Adama Science and Technology University

School of Applied Natural Science

Post Graduate Program

Department of Chemistry

Characterization of some Selected Physicochemical Parameters of Effluent from Anmol Product Ethiopia Paper Factory Discharged in to Upper Awash River at Ginchi, Ethiopia.

A Thesis Submitted to Adama Science and Technology University in Partial Fulfillment of the Requirements for the Degree of Master of Analytical chemistry.

By ZERIHUN FEYISA JEBESA

August, 2015

Adama

ADAMA SCIENCE AND TECHNOLOGY UNIVERSITY

SCHOOL OF APPLIED NATURAL SCIENCE

POST GRADUATE PROGRAM

DEPARTMENT OF CHEMISTRY

STREAM OF ANALYTICAL CHEMISTRY

Characterization of some selected physicochemical parameters of Effluent from Anmol Product Ethiopia Paper Factory Discharged in to Upper Awash River at Ginchi, Ethiopia.

A Thesis Submitted to Adama Science and Technology University in Partial Fulfillment of the Requirements for the Degree of Master of Analytical chemistry.

By ZERIHUN FEYISA JEBESA

ADIVISOR ESHETU BEKELE (PhD)

August, 2015
Adama

APPROVAL SHEET

ADAMA SCIENCE AND TECHNOLOGY UNIVERSITY
SCHOOL OF APPLIED NATURAL SCIENCES
CHEMISTRY PROGRAM

This is to certify that the thesis prepared by Zerihun Feyissa Jebessa, entitled ‘‘Characterization of some selected physicochemical parameters of effluent from Anmol Product Ethiopia paper Factory discharged into upper Awash River at Ginchi, Ethiopia’’ and Submitted in Fulfillment of the Requirements for the Degree of Master of science in chemistry complies with the regulation of the university and meets the accepted standards with respect to originality and quality.

Signed by the Examining Committee

Name	Signature	Date
ESHETU BEKELE (PhD) (Advisor)	_____	_____
_____ (Co-Advisor)	_____	_____
SOLOMON GIRMAY (Department Head)	_____	_____
ALEMAYEHU ABEBAW (PhD) (External Examiner)	_____	_____
DEREGE TSEGAYE (PhD) (Internal Examiner)	_____	_____

Acknowledgement

I would like to express my profound gratitude and sincerest appreciation to my advisor, Dr. Eshetu Bekele for his tireless encouragement, guidance, friendly approach, and willingness for heartfelt discussion and help whenever I need him for the completion of this thesis.

My gratitude is extended to Dr. Dereje Tsegaye for his skillful guidance, unreserved support as well as critical and valuable comments and suggestions in my research proposal, progress reports and final thesis.

I am deeply indebted to Dr. Fufa Lemessa for his love, encouragement and financial support starting from my elementary school up to this level. His moral support and utmost encouragement contributed much to my success.

Last but not least, I would like to express my deepest sense of gratitude to my family, particularly my wife Meseret Dibaba, without her love, support, patience and encouragement this thesis would not have been possible.

Table of Contents

ACRONYMS AND ABBREVIATIONS

APEPM Anmol Product Ethiopia Paper Mill

AOX Absorbable Organic Halides

APHA American Public Health Association

BOD Biological Oxygen Demand

BOD_5 Five Day Biological Oxygen Demand

COD Chemical Oxygen Demand

DO Dissolved Oxygen

EC Electrical Conductivity

EFC Elemental Free Chlorine

EDTA Ethylene Diamine Tetra Acetic Acid

EPA Environmental Protection Authority

EEPA Ethiopian Environmental Protection Authority

FAO Food and Agricultural Organization

MoWR Ministry of Water Resource

NTU Nephelometric Turbidity Unit

pH Power of Hydrogen

SPSS Statistical Package for Social Sciences

TFC Total Free Chlorine

TDS Total Dissolved solid

TN Total Nitrogen

TP Total Phosphorus

TS Total Solid

TSS Total Suspended Solid

UNIDO United Nation Industrial Development Organization

List of Tables

List of Figures

List of Plates

Abstract

Pulp and paper industry wastewaters entering water body represent heavy source of environmental pollution. The objectives of this study were characterization of wastewater from Anmol Product Ethiopia Paper factory and the receiving river water quality. Samples from untreated and treated effluents of the factory, and upper Awash River water were examined using standard procedure over two months of dry season. The result shows the brown untreated wastewater consists of BOD5 (470-2499.3 mg/L),COD(2969-5848.6 mg/L), TP(0.37-0.42 mg/L),TN(7.79 20 mg/L),Turbidity(118.3-499.3 NTU),TS(1512-2592.67 mg/L),TDS(1032-2333.3 mg/L),SS(298-501.3 mg/L),EC(1576-3198.7 µS/cm), pH 3.23–10.66,Na(140-900 mg/L),K(2.9-12.1 mg/L),TH (49.5-3335 mg/L), Ca(11.09-1150 mg/L), Mg (5.23-110.4 mg/L), Cl^- (186.22-3818.7 mg/L),$SO4^{-2}$(26.7-282.3mg/L),the treated effluent consists of BOD5(405-1314.6mg/L),COD(2304-3729.6mg/L),TP(0.35-1.69mg/L),TN(12.41-12.80g/l),Turbidity(50.88-418.65NTU),TS(1230-2854 mg/L),TDS(1118-2650mg/L),SS(112-532mg/L),EC(1705-4020 µS/cm), pH 3.4–10.3, Na(130-800mg/L),K(2.1-11.6mg/L),TH (47.52-3036 mg/L), Ca(8.71-1104 mg/L), Mg (6.18-66.24 mg/L), Cl^-(150.41-815.44 mg/L),$SO4^{2-}$ (219.25-424.22mg/L). The mean variations of all parameters are not significantly varied ($p>0.05$) between untreated and treated effluents at 0.05 significant level. The values of most parameters were found higher than the EEPA and WHO prescribed industrial effluent discharge limit. The result also showed the levels of most parameters of the upper Awash River water quality were generally higher in the effluent discharge point than downstream point. At upstream sampling point lowest values were obtained. Excluding pH, K, Mg, Cl^-, Cu, Zn all the rest examined parameters at discharge and downstream sampling points were much higher than the maximum allowable limit. The study concludes the paper mill does not meet the EEPA and WHO prescribed discharge limits and Upper Awash River is highly polluted while the pollution is due to the discharge of effluents from the factory. There is a need of establishment and improvement of APEPM wastewater treatment system, as well as an intervention of regulatory bodies to ensure release of high quality treated final effluents from the factory.

Key words: Physicochemical characteristics, River Water quality, ANMOL Product Ethiopia Paper Mill effluent.

1. INTRODUCTION

1.1. Background the study

Now days, pollution is a major environmental issue in the world due to its adverse effect on living organisms. The increased industrialization has resulted in indiscriminate release of toxic waste in to the surrounding environment. Majority of the industries are water based and a considerable volume of wastewater emanates from them which are generally discharged into water courses either untreated or inadequately treated causing water pollution (Garnaik et al, 2013).

Pulp and paper industry is considered as one of the major potential sources of pollution in the environment. It is ranked as the third world's largest consumer of water and is consequently discharging huge volumes of highly colored and toxic wastewater in the environment causing pollution of soil, air and receiving water bodies (SevimLi, 2005). It is reported that on average, one ton of paper production produces 1.5 to 50 m^3 wastewater depending on the nature of raw materials and extent of water use (European Commission, 2001). The direct discharge of such effluents in aquatic system spoils fresh water ecosystems which results in series problems for aquatic life (Kesalkar et al.2012).

There are two segments, pulping and paper making in paper manufacturing process. Pulping is the major source of environmental pollution. Black liquor from chemical pulping processes is the most significant and troublesome source of pollution. The majority of pollutants released from Pulp and paper industry are rich in dissolved solids such as chloride and sulphate of Na, Ca and varying amounts of suspended organic materials. The effluents are generally alkaline in reaction with high chemical and biological oxygen demands (Kesalkar et al. 2012). The high organic content of pulping wastewater coupled with the process of chlorine results in the production of highly toxic organic compounds such as chlorinated phenols, furans and aliphatic hydrocarbons. Some members of these families are known to be toxic, mutagenic, persistent bio accumulating and are thought to cause harmful disturbances in biological systems and pose human risk through long term exposure via drinking water and through bioaccumulation along with food chain (Raaz Maheshwari et al 2012).

1.2. Statement of the problem

According to Ethiopia guide lines for drinking water Quality, Ministry of Water Resources, 2007 water pollution due to paper industry in Ethiopia was 6.05%. But recently Anmol recycled paper industry which produces paper from recycled pulp was founded near upper Awash River in Ginchi town in 2009. Awash River emanates at an elevation of about 3000 m in the central Ethiopian Highlands, west of Addis Ababa, and flows northeastwards along the rift valley into Afar region where it terminates in Lake Abe at an elevation of 250 meters. The main river length is about 1200 km. The Awash River basin is divided into upper, middle and lower valleys. People living near the river downstream use it for drinking, bathing and irrigation (MoWR, 2001a). However; many externalities are associated with the river. The main set of problems of the River is generated downstream from the disposal of excess wastewater that may contain harmful concentration of salts, organic wastes, and pathogenic organisms (Wagnew, 2004).

Anmol Product Ethiopia Recycled Paper Factory is one of the industry discharging insufficiently treated wastewater directly in to upper Awash River stream. The direct discharge of this effluent has spoiled most of the fresh water of the river creating social and environment concern among the downstream users as well as serious problem to the aquatic life. The effects of effluents from this industry could be observed in that the colour of the river was changed, fishes present in the river before are all disappeared. People living near Awash River in Dendi Woreda have been asking the government bodies to solve the problem.

However; wastewater management is an inherent aspect of many industrial operations and according to the Guidelines and Standards for Industrial pollution control in Ethiopia, all discharges of effluent with constituents beyond the specified limits into public drains, streams, rivers or underground injection are unacceptable (EEPA, 2010). Hence, it is mandatory for this, paper industry to use a satisfactory wastewater treatment system. To promote this understanding of the physicochemical characteristics of wastewater is important to know the efficiency of the existing wastewater treatment system.

Therefore; the aim of this study is to investigate the physicochemical parameters of wastewater released from Anmol recycled paper industry and to assess the upper Awash River water quality at the vicinity of Anmol product Ethiopia paper mill.

1.3. Objective of the study

1.3.1. General objective

The objective of this study is to determine some selected physicochemical parameters of wastewater of Anmol Product Ethiopia Paper Industry and water quality of the upper Awash River around Ginchi.

1.3.2. Specific Objectives

This study has the following specific objectives

- To determine some selected physical parameters of wastewater of Anmol Product Ethiopia paper factory.
- To determine some selected chemical parameters of wastewater of Anmol Product Ethiopia paper factory.
- To compare some selected physicochemical parameters among the treated and untreated effluents of Anmol Product Ethiopia paper factory.
- To asses upper Awash River water quality at the vicinity of Anmol Product Ethiopia Paper mill
- To address Anmol Product Ethiopia paper industry wastewater compliance issues of discharge by comparing the results with available base line data of WHO and EEPA.

1.4. Significance of the study

The finding of this study is expected to be used to indicate how far the chemicals and wastes from the factory are polluting the Awash River. It addresses the effluent compliance issues of discharge by comparing the results with available base line data of WHO and EEPA so that the factory, regulatory bodies such as EEPA, regional and Dendi Woreda environmental protection agencies may use it as input to monitor the effluents so that public safety and environmental protection is assured. Researchers will also use the outcome of the study as well.

2. LITRATURE REVIEW

2.1. General Production Process of Pulp and Paper Industry

Paper is made by pulping wood, non wood substances such as rags and wastepaper, bleaching this pulp and then spreading it out into sheets to make it in to paper. In Paper industry there are usually two separate mills. One is pulp mill which separates the fibres of wood or from other materials, such as rags, wastepaper or straw in order to create pulp. The other is paper mill primarily are engaged in manufacturing of paper from wood pulp and other fibre pulp, and may also manufacture converted paper products (Irma, 2013).

At various stage of the process, chemicals are used to give the paper particular properties, such as the bleaching chemicals that make paper white (which also enable it to subsequently be coloured). Wood contains cellulose, lignin and hemicelluloses, where celluloses are desirable for production of for example paper and textiles and depending on the end-usage of the pulp the level of the separation can be varied. The pulp and paper manufacturing process can be divided in to four steps; wood preparation, pulping, bleaching, and paper making, which are described in the following section (Irma, 2013).

2.1.1. Wood Preparation

Wood arrives to the pulp mills in the form of logs, and is debarked with the help of debarking drums and chipped in the wood chipper before storage in the stacks. The chips are then discharged from the stack base with the help of screws and conveyors and send to the pulping process (ljunberg and Brannvall, 2011).

2.1.2. Pulping

The objective with pulping is to release and soften the cellulose fibres from the wood matrix or recycled paper with the use of chemicals, mechanical or combination of both depending on the desired fibre quality methods to convert the wood into a smooth, soft

pulp suitable for use in paper making (Pokhrel and Viraraghavan, 2004). In chemical pulping, fibres are released from the wood matrix with the use of chemicals in the presence of heat and pressure. The fibre yield for chemical is often around 40-50%, and the rest is considered as by-product. Chemical pulping may be subdivided in to Kraft (sulphate), Sulphite, and Soda (Ljunberg and Brannvall, 2011).

The Kraft process, also known as the sulphate process, is the dominating chemical pulping technology worldwide (Irma, 2013). The process is based on an alkaline solution of sodium hydroxide (NaOH) and sodium sulphide (Na_2S). The presence of caustic soda in the cooking liquor is suitable for the use of practically all wood species. Thus damage to the fibres is reduced and high strength pulps are produced. An advantage of the kraft pulping process is the possibility of recovering both process chemicals and the heat content of the dissolved lignin (Ljunberg and Brannvall, 2011).

The sulphite pulping process is based on an acidic or neutral cooking with salts of sulphites (SO_3^{2-}) or bisulphates (HSO_4^-) (Irma, 2013). This process is most suitable for non resinous softwood. In this method, the fiber binding lignin is softened and dissolved to a considerable extent in a solution containing dissolved SO_2, hydrogen sulphite ions.

The soda pulping was the first chemical process applied in pulp manufacture. In the process, sodium hydroxide is used as cooking liquor with adding mixture of soda ash (Na_2CO_3) and $Ca(OH)_2$ to the digester. This process is most suitable for agricultural residues pulping (Irma, 2013).

In mechanical pulping, wood is processed mechanically with the use of electrical energy. By utilizing a mechanical approach for fibre disintegration the original composition of the wood is retained within the derived fibre, resulting in a high yield of the process (up to 95%). The quality of the pulp is low grade and contains a lot of lignin which can cause post yellowing if applied to papers (Pokhrel and Viraraghavan, 2004).

In semi-chemical process the pulping of wood raw material pulp is obtained by a series of chemical and mechanical wood treatments. Neutral sulphite, in which the active chemical is sodium sulphite, sufficient alkali (usually sodium carbonate or sodium

bicarbonate) is used to keep the digestion liquor alkaline. Cold Soda, in which chips is soaked for several hours in sodium hydroxide at atmospheric pressure without heating (Irma, 2013).

Recycled pulp is sometimes used instead of fresh pulp for board and newspaper manufacturing. This type pulp has a lower strength and stiffness due to the many different origins of the paper. It is here important to remove detrimental substances such as ink, and prepare a component of a stock with uniform quality (Irma, 2013).

2.1.3. Bleaching

The importance of bleaching is to give paper a specific brightness in order to obtain a certain printing quality and to purify the pulp from undesirable impurities that may be present in the final paper quality (Ljungberg and Brannval, 2011). In the past, chlorine bleaching with elemental chlorine was the most common bleaching technology, but was associated with very high concentrations of Adsorbable Organic Halides (AOX) in the emissions and therefore replaced with other technologies. Today, Elemental Free Chlorine (EFC) bleaching with low AOX or Totally Chlorine Free (TFC) bleaching is used. The ECF bleaching is based on chlorine dioxide (ClO_2), consequently only small portions of AOX are formed. In TCF bleaching, neither elemental chlorine nor chlorine containing agents are used. Instead, hydrogen peroxide (H_2O_2), oxygen (O_2) and peracetic acid ($C_2H_4O_3$) are used (Lenntech, 2011). The bleaching operations sequence widely depends on the type of pulp to be bleached. For mechanical pulp bleaching, hydrosulphites are the agents most frequently used, but zinc hydrosulphites are considered more and more unacceptable. Peroxides can also be used but are more expensive (S.R.paranthaman, 2013).

Chemical pulping is mainly achieved by Kraft and sulphite processes. Bleaching Kraft pulp is much harder than bleaching sulphite pulp because of the initial color of the pulp. Bleaching is mostly conducted with a succession of chlorination, alkaline extraction and oxidation. For Kraft pulps 2 or 3 cycles are still necessary. Effluents from bleaching operations are the main source of coloring agents and often very toxic substances, chlorinated organic compounds can represent 3 to 8 kg/t pulp, in some cases dioxin can be discharged (Irma, 2013).

Recycled pulp can be bleached with the same chemicals used to bleach virgin pulp, but hydrogen peroxide and sodium hydrosulfite are the most common bleaching agents. The preparation of recycled paper requires particular treatments which can produce highly toxic solid wastes, difficult to eliminate (Lenntech, 2011).

2.1.4. Paper making

Paper is produced from new or recycled pulp. Papermaking is generally divided into four main operations: stock preparation, sheet formation, drying and finishing. During the process of paper producing, kaolin, $CaCO_3$, talc and/or TiO_2 are added to the pulp, to give the paper whiter color. Also chemicals like organic fillers (starch, latex), dyes, aluminum sulfate, etc. are used to make paper of different properties or making the process simpler. Paper can be decolored, which can be done with two different processes. Washing the pulp with a high amount of water or washing with a low amount of water plus additions like sodium silicates, sodium carbonate, fatty acids or non ion detergents (S.R.paranthaman, 2013).

2.2. Sources of Water Pollution from Pulp and Paper Production

The pulp and paper industry is one of the largest water using industries not only in terms of the volume specific water use but also in terms of the volume of output. The sources of the wastewater in the pulp and paper industry come from raw material preparation, pulping, rinsing, bleaching and paper making process (Irma, 2013).

Toxicity of pulp and paper mill effluent may also be caused by sulfur compounds introduced into the pulping process, dissolved organic compounds of the raw materials, resin and fatty acids and some cases heavy metal (which are used for wood preservation or raising paper quality). More recent questions have been raised regarding chlorinated dioxins, formed during the bleaching process, that effect water quality for human consumption and other purposes. Color and turbidity of effluents cause aesthetic problems. Color of the pulp and paper industry's wastewater is caused mainly by lignin of the wood as well as in some cases by dye (Lenntech, 2011). The sources of the wastewater in the pulp and paper industry come from raw material preparation, pulping, rinsing, chemical recovery, bleaching and paper making process (Irma, 2013).

The wood material preparation at mill site includes weighing, storage, debarking, washing and chipping. The major source of water pollution from the wood preparation is debarking, especially when wet debarking is used. The effluent contains large amounts of dissolved as well as suspended pollutants. In general, wood has to be washed before chipping to prevent damaging the knives by sand and other impurities. Therefore, the wastewater from the process contains course materials (Ljunberg and Brannvall, 2011).

In Pulping, either mechanical or chemical methods are used to produce fibers. In the chemical method, fibrous raw material is treated with chemical cooking liquor which used to dissolve most of lignin and liberate the fibers. The effluent is called black liquor containing lignin and hemicellulose as well as toxic waste material like dimethyl sulphite, methyl mercaptan etc. The wastewater is highly polluted with brown color and high COD. Bottom deposits of lignin cellulosic materials near the discharge point will lead to DO depletion at the discharge point (sdguide, 2008).

The Kaft process is an alkaline process. The lignin is cracked by NaOH or Na_2S, which is very effective at different kind of woods specially the wood contains pollutions. Disadvantage is the odour problem, based on thiols and sulfides. The pulp has also to be bleached more, compared to the suphite process. Process water of this kind of process contains SO_2 and the pH is between 8 and 9 (Irma, 2013).

The sulphite process is a procedure based on acids. The effect is not the same compared to the alkaline process. The procedure is more sensitive, against pollution. The major problem associated with process is the potential for hydrogen sulphide formation when sulphate is widely used as active cooking chemical in pulp mills (Thompson et al., 2001).

The pulp rinsing after the cooking is one of the most important operations in a pulp mill. The rinsing operation aims to separate pulp fiber from spent cooking liquor that contains inorganic cooking chemicals and organic substances dissolved from the fibrous raw materials. A thorough washing that leaves a low residue of black liquor in the washed pulp is also decisive for the amount of polluting discharges from the following process department, i.e. screening and bleaching **(**S.R.paranthaman, 2013).

In order to obtain good properties like white and strong paper the remaining lignin and resinous bark as well as knot particles must removed. This process is called bleaching. The effluent from a bleaching plant contains large amount of lignin related chlorinated compounds which have a negative impact on environment in receiving area and further more they are degrade very slowly. The effluent of bleached pulp affects the diversity, biomass and distribution of fish, invertebrates and plants reported that Kraft mill effluent interacts with a low DO (dissolved oxygen) content and produces synergism effect. This step has the disadvantage to load the environment more, because of the use of chemicals like chlorine or chlorine dioxide which are restricted, because of the process (WHO, 2010).

The process of paper making involve the use of large amounts of water, chemicals, additives and fillers depending on the type of paper to be produced. The toxicity of some additives has to be addressed, particularly heavy metals like mercury (Ljungberg and Brannvall,2011).

In paper recycling industries, because of the color on written, old papers the pulp has to be bleached, bleaching with peroxides, oxygen and ozone is not as efficient as using chlorine or chlorine dioxide. By using chloride or chloride dioxide, the water contains these agents which increase the AOX. The waste water of paper recycling contains also particles which have to be filtrated. Rests of plastics, metal parts (paper clips, etc.) other waste have to be removed (Sdguide, 2008).

2.3. Waste water characteristics

The effluents from pulp and paper industries are often very complex and it is almost impossible to characterize all types of constituent. The waste water generally contain carbohydrates, fatty acids and low molecular weight compounds (formic acid, oxalic acid) (Irmat, 2013).

Waste water generated from wood preparation stage include mostly solid (bark, branches, dirt, sand etc) and dissolved organic matter as wood is chipped and washed. The wastewater often has a brown colour, and contains mostly wood debris, soluble material and chemicals. The brown colour consists of mainly phenolic lignin derivates, arising from lignin depolymerisation. These types of molecules are very hard to

degrade, because of the strong bonds in their molecular structure and will contribute to a high COD (Kreetachat et al. 2007).

Wastewater that is generated from the bleaching process is generally not higher strength than wastewater discharged from the pulping process; the toxicity is however more of an issue. If molecular chlorine or chlorine dioxide is used in the bleaching step, chlorinated organic substances such as chloro phenols, dioxins, resin and fatty acids and furans can be generated many of these are very toxic, bio-accumulative, and mutagenic (Jitendra , 2013).

Inorganic compounds containing chlorates are also formed when chlorine is used in any of its forms in the bleaching process. These are salts of chloric acid and contain the chlorate ion. Chlorates are powerful oxidizers and will often react easily with organic materials present in the wastewaters. The wastewater from the paper industry is characterized by colour, pH, and extreme quantities of COD, BOD, TDS and TSS etc (Pokhrel et al. 2004).

2.3.1. Previous studies of physicochemical Characterization of Pulp and Paper Industry waste water.

Previous studies in physicochemical characterization of pulp and paper mill wastewaters have been carried out in different countries such as India, Vietnam and Canada to investigate the pollution load of pulp and paper effluents and showed that the effluent of pulp and paper mill is acute toxic containing non biodegradable organic matters. Most of the studies have been made in laboratory scale with wastewaters collected from pulp and paper mill effluents, such as Jitendra Giri (2013), Preeti Nandkumar (2007), Irma Karat (2013) and Jamil, (2011), as it is seen in Table 2 below. However, environmental studies on pulp and paper industry in Ethiopia are scarce in literature.

Table.2 Previous studies of physicochemical characterization of pulp and paper industry waste water**.**

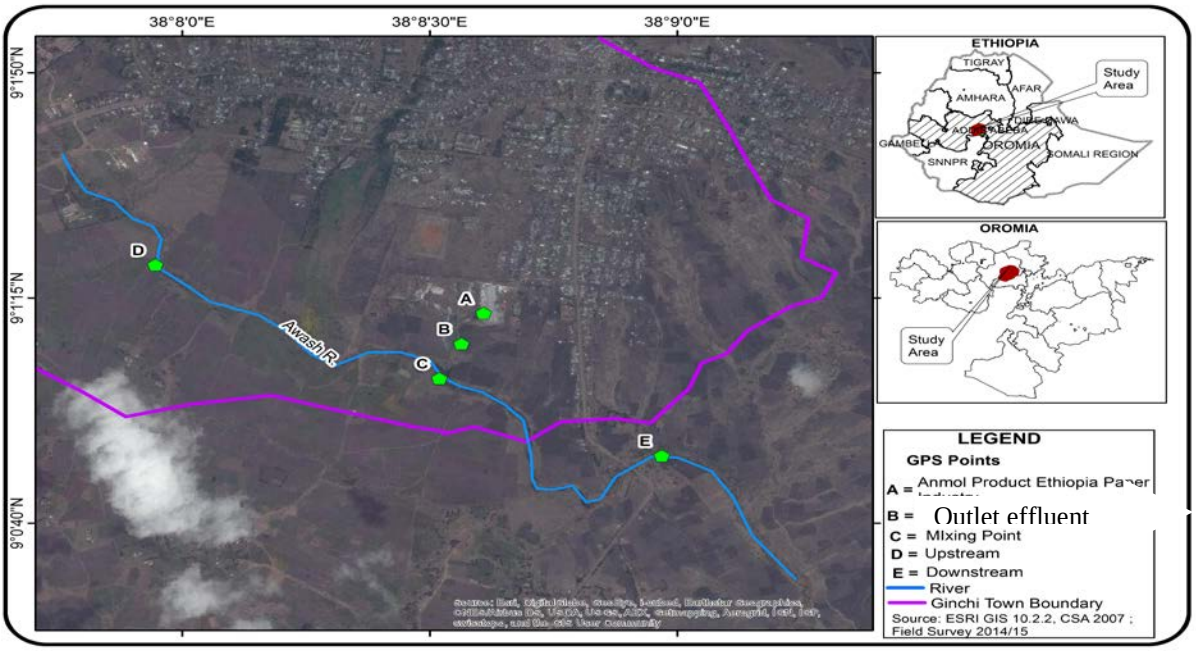
NO	Title	Results of physicochemical characterization	Reference
1	Physico-chemical characteristics of waste water from Egyptian recycled paper Industry	BOD5: 2200 mg/L COD: 10300 mg/L TS: 5950 mg/L	Jamil et al.; (2011)
2	Physicochemical and biological characteristics of paper effluent from the paper mills ofNilakotaiDindigul(Dt), TamilNadu,were analyzed from Nov 2010 to Apr 2011	PH=8.56±0.33 COD(mg/L)=1838±81.85 EC(µs)=1300±26.0 Na(mg/L)=260.99±7.06 TDS(mg/L)=2950±38 Ca(mg/L)=299.66±19.09 BOD5(mg/L)=380±36.55 Mg(mg/L)=184.2±12.48	Surumbar Kuzhali (2010)
3	Effluents from Century Paper and Pulp Industries and their impact on soil properties and chemical composition of plants in Lalkuan, India	PH= 7.32-7.46 , Na(mg/L) = 347-826 Mg(mg/L)= 50-51 , EC(µs)= 790-174 TDS(mg/L) = 486-1380 Ca(mg/L) =1614-2346, BOD5(mg/L)=306-408 Fe(mg/L)=0.17-0.73 ,COD(mg/L)=1736-4357 Cu(mg/L)=0.0003-0.006 ,Chloride(mg/L)=43.5-347.6 Zn(mg/L)=0.010.04 Bicarbonate(mg/L)=352-440	Jitendra Giri (2013)
4	Studies on the effluent generated during the pulping process in paper industry M, Bhilai ,India	PH=11.5 , BOD5(mg/L)= 870 COD(mg/L)=2000 Alkalinity(mg/L)=1159 TS(mg/L)= 2890	Preeti Nandkumar (2007)
5	Advanced Oxidation Processes for Removal of COD from Pulp and Paper Mill Effluents, Stockholm.	t-N=5.89mg/L PH=8.7 t-P= 0.14mg/L *For the treated effluent	Irma Karat (2013)
6	Biodegradation of pulp and paper mill effluent using anaerobic followed by aerobic digestion, India.	PH= 11 , Sulphate = 130mg/L Chloride (Cl^-) =1533mg/L Copper = 0.064mg/L 22. Zn = 0.988mg/L	Narsi R. Bishnoi (2004)
7	studies on different indigenous microorganism in pulp and paper millindustry effluent during march-june,India	 Chloride=1642±2.8 Bicarbonate=280±1.3 PH = 7.54±2.1 Carbonate= nil	**S.**R.parantha man (2013)

3. MATERIALS AND METHOD

3.1. Description of study area

The study area was at Anmol product Ethiopia paper factory which discharges its wastewater into upper Awash River. The location map of the study area is as shown in Figure 3.1 below.

Figure 3.1 Location map of Anmol product Ethiopia Paper factory (Source: *ESRI GIS 10.2.2, CSA 2007)*



The geographical location of Anmol product Ethiopia paper industry is in Oromia region 74 kms west of the capital city Addis Ababa in the Dendi district located at Ginchi town near upper Awash River and it covers over 13-hectare areas. It is the first foreign investment in Ethiopia for manufacturing of paper by Anmol Polymers Company of India and known by the name of Anmol products Ethiopia PLC (APEP). The area has an average annual temperature of 23.8°C and receives mean annual rainfall of 1172 mm. The altitude of the study area is 3000 meter above sea level with dry mid land (wayina daga) climatic condition (Birhanu, 2008). The area lies between 38°8'0"E to 38°9'0"E and 9°0'40"N to 9°1'50"N. The factory collects raw material from different parts of the country as well as from other countries. Sometimes the factory

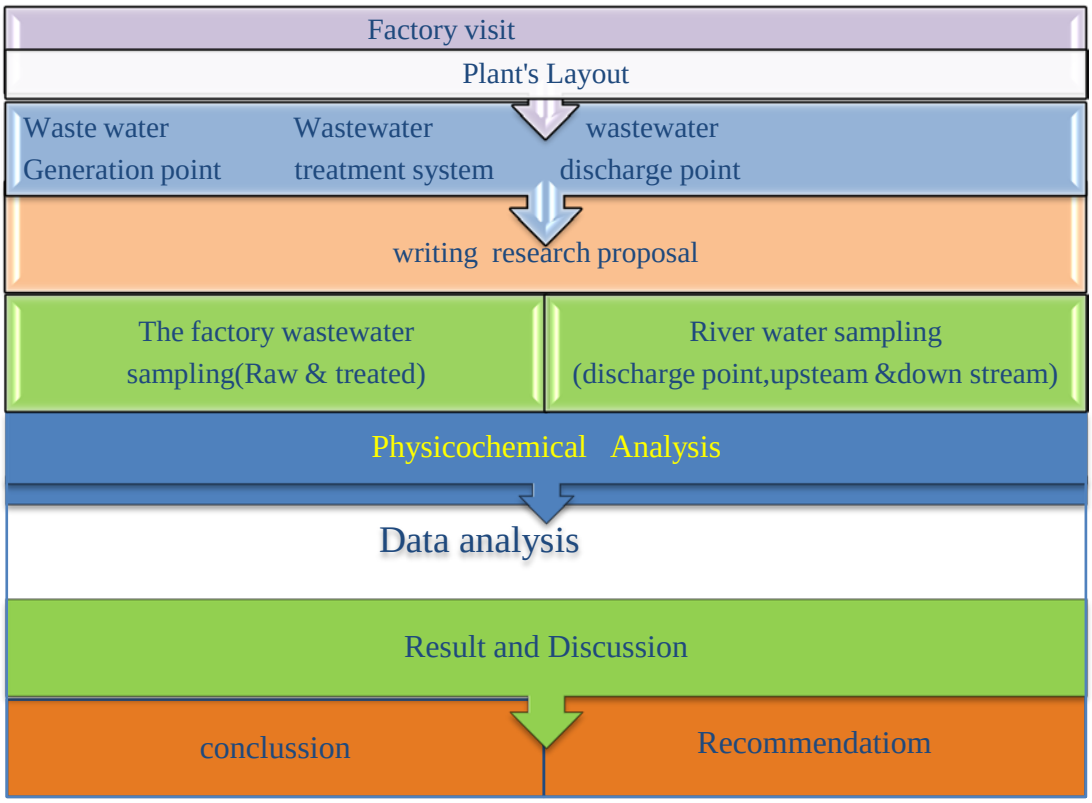
import finished pulp from Indonesia and convert it into paper. The mill uses wheel water from two sedimentation sources pumped to the production area of the mill through plastic tubes which is used for domestic use includes staff housing and office consuming and for steam boiler use after adding chemical to soften the water. The wastewater from the mill is passed through a plastic tube and pumped to a storage pond near the mill. The effluent is screened and the final discharge to nearby land is during night time. The pulp collected here is reused in the Mill. The effluent leaving the pond is directly discharged to river Awash through a small stream as shown in plate 3.1 below.

Plate 3.1 the flow Coarse of the effluent from APEP

3.2. General Research Design

The General design of the approach that was followed in this particular study is summarized in Figure 3.2.

Figure.3.2. Flow diagram of the research design



3.3. Experimental

3.3.1. Apparatus and instruments

Conductivity meter (HI 8733, Singapore) was used to measure electrical conductivity; pH meter (HI9023 microcomputer, Germany) was used to measure pH, drying oven (Digitheat, J.P.Selecta, Spain), digital analytical balance (Mettler Toledo, Model AB104, Switzerland) with ± 0.0001 were used to weigh the solid residues sample. Flame photometer (Halseled-410, England,UK) was used for the determination of Sodium and Potassium concentration. UV-Visible Spectrophotometer (HACH Scientific LTD 6305, Essex, USA) was used for the determination of Sulphate,

turbidity, Cr, Zn, Fe and Cu concentrations. Biochemical Culture Box (SPX 250B, China), 125 mL capacity, round bottom flasks with ground glass joint (300 mL) fitted with reflux condenser (UK) were used to determine concentrations of BOD, Automat digester (B414,Switzerland), Conical flask 500mL (Glascco, Switzerland) were used to determine concentrations of COD), Kjeldahl heating apparatus (K-355, Switzerland) was used to determine concentrations of total nitrogen, UV-Visible Spectrophotometer (T/70/T80,China) was used to determine concentrations of TP, Burette (50 mL) (Shanghai, China) were used during titration procedures. Measuring cylinders, pipettes, Borosilicate volumetric flasks (25, 50 and 100 mL) were made use during measuring different quantities of volumes of sample, acid reagents and standard solutions, Polyethylene bottle, Filter paper 70 µm pore, glass fiber filter (47 mm size).

3.3.2. Chemicals and reagents

All the reagents and chemicals used in this study were analytical grade. Hydroxylamine buffer solution, disodium hydrogen phosphate pH= 7.4 and borax pH= 9.2, (BDH Chemicals Ltd. England), 0.25 N $K_2Cr_2O_7$ solution (Breckland Scientific LTD), 0.25N ferrous ammonium sulfate and Ferroin indicator (Eurostar Scientific LTD), 8N NaOH, manganous sulphate, sodium iodide azide reagent, conc.H_2SO_4, 0.025N $Na_2S_2O_3$ solution, starch indicator and powder $HgSO_4$, methyl red-Bromocresol mixed indicator, 40% NaOH, 2% boric acid, conc. HNO_3, vanado molybdate, conc. HCl, H_3PO_4, H_3BO_3 buffer solution were all supplied by CDH Chemicals Ltd., England. All the chemicals and reagents used at Water Works Design and Supervision Enterprise Water Quality Laboratory Service such as Calmagite indicator, 0.02N EDTA, Calver 2 calcium indicator, phenolphthalein indicator, methyl orange indicator, standard 0.014N silver nitrate solution and potassium chromate indicator, SulfaVer 4 reagent, Na_2SO_4 standard solution , powder Copper sulphate and Potassium sulphate mixture, sodium ascorbate, Zincon reagent, $NH_2OH.HCl$ solution, Sodium meta bisulfite solution, diphenyl carbazide reagent, Phenanthroline reagent, neocuproine reagent, Stock standard solutions containing 1000 mg/L, in 2% HNO_3, of the metal Fe, Zn, and Cu were supplied by HACH Scientific LTD,USA. Distilled water was used for dilution of sample and metal standard solutions as well as for rinsing glassware and sample bottles.

3.4. Sampling Sites

The Anmol product Ethiopia Paper Mill effluents and upper Awash River water samples were collected from five sampling sites. Sampling site (A), this represent the factory site (raw wastewater) which was designated as 0 meter distance. Sampling Site (B), this site was located approximately 100 to 150 m after the effluent leaving the pond. Sampling site (C), this is the effluent discharge point into Awash River. Sampling Site (E), this site was located approximately 2 to 3 km downstream of the effluent entry point. Sampling Site (D) located nearby unpolluted site upstream of the river at 1-2 km around Ginchi town for comparison purpose. The wastewater and river water samples were collected in polyethylene plastic bottles and transported to Jije Labo Glass Analytical Laboratory service and Water Works Design and Supervision Enterprise Water Quality Laboratories, Addis Ababa.

3.5. Sampling Techniques

Grab samples of the raw and treated wastewater from Anmol Product Ethiopia Paper industry were collected in the month of January to March, 2015 of dry season from sampling sites designated as A and B. In addition, grab samples of upper Awash River water samples were also collected at the discharge points, upstream and downstream of the discharge points during the sampling periods of the wastewater and designated as C, D, and E respectively. The grab samples (2L each) were collected in polyethylene plastic bottles from all sites in two weeks interval and transported to each laboratory within 2 hours which were refrigerated at 4°C prior to further treatment. All the bottles were previously washed with detergent and rinsed with the water sample at the point of collection. The reason for the selection of dry season and two weeks gap were by taking in to consideration the time limit given to complete this work. In general, Sample collection and handling procedure were performed according to standard procedures recommended by American Public Health Association (APHA, 2005).

3.6. Analytical procedures

Anmol Product Ethiopia Paper Mill (APEPM) wastewater and upper Awash river water samples collected from different locations were analyzed for chemical parameters such as Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total nitrogen (TN) and Total phosphorus (TP) at Jije Labo Glass Analytical Laboratory service, Addis Ababa while chemical parameters such as Sodium (Na), Potassium (K), Calcium (Ca), Magnesium (Mg), Sulfate, Carbonates, Chloride, Iron (Fe), Zinc (Zn) and Copper (Cu) and also physical parameters such as pH, colour, turbidity, electrical conductivity (EC),Total Dissolved Solids(TDS),Total Solids (TS) were determined at Waterworks Design and Supervision Enterprise Water Quality Laboratory Service using the standard methods of American Public Health Association (APHA, 2005) as explained below.

pH measures the hydrogen ion concentration of a sample. It was determined at room temperature by Systronic digital pH meter. The standardization of the instrument was done with a buffer solution of disodium hydrogen phosphate (pH= 4.7) and borax (pH= 9.2). The pH value was obtained directly from the instrument. Color of the effluent was noted by visual observation.

The measurement of electrical conductivity is an excellent indicator of total dissolved matters (Sarma et al 2008). Conductivity of the Anmol Product Ethiopia paper Industry wastewater and upper Awash River water during this study was determined by using a conductivity meter as per the instruction manual supplied with the instrument and the result was expressed as µS/cm.

Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through the sample. Excessive turbidity in water can cause problem for water purification process such as flocculation and filtration which may increase treatment cost. High turbid waters are associated with microbial contamination. Again turbidity causes decrease in photosynthesis process since turbidity prevents deep penetration of light in water (Muoghalu and Omocho, 2000). Turbidity of the Anmol Product Ethiopia paper Industry wastewater and upper

Awash River water samples were measured in Nephelometric turbidity units (NTU) by UV-Visible Spectrophotometer.

Hardness is mainly due to presence of divalent cations like Ca^{2+}, Mg^{2+}, Sr^{2+}, Fe^{2+} and Mn^{2+} which may be present in the combination with various anions like CO_3^{2-}, HCO_3^-, SO_4^{2-}, Cl^-,NO_3^- etc. Calcium and magnesium are the major scale forming hardness in water. Total Hardness is sum of calcium and magnesium concentrations and is a measure of the capacity of water to precipitate. The general accepted classification for hardness of water is 75 to 150 mg/L of $CaCO_3$ for soft and 150 mg/L and above for hard water (Deat, 2000). In this study 50 mL of the samples were taken and 3 drops of hydroxylamine buffer solution were added into it to give a pH 10. Then Manver 2 Hardness indicator (Calmagite) was added and titrated with 0.02N EDTA, with continuous stirring, at the end point the solution was changed from pink to blue color.

Calculation:

$$\text{Total Hardness (EDTA) as mg } CaCO_3\text{/ L} = \frac{ABX1000}{Volume\ \ of\ sample\ \ used\ ,ml}$$

Where A= volume of EDTA used by the sample

B= mg $CaCO_3$ equivalent to 1mL EDTA titrant.

Calcium hardness: 50mL of each sample was taken and 3 drops of hydroxylamine buffer solution were added into it to give a pH 10. Then Calver 2 calcium indicator and 8N NaOH were added and titrated with 0.02N EDTA, with continuous stirring, at the end point the solution was changed from pink to blue color.

$$\text{Calcium Hardness as } CaCO_3 \text{ as mg/L} = \frac{\text{AXDX 1000}}{\text{Volume of sample used ,mL}}$$

Where A_1 = volume of EDTA used by sample

D =mg CaCO3 equivalent to 1mL EDTA titrant

Mg hardness = Total hardness as $CaCO_3$ in mg/L – Calcium hardness as $CaCO_3$ in mg/L

Total Solid (TS) and Total Suspended Solid (TSS): Both TS and TSS were measured gravimetrically i.e. well mixed measured samples were evaporated in a pre weighed dish at 105°C in an oven. The increase in weight over that of the empty dish was representing for the TS. Similarly, a well mixed water sample was filtered through a pre weighed glass fiber filter (47 mm size) and the residue retained on the filter was dried at

105°C in an oven. The increase in weight of the filter was representing for the TSS. Calculations for both parameters were done as follows:

mg of total solids (TS)/l = $\frac{A-B}{\text{filtrate sample volume ,in mL}} x1000$

Where: A = Weight of dried residue + dish, B = Weight of dish

mg of Suspended solids (TSS)/l = $\frac{A-B}{\text{volume of sample}}$ x 1000.

Where: A=weight of filter + dried residue, and B = weight of filter

Total Dissolved Solids (TDS) is the filterable residue that passes through a standard membrane filter or glass filter disk and remains after evaporation and drying at 180°C. It is the measure of total inorganic salts and other substances that are dissolved in water (Mishra et al, 2009). In this study, a well mixed sample was filtered through a membrane filter (70 mm size). 50mL of the filtrate was transferred in per weighed evaporating dish and evaporated to dryness on steam bath. The evaporated sample was dried for about 1 hour in an oven at 180°C then cooled in desiccators and weighed.

mg/L total filterable residue at 180°C = (A –B) x 1000 / C

Where: A = weight of dried residue + dish, B = weight of dish, C = mL of filtrate used

Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) tests are useful in determining the relative waste loading and its higher degree therefore indicates the presence of large amount of organic pollutant and relatively higher level of microbial activities with consequent depletion of oxygen content of water bodies (Kuforiji et al, 2013). These are important parameters, used to determine whether a water body is polluted or not. The higher the BOD and COD values would be depleting the higher dissolved oxygen concentration in the receiving rivers by organic and inorganic pollutants present in the effluents. Biochemical oxygen demand is the measure of the oxygen required by microorganisms whilst breaking down organic matter. The BOD measurement of waste water and water samples was the difference of dissolved oxygen in the sample before and after incubation in dark. Incubation was made at 20 ºC in BOD incubator for five days (5-Day BOD Test).

Dissolved Oxygen (DO) was determined by Winkler's azide modification of the iodometric method. 300mL samples were taken in BOD Bottles. 1 mL of manganous sulphate and sodium iodide azide solution was added into each bottle. The Bottle was

shaken and then brown precipitate was allowed to settle down. Later 1 mL of conc. H_2SO_4 was added to each bottle to dissolve the precipitate, resulted in yellow colour solution on complete dissolution. 200 mL of this yellow solution was titrated against standard 0.025N $Na_2S_2O_3$ solution in presence of starch indicator. The end point was indicated by disappearance of blue colour. The chemical reactions involved in the method are given below.

a. $MnSO4 + 2NaOH \rightarrow Mn(OH)_2 + Na_2SO4$(white ppt)
b. $Mn(OH)_2 + O_2 \rightarrow 2MnO(OH)_2$(Brown ppt)
c. $MnO(OH)_2 + 2H_2SO4 + 2NaI \rightarrow MnSO_4 + Na_2SO4 + I_2 + 3H_2O$
d. $2Na_2S_2O_3.5H_2O + I_2 \rightarrow Na_2S_4O_6 + 2NaI + 10H_2O$
e. $2NaN_3 + H_2SO4 \rightarrow 2HN_3 + Na_2SO4$
f. $HNO_2 + HN_3 \rightarrow N_2 + N_2O + H_2O$

Calculation for DO: 1mL of 0.025N $Na_2S_2O_3$ = 0.2mg of O_2

Determination of BOD:

Freshly collected Anmol Product Ethiopia paper Industry wastewater and upper river Awash water samples were diluted to about 100 times to get measurable amount of oxygen after five days of incubation. Each sample was filled into four BOD bottles. Initial oxygen concentration was determined immediately in two of the bottles. Remaining two bottles were incubated in BOD incubator at 20ºC for five days, and then oxygen concentration was again determined.

$$\text{BOD as } O_2 \text{ mg/L} = \frac{(D1 - D2) \times 100}{\%\ \text{dilution}}$$

Where, D1 = DO of sample immediately after preparation, mg/L

D2 = DO of sample after incubation period, mg/L after 5 days incubation

Chemical Oxygen Demand (COD) was determined by an open reflux titrimetric method. It is the measure of amount of oxygen required by specified amounts of oxidants (potassium dichromate) in concentrated sulfuric acid to breakdown both organic and inorganic matters. In this study 10 mL samples were taken in 250 mL refluxing flask. 0.2 gm of $HgSO_4$ and 15 mL of conc. H_2SO_4 reagent were added. The Solution was cooled and 5 mL of 0.25 N, $K_2Cr_2O_7$ solution was added. This solution was refluxed for two hours. After 2 hours of reflux, the solution was cooled and diluted to final volume of 70 mL by distilled water. Excess dichromate of 25 mL refluxed solution was titrated against 0.25N ferrous ammonium sulfate in presence of 3 drops of

Ferroin indicator. End point of the titration was indicated by a color change from blue green to reddish brown. The chemical reactions involved in the method are:

a) $2K_2Cr_2O_7 + 8H_2SO_4 \rightarrow 2K_2SO_4 + 2Cr_2(SO4)_3 + 8H_2O + 3O_2$

b) $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

c) $Cr_2O_7^{2-} + 6Fe^{+2} + 14H^+ \rightarrow 6Fe^{+3} + 2Cr^{+3} + 7H_2O$

Simultaneously a blank was also run and COD value was calculated as

$$\text{COD mg/L} = \frac{(A - B) \times N \times 8{,}000}{\text{volume of sample}}$$

Where: A = mL of ferrous ammonium sulfate titrant used for blank.

B = mL of ferrous ammonium sulfate titrant used for sample

N = Normality of ferrous ammonium sulfate titrant.

8000 = Milieq. wt. of O_2 x 1000

Alkalinity is an important parameter in determining a stream's ability to neutralize acidic pollution from rainfall or wastewater (EPA, 2013). It is primarily due to carbonate, bicarbonate and hydroxide contents. Alkalinity is equal to the stoichiometric sum of the bases in solution. In the natural water carbonate alkalinity tends to make up most of the total alkalinity due to the common occurrence and dissolution of carbonate rocks and presence of carbon dioxide in the atmosphere. Aerobic degradation can decrease alkalinity. It results in dissolved organic matter and the production of hydrogen ions. An increase in H^+ clearly decreases alkalinity (Kim et al., 2009). Alkalinity of sample is estimated by titrating with 0.02N standard sulphuric acid at room temperature using phenolphthalein and methyl orange indicator. Titration to decolourisation of phenolphthalein indicator indicates complete neutralization of OH^- and ½ of CO_3^{2-}, while sharp change from yellow to orange of methyl orange indicator indicates total alkalinity. Once the phenolphthalein and total alkalinities are determined hydroxide, carbonate and bicarbonate are easily calculated from the table given below.

Table 3.2 Type of alkalinity

Values of P and T	Types of Alkalinity		
	OH^-	CO_3^{2-}	HCO_3^-
P = O	0	0	T
P<1/2T	0	2P	T-2P
P = 1/2T	0	2P	0
P>1/2T	2P-T	2(T-P)	0
P = T	T	0	0

Source: APHA, 2005

25 mL of each sample was taken in a separate 250 mL conical flask and 4 drops of Phenolphthalein indicator solution was added. Pink color was appeared and then, titrated with sulphuric acid (0.02N) until the solution became colorless. Volume of sulphuric acid used was recorded. Then, 3 drops of methyl orange indicator solution was added and was titrated against sulphuric acid (0.02N) to light pink colour. Total (T) and phenolphthalein (P) alkalinities were calculated as follows:

P-alkalinity, as mg $CaCO_3$/L = A x N x 1000/mL sample

T-alkalinity, as mg $CaCO_3$/L = B x N x 1000/mL sample

Where, A = mL of H_2SO_4 required to bring the pH to 8.3

B = mL of H_2SO4 required to bring the pH to 4.5

N = normality of H_2SO4

Once carbonate and bicarbonate alkalinities are known, then their conversions to milligrams CO_3^{-2} /L or HCO_3^-/L are possible.

mg CO_3^{-2}/L = Carbonate alkalinity mg $CaCO_3$/L x 0.6

mg HCO_3^- /L = Bicarbonate alkalinity mg $CaCO_3$/Lx 1.22

Chloride (Silver nitrate titrimetric method).Chloride was determined by titrating the sample against 0.014N silver nitrate solution in the presence of potassium chromate indicator. End point of titration was indicated by appearance of pinkish yellow colour of silver chromate. A blank was also titrated simultaneously, and the obtained values were computed in the formula.

$$Ag^+ + Cl^- \rightarrow \text{AgCl} \downarrow$$

Chloride mg/L as Cl^-= (A –B) x N x 35.45 x 1000 / volume of sample

Where, A = mL $AgNO_3$ required for sample

B = mL $AgNO_3$ required for blank, and

N = Normality of $AgNO_3$ used

Sulphate (SulfaVer 4 method): 50 mL of each sample was taken and diluted to 100 mL. The diluted samples were treated with SulfaVer 4 reagent powder pillow and Sulfate ions in the samples reacted with barium in the SulfaVer 4 to form a precipitate of barium sulfate. The SulfaVer 4 also contained a stabilizing agent to hold the precipitate in suspension. The amount of turbidity formed is proportional to the sulfate concentration and measured at 450 nm in an absorption cell of 5 cm. A blank prepared

from deionized water, treated and measured equally as the water samples. Sulfate concentration in the sample was estimated by comparing turbidity reading with a calibration curve prepared from Na_2SO_4 standard solution at 5 mg/L increments in the 0 to 40 mg/L SO_4^{2-} range.

$$\boldsymbol{Ba^{+2} + SO4^{2-} \rightarrow BaSO_4 \text{ (Suspension)}}$$

$$\text{mg of } SO_4^{2-}/\text{L} = \frac{\text{mg of } SO_4^{2-} \text{x } 1000}{\text{volume of sample}}$$

Total Nitrogen and Total phosphorus are nutrients which are essential for the growth of algae and other plants. Aquatic life is dependent upon these photo synthesizers, which usually occur in low levels in surface water. Excessive concentrations of nutrients, however, can over stimulate aquatic plant and algae growth. Bacterial respiration and organic decomposition can use up dissolved oxygen, depriving fish and invertebrates of available oxygen in the water and causes eutrophication (Tenagne, 2009).

Total Nitrogen (Kjeldahl method) : The method consists of three basic steps: 1) digestion of the sample in sulfuric acid with a catalyst, which results in conversion of nitrogen to ammonia; 2) distillation of the ammonia into a trapping solution; and 3) quantification of the ammonia by titration with a standard solution. In this study**,** 50mL of each sample was taken on duplicates for digestion into digestion tube. The digestion was performed by adding 10 mL concentrated sulfuric acid and 2 mg mixture of Copper sulphate and potassium sulphate for about 3hrs at 370°C on automatic digester. The digested sample was cooled down and diluted by 50 mL distilled water to overcome serious reaction during NaOH addition. Diluted digest was taken to distillation apparatus and 60 mL of 40% NaOH added to digestion tube to neutralize ammonium sulphate. The distillate was collected in 250 mL conical flask which contains 25 mL of 2% boric acid to trap ammonia and 4 drops of methyl red and methylene blue mixed indicator was added. Then the trapped distillate was titrated against 0.005N standard H_2SO_4. The volume of titrant consumed by sample and blank was recorded.

$$\text{Calculation: mg } NH_3\text{-N /L} = \frac{A-B\ X70}{\text{volume of sample}}$$

A = volume of H_2SO_4 titrated for sample, mL and

B = volume of H_2SO_4 titrated for blank, mL

Total Phosphorous (Vanadomolybdophosphoric acid colorimetric method): 50 mL of each sample on duplicates were taken for digestion. The digestion was performed by using 1 mL conc. H_2SO_4 and 5 mL conc. HNO_3 for 30 minute in a micro Kjeldahl flask. These conditions allowed for hydrolysis of the condensed inorganic and organic phosphates in the samples to be converted to orthophosphates. The digested sample was filtered on 100 mL volumetric flasks through 0.45 µm membrane filters and the extract made to volume by distilled water. Then 40 mL aliquot volume was taken from extract to 50 mL volumetric and 10 mL of vanado molybdate in an acid medium was added to produce phosphate molybdate complex with an intense yellow colour. After 30min (after Color developed) the sample was taken to UV-Visible spectrophotometer and absorbance was measured at 470 nm. The concentration was taken in mg/L on the calibration curve. A blank prepared from deionised water was measured in similar manner.

Calculation, $\text{mg P/L} = \frac{\text{mg P (from the curve) x 1000}}{\text{volume of sample}}$

Sodium and Potassium (Flame photometric method): Blanks, sodium and potassium calibration standards in a range of 0 to 100 mg/L were prepared and the emission intensity was adjusted at 589 nm for sodium and 766.5 nm for potassium. The calibration standards were aspirated into the flame photometer and a calibration curve was constructed from the readings. Then 25 mL of each sample was transferred to 50 mL volumetric flask diluted to the mark and fed in the flame photometer. The readings were noted to get the amounts of sodium and potassium directly as milligrams per liter, by referring to the calibration curve. Sodium and potassium concentration of the samples were determinedd as follows.

mg of Na/L = (mg Na /L in portion) x D

mg of K/L = (mg K/L in portion) x D

Where, D = Dilution factor

Determination of Copper (neocuproine method): 1 mL conc. H_2SO_4 and 5 mL conc. HNO_3 were added to 100 mL sample and boiled until the solution become colourless. 50 mL of this solution was added, into a 100 mL separate funnel and 10 mL neocuproine reagent was added. Shacked and transferred to an absorption cell of 1cm and absorbance was measured at 457 nm. Calibration curve was constructed by plotting

absorbance values against standard Copper concentrations. Milligrams of Copper in the sample determined from the calibration curve.

mg Cu/L = µg Cu (in 25 mL final volume) / volume taken for extraction

Total Iron (Phenanthroline method): 50 mL of the sample was taken and 2 mL $NH_2OH.HCl$ solution was added and boiled to insure dissolution of all the iron. The solution was cooled to room temperature and transferred to a 100 mL volumetric flask. 10 mL sodium acetate solution and 10 mL Phenanthroline solution were added, diluted to the mark with water, mixed thoroughly and allowed for 10 min until an orange colour was developed and measured at a 510 nm, providing a light path of 1cm. Calibration curve was constructed by plotting absorbance values against concentrations of a range of standards containing the same amounts of phenanthroline, hydroxylamine, and sodium acetate as the sample, distilled water was used as a blank and set at zero absorbance. Milligrams of Iron present in the sample determined from the calibration curve.

mg Fe/L= µg Fe (in 100mL) / volume of sample

Determination of Zinc (Zincon method): 1 mL of conc. HCl was added to 50 mL sample, mixed thoroughly, filtered and pH was adjusted to 7 by using 1N NaOH. 5 mL H_3BO_3 buffer solution, 0.5 g sodium ascorbate, 2 mL KCN solution and 3 mL Zincon solution were added. Appropriate portion of the solution was transferred in an absorption cell of light path of 1 cm and measured at 620 nm. Calibration curve was constructed by plotting absorbance values against milligrams of a range of standards of Zinc solutions containing the same amounts of reagents in the sample.

Concentration of Zinc (in mg/L) = directly Read from the calibration curve.

3.7. Contamination Control

Rigorous effort was taken to avoid contamination during processing of samples for analysis of wastewater. This applied to the collection of sample material, separation and preparation of subsamples for analysis as per APHA, 2005. All apparatus were cleaned with tap water and detergents, rinsed with deionized water and dried well before use. Strong oxidizing agents employed for well. After each analysis, the apparatus were soaked in nitric acid, rinsed with deionized water, and dried before the next analysis.

Polyethylene encased magnetic stirrer for mixing solutions was used. Standard solutions were prepared immediately before use.

3.8. Method Validation

A blank was conducted using distilled water and reagents for the characterization of the physicochemical parameters. Samples were analyzed in triplicate and Calibration of the instrument was carried out with range of standard solution. For UV-Visible spectrophotometric and flame determination five working calibration standards were prepared by serial dilution of concentrated stock solution of each metal solution. A calibration curve of Absorbance Vs concentration was established for each metal and used for determination of metal concentration in the samples of effluent and river water

3.9. Statistical Methods

The data analysis for all parameters was made by using SPSS version 15.0 software and excel 2007 program. SPSS was used to determine the Mean, Standard deviation and range of the parameters. The comparison between means of data obtained from physicochemical analysis of effluents was compared using paired t-test at the 0.05 significant levels by using SPSS. The coefficient of correlation between some physicochemical parameters was calculated by Pearson correlation test at 0.05 and 0.01 significant levels and results were presented in terms of Tables, graphs and charts performed using Microsoft office excel 2007 program.

4. RESULTS AND DISCUSSIONS

4.1. Selected Physicochemical Characteristics of Anmol Product Ethiopia Paper Industry Wastewater

Wastewater characteristics based on the analysis of the grab samples from untreated and treated wastewater of Anmol Product Ethiopia Paper factory for two consecutive months (January to March, 2015) are shown in Table 4.1 below. The values of the results were compared with the standard set by EEPA (2010) and WHO (2008) for the discharged of wastewater from industries into surface water. The table summarizes mean, standard deviation and relative standard deviation of the physicochemical properties of untreated and treated wastewater samples of APEPM and the values of physicochemical parameters of each determination date during the study period are summarized in appendix.

The effluent from the digestion step has oily dark brown color at origin in untreated effluent which gradually turned in light brown color in treated wastewater. This may be due to the presence of low and high molecular weight organic compounds generated from the lignin degradation product which are produced during different stages like paper making, bleaching and alkali extraction and dying (Kreetachat et al., 2007). But the color of effluents released from the imported pulp was milky and gradually turned in to green in treated wastewater.

The pH of the wastewater was oscillating between acidic and basic range, with value 3.23 for the untreated and 3.4 for the treated bleached wastewater of the imported pulp. However; the PH value of the wastewater from the digestion step was 10.66 for untreated wastewater and 10.3 for wastewater released from the pond. The low pH values of effluents may be attributed to, the process is based on an acidic digestion with salts of sulphites (SO_3^{2-}) and also due to the metabolic production of acids by indigenous microorganisms (Irma, 2013). The value obtained for alkaline pulping process is comparable with the value reported by Preeti Nandkumar (2007) 11.5 for Kraft paper mill at M. Bhilai (India). The high pH values of effluents may be attributed to caustic treatment during pulping or bleaching process of the raw material and the higher alkalinity levels observed during the process (Ipeaiyeda & Onianwa, 2011). The

values did not meet EEPA and WHO permissible limits of pH as 5-9 for the discharge of wastewater into surface water.

Table 4.1 Average Selected physiochemical characteristics of APEPM wastewater and their mean comparisons with standard discharge limits (n=3).

Parameter	Untreated		Treated		Discharge permit limit	
	Mean ± SD	RSD	Mean ± SD	RSD	WHO (2008)	EEPA (2010)
BOD5(mg/L)	1176.84 ± 88.10	7.5	886.7 ± 63.01	7.1	50	40
COD(mg/L)	4065.86 ± 301.30	7.4	2947.2 ± 224.19	7.6	250	120
TP(mg/L)	0.39 ± 0.004	1.02	1.02 ± 0.03	2.9	2*	-
TN(mg/L)	13.89 ± 0.74	5.3	12.6 ± 0.25	1.9	10*	-
Turbidity (NTU)	270.35 ± 11.09	4.1	198.12 ± 7.24	3.6	5	5
TS(mg/L)	2592.67 ± 297.99	11.4	2197.3 ± 210.94	9.59	1000	
TDS(mg/L)	2333.33 ± 312.67	13.4	2092 ± 268.`9	12.8	1000	1000
TSS(mg/L)	501.33 ± 62.67	12.5	282.66 ± 28.44	10.1	200	100
EC(µS/cm)	3198.67 ± 0.24	0.007	2888.33 ± 0.36	0.01	1000	1000
PH	6.83 ± 0.10	1.4	6.47 ± 0.12	1.85	5-9	5.5-9
Na(mg/L)	556.67 ± 16.59	2.9	493.33 ± 12.83	2.6	400	400
K(mg/L)	6.57 ± 0.18	2.7	8.23 ± 0.21	2.5	-	-
T. Hardness (mg/L	1394.83 ± 58.5	4.19	1291.17 ± 65.84	5.09	-	-
Ca(mg/L)	483.03 ± 22.79	4.7	464.23 ± 16.63	3.5	200	200
Mg(mg/L)	44.94 ± 1.38	3.1	31.34 ± 0.95	3.03	150	150
Alkalinity (mg/L)	1032.68 ± 64.62	6.2	953.09 ± 57.18	5.9	-	-
CO_3^{2-}(mg/L)	93.89 ± 5.08	5.4	129.81 ± 6.25	4.8	-	-
HCO_3^-(mg/L)	1068.97 ± 71.04	6.64	898.84 ± 58.33	6.4	-	-
Chloride (mg/L)	1454.98 ± 101.13	6.9	419.33 ± 25.22	6.01	1000	750
Sulphate (mg/L)	195.31 ± 12.76	6.5	309.09 ± 14.85	4.8	-	-
Fe (mg/L)	1.42 ± 0.02	1.4	1.003 ± 0.01	0.99		
Cu (mg/L)	0.01 ± 0.0001	1	0.01 ± 0.0001	1	2	2
Zn (mg/L)	0.195 ± 0.002	1.02	0.34 ± 0.004	1.17	10	6

** FAO* (2005)*: Food and Agriculture Organization Irrigation water quality Guide value*

The conductivity levels of APEPM wastewater were considerably high, 1476 – 4720 µS/cm for untreated waste water and 664 – 4020 µS/cm for treated wastewater .The mean conductivity values for both sampling points were higher than the EEPA and WHO guideline values of 1000 µS/cm for the discharge of wastewater into river stream. The observed conductivity Values of both untreated and treated effluents were found similar with previous studies obtained by Jitendra (2013) between 790 – 1740 µS/cm for pulp and paper mill effluents of Lalkuan, and S.Surumbar (2010) 1300±26.0 µS/cm for pulp and paper mill effluents of Nilakotai Dindigul both in India. Increase in EC values of APEPM wastewater indicates the presence of higher concentration of dissolved ions (S.Surumbar, 2010).

Total Suspended Solid (TSS) concentrations were 298-726 mg/L for raw wastewater and 112-532 mg/L for treated effluent. The values were more than WHO standard of 200 mg/L for the discharge of wastewater into surface water and generally decreased with the increasing distance downstream. Such elevated value of TSS, in Anmol Product Ethiopia Paper Industry wastewater could be the presence of non dissolved substances including lignin and hemicelluloses, which are not biodegradable and contributed from raw material preparation, pulping, rinsing, bleaching and Paper making process (Ljungberg and Brannvall, 2011).

The value of Total Dissolved Solids (TDS) were ranging from 1032 to 3134 mg/L for raw wastewater and 1118 to 2650 mg/L for treated wastewater respectively and the value of Total Solids (TS) observed were 1512 to 3432 mg/L for untreated wastewater and 1230 to 2854 mg/L for treated wastewater respectively. The values obtained for TDS and TS were more than EEPA and WHO standard of 1000 mg/L for the discharge of wastewater into surface water. The TDS values were found similar with previous studies obtained by S.Surumbar (2010) 2950±38 mg/L for pulp and paper mill effluents of Nilakotai Dindigul in India. The values of Total Dissolved Solids (TDS), Total Suspended Solids (TSS), Total Solids (TS) and EC in effluents were high for untreated wastewater and slightly decreased with the increasing distance downstream may be due to the adsorption of metal ions (precipitation) on distance on soil which could reduce their concentration. The higher TDS and EC may increase salinity of the receiving river water and may render it unfit for irrigation and drinking purposes (Reddy et al., 2001).

Turbidity values were 118.28 to 499.32 NTU for untreated wastewater and 50.88 to 418.655 NTU for treated wastewater. The values obtained for turbidity in both sampling points were higher than EEPA and WHO Standard of 5 NTU to discharge wastewater into stream. The high turbidity of the effluents indicates the presence of various non dissolved solid by products during paper production process such as lignin and hemicelluloses (S.Surumbar, 2010).

The wastewater has COD concentration 2969 to 5848.6 mg/L for untreated wastewater and 2304 to 3729.6 mg/L for treated effluent (Table 4.1). BOD concentration of the wastewater obtained for the untreated effluent was 470 to 2499.36 mg/L and for the treated wastewater ranged between 405 to 1314.6 mg/L. The concentrations of` BOD and COD in both sampling point were higher than the WHO values of 50 mg/L and 250 mg/L for the discharged of wastewater into stream respectively. The BOD value was also higher than value of the paper mill effluent as 306 to 408 mg/L reported by Jitendra (2011) and S.Surumbar (2013) in India. However; the BOD value in this study is comparable with the value 2200 mg/L found by Jamil et al. (2011) for effluents released from digester of Egyptian recycled paper mill. The COD values reported by Jitendra (2011) ranged from 1736 to 4357 mg/L is comparable with COD values obtained in this study. The high BOD and COD values of the APEPM effluents suggest the presence of organic pollutants. The high COD levels indicate toxic state of the wastewater along with the presence of biologically resistant organic substances S.Surumbar (2010). The very high level of Biochemical Oxygen Demand (BOD) is due to the consumption of dissolved oxygen by microorganisms for breaking down of organic matter. It may be also due to the consumption of oxygen during the oxidation of sulphides (kesaker, 2012).

The BOD5/COD ratio is great importance for quantification of biodegradability of a contaminated effluent. A high ratio (>0.5) indicates good biodegradability as reported by Jamil et al. (2011). A ratio less than 0.5 is considered as low and corresponds to low biodegradability of the organic material present in the wastewater. In this study the mean BOD5/COD ratio of the effluent were 0.29 for untreated effluent and 0.3 for treated effluent indicating that low biodegradable organic molecules are present in the wastewater according to Jamil et al. (2011). The mean BOD5/COD ratio of the treated effluents is only slightly increased, showing a small improved biodegradability.

One part of the COD is converted into BOD which potentially can be removed efficiently with further reduction in subsequent treatment stage.

Total nitrogen (TN) and Total Phosphorus (TP) concentrations of Anmol Product Ethiopia Paper Industry were ranged from 7.79 to 20 mg/L, 0.37 to 0.42 mg/L for the untreated wastewater and 12.41 to 12.80 mg/L, 0.35 to 1.69 mg/L for treated wastewater respectively. TN and TP values obtained in this study were found slightly higher than the values reported by Irma (2013) TN (5.89 mg/L) and TP (0.14 mg/L) for treated paper mill in Stockholm. The values of TN recorded were higher than the permissible limit of 10 mg/L and TP was found below permissible limit 2 mg/L set by FAO. But total Phosphorus level in treated effluent was slightly increased which could possibly result from soaps used to clean floor and other materials released into the storage pond and could indicate enough nutrients for algae growth. The discharge of such wastewater with high nutrients TN and TP may cause excessive algae growth and subsequent dying off and mineralization of these algae (eutrophication), may lead to the death of aquatic life because of oxygen depletion of the receiving water bodies (sdguide, 2008).

The sulfate concentration of the wastewater was 26.1 to 282.32 mg/L for the untreated effluent and 219.25 to 424.22 mg/L for treated effluent. Higher concentration of sulfate was observed at the downstream of outlet effluent. This condition occurs in pulping process based on an acidic cooking with salts of sulphites which might be due to the sulphite or sulfide in the effluent oxidized into sulfate in well aerate zone (Hultman, 1997). The discharge of such wastewater with high sulfate content into river stream might cause unpleasant odour in the receiving water body and toxic effect on the aquatic organism upon its reduction and depletion of oxygen in the water body during its oxidation by microorganisms (EEPA and UNIDO, 2003).

The concentrations of chloride observed during the study period were 186.22 to 3818.74 mg/L for the untreated and 150.41 to 815.44 mg/L for outlet effluent. The chloride (Cl^-) contents for untreated bleached effluent was very high (3818.74 mg/L) and decreased downstream of the effluent (815.44 mg/L). Chloride (Cl^-) contents for untreated and treated bleached effluents were higher than WHO 600 mg/L industrial wastewater discharge limit (Table 4.1). The value for chloride (Cl^-) obtained in the

present study are in good agreement with the characteristic of pulp and paper mill bleached effluents 1533 mg/L as reported by Narsi et al (2004) and 43.5 to 347.6 mg/L for Jitendra (2013) both in India.

The high values of chloride indicate either elemental chlorine or chlorine containing agents were used for bleaching purpose. But chlorine in pulp and paper effluents coupled with high organic content of pulping wastewater, results in the production of highly toxic organic compounds such as Chlorinated phenols, furans, aliphatic hydrocarbons, etc (Jitendra G. , 2013). Some members of this family are known to be toxic, mutagenic, persistent, and bio-accumulating and are thought to cause numbers harmful disturbances in biological systems, and pose a human risk through longterm exposure via drinking water and through bioaccumulation along with food chain (Raaz Maheshwari et al 2012).

During this study total alkalinity was not detected both for the untreated and treated effluents which were acidic in nature with pH value ranging from 3.2 to 3.4. The total alkalinity value ranges from 1098.08 to 2000 mg/L for the raw effluent and from 280 to 1700 mg/L for the outlet wastewater both sampling sites with pH value greater than 7. The average Carbonate contents of alkaline untreated and treated effluents were 281.66 and 389.42 mg/L respectively. The bicarbonate concentration of untreated wastewater was ranged from 766.93 (alkaline) to 2440 mg/L (slightly acidic) and 622.51 to 2074 mg/L for the outlet wastewater. There was slight increase in the carbonate and total alkalinity downstream of the wastewater for the alkaline sample. This might be due to the dissolution of $CaCO_3$ and also sulfate reduction processes which consume hydrogen ions and releases H_2S. This consumption of H^+ increases total alkalinity (Garnaik et al, 2013). The carbonate and bicarbonate content of slightly basic effluents of both sampling sites were found similar with previous studies obtained by S.R.Paranthaman (2013) carbonate nil and bicarbonate 280±1.3 mg/L and bicarbonate between 352-440 mg/L reported by Jitendra (2013) for different Paper Mills wastewater both in India.

In the present study the total hardness of APEPM effluents were ranging from 49.6 mg/L for the bleached untreated effluents to 3335 mg/L for the untreated effluents of digestion process. The total hardness of the treated effluent shows similar trends ranging from 47.52 mg/L for the bleached to 3036 mg/L for the pulping process of the

treated wastewater. The result indicates that the effluents released from the pulping process have high total hardness which decreases downstream of the wastewater only slightly. The value was above 150 mg/L and can be categorized as hard wastewater. This might be due to the presence of high amounts of calcium and magnesium ions mixed with the higher carbonate and bicarbonate content observed in the effluent (Garnaik et al, 2013).

The composition of metals in the untreated wastewater samples were ranged from, Na (140-900 mg/L), K (2.9-12.1 mg/L), Ca (11.09-1150 mg/L) and Mg (5.23-110.4 mg/L). In the treated effluent Na (130-800 mg/L), K (2.1-11.6 mg/L), Ca (8.18-1104 mg/L) and Mg (6.18-66.24 mg/L) (appendix). The result shows that Na and Ca concentrations in the untreated and treated effluent are more. This may be due to caustic treatment during pulping or bleaching process of the raw material. It is observed that the same value is less in the treated sample that may be due to the deposition of sludge over a distance and in the treatment process. The average values for Na and Mg obtained in the present study are in good agreement with the value of Na (347-826 mg/L) and Mg (51 mg/L) but Ca is lower than 1614-2346 mg/L as reported by Jitendra (2013) for pulp and paper mill effluent of Lalkuan, India. The average concentrations of Na and Ca in APEPM effluent were much higher than the EEPA and WHO industrial discharging limit while the concentration of Mg was present within EEPA and WHO industrial wastewater discharge limits.

The ranges of values of heavy metals analyzed in APEPM untreated wastewater were recorded as Fe (0.27-2.77 mg/L), Cu (0-0.033 mg/L) and Zn (0-0.59 mg/L) and for the effluent released from oxidation pond Fe (0.18-1.67 mg/L), Cu (0.-0.026 mg/L) and Zn (0.128-0.552 mg/L) (appendix). The result shows that the concentration of the metals decreased in the treated effluents may be due to the deposition of sludge over a distance. Iron was found comparatively higher in concentration compared to other heavy metals, which reflect toxic nature of the paper mill effluents (Ningombam et al, 2011). However; the heavy metal contents of APEPM effluents were within EEPA and WHO industrial wastewater discharge limit (Table 4.1). The concentrations of heavy metals obtained in this study were higher than the concentration of Zn (0.01-0.04 mg/L), Cu (0.003-0.006 mg/L) and Fe (0.17-0.73 mg/L) as reported by Jitendra (2013) in India. The low heavy metal content of the effluents may be due to character of the

raw material or may also be due to the chemicals used during the paper manufacturing process. The concentrations of Zn and Fe are slightly on the higher side. This may be due to the wear and tear or rusting of the old equipments of the plant staples removed during recycling of the paper.

4.1.2. **The Mean Variation and Correlation of the APEPM untreated and treated effluents**

Mean variation

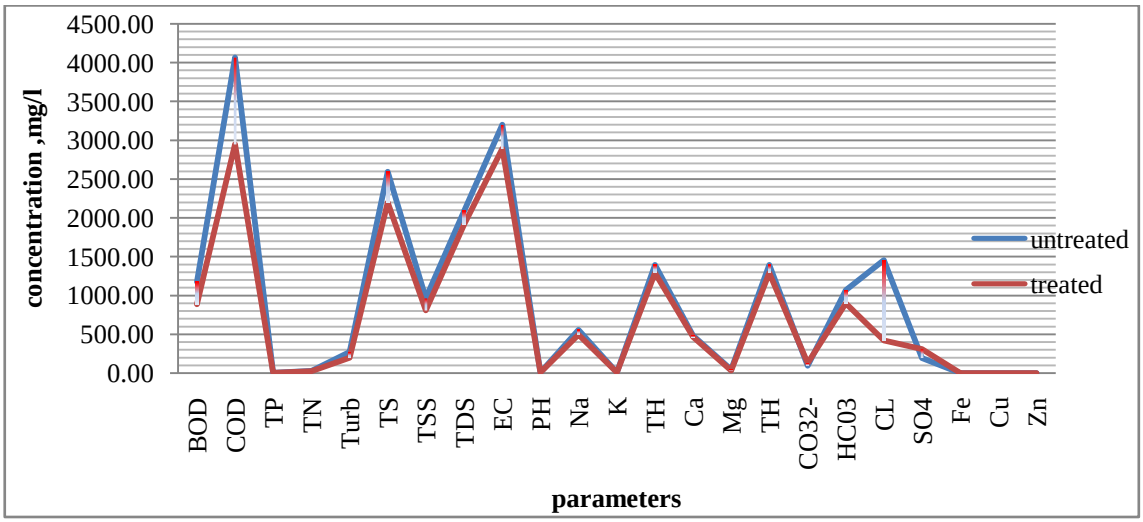
As it can be seen from the above results (Tables 4.1) the average physicochemical characteristics of the untreated wastewater is similar to the treated wastewater. For instance the mean turbidity value of untreated wastewater was 270.35 NTU whereas for treated wastewater 198.12 NTU was obtained. Similarly the mean total dissolved solid values amounted 2333.33 mg /l for the raw wastewater and 2092 mg /l for the treated wastewater, most of the rest parameters also exhibited similar trends. This was also viewed statically using a paired t-test comparison of SPSS version 15 (at the 0.05 significant level) to see whether the mean concentration of pollutants between the untreated and treated wastewater varied significantly or not as shown in Table 4.2. Table 4.2 the paired t-test comparison of untreated and treated wastewater (at 0.05 significant levels).

Variable	p-value	Variable	p-value
BOD5	0.597	Total Hardness	0.40
COD	0.16	Ca	0.304
TP	0.975	Mg	0.467
TN	0.625	T. Alkalinity	0.550
Turbidity	0.1	CO_3^{2-}	0.423
TS	0.05	HCO_3^-	0.251
SS	0.112	Chloride	0.403
TDS	0.399	Sulphate	0.51
EC	0.326	Fe	0.569
PH	0.36	Cu	0.878
Na	0.146	Zn	0.449
K	0.55	-	-

The paired t-test comparison (Table 4.2) indicate the mean variation of physicochemical characteristics of the untreated and treated wastewater at $p<0.05$ significance level.

However; the mean value variations of all parameters monitored are not significantly varied (p>0.05) between the two sites during the triplicate sampling period analyses. This reveals that the waste water treatment system of the industry is not satisfactory.

Figure 4.1 Comparative mean concentration of the selected physicochemical characteristics of Anmol Product Ethiopia Paper Industry untreated and treated wastewater.



(N.B. except EC in Scm^{-1} all the parameters have same unit mg/L).

Correlation analysis

The correlations among some selected physicochemical properties of untreated Anmol Product Ethiopia Paper Industry wastewater are presented in Table 4.3. The results of the analyses for most parameters show the expected trends in waste water quality. BOD has significant strong positive correlation with the parameters such as TN(r = 1), K(r = 0.96), TH(r = 0.98), Ca(r = 0.98) and HCO_3^-(r = 0.94) and non significant positive correlation with EC(r = 0.81), chloride(r= 0.43), total alkalinity(r = 0.81), sulphate (r = 0.45), TDS(r = 0.58) and TS(r = 0.71). However, it has negative correlation with carbonates (r = -0.53), COD (r= -0.58) Fe(r= -0.1) and Turbidity(r = -0.82). This indicate that changing in amount of TN, K, TH, Ca and bicarbonates have caused significant positive change in BOD value of these wastewater and change in EC, total alkalinity, TDS ,TS, chlorides and sulphate concentration brings a little positive change

in BOD. TS and TDS (r = 0.98) have significant strong positive correlation with each other as well as with EC(r = 0.99), total alkalinity, sulphate, carbonate and bicarbonate. They have also moderate positive correlation with pH, K, Mg, Ca, TH, and Na. However, negative correlation with chlorides, COD and Iron. This is pointed out that increase in TS and TDS led to an increment of BOD, EC and decrement in chlorides. Since degradation of both TS and TDS reduce the dissolved oxygen of the wastewater which led to increase BOD and freely moving ions in the wastewater. Total hardness has strong positive correlation with BOD(r= 0.98), Ca(r=1), Mg(r = 1), and moderate positively correlation with TS(r= 0.58), TDS(r = 42), bicarbonate(r= 0.88), and EC(r=0.7). However; it is negatively correlated with turbidity(r= -0.91), COD(r= -0.42), carbonate (r= -0.68). Chemical Oxygen Demand has a negative correlation with almost all parameters such as EC(r=- 0.94), TS(r=-0.98), TDS(r= -1), TH(r= -0.42), HCO_3^-(r= - 0.82), $SO4^{-2}$(r= -0.99) but has positive correlation with turbidity (r= 0.01), chloride (r=0.98) and Fe (r=87). This implies that the presence in a high value of conductivity, TS, TDS, and TH increases COD.

The correlation in treated effluent of APEPM effluent in table 4.4 above follows similar trends to untreated effluent except COD in this case has also positive correlation with sulfate (r= 0.78) in addition to chlorides (r = 0.85).

Table 4.3 Correlation matrix (Pearson) of untreated effluent

Param	BOD	COD	TN	Turb	TS	TDS	EC	PH	TH	Ca	Fe	Cl^-	TA	$CO3^{2-}$	HCO_3^-	SO_4^{2-}
BOD	1															
COD	-0.58	1														
TN	0.96	-0.77	1													
Turb	-0.82	0.01	-0.64	1												
TS	0.71	-0.98*	0.87	-0.19	1											
TDS	0.58	-1 **	0.77	-0.01	0.98*	1										
EC	0.81	-0.94	0.94	-0.34	0.99*	0.94*	1									
PH	-0.09	-0.76	0.18	0.64	0.63	0.76	0.50	1								
TH	0.98	-0.42	0.90	-0.91	0.58	0.42	0.70	-0.27	1							
Ca	0.98*	-0.41	0.89	-0.92	0.56	0.41	0.69	-0.28	1.0	1						
Fe	-0.10	0.87	-0.36	-0.48	-0.77	-0.87	-0.66	-0.98	0.08	0.10	1					
Cl^-	0.43	0.98	-0.65	-0.16	-0.94	-0.98*	-0.87	-0.86	-0.26	-0.24	0.94*	1				
TA	0.81	-0.94	0.94*	-0.34	0.99*	0.94*	1 **	0.50	0.70	0.69	-0.66	-0.87	1			
CO_3^{2-}	-0.53	-0.38	-0.29	0.92	0.21	0.38	0.06	0.89	-.68	-0.69	-0.79	-0.54	0.06	1		
HCO_3^-	0.94*	-0.82	1**	-0.58	0.91	0.82	0.96*	0.26	0.86	0.85	-0.44	-0.71	0.96*	-0.21	1	
SO_4^{2-}	0.45	-0.99*	0.67	0.14	0.95	0.99*	0.88	0.85	0.28	0.27	-0.93	-1**	0.88	0.52	0.73	1

* Correlation is significant at the 0.05 level (2-tailed).

**Correlation is significant at the 0.01 Level (2-tailed)

Table 4.4 Correlation matrix (Pearson) of treated effluent

Param.	BOD	COD	Turb	TS	TDS	EC	pH	TH	Ca	Fe	Cl^-	TA	CO_3^{2-}	HCO_3^-	SO_4^{2-}
BOD	1														
COD	-0.25	1													
Turb.	-0.82	-0.35	1												
TS	0.10	-0.99	0.49	1											
TDS	0.02	-0.96	0.59	0.99	1										
EC	0.37	-0.99	0.22	0.96	0.92	1									
pH	-0.73	-0.48	0.99	0.61	0.70	0.37	1								
TH	0.93	-0.60	-0.55	0.47	0.36	0.69	-0.42	1							
Ca	0.93	-0.60	-0.55	0.47	0.36	0.70	-0.41	1**	1						
Fe	0.99*	-0.18	-0.86	0.02	-0.10	0.30	-0.78	0.90	0.89	1					
Cl^-	0.30	0.85	-0.79	-0.92	-0.96	-0.77	-0.87	-0.08	-0.08	0.37	1				
TA	0.21	-0.99*	0.38	0.99	0.97	0.99	0.52	0.56	0.57	0.14	-0.87	1			
$CO3^{2-}$	-0.91	-0.17	0.98	0.32	0.43	0.04	0.94	-0.69	-0.69	-0.9	-0.7	0.21	1		
HCO_3^-	0.60	-0.92	-0.04	0.85	0.79	0.97	0.11	0.86	0.86	0.54	-0.6	0.91	-0.23	1	
SO_4^{2-}	0.40	0.78	-0.85	-0.87	-0.92	-0.70	-0.92	0.03	0.03	0.47	0.99	-0.81	-0.74	-0.5	1

* Correlation is significant at the 0.05 level (2-tailed).

**Correlation is significant at the 0.01 Level (2-tailed)

4.1.3 An overall reduction in pollution load of APEPM Wastewater Treatment System

After the effluent released from the storage pond, it was sampled at about 150 m (sampling point B) downstream of the effluent before it meets upper Awash River and analyzed for physicochemical characterization. The characterization was done to measure the overall reduction in the selected physicochemical parameters of the wastewater in the storage pond of the paper mill during the raw wastewater analysis. The parameters selected as operational variables in evaluating the wastewater treatment pond were COD, BOD,TN, TP, turbidity, pH, TSS, TDS, sulfate, Chloride, total hardness, Ca, Na, total alkalinity, bicarbonate, carbonate EC and Cu as shown in the following table 4.5.

Table 4.5 Percent reduction of average values of physicochemical parameters in wastewater treatment pond

Parameter	Unit	Average Values		% Reduction
		Untreated	Treated	
BOD	mg/L	1176.84	886.7	24.65
COD	mg/L	4065.87	2947.2	27.49
TP	mg/L	4.03	4.01	0.6
TN	mg/L	27.55	26.07	5.4
Turbidity	NTU	270.35	198.12	26.72
SS	mg/L	501.33	282. 67	43.61
TDS	mg/L	2333.3	2092	10.34
pH		6.83	6.47	5.3
EC	mg/L	3198. 67	2888.33	9.7
Sodium	mg/L	556. 67	493.33	11.37
Potassium	mg/L	6.56	8.23	- 25.4
Total Hardness	mg/L	1394.83	1291.17	7.43
Calcium	mg/L	483.03	464.24	3.89
Total Alkalinity	mg/L	1032.68	953.1	7.706
Carbonates	mg/L	93.89	129.81	-38.26
Bicarbonates	mg/L	1068.97	898.84	15.91
Chlorides	mg/L	1454.98	419.33	71.16
Sulphates	mg/L	195.31	309.09	-58.25
Zn	mg/L	0.31	0.34	- 9.6
Cu	mg/L	0.033	0.03	21.2

The Percent reduction of physicochemical parameters in the pond was calculated as follows

$$R = \frac{\text{Value of untreated effluent} - \text{value of treated effluent}}{\text{values of untreated effluent}} \text{ x100}$$

Where: R = Percent reduction in %

The negative values of R indicate the value of the parameter is increased after treatment by the magnitude of R expressed in percent while the positive values of R indicate the value of the parameter is reduced after treatment by the magnitude of R expressed in percent. Thus, the R values in this study indicate the treatment system of the factory is nominal because it is inefficient in treating all the studied physicochemical parameters of wastewater samples. The treatment pond of the factory even adds further pollution load for some of the studied parameters such sulphates, carbonates, potassium, phosphorus and zinc. Except chlorides and total suspended solids the rest parameters were not reduced more than 27% of their concentrations in untreated form as illustrated in table 4.5. The high chlorine and suspended removal efficiency doesn't guarantee that the quality of effluent is safe for discharge to the environment. The high percentage of chloride reduction might be attributes to the couple of chlorides with high organic content of pulping wastewater, results in the production of highly toxic organic compounds such as Chlorinated phenols (Jitendra, 2013; Raaz Maheshwari et al 2012). The TSS removal efficiency was found to be 43.61%. The removal efficiency seems relatively higher than other chemical parameters but the final discharge of the effluent had still high level of TSS which could not be released directly to water bodies without further treatment to avoid significant impact on the aquatic ecosystem. The discharge limit for TSS to water bodies is 100 mg/L in the Ethiopian industrial effluent discharge guideline (EEPA, 2010). Sulfate and carbonate concentration negatively removed from wastewater treatment pond. The increase in concentration of sulfate probably due to in a more aerated condition sulphites used during digestion process oxidized to sulphates (Hultman, 1997) and the increase in carbonate might be due to the dissolution of $CaCO_3$ (Garnaiket al, 2013). In general the overall performance of the treatment system was not satisfactory for the removal of these pollutants.

4.2. **Some Selected Physicochemical Characteristics of Upper Awash River Water at the Vicinity of Anmol Product Ethiopia Paper Mill**.

The effluent generated from APEPM after released from the oxidation pond allowed to mix with upper Awash River near Ginchi. As a result, the upper Awash River water is expected to be polluted. In the present work an attempt has been made to study the variation in the physicochemical characteristics of upper Awash River water at the vicinity of APEPM at three sampling sites, effluent discharge point, upstream and downstream (2-3 km) of the drain for two consecutive months from January to March, 2015. The data obtained can be believed to provide enough information regarding the impact of the Anmol Paper Industry effluent on the physicochemical properties of upper Awash River to which the effluent is released. The values of the results were compared with standard values of EEPA (2010) and WHO (2008) maximum permissible limits of river water and discussed as below.

The pH value of upstream sampling point was ranged from 7.05 to 7.91. This value was within Maximum allowable concentration of river water standard limit of EEPA, 6.5-8.5. However; a slight increased in pH value 7.16 to 9.16 at discharge points and a slight drop 5.12 to 9.38 at the downstream were observed. This could be attributed to the addition of the Anmol Paper industry effluents along with the eroded soil and trash materials added into the river and slight drop in pH value for the downstream is due to dilution. But this change is not serious still the pH values of the river remain within the EEPA and WHO river water standard limit and may not cause an adverse effect on the survival of aquatic organisms.

It is obvious that unpolluted water is a colorless. In this study at the discharge point the color of the river was light brown and decrease downstream of Awash River. The change in the color of river was arising from discharge of Anmol Product Ethiopia Paper industry wastewater which might be dominated mainly by phenolic lignin derivates, arising from lignin depolymerisation and dying (Kreetachat et al., 2007; Irma, 2013). The color of the River at discharge point and downstream were not meet EEPA standard limit.

Table 4.6 Average concentrations of selected physicochemical parameters of upper Awash River.

Parameter	Discharge point		downstream		upstream	
	Mean ±SD	RSD	Mean ±SD	RSD	Mean ±SD	RSD
BOD5(mg/L)	429.19 ± 27.64	6.4	65.48 ± 3.18	4.8	6.81 ± 0.089	1.3
COD(mg/L)	1066.7± 76.01	7.12	314.37 ± 19.80	6.29	7.53 ± 0.45	5.9
TP(mg/L)	1.04 ± 0.01	0.96	0.815 ± 0.005	0.61	0.78 ± 0.001	0.12
TN(mg/L)	9.06 ± 0.52	5.7	6.30 ± 0.18	2.8	2.40 ± 0.02	0.8
Turbidity(NTU)	198.12 ± 13.5	6.8	129.58 ± 9.6	7.4	22.51 ± 1.4	6.2
TS(mg/L)	1048.67± 118.1	11.2	804 ± 92.79	11.5	327.33± 34.4	10.5
TDS(mg/L)	833.33 ± 68.77	8.2	663.3 ± 36.69	5.5	321 ± 13.57	4.2
TSS(mg/L)	215.33 ± 13.55	6.2	140.67± 10.43	7.4	33.33± 2.44	7.3
EC µS/cm	1247 ± 12.6	1.01	1028.33 ± 10.3	1.0	469.33 ± 8.2	1.7
pH	7.84 ± 0.43	5.49	7.23 ± 0.44	6.08	7.50 ± 0.21	2.8
Na(mg/L)	279 ± 0.68	0.24	161.33 ± 0.87	0.53	28.50 ± 0.07	0.24
K(mg/L)	3.467 ± 0.1	2.88	3.93± 0.08	2.03	2.1 ± 0.02	0.95
T. Hardness (mg/L)	363.09 ± 30.8	8.4	345.08 ± 28.65	8.3	28.20 ± 1.5	5.3
Ca(mg/L)	118.33 ± 6.7	5.6	121.43 ± 5.12	4.2	74.62 ± 3.18	4.3
Mg(mg/L)	16.13 ± 0.92	5.7	9.96 ± 0.76	7.6	7.63 ± 0.49	6.42
Cl^-(mg/L)	97.47 ± 4.76	4.8	50.10 ± 1.34	2.6	5.99 ± 0.27	4.5
T. Alkalinity (mg/L)	428.54 ± 29.42	6.8	353.01 ± 24.5	6.9	237.35± 16.2	6.8
CO_3^{2-}(mg/L)	19.59 ± 0.62	3.1	29.39 ± 1.31	4.4	ND	
HCO_3^-(mg/L)	482.80 ± 19.2	3.9	370.91 ± 17.34	4.7	289.6 ± 11.2	3.8
SO_4^{2-}(mg/L)	56.3 ± 0.95	1.68	194.65 ± 1.84	0.94	4.89 ± 0.03	0.61
Cu(mg/L)	ND		0.005 ± 0.00	0.00	0.029 ± 0.00	0.00
Zn(mg/L)	0.065±0.00	0.00	0.058 ± 0.00	0.00	0.089 ± 0.00	0.00
Fe(mg/L)	0.29 ± 0.001	0.34	0.38± 0. 001	0.26	0.13 ± 0.00	0.00

The mean concentration of total solids at discharging point, downstream and upstream, of Awash river water samples were found 1048.67±118.1, 804.00±92.79, and 327.33± 34.4 mg/L respectively. The total solids at the discharging point were slightly higher and decreased downstream samples which have more total solids than upstream samples as shown in Figure 4.2. The increment in the magnitude of TS at discharging point compared to at downstream and upstream values might be due to the influence of the Anmol Paper Industry wastewater on the river.

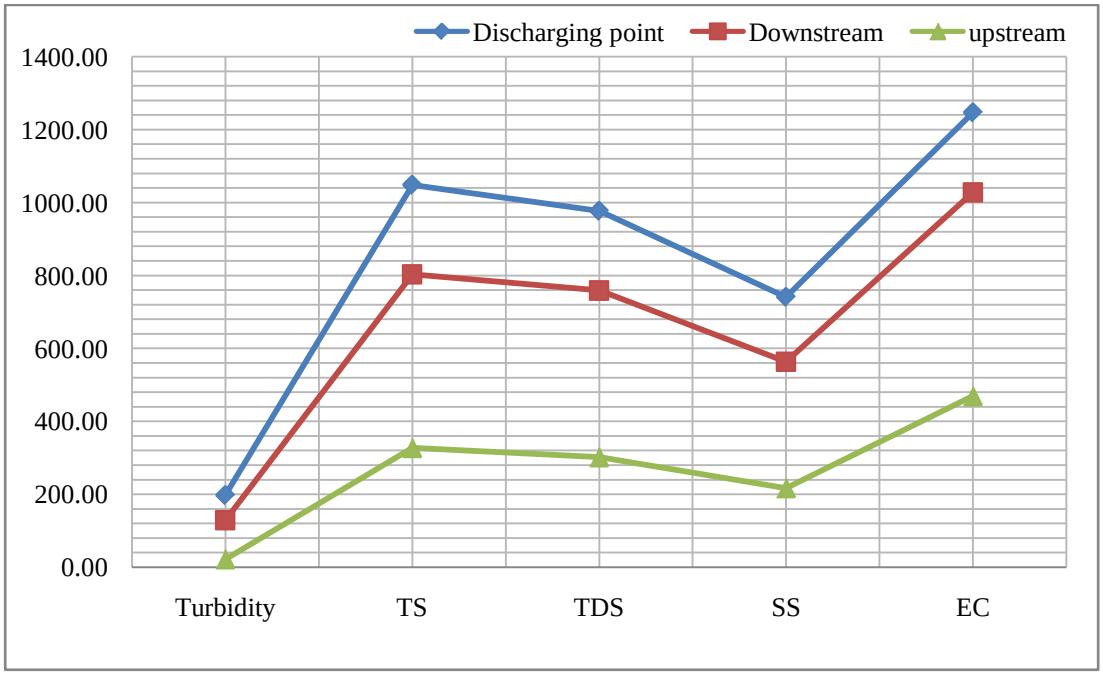
The mean total suspended solids content in upper Awash River water at discharge point, downstream and upstream samples were 215.33±13.55, 140.67±10.43, and 33.33±2.44 mg/L respectively. The suspended solids at the discharging point were slightly higher than the other sampling points. Again the downstream samples have more suspended particles then upstream samples as shown in Figure 4.2. The total suspended solid values obtained for the river at discharge and downstream point was higher than WHO recommended maximum concentration of 100 mg/L in surface water.

The upper Awash River water samples during this study have higher dissolved solids at discharge point (833.33±68.77 mg/L) and the downstream samples have dissolved particles of 663.33±36.69 mg/L which was higher than the value at upstream sampling point (321.00±13.57 mg/L) as shown in Figure 4.2. The total dissolved solid values obtained for the river at discharging point were higher than WHO maximum permissible concentration of 500 mg/L for surface water.

The mean turbidity values of upper Awash River water sample during the study period at discharging point, downstream and upstream were 198.122±13.5, 129.58±9.6, 22.51±1.4 NTU respectively. The turbidity values obtained at all locations were higher than EEPA and WHO standard limit of 5 NTU for river water. There were significant differences in values obtained at the effluent discharge point, in comparing with other sampling points D and E. The excessive turbidity, TSS, TS and TDS in upper Awash River water observed during this study associated with APEPM effluent contamination which may reduce the aesthetic value of the river such as decrease in photosynthesis process and also associated with microbial contamination since turbidity prevents deep penetration of light in water (Muoghalu and Omocho, 2000).

The mean electrical conductivity of the upper Awash river water samples at effluent discharging point, downstream and upstream, during this study period were 1247±12.6, 1028.33±10.3, and 469.33±8.2µS/cm respectively. The EC values obtained at all sampling points exceed EEPA and WHO maximum permissible limit (300µS/cm), which indicates the river is polluted. The EC of discharging point sample were higher than downstream and upstream samples as shown in Figure 4.2. The conductivity value at discharge and downstream point obtained in this study was attributed to the discharge of effluents from APEPM into the river. Conductivity in water analysis is used to indicate the contents of dissolved solids in water because the concentration of ionic species determines the conduction of current in an electrolyte and it is unsafe to aquatic live when it is above the permissible limit (Saidu & Musa, 2012).

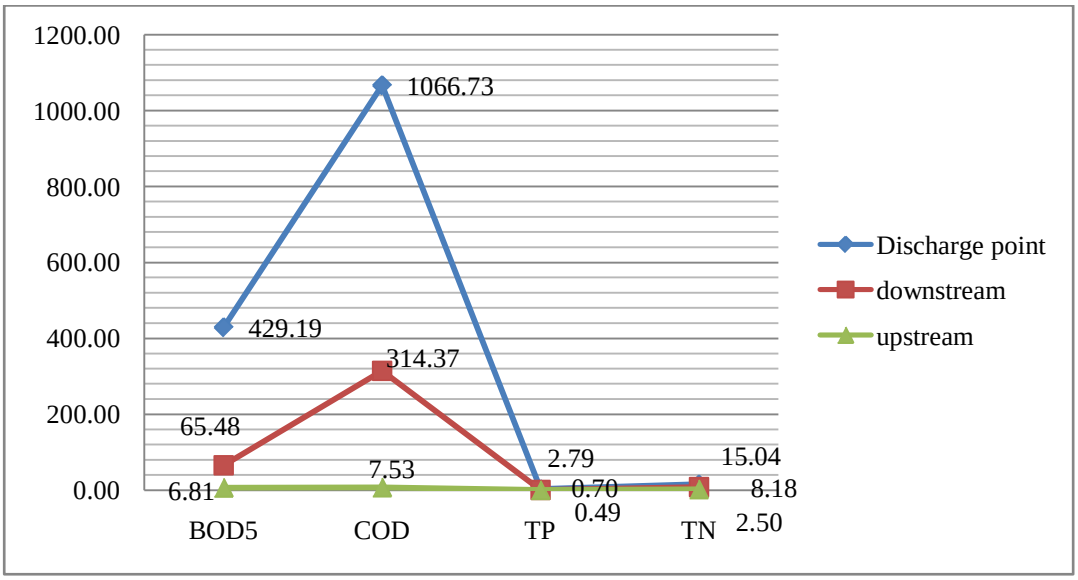
Figure 4.2 Trends of average concentrations of Turbidity, TDS, TSS and EC.



The BOD values measured at effluent discharge point, downstream and upstream sampling sites were 429.19±27.64, 65.48±3.18 and 6.81±0.089 mg/L, and the mean COD values were 1066.73±76.01, 314.37±19.80, and 7.53±0.45 mg/L respectively. The mean BOD and COD concentrations of the river at all sample locations follow similar trend as illustrated in Figure 4.3. The lowest values were recorded in the upstream and the highest values at the effluent discharging point. This is attributed to the discharged of effluents containing high organic matter from Anmol product Ethiopia paper

industries to the upper Awash river. The observed BOD and COD levels (Table 4.6) were also noticed to be above the EEPA and WHO maximum allowable concentration for undisturbed river which is less than 10 mg/L and 40 mg/L (Table 4.7) respectively. These high levels of BOD and COD could deplete the DO in the water system. The result indicated that the water bodies sampled were deteriorated due to continuous discharge of Anmol Product Ethiopia Paper factory effluents.

Figure 4.3 Trends of average concentrations of TN, TP, BOD5 and COD



Total phosphorus**:** The sampling site at effluent discharging point was the highest with mean total phosphorus load of 1.04±0.01mg/L. The total phosphorus content in downstream and upstream of the river was also high with average concentration of 0.815±0.005 and 0.78±0.001mg/L respectively. The elevated TP levels in all sampling sites could possibly result from soap and detergent used by the nearby residents that use the river for bathing, nearby hotels that discharge their domestic effluents to the stream which drains the wastewater to the upper river Awash. At discharging point and downstream the level of phosphorus was higher that might be due to the addition of wastewater from APEPM. The average total phosphorus levels recorded at each sampling site were in excess of 0.14 mg/L maximum allowable concentration WHO (Table 4.7) and can cause eutrophication.

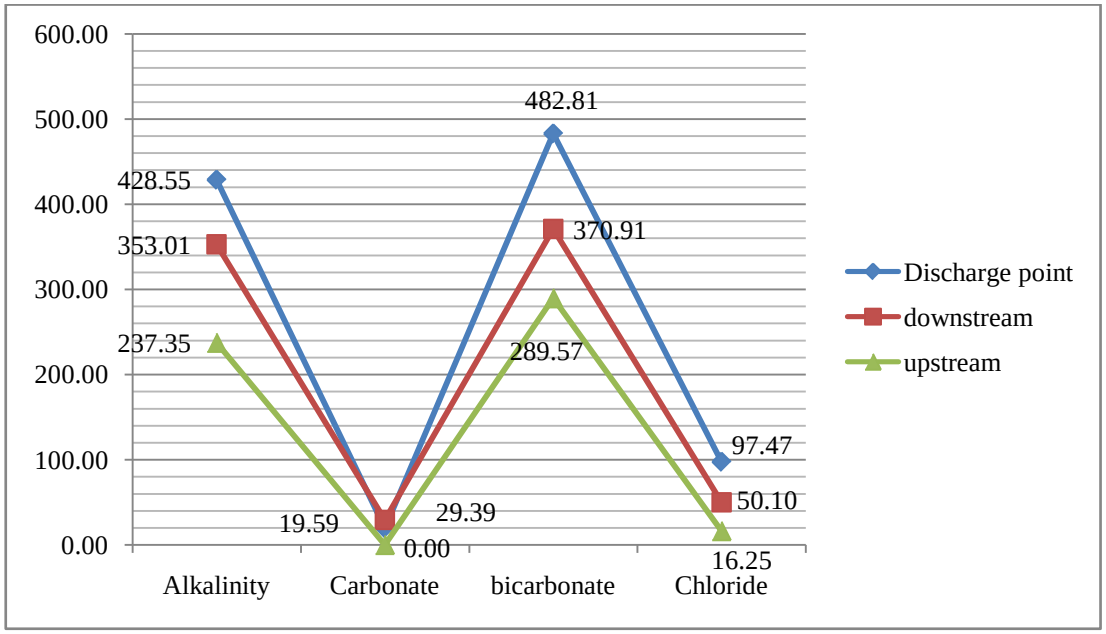
Total nitrogen: The average concentrations of TN at discharging point, downstream and upstream sampling points were 9.06±0.52, 6.30±0.18 and 2.40±0.02 mg/L respectively. The higher concentrations of total nitrogen was observed at the effluent discharging

point and followed by a decline at the downstream and the lowest concentration was registered at the upstream. It is probably due to diffused sources of pollution entering into upper Awash River such as cow's dung and nearby latrines of the residential to the stream which drains the wastewater to the river. The mean total nitrogen level recorded at effluent discharging point is in excess of 10 mg/L maximum allowable concentration WHO (Table 4.7) and can cause eutrophication.

The highest average concentrations of total alkalinity during this study period observed at effluent discharge point (428.54±29.42 mg/L) and followed by a decreased mean value at the downstream (353.01±24.5 mg/L) and the lowest concentration was registered at the upstream (237.4±16.22 mg/L). The total alkalinity values of the river at the three sampling points were in excess of 200 mg/L of EEPA and WHO maximum allowable concentration (Table 4.7) of surface water. The average bicarbonate content also shows similar trends (Table 4.6). The lowest concentration of carbonate was observed at upstream sampling point (ND) but the highest value was obtained in downstream sampling point (29.39±1.31 mg/L). This might be due to the dissolution of carbonate rocks in the river and the lower concentration of carbonate at effluent discharging point could be due to the acidic nature of the APEPM effluent containing organic matters under aerated condition added to the river (Garnaik et al, 2013).

The mean concentrations of total hardness of upper Awash River water at the effluent discharge point, downstream and upstream sampling points during the study period was found to be 363.09±30.8, 345.08±28.65 and 28.50±1.5 mg/L respectively which is shown in the Figure 4.6. The result indicates the total hardness of the river at effluent discharge point and downstream was above the WHO maximum allowable limit of 500 mg/L. Water of hardness level 50-100 mg/L is classified as moderately soft, 100-150 mg/L is slightly hard, while above this value is hard water (Deat, 2000). Hence, upper Awash River water downstream of effluent discharge point categorized as very hard water. This might be due to the addition of wastewater from APEPM which have been accumulating much dissolved calcium and magnesium ions that could possibly cause hardness. An increase in hardness level adversely affects detergent performance which constitutes the major problem to people who rely on the surface water for cleaning purpose (Iwara et al., 2012).

Figure 4.4 Tends of average concentrations of total alkalinity, bicarbonate, carbonate and Chloride.

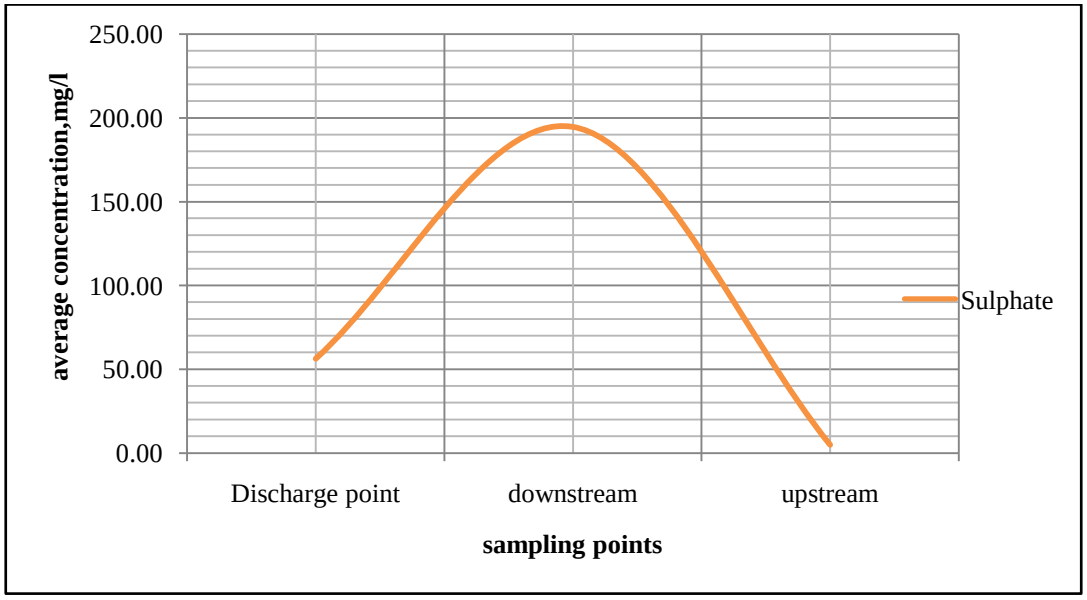


Chloride (Cl^-): The mean concentration of chloride at discharging point, down-stream and upstream sampling sites during this study period were found 97.47±4.76, 50.10±1.34 and 5.99±0.27 mg/L respectively. The highest chloride concentration was found at discharging point which is attributed to the addition of effluent from APEPM that contains chlorine compounds. Chlorides in water are not harmful to human and other animals until a concentration of 600 mg/L (WHO, 2008). Above maximum safe chloride concentration limit was not recorded in all sampling points. However; effects may be worse when the pulp and paper effluents containing chlorine compounds are added to the river. This is because of the chlorine in the effluent coupled with high organic content of the wastewater, results in the production of highly toxic organic compounds which are known to be toxic, persistent and bio accumulating and are thought to cause harmful disturbances in biological systems, and pose a human risk through long term exposure via drinking water and through bioaccumulation along with food chain (Raaz Maheshwar et al, 2012; Jitendra, 2013).

The mean sulfate (SO_4^{2-}) concentration at the discharging point, down-stream and upstream of upper Awash River water sample were found 56.3±0.95, 194.65±1.84 and 4.89±0.03 mg/L which were found unexpected trend. Apparently, more concentration of sulfate (SO_4^{2-}) was obtained in downstream than any other sites. This result may be due to

the high BOD and COD values at discharging point which decreases dissolved oxygen level of the river resulted in the subsequent reduction of sulfate to sulfide. In polluted waters the dissolved oxygen is very low and sulfate is readily reduced to sulfide causing noxious odors (EEPA and UNIDO, 2003). However; in the downstream concentration of sulfate was found increased probably due to the decrease in organic load because of more dilution resulted in the oxidation of sulfides to sulfate. The mean sulphate level of the river at discharging point and downstream were higher than the EEPA and WHO maximum allowable limit of 250 mg/L.

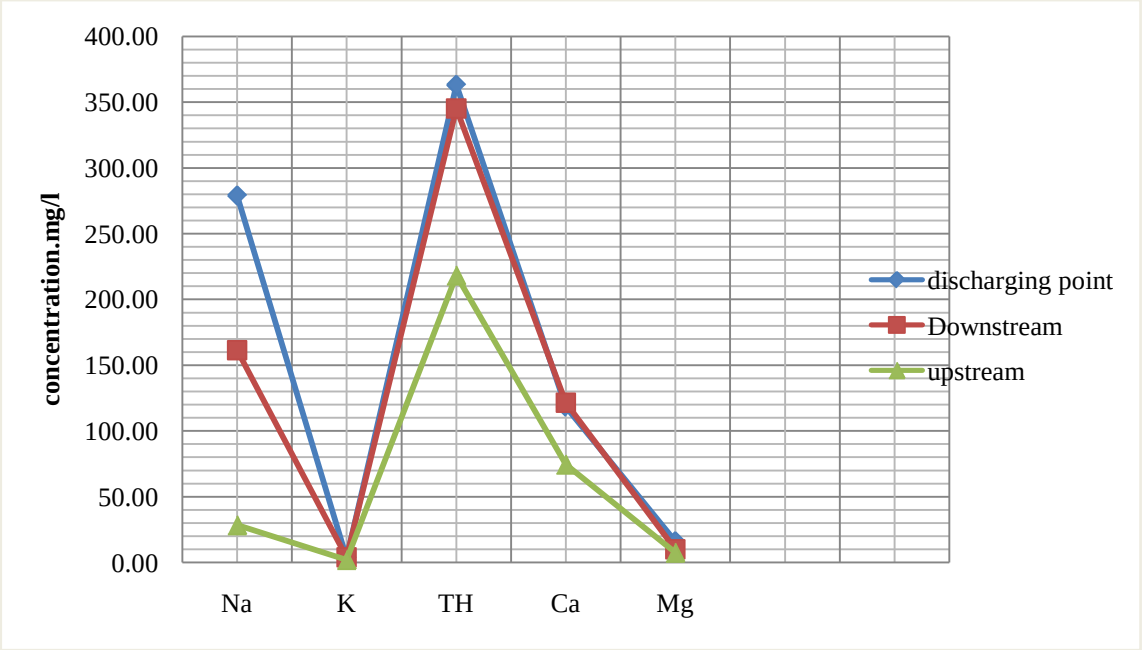
Figure 4.5 Trends of average concentrations of Sulfate



The mean concentration of Magnesium at discharging point, downstream and upstream sampling points were 16.13±0.92, 9.96±0.76 and 7.63±0.49 mg/L and the mean Ca concentrations were 118.33±6.7, 121.43±5.12 and 74.62±3.18 mg/L respectively. High concentrations of Mg and Ca were observed at effluent discharging point. The value decreases downstream and low value of Ca and Mg were recorded at upstream point. The presence of appreciable higher concentration of Ca was consistent with the level of hardness of the water observed during this study period. The concentrations of Ca at the three sampling sites were above the WHO maximum restriction limit of 75 mg/L of surface water while Mg was found below the recommended limit of 50 mg/L.

The mean concentration of sodium at discharging point, downstream and upstream were 279±0.68, 161.33±0.87 and 28.50±0.07 mg/L and potassium were 3.467±0.1, 3.93±0.08 and 2.1±0.02 mg/L respectively. Higher concentrations of K and Na were observed at effluent discharging point. The value decreases downstream and low value of K and Na were recorded at upstream point. The higher concentration of Na at discharging point indicates the effect of APEPM effluent with high content of Na probably from the caustic treatment during pulping or bleaching process of the raw material. The mean sodium level of the river at discharging point and downstream was above WHO 200 mg/L maximum allowable concentration while K was higher at all sampling sites than the EEPA maximum allowable concentration of 1.5 mg/L of surface water.

Figure 4.6 Trends of average concentrations of Na, K, TH, Mg and Ca.



The mean values of various heavy metals analyzed at discharge point, downstream and upstream sampling points were Fe(0.29±0.001, 0.38±0.001, 0.13±0.00mg/L),Cu(ND, 0.005±0.00, 0.029±0.00 mg/L) and Zn (0.065±0.00, 0.058±0.00, 0.089±0.00 mg/L) respectively (Table 4.6). The heavy metal concentrations in upper river Awash water samples at all sampling sites measured were within EEPA and WHO except iron which was slightly higher at effluent discharge point and downstream sampling points which reflects the influence of the APEPM wastewater on the river.

Table 4.7 Average concentrations of selected physicochemical parameters of upper Awash River compared with river water maximum allowable standard concentrations.

Parameter	Mean ±SD			Maximum permit concentration	
	Discharge point	downstream	upstream	EEPA (2010)	WHO (2008)
BOD(mg/L)	429.19 ± 27.64	65.48 ± 3.18	6.81 ± 0.089	10	10
COD(mg/L)	1066.7± 76.01	314.37 ± 19.80	7.53 ± 0.45	40	40
TP(mg/L)	1.04 ± 0.01	0.815 ± 0.005	0.78 ± 0.001	0.24	0.14
TN(mg/L)	9.06 ± 0.52	6.30 ± 0.18	2.40 ± 0.02		10
Turbidity (NTU)	198.12 ± 13.5	129.58 ± 9.6	22.51 ± 1.4	5.0	5.0
TS(mg/L)	1048.67± 118.1	804 ± 92.79	327.33± 34.4		
TDS(mg/L)	833.33 ± 68.77	663.3 ± 36.69	321 ± 13.57		500
TSS(mg/L)	215.33 ± 13.55	140.67± 10.43	33.33± 2.44	100	80
EC µS/cm	1247 ± 12.6	1028.33 ± 10.3	469.33 ± 8.2	300	300
pH	7.84 ± 0.43	7.23 ± 0.44	7.50 ± 0.21	6.5-8.5	6.5-8.5
Na(mg/L)	279 ± 0.68	161.33 ± 0.87	28.50 ± 0.07	200	200
K(mg/L)	3.467 ± 0.1	3.93± 0.08	2.1 ± 0.02	1.5	
TH(mg/L)	363.09 ± 30.8	345.08 ± 28.65	28.20 ± 1.5		500
Ca(mg/L)	118.33 ± 6.7	121.43 ± 5.12	74.62 ± 3.18	75	75
Mg(mg/L)	16.13 ± 0.92	9.96 ± 0.76	7.63 ± 0.49	50	50
Cl^-(mg/L)	97.47 ± 4.76	50.10 ± 1.34	5.99 ± 0.27		600
T .Alkalinity (mg/L)	428.54 ± 29.42	353.01 ± 24.5	237.35± 16.2	200	200
CO_3^{2-}(mg/L)	19.59 ± 0.62	29.39 ± 1.31	ND	ND	ND
HCO_3^-(mg/L)	482.80 ± 19.2	370.91 ± 17.34	289.6 ± 11.2	-	-
SO_4^{2-}(mg/L)	56.3 ± 0.95	194.65 ± 1.84	4.89 ± 0.03	250	250
Cu(mg/L)	ND	0.005 ± 0.00	0.029 ± 0.00	2	1.5
Zn(mg/L)	0.065±0.00	0.058 ± 0.00	0.089 ± 0.00	5	5
Fe(mg/L)	0.29 ± 0.001	0.38± 0. 001	0.13 ± 0.00	0.3	0.3

4.2.1. Analysis of mean variation in upper Awash River water quality at the vicinity of APEPM

The relative concentrations of pollutants at the discharge point, upstream and downstream sampling points of the upper Awash River were illustrated in Figure 4.7 and Figure 4.8 which indicate that the mean concentration of most parameters were generally found in the highest amount at the discharge point due to the increased discharges of the factory wastewater and fall down at the downstream probably due to the assimilation and dilution effects along a distance except sulphate, carbonate, Ca and Fe which were found relatively in more amount at downstream for the reason discussed above. The lowest concentration was recorded at upstream sampling site. This clearly indicates that upper Awash River water is polluted.

Figure 4.7 Comparison of the mean value of selected physicochemical parameters at upstream and discharging point river water samples.

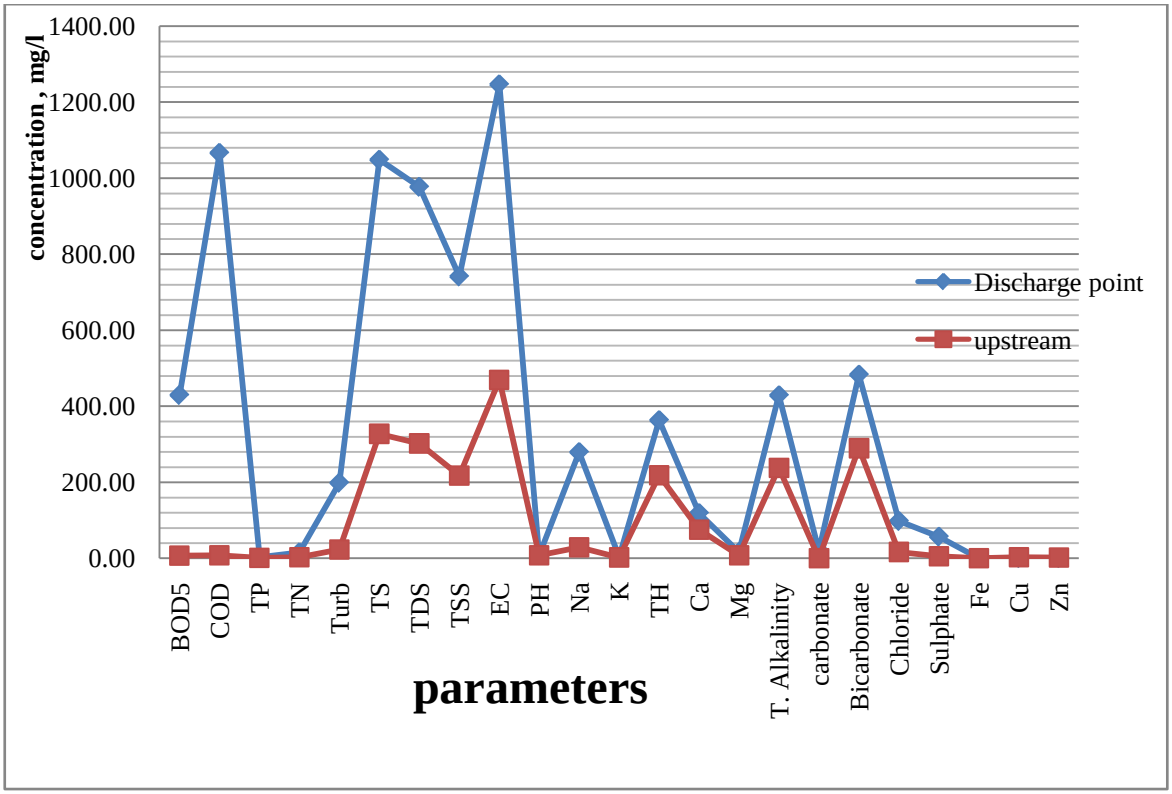
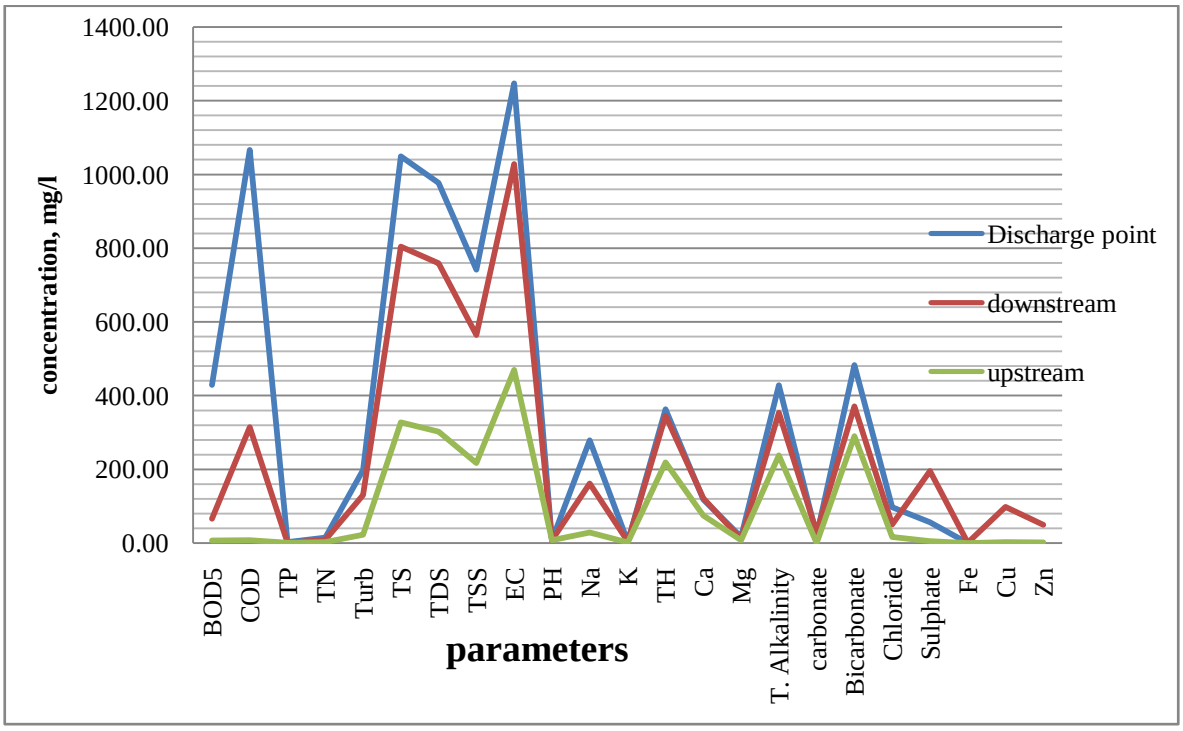


Figure 4.8 Comparison of the mean value of selected physicochemical parameters the three sampling sites



5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

Both untreated and treated wastewater of APEPM were characterized by extremely high concentrations of organic matter (COD & BOD), electrical conductivity, sulphates, TDS, TS, turbidity, Chlorides, Bicarbonate, total alkalinity, carbonates, Ca, Na, TN as well as strong hardness with pH value varies between strongly acidic and basic ranges. While, metals such as, K, Fe, Cu, Zn, and Mg were found in less amount in both untreated and treated wastewater of the factory which were also found within EEPA and WHO Industrial effluent discharge limits to surface water. However, the rest parameters were much higher than these discharge limits.

The Selected physicochemical characteristics of the untreated and treated wastewater were not significantly differing during the study period for most of the parameters. The mean value variations of the parameters such as BOD, COD, Turbidity, TS, TSS, TDS, EC, pH, Na, Mg, Ca, sulfate, carbonates and total alkalinity of untreated and treated effluents were not significantly varied ($p>0.05$) .

Except chlorides, Sulfates, Carbonates and total suspended solids the rest parameters were not reduced more than 27% of their concentration in untreated form. This reveals that the overall wastewater treatment of the oxidation pond is not satisfactory rather it is used only as storage during day time which might expose organisms to toxic effects when discharged to the river bodies.

Statistical analysis showed BOD, COD, Ca, total hardness, Mg, TS, TDS, EC, total alkalinity, bicarbonate and chloride of the wastewater were highly inter correlated. However; no significant association of turbidity was observed with COD and TDS while other parameters were moderately correlated.

The result also indicates that discharge of untreated and inadequately treated effluents from the factory have considerable influences on the upper Awash River water quality. Higher concentration of physicochemical parameters like Turbidity, TS, TDS, EC, BOD,COD, total alkalinity, bicarbonates, total hardness, TN, chlorides, K, Fe, Ca, Mg

and Na was observed at sampling site C (effluent discharge point). This may be due to the addition of Anmol product Ethiopia paper mill effluent which contains dissolved metal ions, organic materials and colloidal particles.

On comparing upstream and downstream of upper Awash river water samples at the vicinity of APEPM, the downstream samples have slightly higher value of parameters like Turbidity, TS, TDS, EC, BOD, COD, total alkalinity, bicarbonates, carbonate, total hardness, TN, chlorides, sulphates, K, Fe, Ca, Mg and Na. The concentration of sulfate was found increased in the downstream sampling point probably due to the decrease in organic load because of more dilution resulted in the oxidation of sulfides to sulfate.

Similarly, the water sampled from Upper Awash river at the vicinity of APEPM excluding pH, K, Mg, chloride, Cu, Zn, all the rest examined parameters at discharge and downstream sampling points were much higher than the EEPA and WHO maximum allowable limit.

5.2. Recommendation

The pulp and paper effluent is very complex so that it is difficult to characterize the wastewater matrix completely (Irma, 2013). This thesis provides a good overview of the selected effluent physicochemical parameters and how they are changing throughout the existing treatment system and their influence on the upper Awash river water but a survey on molecular level for the determination of AOX (such as Chlorinated phenols, dioxins, furans, aliphatic hydrocarbons etc) would be required in the future for a complete characterization.

Data obtain in this study should be used as an input for establishing a satisfactory wastewater treatment plant and further studies should also be conducted on the overall performance of wastewater treatment system in the factory.

Human beings and other animals that are using the upper Awash River water which is contaminated with Anmol Product Ethiopia Paper Industry effluent are may be highly exposed to various types of problems. There should be an intervention of appropriate

regulatory bodies (EEPA) to ensure release of high quality treated final effluents by the paper industries and to protect the natural river water quality.

There should be continuous monitoring and evaluation of the quality of the upper Awash River near the factory site and the wastewater before discharging it to the river.

The massive use of water for paper making purposes in Anmol product Ethiopia paper industries creates excessive amounts of wastewater production. Therefore; recycling the water is advisable to reduce the pollution load and amount of wastewater discharged.

6. REFERENCES

APHA (2005). Standard methods for the examination of water and waste water. Port City Press, Baltimore, Maryland, USA.

Birhanu M. (2008). Assessment of the contamination level of water at collection points and determination of the major sources of contaminants in the Central Highlands of Ethiopia, Yubdo Legebatu PA, Ethiopia.

Deat A. (2000). White paper on integrated pollution and waste management for South Africa. A policy on pollution prevention, waste minimization, impact management and remediation. Department of Environmental Affairs Tourism .

Eddy (2003).Constituents in Wastewater. In Hill, A. Wastewater Engineering. 3 Ed. New York: McGraw-Hill.

Ensis and Csiro (2005). Frequently asked questions on Kraft pulp mills.

Australian Journal of Scientific and jiont research . 78(12): 964-998.

Ethiopia Environmental Protection Authority (EEPA) (2010). Provisional Guidelines and Standards for Industrial Pollution Control in Ethiopia, Addis Ababa, Ethiopia.

Ethiopia Environmental Protection Authority (EEPA) and United Nations Industrial Development Organization (UNIDO)(Q2003). Standards for industrial pollution control in Ethiopia. The Ecologically Sustainable Industrial development Project US/ETH/99/068/ETHIOPIA. Addis Ababa, Ethiopia.

European Commission (2001). Revision of the Eco labeling Criteria for Tissue Paper: Comments and background to the second draft proposal.

Food and Agricultural Organization of the United Nations (FAO) (2005). Wastewater treatment and Use in agriculture, FAO Irrigation and drainage. Viale Delle Terme di Caracalla, Italy.

Garnaik B., Panda S.,and Tripathy S.(2013). Seasonal Variation of Nagavali River Water Quality at the Vicinity of Paper Mill near Jaykaypur, Odisha, India.

Gawas A.D., Lokhade P.B. and Mujawar H.A. (2006). Study of physico-chemical parameters of surface waters in the Mahad industrial area, India.

Ipeaiyeda AR, Onianwa PC. (2011). Pollution Effect of Food and Beverages Effluents on the Alaro River in Ibadan City, Nigeria. *Bulletin of the Chemical Society of Ethiopia* 25(3):347-360.

Irma K. (2013). Advanced Oxidation Processes for Removal of COD from Pulp and Paper Mill Effluents. Technical, Economical and Environmental Evaluation, Stockholm.

Iwara Ai, N. G. (2012). Effect of Adiabo Abattoir on the Water Quality Status of Calabar River in Odukpani,Cross River State. *Continental Journal of Environmental Sciences* 6(2):36-43.

Jamil, T. (2011). A comparative study among different photochemical oxidation processes to enhance the biodegradability of paper mill wastewater. *Journal of Hazardous Materials* 18(5)**:**353-358.

Jitendra G. (2013). Effluents from Century Paper and Pulp Industries and their impact on soil properties and chemical composition of plants in Lalkuan , India.

Kesalkar VP, Khedikar IP and SudameAM (2012). Physicochemical characteristics of waste water from paper industry. *International Journal of Engineering Research and Applications* 2(4): 137-143.

Khan. N, Basheer. F, Singh.D,Farooqi.I. (2011).Treatment of paper and pulp mill wastewater by column type sequencing batch reactor. *Journal of Industrial Research Technology* 1(1): 12-16

Kim, H., and K. Lee (2009). Significant contribution of dissolved organic matter to seawater alkalinity. *Journal of Geophysical Research* 3(6): 20-60.

Kowsalya R., Uma A., Meena S., Saravanabava K., Karrunakaran C.M. and Raman M.D. (2010). Assessment of water quality and pollution of Porur double Lake (Erettaieri). *Journal of Industrial Pollution Control* 26(1**)**: 61-69.

Kuforiji T. and Ayandiran T.(2013). Study of heavy metals pollution and physico chemical assessment of water quality of River Owo, Agbara, Nigeria. *International Journal of Water Resources and Environmental Engineering* 5(7): 434-341.

Kumar V, Chopra AK and Pathak (2010). Agro-potentiality of Paper Mill Effluent on the characteristics of *Trigonella foenum-graecum* L. (Fenugreek). *Journal of Scientific Research* 3(5): 68-77.

Lenntech,*BV*.(2011). Pulp and paper industry water treatment. Netherlands.Available at:*http://www.lenntech.com/effluent/pulp and paper/treatment.: Accessed 21st march 2015*.

Ljunberg .M and Brannvall, E. (2011). Overview of Pulp and Paper Processes. Stockholm, Sweden: KTH Fiber and Polymer Technology.

Martin P. (1998). River pollution in India: An overview, In Chari, K. Ed. Employment News. March 28- April, 13. XXII (82): 1-2.

Mishra D.Mudgal M. Khan M.A. Padmakaran P.and Chakradhar B. (2009). Assessment of ground water quality of Bhavnagar region (Gujarat). *Journal of Scientific and Industrial Research* 68(11): 964-966.

MoWR (Ministry of Water Resources). (2001a). Data collected from different river basin development master plan studies. Planning and Projects Department, Ministry of Water Resources, Addis Ababa, Ethiopia.

MoWR (Ministry of Water Resources) (2001b). Water Sector Development Program Methodological Framework. Addis Ababa, Ethiopia.

MoWR (Ministry of Water Resources) (2002). Ethiopian Guidelines Specification for Drinking Water Quality, Ministry of Addis Ababa, Ethiopia.

Muoghalu LN, Omocho V. (2000).Environmental Health Hazards Resulting from *Awka Abattoir*. *African Journal of Environmental Studies* 2(1):72-73.

Narsi R.Bishnoi (2004). Biodegradation of pulp and paper mill effluent using anaerobic followed by aerobic digestion, India.

Ningombam Li. and Chandra Y. (2011). Belagali Physicochemical characteristics of paper industry effluents a case study of South India Paper Mill.

Preeti N. (2007). Studies on the effluent generated during the pulping process in paper industry M, Bhilai , India.

Pokhrel, D. & Viraraghavan, T. (2004).Treatment of pulp and paper mill wastewater. A Review. *Science of the Total Environment*, 333**:** 37-58.

Reddy, PM and Subba RaoN. (2001). Effects of industrial effluents on the ground water regime Vishakapatnam. *Pollution Research* 20(3):383-386.

Saidu M, Musa J. (2012).Impact of Abattoir Effluent on River Landzu, Bida, Nigeria. *Journal of Chemical, Biological and Physical Sciences* 2(1): 132-136

Sarma K.P. and Talukdar B. (2008). Sediment characteristic and concentration of heavy metals in water and sediment of the effluent discharging water body of Nagaon paper mill, Assam, India. *Asian journal of water, environmental and pollution* 6(4):97-102.

SevimLi, M. F. (2005). Post-treatment of pulp and paper industry wastewater by advanced oxidation processes of ozone. *Journal of Science and Engineering* 27: 37-43.

Sdguide.org. (2008). Environmental Guide for Pulp and Paper Production. European paper Merchants Association. Available *At:http://www.eugropa.com/downloads/Eugropa%20Guide%20Pulp%20&%20Paper.pdf Accessed 6th Sep 2014.*

S.R.Parathaman.K.(2013). Study on different indigenous microorganism in pulp and paper mill industry effluent . *Indian streams research journal* 2(4:) 2230-7850.

Surumbar K. (2004). Physicochemical and biological characteristics of paper effluent from the paper mills of Nilakotai Dindigul(Dt), TamilNadu, India.

Tenagne A. (2009). The Impact of urban storm water runoff and domestic waste effluent on water quality of Lake Tana and local groundwater near the city of Bahir dar, Ethiopia, Cornell University.

Thompson, G., Swain, J., Kay, M. & Forster, C. F. (2001). The treatment of pulp and paper mill effluent: A review. *Bio Resource Technology* 77: 275-286.

Wagnew A. (2004).Socio economic and environmental impact assessment of community based small scale irrigation in the Upper Awash Basin, Addis Ababa, Ethiopia.

World Health Organization (WHO) (2008). Guidelines for Surface water quality. Vol. 1, Geneva.

World Health Organization WHO (2010). Dioxin and their effects on human health.

Appendix: Laboratory Analytical Results

Parameters	Analysis Date	waste-1	waste-2	mixing point	down steam	upstream
	30/01/2015	2499.36±201.32	1314.6±112.1	898±92.21	ND	2.11±0.70
	18/02/2015	561.16±40.72	940.5±48.2	203.58±27.25	84.44±4.34	5.85±0.76
	16/03/2015	470±22.26	405±28.7	186±23.46	112±8.02	12.48±1.19
BOD (mg/L)	Average	1176.84 ± 88.1	886.7± 63.01	429.19±47.64	65.48±6.18	6.81±0.089
	30/01/2015	2969.6±185.25	2304±160.12	1672±114.23	240.57±26.0	2.48±0.24
	18/02/2015	5848±506.2	3729.6±289.3	330.2±53.7	240.54±14.5	8.1±0.51
	16/03/2015	3380±212.45	2808±223.15	1198±60.1	462±33.4	12±0.6
COD(mg/L)	Average	4065.86± 301.3	2947.2± 224.19	764.1±76.01	351.27±19.8	10.05±0.45
	30/01/2015	ND	ND	ND	ND	ND
	18/02/2015	0.37±0.008	1.69±0.04	0.43±0.01	0.83±0.005	0.78±0.001
	16/03/2015	0.42±0.008	0.35±0.02	1.65±0.01	0.8±0.005	0.68±0.001
TP(mg/L)	Average	0.395±0.004	1.02±0.03	1.04±0.01	0.815±0.005	0.78±0.001
	30/01/2015	ND	ND	ND	ND	ND
	18/02/2015	9.79±0.28	12.41±0.25	11.93±0.54	10.41±0.18	3.01±0.02
	16/03/2015	20±1.2	12..8±0.25	6.2±0.50	2.2±0.54	1.8±0.02
TN(mg/L)	Average	14.89±0.74	12.41±0.25	9.06±0.52	6.30±0.18	2.405±0.02
	30/01/2015	279.25±10.91	193.45±6.12	124.83±12.7	89.42±8.79	16.43±1.89
	18/02/2015	446.03±9.06	118.28±7.28	50.88±9.3	39.79±6.45	40.88±1.21
	16/03/2015	699.34±13.3	499.32±8.32	418.65±18.8	259.51±13.56	10.22±1.1
Turbidity(mg/L)	Average	474.86±11.09	270.35±7.24	198.12±13.5	129.57±9.6	22.51±1.4
	30/01/2015	3432±435.86	2854±274.45	1078±158.73	862±97.72	284±33.2
	18/02/2015	1512±170.77	1230±102.91	476±87.93	518±42.13	434±45.2
	16/03/2015	2834±287.34	2508±255.46	1592±107.64	1032±138.52	264±24.8
Total solids(mg/L)	Average	2592.67±297.99	2197.33±210.94	1048.67±118.1	804±92.79	327.33±34.4
	30/01/2015	3134±331.58	2650±356.37	918±85.25	768±46.13	260±17.8
	18/02/2015	1032±108.23	1118±144.22	422±75.66	478±38.95	382±12.06
	16/03/2015	2108±308.2	1976±306.11	1160±45.4	744±24.99	240 ±10.85
TDS(mg/L)	Average	2091.3±312.67	1914.67±268.9	833.33±68.77	663.33±36.69	321±13.57
	30/01/2015	298±56.22	204±18.94	160±25.57	94±14.46	24±2.1
	18/02/2015	480±61.7	112±33.62	54±11.66	40±7.63	52±4.38
	16/03/2015	726±70.09	532±32.12	432±33.42	288±9.2	24±0.84
TSS(mg/L)	Average	501.33±62.67	282. 67±28.44	215.33±13.55	140.67±10.43	33.33±2.44
	30/01/2015	4720±0.28	4020±0.78	1425±12.5	1190±12.6	398±9.8
	18/02/2015	1576±0.1	1705±0.43	664±7.5	765±7.1	598±13.6
	16/03/2015	3300±0.34	2940±0.73	1652±17.8	1130±11.2	412±9.9
EC(µs/cm)	Average	3198.67±0.24	2888.3±0.36	1247±12.6	1028.33±10.3	469.33±11.1
	30/01/2015	6.61±0.1	5.72±0.17	7.19±.32	7.19±0.35	7.73±0.36
	18/02/2015	3.23±0.1	3.4±0.11	7.16±0.22	5.12±0.26	7.05±0.14
PH	16/03/2015	10.66±0.1	10.3±0.08	9.16±0.75	9.38±0.71	7.91±0.13

	Average	6.83±0.1	6.47±0.12	7.84±0.43	7.23±0.44	7.56±0.21
	30/01/2015	630±16.3	550±14.0	121±0.42	77±0.75	25.5±0.04
	18/02/2015	140±10.65	130±10.81	116±0.6	87±0.91	33±0.09
	16/03/2015	900±22.82	800±26.28	600±1.02	320±0.95	27±0.08
Sodium(mg/L)	Average	556.67±16.59	493.33±12.83	279±0.68	161.33±0.87	28.5±0.07
	30/01/2015	12.1±0.1	11±0.09	4.5±0.1	3.8±0.08	2.5±0.02
	18/02/2015	4.7±0.1	11.6±0.19	3.3±0.1	5.4±0.07	1.5±0.02
	16/03/2015	2.9±0.1	2.1±0.06	2.6±0.1	2.6±0.09	2.3±0.02
Potassium(mg/L)	Average	6.567±0.1	8.23±0.12	3.47±0.1	3.93±0.08	2.1±0.02
	30/01/2015	3335±125.5	3036±129.52	828±64.47	690±57.28	218.5±1.68
	18/02/2015	800±41.0	790±53.2	190±14.83	270±23.98	300±1.8
	16/03/2015	49.5±9.0	47.52±14.8	71.28±13.1	75.24±4.69	136.62±1.02
Total Hardness (mg/L)	Average	1394.83±58.5	1291.17±65.84	363.09±30.8	345.08±28.65	218.37±1.5
	30/01/2015	1150±46.2	1104±28.69	276±9.21	242.88±7.83	64.4±3.6
	18/02/2015	288±19.7	280±18.3	65.6±8.49	102.4±5.51	108±4.3
	16/03/2015	11.09±2.47	8.71±3.1	13.46±2.4	19.01±2.02	51.48±2.54
Calcium(mg/L)	Average	483.03±22.79	464.23±16.63	118.35±6.7	121.43±5.12	74.63±3.18
	30/01/2015	110.4±14.54	66.24±1.44	33.12±1.83	19.87±1.05	13.8±1.0
	18/02/2015	19.2±4.1	21.6±0.72	6.24±0.42	3.36±0.81	7.2±0.3
	16/03/2015	5.23±0.5	6.18±0.69	9.03±0.51	6.65±0.42	1.9±0.17
Magnesium(mg/L)	Average	44.94±6.38	31.34±0.95	16.13±0.92	9.96±0.76	7.63±0.49
	30/01/2015	1.22±0.002	1.67±0.001	0.19±0.001	0.46±0.001	0.08±0.00
	18/02/2015	2.77±0.003	1.16±0.001	0.46±0.001	0.56±0.001	0.15±0.00
	16/03/2015	0.27±0.001	0.18±0.001	0.24±0.001	0.12±0.001	0.17±0.00
Total Iron(mg/L)	Average	1.42±0.002	1.0±0.001	0.29±0.001	0.38±0.001	0.13±0.00
	30/01/2015	360±67.3	292.14±15.91	87.37±4.4	55.52±1.58	9.76±0.23
	18/02/2015	3818.74±213.12	815.44±46.3	56.43±1.68	48.23±1.41	30.94±1.07
	16/03/2015	186.22±22.97	150.41±13.45	148.62±8.2	46.56±1.03	8.06±0.11
Chlorides(mg/L)	Average	479.64±101.13	419.33±25.22	97.47±4.76	50.1±1.34	16.25±0.47
	30/01/2015	2000±98.7	1700±79.65	526±36.6	390±27.1	220±22.8
	18/02/2015	ND	ND	280±18.68	220±13.7	290±16.4
	16/03/2015	1098.06±30.54	1159.29±34.69	479.64±32.98	449.02±32.7	202.06±9.4
Total Alkalinity(mg/L)	Average	1032.68±64.62	953.09±57.17	428.54±29.42	353.0±24.5	237.35±16.2
	30/01/2015	ND	ND	ND	ND	ND
	18/02/2015	ND	ND	ND	ND	ND
	16/03/2015	281.66±5.08	389.42±6.25	58.78±0.62	88.17±1.31	ND
Carbonate(mg/L	Average	281.66±5.08	389.42±6.25	58.78±0.62	88.17±1.31	ND
	30/01/2015	2440±97.3	2074±95.56	641.17±26.19	475.8±33.73	268.4±14.1
	18/02/2015	ND	ND	341.6±13.67	268.4±7.96	353.8±11.63
	16/03/2015	766.93±44.78	622.51±21.1	465.65±17. 74	368.52±10.33	246.51±7.87
Bicarbonate(mg/L	Average	1068.9±71.04	898.83±58.33	482.80±19.2	370.90±17.34	289.57±11.2
Sulphate(mg/L)	30/01/2015	276.9±17.88	283.8±22.68	37.05±0.76	421.26±3.3	1.77±0.03

	18/02/2015	26.7±6.2	424.22±30.24	43.06±0.99	124.75±1.6	10.54±0.03
	16/03/2015	282.32±20.2	219.25±	88.79±1.1	37.94±0.62	2.37±0.03
	Average	195.30±14.76	309.09±21.63	56.3±0.95	194.65±1.84	4.89±0.03
	30/01/2015	ND	ND	ND	0.01±	0.058±
	18/02/2015	0.033±0.0001	0.026±0.0001	ND	ND	ND
Copper(mg/L)	Average	0.0165±0.0001	0.026±0.0001	ND	0.005±0.00	0.029±0.00
	30/01/2015	ND	0.128±	ND	ND	0.064±0.00
	18/02/2015	0.59±0.002	0.552±0.0004	0.13±0.00	0.115±0.00	0.115±0.00
Zinc(mg/L)	Average	0.29±0.002	0.34±0.0004	0.065±0.00	0.057±0.00	0.089±0.00

Appendix.2 UV Spectrophotometer determinations of samples

Appendix .3 Filtrations of samples

Appendix .4 Over view of samples