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SCHOOL OF CHEMICAL AND BIO ENGINEERING  
ENVIRONMENTAL ENGINEERING STREAM**

***Technology, Performance and Design Evaluation of Tannery  
Wastewater Treatment Plants in the vicinity of Addis Ababa,  
Ethiopia (The Case of China Africa Tannery)***

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**A Thesis Submitted to the School of Graduate Studies of Addis Ababa  
University in Partial Fulfillment of the Degree of Master of Science in  
Environmental Engineering**



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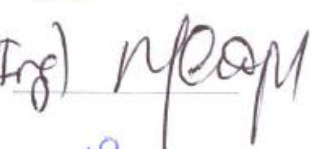

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(with Specialization in Environmental Engineering)

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## List of abbreviations and acronyms

ANOVA:	Analysis of Variance
BAT:	Best Available Technology
BOD:	Biological Oxygen Demand
COD:	Chemical Oxygen Demand
CP:	Cleaner Production
DO:	Dissolved Oxygen
F/M:	Food to Microorganism Ratio
HRT:	Hydraulic Retention Time
LSD:	Least Significant Difference
MLSS:	Mixed Liquor Suspended Solid
NH <sub>3</sub> -N:	Total Ammonia as Nitrogen
NO <sub>3</sub> <sup>-</sup> :	Nitrate
OLR:	Organic Loading Rate
PO <sub>4</sub> -P:	Reactive Phosphate as Phosphorous
PRSCT:	Primary-secondary Treatment
PRT:	Primary Treatment
RAS:	Return Activated Sludge
R-PO <sub>4</sub> :	Reactive Phosphate
S <sup>2-</sup> :	Sulfide
SCT:	Secondary Treatment
SDB:	Sludge Drying Beds
SLR:	Solids Loading Rate
SRT (Θ <sub>C</sub> ):	Sludge Retention Time (Sludge Age)
TDS:	Total Dissolved Solids
TS:	Total Solids
TSS:	Total Suspended Solids
WAS:	Waste Activated Sludge

## Abstract

Industrial water pollution is among the major environmental problems in and around Addis Ababa, Ethiopia while leather-tanneries are among the heavy polluters. Effluent treatment plants already exist in some tanneries with huge concern on their performance. The aim of the study was to evaluate the technology, design and treatment efficiency of tannery wastewater treatment plants in Addis Ababa area based on a case study. Morning hours (10-12 A.M) wastewater sampling for a maximum of five days and then laboratory analysis were conducted at five selected sites in the treatment line for BOD<sub>5</sub>, TSS, TDS, NH<sub>3</sub>-N and pH in both the dry (end of January-February, 2014) and wet (end of June-July, 2014) seasons while COD, chromium, sulfide and R-PO<sub>4</sub> for the dry season and total phosphorous for the wet season were also analyzed. Dissolved oxygen (in the AS aeration basin) and temperature were also measured on-site in both seasons while other additional data were also collected using questionnaire/checklist. Pollutant removal efficiencies were compared with the actual plant design efficiencies, international benchmark efficiencies as well as other similar studies whereas the final effluent quality was compared with national and international effluent release standards to surface waters. The day-to-day and seasonal treatment efficiency variations were also assessed. Technology evaluation for secondary treatment was conducted based on multi-criteria analysis technique (MCA) through stakeholders' participation. The collected data were analyzed by Design Expert Software Version 7.0.0 and MS-Excel 2007. For the overall treatment plant, the dry season mean daily removal efficiencies were 56.3%, 74.9%, 89.5% and 99.7% for BOD<sub>5</sub>, COD, TSS and sulfide respectively while the figures for the wet season were 37.4% for BOD<sub>5</sub>, 80.5% for TSS and 28.3% for total phosphorous. NH<sub>3</sub>-N and TDS were significantly enhanced rather than reduced in both seasons. No statistically significant day-to-day (ANOVA;  $p > 0.05$ ) efficiency variations were observed. Nor was there statistically significant seasonal efficiency variation (t-test;  $p > 0.05$ ) except for the primary-secondary combined treatment in the removal of NH<sub>3</sub>-N and TSS. The mean daily final effluent quality was well within the national standard for BOD<sub>5</sub>, COD, sulfide, total phosphorous, pH and temperature while the standard was significantly exceeded for TSS, NH<sub>3</sub>-N and total nitrogen. The treatment plant was well designed and flexible for the liquid treatment while it was by far deficient for the sludge treatment. WSPs followed by CWs are better than AS and UASBs for secondary treatment of tannery effluent in Ethiopia though the choice depends also on specific local conditions. Efficiency determining factors such as cleaner production are inadequately addressed. To conclude, the treatment plant is well functional, reasonably efficient and is achieving national compliance requirements of major parameters while it has huge limitations in TSS, nitrogen and TDS removal coupled with very poor sludge management.

Key word: Ethiopia, tannery wastewater, treatment technology, design, treatment efficiency, efficiency determining factors, seasonal variation, day-to-day variation

# **1. Introduction**

## **1.1. Background**

Industrial activities have long been greatly contributing to the socio-economic and technological development of human kind. Among the industries mentioned in this regard are manufacturing industries such as leather, textile, food, chemical and other industries, which brought about significant change in their respective domains. However, those huge gains have been overshadowed by undesired consequences of environmental pollution, among which is water pollution caused among others by untreated or unsatisfactorily treated industrial effluents released to water bodies such as rivers and lakes.

Tanneries are the leading among the highest water body polluters, being the oldest and pollution-intensive industries [1-3]. There is a huge concern of water pollution from tanneries in Ethiopia in general and in Addis Ababa in particular. The two major Rivers in Addis Ababa considered highly polluted are the little and great Akaki Rivers, which are used for irrigation, bathing, washing of materials and cattle consumption [4]. They are highly polluted by BOD, COD, dissolved solids (DS) and nitrate while heavy metal pollution was also reported [5]. Heavy metals such as chromium, arsenic, cadmium and copper were found in different proportions in waste water irrigated with vegetables such as cabbage, onion and potato in the city [6].

## **1.2. Statement of the Problem**

The leather-tannery industry sector has been hugely contributing to the socio-economic development of the nation in terms of foreign currency earning, job creation and tax generation. However, this sector in general is among the most polluting industrial sectors, being very pollution-intensive [1-3]. Currently, there are about thirty tanneries in the country, around a dozen of them in the vicinity (in or around) of Addis Ababa according to the Leather Industry Development Institute (LIDI). As the sector is one of the top development priorities of the country, water pollution due to untreated or unsatisfactorily treated tannery effluents is expected to get exacerbated in the future in a business as usual scenario. In Ethiopia, including Addis Ababa, there is a practice of using effluent treatment plants with huge concern on their proper functioning and efficiency according to regulators such as the Addis Ababa Environmental Protection Authority (AAEPA), necessitating a study of this kind for further action.

## **1.3. Objective**

### **1.3.1. General Objective**

The general objective of the research was to evaluate the technology, design and pollutant removal efficiency/performance/ of the selected tannery wastewater treatment system along with assessing factors relevant to plant efficiency.

### **1.3.2. Specific Objectives**

The specific research objectives were the following:

1. To evaluate the technology and design of the treatment plant in relation to the desired purpose and other recommended technologies and designs
2. To evaluate the pollutant removal efficiencies of the treatment system thus comparing the determined efficiencies with the plant design efficiencies and the results of other similar efficiency studies, and the overall effluent quality with national and international tannery effluent release standards to surface waters
3. To check daily & seasonal treatment efficiency variations
4. To assess factors of relevance to treatment efficiency namely treatment system design, operation, administration and maintenance as well as the practice of cleaner production in the manufacturing process

## **1.4. Research Significance**

The results of the current study are 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. Further studies can also be conducted based on the results.

## **2. Literature Review**

### **2.1. Leather Tannery Manufacturing Processes**

Leather production processes involve operations of hide and skin storage, beam house, tanyard, post tanning and finishing [1-3].

Hide and skin storage involves sorting (based on size, weight, quality etc), trimming, curing (using salting, drying, brining, crushed ice or refrigerators along with biocides and fungicides) and storing. Beamhouse operation involves soaking (hydration and cleaning using surfactants, bactericides, enzymes, alkali products etc), dehairing-liming (to remove hair, hair roots, epidermis using inorganic sulfides, lime, enzymes or other alternatives) and fleshing (green flesh or lime flesh, a mechanical process to remove excess organic matter such as fat from the hide). Tanyard operations involve deliming (using ammonium salts and sodium sulfide/bi-sulfide or carbon dioxide or weak acids or esters), bating (using enzymes to remove hair roots and non collagenic proteins thereby improving leather grain and stretch characteristics), degreasing (using paraffin, butyl oxitol, perchloro benzene, ethyl oxitol etc), pickling (to lower pelt pH), pre-tanning (using aluminum salts, syntans, titanium oxides etc to create favorable condition for tanning thereby reducing chrome consumption), tanning (to stabilize the leather using chrome tanning, vegetable tanning or organic tanning), draining-sammying-setting (to reduce moisture content and give good pattern), splitting (cutting at a set thickness) and shaving (to ensure even thickness). Post tanning operations involve neutralization (pH adjustment using weak alkalis such as sodium or ammonium bi-carbonate and acetate), bleaching (to remove stains and the coloring), re-tanning (using vegetable tanning extracts, syntans, aldehydes, resins and mineral tanning agents to improve the leather characteristics and re-wetting properties), dyeing (to give color using water-based acid dyes) and fat liquoring (leather lubrication to return fat lost). Finishing operations achieve required appearance and product specifications in terms of color, feel, flex etc, being classified in to mechanical operations (e.g. moisture optimization, dry milling, polishing and plating) and surface coating operations (e.g. spray coating and roller coating). Coating chemicals include acrylic-based chemicals, silicon, oily and waxy compounds [1].

## **2.2. Environmental Pollution from Leather Manufacturing**

### **2.2.1. General Environmental Pollution**

The socio-economic benefit from leather tanneries is being challenged by the sector's pollution in terms of air emissions, solid waste generation, hazardous materials and toxic effluents [1, 2]. Air pollution includes sulfides due to liming/unhairing and wastewater treatment; dust from operations such as buffing and dry shaving; organic solvents from finishing operations; ammonia from de-liming and post tanning operations, and sulfur dioxide from bleaching, post tanning and other operations [1]. Huge amount of solid waste is also generated from processes of trimming, fleshing, splitting, shaving and wastewater treatment [1, 7]. In a study in Ethiopia, over 850kg of solid waste was generated per ton of wet salted hide processed while the corresponding figure was over 250kg per ton of sheep skin processed, 60% being from beamhouse operations [8].

### **2.2.2. Wastewater Pollution**

#### **2.2.2.1. Physico-chemical and Biological Wastewater Characteristics**

Tanning industries are among the highest water body polluters, being the oldest and pollution-intensive [3, 9]. Process water usage and wastewater characteristics vary greatly among tanneries depending on processes involved, raw materials used and final products, among others [1]. Most leather tanning processes generate huge amount of BOD, COD, TSS, TDS, nitrogen and toxic substances in their wastewater [1, 2]. For example, a conventional process combined raw tannery effluent with water consumption of 45m<sup>3</sup>/ton is reported to have average total pollution load of 2000mg/l for BOD<sub>5</sub>, 4000mg/l for COD, 2000mg/l for TSS, 160mg/l for sulfide, 150mg/l for trivalent chromium, 10,000mg/l for TDS (its main constituents being chlorides and sulfates) and 6-9 units for pH [2]. Most of the organic matter generated from leather processing is not biodegradable [10]. Huge chemicals including toxic substances per unit of output are associated with tanning industries [11-13]. Over 80% of chemicals used in processing are wasted [2]. Chromium, sulfide and nitrogenous substances are also the harmful constituents in tannery wastewaters [13].

### 2.2.2.2. Impacts on Human Health and the Environment

Untreated or inadequately treated industrial including tannery wastewater poses major threat to the environment and human health among others.

In Ethiopia, the impact of water pollution from leather processing industries is already felt. In Addis Ababa, the little and great Akaki Rivers are highly polluted [4, 5]. Heavy metals such as chromium were found in wastewater-irrigated vegetables such as cabbage, onion and potato in the city [6] (Figure 2.1). The pollution of little Akaki River by pollutants such as BOD and ammonia ( $\text{NH}_3$ ) was also reported by other studies [14]. A study conducted in Bahir Dar and Kombolcha industrial sites also claimed that the soil, the irrigation water and the irrigated vegetables were highly polluted, though heavy metal pollution in the irrigation water was not that much, tanneries being among the polluters [15]. The Koka bridge site of the upper Awash River was also found to have low water quality likely due to factors among which is untreated effluent from factories such as Shoa and Ethio tanneries [16]. Severe pollution was also reported regarding the Modjo River (polluted by nutrients and other pollutants) by tanneries along the river [17]. The downward streams of the Sebeta River are also polluted by industries among others [18]. The downstream sites in the river which receive effluent from the Sheba tannery in Tigray region, were also found to have been polluted by hexavalent chromium ( $\text{Cr}^{+6}$ ) exceeding the WHO standard of total chromium in drinking waters (0.05 mg/L) as compared with the levels in the upstream points, hexavalent chromium being very toxic to the environment and human health [19]. Toxic chemicals in tannery effluents pushed communities to lodging serious complaints in the country including in the vicinity of the tannery selected for the actual study.



Figure 2.1. Little Akaki river being used for vegetable irrigation [20]

### **2.3. Cleaner Production (CP) of Relevance to Wastewater Management**

CP as pollution prevention approach does play a huge role in reducing the quality (type of pollutants) and quantity of wastewater generated in leather processing [1, 13]. Material balance in beamhouse processing section (per processing one ton of raw hide) indicated that CP practice in that section enabled a pollution reduction from that section of 50%, 50%, 31%, 52%, 52%, 60%, 30% and 100% for parameters of effluent volume, total lime, inorganic solids, COD, BOD, salt, sulfide and  $\text{NH}_3\text{-N}$  respectively [13]. Significant pollutant reduction was also claimed through CP in beam house processing which is the major source of organic matter (approximately 75% of the total load in the wastewater) and total suspended solids, the liming/dehairing process being the major contributor [1]. Accordingly, hair saving through enzymatic dehairing reduces COD by 40-50%; filtration to recover hair in conventional lime dehairing reduces COD by 15-20% and total nitrogen by 25-30% in mixed tannery effluent; and lime float recycling reduces COD by 30-40%, nitrogen by up to 35%, sulfide use by up to 40% and lime use by up to 50% [1].

Around 60% of total chloride in the tannery effluent is due to the curing process using salt, which is released in the soaking effluent, the rest contributed by pickling and a few by the tanning and dyeing operations. Then, CP in this case to reduce chlorides in the effluent involves natural drying of skins; chilling/ice preservation for short-term storage; antiseptics usage for long-term storage; trimming before curing and other operations; mechanical/manual removal of salt to save it before soaking; salt free pickling; ammonium free deliming (using weak acids or esters);  $\text{CO}_2$  deliming instead of using ammonium salts; short floats in tanning to reduce chemical; direct recycling of pickling float; direct recycling of tanning floats and recycling of chrome recovery plant supernatant. In relation to sulfide reduction from the deliming/hairing waste stream through CP, actions such as enzymatic dehairing (rather than using inorganic sulfide), keeping sulfide-lime overall solution percent of 20-50 for a conventional lime dehairing process and keeping sulfide-containing liquor at alkaline pH ( $\text{pH} > 10$ ) are recommended. Ammonia salts used in the tanning process are the major contributors (up to 40%) of ammonia nitrogen in tannery effluents, other sources being dyeing and animal proteins in beamhouse operations. On the other hand, total kjeldahl nitrogen (TKN) is mainly contributed up to 85% by liming in the beamhouse operations. Accordingly, use of ammonium-free deliming such as weak acids and CP measures used to reduce organic load may also be considered to reduce nitrogen

load in tannery wastewaters. CP for chrome management include fully/partially replacing trivalent chromium; chrome liquor recycling and increasing chrome fixation efficiency [1].

The detailed role of CP in reducing pollutants of effluent was also reported [21] (Table 2.1).

In Ethiopia, CP practices are found to be inexistent or inadequately existent in many tanneries. A study on CP for solid waste management in Addis Ababa Tannery (AAT) reported that CP practices such as proper weighing of chemicals, green fleshing and lime splitting were absent in the tannery [22]. The study claimed that those CP options, if implemented, could have significantly reduced process chemical usage and production cost along with prevention of environmental pollution. The recommended CP options do also have a decisive role in reducing the amount of chemical pollutants in wastewater obviously easing the burden on wastewater treatment plants. Another study on wastewater management in Batu tannery, Ethiopia also reported the inexistence of CP practices creating further burden on the wastewater treatment plant that was physically observed to be inefficient [20].

Table 2.1. Pollution loads discharged in effluents from tannery processing units [21]

Process	Tech.	Pollution load (kg/tonne of raw hide); WW (m <sup>3</sup> )									
		WW	SS	COD	BOD <sub>5</sub>	Cr	S <sup>2-</sup>	NH <sub>3</sub> -N	TKN	CL <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
Soaking	C	7-9	11-17	22-33	7-11	-	-	0.1-0.2	1-2	85-113	1-2
	A	2.0	11-17	20-25	7-9	-	-	0.1-0.2	1-2	5-10	1-2
Liming	C	9-15	53-97	79-122	28-45	-	3.9-8.7	0.4-0.5	6-8	5-15	1-2
	A	4.5	14-26	46-65	16-24	-	0.4-0.7	0.1-0.2	3-4	1-2	1-2
Deliming /Bating	C	7-11	8-12	13-20	5-9	-	0.1-0.3	2.6-3.9	3-5	2-4	10-26
	A	2.0	8-12	13-20	5-9	-	0-0.1	0.2-0.4	0.6-1.5	1-2	1-2
Tanning	C	3-5	5-10	7-11	2-4	2-5	-	0.6-0.9	0.6-0.9	40-60	30-55
	A	0.5	1-2	7-11	2-4	0.05-0.1	-	0.1-0.2	0.1-0.2	20-35	10-22
Post tanning	C	7-13	6-11	24-40	8-15	1-2	-	0.3-0.5	1-2	5-10	10-25
	A	3.0	1-2	10-12	3-5	0.1-0.4	-	0.1-0.2	0.2-0.5	3-6	4-9
Finishing	C	1-3	0-2	0.5	0-2	-	-	-	-	-	-
	A	0	0-2	0	0	-	-	-	-	-	-
Total	C	36-56	83-149	145-231	50-86	3-7	4-9	4.6	12-18	137-202	52-110
	A	12	35-61	96-133	33-51	0.15-0.5	0.4-0.8	0.6-1.2	5-8	30-55	17-37

**Tech.: Technology; C: Conventional; A: Advanced/cleaner production; WW: Wastewater**

## 2.4. Environmental Legal Framework

One of the mechanisms to control water pollution is law promulgation and enforcement. In Ethiopia, citizens' right to a clean, healthy environment and to sustainable development are the two environmental objectives in the national constitution (Article 44 (1), Article 43(1)). Among the specific objectives of the national environmental policy are sustainable use of non-renewable natural resources and cost-effective prevention of pollution with its guiding principles such as pollution prevention and minimization, enforceable pollution standard setting and monitoring, polluter-pays approach and clear linkage between pollution control and other sector policies [23]. In addition, the industrial sector pollution control policy has the objective of limiting the release of industrial (including tannery) hazardous and other pollutants to the environment. The country's environmental pollution control proclamation imposes a legal duty that no person shall pollute the environment, incentive mechanisms such as exemption of custom duty for import of pollution control equipment being part of it (article 10 (1, 2)) [24]. The country also has environmental impact assessment (EIA) law with an incentive mechanism such as financial and technical support by regulators namely regional and federal EPAs (article 16 (1, 2)) [25]. Standards were then set at national level to regulate effluent release from tanneries (Table 2.2).

Table 2.2. National (Ethiopian) and World Bank tannery effluent discharge limit to surface water

Parameter	Unit	National [26]	World Bank [1]
Temperature	°C	40	
pH	pH units	6-9	6-9
BOD <sub>5</sub> at 20°C	mg/l	200 (or 90% removal)	50
COD	mg/l	500	250
SS	mg/l	50	50
Total ammonia (as N)	mg/l	30	10
Total nitrogen (as N)	mg/l	60 (or 80% removal)	10
Total phosphorous (as P)	mg/l	10 (or 80% removal)	2
Total chromium	mg/l	2	0.5
Sulfide (as S <sup>2-</sup> )	mg/l	1	1

## **2.5. Leather Tannery Wastewater Treatment**

### **2.5.1. Best Available Treatment Technologies (BATs)**

Protection of water bodies from harmful pollutants is the main objective of wastewater treatment [2, 27]. Hence the appropriate wastewater treatment technology must be carefully selected considering multiple objectives such as technical, economical, legal and environmental aspects to increase the chance of success of the selected alternative [27-29]. There are a number of available in-use treatment technologies for tannery effluents in the world [3]. However, BAT for a particular industry depends on factors such as land availability, local climate and available resources among others. Although there are BATs in the world, contextualized and adapted use of the technologies for a particular industry is important. Consequently, there are several criteria based on which to select a particular technology among the major ones being efficiency, reliability, land requirement, cost, simplicity, flexibility and sustainability [27-32].

#### **2.5.1.1. Preliminary Treatment**

The role of preliminary treatment in tanneries is to remove large particles such as sand, grit and grease apart from highly reducing the concentrations of chrome and sulfides before the effluent joins the main treatment plant. Accordingly, BAT in pretreatment of tannery effluents includes coarse and fine screens, equalization tanks, sulfide oxidation system-sometimes performed in equalization tanks, chrome recovery system and floating object removing system apart from segregation of streams namely lime stream, chrome stream, soaking stream, post-tanning stream and the rest stream so as to facilitate efficient separate treatments and valuable resource recovery [2]. Consequently, some of the CP techniques that reduce pollutants in the general influent to the conventional wastewater treatment plant may also be considered as vital effluent pretreatment processes as they lessen the burden on the conventional treatment plant

Chrome recovery involves precipitating the spent tanning liquor (after sieving to remove particles and fiber) as chrome hydroxide sludge by treating it with a base such as hydroxide of sodium or magnesium followed by addition of concentrated sulfuric acid to dissolve the sludge to change it to chromium salt solution of  $\text{Cr}(\text{OH})\text{SO}_4$  which is used for tanning [1, 2, 29]. This recovery mechanism can enable 95-98% chrome recovery with very attractive economical implications, with the money saved fully or partially covering the operating costs of treatment

plants [29]. Sulfide catalytic oxidation (in a separate or in equalization tanks) usually using  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  significantly reduces the concentration of sulfide in the liming/dehairing segregated effluent [2]. This technique is the most economical and widely used BAT of sulfide removal in tannery effluents [2, 33].

Equalization tanks are used to homogenize hydraulic and organic loadings to ensure the desired effluent quality of individual units and the overall treatment system [2, 29, 30]. They solve operational problems, enhance overall treatment efficiency, reduce the size and cost of subsequent treatment processes, improve chemical feed control, reduce process variability and improve efficiency of overloaded treatment plants though they have disadvantages such as big land requirement, odor and additional costs [30]. Screening operations protect further treatment process equipments and enhance process efficiency and reliability, being classified in to coarse (mesh size: 6-150mm), fine (mesh size < 6mm) and micro (mesh size much less than 6mm). The coarse screens protect pumps, valves and pipelines from damage and clogging while fine screens are used for preliminary and primary treatment [30]. Mechanically cleaned screens are generally preferable due to enhanced process efficiency, and reduced operational and maintenance frequency and costs [2, 30, 34]. Both coarse and fine screens are highly recommended for leather tannery effluent preliminary treatment, the fine screen having the ability of further reducing fine suspended solids in the effluent [2]. Grit chambers remove large particles such as grit, sand etc that could cause problems such as abrasive wear in mechanical equipment and pipe clogging among others [2, 30]. At least simple non-aerated grit chamber is recommended [2].

### **2.5.1.2. Primary Treatment**

This stage is designed to remove organic and inorganic solids by the action of gravity (sedimentation) or dissolved air under pressure (dissolved air floatation). Floating materials are also removed at this stage through skimming operation. Removal of around 25-50% of  $\text{BOD}_5$ , 50-70% of TSS and 65% of the oil and grease can be achieved during primary treatment [2]. Circular and rectangular tanks are used with continuous scum and sludge removal [2, 35, 36].

Circular clarifiers are better in terms of sludge removal mechanism, maintenance requirement/cost and in-tank thickening while the rectangular ones are better regarding space

requirement, capital cost, easy allowing of separate flow splitting structures and sludge pumping stations [37]. However, circular clarifiers are recommended for tannery wastewater treatment [2].

Chemically enhanced primary treatment is mostly used in wastewater treatment to enhance pollutant removal efficiency of TSS, BOD, heavy metals and nutrients (especially phosphorous) apart from allowing increased solids and hydraulic loading rates. It involves salt (iron and aluminum salts) and/or lime addition for coagulation (destabilization) of particles and polyelectrolyte addition for flocculation (aggregation) of particles, the most common chemicals for this purpose being alum ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  or  $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ ), ferric chloride ( $\text{FeCl}_3$ ), calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), aluminum chloride ( $\text{AlCl}_3$ ) and ferrous sulfate or copperas ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ). Chemical precipitation for phosphorous and heavy metal removal is also achieved with coagulation and flocculation processes by the addition of multivalent ions ( $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ), polymers being effectively used along with alum and lime as flocculation aids. For instance, addition of lime results in reaction with natural bicarbonate alkalinity to precipitate calcium carbonate. But at  $\text{pH} > 10$ , excess calcium ions react with the phosphate to precipitate it as calcium hydroxylapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ). Similarly, addition of trivalent iron and aluminum ions results in precipitation in the form of aluminum and iron phosphates [30]. Although the chemical enhancement of the primary treatment incurs additional cost, it may be compensated by the reduction in cost from the operation of secondary treatment as the burden on it is significantly reduced. It may also be justified by the discharge standard compliance requirements that may incur even much more cost to the industry in question if not achieved.

High rate clarifiers such as inclined plate and tube/lamella/ settlers and dissolved air floatation (DAF) systems permit higher loading rates and enhanced pollutant removal efficiency. Lamella settling is based on the principle of reduced-depth sedimentation (increased surface-area-based settling) where particles are only required to settle to the surface of the tube or plate below. These high rate settlers in primary sedimentation processes are very useful as they are associated with major advantages such as allowing high loading rates, reduced space requirement, rapid start-up times of the system and high effluent quality [30, 38].

DAF is a mechanism involving the bubbling of air into flocculated wastewater to force flocculated particles to the surface where they will be skimmed [30]. Accordingly, the waste water pre-saturated with air will be exposed to a reduction in pressure, which will then be forced

through valves or special orifices so that clouds of bubbles are formed downstream of the constriction [30, 40]. Chemically enhanced DAF system as a primary wastewater treatment can ensure removal efficiency of 70-80%, sometimes up to 90% COD, the floating sludge having 8-10% of solids content that is more cost effective to handle compared to the handling of the only 2-3% solid content sludge achieved by settlement processes [33]. DAF has long been used for sludge thickening and removal of ions, organic solids, dissolved oils volatile organic compounds, and algae, being most commonly used for the treatment of industrial effluents [41]. It has advantages such as small tank size requirement, allowing high and variable solids loading rate, high float concentration, removal of low-density particles, short detention times and less space requirement [33, 41]. However, they are associated with high capital and operating costs such as energy costs associated with the aeration process.

### **2.5.1.3. Secondary (Biological) Treatment**

#### **2.5.1.3.1. General Overview**

Biological treatment is the next step in the treatment of industrial wastewater, both aerobic and anaerobic biological systems being used with different efficiencies across the world [3, 42]. The aerobic system is better than the anaerobic system in that it has excellent effluent quality, low temperature sensitivity or no heat input and less sensitivity to toxic compounds in the wastewater such as chlorinated compounds [42, 43]. It is also associated with low alkalinity requirement, high nutrient removal, less odor production and short start-up time of usually 2-4 weeks unlike the 2-4 months of the anaerobic processes [42]. On the other hand, the anaerobic systems are associated with (and hence better than the aerobic systems) low sludge production, low nutrient and oxygen requirement, low energy input and better resource (e.g. energy) recovery [42, 43].

Both aerobic and anaerobic processes are used in treating tannery wastewater, the widely used technologies being activated sludge (AS) [2, 3] and upflow anaerobic sludge blanket (UASB) [3, 44]. Constructed wetlands (CWs) [3] and pond systems (waste stabilization ponds especially aerated facultative ponds) [2] are also used for tannery wastewater treatment in some cases, though these treatment approaches are not as well established as conventional treatment systems such as the AS. The AS will be focused in this paper as it is the secondary treatment technology used in the actual industry.

### 2.5.1.3.2. Activated Sludge Treatment (AS)

AS is the most widely used secondary (biological) treatment system for tannery wastewater (Figure 2.2). It could be the conventional one or its modifications, the most widely used being the complete-mix extended aeration system. The major operational parameters of the process are total influent volume, aeration tank volume, organic loading rate (OLR), mixed liquor suspended solids (MLSS), food-to-microorganism ratio (F/M) and hydraulic retention time (HRT), other important operational parameters being sludge age (usually not less than 20 days) and return activated sludge (RAS), which is the volume of recycled sludge to the total influent volume (Q) (80-100% in extended aeration process). In addition, the parameters to be regularly monitored are DO in the aeration tank, pH (effective range is 6-9, the optimum being 7.0-7.5), temperature (recommended: 10-30°C), nutrients and sludge volume index (SVI), which is the volume occupied by 1g of activated sludge after settling the aerated mixed liquor in a 1,000ml graduated cylinder for 30 minutes. SVI shows whether the sludge is compact, which is important to control the process and determine pumping requirements of return sludge, well settled sludge having SVI less than hundred [2]. DO must be at least 2mg/l in the aeration tank, the BOD-nitrogen-phosphorous ratio (BOD: N: P) being 100:5:1 [2, 30]. Dissolved oxygen above 2mg/l improves nitrification while above 4mg/l increases aeration cost without improving anything [30].

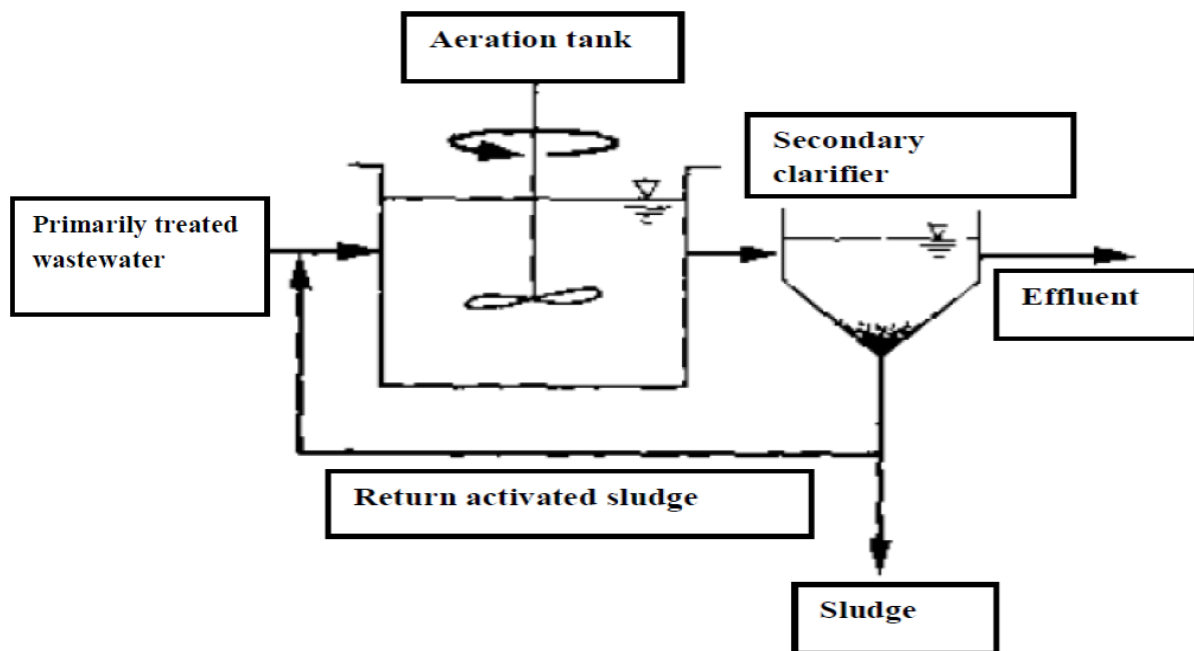


Figure 2.2. Complete-mix activated sludge reactor [30]

### **2.5.1.3.3. Upflow Anaerobic Sludge Blanket Treatment (UASB)**

UASB is a high rate anaerobic reactor popular in treating high strength industrial wastewater including tannery wastewaters [3, 44] (Figure 2.3). It is better than other high rate anaerobic treatment systems such as anaerobic fixed and fluidized bed reactor systems in terms of biomass retention, cost, operation and maintenance requirements and high mean cell residence time, though they are also associated with disadvantages such as long start-up period, significant wash-out of sludge in the initial stages of the process and seed sludge requirement for faster start-up [44]. Its space requirement is also comparable to the AS system, being less than the oxidation pond and aerated lagoon systems, its capital cost being smaller than that of the AS but higher than oxidation ponds and aerated lagoons [36]. However, a comparative study of tannery wastewater treated by UASB and AS technologies in India indicated the superiority (they are better) of AS system over the UASB system in terms of effluent quality, sludge quantity generated, annual cost (capital, maintenance and operating) and space or land requirement [45]. The UASB technologies are also said to be associated with other negative aspects in that they are efficient usually in terms only of removing BOD and TSS; they are sensitive to toxic substances and acids; they are sensitive also to operating conditions of pH (e.g. optimum pH for methanogenic bacteria is 6.8-7.2) and temperature and require high BOD wastes for better efficiency [36]. On the other hand, the technology showed better performance of treating high strength tannery wastewater effectively compared to conventional reactors, the technology being most frequently used in common effluent treatment plants in India as an alternative to the AS technology [3]. A study on the performance of a UASB reactor treating tannery wastewater under different organic loading rates between 5-12kg/m<sup>3</sup>/d resulted in COD and BOD removal efficiencies of the range 46-85% and 65-93% respectively, the gas production being between 2-15L [46].

In the UASB system, wastewater enters at the bottom and moves upward through granular sludge blanket, the main components of the system being influent distribution system, gas solid separator and effluent collection facility [30, 44].

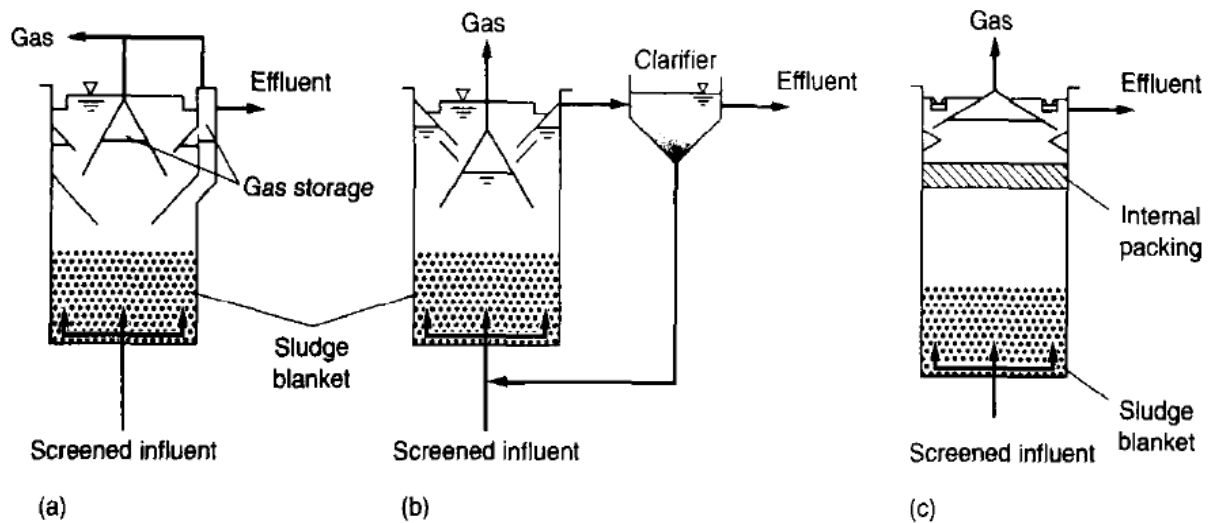


Figure 2.3. The original UASB reactor (a); UASB reactor with clarifier and sludge recycle (b); UASB reactor with fixed film above the sludge blanket (c) [30]

#### 2.5.1.3.4. Wastewater Stabilization Ponds (WSPs)

These are the oldest types of natural-process based effluent treatment methods, associated with higher HRT (in days) than modern electromechanical processes such as AS, which have HRT in hours [29, 31]. Examples of some pond systems are shown in Figure 2.4 and Figure 2.5. The citation of Mara [31] in this section refers to pond treatment of high strength organic wastewater (especially domestic wastewater), leading to limitations of the data and the associated discussion in relation to tannery wastewater treatment which is associated with inhibitory situations of microorganism activity such as high salinity and toxicity. WSPs have been widely used in developing countries because of high economic constraints to run sophisticated systems and the presence of favorable temperature environment for microorganisms to thrive and operate optimally (especially in tropical regions) among others [31, 47]. They can ensure adequate secondary and tertiary wastewater treatment, though big land is required to enable higher hydraulic retention time for enhanced pollutant removal [31]. They are majorly categorized into anaerobic, facultative, aerobic and maturation ponds. The anaerobic ponds produce small amount of sludge and treat high-strength organic wastes and suspended solids, with long (20-50 days) detention time and depth of range 2.5-9 meters [10]. They have less operating and energy costs compared to other ponds [47]. Aerobic ponds are shallow ponds (0.3-0.5 meters deep) with relatively small detention times (3-5 days) whereas facultative ponds are ponds of 1-2.5 meters deep with detention times of 5-30 days, having three layers of upper- aerated, middle-facultative

and lower-anaerobic. Maturation ponds are shallow (1-2 meters) ponds of roughly 20-days of detention time, which serve as tertiary treatment of effluents from AS or trickling filters to further reduce BOD, SS and nutrients [10]. Those different types of ponds may be used as a single unit or in combination depending on the degree of effluent quality required after treatment [31, 47]. More than one pond is usually used in series of anaerobic pond, facultative pond and a series of maturation ponds followed by polishing pond [31].

WSPs are easy-to-use, low cost, resilient to shock loadings (organic and hydraulic), resilient to high levels of heavy metals and highly efficient-mainly in relation to domestic wastewater in removing constituents of BOD, SS and  $\text{NH}_3\text{-N}$  by over 90% apart from reasonable degree of phosphorous removal, especially up on addition of iron or aluminum salts in the pond [31]. Reasonably high amount of nitrogen (40-80%) and better salt-enhanced (iron and aluminum salts) phosphorous removals by ponds were also reported [10]. The fact that the system is less costly, less energy intensive and easy-to-operate was also discussed in [10, 47].

The disadvantages of pond systems are bad odor and serious health disorders due to hydrogen sulfide (from anaerobic pond) and big land required for the pond system. Sulfide exists predominantly as  $\text{H}_2\text{S}$  at low pH ( $\text{pH} < 7$ ) as  $\text{HS}^-$  at moderate pH ( $\text{pH}$  between 7 and 9.5) and as  $\text{S}^{2-}$  at high pH ( $\text{pH} > 10$ ) [48]. However, the odor problem could be avoided by optimal design and operating practices. The system must not be overloaded and the sulfate concentration in the raw wastewater had better be reduced to less than 500 mg/l to minimize the odor problem apart from controlling the sulfide odor by pH adjustment as sulfide exists in different forms at different pH [31]. Similarly, the huge land requirement of WSPs could be adequately justified where there is no land problem. Other environmental problems such as noise pollution are minimal for WSPs. The low capital and operating costs justify the economic sustainability of pond systems, though this is compromised in congested cities where land is very expensive. Social attractiveness is also justified as there is no big and unnecessary cost associated with pond systems, the saved money being invested in other activities that benefit the society.



Figure 2.4. A picture of facultative pond [31]



Figure 2.5. A picture of anaerobic pond [31]

### **2.5.1.3.5. Constructed Wetlands (CWs)**

These are artificially engineered wastewater treatment systems designed through imitation of natural wetlands treating wastewater, but in this case at a more controlled situation [49, 50, 51]. They remove pollutants such as heavy metals, nutrients and BOD with the crucial role of floating, submerged or/and rooted aquatic plants through a combination of physical, chemical and biological processes [47, 51, 52]. The two major types of constructed wetlands namely subsurface horizontal and vertical hydraulic flow types are shown in Figure 2.6 and Figure 2.7 while the free water surface type (the wastewater is seen on the surface) constructed wetland used as biological treatment in Modjo tannery, Ethiopia is shown in Figure 2.8. The performance of CWs in treating wastewater is affected by hydraulic loading, water depth and degree of aquatic plants covering it [10]. Plant type also affects wetland pollutant, especially heavy metal removal efficiency as plant assimilation capacity varies [50, 53, 54]. CWs are very effective for the removal of organic matter (BOD and COD) from tannery wastewaters, though their removal of nutrients is relatively low as compared to organic matter removal [49, 53]. However, the removal of nitrogen may be increased by a combination of different types of CWs whereas high sorption media may be used to enhance phosphorous removal [49]. The choice of plants on wetland performance is evident in that wetlands planted with *typha latifolia* and *phragmites australis* better performed in terms of adaptation and propagation on the wetlands receiving tannery wastewaters [53, 54]. A study on the tannery effluent treatment performance of a two-stage constructed wetland planted with *typha latifolia* and *phragmites australis* reported removal efficiencies of 88% for BOD and 92% for COD along with the removal of nutrients, showing that multistage wetland treatments have better performance [54]. Another study claimed very high chromium removal efficiencies of up to 99.83% and up to 92.53% for vegetated and un-vegetated horizontal sub-surface flow constructed wetlands treating tannery wastewater, the chrome removal mechanism perhaps being due to gravitational settling, chemical precipitation and adsorption on plant surfaces [55]. The operating and maintenance costs of constructed wetlands are very low compared to conventional treatment systems such as AS apart from their being simple to construct [10, 49, 51, 52]. In addition, they render other ecosystem services such as wildlife habitat and biodiversity conservation apart from being aesthetically nice. However, they are associated with big land requirement and clogging [51].

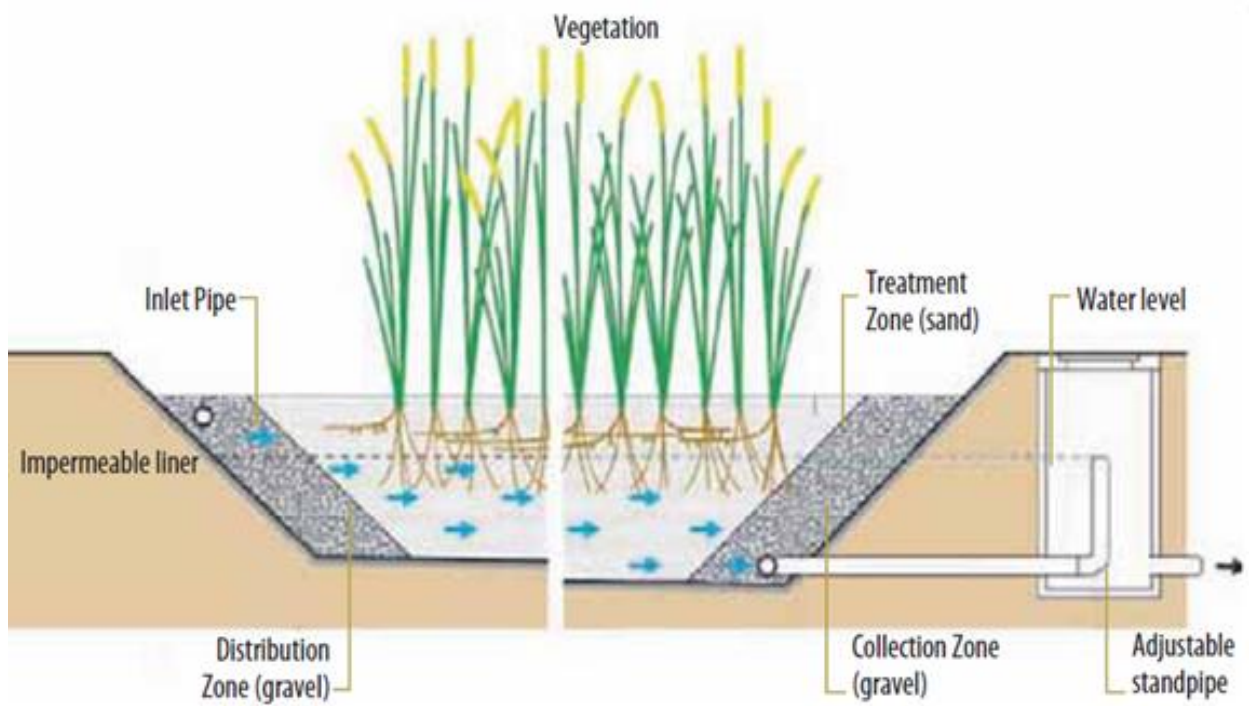


Figure 2.6. Sub surface horizontal flow constructed wetland [51]

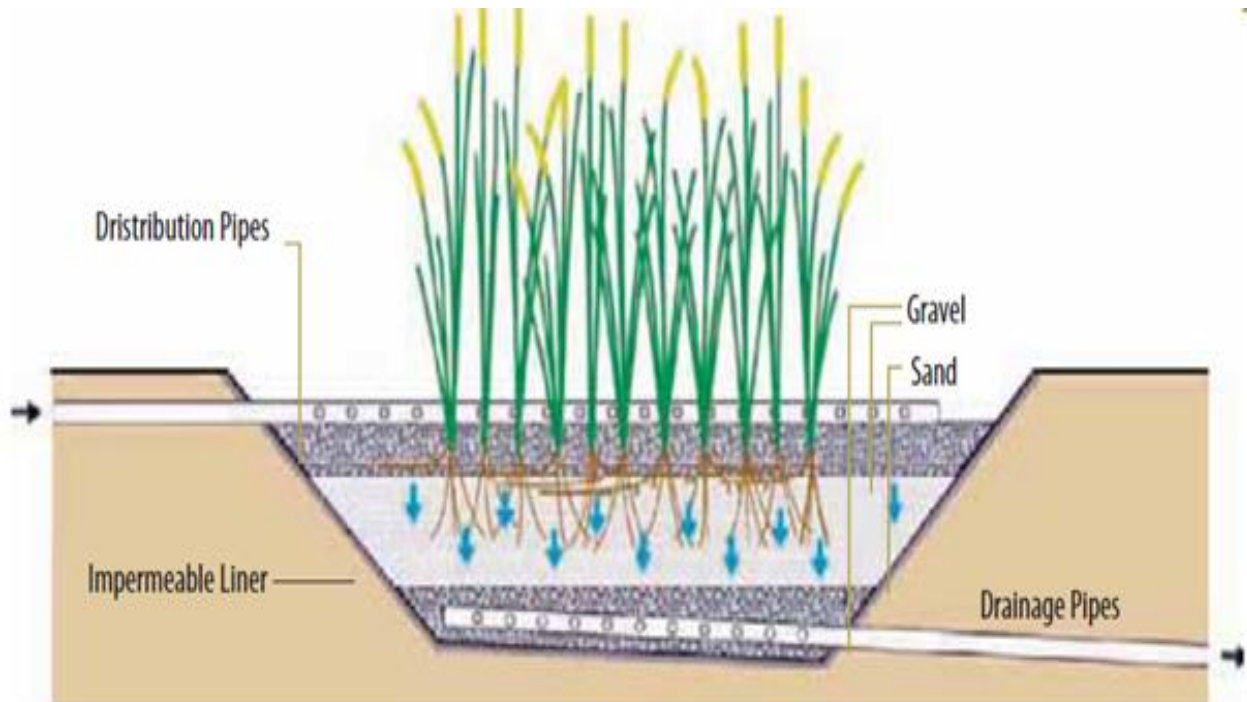


Figure 2.7. Sub surface vertical flow constructed wetland [51]



Figure 2.8. Free water surface type constructed wetland being used for tannery effluent treatment in Modjo Tannery, Ethiopia (actual field visit photo)

#### **2.5.1.4. Emerging Advanced Treatment Technologies**

Emergent advanced treatment technologies such as membrane processes, membrane bioreactors and advanced oxidation processes have so far been attempted in tannery wastewater treatment, though not well practiced at full scale stage as the conventional ones. Microfiltration, ultrafiltration and nanofiltration can be used in tanneries for the removal of chromium (chrome recovery), hair, grease and salt from the wastewater. Chlorides and sulfates can be removed from the wastewater through reverse osmosis, the water being treated this way having the possibility of being reused in the manufacturing process thereby conserving water in the process. Membrane bioreactor technology is found to be advantageous over the classical activated sludge processes in that no secondary clarifier is required thereby avoiding the issue of poor sludge settleability, though the former are associated with problems such as clogging and cake formation on to the membranes. Advanced oxidation processes are also being tried for tannery wastewater treatment by using strong oxidizing agents such as ozone and hydrogen peroxide and/or catalysts (iron, manganese titanium oxide) sometimes with high energy radiation such as UV light to generate and use the very powerful oxidizing agents called hydroxyl radicals that have the ability of oxidizing many organic compounds [50].

## 2.5.2. Design Aspects of BATs of relevance to the Actual Treatment Plant

### 2.5.2.1. Preliminary Treatment

Major design considerations of flow equalizations include the location in the treatment line, flow sheet (in-line/off-line arrangement), required basin volume and control of solid deposition and odor. In-line arrangement is highly preferable to the off-line one in terms of significant influent mass dampening. For in-line arrangement type equalization tanks, continuous flow stirred tank reactor (CSTR) are highly recommended, thereby avoiding elongated designs. Inlet and outlet configurations should minimize short circuiting. Earthen material, concrete or steel may be used for construction. Ground water protection is also important using liners. Proper mixing of the basin constituents is crucial to minimize solid deposition in the basin. The basins are recommended to be preceded by grit chambers to reduce mixing requirements. Proper aeration is also recommended to minimize septic conditions and hence odor. Deposited solid and grease removal, floating materials removal (foam, scum and others) and odor control facilities must also be considered in the design. Flow meter must be used on the outlet to monitor the equalized flow. The volume of the tank may be determined by the subtraction of the design average hourly flow volume (design daily flow volume averaged over 24 hours of the day) from the actual hourly flow volumes and then taking the cumulative positive values (their sum) to be equal to the equalization volume required [30].

Major design considerations of screens include location, influent approach velocity; mesh size, head loss, screen handling/processing/disposal and process control. For most mechanically cleaned coarse screen installations, two or more units should be installed so that one unit may be taken out of service for maintenance. The cleaning (raking) mechanisms of course screens are usually based on differential head loss through the screens or a time clock [30]. Head loss through coarse bar screens can be estimated using the equation [30]:

$$h_L = (1/2gc) (V^2 - U^2) \quad (2.1)$$

Where  $h_L$  = head loss (m);  $U$  = approach velocity in upstream channels (m/s) and

$C$  = discharge coefficient = 0.7 for a clean screen and 0.6 for a clogged screen

$V$  = velocity through the openings (m/s);  $g$  = acceleration due to gravity

On the other hand, head loss through fine screens is estimated using the equation [30]:

$$h_L = (1/2g) (Q/CA)^2 \quad (2.2)$$

Where  $h_L$  = head loss (m);  $g$  = acceleration due to gravity;  $Q$  = discharge through screens ( $m^3/s$ );

$A$  = Effective surface area of submerged screens ( $m^2$ )

$C$  = coefficient of discharge for the screen (typical value for a clean screen = 0.6)

### 2.5.2.2. Primary Treatment

Design criteria for primary sedimentation tanks are surface overflow rate, wall depth, detention time and weir loading rate, with indeed detention time being implicit in depth [30, 35]. Their design criteria (when followed by secondary treatment) are 1.5-2.5h for detention time; 30-70 $m^3/m^2.d$  (when alum or iron floc are used) for average overflow rate and 125-500 $m^3/m.d$  for weir loading rate. Regarding dimension, depth of 3-4.9m, diameter of 3-60m and flight speed of 0.02-0.05 rev/min for circular clarifiers and depth of 3-4.9m, length of 15-90m, width of 3-24m and flight speed of 0.6-1.2m/min for rectangular clarifiers are recommended [30].

In a sedimentation basin, surface overflow rate and detention time can be computed by: [35]

$$V_o = \frac{Q}{A} \quad (2.3)$$

$V_o$  = overflow rate ( $m^3/m^2/day$ );  $Q$  = average daily flow ( $m^3/day$ );  $A$  = tank surface area ( $m^2$ )

Detention time of a tank can then be given by:

$$t = \frac{V}{Q} = \frac{HA}{Q} \quad (2.4)$$

Where  $t$  = detention time;  $V$  = tank volume and  $H$  = depth of wastewater in the tank

Lamella systems are usually inclined parallel metal plates or bundles of hexagonal plastic tubes installed at the surface of the settling tank to a vertical depth of approximately 2 m. Lamella

installation at an angle of 45 to 60 degree (with the horizontal) and spacing of 40 to 120 mm (adequate spacing for the movement of water and sludge is required) results in an increase in the effective settling surface area by a factor of 6 to 12, which then allows higher peak flow to be treated in a given tank surface area [38]. Countercurrent designs (where influent and effluent have the same direction of flow while the settled solids (sludge) slide down in an opposite direction) are most common and preferred as they have less installation and operating costs [56].

Mixing and flocculation play a huge role in wastewater treatment, which usually involves mixing of two substances, blending of miscible liquids, flocculation of particles and heat transfer among others. They are mostly classified as continuous-rapid ( $t < 30$  second) or continuous. Continuous rapid mixing happens in coagulation, blending of miscible liquids and addition of chemicals to sludge and biosolids to improve dewatering characteristics. On the other hand, continuous mixing occurs in equalization basins, flocculation basins, aerated lagoons etc [30].

In the design of mechanical mixers in coagulation tanks, the equation below is applied [30]:

$$G = \sqrt{\frac{P}{\mu V}} \quad (2.5)$$

Where  $G$  = average velocity gradient (1/s);  $P$  = power requirement (Watt);  $V$  = flocculator volume and  $\mu$  = dynamic viscosity (N.S/m<sup>2</sup>). Multiplying both side of equation 2.5 by detention time  $t$ , one can get:

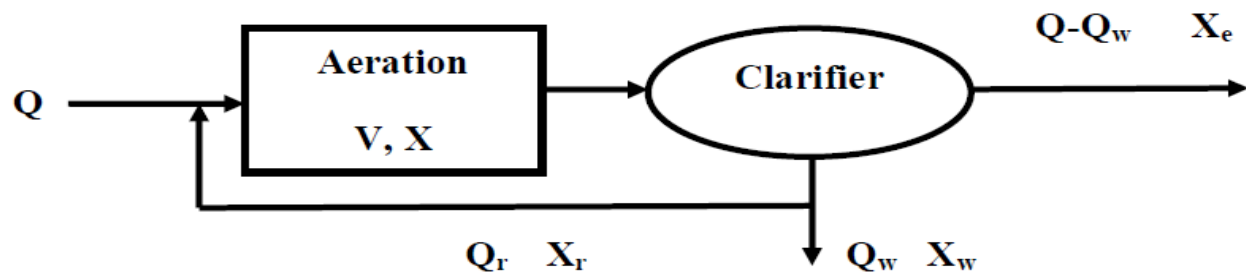
$$Gt = t \sqrt{\frac{P}{\mu V}} \quad (2.6)$$

Typical  $t$  and  $G$  values for rapid mixing operations in wastewater treatment are 5-30s and 500-1500s<sup>-1</sup> whereas the corresponding figures are 30-60min for  $t$  and 50-100s<sup>-1</sup> for  $G$  for flocculation processes [30].

### 2.5.2.3. Secondary (Biological) Treatment

The secondary treatment of concern in this section is activated sludge (AS) treatment as the selected tannery industry for this study consists of this system for secondary treatment. The typical design criteria for AS processes are solids loading rate (SRT) ranges (in days) of 3-15, 20-40 and 15-30 for complete-mix, extended aeration and oxidation ditch respectively. The corresponding figures for F/M (in kg BOD/kg MLVSS.d) are 0.2-0.6, 0.04-0.10 and 0.04-0.10 respectively. Regarding volumetric loading, the corresponding figures (in kg BOD/m<sup>3</sup>.d) are 0.3-1.6, 0.1-0.3 and 0.1-0.3 respectively. The total HRT ranges (in hours) are 3-5, 20-30 and 15-30 for the complete-mix, extended aeration and oxidation ditch respectively, the corresponding MLVSS values (in mg/l) being respectively 1500-4000, 2000-5000 and 3000-5000. Finally, RAS ranges (in % of influent) are 25-100, 50-100 and 75-150 for those activated sludge types respectively. Similarly, the most widely used parameters for the design of secondary clarifiers are surface overflow rate (SOR), sludge loading rate (SLR) and depth while return activated sludge (RAS), MLSS concentration and peak events are also considered in the design. Accordingly, for settlement after extended aeration, the average and peak SOR values are 8-16 and 24-32m<sup>3</sup>/m<sup>2</sup>.d respectively. The recommended SLR is 1-5 and 7kg/m<sup>2</sup>h for the average and peak values respectively. The required depth is 3.5-6m [30].

A typical activated sludge system diagram is shown in Figure 2.9 [36].



$Q$  = influent flow rate;  $Q_r$  = return sludge flow rate;  $Q_e$  = effluent flow rate;  $V$  = aeration tank volume;  $X$  = aeration tank MLSS;  $X_e$  = effluent MLSS;  $X_w$  = wasted sludge MLSS

Figure 2.9. A typical activated sludge system [36]

In relation to an activated sludge plant, the following design equations are usually used: [36]

$$t = \frac{V}{Q} \times 24 \quad (2.7)$$

Where  $t$  = aeration period (hours),  $V$  = aeration tank volume ( $m^3$ ) and  $Q$  = wastewater flow quantity ( $m^3/day$ ) excluding the quantity of recycled sludge.

$$Y_o = \frac{Q}{V} \times S_o \quad (2.8)$$

Where  $Y_o$  = volumetric organic loading ( $gm/m^3$  or  $mg/l$ ) and  $S_o$  =  $BOD_5$  ( $gm/day$ ).  
Food-to-microorganism (F/M) ratio is another important parameter determined by:

$$\frac{F}{M} = \frac{Q}{V} \frac{S_o}{X} \quad (2.9)$$

Where  $X$  = mixed liquor suspended solids (MLSS) in the aeration tank.

Finally, sludge age ( $\theta_c$ ) (the average time that bio-solids spend in the system) is determined by:

$$\theta_c = \frac{VX}{Q_w X_r + (Q - Q_w) X_e} \quad (2.10)$$

In equation 2.10, the numerator represents total solids in the system while the denominator represents the total solids leaving the system. The total solid leaving the system is determined by steady state material balance on the secondary clarifier (Figure 2.2) as shown in equation below.

$$Q_w X_w + (Q - Q_w) X_e = (Q + Q_r) X - Q_r X_r \quad (2.11)$$

Note that  $X_w = X_r$  as recycling is done from the same secondary sludge.

$$\theta_c = \frac{VX}{Q_w X_r} \quad (\text{assuming } X_e = 0) \quad (2.12)$$

## 2.5.3. Treatment Plant Efficiencies and Major Determining Factors

### 2.5.3.1. Treatment Efficiencies-A Review of Previous Studies

Tannery wastewater treatment plant efficiencies are one of the major determinants in the selection of treatment technologies and designs [29-31]. Efficiency studies were conducted in different countries (Table 2.3). Typical efficiencies of individual treatment units up to biological treatment with different technologies and processes were also reported [57] (Table 2.4).

Table 2.3. A summary of tannery wastewater treatment efficiencies (%) of previous studies

Studies	Treatment	BOD <sub>5</sub>	COD	TSS	TDS	Cr	NH <sub>3</sub> -N	P
Shanmugasundaram and Murthy [58]	Preliminary	9.8	12.0	2.5	0.5			
	Primary	35.7	42.1	59.6	2.7			
	Secondary (AS):	89.2	53.1	41.8	1.1			
	Aeration tank:	72.3	48.0	-	0.21			
	Clarifier	61.2	9.9	94.5	0.9			
	Overall	93.8	76.1	77.1	4.3			
Govindasamy et al. [59]	Primary	52.9	65.1	90.7				
	Secondary (AS)	95.2	71.4	62.7	-			
	Tertiary:	12.9	45.9	48.8	-			
	Overall	97.5	93.9	97.0	19.0			
Ezike et al. [60]	Primary	39.6	44.2	32.2	36.4	86.6		
Tadesse et al. [61] A pilot-scale study	Secondary (pond) Advanced FP: Secondary FP: MP: Advanced integrated WSP (Overall)	70-89 34-65 30-40 90-98	86-92				60 20-26 85	75 Erratic
Dejene and Tenalem [62] (Pond system)	Secondary (Industry 1):							
	Chrome OP:	52.5	35	84.3	61.2	65.7**	32.6	59.5*
	Sulfide OP:	64	44.8	93	60.7	-	-	34.8*
	Secondary (Industry 2):	67.7	37	63.3	78.4	50.8**	47.2	56
FP: Facultative Pond; MP: Maturation Pond; OP: oxidation pond; **Cr(III); *Phosphorous as PO <sub>4</sub>								

Table 2.4. Typical efficiencies for tannery wastewater treatment for conventional liquors [57]

Parameter	COD	BOD <sub>5</sub>	SS	Cr	S <sup>2-</sup>	TKN	Sludge
% or mg/l	%	%	%	mg/l	mg/l	%	Kg DS/trh
<b>Pretreatment</b>							
Sulfide oxidation (liming and rinsing liquors)	10				10		
Chromium precipitation				2-10			
<b>Primary treatment</b>							
Mixing + Sedimentation	25-35	25-35	50-70	20-30		25-35	80
Mixing + chemical treatment + sedimentation	50-65	50-65	80-90	2-5	2-10	40-50	150-200
<b>Biological treatment</b>							
Primary or chemical + extended aeration	85-95	90-97	90-98	<1	<1	50	70-150*
Primary or chemical + Aerated facultative ponds	80-90	85-95	85-90	<1	<1	50	100-140
Anaerobic treatment (lagoon or UASB)**	65-75	60-70	50-80	<2	0 (%)	20-30	60-100
Constructed wetlands (after primary treatment)	70-80	85-95					

\*No chemical treatment; \*\* with 75% domestic sewage; salinity unaffected; DS/trh: dry sludge per ton of raw hide

### 2.5.3.2. Major Determining Factors of Treatment Plant Efficiencies

Performance limiting factors of treatment plants are categorized into plant design (e.g. loading rates, flexibility, oxygen transfer), maintenance (e.g. scheduling, recording, skill, equipment availability), administration (e.g. staffing, finance, training) and operation (e.g. process control, sludge removal rate, chemical dose), which need to be optimized for best performance [34].

In relation to design and operation issues, one can mention a number of issues. Accordingly, screening efficiency can decrease due to poor design, poor maintenance, inadequate cleaning and absence of by-pass or reserve unit [2, 30, 34]. Poor hydraulics in tanks and inadequate grit removal and maintenance could affect horizontal flow grit removal systems [34].

Poor primary clarification may result from improper design of inlet/outlet structures (causes flow break-up and scour), inadequate sludge removal, and poor maintenance among others [30, 35]. Inadequate rapid mixing, improper coagulant dosages, and short-circuiting could also reduce clarification efficiency. Accordingly, the primary treatment system can be optimized through

improved hydraulics (e.g. flow splitting), improved process control, adequate scum and sludge removal, and improved/optimum chemical dosing and mixing [30, 34]. Avoiding co-settling of waste activated sludge in primary clarifiers is also recommended for better efficiency [34].

The main problems of activated sludge are bulking sludge (due to poor settling characteristics), rising sludge (due to de-nitrification in secondary clarifier) and nocardia foaming (foam formation) [30, 34]. Sludge bulking is affected by variation in wastewater characteristics (e.g. variations in flow rate, variations in composition, pH, temperature, nutrient), design limitations (e.g. low air supply, poor mixing, short circuiting in the aeration tank and poor secondary clarifier design, sludge collection and removal problems) and operational issues such as insufficient nutrient, low dissolved oxygen, low F/M ratio and insufficient soluble BOD. Measures to control bulking include addition of chlorine (chlorination of return sludge practiced widely) and hydrogen peroxide, though chlorination may result in trihalomethanes and turbid secondary effluents. Rising sludge can be controlled by increased RAS withdrawal rate, decreased entrance of aerated liquor to the secondary clarifier, increased sludge collection from the settling tank and decreased SRT to prevent denitrification. Nocardia foam is due to nocardia and microthrix parvicella which attach themselves to air bubbles to form foam, which is thick, brown color with thickness of up to 1m that can also be controlled by addition of chlorine [30].

Performance limiting factors of secondary clarifiers include uncontrolled flow splitting, rapid flow variations, turbulent influent flow, outlet turbulence, uncontrolled waste activated sludge and return activated sludge. Such issues can be addressed by using multiple weirs for flow splitting, use of variable pump systems for flow variation dampening, inlet baffles for dissipating influent energy, outlet baffles to separate solids from effluent, tube or lamella settlers for enhanced performance, regular measurement and control of waste and return activated sludges, polymer addition for enhanced clarification and rapid sludge withdrawal to prevent blanket wash-out at high flows. Co-settling of WAS in primary treatment must also be avoided [34].

### **3. Materials and Methods**

#### **3.1. Description of the Study Area**

##### **3.1.1. The Selected Industry and Its Manufacturing Processes**

The study was conducted in Sululta (9° 09' 39" N and 38° 45' 03" E) located in the Oromia region of Ethiopia at a distance of around 32km north of Addis Ababa (Figure 3.1). The selected industry for the case study called China Africa Tannery, established in 2003 in Sululta, was selected based on pre-set criteria namely (in order of importance) having well established effluent treatment plant; up to secondary treatment level; operational; and in the vicinity of Addis Ababa. The Ethiopian Leather Industry Development Institute (LIDI) and the Oromia, and Addis Ababa Environmental Protection Authorities (EPAs) were consulted in the selection process.

The industry has around 440 employees most of them local people. It used to process sheep and goat skin (mostly sheep skin) during the first phase (dry season) of wastewater sample collection (end of January to February), with daily soaking capacity of 7000 pieces (9.1 ton) of skin and daily production in the range of 6500-7000 pieces (2.6-2.8 ton) of skin. However, hide skin processing was begun as a trial or pilot scale during the second phase (wet season) of wastewater sample collection (end of June to July) with daily soaking capacity of around 200 hides per day (below 20% of its full capacity). The industry works 7 days a week; 350 days a year. Its final product is finished leather for the sheep/goat skin and crust for the hide skin.

Ground water is the only source of water for the industry with huge daily usage of much more than 600m<sup>3</sup> (though the exact amount is not known as it is not measured) which is said to be the amount treated daily.

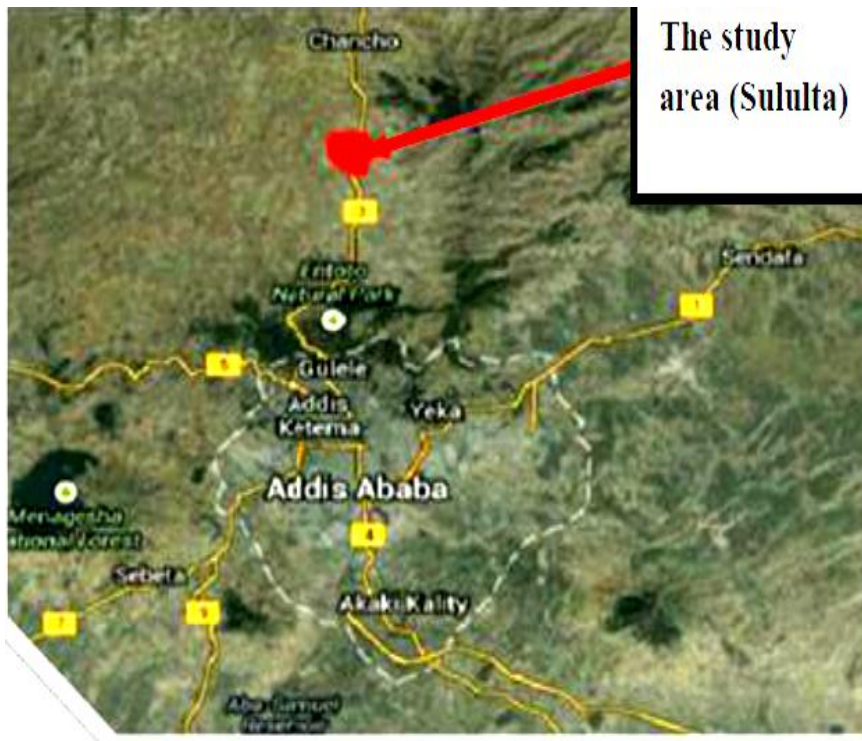


Figure 3.1. Location of the study area (Google Imagery@2014)

In the actual industry, the sheep/goat skins are sorted (by defect and size), trimmed and stored with the sheep/goat skins not further cured while the hides are cured mainly in the industry using sodium chloride. In the beamhouse section for the sheep/goat skin processing, dirt soaking of manually de-dusted skin takes place in drums and pits. As the available drums are not enough, some of the skins by-pass the drum soaking to be soaked in pits (without paddles; it is manually conducted), the soaking efficiency of the drums being better than that of the pits as mechanical operations are involved in the former. Then the skins from the dirt operations are pre-fleshed (green flesh) to facilitate chemical penetration in subsequent processes. Then follows the main soaking of the pre-fleshed skins in drums (the main soaking is fully conducted in drums) using wetting agents, soaking auxiliaries and soda ash (e.g. to remove non structural proteins). For the hide skin, soaking is conducted fully in drums (eight drums available) in two steps namely dirt soaking (conducted in four drums) and main soaking (conducted in the remaining four drums) using water (the main soaking medium) and soaking auxiliaries such as soda ash.

After main soaking, liming-unhairing takes place in two stages for the sheep/goat skins namely paste liming and re-liming. In the first stage (paste liming), unhairing process begins using hair saving approach using sodium sulfide (NaS), sodium bisulfide (NaHS) and lime ( $\text{Ca(OH)}_2$ ) to

loosen hair and flesh for further manual removal. Then after the manual removal of the loosened skins and flesh, the next liming stage (re-liming) takes place using the chemicals used in the first liming stage along with others such as liming auxiliaries and degreasing agents. However, for the hide skins, liming takes place only once (no hair saving) in a single stage using sodium sulfide and liming auxiliaries followed by splitting of the hide into three layers, two of which being used and the rest (the defected one) being sold for glue manufacturers (i.e. lime split is practiced for the hide skin whereas no splitting takes place for the sheep/goat skin). Main fleshing (lime flesh) is then conducted after the liming process for the sheep/goat skins (fleshing takes place after dirt soaking and liming) whereas it takes place only after the dirt soaking operation (before the liming-unhairing process) for the hide skins, which is somehow called green fleshing. Huge water is used in the beamhouse operations due mainly to the partial use of pit soaking for the sheep/goat skins and huge water wastages adding burden on the wastewater treatment plant.

Deliming is then conducted mostly using ammonium sulfate though ammonium chloride is also sometimes used. It is then followed by the bating process using enzymes and degreasing agents to improve the grain characteristics and remove materials such as hairs and non collagenic protein from the skin. After bating, pickling is conducted using chemicals such as sodium chloride, formic acid and sulfuric acid to condition and prepare the pelt for the tanning operation.

The skin then becomes stabilized by the tanning process using basic chromium sulfate solution, sodium formate being also used for masking for chrome fixation. Basification is then conducted using sodium bicarbonate for enhancing chrome fixation on the skin. The wet blue thus produced is treated with anti fungus or mold if it has to be stored. Then, wet blue selection is conducted based on defect assessment in to shoe upper, garment, glove or rejected for the sheep/goat skin. For the hide skin, the wet blue is side-cut into two to facilitate samming and re-tanning. Samming is then followed to dehydrate the skin for the shaving operation to achieve uniform leather thickness. Still huge amount of water is observed to be used in those processes.

The wet processing is finished by post tanning processes of re-chroming and re-tanning using numerous chemicals such as vegetable tannins, synthans, auxiliary re-tanning materials and rasins. This post tanning operation produces crust leather, which is treated then by dry finishing operations to produce finished leather for the sheep/goat skin. Crust is the end product of the hide skin processing as it is done at a pilot scale.

The wet processes were mostly conducted in vessels with huge wastewater use and generation.

There has been public or community reaction in the form of complaints to the pollution of the nearby water bodies and associated human and animal health problems in the area where the industry is located. Although there are also other industries in the locality, the actual industry did also highly suffer from public pressure due to significant pollution of the locality mainly the nearby water body from wastewater and solid waste emanating from the industry, which is said to have caused animal mortality and death as well as serious human health problems. Indeed, it was those pressures from the community that forced the actual industry to install and operate the very costly and highly efficient secondary treatment system called activated sludge system.

### **3.1.2. The Selected Wastewater Treatment Plant**

The actual wastewater treatment plant diagram is shown in Figure 3.2. Accordingly, the chrome precipitation pre-treatment supernatant is mixed with the beamhouse and re-tanning sections effluent to be pretreated with three main manually cleaned screens of mesh size 5-10mm (blue outer border) before stored in three rectangular tanks (2\*) of volume  $108\text{m}^3$  each, also used as pre-sedimentation tanks. The wastewater then goes to a two-compartment in-line equalization tank of volume  $180\text{m}^3$  for organic and hydraulic loading homogenization (3\*), the second compartment (3\*\*) also serving as coagulation basin and sulfide removal by precipitation. Clarification takes place in a circular clarification tank (4) of volume =  $152.4\text{m}^3$  followed by activated sludge treatment (5: aeration tank of volume =  $700\text{m}^3$ ; 6: secondary clarifier of volume =  $181\text{m}^3$ ). The primary and secondary sludge is handled by a sludge drying bed (SBD) of plane area size  $200\text{m}^2$  with four compartments of  $50\text{m}^2$  (Appendix 1 shows technical details).



## 3.2. Wastewater Sample Collection and Laboratory Analysis

### 3.2.1. Sampling and Experimental Design

The sampling and experimental design is shown in Table 3.1. Wastewater samples were taken in end-of-January to February (dry season) and end-of-June to July (wet season) in morning hours (10-12 A.M) over a maximum of five days at five selected sites (S1: at the raw influent; S2: before primary treatment; S3: after primary treatment; S4: after the AS aeration tank and S5: after the secondary clarifier) in the treatment system for laboratory analysis of BOD<sub>5</sub>, TSS, TDS, NH<sub>3</sub>-N, pH and temperature in both seasons while COD, chromium, sulfide and R-PO<sub>4</sub> for the dry season and total phosphorous for the wet season were also analyzed apart from onsite measurements of DO (in the AS reactor) and temperature in both seasons. Some of these parameters (particularly BOD, COD, TDS and SS) were also used as tannery effluent treatment plant performance indicators in other studies [58, 59, 60, 62].

Table 3.1. Sampling and experimental design used in the present research

Sampling days	Day 1 (D1)	Day 2 (D2)	Day 3 (D3)	Day 4 (D4)	Day 5 (D5)
Sampling sites	<b>End of January to February (dry season)</b>				
Site 1 (S1)	D1S1	D2S1	D3S1	D4S1	D5S1
Site 2 (S2)	D1S2	D2S2	D3S2	D4S2	D5S2
Site 3 (S3)	D1S3	D2S3	D3S3	D4S3	D5S3
Site 4 (S4)	D1S4	D2S4	D3S4	D4S4	D5S4
Site 5 (S5)	D1S5	D2S5	D3S5	D4S5	D5S5
	<b>End of June to July (wet season)</b>				
Sampling sites	Day 1 (D1)	Day 2 (D2)	Day 3 (D3)	Day 4 (D4)	
Site 1 (S1)	D1S1	D2S1	D3S1	D4S1	
Site 2 (S2)	D1S2	D2S2	D3S2	D4S2	
Site 3 (S3)	D1S3	D2S3	D3S3	D4S3	
Site 4 (S4)	D1S4	D2S4	D3S4	D4S4	
Site 5 (S5)	D1S5	D2S5	D3S5	D4S5	

### 3.2.2. Methods and Materials for Sample Collection and Analysis

The wastewater sample analysis methods, instruments and materials are shown in Table 3.2. Wastewater samples were collected in plastic bottles cleaned with hydrochloric acid solution followed by repeated washing by distilled water. They were taken at the well mixed (turbulent) section of the wastewater. After sampling, they were preserved at appropriate temperature (around 4°C) using ice till laboratory analysis, which was conducted as quickly as possible. The samples were analyzed in the environmental laboratory of AAEPa with standard methods for the examination of water and waste water [63].

Table 3.2. Methods, instruments, materials and reagents used in the study

Parameter	Method	Instrument	Other major materials/reagents
<b>pH</b>	Electro-analytical	pH meter	-Plastic bottles (for sample collection) -Distilled water (cleaning; blank) -Tissue paper (cleaning) -Thermometer (temperature adjustment) -Weak acids/ bases (neutralization) -Potassium dichromate (for COD analysis) -pH buffer tablets (for pH meter calibration) -Sodiumhydroxide (nitrification inhibitor) -Ammonia salicylate and ammonia cyanurate (for NH <sub>3</sub> -N analysis) -Cooling rack (for cooling samples) -Blenders (for sample homogenization) -Magnetic stirrer (for sample mixing)
<b>Temp.</b>	Onsite measurement	Thermometer	
<b>DO</b>	Onsite measurement	DO meter	
<b>TDS</b>	Electro-analytical	Conductivity meter	
<b>BOD<sub>5</sub></b>	Gravimetric	Thermostatic cabinet	
<b>TSS</b>	Photometric	Spectrophotometer	
<b>COD</b>	Reactor digestion	Spectrophotometer	
<b>NH<sub>3</sub>-N</b>	Salicylate	Spectrophotometer	
<b>Sulfide</b>	Methylene blue	Spectrophotometer	
<b>R-PO<sub>4</sub></b>	Molybdovanadate	Spectrophotometer	
<b>TP</b>	Digestion	Spectrophotometer	
<b>Chromium</b>	Flame	AA spectrophotometer	

### **3.3. Data Collection Using Checklist/Questionnaire**

Factors of relevance to treatment efficiency namely plant design, administrative, maintenance and operational issues [34] as well as the practice of cleaner production in the manufacturing process [1, 21] were assessed. The assessment was made by checklists/questionnaires (see Appendices 9-11) developed based on [1, 2, 20, 22, 30, 34]. Accordingly, physical inspection, factory document analysis (e.g. the design document of the industry which is summarized in Appendix 1) and interview of the plant operators and industry management staff were conducted. The design data of the treatment plant were obtained from the design document and it was checked whether the actual design corresponds to what is stated in the design document in an attempt to look for any design flaw in the system. Similarly, operational aspects (e.g. whether operation is according to design, process control, sludge/scum removal rate, coagulation chemical types and dose), administration issues (e.g. treatment system staffing, treatment system financing and operator training), maintenance issues (e.g. treatment system maintenance scheduling, recording, operator skill and equipment availability) as well as cleaner production practices (e.g. water conservation, chemical reduction and good housekeeping) were assessed.

### **3.4. Data Quality**

Appropriate procedures were followed to ensure the quality of the collected data. For example, wastewater sample collection and analysis was conducted as in the following (among others):

- Standard analysis method used [63]
- Samples taken in a well cleaned plastic bottles
- Samples taken at well-mixed (turbulent), homogenized sections for representativeness
- Samples preserved at 4 °C after sampling and transportation to the laboratory
- Calibration was well conducted during analysis as per required
- Samples analyzed as quickly as possible upon reaching the laboratory
- Analysis conducted more than once when odd results obtained

### **3.5. Treatment Efficiency Determination**

The treatment efficiency of individual unit operations and the whole treatment plant was determined using the following equation:

$$\eta (\%) = \frac{(I-E)}{I} \times 100 \quad (3.1)$$

Where  $\eta$  = efficiency; I = Influent concentration and E =Effluent concentration

### 3.6. Secondary Treatment Technology Evaluation and Selection

Multi-criteria analysis technique (MCA) was used to evaluate the secondary treatment technology of the actual industry along with other technologies used in tanning industries. The process involved aim setting, key stakeholder identification, option identification, criteria/sub-criteria setting, criteria weighting, scoring per criteria and score aggregation to develop performance matrix. MCA was also used in other engineering studies for decision making [22, 32]. Criteria setting and weighting in the MCA process was also based on literature review (e.g. [32]) in addition to consensus (through discussions/consultations) reached by relevant stakeholders namely the Addis Ababa Environmental Protection Authority (AAEPA), the environmental unit of the national Leather Industry Development Institute (LIDI) and some tannery industries. Scoring was based on comprehensive literature review. Finally, weighted linear average (the commonly used linear additive model) approach given below was used for aggregation of scores to generate performance matrix [64]:

$$U(O_i) = \sum_{k=1}^M Z_k(O_i) \times W(C_k) \quad (3.2)$$

Where U (O<sub>i</sub>) is the aggregate score of option O<sub>i</sub>, Z<sub>k</sub>(O<sub>i</sub>) is the normalized score of option O<sub>i</sub> on criterion C<sub>k</sub> and w(C<sub>k</sub>) is the normalized weighting of criterion C<sub>k</sub> and k = 1...M are the criteria.

### 3.7. Treatment Plant Design Evaluation

Design evaluation of the actual treatment system was conducted based on comparison with published works [2, 30] apart from sizing calculation based on the already adopted values for design parameters such as average daily flow rate (Q), surface overflow rate (SOR), detention time, weir loading rate, AS aeration period, F/M, SRT, SLR and MLSS.

### 3.8. Statistical Data Analysis

The wastewater data were analyzed using Design Expert Software Version 7.0.0 for ANOVA and LSD tests to check the significance of day-to-day pollutant concentration and treatment efficiency variations. MS-Excel 2007 was also used for T-tests and other statistical analysis.

## 4. Results and Discussion

### 4.1. Actual Wastewater Pollutant Concentrations and Treatment Efficiencies

#### 4.1.1. Wastewater Pollutant Concentration

Wastewater pollutant concentrations (averages and standard deviations) at different stages from entrance to exit of the treatment plant for the two seasons are shown in Table 4.1 and Table 4.2.

Table 4.1. Laboratory analysis results of wastewater samples for the dry season (units are mg/l for all except for pH and temperature)

Parameter	Statistics	S1	S2	S3	S4	S5
	<i>No of samples</i>	5	5	5	5	5
<b>BOD<sub>5</sub></b>	<i>Average ± STD</i>	353.3 ± 139.8	742.1 ± 237.2	356.0 ± 169.4	600.0 ± 201.5	136.8 ± 23.2
<b>COD</b>	<i>Average ± STD</i>	1761.1 ± 944.8	3366.7 ± 1051.6	1575.5 ± 619.0	3160.0 ± 1285.7	337.6 ± 69.6
<b>TDS</b>	<i>Average ± STD</i>	1590.1 ± 507.5	3277.5 ± 488.5	3182.0 ± 414.1	3278.0 ± 175.7	2960.0 ± 222.6
<b>pH (unitless)</b>	<i>Average ± STD</i>	11.2 ± 0.8	7.8 ± 0.7	6.9 ± 0.5	7.8 ± 0.4	7.8 ± 0.2
<b>NH<sub>3</sub>-N</b>	<i>Average ± STD</i>	33.8 ± 22.5	69.7 ± 15.9	65.6 ± 23.3	82.1 ± 20.2	79.4 ± 25.7
<b>TSS</b>	<i>No of samples</i>	4	5	4	4	5
	<i>Average ± STD</i>	1039.5 ± 437.8	5789.4 ± 2365.6	1014.0 ± 564.6	5249.9 ± 1602.8	89.5 ± 9.1
<b>Sulfide</b>	<i>No of samples</i>	4	5	5	4	4
	<i>Average ± STD</i>	92.1 ± 53.7	82.9 ± 56.9	14.6 ± 8.5	4.9 ± 4.1	0.3 ± 0.3
<b>R-PO<sub>4</sub></b>	<i>No of samples</i>	4	4	4	4	4
	<i>Average ± STD</i>	62.7 ± 31.3	170.8 ± 61.8	40.3 ± 14.4	188.9 ± 115.6	11.5 ± 4.2
<b>Chromium*</b>	<i>No of samples</i>	5	5	5	5	4
	<i>Average ± STD</i>	14.6 ± 14.0	27.7 ± 25.9	1.0 ± 0.6	30.6 ± 29.3	0.6 ± 1.3
<b>Temp. (°C)</b>	<i>No of samples</i>	3	4	3	4	3
	<i>Average ± STD</i>	20.3 ± 1.9	18.4 ± 0.8	19.2 ± 1.1	18.0 ± 0.6	18.0 ± 1.2

DO in AS aeration tank (mg/l) = day two: 1.93-2.01; day three: 0.9-1.03; day four: 4-4.10 and day five: 0.86-0.98  
 \*Chromium: the freely available chromium, not the total chromium in the wastewater

Table 4.2. Laboratory analysis results of wastewater samples for the wet season (units are mg/l for all except for pH and temperature)

Parameter	Statistics	S1	S2	S3	S4	S5
	<i>No of samples</i>		4	4	4	4
<b>TDS</b>	<i>Average ± STD</i>	1963.5 ±983.6	4207.5 ±480.1	4087.5 ±180.8	3927.5 ±589.0	3950.0 ±686.3
<b>pH</b>	<i>Average ± STD</i>	9.6 ±1.2	5.8 ±0.8	6.2 ±1.0	7.5 ±0.2	7.8±0.1
<b>NH<sub>3</sub>-N</b>	<i>Average ± STD</i>	61.4 ±45.3	204.1 ±23.0	184.0 ±36.0	175.5 ±20.1	161.0 ±16.3
<b>TSS</b>	<i>Average ± STD</i>	1073.8 ±735.2	6178.3 ±2079.1	637.8 ±427.6	7096.9 ±898.9	132.0 ±19.7
<b>TP</b>	<i>Average ± STD</i>	6.6 ±3.7	7.0 ±0.9	2.9 ±1.1	16.4 ±4.6	4.4 ±2.4
<b>Temp. (°c)</b>	<i>Average ± STD</i>	20.7 ±0.8	18.2 ±0.6	18.7 ±0.5	18.0 ±0.8	18.5 ±0.9
<b>BOD<sub>5</sub></b>	<i>No of samples</i>	3	3	3	3	3
	<i>Average ± STD</i>	289.3 ±139.6	178.7 ±92.5	89.3 ±80.1	568.0 ±115.4	149.3 ±13.3
DO in AS aeration tank (mg/l) = day one: 2.9-3.15; day two: 2.8-3.8; day three: 1.3-3.9 and day four: 3.3-4.7						

For the dry season, there was statistically significant (ANOVA test,  $p < 0.05$ ) day-to-day variation of pollutant concentrations for the parameters of chromium, SS and NH<sub>3</sub>-N. The day-to-day variation of pH readings was statistically insignificant ( $p > 0.05$ ) while that of temperature was statistically significant ( $p < 0.05$ ). For the wet season, however, no statistically significant day-to-day variation of pollutant concentration was observed for the then analyzed parameters of BOD<sub>5</sub>, NH<sub>3</sub>-N, TDS, TSS, total phosphorous and pH while that of temperature was statistically significant ( $p < 0.05$ ) like in the dry season (the summary of the design expert software version 7.0.0 ANOVA and LSD results is shown in Appendix 2). Indeed, the significance of the variation may also be inferred from the calculated standard deviation values for those parameters (Table 4.1 and Table 4.2). Some of the factors causing those day-to-day pollutant concentration variations could be poor housekeeping in the treatment plant area (causing re-entrance); operational inconsistencies (of production and wastewater treatment); irregular screen cleaning; irregular settled sludge removal rate; inadequate treatment process control and occasional failure of treatment units. Other factors could be power interruption; discontinuous operation of energy-intensive units (e.g. the activated sludge system); variation in daily production capacity and side-stream return (e.g. settled sludge) to equalization tank and sometimes to primary clarifiers.

### 4.1.2. Treatment Plant Removal Efficiencies

The pollutant removal efficiencies of the individual treatment units (PRT: primary treatment; SCT: secondary treatment; PRSCT: primary plus secondary treatment) and the overall treatment plant (comparison between inlet and outlet points of the whole treatment plant) of the actual wastewater treatment system were determined using equation 3.1 in terms of major parameters (Table 4.3 and Table 4.4).

Table 4.3. Actual treatment plant pollutant removal efficiencies (%) (wet season)

Parameter	Day	Day1	Day2	Day3	Day4	Average daily $\pm$ STD
	Operation					
BOD <sub>5</sub>	PRT	87.7	16.7	23.7	-	42.7 $\pm$ 39.1
	SCT	-378.6	-160.0	12.2	-	-175.4 $\pm$ 195.9
	PRSCT	41.2	-116.7	33.1	-	-14.1 $\pm$ 88.9
	Overall	69.3	43.1	0.0	-	37.4 $\pm$ 35.0
TSS	PRT	96.8	90.4	93.8	67.1	87.0 $\pm$ 13.5
	SCT	40.3	75.1	72.5	90.5	69.6 $\pm$ 21.1
	PRSCT	98.1	97.6	98.3	96.9	97.7 $\pm$ 0.6
	Overall	91.9	69.1	67.0	94.1	80.5 $\pm$ 14.4
Total phosphorous	PRT	76.0	59.4	65.4	30.7	57.9 $\pm$ 19.4
	SCT	-44.4	-46.2	-22.2	-80.9	-48.4 $\pm$ 24.2
	PRSCT	65.3	40.6	57.7	-25.3	34.6 $\pm$ 41.3
	Overall	54.8	19.1	4.3	34.9	28.3 $\pm$ 21.6
TDS	PRT	12.7	2.5	5.6	-12.9	2.0 $\pm$ 10.8
	SCT	0.3	-14.9	17.4	11.4	3.5 $\pm$ 14.2
	PRSCT	12.9	-12.0	22.1	0.0	5.7 $\pm$ 14.9
	Overall	-59.3	-254.7	-274.5	-13.3	-150.4 $\pm$ 133.4
NH <sub>3</sub> -N	PRT	29.0	-23.0	10.3	18.9	8.8 $\pm$ 22.5
	SCT	-19.7	20.9	14.3	24.7	10.0 $\pm$ 20.3
	PRSCT	15.0	2.7	23.1	38.9	19.9 $\pm$ 15.2
	Overall	-475.1	-56.5	-700.0	-75.8	-326.9 $\pm$ 314.8

Negative values: pollutants are increased (enhanced) rather than reduced

Table 4.4. Actual treatment plant pollutant removal efficiencies (%) (dry season)

Parameter	Day	Day1	Day2	Day3	Day4	Day5	Average daily $\pm$ STD
	Operation						
BOD <sub>5</sub>	PRT	50.0	40.0	48.1	65.5	62.7	53.3 $\pm$ 10.6
	SCT	53.3	71.1	69.6	55.4	32.0	56.3 $\pm$ 15.8
	PRSCT	76.7	82.7	84.2	84.6	74.6	80.6 $\pm$ 4.6
	Overall	46.7	39.1	48.8	79.3	67.6	56.3 $\pm$ 16.6
COD	PRT	51.0	36.7	60.2	59.2	58.6	53.1 $\pm$ 9.9
	SCT	72.9	83.3	78.8	76.8	74.8	77.3 $\pm$ 4.0
	PRSCT	86.7	89.4	91.5	90.5	89.6	89.5 $\pm$ 1.8
	Overall	74.2	46.9	78.0	85.4	89.8	74.9 $\pm$ 16.8
TSS	PRT	-	79.2	85.3	76.9	96.6	84.5 $\pm$ 8.8
	SCT	-	91.1	91.4	94.6	64.1	85.3 $\pm$ 14.2
	PRSCT	-	98.2	98.7	98.8	98.8	98.6 $\pm$ 0.3
	Overall	-	82.9	87.0	93.8	94.3	89.5 $\pm$ 5.5
Sulfide (S <sup>2-</sup> )	PRT	-	55.1	84.3	81.2	96.9	79.4 $\pm$ 17.5
	SCT	-	98.9	99.7	98.8	75.0	93.1 $\pm$ 12.1
	PRSCT	-	99.5	99.9	99.8	99.2	99.6 $\pm$ 0.3
	Overall	-	99.6	99.8	99.8	99.4	99.7 $\pm$ 0.2
R-PO <sub>4</sub>	PRT	-	73.0	57.6	77.3	87.1	73.8 $\pm$ 12.3
	SCT	-	83.0	70.3	56.3	70.4	70.0 $\pm$ 10.9
	PRSCT	-	95.4	87.4	90.1	96.2	92.3 $\pm$ 4.2
	Overall		39.3	86.1	75.9	91.1	73.1 $\pm$ 23.4
TDS	PRT	-11.7	12.3	2.5	11.6	-3.3	2.3 $\pm$ 10.2
	SCT	8.2	-4.8	19.9	-1.8	9.3	6.2 $\pm$ 9.8
	PRSCT	-2.6	8.1	22.0	10.0	6.3	8.8 $\pm$ 8.8
	Overall	-81.5	-48.2	-260.1	-90.4	-51.9	-106.4 $\pm$ 87.8
NH <sub>3</sub> -N	PRT	41.4	-10.7	-22.2	-6.9	23.1	4.9 $\pm$ 26.4
	SCT	-89.4	-20.4	22.7	5.9	-57.6	-27.8 $\pm$ 45.9
	PRSCT	-11.0	-33.3	5.6	-0.6	-21.2	-12.1 $\pm$ 15.6
	Overall	-108.0	-2698.3	-142.9	-45.5	-46.6	-608.3 $\pm$ 1169.1
Chromium*	PRT	96.8	100.0	-51.5	96.9	97.9	68.0 $\pm$ 66.8
	SCT	100.0	0.0	16.8	100.0	-104.0	22.6 $\pm$ 84.5
	PRSCT	100.0	100.0	-26.0	100.0	95.6	73.9 $\pm$ 55.9
	Overall	100.0	0.0	-	100.0	87.5	71.9 $\pm$ 48.3

Negative values: pollutants are increased (enhanced) rather than reduced  
 \*Chromium: the freely available chromium, not the total chromium in the wastewater

The dry season primary treatment pollutant removal efficiency ranges and (average daily values) of the primary treatment unit were found to be 40-65.5% (53.3%) for BOD<sub>5</sub>, 36.7-60.2% (53.1%) for COD, 76.9-96.6% (84.5%) for TSS, 55.1-96.9% (79.4%) for sulfide and 57.6-87.1% (73.8%) for R-PO<sub>4</sub>. The 5-day average TDS, NH<sub>3</sub>-N and chromium removal efficiencies of the primary treatment unit were 2.3%, 4.9% and 68% respectively, the efficiency of the individual days being erratic with some days associated with negative values (amount of pollutants increased) and others with positive values (pollutant amount reduced) especially for TDS and NH<sub>3</sub>-N. For the wet season, the corresponding values were 16.7-87.7% for BOD<sub>5</sub> (42.7%) and 67.1-96.8% (87%) for TSS, the mean daily values being 2% for TDS and 8.8% for NH<sub>3</sub>-N.

For the secondary treatment, removal efficiencies in the dry season ranged from 32-71.1% for BOD<sub>5</sub> (average: 56.3%), 72.9-83.3% for COD (average: 77.3%), 64.1-94.6% for TSS (average: 85.3), 75-99.7% for sulfide (average: 93.1%) and 56.3-83% for R-PO<sub>4</sub> (average: 70%). The 5-day average TDS, NH<sub>3</sub>-N and chromium removal efficiencies were 6.2%, -27.8% (increased amount) and 22.6% respectively. Erratic daily efficiencies were found especially for TDS and NH<sub>3</sub>-N, some days being associated with an increase (negative efficiencies) while others associated with a decrease (positive efficiencies) of pollutants upon leaving the treatment unit. On the other hand, removal efficiencies of -378.6-12.2% (average: -175.4%) for BOD<sub>5</sub> and 40.3-90.5% (average: 69.6%) for TSS were found for the wet season while average daily removal efficiencies of 3.5% and 10% were found for TDS and NH<sub>3</sub>-N respectively.

The efficiency analysis of the combined primary-secondary system resulted in dry season removal efficiencies of 74.6-84.6% for BOD<sub>5</sub> (average: 80.6%), 86.7-91.5% for COD (average: 89.5), 98.2-98.8% for TSS (average 98.6%), 99.2-99.9% for sulfide (average: 99.6%) and 87.4-96.2% for R-PO<sub>4</sub> (average: 92.3%). The TDS, NH<sub>3</sub>-N and chromium average (5-days) removal efficiencies of the system were found to be 8.8%, -12.1% (amount of pollutant increased) and 73.9% respectively. The daily TDS removal efficiencies, in this case, ranged from 6.3-22% for the four individual days whereas it was negative (-2.6% showing an increase in the amount of TDS) only for one day. Similarly, for chromium, the daily removal efficiencies ranged from 95.6-100% for the four individual days while it was -26% only for one day showing an increase upon leaving the treatment system. The NH<sub>3</sub>-N daily efficiencies were erratic. The wet season efficiencies were -116.7-41.2% (average: -14.1%) for BOD<sub>5</sub> and 96.9-98.3% (average: 97.7%) for TSS. The removal efficiencies of TDS and NH<sub>3</sub>-N were found to be 5.7% and 19.9% respectively.

The dry season overall removal efficiencies of the treatment plant (i.e. comparison between inlet and outlet- points of the overall treatment system) were 39.1-79.3% for BOD (average: 56.3), 46.9-89.8% for COD (average 74.9%), 82.9-94.3% for TSS (average: 89.5), 99.4-99.8% for sulfide (average 99.7) and 39.3-91.1% for R-PO<sub>4</sub> (average 73.1%). The corresponding wet season values were 0-69.3% (average: 37.4%) for BOD<sub>5</sub> and 67.0-94.1% (average: 80.5%) for TSS. The 5-day average dry season removal efficiencies of TDS and NH<sub>3</sub>-N for the whole treatment system were -106.8% and -608.3% respectively, the corresponding values for the wet season being -150.4% for TDS and -326.9% for NH<sub>3</sub>-N. The TDS and NH<sub>3</sub>-N removal efficiencies in this case were negative for both seasons for all the sampling days (i.e. TDS and NH<sub>3</sub>-N significantly increased) showing that the overall effect of the whole treatment plant was to highly enhance those pollutants rather than reduce them.

Total phosphorous in the wastewater was also determined for the wet season. Accordingly, average daily pollutant removal efficiencies of 57.9%, -48.4%, 34.6% and 28.3% were found for the primary, secondary, combined primary-secondary and overall treatment plant respectively.

One major reason for the significant enhancement and erratic removal efficiencies of TDS and NH<sub>3</sub>-N by the overall treatment plant is the fact that the reduction of those pollutants was not considered in the design and operation of the treatment plant, the main objective being to reduce BOD<sub>5</sub>, COD, TSS, sulfide and chromium. The assessment of the treatment system removal efficiencies of TDS and NH<sub>3</sub>-N was conducted in this paper (though the system was not designed for that purpose) to check how the already existing system is responding to those parameters thereby generating useful data based on which to recommend future actions in this regard. The enhancement of chromium in some minor cases may be explained by the re-entrance of chrome sludge damped in the area, among others.

The amount of pollutants as they just leave the equalization tank and the aeration basin of the AS system were also analyzed (Appendix 3). Accordingly, the equalization tank had the effect of considerably raising the amount of pollutants in both seasons to go to the subsequent treatment processes. This could mainly be due to the simultaneous use of the second compartment of the equalization tank for homogenization, sulfide oxidation and chemical coagulation. This huge pollutant enhancement by the equalization tank may explain the significant difference between overall treatment efficiencies and the efficiencies of the combined primary-secondary system, the overall treatment efficiency being in most cases lower than the primary-secondary combined

treatment efficiency. The aeration process of the AS system also resulted in a significant increase in the amount of pollutants, mainly BOD<sub>5</sub>, COD, TSS and R-PO<sub>4</sub>, which could be explained by the very old sludge age with probably a great deal of dead microorganisms present in the aeration tank, among others.

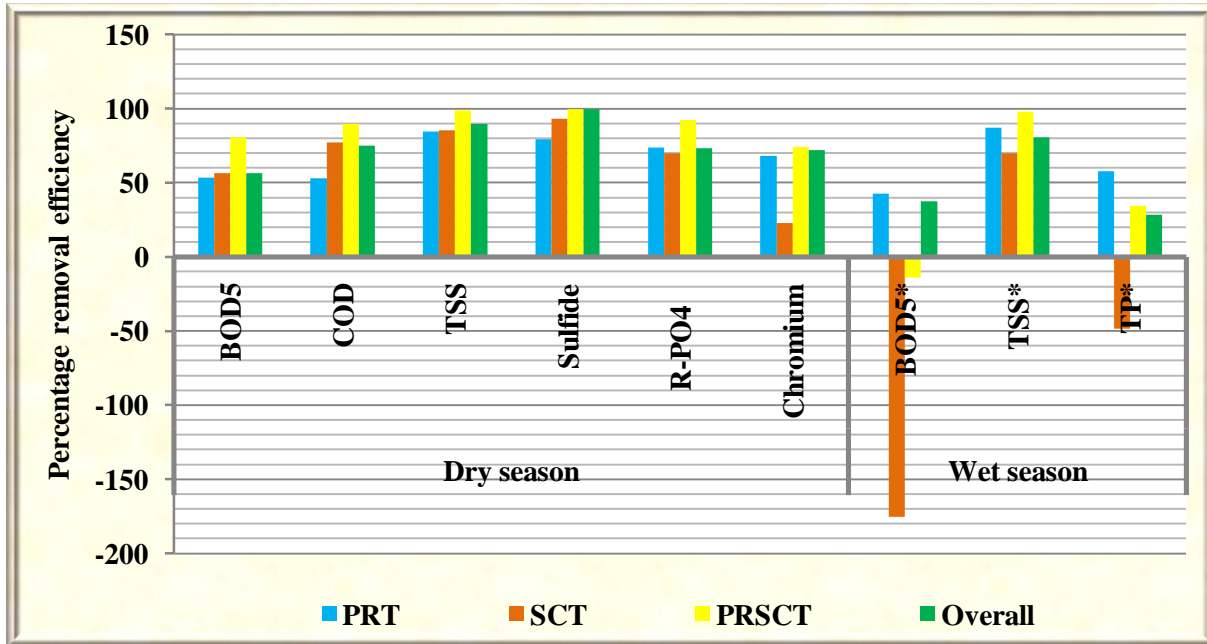


Figure 4.1. Actual mean treatment efficiencies of major parameters

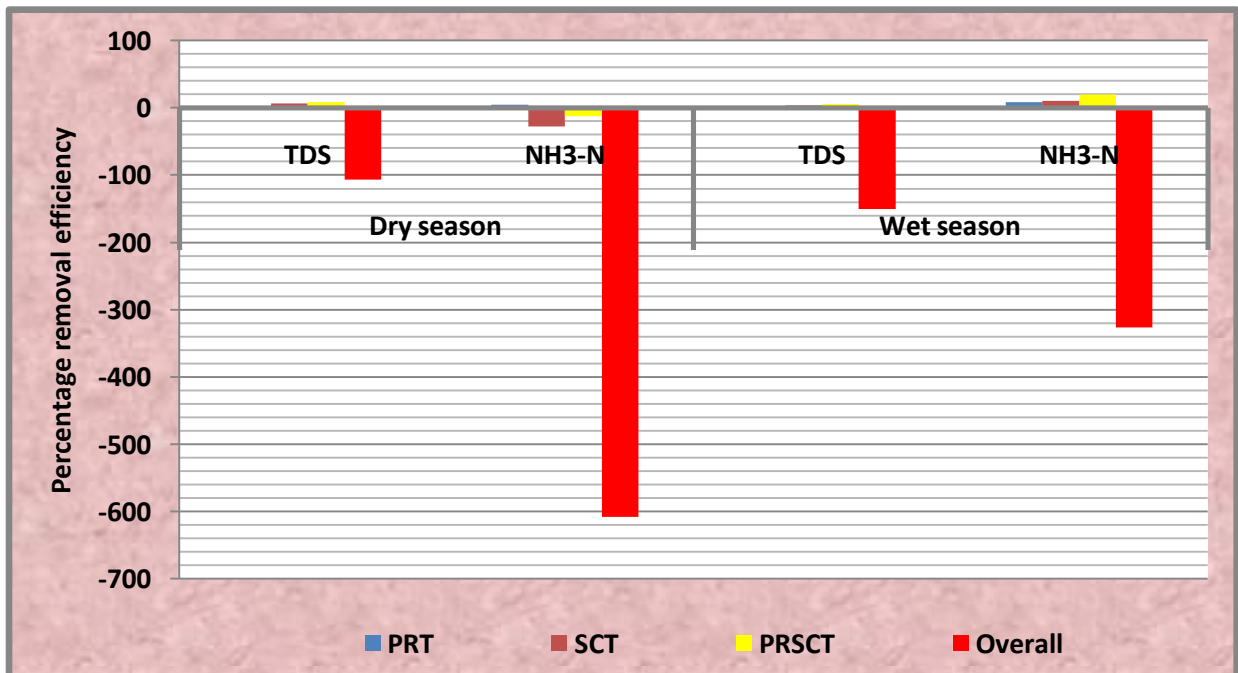


Figure 4.2. Actual mean treatment efficiencies of parameters with erratic values

The comparison of different treatment processes based on their pollutant removal efficiencies is well shown in Figures 4.1 and 4.2 above. Accordingly, for the dry season, the combined primary-secondary system had the highest removal efficiency for most parameters such as BOD<sub>5</sub>, COD, TSS and R-PO<sub>4</sub>. Similarly, the secondary treatment alone had higher removal efficiencies than the primary treatment alone for parameters such as BOD<sub>5</sub>, COD, TSS and sulfide (Figure 4.1). For the wet season, however, the combined primary-secondary treatment gave greater efficiency than the overall treatment for total phosphorous and suspended solids whereas it gave much lesser efficiency than the overall treatment for BOD<sub>5</sub>. The primary treatment alone in this case gave much better removal efficiencies than the secondary treatment alone for BOD<sub>5</sub>, TSS and total phosphorous. On the other hand, the fact that pollutants of TDS and NH<sub>3</sub>-N were highly enhanced by the overall treatment plant in both seasons is well depicted in Figure 4.2.

An attempt was also made to compare the pollutant removal efficiencies of the primary and secondary clarifiers/sedimentation tanks alone (based on comparing influent and effluent of the two tanks). Accordingly, the secondary clarifier alone seemed to be more efficient than the primary clarifier alone for most of the compared parameters such as BOD<sub>5</sub>, COD, TSS, sulfide, R-PO<sub>4</sub> and total phosphorous, which could be explained by several factors such as the difference in the design of the two clarifiers and the influent wastewater characteristics to the two tanks (e.g. chemically coagulated floc is settled in the primary clarifier whereas bio-floc is settled in the secondary clarifier).

The enhanced primary clarification (chemical precipitation) in the actual treatment plant was carried out by the addition of alum (mostly used), ferrous sulfate and calcium hydroxide. Alum (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.18H<sub>2</sub>O) was mostly used for coagulation, being replaced by ferrous sulfate (FeSO<sub>4</sub>.7H<sub>2</sub>O) and lime (Ca (OH)<sub>2</sub>) usually together (sometimes they are used alone if one is missing) only if alum is not available. The lime was also used to manipulate the pH of the wastewater to somehow optimize coagulation efficiency. The main purpose of using the ferrous sulfate in the actual industry is for sulfide precipitation as iron sulfide apart from coagulation. The variation of chemicals used in the enhanced primary clarification along with improper dosing and inadequate process monitoring and control might have contributed to the day-to-day treatment efficiency variations of the enhanced primary treatment as well as other subsequent processes of the treatment plant.

## 4.2. Seasonal and Daily Treatment Efficiency Variations

### 4.2.1. Seasonal Efficiency Variations

The seasonal variation of pollutant removal efficiencies was also assessed (Figure 4.3). End-of-June to July was considered wet season while end-of-January to February was considered dry season. The year 2014 monthly rainfall data for Sululta were 0.0mm for January; 25.2mm for February; 60.4mm for June and 252.1mm for July (National Meteorological Agency of Ethiopia).

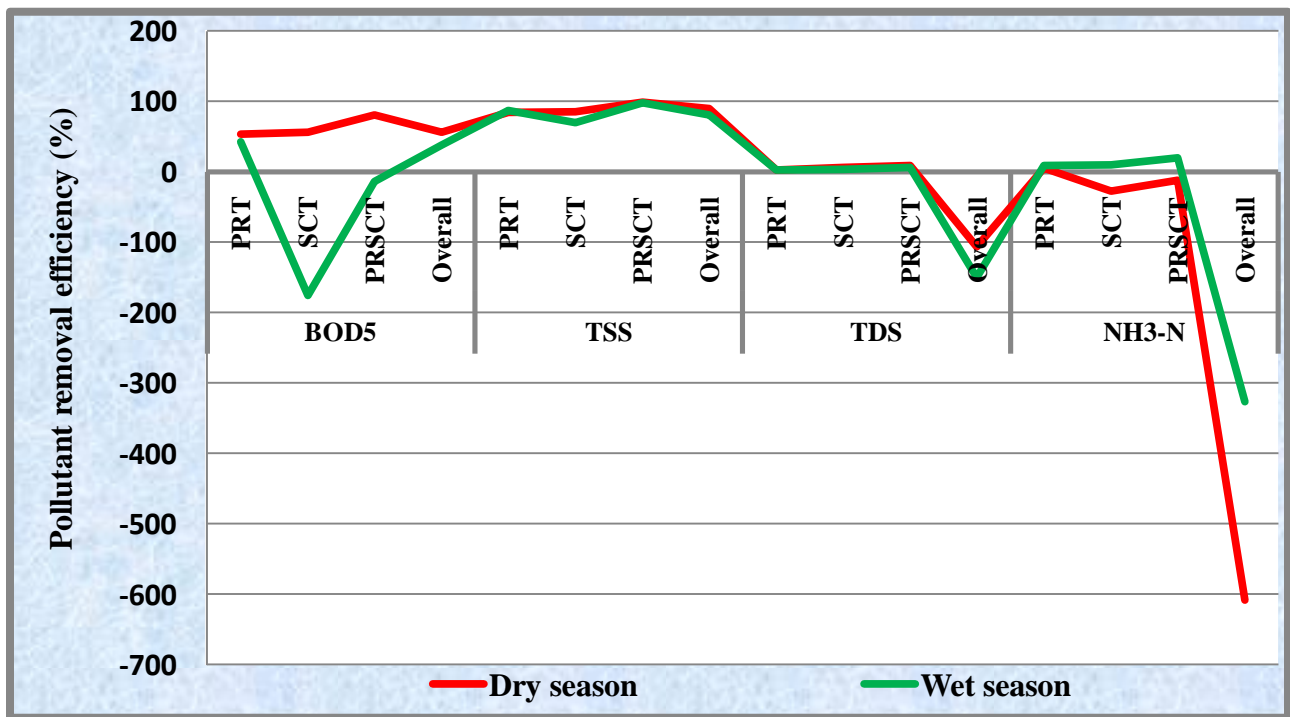


Figure 4.3. Seasonal variation of actual mean-daily removal efficiencies of treatment units

The pollutant removal efficiencies of the treatment plant were greater in the dry season than in the wet season for BOD<sub>5</sub>, TSS and TDS for all treatment units except for that of primary clarifier in TSS removal and the overall plant in TDS removal. This might be due to the relatively high temperature in the dry season possibly enhancing the chemical (coagulation process) and biochemical (in the biological reactor of the AS) reaction enhancing the removal efficiencies of BOD<sub>5</sub> and TSS. The increased efficiency of TDS in the dry season might also be due to increased evaporation rate, among others. On the other hand, the wet season removal efficiency exceeded that of the dry season for all the treatment units including for the overall treatment for

NH<sub>3</sub>-N, which might be due to increased nitrification in the biological system due to high dissolved oxygen in the bioreactor of the AS system. However, the seasonal efficiency differences were not statistically significant ( $p > 0.05$ ) in all cases except for the TSS and NH<sub>3</sub>-N removal of the combined primary-secondary treatment unit. At higher significant levels, however, the variations start to be significant (Appendix 4). For example, the secondary and the combined primary-secondary treatment units had significant seasonal variation in removing BOD<sub>5</sub> ( $p < 0.2$ ), the same being true for the removal of NH<sub>3</sub>-N by the secondary treatment unit.

The statistical insignificance of seasonal efficiency variations ( $p > 0.05$ ) could be partly explained by the neutralizing effect of efficiency enhancers and reducers. For example, the wet season might have caused turbulence in clarifiers reducing efficiency; the dissolved oxygen in the biological reactor did, however, increase that was good for secondary treatment efficiency.

#### **4.2.2. Day-to-day Efficiency Variation**

The day-to-day treatment efficiency variation of individual treatment units and the whole treatment plant was conducted using design expert software version 7.0.0 to conduct ANOVA analysis and Fisher LSD (Least Significant Difference) tests on the basis of normality and randomness assumptions. The statistical test results are presented in Appendix 2 and Appendix 5.

Accordingly, there were no statistically significant differences of day-to-day treatment efficiencies of the treatment plant in both the dry and wet seasons for all the parameters considered in the study (ANOVA test;  $p > 0.05$ ). Similarly, no two compared days (for most parameters) had efficiency differences that were statistically significant (LSD test;  $p > 0.05$ ).

Normal probability plot of residuals (Appendix 6) indicates that there is no as such non-normality of efficiency data distribution for the parameters of BOD<sub>5</sub>, COD, TSS, R-PO<sub>4</sub> and total phosphorous. Nor are there significant outliers (those that significantly deviate from the normal probability line) for those parameters. However, for the parameters of sulfide, TDS, NH<sub>3</sub>-N and chromium, one can't ascertain the normality of the efficiency data from the normal probability plot leading to the limitations of statistical data analysis such as ANOVA for those parameters. There are many outliers from the normal probability line for those parameters especially in the dry season.

### 4.3. Comparative Analysis

#### 4.3.1. Comparison of Actual Plant Efficiencies with Design Efficiencies and International Benchmark

A comparison was made between the actual treatment plant efficiencies and international benchmark efficiencies (Table 4.5). Green-shaded cells indicate values within the benchmark.

Table 4.5. A comparison of actual efficiencies with international benchmark [57]

Parameter	Unit	Day1	Day2	Day3	Day4	Day5	Mean	IUE IULTCS [57]
BOD <sub>5</sub> (%)	PRT	50	40	48.1	65.5	62.7	53.3	50-65
	PRSCT	76.7	82.7	84.2	84.6	74.6	80.6	90-97
BOD <sub>5</sub> * (%)	PRT	87.7	16.7	23.7	-	-	42.7	50-65
	PRSCT	41.2	-116.7	33.1	-	-	-14.1	90-97
COD (%)	PRT	51	36.7	60.2	59.2	58.6	53.1	50-65
	PRSCT	86.7	89.4	91.5	90.5	89.6	89.5	85-95
TSS (%)	PRT	-	79.2	85.3	76.9	96.6	84.5	80-90
	PRSCT	-	98.2	98.7	98.8	98.8	98.6	90-98
TSS* (%)	PRT	96.8	90.4	93.8	67.1	-	87	80-90
	PRSCT	98.1	97.6	98.3	96.9	-	97.7	90-98
Sulfide (mg/l)	PRT	10.25	15.375	25.45	19.06	3	14.6	2-10
	PRSCT		0.175	0.085	0.225	0.75	0.3	<1
Chromium (mg/l)	PRT	1.281	<0.0001	1.306	1.196	1.248	1	2-5
	PRSCT	<0.0001	<0.0001	1.0861	<0.0001	2.546	0.7	<1

\*Wet season

Consequently, the dry season average daily pollutant removal efficiency of the actual primary treatment unit was within the range of the benchmark for BOD<sub>5</sub>, COD, TSS and chromium. In the wet season, the average daily removal efficiency of BOD<sub>5</sub> was outside (less than) the benchmark value whereas that of TSS was well within the range. The combined primary-secondary treatment average daily efficiency in the dry season was well within the benchmark for COD, TSS, sulfide and chromium while that of BOD<sub>5</sub> was below the benchmark. For the wet season, all the daily and average daily removal efficiencies were well within the benchmark for TSS removal while they were below the benchmark for BOD<sub>5</sub> removal.

Some design efficiencies of the plant were also compared with the actual efficiencies (Table 4.6)

Table 4.6. A comparison of actual efficiencies with some design efficiencies of the plant

Parameter	Preliminary Treatment		Primary-secondary treatment		Overall treatment	
	Design Value (mg/l)	Actual average daily value (mg/l)	Design efficiency (%)	Actual average daily efficiency (%)	Design (objective)	Actual
COD	1500*	3366.7 *	87-95	89.5	Compliance with national standard for release to surface waters	Compliance well achieved
BOD5	600*	742.1*	95	80.6		
BOD5*	600*	178.7*	95	-14.1		
Sulfide	40*	82.9*	99	99.6		
Cr (total)	20**	9.43**	NA	73.9		
* Just before primary clarifier; ** Chromium precipitation supernatant value; NA: not available; *wet season						

Accordingly, the overall efficiency of the treatment plant at design was in such a way to comply with the national effluent release standard to surface water, which was well achieved for COD, BOD<sub>5</sub>, sulfide and chromium. On the other hand, TDS and nitrogen nutrient removal was not the focus of the treatment plant at design according to the design document leading to significant enhancement of the amount of those pollutants in the final effluent released to the nearby river (e.g. the standard for release of NH<sub>3</sub>-N and total nitrogen was not attained). The primary-secondary combined treatment efficiencies at design, which were 87-95% for COD and 99% for sulfide were achieved by the treatment plant whose average daily efficiencies were 89.5% for COD and 99.6% for sulfide. Nevertheless, the design removal efficiency for BOD<sub>5</sub> which is 95% was not achieved by the plant in both seasons.

Among the possible reasons for the low BOD<sub>5</sub> removal efficiencies of the secondary and the primary-secondary combined treatment units are the presence of very high MLSS (with high dead microorganisms) within the AS aeration tank and the variable organic loading to the aeration tank of the AS.

### 4.3.2. Comparison of Final Effluent Quality with National and International Tannery Effluent Release Standards to Surface Waters

The actual final effluent quality at the outlet of the treatment plant was compared with national and international (World Bank) tannery effluent release standards for discharge to surface waters (Figure 4.4 highlights the comparison for some parameters; see also Appendix 7). Accordingly, the final effluent daily and mean daily qualities were much below (within) the national standard for BOD<sub>5</sub>, COD, sulfide, temperature and pH while they well exceeded the national standard for TSS and NH<sub>3</sub>-N and obviously for total nitrogen. The final effluent daily and mean daily sulfide and pH values were also below (within) the World Bank standard though it was not the case for BOD<sub>5</sub>, COD (except for one day), TSS and NH<sub>3</sub>-N. The dry season daily and mean daily PO<sub>4</sub>-P values were above the world bank total phosphorous release standard to surface waters, which is 2 mg/l. In the wet season, all the final effluent daily and mean daily total phosphorous values were below the national release standard, though they somehow exceeded the world bank standard. The dry season final effluent mean daily chromium (the freely available which is only part of the total chromium) amount (0.6mg/l) already exceeded the world bank total chromium release standard of 0.5mg/l. However, nothing can be said about compliance with the national total chromium release standard as total chromium was not analysed in the present study. The national standard is quite relaxed as compared to the World Bank standard for BOD<sub>5</sub> and COD.

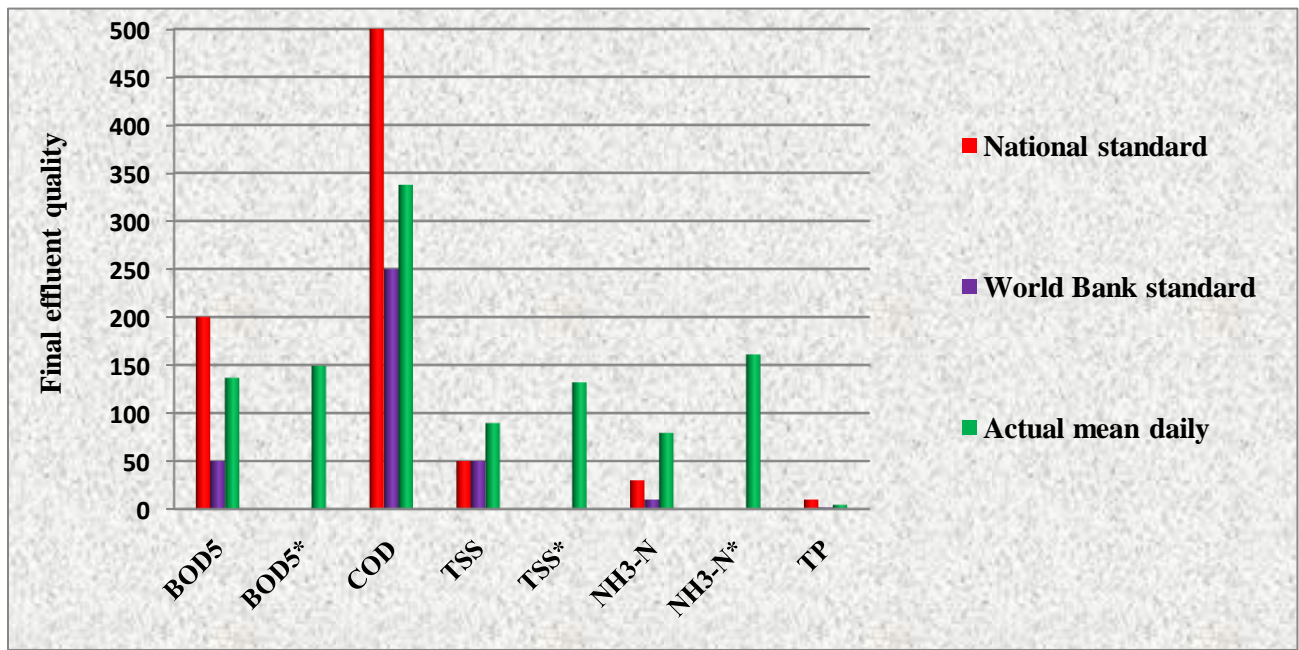


Figure 4.4: Comparison of final effluent mean daily quality with the standards (\*wet season)

### **4.3.3. Comparison of Actual Results with Results of Other Studies**

The dry season treatment efficiency of the primary clarifier of the actual treatment plant was much better than those reported by Shanmugasundaram and Murthy [58] and Ezike et al. [60] for BOD<sub>5</sub>, COD and TSS (Figure 4.5). However, its TDS removal efficiency was much below that reported by Ezike et al. [60], being almost equal to that of Shanmugasundaram and Murthy [58]. The COD and TSS removal of the primary clarifier as reported by Govindasamy et al. [59] was, however, somehow better than that found in the actual study. Its wet season TSS removal efficiency was also much better than those of Shanmugasundaram and Murthy [58] and Ezike et al. [60] whereas that of TDS was much lower than that reported by Ezike et al. [60]. Similarly, its BOD<sub>5</sub> removal efficiency in wet season was a little better than those of Shanmugasundaram and Murthy [58] and Ezike et al. [60].

The dry season secondary treatment was much more efficient than that of Govindasamy et al. [59] and Shanmugasundaram and Murthy [58] for COD and TSS removal. Its TDS removal was also better than that reported by Shanmugasundaram and Murthy [58]. On the other hand, it was by far less efficient than that of Govindasamy et al. [59] and Shanmugasundaram and Murthy [58] in terms of BOD<sub>5</sub> removal. Its wet season TSS removal efficiency was somewhat better than that reported by Govindasamy et al. [59] and Shanmugasundaram and Murthy [58] while its TDS removal efficiency was a bit better than that of Shanmugasundaram and Murthy [58].

One major difference between the actual study and the other studies is the low BOD<sub>5</sub> removal efficiency of the actual secondary treatment which could be due to operational problems of the actual plant such as very high MLSS (with high dead microorganisms) within the AS aeration tank and the varying organic loading to the aeration tank of the AS, among others. The actual plant primary and secondary treatment units TSS removal efficiency is found to be better than others in most cases may be due to differences in the design of the primary and secondary clarifiers as well as coagulation efficiencies among others.

The activated sludge aeration tank alone had the effect of significantly reducing BOD<sub>5</sub> and COD as reported by Shanmugasundaram and Murthy [58] whereas that of the actual treatment plant significantly enhanced those pollutants (Appendix 3), which could be partly due to a great deal of dead microorganisms in the aeration tank demanding additional oxygen.

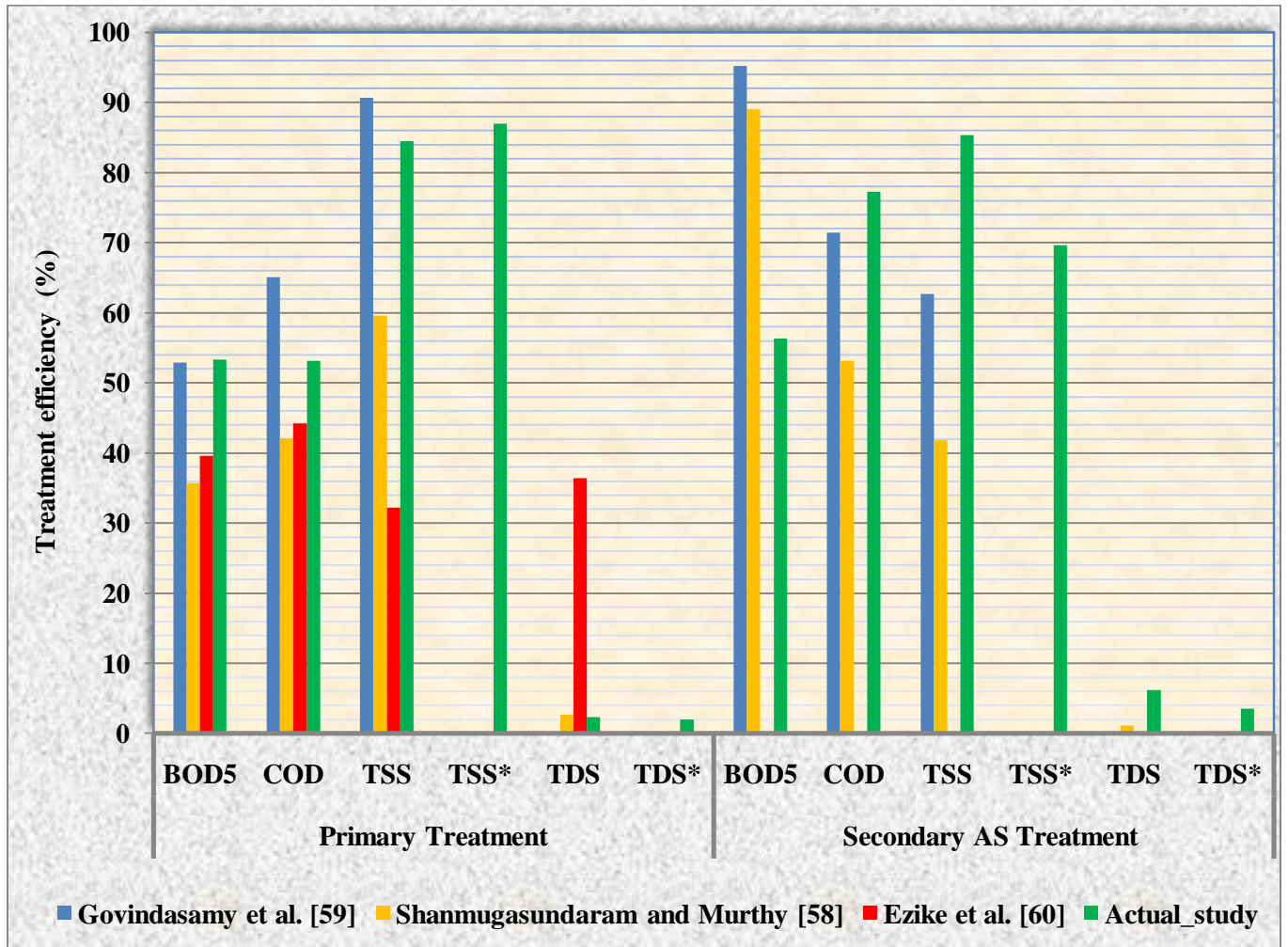


Figure 4.5. Comparison among treatment efficiency studies on similar technologies (\*wet season)

#### **4.4. Assessment of Factors of Relevance to Actual Treatment Plant Efficiency**

The factors of relevance to the performance of the actual treatment plant were assessed through physical observation, document analysis and interview by classifying them into prevention factors (CP practices) and direct factors (design, operation, maintenance and administration).

##### **4.4.1. Wastewater and Pollutant Reduction through Cleaner Production**

Good housekeeping is well practiced in most production areas though some flaws were observed in the beamhouse and tanyard sections. Very poor housekeeping was, however, observed in the compound in the vicinity of the treatment plant as was evidenced by the careless dumping of solid waste including precipitated chrome sludge, screenings and primary/secondary sludge in the compound creating huge aesthetic and odor problems. The openly dumped solid waste could further enter the different treatment units of the treatment plant through wind, rainfall erosion or other mechanisms thereby affecting the operation and efficiency of the treatment plant. CP options such as water conservation, process liquor recycling and short process floats can reduce up to 65% of water consumption and wastewater generation significantly reducing the burden on treatment plants [21, 66]. However, the actual industry is found to have huge wastewater generation (much more than  $600\text{m}^3$  per day) than that normally required at the current soaking capacity of around 9.1 ton/day under conventional processing practices, which is  $328\text{-}510\text{m}^3$  based on [21]. Indeed, through proper cleaner production approach, even only around  $109\text{m}^3$  (82% reduction of actual use) of wastewater generation could have been achieved in the actual industry [21]. The main reason for this huge wastage is the full dependence of the industry on ground water accessible without any charge except the initial investment to make the ground water available. There is no re-use of treated wastewater and recycling of process liquors. COD, nitrogen and sulfide could have reduced had process water been recycled as claimed by [1].

The inability of the actual treatment plant for nitrogen and TDS reduction and compliance can be partially addressed by strong CP practices as overall reduction of 74-87% for  $\text{NH}_3\text{-N}$ , at least 33-56% for TKN, 28-66% for sulfate and 60-72% for chloride can be achieved [21].

A study in the country stressed the importance of proper weighing and preparation of process chemicals as a crucial CP measure to reduce chemical wastage [22]. Indeed, the chemicals that join the wastewater can also decrease if chemical wastage is minimized. In the actual industry, process chemical weighing and recipe preparation is well practiced in all sections using analogue

and digital beam balances, which are fully operational. Regular training on how to operate such as on chemical weighing and recipe preparation does also play a role as a CP measure to manage chemical wastage and waste management [22]. However, no regular on-the-job training is offered in the actual industry to workers on how to optimize their operation.

No further salt curing of sheep/goat skin and mechanical de-dusting of salt-preserved skin in the actual industry are believed to have significantly lowered chlorides and hence TDS in the wastewater as beamhouse contributes up to 60% of total chloride in wastewater as reported by World Bank [1]. However, sodium chloride is also used by the actual industry in pickling processes coupled with the absence of important CP measures in this regard such as short floats and pickling float direct recycling. Deliming also takes place sometimes using ammonium chlorides, though the most commonly used is ammonium sulfate, which clearly shows the lack of CP practices in this case such as salt free deliming using other approaches such as CO<sub>2</sub> deliming to reduce the introduction of further chlorides and TDS in the wastewater. CP measures such as ammonia free deliming, ammonia free pickling/tanning, hair saving and lime float recycling play vital role in nitrogen reduction in the wastewater, lime float recycling alone reducing up to 35% of total nitrogen in the wastewater generated [1]. In the actual industry, the pickling/tanning process is ammonia free coupled with the practice of hair saving for the sheep/goat skin (hair saving not used for hide skin). However, the deliming process is not ammonia free, nor is there lime float recycling. Chromium reduction through CP measures such as short tanning floats and tanning float direct recycling are absent, though chrome precipitation and enhanced chrome fixation are undertaken. Lime float recycling is not practiced in the actual industry, which could have well reduced the wastewater sulfide content according to [1]. Other CP options such as reducing the use of inorganic sodium sulfide and sodium bi-sulfide are completely absent.

Hence, CP practices were observed to be partially implemented in the actual industry necessitating much further action in the future in this regard to lessen the burden on the treatment plant thereby reducing its operational cost and enhancing its treatment performance.

## **4.4.2. Design, Operation, Maintenance and Administration Factors**

### **4.4.2.1. Actual Design Parameters: Evaluation and Comparison with Benchmarks**

#### **4.4.2.1.1. Preliminary Treatment**

Proper segregation (into effluents of soaking, liming, tanning, post tanning and sanitary) and separate treatment of the liming liquor (through sulfide oxidation) and the tanning liquor (through chrome recovery) is highly recommended before the streamlines join other streams for combined treatment. The two streamlines are also recommended to pass a set of two screens of size 20 mm and 10 mm before the sulfide oxidation and chrome recovery processes [2]. However, the wastewater in the actual industry is segregated only into two stream lines namely for the beamhouse and re-tanning section, and for the tanning section. The tanning liquor is chrome precipitated whose supernatant is then mixed with liquor from the beamhouse and re-tanning sections for combined treatment in the treatment plant. The two stream lines each have coarse screens to separate substances that can be screened though they are not of design recommended by UNIDO [2]. Hence, proper wastewater stream segregation and separate treatment is not adequately part of and well integrated in to the design of the preliminary treatment system of the actual treatment plant.

The combined effluents are then strongly recommended to be treated by screening and de-gritting operations as part of preliminary treatment. To this end, the combined wastewater is to pass through screens of mesh size 20 mm followed by 10 mm, which is then to pass through a simple non-aerated grit and floating object removal chamber followed by a 6 mm mesh size screen [2]. In the actual industry, however, there are three major screens of size 5-10 mm while there is no grit removal chamber. Consequently, though the screening system is somehow well designed, the de-gritting operation is absent while it is also recommended to prevent operational problems in subsequent treatment processes. Manually cleaned screens are used in the actual industry while mechanically cleaned ones are recommended for better operational consistency and process efficiency of the screening operation as claimed by [2].

The three rectangular wastewater collection tanks in the actual industry ( $108\text{m}^3$  of volume each) were mainly designed to collect and store screened wastewater, though it is also desired that they serve as pre-sedimentation tanks. Additional three collection tanks were also constructed and operated during the second phase (wet season) of wastewater sample collection to serve for storing the non-tanning wastewater coming from the trial/pilot-scale hide processing section. However, the design of the tanks didn't incorporate issues of sludge removal leading possibly to further concentrated accumulation of pollutants in the tanks resulting from re-suspension of settled sludge, which in turn creates a significant burden on the subsequent treatment operations and processes.

The actual industry has a two-compartment equalization tank for flow and organic loading homogenization, the second compartment also serving as coagulation basin for enhanced primary clarification. In-line equalization is practiced for much better flow and influent pollutant concentration dampening and equalization effects as claimed by [30]. Aeration based (not mechanical) mixing is used, which also provides the required air for sulfide oxidation and prevention of odor and septic conditions in the tank. Having two compartments in the design is important during purposes such as cleaning as recommended by [30]. However, the design of the equalization system didn't incorporate flow monitoring using flow meter leading to a huge limitation in hydraulic loading monitoring and control. Liners (clay or synthetic) were not used in the design to protect ground water contamination as the industry is found where ground water (the only water source of the industry) is found. The simultaneous use of the second compartment of the equalization tank for sulfide removal and coagulation basin significantly reduced space or land use (less ecological foot print) as no separate sulfide removal and coagulation basin was designed and constructed. However, such approach of sulfide removal must be cost and efficiency-wise compared with the lime liquor segregation and catalytic oxidation based removal of sulfide in a separate tank as recommended by [2].

#### 4.4.2.1.2. Primary and Secondary Treatment

The primary and secondary treatment design values were evaluated based on recommended values (Table 4.7) [30]. Accordingly, most design values are in the recommended range.

Table 4.7. Primary and secondary treatment design evaluation result of the actual plant

Primary clarifier			
Design parameter	Recommended range [30]	Actual	Within recommended range
$\phi$ (m)	3-60 (typical: 12-45)	7.1	Yes
H (m)	3-4.9 (typical: 4.3)	3.85	Yes
$u_o$ ( m <sup>3</sup> /m <sup>2</sup> .d)	Alum floc: 30-70	26.4	No
	Iron floc: 30-70		
	Lime floc: 35-80		
t (h)	1.5-2.5 (typical: 2)	3	No
WLR ( m <sup>3</sup> /d/m)	≤ 125 m <sup>3</sup> /d/m (average flow)	26.95	Yes
Activated sludge aeration			
$X_i$ (mg/l)	3000-5000	3000	Yes
F/M (kg BOD/kg MLSS.d)	0.04-0.10	0.085	Yes
OLR (kg BOD/m <sup>3</sup> .d)	0.1-0.3	0.26	Yes
$\tau$ (h)	15-30	28	Yes
$\theta_c$ (day)	15-30	25	Yes
RAS	75-150	100	Yes
Secondary clarifier			
$\phi$ (m)	-	8	-
H (m)	3.5-6	3.6	Yes
$u_o$ ( m <sup>3</sup> /m <sup>2</sup> .d)	Average: 8-16 (peak: 24-32)	15.6	Yes
SLR (kg/m <sup>2</sup> .h)	Average: 1-5 (peak: 7)	3.96	Yes
WLR ( m <sup>3</sup> /d/m)	≤ 125 m <sup>3</sup> /d/m (average flow)	23.9	Yes
$\phi$ : diameter; H: Depth; t: detention time; $\theta_c$ : sludge age; $\tau$ : aeration period; WLR: Weir loading rate $u_o$ : Surface overflow rate (SOR); $X_i$ : MLSS SLR: solids loading rate			

Circular clarifier is used for clarification as recommended by [2]. The mixing system for coagulation is aeration-based that didn't incorporate gentle mixing for flocculation.

The design of the actual primary and secondary treatment units along with the sludge drying beds was determined to check for any design deficiencies or limitations based on the actual average daily treatment (design average daily flow) of 600m<sup>3</sup> of wastewater.

### I. Design of the Primary Sedimentation Tank

The assumed surface overflow rate and detention time for designing the actual primary clarifier tank are 26.4 m<sup>3</sup>/m<sup>2</sup>.d and 3 hours respectively. With these assumed data, the actual sizing of the tank is calculated as in the following:

$$t = \frac{V}{Q} \Rightarrow V = Q \cdot t = (600\text{m}^3/\text{day}) \left(\frac{3}{24} \text{ day}\right) = 75\text{m}^3$$

$$\text{SOR} = u_o = \frac{Q}{A} \Rightarrow A = \frac{Q}{u_o} = (600\text{m}^3/\text{day}) / (26.4\text{m}^3/\text{m}^2 \cdot \text{d}) = 22.73 \text{ m}^2$$

Where t = detention time; u<sub>o</sub> = surface overflow rate; V = tank volume; Q = daily wastewater flow rate

Then, the diameter (Φ) becomes,

$$A = (\pi\Phi^2)/4 \Rightarrow \Phi = \sqrt{\frac{4A}{\pi}} = \sqrt{\frac{4 \times 22.7\text{m}^2}{\pi}} = 5.38\text{m}$$

The depth of the tank is calculated as:

$$H = \frac{V}{A} = (75\text{m}^3) / (22.73\text{m}^2) = 3.3\text{m}$$

Finally,

$$\text{Weir loading rate} = \text{WLR} = \frac{Q}{L} = (600\text{m}^3/\text{day}) / (\pi \times 5.38\text{m}) = 35.5\text{m}^3/\text{day}/\text{m}$$

Where L is weir length, which is the perimeter of the tank.

Consequently, under the assumed u<sub>o</sub> and t in the design, the volume, base area, diameter, depth and weir loading rate of the primary sedimentation tank should have been 75m<sup>3</sup>, 22.73m<sup>2</sup>, 5.38m, 3.3m and 35.5m<sup>3</sup>/day/m respectively. But now, the actual values are 7.1m and 3.85m for the diameter and depth respectively, which make the actual volume and base area of the tank to be

152.4m<sup>3</sup>, 39.6m<sup>2</sup> respectively. Similarly, the actual weir lading rate is 26.95m<sup>3</sup>/day/m for the actual diameter of 7.1m. Hence, the tank is by far oversized (over-sized) for the treatment of an average of 600m<sup>3</sup> of wastewater daily. However, as the industry is operating at about half of its full capacity now, the overdesigning of the system is quite reasonable for future expansion of the treatment plant. The actual surface overflow rate and detention time ensure more clarification efficiency than would have been obtained had the tank not been over-sized.

## II. Design of the AS Aeration Tank

The AS is extended aeration type as is recommended for tannery wastewater treatment by [2]. The sizing of the aeration tank is determined based on the assumed aeration period ( $\tau = 28$  hours) or food-to-microorganism ratio ( $F/M = 0.085$ ). Accordingly,

$$\tau = \frac{V}{Q} \Rightarrow V = Q \cdot \tau = (600\text{m}^3/\text{day}) \left(\frac{28}{24} \text{day}\right) = 700\text{m}^3$$

$F/M = \frac{Q \cdot S_o}{V \cdot X_t} \Rightarrow V = \frac{M \cdot Q \cdot S_o}{F \cdot X_t} = 700\text{m}^3$  (taking  $S_o = 300\text{mg/l}$  as assumed BOD<sub>5</sub> to reach secondary treatment)

Where  $S_o$  = average BOD<sub>5</sub> input to the aeration tank;  $X_t$  =MLSS

The whole treatment plant was designed to treat 600mg/l of BOD<sub>5</sub>, 50% by primary and 50% by secondary treatment. Accordingly, the volume of the actual aeration tank is neither undersized nor oversized. Future plant expansion might have been considered in the design that the volume could be made to increase (size modification) to operate at the unchanged aeration period or the aeration period could be reduced so far as within recommended range without modifying the volume of the tank.

The volumetric organic loading rate (VLR) to the aeration tank is determined to be:

$$\text{VLR} = \frac{Q}{V} \cdot S_o = ((600\text{m}^3/\text{day}) / (700\text{m}^3)) (300\text{g}/\text{m}^3) = 0.26\text{kg BOD}/\text{m}^3 \cdot \text{d}$$

This loading rate is well within the range recommended by [30].

### III. Design of the Secondary Sedimentation Tank

The sizing of the actual secondary clarifier was also checked based on the assumed surface overflow rate and detention time for designing the actual secondary clarifier tank given as 15.6 m<sup>3</sup>/m<sup>2</sup>.d and 3.5 hours respectively. With these data, the actual sizing of the tank is calculated as:

$$t = \frac{V}{(Q+Qr)} \Rightarrow V = (Q + Qr).t = (1200\text{m}^3/\text{day}) \left(\frac{3.5}{24} \text{ day}\right) = 175\text{m}^3$$

Where  $Qr$  = return sludge flow rate =  $Q$  (since the sludge recycle design value is 100%).

$$\text{SOR} = u_o = \frac{Q}{A} \Rightarrow A = \frac{Q}{U_o} = (600\text{m}^3/\text{day}) / (15.6 \text{ m}^3/\text{m}^2.\text{d}) = 38.46 \text{ m}^2$$

The base area can also be determined using the design solids loading rate (SLR) as follows:

$$A = \frac{\text{Total solids}}{\text{SLR}} = \frac{(Q+Qr)(\text{MLSS})}{\text{SLR}} = \frac{(1200\text{m}^3)(3000\text{g}/\text{m}^3)}{(95\text{kg}/\text{m}^2.\text{d})(1000)} = 37.89\text{m}^2$$

Then, the diameter ( $\phi$ ) becomes,

$$A = (\pi\phi^2)/4 \Rightarrow \phi = \sqrt{\frac{4A}{\pi}} = \sqrt{\frac{4 \times 38.46\text{m}^2}{\pi}} = 7\text{m}$$

The depth is calculated as:

$$H = \frac{V}{A} = (175\text{m}^3) / (38.46\text{m}^2) = 4.55\text{m}$$

Consequently, the secondary clarifier is a little bit oversized (to treat 600m<sup>3</sup> of wastewater) in terms of volume as its actual volume is 181m<sup>3</sup> (may be it so for safety factor). Its actual base area (50.3m<sup>2</sup>) and diameter (8m) are also higher than the required values. However, it is under-designed in terms of depth whose actual value is 3.6m. Its actual weir loading rate is 23.9 m<sup>3</sup>/d/m rather than 27.3 m<sup>3</sup>/d/m showing that it is also oversized.

#### 4.4.2.1.3. Primary and Secondary Sludge Treatment

Sludge drying beds (SDBs) are the recommended sludge dewatering methods due to low cost, infrequent attention requirement, low operation skill and high solids in final dewatered sludge, though also associated with large space requirement, unfavorable weather/climate (e.g. rain) and problems such as insects and odors [30]. However, SDBs had better be preceded by sludge thickening and digestion mechanisms especially in cold climates [2]. Dried sludge to be already removed from an SDB needs to have moisture content around 60% after 10-15 days of drying under favorable circumstances. As such, the recommended dry solids loading rate for SDBs is 60-100 kg dry solids/m<sup>2</sup>/yr for the digested primary and waste-activated sludge. Adequate drainage system must be incorporated as most of the water in the sludge is removed by drainage rather than by evaporation. Facilitation for cleaning and dried sludge removal must also be considered in the design [30]. In the actual industry, however, only SDBs of size 200m<sup>2</sup> were designed and used in the absence of any other thickening mechanisms (except in-tank thickening in the circular clarifier), mechanical dewatering mechanisms (e.g. filter press) and sludge digestion (aerobic or anaerobic). No adequate drainage system and convenience for cleaning and dried sludge removal was considered in the actual SDBs design.

Liquid sludge and dry solids generated per ton of wet-salted hide/skin are 2000-3000 liters and 80-120kg for primary sludge [2]. Consequently, in the actual treatment plant, the daily primary sludge production was estimated (for 9.1 ton wet-salted hide processes per day) to be 18.2-27.3m<sup>3</sup> (728-1092kg of dry solids). On the other hand, the sludge wasted per day from the activated sludge system is given by:

$$\theta_c = \frac{V.Xt}{XrQ_w + (Q - Q_e)X_e} = \frac{V.Xt}{XrQ_w} \quad (\text{Assuming } X_e \approx 0)$$
$$\Rightarrow XrQ_w = \frac{V.Xt}{\theta_c} = ((700\text{m}^3/\text{day}) (3000\text{gm}/\text{m}^3))/25\text{days} = 84 \text{ kg/day}$$

Therefore, total sludge (primary plus secondary) with dry solid of 812-1176kg/day goes to the drying beds. The total dry solids generation per year with 350 working days then becomes 284,200-411,600kg, making the actual dry solids loading rate to the SDBs 1421-2058kg DS/m<sup>2</sup>/year, which by far exceeds the range of 60-100 kg Ds/m<sup>2</sup>/year recommended by [30]. The drying bed area required at that recommended solids loading rate was rather:

$$BA = \frac{DS/Year}{RDSLRL} = \frac{84,200-411,600kg}{60-100kg DS/m^2/yr} = 2842-6860m^2$$

BA = drying bed area; DS = dry sludge; RDSLRL = Recommended dry solid loading rate.

Hence, the actual SDB of 200m<sup>2</sup> was by far under-designed for the actual daily wastewater treatment of 600m<sup>3</sup> coupled with the fact that the industry is running at about half its total capacity (big future expansion is expected). This overloading condition of the drying bed is well evident in the fact that inadequately dewatered and even raw sludge is openly damped in the compound in the vicinity of the treatment plant, thereby affecting the operation of the system.

In summary, design flexibility was found to be incorporated in to the design of the primary and arguably secondary clarifiers considering future expansion of the industry. The aeration tank may also be arguably considered flexible as the actual aeration period of 28 hours may be varied in response to future expansions in the range of 15-30 hours recommended by [30]. However, the sludge processing system is by far inadequate for the actual sludge generation rate, let alone incorporating design flexibility in case of future plant expansion. The over-sizing of the sedimentation units and the high aeration period of the biological reactor might have overshadowed the adverse effects of the non-design related factors of operation, maintenance and administration on treatment efficiency.

#### **4.4.2.1.4. Nutrient (nitrogen and phosphorous) treatment**

The actual treatment plant design didn't incorporate nitrogen removal as it was evidenced by the failure of compliance with national NH<sub>3</sub>-N release standard to surface waters. However, the national total phosphorous release standard was attained based on the wet season data.

Treatment plants may be modified to incorporate biological nitrification-denitrification (BND) system for nitrogen removal in an anoxic zone in single sludge systems, the anoxic zone being before (pre-anoxic), after (post anoxic) or within (simultaneous nitrification-denitrification-SND) the aerobic zone. The pre-anoxic system is widely used for its provision of selector operation for controlling sludge bulking; for alkalinity production for the nitrification stage and for reduced oxygen demand in the aeration zone among others [30]. Hence for the actual industry, either pre-anoxic or simultaneous nitrification-denitrification processes (as the actual sludge age is within the range of 18-40 days) may be considered the later being attractive especially for its cost

effectiveness and simplicity of incorporation to the existing plant. The pre-anoxic process incurs additional cost while the simultaneous BND process in a single tank requires more strict process control. However, the BND along with other mechanisms (e.g. ammonia stripping, breakpoint chlorination, ion exchange) must undergo cost effectiveness analysis for final decision. Huge chemical cost and sludge production in chemical precipitation of phosphorous removal may also lead to the importance of biological phosphorous removal though the standard is already met.

#### **4.4.2.2. Treatment Plant Operation**

Best technology and design of treatment plants are not enough in relation to their performance if not coupled with consistent operation as claimed by [30, 34].

In the actual industry, screen cleaning takes place somehow regularly though there are still concerns on how often it takes place. However, the wet and dried screenings are usually left right in the vicinity of the screens for being dried and then dumped in the open dumping site in the compound, which may reach the treatment plant through wind and rainfall affecting its performance. The wastewater collection tanks are not treated as sedimentation basins in terms of operation though they are also desired to serve as pre-sedimentation tanks. There is very low sludge removal rate that could lead to re-suspension of settled sludge to go to the equalization tank in concentrated form. The actual equalization tank is found to be continuously agitated to prevent solid deposition though process monitoring is inadequate as no flow meter is installed in the system to check the extent to which flow is equalized. Homogenization efficiency is not regularly monitored through continuously taking wastewater samples in the influent and effluent of the equalization tank. There is a huge concern on the operational consistency of coagulation chemical (different chemicals used based on availability), dosing (based on guessing) and process monitoring and control of pH and temperature which have big impact on coagulation efficiency. There is only rapid mixing, gentle mixing being absent for flocculation purposes.

The operational aspects observed to possibly negatively affect the performance of the actual primary treatment are improper coagulant dosage (based on guessing), absence of flocculation, inadequate process control (pH and temperature not well monitored), rain dilution and possible re-entrance of dry and wet sludge from the surrounding (due to wind, rain etc) due to poor housekeeping in the area. Monitoring of hydraulic loading to the clarifier was absent as no flow

meter is installed. The secondary clarifier might have also been affected by inadequate process control, wind current, rain dilution, and re-entrance of sludge due to poor housekeeping in the area. Hydraulic loading to the secondary clarifier was not objectively monitored as there is no flow meter in the system. The inadequate operation of sludge drying beds could also affect clarification efficiency as it could cause infrequent sludge removal from the clarifier.

The operating values (in the AS biological reactor) for pH (6-9) and temperature (10-30°C) were well attained in the actual treatment plant as recommended by [2]. The recommended BOD<sub>5</sub>/N/P for biological treatment is 100/5/1 [2, 30]. For the dry season, the five-day average BOD<sub>5</sub>/NH<sub>3</sub>-N/PO<sub>4</sub>-P in the influent to the aeration tank was around 100:19:4 showing that there is excess nutrient. The corresponding ratio (average) in the aeration tank was around 100:14:10 again indicating excess nutrient. For the wet season, the BOD<sub>5</sub>/NH<sub>3</sub>-N/TP (TP: total phosphorous) in the influent to and within the aeration tank were 100:203:3 and 100:31:3 respectively showing excess nutrient presence. However, the dissolved oxygen in biological reactors of at least 2mg/l was not consistently achieved in the dry season though recommended by [2, 30]. However, it was well achieved (even much higher) in the wet season.

Operation with F/M, MLSS and OLR (BOD<sub>5</sub>) outside the design range is believed to have negatively impacted the efficiency of the primary-secondary combined treatment system in terms, especially, of removing BOD<sub>5</sub> from the wastewater (Figure 4.6 and Figure 4.7). The regular monitoring of hydraulic and organic loading to the aeration basin of the AS is very crucial [30]. However, there is no flow meter to monitor the hydraulic loading and regular BOD<sub>5</sub>/COD analysis to monitor organic loading. Process control variables of MLSS, F/M and/or sludge age should also be regularly monitored and controlled by dissolved oxygen in the basin, RAS and WAS [2, 30]. However, it is not usually practiced in the actual industry. The inadequate operation of the already under-designed sludge drying beds of 100m<sup>2</sup> for the secondary sludge is also believed to have been significantly affecting the operation of the biological reactor. The beds are placed in a location where it is difficult for the dewatered-sludge collection and disposal leading to operational limitations. The activated sludge system requires well skilled operators as it requires good process control and operation. However, there is limitation in this regard as well though some basic skill is already available.

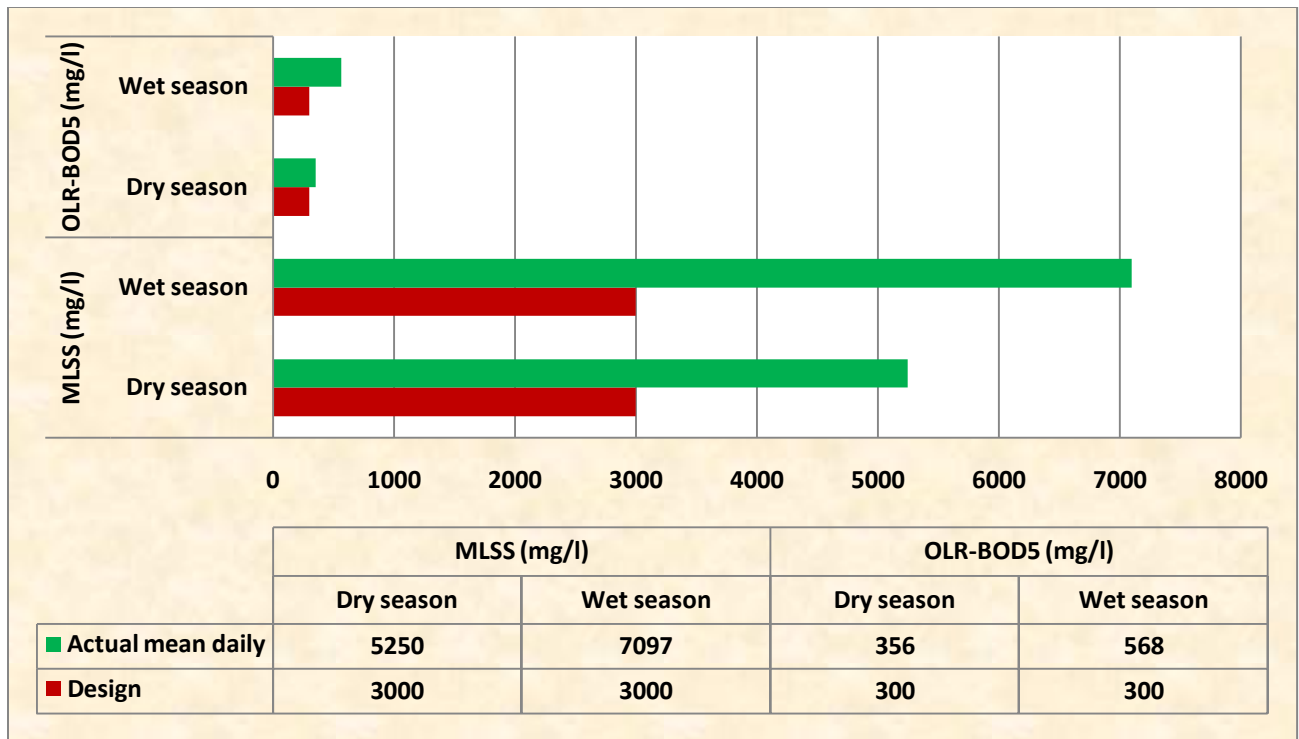


Figure 4.6. Comparison of AS system design and actual values of MLSS and OLR

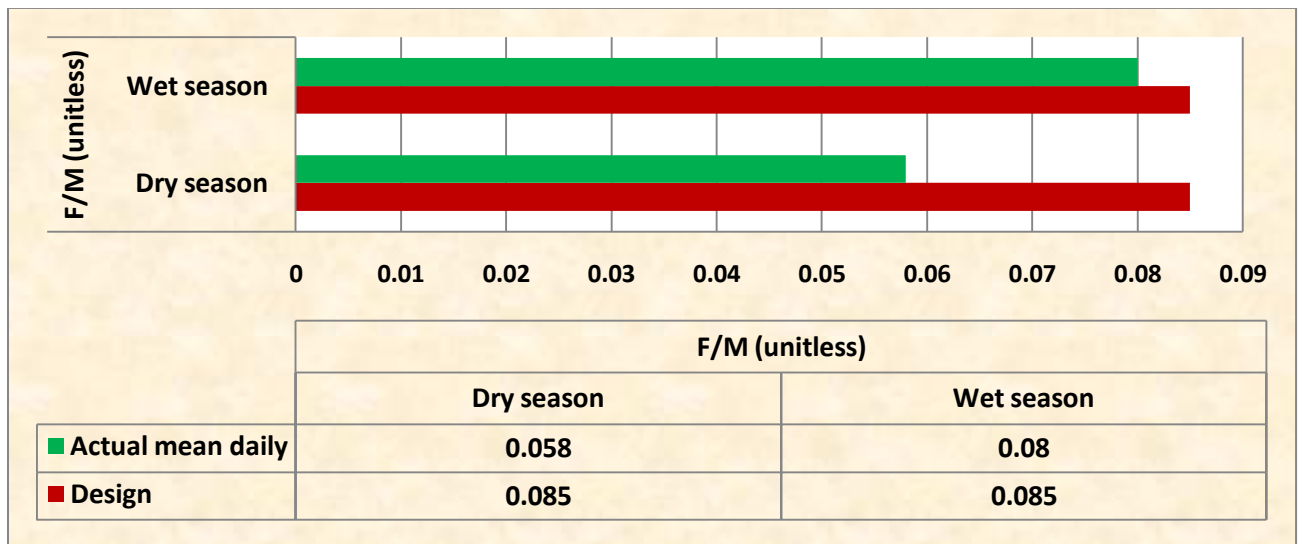


Figure 4.7. Comparison of AS system design and actual values of F/M

Threshold concentrations above which may inhibit biological activity in aeration tanks were reported by [67]. Those values are 480mg/l for  $\text{NH}_3\text{-N}$  and 25mg/l for sulfide whereas the actual values in the aeration tank were much below those threshold values. Regarding trivalent chromium, which is also poisonous to biological activity in the aeration tank, actual values don't

seem to be consistently below the threshold value of 50mg/l. If de-nitrification is desired in aeration tanks, the threshold value for the trivalent chromium is 0.01mg/l whereas the average daily measured chromium value in the actual aeration tank was found to be 30mg/l. Finally, for proper nitrification in the aeration tank, the sulfate in the tank should also be kept below 500mg/l, though actual values of sulfate were not determined in this regard. Consequently, the less BOD<sub>5</sub> removal efficiency and nitrogen enhancement of the actual biological treatment might have also been due to high toxicity in the tank such as chromium and salinity (e.g. sulfate). Other operational problems observed to affect the operation of the biological reactor were power-cut induced plant interruption (e.g. activated sludge interruption) and poor housekeeping in its vicinity among others.

The pipelines, pumping systems and other components of the treatment system were functional with no damaged component.

#### **4.4.2.3. Treatment Plant Maintenance and Administration**

Proper and scheduled maintenance is crucial along with regular maintenance record keeping for the good operation and performance of wastewater treatment plants [30, 34]. The assessment in the actual study shows that maintenance in the actual treatment plant takes place as problems just happen, scheduled maintenance and record keeping being absent. The required maintenance equipment and accessories are said to be available in the factory's equipment store along with skilled maintenance personnel and allocation of adequate financial resource. Scheduled maintenance and servicing is important for early problem detection and handling at much lower cost than the cumulative and costly problems. Similarly, record keeping is crucial to assess the frequency and type of dysfunctions, which will be important input to next maintenance scheduling and operation issues. Regarding administration, the treatment plant has enough number of operators (one supervisor and 7 operators working on shift basis) with some basic treatment plant operation knowledge and skill along with allocation of adequate financial resources to the plant. However, the lack of staff motivation such as continuous on-the-job training and adequate payment for their service seems to have negatively impacted the operators. The industry doesn't have its own environmental policy which will have positive impact on the performance of the treatment plant.

#### **4.5. Technology Evaluation of the Actual Treatment Plant**

The actual treatment plant secondary treatment technology (AS) was evaluated along with UASB, WSPs and CWs using Multi Criteria Analysis Technique (MCA). The evaluation process involved aim setting, key stakeholder identification, option identification, criteria/sub-criteria setting, criteria weighting, scoring per criteria and score aggregation to develop performance matrix, which is constituted by rows (options) and columns (criteria), the entries being weighted scores. The evaluation aggregate score (aggregated using equation 3.2) results are summarized in Figure 4.8, the detail being given in Appendix 8. The technology evaluation was based on a comprehensive literature review [3, 10, 30, 31, 32, 36, 42-44, 47, 49, 52, 53, 57].

Accordingly, AS is the most efficient treatment system while CWs followed by WSPs are found to be better than the other systems in terms of reliability, sustainability, cost and simplicity. UASBs are best in terms of space requirement. On aggregate (all criteria considered), indicated by the aggregate score, WSPs are much better than AS and UASBs to be used in Ethiopia. CWs are the second best alternatives of biological wastewater treatment in the country. However, the current technology ranks may be somehow changed based on some specific local conditions. For example, CWs may be best rather than WSPs if land is not a problem and more efficiency is required. Similarly, even AS which is the least favorable in the current technology ranking may be the only option to be considered if space is very scarce and high effluent quality is required.

Although WSPs followed by CWs are recommended as discussed above, the next concern is which type of WSPs and CWs to use. In relation to WSPs, a series of anaerobic, facultative and then aerobic ponds are better used for best performance through utilizing the advantages of each. Tadesse et al. [61] claimed, for instance, that effective treatment of tannery wastewaters can result using a pond system in a series of advanced facultative pond, secondary facultative pond and maturation ponds. Similarly, subsurface flow CWs are usually used in most cases as compared to the free water surface ones due mainly to aesthetic, environmental and efficiency considerations. A series of subsurface flow CWs [49, 54] may be used for better performance.

The major limitation in this technology evaluation process is the fact that MCA technique is subjective, though the subjectivity has been minimized as much as possible. Hence the actual evaluation results give at least some direction on the selection of secondary treatment technologies not only in tanneries but also in other industries.

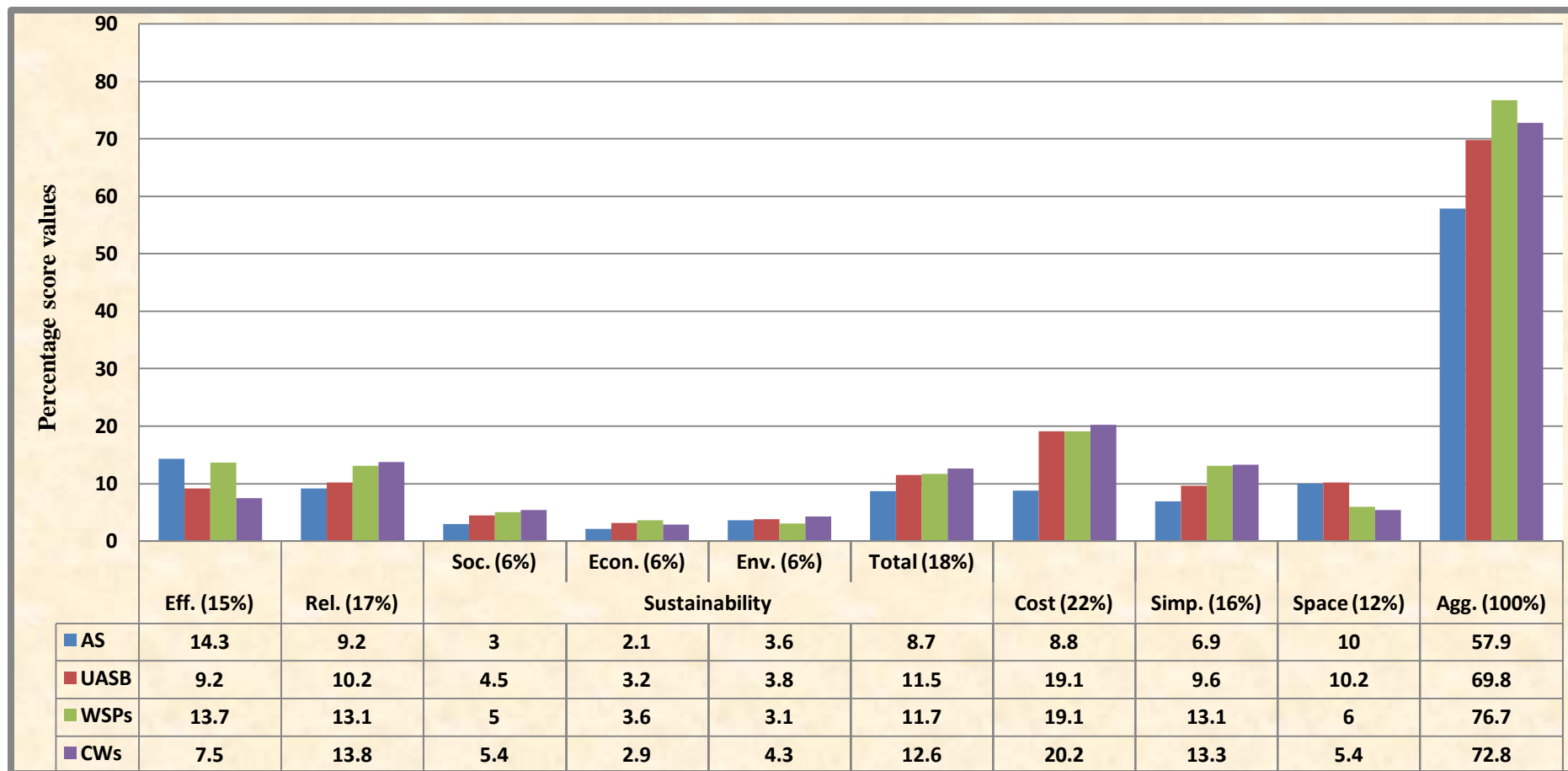


Figure 4.8. MCA individual and aggregate score results of the evaluation of secondary tannery wastewater treatment technologies (Eff.: efficiency; Rel: reliability; Simp.: simplicity; Agg.: aggregate; Soc.: social; Econ.: economical; Env.: environmental)

## **5. Conclusion and Recommendation**

### **5.1. Conclusion**

Technology, design and efficiency evaluation along with assessment of CP practices and efficiency determining factors of the wastewater treatment plant in the selected industry gave results based on which can be made conclusive remarks. The technologies used for the preliminary and primary effluent treatment in the actual industry are the ones recommended for tannery industries. The secondary treatment technology is AS whereas the actual study showed that WSPs are best recommended in Ethiopia followed by CWs and UASBs, the AS being the least recommended. Hence either WSPs or CWs should have been used in the actual industry for sustainable operation owing to the huge land that the industry possesses coupled with the less stringent national tannery effluent release standards (relaxed standards giving more flexibility to the industry for compliance).

The treatment plant is well functional, reasonably efficient and achieving national compliance requirements of major parameters such as BOD<sub>5</sub>, COD, sulfide, chromium and total phosphorous. No seasonal (except for the combined primary-secondary treatment in removing NH<sub>3</sub>-N and TSS) and day-to-day treatment efficiency variations were observed though further research is essential in this regard. Actual plant design and international bench mark treatment efficiencies are also well achieved for some parameters. However, huge limitation exists in terms of nitrogen and dissolved solids removal as well as sludge management. There is no as such design deficiency in the liquid treatment system. However, a serious design flaw is found to exist in the sludge management system. Although cleaner production has a vital role in reducing the burden on treatment plants, it is only partially implemented in the actual industry. There exist serious operational problems though administration and maintenance of the plant are somehow good but need to be further strengthened.

## 5.2. Recommendation

Based on the findings of the study, the following are strongly recommended:

- Due attention must be given to appropriate technology selection especially for secondary treatment based on pre-set criteria and specific local conditions
- Better cleaner production practices to aid end-of-pipe treatment of pollutants, mainly ammonia and total dissolved solids, which were poorly addressed by the system
- Incorporation of nutrient (mainly nitrogen) removal systems in to the existing plant through intermittent aeration or pre-anoxic tank approaches; enhanced phosphorous removal may also be implemented (to complement the phosphorous removal by chemical precipitation and reduce chemical cost) through incorporation of anaerobic tank in the system before the pre-anoxic tank
- Adequate monitoring and control of process variables such as pH, temperature, OLR, F/M, MLSS and toxic substances, among others to further improve system efficiency
- Incorporation of flow meters in the treatment system to monitor and control hydraulic loading rates to different units of the treatment plant
- Better sludge management through re-designing or upgrading the existing sludge drying beds and properly and regularly disposing of the dried sludge.
- Implementation of chrome recovery and reuse rather than simply precipitating the chrome and disposing it of freely in the factory compound; chrome reuse can significantly reduce chrome associated cost, the cost saved in turn being allocated to at least partially fund the operation of the costly activated-sludge treatment system
- Strengthening and optimizing efficiency influencing factors such as plant maintenance (should be scheduling and recorded) and plant administration (staff training and motivation must be regularly undertaken)
- Further research on the performance of sludge dewatering systems, especially sludge drying beds (SDBs) and the seasonal variation of treatment system efficiency

## References

- [1] World Bank Group (2007) Environmental, Health and Safety Guidelines for Tanning and Leather Finishing.
- [2] UNIDO (2011) Introduction to Treatment of Tannery Effluents: What every tanner should know about effluent treatment, Vienna.
- [3] Durai, G. and Rajasimman., M. (2011) Biological treatment of tannery waste water-a review. Journal of Environmental Science and Technology. Asian Network for Scientific Information, 4(1), 1-17.
- [4] Gebre G. and Van Rooijen, D. (2009) Urban water pollution and irrigated vegetable farming in Addis Ababa, 34 th WEDC International Conference, Addis Ababa, Ethiopia.
- [5] Mersha Z. (2008) Water Quality Monitoring Design for Little Akaki River. Unpublished M.Sc. thesis.
- [6] Itanna F. (1998) Metal concentrations of some vegetables irrigated with industrial liquid waste at Akaki, Ethiopia. Ethiopian Journal of Science, 21(1), 133-144.
- [7] Palanisamy T. et al. (2005) Recent Trends in Leather Making: Processes, Problems, and Pathways, Critical Reviews in Environmental Science and Technology.
- [8] Zulfikar, A. (2012) Assessment of Tannery Solid Waste Management and Characterization: A Case of Ethio-Leather Industry Private Limited Company (ELICO), MSC Thesis in Environmental Engineering, Addis Ababa University, Addis Ababa, Ethiopia.
- [9] Banuraman, S. and Meikandaan, T.P. (2013) Treatability Study of Tannery Effluent by Enhanced Primary Treatment. International Journal of Modern Engineering Research (IJMER), 3(1), 119-122.
- [10] Bitton, G. (2005) Wastewater Microbiology, 3<sup>rd</sup> Edition, John Wiley and Sons, Inc.
- [11] L.A.H.M. Verheijen D. Wiersema, L.W. Hulshoff Pol, J. De Wit (1996) Livestock and the Environment: Finding a Balance Management of waste from animal product processing, International Agriculture Centre, Wageningen, The Netherlands.
- [12] Khan, S.R., Kawaja, M.A., Khan, A.M., Ghani, H. and Kazmi, S. (1999) Environmental Impacts and mitigation costs associated with cloth and leather exports from Pakistan. Islamabad, Pakistan.
- [13] UNEP (1996) Cleaner Production in Leather Tanning, A Workbook for Tanneries, first edition, France.

- [14] Melaku, S., Wondimu, T., Dams, R. and Moens, L. (2007) Pollution status of Tinishu Akaki River and its tributaries (Ethiopia) evaluated using physico-chemical parameters, major ions, and nutrients, *Bull. Chem. Soc. Ethiop.*, 21(1), 13-22.
- [15] Getahun, M. and G.Selassie, Y. (2013) Pollution of Water, Soil and Vegetables: Challenges to Growing Cities of Bahir Dar and Kombolcha, Amhara Region, Ethiopia. *Journal of Agricultural Science*, 5(9), 22-28.
- [16] Degefu, F., Lakew, A., Tigabu, Y. and Teshome, K. (2013) The Water Quality degradation of Upper Awash River, Ethiopia. *Ethiopian Journal of Environmental Studies and Management*, 6(1), 58-66.
- [17] Zeleke, A., Seyoum, M. and Seyoum, L. (2010) Assessment of Water Pollution and Biological Integrity Along Modjo River, Ethiopia Using Macroinvertebrate Metrics and Physicochemical Parameters, presented on a conference on Water Resources in Ethiopia, A.A., Ethiopia.
- [18] Tassew, A. (2007) Assessment of Biological Integrity Using Physico-chemical Parameters and Macroinvertebrate Community Index Along Sebeta River, Ethiopia, *MSC Thesis*, Addis Ababa University, Addis Ababa, Ethiopia.
- [19] Gebrekidan, A., Gebresellasie, G. and Mulugeta, F. (2009) Environmental impacts of Sheba tannery (Ethiopia) effluents on the surrounding water bodies, *Bulletin of the Chemical Society of Ethiopia* 23(2), 269-274.
- [20] Zeleke, A. (2011) Tannery Waste Water Management Problems in Ethiopia, *MSC Thesis*, Electronic Thesis and Dissertations Digital Library, Addis Ababa University. (<http://hdl.handle.net/123456789/4168>).
- [21] International Union of Environment (IUE) Commission of the International Union of Leather Technologists and Chemists Societies (IULTCS) (1997), *Typical Pollution Values Related to Conventional Tannery Processes*, London, UK.
- [22] Belay, W. and Andualem, A. (2008) Cleaner Production for Solid Waste Management in Leather Industry, *Journal of EEA*, 25, 1-7.
- [23] Conservation Strategy of Ethiopia (CSE) (1997), Volume 2: Federal Policy on the Environment, Federal Democratic Republic of Ethiopia, Addis Ababa, Ethiopia.
- [24] Environmental pollution control proclamation number 300/2002, Federal Negarit Gazeta, Federal Democratic Republic of Ethiopia, Addis Ababa, Ethiopia.

- [25] EIA proclamation number 299/2002, Federal Negarit Gazeta, Federal Democratic Republic of Ethiopia, Addis Ababa, Ethiopia.
- [26] FEPA and UNIDO (2003) Guideline Ambient Environment Standards for Ethiopia, Addis Ababa, Ethiopia.
- [27] Flores-Alsina, X., Gallego, A., Feijoo, G. and Rodriguez-Roda, I. (2010) Multi-objective evaluation of wastewater treatment plant control alternatives, *Journal of Environmental Management*, Elsevier Ltd, 91, 1193-1201.
- [28] Flores-Alsina, X., Rodriguez-Roda, I., Sin, G. and Gernaey, K.V. (2008) Multi-criteria analysis of wastewater treatment plant control strategies under uncertainty. *Wat. Res.* 42 (17), 4485–4497.
- [29] WHO and UNEP (1997) *Water Pollution Control - A Guide to the Use of Water Quality Management Principles*.
- [30] Metcalf and Eddy (2003) *Wastewater engineering: Treatment and reuse*, 4th edition, Metcalf and Eddy Inc.
- [31] Mara, D. (2003) *Domestic wastewater treatment in developing countries*, Earthscan, UK.
- [32] Von Sperling, M. (1996) *Comparison Among the most Frequently Used Systems for Wastewater Treatment in Developing Countries*, *Water Science and Technology*, Elsevier Science Ltd, 33(3), 59–72.
- [33] *Leather international news and technology* (2009) free newsletter, best available technology for tannery effluent treatment (<http://www.leathermag.com/features/featurebest-available-technology-for-tannery-effluent-treatment/>).
- [34] Federation of Canadian Municipalities and National Research council (FCMNRC) (2003) *Wastewater Treatment Plant Optimization*, Canada.
- [35] Hammer, M, J. and Hammer Jr., M.J. (2001) *Water and Wastewater technology*, Prentice Hall of India Private Limited, Fourth Edition, New Delhi, India.
- [36] Garg, S.K. (2006) *Sewage Disposal and Air Pollution Engineering*, *Environmental Engineering (Volume II)*, 19<sup>th</sup> Edition, Payal offset press, New Delhi.
- [37] City of Riverside (2008) *Wastewater Collection and Treatment Facilities Integrated Master plan*, Volume 4: *Wastewater Treatment System*, Chapter 6: *Primary treatment*, USA.
- [38] Water Environment Federation (2005) *Clarifier Design*, Manual of Practice No. FD-8, 2<sup>nd</sup> Edition, USA.
- [39] Bratby, J. and Marais, G.V.R. (1977) *Flotation*. In: Purchas, D.B. (Ed.), *Solid/Liquid Separation Equipment Scale-Up*. Upland Press, 155–168.

- [40] Lazaridis, N.K., Matis, K.A., Stalidis, G.A., Mavros, P. (1992) Dissolved air flotation of metal ions. *Separation Science and Technology* 27, 1743–1758.
- [41] Rubio, J., Souza, M.L. and Smith, R.W. (2002) Overview of floatation as a wastewater treatment technique, *Mineral engineering*, 15, 139-155 (available on [www.elsevier.com/locate/mine](http://www.elsevier.com/locate/mine)).
- [42] Chan, Y.J., Chong, M, F., Law, C.L. and Hassell, D.G. (2009) A review on anaerobic–aerobic treatment of industrial and municipal wastewater, *Chemical Engineering Journal*, 1–18, ELSEVIER (available on: [www.elsevier.com/locate/cej](http://www.elsevier.com/locate/cej)).
- [43] Vochten, P., Schowanek, S., Schowanek, W. and Verstraete, W. (1988) Aerobic versus anaerobic wastewater treatment, *Proc. of the 5th Int. Symp. on Anaerobic Digestion*, Bologna, Italy. Hall, E. R. and Hobson, P. N. (Eds.), Pergamon Press, UK, 91-104.
- [44] Saleh, M.M.A. and Mahmood, U.F. (2004) Anaerobic Digestion Technology for Industrial Wastewater Treatment, Eighth International Water Technology Conference, IWTC8, Alexandria, Egypt.
- [45] Tare, V., Gupta, S and Bose, P. (2003) Case Studies on Biological Treatment of Tannery Effluents in India. *Journal of the Air & Waste Management Association*, 53 (8), 976-982.
- [46] Rajasimman, M., Jayakumar, M., Ravindranath, E. and Chitra, K. (2007) Treatment of solid and liquid wastes from tanneries in an UASB reactor, *Proceedings of the 60th Annual Session of Indian Institute of Chemical Engineers*, Kolkotta, India.
- [47] Mahmood, Q., Pervez, A., Zeb, B.S., Zafar, H., Yaqoob, H., Waseem, M., Zahidullah and Afsheen, S. (2013) Natural Treatment Systems as Sustainable Ecotechnologies for the Developing Countries, *BioMed Research International* (<http://dx.doi.org/10.1155/2013/796373>)
- [48] Sawyer, C N, McCarty, P L and Parkin, G. F. (2002) *Chemistry for Environmental Engineering and Science*, 4th ed, McGraw-Hill, New York.
- [49] Vymazal, J.J. (2010) *Constructed Wetlands for Wastewater Treatment-a review*, 2, 530-549. (available on: [www.mdpi.com/journal/water](http://www.mdpi.com/journal/water)).
- [50] Lofrano, G., Meriç, S., Zengin, G.E. and Orhon, D. (2013) Chemical and biological treatment technologies for leather tannery chemicals and wastewaters: A review, *Science of the Total Environment*, 461–462 (2013) 265–281
- [51] UN-HABITAT (2008) *Constructed Wetlands Manual*, UN-HABITAT Water for Asian Cities Programme, Nepal, Kathmandu.
- [52] Mthembu, MS., Odinga, CA., Swalaha FM. and Bux F. (2013) Constructed wetlands: A future alternative wastewater treatment technology, a Review. *African Journal of Biotechnology*, 12(29), 4542-4553.

- [53] Calheiros, C.S.C., Rangel, A.O.S.S. and Castro, P.M.L. () Constructed wetland systems vegetated with different plants applied to the treatment of tannery wastewater, CBQF/Escola Superior de Biotecnologia, Universidade Católica Portuguesa, Rua Dr. António Bernardino de Almeida, Portugal.
- [54] Calheiros, C.S.C., Rangel, A.O.S.S. and Castro, P.M.L. (2009). Treatment of industrial wastewater with two-stage constructed wetlands planted with *Typha latifolia* and *Phragmites australis*, *Bioresource Technology*, 100, 3205–3213.
- [55] Kaseva M.E. and Mbuligwe S.E. (2010) Potential of constructed wetland systems for treating tannery industrial wastewater, *Water Sci Technol*, 61(4), 1043-52. (available on: 10.2166/wst.2010.474.).
- [56] Dudley, J.; Mulhall, E.; Solomon, S. (1994) Primary Treatment Processes to Reduce BOD and Suspended Solids—Final Report; UM 1458; WRc: Swindon, Wiltshire, UK.
- [57] International Union of Environment (IUE) Commission of the International Union of Leather Technologists and Chemists Societies (IULTCS) (2008). IUE Document on Recent Developments in Cleaner Production and Environment Protection in World Leather Sector, Typical Performance for tannery Wastewater Treatment (IUE 5).
- [58] Shanmugasundaram, S. and Murthy, D.V.S. (2000) Performance evaluation of the common effluent treatment plant for tanneries at Pammal-Pallavaram Tamil Nadu (India). *Bioprocess Engineering*, 23, 431-434.
- [59] Govindasamy, P., Madhavan, S.D., Revath, S. and Shanmugam, P. (2006) Performance Evaluation of Common Effluent Treatment Plant for Tanneries at Pallavaram CETP. *Journal of Environmental Science and Engineering*, 478(43), 213-220.
- [60] Ezike, N.N., Udiba, U.U., Ogabiela, E.E., Akpan, N.S., Odey, M.O., Inuwa, B., Sule, Gauje B, A.M. (2012) Assessment of the Performance of Primary Effluent treatment Plant of Major Tanneries in Kana, Nigeria, , *Trends in Advanced Science and Engineering*, Science Road Publishing Corporation, 38-45.
- [61] Tadesse, I., Isoaho, SA., Green, FB. And Puhakka, JA. (2003) Removal of organics and nutrients from tannery effluent by advanced integrated Wastewater Pond Systems technology, *Water Sci Technol*, 48(2), 307-14.
- [62] Dejene, B. and Tenalem, A. (2012). Effectiveness of Oxidation Ponds in Industrial Wastewater Treatment: The case of Mesaco Global and Ethiopia Tanneries, Modjo Area, MSC Thesis, Addis Ababa University.

- [63] American Public Health Administration-APHA (1995) Methods for the examination of water and wastewater, 19th ed., Whashington, DC, USA.
- [64] Steele, K., Carmel, Y., Cross, J. and Chris Wilcox, C. (2008) Uses and Misuses of Multi-Criteria Decision Analysis (MCDA) in Environmental Decision-Making, Manuscript, Australian Center of excellence for Risk Analysis (acera).
- [65] Department for Communities and Local Government (2009) Multi-criteria analysis: a manual, London.
- [66] Sundar, V.J., Ramesh, R., Rao PS., Saravanam, P., Sridharnath, B. and Muralidharan, C. (2001) Water Management in Leather Industry. Journal of Scientific and Industrial Research, 60, 443-450.
- [67] M. Sykes, R. (2003) Biological Wastewater Treatment Processes, Book Chapter, Environmental Engineering section, The Civil Engineering Handbook, 2<sup>nd</sup> Edition, Press LLC.

**Appendix 1: Design technical details of the actual wastewater treatment plant**

(Source: design document of the industry, 2011)

Operation/process	Equipment	Qt.	Volume	Dimension	HLR (SOR)	HRT
<b>Chrome precipitation</b>	Chrome liquid collection tank	1	40m <sup>3</sup>			
	Chrome and liquid separation tank	1	15m <sup>3</sup>			
	Chrome sludge collection tank	1	12m <sup>3</sup>			
<b>Screening</b>	Manually cleaned major screens	3		-Mesh size =0.5-1cm -Grille gate width = 40cm		
<b>Storage and pre-sedimentation</b>	Pre-sedimentation tanks	3	108m <sup>3</sup> each (effective volume)	L=12m, W =9m Effective H =1m (each)		
<b>Equalization</b>	Equalization tank	2	180m <sup>3</sup> (each)	L = 12m, W = 6m Effective H = 2.5m		
	-Aeration equipment -Air consumption = 6.19m <sup>3</sup> /min; Aeration intensity = 3.41m <sup>3</sup> /m <sup>2</sup> .h -Two submersible sewage pumps: Q =30m <sup>3</sup> /h; N = 2.2Kw; H = 8m					
<b>Primary sedimentation</b>	Circular tank	1		ϕ =7.1m; H = 3.85m	1.1m <sup>3</sup> /m <sup>2</sup> .h	3h
	Center turn sludge scrapper	1		ϕ =7.1m		
	N = 0.75Kw for the sludge scrapper					
<b>Activated sludge aeration</b>	No pump; gravity					
	Aeration tank or ditch	1	700m <sup>3</sup>			28h
-The type of activated sludge used is CARROUSEL oxidation ditch -The aerator type is Inverted Umbrella Surface Aerator: N = 22Kw -Sludge age (θc) = 25 days; MLSS = 3000mg/l; F/M = 0.085kgBOD/kg MLSS.d -Oxygen demand = 44kg/h (clean water) -The capacity of a Single Inverted Umbrella Surface Aerator = 46kg O <sub>2</sub> /h (clean water)						
<b>Secondary sedimentation</b>	Circular tank	1		ϕ =8m H = 3.6m (effective)	0.65m <sup>3</sup> /m <sup>2</sup> .h	3.5h
	Central rotating hanging sludge scrapper	1		ϕ =8m		
	Sludge return pump	1		H = 6m		
	-Solids loading rate (SLR) = 95kg/m <sup>2</sup> .d; Sludge return (RAS) rate = 100%					
<b>Sludge dewatering</b>	Drying bed	4		50m <sup>2</sup> (each)		

Note: ϕ = Diameter; H = Depth; L = Length; W = width; N = Power requirement; Q = Capacity

**Appendix 2: The summary of design expert software version 7.0.0 ANOVA and LSD test results of the significance of day-to-day variations of treatment efficiency and pollutant concentration**

<b>Day-to-Day treatment efficiency variation of the treatment system</b>						
	<b>Dry season</b>			<b>Wet season</b>		
<b>Parameter</b>	<b>F<sub>value</sub></b>	<b>P-value</b>	<b>LSD with p &lt; 0.05</b>	<b>F<sub>value</sub></b>	<b>P-value</b>	<b>LSD with p &lt; 0.05</b>
BOD <sub>5</sub>	0.77	0.5646	Not any	0.42	0.6734	Not any
COD	1.79	0.1950	2:5			
TSS	0.098	0.9592	Not any	0.082	0.9683	Not any
R-PO <sub>4</sub>	0.64	0.6081	Not any			
Sulfide	0.34	0.7974	Not any			
TDS	0.62	0.6544	Not any			
NH <sub>3</sub> -N	1.04	0.4287	Not any	1.00	0.4378	Not any
Chromium	1.00	0.4446	Not any			
Total phosphorous				3.46	0.0644	1:4;3:4
<b>Day-to-Day pollutant concentration variation of the treatment system</b>						
BOD <sub>5</sub>	2.67	0.0706	1:2;1:3	0.32	0.7331	Not any
COD	2.25	0.1092	1:3;1:5			
TSS	4.51	0.0124	1:3;1:4;1:5	0.54	0.6648	Not any
R-PO <sub>4</sub>	0.19	0.9016	Not any			
Sulfide	2.11	0.1263	1:4			
TDS	1.29	0.3143	Not any	0.93	0.4551	Not any
NH <sub>3</sub> -N	2.97	0.0516	1:3;2:3;3:4;3:5	3.22	0.0614	1:2;2:3
Chromium	4.67	0.0109	1:4;1:3;2:4;2:5;3:4;3:5			
Total phosphorous				1.32	0.3130	Not any
pH	0.76	0.5654	Not any	0.61	0.6231	Not any
Temperature	21.22	0.0006	1:2;1:3;2:3	5.41	0.0138	1:2;2:3;3:4
<ol style="list-style-type: none"> <li><b>LSD</b> (Least Significant Difference) tests show the statistical significance of the difference between any two compared days.</li> <li><b>Not any</b>: no two compared days have statistically significant difference</li> <li><b>Numbers separated by columns</b>: indicate those days with statistically significant difference (e.g. 1:2 means day 1 and Day2 have statistically significant difference)</li> </ol>						

Appendix 3: Actual pollutant treatment efficiency of some individual treatment units

Parameter	Day	Day1	Day2	Day3	Day4	Day5	Average ± STD
	Operation						
BOD <sub>5</sub>	EQT	-128.2	-251.6	-225.0	-34.8	-27.6	-133.4 ± 104
	AT	-16.7	-25.9	-22.2	-115.4	-310.0	-98.0 ± 125.3
	SC	60.0	77.1	75.2	79.3	83.4	75.0 ± 8.9
BOD <sub>5</sub> *	EQT	47.7	73.7	-49.4	-	-	24.0 ± 64.9
	AT	-2042.9	-1006.7	-144.4	-	-	-1064.7 ± 950.5
	SC	77.7	76.5	64.1	-	-	72.8 ± 7.5
COD	EQT	-94.5	-403.2	-159.7	-54.2	2.0	-141.9 ± 157.5
	AT	-148.0	33.6	-138.6	-107.4	-277.0	-127.5 ± 111
	SC	89.1	74.9	91.1	88.8	93.3	87.4 ± 7.2
TSS	EQT		-826.6	-931.3	-396.8	-369.0	-630.9 ± 289.8
	AT		-232.1	-257.4	-337.7	-2643.5	-867.7 ± 1184.7
	SC		97.3	97.6	98.8	98.7	98.1 ± 0.8
TSS*	EQT	-329.8	-1191.3	-1821.4	-90.1	-	-858.2 ± 797.5
	AT	-4206.3	-948.7	-1240.9	-441.0	-	-1709.2 ± 1697.2
	SC	98.6	97.6	98.0	98.2	-	98.1 ± 0.4
Sulfide	EQT		14.9	-215.8	29.3	28.7	-35.7 ± 120.2
	AT		97.6	75.4	84.1	-225.0	8.0 ± 155.6
	SC		53.3	98.6	92.6	92.3	84.2 ± 20.8
R-PO <sub>4</sub>	EQT		-1224.4	-10.6	-143.0	-132.2	-377.6 ± 567.7
	AT		-84.3	-900.0	-387.5	-283.8	-413.9 ± 347.6
	SC		90.8	97.0	91.0	92.3	92.8 ± 2.9
TDS	EQT	-77.0	-61.3	-361.5	-111.5	-62.0	-134.7 ± 128.4
	AT	-8.5	3.2	8.5	-20.1	-3.2	-4.0 ± 11
	SC	15.4	-8.2	12.5	15.2	12.1	9.4 ± 10
TDS*	EQT	-82.9	-216.5	-380.5	-13.3	-	-173.3 ± 161.8
	AT	2.8	-11.7	15.0	10.2	-	4.1 ± 11.6
	SC	-2.6	-2.9	2.8	1.4	-	-0.3 ± 2.9
NH <sub>3</sub> -N	EQT	-87.3	-1998.8	-157.1	-44.5	-20.9	-461.7 ± 860.8
	AT	-147.1	10.7	9.1	5.9	-80.0	-40.3 ± 71
	SC	23.3	-34.9	15.0	0.0	12.4	3.2 ± 22.9
NH <sub>3</sub> -N*	EQT	-577.0	-60.9	-940.0	-187.9	-	-441.4 ± 398.4
	AT	-25.5	11.0	11.4	13.0	-	2.5 ± 18.7
	SC	4.6	11.1	3.2	13.4	-	8.1 ± 4.9
Chromium	EQT	-91.8	-482900.0	-861900.0	-21.4	-186.0	-269019.8 ± 391856.4
	AT	-2783.7	0.0	100.0	-4547.2	-4739.7	-2394.1 ± 2358.1
	SC	100.0	0.0	-1086000.0	100.0	95.8	-217140.8 ± 485707.0

EQT: Equalization tank; SC: Secondary clarifier; AT: Aeration tank of activated sludge S; \*Wet season values

**Appendix 4: Statistical significance (t-test) results of seasonal treatment efficiency variations**

Parameter	Unit	Null hypothesis: no seasonal difference			
		$\alpha = 0.05$	$\alpha = 0.1$	$\alpha = 0.2$	$\alpha = 0.5$
BOD <sub>5</sub>	PRT	A	A	A	A
	SCT	A	A	R	R
	PRSCT	A	A	A (border)	R
	Overall	A	A	A	R
TSS	PRT	A	A	A	A
	SCT	A	A	A	R
	PRSCT	A (border)	R	R	R
	Overall	A	A	A	R
TDS	PRT	A	A	A	A
	SCT	A	A	A	A
	PRSCT	A	A	A	A
	Overall	A	A	A	A
NH <sub>3</sub> -N	PRT	A	A	A	A
	SCT	A	A	R	R
	PRSCT	R	R	R	R
	Overall	A	A	A	A
<p>Two sample (of unequal variance) t-test was conducted for each parameter under each treatment unit</p> <p>Null hypothesis: no seasonal treatment variation exists</p> <p>A: null hypothesis accepted; R: null hypothesis rejected</p>					

**Appendix 5: Sample design expert software version 7.0.0 ANOVA and LSD test results for day-to-day pollutant removal efficiency difference significance for TSS**

**Dry season**

Response	1	TSS			
<b>ANOVA for selected factorial model</b>					
<b>Analysis of variance table [Classical sum of squares - Type II]</b>					
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Block	503.62	3	167.87		
Model	29.44	3	9.81	0.098	0.9592
<i>A-Day</i>	29.44	3	9.81	0.098	0.9592
Residual	901.83	9	100.20		
Cor Total	1434.88	15			

The "Model F-value" of 0.10 implies the model is not significant relative to the noise. There is 95.92 % chance that a "Model F-value" this large could occur due to noise.

**Treatment Means (Adjusted, If Necessary)**

	Estimated Mean	Standard Error
1-D2	87.85	5.01
2-D3	90.60	5.01
3-D4	91.03	5.01
4-D5	88.45	5.01

Mean Treatment	Difference	Standard df	t for H <sub>0</sub> Error	Coeff=0	Prob >  t
1 vs 2	-2.75	1	7.08	-0.39	0.7067
1 vs 3	-3.17	1	7.08	-0.45	0.6644
1 vs 4	-0.60	1	7.08	-0.085	0.9343
2 vs 3	-0.42	1	7.08	-0.060	0.9534
2 vs 4	2.15	1	7.08	0.30	0.7682
3 vs 4	2.58	1	7.08	0.36	0.7244

Values of "Prob > |t|" less than 0.0500 indicate the difference in the two treatment means is significant.

Values of "Prob > |t|" greater than 0.1000 indicate the difference in the two treatment means is not significant.

## Wet season

Response	1	TSS			
<b>ANOVA for selected factorial model</b>					
<b>Analysis of variance table [Classical sum of squares - Type II]</b>					
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Block	1666.58	3	555.53		
Model	66.68	3	22.23	0.082	0.9683
<i>A-Day</i>	66.68	3	22.23	0.082	0.9683
Residual	2445.43	9	271.71		
Cor Total	4178.68	15			

The "Model F-value" of 0.08 implies the model is not significant relative to the noise. There is a 96.83 % chance that a "Model F-value" this large could occur due to noise.

### **Treatment Means (Adjusted, If Necessary)**

	Estimated Mean	Standard Error
1-D1	81.78	8.24
2-D2	83.05	8.24
3-D3	82.90	8.24
4-D4	87.15	8.24

Mean Treatment	Difference	Standard df	t for H <sub>0</sub> Error	Coeff=0	Prob >  t
1 vs 2	-1.27	1	11.66	-0.11	0.9153
1 vs 3	-1.13	1	11.66	-0.097	0.9252
1 vs 4	-5.37	1	11.66	-0.46	0.6556
2 vs 3	0.15	1	11.66	0.013	0.9900
2 vs 4	-4.10	1	11.66	-0.35	0.7331
3 vs 4	-4.25	1	11.66	-0.36	0.7238

Values of "Prob > |t|" less than 0.0500 indicate the difference in the two treatment means is significant.

Values of "Prob > |t|" greater than 0.1000 indicate the difference in the two treatment means is not significant.

**Appendix 6: Sample design expert software version 7.0.0 treatment efficiency normal probability plot (normal plot of residuals) for TSS and NH<sub>3</sub>-N**

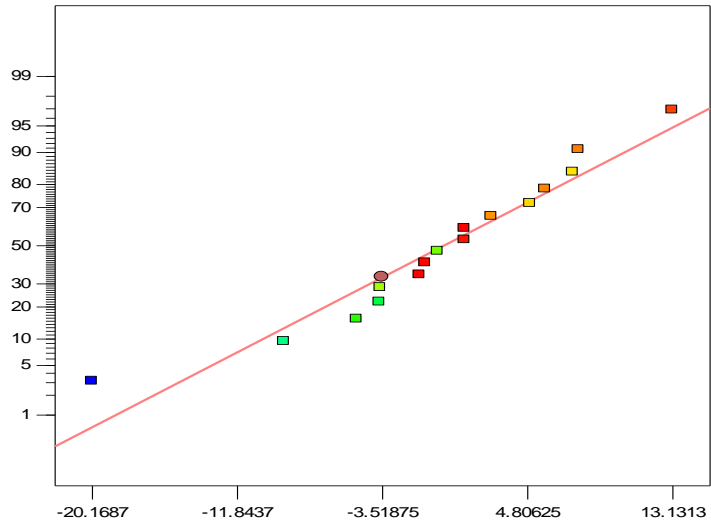
**Note: BOD<sub>5</sub>, COD, R-PO<sub>4</sub> and total phosphorous have a pattern more or less similar to that of TSS while TDS, chromium and sulfide have somehow similar pattern to that of NH<sub>3</sub>-N.**

**Dry season**

Design-Expert® Software  
TSS

Color points by value of  
TSS:  
98.8  
64.1

**Normal Plot of Residuals**

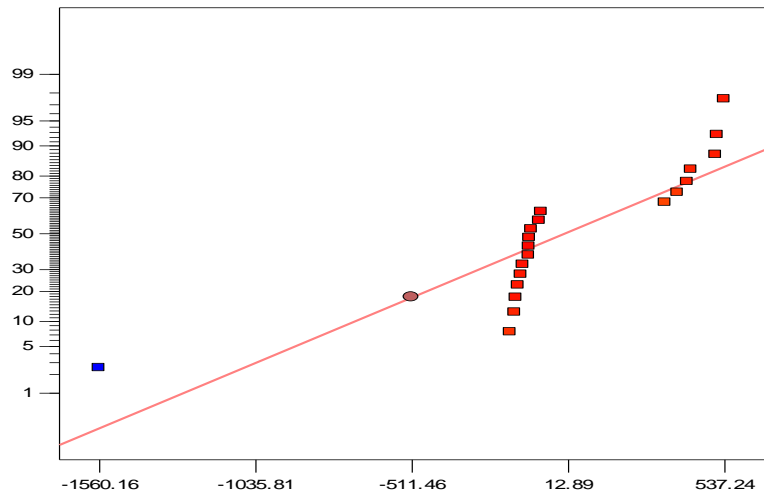


X: Residual  
Y: Normal % Probability

Design-Expert® Software  
NH<sub>3</sub>-N

Color points by value of  
NH<sub>3</sub>-N:  
41.4  
-2698.3

**Normal Plot of Residuals**



X: Residual  
Y: Normal % Probability

# Wet season

Design-Expert® Software  
TSS

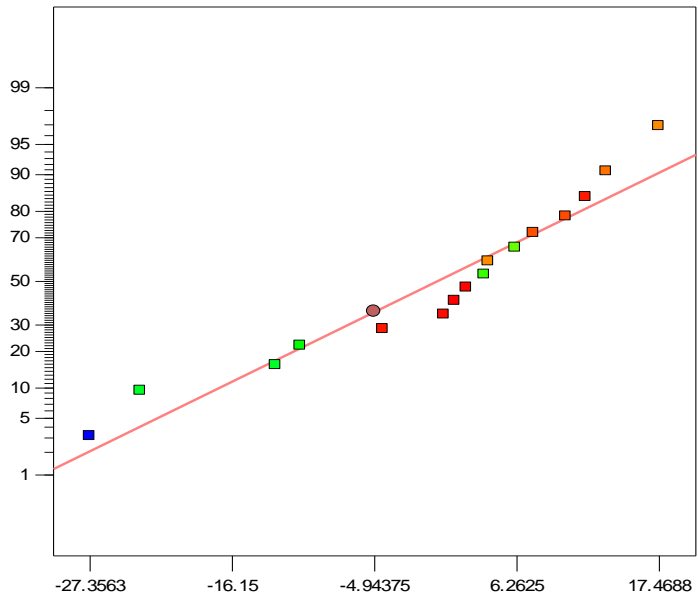
Color points by value of

TSS:

98.3

40.3

## Normal Plot of Residuals



X: Residual  
Y: Normal % Probability

Design-Expert® Software  
NH3-N

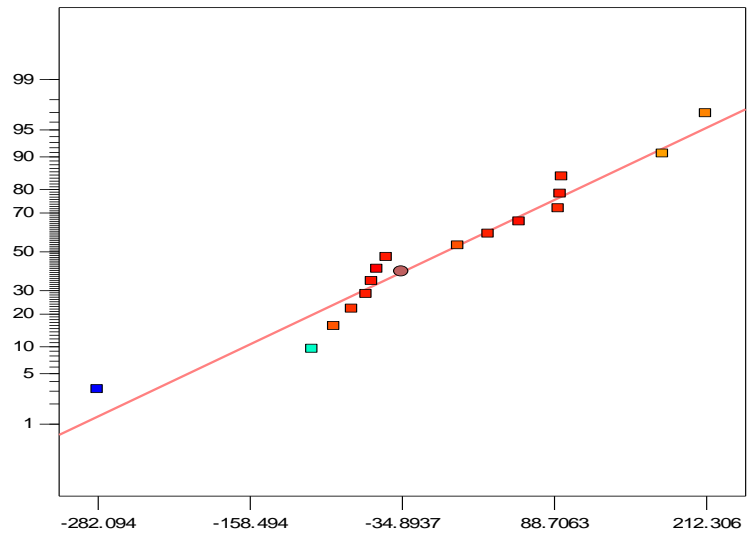
Color points by value of

NH3-N:

38.9

-700

## Normal Plot of Residuals



X: Residual  
Y: Normal % Probability

**Appendix 7: Comparison of actual effluent quality with national and international standards**

Parameter	Unit		Day 1	Day2	Day 3	Day 4	Day5	Average	
<b>BOD<sub>5</sub></b>	mg/l	AFEQ	112	156	164	116	136	136.8	
		AFEQ*	134	156	158	-	-	149.3	
		NS	200						
		WBS	50						
<b>COD</b>	mg/l	AFEQ	237	417	383	343	308	337.6	
		NS	500						
		WBS	250						
<b>TSS</b>	Mg/l	AFEQ	83.3	93.0	104.0	84.0	83.0	89.5	
		AFEQ*	114	147	151	116	-	132	
		NS/WBS	50						
<b>Sulfide</b>	mg/l	AFEQ	-	0.175	0.085	0.225	0.75	0.3	
		NS/WBS	1.0						
<b>TP</b>	mg/l	AFEQ*	2.6	4.8	2.8	7.7	-	4.4	
		NS	10						
		WBS	2						
<b>NH<sub>3</sub>-N</b>	mg/l	AFEQ	80.5	115.3	42.5	80	78.8	79.4	
		AFEQ*	168.8	180	150	145	-	161	
		NS	30						
		WBS	10						
<b>pH</b>	pH units	AFEQ	7.9	8.1	7.5	7.7	7.6	7.8	
		AFEQ*	7.7	7.8	7.9	8.0	-	7.8	
		NS/WBS	6-9						
<b>Temperature</b>	°C	AFEQ	-	-	18.0	16.8	19.1	18.0	
		AFEQ*	19.3	17.6	19.2	17.9	-	18.5	
		NS	40						
<p>1. <b>AFEQ</b>: Actual Final Effluent Quality (AFEQ: dry season; AFEQ* : wet season); <b>NS</b>: National Standard; <b>WBS</b>: World Bank Standard</p> <p>2. The shaded cells indicate that the national release standards are complied with (not exceeded)</p>									

**Appendix 8a: Secondary treatment technology evaluation weighting and score per indicator**

Criteria and technologies	Weighting (on a 0-1 scale)	Score per indicator (%)					Average score (%)
<b>Efficiency**</b>	<b>0.15</b>	I1	I2				
AS (extended aeration)		95	95				<b>95</b>
UASB		50	71				<b>61</b>
WSP		86	95				<b>91</b>
CW		71	29				<b>50</b>
<b>Reliability</b>	<b>0.17</b>	I1	I2	I3	I4	I5	
AS		50	70	60	50	40	<b>54</b>
UASB		70	60	40	70	60	<b>60</b>
WSP		80	80	60	85	80	<b>77</b>
CW		90	65	80	90	80	<b>81</b>
<b>Sustainability</b>	<b>0.18</b>	I1	I2				
✓ Social	<b>0.06</b>						
AS		50	50				<b>50</b>
UASB		75	75				<b>75</b>
WSB		85	80				<b>83</b>
CW		90	90				<b>90</b>
✓ Economic	<b>0.06</b>	I1	I2				
AS		20	50				<b>35</b>
UASB		65	40				<b>53</b>
WSP		70	50				<b>60</b>
CW		45	50				<b>48</b>
✓ Environmental	<b>0.06</b>	I1	I2	I3	I4		
AS		90	25	50	75		<b>60</b>
UASB		60	70	50	70		<b>63</b>
WSP		50	90	25	40		<b>51</b>
CW		70	90	75	50		<b>71</b>
<b>Cost</b>	<b>0.22</b>	I1	I2	I3			
AS		40	40	40			<b>40</b>
UASB		80	90	90			<b>87</b>
WSP		80	90	90			<b>87</b>
CW		85	95	95			<b>92</b>
<b>Ease-of-use</b>	<b>0.16</b>	<b>I1</b>	<b>I2</b>	<b>I3</b>			
AS		40	40	50			<b>43</b>
UASB		60	60	60			<b>60</b>
WSP		90	80	75			<b>82</b>
CW		70	90	90			<b>83</b>
<b>Land/space requirement</b>	<b>0.12</b>	I1	I2				
AS		85	80				<b>83</b>
UASB		90	80				<b>85</b>
WSP		50	50				<b>50</b>
CW		40	50				<b>45</b>

## **Appendix 8b: Description of wastewater treatment technology evaluation criteria indicators [30]**

### **1. Pollutant removal efficiency indicators:**

- I1: BOD/COD/TSS removal
- I2: Nutrient removal (Total Kjeldahl nitrogen)

### **2. Reliability indicators**

- I1: Possibility of high failure frequency of the whole plant or its components
- I2: Plant response to shock organic and hydraulic loadings (high or low loadings)
- I3: Plant response to toxic substances (e.g. biological reactor's response)
- I4: Possibility of high frequency of unplanned plant maintenance
- I5: The extent to which the above conditions affect effluent quality

### **3. Sustainability indicators**

#### **3.1. Social sustainability indicators**

- I1: Public acceptance of the plant operation
- I2: Public participation in plant operation and maintenance

#### **3.2. Economic sustainability indicators**

- I1: Resource such as energy recovery possibilities and other byproducts
- I2: Treated wastewater reuse possibilities in the industry or elsewhere

#### **3.3. Environmental sustainability indicators**

- I1: Air pollution (emission of odor, methane, hydrogen sulfide etc)
- I2: Noise pollution
- I3: Aesthetic pollution
- I4: Insect and other vector breeding possibilities

### **4. Cost**

- I1: Capital cost (plant construction and land costs)
- I2: Operational costs (personnel, administration, energy, chemicals, sludge management)
- I3: Maintenance costs (personnel, equipments)

### **5. Ease-of-use**

- I1: Ease of plant construction
- I2: Operational requirements (skill, personnel etc)
- I3: Maintenance requirements (frequency, skill, spare part, scheduling etc)

### **6. Land/space requirement**

- I1: Plant ecological footprint (total area required for the plant)
- I2: Requirement of land type (permeability, ground water presence)

**Appendix 9: Checklist/questionnaire for the physical observation and interview based data collection about the wastewater treatment plant under study**

1. Wastewater stream segregation practices (chrome, sulfide, other streams)
2. Energy source of the treatment plant for pumps, aeration, sludge scrappers (electric, fuel)
3. Power failure consequences in the treatment plant-wastewater bypassing of the treatment plant for direct release to the environment or there exists stand-by power
4. Screen-cleaning, maintenance and screenings management issues
5. Whether damaged component is there (sludge scrappers, pumps, aerators, pipelines)
6. Whether the treatment plant operates continuously-day and night (hours/day)
7. Whether the equalization tank is agitated continuously to avoid solid settling in the tank
8. Whether there is continuous dosing of coagulant ( $\text{FeSO}_4$ ) and flocculent (polyelectrolyte)
9. Sludge removal rates from primary/secondary clarifiers (per day/per week)
10. Whether flow meters are installed in the system
11. The issues of proper operation, volume and adequacy of sludge drying beds
12. Whether there is good housekeeping in the treatment plant area
13. Whether the system is covered (drains, tanks etc) to prevent it from negative consequences of the environment such as wind current, rainfall etc
14. Existence and status of filtration media and filtrate line in the sludge drying beds
15. The status of sludge recirculation line and pumping system in the activated sludge system
16. The status of the chrome recovery system (pipelines/pumps etc)

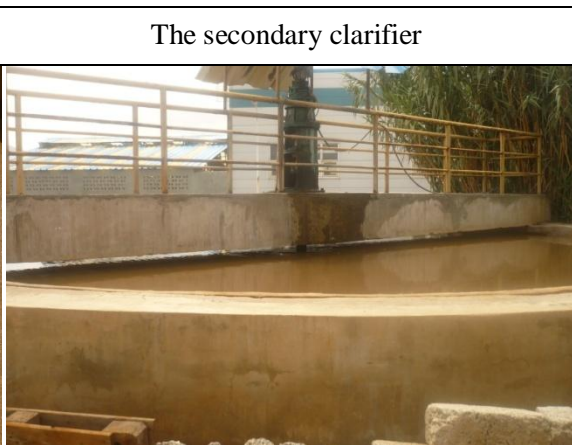
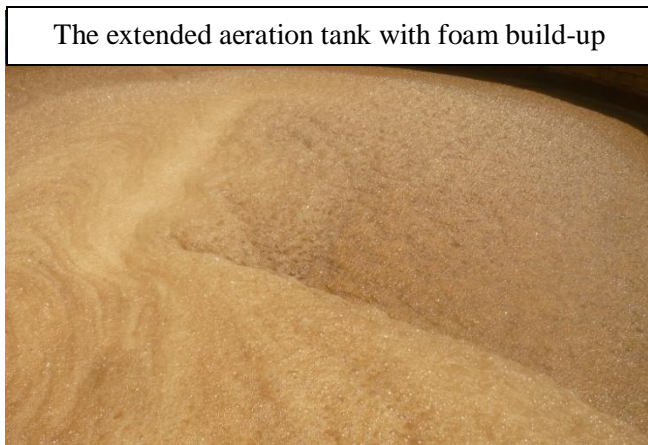
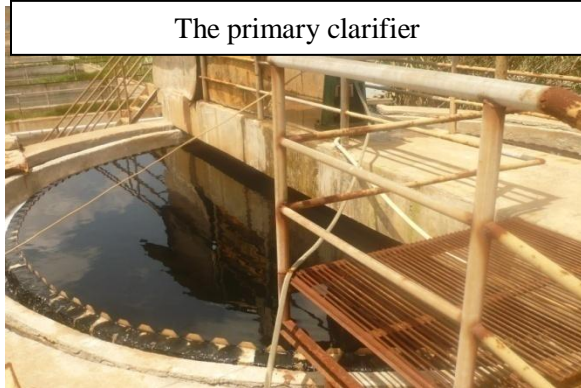
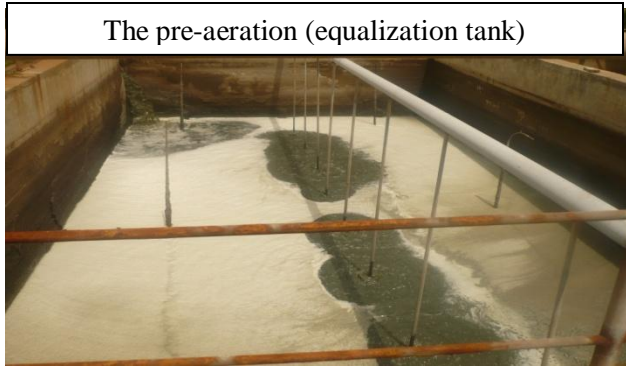
**Appendix 10: Checklist/questionnaire for the physical observation and interview based data collection about cleaner production practices in the industry**

1. Existence of good housekeeping in the production process
2. Chemical weighing and preparation practices (the existence of equipments such as beam balance; maintenance and calibration issues)
3. Green flesh or lime flesh practiced?
4. Where splitting happens (lime split/blue split after tanning or else)
5. The practice of hide classification/sorting upon arrival and proper de-dusting
6. Existence of regular/scheduled awareness raising/training on water/wastewater management and good operations (on how to trim, split, shave, weigh and prepare chemicals for recipe optimization)
7. Process chemical storage and handling practices in the industry
8. Source of water in the industry
9. The practice of using treated water for some purposes in the industry
10. Wastage of water between production stages
11. Process water or liquor reuse/recycling practices in new bathing operations
12. Existence of wasteful production processes in relation to wastewater generation

## Appendix 11: General data collection checklist/questionnaire

Issues	Physical observation	Interview
<b>1. General information</b>		
<b>About the industry:</b>		
• Number of employees		
• Working days per week/year; working hours/day (on average)		
• Main products		
• Daily soaking and production capacity		
• Daily process water usage and wastewater production (m <sup>3</sup> )		
<b>2. Treatment plant efficiency determiners</b>		
✓ <b>Operational issues (design-operation compatibility)</b>		
Treatment chemical usage (type; dose)		
Treatment process monitoring and control		
• Preliminary treatment (screen cleaning rate, mixing in equalization etc)		
• Primary treatment (HLR, OLR, pH, Temp etc)		
• Secondary (HLR, OLR, sludge age, F/M, MLSS etc)		
Primary/secondary clarifier sludge removal rate		
Operator/staff knowledge/skill		
✓ <b>Maintenance issues</b>		
Maintenance scheduling and recording		
Availability of required equipment/accessory		
Skilled manpower for maintenance		
Allocated resource for maintenance		
✓ <b>Administration issues</b>		
Level of treatment plant staffing and motivation		
Organization/industrial environmental policy/		
Operational/maintenance record keeping		
Financial /facility support for the plant		
Other administrative support		
✓ <b>Design issues/deficiencies</b>		
Preliminary treatment; primary treatment; secondary treatment; sludge management		

**Appendix 12: Pictures of some major components of the actual wastewater treatment plant**



**Appendix 13: Pictures of poor housekeeping and solid waste management in the vicinity of the actual treatment plant**

Openly left screenings near screens



Chromium precipitation plant



Openly damped saved hair




Chromium sludge openly damped in the compound

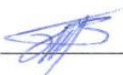


## Declaration

I declare that this thesis entitled "Technology, Performance and Design Evaluation of Tannery Wastewater Treatment Plants in the vicinity of Addis Ababa, Ethiopia (The Case of China Africa Tannery)" is my original work and has not previously been submitted in any form for another degree, diploma or an award at any university or other institution of the tertiary education. Whenever contributions of others are involved, every effort was made to indicate this clearly, with due reference to the literature and discussions. All reference materials contained therein have been acknowledged.

Name: Aberra Birhanu Tsegaye  
Signature:   
Place of Submission: Addis Ababa, Ethiopia  
Date of submission: 25/12/14

This thesis has been submitted to the university with my approval as the university advisor.

Name: Dr. Tassisa Kebea  
Signature:   
Date: 25/12/14