also extends to all my colleagues and others who have provided assistance at various occasions. I would like to thank Fikadu Demboba for his technical support during the research work. My appreciation and special thanks also extends to Mr. Chrisogan Paschal for his valuable advice, technical support as well as his encouragement and contribution to make my study become reality. And also, Special thanks and deepest appreciation goes to Demeke (Ph.D Student) for assisting in editing the research paper. I would like to thank my beloved friend Dejene Tsegaye for his advice and for providing a loving environment for me.

I am also grateful to all my family members. Finally, special thanks and deepest appreciation goes to my Mother Gudi Dugassa, my dearest sisters, Demeshe and Ebsitu for providing financial and giving good environment for me. They always have been behind me with love, support and endless patient.

Abstract

Environmentally friendly way of handling industrial effluents is the most important concept for industries direct and/or indirect contribution of a country's sustainable development. In order to achieve such goals biological processes considered to play the major role. The study to evaluate the treatment performance of horizontal subsurface flow constructed wetland (SSFCW) systems planted with selected emergent wetland plants for the removal of pollutants from brewery wastewater was initiated. For this purpose the treatment plant was fed with raw brewery wastewater collected from St. George Beer Industry of Ethiopia. The constructed wetland for wastewater treatment was operated for six months (August, 18/2010 to February, 20/2011).The four SSFCWs cells packed with gravel media and with HRT of 7 days. One bed was left unplanted and used as a control while each of the remaining beds was planted with *Cana. indica*, *Phragmite. karka* and *Colocasia. gigantea* to each unit. Each set of SSFCW cells had influent parameters such as hydraulic loading rates of 26 L/d with high-strength 4798 mg COD/L and 1714 mg BOD_5/L from brewery wastewater. After six month operation, the laboratory analysis gave a witness that the average removal efficiencies for the planted and unplanted wetlands were as follows: COD (78.9 % and 76.8 %), BOD_5 (74.4% and 70.5%), TN (77.4% and 59.8 %), NH_4-N (62.8% and 58%), NO_3-N (55.2% and 42.5%), TP (68 % and 56.1%), PO_4 (81.4% and 58.4%), sulfate (36.1% and 30.1%), sulfide (97.3% and 93.4%), TSS (61.7% and 50%) ,TDS (54.1% and 45.5%) and EC (27.4% and 30%), respectively. While the amount of DO was increased for planted and unplanted (65.6% and 38.6%) respectively.

Therefore, the influent concentration with the average composition of COD (4798 mg/L), BOD_5 (1714 mg/L), TN (106 mg/L) and TP (83.3 mg/L) has a great effect on pollutant removal efficiency in horizontal subsurface flow constructed wetland systems.

Keywords: *Constructed wetlands, Horizontal subsurface flow, Wetland plants, Treatment Technology, Brewery wastewater.*

List of Tables

List of figures

Lists of Abbreviations

AAWSA	Addis Ababa water and sewage authority
APHA	American public health Association
BGI	Brewery St.Gorgea Industry
BOD	Biological Oxygen Demand
CIP	Cleaning-In-Place
COD	Chemical Oxygen Demand
CW	Constructed Wetland
DO	Dissolved oxygen
EC	Electrical Conductivity
EEPA	Ethiopian Environmental Protection Authority
EPA	Environmental Protection Authority
HLR	Hydraulic loading Rate
HRT	Hydraulic Retention Time
ITRC	Interstate Technology and Regulatory Council
OLR	Organic Loading Rate
SF	Surface Flow
SSFCWs	Sub Surface Flow Constructed Wetlands
TDS	Total dissolved solid
TOC	Total Organic Carbon
TSS	Total suspended solid
UNEP	United Nations Environmental Protection
UNESCO	United Nations Educational, Scientific and Cultural Organization
UNIDO	United Nations Industrial Development Organization.
USEPA	United States Environmental Protection Authority
WHO	World Health Organization

Table of Contents

CHAPTER ONE

1. INTRODUCTION

1.1 Background

In pursuit of a better life, industrialization is growing day by day leaving behind the pollutants in our environment. Environmental pollution is an inevitable consequence of economic development and people's desire to improve their quality of life [1]. Efforts to clean up the environment and keep it clean have been made by government agencies at national, state and local levels by establishing guidance and regulations. One of the primary concerns is water quality. Accelerated water quality change due to industrial pollution is one of the major environmental concerns throughout the world [2].

Similarly, industrial and chemical pollution constitute the major problem in Ethiopia and it is now one of the great environmental concerns in the country. The effects of industrial activities on the environment in the country are becoming evident through the pollution of water bodies and human habitat in the major cities, rivers and lakes. In developing countries like Ethiopia, industrial wastewater has become the most vital problem because of the high growth rate and enormous discharge quantity to the environment. Industrial effluents and domestic sewage contribute large quantities of nutrients and toxic substances that have a number of adverse effects on the water bodies and the biota [2].

It is estimated that 90 percent of wastewater in developing countries is still discharged directly to rivers and streams without any waste processing or treatment. Likewise, in Ethiopia most of the factories have no effluent treatment plants. They directly discharge untreated colored and toxic effluent into the nearby rivers, lakes, and streams. All organic and inorganic chemicals in water are much higher than allowable limits and extremely harmful to aquatic flora and fauna and through food chains to human beings [1]. This wastewater has serious negative impact not only on underground and surface water bodies and land in the surrounding area but also has an adverse effect on the aquatic ecological systems [2].

Breweries for beer production generates wastewater mainly from the following sources: Wheat malt production process where wastewater is from wheat washing water, water-soaked wheat, germination cooling spray water, wheat trough water, condensate wash water. Further, it has been estimated that approximately 3 to 10 liters of wastewaters are generated per liter of beer produced in breweries. The quantity of brewery wastewater also depends on the production and the specific water usage. Other materials make up only a small portion of wastewater, but can be present in large enough quantities that may require some pretreatment or full treatment before discharging into the sewage system [3].

The physical characteristics of brewery wastewater are physical parameters include color, odor, temperature, turbidity. Insoluble contents include total solids (TS), oil and greases [4]. Thus, all parameters, causes pollution of water bodies and the soils in the surrounding environment and create a serious human and ecological health hazards. For instance, the areas in the vicinity of Akaki river excessive industrial discharges have heavily polluted the river and lead to serious health and ecological consequences [5].

In developing countries, low cost and appropriate wastewater treatment technology like constructed wetlands is necessary for sustainable development. In order constructed wetland can be one of the important tools for assimilating pollutants in municipals and industrial wastewater. Therefore, in this thesis the potential of constructed wetland in sought to be investigated.

1.2 Statement of the Problem

The practice of discharging effluent of low quality into the environment causes numerous problems. These industries include breweries in Ethiopia does not meet the national discharge standards. They do not treat their wastewater and discharge to the river loaded wastewater. This practice causes a risk to other water users downstream. For this reason, environmental issues are a critical factor in today's industrial competitiveness [13]. The Ethiopia Environmental Protection Authority (EEPA) is working on address the problem. This include enforce regulation and asking industries to treat their wastewater to meet standard limits and keep the environment.

Brewery plants produce large quantities of highly polluting wastewater rich in organic substances. Generally, the wastewater from a brewery is the combined effluent comprising discharges from various sources of unit operation in the plant. These discharges may include spent grain, yeast, and dripped beer from fillers packaging and washing wastewater. As a result, wastewater is usually characterized by wide variation both in the discharge volume and the strength of pollutants such as biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total solids and pH [3, 4].

Since, untreated brewery wastewater discharged in surface waters can bring about a rapid deterioration of their physical, chemical and biological qualities. Their decomposition depletes the dissolved oxygen in the water that is vital for aquatic life and also release of nitrogenous and phosphorous compounds in the wastewater will stimulate aquatic plant growth contributing to eutrophication of water bodies. Further, due to turbidity and color photosynthesis may be restricted and thereby affecting the primary link in the food chain [14]. Hence, they are target of EPA short term action when it starts enforcement. Moreover, the public images of the industries will unacceptable if they do not act with social and environment.

BGI Ethiopia is one of industries poor environmental performance in managing its wastewater. Introduction of appropriate wastewater treatment is fundamental for maintaining people's health, protecting the quality of the environment and ultimately promoting economic development [10]. Subsurface flow constructed wetland treatment is one of the low cost technology methods. However, there is no data generated on such wastewater. Thus, investigating the suitability of SSFCW for treating the wastewater of industry found to be necessary.

1.3 Objectives of the Study

1.3.1 General Objective

The overall objective of this study is to evaluate the performance of horizontal subsurface flow constructed wetland systems planted with selected emergent wetland plants for the removal of pollutants from brewery wastewater.

1.3.2 Specific Objectives

The specific objectives of this study are:

- To characterize brewery wastewater for selected parameters.
- To evaluate the removal efficiency and performance of horizontal SSFCWs systems for treatment of brewery wastewater for selected parameters such as: BOD_5, COD, TN, NO3-N, NH_4-N, TP, PO_4^{3-}, $SO4^{2-}$, S^{2-}, TSS, TDS, EC, DO, temperature and pH.
- To compare the removal efficiency of horizontal SSFCWs planted with three selected plants: *Canna indica*, *phragmites karka and Colocasia gigantea* for the above parameters.
- To generate baseline data on horizontal SSFCWs for effluent from factories

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Ethiopia Brewery Industry Wastewater Management

Ethiopia's beer industry is currently comprised of five major breweries. The industry at present includes five major breweries, namely Meta Abo, Harar, Bedele, Dashen and BGI Ethiopia [16]. In Ethiopia, most breweries are located in rural areas where they compete for water with crop farming while BGI is at the centre of capital city (Addis Ababa). By far the most dominant brewer is BGI Ethiopia with a market share of around 50 percent nation-wide and even higher in Addis Ababa. Ethiopia's beer industry has seen much activity in recent years including a flow in demand associated with increased urbanization, population growth, and rising incomes.

The effluent discharged by the breweries in the country does not meet the national discharge standards as all of them release their effluent with little or no prior treatment. The practice of discharging effluent of low quality into the environment causes numerous problems. The effluent from rural breweries is used for irrigation purposes in rural area. However, the breweries effluent in urban areas is directly discharged into rivers without any prior treatment. This practice poses a threat to other water users downstream [13].

If we take BGI Ethiopia, wastewater is the subject of this study, its beer production level in year 2010 is around 107.7 thousand hectoliter (hL) and the total water used for the brewing and other purpose was about 7.5 million hL annually. The total volume of water leaving the factory as wastewater and evaporation was about 6.47 million hL. Therefore, daily wastewater discharged from the factory is about 18 thousand hL to nearby river without any treatment [16]. Breweries have a specific consumption of water ranging from 4 to 11 hL water/hL beer with the average water consumption of around 5 to 6 hL water/hL beer. Also water consumption is divided into 2/3 used in the process and 1/3 in the cleaning operations [4]. So, water and wastewater management in breweries remains a critical and practical problem. Therefore, industries that use large amounts of water for processing have the potential to pollute water catchments such through the discharge of their waste into streams and rivers.

2.2 Nature of Brewery Wastewater and Environmental Concerns

In Ethiopia the establishments of many industries were only based on their economic benefits to the society as well as to the country. Many of the industries are concentrated in Addis Ababa and the establishment of these industries did not consider their potential harm on the environment. As result most of the rivers found around these industries indicate high organic pollution load and higher level of toxic substances than the acceptable level for human health. Like other sectors of industries, breweries in Ethiopia have also got attention in terms of their pollution contribution to the environment [18].

Wastewater quality may be defined by its physical and chemical factors. The physical characteristic of wastewater parameters including color, odor, temperature, turbidity and insoluble contents such as total solids (TS), total dissolved solid (TDS), oil and greases. Chemical parameters include organic content of wastewater such as total organic carbon (TOC), and total oxygen demand [19]. Organic materials will mainly leave the brewery as beer, by-products and wastewater. The potential largest organic matter discharging processes are: brewers grains, yeast and surplus yeast, trub, weak wort discharge, emptying of and rinsing water from kettles, emptying of process tanks, pre- and after-runs from kieselguhr filtration and filling, follow water from process pipes, rejected beer in the packaging area, returned beer, breakage of bottles in the packaging area, ancillary materials used in packaging area e.g. adjective for bottle washer, conveyor lubrication and label glue.

Suspended solids in the wastewater originate from the discharge of byproducts, kieselguhr and possible label pulp from the bottle washer. Nitrogen in the wastewater originates from discharge of yeast and cleaning agents e.g. nitric acid that can be a part of the detergents used for tank cleaning. Phosphorus in the wastewater originates mainly from the detergents used for tank cleaning. The usage of acids and caustic soda for the cleaning of process equipment and reuse bottles results in large variation of the pH in the wastewater. The main sources for discharge of acid and caustics are water treatment plant, CIP plant and brew house, acid and caustic storage tanks [3]. Untreated brewery effluents typically contain suspended solids (200-1000 mg/l), biochemical oxygen demand (BOD) (1,200–3,600 mg/l), chemical oxygen demand (COD) (2,000 – 6,000 mg/l), nitrogen (N) (25 – 80 mg/l), phosphorus (P) (10 – 50 mg/l), temperature in the range of 18-40 ^{0}C and between 3-12 for pH value [24]. And also contains total dissolved solid (761-2500mg/l), nitrate (NO_3-N) (13-36mg/l), ammonium ion (NH_4-N) (12.2-54.2mg/l) orthophosphate (PO_4) (31.9-121.2mg/l) Electric conductivity (EC) or ionic strength (1731-3260 μS/cm) [18].

Because the problems facing the environment are vast and diverse, environmentalists have expressed concerns about issues such as global warming, depletion of the Ozone layer, population growth, air pollution and water pollution. Thus, water pollution is a serious problem globally involving the discharge of dissolved or suspended substances into groundwater, streams, rivers and oceans. Major sources of pollutions in developing countries are industrial activities and these have gradually increased the problem of waste disposal. Discharging of wastewater to open grounds or into nearby water bodies results in significant impacts on the water and surrounding environment. Excessive release of nutrients nitrogen and phosphorus to a water body can lead eutrophication, which can in turn encourage the overgrowth of weeds, algae, and cyanobacteria (blue-green algae). This may cause an algal bloom, a rapid growth in the population of algae. The decomposition of the algae by bacteria depletes so much amount of oxygen in the water that most or all of the animals die, which creates more organic matter for the bacteria to decompose [21].

In addition eutrophication causes deoxygenation and some algal species produce toxins that contaminate drinking water supplies [14]. Nitrate and nitrite nitrogen constitute a public health concern, primarily related to methemoglobinemia and carcinogenesis [9]. Ammonia nitrogen may deplete dissolved oxygen in natural waters by way of microbial nitrification reactions. Therefore, it is important to note that when evaluating the performance of wetlands relative to nitrogen, both total nitrogen and the species of nitrogen are important [22]. Consequently, there is a direct need to control the pollution of surface and ground water since the public health and well being of the people have a direct link with the availability of adequate quantity of good quality water.

2.3 The Sources of Wastewater in Brewery Industry

High consumption of good-quality water is a characteristic of beer brewing. More than 90 percent of beer is water and an efficient brewery will use 3.5L of water to produce 1L of beer. Also breweries use water for heating and cooling, cleaning equipments, cleaning vehicles, and sanitary water [4]. During beer production process, wastewater main sources are wheat malt production process water, water-soaked wheat, germination cooling spray of water, wheat trough of water, condensate wash water, saccharification process, filter wash water, the fermentation tank cleaning, filter washing water, canning process of cleaning, sterilization, and broken bottles of beer, cooling water and the finished product workshop washing water, and representatives from the office, cafeteria and bathroom domestic sewage [3].

2.3.1 Brewery Process Description

The raw materials for beer generally include barley malt, adjuncts, hops, water and yeast. Production methods will differ from brewery to brewery as well as according to beer types, brewery equipment and national legislation. The main processes are the same: Wort production, Fermentation and Packaging [3].

Wort production process: Milling of the malt and preliminary treatment of the adjuncts are mixed with brewing water to form a mash. Adjuncts are a supplementary carbohydrate supply added as sucrose or glucose. The mash is heated following a pre-set time-temperature and extracted [4]. The solution of the extract and water is called the “wort”. When the mashing is completed the insoluble solids called the “brewers grains” are separated from the wort by straining. The wort is boiled with hops and then finished wort is cooled to 8-20°C depending on the yeast and the fermentation process chosen. The cooled wort is hereafter transferred to the fermentation area [3].

Fermentation Processes: Fermentation can be preceded by separation of the cold break consisting mainly of protein formed during cooling of the wort. This separation is performed by wort sedimentation in kettles, flotation, centrifugation or filtration. Then yeast is added to the cold wort and aerated to support development of the yeast. The yeast metabolizes the fermentable carbohydrates in the wort forming alcohol and carbon dioxide and decomposes certain undesirable constituents of the green beer [4]. Kieselguhr is used as filtration aid in filtering yeast cells contained in the beer and other substances causing turbidity and any bacteria that might cause the beer to spoil. In order to achieve the finished product specification for CO_2, the beer is carbonated before being sent to the bright beer tanks. It is important that all process equipment and pipes are kept clean and disinfected. Cleanness is done by means of CIP plants (Cleaning-In Place) where cleaning agents are circulated through the equipment or spread over the internal surface of the tanks [3].

Pasteurization and Packing Processes: From the bright beer tanks the beer is pumped to the packaging area where it is bottled or canned. In addition to the packaging lines and reuse bottles require systematic cleaning. Since the bottle washer consumes large quantities of energy, water and caustic, large quantities of wastewater are discharged. The use of non-returnable packaging material reduces the consumption of energy, water and caustic, therefore reducing wastewater generation [3].

In general, the amount of wastewater produced is related to the specific water consumption with the exception of the water which is contained in the beer itself and evaporated, every drop of water ends up as wastewater [23, 24]. A simplified water balance of the water used within a brewery is shown in Fig. 2.1 whereby the water either becomes part of the beer, part of the effluent or is evaporated. The actual discharge limits for breweries might vary for each location, region and country. The Ethiopian Environmental Protection Authority sets provisional limit for the pollutants that brewery wastewater should contains when discharged to surface waters [25]. Therefore, in order to achieve this allowable brewery wastewater discharge limits appropriate, cost-effective as well as environmentally friendly wastewater treatment method is required.

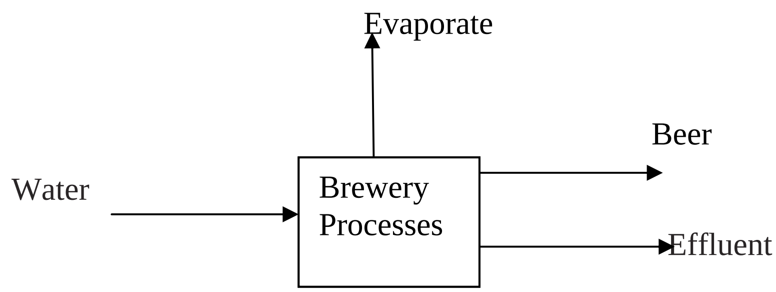

Figure 2.1 Typical water balances within a brewery [25].

2.4 Brewery Wastewater Treatment Technology

A number of pollution related studies have confirmed that about 90% of industries including breweries in Addis Ababa are simply discharging their effluent into nearby water bodies, streams and open land without any form of treatment [26]. Basically wastewater treatment technologies can be divided into three categories which are physical, chemical and biological wastewater treatment processes [18]. For almost all combinations of requirements in terms of effluent quality, land availability, construction and running costs, mechanization level and operational simplicity there will be one or more suitable treatment processes [27]. The selections of specific unit processes depend not only on the nature of wastewater, including degradability and treatability by selected processes, but also on discharge requirements. Other important factors are environmental impact, land availability, projected life of plant design and cost [28, 29].

2.4.1 Physical Wastewater Treatment Technology

Physical treatment processes are operations used for the treatment of wastewater in which change is brought about by means of or through the applications of physical forces. The physical units most commonly used in wastewater treatment include screening, grit removal, mixing and flocculation, sedimentation, clarification, aeration, and volatilization and stripping of volatile organic compounds (VOCs). These processes are mostly used at pre-treatment stage [19].

2.4.2 Chemical Wastewater Treatment Technology

Chemical treatment processes are the processes used for the treatment of wastewater in which change is brought about by means of or through chemical reactions. The principal chemical processes used for wastewater treatment include chemical coagulation, precipitation, disinfection and oxidation, ion exchange and others. This type of treatment mainly relies on addition of chemicals and is applied when the wastewater cannot be treated biologically [30]. A significant disadvantage of this treatment process is additive processes involve. As a result there is a net increase in the dissolved constituent and secondary pollutants in the wastewater. Besides that another disadvantage of chemical treatment process is that the cost of most chemicals is related to the cost of energy [12].

2.4.3 Biological Wastewater Treatment Technology

Biological treatment is the most appropriate industrial wastewater treatment technology. Organic components in brewery effluent are generally easily biodegradable as these mainly consist of sugars, soluble starch, ethanol, volatile fatty acids, etc [24]. The effluent has a low content of non-biodegradable components. Brewery wastewater normally has a COD: BOD ratio of 1.5 to 1.7 indicating that the wastewater is easily degradable [3]. The objective of biological wastewater treatment processes is to remove or reduce the concentration of organic and inorganic compounds. The principal process used for the biological treatment of wastewater can be classified with respect to their metabolic function as aerobic and anaerobic [28].

Aerobic Wastewater Treatment process: Aerobic treatment is a process with the presence/supply of air/oxygen. The overall basic reactions during aerobic treatment can be summarized as:-

Organic matter + $O_2 \rightarrow CO_2 + H_2O$ + Aerobic Biomass

Organic matter which is fed to an aerobic biological treatment plant maybe exposed to oxidation to carbon dioxide and different nutrients (in the form of N, P and S), assimilation in biomass (sludge), unchanged passage for biologically non degradable matter, and finally conversion into other organic matter. Furthermore, since it is an oxidative biological reaction, large amounts of biomass are produced which settle as sludge which requires further disposal. The aerobic treatment of brewery effluent requires a comparatively large energy input compared to anaerobic treatment [31]. In contrast to the anaerobic process, this process is quite fast which means that bacteria are able to make better use of the substrate and can create biomass more readily [24, 30].

Anaerobic Wastewater Treatment Process: Anaerobic treatment of wastewater is a process that takes place in the absence of electron acceptor. The overall basic reactions during anaerobic system can be summarized as: -

$$\text{Organic matter} \rightarrow CH_4 + CO_2 + \text{Anaerobic Biomass}$$

This process is characterized by biological conversion of organic compound into biogas (methane 70-85 % and carbon dioxide 15-30 % with traces of hydrogen sulphide) [27]. Furthermore, the process is known for its less energy consumption as well as smaller sludge generation [24]. The main advantages of anaerobic treatment are the very high loading rates that can be applied (10 to 20 times as high as in conventional activated sludge treatment) and the very low operating costs. Anaerobic treatment often is very cost-effective in reducing discharge taxes combined with the production of reusable energy in the form of biogas [32].

Constructed Wetlands: Constructed wetland is a imitate of natural wetland and ecological system that combines physical, chemical and biological treatment mechanisms, in removing pollutants from wastewater as it flow through the wetland [34]. Constructed wetlands offer all of the treatment capabilities of the natural wetlands but without the limitation associated with discharging to a natural ecosystem. Additionally, the constructed wetland treatment units are not restricted to the special requirements on influent quality. They can ensure much more reliable control over the hydraulic regime in the system and therefore perform more reliably than the natural wetlands [33]. Constructed wetlands represent an emerging eco-technological treatment system, which are designed to overcome the disadvantages of natural wetlands. It is man-made systems that involve altering the existing land to simulate wetlands conditions. It has developed in popularity for wastewater treatment since the early 1980s [35].

2.5 Treatment of Brewery Wastewater using Constructed Wetlands

For developing countries like Ethiopia, that has limited resources for the construction and operation of convectional treatment plant, there should be an option which is economical but produce an effluent with the same or even better quality from that of conventional treatment system [6]. This necessities the provision of energy and cost effective secondary wastewater facilities for small communities such as schools, hospitals, military camps, colleges, farms, industries and universities where onsite wastewater disposal technology is predominant [34].

A constructed wetland system has selected that advantage. Thus, it may be investigated for brewery wastewater treatment. Constructed wetlands are a cost-effective and technically feasible approach to the treatment of wastewater for several reasons: Wetlands can often be less expensive to build than other treatment options, operation and maintenance expenses (energy and supplies) are low, wetlands are able to tolerate high fluctuations in flow and wetlands are able to treat wastewaters with very different constituents and concentration. In addition, the use of constructed wetlands is now recognized as an accepted eco-technology, especially beneficial to small towns or industries that cannot afford expensive conventional treatment systems. This system seems to have the potential to be one of solutions in discharging the huge amount of wastes and getting access to safe drinking water [36].

Constructed wetlands are engineered systems that have been designed and constructed to utilize the natural processes involving wetland vegetation, soils (substrates), and the associated microbial assemblages to assist in treating wastewaters. They are designed to take advantage of many of the same processes that occur in natural wetlands, but do so within a more controlled environment. Engineered wetlands, as other kinds of wastewater treatment plant, may also consist of a series of treatment steps that have been built according to the expected flow and loading rates. In general, the heavier the load a system receives, the larger the wetlands system will need to be to effectively remove contaminants [33]. A better understanding of the benefit that wetlands provide has led to the use of constructed wetlands to mimic the filtration process that takes place in the fragile ecosystem of a natural wetland. Also constructed wetland are planned systems, designed and constructed to employ wetland vegetation to assist in treating wastewater in a more controlled environment than occurs in natural wetland [11]. Constructed wetlands can be built with a much greater degree of control, thus allowing the establishment of experimental treatment facilities with a well-defined composition of substrate, type of vegetation and flow pattern.

In addition, constructed wetlands offer several additional advantages compares to natural wetlands including site selection, flexibility in sizing and most importantly, control over the hydraulic pathways and retention time. In such systems, water goes through a series of purification process, which includes biological degradation, filtration, sedimentation and adsorption resulting in the significant reduction of organic compounds, suspended solids and also to some extent nitrogen compounds, phosphorous and pathogens [12].

2.5.1 Treatment Mechanisms in Constructed Wetlands

In the natural environment, physical, chemical, and biological processes occur when water, soils, plants, microorganisms and atmosphere interact. These processes are sedimentation, filtration, gas transfer, adsorption, ion exchange, chemical precipitation, chemical oxidation and reduction, and biological conversions plus other unique processes such as photosynthesis, photo-oxidation and aquatic plant uptake. Generally, a natural system might typically include pumps and piping for wastewater conveyance but would not depend on external energy sources exclusively to maintain the major treatment responses [33].

Factors affect CWs are climate, type of vegetation, effects of the local environment, operating strategies. Among these factors, the type of macrophyte and loading rate are the only items controlled by the designer [37]. The basic design considerations for CWs are site selection, plants types, physical facilities, hydrologic factors, organic loading factors, and performance expectations [33]. In order that the design and operational characteristics of wetland treatment systems are satisfactorily specified, it is necessary to have an understanding of the basic pollution removal mechanisms. Various processes of wetlands are improving water quality are summarized in table 2.1. Due to the complex interactions between the physical and biochemical processes which occur in wetland systems, these removal mechanisms are not independent.

Table 2.1: Wastewater Treatment Processes Occurring in Constructed Wetlands

Physical	Sedimentation of denser particle fractions
	Filtration of lighter particle fractions by macrophytes and biofilms
	Aggregation of particles leading to removal by either sedimentation or filtration
	Exposure of influent to UV radiation via sunlight
Chemical	Precipitation
	Adsorption onto wetland substratum and detritus
	Volatilisation
Biological	Microbial decomposition and mineralisation of organic material
	Microbial nutrient transformation (nitrification/denitrification)
	Direct biological uptake from the water column (algal and bacterial biofilms)
	Indirect biological uptake from within the root-zone (benthic biofilms and emergent aquatic macrophytes)
	Microbial competition resulting in the die-off of pathogens
	Direct animal grazing of influent organic material (including pathogens)

Sources: [45].

A constructed wetland has been traditionally thought to provide a combined aerobic and anaerobic environment [10]. The anaerobic zone surrounds the root zone and at the same time provides a mini-aerobic zone surrounding the root hairs formed by the oxygen passed down from the stems and/or leaves of the aquatic vegetation and contributing to the degradation of oxygen-consuming substances and to nitrification. Ammonia is also oxidized into nitrate by nitrifying bacteria in aerobic zones with denitrification converting nitrate to free nitrogen or nitrous oxide in the anaerobic bottom layers and substrate by denitrifying bacteria [22]. Solids, settle able organics and solid associated pollutants such as bacteria, metals and oils are very effectively removed by the physical filtration offered by the vegetation which imposes a considerable hydraulic resistance to the incoming flow [34].

Macrophytes and photosynthetic micro-organisms also improve overall water quality by producing oxygen during photosynthesis which diffuses into the water column. Macrophytes transport oxygen down their stems into the roots where it diffuses into the sediment to produce an aerobic microenvironment around the root zone (rhizosphere) [38]. Diffusion of oxygen from the roots of macrophytes maintains an oxidized sediment surface layer and microenvironment around the root zone. This modifies the sediment redox conditions facilitating aerobic microbial processes including nitrification. In gravel bed wetland systems, solids accumulation and associated biofilm development can delay influent contact with both the macrophyte roots and the underlying media especially adjacent to the inlet where most sedimentation occurs [39]. Efficient inlet distribution and carefully selected washed gravel media sizes can help to improve this problem [40].

Adsorption processes are therefore enhanced by increasing the contact of the surface runoff with the wetland mineral substrates and with the vegetative surfaces and plant detritus which provide large surface areas for adsorption. In addition, high retention times, shallow water depths and an even distribution of influent will further enhance the interactions of the wastewater with substrate and plant surfaces thereby increasing the adsorption potential [10]. A dense vegetation cover can also be very effective at removing gross solids, litter and floatable material from the incoming influent flows [41]. The removal mechanisms of pollutant in constructed wetlands is summarised in Table 2.2.

Table 2.2 Overview of pollutant removal processes

pollutant	Removal process
Organic material (BOD)	Biological degradation, sedimentation, microbial up take
Suspended solids	Sedimentation and filtiration
nitrogen	Sedimentation,filtiration,nitrification/denitrification,microbial uptake, volatilization, plant uptake
phosphorus	Sedimentation, filtiration, adsorption microbial and plant uptake
phathogens	Natural die off, Sedimentation, filtiration, adsorption
Heavy metals	Sedimentation, adsorption, plant uptake

Source: [46].

2.5.2 Hydrology of Constructed Wetlands

The hydrology of constructed wetlands is the most important factor in their effectiveness. Hydrologic considerations include climate, hydroperiod, hydraulic residence time, hydraulic loading rate, groundwater exchanges (infiltration and exfiltration), losses to the atmosphere (evapotranspiration) and overall water balance [33]. The hydroperiod is a result of the balance of inflow, outflow and storage in the system and depends further on seasonal differences in precipitation and evapotranspiration. Evapotransporation (ET) decreases the hydraulic loading and will not contribute to surfacing. Precipitation dilutes pollutants in the system, temporarily raises the water level and decreases the HRT while ET concentrates pollutants, temporarily lowers the water level and increases the HRT. The overall water balance for a constructed wetland is an account of the inflow, storage and outflow of water.

During design and operation, the wetland water balance is important for determining conformance with desired limits for HLR, HRT and mass balances. A simple water balance equation for a constructed wetland is expressed as equation 2.1 [38].

$$[dV/dt] = Q_i - Q_o + P + I - ET \quad (2.1)$$

Where, Q_i = influent wastewater flow, m^3/d

Q_o = effluent wastewater flow, m^3/d

P = precipitate precipitation, m^3/d

I = net infiltration (infiltration less exfiltration)

ET = evapotranspiration, m^3/d

V = volume of water, m^3 and

t = time, d.

The hydraulic residence time (HRT) is defined as the average residence time during which the water remains within the wetland system. In subsurface flow systems, the "reactive" volume is defined as the volume of water in the media in consideration of the void fraction that is defined as the fraction of the total media volume through which water can flow. The void fraction, also termed media porosity, ranges usually from 0.3 - 0.45 depending on the media material chosen [7]. If short circuiting occurs, the actual HRT can be less than the theoretical one which can result in lower removal efficiencies. To meet advanced treatment standards in surface flow as well as in subsurface flow wetlands, the HRT should be at least 5 days. A hydraulic retention time of at least 6 to 8 days recommended ensuring an adequate nitrification rate [42]. It can be calculated from equation 2.2.

$$HRT = LWnd/Q_{av} \quad (2.2)$$

Where, L = length of wetland (m)

W = width of wetland (m)

n = media porosity

d = water depth (m)

HRT = hydraulic retention time (day)

Q_{av} = average flow rate (m^3/d)

The hydraulic loading rate (HLR) refers to the loading on a water volume per unit area over a specified time interval. It is defined as the volumetric averaged flow rate divided by the wetland surface area. Typically, hydraulic loading rates are specified in [cm/d] or [mm/d]. It depends on media material, which is a critical parameter for subsurface flow wetlands, flow rate, area-size and the resulting hydraulic residence time. A hydraulic loading rate of $0.2m^3/m^2/day$ provides for maximum treatment efficiency [8]. Because high organic loading will cause anaerobic conditions, and plants die off. Therefore, the maximum organic loading rate for both type of systems (SF and SSF) should not exceed (1.12 mg $BOD_5/cm^2.d$) [33]. Hydraulic loading rate (HLR) is calculated from equation (2.3).

$$HLR = Q_{av}/As \quad (2.3)$$

Where, Q_{av} = average flow rate (m^3/d)

A_s = surface area of wetland (m^2)

2.5.3 Wetland Plants

The basis for employing constructed wetlands for wastewater treatment is the ability of plants to transfer oxygen to their roots, and the surrounding wastewater environment. Frequently used macrophytes species are cattails (Typha sp.), reeds (Phragmites sp.), bulrushes (Scirpus sp.), and rush (*Juncus* spp.). The general requirements of plants suitable for use in constructed wetland wastewater treatment systems include: Ecological acceptability, tolerance of local climatic conditions, tolerance of pollutants loading, ready propagation and rapid establishment, rapid growth and high pollutant removal capacity [41]. When selecting plants for constructed wetlands, the main factors to be considered are their pH, temperature and organic loading tolerances.

A study conducted by [52], SSFCWs planted with C.indica and C.gigantea for the treatment of dormitory wastewater with concentration range for BOD (155-286 mg/l) and TSS (155-330 mg/l) showed the treatment performance of a SSF constructed wetland the removal efficiency of 97.2% and 99%, respectively. As study by [54], SSFCW planted with *P.karka* for treatment of tannery wastewater with concentration range for COD (2202-8100mg/l) and BOD_5 (572-1950mg/l) showed removal efficiencies of 80.9% COD and 77% BOD_5, 61% TN, 53% NO_3, 82.5% NH_4-N.

Study conducted by [15], the average treatment performance of HSSFCWs for domestic wastewater in India with *phragmite karka* showed that 77.8% for COD, 65.7% for BOD, 79% for TSS and 71.2% for TDS. However, there is no studies investigate on using these plants for the treatment of brewery wastewater which has high strength of concentration. So, the study be consider the tolerance and treatment performance of the wetland plants for brewery wastewater which ranges COD (2206 – 9686mg/l), BOD (1300-2215mg/l), TN (97-125 mg/l) and TP (74-90 mg/l). The three wetland plants' characteristic is summarized in the Tables 2.3, 2.4 and 2.5.

Tables 2.3 Characteristics *Canna indica*

Characteristic	**Description**
Family	Cannaceae
Local Name	Canna, Indian shot, "Set Akuri"
Origin	Brazil
Brief description	All varieties love rock media systems but will not grow in standing open water. All varieties produce wonderful color in the landscape from spring to late summer. Succulent stalks and leaves. Roots with well developed tuberous rhizomes [52].

Table 2.4: Characteristics of *Phragmites karka*

Characteristic	Description
Family	*Poaceae (Arundineae).*
Local Name	"Shembeko"
Origin	India
Brief description	They are robust perennial which forms an extensive creeping woody rhizomes, stems /culms 2-8m high, very tubby often woody and a bamboo like. It grows in marshy or seasonally flooded alluvial soils along river banks; widely distributed in many regions of Ethiopia, Tropical Africa, Tropical Asia and other parts of the world. [54].

Table 2.5: Characteristics of *Colocasia gigantean*

Characteristic	**Description**
Family	Araceae
Local Name	"Godare"
Origin	South-eastern Asia
Brief description	Up to 275cm high; each leaf can reach 150cm long; ample water; protect from strong winds, part sun to sun exposure. Make an attractive contribution to the landscape, no doubt. Have an enhanced thick tap root system [52].

Wetlands plants are the principal component of a wetland system [44]. In addition, wetland plants can assimilate pollutants in their tissue; provide a surface and an environment for microorganisms to grow. The growth of roots within aggregates helps to decompose organic matter and prevents clogging by creating channels for the water to pass through the system. In general the role of vegetation in Constructed Wetlands is summarized in table 2.6.

Table 2.6: Roles of Vegetations in Constructed Wetlands

Macrophyte part	Role in treatment process
Aerial plant tissue	-Light attenuation: reduce growth of phytoplankton - Reduce wind velocity: reduces risk of resuspension - Aesthetically pleasing appearance of system - Storage of nutrients
Roots and rhizomes in the sediment	- Filtering effect: filter out large debris - Reduce current velocity: increases rate of sedimentation, reduces risk of resuspension - Provide surface for attached biofilms, bacteria and other micro organisms - Stabilizing the sediment surface: less erosion - Prevents the medium from clogging - Release of oxygen increase aerobic degradation and nitrification - Uptake of nutrients -Release of antibiotics

Source: [44]

2.5.4 Types of Constructed Wetlands

Constructed wetlands can be classified based on different criteria. These include their dominating macrophyte, size and according to their flow type [7].

- Based on dominating macrophyte CWs can be classified into three types and shown in Fig. 2.2.
  - ☞ Free-floating macrophyte-based system
  - ☞ submerged macrophyte-based system,
  - ☞ rooted emergent macrophyte-based system
- According to [39] experimental wetlands can be classified by their size (surface area) in to:
  - ☞ Microcosms CW whose surface areas are less than $0.5m^2$ (columns, buckets)
  - ☞ Mesocosms CW with sizes ranging from 0.51 up to $5m^2$
  - ☞ Pilot scale and full size CW with surface areas greater than 5 m^2
- According to flow type two basic types of constructed wetland treatment systems and shown in Fig. 2.3 and 2.4.
  - ☞ Surface Flow constructed wetlands (SFCW)
  - ☞ Subsurface Flow constructed wetlands (SSF)

Surface Flow Constructed Wetland (SFCW): It is densely vegetated by a variety of plant species and typically has water depths less than 0.4 m with water flowing above the surface. The typical hydraulic loading rates are between 0.7 and 5.0 cm/d in (SF) wetlands [38]. In SFCW, the near surface layer is aerobic while the deeper waters and substrate are usually anaerobic. Surface flow systems require more land, but generally are easier to design, construct and maintain. These systems provide habitat and public access [47]. The advantages of SFCWs are that their capital and operating costs are low, and that their construction, operation, and maintenance are simple. But the main disadvantage of FWS systems is that they generally require a larger land area than other systems. Fig. 2.3 provides a schematic flow diagram of surface flow wetlands [33].

Subsurface Flow Constructed Wetland (SSFCW): It uses a bed of gravel as a substrate for the growth of rooted emergent wetland plants. The bed depth in SSF wetlands is typically between 0.3 and 1.0 m with water under the surface and as shown in Fig. 2.4. The typical hydraulic loading rates in SSF wetlands range from 2 to 20 cm d^{-1}. Subsurface flow systems consist of an underground flow of wastewater through some kind of substrate such as gravel. These systems demonstrate higher rates of contaminant removal than surface flow wetlands. The earth provides insulation for subsurface flow wetlands in cold climates. Subsurface flow systems limit human and animal exposure, and do not provide habitat for birds [51].

Depending on the direction of flow of applied wastewater, SSF wetlands can be either horizontal flow type or vertical flow type. In horizontal SSF systems the substrate is maintained water-saturated through continuous application of wastewater. The bed depth of horizontal SSF wetlands is typically less than 0.6 m and the bottom of the bed is sloped to minimize flow above the surface. Because of the hydraulic constraints imposed by the substrate, SSF wetlands are best suited to wastewaters with relatively low solids concentrations and under relatively uniform flow conditions. It has been claimed that the porous medium provides greater surface area for treatment contact than is found in SF wetlands, so that the treatment responses should be faster for SSF wetlands which can, therefore, be smaller than a SF system designed for the same volume of wastewater.

SSFCW systems have several advantages over the surface flow CW. These include: greater ability to treat high organic loads, higher colder weather tolerance, greater treatment per unit area of land when compared with SFCW, SSFCWs the filter media provides greater available surface area for wastewater treatment than the free water phase, since there is no body of open water, reduction of odors and insects (especially; breeding mosquitoes), reduction of the risk of exposure of persons and animals to hazardous substances and microbial pathogens. Thus, it is not a public safety problem. Low operating costs and low level of operator training required and aesthetically pleasing [52].

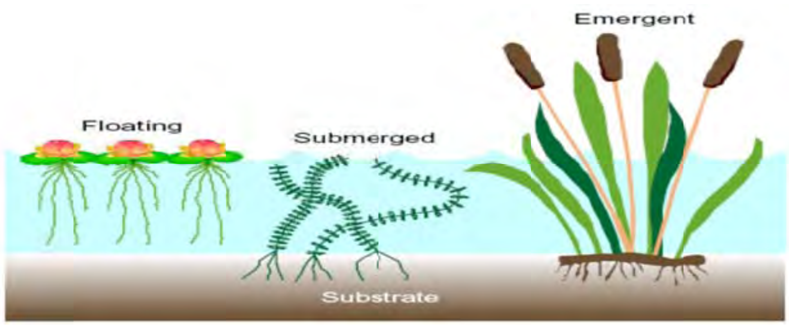

Figure 2.2 Types of Wetland Plants

Figure 2.3 Surface Flow Constructed Wetland

Figure 2.4 Subsurface Flow Constructed Wetland

The cost constructions of SSFCW systems are more expensive, on a unit basis than SFCW systems. Moreover, SSFCWs may be more difficult to regulate than SFCWs, and thus, maintenance and repair costs are generally higher than for SFCWs. A number of systems have had problems with clogging and accidental surface flows. The major problem is associated when compared with SFCWs [52]. However, the advantage outweigh when aesthetic value is given preference. The clogging problems can be managed by introducing appropriate pre -treatment and improved design and operation of SSFCWs.

2.5.5 Structural and Functional element of SSFCW

The media of a SSFCW system perform several functions; they are rooting material for vegetation, help to evenly distribute/collect flow at the inlet/outlet, provide surface area for microbial growth, and filter and trap particles. For successful plant establishment, the uppermost layer of media should be conducive to root growth. A variety of media sizes and materials have been tried, but there is no clear evidence that points to a single size or type of media. The media in the inlet and outlet zones was used, sizes between 40mm and 80 mm in diameter to minimize clogging and was extend from the top to the bottom of the system. Therefore, it is recommended that the average diameter of the treatment zone media be between 20mm and 30 mm in diameter as a compromise between the potential for clogging and ease of handling. These media with 20 and 30 mm in diameter have porosity and hydraulic conductivity of 0.35-0.38 (35%-38%) and 100,000m/d respectively.

Hydraulic Conductivity (K) is the rate at which soil or substrate can transmit water. For an operating SSFCW, K varies with time and location within the media and it has a major impact on the head loss. Clogging of wetland media decreases the hydraulic conductivity, resulting in the surface flow of wastewater. This would negatively affect the overall treatment performance as well as its operation lifetime.

Estimating the elevation of the water surface throughout the SSFCW helps to ensure that surfacing of the wastewater does not occur. As in all gravity flow systems, the water level in a SSFCW system is controlled by the outlet elevation in Fig. 2.5 and the hydraulic gradient or slope, which is the drop in the water level (head-loss) over the length from the inlet to the outlet [38].

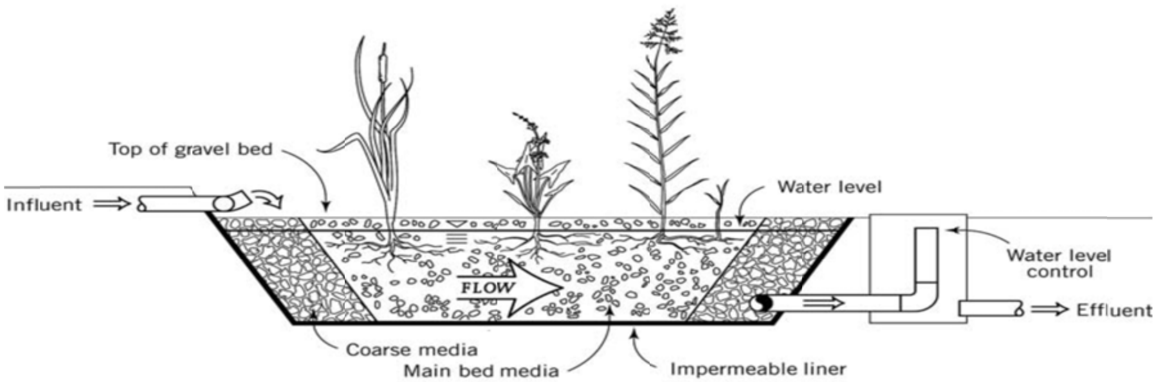

Figure 2.5 Cross-sectional View of a Typical SSFCW

The relationship between flow through a porous media and the hydraulic gradient is typically described by the general form of Darcy's Law Equation 2.4 and 2.5. To be able to use Darcy's Law, a few assumptions need to be made, the flow through the porous media assumed uniform and laminar flow [22].

$$Q = K A_c (dh/dL) \quad (2.4)$$

Or, for a defined length of the SSFCW,

$$dh = Q L / K A_c \quad (2.5)$$

Where, Q= flow rate, m^3/d

K = hydraulic conductivity, m^3/m^2d^{-1} or m/d

A_c = cross-sectional area normal to wastewater flow, m^2

$A_C = (W)(D_w)$

W = width of SSFCW, m

D_w = water depth, m

L = length of SSFCW, m

dh = head loss (change in water level) due to flow resistance, m

dh/dL = hydraulic gradient, m/m

The piping of the system used was inlet distribution and outlet collection pipes. Inlet distribution pipes were pipes delivering the wastewater into the system. These pipes were designed to minimize the potential for short-circuiting and clogging in the media, and maximize even flow distribution. This can be taken as the most important part of the system as it determines the amount of wastewater to be fed into the system which in turn affects the HRT and the overall treatment or removal efficiency of the whole system. A weir made of slotted pipe extending across each CW then received the wastewater from the inlet pipe and distributed it all over the width of the CW. The outlet piping was designed to minimize the potential for short-circuiting, to maximize even flow collection, and to allow the operator to vary the operating water level and drain the bed. The collection header is designed with the same hydraulic principles used for inlet distribution piping.

The depth of media selected was depending on the design intentions for the system in which vegetation was considered as a major oxygen source for nitrification in the system, then the depth of the bed chosen was not exceed the potential root penetration depth for the plant species to be used. Typical average media depths in SSFCW systems have ranged from 0.3 to 0.7 m. The overall width of a treatment system using SSFCW is defined by Darcy's Law, Equation 2.4 which is a function of the flow rate, ALR, water depth and hydraulic conductivity. The width of an individual SSFCW was set by the ability of the inlet and outlet structures to uniformly distribute and collect the flow without inducing short-circuiting.

Theoretically, the bottom slope should match the slope of the water level to maintain a uniform water depth throughout the SSF. No research has been done to determine an optimum slope, but a slope of 1/2 to 1% is recommended for ease of construction and proper draining. The aspect ratio (L: W) of the wetland bed is a very important consideration in the hydraulic design of SSFCW systems, since the maximum potential hydraulic gradient is related to the available depth of the bed divided by the length of the flow path. The aspect ratio the recommended value is between 0.25:1 and 4:1 [38].

2.6 Performance Expectation of SSFCWs

The pollutant removal performance of SSF systems depends on many factors including influent wastewater quality, hydraulic pollutant loading, climate, and the physical characteristics of the system [47]. Constructed wetland systems can significantly remove the biochemical oxygen demand (BOD), total suspended solids (TSS), nitrogen and phosphorus, as well as metals, trace organics and pathogens [48]. SSFCW systems are effective for TSS and BOD removal because of relatively low flow velocities and a high amount of media surface area [49]. The performance of many well known constructed wetlands in terms of BOD_5, TSS, nitrogen, sulfur and total phosphorus are discussed in the following sections [50].

Chemical Oxygen Demand: COD is defined as the quantity of specified oxidant that reacts with the sample under control conditions. It often measured as a rapid indicator of organic pollutant in water and wastewater.

Biochemical oxygen demand: BOD is a measure of the quantity of organic compounds in the wastewater that tie up oxygen. BOD_5 is removed by the microbial growth on the media and the plant roots. BOD_5 is the basis for determining the area of wetland required using a first order plug flow model. Removal of BOD_5 is expressed by Equation (2.6). This is also a first order equation and the hydraulic residence time, t, can be determined from equation (2.7) .Then combining these two equations (2.6 and 2.7) and rearranged give equation (2.8) to calculate the area required for the subsurface flow system [33].

$$Ce/Co = e^{(-k_T t)} \qquad (2.6)$$

$$t = And /Q \qquad (2.7)$$

$$A = Q\,[\ln(Co/Ce)] / KT\ d\ n \qquad (2.8)$$

Where, C_e = Effluent BOD_5 (mg/L)

C_o = Influent BOD_5 (mg/L)

$K_T = K_{20}(1.06)^{(T-20)}$ = Temperature dependent rate constant (d^{-1})

K_{20} = Rate constant at 20^o C = 1.04 d^{-1}

t = Hydraulic residence time (d)

T = Temperature of liquid in the system (^oC)

n = the porosity of the media as a fraction

A = the area of the bed (m^2)

d = Average depth of water in bed (m)

Q = Average flow rate (m^3/d)

The removal of BOD appears to be faster and somewhat more reliable with SSF wetlands than for SF wetlands, partly because the decaying plants are not in the water column, thereby producing slightly less organic matter in final effluent. The settled BOD undergoes aerobic or anaerobic decomposition, depending on oxygen status at the point of deposition. The remaining BOD, in colloidal and dissolved forms, continues to be removed as wastewater comes in contact with the attached microbial growth in the system [48]. The BOD loading can be limiting design factor for wetland systems [47]. For the SSFCWs, oxygen is transmitted by the vegetation to the root zone. In most cases, there is very little direct atmospheric re-aeration as water surface remains below the surface of the media.

It is possible that some aerobic metabolism would occur in these beds, but the predominant biological mechanism is likely to be facultative/ anaerobic. Typical values of DO in SSF systems are very low (<0.1 mg/l). Exact BOD removal only occurs when the material causing the BOD is completely converted by anaerobic biological processes to gaseous end products. The two most likely anaerobic pathways are methane fermentation and sulfate reduction. Since methane fermentation is severely inhibited at temperatures below 10°C, Sulfate reduction predominates for soluble BOD removal during colder months. Microbial degradation plays a dominant role in the removal of biodegradable organic matter. Organics can create oxygen deficiencies in receiving waters; however, aquatic plants supply oxygen to the wetland floor through their roots, thus promoting the aerobic digestion of organic material. Some anaerobic degradation of organic material also occurs in the bottom sediments; therefore, wetlands provide a diversified micro environment which plays an important role in pollutant processing [51].

Total suspended solids: The results for TSS removal have been similar to BOD_5 in that the majority is removed in the first few meters beyond the inlet of the bed and a system properly sized for BOD_5 removal would be properly sized for TSS removal. Removal of TSS is very effective in both types of constructed wetlands. Control distribution of the inlet flow will enhance removal near the inlet zone. Proper distribution of solids can be achieved by low inlet velocities, even cross sectional loadings and uniform flow of influent [33]. The suspended solid content of wastewater is not a limiting design parameter for sizing wetland because TSS removal is very rapid as compared to either BOD or nitrogen. Optimal removal of TSS requires a full stand of vegetation to facilitate sedimentation and filtration and prevent the re-growth of algae. Most of the solids are removed through sedimentation and filtration, as vegetation obstructs the flow and reduces velocities [49].

Nitrogen: Organic nitrogen may be found in both soluble and particulate forms. The other nitrogen species are water soluble such as un-ionized form NH_3 or the ionized form NH_4^+, depending on water temperature and pH. The ionized form is predominant in wetlands and at 25^oC and pH of 7.0, the % un-ionized ammonia is approximately 0.6% [10]. The removal of nitrogen in the form of ammonia and organic nitrogen requires a supply of oxygen for nitrification. Nitrogen removal is mainly accomplished by the successive microbial pathways ammonification, nitrification and denitrification. Nitrogen removal is very effective in both the free water surface and subsurface flow constructed wetlands. Total nitrogen removals of up to 79% are reported at nitrogen loading rates of elemental N (0.44 mg/cm^2.d), in a variety of constructed wetlands [33].

Biological transformation of organically combined nitrogen to ammonium nitrogen during ammonification process under aerobic and anaerobic conditions, but slower for anaerobic conditions [51]. The bacteria present in the water (*Nitrosomonas*) oxidize ammonia to nitrite in an aerobic reaction and nitrite is then oxidized aerobically by another bacteria (*Nitrobacter*) forming nitrate. Denitrification also occurs as nitrate is reduced to gaseous forms under anaerobic conditions in the litter layer of the wetland substrate. This reaction is catalyzed by the denitrifying bacteria *Pseudomonas spp*. and other bacteria [38]. Consequently, interaction between macrophytes and microbes is essential for nitrogen removal [49].

Phosphorus: It occurs in natural water and wastewater primarily as phosphates. They are classified as orthophosphates and organically bound phosphates. Phosphorus removal in many wetlands is not very effective because of the limited contact opportunities between the wastewater and the substrates. However, in the subsurface flow bed design when proper substrates are selected as the medium for the system be effective. Significant clay content and the presence of iron, and aluminum will enhance the potential for phosphorus removal [48]. The mechanism of phosphorus is through adsorption and uptake by plants. Phosphorus removal in wetlands is based mainly on the phosphorus cycle and can involve a number of processes such as adsorption filtration, sedimentation, precipitation and assimilation/uptake. Because phosphorus removal in wetlands is less effective than nitrogen removal, a post wetland polishing step may be required in the form of vegetated filter strips, irrigation or phosphorus adsorption media. Soluble inorganic phosphate is taken up by plants, and cycled through their growth and decomposition. Micro-organisms also take up P but most of it is released again after cell death [51].

Sulfur: Influent sulfur to wetlands is typically in the form of sulfate in oxidized environments and sulfide in reduced environments. Sulfate is highly soluble under all temperature and pH conditions, whereas sulfide solubility is pH-dependant. Sulfide solubility increases ten-fold between pH 6–8. At acidic pH (< 6) sulfide will be present as H_2S, which has a much lower solubility. Sulfate reducing bacteria can be utilized to convert sulfate (SO_4^{2-}) to sulfide (S^2). Therefore, sulfate behaves as an alternative electron acceptor to support anaerobic respiration. Sulfides can be partially reoxidized under micro aerophilic conditions or at low oxygen concentrations by chemotrophic bacteria to form insoluble elemental sulfur (S) and the elemental sulfur sediment from the wastewater [51].

CHAPTER THREE

3. MATERIALS AND METHODS

3.1 Materials

Materials used to achieve all the objective for study were discussed in the following Sedimentation tank (700L) - where some of the settleable and suspended solids would settle down at the bottom of the tank

- Equalization tank (80L) - to regulate the flow of wastewater into the system by ensuring that the delivery head is always constant with the help of a floating ball valve.
- Plastic pipes – PPR (polypropylene) of one inch or 2.54cm diameter pipes with controlling valve - The piping of the system used for the supply, distribution and collection of wastewater comprised of 2.54 cm diameter plastic pipes.
- Sample collector of plastic bottles- used to collect sample for laboratory analysis
- Gravel size selected.
  - size 20mm-30mm diameter-used in treatment zone of the wetland
  - size 40mm-80mm diameter- used in inlet and outlet zone of the wetland
- Wetland plants- selected plants were *C.indica, P.karka and C. gigantean* and shown in Fig 3.1

Figure 3.1a
Canna indica

Figure 3.1 b
Phragmite karka

Figure 3.1c
Colocasia gigantean

3.2 Equipments

- BOD incubator (TS606/4)
- Drying oven (BSchickUNG-loading model100-800)
- BOD bottle, Erlenmeyer flasks (500mL), Aluminum weighing dishes, Glass-fiber filter disks, Suction flask, Membrane filter funnel, Gooch crucible, Filter paper (110mm), measuring cylinder (50mL and 100mL), weighing scale, evaporating dishes, desiccators, beaker(100mL)
- DO meter (HACH P/N HO30d LOVELAND. CO, USA)
- EC meter(Wagtech International N374,+M207/03 IM ,USA)
- pH meter (Wagtech N374, M128/03IM, USA) were used for the analysis of samples throughout the experiment.

3.3 Methods

Analytical reagents were used for the analysis of brewery wastewater composition and analysis was conducted for samples from St. George Brewery (BGI Ethiopia). The wastewater was analyzed for COD, BOD_5, TN, NH_4-N, NO_3-N, TP, PO_4^{3-}, SO_4^{2-}, S^{2-}, TSS, TDS, DO, EC, Temperature and pH.

3.3.1 Experimental set up

The horizontal SSFCW systems used built by Environmental Science, Faculity of Addis Ababa University (AAU), used for the experiment. Its dimension and components summarized in Table 3.1.

Table 3.1 Dimensions and Components of SSF Constructed Wetland.

Dimension	Typical value
Length of wetland (L)	2m
Width of wetland (W)	0.65m
Aspect ratio (L/W)	3:1
Depth of wetland (D)	0.6m
Depth of media /gravel	0.5m
Water depth (d)	0.4m
Surface area of wetland (As)	$1.3m^2$
Average Flow rate (Q_{av})	26 L/day
Bottom Slope (S)	1%
Hydraulic retention time (HRT)	7 day
Media size	20mm-30mm
Number of cells	4 SSFCWs

The system consists of four analogous horizontal SSFCWs each with a dimmension of 2 meters length, 0.65 meters width and 0.6 meters depth with surface area of $1.3m^2$ aligned in parallel. The floor of the system has 1% slope from inlet to outlet to achieve a hydraulic head-loss. The empty-bed volume of each SSFCW up to the level of gravel was approximately 0.65 m^3 (650 L). This was done by filling water in empty CW up to gravel level, 0.5m. The void volume or the free volume after the system was filled with gravel size 20mm-30mm was around 0.227 m^3 (227 L). Then the porosity of the media was calculated by dividing void volume to total volume, which give 0.35 or 35%. This system is designed with an average wastewater flow-rate of 26 L/d ($0.026m^3$/d) into each SSFCW and a theoretical HRT of 7 days.

The brewery wastewater is first settled in a sedimentation tank. The septic tank served as a primary treatment to stay one day to settle and passes out to SSFCWs. About sixty litres of pre-settled wastewater is then passed from the sedimentation tank to an equalization tank before getting into the SSFCW system with gravitational force. The photograph of sedimentation tank and equalization tank are shown in Fig 3.2

Figure 3.2 Sedimentation Tank and Equalization Tank with a Floating Ball valve inside

The piping of the system used for the supply, distribution and collection of wastewater comprised of one inch (2.54 cm) diameter PPR (polypropylene) plastic pipes and shown in figure 3.3 (a, b and c). The sedimentation and equalization tank were connected through a single pipe. The two major components of the piping system in the SSFCW were the inlet and outlet pipes.

(a) **(b)** **(c)**

Figure 3.3 Inlet Piping (a), Wastewater Distribution Weir (b) and Adjustable Outlet Piping (c)

The substrate or plant growth media used in this SSFCW system was 20mm-30mm diameter sized gravel. This gravel was carefully washed before it was filled into the four cells. The substrate was filled to a height 0.5m. Gravel size 20mm-30mm was selected based on the recommended gravel size range of 20mm-40 mm for SSFCWs on different literatures [38].

The three plant species selected for this research purpose were *Canna indica, Phragmites karka* and *Colocasia gigantea.* The selection criteria for these plants were based on prior information on their use in CW from various literatures, their “aesthetic” landscaping applications their ease of accessibility and their potential treating wastewater. With the use of these plants on horizontal SSFCWs, combined gains of wastewater treatment, landscape beautification and household material made can be achieved. Especially, *C.indica* and *C.gigantea* being famous for their gardening application can add-up to appealing appearances to the system. *Phragmites karka* is also used for making household materials (as baskets), used to build traditional house roof which is for better looking smarts, which is common in big city for cultural houses which serves as a hotel and restaurant and also used for fencing rural area.

Plant establishment was made right after the cells were filled with gravel substrate on August18, 2010 as shown in Fig3.4a. The first SSFCW was planted with *C. indica*, the second with *Phragmites karka*, the third with *C. gigantea* and the final SSFCW was left unplanted to serve as a control and shown in Fig 3.4b. All three of the plants were picked up from the premises of Arat kilo campus of AAU and transplanted into their respective SSFCW. Before transplantation, soil and litter from the roots were removed by washing to prevent debris from exerting organic matter into the system and minimize their effect on the treatment. Right after transplantation, the plants were reduced and allowed to grow back again.

(a) **(b)**

Figure 3.4 SSFCW Pre-Plantation (a) and after plantation (b)

After the establishment of plants, the SSFCWs were fed only with tap water for the first five days. Then, the wastewater used was diluted with tap water at different percentage was summarized in Table 3.2 and was introduced for the first four months, because gradual rather than sudden increase in the concentration of the wastewater applied reduces shock to the vegetation and provide adaptation period for the plants. The purpose of acclimatization is to avoid the shock or stress of the plants that could be caused by the high concentration of pollutants in the wastewater. Each SSFCW is fed with the same type of wastewater and the same average flow rate of influent from equalization tank through pipe. Wastewater feeding was semi continuous over the entire period of the study. The operating parameters during the experimental study were flow rate (Q), hydraulic retention time (HRT) and hydraulic loading rate (HLR). These HRT and HLR were controlled by controlling the flow rate of wastewater entering the CWs by using control valves. Short-circuiting was prevented (reduced) in the treatment cells by replacing the single-point inlet and outlet structures with weir pipe extending the full width of the cell, by controlling water depth and by uniformly compacting gravel.

Based on the literatures hydraulic retention time of at least 6 to 8 days recommended ensuring an adequate nitrification rate, 7days was taken as hydraulic retention time for the study and then the theoretical flow rat calculated from equation 2.2. However, practically the inflow and outflow rate was measured using a stopwatch and measuring cylinder. The inflow rate and outflow rate was 19.5 mL/min and 16.5 mL/min respectively. The average inflow to each CW was 28 L/d and outflow rate was 24 L/day. Therefore, the average flow rate of each SSCW was 26 L /d. The minimum inlet flow rate was 23L/d where the control valve closed (the flow was stopped). And the maximum inlet flow was not exceeded 32 mL/d. If it exceed the maximum flow rate, cause water surfacing problem.

Table 3.2 Percentage ratio used to dilute the wastewater with tap water

Days	**Tap water (%)**	**Wastewater (%)**
18-24/8/2010	100	0
24/8/2010 – 24/10/2010	95	5
26/10/2010 – 6/11/2010	90	10
06 -18/11/2010	80	20
20/11/2010- 02/12/2010	60	40
04 -15/12/2010	50	50
17-28/12/2010	25	75
01/01/2011 onwards	0	100

3.3.2 Sample collection

Samples were collected from five different points at an interval of seven days, a total of 15 samples, were taken during the study period. Three replica samples were taken for the analysis of each parameter. These points were labeled S_1, S_2, S_3, S_4 and S_5 as shown in Fig 3.5. S_1 represents sampling point for the influent wastewater into the system and is situated at the equalization tank. S_2, S_3, S_4 and S_5 represent sampling points for the treated effluent coming out of SSFCW 1, SSFCW 2, SSFCW 3 and SSFCW 4, respectively.

Samples were taken over the period of one month after established plants grown fully and extended from January 20 to February 20, 2011. The grab samples were taken for water quality analysis every seven days (HRT=7days). Putting in mind the assumption that wastewater fed at a given day will come out of the system after seven days. The samples were collected using sterile plastic sampling bottles and transported to the laboratory, for analysis.

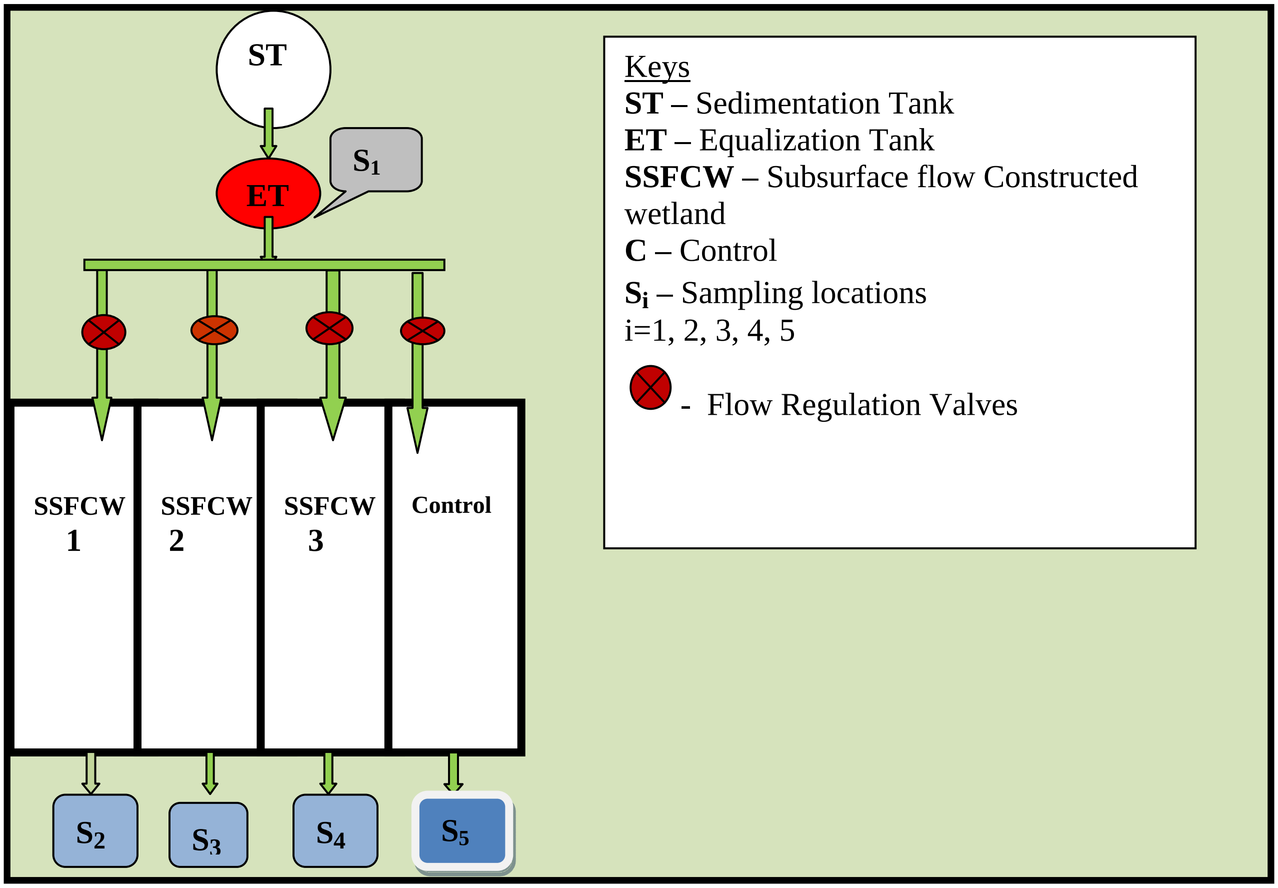

Figure 3.5 Schematic Diagram of the Experimental SSFCW System

3.3.3 Laboratory Analysis and Measurement

BOD_5 and TS were analysed in the Environmental Engineering, Chemical Engineering Department laboratory. DO, EC, wastewater pH and temperature were measured on-site during sampling time at the inlet and outlet using portable DO meter, EC meter, Thermometer and pH meter respectively. Some parameters were analyzed in JIJE LABOGLASS PLC Laboratory.

Parameter tested and Method

COD - Open Reflux Method (APHA 5220B)

BOD5 - Lovibond BOD system oxidirect method

TN - In-Line UV/Per sulfate Digestion and Oxidation with Flow Injection Analysis and Titrimetric Method

NH_4-N and NO_3-N- Kjeldha Distillation with Magnesium Oxide

TP - Manual Digestion and Flow Injection Analysis (APHA 4500 P H)

PO_4 - HACH method 8190: Molybdovanadate with acid per-sulfate digestion (APHA 1998)

Sulfide- Methylene Blue Method 8131 (DR/2400 USA) according to HACH instructions

Sulfate - Spectrophotometer (DR/2400 USA) according to HACH instructions

TSS - procedure (APHA, 1998) 2540D and 2540E

TDS – procedure (APHA, 1998) 2540C

3.4 Statistical Analysis

Statistical analysis was performed using SPSS program (SPSS; Version 15.0). The data was analyzed through one-way analysis of variance (ANOVA) at 95% confidence level to compare the performance efficiency of each CW concerning the removal of BOD_5, COD, total nitrogen (TN), nitrate nitrogen (NO_3-N), ammonium nitrogen (NH_4^+-N), total phosphorus (TP), orthophosphate (PO_4^{3-}), sulfate (SO_4^{2-}), sulfide (S^{2-}), total suspended solids (TSS), total dissolved solids (TDS), electrical conductivity (EC), dissolved oxygen (DO), wastewater pH, and temperature (T^o). The statistical analysis was done using this SPSS included mean, standard error of mean, standard deviation, the Analysis of variance (ANOVA) with LSD (Fisher’s Least Significant Difference) as a Post Hoc Analysis.

The removal efficiency of the SSFCWs for each wastewater quality parameters were calculated using the following formula.

Removal Efficiency (%) = $[(C_i - C_e)/C_i]\ 100$ ....(3.1)

Where, C_i = is the concentration of the waste material in the influent

C_e = is the concentration of the waste material in the effluent

CHAPTER FOUR

4. RESULTS AND DISCUSSION

The brewery wastewater characteristics and the removal efficiency of the different emergent plants in the different horizontal SSFCWs were examined. The results obtained from the laboratory analysis of raw brewery wastewater characterized and the average values of the influent and effluent characteristics of the SSFCW systems for selected physic-chemical parameters were summarized in Table 4.1. The results obtained for the removal efficiency of septic tank and the four SSFCWs and the organic loading rate of the pollutants were summarised in table 4.2.

The wastewater before treatment figure 4.1a and after treatment figure 4.1b was observed.

(a)

(b)

Figure 4.1a wastewater before treatment **Figure 4.1b wastewater after treatment**

Table 4.1: Influent and effluent characteristics of brewery wastewater and the experimental SSFCW system

Parameter	Mean Influent and Effluent Concentrations					
	Raw Brewery wastewater	**Influent Concentration**	**Effluent Concentration**			
	Mean±SD	**Mean±SD**	**SSFCW 1** (*C. Indica*)	**SSFCW2** (*p.karka*)	**SSFCW 3** (*C.giganteae*)	**SSFCW 4** (Control)
COD	13901±1592	4798 ± 423	1089 ± 87	947 ± 12	1003 ± 73	1115 ±109
BOD_5	5196 ± 389	1714 ± 163	453 ± 37	421 ± 27	443 ± 29	506 ± 36
TN	200 ± 24	106 ± 16	30 ± 3	17 ± 7	24± 2	42 ± 2.5
NH_4-N	22 ± 12	61 ± 31	22 ± 7	22 ± 2	24 ± 2	25 ± 7
NO_3-N	11 ± 4	44 ± 11	19 ± 6	18 ± 3	22 ± 4	25 ± 4
TP	97 ± 12	83 ± 8	30 ± 4	24 ± 3	25 ± 3	36 ± 1
PO_4	76 ± 11	62 ± 6	13 ± 2	8 ± 2	13 ± 3	25 ± 6
SO_4	15 ± 3	12 ± 2	8 ± 0.3	7.4 ± 0.2	7.6 ± 0.7	8.3 ± 0.4
S^{2-}	0.62 ± 0.2	0.61 ± 0.2	.02 ± 0.006	.01±0.003	0.02±0.006	0.04 ±0.02
TS	12806±3821	2098 ±623	973±122	936 ±120	958±128	1139 ±24
TSS	5061 ± 2088	100 ± 10	40 ± 10	32 ± 8	43 ± 15	50 ± 10
TDS	7738 ± 1941	1998 ± 618	933 ± 112	905 ± 113	915 ± 113	1089 ± 32
DO	1.4 ± 0.4	0.86 ± 0.1	2.3 ± 0.1	2.9 ± 0.2	2.4 ± 0.3	1.4 ± 0.16
EC(µS/cm)	1904 ± 43	1758 ± 60	1218 ± 42	1330 ± 85	1279 ± 69	1230 ± 33
T(^{o}C)	36 ± 2	21 ± 0.8	20.9 ± 0.5	20.7 ± 0.5	21.8 ± 0.8	20.6 ± 0.9
pH	5 ± 0.4	5.6 ± 0.9	6.2 ± 1	6.3 ± 0.5	6.5 ± 0.6	6.9 ± 0.7

All units in mg/l except EC, T and pH

Table 4.2 Organic loading rate of Pollutants and Removal Efficiency of Different Pollutants by the four SSFCWS were summarized

Parameters	Loading rate ($g/m^2.d$)	Percentage Removal (%)				
		Sedimetation tank	**SSFCW 1** (*C. indica*)	**SSFCW 2** (*P.karka*)	**SSFCW 3** (*C.giganteae*)	**SSFCW 4** (Control)
COD	96	65.5	77.3	80.3	79.1	76.8
BOD_5	34.3	67	73.6	75.4	74.1	70.5
TN	2.12	47	71.1	84.1	77.1	60
NH_4-N	1.2	-182	64	64.3	60	58
NO_3-N	0.87	-285	56	59	50	43
TP	1.66	14	63	71	69	56
PO_4	1.23	19	79	85.7	80	58
Sulfate	0.24	21.5	33	38	36.6	31
Sulfide	0.01	1.6	97	98.4	97	93
TS	42	84	53.6	55.3	54	46
TSS	2	98	60	68	57	50
TDS	40	74.2	53.3	54.7	54.2	46
EC	35.2	7.7	30.7	24.3	27	30

4.1 Brewery Wastewater Characteristics

Brewery effluent had BOD_5 value ranging from 2650 mg/l to 9685 mg/l with the average value of 5196.3 ± 389 mg/l) and COD value ranging from 4412.8 mg/l to 32286 mg/l with the average value of 13901 ± 1592 mg/l. (Table 4.1). The high value of standard deviation showed that the variability of brewery wastewater composition. Because the brewery production activities were varied by season, by day of the week and by the time of day, wastewaters are extremely variable [3]. Therefore variations have been observed in the analysis of the different physico-chemical parameters while characterizing brewery wastewater. This value of BOD_5 and COD is out of range of Ethiopian EPA standard and when compared to the value reported by [24] (2000 mg/l to 6000 mg/l COD), [18] (1860 mg/l to 3880 mg/l COD) and [3] (8240-20000 mg/l COD). According to the [3], the high organic loads in the wastewater arise from dissolved carbohydrates, the alcohol from beer wastes, and a high content of suspended solids, such as spent grain, malt and yeast. It is also explained in many reports that the raw materials like malt and adjuncts, and the discharge of trub, weak wort, surplus yeast, emptying and rinsing of process tanks, pre- and after- runs of kieselguhr filtration and drip beer could possibly be the sources of high COD and BOD_5 in the wastewater.

For any level of BOD and COD that resulted in BOD/COD ratio of more than 0.1 is classified as biodegradable organic matter. The composition of brewing effluents can fluctuate significantly as it depends on various processes that take place in the brewing. Organic components in brewery effluent which have BOD_5/COD ratio of 0.6 to 0.7 are generally easily biodegradable. The results indicated that the BOD_5 /COD ratio was 0.40, which indicates a medium biodegradability of organic matters.

The brewery wastewater is also characterized for its nutrients (N and P) contents. In this study the result show that the brewery effluent had TN, NH_4-N, NO_3-N, TP and $PO4^{3-}$ that ranged from 178 mg/l to 225 mg/l, 13 mg/l to 35 mg/l, 7 mg/l to 15 mg/l, 87 mg/l to 110 mg/l, 68 mg/l to 88 mg/l with average values of 200 ± 24 mg/l, 21.6 ± 12 mg/l, 11.3 ± 4 mg/l, 97 ± 12 mg/l and 76 ± 11 mg/l, respectively (Table 4.1). The high $PO4^{3-}$ levels obtained in the study could be recognized to the use of phosphorous containing chemicals like phosphoric acid used in the CIP (Cleaning in place) units and the variation in the concentration resulted from the variation in the amount of cleaning agents [3].

The sources of the nitrogen forms could be malt processing followed by protein hydrolysis for NH_4^+-N and NO_3-N. Also it might come from dissociation of the nitric acid used in the CIP units as well as ammonification and nitrification of the ammonium nitrogen in the wastewater during the periods of sample collection and transportation for analysis. The TS, TSS and TDS analysis of the wastewater results the values ranging from 9240 mg/l to 16840 mg/l, 3644 mg/l to 7460 mg/l and 5596 mg/l to 9338 mg/l, with an average value of 12806 ± 3821mg/l, 5061 ± 2088 mg/l and 7738 ± 1941 mg/l, respectively (Table 4.1). Brewing activities like malt processing, filtration and packaging could be the cause for the high TSS values, which indicated that brewery solids mainly consisted of spent grains, kieselguhr, surplus yeast, trub and possible label pulp from the bottle washer.

The wastewater analysis also showed pH values ranging from 4.6 to 5.4 pH units (Table 4.1). The wide range (2-12) pH unit values are reported by different researchers for the discharges from different sections of a brewery [3]. The variation in the wastewater's pH could be recognized to the batch processing nature of the brewery and the amount and type of chemicals (caustic soda, phosphoric acid, nitric acid, etc.) used at the CIP units. On site measurement of the wastewater temperature ranges from 34^oC to 38^oC. This temperature range was below the temperature limit set [26] which is 40^oC.

4.2 Sedimentation Tank Removal

The raw wastewater is to be treated in a sedimentation tank as a primary treatment in order to reduce the amount of suspended solids and BOD coming into the wetland, the average sedimentation tank removal efficiencies with one day retention time as COD (65.5%), BOD_5 (67%), TS (83.6%), TSS (98%) and TDS (74.2%). This result falls within the range of the reported value by [53] which the septic tank able to reduce at least 60% to 70% of the incoming BOD_5 and TSS in order to reduce the length of the wetland. The volume of the accumulated sludge in the tank and the retention time is used as design parameters to size sedimentation tank that feed for subsequent process. Based on empirical evidence, the retention time for a septic tank recommended that at least one day in order to remove 60 to 70% of the incoming BOD_5. Because of sludge accumulation on the bottom of the tank, the volume of the tank reduces with time. Therefore the recommended volume of the tank is at least two times the daily average flow [53]. Thus, in this study, a volume of 700L sedimentation tank was used which is greater than five times the daily used volume.

4.3 Influent and Effluent Characterization of Horizontal SSFCWs

After laboratory analysis the mean influent BOD_5 and COD concentrations were 1714 mg/l and 4798.2 mg/l respectively, which had the mean daily organic loading rate (OLR) of 34.3 $g/m^2.d$ and 96 $g/m^2.d$, respectively. The mean effluent concentration of all four SSFCWs for BOD_5 and COD were in the range of 421 to 506 mg/l and 947.6 to 1115 mg/l, respectively. For nitrogen, the mean influent parameter values were: 106 mg/l for TN, 43.5 mg/l for NO_3-N, and 61.0 mg/l for NH_4-N. These values are equivalent to the mean daily loading rate of 2.12 $g/m^2.d$, 0.87 $g/m^2.d$ and 1.2 $g/m^2.d$ for TN, NO_3-N and NH_4-N, respectively. The mean effluent concentration of all four SSFCWs for TN, NH_4-N and NO_3-N were in the range of 16.9 to 42.6 mg/l, 21.8 to 25.6 mg/l and 17.7 to 25 mg/l, respectively. The mean influent parameter values for phosphorus were 83.3 mg/l for TP and 61.6 mg/l for PO_4^{3-}. The effluent concentrations were between the range of 23.8 mg/l to 36.6 mg/l for TP and 8.1 mg/l to 25.6 mg/l for PO_4^{3-}.

In case of Sulfate and sulfide mean concentrations in the influent were 12 mg/l and 0.61 mg/l, respectively. The mean concentration of sulfate and sulfide in the effluent ranged from 7.4 mg/l to 8.3 mg/l and 0.01 mg/l to 0.04 mg/l respectively. While, mean influent concentration for TS, TSS and TDS were 2098 mg/l, 100 mg/l and 1998 mg/l, respectively. The effluent values were in the range of 936.6 mg/l to 1139 mg/l, for TS, 31.6 mg/l to 50 mg/l for TSS, 905 mg/l to 1089 mg/l for TDS. For the physical parameters, EC, DO, pH and temprature mean influent values were 1758 µS/cm, 0.86 mg/l, 5.6 pH units and 20.6^{o}C, respectively. The effluent mean of EC, DO, pH and temperature were in the range of 1218 µS/cm to 1279 µS/cm, 1.4 mg/l to 2.9 mg/l, 6.2 to 6.9 pH units and 20.6 to 20.9^{o}c, respectively.

4.4 Removal Efficiencies of Horizontal SSFCWs

General comparison of removal efficiencies showed that planted SSFCWs performed better than unplanted SSFCW for many of the parameters. But these differences in removal were statistically significant ($P < 0.05$) only for TN, TP, $PO4^{3-}$ and DO of the parameters.

The Ethiopian brewery effluent standard limits for COD (250 mg/l), BOD_5 (60 mg/l), TN (40 mg/l), NH_4-N (20mg/l), NO_3-N (20mg/l), TP (5mg/l), PO_4 (5 mg/l), SO_4 (200 mg/l), S^{2-}(1mg/l), TSS (50 mg/l),TDS (3000 mg/l), T (40^{o}c) and pH (6-9 pH units), respectively [26]. Some of the effluent parameters from all four SSFCWs are out of the range of this standard. However, for TN, NH_4-N, sulfate, sulfide, T^{o}c and pH, which are within the range of the standard. The effluent discharge limit of a brewery has to comply with depends on local environmental legislation. It is obvious that in case of discharging to a municipal sewer discharge limits are less stringent than when the effluent is to be discharged into a sensitive receiving surface water body (river, Lake Sea, etc). For that reason, removal of organic compounds from the wastewater is important to avoid anaerobic conditions in the receiving waters. The presence of oxygen depleting substance like organic matter lead to very low concentration of dissolved oxygen in the influent. This in-turn has adverse effects on different aquatic life forms.

Effluents from the SSFCWs planted with by *phragmite.karka* had improved dissolved oxygen concentration from 0.86 to 3.1 mg/l. There were only slight differences in temperature and pH between influent and the effluents from the four SSFCWs. ANOVA results confirm that values of T^{o}c and pH showed no statistically significant differences ($P>0.05$) between planted and unplanted SSFCWs and for DO showed statistically significant difference($P<0.05$) between planted and unplanted SSFCWs.

4.4.1 BOD_5 and COD Removal

Figure 4.2 shows the average BOD_5 and COD removal efficiency of each SSFCW cells. The removal efficiency of the three planted SSFCW was between 73.6 % and 75.4 % for BOD_5 and 77.3% to 80.2 % for COD. As shown in Table 4.2 the maximum BOD_5 removal (75.4%) was observed in the SSFCW planted with *P.karka* followed by *C.gigantea* (74.1%) and *C.indica* (73.6%). In case of BOD_5 removal, no statistical difference among the units was observed ($p > 0.05$). COD removal trend was as follows *P.karka* (80.3%), *C.gigantea* (79.1%) and *C.indica* (77.3%). Therefore, *P. Karka* had a better BOD_5 and COD removal efficiencies of 75.4% and 80.3%, respectively and followed by C.gigantea removal efficiencies of 74.1% and 79.1%, respectively. Whereas

SSFCW planted with *C.indica* showed a removal efficiency of 73.6% and 77.3%, for BOD_5 and COD, respectively. The minimum removal efficiency of BOD_5 and COD were observed in the Control 70.5% and 76.8%, respectively. The ANOVA test results showed differences in removal efficiency were not statistically significant ($p > 0.05$) for BOD_5 and COD.

The result indicated that almost similar trend has been repeated by [15]. The average treatment performance of HSSFCWs for domestic wastewater in India with *phragmite karka* showed 77.8% for COD, and 65.7% for BOD. A study conducted by [54] using tannery wastewater CW cells under 5 days HRT showed that the maximum BOD_5 and COD removal was observed in the cell planted with *P. karka* 77% and 80.9%, respectively. The findings from this study showed that most CWs containing plants lead to higher organic matter removal when compared to the control unit (unplanted). This indicates that plants contribute to wastewater treatment processes in a number of ways, such as providing surface area for microorganisms, increasing uptake of nutrients and trace elements, and oxygen transfer by their tissue, to their roots [41].

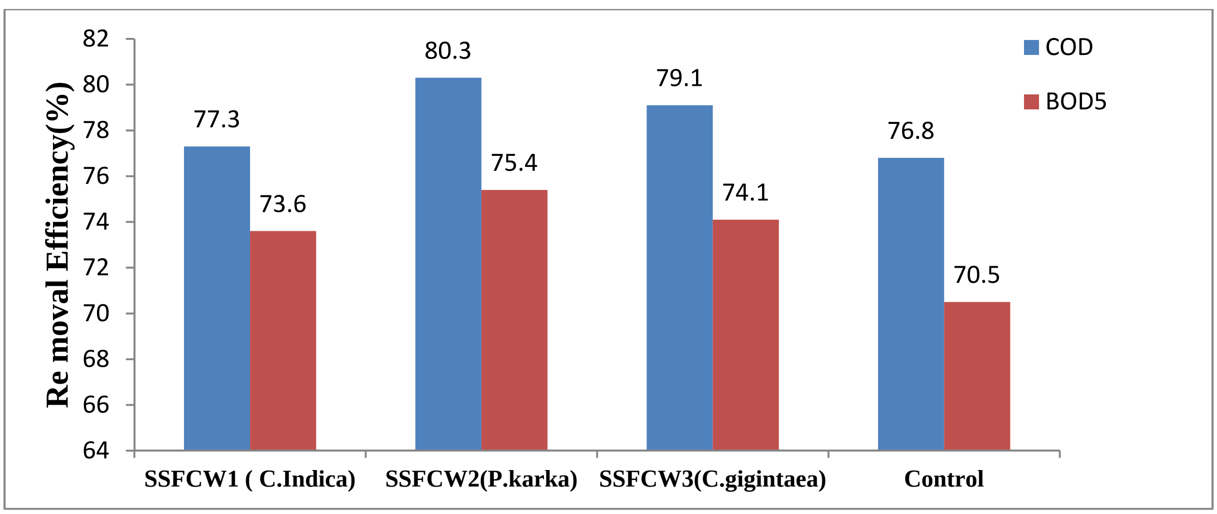

Figure 4.2 BOD_5 and COD Removal Efficiencies of Experimental SSFCWs

A study conducted by [15] noted the treated water dissolved oxygen (DO) level increased by 139 % and reached 3.1 mg/l indicating the existence of aerobic condition in the root zone bed. Similarly in this study, the treated water DO level increases for four SSFCWs planted with *C.indica* (62.6%), *P.karka* (70.3 %), *C.gingantea* (64.2%) and unplanted SSFCW (39.8%). The high BOD_5 and COD removal in *P. karaka* may be due to its capacity to supply oxygen via it's hallow stems that helps to oxidize organic matter in root zone.

Dissolved oxygen is an important parameter to take into consideration when working with a wetland since the amount of DO in the water is directly related to the population size and community of aerobic bacteria that the system can sustain. In this study, the analysis of DO variations in CW cells planted and unplanted indicated that DO increased from the influent to the effluent as shown in Table 4.1. There was an increase of DO from 0.86 mg/l to 3.1 mg/l in the planted SSFCWs and 0.86 mg/l to 1.43 mg/l in control SSFCW.

Further according to [22], Wetland plants also improve organic matter removal due to the growth of biofilms on the root surface, releasing chelating substances and enzymes by their roots which enhance adsorption and degradation of organic compounds and adsorption of certain organic matter on clay soil and sand. In this experiment, the COD and BOD_5 the effluents from the constructed wetland do not meet the discharge limit set by the EEPA for brewery industry. This may be due to the fact that the organic loading rate used in this study was 34.3 $BOD_5 g/m^2.d$ and 96 COD $g/m^2.d$, which was higher than the recommended value, the maximum recommended by [22], organic loading rates for wastewater treatment by constructed wetlands is 11 g $BOD/m^2.d$ and 20 g $COD/m^2.d$, this may be decreases the removal efficiency of the CWs.

4.4.2 TSS and TDS Removal

Mean influent and effluent concentrations and removal efficiency of each SSFCWs for TSS, TDS and EC are presented in table 4.1 and Fig 4.3. The better removal efficiency for both TSS (68.4 %), and TDS (54.7%) was recorded by the SSFCW planted with *P.karka* followed by *C.indica* for TSS (60%), *C. gigantae* for TDS (54.2%) and *C. gigantae* for TSS (56.7%), *C.indica* for TDS (53.3%). Whereas, the minimum observed in unplanted SSFCW with TSS was (50%) and TDS (45.5%). The maximum removal efficiency of EC was observed by the SSFCW planted with *C.indica* (30.7%) followed by the unplanted SSFCW (30%), planted with *C.gigantae* (27.3%) and *P.karka* (24.3%).

Here, the test showed that there was no statistically significant difference ($P>0.05$) in the removal efficiency of TDS & TSS among the four SSFCWs. Also according to [38] one of the primary intermediate mechanisms in the removal of suspended solids by CW systems is the flocculation and settling of colloidal particulates. These systems are relatively effective in TSS removal because of the relatively low velocity and high surface area in the SSFCW media. Also, SSFCW acts like filters and thereby provide opportunities for TSS separations by gravity sedimentation, straining and physical capture, and adsorption on biomass film attached to gravel and root systems.

The TSS discharge limit set by the EEPA for discharge to water is 50 mg/l and the result obtained from this study, is in range of 31.6 to 50 mg/l, hence within the limit value. For the TDS discharge limit set by the EEPA is 3000mg/l and the result obtained, in the range of 905 mg/l to 1089 mg/l. The resulted effluent from the four SSFCWs for TSS and TDS were conformed to the standard limit.

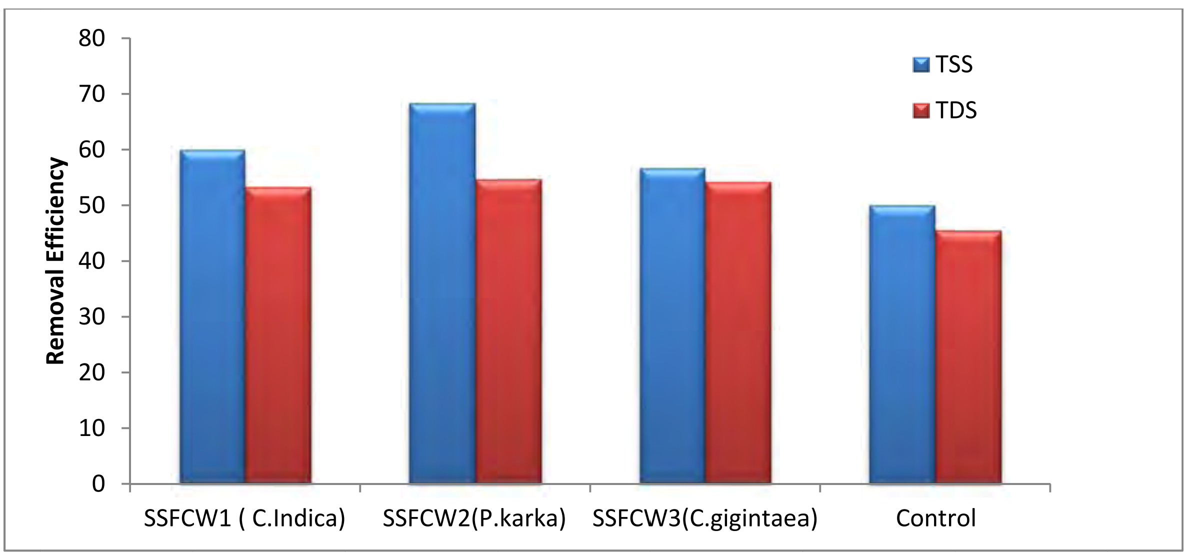

Figure 4.3 TSS and TDS Removal Efficiency of the SSFCWs

Since, ionic strength measures the solution's amount of dissolved salts in a solution, in this study, most breweries use NaOH (sodium hydroxide), H_2SO_4 (sulfuric acid), H_3PO_4 (phosphoric acid) and HNO_3 (nitric acid) for cleaning agent without doubt increases the ion concentration in the wastewater and led to high ionic strength during the study period.

A study conducted by [15], the average treatment performance for domestic wastewater in India, using horizontal SSFCWs with *phragmite karka* was 79% for TSS and 71.2% for TDS and other study, in Central India, *Phragmites karka* was planted in a horizontal subsurface flow gravel bed for treatment of primary municipal wastewater showed the removal efficiency of TSS (78 %). However, in this study, the removal of TSS and TDS were slightly less as compared to the above study. So, the relative low removal of solids in this study may be due to the plants are not as much as necessary matured for effective removal of solids and because of the study carried out for the short period.

4.4.3 Nitrogen Removal

The average influent TN, NH_4- N and NO_3-N concentration was 106 mg/l, 61 mg/l and 43.5 mg/l, respectively. After 7 days of HRT, the constructed wetlands were able to show some reduction of concentration in the effluent. Table 4.1 and 4.2 shows the average concentration of TN, NH_4-N and NO_3-N in the effluent and removal efficiency of the system. The nitrogen removal efficiency of the three planted SSFCWs and control were shown in figure 4.4. The maximum TN removal was observed in CW planted with *P.karka* (84.1%) followed by *C.gigantae* (77.1%), *C.indica* (71.1%) and unplanted CW (59.8%). In general, SSFCW planted with *P.karka* showed better removal efficiency for TN (84.1%), NH_4-N (64.3%) and NO_3-N (59.3%) followed by SSFCW planted with *C.gigantae* for TN (77.1%).

When carrying out ANOVA and LSD Post Hoc tests for these diferences in performance, removal efficiency of planted SSFCWs for TN showed statistically significant differences ($P<0.05$) with each other and with the control. However, the removal efficiency for NH_4-N and NO_3-N showed that the differences is not statistically significant ($P>0.05$) within planted and unplanted SSFCWs (control).

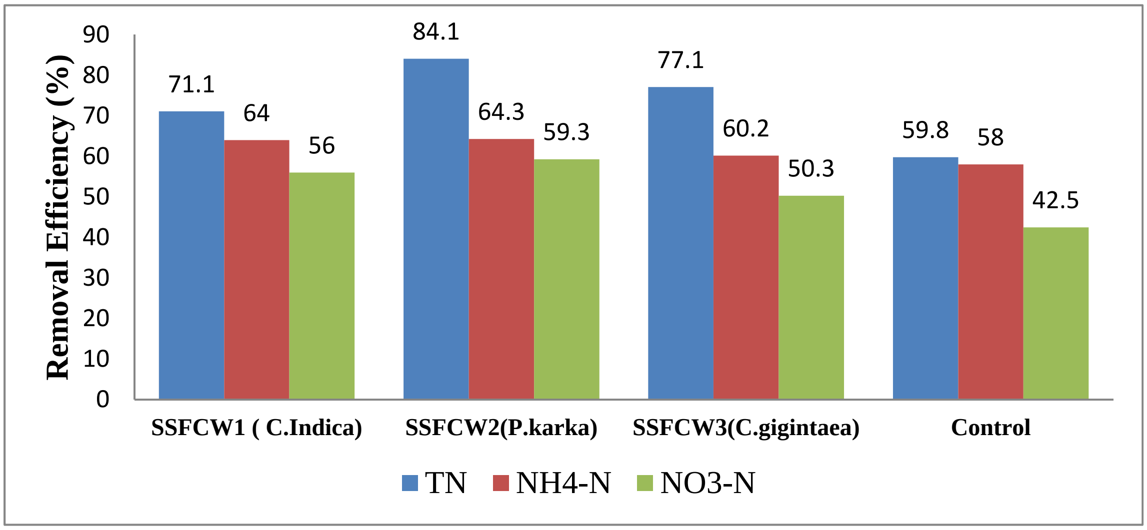

Figure 4.4 Nirogen Removal Efficiencies of the SSFCWS

A study conducted by [52], the removal efficiency of TN, NH_4- N and NO_3-N was 96.5%, 98.7% and 93.6%, respectively for pilot scale plants with 7 day HRT for treatment of dormitory wastewater and a study conducted by [12], the findings for removal of TN, NH_4-N and NO_3-N were 58.3%, 26.8% and 73.1%, respectively for scale plants with 5 day HRT for treatment of tannery wastewater. Also a similar study was carried out by [54], for removal efficiency of TN, NH_4-N and NO_3-N were 61%, 82% and 53%, respectively for scale plants with 5 day HRT for treatment of tannery wastewater.

From study conducted by [15], the average treatment performance for domestic wastewater in India, using horizontal SSFCWs with *phragmite karka*, 100% for organic nitrogen, 62% for NO_3-N and 53.3% for NH_4-N. In this study, the results were almost similar to that of the studies done by [12] and [54] on SSFCWs, which showed the removal efficiency of TN, NH_4-N and NO_3-N picked was 85.4%, 64.3% and 55.8%, respectively. The result obtained for the removal of NH_4-N and NO_3-N also agreed with the result obtained by [15].

Concentrations of TN, NH_4-N and NO_3-N from the effluent of the experimental study were compared with the National effluent emission standard limit for brewery wastewater set by EEPA. These standards were met by the effluents from all four SSFCWs for TN and NO_3-N except effluents from SSFCW3 for NO_3-N (21.6 mg/l). Whereas, for NH_4-N removal the standard limit was not met by effluents from all four SSFCWs.

As showed in this experimental study, the removal of TN was slightly higher than NH_4-N and NO_3-N in four SSFCWs, this may be due to the transformation of nitrogen through ammonification and nitrification processes occurred in the presence of high dissolved oxygen in the systems. Ammonification process occurs under both aerobic and anaerobic conditions the improved removals were shown within planted SSFCWs because of macrophytes transport oxygen down their stems into the roots where it diffuses into the sediment to produce an aerobic microenvironment around the root zone. In this experimental study, the high nitrogen removal in CWs planted with *P. karaka* may be due to its high biomass content and root mat, which enables the plant to take up more soluble inorganic nitrogen. In contrast, the SSFCW for control has lower nitrogen removal efficiency. This shows that plants can improve nitrogen removal in Constructed wetlands.

As [40] reported that the nitrification process is affected by the BOD level of the wastewater because of the competition for available oxygen between the nitrifying bacteria and the microorganisms removing biodegradable organic matter. In this experiment, the lower removal efficiency of ammonium ion relative to total nitrogen may be due to the available oxygen in the systems is not sufficient for both BOD decomposition and nitrification processes. Also nitrification requires a minimum of 2 mg O_2/l to proceed at a maximum rate, it is evident that the rate of nitrification is most likely the rate limiting factor for overall nitrogen removal from a constructed wetland system. Furthermore, the result showed that the removal efficiency of NH_4-N is greater than NO_3-N removal for four SSFCWs systems. This indicates that the nitrification process occurs sufficiently than denitrification processes. This condition contributes the formation of high amount of nitrate nitrogen and reduces NH_4-N.

In general, the possible reason for the lower removal of TN, NH_4-N and NO_3-N in the present study may be the SSFCWs in this study have only operated for short period of time, which is not enough for good root mat development of the plants. This indirectly decreases the aerobic region in the constructed wetland. Therefore, the short operation period, short HRT, high organic loading and less root mat development, which may decrease the aerobic region in the constructed wetland, accounts for a decrease in nitrogen removal.

4.4.4 Phosphorus Removal

The average removal efficiency for TP and PO_4 of the SSFCWs in Fig. 4.5 are 63.3% and 78.9% for *C.indica*, 71.4% and 85.7% for *P.karka*, 69.4% and 79.5% for *C.gigantea,* and 56.1% and 58.4% for the control (unplanted). ANOVA and Post Hoc LSD tests showed that statistically significant differences ($P<0.05$) in removal of TP and PO_4 between planted SSFCWs and control. However, the test showed that the removal of TP between SSFCW1 (*C.indica*) and SSFCW3 (*C.gigantea*), SSFCW2 (*P.karka*) and SSFCW3 (*C.gigantea*) were not statistically significant different ($P>0.05$). These test also showed that the removal of PO_4 between planted SSFCWs were not statistically significant different ($P>0.05$). It can be seen that all of the planted SSFCWs have better improvement in the removal of TP and PO_4 removal compared with the cell unplanted. It is generally accepted that planted in SSFCWs improve phosphorus removal which may be due to combination of mechanisms favored by the plants and adsorption of certain phosphorus. The maximum removal efficiency of TP and PO_4 was observed by SSFCW2 planted with *P.karka*, 71.4% and 85.7%, respectively.

Concentrations of TP and PO_4 from the effluent of the experimental study were compared with the National effluent emission standard limit for brewery wastewater not met standards. The removal efficiency of both TP and PO4 in planted SSFCW systems was higher than unplanted. This may be assumed that phosphorus is removed by precipitation and adsorption on to the media, also phosphorus is biologically removed by plant and micro-organisms uptake. As a result, the amounts of phosphorus in the influent tend to decreases in the effluent. Since the wastewater pH ranges from 6.2 to 6.9, the phosphorus cannot precipitate out of solution with metals and phosphorus was again released after micro-organisms were died. This showed that again the addition of phosphorus species to the systems which leads to the removal of phosphorus lowers

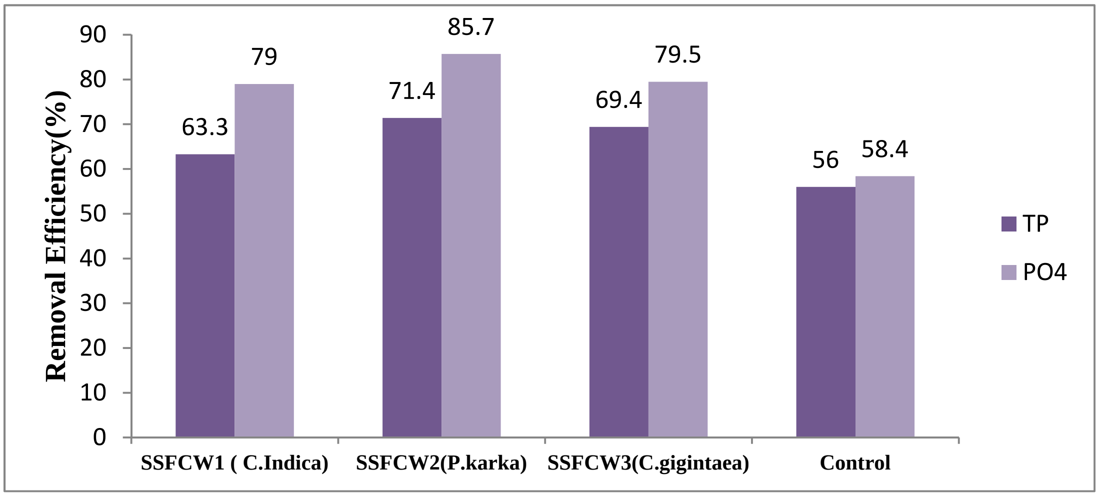

Figure 4.5 Phosphorus Removal Efficiency of the horizontal SSFCWs

4.4.5 Sulfur Removal

Sulfur compound is mostly found in brewery wastewater in the form of sulfate and sulfide. Table 4.1 and 4.2 showed the average concentration of sulfate and sulfide in the effluent and corresponding removal efficiency from the constructed wetland cells. Very low sulfate removal efficiency was recorded by all four SSFCWs. However, planted SSFCWs performed better removal for sulfate and sulfide than the unplanted SSFCW system. ANOVA and LSD Post Hoc tests showed that there was no statistically significant difference ($P>0.05$) between the SSFCWs. But for sulfate removal between SSFCW 2 (*C.indica*) and control showed statistically different ($P<0.05$).

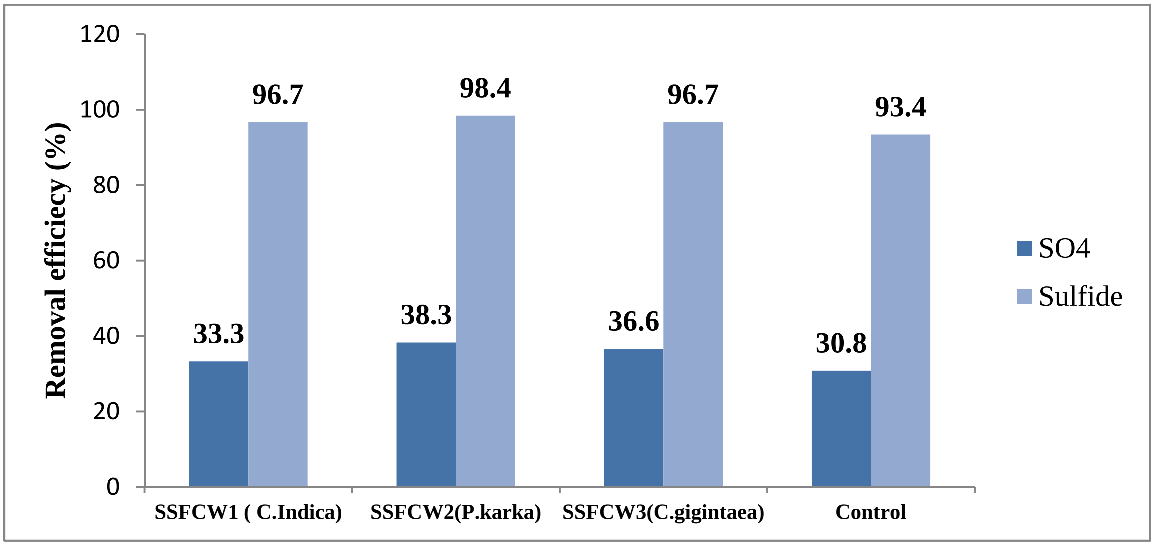

Figure 4.6 Sulfates and Sulfide Removal Efficiency of the Horizontal SSFCWs

As shown in figure 4.6, the maximum removal for sulfate and sulfide were observed in SSFCW planted with *p.karka* (38.3%) and (98.4%), respectively. The tests showed that the removal of Sulfide was not statistically significant differences ($P>0.05$) between planted SSFCWs and control. The low removal of Sulfate is not to be a source of environmental concern since the ambient surface water quality standard of Ethiopia for Sulfate is 200 mg/l and for sulfide 1mg/l and also effluents from all four of the SSFCWs were within the standard limit.

As study conducted by [52] showed sulfate and sulfide removal of 13.8% and 99.2% (*C.indica*), 10.7% and 98.9% (*C.altemifolius*) and 13.3% and 98.8% (*C.gigantea*) for dormitory wastewater using SSFCWs. The result obtained for the sulfate and sulfide removals were ranged between the results of above study. The low removal of Sulfate recorded may be due to the higher dissolved oxygen content in the effluents of SSFCWs, which the oxygen transferred to the systems as a result of root penetration (for planted SSFCWs). Ultimately the oxygen rich conditions deny the sulphate reducing bacteria of a suitable environment to survive and the low sulfate removal can be attributed to this fact. Better removal of sulfate also showed with planted SSFCWS in this study may be due to the usage of sulfate by microbial and plants.

On the other hand, the high removal of sulfide may be due to its unstable nature, readily reacts with metal to form precipitate metal sulfide. Further, sulfides can be oxidized to elemental sulfur and sulfates in the aerobic zones by microorganisms. This leads to the addition of sulfate amounts to the system, which lowers removal of sulfate from the systems. As well as the average temperature of the system ranges from 20.6 to 21.8^{O}C this may inhibit sulfate reduction.

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Considering the continuous variation in the discharge of wastewaters both quantity and quality due to the nature of the factory's operation, a brewery effluent can generally be characterized as medium to high strength waste. And the high proportion of these wastes can easily be degraded biologically and transformed to environmentally friendly substances and/or serve as potential resources. During the experimental study, the feeding of high strength brewery wastewater created very poor growing conditions for the plants, especially at the inlet parts. However, the three plants *C.indica*, *P.karka* and *C.gingantea* were able to withstand again the wastewater from the brewery.

From the result, it is clear that constructed wetland can remove and retain nutrients and pollutants from brewery wastewater. During the study, high removal efficiency for COD (80.3%), BOD_5 (75.4%), TN (84.1%), NH_4-N (64.3%), NO_3-N (59.3%), TP (71.4%), PO_4 (85.7%), sulfide (98.4%), TSS (68.4%) and TDS (54.7%) were observed in SSFCW planted with *P.karka.* The removal efficiency between the planted and the unplanted SSFCWs, during the study was much different for TN, TP and PO_4 of the parameter tested. This performance of the planted and unplanted SSFCW obtained in the present study may be explained due to nutrients can be up taken by plants. Therefore, the average removal efficiency of the three planted SSFCWs was much higher than unplanted SSFCW.

Comparison of planted SSFCWs for removal efficiency showed that SSFCW 2 planted with *P.karka* has better removal efficiency for the parameters and improved value of DO (2.9 mg/l). Therefore, from the three selected plants, *P. karka* was capable of removing organic pollutants and nutrients from brewery wastewater. Further comparing concentrations and values of the wastewater parameters under this investigation for the effluents of planted SSFCWs discovered that some of the results were within the range of National effluent emission standard limits for Ethiopia.

Generally, it can be concluded from the treatment performance of this experimental SSFCW systems that, data generated from this study can give an insight for the potential use of constructed wetlands as an alternative wastewater treatment system. The findings from this study indicate that, for brewery industry, with no land scarcity, CWs using selected plant species, could achieve a level of clean up and are often very cost effective and environmentally friend. Therefore, the development of this experimental system into a large-scale working unit offers an attractive alternative for low-level income countries to protect their environment.

5.2 Recommendation

The following recommendations are suggested for further application of SSFCWs and research on the area in order to begin horizontal subsurface constructed wetland system for the treatment of brewery wastewater in developing countries like Ethiopia, further study should be done on:

1. Horizontal subsurface flow constructed wetland using a combination of more than one type of plant is essential, as the various types of plants tolerate wastewater differently and their ability to remove nutrients from the effluent also differs.
2. Hydraulic retention time of 7 days has proven to give improved removal efficiency for nitrogen removal, so future works need to take longer HRT in to consideration.
3. Since secondary effluent of industrial wastewater from CWs were not met the standard limits for BOD_5, COD, TP and NH_4-N, further treatment is recommended.
4. A series combination of SSFCWs be used for further treatment to improve the removal efficiency of the system and the effluent be met the standard limits.
5. Further research on pilot scale or full scale SSFCWs need to be done to get more reliable results on their treatment capacity.

References

1. Seyoum Leta, Fasil Assefa, Gumaelius. L and Dalhammar G. (2004). Biological nitrogen and organic matter removal from tannery wastewater in pilot plant operations in Ethiopia. *Applied Microbiology, Biotechnology*. Springer-Verlag.
2. Zinabu Gebre-Mariam and Zerihun Desta (2002).The Chemical Compostion of of the effluent from Awassa Textile Factory and Its Effects on Aquatic Biota. *SINET: Ethiopia Journal Science*, 25 (2).
3. The Brewers of Europe Guidance Note for establishing BAT in the brewing industry(2002) http://www.brewersofeurope.org/asp/publications/publications.asp
4. Fillaudeau, L. (2006). Water, wastewater and waste management in brewing industries, *Journal of Cleaner Production* 14.
5. Mohammed Ali. (2002). Industrial pollution and its impact on little Akaki River, Addis Ababa.
6. Berhanu Genet (2007). Constructed wetland system for domestic wastewater treatment, a case study in Addis Ababa, Ethiopia, Master's thesis, in Environmental science. Addis Ababa University.
7. Vymazal, J. (1998). Constructed Wetlands for Wastewater Treatment in Europe, Backhuys Publishers and Leiden, Netherlands.
8. Heers, M. (2006). Constructed wetlands under different geographic conditions, Evaluation of the suitability and criteria for the choice of plants including productive species. Master thesis, Institute of Wastewater Management and Water Protection, Hamburg University of Technology, Department of Environmental Engineering.
9. Kumar, S. (2008**).** Performance Evaluation of Central Wastewater Treatment Plant. *Environment and Natural Resources Journal*, 6 (2).
10. Joseph, K. (2005). Nitrogen and phosphorus removal in substrate-free pilot constructed wetlands with horizontal surface flowin Uganda. Makerere University Institute of Environment and Natural Resources, Uganda, Stocholm, Sweeden.

11. USEPA (1993). Subsurface Flow Constructed Wetlands for Wastewater Treatment: A Technology Assessment, U.S. EPA Office of Water, EPA 832-R-93-008, Washington, D.C.
12. Asaye Ketema (2009). Evaluation of Selected Plant Species for the Treatment of Tannery Effluent in a Constructed Wetland System. Master's thesis, in Environmental science, Addis Ababa University, Addis Ababa.
13. UNEP (2007). Sustainable Water Utilization in African Breweries Current Practices and Prospects. A sector study and framework analysis of water consumption in African breweries with focus on the situation in Ethiopia, Ghana, Morocco and Uganda.
14. R.F. Weiner and R. Matthews (2003).Water pollution, Department of Nuclear Engineering and Radiation Sciences, University of Michigan, Ann Arbor, MI and Huxley College of Environmental Studies Western Washington University, Bellingham, WA, Environmental Engineering , 4th Edition.
15. Billore, S.K, Vipat, V. and Singh, U.R. (2008). Efficacy of Root zone Technology for Treatment of Domestic Wastewater. In proceeding of the 12th World Lake Conference on Field Scale study of pilot Project in Bhopal (MP), India, 995-1003.
16. BGI Ethiopia (2010). Sector report. http://www.accesscapitalsc.com/downloads/sector%20report--beer.pdf
17. Olajumoke, A. (2010**).** Impact Assessment of brewery effluent on water quality in Majawe, Ibadan and southwestern Nigeria**,** 2(5).
18. Yared Shumate (2008). Biological Nutrient Removal from Brewery Wastewater using a Laboratory Scale Anaerobic/Anoxic/Aerobic Bioprocess. Master's thesis, in Environmental science. Addis Ababa University.
19. Arcadio, P. and Gregoria, A. (2002). Physical-Chemical Treatment of water and wastewater. Morgan State University, Department of Environmental, Baltimore, Maryland.
20. Vymazal, J. and Kr^{+}opfelova, L.(2008). Wastewater Treatment in constructed wetland with horizontal subsurface flow Czech University of Life Sciences Prague Faculty of Environmental Sciences, Czech Republic.

21. Hagberg, A. (2007). Industrial wastewater treatment and other environmental problems in Wuhan-Is Swedish technology a solution. Department of Earth Sciences, Geotryckeriet, Uppsala University, Uppsala.
22. USEPA (1998). Constructed Wetlands and Aquatic Plant Systems for Municipal Water Treatment, Design Manual, United States Environmental Protection Agency, Office of Research and Development, EPA/625/1-88/022. September, 1998.
23. UNEP (1996). Division of Technology, Industry and Economics (DTIE). Cleaner Production in Breweries: A Workbook for Trainers, 1st edition, Paris.
24. Driessen, W., Vereijken, T. and Paques, B. (2003). Recent Developments in Biological Treatment of Brewery Effluent. *Institute and Guild of Breweryof Africa Sector. Proceeding 9th Brewing Convention, Victoria Falls, Zambia*, Netherlands.
25. Merwe, AI. V. d., and Friend, J.F.C. (2002). Water management at a malted barley brewery. Environmental Engineering Group, Department of Chemical Engineering, University of Pretoria, Pretoria, South Africa. *Water SA* 28**(**3). ISSN 0378- 4738.
26. EEPA (2003). Water Pollution in Ethiopia, Ethiopian Environmental Protection Agency, Addis Ababa, Ethiopia.
27. Metcalf and Eddy, Inc. (2003). Revised by: Tchobanoglous, G. and Burton, F.L. Wastewater Engineering–Treatment, Disposal and Reuse, McGraw-Hill, New York.
28. IWA (2006). Biological Wastewater Treatment in Warm Climate Regions, Marcos von Sperling and Carlos Augusto de Lemos Chernicharo Vol.1. Department of Sanitary and Environmental Engineering Federal University of Minas Gerais, Brazil.
29. Metcalf and Eddy, Inc. (1991). Revised by Tchobanoglous, G. and Burton, F.L. Wastewater Engineering Treatment, Disposal, and Reuse, McGraw-Hill, New York.
30. Manual of practice No 11, Operation of municipal Wastewater Treatment Plants, 6th edition, volume 1.
31. Bitton, G. (2005).Wastewater Microbiology.Department of Environmental Engineering Sciences University of Florida, Gainesville, Florida, Wiley-Liss, Inc, 3rd edition.

32. Indian Environmental Protection Agency (EPA) (1992). Fermentation Industry Wastewater Discharge Standards (Distilleries, Maltries & Breweries), Indian EPA, Delhi.
33. J.R. Pfafflin and E.N. Ziegler (2006). Encyclopidia of Environmental Science and Engineering, volume 2, 5th edition.
34. Franklin, J. and Patrick. J (2009). Enviromental Enginerring Water, wastewater, soil and Groundwater Treatment and Remediaation, 6th edition. John Wilery and Sons, Inc. ISBN: 978-0-470-08303-1
35. Ayaza, S. (2001).Treatment of wastewater by natural systems. *Environment International* 26.
36. Wikipidea (2007). Constructed wetland. Accessed on March 19th, 2009.
37. Oketch, M. A. (2006). The Potential Role of Constructed Wetlands in Protection and Sustainable Management of Lake Catchments in Kenya. Department of Environmental Science, Egerton University, Njoro, Kenya.
38. USEPA (2000). Constructed Wetlands Treatment of Municipal Wastewaters, Design Manual, United States Environmental Protection Agency, Office of Research and Development. Cincinnati, Ohio 45268. EPA/625/R-99/010, September, 2000.
39. Brisson, J. (2009). Maximizing pollutant removal in constructed wetlands. Should we pay more attention to macrophyte species selection? *Science of total environment* 40.
40. Vaillant, N., Monnet, F., Sallanon, H., Coudret, A. and Hitmi, A. (2004).Use of commercial plant species in a hydroponic system to treat domestic wastewaters. Journal of environmental Quality.33.
41. Scholz, M. (2007). What is the role of *Phragmites australis* in experimental constructed wetland filters treating urban runoff? Institute for Infrastructure and Environment, School of Engineering and Electronics, College of Science and Engineering, The University of Edinburgh, Scotland, *UK Ecological engineering* 29.

42. Brovelli, A. (2010).Design methodology accounting for the effects of porous medium heterogeneity on hydraulic residence time and biodegradation in horizontal subsurface flow constructed wetlands. *Ecological Engineering.*
43. APHA (1998). Standard Methods for the Examination of Water and Wastewater 20th ed. American Public Health Association/ American Water Works Association/Water Environment Federation, Washington DC, USA
44. Lee, Y.F. (2004). Rainfall Effects to the Performance of SSF Constructed Wetlands in Leahate Treatment. University of Technology Malaysia, Master's Thesis.
45. Kadlec, R.H. and Knight, R.L. (1996). Treatment Wetlands. CRC Press LCC: Boca Raton, Lewis Publishers, Florida.
46. Crolla, A. (2004). Constructed wetlands in Canada. ATAU Seminar, Morocco.
47. Kaseva, M. (2003). Performance of Subsurface Flow Constructed Wetland in Polishing Pre-treated water; a tropical case study. *Water Research.* 38.
48. Vymazal, J. and Kr+opfelova, L. (2009). Removal of organics in constructed wetlands with horizontal sub-surface flow. A review of the field experience *Science of the total environmen*t 407.
49. Reed, S.C., Crites, R. W., Middlebrooks, E. J. (1995). Natural Systems for Waste Management and Treatment; 2nd edition. McGraw - Hill, New York.
50. K.N. Njau and M. Renalda (2010). Performance of horizontal subsurface flow constructed wetland in the removal of tannins. Vol. 37, Department of Chemical and Process Engineering, University of Dares Salaam, Tanzania, Published by NRC Research Press.
51. Vymazal, J. and Kr+opfelova, L. (2008). Wastewater Treatment, Plant Dynamics and Management in Constructed and Natural Wetlands Institute of Systems Biology and Ecology, Czech Academy of Sciences, Czech Republic
52. Firew Eshetu (2010). Constructed Wetland as Municipal Wastewater Treatment Solution: A case study on experimental Vegetated Submerged Beds at Addis Ababa University. Master's Thesis, Addis Ababa University, Faculty of Science, School of Graduate Studies, Department of Environmental science.

53. Stewart, E. (2005). Evaluation of Septic Tank and Subsurface Flow Wetland for Jamaican Public School Wastewater Treatment. Master's of Science in Environmental Engineering, Michigan Technological University.

54. Tadesse Alemu (2010). Evaluation of Selected Wetland Plants for the Removal Efficiency of Chromium and Organic Pollutants from Tannery Wastewater in Constructed Wetlands at Modjo Tannery. Master's Thesis, Addis Ababa University, Faculty of Science, School of Graduate Studies, Department of Environmental science.

Annex-1 Laboratory procedures for wastewater parameter determination

1.1 COD Determination

Method: Open Reflux Method (APHA 5220 B)

Reagent: Standard potassium dichromate solution ($K_2Cr_2O_7$), Sulfuric acid reagent, Ferroin indicator solution, Standard ferrous ammonium sulfate (FAS) titrant, Mercuric sulfate ($HgSO_4$), Sulfamic acid and Potassium hydrogen phthalate (KHP) standard.

Materials: Reflux apparatus, consisting of 500-mL or 250-mL Erlenmeyer flasks with ground-glass 24/40 neck and 300-mm jacket Liebig, West, or equivalent condenser with 24/40 ground-glass joint, and a hot plate having sufficient power to produce at least 1.4 W/cm^2 of heating surface, Blender and Pipets.

Measurement procedure:

- Blend sample and pipet small portion diluted to 50 mL into 500-mL refluxing flask
- add 1 g $HgSO_4$, several glass beads and very slowly add 5.0 mL sulfuric acid reagent
- with mixing to dissolve $HgSO_4$, Cool while mixing to avoid possible loss of volatile materials
- add 25 mL 0.04167M $K_2Cr_2O_7$ solution and mix and attach flask to condenser and turn on cooling water, add remaining sulfuric acid reagent (70 mL) through open end of condenser
- Continue swirling and mixing while adding sulfuric acid reagent
- Cover open end of condenser with a small beaker to prevent foreign material from entering refluxing mixture and reflux for 2 h
- Cool and wash down condenser with distilled water, Disconnect reflux condenser and dilute mixture to about twice its volume with distilled water
- Cool to room temperature and titrate excess $K_2Cr_2O_7$ with FAS, using (2 to 3 drops) ferroin indicator
- Take as the end point of the titration the first sharp color change from blue-green to reddish brown that persists for 1 min or longer
- Evaluate the technique and quality of reagents by conducting the test on a standard potassium hydrogen phthalate solution

- Calculation

$$\text{COD as mg } O_2/\text{L} = \frac{(A - B) \times M \times 8000}{\text{mL sample}}$$

Where, A = mL FAS used for blank

B = mL FAS used for sample

M = molarity of FAS, and

8000 = milliequivalent weight of oxygen × 1000 mL/L.

1.2 Phosphorus Determination

Method: HACH method 8190 Molybdovanadate with acid per-sulfate digestion (APHA 4500-P C)

Reagent: Potassium per-sulfate powder pillows, 1.54NNaOHsolution, Molybdovanadate reagent, Deionized water

Materials: HACH reactor, HACH spectrophotometer model DR / 2010, Measuring cylinder and Pipette.

Measurement procedure:

- Reagent blank correction was prepared, For most accurate measurement, a blank used for each set of measurements ,
- The HACH reactor preheat to 150 ^{0}C and the cap removed from two reagent vials , 5ml of sample added exactly to one vial (sample vial) and 5 ml of deionized water added exactly to the other (blank vial).
- then one potassium per-sulfate reagent powder pillows for phosphorus analysis added to each vials , Each sample was shaked gently until all the powder is completely dissolved, Insert the vials into the reactor and heated them for 30 minute at 150 ^{0}C,
- At the end of digestion period the reactor switched off and allowed to cool to room temperature , 2ml of sodium hydroxide solution (1.54 N) added to each vial while keeping the vial at 45 degree,

- Replace the cap tightly and mix by inverting the vial a couple of time, 0.5 ml of molybdovanadate reagent added to each vial while keeping the vial at 45 degree
- Place the blank vial placed into the holder and push it completely down, Press timer and the display show the countdown prior to the measurement, alternatively, wait for 7 minute and pres zero in both case 'sip' will blink on the display, Press read direct and 'sip' will blink during measurement, Instrument directly displays concentration in mg/l of total phosphorus on the liquid crystal display

1.3 Total Dissolved Solids (TDS)

Method: Procedure 2540C and 2540E (APHA, 1998)

Apparatus: Evaporating dishes, Desiccator, Analytical balance, Graduated cylinder, Beaker Glass-fiber filter disks, Filtration apparatus (Membrane filter funnel and Gooch crucible), Suction flask, drying oven, for operation at 180 ± 2°C.

Procedure:

- Evaporating dish was prepared, Clean dish heat to 180 ± 2°C for 1 h in an oven, then the dish was stored and cooled in desiccator until needed,
- the dish Weigh immediately before used.
- Volume of well mixed sample was measured, the sample well mixed with magnetic stirrer and filtered with suction flask
- then washed with reagent grade water and continued suction for 3 min after filtration completed, Total filtrate was transferred to a pre-weighed dish,
- Drying the filtrate to 180 ± 2°C for at least 1h, the dish with sample cooled in desiccator to balance temperature, and weigh. Total weight of the sample was calculated as follows.

$$\text{mg total dissolved solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

Where, A = weight of dried residue + dish, mg, and

B = weight of dish, mg.