EFFECTS OF COUPLING ELECTROCOAGULATION WITH DUCKWEED BASED TREATMENT PROCESS IN THE MANAGEMENT OF INDUSTRIAL TEA EFFLUENT

GILBERT MAGUTT

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN ENVIRONMENTAL HEALTH AND BIOLOGY IN THE SCHOOL OF ENVIRONMENTAL STUDIES UNIVERSITY OF ELDORET, KENYA

SEPTEMBER, 2015

DECLARATION

Declaration by the Student

This thesis is my original work and has not been presented for a degree in any other University.

_____ _____

Gilbert Magutt Date

SES/PGH/09/ 09

Declaration by the Supervisors

This thesis has been submitted for examination with our approval as university supervisors.

_____ _____

Prof. Odipo Osano Date

School Environmental Studies,

Department of Environmental Health and Biology,

University of Eldoret

_____ _____

Prof. E. C. Kipkorir Date

School of Engineering,

University of Eldoret,

DEDICATION

I wish to dedicate this study to my family, in particular my wife and my two daughters Lindsay and Joy.

.

ABSTRACT

Discharge of untreated waste water into the receiving water bodies could cause ecological disruption which include but not limited to eutrophication. Any continued deterioration of water quality and quantity may lead to the decline in aquatic biodiversity. Tea factories have been singled out as industries that have a potential to compromise ecosystems with their waste waters. In spite of the industries' attempt to alleviate their wastes water problems with constructed wetlands, there is still a lot of discharge of effluents with high level of colour and other contaminants coupled with long treatment time needed. This study sought to assess the effects of coupling electrochemical technology with duckweed based treatment technology in the management of industrial tea effluent. The study used a complete block design, 36 basins were arranged into two distinct blocks of 18 basins each, i.e. raw effluent block (RE) and electrochemically treated effluent block (EC). Each of the blocks (RE) and (EC) were further sub divided into two sets of 9 basins each, one set of (RE) basins were treated with 50gms of duckweed plants *Lemna spp*, while the other set remain untreated. Similarly, EC treated effluents of 18 basins were sub-divided into two sets of nine basins each. One set of EC pre- treated effluent was further treated with 50gms of duckweed plants *Lemna spp* while the second set of nine basins were untreated It was found out that electrocoagulation process reduced colour intensity of industrial tea effluents by 53.6%, BOD by 55.0% and electrical conductivity by 32.5%. In addition, electrochemical process reduced the concentration of nitrates, nitrites, and total phosphates by 94.7%, 80.5% and 69.90%, respectively. Further, it was found that electrochemical process coupled with DWT reduced effluent retention by 5 days. The relative growth rate of duckweed plants grown on electrochemically pre-treated tea effluents was higher (62.7%) than those in non-electrochemically treated effluent (50.8%) after 15 days. The electrochemical process coupled with DWT in the treatment of tea effluents was found be cost effective and efficient in the management of tea effluents. EC technology also showed the ability to remove toxins that inhibit the growth of duckweed plants as well as its utilization of other nutrients. It is recommended that EC treatment should be integrated with plants of different species and rooting systems to achieve better results in nutrients uptake. Moreover, a combination of different plant species with different root structures be selected so that effective extraction of N and P lodged in the bottom of the basin is achieved. In addition, the EC reactor should be designed to automatically separate precipitated organic matter that would otherwise have undergone oxidation resulting in more colour formation.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF ABBREVIATIONS ACRONYMS

ADSW	Anaerobically digested swine effluent
BOD	Biological Oxygen Demand
CFU	Continues Fermentation Unit
COD	Chemical Oxygen Demand
CTC	Cut Tear Curl
D O	Dissolved Oxygen
D WT	Duckweed Based Treatment
DO	Dissolved Oxygen
DWT	Duckweed Treatment
E P K	Eastern Produce Kenya
ECF	Electrochemical Floatation
EEC	Electrochemically pre-treated effluent Control
EET	Electrochemically pre-treated effluent Treatment
EM	Effective Microorganisms
ERT	Effluent Retention Time
G.O.K	Government of Kenya
GBH	Gravel Bed Hydroponics’
KTDA	Kenya Tea Development Authority
NEMA	National Environment and Management Authority
PWC	Portable water control
PWG	Percentage Weight Gain
PWT	Portable water treatment

REC	Raw Effluent Control
RET	Raw Effluent Treatment
RGR	Relative Growth Rate
T F	Theaflavins
T R	Thearubigins
TDS	Total Dissolve Solids
WRMA	Water Resource Management Authority
WHO	World Health Organization

ACKNOWLEDGEMENTS

I am grateful to the University of Eldoret for giving me the opportunity to pursue this course in Master of science in Environmental Studies-(Health and Biology option).I also wish to extend my sincere thanks to my very able supervisors; Prof. Odipo Osano from the school of Environmental studies, department of environmental health and biology and Prof. E.C. Kipkorir Dean school of engineering who mentored and guided me throughout my research studies particularly for their informative and focused discussions on various aspect of my study that includes research design, data collection, data analysis and presentations of data among other issues. I also wish to acknowledge the contribution made by Mr. J. Maghanga, lecturer school of Agriculture, department of soil science for informative discussion too. I also acknowledge the assistance by Assistant General Manager Eastern Produce Kenya limited Chemomi Estate Mr. Paul Mbogua who allowed me collect samples from the company constructed wetlands for my research. I also thank the following; Prof. Etiegni Dean School of Natural Resources, Mr Orori lecturer in the department of wood science for their invaluable support in providing me with EC reactor , iron plates and for allowing me use their wood science laboratory. I am also indebted to the Department of chemistry and physics for allowing me use their laboratories and equipments too. Last but not least a big thanks to the M.D Eldoret Water And Sanitation Company and the chief technician Mr. Olal for allowing me use their laboratory for analysis of some of my effluent samples. And lastly I am also grateful to all the people who have in one way or another contributed to my successful collection of data, data analysis and editorial work. And finally I wish to thank all my colleagues in the department of Environmental studies (Biology and Health) for their encouragement

CHAPTER ONE

INTRODUCTION

1.1 Background of Study

Tea was introduced into Kenya from India in 1903 by European settlers. With an annual production of approximately 395.5 million kilograms, Kenya is the world's leading exporter of black tea (Tanui *et al.,* 2012). According to Kenta Tea Development Authority (KTDA), there are over 66 tea factories in Kenya most of which are in the Rift Valley region (KTDA, 2011). The tea industry in the country is structured into two main sub-sectors: the large estate and small holder sub-sectors. The latter sub-sector, with average holdings ranging from less than one hectare to twenty hectares, accounts for about 66% of the total area under the crop and 62% of the total production (Oriere, 2014; Anon, 2006).

Tea manufacture is such an elaborate process with a number of stages. Firstly the green leaves from the fields, are received; weighed and withered to reduce moisture content to a range between 65% - 67% to initiate vital chemical reactions. Secondly, they are then macerated (cut and curl) fermented and dried to about 13% moisture content. Thirdly tea fibre are systematically removed before black tea are sorted into various grades for packing (Kenya Tea Development Agency, 2011). Tea manufacture is a reduction of the leaf moisture content without any addition of water. The waste water generated from the tea factory emanates from the washing of the factory equipments such as; Cutting Tearing and Curling (CTC) machine, Continuous Fermentation Unit (CFU) troughs and the driers(Eastern Produce.Kenya Ltd, 2012; Wasewar *et al.,* 2009).

Since all the products formed during tea processing are coloured, the resultant waste water is also coloured. The coloured segments of waste water are usually theaflavins (TF) and thearubigins (TR) which are brown in colour (Liu *et al.,* 2005). After firing the dhool, benzotopoloneny ring forms the black colour that is usually seen in black tea (Maghanga, *et al.,* 2009; Liang *et al.,* 2003). This indeed explains the brick red colour

that is associated with infused tea. Tea factories are required to treat their effluents to standards set by National Environment Management Authority (NEMA), before being discharged into the environment (Murunga, 2012). There has been an upsurge in agro-based, industries, and use of fertilizers in growing tea that has led to environmental pollution. For efficient treatment of wastewaters from tea industries to be attained, reliable technologies are required. Even though remedial measures are being put in place, most remedial options are either too expensive or suffer from lack of technical knowhow (Singh *et al.,* 2003) (Dalu & Ndamba, 2003). Phytoremediation, which involves use of plants in waste water treatment, is an acceptable remedial technology that is not only efficient, and cost saving but also driven by natural energy and does not need a lot of capital to run (Pilon-Smits, 2005). It has also been found to be non-invasive alternative technology for engineering-based remediation systems (Singh *et al.*, 2003; Susarla *et al.,* 2002). The floating *Lemna* species has been identified to be one of most conducive plants for use in phytoremediation of wastewater treatment (Mkandawire & Dudel, 2007; Parra *et al.,* 2012).

1.2 Electrochemical Process

Electrocoagulation (EC) and electrocoagulation and flotation (ECF) processes was used in effluent treatment systems and was found efficient in the removal of inorganic pollutants and pathogens (Chen *et al.,* 2000; Amuda & Alade, 2006). EC technology was used in groundwater and surface water (Joffe & Kniopper, 2000; Rajeshwar & Ibanes, 1997). This study presents information pertaining to the removal of pollutants by electro coagulating wastewater sampled from Chemomi tea factory and integrating it with DWT. The main purpose of this study was to determine the applicability of EC process coupled with duckweed based treatment in industrial tea wastewater treatment. An electrocoagulation reactor used was made up of an electrolytic cell with anode on one side and cathode on the other. The conducting metal was iron metal sheet both at the anode and at the cathode (Mollah, *et al.*, 2001).

1.2.1. Electrocoagulation effects

The electrical current applied caused the dissolution of iron electrodes. The dissolved iron metal ions formed coagulating species and iron hydroxides that destabilize and bind the suspended particles and absorbs dissolved contaminant (Chen, 2004) and (Ganizares, *et al.*, 2005) this form the basis with which EC was used to clean the waste water.

1.3 Statement of the problem

Kenya is currently being faced with a fast growing population, increased demand for industrialization particularly Agro based industries and rise in the use of water. The consequence of this could lead to pollution of the stream, rivers and lakes by effluent from the fast growing tea industries that are discharging effluent into the receiving water bodies. Tea industries operating in Nandi County have set up constructed wetlands to help them purify tea effluent but with no much success. Tea effluent being discharged from these tea factories develops more colour as they flow from one surface cell to the next begging the question why? Discharge of such coloured effluent into the receiving water bodies could cause decline in aquatic biodiversity and limit the usage of such water. Any continued deterioration of water quality and quantity may lead to the ecological disruption which includes but not limited to eutrophication

1.4 Justification

Tea factory and other related agro-based industries are important to the economy of Kenya as a source of employment to the growing population, and foreign exchange earner. However, these industries could be polluting streams and rivers through their effluents. The Environmental Management and Coordination Act no 8 of 1999 Water Quality Regulation of 2006, Wetlands and River bank Regulations of 2006, and Water Act of 2002 (G.O.K, 1999) prohibit discharge of any liquid, fluid or substance into a flowing river, lake or wetland on or under its bed if the substance is likely to have an adverse effect on the water quality. Many tea factories have since constructed wetlands as cost effective means to treat / purify the effluent. However these constructed wetlands

have been found less effective in the removal of colour from tea effluent. *Lemna spp,* a predominant plant used, has several other benefits including livestock, pig and poultry feeds.

The Study of effects of coupling duckweed based treatment with electrochemical technology in the management of industrial tea effluent provided an excellent opportunity to interrogate the efficacy of Duckweed (*Lemna spp*) grown in the constructed wetland for the purposes of removing pollutants in the tea wastewater. The results of this study will be made available to the company management to assist them make informed decisions about factory waste water treatment.

1.5 General objective

This study sought to assess the effects of coupling electrochemical technology with duckweed based treatment process in the management of industrial tea effluent.

1.5.1 Specific objectives

i. To determine the effects of coupling electrochemical (EC) technology with duckweed based treatment (DWT) on the overall quality of tea effluent.
ii. To compare the relative uptake of Phosphate (P) and nitrogen (N) from raw and the electrochemically pre-treated tea effluents by Duckweed plants (*Lemna spp*).
iii. To assess and establish the effects of EC treatment on the relative growth rate (RGR) of *Lemna spp.*

1.6 Research Hypotheses

HA_1: There was a significant difference in the physico-chemical characteristics of tea effluents treated with DWT alone compared with those treated with DWT coupled with EC process.

HA_2: There was a significant difference in the relative uptake of Phosphates and Nitrogen between duckweed plants stocked in raw effluent compared to those in EC treated tea effluents.

HA_3: There was a significant effect on the relative growth rate (RGR) of duckweed

grown in EC treated effluent compared to those in raw industrial tea effluents.

CHAPTER TWO

LITERATURE REVIEW

2.1 Production of tea in Kenya

The world tea producing and exporting countries are: India, China Sri Lanka, Indonesia and Kenya which produce about 75% of the world production (Kinyili 2003). In Kenya, tea is grown in several counties namely; Kericho, Bomet, Nandi, Trans-Nzoia, Kiambu, Muranga, Kisii, Meru, Nyamira, Nyeri, Kakamega and Nakuru, these areas receives adequate amount of rainfall to support tea farming all year round (Gesimba, *et al.*, 2005). Tea industry in Kenya is the largest private sector employer for more than 80,000 people working directly in the tea farms and over 3 million earn their living from the sector indirectly (Kinyili, 2003). There are over fifteen tea factories and several tea estates in Nandi County, they are either owned by multinationals, government agency or individuals. Those owned by multinationals are; Eastern Produce Kenya Ltd and Williamson tea while Kenya tea development agency (KTDA) own and managed its factories while the rest are owned and managed by individual investors. EPK factories are, Chemomi, Savani, Kibwari, Kipchamo, Kapsumbeiywo, Kipkoimet and Siret all in Nandi Hills, while Williamson tea factories are Kapchorua, Kaimosi, and Tindiret while Kenya Tea Development Agency (KTDA) factories are Chebut and Chepkong'ony. Individually owned factories are Nandi tea, Ogirgir and Koisagat.

2.2 State of Environment at Chemomi tea factory

Chemomi estate supports a forest consisting of interspersed tall trees dominated by a mixture of indigenous trees, and a dense undergrowth mat of herbs dominated by climbers and several pockets of cypress, pines, and eucalyptus plantations. Agricultural activities within and around Chemomi area revolve around tea farming (*Camellia sinensis*) which is an important cash crop species in Kenya.

Chemomi factory receives and manufacture tea from leave supplied from its own farms surrounding the factory estimated to be about 1506 Ha. These farms are; Kapkeben tea estate 536 Ha, Kaitet tea estate 330Ha, and Kapsigak tea estate 640Ha. The factory also

receives green leave from their sister estates namely; Kipsitoi and Valerie divisions. Other sources of green leave are several small scale cooperative societies ran by farmers namely; Kapsean, Kirondio, Kosoiywo, Siksik, Kaboi, Sarma, Mugundoi and Chesuwe all located in Nandi hills Sub-County. (Eastern.Produce Kenya 2010). Owing to regular fertilizer application in their farms notably, NPK, Urea, Zinc oxides among other forms of foliar feeds, waste water generated from the washings of the factory equipment's are rich in nitrogenous and phosphate fertilizers. The Levels of Phosphorous and Total nitrogen in the effluents produced from these factories vary from one factory to another and use of bio remediation to treat them was assessed to determine their efficacy. A number of processes like activated carbon, burn charcoal, activated sludge, hey and saw dust have been tried but they suffer from several draw backs such as high cost and many absorbent materials needs to be chemically activated to increase their absorption efficiency (Garge, *et al.*, 2005).

Tea factory wastewaters contribute to a greater extend to the pollution of the surrounding rivers and streams. The rise in water pollution has resulted in the formulation of laws and regulations on wastewater discharge into the aquatic environment. Many tea industries are now faced with the challenges of upgrading their existing wastewater treatment works in order to comply with wastewater regulations set by NEMA and WRMA. However, high construction costs, Land requirement, maintenance expenses and rising labour costs, in wastewater treatment systems have become uneconomical to run. Nitrogenous and phosphorus based form of fertilizers are some of the key pollutants which are released into the aquatic environment through effluents generated from these tea factories.

Millennium Development Goal No.7 provides that: "To ensure environmental sustainability, adequate treatment and disposal of wastewater contribute to better ecosystem conservation and less stress on scarce freshwater resources" (Gleick *et al.*, 2002). The state is bestowed with the duty of eliminating processes and activities that are likely to endanger quality environment (G.O.K., 2010). The Act prohibits deposit of any substance in a lake, river, wetland or under its bed, if that substances would or is likely to have adverse environmental effects on river, lake quality or quantity of water (G.O.K,

1999; G.O.K., 2006). The Act further outline various environmental offences and related penalties associated with noncompliance. Right to clean and health environment has been provided for by the Kenyan constitution under the bill of right, and therefore everyone is entitled to it. Safeguarding the environment is everyone's responsibility and its everyone's duty to enhance it (G.O.K., 2010). Environmental agencies have been established to supervise and coordinate matters of environment and develop local standards for waste water being discharge into the aquatic environment**.** These authorities have developed guidelines for sound environmental management. These institutions are; National Environmental Management Authority (NEMA) and Water Resource Management Authority (WRMA).

2.3 Remedial Measures

2.3.1 Phytoremediation

Phytoremediation involves the use of plants to clean and restore polluted wastewater. Duckweed are naturally floating plants found in water and they are applied to remove both organic and inorganic pollutants from the effluent. Bioremediation and phytoremediation are new technologies used in restoration of contaminated environment back to health (Salt *et al*., 1995). Conventional chemical methods used in the removal of toxic metals were found to be inefficient when their concentrations in the waste water were very low for example between 10-100 mg/cm^2 (Volesky, 1990). Duckweed plants (*Lemna spp)* were able to remove heavy metals ions from the effluent through bio sorption process (Aravindan, *et al.*, 2004). Studies have also showed that there has been an increasing interest in designing cost saving and environmentally friendly systems for the restoration of contaminated soils and water (Zayed, *et al.*, 1998). Some plants were capable of accumulating heavy metals and other nutrients from contaminated wastewaters and could be exploited for cleaning industrial waste waters (Jain, *et al.*, 1989) and (Boonyapookana, *et al.*, 2005).

2.3.2 The Duckweed plants

Duckweeds are aquatic plants composed of a large family of a number of genera one of which is *Lemna species.* Duckweed family has five genera, *Lemna, Landoltia, Spirodela, Wolffia and Wolffiella* and are naturally occurring in fresh on waste water and are found floating on calm water surface (Les, *et al.,* 2002).Duckweed plants prefer full sunlight but could adapt well to low light conditions (Iqbal, 1999; Leng, *et al.,* 1995).Other researchers observed that duckweed could tolerate a wide pH range of 4.5 – 8.0, however, a pH greater than 9.5 inhibits duckweed growth (Caicedo, *et al.,* 2000; Cross, 2004). The optimum water temperature range for duckweed growth was found to be between 17^{o}C and 35^{o}C (Iqbal, 1999).

Duckweed plants occur naturally in water with decaying organic matter (Smith & Moelyowati, 2001). Ammonia nitrogen in its ionized form (ammonium NH_4^+) and phosphate has been found critical and a pH above 8.5 gradually transform ammonium into the un-ionized state (NH_3) resulting in the release of free ammonia molecules attributed to toxicity in duckweed plants (Caicedo *et al.,* 2000).

When ammonium levels are limited, duckweed plants are able to use other forms of nitrogen present especially nitrate (NO_3) and simple organic molecules to sustain its growth (Skillicorn, *et, al.,* 1993) Duckweed plants reproduce vegetatively, about 10 times in its lifecycle (Skillicorn *et al.,* 1993).

2.3.3 Duckweed Capacity in wastewater treatment

Since early 1970s, a lot of work has been done on the use of duckweed plants as a means of treating agricultural and domestic wastewater (Obek & Hasar, 2002; Smith & Moelyowati, 2001). Duckweed grows well in nutrient-rich effluents creating an anaerobic environment in the waste water which encourages anaerobic condition for digestion and denitrification of wastewater (Cheng, *et, al.,* 2002; Landesman, 2000; Landesman, *et al.,* 2005).

The capacity of duckweed to eliminate organic material in waste water was found to be lower compared to other higher plants (Gerard, *et, al.,* 2002). Phosphate elimination was

however, higher in halophytes compared to the duckweed-dominated systems because phosphates were found lodged on the gravel beds in the benthic zone of the constructed wetlands (Vyamazal, 2005).

Duckweed plants species have been used to recover nutrients from wastewater for over 30 years (Mohedano, *et, al.,* 2012). These plant materials are a good source of proteins and starch, for improving the nutritive value of the animal feeds and bio-ethanol (Landesman, *et al.*, 2011).

The ability of duckweed and azolla culture plants to grow and remove nutrients from different dilutions of anaerobically digested swine effluent (ADSW) sampled , and prepared from swine lagoon wastewaters showed inhibitory effects on duckweed growth (Muradov *et al.,* 2014).However, the rate of nutrient uptake was lower than when *Spirodela punctata* was grown under lab conditions using anaerobically digested swine wastewater (2.03g/m^2/day of Total nitrogen and 0.4g/m^2/day for total phosphorus (TP) (Cheng *et al.*, 2002; Cheng & Stomp, 2009).

2.3.4 Duckweed-based Wastewater Treatment

Duckweed based waste water treatment (DWT) is different from the conventional lagoon systems because they prevent planktonic algal growth. Nutrients contained in phytoplankton was found difficult to harvest and as such they could be released back into the waste water, whereas duckweed was easy to harvest (Bonomo, *et al.*, 1997).

Heterotrophic bacteria decompose organic matter into some forms of ammonia nitrogen and orthophosphates that are readily taken up by the duckweed plants (Smith & Moelyowati, 2001). Duckweed mat was also found to maintain the bottom layer of about 10cm of the effluent anaerobic by blocking oxygen, leaving surface layer aerobic due to atmospheric oxygen being transferred by duckweed roots (Hancock & Buddhavarapu, 1993). Sedimentation of organic matter and volatilization of ammonia were the processes that help in the removal of nitrogen in DWT system (Smith & Moelyowati, 2001). They also reported that the amount of Phosphorous in the effluent was reduced in DWT system

by; plant uptake, absorption of Phosphorus into organic matter, chemical precipitation and sludge removal. Figure, 1, shows nitrogenous nutrient flow in the environment.

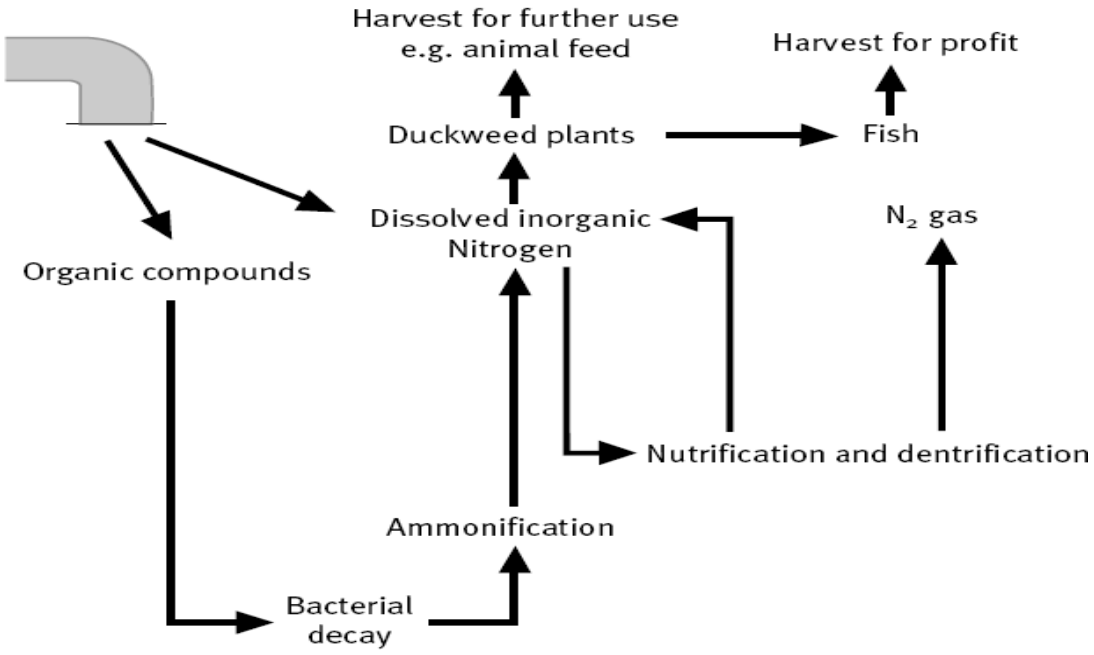


Figure 1: Nitrogenous nutrients flow within a DWT system.

(Source: Iqbal 1999)

2.3.5 DWT Effectiveness

The effectiveness of DWT was found to vary with the design of the system and other factors which includes; organic loading rate, water depth and hydraulic retention time which was further found to vary with effluent source and the level of pre-treatment (Skillicorn *et al.*, 1993).

Duckweed required acclimatization period to adjust to high Nitrogen levels in raw industrial wastewaters (Phan, 2002). Efficiency of DWT was enhanced by removing organic sludge and transforming it into simple organic and inorganic molecules that were readily used by duckweed (Caicedo *et al*., 2000; Dalu & Ndamba, 2003; Smith & Moelyowati, 2001).

2.3.6 Nutrient uptake

Duckweed was used as a nutrient sink in the effluent treatment works, and a lot of nutrients extraction occur from the effluents into the duckweed resulting in high biomass achieved leading to nutrient depletion (Skillicorn *et al.*, 1993). Duckweed plants when starved of N and P nutrients could scavenge for nutrients, heavy metals and toxins present in the effluent (Skillicorn *et al*., 1993)

2.3.7 Duckweed Harvesting

Biomass produced by duckweed *Lemna spp* was found to be proportional to the amount of nutrients present in the waste water. Biomass growth gradually increases exponentially until overcrowding occurred inhibiting reproduction. The growth of the duckweed was found to be dependent on the sites, local climatic conditions, available nutrient and duckweed species (Landesman *et al*., 2005). A trial conducted in Burdekin showed that the duckweed biomass could double from the density of ($1kg/m^2$) before overcrowding could occur and causing slow growth (Willett, *et al.*, 2003).

2.4 Electrochemical treatment of Wastewater

Electrocoagulation (EC) reactor consists of a pairs of iron metal plates referred to as electrodes, anodes on one side and cathodes on the other end. Using the principles of electrochemistry, the cathode losses electrons, while the waste water gains electrons, making the effluent quality improved. The electric current applied is able to remove small organic matter by electrocoagulating them and causing them to float. The EC process, makes the particulates matter float at the top of the tank aided by hydrogen bubbles created and released from the anode (Butler, *et al*., 2011).

Coagulation of particle matter occurs when the electric current is applied into effluent setting the dissolved particles into motion making them attracted to each other consequently forming small flocs (Shammas, *et al.*, 2010) . Electrocoagulation electro flotation processes could achieve a higher level of COD removal from the effluent by optimizing various parameters which includes; electrical intensity, effluent pH and

temperature, and the type electrodes used (Yang, 2009). EC effluent treatment system is depend on the electrical current and the type of electrode used (Chen, 2004; Chen, *et al.*, 2002). Electrochemical treatment technology is effective with low maintenance cost, minimum labour requirement and gives the desired results when used in water treatment (Feng, *et al.*, 2003).

Electrocoagulation-flotation was found to remove a higher COD and SS from effluents when compared with the usual coagulation (Jiang, Graham, Andre, & Kelsall, 2002). The insoluble iron hydroxide removes pollutants from the effluent by way of surface complexation and or electrostatic attraction (Maghanga *et al.,* 2009). The prehydrolysis of Fe^{3+} cations has been found to lead to the formation of reactive ions for effluent treatment (Mollah *et al.*, 2001). Electrochemical technology has been used effectively in the removal of effluent colour from Kraft mill in paper industry in Kenya (Orori, *et al.*, 2005).

Electrochemical process (EC) efficiency is influenced by factors that includes; electrode materials used, applied current density, treatment time and solution chemistry of the effluent i.e. (pH, chemical solution of the effluent, solution temperature and conductivity) and the gap between electrodes (Kuokkanen, *et al.*, 2013). However, electrocoagulation combined with wood ash leachate, applied on the pulp and paper mill effluent, reduced COD by 80.6% (Etiégni *et al.*, 2010). When EC electrocoagulation was applied on domestic sewer using iron electrodes, COD was removed by 60% (Ilhan, *et al.*, 2008). Electrochemical processes through oxidative and reductive reactions could destroy Nitrate ions into harmless constituents such as water, nitrogen and oxygen (Paidar, *et al.*, 1999). The following cathode reaction is an EC reduction of nitrate ions to nitrogen and ammonia (Rezaee, *et al.*, 2011).

$NO_3^- + H_2O + 2e \leftrightarrow NO_2^- + 2OH^-$, ……*eq.1*

$NO_3^- + 3H_2O + 5e \leftrightarrow 12N_2 + 6OH^-$,……*eq.2*

$NO_3^- + 6H_2O + 8e \leftrightarrow NH_3 + 9OH^-$,……*eq3*

$NO_2^- + 2H_2O + 3e \leftrightarrow 12N_2 + 4OH^-$, ……*eq.4*

$NO_2^- + 5H_2O + 6e \leftrightarrow NH_3 + 7OH^-$, ……*eq. 5*

$NO_2^- + 4H_2O + 4e \leftrightarrow NH_2OH + 5OH^-$, ……..*eq.6*

The reaction at cathode is hydrogen evolution

$2H_2O + 2e \leftrightarrow H_2 + 2OH^-$ ……...eq.7

While the main anode reaction is oxygen evolution

$4OH^- \leftrightarrow O_2 + 2H_2O + 4e$ ……....eq.8

A high concentration of nitrite in drinking water was found to cause temporary blood disorder in young children called methemoglobinemia (blue baby syndrome) (European Commission, 2006). Nitrate could also convert to nitrite in the human body reacting with certain amine containing substances found in food to form nitrosamines, which are potential cancer causing chemicals. Ammonium ion in effluent retards the nitrite removal due to oxidation reaction of ammonium ion to nitrite then oxidized to nitrate (Benefield, 1998). Nitrate is harmful when present in water and should be removed. High nitrate concentration in water has detrimental effect on environment and limits the use of water for both domestic and industrial use. According to European Environmental Commission (EEC), the maximum allowable concentration of nitrate as NO_3 in drinking water is 50 mg/ l (15 mg/ l for young children).

2.4.1 Applied voltage effects

The amount of current supplied to EC system determines the amount Fe^{2+} ion released from the electrodes and the amount of coagulants resulting from the process. The iron ions get dissolved and forms $Fe(OH)_2$. Electrical potential also determine coagulants dosage rates as well as bubble production rate and floc size (Letterman, *et al*., 1999).

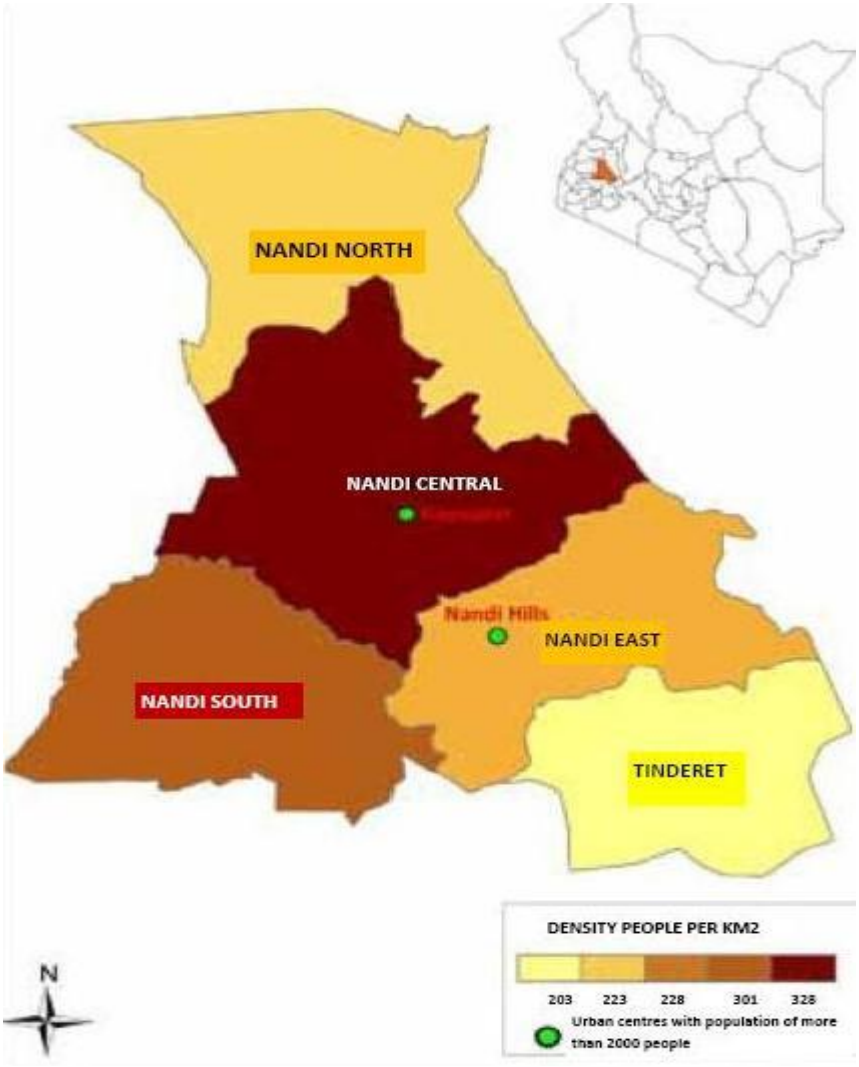
CHAPTER THREE

MATERIALS AND METHODS

3.1 Source of the test plants and the effluent

The effluent samples and duckweed plants under study were collected from Chemomi tea factory constructed wetland in Nandi County. The area is described by latitude 0 06N to 0 08N and longitude 35 08'E to 35 10'E- 2000 metres above sea level.

Figure 2: Map of Nandi County



(Source: Nandi county website)

3.2 Climatic conditions of the area

The area is hilly and generously cool and moderately wet with average rainfall of between 1,200mm-2000mm per annum. This climatic condition is favourable for tea and other agricultural activities such as livestock rearing. Chemomi tea estate lies within climatic zone 11; humid and high tea production area (Pratt & Gwynne, 1977).

3.2.1 Description of the sampling site

Chemomi constructed wetland is situated on a gentle slope. The constructed wetland is used to treat and clean factory effluent generated from the washing of factory machinery used in tea manufacture. After day long tea manufacture, machines are washed which generates about $50m^3$/day of effluent. Monday is maintenance day and all machines are cleaned and serviced generating about $70m^3$ of waste water,(E.P.K, 2010).Chemomi constructed wetland is a biological treatment system established in 1999, designed to treat tea effluent from the factory. The process of cleaning the effluent begins with separating suspended tea particles from the effluent through sedimentation process. Sedimentation tanks are designed to remove suspended tea particles at this stage and effective micro Organisms added (EM). Tea effluent is then allowed to flow into gravel bed hydroponics (GBH) with eight chambers. The (GBH) chamber is designed to hold the factory effluent for a week. It is at this stage that the effective microorganisms (EM) are given an ample time to break down the organic matter (decomposition) so that the nutrients are released to the plants. The (EM) technology was developed in 1970's at the University of Ryuku Okinawa, Japan(Sangakkara, 2002).Studies have shown that EM have a wider applicability including agriculture, livestock, composting, bioremediation, cleaning of septic tanks, control of algae among others (Higa & Chinen, 1998). EM is a multi-culture of coexisting anaerobic and aerobic beneficial microorganism (Higa & Chinen, 1998).The main species involved in EM includes; lactic acid -bacteria- *Lactobacillus Plantarum, L, Casei*, *Streptococcus Lactis*, photosynthetic bacteria *Rhodopseudomonas Palustus; Rhodobacteria Spearoides*; yeast and fermenting fungi. EM is preferred because it contains various organic acids due to the presence of lactic acid bacteria. EM can be used as a sterilizing compound and enhances decomposition of

the tea particles (Samson, 2010). Once organic sludge is removed at the sedimentation tank, tea effluent rich in nutrient such as nitrogenous and phosphates fertilizers are passed through the gravel bed hydroponics (GBH**).**

The sample site at the Chemomi constructed wetland marked as sample point **1** as shown by the Figure 3 was purposively chosen during a reconnaissance visit site. Effluent sample used in the treatment were collected using sterilized containers of 20litres each and transported to the University of Eldoret for treatment, to evaluate the effectiveness of coupling duckweed with EC technology in the management of industrial tea effluent.

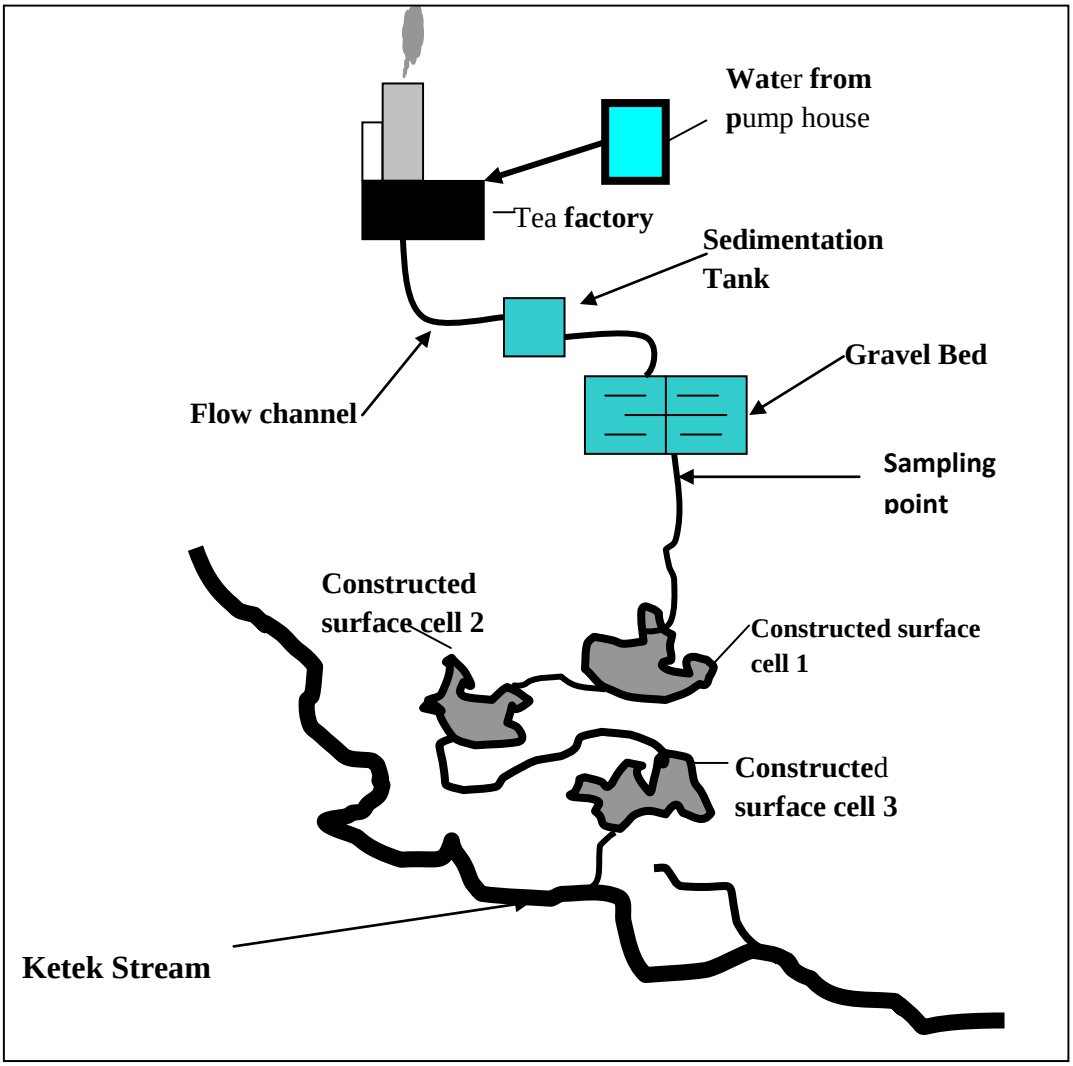


Figure 3: Sampling sites at Chemomi Constructed Wetlands

3.3 Research Design

The experiment was set up at the University of Eldoret, school of natural resources where a greenhouse was constructed The study adopted a complete block design, briefly, 36 basins were arranged into two distinct blocks of 18 basins each, i.e. raw effluent block (RE) with 18 basins and electrochemically treated effluent block (EC) with 18 basins. Each of the (RE) and (EC) blocks were further sub divided into two sets of basins each with one set of each (RE) and (EC) basins being treated with 50gms of about 8 young duckweed plants *Lemna spp*, while the replicate of (RE) and (EC) set remained untreated (control), as shown in Figure, 4.

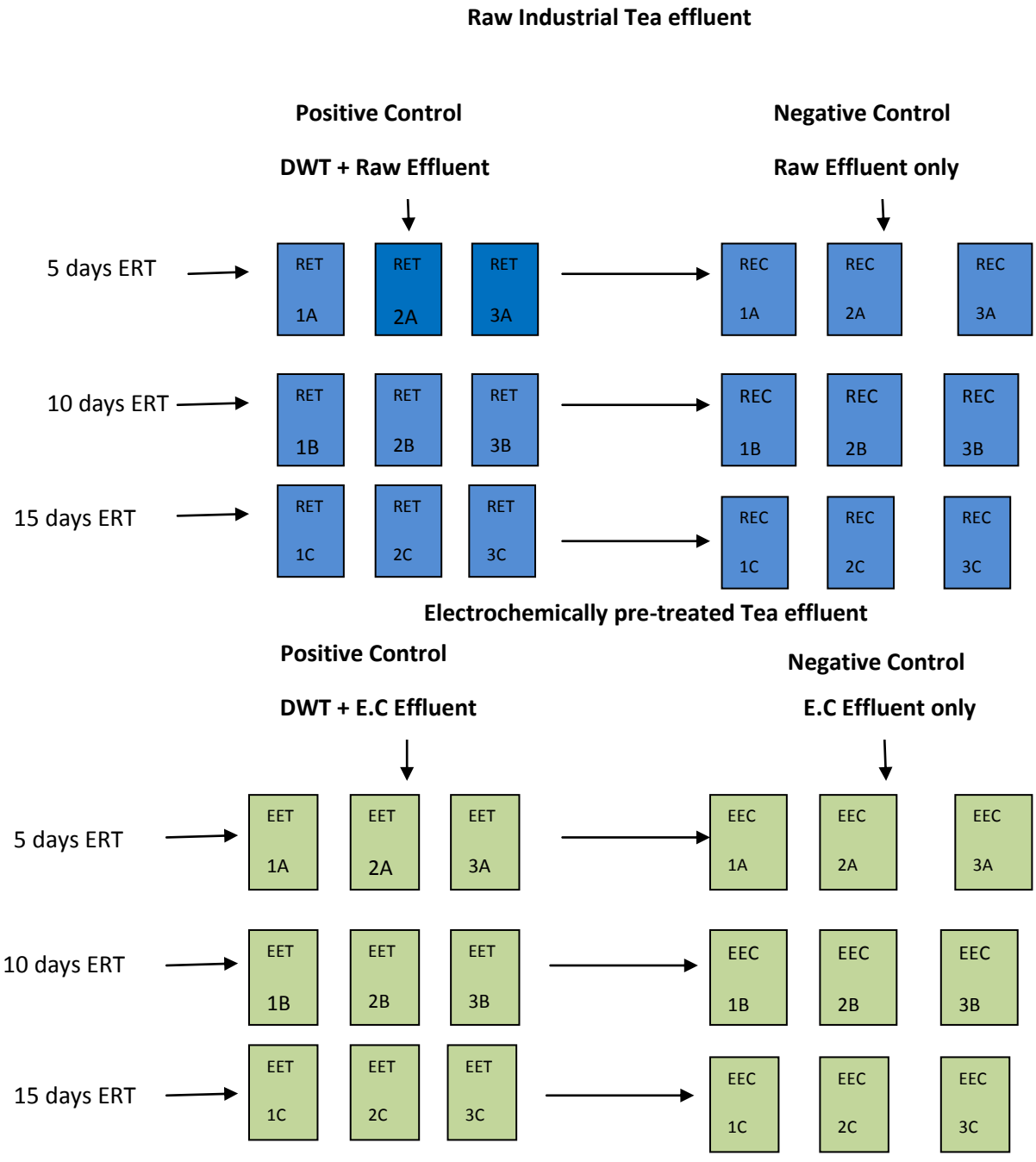


Figure 4: Schematic diagram of experimental Design

Where

RET – Raw effluent Treatment

REC- Raw effluent control

A: 5 days ERT

B 10 days ERT

C: 15 days ERT

1st Column

Second column

3rd Column

ECT- Electrochemically pre-treated effluent treatment

ECTC- Electrochemically Pre-treated Effluent Control

Figure 4 shows 36 basins in blocks of nine each. Each block had 18 basins divided into a treatment set and a control set. Block one had been divided into two sets of 9 basins each, one with wastewater treated with duckweed and another without duckweed treatment (control).while the second block similarly had two set of 9 basins each with waste water treated with EC, one set of 9 basins were further treated with duckweed plants, while the second set of 9 basin were not treated with any plants (control).

3.3.1 Sample collection site

The sampling site was systematically identified as shown in the figure 3 above so that effluent sampled would be a true representative sample from the tea factory and that they were inoculated with Effective Microorganisms (EM) solution to facilitate the decomposition of tea organic waste. The site chosen was also ideal because the tea

effluent at this stage was in the process of decomposition after being held in the area (GBH) for one week.

3.3.2 Sampling procedures, sample collection and handling

Industrial tea effluent was sampled on a Monday of October, 2012 at 9.00am. The total amount of effluent required was 200litres, where 100litre of these would be pre-treated with electrocoagulation process before subjecting to DWT. Raw tea effluent was collected from GBH outlet. Ten containers of about 20 litres each were used to carry sample effluent. The containers were thoroughly cleaned, and rinsed with some wastewater from the GBH to ensure that no contamination occurred. The waste water was then filled in each of the containers before; their pH and temperature determined and recorded and transported in cooled chambers to the University of Eldoret laboratories for electrochemical treatment and later to the School of Natural Resources nursery for subsequent treatment with the Duckweed based treatment(*Lemna spp)* for 5,10,15 days respectively.

3.3.3 Pre-treatment of industrial tea effluent

Industrial tea effluents were systematically divided into two equal volumes of 100 litres each. Portion one was subjected to electrochemical treatment for 3 hours before they were taken to the school of Natural resources Tree Nursery together with the other batch of 100 litres raw effluent for further treatment with the duckweed based treatment (*Lemna spp*).

3.3.4 Electrochemical treatment of tea Effluent

Wastewater was collected from Chemomi tea factory constructed wetlands (GBH) outlet. Chemomi tea factory generates about $50m^3$ of wastewater per day. The wastewater was first filtered to remove large suspended solids before it was used for the subsequent studies. The experimental setup is shown in Figure 5. The electrocoagulation reactor (tank) was made of plastic tank with capacity of 100 litres and the dimensions 48cm x 40cm x 60cm. There were eighteen iron electrodes used, (nine anodes and nine cathodes

of the same dimensions) measuring 48.5cm long, 30cm in width and 10.2mm thick. The total effective electrode area was 1455 cm^2 and the spacing between electrodes was 1.5cm. The electrodes were connected to a digital dc power supply (Top ward; 12V, 6A). All the runs were performed at constant temperature of about 20 ^{0}C and manual stirring using a non-conducting rod. The current density was adjusted to a desired value of 6V and then the operation was started. At the end of EC process, the solution was filtered, and then the filtrate were collected for further treatment with duckweed plants *Lemna spp* and was later sampled for analysis after 5days, 10 days and 15 days ERT respectively. After 1.5hours run, the electrodes were scrapped with steel wire and washed with clean running tap water to remove coagulants and the impurities on the iron electrode surfaces then resumed operation. At the end of the run, the electrodes were washed thoroughly with water to remove solid residues on the surfaces, and dried. The experiment was operated as a batch.

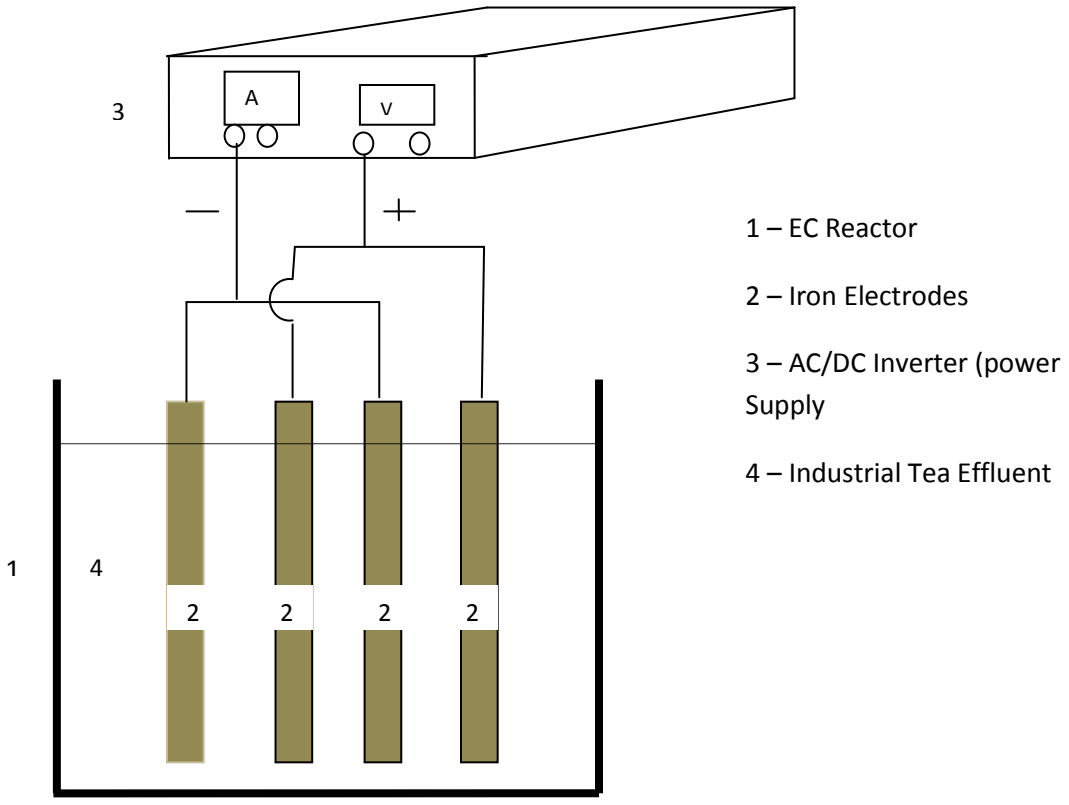


Figure 5: Schematic Diagram of Electro-coagulation Process

3.4 Duckweed Based Wastewater Treatment

3.4.1 Preparation steps

A system of growing duckweed in opaque PVC basins was constructed in a shade made of polythene and some scattered leaves at the University of Eldoret. Each basin was measuring 30cm in diameter and 10 cm high. These basins were arranged in sets of nine. Each basin in the first block was supplied with 5litres of raw industrial tea effluent and the second block was supplied with 5litres of EC treated industrial tea effluent. 50g of fresh young duckweed plants about (8) *Lemna spp* were stocked in each set of nine basins in each block i.e. in (RE) block (treatment) and similarly in the EC (treatment) block as shown in plate 1.. The level of industrial effluent in each basin was marked and topped up with distilled water after every two days to make up for water loss due to evaporation.

Plate 1: Experiment Showing Duckweed Based Treatment

(Source: Author 2012)

After every five days, duckweed plants *Lemna spp* used in effluent treatment tea effluent were harvested from the identified basin at once, weighed and dried for Total nitrogen (TN), and Total phosphates (TP) analysis. This system was used to test the effects of two different setups on the growth rate of duckweed as well as accumulated nitrogen and

phosphate content in the plant. Duckweed plants from the identified basin were collected at the end of each trial run, dried and analyzed for their TN and TP content.

The growth responses of duckweed plants (*Lemna spp)* were determined by using two measures:

- Relative growth rate (RGR or $\log_e$ Final Wt - $\log_e$ Initial Wt) / days of growth)
- Percentage Weight Gain (PWG or wet weight increase divided by the initial wet weight / days of growth).

Together these two parameters compared growth rates in a way that corrects for the differences in scale between 250 ml beaker in a growth chamber and a 3 m long tank in a greenhouse (South, 1995).

3.4.2 Duckweed Sampling

Duckweed from identified basin was all harvested at once whenever it was due. Systematic selection was used to collect samples from identified basin every five days. Subsurface (under duckweed mat) water samples were collected in polyethylene bottles from all sides of each identified basin for analysis of physico-chemical parameters as well as total nitrogen, nitrites, nitrates and Phosphate elements. The procedure of collecting samples was repeated every 5,10 and 15 days respectively.

3.5 Chemical analysis

This section presents methods, equipment and procedures followed to determine various parameters.

3.5.1 Biochemical Oxygen Demand

Biochemical Oxygen Demand (BOD) is a biochemical test which determines the amount of organic matter oxidized by the activities of aerobic bacteria in a period of *5* days at 20°C.

Reagents

Reagents used include phosphate buffer solution which was prepared by dissolving 8.5g KH_2P0_4 , 21.75g K_2HP0_4, 83.49 Na_2HPO_4. $7H_20$ and 1.7g NH_4CL in 500ml distilled water and diluted to 1 litre and the PH was kept at 7.2; magnesium sulphate solution was prepared by dissolving 22.5 $MgS0_4.7H_20$ in distilled water and diluted to 1litre; calcium chloride solution was prepared by dissolving 0.25g $FeCl_2$ in distilled water and diluted to 1 litre; and Glucose –glutamic acid solution was prepared by drying reagent –grade glucose and reagent –grade glutonic acid at 130^0c for one hour. Then 105 mg glucose and 150 mg glutonic acid were added to distilled water and diluted to 1 litre for a standard to check the seed and dilution water.

Dilution Water

The distilled water is aerated for use as dilution water

Procedure

The pH of the sample was first adjusted to 7 with 1N. H_2SO_4 or 1 N.NaOH , prior to the analysis to ensure that not all the oxygen of the sample is exhausted during incubation. The required volume of dilution water is carefully added into a graduated cylinder of 1 or 2l capacity and the known quantity of the sample is added to it. The diluted sample is then transferred to two BOD bottles. One of them is incubated at 20°C for 5 days in a BOD incubator. The dissolved oxygen in the second bottle is determined immediately by the Winkler titration method. This will give the initial dissolved oxygen content of the sample. The succeeding dilutions of lower concentrations are prepared in the same manner. All the samples and blank dilution water is determined by the above method. Those dilutions showing residual dissolved oxygen of at least 2mg/I are considered to the most reliable. (APHA, 1998).

BOD was determined as follows'

Calculation

$$BOD\ (mg/l) = \frac{(I-F) - (I'-F')\ (X/Y)}{D} \quad \text{.....equ 9}$$

Where, I = initial dissolved oxygen content (DO) of the sample and seeded dilution water

F = Final DO of the sample and seeded

I' = Initial DO of the seeded dilution water

F' = Final DO of the seeded dilution water

X = ml seeded dilution water in the sample bottle

Y = ml in the bottle with only seeded dilution water

D = Dilution of the sample

3.5.2 Chemical Oxygen Demand (COD)

The chemical oxygen demand is a measure of the total amount of oxygen which is required to completely oxidize all the organic matter in a sample to carbon dioxide. It is based on the principle that almost all organic compounds in water can oxidized to carbon dioxide and water by the action of strong oxidizing agents under acid conditions. The excess chromate can be measured by back titration with ferrous ammonium sulphate using the ferrion indicator to detect the end point.

A reflux apparatus consisting of a 250-ml Erlenmeyer flask with ground –glass neck, and a 300-mm double surface condenser (Liebig, Friedrichs,West) with a ground glass joint, and a heating mantle were used in determination of COD.

Reagents

Reagents used include; 0.0417mol per litre Sulphuric acid ; standard potassium dichromate solution(made by dissolving 12.259g of K2Cr207 primary standard grade, dried at 103^0C for 2 hours, in distilled water and diluted to 1.000 litre); 0.00417 mol per litre dilute standard potassium dichromate solution (made by diluting 100ml of the standard potassium dichromate solution to 1.000 litre); 0.25 mol per litre of standard ferrous ammonium sulphate solution(made by dissolving 98g of $Fe(NH4)_2$ (SO_4) $2.6H_20$ analytical grade crystals in distilled water added to 20ml of H_2SO_4(d=1.84,cooled and

diluted to 1.000litre;) 0.025mol per litre dilute standard ferrous ammonium sulphate solution (made by diluting 100ml of the standard ferrous ammonium sulphate solution to 1.000litre), standardized against the 0.00417 mol per litre dilute standard potassium dichromate; silver sulphate, reagent powder directly in powder form; mercuric sulphate, analytical grade crystals; ferroin indicator solution 0.695g of ferrous sulphate,$FeS0_4.7H_20$ dissolved in water to which 1.485g of 1,10-phenanthroline monohydtrate was added , shaking until dissolved and diluted to 100ml, sulphamic acid , analytical grade(to eliminate interference of nitrites , and anti –bumping granules previously heated to 600^0 for one hour.

Procedure

A 20 ml of the water sample and 10 ml of the standard dichromate solution were taken in a 125 ml flask and to which 0.4 g of mercuric sulphate and 30 ml of the concentrated, sulphuric acid was carefully added and the solution was thoroughly swirled, The flask containing the solution is covered with a clean cover glass and was allowed to stand for about 30 minutes in a boiling water bath. The content of the flask was diluted to 75 ml with distilled water. 2 or 3 drops of ferrion indicator was then added to the sample and the sample was titrated with ferrous ammonium sulphate. The initial colour of the solution may be yellowish - orange to blueish green. At the end point, the addition of a single drop of titrant causes the colour to change from blueish green to redish brown. A Reagent blank was also prepared using 20ml of distilled water

Calculation

$$\text{COD (mg/l)} = \frac{\text{(B-S) (N) (8) 1000}}{\text{Sample volume (ml)}} \quad \text{.....eq10}$$

Where,

B = ml of ferrous ammonium Sulphate (FAS) used in the titration of the reagent blank

S = ml of FAS used in the titration of the sample

N = Normality of FAS

M = Equivalent weight of oxygen

Note: Mercuric sulphate is added to precipitate chloride as mercuric chloride
A reflux apparatus consisting of a 250-ml Erlenmeyer flask with ground glass neck, and a 300-mm double surface condenser (Liebig, Friedrichs,West) with a ground glass joint, and a heating mantle were used in determination of COD.

3.5. 3 Total dissolved solids

Apparatus: Evaporating dish, Oven, Electronic balance, Measuring cylinder, Filter paper (standard).

Procedure

Evaporating dish was weighed, then 50ml of filtered sample was taken and**,** evaporated in the oven at 100-103^0 C, evaporating dish was then cooled and weighed again.

Calculation

$$T.D.S.\ \text{mg/l} = \frac{A-B*1000}{volume\ of\ sample\ (ml)} \quad \text{.....equ 11}$$

Where

A: Final weight of dish (with sample)

B: Initial weight of dish (without sample**)**

3.5.4 Total suspended solids

Apparatus –Measuring cylinder, Filter paper, Oven, Beaker

Procedure-Filter paper of standard size was weighed then 50ml of sample was filtered through pre-weighed filter paper. The filter paper was then dried in an oven at 90^{0}c for 1 hour and weighed.

Calculation

T.S.S

$$\text{mg/l} = \frac{(X-Z)x100}{volume\ of\ sample(ml)} \quad \text{.....equ 12}$$

Where

X: Final weight of filter paper

Z: previous weight of filter paper

3.5.5 Measurement of Colour using spectrophotometer

Working standard(s) were prepared by diluting an appropriate volume of the 500 mg/L Pt-Co standard with distilled water in 100 ml volumetric flask. The spectrophotometer was turned on and allowed to warm up. 25 mm cells were chosen with appropriate cell holder in position.

The equipment was calibrated using distilled water in the cell as blank, to set it at zero. The cell was emptied and filled with a colour standard of 50 mg/L. It was placed into the sample holder and the display recorded. The cell was cleaned by rinsing with distilled water. The clean sample cell was filled with the sample and inserted into the sample holder. The lid of the sample holder was closed and the display read and recorded in mg/L. This procedure was repeated for all the samples.

3.5.6 Determination of Dissolved Oxygen using Winkler method

The Winkler Method was used for the determination of DO. The Winkler Method uses titration to determine dissolved oxygen in the water sample. A sample bottle was filled completely with water (to exclude air). The dissolved oxygen in the sample was then fixed by adding a series of reagents that form an acid compound that is then titrated with a neutralizing compound that results in a color change. The point of color change coincides with the dissolved oxygen concentration in the sample. Dissolved oxygen analysis was done in the lab.

3.5.7 Measurement of conductivity by use of conductivity meter

Conductivity meter was prepared for use according to the manufacturer's directions. Conductivity standard solution (sodium chloride) was prepared and used to calibrate the

meter for the required range. The probe was rinse with distilled water. The appropriate range was selected and the meter was read to give the conductivity.

3.5.8 Determination of Turbidity using Turbidity meter

Turbidity meter was prepared for use according to the manufacturer's directions. A turbidity standard is used to calibrate meter in the working range. Samples were vigorously shaken and the bubbles left to disappear. A lint-free cloth was used to wipe the outside of the tube into which the sample will be poured. The sample was poured into the tube. Drops on the outside of the tube were wiped off. The meter was set for the appropriate turbidity range. The tube was placed in the meter and the turbidity measurement read directly from the meter display.

3.6 Nutrient Analysis

The HACH DRI4000 Spectrophotometer was used to determine Total Nitrogen (N), Total Phosphorus (P), and orthophosphate in the wastewater samples.

3.6.1 Phosphate Analysis

Phosphate concentrations in water samples were measured using absorbance. This process involved a chemical reaction, creating an *in situ* reduced heteropoly acid complex that produces a blue solution, which has extinction at 885-nanometer wavelength (nm). The intensity of the blue solution was related to the concentration of phosphorus in the water samples.

Total phosphorus

Principle

In this method the total phosphorus content of the sample is oxidized by persulphate which liberates organic phosphorus as inorganic phosphate. The total phosphorus is determined by a method similar to inorganic phosphorus. Total phosphorus concentration of an unfiltered water sample minus dissolved PO_4-P fraction, approximately equals the organic phosphorus content of the sample. The analysis should be completed within one

hour of sample collection. If analysis is not performed immediately, then the filtrate should be frozen at once to 20°C in polyethylene bottles. The thawed samples should not be refrozen.

Reagents

All reagents as for the inorganic phosphate (ref: Phosphate) Persulphate solution 5% W/V of is prepared with distilled water. This reagent should be prepared daily.

Procedure

16 ml of the 5% persulphate solution is added to a 250 ml flask containing 100 ml of the sample. The flask is placed in a boiling water bath for about one hour. Alternatively, this mixture may be autoclaved for 1-1/2 hrs at 15 lbs/ in^2. The solution is then cooled and the volume is made up to 120 ml. The liberated P04-P is then analysed using the method for the determination of inorganic $P0_4$- P (10µg PO_4-P/1). If the PO_4-P/1 content of the samples is 10µg P/1, then the extraction procedure given earlier may be used to measure the liberated P04-P by increasing the sample and reagent volumes approximately. The $P0_4$- P standards and reagent blanks are made and are subjected to identical boiling and volume adjustment procedures. The calculations pertaining to the concentration of the samples are done using a standard curve.

3.6.2 Nitrogen analysis

Reagents

A system of standard solutions, blanks, duplicates, and spikes (standard additions), was used to check the laboratory techniques for the Bach DR/4000 Spectrophotometer. A blank and a spike were incorporated into each set of samples for each parameter measured. Blanks are samples of demineralized water that are treated in the same manner as the samples tested while spikes are used to determine the accuracy and precision of the analysis methods in the sample matrix. They were created by mixing the sample water with a known volume of solution of known concentration and incorporated with other samples. The resulting concentration represented a mass balance of the known addition and the sample concentration.

An alkaline persulfate digestion converted all forms of nitrogen to nitrate. Sodium metabisulfite was added after the digestion to eliminate halogen oxide interferences. Nitrate was then reacted with chromotropic acid under strongly acidic conditions to form a yellow complex with an absorbance maximum at 410 nm. In the TP method, orthophosphate will react with rnolybdate in an acid medium to produce a Phosphomolybdenum complex. Ascorbic Acid then reduced the complex, giving an intense niolybdenam blue color. In the orthophospate method, orthophosphate will react with molybdate in an acid medium to produce a Phophomolybdate complex, giving an intense molybdenum blue color. This method is a persulfate oxidation technique for nitrogen and phosphorus where, under initially alkaline conditions, nitrate is the sole nitrogen product. Phosphate is the sole phosphorus product after acidic conditions are achieved following further auto decompositon of the persulfate in the heated oxidation tubes.

Digested samples were passed through a granulated copper-cadmium column to reduce nitrate to nitrite. The nitrite was then determined by diazotizing with sulfanilamide and coupling with N-I- naphthyl ethylene diamine dihydrochioride to form a colored azo dye. Color was proportional to nitrogen concentration.

3.6.3 Determination of nitrate in waste water by use of spectrophotometer

EPA method 4500 NO_3-N was used to determine nitrates in water.
An aliquot of 50 ml sample was taken in a china dish and evaporated on hot plate until it become dry. Then 0.5 ml of phenol disulphonic acid was added to the sides of china dish. It was cooled at room temperature and 6 to 8 ml of conc. NH_3 solution was added and mixed well. The sample was then diluted up to 100 ml with distilled water and then absorbance was measured at 410nm. Standard curve was prepared against nitrate concentration. The nitrate concentration of the sample was computed by comparing it with standard curve.

3.6.4 Determination of nitrite in waste water by use of spectrophotometer

4500 NO_2-N method was used to determine nitrites in water sample. An aliquot of 50 ml of well filtered sample was taken in 100 ml Nessler's tube and 2 ml of buffer reagent was added into it and mixed thoroughly until the colour appears within 15 minutes. Then absorbance was measured at 540nm. Standard curve was prepared against nitrite concentration. The nitrite concentration of the sample was computed by comparing it with standard curve.

3.6.5 Determination of Orthophosphates by use of mass spectrophotometer

Standard method 4500-P was used to determine orthophosphate contents. An aliquot of 50 ml of solution was taken in a flask and few drops of phenolphthalein indicator were added into it. upon the development of a pink colour, small amount of strong acid solution was added drop wise, just to discharge the color. An aliquot 4 ml of ammonium molybdate was added slowly followed by the addition of 4-5 drops of stannous chloride with through mixing after each addition. Samples were left unshaken for 10 minutes at room temperature for colour development. The absorbance was measured at 610nm wavelength. Standard curve was prepared against phosphate concentration. The phosphate concentration of the sample was computed by comparing with standard curve.

3.7 Total Nitrogen and Phosphorous In Plants

The reagents (analytical reagent grade, 'AR') used included selenium powder, (Se), salicylic acid, hydrogen peroxide, 30%, $H_2 O_2$ (or 100 vols), sulphuric acid H_2SO_4, concentrated, sulphuric acid and selenium powder mixture and digestive mixture.

Procedure using a block digester

Oven dried ground duckweed tissue was weight (0.3g) into a labeled dry and clean digestion tube this was followed by addition of 2.5 ml digestion mixture to each tube and the reagent blanks for each of samples. Digestion of the mixture at 110^0C for 1 hour was done, removed allowed to cool and three successive 1 ml portions of hydrogen peroxide were added. The temperature was raised to 330^0 c and heating continued till the solution

turned colourless and the remaining sand turned white. After this was achieved, the contents were allowed to cool and about 2.5ml distilled water were added and mixed well until no more sediment dissolved. This mixture was allowed to cool and made up to 50ml with water. The solution was allowed to settle so that a clear solution could be taken from the top of the tube for analysis of total N and P from the sample.

3.7.1 Colorimetric determination of Total Nitrogen

Reagents

Sodium citrate, sodium hydroxide, sodium hypochlorite, sodium nitroprusside, Sodium salicylate, Sodium tartrate and reagent N1 where 34g sodium salicylate , 25g sodium citrate and 25g sodium tartrate were dissolved together in about 750ml water and 0.12g sodium nitroprosude added to make up to 1 litre of distilled water.

Reagent N2 was made by dissolving 30g sodium hydroxide in about 750ml distilled water and allowed to cool. Further, 10ml sodium hypochlorite was added and mixed well and made up to 1 litre. Stock solution of 2500mg N/Litre was made by dissolving 11.793 g of ammonium sulphate $(NH_4)_2 SO_4$ in 1000ml volumetric flask and made up to the mark with distilled water

Standards

In to a clean set of 100ml volumetric flask containing 20ml water, 2.5ml digestion mixture was added. In addition, 0, 1.0, 2.0, 4.0, 5.0, 6.0 of the stock solution were added. The standard series contained 0, 25, 50, 75,100, 125, 150mg N/litre. The standards series were diluted at a ratio of 1.9 (v/~v) with distilled water, the actual concentration were 0.2., 5.0, 7.5, 10.0 and 15mg N/Litre

Procedure

The entire digests and the blanks were diluted to a ratio of 1:9 (v/v) with distilled water to match the standards. With a micropipette 0.2ml sample digest and the blanks were taken into clearly labeled test tube. Further, 5.0 ml of the reagent N1, vortex were added with a similar addition of 5ml reagent N2 and vortex. This was allowed to stand for 2 hours and the absorbency was measured at 655nm. A calibration curve was plotted and the concentration of N solution was read.

Calculation:

The nitrogen concentration in the sample material expressed in %N was calculated as follows:

$$N\% = \frac{(a-b)\ x\ V\ x\ 100}{1000\ x\ w\ \ x\ al\ x\ 1000} \quad \text{.....equ 14}$$

Where: a – concentration of N in solution

b – Concentration of N in the blank

v – Total volume at the end of analysis procedure

w – Weight of dried sample

al - aliquot of the solution taken

3.7.2 Total phosphorous without pH adjustment using ascorbic acid

Reagents

Sulphuric acid, H_2SO_4, 5N, Ammonium molybdate/antimony potassium tartrate solution, Ascorbic acid reducing agent, Standard phosphorous stock solution, 100ppm P and 10ppm P working solution

Procedure

5ml of the supernatant clear wet- ashed digested solution were pipetted into a 50 ml volumetric flask and about 20ml distilled water were added to each flask. Further, 10ml of the ascorbic acid reducing agent were added to each flask, beginning with the standards and made to 50ml with water, stoppered and shaken well. The mixture was allowed to stand for 1 hour to permit full colour development and the standards and sample absorbance blue colour were measured at 880nm wavelength setting in a suitable colorimeter

Standards

Working solutions of 0, 1, 2, 3, 4, 5, and 6 ml of the 10ppm P were pipetted into 50ml volumetric flasks. 10ml of the ascorbic acid reducing solution were added to each flask and made to the mark with distilled water and allowed to stand for 1 hour and absorbance read exactly like the sample solutions. The standards contained 0, 0 .2, 0.4, 0.6, 0.8, 1.0 and 1.2 ppm P respectively.

Calculations

A graph of absorbance against standard concentration was plotted and solution concentrations for each unknown and the 2 blanks were determined. The mean blank value were subtracted from the unknowns, this gave a value for the corrected concentration.

$$\boldsymbol{P\ in\ sample}\ (\%) = \frac{c\ x\ v\ x\ f}{w} \quad \textbf{.....equ 15}$$

Where c = the corrected concentration of P in the sample

v = Volume of the digest

f = dilution factor

w = weight of the sample

With a 10ml digest aliquot (pH adjustment technique) and a 50ml final dilution used for color intensity (absorbance) measurement;

$$\text{P in sample}\ (\%) = \frac{c*0.025}{w} \quad \text{.....equ 16}$$

Where c=the corrected concentration for sample solution

W =weight of sample taken for example 0.3g

3.8 Determination of Duckweed Growth Rate

This was determined for fresh and dry weights. Systematic sampling of basins harvested was done periodically at the designated time periods (5, 10, 15 days respectively) and

each time they were filtered using filter paper and fresh weights determined. These samples were dried at 60^{o}C for 48 h to a constant weight and then dry weights were calculated using the relative growth rate formula or percentage weight gain.

3.9 Data Analysis

Statistical analyses of physico-chemical parameters of the effluent and the Macro-elements (N and P) available both in the effluent and in the duckweed plant also known as *lemna spp* were performed using; Percentages and Pearson correlation analysis (relationships). They were then presented in tables and graphs.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Physico-Chemical Parameters

This chapter presents results and discussions of Changes in selected Physico-chemical parameter in tea effluent as a result of coupling electrochemical technology with duckweed based waste water treatment in the management of industrial tea effluent. These parameters were studied and presented as below;

4.1.1 pH

The changes in the pH of the two experimental treatment of effluent are presented in Table 1

Table 1: Effects of effluent retention time on pH levels for the EC pre-treated and RE effluent treated with duckweed plants.

Type of Treatment		ERT in days	0 days	After 5 days	After 10 days	After 15 days
Raw effluent + DWT	Treatment	pH	6.70	7.17 ± 0.12	7.03 ± 0.06	6.77 ± 0.06
	Control	pH	6.70	6.97 ± 0.06	7.27 ± 0.06	7.1 ± 0.12
EC Treated effluent + DWT	Treatment	pH	6.70	7.13 ± 0.12	7.03 ± 0.06	6.73 ± 0.06
	Control	pH	6.70	6.83 ±0.15	7.5 ± 0.1	7.3 ± 0.0

Nema Guide value (6.5-8.5) ± = SD

From Table 1 above, it was observed that the level of pH ranged from 6.70 to 7.17 in raw effluent and 6.70 to 7.1 in EC pre-treated tea effluent, respectively. This therefore shows that the pH values for both the raw and electrochemically treated tea effluents were not affected by the electrolysis process applied. This concurred with the study by Zaroul, *et al.*, (2006) where the pH of the effluent did not change with the electrolysis, in their study on decoulorisation of waste water by electrolysis. The introduction of duckweed based

treatment, plants showed no effects on the effluent pH too. The above pH range of 6.7 to 7.17 were found to be conducive to support the growth of duckweed plant *Lemna spp* (Caicedo et al., 2000; Cross, 2004). Further, they observed that duckweed can tolerate a wide pH range of 4.5 – 8.0. However, a pH greater than 9.5 they argue inhibits duckweed growth. It is also observed that at the pH of 7 majority of iron complexes (coagulants) are formed since this is an optimum pH for carrying out electrocoagulation.

4.1.2 Colour

Changes in the colour of tea effluents after treatment are presented in Table 2 below.

Table 2 Effects of effluent retention time on the overall Colour changes on EC pre-treated and RE effluent treated with duckweed plants.

Type of treatment		ERT in Days	0 days	After 5 days	After 10 days	After 15 days
Raw effluent + DWT	Treatment	Colour (mg/l)	2030	1823.33 ± 138.68	1906.67 ±159.48	1965.33 ±136.50
	Control	Colour (mg/l)	2030	2310 ±281.60	2030 ± 108.17	2110.33 ±166.53
EC Pre-treated effluent + DWT	Treatment	Colour (mg/l)	942	628 .33 ±163.12	1540 ± 36.06	1706.67 ±119.
	Control	Colour (mg/l)	942	521.67 ±177.86	502.67 ±128.36	688.33 ±183.

Guide Value (max allowable value): 15mg/l ± = SD

Results in Table 2 shows that the electrolysis process had some effects on the effluent colour. From the data, the EC process was able to reduce the intensity of colour from an initial level of 2030 mg/l to 942 mg/l representing a decrease of 53.6%. However, upon the introduction of duckweed based wastwater treatment in the purification of tea effluent, a gradual decrease in colour intensity, was observed in the first 5 days followed by a gradual increase in colour intensity in both cases with time. For instance from the 5th

day of effluent retention to the 15th day effluent retention, colour was gradually increasing.This was attributed to the formation of organic compounds due to oxidation over time for instance the formation of theaflavins from catechins oxygen is required (Maghanga *et al.*, 2009).

During Electrocoagulation process, the iron anode electrodes is dissolved and goes into solution, reacting with hydroxyl ions (from the cathodes) to form iron hydroxide. The iron hydroxide formed flocculates and coagulates the suspended and dissolved solids purifying the effluent (Matteson, *et. al.,* 1995). The findings further showed that electrocoagulation was able to remove some amount colour from tea effluents which was highly dependent on the chemistry of the wastewater, especially its conductivity and the intensity of electric energy supplied (Maghanga *et al.*, 2009). The insoluble hydroxides of iron could remove pollutants by surface complexation or electrostatic attraction. Electrochemical method was effective in the removal of colour from Kraft mill effluent in paper industries(Orori *et al.*, 2005). Iron Electrocoagulation process was more effective for the colour removal of textile effluents while the Al electrocoagulation was more effective for disperse dyes (Yang & McGarrahan, 2005).

Table 3 shows effects of effluent retention time on colour (mg/l) and dissolved oxygen in (mg/l).

Table 3: Effects of effluent retention time on the overall Colour and level of Dissolved Oxygen in EC pre-treated and RE effluent both treated with duckweed plants. ± = *SD*

Effluent type	Effluent Retention Time (ERT) (Days)	Colour (mg/l)	Dissolved Oxygen (mg/l)
Raw Effluent + DWT	0	2030	4.10
	5	1823.33	1.64
	10	1906.67	2.35
	15	1965.33	2.31
Electrochemically treated effluent + DWT	0	942	4.02
	5	628.33	2.13
	10	1540.00	2.20
	15	1706.67	2.14

Table 3 shows that Dissolved Oxygen dropped in the first 5 days of the treatment, from 4.10mg/l to 1.64 mg/l and 4.02mg/l to 2.13mgs/l in raw and EC pre- treated effluents respectively. The reduction in Dissolved Oxygen concentration was attributed to the oxidation process of catechins resulting in the formation of colour while the increase in colour was attributed to the formation of organic compounds in the effluent. Due to oxidation process a reduction in Dissolved Oxygen in the tea effluents was recorded (Maghanga *et al.*, 2009). The above data indicated that Dissolved O_2 was consumed by organic matter during decomposition resulting in oxygen reduction by 43% and 46% in raw and EC treated effluents respectively. The sudden drop in Oxygen concentration in the effluent with ERT was attributed to occasional top up of effluent with distilled water to replenish the lost moisture due to evapotranspiration; this replenished some oxygen in the effluent as well. The data obtained from the control treatment of both EC treated and

raw effluent shows a steady and gradual colour increase with ERT indicating that colour formation continued even as organic matter was undergoing decomposition.

4.1.3 BOD

The changes in BOD (mg/l) in the two experimental treatments of tea effluents with time are presented in Table 4.

Table 4: Effects of effluent retention time on BOD levels in EC pre-treated and RE effluent treated with duckweed plants.

Treatment	ERT in days	ERT	0 days	After 5 days	After 10 days	After 15 days (mg/l)
Raw effluent + DWT	Treatment	(BOD mg/l)	120	63.00 ±4.00	27.67 ± 2.08	8.33 ±2.01
	Control	(BOD mg/l)	120	39.67 ±6.43	30.67 ±2.52 -33)	4.67 ±1.53
EC Pre-treated effluent +DWT	Treatment	(BOD mg/l)	54	32.67 ±7.57	15.67 ±1.53	9.33 ± 2.52
	Control	(BOD mg/l)	54	30.67 ±5.68	9.0 ± 2.0	5.33 ±1.53

Guide Value (max allowable value): 30mg/l ± = SD

The electrolysis process was able to reduce BOD levels from 120 mg/l to 54 mg/l representing a percentage reduction of 55.0%. This study showed that iron hydroxide in solution acting as a coagulant facilitated the precipitation of the organic matter resulting in the reduction of dissolved and suspended matter in the effluent. However, upon introduction of the duckweed based treatment for 15 days ERT, the BOD levels reduced from 120.00 mg/l to 8.33 ± 2.01 mg/l in raw tea effluent while EC pre-treated tea effluent reduced from 54.00 mg/l to 9.33 ± 2.52 mg/l representing a percentage reduction of 93.1% and 82.7% in raw and electrochemically pre-treated tea effluents respectively. This shows that the statutory allowable value for Effluent discharge into the environment of 30mg/l was achieved and surpassed within the 15 days ERT. From the statistical data, it showed that EC treated effluent coupled with duckweed based treatment (DWT)

required at least 5 days effluent retention time (ERT) to attain the statutory BOD levels of 30mg/l for discharge while raw tea effluent treated with only duckweed based treatment required at least 10 days ERT to attain the 30mg/l of BOD required for discharge into the aquatic environment. Most researchers have suggested that the efficiency gained using DWT are greater in secondary and tertiary treatment of effluents where organic sludge have already been removed or converted into simple organic and inorganic molecules that can be used directly by Duckweed (Alaerts, *et al.*,1996; Caicedo *et al.,* 2000; Dalu & Ndamba, 2003; Smith & Moelyowati, 2001). The EC process had the capacity to reduce the amount of dissolved organic matter in the effluent hence improving the quality of the effluents (Butler *et al.*, 2011). In this study the significant biomass growth of the duckweed plants grown in EC treated effluents was associated with the EC process which converted organic matter into simple organic and inorganic molecules which are readily available for the duckweed plants to utilize.

It was also noted that duckweed plants grown in the two sets of effluents treatments showed different responses to the different effluent quality. Growth nutrients, such as ammonia nitrogen in its ionised form (ammonium $NH4^{+}$) and phosphate are the most critical (Smith & Moelyowati, 2001) This preference for ionised ammonium helps explain the optimum pH range for duckweed growth, alkaline pH above 8, ammonium is progressively transformed into the un-ionized state (NH_3). This results in the liberation of free ammonia molecules, which has been associated to cause toxicity in duckweed plants (Caicedo *et al.,* 2000) When ammonium concentrations are limited, duckweed is able to utilize other forms of nitrogen especially Nitrate (NO^{-}_3) and simple organic molecules to maintain growth (Skillicorn *et al.,* 1993). Ionization of nutrients by electrolysis process also may have broken down, Nitrogen and its constituent's forms such as ammonia nitrogen in its ionized form (ammonium $NH4^{+}$) becoming bio-available for assimilation by the duckweed plants hence boosting its biomass growth significantly. In this study iron electrodes were used in electrocoagulation process and the iron is thought to dissolve at the anode and hydrogen gas is released at the cathode. The coagulating agent (iron hydroxide) combined with the pollutants to form large flocs subsequently precipitating at the base of the tank (Shammas *et al.*, 2010). It was also observed that whereas

pretreatment of the waste water by both EC and DWT showed remarkable results, the controls of raw waste treated with DWT and EC combined with DWT show that the amount of BOD was reduced from 39.67 to 4.67 mg/l and 30.67 to 5.33mg/l respectively. This was attributed to the effective microorganisms working on the organic matter hence drastically reducing the amount (BOD). EM have been used widely in composting and bioremediation of waste and waste water (Higa & Chinen, 1998).

4.1.4 COD

The change in chemical oxygen demand (COD) of both EC and raw industrial tea effluents are presented in Table 5.

Table 5: Effects of effluent retention time on COD levels in EC pre-treated and RE effluent treated with duckweed plants

Type of treatment	0 days ERT	5 days ERT	10 days ERT	15 days ERT
Raw effluent + DTW (a) (COD, mg/l) z	365.00	274.33 ± 3.21	267.00 ± 30.32	221.33 ±18.50
Electrochemically Treated effluent + DTW (b) (COD, mg/l)	256.00	120.33 ± 50	72.33 ± 8.62	66.33 ± 8.39
Difference (a-b) (COD, mg/l)	109.00	154.00	194.67	155.00
% difference in COD (mg/l)	29.86	56.14	72.91	70.08

The findings in this study indicated that electrocoagulation process significantly reduced the levels of COD by 29.8% before the introduction of Duckweed based treatment. Upon the introduction of the plants into the system, it was observed that 74.09% of COD was removed from EC treated effluent and 54.22% from raw effluent in 15 days ERT. This show that the effectiveness of COD removal from tea effluent can be improved by coupling EC with DWT. Optimizing operating parameters such as electrolysis time and electrolysis potential also enhance treatment efficiency. It was also found that removal efficiency of the COD and Colour was dependent on the quantity of iron electrodes

generated (Zaroul *et al.*, 2006). It was further observed that important factors influencing the efficiency of the Electrochemical process (EC) are the electrode materials used, applied current density, treatment time and solution chemistry (pH, chemical solution of the effluent, solution temperature and conductivity) and electrode gap (Kuokkanen *et al.*, 2013). Electrocoagulation combined with wood ash leachate was applied to the pulp and paper mill effluent, it reduced COD by 80.6% (Etiégni et al., 2010) while COD could be removed at 60% from domestic wastewater with electrocoagulation using iron-iron electrodes (Ilhan *et al.*, 2008). This findings concurred with studies by Etiégni *et al.*, (2010); Ilhan *et al.*, (2008); Kuokkanen *et al.*, (2013) which showed that EC process is influenced by several factors.

The COD difference for the two sets of industrial tea effluent ie the COD values for the EC pre- treated effluent subjected DWT and COD values for the RE effluent subjected to duckweed based treatment exhibited an increase in their resultant values.The diference in COD values between EC effluent treated with DWT and RE effluent treated with DWT recorded an increase in the 5^{th} and 10^{th} ERT before it started to increase at a decreasing rate at the 15^{th} ERT. Figure 4.1 below shows the COD values of the resultant diference between COD of EC tea effluent and RE tea effluent expressed as a percentage and plotted against the efluent retention time in days

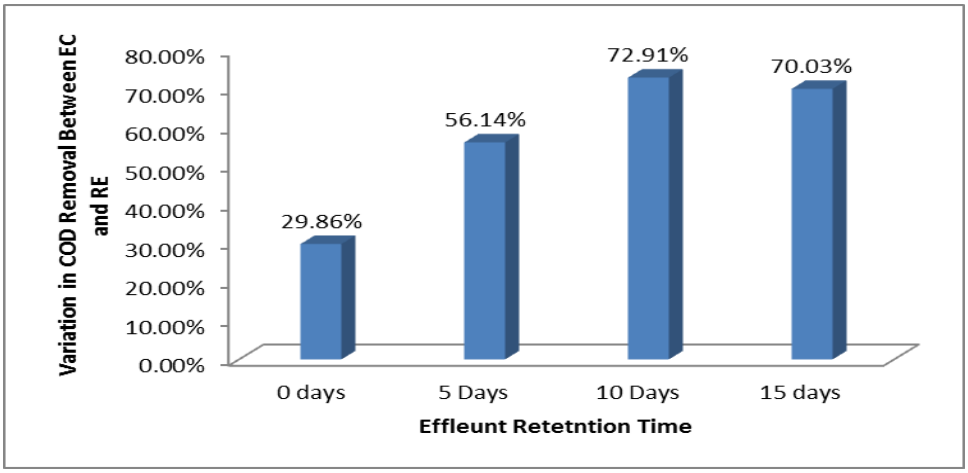


Figure 6: Effect of effluent retention time on the resultant difference between RE.COD levels and the EC.COD levels expressed as a percentage.

Figure 6 above demonstrated that electrochemical treatment enhanced the removal of COD in the Duckweed based wastewater treatment. This study finding supports other studies which concluded that COD and Conductivity could be removed by electrocoagulation process from tea effluents by 96.6% and 31.5% respectively (Maghanga *et al*., 2009). This findings shows that COD statutory allowable levels of 50mg/l could not be achieved within 15 days ERT. However, EC combined with DWT could achieve 66mg/l within 15 days ERT.

4.1.5 TDS

Table 6 below presents the change in TDS with respect to ERT between Raw and EC treated effluents.

Table 6: Effects of effluent retention time on Electrical conductivity and TDS levels in EC effluents and RE effluent treated with duckweed plants.

Parameter	ERT (days)				
	Effluent	0 days	5days	10days	15days
Electrical conductivity (**µS/cm**)	Raw	490.00	387.67	310.67	330.67
	Raw $_{Control}$	490.00	454.33	446.67	361.67
	ECT	433.00	420.67	414.67	371.33
	ECT $_{Control}$	433.00	485.67	508.00	538.00
TDS (mg/l)	Raw	343	271.00	231.33	217.33
	Raw $_{Control}$	343	318.00	313.00	286.67
	ECT	303	294.67	290.67	260.00
	ECT $_{Control}$	303	340.00	355.67	376.33

Guide Value (max allowable value): 1200mg/l ± = SD

Table 6 shows that the EC process merely reduced TDS levels by 11.7% prior to the introduction of duckweed based treatment. This demonstrates that electrocoagulation process was able to remove some dissolved substance to some degree. However, upon introduction of the duckweed based treatment, TDS levels were reduced by 36.7% and 14.2% in raw and EC treated tea effluent respectively. This shows that duckweed plants were useful in the removal more TDS in raw effluent as compared to electrochemically treated tea effluents. This was attributed to the dissolution of iron electrode cathode (sacrificial electrodes') which dissolved to form coagulants (iron hydroxide) hence increasing the level of TDS in the solution as demonstrated in the EC treated effluent control experiment (Butler *et al*., 2011). From the data obtained, TDS levels were reduced from 303mg/l to 260mg/l and from 343mg/l to 217.3mg/l in EC treated and raw effluents respectively when duckweed plants were applied over 15 days ERT. In this study the allowable value of 1200mg/l of TDS was achieved and surpassed within same time. However, control experiments showed that raw effluent left untreated reduced somehow the amount of TDS from 318.00 mg/l to 286.67mg/l while EC treated effluent control showed exactly the opposite that the TDS in fact increased from 303.0 mg/l to376.33mg/l over 15 days ERT. This was again attributed to the iron electrode used in electrolysis which dissolved to form coagulants in the effluent. The dissolved iron plates formed iron ions subsequently increased the amount of TDS in the effluent,(Butler *et al.*, 2011).

Table 6 showed that electrochemical (EC) process used in the purification of effluent reduced electrical conductivity from 490µS/cm to 433 µS/cm representing 11.6% efficiency. The Electrochemical process didn't achieved higher efficiency due to several intervening factors that were not optimized which includes; electrode materials used, applied current density, treatment time and solution chemistry (pH, chemical solution of the effluent, solution temperature and conductivity) and electrode gap affects the efficiency of electrolysis process(Kuokkanen *et al.*, 2013) The data above further indicate that electrical conductivity was gradually reducing with effluent retention time in the experiment under duckweed treatment. With the introduction of plant based treatment,

Electrical conductivity reduced by 32.5% and 14.2% for raw and electrochemically treated effluents respectively over 15 days ERT.

On the contrary EC treated effluent control experiment showed an increase in electrical conductivity with increase in ERT. This is attributed to the dissolution of iron cathode electrode (sacrificial electrode) that went into solution (iron hydroxide) increasing the concentration of TDS levels in the effluent. However, the data shows that conductivity of the raw effluent reduced gradually over time when treated with duckweed plants. Similarly, electrical conductivity for EC treated effluent treated with Duckweed plants decreased over time too. Duckweed plants were noted to reduce TDS levels and electrical conductivity from both raw and EC treated tea effluent. Other studies shows that when duckweed plants are starved of N and P nutrients, they scavenge for nutrients and in the process they absorb heavy metals and toxins present in the effluent (Skillicorn *et al*., 1993). However, it was noted that while electrical conductivity for raw effluent decreases by 32.65%, EC treated effluent decreased electrical conductivity by 14.3% over 15 days ERT. Iron electrodes when used in electrolysis reduces the concentration of metals such as Al, Zn, Cr, Cd while at the same time Fe is itself increased in the treated effluent (Etiégni *et al*., 2010). This explains why electrical conductivity and TDS is substantially increasing with an increase in ERT.

4.1.6 Turbidity

Table 7 below shows the effects of ERT on Turbidity.

Table 7: Effects of effluent retention time on Turbidity levels in EC pre-treated and RE effluent treated with duckweed plants

Type of treatment		ERT in days	0 days	5 days	10 days	15 days
Raw effluent + DWT	Treatment	Turbidity in NTU	41.00	14.97 ± 4.40 (11.00 – 19.70)	4.83 ±1.00 (3.90 – 5.90)	7.37 ± 2.10 (5.30 – 9.50)
	Control	Turbidity in NTU	41.0	22.07 ± 5.49 (17.00 – 27.90)	2.73 ± 0.15 (2.60 – 2.90)	3.40 ± 2.75 (1.60 – 6.60)
Electrochemically Treated effluent + DWT	Treatment	Turbidity In NTU	21.00	21.83 ±0.06 (21.80 – 21.90)	20.90 ± 0.12 (16.70 25.10)	15.57 ± 0.89 (12.40 – 17.20)
	Control	Turbidity In NTU	21.0	32.77 ± 9.83 (26.50 – 44.10)	24.43 ± 0.75 (23.70 25.20)	30.97 ± 3.69 (28.00 – 35.10)

± = SD

Table 7 shows that turbidity levels were reduced from 41.0 NTU to 21.0 NTU when electrochemical treatment was applied on raw tea effluent, this represent 48.8% efficiency. The data further shows that turbidity was further reduced when DWT was applied. It was observed that with increase in the effluent retention time in both case i.e. EC treated and raw effluent turbidity levels decreased. From the data, raw effluent subjected to duckweed based treatment reduced turbidity levels from 41.0 NTU in 0 days ERT to 7.37 NTU in 15 days ERT representing 82.0% while electrochemically treated tea effluent reduced its turbidity levels from 21.00 NTU at 0 days ERT to 15.57 NTU in 15 days ERT representing 28.9% efficiency. However, control experiment for RE effluents shows a different picture of slight decrease in turbidity levels from 32.8NTU to 30.97NTU representing a 5.49% efficiency while control experiment for the raw effluent

showed that turbidity levels was reduced from 22.07 NTU to 3.40 NTU representing 84.59% efficiency. The significant change in turbidity levels in EC treated effluent was attributed to effective microorganism (EM) that was added to the effluent at the GBH. Studies have shown that effective microorganisms (EM) breakdown organic matter into its constituent elements hence affecting the amount of suspended and dissolved organic matter(Higa and Chinen, 1998).

4.2 Results of Nutrients Analysis

This section provides results and discussions of effects of coupling duckweed based treatment with electrolysis process on the levels of nutrients availability in the tea effluent after treatment.

4.2.1. Total Nitrogen

Table 8 below presents the levels of Total Nitrogen in the industrial tea effluent subjected to integrated treatment.

Table 8: Effects of effluent retention time on Total Nitrogen levels.in EC pre-treated and RE tea effluent treated with duckweed plants.

Type of treatment	ERT in days	0 days	5 days	10 days	15 days ERT
TN in Raw effluent +DWT	TN in mg/l	7.12	7.24 ±1.67	6.65 ± 0.72	5.00 ± 0.63
TN in Electrochemically Treated effluent +DWT	TN in mg/l	2.5	0.17 ± 0.04	0.17 ± 0.06	0.02 ±0.02

± = SD

From Table 8, it was observed that electrocoagulation process was able to reduce the level of total nitrogen from 7.12 mg/l in raw effluent to 2.5 mg/l in EC treated tea effluents representing 64.9% percentage reduction. Upon the introduction of duckweed based treatment into the tea effluent, total nitrogen in raw industrial tea effluents were

further reduced from 7.12mg/l to 5.0mg/l while its levels in the electrochemically pre-treated tea effluents was too reduced from 2.5mg/l to 0.02mg/I in 15days ERT respectively. This shows that duckweed plants used in the treatment of raw effluent was able to take up and assimilate 29.8% of TN within 15 days ERT while DWT used on EC treated tea effluents took up 99.2% of TN within 15 days ERT respectively. The study findings suggested that duckweed plants were more effective in the uptake of TN levels from EC treated tea effluents as opposed to the uptake of TN from the raw tea effluents.

4.2.2 Total Nitrogen levels in the duckweed plants

Table 9 below presents the total nitrogen levels taken up by duckweed plants used in the treatment of tea effluents.

Table 9 Effects of effluent retention time on Total Nitrogen levels taken up by duckweed plants used in the treatment of EC and RE tea effluent respectively.

Treatment	ERT in days	0 days	5 days	10 days	15 days ERT
Raw effluent +DWT	TN in mg/l	3.69 mg/l	4.18 ± 1.66	5.06 ± 0.27	4.24 ±0.21
Electrochemically Treated effluent +DWT	TN in mg/l	3.69 mg/l	4.26 ± 2.19	4.65 ± 0.20	4.50 ± 0.15

Initial Total Nitrogen levels in the duckweed plants 3.69 mg/l ± = SD

The results in Table 9 above shows that TN levels in the duckweed plants used in the treatment of industrial tea effluent increased as follows; in the duckweed plants tissues used on raw tea effluents TN levels rose from 3.69mg/l to 4.18mg/l representing a percentage increase of 11.7% while TN levels in the duckweed plants grown on electrochemically pre-treated tea effluents rose from 3.69mg/l to 4.26mg/l representing a percentage increase of 15.4% in 5 days ERT. On continued exposure of the duckweed plant to the two types of effluents, it was noted that TN levels increased by 14.98% in

plants tissues grown in raw tea effluent and 21.8% in EC treated tea effluents in 15 days ERT as shown in Figure 6 This demonstrate that duckweed plants grown in EC treated tea effluents had a lot more readily TN which was taken up by the plants as opposed to duckweed plants grown in raw tea effluents. This was attributed to the availability of nitrogen in the form (nitrates) that is readily absorbable by the plant from the EC effluent.

Figure 6 shows effects of ERT on TN uptake and TN assimilation by the duckweed plants. The figure 6 illustrates the overall flow of TN flow from the tea effluent to the duckweed plant tissues over 15 days ERT.

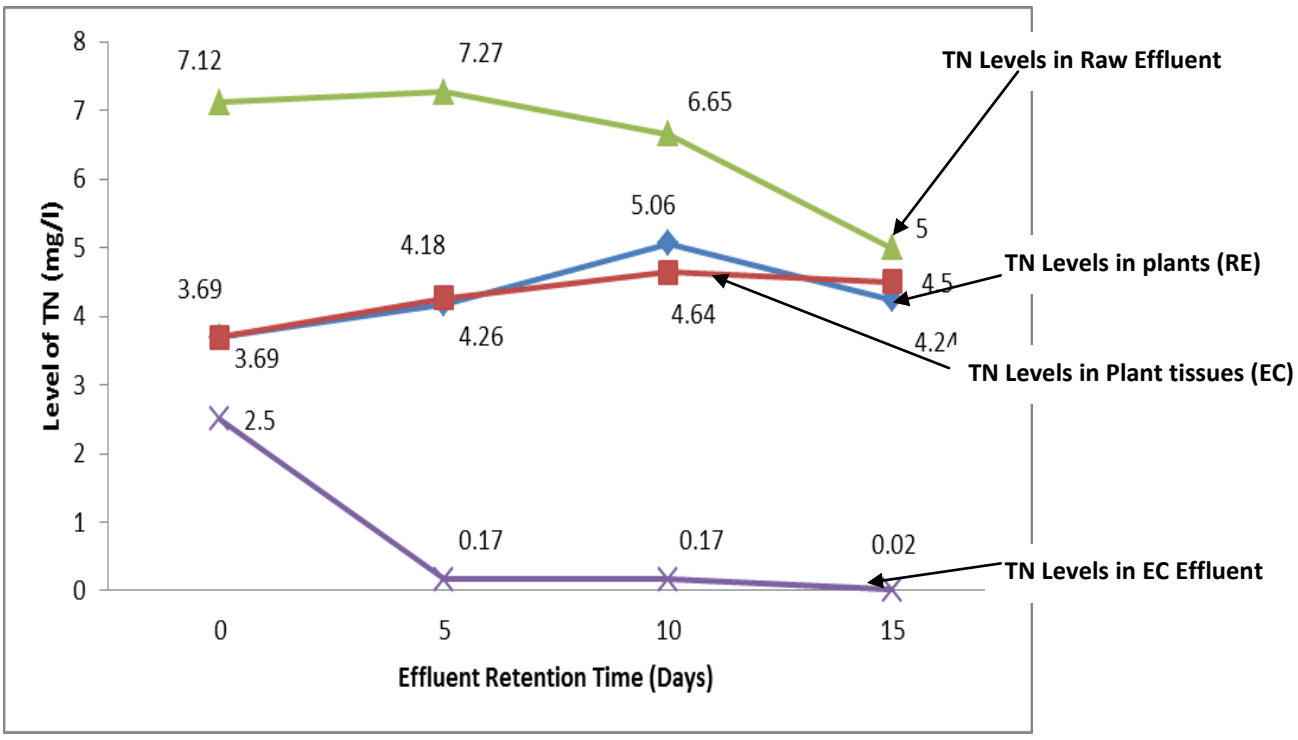


Figure 7 Effects of ERT on TN uptake and TN assimilation by the duckweed plants used in the experiment

4.2.3 Uptake of TN and TP efficiency by DWT

Table10 below presents the TN and TP uptake efficiency by the duckweed based treatment (DWT) alone and when combined with EC.

Table 10 Effects of effluent retention time on TN and TP uptake by the duckweed plants used in the treatment of EC effluent and RE tea effluent respectively

Treatment Effects	Type of treatment	5 days E.R.T	10 days E.R.T	15 days E.R.T
TN uptake in(mg/l)	Raw Effluent	0.49	0.14	0.55
	EC	0.57	0.96	0.81
TN uptake efficiency (% removal)	Raw Effluent	2.65%	3.7%	14.90%
	EC	3.09%	9.57%	21.82%
TP uptake (mg/l)	Raw Effluent	0.13	0.92	0.04
	EC	0.735	0.41	0.01
TP uptake efficiency (% removal)	Raw Effluent	5.0%	37.1%	2.6%
	EC	41.6%	39.8%	1.6%
Biomass produced (g/day)	Raw Effluent	1.34	2.48	1.69
	EC	2.30	2.69	2.09
% weight gain	Raw Effluent	2.68%	4.97%	1.69%
	EC	4.59%	5.38%	2.09%

± = SD

Table 10 shows that duckweed plants applied on EC treated effluents enhanced the uptake of total nitrogen from 3.09% in 5 days to 21.82% in 15 days ERT as compared to that of raw tea effluent which showed 2.65% uptake in 5 days to 14.90% in 15days ERT. Duckweed plants used in the trreatment of raw effluent similarly, shows a TP uptake efficiency of 5.0% in 5 days to 2.6% in 15 days ERT While duckweed plants used in the treatment of EC effluent shows a TP uptake efficiecy of 41.6% in 5 days ERT to 1.6% in 15 days ERT. This shows that EC process made nitrates readily available for plant uptake while TP levels appeared to be dwindling or unavailable.Phosphate elimination is higher in deep rooted plants (halophyte) compared to the duckweed-dominated systems because phosphates are usually found lodged at the bottom zone of the basin(Vyamazal, 2005).

Generally this is corroborated by the higher biomass produced in duckweed grown on EC treated effluents compared to those grown in raw effluent as shown in the Table10.

4.2.4 Nitrates concentration in the effluent

Table 11 below shows the effects of ERT on nitrate levels in the duckweed plants used in the experiments.

Table 11: Effects of effluent retention time on the nitrate levels in EC pre-treated and RE effluent treated with duckweed plants.

Type of effluent on treatment	ERT in days	0 days ERT	5 days ERT	10 days ERT	15 days ERT
Nitrates (mg/l) in Raw effluent + DWT	NO_3^- (mg/l)	2.678	1.87 ± 0.24	0.40 ± 0.10	0.27 ± 0.06
	% NO_3^-	0.0%	30.2%	78.6%	32.5%
Nitrates (mg/l) in Electrochemically Treated effluent + DWT	NO_3^- in mg/l	0.142	0.133 ± 0.06	0.102 ± 0.06	0.07 ± 0.06
	% NO_3^-	0.0%	6.3%	23.3%	31.4%

Guide value max allowable; 100mg/l ± = SD

Table 11 showed that electrochemical process significantly reduced nitrates levels by 94.7%. The data obtained above concur with other studies on inorganic compounds such as nitrate, nitrite, and ammonium ions from paper mill effluents that were removed by electrocoagulation process using iron and aluminum electrode plates resulting in 95% and 65% nitrate removal when Fe and Al electrodes were used respectively(Urgulu, 2004).In this study, the introduction of duckweed based treatment shows that nitrate levels in raw tea effluent reduced from 2.67mg/l in 0 days ERT to 0.27mg/l in 15days ERT representing 89.90% reduction, while total nitrates reduced from 0.14mg/l in 0 days ERT to 0.07 mg/l in 15 days ERT representing 50.70% of nitrate removal as shown in Figure 9 above. It was found that electrocoagulation process was fairly efficient in nitrate removal before any biological treatment was introduced (at 0 days ERT). Nitrate is harmful to human and infants when present in water and should be removed from the effluents before discharge into the environment. High concentrations of nitrates in water have a detrimental effect on the quality of environment and also limit the usage of water for

industrial use. The maximum allowable concentration of nitrate as NO_3 in drinking water according to the EEC recommendations is 50 mg/l and 15 mg/l for infants.

The standard of effluent discharge into the environment which is the sum total of ammonia, nitrates and nitrites maximum allowable was 100mg/l (GOK, 2006) which according to this study was attained and surpassed as shown in the Figure 10 below

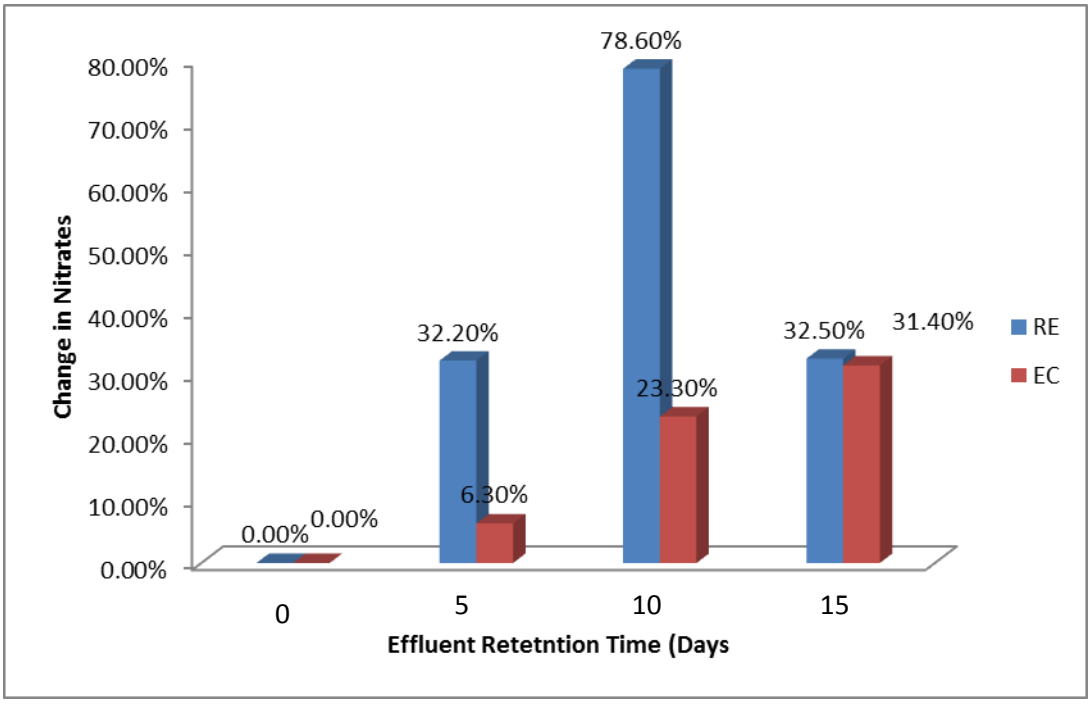


Figure 8: Effects of effluent retention time on percentage nitrate removal from industrial tea effluent

4.2.5Nitrites levels in the industrial tea effluent

Table 12 shows the effects of ERT on nitrite levels in the two types of tea effluents.

Table 12: Effects of effluent retention time on nitrite levels.in EC pre-treated and RE effluent treated with duckweed plants.

Type of treatment	ERT (days)	0 days	After 5 days	After 10 days	After 15 days
Nitrites (mg/l) in Raw effluent +DWT	NO_3^- (mg/l)	0.23	0.23 ± 0.09	0.15 ± 0.09	0.06 ± 0.04
	% NO_3^-	-	2.2%	33.5%	61.6%
Nitrites (mg/l) in Electrochemically Treated effluent +DWT	NO_3^- (mg/l)	0.05	0.04 ± 0.01	0.03 ± 0.01	0.01 ±0.01
	% NO_3^-	-	16.4%	14.3%	73.7%

± = SD

Table 12 indicated that electrochemical treatment of industrial tea effluents was able to reduce nitrites levels in the tea effluents by 80.5%. Other studies showed that the removal efficiencies of nitrites turned out to be rather low when cast iron was used to investigate the efficiencies of nitrite and ammonia removal from the aqueous solution, being no more than 20% for a 2-hour test run (Lin & Wu, 1996).In the study of raw effluent experiment subjected to duckweed based treatment, the levels of nitrites reduced from 0.23mg/l in 0 days ERT to 0.06 ± 0.04mg/l in 15 days ERT showing a significant reduction of 75.02% of nitrites. Similarly, nitrites in the EC treated tea effluents subjected to duckweed based treatment reduced its nitrites levels from 0.05mg/l in 0 days ERT to 0.01 ±0.01mg/l in 15 days ERT representing 81.2% reduction as shown in Figure 10.below. This confirms that electrochemical process combined with biological process (duckweed based treatment) is effective in the removal of nitrites from industrial tea effluents before discharge. Nitrites are precursors of cancers and therefore its removal from tea effluent helps in reducing cases of cancer related diseases. Nitrite once in the blood changes the normal form of hemoglobin, which carries oxygen in the blood to the rest of the body, referred to as methemoglobin that cannot carry oxygen. High enough concentrations of nitrite in drinking water can result in a temporary blood disorder in infants referred to as methemoglobinemia (blue baby syndrome) (Environmental Fact Sheet, 2006). In addition, it is believed that after nitrate is converted to nitrite in the body, it can react with

certain amine containing substances found in food to form nitrosamines, which are known to be potent cancer causing chemicals.

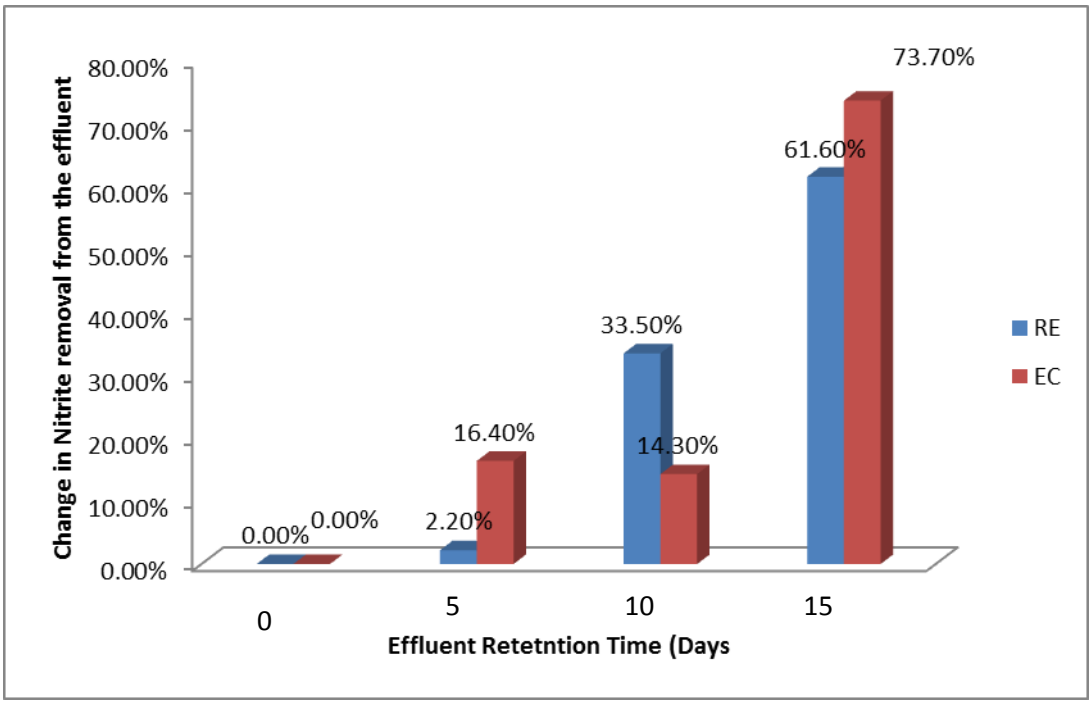


Figure 9: Effects of effluent retention time on percentage nitrite removal from the tea effluents over time.

Figure 9 shows that duckweed plants used in both treatment of EC pre-treated and Raw effluent resulted in the removal of 73.7% and 61.6% of nitrite levels respectively in 15 days ERT The presence of ammonium ion in effluent retards the nitrite removal due to oxidation of ammonium ion to nitrite which is then further converted to nitrate. Hence, during the electrochemical oxidation process, certain amount of nitrite is generated. The actual amount of nitrite existing in the aqueous solution would be more than that derived from the initial nitrite(Benefield, 1998).

4.3 Total Phosphorus level in the effluent after treatment with duckweed plants.

The analytical data in Table 11 indicate that electrocoagulation process applied on raw tea effluent reduced TP from 12.51mg/l to 3.77mg/l representing 69.90%.Upon introduction of duckweed plants into the effluent treatment 47.2% and 20.01% of total

phosphate was taken up from the raw and electrochemically treated tea effluent respectively over 15 days ERT as shown in Table 11.

Table 13: Effects of effluent retention time on Total phosphorus levels in EC pre-treated and RE tea effluent after treatment with duckweed plants.

Type of treatment	0 days ERT	5 days ERT	10 days ERT	15 days ERT
phosphorus (mg/l) in Raw effluent + DWT	12.51	8.20 ± 3.05	7.44 ± 1.08	6.81 ± 2.29
phosphorus (mg/l) in Electrochemically Treated effluent + DWT	3.77	3.42 ± 1.45	2.64 ± 0.23	2.39 ± 0.64

± = SD

Total phosphate (TP) uptake efficiency gradually increases from 0 days to 15 days reaching a high of 37.1% on 10 days effluent retention time. It further shows that increasing the effluent retention time, results in a higher TP uptake efficiency though at a decreasing rate. This shows that the TP levels available for duckweed plant uptake were either depleted or unavailable. Similarly, the percentage weight gains gradually increased with increase in effluent retention time (ERT) to a high of 4.96% in the 10 days of effluent retention time. This infers that optimum retention time for the raw effluent under duckweed based treatment has been reached. Figure 7 shows that electrochemically pre-treated tea effluent and raw effluent exhibited a similar trend as DWT used in the treatment of raw tea effluents. Percentage TP levels in raw industrial tea effluent reduced upon the introduction of DWT treatment from 41.1% to 39.9% then to 1.6% for EC effluent and 5.0%,37.10%, 2.60% for RE effluent in 5, 10,and 15day Effluent Retention time respectively. These resulted in duckweed plants growth weight gained of 4.9%, 5.38% and 2.09% for duckweed plants grown on EC effluent and 2.68%,4.98% and 1.69% for duckweed plants grown on RE effluent in 5,10 and 15days effluent retention time in EC and RE treated effluents respectively.

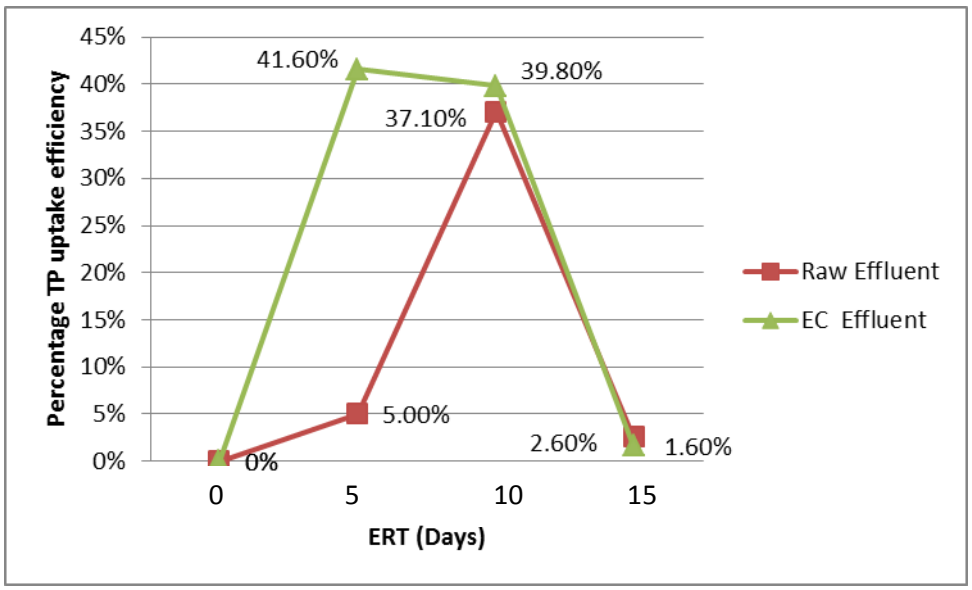


Figure 10: Effects of ERT on Percentage TP uptake by the duckweed plants

This indicates that though there was nutrient depletion with increase in effluent retention time, duckweed plants used in EC treated effluent acquired more weight than the duckweed plants grown on the raw effluents.

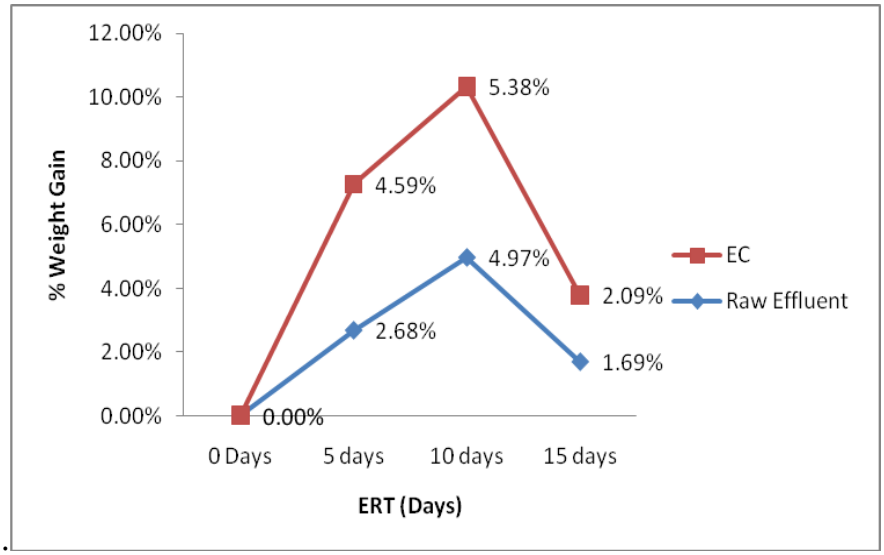


Figure 11: Effects of effluent retention time on percentage weight gain

4.3.1Plant TP levels taken up by Duckweed plants used in the treatment.

The total phosphorus levels in raw effluent varied from 0.17 mg/l in 0 days to 0.28 mg/l in 15 days effluent retention time as indicated in Table 14. This represented an increase of 64.4% of TP taken up and assimilated by the duckweed plants. However, TP levels in duckweed plants tissue used in electrochemically treated tea effluents varied from 0.17mg/l in 0 days to 0.21 mg/l in 15 days effluent retention time This represented a TP increase of 27.0% assimilated by the plant as shown in Table14

Table 14 Effects of effluent retention time on Total phosphorus levels taken up by duckweed plants used in the treatment of EC pre-treated and RE tea effluent respectively

	Treatment	Effluent Retention Time			
		0days	5 days	10 days	15 days
Level of TP in plant tissues	Raw effluent + DWT	0.17	0.15 ± 0.07	0.28 ± 0.00	0.28 ± 0.00
	Electrochemically Treated effluent + DWT	0. 17	0.14 ± 0.09	0.20 ± 0.01	0.21 ± 0.00
Level of TP in Tea effluent	Raw effluent + DWT	12.51	8.20 ± 3.048	7.44 ± 1.0858	6.81 ± 2.29
	Electrochemically Treated effluent + DWT	3.76	3.42 ± 1.45	2.64 ±.22	2.39± 0.64

Initial phosphorus Level in the duckweed = **0.17 mg/l** ± = SD

4.4 Relative Growth

Table 14 shows that the relative growth rate of *Lemna spp* stocked in raw effluent was 0.27, 0.50, 0.34 g/day representing 2.68%, 4.97%, 1.69% of biomass produced over 5, 10 and 15 days effluent retention time respectively while relative growth rate of *Lemna spp* stocked in EC pre-treated effluent varied in biomass produced per day from 0.46, 0.54, 0.42 g/day representing 4.59%, 5.38%, 2.09% over 5, 10, 15 days effluent retention time respectively. From the analysis, more growth was recorded in the EC pre-treated effluent. Table 4.17 also showed the effects of effluent retention time on overall weight gain by (*Lemna spp*). Phosphate elimination was higher in deep rooted plants compared to the duckweed-dominated systems because phosphates are found lodged in bottom zone of the

effluent basin. (Vyamazal, 2005). The amount phosphates taken up by the duckweed plant in the 15 days ERT could not match that of TN. This showed that the phosphates fertilizers in the effluent were not available in the effluent but rather lodged in the formed flocs, and other settle able matter at the base of the basin and due to the short *Lemna spp* roots the phosphate nutrients could not be taken up by the plant roots.

Table 15: Effects of effluent retention time on the relative growth rate of duckweed plants used in the treatment of EC pre-treated and RE tea effluent respectively

Treatment	After 5 days ERT		After 10 days ERT		After 15 days ERT	
	Av. Wet weight (g)	Av .Dry weight (g)	Av. Wet weight (g)	Av. Dry weight (g)	Av. Wet weight (g)	Av. Dry weight (g)
Raw effluent + DWT	56.67 ± 5.79	1.93 ± 0.05	74.84 ± 4.86	3.04 ± 0.13	75.40 ± 2.62	3.26 ± 0.11
Electrochemically Treated effluent + DWT	61.48 ± 3.07	2.10 ± 0.10	76.88 ± 2.09	3.11 ± 0.19	81.36 ± 6.73	3.42 ± 0.21)
% weight gain in Raw effluent	13.4%		49.7%		50.8%	
% weight gain in Electrochemically Treated effluent	22.96%		53.76%		62.7%	

Initial duckweed weight before treatment = **50g** ± = SD

The percentage weight gain of *Lemma spp*. Grown in the two qualities of industrial tea effluents is illustrated in Figure 12 below**.**

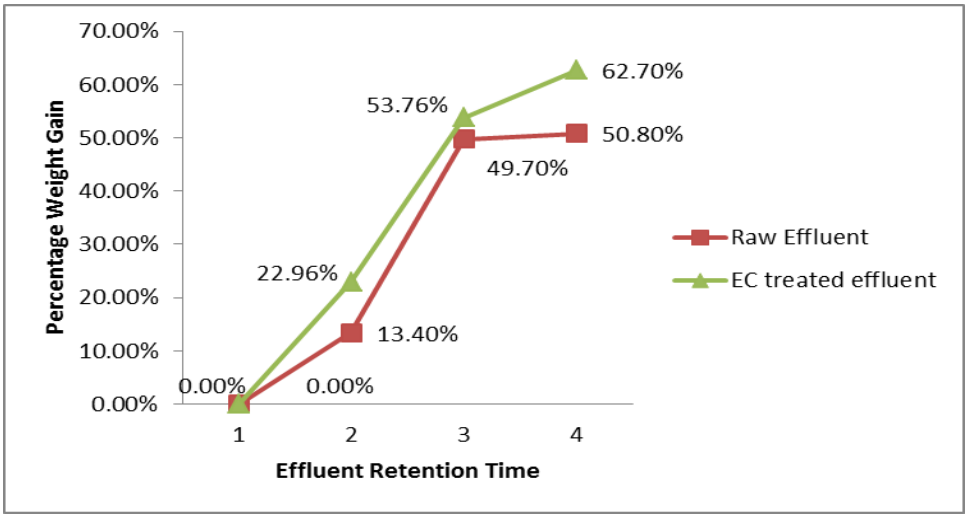


Figure 12: Effects of effluent retention time on Overall weight gain by *Lemna spp* used in the treatment of tea effluent

Figure 12 shows that percentage weight gain of 50.8% was attained by duckweed plants used in the treatment of raw tea effluent in 15 days effluent retention time while a percentage weight gain of 62.70% was obtained by duckweed plants used in the treatment of electrochemically treated tea effluent in 15 days effluent retention time. More weight gains were achieved in the first 10 day of effluent retention time. This was attributed to sufficient nutrients availability in the effluents sampled. The percentage weight gained increased at a decreasing rate after 10 days of effluent retention. This signifies that the overall retention time required in duckweed treatment system for industrial tea effluents could possibly be 10 days. The 10 days optimum effluent retention time was obtained under experimental depth of 10cm, temperature range of 16^{o}C to 21^{o}C and a pH range of 6.7 to 7.8. The overall retention time required in a DWT system vary depending on; nutrient levels, temperature and the discharge standards that must be met (Skillicorn *et al.*, 1993). According to his studies, 20 days hydraulic retention time was found to be the minimum requirement for DWT to achieve acceptable effluent standard for discharge into the environment. However, according to this study coupling EC with DWT treatment would reduce hydraulic retention time to 10 days for industrial tea effluent.

Hypothesis testing

Table15 presents the p and r values for physicochemical parameters tested for their significance in coupling DWT with EC treatment.

Hypothesis (1) testing for physico chemical parameters

Table 16: p Values for physic-chemical parameters

Variable	p values	r values
pH	.005	.995
Colour	.661	.339
BOD	.002	.998
COD	.041	.959
Dissolved Oxygen	.043	.957
TDS	.226	.774
Turbidity	.634	.336
Electrical Conductivity	.352	.648
TSS	.049	.951

The results in Table 16 shows that pH (p=.005), BOD (p=.002), COD (p=.041), Dissolved oxygen (p= .043) and TSS (p=.049) of raw and EC treated effluents were significantly different and positively correlated while colour (p=.661), TDS (p=.634), turbidity (p=.634) and electrical conductivity (p=.352) of raw and EC treated effluents were not significantly different but were positively correlated.

There was a significant difference in the concentration of physico-chemical parameters between tea effluents treated with only DWT compared with DWT coupled with EC process and therefore the hypothesis was accepted.

H_2Hypothesis (2) testing for nutrients uptake

H_2: There was a significant difference in the relative uptake of Phosphates and Nitrogen between duckweed plants stocked in raw and EC treated tea effluents.

Table 17: Pearson Correlation table

		Raw	EC
Phosphorus	Pearson Correlation	1	.863
	Sig. (2-tailed)		.137
Nitrogen	Pearson Correlation	1	-.709
	Sig. (2-tailed)		.499

The results in table 17 shows that there was no significant relationship in phosphorus and nitrogen uptake between duckweed plants stocked in raw and EC treated tea effluents (p =.137; p= .499for P and N respectively). At the same time, phosphorus uptake in *Lemna spp* plants grown in the two types of effluents were positively and strongly correlated (r=.863). However, Nitrogen uptake in *Lemna spp* plants grown in the two types of effluents were negatively and strongly correlated (r= -.709) and therefore the hypothesis was rejected.

H_3: Hypothesis (3) testing for relative growth rate (RGR) between duckweed grown in raw effluent and those grown in industrial tea effluents treated with EC over time.

Table 18: Correlation coefficient tests in growth rate of *Lemna spp* grown in Raw the EC treated effluents

	Raw	EC
Pearson Correlation	1	.972
Sig. (2-tailed)		.152

There was no significant difference (p=.152) between the relative growth rate of *Lemna spp* grown in EC effluent and those grown on raw effluents. At the same time, the relative growth rates for the *Lemna spp* grown on the two types of effluents were strongly correlated (r=.972) and therefore the hypothesis was rejected.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusions

The results from this study have led to the following conclusions;

That Electrochemical Technology coupled with duckweed based treatment was found to be effective and efficient in the purification of industrial tea wastewater. The electric current applied combined with DWT was able to remove small organic matter by electrocoagulation flotation process reducing COD, BOD, Electrical conductivity by 74%, 93% and, 32.5% respectively. This study also demonstrates that electrochemical treatment enhanced duckweed based treatment removal of these parameters: BOD, COD, TDS,TSS and Colour from the effluent thus improving effluent quality. It was further found that duckweed plants when starved of N and P were able to scavenge for nutrients and in the process absorbs iron ions and other pollutants hence reducing the amount of TDS and Electrical conductivity.

The combined effects of electrochemical technology showed that the relative uptake of N and P varied with effluent treatment. TN uptake efficiency started with 0.57mg/l representing 3.09% in 5 days and rose to 0.81mg/l representing 21.08% in 15days effluent retention times. The study finding showed that EC process made nitrogen and its other forms available for the plant uptake while the TP uptake efficiency started with 0.735mg/l representing 41.6% and drop to0.01mg/l representing 1.6%. TP appeared to be getting depleted with ERT. The depletion of TP was attributed to phosphate being lodged in the flocs and at the bottom zones of the effluent that was beyond the reach of duckweed roots.

EC process has the capacity to ionise the nutrients in the effluents making them bio-available for the plants to utilise while removing toxins (pollutants) that are known to inhibit the growth of plants. This was demonstrated by the higher weight gained by duckweed plants grown on electrochemically pre-treated industrial tea effluents where a percentage average wet weight gain of 31.36g wet weight was obtained representing a

62.7% while duckweed plants grown on raw industrial tea effluent gained an average of 25.4g of wet weight representing 50.8% in 15 days effluent retention time.

6.2 Recommendations

The following are the recommendations of this study

i. Electrochemical technology (E C) treatment should be integrated with biological systems (hydrophytes) of different species and rooting systems to achieve desired statutory levels of colour, BOD, COD, TSS, TDS, and conductivity.

ii. A combination of different aquatic plant species (hydrophytes) with different root structures should be used in phytoremediation so that effective extraction of N and P in solution and those lodged in the bottom of the basin is removed.

iii. The EC reactor should be designed to automatically separate precipitated organic matter that would otherwise have undergone oxidation resulting in more colour formation.

iv. EC technology should be employed in industrial tea purification and treatment because it enhance nutrient extraction by the plants from the effluent thus reducing effluent retention time

6.3 Suggestions for Further Research

Duckweed plants (Lemna *spp)* are a small floating plant that is easily blown away by wind and can be moved from one surface to another. This makes it unsuitable for use in large scale waste water treatment alone when not combined with other aquatic plant species with long roots. More research should be done to determine the effects of coupling EC technology with an integration of deep and shallow rooted plants (halophyte) and duckweed plants species in effluent treatment.

REFFERENCES

Alaerts, G. J., Rahman, M. D. M. , & Kelderman, P. (1996). Performance analysis of a full-scale duckweed-covered sewage lagoon. *Water Resource, 30*(4), 843-852.

APHA. (1998). Standard methods for examination of water and wastewaters, *American Water Works Association and Water Pollution Control Federation* (20 ed.). Washington, D C AWWA WPCF

Aravindan, S., Manivel, M., & Chandrasekar, S.V.N (2004). Groundwater quality in the hard rock area of the Gadilam river basin, Tamilnadu. *Journal of Geological Society of India, 63*, 625-635.

Benefield. (1998). process chemistry for water and waste water treatment. . (Prentice Hall Inc new jersey).

Bonomo, L., Pastorelli, G., & Zambon, N. (1997). Advantages and limitations of duckweed-based wastewater treatment. *Water Science and Technology, 35*(239-246).

Boonyapookana, B., P., Parkpian, Techapinyawat, S., Delaune, R.D., & Jugsujinda, A. (2005). Phytoaccumulation of lead by Sunflower (Helianthus annus), Tobacco (Nicotiana tabacum), and Vetiver (Vetiveria zizanioides). *Journal of Environmental Science and Health, 40*, 117-137.

Butler, E. , Tse Hung, Y. , Yeh Li, R. , & Ahmed, S. M. (2011). Electrocoagulation in waste water treatment. *department of civil & environmental engineering,Cleveland state university*.

Caicedo, J.R., Van der Steen, N.P., Arce, O., & Gijzen, H.J. . (2000). Effect of total ammonia nitrogen concentration and pH on growth rates of duckweed (Spirodela polyrrhiza). . *Water Research, 34*, 3829-3835.

Chen, G. (2004). Electrochemical technologies in wastewater treatment. *Separation and Purification Technology, 38*(1), 11-41.

Chen, X., Chen, G., & Yue, P.L. . (2002). Investigation on the electrolysis voltage of electrocoagulation. *Chemical Engineering Science., 57*, 24-49.

Cheng, J, Bergmann, B.A., Classen, J.J. , Stomp, A.M., & Howard, J.W. . (2002). Nutrient recovery from swine lagoon water by Spirodelapunctata. *Bioresource Technology, 81*, 81–85.

Cheng, J. J., & Stomp, A. M. (2009). Growing duckweed to recover nutrients from wastewaters and for production of fuel ethanol and animal feed. *Clean-Soil Air Water 37*, 17-26.

Cross, J. W. (2004). The Charms of Duckweed.http://www .mobot. org/ jwcross/ duckweed.htm (accessed 10 may, 2014).

Dalu, J.M., & Ndamba, J. (2003). Duckweed based wastewater stabilization ponds for wastewater treatment (a low cost technology for small urban areas in Zimbabwe *Physics and Chemistry of the Earth* (Vol. 28, pp. 1147–1160).

E.P.K. (2010). *Eastern Produce Kenya Ltd. Technical report*.

E.P.K. (2012). *Eastern Produce Kenya Ltd. Standing instruction on tea manufacture.*

European Commission,(2006). Environmental fact sheet *Nitrate and nitrite: Health information summary*.

Etiégni, L, Senelwa, K, Balozi, B K, Ofosu-Asiedu, K, Yitambé, A, Oricho, D O, & Orori, B. O. (2010). Treatment of wastewater by electrocoagulation method and the effect of low cost supporting electrolytes. In K. W. Canton (Ed.), *Fluid Waste Disposal*. Oser Avenue, Suite, Hauppauge, N.Y. 11788-3619, USA.: Nova Science Publishers, Inc.

Feng, C., Sugiura, N., Shimada, S., & Maekawa, T. . (2003). Development of a high performance electrochemical wastewater treatment system. *Hazard. Mater, B103*(65).

GoK (1999) Environmental Management and Coordination Act. Government Printers, Nairobi.

GoK (2006). Environmental Management and Coordination Act : Water quality regulation. Government Printers, Nairobi.

G.O.K. (2010). *The Kenya constitution*. Government printers.

Ganizares, P., Carmona, M., Labato, J., Martines, F., & Rodrign, M.A. (2005). Electrodissolution of alluminium electrode in electrocoagulation processes industrial engineering chemistry *44*, 4178-4185.

Garge, N., Page, G.P. , Spargue, A.P., Gorman, B.S., & Allison, D.B. (2005). Reproducible clusters from micro array research: Whither? *BMC Bioformatics, Suppl. 2*(10).

Gerard, M., Jean-Luc, P. , & Thierry, L. . (2002). Performances of constructed wetlands for municipal wastewater treatment in rural mountainous area. *Hydro-biologia, 469*, 87-98.

Gesimba, R. M., Langat, M. C., Liu, G., & Wolukau, N. J. . (2005). The tea industry in kenya; the challenges and positive developments. *Journal of applied sciences, 5(2)*(1812-5654), 334-336, 2005.

Gleick, P. H., Burns, W. C. G., Chalecki, E. L., Cohen, M., Cushing, K. K. , Mann, A. S. , Wong, A. K. (2002). The world's water 2002-2003 *The biennial report on freshwater resources.* . Washington,D.C: Island press.

Hancock, S. .J., & Buddhavarapu, L. R. (1993). Control of algae using duckweed (lemna) systems. In: Constructed wetlands for water quality improvement. *399-406*.

Higa, T. , & Chinen, N. (1998). EM treatment of oudor, wastewater and environmental problems. Okinawa,Japan: University of Ryuku, College of Agriculture.

Ilhan, F., Kurt, U., Apaydın, O., & Gonullu, T. (2008). Treatment of Leachate by electrocoagulation using aluminum and iron electrodes. *Journal of Hazardous Materials, 154*, 381-389.

Iqbal, S. . (1999). Duckweed aquaculture: Potential, possibilities and limitations for combined wastewater treatment and animal feed production in developing countries. *6/99*. Switzerland.

Jain, S.K., Vasudevan, P., & Jha, N.K. . (1989). Removal of some heavy metals from polluted water by aquatic plants: Studies on duckweed and water velvet. *Biology of Wastes, 28*, 115-126.

Jiang, Q. J., Graham, N., Andre, C., & Kelsall, H. G. (2002). Laboratory study of electro-coagulation–flotation for water treatment. *Water Research, 36*(16), 4064–4078.

Joffe, L. , & Kniopper, L, . (2000). Electro coagulation, industrial waste water. *20*, 1067.

K.T.D.A. (2011). From Tea to cup "Tea life cycle": Kenya Tea Development Agency Ltd.

Kinyili, J.M. (2003). Diagnostic study of the tea industry in kenya. *Export promotion council*.

Kuokkanen, V., Lassi, U., Kuokkanen, T., & Rämö, J. (2013). Recent applications of electrocoagulation on treatment of water and wastewater; A review. *Green and Sustainable Chemistry, 3*, 89-121.

Landesman. L,(2000). effects of herbivory and competition on growth of lemnacea in systems for waste water treatment and livestock feeds production,. 150.

Landesman , L, Parker, N.C., Fedler, C.B &, & Konikoff, M. . (2005). Modeling duckweed growth in wastewater treatment systems. Livestock Research for Rural Development *Livestock research for rural development 17*.

Landesman, L., Fedler, C. , & Duan, R.B. . (2011). Plant nutrient phytoremediation using duckweed In G. S. Edited by Ansari AA, Lanza GR, Rast W. (Ed.), *Eutrophication: Causes, Consequences and Control.* . Beilin Springer-Verlag.

Leng, R.A. , Stambolie, J.H., & R., Bell. (1995). Duckweed - a potential high-protein feed resource for domestic animals and fish. *Livestock Research for Rural Development, 7*(1), 36.

Les, D.H., Crawford, D.J., Landolt, E., Gabel, J.D. , & Kimball, R.T. (2002). Phylogeny and Systematics of Lemnaceae, the Duckweed Family. *Systematic Botany, 27*, 221–240.

Letterman, R. D., Amirtharajah, A. , & O'melia, C. R. (1999). Coagulation flocculation in water quality treatment (5th ed.). new york,: AWWA McGrans-Hill, .

Liang, Y., Lu, J., Zhang, L., Wu, S., & Wu, Y. (2003). Estimation of black tea quality by analysis of chemical composition and colour difference of tea infusions. *Food Chemistry*, *80*(2), 283-290.

Lin, S., & Wu, C. . (1996). Electrochemical removal of nitrite and ammonia for aquaculture. *Water resource, 30*, 715- 721 (716 pages).

Liu, S., Lu, H., Zhao, Q., He, Y., Niu, J., Debnath, A. K., ... & Jiang, S. (2005). Theaflavin derivatives in black tea and catechin derivatives in green tea inhibit HIV-1 entry by targeting gp41. *Biochimica et Biophysica Acta (BBA)-General Subjects*, *1723*(1), 270-281.

Maghanga, J, Segor, F, Etiegni, L, & Kituyi, J. (2009). Electrochemical treatment of a Kenyan tea factory waste water. *Journal of Agriculture, Pure and Applied Science and Technology*, *2*, 68-75.

Matteson, Michael, J, Dobson, & Regina, L. . (1995). Electrocoagulation and separation of aqueous suspension of ultrafine particles, colloids and surfaces *A physicochemical and engineering aspects, , 104*, 101- 109.

Mohedano, R.A., Costa, R.H.R., Tavares, F.A, & Belli, P (2012). High nutrient removal rate from swine wastes and protein biomass production by full-scale duckweed ponds. *Bioresour Technology, 112*(98-104).

Mollah, M.Y.A, Schennach, R., Parga, J.R., & Cocke, D.L. . (2001). Electro coagulation (EC)- Science and applications. *Hazard mater, 84*(1), 29-41.

Mkandawire, M., & Dudel, E. G. (2007). Are Lemna spp. effective phytoremediation agents. *Bioremediation, Biodiversity and Bioavailability*, *1*(1), 56-71.

Muradov, N., Tana, M. , Miranda, F., Kadali, K., Gujar, A. , Rochfort, S.,Ball, S. S. . (2014). Dual application of duckweed and Azolla plants for waste water treatment and renewable fuels and petrochemicals production:. *Biotechnol Biofuel 7*.

Murunga, S. R. (2012). *An efficient and cleaner production system for tea processing industry in Kenya (a case study of Mudete tea factory)* (Doctoral dissertation, University of Nairobi, Kenya).

Obek, E., & Hasar. (2002). Role of duckweed (Lemna minor L.) harvesting biological phosphate removal from secondary treatment effluents. *Fresen. Environmental bulletin, 11*, 27–29.

Orori, O. B. , Etiégni, L., Rajab, M. S., Situma, L. M., & K, Ofosu-Asiedu. (2005). Decolorization of a pulp and paper mill effluent in Webuye Kenya by a combination of electrochemical and coagulation methods. *Pulp and Paper Canada, 106*(3), 21-26.

Paidar, M., Rousar, I., & Bouzek, K. (1999). Electrochemical removal of nitrate ions in waste solutions after regeneration of ion exchange columns. *Journal of Applied Electrochemistry, 29*, 611-617.

Parra, L. M. M., Torres, G., Arenas, A. D., Sánchez, E., & Rodríguez, K. (2012). Phytoremediation of low levels of heavy metals using duckweed (Lemna minor). In *Abiotic Stress Responses in Plants* (pp. 451-463). Springer New York.

Phan, T.B. . (2002). Duckweed: bioremediation of wastewater. *Internal Report for the School of Land and Food Sciences.* (pp. 28): The University of Queensland.

Pilon-Smits, E. (2005). Phytoremediation. *Annu. Rev. Plant Biol., 56*, 15-39.

Pratt, D. J., & Gwynne, M. D. (1977). Rangeland management and Ecology in East Africa. In H. a. Stoughton (Ed.). London.

Rajeshwar, K. , & Ibanes, J. G. (1997). Environmental electro chemistry *Fundamentals and applications of pollution sensors and pollutant treatment*. USA: Academic press.

Rezaee, A., Hossini, H. , Masoumbeigi, H. , & Soltani, R. D . C. . (2011). Simultaneous removal of Hexavalent Chromium and nitrate from Wastewater using Electrocoagulation method. *International Journal of Environmental Science and development, 2*(4).

Salt, D. E., Blayleck, M., kumar P. B. A. N., Dushenkov, v., Ensley, B. D., Chet, L. , & Raskin, L. . (1995). Phytoremediation a novel strategy for the removal of toxic metals from the environment using plants. *Biotechnology, 13*(2), 468-474.

Samson, M. M. . (2010). *Bioassment of the tea Effluent treatment by constructed wetlands, at chemomi tea factory.* (Master of Philosophy in Environmental studies -Biology M.phil. in environmental studies biology), Moi university.

Sangakkara, U.R. (2002). The technology of effective microoganisms: *Case studies of applications.* Cirencester, U. K Royal Agriculture College.

Shammas, N. K. , Pouet, M., & A., Grasmick;. (2010). Waste water treatment by electro coagulation in flotation technology. 99-124.

Singh, O.V., Labana, S., Pandey, G. , Budhiraja, R., & Jain, R.K. (2003). Phytoremediation: an overview of metallic ion decontamination from soil. *Applied Microbiology Biotechnology, 61*, 405- 412.

Skillicorn, P., Spira, W., & Journey, W.. The World Bank: Washington D.C. (1993). *Duckweed aquaculture: a new aquatic farming system for developing countries*. Washington D.C.: The World Bank.

Smith, M.D., & Moelyowati, I. . (2001). Duckweed based wastewater treatment (DWT): design guidelines for hot climates. *Water Science and Technology, 43*, 291-299.

South, D.B. . (1995). Relative growth rates. *A critique of South African forestry journal, , 173*, 43-48.

Susarla, S., Medina, V. F., & McCutcheon, S. C. (2002). Phytoremediation: an ecological solution to organic chemical contamination. *Ecological Engineering, 18*(5), 647-658.

Tanui, J. K., Fang, W., Feng, W., Zhuang, P., & Li, X. (2012). World black tea markets: Relationships and implications for the global tea industry. *Journal of International Food & Agribusiness Marketing, 24*(2), 148-168.

Urgulu, M. (2004). The removal of some inorganic compounds from paper mills effluents by the electrocoagulation method. *G.U.J. Science 17*(3), 85 -99 (14 pages).

Volesky, B. (1990). Biosorption of heavy metals.Bola Raton,FL.CRC Press396p ISBN 0-8493-4917-6.

Vyamazal, J. . (2005). Removal of nutrients via harvesting of emergent vegetation in constructed wetlands for wastewater treatment in natural and constructed wetlands. In Giden (Ed.), *Nutrients, Metals and Management* (ed ed., pp. 209-221). Netherlands: Backhuys publishers.

Wasewar, K. L., Atif, M., Prasad, B., & Mishra, I. M. (2009). Batch adsorption of zinc on tea factory waste. *Desalination, 244*(1), 66-71.

Willett, D. , Rutherford, B., Morrison, C. , & Knibb, W. . (2003). Tertiary treatment of Ary municipal waste water bioremediation; a pilot study. (Q. l. d. o. p. industries, Trans.) (pp. 14): Report to the burdekin shire council and burdekein rangeland reef initiatives.

Yang, Chen-Lu, & McGarrahan, J. (2005). Electrochemical Coagulation for Textile Effluent Decolorization. *Hazardous Materials, 127*, 40- 47.

Yang , Y. . (2009). Electrochemistrical decolourization of C.I. Reactive black K N-B Simulated waste water,chin. *Environmental .science 9*.

Zaroul, Z., Azzi, M. , Saib, N. , & Chainet, N. J. (2006). Contribution to the study of electrocoagulation mechanism in basic textile effluent. *Hazard. Mater, 131*, 73-78.

Zayed, A., Gowthamans., & Terry, N. . (1998). Phytoremediation of trace elememts by wetland plants;duckweed. *Environment quality 127*(3), 715-725.

APPENDICES

APPENDIX I: RESULTS

Results of Physico-chemical parameters

pH

Table 1: Effects of effluent retention time on pH levels for the EC pre-treated and RE effluent treated with duckweed plants.

Type of Treatment		0 days	After 5 days	After 10 days	After 15 days
Raw effluent	Treatment	6.70	7.17 ± 0.1155 (7.1 – 7.3)	7.03 ± 0.06 (7.0 – 7.1)	6.77 ± 0.06 (6.7 – 6.8)
	Control	6.70	6.97 ± 0.0577 (6.9 – 7.0)	7.27 ± 0.06 (7.2 – 7.3)	7.1 ± 0.17 (6.9 – 7.2)
Electrochemically Treated effluent	Treatment	6.70	7.13 ± 0.1155 (7.0 -7.2)	7.03 ± 0.06 (7.0 – 7.1)	6.73 ± 0.06 (6.7 – 6.8)
	Control	6.70	6.83 ±0.1528 (6.7- 7.0)	7.5 ± 0.1 (7.4 – 7.6)	7.3 ± 0.0 (7.3 -7.3)

± = SD

Colour

Table 2: Effects of effluent retention time on Colour levels on EC pre-treated and RE effluent treated with duckweed plants.

Type of treatment		0 days mg/l)	After 5 days (mg/l)	After 10 days (mg/l)	After 15 days (mg/l)
Raw effluent	Treatment	2030	1823.33±138.68 (1670 -1940)	1906.67 ±159.47 (1730 – 2040)	1965.33 ±136.50 (1850-2120)
	Control	2030	2310 ±281.6026 (2000 – 2550)	2030 ± 108.17 (1940 – 2015)	2110.33±166.53 (2050 -2170)
Electrochemically Treated effluent	Treatment	942	628.33 ±163.12 (450-770)	1540 ± 36.06 (1500 – 1570)	1706.67 ±119.30 (1570-1790)
	Control	942	521.67 ±177.86 (395 -725)	502.67 ±128.36 (415 -650)	688.33 ±183.39 (545 -895)

± = SD

BOD (mg/l)

Table 3: Effects of effluent retention time on BOD levels in EC pre-treated and RE effluent treated with duckweed plants.

Type of treatment		0 days (mg/l)	After 5 days (mg/l)	After 10 days (mg/l)	After 15 days (mg/l)
Raw effluent	Treatment	120	63.00 ±4.00 (59 – 67)	27.67 ± 2.08 (26 -30)	8.33 ±2.012 (6 -10)
	Control	120	39.67 ±6.43 (37 - 47)	30.67 ±2.52 (28 -33)	4.67 ±1.53 (3 – 6)
Electrochemically Treated effluent	Treatment	54	32.67 ±7.57 (24 -38)	15.67 ±1.53 (14 – 17)	9.33 ± 2.52 (7 -12)
	Control	54	30.67 ±5.68 (26 -37)	9.0 ± 2.0 (9 – 11)	5.33 ±1.53 (4 -7)

± = SD

COD (mg/l)

Table 4: Effects of effluent retention time on COD levels in EC pre-treated and RE effluent treated with duckweed plants

Type of treatment		0 days (mg/l)	After 5 days (mg/l)	After 10 days (mg/l)	After 15 days (mg/l)
Raw effluent	Treatment	365	274.33 ± 3.21 (272 – 278)	267.00 ± 30.32 (249 – 302)	221.33 ±18.50 (203.00 –240.00)
	Control	365	359.67 ±16.62 (342 – 375)	259.67 ± 24.58 (232 – 279)	233.67 ±30.66 (205 – 266)
Electrochemically Treated effluent	Treatment	256	120.33 ±5.011 (94 – 162)	72.33 ±8.62 (62-80)	66.33 ±8.38 (61 – 76)
	Control	256	64.67 ± 4.04 (61 – 69)	56.33 ±2.08 (54 – 58)	135.67 ±30.89 (108 – 169)

Dissolved Oxygen (mg/l)

Table 5: Effects of effluent retention time on Dissolved Oxygen levels in EC pre-treated and RE effluent both treated with duckweed plants.

Type		0 days (mg/l)	After 5 days (mg/l)	After 10 days (mg/l)	After 15 days (mg/l)
Raw effluent	Treatment	4.10	1.64 ±0.13 (1.56 – 1.79)	2.35 ± 0.11 (2.22 – 2.41)	2.31 ±0.13 (2.16 – 2.42)
	Control	4.10	1.93 ±0.14 (1.8 – 2.07)	2.24 ± 0.13 (2.1 – 2.36)	1.93 ±0.13 (1.78 – 2.03)
Electrochemically Treated effluent	Treatment	4.02	2.13 ± 0.12 (1.99 – 2.23)	2.20 ± 0.11 (2.12 – 2.32)	2.14 ± 0.42 (1.66 – 2.42)
	Control	4.02	2.08 ±0.12) (2.00 – 2.20)	2.24 ±0.14 (2.15 – 2.40)	1.85 ± 0.26 (1.69 – 2.15)

± = SD

TSS (mg/l)

Table 6: Effects of effluent retention time on TSS levels in EC effluents and RE effluent treated with duckweed plants.

	Type	0 days **(mg/l)**	After 5 days (mg/l)	After 10 days (mg/l)	After 15 days (mg/l)
Raw effluent	Treatment	0.08	0.03 ± 0.00 (0.03 – 0.03)	0.003 ± 0.001 (0.002 – 0.003)	0.023 ± 0.006 (0.02 – 0.03)
	Control	0.08	0.03 ± 0.01 (0.03 – 0.04)	0.0028 ± 0.001 (0.002 – 0.003)	0.05 ± 0.016 (0.03 – 0.06)
Electrochemically Treated effluent	Treatment	0.76	0.04 ± 0.01 (0.03 – 0.05)	0.0057 ± 0.005 (0.003 – 0.011)	0.04 ± 0.015 (0.03 – 0.06)
	Control	0.76	0.04 ± 0.015 (0.03 – 0.06)	0.0017 ±0.001 (0.001 – 0.002)	0.02 ± 0.00 (0.02 – 0.02)

± = SD

TDS (mg/l)

Table 7: Effects of effluent retention time on TDS levels in EC effluents and RE effluent treated with duckweed plants.

Raw effluent	Type	0 days	After 5 days	After 10 days	After 15 days
		TDS**(mg/l)**	**(mg/l)**	**(mg/l)**	**(mg/l)**
	Treatment	343	271.00 ± 8.7178 (265.00 – 285.00)	231.33 ±22.98 (213.00 – 257.00)	217.33 ± 19.86 (200.0-239.00)

	Control	343	318.00 ±3.46 (314 – 320)	313.00 ± 16.09 (295.00 – 326.00)	286.67 ± 27.02 (256.00 – 307.00)
Electrochemically Treated effluent	Treatment	303	294.67 ± 3.06 (292.0 – 298.0)	290.67 ±10.21 (279.00 – 298.00)	260.00 ±6.25 (255.00 – 267.00)
	Control	303	340.00 ±3.00 (337.0 – 343.0)	355.67 ± 1.53 (354.00 – 357.00)	376.33 ± 14.29 (364.00 – 392.00)

± = SD

Turbidity (NTU)

Table 8: Effects of effluent retention time on Turbidity levels in EC pre-treated and RE effluent treated with duckweed plants

Type of treatment		0 days	After 5 days	After 10 days	After 15 days
		Turbidity (NTU)	**(NTU)**	**(NTU)**	**(NTU)**
Raw effluent	Treatment	41.00	14.97 ± 4.40 (11.00 – 19.70)	4.83 ±1.01 (3.90 – 5.90)	7.37 ± 2.10 (5.30 – 9.50)
	Control	41.0	22.07 ± 5.49 (17.00 – 27.90)	2.73 ± 0.15 (2.60 – 2.90)	3.40 ± 2.75 (1.60 – 6.60)
Electrochemically Treated effluent	Treatment	21.00	21.83 ±0.06 (21.80 – 21.90)	20.90 ± 0.12 (16.70 – 25.10)	15.57 ± 0.89 (12.40 – 17.20)
	Control	21.0	32.77 ± 9.83 (26.50 – 44.10)	24.43 ± 0.75 (23.70 – 25.20)	30.97 ± 3.69 (28.00 – 35.10)

± = SD

Electrical Conductivity (µS/cm)

Table 9: Effects of effluent retention time on Electrical conductivity in EC effluents and RE effluent treated with duckweed plants.

Type of treatment		0 days **(µS/cm)**	After 5 days **(µS/cm)**	After 10 days **(µS/cm)**	After 15 days **(µS/cm)**
Raw effluent	Treatment	490.00	387.67 ± 12.50 (382.00-402.00)	310.67 ± 28.58 (286.00 –342.00)	330.67 ± 33.31 (304.00 – 368.00)
	Control	490.0	454.33 ±4.6188	446.67 ± 22.8983	361.67 ±79.05 (281.00 –

			(449.00 – 457.00)	(421.00 – 465.00)	439.00)
Electrochemically Treated effluent	Treatment	433.00	420.67 ± 4.0414 (417.00 – 425.00)	414.67 ± 14.5717 (398.00 – 425.00)	371.33 ± 8.74 (364.00 – 381.00)
	Control	433.0	485.67 ± 4.51 (481.00 – 490.00)	508.00 ± 2.0 (506.00 – 510.00)	538.00 ±20.95 (520.00 – 561.00)

± = SD

Nutrients Analysis

Total Nitrogen (TN) (mg/l)

Table 10: Effects of effluent retention time on Total Nitrogen levels.in EC pre-treated and RE tea effluent treated duckweed plants

Type of treatment		0 days **(mg/l)**	After 5 days **(mg/l)**	After 10 days **(mg/l)**	After 15 days **(mg/l)**
Raw effluent	Treatment	7.12	7.24 ±1.67 (6.2 - 8.5)	6.65 ± 0.72 (5.9 -7.34)	5.00 ± 0.63 (4.36 -5.62)
	Control	7.12	6.57 ± 0.80 (5.8 - 7.4)	7.03 ± 0.50 (6.50 - 7.50)	6.5 ± 0.64 (5.8 - 7.0)
Electrochemically Treated effluent	Treatment	2.50	0.17 ± 0.04 (0.126 - 0.21)	0.17 ± 0.06 (0.1 - 0.2)	0.02 ±0.02 (0.00 -0.03)
	Control	2.50	0.15 ± 0.033 (0.11 - 0.14)	0.13± 0.84 (0.00 - 0.3)	0.05 ± 0.05 (0.01 -0.1)

± = SD

Total Pant Nitrogen (T.N) levels in the duckweed used in experiment (mg/l)

Table 11: Effects of effluent retention time on Total Nitrogen levels taken up by duckweed plants used on EC pre-treated and RE tea effluent respectively

Treatment	T.N. After 5 days (mg/l)	T.N. After 10 days (mg/l)	T.N. After 15 days (mg/l)
Raw effluent	4.18 ± 1.66 (4.1743- 4.478)	5.06± 0.27 (4.78 – 5.32)	4.49 ± 0.15 (4.37 – 4.66)
Electrochemically Treated effluent	4.26 ± 2.19 (4.09-4.44)	4.6465 ± 0.19 (4.42 – 4.77)	4.24 ±0.21 (4.03 – 4.46)

± = SD

Initial Total Nitrogen value in the duckweed = 3.68984 mg/l

Nitrites concentration in the effluent (mg/l)

Table 12: Effects of effluent retention time on nitrite levels.in EC pre-treated and RE effluent treated with duckweed plants.

Type of treatment		0 days **(mg/l)**	After 5 days **(mg/l)**	After 10 days **(mg/l)**	After 15 days **(mg/l)**
Raw effluent	Treatment	0.23	0.2263 ± 0.09 (0.1421 – 0.3212)	0.1505 ± 0.09 (0.0906 – 0.2566)	0.0578 ± 0.04 (0.012 – 0.101)
	Control	0.23	0.0922 ± 0.027 (0.061 – 0.113)	0.026 ± 0.003 (0.024– 0.03)	0.0125 ± 0.013 (0.001 – 0.026)
Electrochemically Treated effluent	Treatment	0.045	0.038 ± 0.005 (0.033 – 0.043)	0.032 ± 0.005 (0.027 – 0.036)	0.008 ±0.007 (0.0026 – 0.016)
	Control	0.045	0.0043 ± 0.003 (0.001– 0.007)	0.022 ± 0.019 (0.008– 0.044)	0.0095 ±0.012 (0.002 – 0.023)

± = SD

Nitrate levels. in the effluent (mg/l)

Table 13: Effects of effluent retention time on nitrate levels in EC pre-treated and RE tea effluent after treatment with duckweed plants

Type of treatment		0 days **(mg/l)**	After 5 days **(mg/l)**	After 10 days **(mg/l)**	After 15 days **(mg/l)**
Raw effluent	Treatment	2.68	4.00 ± 1.00 (3.00 – 5.00)	0.40 ± 0.10 (0.30 – 0.50)	0.27 ± 0.06 (0.20 – 0.30)
	Control	2.68	2.033 ± 0.4509 (1.6 – 2.5)	0.47 ± 0.046 (0.42 – 0.50)	0.37 ± 0.058 (0.30 – 0.40)
Electrochemically Treated effluent	Treatment	0.142	0.133 ± 0.058 (0.1 – 0.2)	0.17 ± 0.058 (0.10 – 0.20)	0.07 ± 0.058 (0.00 – 0.100)
	Control	0.14	0.133 ± 0.058 (0.1 – 0.2)	0.13 ± 0.15 (0.00 – 0.30)	0.07 ± 0.058 (0.00 – 0.100)

± = SD

Total Phosphorus levels in effluent (mg/l)

Table 14: Effects of effluent retention time on Total phosphorus levels in EC pre-treated and RE tea effluent after treatment with duckweed plants

Type of treatment		0 days **(mg/l)**	After 5 days **(mg/l)**	After 10 days **(mg/l)**	After 15 days **(mg/l)**
Raw effluent	Treatment	12.51	8.20 ± 3.048 (4.77 – 10.63)	7.44 ± 1.0858 (6.45 – 8.60)	6.81 ± 2.29 (4.83 – 9.32)
	Control	12.51	15.14 ± 1.82 (13.43 – 17.06)	14.16 ± 1.24 (12.73-14.90)	13.16 ± 1.05 (11.97 – 13.94)
Electrochemically Treated effluent	Treatment	3.76	3.42 ± 1.45 (4.8 – 7.6)	2.64 ±.22 (2.38 – 2.80)	2.39± 0.64 (1.81 – 3.08)
	Control	3.76	1.11 ± 0.48 (0.65 – 1.615)	1.70 ± 0.08 (1.61 – 1.76)	3.01 ± 0.72 (2.53 – 3.83)

± = SD

Plant Total phosphorus concentration in duckweed used in experiment (mg/l)

Table 15: Effects of effluent retention time on Total phosphorus levels in duckweed plants used in treatment of EC pre-treated and RE tea effluent after treatment .

Treatment	T.P After 5 days**(mg/l)** (mg/l)	T.P After 10 days **(mg/l)** (mg/l)	T.P After 15 days **(mg/l)** (mg/l)
Raw effluent	0.152 ± 0.072 (0.098 – 0.233)	0.279 ± 0.0016 (0.278– 0.281)	0.277 ± 0.002 (0.275 - 0.279)
Electrochemically Treated effluent	0.136 ± 0.092 (0.032 – 0.209)	0.202± 0.011 (0.1912 – 0.213)	0.214 ± 0.001 (0.213 – 0.215)

± = SD

Initial phosphorus in the duckweed = 0.1687 mg/l

Relative weight analysis

Weight of duckweed plants as used in the Experiment

Table 16: Effects of effluent retention time on the relative growth of the duckweed plants used in the treatment of EC pre-treated and RE tea effluent respectively

Treatment	After 5 days		After 10 days		After 15 days	
	Wet weight (g)	Dry weight (g)	Wet weight (g)	Dry weight (g)	Wet weight (g)	Dry weight (g)
Raw effluent	56.70± 5.79 (52.41 – 63.29)	1.93 ± 0.05 (1.89 – 1.98)	74.84 ± 4.87 (70.79 - 80.303)	3.037 ± 0.13 (2.94 – 3.19)	75.40± 2.62 (72.49 – 77.69	3.26 ± 0.11 (3.19 - 3.39)
Electrochemically Treated effluent	61.48±3.08 (57.94 – 63. 54)	2.10±0.09 (2.01 – 2.20)	76.88 ±2.09 (75.28 – 79.25)	3.11 ± 0.19 (2.99- 3.33)	81.36 ± 6.73 (76.36 – 89.00)	3.42 ± 0.21) (3.25 – 3.65)

± = SD

Initial duckweed weight before treatment = 50g