PHYSICO-CHEMICAL CHARACTERIZATION OF KOMBOLCHA TANNERY EFFLUENT AND ITS IMPACT ON ABBA SHARO RIVER WATER DURING A DRY SEASON, SOUTH WOLLO, ETHIOPIA

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Physico-Chemical Characterization of Kombolcha Tannery Effluent and its Impact on Abba Sharo River Water during a Dry Season, South Wollo, Ethiopia

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DEDICATION

If this paper is an achievement, I dedicated this work in remembrance of my late brother, Mr. Mekin Sani. His advice was my strength made a way for me and helped achieve this success.

BIOGRAPHICAL SKETCH

The author was born in February, 1992 in Bati District, Special Oromia Zone, Amhara National Regional State of Ethiopia. He attended elementary education at Bati elementary school and secondary and preparatory education at Bati Red Cross 77 Senior secondary and preparatory school. After completion of his secondary school education he joined Haramaya University in 2013 and graduated with BSc degree in Environmental Science in 2015. Then, he was employed as Graduate Assistant I at University of Adigrat. After serving for one year, he then joined the postgraduate program of Haramaya University in October, 2017 to pursue his study leading to Master of Science Degree in Environmental Science and Management.

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ABBREVIATIONS AND ACRONYMS

ANOVA	Analysis of Variance
AOP	Advanced Oxidation Process
APHA	American Public Health Association
ATSDR	Agency for Toxic Substances & Disease Register
BAT	Best Available Technology
BOD_5	Biochemical Oxygen Demand of five days
COD	Chemical Oxygen Demand
ECPC	Environmental Cleaner Production Center
EDC	Endocrine Disrupting Chemical
EIA	Environmental Impact Assessment
EPA	Ethiopian Privatization Agency
EPCP	Environmental Pollution Control Proclamation
EPE	Environmental Policy of Ethiopia
FEPA	Federal Environmental Protection Agency
GTP	Growth and Transformation Plan
HMBR	Hybrid Membrane Bioreactor
ILTIP	Indian Leather and Tanning Industry Profile
IPPC	Integrated Pollution Prevention and Control
LIDI	Leather Industry Development Institute
LSD	Least Significant Difference
MBR	Membrane Bioreactor
MELCA	Movement for Ecological Learning and Community Action
MoI	Ministry of Industry
MT	Membrane Technology
SPSS	Statistical Package for the Social Sciences
TDS	Total Dissolved Solid
TWW	Tannery Waste Water
UNEP	United Nation Environmental Program
ESA	Ethiopian Standard Agency
WQM	Water Quality Monitor
QSAE	Quality and Standard Authority of Ethiopia

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ABSTRACT

Kombolcha leather industry produces huge amounts of inorganic and organic wastes which pollute the adjacent environment including Abba Sharo River. This study was focused on characterizing the physic-chemical parameters of Kombolcha tannery effluent and evaluates its impact on the water quality of receiving Abba Sharo River water. Accordingly, two tannery effluent samples along wastewater channel at different distances have been taken and three river water samples were collected along the river to evaluate its impact on the river and samples were collected and examined according to standard methods during period of dry season. The analyzed parameters were pH, EC, TDS, T^o, COD, NH_3-N, Cl^-, S^{-2} and Cr^{6+}. The observed mean values for the above parameters revealed that except for pH, T^o, COD and the observed mean values for the remaining all parameters analyzed were beyond the EEPA standard limit values and pH, T^o and Cl^-, values detected in the downstream of the river were within the permissible limit of the WHO guidelines (2013) and Ethiopian recommended values (QSAE, 2013) whereas EC, TDS, NH_3-N, S^{-2} and Cr^{6+} were beyond the permissible limit of the WHO guidelines (2013) and Ethiopian recommended values (QSAE, 2013). The T- test also showed that, except for pH the variation between tannery effluents sampling points were statistically significant ($p < 0.05$). ANOVA also indicated that variation among the sampling points of river water samples were highly statistically significant ($p < 0.05$). In addition to this, the observed mean values for all analyzed parameters in downstream of the river were greater than the values obtained at upstream of the river that were considered to be free of Kombolcha tannery effluent. This shows that the downstream of the river is polluted, indicating the need to remediate the contaminated river due to direct discharge of tannery effluent by launching treatment plant and implementing rules and regulations.

Keywords: Abba Sharo River, Kombolcha, River water, Tannery, Wastewater

1. INTRODUCTION

The rapid urbanization and industrialization that has been taking place during the 20th century virtually transformed the world in to communities of cities and towns facing similar challenges on environmental issues in which most of them have to be addressed at international level. Among those environmental issues, wastewater effluent is a critical one. As long as industries consume a lot of water, liquid waste generation has been an unavoidable and critical issue both in developed and developing nations (Smith, 2010).

The pollutants are generated by various human activities, and improper management of the wide amount of these wastes has become one of the most critical problems of developing countries as they are harmful to the public health and the environment, and they are toxic to the aquatic organisms as well and wastewater treatment helps to remove contaminants from water to reduce pollutant load (Zhang *et al.,* 2010).

Tanning is the chemical process that converts animal hides and skin into leather and related products. The transformation of hides into leather is usually done by means of tanning agents and the process generates highly turbid, coloured and foul smelling waste water (Buljan and Kral, 2011). These have an adverse effect on plant growth, health of animals and people existing in that area (Bhatnagar *et al.,* 2013). Excessive amount of effluent is released as by-product of several industries including tanning. Unlike, municipal wastewater, tannery effluent contains huge amount dangerous chemical and elements such as chromium, sulphur, etc. which are discharged to rivers or other water areas or to open field land areas. If it is not properly managed, discharge of effluent generated from tannery in to surface water bodies could have detrimental effect on environment and human (Favazzi, 2003).

These industries are characterized as highly polluting industries which generates high strength of wastewater that is difficult to treat (Durai and Rajasimman, 2011). There are extensive amounts of dangerous pollutants in tannery wastewater in which heavy metals are very common (Saranraj and Sujitha, 2013). The major components of the effluent include sulphide, chromium, volatile organic compounds, large quantities of solid waste, suspended solids like animal hair and trimmings (Hayelom and Adhena, 2014). Water bodies especially freshwater reservoirs are the most affected. This has often rendered these natural resources unsuitable for both primary and/or secondary usage (Beckley *et al.*, 2014). Tannery effluents mostly influence the river ecosystem and reduce seeds germination in cultivable crops (Koizhaiganova *et al*., 2014) and it is a key resource of chromium to the nature and its removal is One of the greatest environmental problems in the tanneries (Aklilu *et al*., 2013). According to Krishnamoorthi and Saravanan (2011) the heavy metals can create cancer, brain or kidney damage.

Tanning industries are among the major export earning industries in Ethiopia, but it is a great challenge to increase its profit by decreasing its pollution effect to the environment. There is conflict between the economic interest and environmental sustainability because of the fact that most of the tanneries discharge their waste from the tanning process without proper treatment (FDRE, 2010).

More than 20 tanning industries operating in Ethiopia and only 10% of the existing tanning industries treat their wastewater to any degree, while the majority (90%) discharges their wastewater into nearby water bodies, streams and open land without any kind of treatment (EPA, 2002) and the annual volume of liquid waste discharge from the 15 tanneries based on their annual production capacities are estimated to vary between 2,000,000 and 2,500,000 cubic meters (Birhanu, 2017).

There are greater number of large-scale manufacturing plants including Textile Factory, ELFORA-Meat Processing Factory, Tannery, BGI-Brewery Factory, Steel Product Industry and Flour Factory in Kombolcha town. On top of this, the town is selected to be an industrial town by Amhara National Regional State of Ethiopia, which indicates the industrial development and its associated pollution risk may increase in the future.

Kombolcha tannery is one of the tanneries in Ethiopia that use chrome tanning method and have been discharging its wastes in to the nearby rivers such as, Worka and Abba Sharo and these rivers are tributary of Borkena River that flows from North to South West and finally join to the Awash River. As a result of these waste waters (i.e. tannery effluents) that are discharged to streams are being used as a source of irrigation water in several parts of Ethiopia (Eskinder *et.al.*, 2010), where Kombolcha is a case in point.

The inhabitant in the downstream part of the river is used not only for irrigation but also for domestic activities including recreation (swimming and bathing). No study has been conducted yet on the chemistry of the polluted river water for its suitability for bathing, drinking and for other commercial and domestic purpose and effects of tannery on receiving river. Therefore, the aim of this study is to determine the concentration of physico-chemical pollutants in effluent of Kombolcha tannery as well as to characterize its impacts on nearby Abba Sharo River water.

The current study focuses on the assessment of effect of Kombolcha tannery effluent on water quality status of Abba Sharo River. It is of high significance to tanneries; city planners; environmental regulators (e.g. EPA) and even industries other than tanneries in their effort to upgrade or newly establish treatment plants and designing appropriate preventive measures to ensure that the water quality in the Abba Sharo River. The general objective of the study was to analyze the physico-chemical characteristics of Kombolcha tannery effluent and assessing its impact on Abba Sharo River water, South Wollo, Ethiopia with the specific objectives:-

To determine the values of selected physicochemical parameters of effluent from Kombolcha tannery

To assess the impact of tannery effluents on the selected physico-chemical parameters of Abba Sharo river water

2. LITERATURE REVIEW

2.1. Water Pollution

Water pollution occurs when unwanted materials enter into water bodies such as lakes, rivers, oceans, aquifers and groundwater and contaminate the quality of water. This form of environmental degradation occurs when pollutants are directly or indirectly discharged into water bodies without adequate treatment to remove harmful compounds. Safe drinking water is necessary for human health all over the world. Being a universal solvent, water is a major source of infection. According to WHO 80% diseases are water borne. 3.1% deaths occur due to the unhygienic and poor quality of water (Pawari and Gawande, 2015).

Among different kinds of environmental pollution (air, water, land, noise and radiation), water pollution is the most severe in its implications for the health and well-being of people. Water pollution inflicts economic burdens on the users of water resources. It imposes costs on municipal and industrial water supply and human health and damages variety of water based activities including recreational activities and commercial fishing.

The specific contaminants leading to pollution in water include a wide spectrum of chemicals domestic and industrial effluent, leakage from water tanks, marine dumping, radioactive waste and atmospheric deposition are major causes of water pollution (Shahid and Saba, 2018).

2.2. Environmental Pollution and Toxicity Profile of Tannery Wastewater

Tannery wastewater is ranked as one of the major environmental pollutants among all the industrial waste waters (Gupta *et al*., 2012). The presence of a variety of toxic and hazardous chemicals such as chromium, chloro phenols, formaldehydes, oils, resins, biocides, detergents and phthalates etc. in tannery wastewater creates a negative image of leather industries (Lofrano *et al*., 2013). The waste-water generated from Common Effluent Treatment Plant contains high BOD, COD, TDS and a variety of toxic heavy metals especially chromium, which makes it potentially toxic for humans and other living beings (Mondal *et al*., 2012). Tannery wastewater also contains a mixture of chemical compounds, which are used during leather processing and are not get properly degraded even after the conventional treatment and have a negative impact on living organisms and environment (Saxena and Bharagava, 2015). The toxicity of some chemicals used during leather processing is summarized in Table 1.

Table 1: Applications, toxicity and LD_{50} for some chemicals used during leather production in leather industry

Name of chemicals	Applications	LD_{50} In rats (oral mg/kg)	Target organs
Pentachlorophenol (PCP) (a carcinogen)	Applied as a biocide in preservative for raw hides/ skins	2000	Eyes, nose, skin, respiratory tract, blood, kidney, liver, immune system and reproductive system
Bis (2-ethylhexyl) phthalate (DEHP)	Applied as a plasticizer in artificial leather manufacturing	30000	Liver and testes
Azodyes (Orange II) (a carcinogen)	Applied as a dyeing agent	3418	Blood, liver and testes
Hexachlorobenzene, (a carcinogen)	Applied for raw hide/skins preservation	10000	Reproductive system
Chromium (a carcinogen)	Applied as a tanning agent	3250	Kidneys, central nervous system and hematopoietic system
Anthracene (a carcinogen)	Additive during tanning	16000	Kidneys and liver

(Adapted from Kumar *et al*., 2008; Dixit *et al*., 2015)

2.2.1. Leather Production and Chemicals Used in Tanning Process

Leather Industries are specialized in processing of hide (skins of large animals like cows, buffaloes and horses) and skins (skins of small animals like sheep, goats and calves) for leather production. The tanning process used to convert the hide /skins (a highly putrescible material) into stable and im-putrescible products termed as leather, which is used for various purposes (Dixit *et al*. 2015). Tanning processes are classified into vegetable or chrome tanning depending on the type of tanning reagent (tannins or chromium) applied (Mannucci *et al*. 2010).

Table 2: Comparison between vegetable tanning and chrome tanning process

S. No.	**Parameters**	**Vegetable tanning**	**Chrome tanning**
1	Tanning agent	Vegetable tannins (VTs)	Chromium salt
2	Nature	Organic tanning	Inorganic (mineral) tanning

3	Action	Slow process	Fast process
4	Cost	Costly affairs	Cost effective
5	Time	time consuming	Less time consuming
6	Geographical use	Used in developed countries and few developing countries	Used in developing countries
7	Products	Heavy leather like shoe soles, luggage, saddler and belt etc.	Light weight leathers like shoe uppers, garments and bag etc.
8	Product characteristics	Higher thermal stability and water resistant	Softer and more pliable leather
9	Processing steps	All the steps are same as in chrome tanning process	Additionally, retanning, dyeing and fat liquoring are usually performed to produce finished leather and a preliminary degreasing step may be necessary when using animal skins, such as ship skins
10	Impact on environment	Does not require prior preparation of pickling and therefore contribution to pollution load from sulfate salts are lower hence eco-friendly, but VTs are hard to biodegrade. Thus, waste bearing VTs degrade slowly	Generation of chromium containing sludge and wastewater is still a major environmental problem of chrome tanning process

(Adapted from ILTIP, 2010; Dixit *et al*., 2015).

However, the tanning process involves different steps and chemicals for different end products and the type and amount of waste generated may vary in a wide range of quantity and nature (Lofrano *et al*., 2013). During the tanning process, a large amount of chemicals such as acids, alkalis, chromium salts, tannins , sulfates, phenolics, surfactants, dyes, auxiliaries, sulphonated oils and biocide etc. are used to convert the semi-soluble protein “collagen” present in hide/skins in to highly durable commercial forms of leather, and the chemical s used are not completely fixed by the hide /skins and end up in waste water (Mannucci *et al*., 2010).

The poor up take of chromium salt (50–70 %) during the tanning process results in the material wastage on one hand and disturbance of the ecological balance on the other hand (Dixit et al., 2015). Moreover, the sulfonated oils and synthetic tannins or syntans (an extended set of chemicals such as phenol, naphthalene, formaldehyde, melamine and acrylic resins) are also used in tanning/ retanning process to make the leather more softer (Lofrano *et al*., 2013).

The inorganic compounds such as lead chromate (fastening agents) and cadmium sulfate are highly toxic in nature (ATSDR, 2008). Further, there is no any particular restriction to use of syntans yet in Leather Industries worldwide but, the EU Azo Colorants Directive (2002) has prioritized several azo dyes and restricted their use in Leather Industries due to higher toxicity (Dixit *et al*., 2015).

2.2.2. Tannery Wastewater: Nature and Characteristics

Water is essential for life and also used in different types of industrial processes. In the tanning process, a large quantity of water and chemicals are used to treat raw hide/skins and approximately 30–35 m^3 of waste water is generated per ton of raw hide /skins processed (Islam *et al*., 2014). However, the wastewater generation depends on the nature of raw material, finishing product and production processes applied (Lofrano *et al*., 2013). This presents two major problems for leather industries: First, the lack of good quality water and second is it involves adequate treatment of such a large volume of highly polluted wastewater.

Tannery wastewater is a basic, dark brown coloured waste having BOD_5, TDS, COD, chromium (III) and Phenolics with high pH and strong odour (Suganthi *et al*., 2013). However, the characteristics of tannery wastewater may be vary from factory to factory, chemicals used and raw materials, type of final product and the production processes adopted by Leather Industries. The beam house and tanning operation during leather production, are the high pollution causing steps because tanning operation contributes high salts (of chloride, ammonium, chromium and sulfate) concentrations in tannery wastewater whereas beam house operation contributes high organic and sulphide content (Rameshraja and Suresh, 2011). Hence, the beam house wastewater is characterized by an alkaline pH and tanning wastewater by a very acidic pH as well as a high COD value (Lofrano *et al*., 2013). Generally, TWW is highly rich in nitrogen, especially organic nitrogen, but very poor in phosphorous (Durai and Rajasimmam, 2011).

The retanning streams relatively have a low BOD_5 and TSS (Total suspended solids), but high COD and contain trivalent chromium (III), tannins, sulfonated oils and spent dyes whereas the wet finishing, retanning, dyeing and fat liquoring processes contribute low fractions of salt in TWW that is predominantly originating from the hide/ skins in the soak liquor. Further, BOD_5/COD (due to inhibitors) or BOD_5/TOC (due to high sulphide and chloride concentration) ratio is used for the biodegradation study of tannery wastewater (Lofrano *et al*., 2013).

2.3. Tannery Wastewater and River Pollution

Environmental pollution causes to a huge health hazard to human, animals and plants or non living and living components with local, regional and global implications. Effluents from industries are normally the main environmental contaminants containing organic and inorganic compounds. Tannery wastewater is a major source of water and soil pollution. The dark brown colour blocks the sunlight penetration, and thus, decreases the photosynthetic activity and oxygenation of receiving water bodies and hence, becomes detrimental to aquatic life (Carpenter *et al*., 2013). In addition, the depletion in dissolved oxygen encourages the anaerobic condition, which leads to the putrefying odour of receiving water bodies (Verma *et al*., 2008).

This wastewater eutrophicates the water bodies, causing the mortality of aquatic biological resources. Hence, the role of treatment plants is in the sustainable use of wastewater as they make the water usable for various purposes (Durai and Rajasimmam, 2011). The increase in the salinization of rivers and ground water has led to the reduction in soil fertility and quality of drinking water (Money, 2008). It has been estimated that over 55,000 ha of land has been contaminated by tannery wastewater in Tamil Nadu, India and around five million peoples are affected by low quality of drinking water and social environment (Sahasranaman and Jackson, 2005).

Tannery wastewater is also reported to inhibit the nitrification process and as well as to cause a huge foaming problem on surface waters (Schilling *et al*., 2012). Afaq and Rana (2009) also studied the impact of leather dyes (Bismarck brown and acid leather brown) on the protein metabolism in fresh water teleost, Cirrhinusmrigala and reported a significant decrease in total protein content in teleost treated with leather dyes. Tannery wastewater also interfere with the metabolic activities by changing the activity of oxidative enzymes in different organs of guppy fish, Poecilia reticulate and thereby causing cellular injury as a result of exposure (Aich *et al*., 2015).

Tannery wastewater are also highly rich in organic and inorganic constituents and thus, may provide a chance to a variety of pathogenic bacteria to flourish and contaminate the receiving water bodies as these constituents may act as a source of nutrients (Bharagava *et al*., 2014). Chandra *et al*. (2011) have reported the presence of various types of organic pollutants and bacterial communities in two aeration lagoons of a CETP used for the degradation and detoxification of tannery waste water in India and also tested the toxicity of tannery wastewater on mung bean (Phaseolus mungo) in terms of seed germination and seedling growth.

Generally, Leather Industries discharges their effluent into nearby canals/ rivers, which are directly/ indirectly being used by farmers for the irrigation of agricultural crops (Gupta *et al*., 2012). This practice leads to the movement of potentially toxic metals like chromium from water to crop plants that ultimately reach in to the human/animal body and cause toxicity (Sinha *et al*., 2008). However, the chromium toxicity mainly depends on the chemical speciation and thus, the associated health effects are influenced by the chemical forms of exposure (Rameshraja and Suresh, 2011).

It is well reported that chromium (VI) is a potent carcinogen for humans, animals, plants as well as microbes as it enters the cells via surface transport system and get reduced into chromium (III) form and causes various genotoxic effects (Raj *et al*., 2014). Thus, the use of Cr loaded tannery effluent for the irrigation of agricultural crops disrupts the several physiological and cytological processes in cells (Gupta *et al*., 2012) leading to the reduction in root and shoot growth and biomass, seed germination, seedling growth (Hussain *et al*., 2010), and also induces the chlorosis, photosynthetic impairment and finally leading to the plant death (Asfaw *et al*., 2012).

However, the effect of tannery wastewater on seed germination and seedling growth is governed by its concentration and it is crop- specific. In a recent study conducted on mung bean by Raj *et al*. (2014) the % inhibition of seed germination was 90 % and 75 %, when seeds were treated with 25 % untreated and treated tannery effluent respectively. According to Alam *et al*. (2009 and 2010) the genotoxic and mutagenic effects of tannery wastewater and agricultural soil irrigated with tannery effluent has been recently studied. Inappropriate discharge of tannery wastewater also leads to significant levels of contamination on soil as well as acidification because of high salt loads in wastewater. High sulphide content in tannery effluent also causes the deficiency of some micro nutrients in soil such as Zn, Cu and Fe etc. (Raj *et al*., 2014). However, Cr (VI) alters the structure of soil microbial communities and reduces their growth and finally retards the bioremediation process and if it enters into the food chain, causes skin irritation, eardrum perforation, nasal irritation, ulceration and lung carcinoma in humans as well as animals along with accumulation in placenta impairing the fatal development in mammals (Asfaw *et al*., 2012).

The exposure to chlorinated phenols is possible particularly to pentachlorophenol, which is highly carcinogenic, teratogenic and mutagenic in nature and causes toxicity to living beings by inhibiting the oxidative phosphorylation, inactivating the respiratory enzymes and damaging the mitochondrial structure (Verma and Maurya, 2013). The high concentration of pentachlorophenol can also cause the obstruction in circulatory system of lungs, heart failure and damage to central nervous system (Tewari *et al*., 2011).

In addition, tannery wastewater also contains azo dyes that are highly persistent in nature due to their complex chemical structure and xenobiotic nature leading to the environmental pollution (Mahmood *et al*., 2013). Thus, the removal of azo dyes from tannery effluent is essential because of their high mutagenicity, carcinogenicity and intense coloration problems of contaminated aquatic resources (Saratale *et al*., 2010). The discharge of azo dyes into the surface water also leads to the aesthetic problems and obstructs the light penetration and oxygen transport into the water bodies and finally affecting the aquatic life and cause some other serious problems such as dermatitis, skin and eye irritation and respiratory problems in human beings (Chen *et al*., 2011). Further, there has been an increasing concern regarding the release of many endocrine disrupting compounds along with tannery effluent in environment. Endocrine disrupting compounds disturb the delicate hormonal balance and com promise the reproductive fitness of living beings and ultimately may lead to carcinogenesis (Dixit *et al*., 2015).

2.3.1. Wastewater and Irrigation

Wastewater is not just sewage. All the water used in the home that goes down the drains or into the sewage collection system is wastewater. This includes water from baths, showers, sinks, dishwashers, washing machines, and toilets. Small businesses and industries often contribute large amounts of wastewater to sewage collection systems (Lokeshwari and Chandrapa, 2006). Irrigation is a supply of water to agricultural crops by artificial means, designed to permit farming in arid regions and to offset drought in semi-arid regions. The wastewater irrigation practices give very good crop yields because wastewater contains large amounts of organic material and some inorganic elements essential for plant growth. But it may also contain large amounts of non-essential heavy metals which can be transferred to animal and human beings through food chain (Murtaza *et al*., 2010).

The main sources of pollution that enter surface water bodies are industries, municipal solid waste and oily wastes from garages and fuel stations. Most of the water resources are gradually becoming contaminated due to the addition of foreign materials from the surroundings. These include organic matter of plant and animal origin, land surface washing and industrial and sewage effluents. Rapid urbanization and industrialization with improper environmental planning often lead to discharge of industrial and sewage effluents into rivers (Lokeshwari and Chandrapa, 2006).

Worldwide, it is estimated that 20 million hectares of arable land are irrigated with waste water. In several Asian and African cities, studies suggest that agriculture based on wastewater irrigation accounts for 50% of the vegetable supply to urban areas. Waste water has deleterious effects on soil and it cannot be properly used for agricultural practices due to salinity and sodicity problems which impose harmful effects on seedlings of plants. Most of the leafy vegetables which were grown in contaminated soil accumulate higher amount of heavy metals in their leaves (Ansari and Malik, 2007). Wastewater irrigation may lead to transport of heavy metals to soils and may cause crop contamination affecting soil flora and fauna. Some of these heavy metals may bio-accumulate in the soil while others, e.g., Cd may be redistributed by soil fauna such as earthworms.

In Ethiopia, from the increasing human population, uncontrolled urbanization and inadequate sanitation infrastructure cause serious quality degradation of surface waters. Now a day’s water pollution from disposal of industrial wastewater is becoming an environmental concern in Addis Ababa city and its vicinity areas, where most (More than 40% of large and medium scale manufacturing industries are located (Abraha and Tenalem, 2015).

2.3.2. Industrial Pollution Problem in Ethiopia

Industries have been accompanied by industrial waste problem due to industrial development which could be classified into hazardous and non-hazardous waste. Improperly managed Industrial waste can pose dangerous health problem and environmental degradation. Several environmental problems are the major challenging issues in urban parts of Ethiopia as the result of industrial waste because of its better infrastructure they are home to small and medium scale industries and consequently, they are the primary areas affected by industrial pollution (Birhanu, 2017).

For instance, the major pollutant industries in Addis Ababa include: “food and beverage, textile, tanneries, chemicals, metal, rubber and plastic, paper and paper product, metallic, non-metal mineral products and wood industries. The rivers in Addis Ababa are simply used as a receptacle of all kinds of wastes released in the city. There is a high amount of waste disposal in the river and riverbanks from these industries in addition to municipal source (municipal solid and liquid wastes), liquid wastes from toilet, open urination and defecation (Hamere and Eyasu, 2017).

According to Hunegnaw (2015) during his visit he was observed that animals drink Sebeta River which carries discharge of factories alongside to the river. One of the farmers during focus group discussion said the following: “I lost one cow during 2013. It drank this river and passed away”. Other participants of the focus group discussion also share this problem and added that, had it not been the situation improving we could have lost many animals.

This shows the severity of the problem and also supported by other similar studies. Most of the high water consuming industries in the Awash basin area draw water for production purposes from water supply sources and discharge their by-product wastes in to streams and rivers without any kind of treatment. Besides this, there is no restriction on industrial plants discharging their wastewater into the rivers and watercourses. The former EPA and It is realized that the tanneries built along the Awash river basin especially on the Akaki and little Akaki rivers carrying all the devastating pollutant wastes on their way to the neighboring peripheral Oromiya region need due attention (ECPC, 2002). Investigation made on the presence and concentration of heavy metals including toxic hexavalent chromium from tanneries, in vegetable leafs irrigated by the Akaki River was found to be more than the maximum limit that may induce gastrointestinal ulceration and cancer (Prabu , 2009).

The issues of environmental problem in Ethiopia are not only limited to Capital city but also the major issue in the other part of the country. For example there are a number of huge manufacturing industries in Kombolcha town of Amhara National Regional State including but not limited to Tannery, Textile Factory, ELFORA-Meat Processing Factory, BGI-Brewery Factory, Steel Product Industry and Flour Factory. These existing industries have been discharging their wastes in to the nearby rivers such as, Worka and Abba sharo Rivers. These rivers are tributary of Borkena River that flows from North to South West and finally join to the Awash River (Tesfalem, 2017).

These rivers receive untreated domestic wastewater from residential areas and industrial effluents directly or indirectly and then, the local farmers are used these rivers for agricultural purpose without any treatment. In addition, the products of farmlands could be contaminated as farmers wash them with contaminated water before bringing them to market and are the major source for irrigation, bathing, washing clothes and other home uses in this town and nearby kebeles. As result of these the waste waters (i.e. Industrials effluents) that are discharged to streams are being used as a source of irrigation is affecting agricultural lands, water bodies and human health water in several parts of Ethiopia (Eskinder *et.al*., 2010).

In additions unlike developed nations where stringent regulations have been implemented to restrict the discharge of untreated wastewater into rivers, weakness of existing pollution legislation in developing countries, including Ethiopia, and generally they are not adequately enforced (Aberra and Helmut, 2006). As the result the rivers in Kombolcha flowing through larger communities become heavily polluted when they are widely used for domestic, commercial, and industrial purpose.

2.4. Policy and Legal Framework for Environmental Management in Ethiopia

2.4.1. The constitution of Ethiopia

Article 43 of the Ethiopian constitution speculates “The Right to Development” which identifies peoples' right to improved living standards and to sustainable development; and participate in national development and, in particular, to be consulted with respect to policies and projects affecting their community. Similarly, according to Article 44; Environmental Rights, all persons have the right to a clean and healthy environment; and who have been displaced or whose livelihoods have been adversely affected as a result of

State programs has the right to commensurate monetary or alternative means of compensation, including relocation with adequate State assistance.

Moreover, in Article 92: Environmental objectives are identified as,

“Government shall endeavour to ensure that all Ethiopians live in a clean and healthy environment, the design and implementation of programs shall not damage or destroy the environment, people have the right to full consultation and to the expression of views in the planning and implementation of environmental policies and projects that affect them directly and Government and citizens shall have the duty to protect the environment” (FDRE, 1995).

2.4.2. Environmental policy of Ethiopia

Ethiopia is highly vulnerable to grave environmental degradation mainly due to unwise use of natural resources and poorly planned development projects, prompted by rapid population growth. This is because the environment has not featured on the development agenda in the past, since project evaluation and decision-making mechanisms have focused only on short-term technical feasibility and economic benefits. Thus, neglected environmental and social, as well as long term economic dimensions, have resulted in a situation where the country experiences a seriously degraded natural environment that has consequences on negatively impacting the public health (Yonas, 2006).

Experience in the past has shown that different development schemes have caused massive environmental problems as traditional project preparation and decision-making mechanisms were based on short-term technical feasibility and economic benefits (Tsion, 2008). As the concern for environmental degradation has increased in recent years, the Environmental Policy of Ethiopia (EPE henceforth) was issued in 1997 to provide guidance in the conservation and sustainable utilization of the country’s natural resources in general. Among the specific objectives that the EPE seeks to achieve are ensuring conservation, development and sustainable use of essential ecological processes and life support systems, biological diversity and renewable natural resources and the empowerment and participation of the people in environmental management (Mellese and Mesfin, 2008).

For the effective implementation of the Environmental Policy of Ethiopia, the policy encourages creation of an organizational and institutional framework from federal to community levels. The Environmental Policy of Ethiopia provides a number of guiding principles that require adherence to principles of sustainable development; in particular, the need to ensure Environmental Impact Assessment. It considers impacts on human and natural environments, provides for early consideration of environmental impacts in projects and programs design, recognizes public consultation, includes mitigation and contingency plans, provides for auditing and monitoring; and is a legally binding requirement (EPA, 1997).

2.4.3. Establishment of Environmental Protection Organs

Proclamation 295/2002 establishes the organizational requirements and identifies the need to establish a system that enables coordinated but different responsibilities of environmental protection agencies at federal and regional levels. The Proclamation indicates the duties of different administrative levels responsible for applying federal law. Depending on the decisions made, resources available and specific organizational situation in each Region, Regional States have devolved duties and responsibilities to *woredas* and *kebeles*.

2.4.4. Environmental Impact Assessment

The formulation of environmental policy in Ethiopia has led to the enactment of the EIA proclamation in 2002. Fortunately, Ethiopia's earliest commitment to use EIA came into being when it ratified the Convention on Biodiversity in 1994 where Article 14(1) (2) of the convention specifically requires every contracting party to use EIA to protect and conserve biodiversity (Dejene, 2013). The Federal Government has issued a Proclamation on Environmental Impact Assessment, (Proc, 299/2002) and the primary aim of this Proclamation is to make EIA mandatory for specified categories of activities undertaken either by the public or private sectors, and possibly, the extension of EIA to policies, plans and programmes in addition to projects.

Similarly, given the fact that natural resources are the foundation of Ethiopia's economy, the country has made a significant attempt to develop a policy which protects its ecosystems. One of the main achievements is the approval of "the first comprehensive statements of Environmental Policy for the Federal Democratic Republic of Ethiopia by the Council of Ministers in April 1997", which was intended to promote sustainable social and economic development of the country through conservation and sustainable utilization of natural, manmade and cultural resources and the environment of the country.

2.4.4. Incentives for pollution control

The Environmental Pollution Control Proclamation provides incentives to encourage industries to control pollution. For instance, it mandates the FEPA to exempt new imported equipment for controlling pollution from customs duty (EPCP, 2002). To implement the incentive mechanisms envisaged in the Proclamation, the Council of Ministers is mandated to issue regulations. Although the Council has issued a Regulation on the prevention of industrial pollution in 2008, this did not contain specific provisions (FDRE Industrial Pollution Regulation, 2008).

According to Art.12 (1) of the Regulation, factories established before its effective date are given a grace period of five years to comply with its provisions. In effect this means that no measure is to be taken on the previously existing polluting factories until 2013. After the grace period expires in 2013, the competent environmental agency (federal or regional) can "take any measure it deems appropriate to avoid the adverse impacts". These may include "either the relocation or closure of the factory".

2.4.5. Public Health Proclamation

The Public Health Proclamation (200/2000) comprehensively addresses aspects of public health including among others, water quality control, waste handling and disposal, availability of toilet facilities, and the health permit and registration of different operations. The Proclamation prohibits the disposal of untreated solid or liquid hazardous wastes into water bodies or the environment that can affect human health.

2.4.6. Environmental Guidelines and Standards

During 2005 – 2010 Ethiopian Privatization Agency had prepared draft environmental standards for several industrial sector activities and ambient environmental qualities. During the same period, the EPA also prepared several draft guidelines that includes the draft Guideline on Sustainable Industrial Zone/Estate Development. Few years back, the

Environment Council, which is a higher body with a mandate to endorse guidelines, have selectively accepted the industrial environmental standards for twelve specified industrial sub-sectors. The accepted industrial emission standards includes tanning and leather finishing, Manufacturing and finishing of textiles, pharmaceutical manufacturing etc. (MoI, 2014).

2.5. Emerging Wastewater Treatment Technologies

The tannery wastewater which discharged even after the conventional treatment process still contains many refractory and recalcitrant organic pollutants and thus, require further treatment for environmental safety. Therefore, in order to overcome this problem, the use of emerging treatment approaches is increasing in recent years.

2.5.1. Membrane Bioreactors

Widely used method for municipal and industrial wastewater treatment is membrane bioreactor (MBR). It is the combination of a membrane process like micro filtration or ultrafiltration with a suspended growth bioreactor. MBRs offer several advantages over the conventional activated sludge treatment process such as elimination of sludge from settling basins, independence of process performance from filamentous bulking or other phenomena that affect the sludge settle ability (Suganthi *et al*., 2013). However, the major drawbacks of membrane application are the significant fouling due to clogging, adsorption and formation of cake layer by pollutants like residual organics, dyes, and other impurities onto the membrane (Stoller *et al*., 2013). However, the extensive work is in progress to reduce the bio-fouling problem in MBRs.

Further, a hybrid membrane bioreactor (HMBR), which is the integration of various treatment technologies, may be an ideal solution to overcome the bio-fouling problem of MBRs. More recently, the efficiency of HMBR (activated sludge process + electro-coagulation) for the effective removal of COD and colour from tannery wastewater satisfying the discharge limits set by Tamil Nadu Pollution Control Board India has been evaluated (Suganthi *et al*., 2013).

2.5.2. Advanced Oxidation Processes

Advanced oxidation processes (AOPs) refers to the set of chemical treatment processes that use strong oxidizing agents (O_3, H_2O_2) and/or catalysts (Fe, Mn, TiO_2) and sometimes also use the high-energy radiation, e.g., UV light (Srinivasan *et al*., 2012; Dixit *et al*., 2015). AOPs are based on the production and utilization of hydroxyl radicals, which are strong oxidizing agents and quickly and non-selectively oxidize a broad range of recalcitrant organic pollutants such as benzoquinone, benzene, phenols, chlorophenols, dyes and formaldehyde in less time (Lofrano *et al*., 2013; Dixit *et al*., 2015). Generally, the AOPs are used to treat the secondary treated wastewater and therefore known as tertiary treatment (Audenaert *et al*., 2011).

The overall goal of AOPs used for tannery effluent treatment is to reduce the pollution load and toxicity to such an extent that the treated tannery wastewater may be reintroduced into the receiving water bodies or reused during the process. Despite of a broad range of applications, AOPs also have some drawbacks that should also be considered before its applications. The presence of scavenger compounds such as an excess amount of H_2O_2 sometime can act as a hydroxyl scavenger instead of hydroxyl radical source, which interferes with the COD determination and reduces the reaction kinetics making the process uneconomical (Lofrano *et al*., 2013).

Moreover, AOPs still have not been put commercially at large scale (especially in the developing countries) even up to today mostly because of the relatively high costs. The increasing interest in wastewater reuse and more stringent regulations regarding the water pollution prevention and control are currently accelerating the implementation of AOPs at large scale.

Table 3: Findings of some advanced oxidation processes applied for the treatment of tannery wastewater

AOPs	Wastewater Type	Influent COD (mg/l)	Operation parameters and reduction in pollutants	References
Electrochemical Treatment	Raw tannery Wastewater	2810	COD removal (70 %),Electric current(15W),Time (10 min) and pH (3)	Kurt *et al*., (2007)
Electrochemical Treatment	Equalized tannery	17618	COD removal (51–56 %), TSS removal (30–70 %), Electric	Costa *et al*., (2008)

	wastewater		current flow rate (0–10 A at 0–30 V), Time (30–45 min)	
Ozone	Biologically treated tannery wastewater	2900	COD removal (97 %), TSS removal (96 %), TKN removal (91 %), and Surfactant removal (98 %), Colour removal (96 %)	Di Iaconi *et al.*, (2010)
Photo-Fenton ($UV/Fe^{2+}/H_2O_2$)	Equalized tannery wastewater	11,878	COD removal (90 %), TSS removal (50 %), Fe^{2+} (0.4 g /L) and H_2O_2 (15 g /L), Irradiation time (540 min)	Modenes *et al.*, (2012)

(Adapted from Saxena *et al.*, 2016)

2.5.3. Anammox Technology

The Anammox technology is used for the anaerobic removal of ammonia from tannery effluent and it is currently emerging because of its low cost and energy consuming nature. It involves the anoxic oxidation of ammonia with nitrite as a preferred electron acceptor and consumes 50 % les s oxygen, 100 % less organic carbon and saves 90 % of operational costs in sludge disposal as compared to the conventional nitrification/ denitrification processes (Anjali and Sabumon, 2014). Therefore, industries, producing wastewaters having a high concentration of ammonia, are showing increased interest in the Anammox process. However, the long start-up time and inhibitive nature in the presence of organic carbon and NH_4-N limits its field applications. Therefore, it is imperative to develop the mixed consortium capable of Anammox in the presence of organic compounds.

2.5.4. Membrane Technologies

Membrane technologies (MTs) are used for the mechanical separation/purification of industrial wastewater with the help of permeable membranes. MTs operate without heating and therefore use less energy than conventional thermal separation processes such as distillation, sublimation or crystallization. The use of MTs in Leather Industries is becoming popular in current years because of continually reducing cost and ever extending application possibilities.

The MTs offer many economic benefits to the Leather Industries, especially the recovery of chromium from TWW (Ranganathan and Kabadgi, 2011) and are used for purification/re use of waste water and chemicals of deliming/bating liquor (Gallego–Molina *et al*., 2013), reduction of pollution load due to unharing and removal of salts as well as in the biological treatment of TWW for its reuse (Lofrano *et al*., 2013).

Several membrane-based technologies such as cross flow micro filtration, ultra filtration, Nano filtration, reverse osmosis and supported liquid membranes can be used for the removal of pollutants from tannery wastewater (Dixit *et al*., 2015). However, the use of reverse osmosis with a plane membrane has been suggested as a post treatment for the removal of refractory compounds such as chlorides and sulphates, and resulted in the production of high quality of permeate that allowed the reuse of tannery waste water within the production cycle and thus, reduced the ground water consumption (De Gisi *et al*., 2009).

2.5.5. Combinatorial Treatment Approaches

In the previous section, various treatment approaches applied for tannery wastewater have been discussed. However, these treatment approaches have some serious limitations that need to be addressed further. The presence of residual organics, dyes, and other impurities in tannery wastewater even after the biological treatment processes followed by the reverse osmosis based membrane technologies have been reported as the major drawbacks leading to membrane fouling and finally failure of treatment processes (Srinivasan *et al*., 2012). Therefore, a combined application of physico-chemical treatment methods with biological treatment methods or various oxidation processes is generally preferred for the effective tannery wastewater treatment.

Table 4: Combined treatment approaches reported for tannery wastewater

Combined treatment Applied	Optimum parameters	Pollutants	References
Photo-electrochemical treatment with electro dialysis	Electric current density (36 mA/cm^2), Ti electrode, Membrane area (1.72 dm^2), Membrane spacing (0.75 mm)	COD and NH_3-N	Rodrigues *et al*., (2008)
SBBR with Ozonation	Sludge production (0.4 kg TSS/kg COD), Time (5760 and 2160h)	COD, BOD, TSS, TKN and colour	Iaconi *et al*., (2009)
Biological treatment with fenton oxidation	Fenton reagent (6g $FeSO_4$ and 266 g H_2O_2), Time (30 min: fenton oxidation, 72h: biological oxidation), pH (2.5), Temperature (30 ^oC)	COD, BOD, Chromium, Sulphide and Colour	Mandal *et al*., (2010)
Biological treatment with ozonation	Ozone flow rate (3 g/h), Time (24 h), pH (12), Hydraulic retention time (36 h), sludge age (10 days)	COD and colour	Srinivasan *et al*., (2012)

Hybrid membrane Bioreactor	Electric current density (15 mA/cm^2), Electro coagulation time (15 min), Membrane area (0.0143 m^2), Membrane spacing (0.22µ m), pH (7.4 and 9)	COD and colour	Suganthi *et al*., (2013)

(Adapted from Saxena *et al*., 2016)

Clean Technologies for Hazardous Minimization

Environmental pollution due to Leather Industries are a major cause of concern and its mitigation requires some cleaner technologies or also regarded as greener technologies for pollution prevention and hazards minimization. Cleaner technologies utilize the processes that avoid the use of harmful chemicals or promote the use of eco- friendly chemical and cut or eliminate the gaseous emissions and wastes and therefore are cost-effective. Various CTs for the tannery waste minimization and control have been reviewed by many workers (Islam *et al*., 2014).

The development and implementation of cleaner technologies at large scale require (a) careful auditing and assessment of the toxicological effects of chemicals used in leather processing, (b) to avoid the use of environmentally susceptible chemicals, (c) to ensure the maximum uptake of chemicals used, (d) assessment of environmental impact of waste generated during leather processing, and (e) optimization of processes for the best economic returns. However, the success of clean technologies depends on the following parameters: (a) reduction of pollution load in terms of quantity and quality, (b) tanner's benefit in terms of leather quality and/or cost reduction, (c) reproducibility of the process, (d) economic feasibility of process (e) wide market opportunities. Further, the use, assessment and selection of best available techniques (BAT) for the tanning of hides and skins have been discussed (IPPC, 2013).

3. MATERIALS AND METHODS

3.1. Description of the Study Area

Kombolcha is a town located on the north central part of Ethiopia placed immediately south east of Dessie and has a latitude and longitude of 11˚ 06' N and 39 ˚ 45' E respectively. One of the industrial zones in Ethiopia is found in Kombolcha and Kombolcha tanning industry of them, which is found in Kombolcha town is located in *kebele* 3 and is a medium- sized leather industry in Ethiopia (Figure 1). The plant is sited near the Abba Sharo River and channels its effluents directly to the river course. The study was carried out in Abba Sharo River. It is the tributary of Borkena River that flows from North to South West and finally joins to the Awash River.

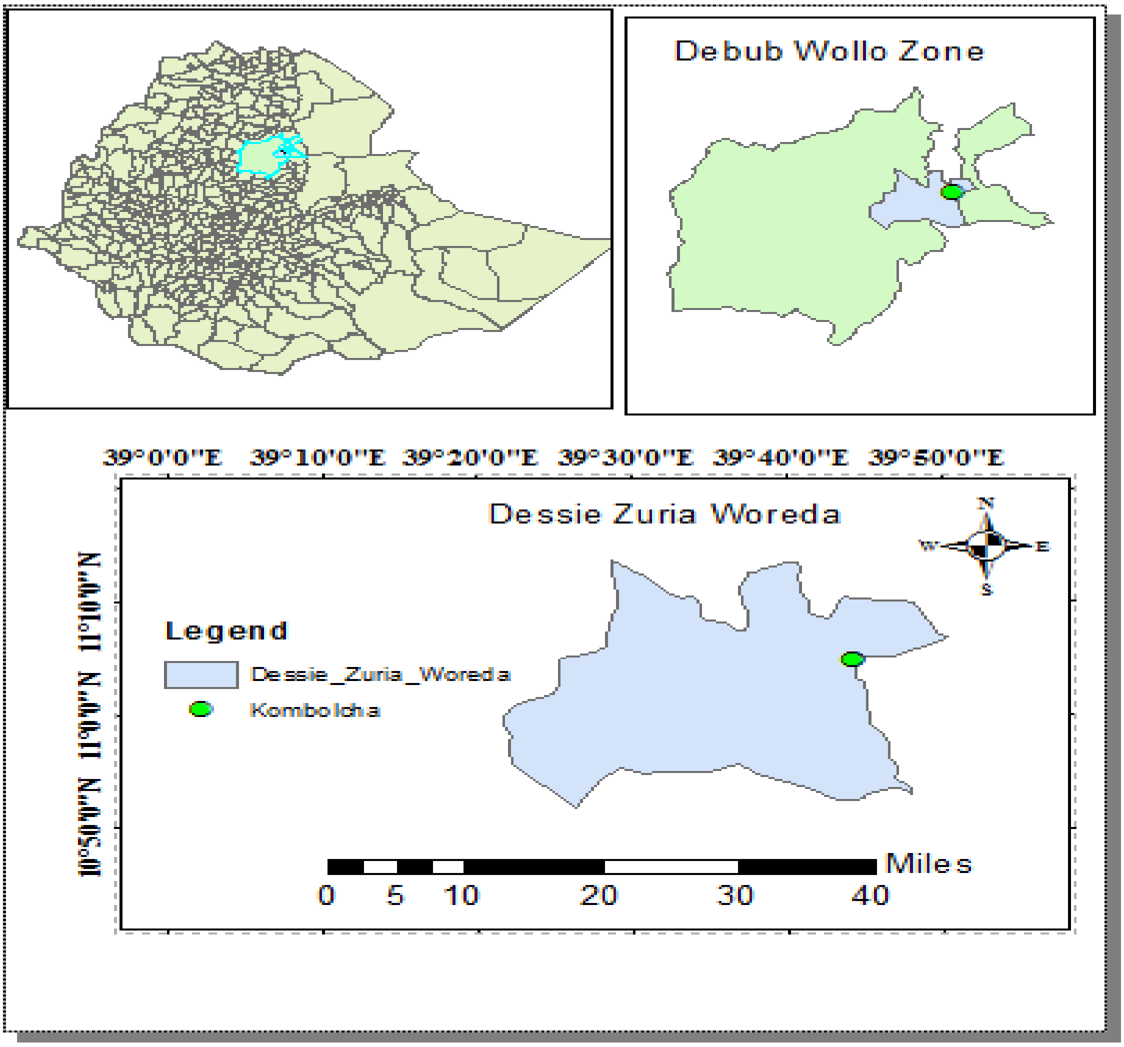

Figure 1: Map of the study area

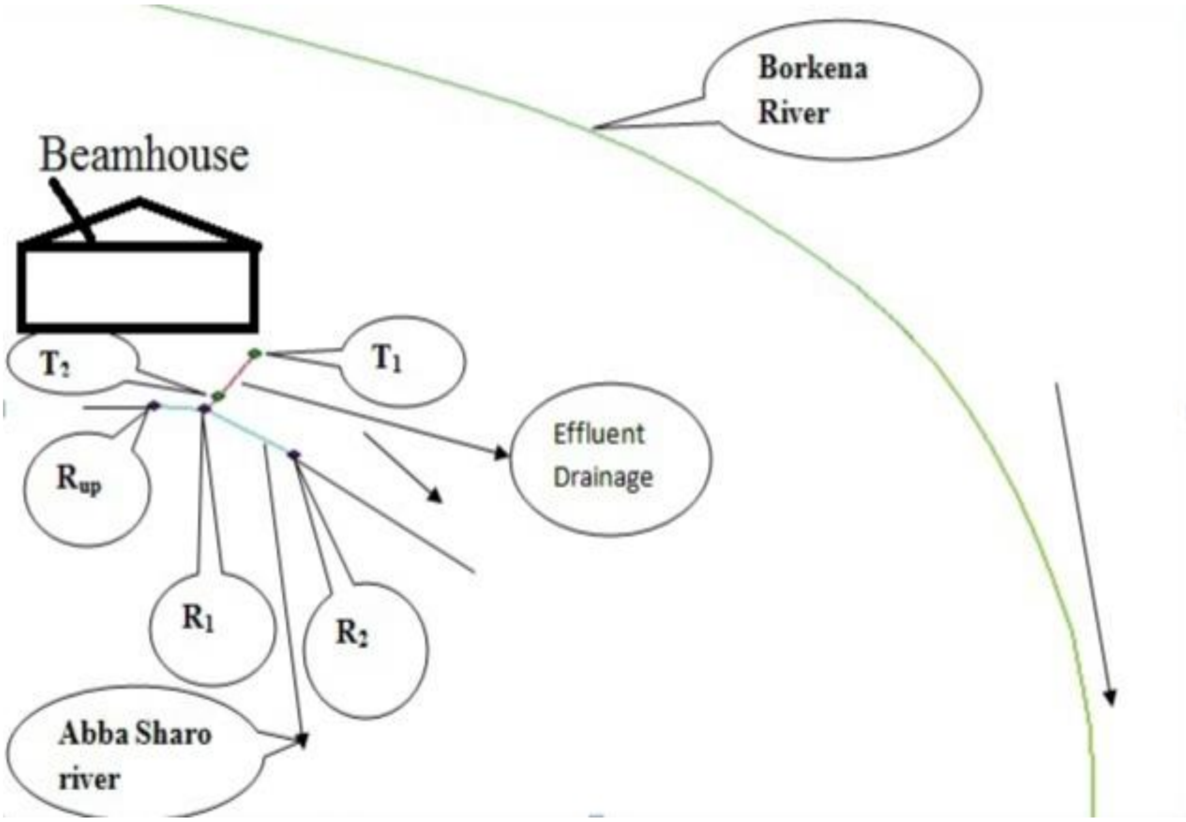

Figure 2: Sketch of tannery beam house, tannery effluent and river water sampling points

3.2. Climatic Condition of the Study Area

The altitude of the town ranged between 1842 and 1915 meters above sea level. The capital of the district, kombolcha town, had an elevation of 1828 m above sea level. Mean annual precipitation was 1,027 mm with mean maximum and minimum temperatures of 25.8 and 11.3 °C respectively. The major portion of the total annual rain fall was received between July to September (NMA, 2019).

3.3. Materials

Table 5: Instruments/methods that were used to determine the physico-chemical properties of tannery effluents and river water samples

No.	Parameters	References	Methods	Instruments
1	pH, EC, TDS and Temperature	APHA (1998)	On site measurement	pH/T ˚ /TDS and conductivity meter
2	Chemical Oxygen Demand	APHA (1998) Section 5220-(B)	Open Reflux Method	Spectrophotometer
3	Ammonia Nitrogen (NH_3-N)	APHA (1998) Section 4500-NH_3(C)	Titrimetric Method	Spectrophotometer
4	Chloride	APHA (1998) Section 4500-Cl^- (C)	Mercuric Nitrate Method	Spectrophotometer
5	Sulphide	APHA (1998) Section 4500 S^{2-}(E)	Gas Dialysis, an Automated Methylene Blue Method	Spectrophotometer
6	Chromium	APHA (1998) Section 3500-Cr^{6+}(C)	Ion Chromatographic Method	Spectrophotometer

3.4. Sampling Techniques

The study utilized grab sampling techniques. Samples were collected from each sample site to different container so that, it is representative of the condition that is to be investigated and in a manner consistent with the collection, handling and preservation principles enunciated in APHA (1998).

Effluent (wastewater) samples were collected along the wastewater channel (drain) at two different distances and were designated as T_1 and T_2 to represent effluents from tannery. Where, T_1 = the point of immediate discharge of mixed tannery effluents and T_2 = the point about 200 m from T_1. Three sampling sites (one upstream and two downstream sites) were established along the river length to assess the impact of the effluent on the river and were designated as R_{up}, R_1 and R_2.

Where, R_1 = downstream site of the river at confluence point where the tannery wastewater joins the river, R_2 = downstream site of the river at about 200 m from R_1 and R_{up} = upstream site of the river at about 200 m from the confluence point where the tannery wastewater joins the river. The control site was established from the upstream site of the river where it is believed to be free of the Kombolcha tannery Factory effluent. All samples were collected from the sites in time of dry season and transferred into the storage bottle without agitation or aeration. Prior to sampling, the polyethylene bottle were cleaned with nitric acid and then washed and rinsed with distilled water. Finally, effluent from both factories and river water samples were sealed and stored in icebox and were transported from sampling sites to the laboratory for the analyses of physico-chemical parameters.

3.4.1. Physicochemical Analysis Method

The parameters of physico-chemical characteristics of tannery effluent such as pH, T^o, EC, COD, NH_3-N, TDS, S^{2-}, Cr^{6+} and Cl^- were analyzed as per standard procedures. These parameters were selected because they were included in the discharge limit and considered to be deleterious on the receiving environment. Shortly before sample collection, water T^o, EC, TDS and pH were measured *in situ* using combined pH/T^o /TDS and conductivity meter. COD, ammonia nitrogen, sulfide, chromium and chloride were analyzed in Addis Ababa City Government Environmental Laboratory according to standard methods for examination of water and waste water (APHA, 1998).

3.4.2. Analytical Procedures

Both field measurement and laboratory analysis were used to analyze each parameter. **Chemical oxygen demand (COD)**: To determine the COD 2.5 ml of the sample was taken in tube, 1.5 ml of 0.25 N $K_2Cr_2O_7$ (potassium dichromate), spatula of H_2SO_4 and 3.5ml of $HgSO_4$ were added and kept in COD reactor for 2hrs at 150^{o}C. After cooling, the sample was titrated against FAS 0.1N and used ferrion as indicator. The end point was reddish brown color. In the blank tube 2.5 ml of distilled water was taken and then follow the same procedure in the sample.

Calculation

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

Where:

A = mL FAS used for blank,

B = mL FAS used for sample,

M = molarity of FAS, and

8000 = milliequivalent weight of oxygen × 1000 m/l.

Ammonia Nitrogen: It was determined by using indicating boric acid solution as absorbent for the distillate. Ammonia was titrated in distillate with standard 0.02NH_2SO_4 titrant until indicator turns pale Lavender and Carry a blank through all steps of the procedure and apply the necessary correction to the results.

Calculation

$$\text{mg } NH_3\text{-N/L} = \frac{(A - B) \times 280}{\text{mL sample}}$$

Where:

A = volume of H_2SO_4 titrated for sample, ml, and

B = volume of H_2SO_4 titrated for blank, ml.

Chloride: Chloride was determined by using a sample portion (5 to 50mL) requiring less than 5 mL titrant to reach the end point. Measure into a 150ml beaker. Add approximately 0.5 mL mixed indicator reagent (i.e NHO_3) and mix well. The color should be purple. Add 0.1NHNO3 drop wise until the color just turns yellow. Titrate with strong Hg $(NO3)_2$ titrant to first permanent dark purple. Titrate a distilled water blank using the same procedure.

Calculation

$$\text{mg } Cl^-/L = \frac{(A - B) \times N \times 35\,450}{\text{mL sample}}$$

Where:

A = mL titration for sample,

B = mL titration for blank, and

N = normality of Hg $(NO3)_2$.

Sulphides: Add 0.5 ml 6*N* NaOH and 400 mg ascorbic acid/100 ml. Shake well. It were precipitated by settling for at least 30 min. pour a portion of well-mixed sample or working standard into a sample cup. Set up manifold as shown in Figure 4500-S^{2-} and follow the general procedure described by the manufacturer. Determine absorbance at 660 nm.

Calculation

Prepare standard curves by plotting peak heights of standards processed through the manifold against S^{2-} concentration in the standards. Compute S^{2-} sample concentration by comparing sample response with standard curve.

Chromium: Ion chromatographic method was applied to determine dissolved hexavalent chromium in wastewater effluents and river water sample. Aqueous samples were filtered and its pH adjusted to 9 to 9.5 with a concentrated buffer. This pH adjustment reduces the solubility of trivalent chromium and preserves the hexavalent chromium oxidation state. The samples were introduced into the instrument's eluent stream of ammonium sulfate and ammonium hydroxide. Trivalent chromium in solution was separated from the hexavalent chromium by the column. After separation, hexavalent chromium reacts with an azide dye to produce a chromogen that was measured at 530 nm. Hexavalent chromium was identified on the basis of retention time. A calibration line was produced by regressing peak area (or height) against standard concentration in mg/l. The concentrations of Cr (VI) were calculated concentration by interpolating from the calibration line.

3.5. Data Quality Control

The procedure of the experiments was done consistently through the whole study to minimize the sources of error. Appropriate procedures were followed to ensure the quality of the collected data. All equipment was calibrated. The analyses of physico-chemical were done following the standard protocols in order to get satisfactory result. For example, wastewater sample collection and analysis were conducted as in the following (among others):

- ✓ Standard analysis method were used
- ✓ Samples were taken in well cleaned plastic bottles
- ✓ Samples were taken at well-mixed (turbulent), homogenized sections for representativeness
- ✓ Samples were preserved at $4^{o}C$ after sampling and transportation to the laboratory

- ✓ Calibration were well conducted during analysis as per required
- ✓ Samples were analyzed as quickly as possible upon reaching the laboratory
- ✓ Analysis were conducted more than once when odd results obtained

3.4. Statistical Analysis

Statistical significance was tested using T-test and one- way analysis of variance (ANOVA) for effluent (wastewater) and river water samples respectively. Least Significant Difference (LSD) method was applied to test the mean differences at the 5% level of significance. All statistical analysis was carried out using statistical package for social sciences (SPSS) soft-ware version 25. Normality test of the data were carried out using statistical method (Shapiro-wilk). The result of the tests shows that the data were normally distributed (Appendix Table 4).

4. RESULTS AND DISCUSSIONS

4.1. Physico-chemical characteristics of Tannery Effluent

The physical and chemical parameters characteristics of tannery effluent and comparison with the Ethiopian tannery effluent discharge limit values are presented in Table (6).

Table 6: Average concentration (mean ± SD, n = 2) values of physicochemical parameters of tannery effluent samples along with Ethiopian tannery effluent discharge limit values

Parameters	Tannery effluent		Discharge limit value	**Remarks**
	T_1	T_2	FEPA	
pH (pH units)	9 .03± 0.15	8.78± 0.15	6-9	Within
EC (µScm^{-1})	14556.67± 15.27	11223.00± 7.55	2500 µScm^{-1}	Beyond
TDS (mg/l)	7330.33±5.50	5599.33±4.04	2000 mg/l	Beyond
Temperature (^{0}C)	24.63±0.21	23.46±0.15	>40	Within
COD (mg/l)	630±12.53	370±7	500 mg/l	Within
NH_3-N (mg/l)	250±3	212.5±2.78	30 mg/l	Beyond
Chloride (mg/l)	7200±3	4640±4	600 mg/l	Beyond
Sulphide (mg/l)	1.1±0.1	0.52±0.02	0.1 mg/l	Beyond
Chromium(mg/l)	267.66±2.55	247±4	0.1 mg/l	Beyond

T_1 = the point of immediate discharge of mixed tannery effluents, T_2 = the point about 200m from T_1 and FEPA= Federal Environmental Protection Authority

The above Table indicates that, at the sites near to the Kombolcha tannery beam house (T_1), the highest concentration of physico-chemical pollutants values were measured and while the sampling site away from the beam house values were recorded decreasing of their values (Figure 6). This is indicated that, the natural treatment of industrial wastewater effluents. But, the result was confirmed that, kombolcha leather industry is contributing and threatening the downstream of the river and environment.

pH

pH is most important in determining the corrosive nature of water. Lower the pH value higher is the corrosive nature of water. pH was positively correlated with electrical conductance and total alkalinity (Gupta *et al.*, 2012). As summarized in Table 6 above, higher value of pH 9.03 was recorded at T_1 and lowest 7.27 for R_{up} (Table 8). The observed values for T_1 (9.03) were greater than and the value (8.78) obtained at T_2 were within standard discharge limits pH value of 6-9 set by the Ethiopian Environmental Protection

Authority (2005) for tannery effluents to be discharged to the nearby environments. The reduced rate of photosynthetic activity the assimilation of carbon dioxide and bicarbonates might be partly responsible for increase in pH. The higher pH values observed suggests that carbon dioxide, carbonate-bicarbonate equilibrium is affected more due to change in physico-chemical condition (Karanth, 1987).

Electrical conductivity

Electrical conductivity is a valuable measure of salt content present in water and its ability to conduct electricity. The maximum obtained EC values were 14556.67 μScm^{-1} and 11223.00μScm^{-1} along the effluent channel at both tannery effluent sample sites T_1 and T_2 respectively. These observed values were greater than the EEPA standard value (2500μScm^{-1}) for tannery effluent to be discharged in to nearby environment. The High EC values indicate the presence of high amount of ionized dissolved inorganic substances in ionized form. The fluctuations in EC in any particular location depend on the change in TDS and salinity and presence of chloride ions and inorganic salt cations ($Na^{2+,}$ K^+, Ca^{2+} and Fe^{3+}) that creates more salinity in water leads to increased capacity of water to conduct electricity (Wright, 1982).

Total Dissolved Solid

Total dissolved solids are measure of total organic salts and other substances that dissolved in water (Nasrullah, *et al.*, 2006). In this study, the TDS values of tannery effluent were found to be much greater than the discharge limit set by EEPA (i.e. 2000 mg/l). The observed values for TDS were 7330.33mg/l and 5599.33mg/l for T_1 and T_2 respectively (Table 6). These higher value of TDS were induced by inorganic impurities including bicarbonates, carbonates, sulphates, chloride, nitrates, nitrogen, phosphates, iron, calcium, sodium and potassium (Kannan *et al.*, 2009).

Temperature

Temperature is the most crucial factors which affects the chemical and biological characteristics of the aquatic system. The observed temperatures for tannery effluent in each of sampling points were 24.63 ^oC and 23.46 ^oC for T_1 and T_2 respectively. These values are below the standard limit values set by EPA for the temperature of tannery effluent, 26 ^oC-40 ^oC (Table 6).

Chemical Oxygen Demand

It is one of the methods used to determine the quality of water (Ram *et al*., 2011). It is similar in function to BOD, in which both of them are an ideal test used to measure the amount of the organic matter found in the water that is not degraded by microbial activity (Abida and Harikrisha, 2008). These are important parameters that are used to determine total oxygen demand by the organic matter present in then water and more realistic parameters to indicate the pollution status of the water body because these parameters are related with organic matter found in the water bodies (WQM, 1999).

The study concludes the average value of COD of the tannery effluent sample as 630 mg/l and 370 mg/l for T_1 and T_2 respectively. It was noticed that comparatively higher concentrations of COD in tannery effluent sample at T_1 (630 mg/l) was against FEPA discharge limit but, the observed COD level (370 mg/l) at T_2 was far below the standard limit value of 500mg/l (Table 6).

Ammonia Nitrogen

Ammonia Nitrogen is present in the form of ammonia and ammonium ions in water bodies. It is a measure of the amount of ammonia, toxic pollutants that often found in landfill leachate and in waste products, like sewage, liquid manure and tannery effluents. It can also be used as indicator for the health of natural water bodies such as rivers, lakes and man-made water reservoirs (Manios *et al.*, 2002). The NH_3-N values along the wastewater drain were 250 mg/l and 212.5 mg/l for T_1 and T_2 respectively. Munz e*t al*. (2008) also reported within an interval of 102-324 mg/l of ammonia nitrogen in tannery effluents. The values obtained along the tannery effluent channel at (T_1 and T_2) were far greater than the acceptable limit values set by FEPA that is 30 mg/l (Table 6). According to Buljan *et al.* (2000) NH_3-N is one of the major components in tannery waste water and its concentration is higher that might be resulted from nitrogen that is found in several components of tannery effluent as a part of the chemical structure and the nitrogen contained in the protenaceous substances of the skin.

Chloride

The obtained chloride values of tannery effluent were 7200 mg/l and 4640 mg/l for T_1 and T_2 respectively. It indicates that the discharge chloride values recorded at T_1 and T_2 for both tannery effluent samples were above the permissible levels of chloride for safe effluent discharge in to water bodies and surrounding areas according to FEPA (600mg/l) (Table 6). Bhattacharya *et al*. (2013) also reported chloride concentration of 6580 mg/l in tannery effluent. The higher concentration of chloride in tannery effluent resulted from the use of significant amount of sodium chloride for skin and hide preservation and pickling process (UNIDO, 2000).

Sulphide

The discharge recorded levels of sulphide along the effluent drain were extremely higher which couldn't be released directly to the Abba Sharo River without prior advanced treatment to reduce its substantial impact on the river ecosystem and to the environment in general. The observed concentrations of suphide along the wastewater channel were 1.1 mg/l and 0.52 mg/l for T_1 and T_2 respectively. This study revealed that the mean sulphide level from tannery effluents were higher than the sulphide discharge limiting values set by FEPA (0.1mg/l) (Table 6). The sulphide content in tannery effluent results from the use of sodium sulphide and sodium hydrosulphide and from breakdown of hair in the unhairing process (UNIDO, 2016). Varsha and Apurba (2008) reported that the use of these two chemicals in the tanning process for dehairing the hides resulted in the higher sulphide content in its effluent. Tesfalem (2017) reported comparable levels of sulphide in effluent generated from Debreberhan tannery.

Chromium

In the present investigation, the chromium content of the tannery effluent samples were 267.66 mg/l and 247 mg/l for T_1 and T_2 respectively. The result revealed that the concentration of chromium were more than the prescribed limit by FEPA (0.0l mg/l) (Table 6). Gebru *et al*. (2012) and Mandal *et al*. (2010) also reported higher concentration of chromium in the tannery effluent sample. According to Sarker *et al*. (2013) the higher concentration of hexavalent chromium in the tannery effluent usually resulted from sulphate salts of chromium that are applied as tanning agent, almost 90% of the tanning industry uses basic chromium sulfate. Out of the total chromium applied in the tanning process, 60-70% is actually consumed, whereas 30-40% remains unconsumed. It is this unconsumed chromium that goes away with the industrial effluent.

T-test for Analyzed Physico-chemical Parameters of Tannery Effluent

For this study, the significance of variation between tannery effluent (wastewater) samples was studied by using T-test method and the result is as presented in Table 7.

Table 7: Mean value of paired t -test result values of physicochemical parameters of tannery effluent samples

Paired Samples Test[a]

Pair		Paired Differences					T	df	Sig. (2-tailed)	
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference					
					Lower	Upper				
1	T_1pH - T_2pH	.26667	.15	.09	-.1	.64612	3.0	2	.094	NS
2	T_1EC - T_2EC	3333.6	7.7	4.5	3314.4	3352.96209	743.3	2	.000	**
3	T_1TDS - T_2TDS	1731.0	5.2	3.0	1717.8	1744.14482	566.6	2	.000	**
4	T_1T^o - T_2T^o	1.1	.3	.1	.4	1.92558	6.6	2	.022	**
5	T_1CoD - T_2CoD	260.0	17.4	10.0	216.7	303.31242	25.8	2	.001	**
6	T_1NH_3N - T_2NH_3N	37.5	2.5	1.4	31.3	43.71034	25.9	2	.001	**
7	T_1Cl^- - T_2Cl^-	2560.0	1.0	.6	2557.5	2562.48414	4434.0	2	.000	**
8	$T1S^{-2}$- T_2S^{-2}	.58	.1	.06	.3	.85662	9.0	2	.012	**
9	T_1Cr^{6+} - T_2Cr^{6+}	20.6	3.8	2.2	11.2	30.07146	9.4	2	.011	**

a. No statistics are computed for one or more split files
NS= not significant and **= highly significant

From the above T-test Table, we can conclude that except for pH, the remaining physico-chemical parameters were highly statistically significantly ($p < 0.05$) varied between tannery effluents sampling points.

4.2. Effects of Tannery Effluent on Physico-chemical Quality of Abba Sharo River Water

The Experimental results of analysis of river water sample for various physical and chemical parameter and comparison of Rivers water quality with WHO and Ethiopian drinking water quality standard are presented in Table (8).

Table 8: Average concentration (mean ± SD, n = 3) values of physicochemical parameters of river water samples along with drinking water quality standards

Parameters	**River water**			**Drinking water quality standards**	
	R_1	R_2	R_{up}	*Ethiopian(QSAE,2013)*	*WHO (2013)*
pH (pH units)	8.23± 0.15	7.67± 0.21	7.27 ± 0.15	6.5-8.5	6.5-8
EC (μScm^{-1})	1484.67 ± 5.50	1111.67±3.05	824±2.00	-	750
TDS (mg/l)	741.66±1.53	555.33±1.53	413±1.00	1000	500
Temperature (^{0} C)	23.06±0.15	21.33± 0.15	20.06±0.35	-	-
COD (mg/l)	169±3	149±4	84 ± 2	10	-
NH_3-N (mg/l)	120±2	65±2	6.5±0.2	1.5	0.2
Chloride (mg/l)	242.6±2.3	208.4±1.21	203.2±0.8	250	250
Sulphide (mg/l)	0.47±0.02	0.16±0.01	0.14±0.02	-	0.01
Chromium(mg/l)	2.13±0.15	1.56±0.15	0.08±0.01	0.05	0.05

The above Table shows that, the lowest concentrations of physico-chemical parameters investigated under this study were measured at the site that is far away from the kombolcha tannery (R_2) than the values recorded at the site that is near the tannery (R_1). It is evidence that, the natural water bodies can ride itself free of pollutants by nature through the process called self purifications of natural streams. On comparing the results against national drinking water quality standards laid by Ethiopian Standard Agency (ESA) and World Health Organization (WHO), it was found that the river water samples are non-potable for human being and account for health hazards for other human uses due to high concentration of one or the other potential contaminants.

pH

Table 8, shows the mean pH value for river water samples at R_{up}, R_1 and R_2 were 7.27, 8.23 and 7.67 respectively, indicating that the effluent from the river affected the receiving part of the river and the pH of the river water was found to be alkaline. This may play havoc with the growth, health as well as the existence of aquatic life. Most metals get soluble in water at low and high pH (Hossain *et al*., 2015). According to Noorjanan (2014), if highly alkaline water consumed would affect the mucous membrane and may cause metabolic alkalosis. In addition to this, the toxicity of the certain substances found in water may be increased due to their interactions with high or low levels of pH prevailing that may further be detrimental to aquatic living beings (Jerin, 2011).

Electrical Conductivity

The EC values of the most fresh waters range from 10 μScm^{-1} to 1000 μScm^{-1} and in polluted water it may exceeds 1000 μScm^{-1} but, the observed EC values for river water samples were 1484.67μScm^{-1}, 1111.67μScm^{-1} and 824 μScm^{-1} for R_1, R_2 and R_{up} respectively (Table 8). This study indicated that the river is somehow polluted and the discharge of the tannery effluent aggravated the situation. Hence, it has been observed that the river being utilized by the nearby inhabitants especially by downstream dwellers for irrigating of the vegetable and bathing. It may cause human health risk and degrade the quality of goods and services that gained from the surrounding environments.

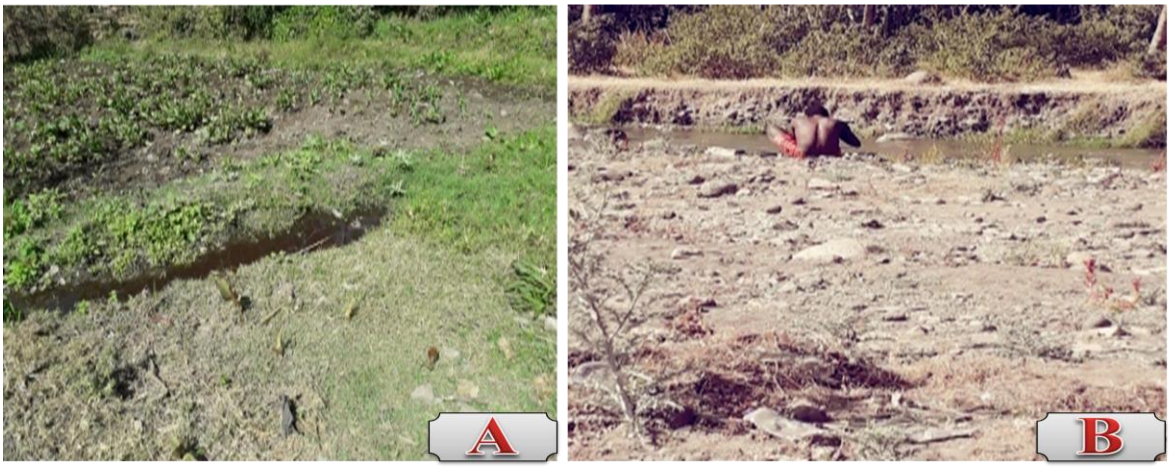

Figure 3: Abba Sharo River used for irrigation (a) and bathing (b) by the nearby resident

There was variation in EC values and decreased in the downstream of the river and along the drainage from T_1 to T_2 for tannery effluent and it might be due to dilution. Generally, the EC values obtained in the control site (824μScm^{-1}) were much lower than the values observed in the downstream of the river 1484.67μScm^{-1} and 1111.67μScm^{-1} for R_1 and R_2 that were polluted due to the addition of Kombolcha tannery effluent. This result indicated that the direct discharge of the effluent in to the river without any prior treatment were polluted the downstream part of the river which might increase the deterioration of the downstream ecosystem.

Total Dissolved Solid

The observed values of TDS for river water samples were 741.66 mg/l, 555.33 mg/l and 413 mg/l at R_1, R_2 and Rup respectively (Table 8). Haile (2016) also reported similar results of higher concentration of TDS in Modjo tannery effluents and nearby river water. Higher concentrations of dissolved solid substances obstruct the density of water. So that, it generates impact on osmo regulation of water and also lessens solubility of gaseous compounds (Azike *et al*., 2011). According to Patel *et al*. (2009), high levels of TDS are aesthetically unsatisfactory and may cause stress on human and livestock and may lower the suitability of water for various uses. The TDS values that were observed in downstream site of the river that were receiving the effluent were greater than the TDS values that were recorded in the control site (Rup). These scenarios can be concluded as the downstream of the river is contaminated due to tannery wastewater that was discharging on it.

Temperature

Table 8 indicates that the analyzed water temperatures for river water sample were 23.06 ^{o}C, 21.33 ^{o}C and 20.06 ^{o}C for R_1, R_2 and R_3 respectively. These values were also within the range of surface waters temperature, 0 ^{o}C – 30 ^{o}C and the little variation among each sampling points of the rivers may be influenced by air circulation, flow and depth of the water body (Chapman, 1996).

Chemical Oxygen Demand

The study concludes the average value of COD of the river water sample as 169 mg/l, 149 mg/l and 84 mg/l for R_1, R_2 and R_{up} respectively (Table 8). The higher COD values in the tannery effluent (Table 6) were increased the COD concentration in the receiving rivers due to the direct addition of wastewater from tannery that contain organic and inorganic pollutants. The magnitude was much higher at R_1 (169 mg/l) and low in R_2 (149 mg/l). The lowest COD values recorded at R_2 were large enough to cause damage on the normal functions of the river. The higher the COD concentration the more rapidly oxygen is depleted in the water. This indicates that less oxygen is available to the higher forms of aquatic living beings due to the effect of waste contaminants. The presence of high COD levels in water may also affect the survival of gill breathing animals found in the receiving river water. It also shows that the toxic state of the river water with the presence of higher concentration of biologically non-degradable organic substances.

Ammonia Nitrogen

The term NH_3-N removal is commonly used in scientific publications as a short way to depict Ammonia in water (Richard *et al.,* 2011). The NH_3-N values of 120 mg/l, 65 mg/l and 6.5 mg/l were recorded at R_1, R_2 and R_{up} respectively (Table 8). The concentrations of NH_3-N that were obtained in the downstream were higher as compared to the values recorded at the upstream site(Rup) that is believed to be free of the kombolcha tannery effluent. This shows that there is increment in the concentrations of this pollutant as the results of the direct discharge of tannery effluent. The higher concentration of NH_3-N can lead to eutrophication of water bodies. Moreover, it can directly poison humans, upset the equilibrium of water system and highly toxic to fish and other aquatic animals (Gupta *et al.,* 2015).Therefore, excessive discharge of NH_3-N has been a serious environmental problem that we need to struggle and solve its potential environmental effect such as unwarranted algae growth and extreme sludge generation producing poor water quality for the sustenance of river aquatic system.

Chloride

Table 8 also depicts that the mean chloride values of river water sample as 242.6 mg/l, 208.4 mg/l and 203.2 mg/l for R_1, R_2 and R_{up} respectively. The comparison between chloride content detected in the downstream (contaminated) of the river (i.e. R_1 and R_2) with the chloride concentration that were recorded at upstream (control) of the river (R_{up}) shows that the chloride concentration were higher in the downstream than upstream, indicating chloride pollution due to direct discharge of tannery effluent that contain higher concentrations of chloride. High levels of chloride in water inhibits the growth of plants, cause human illness, affect bacteria and fish in surface water and it can also lead to the breakdown in cell structure (Chowdhury *et al.*, 2015). Arasappan and Kalyanaraman (2015) also reported that irrigating with water containing high chloride concentration enhance the surface salinity through evaporation which reduce crop yields.

Sulphide

The results of Sulphide in the river water samples were 0.47 mg/l, 0.16 mg/l and 0.14 mg/l for R_1, R_2 and R_{up} respectively. The recorded mean sulphide levels of both R_1 and R_2 at downstream of the river were higher than the WHO drinking water quality standard (0.01mg/l) (Table 8). These results may be due to very low dissolved oxygen level in the river which leads to subsequent reduction of sulfate to sulphide by bacterial decomposition. Both of the values that were recorded at downstream sites were higher as compared to the values obtained from the upstream site of the river (R_{up}) that is taken as control, showing sulphide pollution due to direct discharges of tannery effluent. According to UNIDO (2016) the higher levels of sulphide in water poses many problems such as enhancing the salinity and acidity of water that can harm and will have serious threat to aquatic and human life.

Chromium

Regarding the value of chromium obtained in the river water samples, the downstream river water samples showed much presence of contaminants, as the mean values were 2.13 mg/l and 1.56 mg/l for R_1 and R_2 respectively (Table 8). Both values were greater than the values 0.08 mg/l that was recorded at Rup. De Sousa *et al*. (2016) reported 1.77 mg/l of chromium content in Amazonian river water exposed to tannery effluent. Chromium is an essential metal that is involved in the metabolism of glucose in humans and animals, but its Cr (VI) form is very toxic, mutagenic, and carcinogenic (Rahmaty and Khara, 2011). According to Hany *et al*. (2018) Cr (VI) is highly mobile in most environments, mainly due to its soluble nature and it negatively affects the environment due to its eminent solubility, mobility and responsiveness. Several toxicological studies revealed potential impacts' of chromium (IV) on plant and vegetable growth, animals and humans. Geremew and Tekalign (2017), reported temporary effects such as dizziness, headache, irritation of eyes, skin or lungs, allergic reactions, poisoning of liver, kidney or nervous system or collapse due to lack of oxygen as well as long term illness like occupational asthma, ulcers, bronchitis, genetic defects and dermatitis in humans and animals health due to their unawareness of the toxic effluents of chromium, hydrogen sulphide, lead, zinc, cadmium and formaldehyde released from tanneries.

ANOVA for Physico-chemical parameters of Abba Sharo River water Samples

In the current study, the one- way analysis of variance (ANOVA) were used to test the significance of variation among the river water samples. The least significant difference (LSD) methods were applied to test the mean differences at the 5% level of significance and the result is presented below in Table 9.

Table 9: Multiple comparisons of physicochemical parameters of river water samples

Dependent Variable		Independent Variable I	Independent Variable J	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
pH	LSD	R_{up}	R_1	-1.10*	.14	0.000**	-1.4	-.7540
			R_2	-.57*	.14	0.007**	-.9	-.2206
EC(mg/l)			R_1	-10*	4.63	0.000**	-10122.6	-10099.9
			R_2	-37*	4.63	0.000**	-384.3	-361.7
TDS(mg/l)			R_1	-50*	2.16	0.000**	-5049.2	-5038.7
			R_2	-18*	2.16	0.000**	-191.6	-181.05
T (Celsius)			R_1	-2*	.12	0.000**	-2.4	-1.83
			R_2	-1.7*	.125	0.000**	-2.03	-1.43
COD(mg/l)			R_1	-22*	4.05	0.000**	-230.9	-211.07
			R_2	-20*	4.1	0.000**	-29.9	-10.07
NH_3-N (mg/l)			R_1	-147*	1.9	0.000**	-152.1	-142.9
			R2	-55*	1.9	0.000**	-59.6	-50.4
Cl^-(mg/l)			R_1	-4431*	2.25	0.000**	-4437.1	-4426.1
			R_2	-34*	2.25	0.000**	-39.7	-28.7
S^{-2}(mg/l)			R_1	-.360*	.02	0.000**	-.4	-.32
			R_2	-.310*	.02	0.000**	-.35	-.27
Cr^{6+}(mg/l)			R_1	-.21*	.002	0.000**	-.3	-.22
			R_2	-.20*	.001	0.000**	-.25	-.17

**. The mean difference is highly significant, *. Is significant & Ns. Is not significant at the 0.05 level.

The above Table shows that the concentration of the physico-chemical parameters that were recorded in the downstream (contaminated) of the river were significantly higher than the values physico-chemical parameters that were recorded at upstream (controlled) of the river ($P < 0.05$). This shows that the river is experiencing the higher concentration of physico-chemical pollutants due to the direct discharge of tannery effluent without any prior chemical treatment.

5. SUMMARY, CONCLUSION AND RECOMMENDTIONS

5.1. Summary and Conclusion

The diminishing quality of water seriously delimits its use for human consumption and for aquatic life. Therefore, the continuous and periodical monitoring of water quality is necessary to promote appropriate preventive and remedial measures can be undertaken. In this study, several attempts were carried out to analyze the physico-chemical parameters of tannery effluent and its effect on Abba Sharo river water quality. From the results of analyzed physico-chemical parameters of untreated tannery effluents, it has been concluded that except for pH, temperature and chemical oxygen demand, among the analyzed parameters, the remaining all parameters were exceeded the Ethiopian Federal Environmental Protection Authority (2005) standard limit values. The laboratory results also shown that pH, temperature and chloride values detected in the downstream of the river were within the permissible limit of the WHO guidelines (2013) and Ethiopian recommended values (QSAE, 2013) whereas EC, TDS, NH_3-N, S^{2-} and Cr^{6+} were beyond the permissible limit of the WHO guidelines (2013) and Ethiopian recommended values (QSAE, 2013).

In addition to this the levels of all physicochemical parameters recorded in the downstream (contaminated) site of the river were also high as compared to upstream site which was used as control. This shows that, the untreated effluents from tannery have a considerable effect on the water quality of the receiving river water. The exposure to water contaminated with tannery effluent may pose potential health risk to humans, animals and the environments (soil, water, sediments plants and etc). Similarly, direct discharge of kombolcha tannery effluent to Abba Sharo River affected its downstream part that may have impact on downstream users as they use it for several purposes including for domestic, agricultural and recreational value because the river water is certainly unfit for such purposes without any form of treatment.

5.2. RECOMMENDATIONS

This study suggests that there is a need of remediation of the rivers. To solve the problem tannery should launch treatment plant, hire environmental experts and follow the right procedures to treat the effluent by applying accurate amounts of chemical, good maintenance, and continuous checking and evaluation and intervention of appropriate regulatory bodies (i.e. EPA at federal and regional level) to ensure release of high quality treated final effluents that enable them to meet tannery effluent standard limit set by FEPA before releasing to nearby environments through dissemination and enforcement of the prepared standards. It is therefore recommended that the careless disposal of tannery wastes without pretreatment should be discouraged. Imposition of direct charges on tannery effluents by the regulating agency, as well as continuous monitoring and surveillance is imperative in order to ensure the protection of water resources from further degradation.

Analysis of effluents only by the parameters selected under this research study is not adequate and it was not able to study the effects of effluent on soil and polluted river irrigated crop quality and quantity. But, several heavy metals, Organic and synthetic pollutants are suspected to be discharged with the liquid wastes. So that, further investigation are recommended, in order to have better perspective of the effluents impact on nearby soils, phytoplankton and an overall river ecosystems through ecotoxicological studies.

The communities lived in around the Kombolcha tannery and downstream of Abba Sharo river should be educated to create awareness on impacts of the tannery waste disposal towards the health and environment. Finally, it could be said that adequate preventive measures should be taken in tanning activities with a view to ensuring safe, sound and healthy environment for greater benefit of nearby communities.

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6. APPENDICES

Appendix Table 1: Ethiopian tannery effluent discharge limit value

Parameters	Discharge limit value
pH	6 – 9
EC	2500 µScm^{-1}
TDS	2000 mg/l
Temperature	>40 ^{o}C
BOD5 at 20 ^{o}C	90% removal or 200mg/l, whichever is less
COD	500 mg/l
Total ammonia (as N)	30 mg/l
Total Phosphorus (as P)	80% removal or 10 mg/l, whichever is less
Oils, fats, and grease	15 mg/l
Mineral oils at oil trap or interceptors	20 mg/l
Chromium (as total Cr)	2 mg/l
Chromium (as Cr VI)	Chromium (as Cr VI) 0.1 mg/l
Chloride	600 mg/l
Sulphide	0.1 mg/l
Phenols	1 mg/l

Source: (EEPA, 2005)

Appendix Table 2: Compulsory Ethiopian Standard for Drinking Water specifications

Substances or characteristics	Maximum permissible level
pH	6.5-8.5
Anionic surfactants	1 mg/l
TDS	1000 mg/l
Magnesium (as Mg)	50 mg/l
Manganese (as Mn)	0.5 mg/l
Total iron (as Fe)	0.3 mg/l
Calcium (as Ca)	75 mg/l
Copper (as Cu)	2 mg/l
Sodium (as Caco3)	200 mg/l
Sulfate (as So_4)	250 mg/l
Chromium (as total Cr)	2 mg/l
Chromium (as Cr VI)	Chromium (as Cr VI) 0.05 mg/l
Chloride	250 mg/l
Anionic surfactants	1 mg/l
Potassium (as K)	1.5 mg/l

Sources: (ESA, 2013)

Appendix Table 3: WHO Guideline for drinking water quality

Substances or characteristics	Maximum permissible level
pH	6.5-8
EC	750mg/l
Colour	Not exceeding 5 Hazen units
Hardness	200ppt
TDS	500 mg/l
BOD	6mg/l
COD	10mg/l
Ammonia Nitrogen	0.2 mg/l
Manganese (as Mn)	Not exceeding 0.05 mg/l
Total iron (as Fe)	Not exceeding 0.1 mg/l
Calcium (as Ca)	Not exceeding 0.1 mg/l
Copper (as Cu)	2 mg/l
Cadmium	0.003mg/l
Sulfate (as So4)	250 mg/l
Sulphide	0.01mg/l
Chromium (as total Cr)	0.05 mg/l
Chromium (as Cr VI)	Chromium (as Cr VI) 0.05 mg/L
Chloride	250 mg/l
Nitrate (as $NO3^-$)	50 mg/l
Nitrite (as NO2-)	3 mg/l
Nickel	0.07 mg/l

Sources: (WHO, 2013)

Appendix Table 4: Shapiro-Wilk statistical method to test normality

Parameters	Factor	Shapiro-Wilk		
		Statistic	Df	Sig.
pH	Rup	0.964	3	0.637
	R1	0.964	3	0.637
	R2	0.923	3	0.463
	T1	0.964	3	0.637
	T2	0.964	3	0.637
EC	Rup	1	3	1
	R1	0.997	3	0.9
	R2	0.964	3	0.637
	T1	0.964	3	0.637
	T2	0.987	3	0.78
TDS	Rup	1	3	1
	R1	0.964	3	0.637
	R2	0.964	3	0.637
	T1	0.997	3	0.9
	T2	0.98	3	0.726
Temperature	Rup	0.993	3	0.843
	R1	0.964	3	0.637
	R2	0.964	3	0.637
	T1	0.923	3	0.463
	T2	0.964	3	0.637
COD	Rup	1	3	1
	R1	1	3	1
	R2	1	3	1
	T1	0.995	3	0.868
	T2	1	3	1
NH_3-N	Rup	1	3	1
	R1	1	3	1
	R2	1	3	1
	T1	1	3	1
	T2	0.976	3	0.702
Chloride	Rup	0.893	3	0.363
	R1	1	3	1
	R2	0.98	3	0.726
	T1	1	3	1
	T2	1	3	1
Sulphide	Rup	1	3	1
	R1	1	3	1
	R2	0.75	3	0.57
	T1	1	3	1
	T2	0.987	3	0.78
Chromium	Rup	0.964	3	0.637
	R1	0.964	3	0.637
	R2	0.964	3	0.637
	T1	0.987	3	0.78
	T2	1	3	1

a. Lilliefors Significance Correction. data is normally distributed at $p > 0.05$