

**QUANTIFICATION OF Cr⁺³, Cr⁺⁶, TOTAL CHROMIUM, AND
PHYSICOCHEMICAL CHARACTERISTICS OF TANNERY**

WASTEWATER EFFLUENTS:

A case study of Bata Tanneries, Kenya

BY

MARITIM GEOFFREY KIPLANGAT

**A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE AWARD OF DEGREE OF MASTER OF
SCIENCE IN ANALYTICAL CHEMISTRY, SCHOOL OF SCIENCE,
UNIVERSITY OF ELDORET, KENYA**

OCTOBER, 2022

DECLARATION

Declaration by the Student

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

No part of this thesis may be reproduced without the prior written permission of the author and /or University of Eldoret.

Maritim Geoffrey Kiplangat

SC/PGC/18/2012

Date

Declaration by the Supervisors

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

Prof. Pius Kipkemboi

Department of Chemistry and Biochemistry,
University of Eldoret, Kenya.

Date

Prof. Lusweti Kituyi

Department of Chemistry and Biochemistry,
University of Eldoret, Kenya

Date

DEDICATION

I dedicate this thesis to my wife Lily Cherotich Chepkoech, my sons Arnold and Alvan, my late father Alexander Bii and my mother Sarah Bii.

ABSTRACT

Kenya's tanning industry is a key economic sector. Leather processing generates toxic effluents depending on the process. Bata leather industries in Kenya have been discharging effluent to nearby rivers leading to human and environmental pollution. The current study sought to carry out quantification of chromium and physicochemical characteristics of tannery wastewater effluents: "A case study of Bata Tanneries, Kenya". Using grab sampler, water samples were obtained from four sites (S1 – Pre-tanning, S2 – Tanning, S3 – Post-tanning, and S4 – Drainage to the river). The samples were transported to the Tea Research Foundation of Kenya in a cold box for chemical analysis. Bis(salicylaldehyde) orthophenylenediamine reagent was used to complex Cr⁶⁺ in non-ionic micellar media to determine the concentration of Cr⁶⁺. Double beam uv/vis spectrophotometer (perkinelmer) was used in the analysis. Physicochemical parameters were determined from the collected samples and results were compared with NEMA, KEBS and WHO set standards. Total Cr level was analysed using inductively coupled plasma atomic emission spectrometry (ICP-AES). The mean range levels obtained from (S1, S2, S3 and S4) Bata leather tanneries in Kenya were as follows; total dissolved solids (TDS) 137.70 and 270.00 mg/L, DO 8.40 and 10.60 mg/L, pH concentrations ranged between 1.52 and 8.20. EC 1348.8 and 1385.00 mS/cm at S3, temperature 22.70 and 27.90°C, biological oxygen demand (BOD) 3141.20 and 5477.70 mg/L, total suspended solids (TSS) 148.00 mg/L to 284.00 mg/L, total solids (TS) 286.00 and 554.00 mg/L. Chemical oxygen demand (COD) 5986.70 to 9093.20 mg/L, colour (Pt-Co) 488.50 and 787.20 Pt-Co. The mean levels of total chromium, Cr³⁺ and Cr⁶⁺ in effluent samples were 573.71 and 72.370, 12.08 and 1.37, and 560.38 and 70.69 mg/L, respectively. It is evident from the results of this study that high percentage of 98.05 ± 0.15 % from the initial concentration, added and found concentration of 2.00 ± 0.00, 2 ± 0.00 and 2.25 ± 0.31, respectively. All values of physicochemical parameters exceeded WHO standards except for temperature which was within the range. In comparison with the two methods, UV spectroscopic did best in comparison with ICP-AES in a non-ionic micellar media though with no significant difference (t = 0.2222, p= 0.8350). The ministry of Environment should therefore enforce the law concerning water pollution and prosecute those who are found culpable. Polluter pay principle should be applied to the company.

TABLE OF CONTENTS

DECLARATION	ii
DEDICATION	iii
ABSTRACT.....	iv
TABLE OF CONTENTS.....	v
LIST OF FIGURES	ix
LIST OF TABLES	x
LIST OF ACRONYMS AND ABBREVIATIONS	xi
ACKNOWLEDGEMENT	xiii
CHAPTER ONE	1
INTRODUCTION.....	1
1.1 Background Information.....	1
1.2 Statement of the Problem.....	2
1.3 Justification	5
1.4 Objectives of the Study.....	8
1.4.1 General Objective	8
1.4.2 Specific Objectives	8
1.4.3 Research Hypothesis.....	8
1.5 Significance of the Study	9
1.6 Scope of the Study	9
CHAPTER TWO	10
LITERATURE REVIEW	10
2.1 Historical Developments of Tanning	10
2.2 Tanning Industry: A Global Outlook.....	10
2.3 Leather Industry in Kenya	10
2.4 Importance of Chromium in Tanning Industry	12
2.4.1 Chromium Compounds and their Toxicity	13
2.4.2 Chrome ³⁺ (Trivalent Chrome, Chrome III).....	13
2.4.3 Chrome ⁶⁺ (Hexavalent Chrome).....	14
2.5 The Tanning Process.....	14
2.5.1 Soaking	14
2.5.2 Fleshing and Trimming.....	15
2.5.3 Bating.....	15

2.5.4 Pickling	15
2.5.5 Tanning Operations.....	15
2.5.6 Chrome Tanning	17
2.6 Post-Tanning Operations	17
2.6.1 Pre-Tanning.....	19
2.6.2 Tanning	19
2.6.3 Selecting.....	19
2.6.4 Dressing	20
2.6.5 Finishing	20
2.7 Tanneries as a Source of Pollutants	21
2.7.1 Emissions from the Tanning Process.....	21
2.7.2 Organic Matter (BOD).....	22
2.7.3 Nitrogen	23
2.7.4 Sulphides (S ²⁻).....	24
2.7.5 Fat and Oils	24
2.8 Tannery Effluents Treatment	25
2.8.1 Mechanical Treatment	25
2.8.2 Effluent Treatment.....	26
2.9 Post Purification.....	26
2.9.1 Biochemical Treatment.....	26
2.9.1.2 Anaerobic Treatment	27
2.10 Instrumentation	28
2.10.1 UV-Visible Spectrophotometer	28
2.10.2 Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).....	29
2.10.3 Strengths of ICP-AES	30
2.10.4 Limitations of ICP-AES.....	30
2.11 Related Studies.....	31
CHAPTER THREE	34
MATERIALS AND METHODS	34
3.1 Study Area	34
3.2 Wastewater Sampling	36
3.3 Sample Preservation.....	36
3.4 Laboratory Tests	37
3.4.1 Preparation of Standard Solutions for UV-Visible Spectroscopy.....	37

3.4.2 Calibration Curve for Chromium.....	37
3.4.3 Determination of Cr ⁶⁺ And Cr ³⁺ Ions Using (BSOPD) Complex in Non-Ionic Micellar Media.....	38
3.4.4 Method Validation	39
3.4.5 Procedure	40
3.6 Analysis of Physicochemical Parameters of Treated and Untreated Tannery Effluent Samples.....	40
3.7 Physicochemical Parameters and Analytical Methods	41
3.8.1 DO (Dissolved Oxygen)	41
3.8.2 Biochemical Oxygen Demand Determination (BOD ₅).....	42
3.8.3 COD Determination	44
3.8.4 pH Determination.....	46
3.8.5 TSS (Total Suspended Solids)	47
3.8.6 Total Dissolved Solids (TDS).....	48
3.8.7 Colour	49
3.8.8 Temperature	50
3.8.9 Electrical Conductivity (EC).....	50
3.8 Data Analysis	51
CHAPTER FOUR.....	53
RESULTS	53
4.1 Concentration of Cr ³⁺ and Cr ⁶⁺ in Bata Tannery Effluents using a Simple and Rapid Spectroscopic Method and ICP-AES in Non-Ionic Micellar Media.....	53
4.2 The Levels of Physicochemical Parameters in the Samples of Tannery Effluent from Bata Tannery at Different Sites.....	54
4.2.1 Dissolved Oxygen (DO)	54
4.2.2 Biological Oxygen Demand (BOD ₅)	54
4.2.3 Chemical Oxygen Demand (COD).....	55
4.2.4 pH.....	57
4.2.5 Total Suspended Solids (TSS)	58
4.2.6 Total Dissolved Solids (TDS).....	59
4.2.7 Colour (TCU).....	59
4.2.8 Temperature (°C)	60
4.2.9 Electrical Conductivity (EC).....	61
4.2.10 Total Solids	62

4.2.11 Chromium Levels.....	63
4.3 Recovery Tests.....	65
CHAPTER FIVE	69
DISCUSSIONS.....	69
5.1 Physicochemical Characteristics.....	69
5.1.1 Total Dissolved Solids (TDS).....	69
5.1.2 Dissolved Oxygen (DO)	69
5.1.3 pH.....	70
5.1.4 Electrical Conductivity (EC).....	70
5.1.5 Temperature (⁰ C)	71
5.1.6 Biochemical Oxygen Demand (BOD)	71
5.1.7 Total Suspended Solids (TSS)	72
5.1.8 Total Solids (TS).....	72
5.1.9 Chemical Oxygen Demand (COD).....	73
5.1.10 Colour (Pt-Co)	73
5.1.11 Chromium Levels (Cr).....	74
CHAPTER SIX	75
CONCLUSION AND RECOMMENDATIONS.....	75
6.1 Conclusions.....	75
6.2 Recommendations.....	76
REFERENCES.....	77
APPENDICES.....	93
Appendix I: Process Flowchart for Tannery and Associated Pollution.....	93
Appendix II: Chemical Properties of Water	95
Appendix III: Physical Properties of Water Comparison with WHO Standards.....	97
Appendix IV: Similarity Report.....	98

LIST OF FIGURES

Figure 2.1: Cr-O-Cr bridges in tanning.....	12
Figure 2.2: Complexion Between the Oxo Compound of Collagen Chains in Skins..	13
Figure 2.3: The Flow Chart Summary Of Tanning Operations	18
Figure 2.4: Schematic Diagram of Double Beam UV-VIS Spectrophotometer	28
Figure 2.5: Schematic Diagram of ICP- AES	29
Figure 3.1: The Map Showing the Location of the Tannery and The Sampling Points	35
Figure 3.1: Synthesis of BIS (salicylaldehyde) Orthophenylenediamine (BSOPD)..	39
Figure 4.1: Calibration curve of Cr ⁶⁺	53
Figure 4.2: The Mean Levels of Dissolved Oxygen	54
Figure 4.3: The Mean Levels of Biological Oxygen Demand.....	55
Figure 4.4: The Mean Values of Chemical Oxygen Demand.....	56
Figure 4.5: The Mean Levels of pH Levels	57
Figure 4.6: The Mean Levels of Total Suspended Solids.....	58
Figure 4.7: The Mean Levels of Total Dissolved Solids (TDS).....	59
Figure 4.8: The Mean Levels of Colour (TCU).....	60
Figure 4.9: The Mean Levels of Temperature (°C).....	61
Figure 4.10: The Mean Levels of Electrical Conductivity (EC).....	62
Figure 4.11: The Mean Levels of Total Solids	63
Figure 4.12: The mean concentration of Cr ⁶⁺ and Cr ³⁺ as Obtained by UV Spectroscopic Method.....	64
Figure 4.13: The Mean Concentration of Total Chromium, Cr ⁶⁺ and Cr ³⁺ as Obtained by ICP- AES in A Non-Ionic Micellar Media	65
Figure 4.14: Recovery Tests by UV Spectroscopic Method.....	66
Figure 4.15: Recovery Tests by ICP- AES in a Non-Ionic Micellar Media	67

LIST OF TABLES

Table 2.1: Estimated total production of hides and skins in million (Wangui, 2016).	11
Table 2.2: Chemicals usually Used in the Entire Tanning Process	16
Table 3.1: The Working Concentration for Chromium (Cr^{+6}).....	38
Table 3.2 Distribution of Total Cr, Cr^{6+} and Cr^{3+} Concentration (Mean (Mg/L) at Four Different Sites of Bata.	40
Table 3.3 Working Standards for Colour.....	50
Table 4.1: Spearman's Correlation	68

LIST OF ACRONYMS AND ABBREVIATIONS

APHA	: American Public Health Association
ASALS	: Arid and Semi-Arid Lands
ATSDR	: Agency for Toxic Substances and Disease Registry
BOD	: Biological Oxygen Demand
BSOPD	: Bis(salicylaldehyde)orthophenylenediamine
CNS	: Central Nervous System
COD	: Chemical Oxygen Demand
COTANCE	: Confederation of National of Associations of Tanners and Dresser
DNA	: Deoxyribonucleic Acid
DO	: Dissolved oxygen
DOC	: Dissolved Organic Carbon
EDTA	: Ethylenediaminetetraacetic acid
FAAS	: Flame Atomic Absorption Spectroscopy
FAO	: Food and Agriculture Organization
FAS	: Ferrous ammonium sulfates
GDP	: Gross Domestic Product
GOK	: Government of Kenya
ICP-AES	: Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	: Inductively Coupled Plasma Mass Spectrometry
ITC	: International Trade Centre
KEBS	: Kenya Bureau of standards
MPB	: Methane producing bacteria
NEMA	: National Environmental Management Agency

RNA	: Ribonucleic Acid
SAB	: Syntrophic Acetogenic Bacteria
SRB	: Sulfate-Reducing Bacteria
TDS	: Total Dissolved Solids
TS	: Total solids
TSS	: Total soluble solids
UNEP	: United Nations Environmental Program
UNIDO	: United Nations Industrial Development Organization
USAB	: up flow anaerobic sludge blanket reactor
VFA	: Volatile Fatty Acids
WDXRF	: Wavelength Dispersive X-ray Fluorescence
WHO	: World Health Organization?

ACKNOWLEDGEMENT

My deepest gratitude to God who gave me good health and strength during this project. It is pertinent to thank my supervisors, Prof. Pius Kipkemboi and Prof. Lusweti Kituyi who gave me great encouragement, straight talk, professional advice in their fields and guiding comments despite their busy schedules. I am indebted to the entire Laboratory staff of Tea Research Foundation of Kenya, Kericho who availed me facilities to use. Many thanks go to both my parents for providing insurmountable financial assistance for which it would not have been possible to achieve this goal. My special thanks go to my cherished wife for her lots of encouragements and support in the fulfilment of this research. Finally, my sons Arnold and Alva who gave me determination to carry on.

CHAPTER ONE

INTRODUCTION

1.1 Background Information

Various industrial processes often result in the production of industrial waste. Consequently, the quantity and toxicity of waste produced by industrial activities vary (Alvarez-Bernal *et al.*, 2006). Tanning effluents are among the most harmful industrial wastes. Tanneries are the principal source of chromium pollution in aquatic environments. Toxic surface water and sediments may be contaminated if wastewater from tanneries is not effectively handled (Apaydin *et al.*, 2009). The tannery sector in East Africa is a key economic contributor and provides significant employment (Cassano *et al.*, 2009).

Based on the leather process, tanneries generate substantial amounts of solid waste and effluent containing highly harmful substances (Nyabaro *et al.*, 2013). These chemicals make animal skin dye-resistant and boost its mechanical and hydrothermal resilience. Because most organic wastes are resistant to chemical and biological treatment, they contribute to environmental contamination and health concerns (Srivastava *et al.*, 2018). Due to the vast variety of chemical compounds added in various amounts, treating this solid waste and wastewater is challenging (Kurt *et al.*, 2007). Because almost all leather-producing countries have strict environmental laws, efforts have been made to treat polluted ecosystems (Schrank *et al.*, 2004; Hasegawa *et al.*, 2011).

Literature describes numerous methods for treating tannery effluents (Dawood & Sen, 2014) with Coagulation and adsorption being the most frequently used physical chemical processes for the removal of coloured effluents (Song *et al.*, 2004). However, these treatments do not resolve the issue because contaminants are transferred from one

phase to the next. As a result, tannery effluents are disposed of with pollutants. Due to transformation of some of the harmful components from one state to another, it becomes hard for the conventional analytical methods to detect them (Saxena *et al.*, 2016). Among these are the heavy metals especially (Cr) which is easily oxidized from Cr^{3+} to Cr^{6+} . Only few if any methods can effectively quantify the ions in certain oxidation state. This study therefore determined the concentration of Cr^{3+} and Cr^{6+} ions and levels of physicochemical parameters in effluents from Bata tannery.

1.2 Statement of the Problem

There have been complaints related to factory operations from people living from the surroundings. There is application Cr^{6+} and its related compound in Bata tannery that may cause an effect on human and fauna (Mwonderu, Ombui & Onyuka, 2020). It can cause long term effects like cancer in human beings. Hexavalent chromium has been demonstrated to have several adverse effects ranging from irritation to cancer. It cannot be determined alone without the determination of Cr^{3+} ions. It was therefore necessary to determine the levels of chromium because of the known effects of chromium using simple and rapid UV - spectroscopic method in non-ionic micellar medium. There is possibility of the industry discharging the effluents of the Ndurumo river without proper treatment. Water from this river is used for irrigation and for domestic purposes. Determination of physiochemical parameters was done to assess the level of pollution on the river.

Since independence on 12 December 1963, Kenya has prioritized industrialization (Mwinyihija and Killham, 2006). Kenya's tanning business is one of the largest in East and Central Africa (Muchie, 2001). The main tanneries get raw materials from several infrastructure entities. These facilities in Kenya have led to the processing of hides and

skins from neighboring countries, with tanning enterprises expanding to meet demand (Onyango *et al.*, 2019). The tanning process requires a lot of water and generates 90% effluent. Tannery effluents comprise chrome salts, sodium chloride, heavy metals, sulphate, organic and inorganic pollutants, physiologically oxidizable tanning materials, and putrefying floating detritus. Untreated or inadequately treated contaminants from these industries harm local health, cattle, wetland, and vegetable crops (Chowdhury *et al.*, 2015).

Chromium is a leather tanning/softening ingredient in tanneries (Tünay *et al.*, 2006). Determining an element's redox state in solution affects its toxicity. Hexavalent and trivalent chromium are stable oxidation states. In nature, chromium is trivalent, not hexavalent (Ashwini, 2009). Once tanning effluent isn't treated, it can pollute ground water as Cr^{3+} is oxidized to creating high dangers to the environment and people. Determining the chromium concentration in tanning wastewater was deemed necessary. The lethality, mobility, and biodistribution of Cr are determined by its chemical forms, Cr^{3+} and Cr^{6+} (Barrera, 2006)

Cr^{6+} is harmful to biological systems, and occupational exposure leads to clinical issues (Ashwini, 2009). Hexavalent chromium is hazardous to humans. Hexavalent chromium is a cancer-causing health danger (Machado, 2002). Inhaling and retaining Cr^{6+} can cause nasal septum protrusion, asthma, bronchitis, larynx and liver inflammation, and broncogenic cancer (Barrera, 2006). Cr^{6+} compounds can cause dermatitis, dermal necrosis, and dermal corrosion. Cr^{6+} is hazardous due to its oxidising and free radical-forming properties.

According to (Baysal *et al.*, 2013), Cr^{3+} and Cr^{6+} are biologically important. For toxicological and environmental reasons, Cr^{3+} and Cr^{6+} must be examined individually. Chromium is like bound lead. Chromium does not bioaccumulate and does not rise in food chains. A 50-200 g/day of hexavalent chromium is required for men. Insulin metabolism requires chromium. Animals need it, but it's unknown if plants do; all plants possess it. Cr^{3+} is less poisonous than Cr^{6+} . Hexavalent chromium causes inflammation and cancer.

Hexavalent chromium is more hazardous than trivalent chromium. Human activities cause almost all environmental Cr^{6+} (Mishra & Bharagava, 2016). High quantities of chromium affect aquatic organisms with 0.01 mg Cr^{6+} /L affects *Daphnia* reproduction (Baysal *et al.*, 2013). Aquatic creatures passively absorb hexavalent chromium. Several aquatic and terrestrial invertebrates have a fatal chromium threshold of 0.05 mg/L during Cr^{6+} to Cr^{3+} cell reduction (Blázquez, 2009; Calero *et al.*, 2016).

There exist several analytical methods of determining the concentration of total Cr in wastewaters. Atomic spectrometric techniques: Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), Radiochemical-Neutron Activation Analysis (NAA), Graphite Furnace Atomic Absorption Spectrometry (GFAAS), and Inductively Coupled Plasma Mass Spectrometry (ICP-MS), and x-ray, that is wavelength dispersive X-ray fluorescence (WDXRF) spectrometry (Yun *et al.*, 2001; Blázquez, 2009; Liang & Sang, 2008). However, the methods outlined here are incapable of distinguishing individual species of chromium that is the oxidation state. Equally they are expensive methods to carry out. Therefore, this study aimed at employing a new effective method of determining the concentration of Cr^{6+} and Cr^{3+} in industrial wastewaters from Bata tannery in Kenya. In this study, a simple, sensitive, selective, and rapid procedure for

the determination of chromium in tannery wastewater and agriculture samples was employed where large excess quantities (> 50) of cations, anions and complexing agents do not interfere in the determination.

1.3 Justification

In September 2015, 193 developing and developed countries adopted the Sustainable Development Goals (SDG) (Resolution, 2015). The UN set 17 SDGs to give everyone a better, more sustainable future, and achieving them is a global goal. Pollution threatens air, water, soil, and human growth. UN SDGs emphasize at minimizing pollution. SDG 3.9 aims to reduce fatalities and diseases from hazardous chemicals, air, water, and soil pollution by 2030. SDG 9.4 focuses on clean tech and industry (Wang *et al.*, 2022). Kenya Vision 2030's social pillar strives to offer a clean, secure, and sustainable environment by 2030 (Radeny *et al.*, 2020; Sempele, 2017). Therefore, it is necessary to monitor industrial effluents to ensure that no health-threatening substances are released into the environment.

The lack of proper and efficient way of determination of the concentration of Cr^{3+} and Cr^{6+} in industrial wastewater can result in the disposal of the wastewaters with high levels of these dangerous ions and thus cause deleterious effects on the ecosystem, human and animals (Bielicka *et al.*, 2005). The already existing methods of determination of concentrations of Cr in industrial wastewaters cannot effectively determine the exact levels of Cr^{3+} and/or Cr^{6+} (Rakhunde *et al.*, 2012). This research aimed at employing a new method capable of overcoming the limitations in the already existing methods. The method used bis(salicylaldehyde) orthophenylenediamine (BSOPD) in non-ionic micellar media.

BSOPD is produced by condensing o-phenylenediamine with salicylaldehyde (Memon *et al.*, 2014). These chemicals are employed in optical, electrochemical, and chromatographic sensors to improve selectivity and sensitivity. BSOPD generates stable metal compounds (Uddin & Salam, 2014). Bis(salicylaldehyde) phenylenedamine was employed to detect Cr ions (Uddin *et al.*, 2020). After human societies industrialised, pollution became a severe environmental hazard (Agudelo-Vera *et al.*, 2011). It has harmed air, land, and water. Ineffective wastewater treatment plant operations and management standards decrease the water quality of Nairobi's River Ndurumo.

A holistic methodology was needed to study the pollution loads of industrial wastewater discharge into rivers. The study sought to analyze contamination loads in Bata Company effluents based on pH, temperature, BOD, COD, TDS, TSS, and colour, and compare actual wastewater pollution loads with national and international standards.

In September 2015, 193 countries, developing and developed countries adopted the Sustainable Development Goals (SDG) (Resolution, 2015). The UN set 17 SDGs to give everyone a better, more sustainable future, and achieving them is a global goal. Pollution threatens air, water, soil, and human growth. UN SDGs emphasize at minimizing pollution. SDG 3.9 aims to reduce fatalities and diseases from hazardous chemicals, air, water, and soil pollution by 2030. SDG 9.4 focuses on clean tech and industry (Wang *et al.*, 2022). Kenya Vision 2030's social pillar strives to offer a clean, secure, and sustainable environment by 2030 (Radeny *et al.*, 2020; Sempele, 2017). Therefore, it is necessary to monitor industrial pollution to ensure that no health-threatening substances are released into the environment.

The lack of proper and efficient way of determination of the concentration of Cr^{3+} and Cr^{6+} in industrial wastewater can result in the disposal of the wastewaters with high levels of these dangerous ions and thus cause deleterious effects on the ecosystem, human and animals (Bielicka *et al.*, 2005). The already existing methods of determination of concentrations of Cr in industrial wastewaters cannot effectively determine the exact levels of Cr^{3+} and/or Cr^{6+} (Rakhunde *et al.*, 2012). This research aimed at employing a new method capable of overcoming the limitations in the already existing methods. The method used bis(salicylaldehyde) orthophenylenediamine (BSOPD) in non-ionic micellar media. BSOPD has been used to complex Cr^{6+} in non-ionic micellar media (Memon *et al.*, 2014).

BSOPD is produced by condensing o-phenylenediamine with salicylaldehyde (Memon *et al.*, 2014). These chemicals are employed in optical, electrochemical, and chromatographic sensors to improve selectivity and sensitivity. BSOPD generates stable metal compounds (Uddin & Salam, 2014). Bis(salicylaldehyde) phenylenedamine was employed to detect Cr ions (Uddin *et al.*, 2020). After human societies industrialised, pollution became a severe environmental hazard (Agudelo-Vera *et al.*, 2011). It has harmed air, land, and water. Ineffective wastewater treatment plant operations and management standards decrease the water quality of Nairobi's River Ndurumo.

A holistic methodology was needed to study the environmental effects of industrial wastewater discharge into rivers. Analyzing water quality metrics helped determine the performance of wastewater treatment plants, monitor, and regulate water quality degradation. Determining River Ndurumo water pollution loads generated by Bata tannery is a necessity for rational decision-making and river management. The study also sought to analyze contamination loads in Bata Company effluents based on pH,

temperature, BOD, COD, TDS, TSS, and colour, and compare actual wastewater pollution loads with national and international standards.

1.4 Objectives of the Study

1.4.1 General Objective

To determine the concentration of Cr^{3+} , Cr^{6+} and total chromium ions in the samples of tannery effluent from Bata tannery at different sites using a simple and rapid spectroscopic method in non-ionic micellar media.

1.4.2 Specific Objectives

- i. To determine the concentration of Cr^{3+} , Cr^{6+} and total chromium in Bata Tannery effluents.
- ii. To assess the level of pollution loading on River Ndurumo by analyzing the physicochemical parameters of treated and untreated tannery effluent samples.
- iii. To determine the recovery test of environmental waters of effluents by Uv-visible spectroscopic method and ICP-AES.

1.4.3 Research Hypothesis

- i. There is no known concentration of Cr^{3+} , Cr^{6+} and total chromium in Bata Tannery effluents.
- ii. There is no difference between treated and untreated tannery effluent samples on River Ndurumo.
- iii. There is no difference in recovery test of environmental waters of when using UV and ICP-AES methods.

1.5 Significance of the Study

The aim of this research was threefold: one was to provide a simple, sensitive, versatile, precise, and affordable UV-Vis spectroscopic method for monitoring trace levels of chromium ions in environmental effluents in a developing country like Kenya. Secondly, physicochemical parameters can help establish sewage treatment plant effectiveness, evaluate, and control river Ndurumo water quality degradation. The study also compared actual wastewater pollution loads with KEBS, NEMA and WHO tannery effluent samples. Thirdly was to determine the recovery test of environmental waters of effluents by Uv-visible spectroscopic and ICP-AES methods.

1.6 Scope of the Study

The study determined the concentrations of Cr^{3+} , Cr^{6+} and total Cr in the samples of tannery effluent from BATA company and seven salient physicochemical parameters namely pH, temperature, BOD, COD, TDS, TSS and colour. The study also determined the recovery test of environmental waters of effluents by Uv-visible spectroscopic method and ICP-AES.

The study used samples collected from Bata tannery, Limuru town in Kenya.

CHAPTER TWO

LITERATURE REVIEW

2.1 Historical Developments of Tanning

Tanned hides and skins become leather (Hashmi *et al.*, 2017). Tanners are second-oldest. Ancients thought tannery was harmful (Nyabaro *et al.*, 2013). The leather business makes many products from one of the country's greatest organic fibers (Heideman, 2005). The tanning industry is sometimes critiqued for ecological reasons, but disregarding desiccated animal skins is more harmful (UNIDO).

2.2 Tanning Industry: A Global Outlook

Leather is a worldwide famous product with growing demand (Dhiman & Mukherjee, 2021). The leather industry is worth over \$70 billion each year. With developing countries generating more than 60% of global leather, or 18 billion square feet. Leather footwear uses over 65% of the world's leather manufacturing (Zywicki *et al.*, 2002). Its expansion is in developing and newly industrialised countries, not developed ones. Solid waste and wastewater treatment aren't modern in emerging and newly industrialised countries, and leather production is labour-intensive (Tchobanoglous *et al.*, 2004). China dominates leather exports, while the US and European countries import (FAO/WHO Codex Alimentarius Commission, 2001).

2.3 Leather Industry in Kenya

Kenya's leather industry is well-established. Kenya's enormous animal resource. The industry also uses skins from fish (Nile perch), ostriches, and crocodiles as raw materials. The sector contributes Kshs.10.6 billion to Kenya's GDP and employs 22,540 people. About 14 tanneries in the country currently create employment. Kenya has 85 leather/cottage industries that provide jobs (Kenya Embassy Rome 2010 - 2014).

Kenya's annual production of hides and skins might provide significant leather export money. Table 2.1 shows the hides and skins production statistics of the three East Africa Community countries.

Table 2.1: Estimated total production of hides and skins in million (Wangui, 2016).

Country	Quantity of Goat Skins (Million)	Quantity of Sheep Skins (Million)	Quantity of Hides (Million)	Totals – Hides and Skins (Million)
Kenya	4.2	3.1	1.5	8.8
Tanzania	3.1	0.88	2.6	6.8
Uganda	2.04	0.22	1	3.26

Table 2.1 shows that Kenya's leather sector is increasing faster than any EAC country. Raw material scarcity is to blame. Almost 70 percent of the nation's Drylands provide hides and skins as a results of slaughtering farm animals. Hides, skins, and leather contribute 4% to agricultural GDP (Roether *et al.*, 1998).

Kenya's tanning business has environmental impacts. NEMA closed two tanneries in 2008 for improper effluent disposal, which caused pollution (GOK, 2002). Chemicals used in leather tanning are causing concern and the manner its effluents, which contain toxic elements like chromium salts, are disposed of. High quantities of organic and inorganic chemicals in tannery effluents pose a health and environmental danger (Kurt *et al.*, 2007). Inadequately treated tannery effluents used for irrigation have contaminated food chains and reduced crop, soil, vegetable, and livestock output (Muchangi, 2012). This has caused controversy about controlling tanneries to safeguard

human health and the ecosystem. Continued expansion due to a liberalised economy has required strong and well-equipped regulatory organisations (Apaydin *et al.*, 2009).

2.4 Importance of Chromium in Tanning Industry

Chromium, a transition metal that produces coordination compounds using three-dimensional orbitals, is the best tanning agent. By nature, chromium compounds are basic and include hydroxyl groups (Kotas & Stasicka, 2000). Two chromium chemical properties contribute to its tanning ability; the transitional stability of the complexes allows for easy ligand exchange (Sreeram & Ramasami, 2003). Chromium can form Cr-O-Cr polynuclear complexes.

These result in from scheme 2.1.

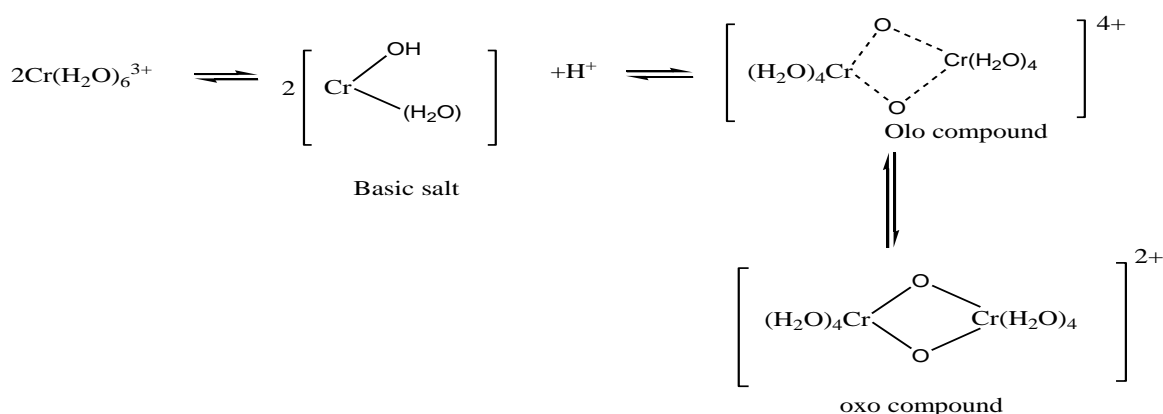


Figure 2.1: Cr-O-Cr bridges in tanning

The ultimate step is oxolation, which is a lengthy and irreversible process. Similarly, long chains can be constructed in the same manner. These polynuclear units can be used to bridge gaps between collagen chains in the skin structure, resulting in the tanning action. These two features are found in the chemistries of many other elements and do not confer any significant tanning ability. However, the combination of the two qualities results in a high tannin potency (Vincent, 2007).

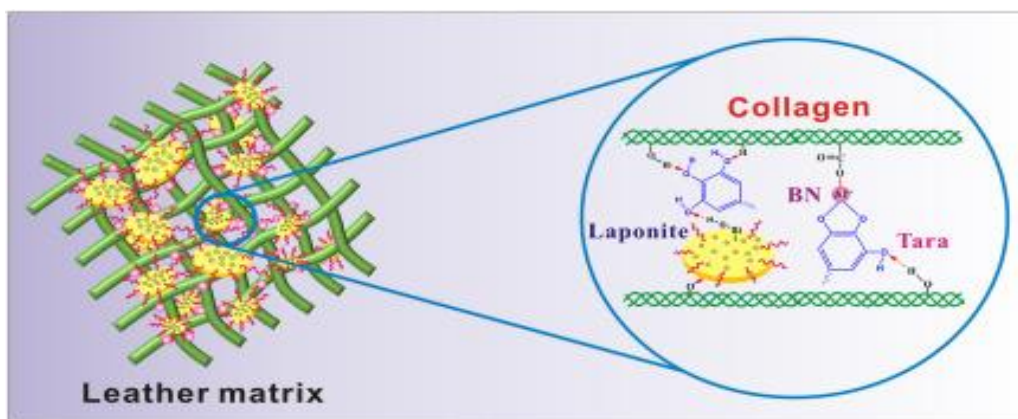


Figure 2.2: Complexion Between the Oxo Compound of Collagen Chains in Skins

2.4.1 Chromium Compounds and their Toxicity

Chromate compounds such as Ammonium dichromate, barium chromate, calcium chromate, chromium trioxide, lead chromate, sodium dichromate, strontium chromate, potassium chromate, potassium dichromate, sodium chromate, and zinc chromate hexavalent chromium compounds (VI) are not biodegradable (Shrivastava *et al.*, 2002). They're long-term environmental attributes. Because they may possibly possess accumulative qualities, they warrant close examination (Papp & Lipin, 2006). Two types of chrome are employed in the tanning business, and their properties are frequently misunderstood.

2.4.2 Chrome ³⁺ (Trivalent Chrome, Chrome III)

The hexavalent state of chromium (Cr^{6+}) is more dangerous than the trivalent state, which precipitates at higher pH. Cr^{6+} enters cells via anionic membrane transporters, but Cr^{3+} cannot be metabolised into Cr^{3+} intracellularly (Alam *et al.*; 2011). Cr^{6+} do not react with DNA, RNA, proteins, or lipids. Both Cr^{3+} and Cr^{5+} can covalently bond to macromolecules (Shrivastava *et al.*, 2002).

Chromium is a by-product of chrome tanning and comes out as leathers during retanning and dyeing. Chrome is soluble; however, it reacts quickly with tannery wastewaters (especially if proteins are present). Protein-chrome precipitates help generate sludge (UNIDO). The chromium solidifies fine colloids, browning the protein. Components are resistant to biological degradation, limiting biological activities in surface waters and treatment facilities.

When chromium hydroxide is degraded, it precipitates in the ecosystem. Chrome may stay in solution if substantial amounts are released. Even in small amounts, it harms daphnia, altering the fish food chain and impairing photosynthesis (UNIDO, 2011).

2.4.3 Chrome ⁶⁺ (Hexavalent Chrome)

Tannery effluents are highly likely to Cr ⁺⁶. Dichromates are harmful to fish due to their rapid penetration of cell walls. They are assimilated through fins and accumulate through the physiology of the fish. (UNIDO, 2011). Another unavoidable environmental impact of tannery effluent is salinity, which reaches conductivity values of 10,000-12,000 s/cm (Kotaś & Stasicka, 2000).

2.5 The Tanning Process

Pre-tanning process/beam house operations. These methods prepare skins/hides for tanning. The processes include:

2.5.1 Soaking

Soaking cleans skin, removes salt and preservatives, rehydrates and disintegrate enzymes. Oversoaking can deplete skin nutrients and cause liming (Covington, 1997).

2.5.2 Fleshing and Trimming

Extra tissue is removed. Dehairing dissolves hair and epidermis using sulphide and lime. After slaughterhouse peeling, the hide looks meaty; fleshing precedes dehairing and liming. (Covington, 1997).

2.5.3 Bating

The de-haired, fleshed, and alkaline hides are treated with digestive enzymes to extract hair and decimate enzymes. Roots and pigments are removed. Enzyme treatment softens hides. (Covington, 1997).

2.5.4 Pickling

This acid wash prepares skin for bleaching and tanning using synthetic or mineral tans. Ossified skins must be pickled to remove bone. Softly agitating skin in an acid bath takes several days. Hydrochloric acid, salts, and other acids are used to treat crocodile skin. Pickled skin can last months if the solution contains preservatives (Cassano *et al.*, 2001).

2.5.5 Tanning Operations

Tanning is a mechanical-chemical process. Tannins chemically bond to the hide's protein complexes, preventing it from decaying, during the leather processing. Chromium or chestnut bark are used for tanning. These tanning agents results in chrome and tanning categories (Covington, 1997; Cassano, *et al*, 2001). Leather tanning uses salts (sodium chloride) and fine finishing chemicals. Depending on the raw material and product, leather manufacture uses about 150 chemicals. Table 2.2 lists tanneries' chemical consumption.

Table 2.2: Chemicals usually Used in the Entire Tanning Process

High Potential Hazard Group						
Acetic acid	Ammonia	Calcium hydroxide	Formaldehyde	Formic acid	Glutaraldehyde,	hydrochloric acid
Hydrogen peroxide	Oxalic acid	Sodium chloride	Sodium hydroxide (Caustic soda)	Sulphuric acid	Sulphides and hydrosulphides	Chromium salts (trivalent) enzyme
Moderate Potential Hazard Group						
Aluminium sulphate (as lacquerconstituents	Amyl alcohol (as lacquerconstituents	Benzyl alcohol (as solvent	carbon black	lacquer	Isopropyl perchloroethene toluene	White spirit

Source: Wiemann *et al.*, 2018)

2.5.6 Chrome Tanning

Chrome-tanning is common. Chrome-tanned leather is softer, more pliable, and water-resistant than vegetable-tanned leather (Covington, 1997). Chrome-tanned leather is made from sheep, lambs, goats, and pigs. Soaking, fleshing, liming/dehairing, deliming, bating, and pickling are similar to vegetable tanning (Machado, 2002). When using animal skins like sheepskin, additional processes like retanning, dyeing, and fat-liquoring are required to produce serviceable leathers (Ashwini, 2009).

Chromium - based tanning is a one-bath process that uses chromium sulphate. Standard one-bath process starts with pH 3 or lower pickled hides, then adds chromium - based tanning chemicals such as chromium (III) hydroxide sulphate and $\text{Cr}(\text{OH})\text{SO}_4$ which raises pH. Stacking, wringing, and grading chrome-tanned leather follows tanning. It's shaved into flesh and grain layers. Shaved grain leathers are retanned, dyed, and fat-liquored. Uncuffed leather can only be surface-coloured. Other leathers (like shoe leather) require deeper dye penetration. When mixed with skin, aniline-based colours create an insoluble compound (Covington, 1997). Fat-liquoring restores natural oils lost during beam house and tan-yard operations by injecting oil into the skin which takes 30–40 minutes in a 60°C drum before drying (Covington, 1997). It is then wrung, dried, and finished fat-liquored leather (Barrera, 2006).

2.6 Post-Tanning Operations

Rechroming, neutralising, dyeing, fat liquoring, and finishing are post-tanning processes. Vegetable-tanned semi-finished leather is semi-chrome tanned, neutralised, dyed, liquefied, and finished output-based operations (Heidemann, 2005). Fat liquoring agents, chlorinated organic compounds, impregnating agents, sequestration agents, disguising agents, and colours are used post-tanning. Impregnating agents reduce gas

permeability, limit abrasion, improve wear, and retard flames. Chrome tanning masks with carboxylic acids, di-carboxylic acids, and their salts. Di-sodium phthalates (DSP) are also used (EHS, 2007). The figure 2.2 below shows a summary chart of tanning operations.

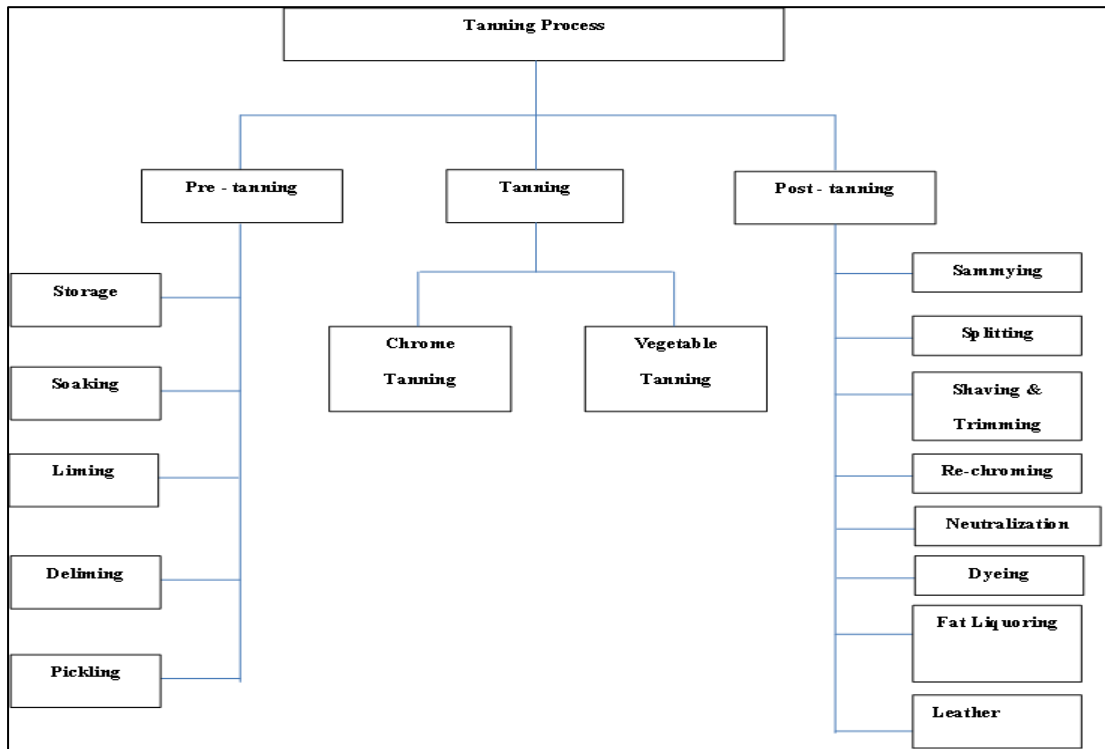


Figure 2.3: The Flow Chart Summary Of Tanning Operations

Source: UNIDO, 2002. Tanneries and the environment: A Technical Guide

The process of tanning involves five distinct stages:

selecting, dressing, finishing, and pre-tanning. These procedures are very intricate and involve several phases. A summary of some of the key components of each stage is provided below.

2.6.1 Pre-Tanning

Soaking - To remove salts needed to preserve leather, the leather may be soaked as it arrives at the tannery. 200 hides can fit inside revolving drums that are used for this.

Liming is a procedure that softens and improves the hide to give it the flexibility and suppleness required for upholstery leather. After the epidermis and hair have been removed, a lime (calcium hydroxide) and sodium sulfide solution has been applied.

By splitting, the hide is separated into layers. The top, or grain, layer will provide a lovely, smooth grain leather. On the bottom, suede or split leather is used for extra reasons.

2.6.2 Tanning

This process is used to create leather from pre-tanned hide. Mineral tanners frequently employ alkaline chrome-3 salts. It goes straight into the hide (24-48 hours). When processed, this results in a light duck-egg blue with a delicate, soft, modern finish. When chromium tanning is not an option, there are alternate methods that combine vegetal with polymers and syntans.

Other tanning methods are:

Pure Vegetable Tanning

Synthetic Tanning

Oil Tanning

Combination Tanning

2.6.3 Selecting

Excess water is drained from the hide after tanning. The number and distribution of natural traits and defects are then taken into account when grading hides. The highest

caliber hides are necessary for aniline and nubuck leathers. Less desirable skins may be used in leather that has been heavily coated or embossed.

2.6.4 Dressing

The following is involved in dressing the hides:

Shaving: The regular thickness of the hides is achieved.

Dyeing: To provide leather color, dyes are used.

Re-tanning: To change the physical properties of the leather to fit its intended usage, additional tanning agents are occasionally applied.

Setting is the mechanical removal of wrinkles and extra water.

Drying: The skins are either vacuum-dried or stretched-dried on substantial frames.

Trimming: The jagged and rough edges are taken off.

2.6.5 Finishing

The goals of finishing are:

- To reduce the appearance of grain imperfections without sacrificing the leather product's inherent beauty.
- To provide the necessary level of gloss.
- Must make sure the leather is pliable, moldable, and supple.
- Provide a surface that is more protective.
- To offer a surface that is simple to clean.
- To create a unique impression, like an aged appearance.

Combinations of surface coating methods, including cushioning, spraying, and roller coating, are used throughout the finishing process. Then there are mechanical procedures like embossing, staking, and polishing.

2.7 Tanneries as a Source of Pollutants

Throughout tanning, hides and skins transfer through liquors with specific chemical makeups to transform a destabilising fibrous organic protein into stable non-putrescible leather (Heidemann, 2005). During each process and subsequent washing, a tannery generates effluent. While spent liquors are disposed of in batches, washing is released sporadically or constantly, causing in significant variance in mainstream discharge (CCB, 2005).

Tanneries are extremely polluting industrial complexes that produce strong wastewaters. Tannery wastewaters vary owing to fill and draw operations and hide preparation, tanning, and finishing. The type of raw hides and final product's desired qualities determine these procedures (Zywicki *et al.*, 2002). Tannery wastewater is dark and smelly. Liming and tanning streams are polluted in the tanning process. Sodium sulphide and chromium salts pollute lime and chrome tanning streams. This means tannery wastewater should not be dumped in public sewers (Wiemannet *et al.*, 2018).

2.7.1 Emissions from the Tanning Process

The solid, liquid, and gas emissions during tanning might be dangerous or not. The ability to classify anything as consumable, recyclable, or reusable relies on the legal system, market environment, and facilities for reuse and disposal in each nation (European Commission, 2003). Traditional tanning requires a lot of water (40 m³ of water per raw hide; European commission, 2009). Wastewater is an issue because of its volume and high organic content (BOD, 14,000 mg/L from dehairing and tanning) (CCB, 2005), with 62% of the original skin turning into solid waste. In certain tanneries, solid waste is either buried or repurposed by the composting of hair and fat. Immediate discharge of tanning wastewater into a body of water has a negative impact on aquatic

life and subsequent use of these waters. Chromium, sulphates, and the organic load are the specific components that cause difficulties in water bodies (CONAMA, 1999).

According to the biosphere's elemental cycles, the river can absorb organic molecules including carbon, nitrogen, phosphorus, chromium ions, and sulfur. Self-purification is what it is termed. Chromium and its ions cannot be removed from rivers by self-purification because terrestrial weathering converts trivalent chromium to hexavalent chromium, which is subsequently cycled down rivers to the ocean. Chromium is released into rivers via estuaries, increasing the amount that is dispersed into the ocean (Wei *et al.*, 2020). The impacts of river contamination by organic materials are aesthetic, terrible odours, the loss of superior aquatic life, and the transmission of diseases due to coliforms and *E. coli*. Inorganic nutrients in excess cause eutrophication in hydrologic sources. Sulphides decompose organic molecules (Chapra, 1997). Consuming water downstream from untreated pollutants can harm entire populations' health. Chlorides are stable in water and only lose concentration through transverse scatter and dilution (Santos, 2010).

2.7.2 Organic Matter (BOD)

Excess BOD in water causes deoxygenation, unpleasant odours, and the death of aquatic life (COTANCE, 2002). During beam house soaking, organic load increases. Biodegradable organic compounds in effluents increase BOD levels, which, depending on the receiving water body's absorption ability, can cause extinction (Bosnic *et al.*, 2000; European Commission, 2003).

2.7.3 Nitrogen

Nitrogen affects dissolved oxygen and is crucial for water quality (Crossman *et al.*, 2019). Plants and microbes in water transform synthetic ammonia into natural foods, ammonia, nitrate, and ammonia (Mook *et al.*, 2012). Tannery effluents contain numerous components. Deliming produces ammonia (from deliming and dyeing) and nitrogen from proteinaceous material (Kanagaraj *et al.*, 2006). These nitrogen sources cause two problems. Nitrogen is necessary for plant growth; a high quantity of nitrogen in the water causes overgrowth of plants. When plants die, they create a lot of organic stuff that cannot be digested (without bacteria), promoting anaerobic conditions.

Bacteria transform nitrogen released during deliming into gaseous nitrogen and release it into the atmosphere. This process needs a lot of oxygen and can quickly lead to anaerobic conditions (Bosnic *et al.*, 2000).

Organic nitrogen or inorganic materials breakdown to create ammonia (NH₃). This substance is a by-product of dehairing and liming during tanning. Water contains NH₄⁺ and NH₃. The nitrification process oxidises organic and inorganic nitrogen in two steps, forming nitrite (NO₂⁻) and nitrate (NO₃⁻). Because this process involves oxygen, the water's concentration of 0.01-0.1 mg/L NH₃, which is harmful to aquatic, will be reduced. Temperature and pH affect this chemical's concentration. Ammonia exposure from consuming 2 litres of water each day is 0.36 mg/day (Bosnice *et al.*, 2000; Commission European, 2003). Animals with metabolic acidosis consume 500 to 1,000 mg/kg/day of ammonium chloride for 1 to 8 days (mice, dogs, pigs, and rabbits). Ammonium in excess is processed in the liver and can be eliminated through the urine. Even for susceptible individuals, additional exposure to ammonium from water at the defined range is insignificant and does not represent a danger to human health (European Food Safety Authority, 2012).

2.7.4 Sulphides (S²⁻)

The tanning process is intrinsically tied to the production of hydrogen sulphide, which happens predominantly in lime yards and anaerobic lagoons (Mwinyihija, 2007). The toxicity of sodium sulphide and sodium hydrosulphide to the environment is well-known. Sulphides remain dissolved in alkaline solutions, but when the pH goes below 9.5 due to the presence of acids in effluents, hydrogen sulphide is generated. The rate of production increases as the pH decreases. This results in disagreeable scents and raises the possibility of breathing these harmful vapours. Sulphides, even in trace amounts, pose a danger when deposited into surface waters. This condition is avoidable by neutralizing acid effluents prior to their discharge into general effluents (EPA, 2003). In ventilated waters, bacteria may reduce sulphides to benign chemicals, but at the expense of oxygen, damaging aquatic life. Depending on the route of exposure, sulphides might create health concerns. Inhaling it damages the mucous pulmonary membranes, causing cough, dyspnea, and pulmonary oedema.

It burns skin and eyes and increases the risk of blindness from corneal damage. Oral and digestive burns, vomiting, GI bleeding, and visceral perforation result from consumption, the central nervous system (CNS) is affected. There is no data on hydrogen sulphide's chronic toxicity in humans. Numerous adverse effects on employee health (dermal lesions, respiratory tract irritations, and burns, to name a few) can be observed because of direct contact with chemicals during the tanning process.

2.7.5 Fat and Oils

Throughout leather production, skin oils and lipids are extracted. Floating fat and fat particles accumulate in treatment facilities, causing blockages. Fat or oil coatings in

surface waters limit oxygen delivery to the atmosphere. If fat particles emulsify, oxygen requirement rises (Bosnic *et al.*, 2000).

2.7.6 Chlorides (Cl⁻)

The substantial use of sodium chloride (NaCl) in raw material preservation and pickling produces these in effluents. The beamhouse stage yields 40% of the leather manufacturing process' dissolved solids. Conventional methods can produce effluents with 22,800 mg/L NaCl (COTANCE, 2002).

2.8 Tannery Effluents Treatment

As was previously indicated, a number of hazardous chemical and physical pollutants are produced during the manufacturing of leather and leather items (COTANCE, 2002). As a result, there are more dangers to human health and environmental harm when tannery effluents are released into natural bodies of water without supervision. Tannery wastes should be handled before being dumped into water or the surrounding environment to prevent these negative effects. To prevent the harmful impacts of untreated tannery effluents and sludge on the environment, tannery wastewater/effluents can be treated using a number of techniques. Mechanical treatment, Effluent treatment and post-purification, sedimentation, and sludge management are the main stages of tannery wastewater treatment.

2.8.1 Mechanical Treatment

Raw wastewater treatment begins with clarification. Screening removes large particles. Screens may remove 30-40% of gross suspended particles in raw trash. Fat, grease, and oil skimming and gravity settling are mechanical treatments. Coagulation and flocculation remove chemical oxygen demand (COD) and suspended particles (Mollah *et al.*, 2001). Physicochemical therapy, including chrome precipitation and sulphide

treatment, follows mechanical treatment. Tannery effluent is frequently easily biodegradable after mechanical and physicochemical treatment (Mollah *et al.*, 2001).

2.8.2 Effluent Treatment

Flow segregation treats sulphide- and chrome-rich wastewater streams. Reduced water use may not decrease pollution load because concentrated effluents are easier to treat. Full blending of chrome-bearing wastewaters with other pollutant streams helps boost wastewaters treatment plant efficiency because chromium precipitates with protein all through pre-treatment (Kobyas *et al.*, 2003).

As pH values below 9 can produce toxic H₂S gas, sulphide-containing beam-house effluent is usually kept separate and at a high pH until the sulphide is handled. Hydrogen peroxide, sodium metabisulphite, or sodium bisulphite can swiftly oxidise sulphides in delimiting and pickling liquors (UNIDO, 2011). After sulphide treatment, a random sample of separate effluent emits 2 mg/L. Where sulphide-containing liquors cannot be separated, iron (II) salts and aeration are used to remove the sulphides (Mollah *et al.*, 2001).

2.9 Post Purification

2.9.1 Biochemical Treatment

2.9.1.1 Aerobic

Good results were obtained from combining chemical and biological ozonation of tannery effluent. The first step was the removal of 95, 98, and 99.9% of COD, NH₄-N, and TSS in an up-flow sequencing batch biofilm reactor with external recycling (Di Iaconi *et al.*, 2002). The combined process produced significantly less sludge than typical biological systems, 0.03 kg TSS/kg COD eliminated.

Aerobic digestion of wastewater sub streams, followed by ozone combustion and a 2nd aerobic treatment, improved refractory organic compound biodegradability. Ammonia was removed during the subsequent aerobic breakdown (Jochimse *et al.*, 1997). After sulphide compound oxidation, a membrane sequencing batch reactor handled beam house effluent better. First reactor removed 100% ammonium and 90% COD, second 10% ammonium and 90% COD. The sequences batch reactor lasted 90 days, while the membrane bioreactor lasted 120 (Martinez *et al.*, 2003; Goltara *et al.*, 2003).

A lab-scale continuous-flow facility managed vegetable tanning wastewater. Under steady-state conditions, BOD and COD removal were 85 to 96% and 86 to 97%. (Murugesan &fox, 1989). Activated sludge combined with wastewater deleted 87 to 96% BOD (Murugesan *et al.*, 1996) 84–92% of influent BOD was removed in a sludge reactor. (Ram *et al.*, 1999; Orhon *et al.*, 1999).

2.9.1.2 Anaerobic Treatment

Anaerobic treatment of tannery effluent seems practical, but hydrogen sulphide inhibits methanogenic bacteria (Sabumon, 2016). Unable-to-dissociate H₂S diffuses "freely" across cell membranes, denatures proteins and enzymes (sulphide crosslinking), and affects cell pH. (Tang *et al.*, 2009). A 100 mg/L undissociated sulphide reduces continuous-flow fixed-film reactor efficiency and degradation. Sulphide tripping reduced the concentration to 30 mg/L. Change reduced degradation by 15%. H₂S inhibits acidogenic bacteria (Suthanthararajan *et al.*, 2004). Anaerobic and aerobic treatment removed 85% of organic carbon from 900 mg/L dissolved organic carbon (DOC) tannery effluent (Harvey, 2000). In anaerobic environments, sulphate-reducing bacteria convert sulphate to sulphide, a toxic chemical that inhibits methanogenesis.

Syntrophic acetogenic bacteria (SAB), methane-producing bacteria, and sulphate-reducing bacteria compete for acetate and hydrogen (MPB). When a (USAB) reactor was used in conjunction, sulphur recovery and biogas production both improved (Suthanthararajan et al., 2004). The sulphur removal apparatus, which was made up of a stripper column, an absorber column, a regeneration unit, and a sulphur separator, eliminated 65 to 95% of the sulfide while boosting the degradation efficiency of the fixed-film reactor by 15%. With ongoing sulphide treatment, the content was reduced to 30 mg/L (Kieu et al, 2011).

2.10 Instrumentation

2.10.1 UV-Visible Spectrophotometer

To determine the absorbance or transmittance in the ultraviolet spectrum, a UV-visible spectrophotometer is utilized. An energy source, a monochromator to isolate a certain range of wavelengths, a detector to measure the signal, and a signal processor (amplifier) to present the signal in an easy-to-read manner are all components of spectroscopy devices (Harvey, 2000).

The UV-Vis spectrophotometric approach is based on the straightforward link between a solution's absorption of radiation and the concentration of colored species in the solution. To determine a species using spectrophotometry, it is typically turned into a colored complex.

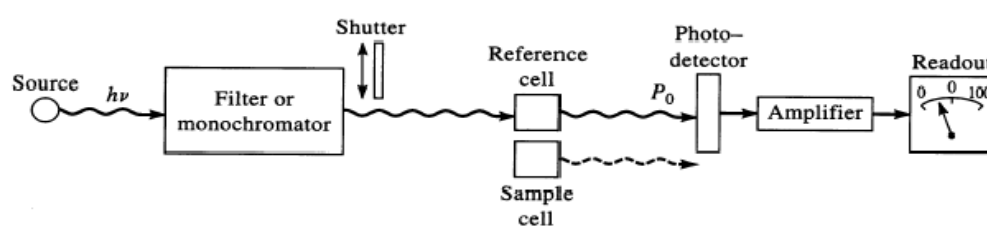


Figure 2.4: Schematic Diagram of Double Beam UV-VIS

Spectrophotometer

The color of the determinant is used significantly less frequently. Indirect spectrophotometric approaches may be used to determine a determinant that is not colored or does not generate colored compounds. The adaptability, sensitivity, and precision of spectrophotometric approaches are unmatched. Almost all are direct and, except for noble gases, are applicable to all elements. A wide variety of concentrations is possible, from macro amounts to traces (10^{-2} – 10^{-8} %).

Spectrophotometric approaches are the most precise. It's the most selective approach for identifying metals in alloys, minerals, and complexes. It has linear calibration graphs across a wider range than atomic emission and absorption spectroscopy.

2.10.2 Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) indicates the fact that high energy electrons emit energy as they return to lower energy (Nölte, 2021). The orbital's electrical setup helps determine transfer of energy when electrons return to initial state. The frequency of light emitted is unique even though energy transfer is inversely related to wavelength ($E = hc/\lambda$).

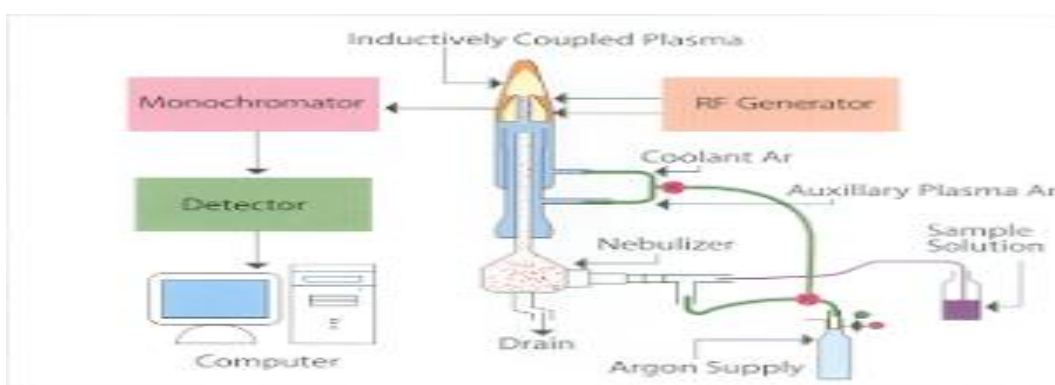


Figure 2.5: Schematic Diagram of ICP- AES

Source : <http://www.rsic.iitb.ac.in/Icp-Aes.html>

Despite the fact that each element emits energy at a variety of wavelengths, ICP-AES only employs one (or a small number of) wavelengths for each element. The intensity of the wavelength depends on the quantity (concentration) of the element in the sample. An analyst can identify a sample's contents both subjectively and quantitatively by identifying the wavelengths and intensities of the sample. From the strongest vacuum ultraviolet (160 nm) to visible light, AES wavelengths are available (800 nm).

Quartz glass is utilized for optical lenses and prisms, and optical paths are evacuated or filled with Argon despite the fact that borosilicate glass absorbs photons below 310 nm and oxygen in air absorbs light below 200 nm. Even undesirable components are atomized when samples are heated to 10,000 °C by ICP. Flame atomic absorption spectroscopy detection limits are 1–10 ppb higher than those of ICP (FAAS). Modern systems examine the emission channel horizontally using the axial approach. The limit of detection is lowered by axisymmetric viewing because it lengthens the journey and reduces the plasma signal to noise ratio. Without compromising accuracy or detection limitations, ICP technology can test for 60 elements in under a minute (Nölte, 2021).

2.10.3 Strengths of ICP-AES

It is simple to use and it is productive at a high level, extremely cost-effective for large numbers of samples and/or components, few interferences from chemical substances, interface that is not fragile, excellent capabilities in screening, solid and organic samples with a high total concentration of dissolved solids (Nölte, 2021).

2.10.4 Limitations of ICP-AES

With the potential of spectrum interferences and other element restrictions, it has moderate to low detection limits. It regularly outperforms FAAS, though.

2.11 Related Studies

Chromium was found in tap water, industrial river water, Mancher lake, and drain water in Pakistan (Soomro *et al.*, 2011). In Chile, toxicity tests revealed that a discharge from various leather processing procedures had elevated COD, sulphates, and total soluble solids (TSS) values. All effluents were dangerous (Cooman *et al.*, 2005). These effluents are regularly discharged on soils. The solid component of soil absorbs heavy metals quickly and selectively (Khan & Anjaneyulub, 2005). India has 800-1400 mg/L Cr. Egypt's Cr ranged from 600 to 1300 mg/L. Khan & Anjaneyulub, 2005; Cooman *et al.*, 2005. Salt-free can reduce pollution loads, including COD and BOD by more than 30%, sulphides by 80-90 percent, ammonia nitrogen by 80%, and total nitrogen by 80% (Akan *et al.*, 2008).

Numerous studies on wastewaters show that oxidation products limit Cr^{3+} in soil such as $\text{Cr}(\text{OH})_3$ and $\text{Cr}_2\text{O}_3(\text{H}_2\text{O})$, at pH values of 6-12, or by co-precipitation with Fe, resulting in the formation of $(\text{Cr}_x, \text{Fe}_{1-x})(\text{OH})_3$, $(\text{Cr}_x, \text{Fe}_{1-x})\text{OOH}$, Fe_x , Cr_{2x} (Stepniewska *et al.*, 2004). Leather process wastewater contaminants were significantly over Bureau of Indian Standards permissible levels, and tanneries pollute quickly, degrading ground water quality (Akan *et al.*, 2008). BOD in tannery effluent in Malawi varies between 2906 and 9000 mg/L, while similar levels are found in Zambia, between 2800 and 12000 mg/L (Tamilchelvan & Dhinakaran, 2012). Chromium concentrations in leather effluents and river water range from 0.12 to 345.00 mg/L (Shukla *et al.*, 2006). Indian tannery effluent had 27.33 to 38.22 mg/L of dissolved oxygen (DO). Tannery chemicals may increase organic matter, lowering DO. Despite differences in DO across industries, seasonal patterns show consistent industry activity. Rainy season BOD ranged from 52.91 to 672.70 mg/L, while dry season BOD ranged from 52.91 to 664.30 mg/L (Tamilchelvan & Dhinakaran, 2012).

The average chromium content in tannery effluents was 2.38 and 7.21 mg/L. Chromium metal concentrations were 89.30% greater than the 0.255 mg/L stated for Lagos textile wastewater. Cr⁶⁺ level in tannery effluent was 7.21 mg/L, 9.89% lower than the reported threshold of 9.0 mg/L. (Apaydin *et al.*, 2009). Chromium can cause skin, lung, and asthma responses. Studies at the Challawa Tannery in Kano State found 1.56 to 4.13 mg L⁻¹ chromium (Aboulhassan *et al.*, 2008).

According to research in Argentina (Cooman *et al.*, 2005), tannery effluents have a pH range of 4.5-7.5, while those in Kanpur (Tariq *et al.*, 2006) have a pH range of 3.7-5.9 and those in Nepal range from 1-6 (Suthanthararajan *et al.*, 2004b). TSS is a problem in various countries. South African research (Bosnic *et al.*, 2000) shows Total Suspended Solids concentration between 250 and 750 mg/L; Italian research (Kurt *et al.*, 2007) shows values between 200 and 800 mg/L; and Indian research shows values between 310 and 900 mg/L (Tamilchelvan & Dhinakaran, 2012).

In India, Gupta *et al.* (2014) reported that textile and tannery industries had high TDS (500 mg/L), hardness (80-100 mg/L), chloride (250 mg/L), and BOD (30 mg/L). Tannery effluents (1190-1240 mg/L) had the highest TDS, followed by textile effluents (1190-1210 mg/L) and Yamuna water (530-1180mg/L). Tannery effluents had 828-898 mg/L chloride. Yamuna water was neutral in textile effluents and acidic in tannery samples. The hardest effluents were tannery (860-880 mg/L) and textile (760-860 mg/L). All BOD values were similar, except tannery effluents (42-48 mg/L).

Bangladeshi tannery effluent (Sabur, 2012) was acidic (pH 3.94), with total Cr, COD, TSS, TDS, and conductivity at 30°C of 987 mg/L, 3175.32 mg O₂/L, 22915 mg/L, and

13360 mg/L, respectively. Leather units line Kanpur's riverbanks (India) with 27 mg/L Cr, pH 8.4, and 16141 moles/cm in effluent, BOD, COD, TS, and TSS exceeded limits (Bhatnagar *et al.*, 2013). The samples gathered from tanneries in India's Korangi industrial district exhibited a high chromium concentration that exceeded the permissible limit by WHO (Shahzad *et al.*, 2006). Tannery effluents were discharged straight into streams without treatment or were treated ineffectively.

The residue had 18.57-170.12 mg/L chromium while the filtrate contained 15.20-185.50 mg/L Cr, respectively. Conductance measurements ranged between 6.7 and 175 m S/m, indicating a significant concentration of ionic species.

The pH of the samples was found to be predominantly alkaline, ranging from 7.0 to 8.9 (Onyango *et al.*, 2019).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Area

On the eastern rim of the Great Rift Valley, at 1°16'S latitude and 36°48'E longitude, a community by the name of Limuru may be located 30 miles north of Nairobi, the capital of Kenya. Most Limuru residents work in agriculture and the shoe industry. According to the 2019 census conducted by the KNBS, the town's population rose from 4,800 in 2004 to 159,314 in 2019. (2019). Limuru is a town of Kiambu county, which was previously included in Kiambu. The majority of Limuru is now covered by what was formerly known as the "white highlands," a fertile agricultural region just south of the equator (Njiru, 2009). The epithet "white highlands" originated with the British and other Europeans who recognized the area's agricultural potential and came in huge numbers with the assistance of the colonial administration, establishing coffee and tea plantations, cereal farms, and ranches. The village is located at an elevation of around 2,500 meters. Limuru's year-round temperature ranges between 10 and 28 degrees Celsius.

Kenyans are familiar with Limuru's business because of how much tea it produces. Limuru Tea Plc produced 3,207,330 kilograms of green leaf in 2021 (compared to 3,882,430 kilograms in 2020), which was then processed into 743,453 kilos of black tea (compared to 844,103 kilograms in 2020). (Kagira et al., 2012). The tea plantations established at Limuru from 1903 on provided the foundation for Kenya's largest export industry, which produces some of the world's best tea. The Bata Shoe Company's main office is in Limuru. The largest country in East and Central Africa. Uganda Railway provides service to Limuru. The railway, the tea industry (especially after major

development in the 1920s), and the Bata shoe plant and headquarters all contributed to Limuru's rising significance (Kimani, 2013).

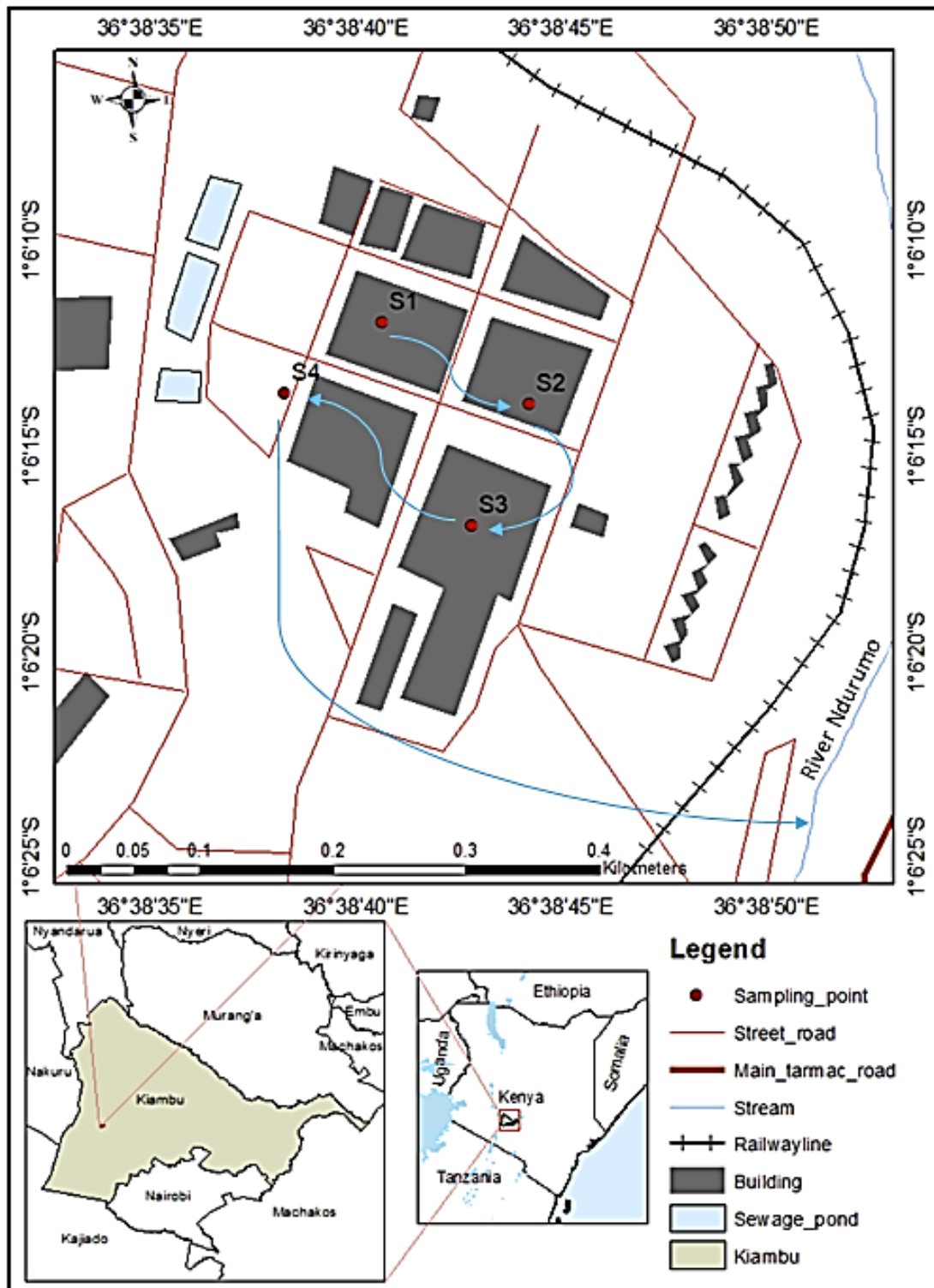


Figure 3.1: The Map Showing the Location of the Tannery and The Sampling Points

3.2 Wastewater Sampling

The locations of the effluent samples that were taken near the tannery are shown in Figure 3.1. The discrete grab sampling approach was applied. Three times daily for four weeks, three times a day for a month, spot samples of 500 mL were taken from each location using a sterile grab sampler. Samples were collected throughout industrial activities. The grab sampling approach is a clear six-step procedure for capturing a single sample or measurement at a given time, location, and depth, providing a snapshot or single depiction of the water quality at that exact instant in time. First, samples of soaking, liming, and de-liming effluents were taken. 500 mL of the sample were utilized at S1 at this time. The second sample site was S2, which was the site of the operations for chrome and vegetable tanning effluents. The third sample site was at the point where water entered the treatment facility, right before post-tanning/finishing (influent). The 500 mL sample from this moment was S3. The last test location was the Ndurumo River, where wastewater is pumped (after basic treatment) (effluent). S4 was produced at this moment from a 500 mL sample. To avoid chromium ion adsorption, 500 mL Teflon bottles were utilized for sampling rather than glass ones. Over the course of the whole month, 30,000 L of samples were obtained from the four locations, with each sample being taken three times and composited for the day.

3.3 Sample Preservation

After collection, the samples were put into Teflon containers and maintained and transported in a cool box. The materials were kept in a cold box to avoid any biological activity (4 °C). After that, they were taken to the lab for inspection.

3.4 Laboratory Tests

3.4.1 Preparation of Standard Solutions for UV-Visible Spectroscopy

These methods followed the procedures done by Memon *et al.* (2014) which used BSOPD to complex Cr⁶⁺ in non-ionic micellar media. The chemicals used were standard Cr⁶⁺ solution, standard Cr³⁺ solution, 0.00158 M, (bis(salicylaldehyde) orthophenylene diamine (BSOPD), absolute ethanol, non-ionic micellar media, (10%), (polyoxyethyleneoctylphenyl ether (TX-100)), 1M H₂SO₄, Concentrated HNO₃, NH₄OH, potassium permanganate solution, EDTA as a masking agent and de-ionized water. All chemicals were of analytical reagents grade .0.565 g of K₂ Cr₂O₇ was dissolved in 100 mL of water that yielded a 1000 mg/L stock solution. Polyoxyethylene-octylphenylphenyl ether (TX-100): 50 mL of pure polyoxyethylene-octylphenylphenyl ether were diluted in 250–300 mL of doubly distilled deionized water to create 500 mL of TX-100 solution.

3.4.2 Calibration Curve for Chromium

Concentrations from 0.01 to 18 ppm of Cr⁶⁺ ions standards were plotted against absorbance and regression curves obtained. This was used to obtain the concentrations of unknown chromium trace ions in the effluents.

The effect of metal concentration was investigated over the range of 0.01-18 mg /L, which was distributed in a single set (0.01-18 mg /L) for measuring ease. In aqueous surfactant medium, 0.01 to 12 mg/L Cr⁶⁺ measurements gave a linear graph.

Table 3.1: The Working Concentration for Chromium (Cr⁺⁶)

Concentration (ppm)	Absorbance
0	0.021
0.02	0.050
0.04	0.090
0.06	0.126
0.08	0.173
0.10	0.210
0.12	0.247
0.18	0.286

3.4.3 Determination of Cr⁶⁺ And Cr³⁺ Ions Using (BSOPD) Complex in Non-Ionic Micellar Media

Into a 10 mL calibrated flask, 1.0 mL of Cr⁶⁺ neutral aqueous solution was added, followed by 2 mL of 1 M sulfuric acid, 1 mL of 10% TX-100 solution, and 1 mL of EDTA solution. After mixing, 1.0 mL of bis (salicylaldehyde) orthophenylenediamine (0.00158 M) reagent solution was added. Bis(salicylaldehyde)orthophenylenediamine (0.00158 M) was obtained from (Mohammad & Abbas, 2014). (Sigma Aldrich). The solution was produced by dissolving BSOPD in double-distilled ethanol (Merck, Darmstadt, Germany). The reagent was diluted as needed.

A 2 mL of chromium (Cr⁺³ and Cr⁺⁶) was aliquoted into a 25 mL conical flask. 2 drops 1M H₂SO₄ and 2 mL 1% potassium permanganate oxidise trivalent chromium. The mixtures were boiled for 10-15 minutes and then cooled. The neutralised solution was transferred into the mixture to 10-mL flask. The total chromium (Cr⁺³ and Cr⁺⁶) was then calculated. Equal volumes of each of the aforementioned Cr⁺⁶ and Cr⁺³ combinations (preferably 1:1). After transferring the beaker's contents to a 10-mL

volumetric flask, the Cr^{6+} concentration was estimated. Subtracting Cr^{6+} from total chromium gave Cr^{3+} concentration.

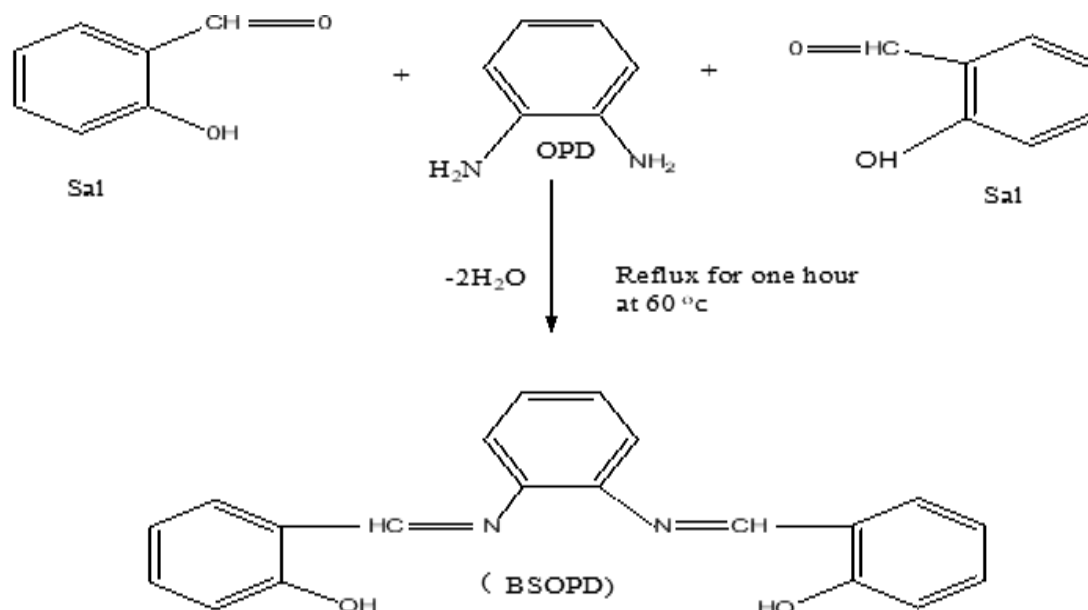


Figure 3.1: Synthesis of BIS (salicylaldehyde) Orthophenylenediamine (BSOPD).

3.4.4 Method Validation

3.4.4.1 Determination of Cr Concentrations in The Samples (Recovery Tests)

Each filtered influent and effluent sample (100 mL) were evaporated almost entirely and dried in a fume cabinet using 5 mL concentrated H_2SO_4 and 10 mL concentrated HNO_3 , then cooled to room temperature. Ten millilitres of deionized water were then added to the residue to dissolve the salts. The surrogate ion used in this recovery test was Fe (II).

Table 3.2 Distribution of Total Cr, Cr⁶⁺ and Cr³⁺ Concentration (Mean (Mg/L) at Four Different Sites of Bata

Sampling point	S1	S2	S3	S4
ICP-AES Data of Total Cr Conc.	0.00±0.00	935.00	690.00±0.00	670.00±0.00
Spectrophotometric Data of Cr ⁶⁺ Conc.	0.00±0.00	12.00±0.00	18.00±0.00	14.00±0.00
Concentration of Cr ³⁺ obtained through difference	0.00±0.00	923.00±0.00	672.00±0.00	656.00±0.00

3.4.4.2 Determination of Chromium by ICP-AES

Samples were filtered through a 0.45 µm membrane filter as soon as possible after collection to determine dissolved elements. The remaining filtrate was collected. Following filtration, the filtrate was acidified to pH 2 with nitric acid.

3.4.5 Procedure

Organic material was removed to estimate Cr concentration in real tannery effluent samples. A 25 mL material was mixed with 5 mL H₂SO₄:HNO₃ (1:1). At 120 °C, dense white SO₃ fumes managed to escape. In 5 mL increments of strong HNO₃, the solution was heated until clear and brown scents evaporated away.

3.6 Analysis of Physicochemical Parameters of Treated and Untreated Tannery Effluent Samples

More than 90% of nations base their discharge restrictions for tannery effluents primarily on characteristics such as pH, temperature, biological oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), total soluble solids (TSS), conductivity, and color. As a consequence, established procedures were used to examine the parameters in treated and untreated samples of tannery effluents (Baird et al., 2012).

3.7 Physicochemical Parameters and Analytical Methods

3.8.1 DO (Dissolved Oxygen)

Apparatus

- a. DO sampler
- b. 4 (500 mL) BOD bottles
- c. A siphon tube, for laboratory use.
- d. Manganous sulphate solution. 480 gm of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ was dissolved in distilled water. It was then filtered and diluted to IL.
- e. Alkali-iodide-azide reagent. 500 g of NaOH and 135 g of NaI was dissolved in distilled water and diluted to IL. A 10 g of NaN_3 was then added and dissolved in 40 mL distilled water.
- f. concentrated Sulphuric acid (specific gravity 1.84)
- g. Starch indicator. 2 g of laboratory grade soluble starch was dissolved in 100 mL and boiled with distilled water and 0.2 g of salicylic acid was added as a preservative.
- h. Standard sodium thiosulphate titrant, 0.025 M or 6.205 g of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ was dissolved in distilled water. 1.5 mL of 6 N of NaOH was added and diluted to 1000 mL. This solution was then standardised with bi-iodate solution.
- i. Standard potassium bi-iodate solution, 0.0021 M of $\text{KH}(\text{IO}_3)_2$ was dissolved in distilled water and diluted to 1000 mL.

Standardisation: 150 mL distilled water was transferred into an Erlenmeyer flask. Approximately 2 g of KI was added and dissolved in distilled water. 1 mL of 6N H_2SO_4 or a few drops of concentrated H_2SO_4 and 20 mL bi-iodate solution was added in this solution. It was then diluted with 200 mL and titrated with thiosulphate to liberate iodine until a pale straw colour developed. A few drops of starch were added as an indicator. Titration was continued until the first disappearance of blue colour.

The morality, M of thiosulphate was calculated as:

$$M = \frac{20 \times 0.0126}{V}$$

where: V = mL of thiosulphate used.

The stopper was removed and 1 mL of MnSO₄ was added followed by 1 mL alkali-iodide-azide reagent. The pipette was held by tip just below the liquid surface touching the side of the bottle. The pipette was washed before returning to the reagent bottles. It was then stoppered carefully to exclude air bubbles. The bottle was then mixed by inverting several times. The brown colour of manganese hydroxide flocculent appeared which indicated the absence of DO, 1.0 mL of concentrated H₂SO₄ was added and re-stoppered. This solution was then mixed thoroughly by inverting several times until dissolution was completed. 20 mL of the solution was then titrated with standard Na₂S₂O₃ and standardized as follows.

$$\text{mg. DO/L} = \frac{V \times M}{0.25}$$

Where: V = mL thiosulphate solution used and M = morality of thiosulphate titrant.

3.8.2 Biochemical Oxygen Demand Determination (BOD₅)

Apparatus

- a. Six 550 mL dark coloured and stoppered bottles.
- b. Two 250 conical flasks
- c. 50 mL burette
- d. 10 mL pipette
- e. stand and clamp
- f. 100 mL conical flask.

(a) Manganese sulphate solution

A 364 g of manganese sulphate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) was dissolved with distilled water in 500 mL conical flask. The solution was then prepared from freshly boiled, distilled water. The solution was filtered and made up to 1000 mL volumetric flask.

(b) Alkaline iodide solution sodium azide solution

A 700g of potassium hydroxide and 150g of potassium iodide was dissolved in freshly boiled and cooled water and was made up to 1000 mL volumetric flask. A 10 g of sodium azide (NaN_3) was dissolved in 40 mL of distilled water and constant stirring was ensured to cool the alkaline iodide solution prepared.

(c) Sodium thiosulphate stock solution; A 25 g of sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) was weighed and dissolved in 250 mL beaker. The solution was then transferred into 1000mL volumetric flask and made up to the volume. A 1 g of NaOH was added for preservation.

(d) Starch indicator.

2 g of starch was weighed and dissolved in 100 mL of hot distilled water.

(e) Concentrated H_2SO_4 concentrated sulphuric acid of specific gravity (1.84).

Samples were collected from the factory from the four sampling points respectively. Raw water was collected from entrance into the factory treatment plant and was used as blank. 550 mL of raw water was transferred into bottles containing the samples .5mL of the of the four sampling points were added into 550 mL-coloured bottles respectively. Oxygen was removed by adding 2 mL each of manganese sulphate and alkali-iodide-azide. The bottles were shaken for 5 minutes after which 2 mL of concentrated H_2SO_4 was added. The brown colour that appeared showed availability of oxygen. They were then titrated with 0.025 N ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) .2 drops of starch indicator was added before the end point. The presence of deep blue colour showed the end point.

$$\text{BOD}_5 \text{ was then calculated as } = \frac{\text{DO}_d - \text{DO}_5}{P}$$

Where DO_d was the initial amount of dissolved oxygen, DO_5 was the amount of dissolved oxygen after 5 days of incubation and p was the decimal fraction of the sample used.

$$\text{Seed correction} = (\text{DO}_{d-\text{seed}} - \text{DO}_{5-\text{Seed}}) \times f$$

The dilution was done as; BOD

$$, \text{ mg/l} = \frac{(\text{D}_d - \text{D}_T) - f \times (\text{B}_0 - \text{B}_T)}{P}$$

where D_d = DO of diluted sample initially, mg/l D_T = DO of diluted sample after 5-day incubation at 25°C, mg/l, P = decimal volumetric fraction of sample used B_0 = DO of seed control initially, mg/l B_T = DO of seed control after incubation, mg/l f = ratio of %seed in diluted sample to %seed in seed control.

3.8.3 COD Determination

Apparatus

- a. Reflux flasks, consisting of 250 mL flask.
- b. Condensers
- c. Hot plate- 1.4 W/cm² of heating surface
- d. Standard potassium dichromate solution, 0.0417M $\text{K}_2\text{Cr}_2\text{O}_7$ primary standard grade previously dried at 103°C for 2 hours was dissolved in distilled water and diluted to 1L.
- e. Sulphuric acid reagent: 5.5 g of Ag_2SO_4 technical or reagent grade was added to concentrated H_2SO_4 , and was kept for a day or two to dissolve.
- f. Ferroin indicator solution: 1.485 g of 1, 10-phenanthroline monohydrate. A 695 g of $\text{Mg FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in distilled water and diluted to 100 mL.

g. Standard ferrous ammonium sulphate (FAS), titrant, 0.25 M or 98 g of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in distilled water, 20 L of concentrated H_2SO_4 was then added, cooled and diluted to 1L, standardised daily as follows.

h. Standardisation: 10 mL of standard $\text{K}_2\text{Cr}_2\text{O}_7$ was then diluted to about 100 mL of distilled water, 30 mL of conc H_2SO_4 was added and cooled. Then 2 drops of ferroin indicator were added and titrated with FAS.

$$\text{i. Morality FAS} = \frac{\text{Volume of 0.0417 M of K}_2\text{Cr}_2\text{O}_7 \text{ (mL)} \times 0.25}{\text{Volume of FAS used (mL)}}$$

j. Mercuric Sulphate (HgSO_4) powder

k. Potassium hydrogen phthalate (KHP) standard: Dry potassium hydrogen phthalate ($\text{HOOC}_6\text{H}_4\text{COOK}$) was lightly crushed, at 120°C , cooled in desiccators, 425 mg was then weighed and distilled water was added and diluted to 1L. This solution had theoretical COD of $500 \mu\text{g O}_2/\text{mL}$.

Chemical Oxygen Demand (COD) loading was determined by use of Open Reflux Method. A sample was refluxed in strongly acid solution with excess of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). After digestion, the remaining unreduced $\text{K}_2\text{Cr}_2\text{O}_7$ was titrated with Ferrous Ammonium Sulfate (FAS) to determine the amount of $\text{K}_2\text{Cr}_2\text{O}_7$ consumed and the oxidizable matter was calculated in terms of oxygen equivalent. A sample size of 50mL was pipette into refluxing flask and to it, 1 g HgSO_4 was added, several glass beads, 5mL sulfuric acid reagent, with mixing to dissolve HgSO_4 , and 25 mL of 0.04167 M $\text{K}_2\text{Cr}_2\text{O}_7$ solution. The flask was attached to condenser and cooling water turned on. Remaining sulphuric acid reagent (70 mL) was added through open end of condenser and continued swirling and thoroughly mixing while adding sulphuric acid reagent as heat was applied and refluxed for 2 hrs. The condenser was cooled, washed down, disconnected and the mixture diluted to twice its volume with distilled water. It

was then cooled to room temperature and excess $K_2Cr_2O_7$ titrated with FAS, using 2 to 3 drops of ferroin indicator. This was then titrated with N/10 Ferrous Ammonium Sulphate solution, till the colour changes from green to wine red and the end point noted.

COD was then calculated as, $mg\ O/l = \frac{(A - B) \times M \times 8 \times 1000}{mL\ sample}$

Where: A = FAS used for blank, mL

B = FAS used for sample, mL

M = Morality of FAS

8 = was the equivalent weight of oxygen (i.e $\frac{16}{2} \times 1000\ mg/l$).

2

3.8.4 pH Determination

- pH meter with temperature compensating device, accurate and reproducible to 0.1 pH unit with a range of 0 to 14.
- Reference electrode preferably with quartz liquid junction
- Glass electrode.

Reagents used were;

- Potassium hydrogen phthalate buffer, 0.05M.

10.12 g of $KHC_8H_4O_4$ (Potassium hydrogen phthalate) was dissolved in 1000 mL freshly boiled and cooled with distilled water.

- 0.025M of Potassium dihydrogen phosphate and 0.025 M of disodium hydrogen phosphate buffer, pH 6.86. Then 3.533 g of Na_2HPO_4 was dissolved in 1000 mL freshly boiled and cooled with distilled water.

- 0.01 M sodium borate decahydrate (borax buffer), pH = 9.18. 3.80 g of $Na_2B_4O_7 \cdot 10H_2O$ was dissolved in 1000 mL freshly boiled and cooled with distilled water.

d. Buffer solutions was stored in polyethylene bottles. Buffer solutions was then replaced for every analysis done.

Electrodes was removed from storage solution, rinsed, blot dried with soft tissue, placed in initial buffer solution and standardised and the pH meter according to manufacturer's instructions. Electrodes was removed from the first buffer, rinsed thoroughly with distilled water, blot dried and immersed in second buffer preferably of pH within 2 pH units of the pH of the sample. The pH was read for each of the four sampling points after calibration with the buffers which was within 0.1 unit of the pH of the second buffer. pH of the sample was determined using the same procedure as above after establishing equilibrium between electrodes and sample. For buffered samples this was done by dipping the electrode into a portion of the sample for 1 min. The electrode was blot dried, immersed in a fresh portion of the same sample, and pH was read. With dilute poorly buffered solutions, electrodes were equilibrated by immersing in three or four successive portions of the sample. Fresh sample was taken to measure pH. The sample was then gently stirred while measuring pH to insure homogeneity.

3.8.5 TSS (Total Suspended Solids)

a. Glass-fibre filter disk, Whatman grade 934 AH, Gelman type A/E.

Diameter 2.2 to 12.5 cm.

b. Filtration equipment, such as a membrane filter funnel or a Gooch crucible with an adapter and a suction flask with enough volume for the chosen sample size.

c. 104 + 1 0C drying oven

d. An analytical balance with a 0.1 mg weight limit.

e. Dishes for weighing in aluminum.

The filter paper was cleaned by putting it on the filtration assembly and filtered with three different 20 mL amounts of distilled water. After that, it was placed on an aluminum plate and dried for an hour in a 104°C oven. Before the filtration system was assembled, the filter paper was cleaned, dried, and weighed. A small amount of distilled water was used to seat the filter paper. As the material was being stirred using a magnetic stirrer, a little volume was measured onto the filter using a large diameter pipette. The sample size was selected to provide between 10 and 200 mg of dry solids. After that, it was cleaned with three subsequent 10 mL amounts of distilled water. After filtering was finished, suction was maintained for around three minutes. Carefully removing the filter paper, it was then placed in the weighing dish made of aluminum. After drying, cooling, and weighting, it was done.

$$\text{mg/mL sample} = (A - B) \times 1000 \text{ mg Total Suspended Solids} / L$$

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

3.8.6 Total Dissolved Solids (TDS)

Apparatus

- a. Evaporating dishes, 100 mL capacity of porcelain, platinum or high-silica glass made
- b. Drying oven, $104 \pm 1^\circ\text{C}$
- c. Desiccator
- d. Magnetic stirrer
- e. Glass-fibre filter disk, Whatman grade 934 AH, Gelman type A/E,
Diameter 2.2 to 12.5 cm.
- f. Filtration apparatus, Membrane filter funnel or Gooch crucible with adapter and suction flask of sufficient capacity for sample size selected.

The filter paper was cleaned by inserting it into the filtration assembly and passing it through a series of 20 mL quantities of distilled water. Any remaining water was sucked out with continued suction. The washes were thrown away, and the evaporated dish was dried at 1040 °C for an hour before being cooled and put in a desiccator for storage. It was instantly weighed before use. The sample was stirred using a magnetic stirrer and a large bore pipette, and a measured volume was pipetted onto the filter. Dry residue sample amounts of 10gm. It was washed three more times with 10 mL each of distilled water after that. The entire filtrate was then placed in a weighted, washing-filled evaporating dish. In a 104 °C oven, the liquid was then dried by evaporation. The same plate was used again after evaporation to obtain between 10 and 200 mg of dried residue. To reduce splattering, the oven temperature was first set at 20 degrees below boiling point. After an hour of evaporation, it was raised to 1040 °C. The sample was cooled in a desiccator before being weighed.

TDS was calculated as:

Dissolved Solids/L = $(A - B) \times 1000$ mg/ mL sample where: A = weight of dried residue + dish, mg B = weight of dish, mg

3.8.7 Colour

a. 50 mL Nessler tubes:

b. Stock standard equivalent to 500 colour units

K₂PtCl₆ and 1.00 g of crystallized cobaltous chloride were dissolved in distilled water with 100 mL of strong HCl and then diluted to 1000 mL with distilled water.

Working standards: The standards have evaporation protection and weren't being used.

The four samples were added to the 50 mL mark in a Nessler tube. Four tubes that matched the color of the sample were each similarly filled with color standards. By looking vertically downwards at the tubes while they were set up on a white surface,

the sample's color was contrasted with that of the standards. There was a color comparator stand utilized. The sample contained turbidity and the result was reported as apparent colour. For diluted samples the colour was calculated in colour

$$\text{units as: } \frac{A \times 5}{B}$$

where: A = estimated colour of diluted sample B = mL sample in 50 mL diluted sample.

3.8.8 Temperature

A thermometer was immersed in the sample up-to the mark specified by the manufacturer and the temperature was read after equilibration.

Table 3.3 Working Standards for Colour

Colour units	5	10	15	20	25	30
Stock std., mL	0.5	1	1.5	2	2.5	3
Distilled water mL	49.5	49	48.5	48	47.5	47
Colour units	40	45	50	55	60	65
Stock std., mL	4	4.5	5	5.5	6	6.5
Distilled water mL	46	45.5	45.0	44.5	44	43.5

3.8.9 Electrical Conductivity (EC)

- Conductivity meter capable of measuring conductivity with an error not exceeding 1%.
- Conductivity cell (Pt electrode type).

The cell was cleansed using a mixture of sulfuric and chromic acids. The platinizing solution was made by dissolving 1g of chloroplatinic acid, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, and 12mg of lead acetate in 100 mL of distilled water. Both electrodes were connected to the negative terminal of a 1.5V dry cell battery and dipped into this solution (in some

meters this source was built in). The positive terminal was connected to a platinum wire, which was submerged in the solution. Electrolysis was performed on both cell electrodes until platinum black was applied to them.

a. Conductivity water - Distilled water was used and boiled shortly before use to minimise CO₂ content of which its electrical conductivity was less than 0.01 mS/m (< 0.1 μmho/cm).

b. Standard potassium chloride solution, KCl, 0.01 M, conductivity 141.2 mS/m at 25°C.

745.6mg anhydrous KCl (dried 1 hour at 180°C) was dissolved in conductivity water and diluted to 1000 mL.

The conductivity cell was rinsed with a 0.01M KCl solution at least three times. A fourth component's resistance and temperature were noted. The device has built-in temperature adjustment and a direct conductivity indicator. The temperature adjustment dial was set to 0.0191/°C after cleaning as previously mentioned, and the meter was adjusted to read 141.2 mS/m (or 1412 mho/cm) with the probe in standard KCl solution.

The cell constant, K_c, was derived with the method below:

$$K_c = \frac{1422}{K_{c\text{KCl}}} \times [0.0191 \times (t-25) + 1]$$

Where: K_c = the cell constant, 1/cm K_cKCl = measured conductance, μmho m t = observed temperature of standard KCl solution.

3.8 Data Analysis

The data were examined using SPSS version 17 (Statistical Package for Social Science).

The data and conclusions displayed in the graphs and tables were condensed using descriptive statistics (frequency, mean, and standard deviation). To evaluate the

significance of a difference between two or more groups, one-way analysis of variance and the T-test were utilized.

CHAPTER FOUR

RESULTS

4.1 Concentration of Cr³⁺ and Cr⁶⁺ in Bata Tannery Effluents using a Simple and Rapid Spectroscopic Method and ICP-AES in Non-Ionic Micellar Media

Concentration of Cr⁶⁺ was determined by simple spectroscopic approach. This was done by use of a calibration curve (Figure 4.1). Absorbance by Cr⁶⁺ ions increased with increase in its concentration;

$$y = 1.5922x + 0.031 \quad (r=0.96, p=0.0001).$$

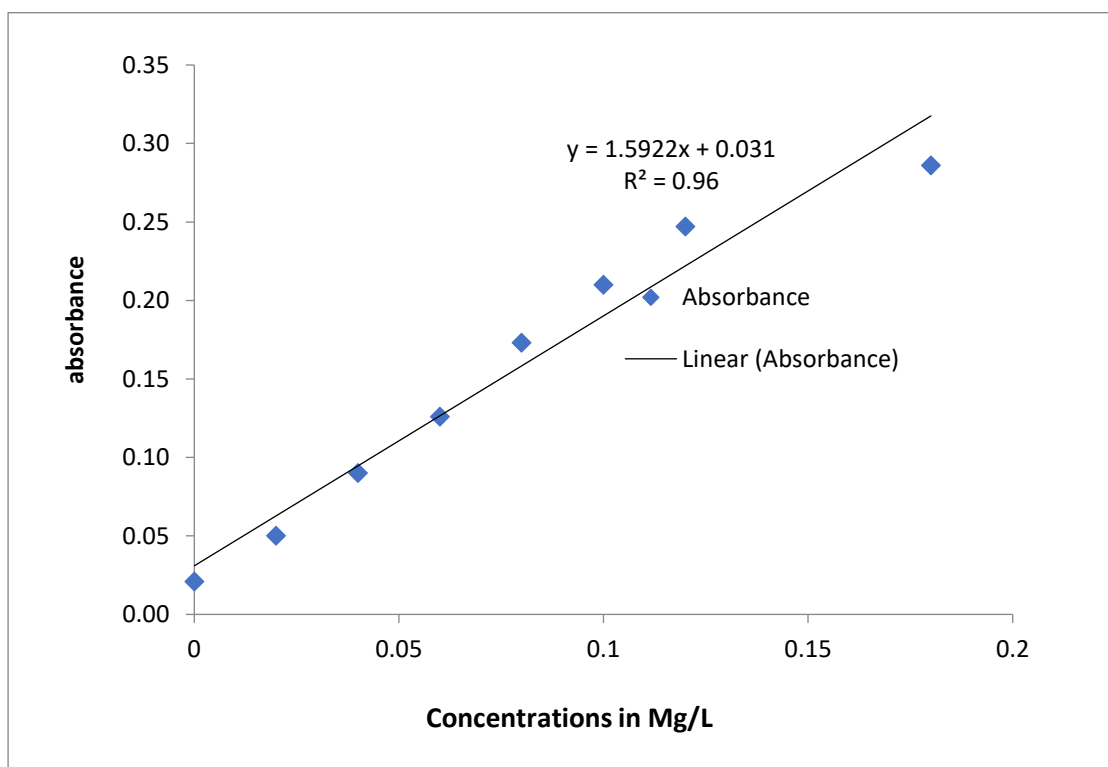


Figure 4.1: Calibration curve of Cr⁶⁺

4.2 The Levels of Physicochemical Parameters in the Samples of Tannery Effluent from Bata Tannery at Different Sites

4.2.1 Dissolved Oxygen (DO)

The four Bata leather tanneries in Kenya that produce wastewater had an overall mean DO level of 9.17 \pm 0.27, which was just a tiny bit more than what was recommended by WHO rules. The average DO concentrations at each of the four sites varied from 8.4 to 10.6 mg/L, with S3 recording the greatest amount of 10.6 mg/L at 10.62 mL/L and S1 recording the lowest at 8.10 mL/L, according to Figure 4.4. This suggests that concept 2 was incorrect. At all four locations, the acceptable DO limit of 7 mg/L was surpassed.

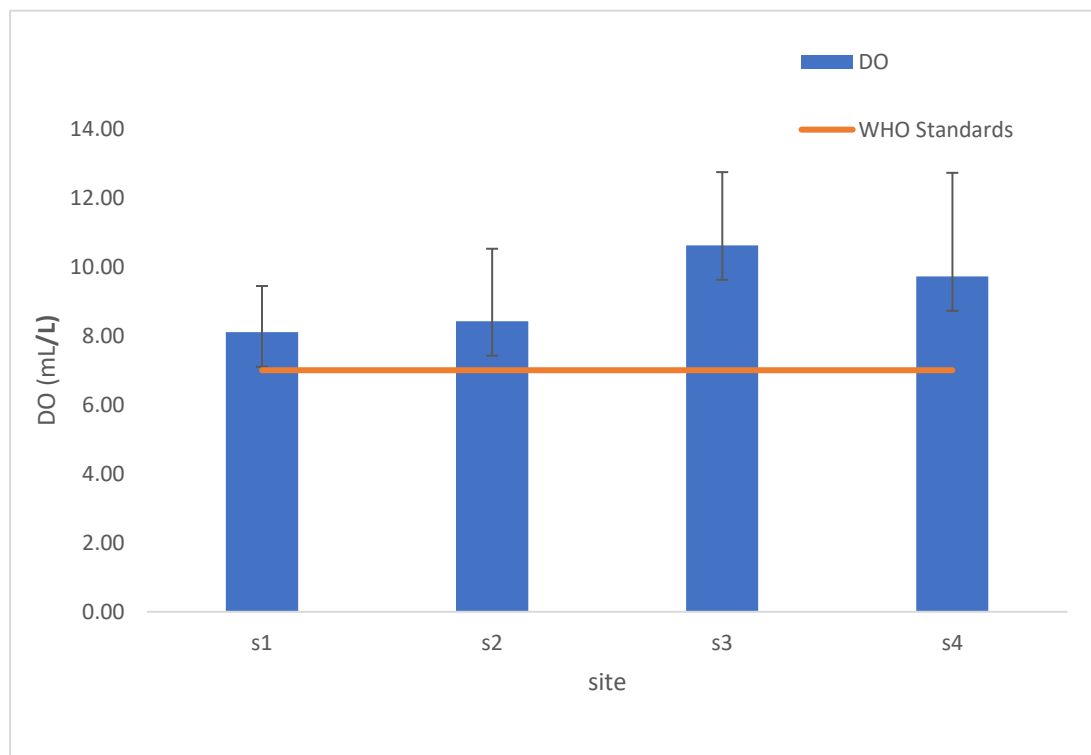


Figure 4.2: The Mean Levels of Dissolved Oxygen

4.2.2 Biological Oxygen Demand (BOD₅)

The average biological oxygen demand from the Bata leather tanneries' effluent in Kenya was found to be 4721.34 \pm 130.5 mg/L, far higher than the WHO's 6 mg/L standards. The findings in Figure 4.2 demonstrate that the four sites' BODs ranged

between 3141 and 5477.7 mg/L, with site 2 recording the highest quantity with the biggest difference (5477 ± 139.34) and the highest $F_{0.05, (3, 20)} = 25100$, $p=0.0000$). As a result, theory 2 is proven false. BOD levels in all four locations above the limits recommended by KEBS, NEMA, and WHO standards.

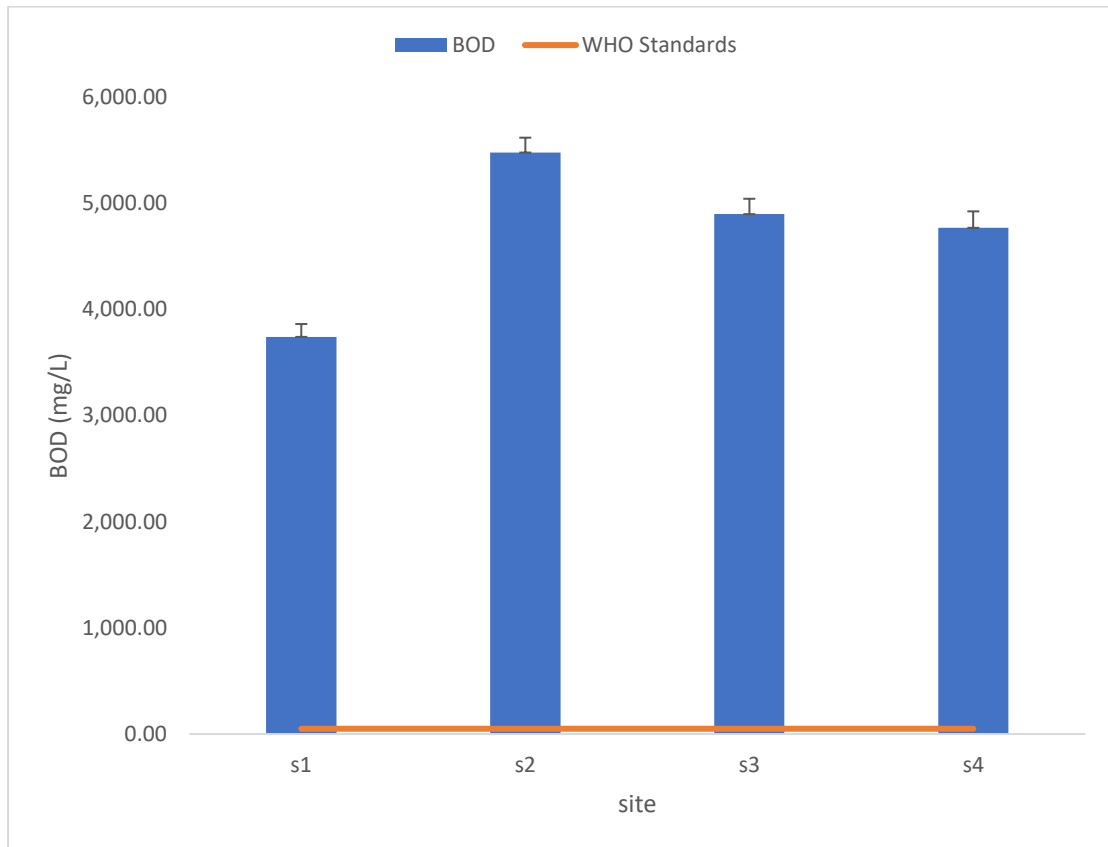


Figure 4.3: The Mean Levels of Biological Oxygen Demand

4.2.3 Chemical Oxygen Demand (COD)

The average COD content for the four locations from the Bata leather tanneries' effluent in Kenya was 7772.92 ± 234.63 mg/L, which was again much higher than the necessary quantity of 10 mg/L for WHO criteria. According to the findings displayed in Figure 4.3, the effluent samples exhibited high COD values, ranging from 5986.7 to 9093.2 mg/L, with site 2 reporting the highest values at 9093.31 ± 254.63 mg/L and site 1 recording the lowest at 5986.252 ± 24.63 mg/L. In terms of statistics, this difference was significant ($F_{0.05, (3, 20)} = 5286.00$, $p=0.0000$). As a result, hypothesis 2 is proven false.

Additionally, each of these measured quantities was higher than the WHO's 500 mg/L standard.

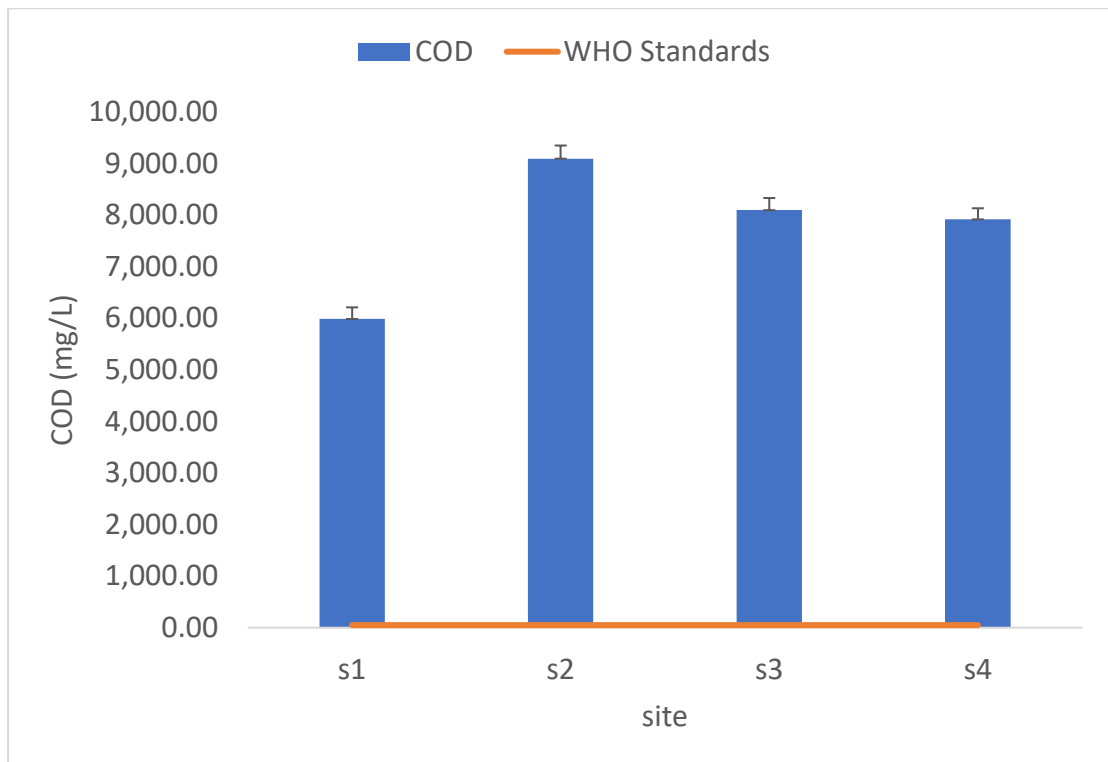


Figure 4.4: The Mean Values of Chemical Oxygen Demand

4.2.4 pH

The effluent from Bata leather tanneries in Kenya had an average pH of 5.030.5, which suggests that it was somewhat acidic and outside of the WHO values' recommended range. According to Figure 4.4, the pH levels at each of the four locations ranged from 1.52 to 8.2, with site 3 having the highest pH at 8.21 ± 2.21 . Sites 1 (1.52 ± 0.14) and S2 (4.41 ± 1.21) had pH levels that were outside of what the WHO considers to be acceptable ranges. The pH levels in the effluent samples varied significantly among the four locations ($F_{0.05, (3, 21)} = 75.71, p = 0.0000$). This leads to the rejection of hypothesis 2.

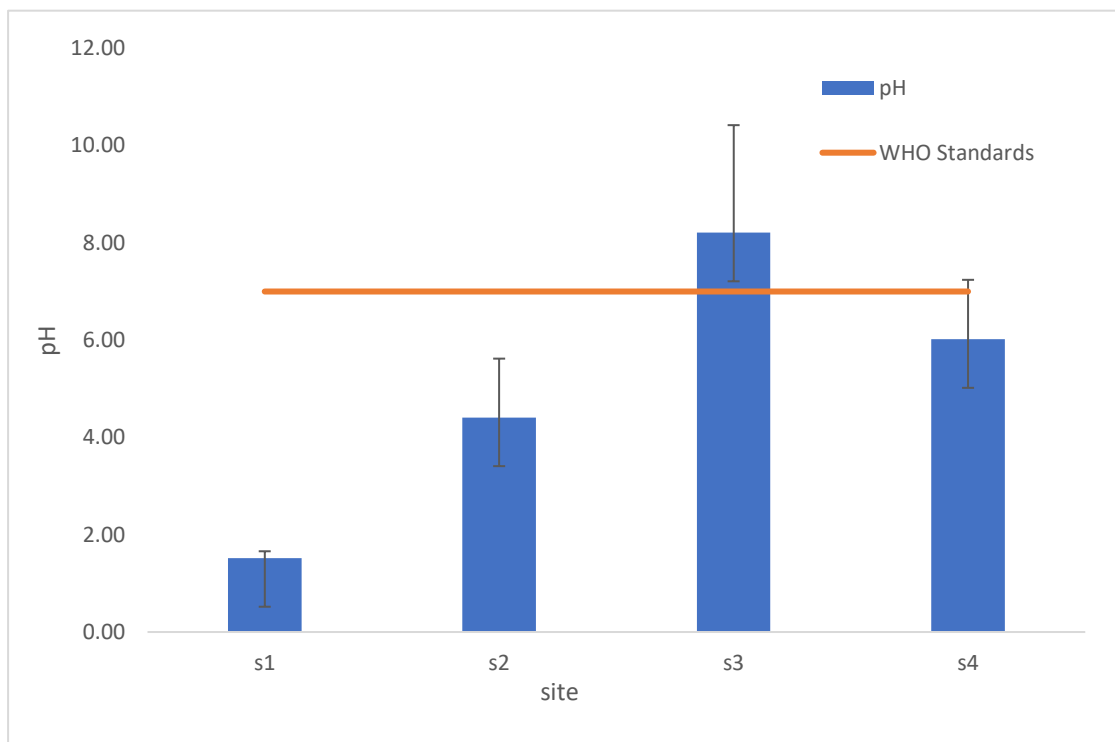


Figure 4.5: The Mean Levels of pH Levels

4.2.5 Total Suspended Solids (TSS)

According to the current study's findings, the mean Total Suspended Solids (TSS) total mean values from wastewater from Kenya's Bata leather tanneries were 213.50 ± 10.1 mg/L, which is much higher than the equivalent recommended threshold of 30 mg/L for WHO standards. Figure 4.5 below shows the mean values for each site. The TSS values ranged from 148 mg/L to 284 mg/L, with S1 recording the highest value (284 ± 10.63) and S4 recording the lowest value (204.23 ± 16.45), with a significant difference ($F_{0.05, (3, 20)} = 1856.00, p = 0.0000$). Consequently, the second theory was found to be false. At all four sites, the TSS levels were above WHO standards.

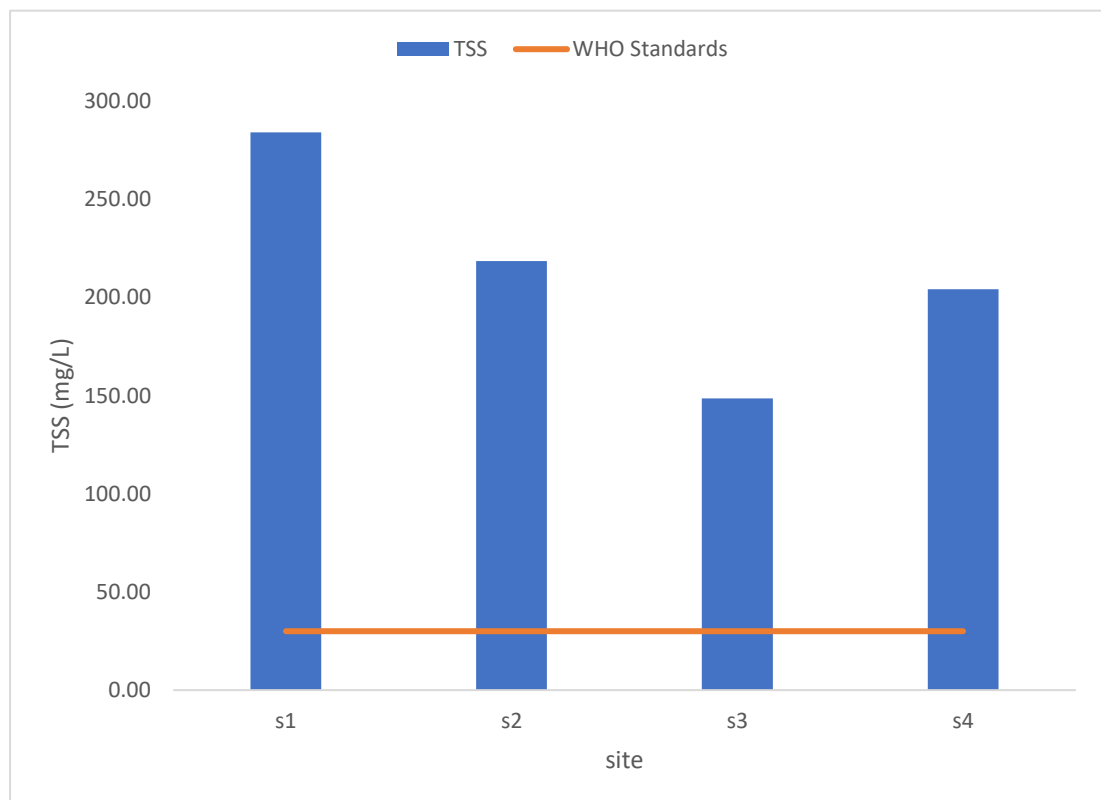


Figure 4.6: The Mean Levels of Total Suspended Solids

4.2.6 Total Dissolved Solids (TDS)

The assessed TDS levels were in high concentration in water sampled from S1 (270.21±9.23) followed in S2 (201.81±7.25) while S3 recorded the lowest (137.71±6.23) with a significant difference ($F_{0.05, (3, 21)} = 10930.00, p = 0.0000$). All the assessed sites had TDS levels below the KEBS, NEMA and WHO standards (1200 mg/L) as illustrate in Figure 4. Therefore hypothesis 2 was rejected.

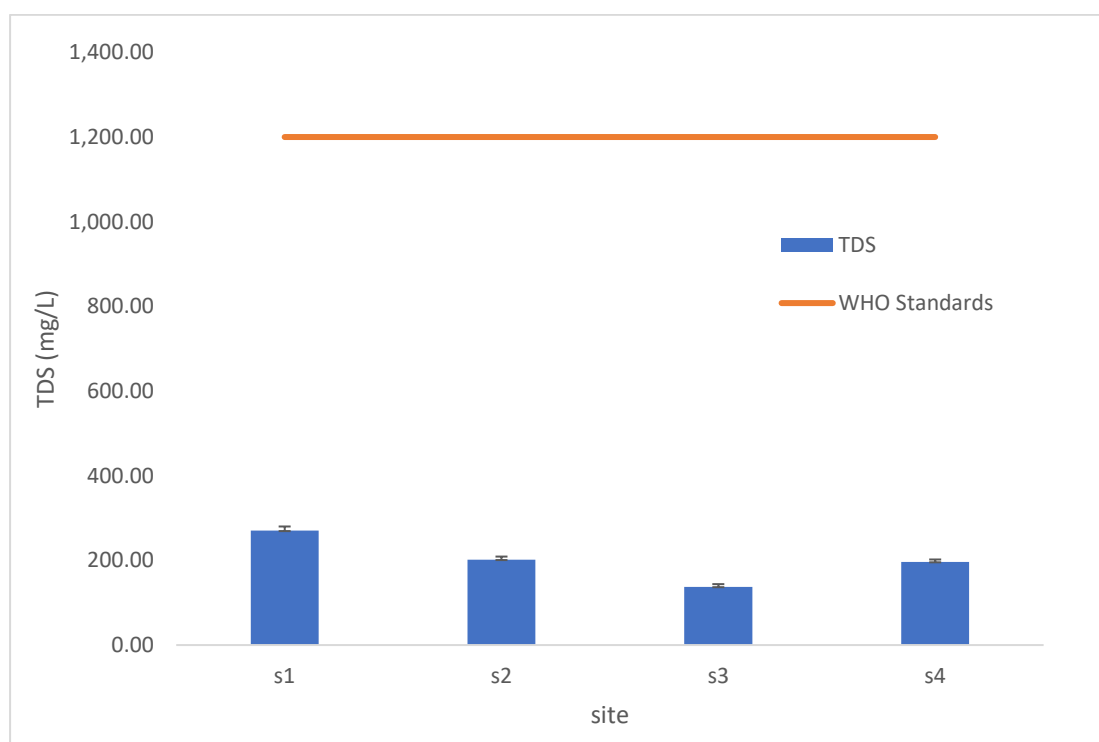


Figure 4.7: The Mean Levels of Total Dissolved Solids (TDS)

4.2.7 Colour (TCU)

The four Bata leather tanneries in Kenya had an average color (TCU) of 667.00±23.12 Pt-Co, which is also much greater than the acceptable level of 15 Pt-Co for WHO requirements. In Figure 4.11 below, the median levels for each area are shown. S2 (787.20±23.12) had the highest color value of the effluent samples, while S4 (488.45±23.12) had the lowest. The color values ranged from 488.5 to 787.2 Pt-Co. In terms of statistics, this difference was significant ($F_{0.05, (3, 20)} = 25360.00, p = 0.0000$).

This resulted in hypothesis 2 being rejected. The colour values for all the four sites were above the recommended levels set by WHO standards.



Figure 4.8: The Mean Levels of Colour (TCU)

4.2.8 Temperature ($^{\circ}\text{C}$)

The four Bata leather tanneries' wastewater treatment facilities in Kenya had an average temperature of $25.59 \pm 0.5^{\circ}\text{C}$, which suggests that it was within the $20\text{-}35^{\circ}\text{C}$ WHO recommended range. As shown in Figure 4.8, the mean temperature for each of the four locations ranged from 22.7 to 27.9°C , with S3 (27.90 ± 1.00) recording the highest temperature and S4 (22.7 ± 1.43) demonstrating a significant difference between the four sites ($F_{0.05, (3, 20)} = 22.55, p = 0.0000$). As a result, hypothesis 2 fooling was disproved. The temperatures, however, were all within the WHO-recommended range at each of the four sites.

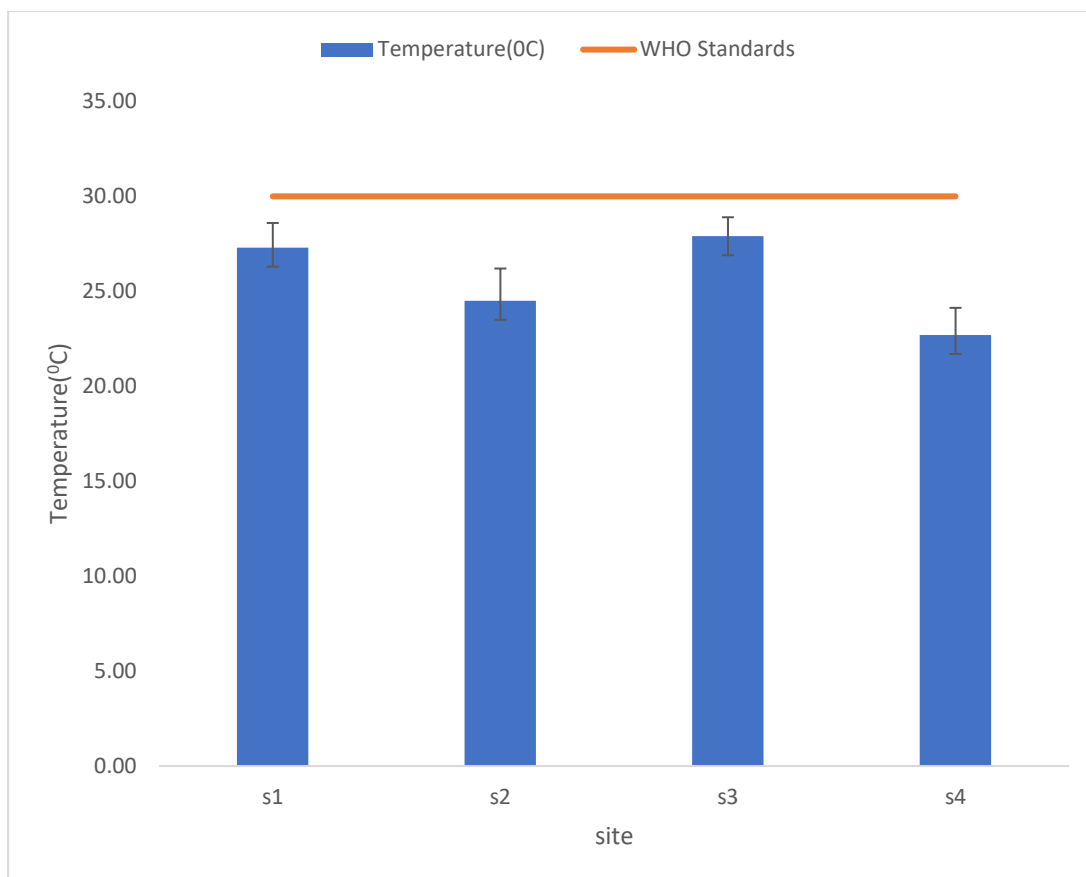


Figure 4.9: The Mean Levels of Temperature (°C)

4.2.9 Electrical Conductivity (EC)

The average mean values of EC in the effluent from Kenya's Bata leather tanneries were 1363.38 ± 2.83 mS/cm, which is much higher than the 25 mS/cm WHO recommended level. Each of the four sites' average EC values varied between 1348.8 and 1385 mS/cm, as shown by Figure 4.9, with S3 (1385.64 ± 35.34) obtaining the highest value. The electrical conductivity values at all four locations were much greater than the WHO-recommended limit of 25 mS/cm. The average EC values across the four locations varied significantly from one another ($F_{0.05, (3, 20)} = 153.61, p = 0.0000$).

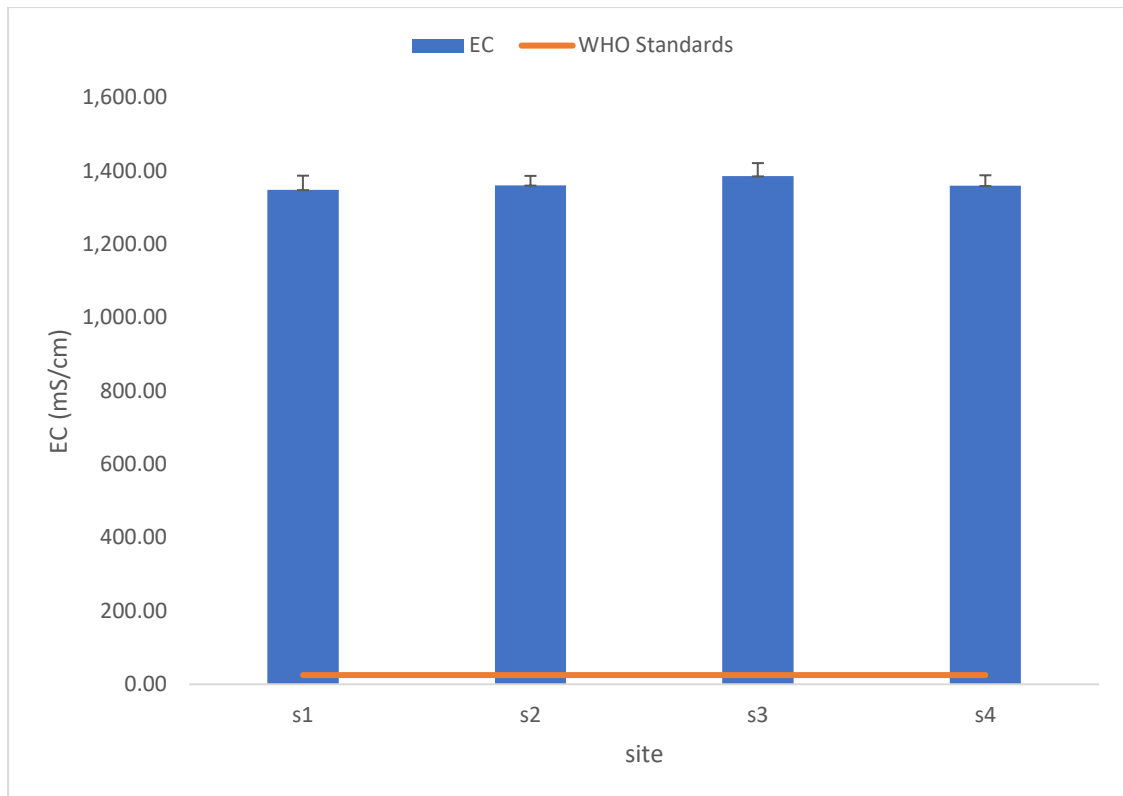


Figure 4.10: The Mean Levels of Electrical Conductivity (EC)

4.2.10 Total Solids

TS values from Kenyan Bata leather tanneries were 413.58 ± 11.87 mg/L, which is higher than WHO standards of 6 mg/L respectively. Figure 4.10 shows site mean values where S1(554.20 ± 23.61) recorded the highest with S3 (285.89 ± 12.56) recording the lowest with a significant difference ($F_{0.05, (3, 20)} = 9254.00$, $p = 0.0000$). TS values ranged from 286 to 554 mg/L. It means that hypothesis 2 was rejected.

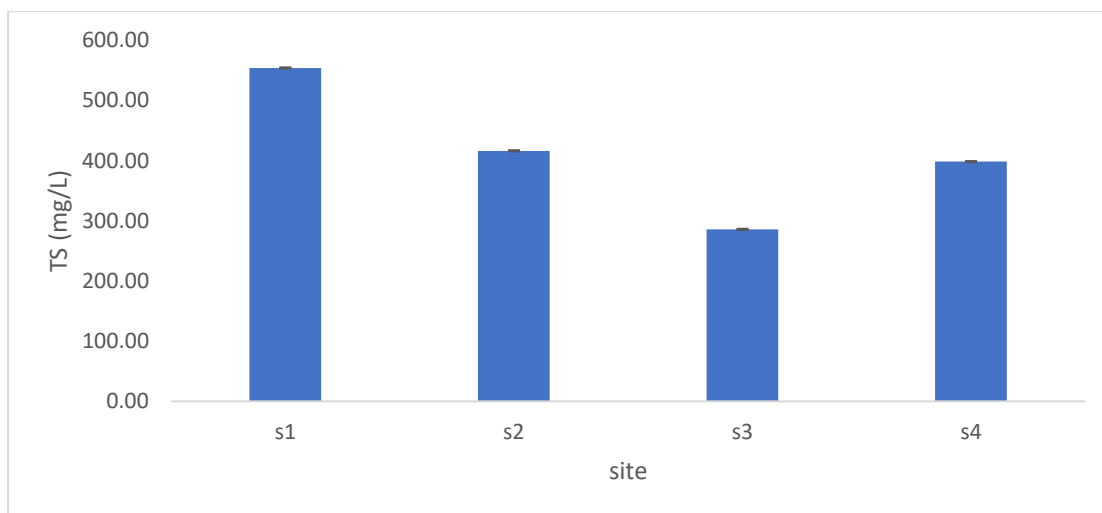


Figure 4.11: The Mean Levels of Total Solids

4.2.11 Chromium Levels

The mean concentration results of Cr from wastewater Bata leather tanneries in Kenya as obtained by UV spectroscopic method are presented in Figure 4.12. The overall mean effluent chromium samples for total chromium, Cr⁶⁺ and Cr³⁺ at S1, S2, S3 and S4 were 573.71 ± 72.37 , 12.08 ± 1.37 and 560.38 ± 70.69 mg/L respectively. There was a significant difference between levels of the total Cr⁶⁺ and Cr³⁺ in the area ($t=7.872$, $df=22$, $p=0.0000$). The amount of Cr ions at different sites of the Bata leather industry had significant differences. Therefore hypothesis 2 was rejected. The mean total chromium, Cr⁶⁺ ($F_{0.05, (3, 20)}=37.74$, $p=0.0000$) and Cr³⁺ ($F_{0.05, (3, 20)}=748.03$, $p=0.0000$) level recorded differed significantly among the four sites as portrayed in Figure 4.11.

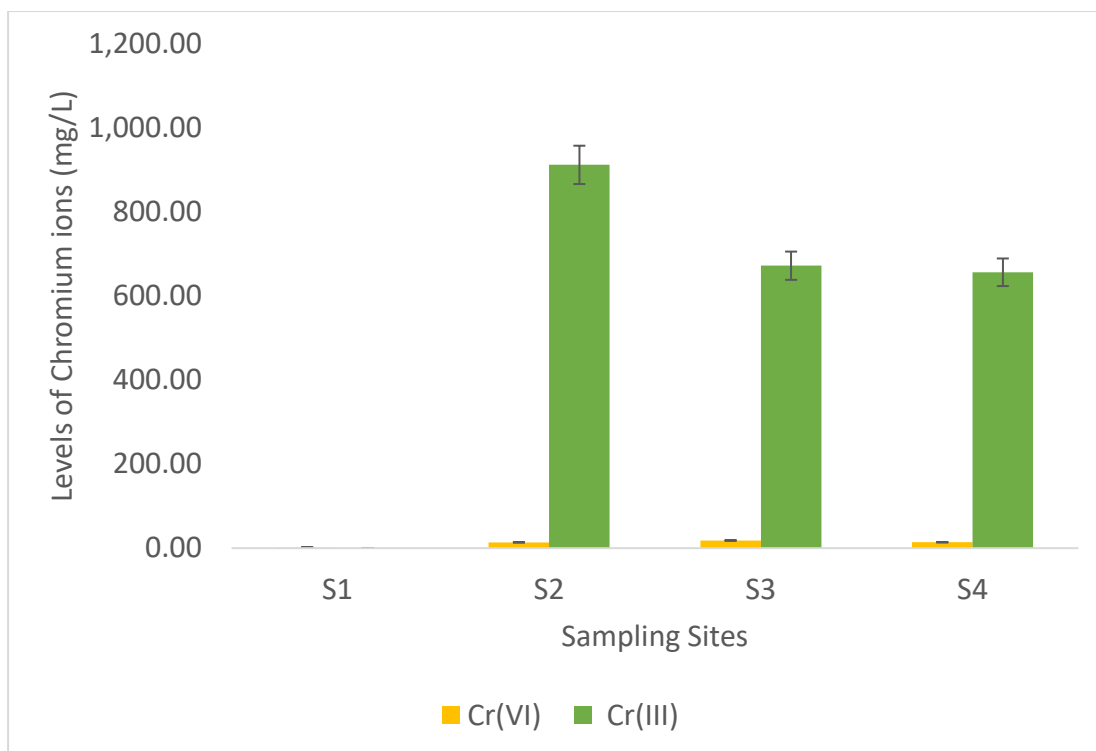


Figure 4.12: The mean concentration of Cr⁶⁺ and Cr³⁺ as Obtained by UV Spectroscopic Method

The mean concentration results of Cr from wastewater Bata leather tanneries in Kenya ICP- AES in a non-ionic micellar media are presented in Figure 4.13. The overall mean effluent chromium samples for total chromium, Cr⁶⁺ and Cr³⁺ at S1, S2, S3 and S4 were 1.70 ± 0.23 , 13.08 ± 1.34 and 18.00 ± 11.7 mg/L. For Cr³⁺ S1, S2, S3 and S4 were 0.00 ± 0.00 , 887.00 ± 17.24 , 649.34 ± 11.70 and 625.60 ± 12.03 mg/L. There was a significant difference between levels of the total Cr⁶⁺ and Cr³⁺ in the area ($t=6.4520$, $df=22$, $p=0.0000$). The amount of Cr ions at different sites of the Bata leather industry had significant differences. It means that hypothesis 2 was rejected. The mean total chromium, Cr⁶⁺ ($F_{0.05, (3, 20)}=42.23$, $p=0.0000$) and Cr³⁺ ($F_{0.05, (3, 20)}=63.78$, $p=0.0000$) level recorded differed significantly among the four sites as portrayed in Figure 4.12.

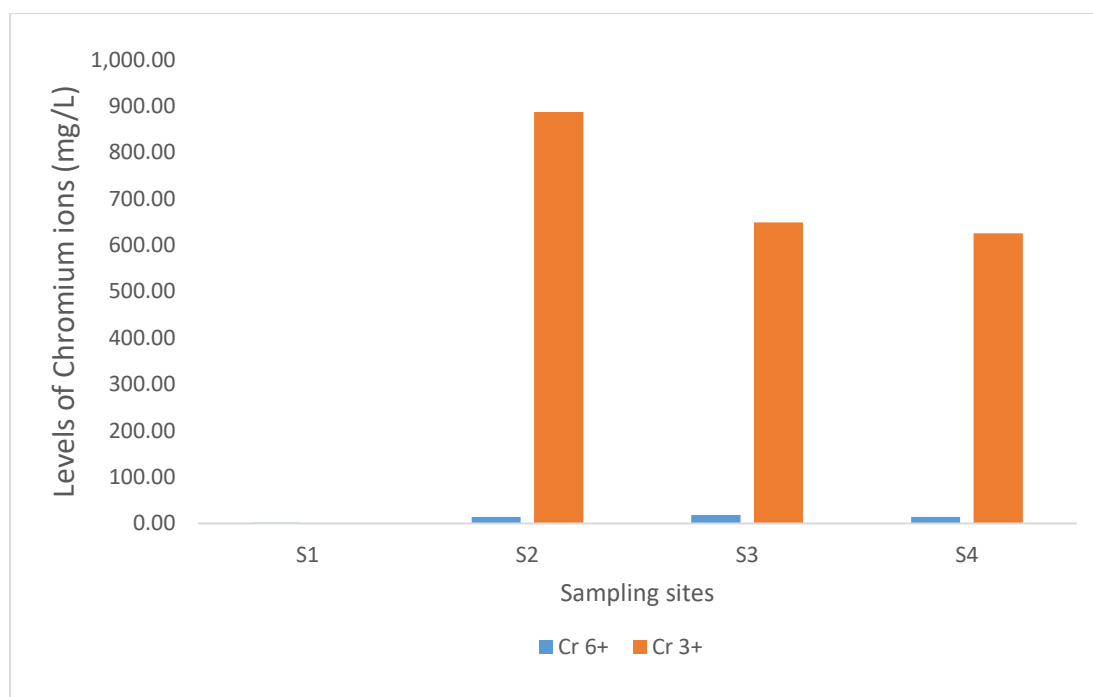


Figure 4.13: The Mean Concentration of Total Chromium, Cr⁶⁺ and Cr³⁺ as Obtained by ICP- AES in A Non-Ionic Micellar Media

In comparison with the two methods, UV spectroscopic did best in comparison with ICP- AES in a non-ionic micellar media though with no significant difference ($t = 0.2222$, $p = 0.8350$).

4.3 Recovery Tests

The results showed a high percentage of 98.05 ± 0.15 % from the initial concentration, added and found concentration of 2 ± 0.00 , 2 ± 0.00 and 2.25 ± 0.31 , respectively. In addition, a t- test between added and found was carried out and reported a significant difference between the two ($p = 0.000$, $df = 11$, $t = -7.975$). Further on recovery and found that there was no significance difference ($t = 0.01$, $df = 11$, $p = 0.9930$).

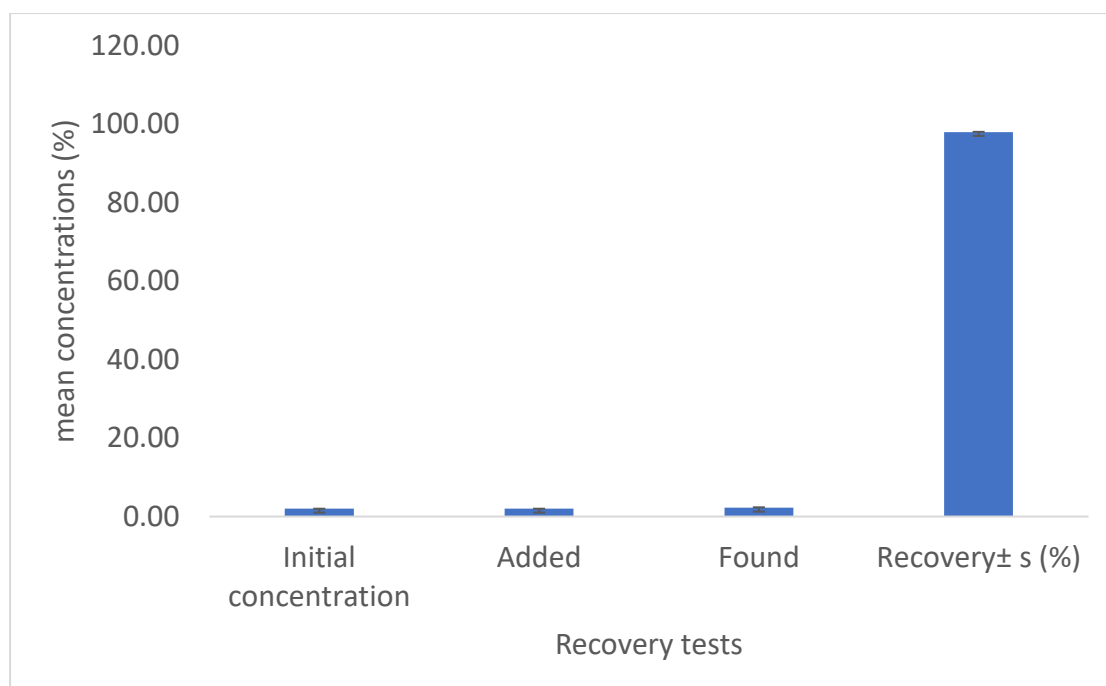


Figure 4.14: Recovery Tests by UV Spectroscopic Method

For the recovery test by ICP- AES in a non-ionic micellar media, the results showed a high percentage (%) of 98.13 ± 0.12 from the initial concentration, added and found concentration of 2.21 ± 0.00 , 2.20 ± 0.00 and 1.25 ± 0.03 , respectively. In addition, a t-test between added and found was carried out and reported a significant difference between the two ($p=0.000$, $df= 11$, $t=-7.975$). Further on recovery and found that there was no significance difference ($t=0.01$, $df= 11$, $p=0.9930$). Therefore, hypothesis 3 was rejected.

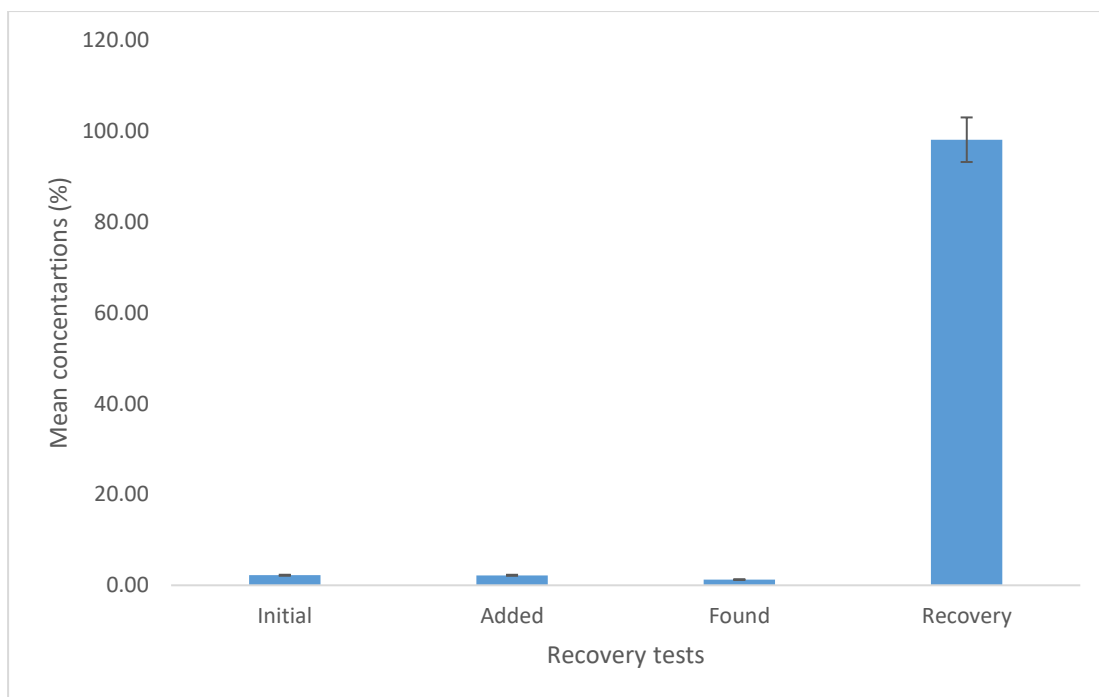


Figure 4.15: Recovery Tests by ICP- AES in a Non-Ionic Micellar Media

The assessed samples showed significant positive correlation between TSS and TDS ($r=0.9979$, $p=0.0021$), TSS and TS ($r=0.9995$, $p=0.0005$), COD and BOD ($r=0.9994$, $p=0.0006$), BOD and Cr^{6+} ($r=0.9897$, $p=0.0103$) and Cr^{3+} , $r=0.9897$, $p=0.0103$), COD and Cr^{6+} ($r=0.9939$, $p=0.0061$) and Cr^{3+} ($r=0.9939$, $p=0.0061$). there was a negative significant correlation between pH and TDS ($r=-0.9807$, $p=0.0193$) as illustrated in Table 4.1.

Table 4.1: Spearman's Correlation

TDS	pH	BO D	TSS	TS	COD	Colour (TCU)	Cr ⁶⁺	Cr ³⁺
	-0.98*	-0.67	1.00*	1.00*	-0.68	-0.11	-0.72	-0.72
		0.59	-0.99*	-0.99*	0.60	-0.09	0.67	0.67
			-0.64	-0.67	1.00*	0.32	0.99*	0.99*
				1.00*	-0.65	-0.05	-0.70	-0.70
					-0.68	-0.08	-0.72	-0.72
						0.29	0.99*	0.99
							0.19	0.19
								1.00*

*Figure which are Significantly different are shown with **

CHAPTER FIVE

DISCUSSIONS

5.1 Physicochemical Characteristics

5.1.1 Total Dissolved Solids (TDS)

The average result for this research was 201.46 mg/L, but the mean values for the four locations ranged from 137.7 to 270 mg/L, with site 1 having the highest value. The readings at all four sites were below WHO guidelines. Elevated TSS and TDS levels might be caused by the wastewater containing organic and inorganic components that are difficult to dissolve (Aniyikaiye et al., 2019; Singh et al., 2012). Sugasini and Rajagopal (2015) reported results for untreated sewage that were marginally higher than those in this study at 318.5 mg/L, whereas Smrithi and Usha (2012) reported values for untreated effluent that were substantially higher at 600 mg/L. The different phases of treatment throughout the tanning process were blamed for the substantial variation between sample locations.

5.1.2 Dissolved Oxygen (DO)

Water contains oxygen that is dissolved (DO). Overall, DO was 9.17 mg/L, ranging from 8.4 to 10.6 mg/L on average at each of the sites, with S3 having the highest concentration. The 7mg/L standard set by KEBS, NEMA, and WHO was exceeded by all measurements. The tannery wastewater's high organic content stimulates microbial growth, which decomposes organic materials and uses up dissolved oxygen.

Similar findings were made by Sugasini and Rajgopal (2015) and Noorjahan et al. (2004). Parveen et al. (2017) investigated the physicochemical characteristics and fresh water quality of tannery waste water. Maximum DO values of 6.96 mg/L and minimum DO levels of 5.09 to 5.76 mg/L were recorded in the control group. Because of the various amounts of treatment used in tanning, sample points varied.

5.1.3 pH

The pH of the wastewater from Kenya's Bata leather tanneries was 5.030.05 on average. Each of the four locations had an average pH between 1.52 and 8.2, with site 3 having the highest pH at 8.2. The pH levels at Sites 1 and S2 are higher than those recommended by KEBS, NEMA, and WHO. The tannery effluent was more acidic and alkaline than what was permitted by NEMA, KEBS, and WHO, as shown by higher pH measurements outside of the permissible range of 5.0 to 9.0. Chrome tanning effluent pH was 3.8, below guidelines. Pickling may lower the pH of chrome tanning wastewaters. Liming harmful byproducts had the highest mean pH because of too much lime and sodium chloride in lime pelt production.

This basic effluent exceeded pH restrictions. A substantial pH value variation strains the aquatic ecosystem and may harm sensitive flora and animals (Welker *et al.*, 2013; Navaraj and Yasmin, 2012). Alkaline effluent used for irrigation may harm aquatic biota like zooplankton and fish. Alkaline tannery effluent may be caused by carbonates and bicarbonates, according to Saxena *et al.* (2002). The use of acidic or basic salts in leather tanning caused a spatially significant pH variation. Alkaline pre-tanning/preparation effluents. The liming section uses CaCO_3 , Na_2S , and NaHS , which are all basic and raise effluent pH.

5.1.4 Electrical Conductivity (EC)

Electrical conductivity is a measurement of how well a water sample conducts electricity. Temperature and the concentration of dissolved ionized material both affect the value. It efficiently assesses effluent quality. In Kenya, the average EC of effluent from Bata leather tanneries ranged from 1348.8 to 1385 mS/cm at S3. In pickling and chrome tanning effluents, EC was highest. Salts of sodium and chromium are greatly

increased during pickling and tanning. Salt concentration is high when the effluent EC values are high. All four locations went beyond the 25 mS/cm benchmark set by KEBS, NEMA, and WHO. Chloride ions and inorganic salt cations (Na^+ , K^+ , Ca^{2+} , and Fe^{3+}) enhance water salinity and conductivity. Murali *et al.*, (2013) found increased conductivity in untreated and treated tannery effluents, indicating more cations and anions. Increased conductivity leads in an imbalance of free metals available to plants and animals due to water chelating characterize (Akan *et al.*, 2008).

5.1.5 Temperature ($^{\circ}\text{C}$)

The mean temperature for each of the four waste water Bata leather tanneries in Kenya locations ranged between 22.7 and 27.9 $^{\circ}\text{C}$, with S3 recording the highest temperature at 27.9 $^{\circ}\text{C}$. The average temperature for all four sites was 25.59 $^{\circ}\text{C}$. All four locations had temperatures that fell within the acceptable limits set by the KEBS, NEMA, and WHO guidelines. In order for aquatic organisms to survive, temperature is a crucial indication of water quality. Wosnie and Wondie (2014) stated that the effluents had a temperature of 25.5 $^{\circ}\text{C}$, which is a comparable observation.

5.1.6 Biochemical Oxygen Demand (BOD)

The Biochemical Oxygen Demand (BOD) is a crucial measure in research on water pollution since it is used to assess the impact that wastewaters have on receiving waterways. The biological oxygen demand (BOD) levels for the four sites ranged between 3141.2 and 5477.7 mg/L, with site 2 having the highest values at 5477.7 mg/L, according to the study's findings, which showed that the biological oxygen demand in the effluents of the Bata leather tanneries in Kenya was high at 4721.34 mg/L. At all four locations, BOD concentrations were higher than those advised by KEBS, NEMA and WHO norms.

The results show how organic materials are used in the tannery sector (skins and hides). High dissolved organic matter reduces oxygen levels, raises BOD, and causes anaerobic reactions that result in the production of ammonia and organic acids. Microorganisms' decomposition of organic materials lowers the amount of dissolved oxygen in stream waters, which in turn promotes anaerobic activity and the release of hazardous gases (Song *et al.*, 2000). In their study, Mwinyihija *et al.* (2006) reached similar conclusions.

5.1.7 Total Suspended Solids (TSS)

The wastewater discharged by Kenya's Bata leather tanneries had an average TSS level of 213.50 mg/L, with values ranging from 148 mg/L to 284 mg/L with S1 registering the highest concentration at 284 mg/L. The standard deviation approach was used to calculate these values. For the NEMA, KEBS, and WHO standards, respectively, TSS levels were discovered to be larger than 100, 30, and 30 mg/L. Due to the processing of leather, TSS in tannery effluent is high. Additionally, the presence of total suspended solids causes turbidity, which limits the amount of light that enters the aquatic system and hinders the activity of photosynthetic organisms (Anantnarayan *et al.*, 2018). Colloidal debris may settle on soil and soil life, changing the soil's porosity, texture, and ability to hold water, as well as blocking fish gills and respiratory surfaces (Chowdhary *et al.*, 2020). In comparison to this work, Chowdhury *et al.* (2015)'s analysis of tannery effluents revealed considerably higher suspended matter (TSS) values.

5.1.8 Total Solids (TS)

Wastewater from Kenya's Bata leather tanneries included 413.58 mg/L of total solids and varied between 286 and 554 mg/L. These results are all higher than the WHO guideline of 500 mg/L. The TS findings demonstrated that more purification is required

before releasing the tannery's effluents. The sample's high results for carbonate and bicarbonate suggest improper liming. The required alkalinity limits were surpassed at every test location, claims Chowdhury et al (2015).

5.1.9 Chemical Oxygen Demand (COD)

The COD test is the fastest way to ascertain the total oxygen demand of the organic matter contained in a sample while also providing the most accurate estimates of organic matter. At 7772.92 mg/L across all stations, COD levels were greater above WHO Standards, with a mean range of 5986.7 to 9093.2 mg/L at the four sample locations. Hypothesis 2 was rejected since the values were considerably higher than the corresponding 100, 50, and 10 mg/L NEMA, KEBS, and WHO criteria. COD levels were reported to range from 2286 to 9600 mg/L by Noorjahan (2014). High concentrations of organic compounds that are not degraded by microbes might greatly increase COD (Nagarajan and Ramachandramoorthy, 2002). These results support the conclusions of earlier study by Alvarez-Bernal et al. (2006).

5.1.10 Colour (Pt-Co)

The color of the effluents changed at different phases. The four wastewater Bata leather tannery sites in Kenya had a mean color value of 667 Pt-Co and a range of 488.5 and 787.2 Pt-Co, with S2 having the highest value of 787.2 Pt-Co because of its yellowish-brown color. These values were much higher than the comparable 300, 40, and 15 Pt-Co thresholds advised by the KEBS and WHO. S1, S3, and S4 monitoring locations all showed lower color units. The color of the effluent may be caused by high molecular weight organic compounds that are both biodegradable and not, as well as salt and chromium used in processing. Odor may be caused by the putrefaction of processed skin and hides (Smrithi et al., 2010). The yellowish-brown hue may deflect sunlight

and lessen pollutant oxidation, claim Verma et al. in 2008. This study supports the conclusions of Dhungana and Yadav (2009).

5.1.11 Chromium Levels (Cr)

The respective mean levels of total chromium, Cr^{6+} , and Cr^{3+} in effluent samples were 573.71 72.370, 12.08 1.370, and 560.38 70.691 mg/L, respectively. NaCl, H_2SO_4 , formic acid, and salts of Cr^{3+} and Cr^{6+} . Acidic environments are more stable and have higher Cr^{6+} . Complexation and coagulation of certain Cr in river water by chelating chemicals resulted in lower Cr levels at S4 than at S3 (Nyabaro *et al.*, 2013). The greatest Cr concentration of the four hazardous elements tested was found in pickling and chrome-tanning effluents (stage 4). Metal levels were above standard limits.

CHAPTER SIX

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusions

The corresponding overall mean effluent chromium samples for total chromium, Cr^{6+} and Cr^{3+} at S1, S2, S3 and S4 were 1.70 ± 0.23 , 13.08 ± 1.34 and 18.00 ± 11.7 mg/L. The overall mean effluent chromium samples for total chromium at these stations differed significantly in the area. The estimated TDS levels were high in the water collected from S1 and S3, respectively, even though all the investigated sites reported values below the KEBS, NEMA, and WHO criteria (1200 mg/L). The pH values at Sites 1 and S2 were acceptable by WHO standards. While the combined mean DO value for all four sites only just above WHO standards, the EC from effluent from Kenya's Bata leather tanneries was much higher than the permitted limit of 25 mS/cm. Similarly, the temperature levels for all the four sites were, however, within the recommended values set by WHO. The BOD, TSS, TS and colour values for all the four sites were above the acceptable set standards by WHO. The assessed samples showed significant positive correlation between TSS and TDS, TSS and TS, COD and BOD, BOD and Cr^{6+} and Cr^{3+} , COD and Cr^{6+} and Cr^{3+} . There was a negative significant correlation between pH and TDS. In comparison with the two methods, UV spectroscopic did best in comparison with ICP- AES in a non-ionic micellar media though with no significant difference. For the recovery test by ICP- AES in a non-ionic micellar medium, the results showed a high percentage of 98.13 ± 0.12 % from the initial concentration.

6.2 Recommendations

This research recommends that developing countries like Kenya should employ UV-vs spectroscopic Method for quantification of Cr trace levels which has been supported by the findings where both methods did not differ significantly. The UV-spectroscopic method showed high percentage of recoveries in determining chromium levels. Therefore, UV-method should be used to test recoveries in environmental waters.

Proper treatment of the effluents from the industry should be done to ensure that no high levels of pollution are discharged to river Ndurumo. There is need to explore other methods of decontaminating of waste rather than the currently used so that it can be utilized in other economic methods. The ministry of environment should enforce the law concerning water pollution and to prosecute those who are found culprits.

REFERENCES

- Aboulhassan, M. A., Souabi, S., and Yaacoubi, A. (2008). Pollution reduction and biodegradability index improvement of tannery effluents. *International Journal of Environmental Science & Technology*, *5*(1), 11-16.
- Agency for Toxic Substances and Disease Registry, (ATSDR) (2005). *Toxicological profile for Chrome and Sulphuric Acid*. Atlanta, GA. US Department of Health and Human Services.
- Agudelo-Vera, C. M., Mels, A. R., Keesman, K. J., and Rijnaarts, H. H. (2011). Resource management as a key factor for sustainable urban planning. *Journal of environmental management*, *92*(10), 2295-2303.
- Akan, J. C., Abdulrahman, F. I., Dimari, G. A., and Ogugbuaja, V. O. (2008). Physicochemical determination of pollutants in wastewater and vegetable samples along the Jakara wastewater channel in Kano Metropolis, Kano State, Nigeria. *European Journal of Scientific Research*, *23*(1), 122-133.
- Alam, M. Z., & Ahmad, S. (2011). Chromium removal through biosorption and bioaccumulation by bacteria from tannery effluents contaminated soil. *Clean–Soil, Air, Water*, *39*(3), 226-237.
- Alvarez-Bernal, D., Contreras-Ramos, S. M., Trujillo-Tapia, N., Olalde-Portugal, V., Frías-Hernández, J. T., and Dendooven, L. (2006). Effects of tanneries wastewater on chemical and biological soil characteristics. *Applied Soil Ecology*, *33*(3), 269-277.
- Anantnarayan, H. S., Beretto, T., Desai, A., and Hegde, G. (2018). Water Quality Assesment of Kotithirta–A Holy Temple Lake of Gokarna, Karnataka. *Inter Res J EngiTechno (IRJET)*, *5* (4): 624, 634.

- Aniyikaiye, T. E., Oluseyi, T., Odiyo, J. O., and Edokpayi, J. N. (2019). Physico-chemical analysis of wastewater discharge from selected paint industries in Lagos, Nigeria. *International journal of environmental research and public health*, **16**(7), 1235.
- Apaydin, O., Kurt, U. and Gonullu, M.T. (2009). An investigation on tannery wastewater by electro coagulation. *Glob Nest Journal*; **11**: 546–55.
- Ashwini. C. (2009). Studies on biological reduction of chromate by *Streptomyces griseus*. *J. Hazard. Mater*, **169**(1-3): 539-545.
- Assefa, R., Bai, R., Leta, S., & Kloos, H. (2019). Nitrogen removal in integrated anaerobic–aerobic sequencing batch reactors and constructed wetland system: a field experimental study. *Applied Water Science*, *9*(5), 1-11.
- Baird, R. B., Eaton, A. D., & Clesceri, L. S. (2012). *Standard methods for the examination of water and wastewater* (Vol. 10). E. W. Rice (Ed.). Washington, DC: American public health association.
- Barrera, H. (2006) Removal of chromium and toxic ions presents in mine drainage by Ectodermis of *Opuntia*. *J. Hazard. Mater*, *136*: 846-853.
- Baysal, A., Ozbek, N., and Akman, S. (2013). Determination of trace metals in **wastewater** and their removal processes. *Wastewater-Treatment Technologies and Recent Analytical Developments*, 145-171.
- Bhatnagar, M. K., Raviraj, S., Sanjay, G., and Prachi, B. (2013). Study of tannery effluents and its effects on sediments of river Ganga in special reference to heavy metals at Jajmau, Kanpur, India. *Journal of Environmental Research and Development*, **8**(1), 56.
- Bielicka, A., Bojanowska, I., and Wisniewski, A. (2005). Two Faces of Chromium-Pollutant and Bioelement. *Polish Journal of environmental studies*, **14**(1).

- Bosnic, M., Buljan, J., and Daniels, R. P. (2000). Pollutants in tannery effluents. *United Nations Industrial Development Organization*, 26.
- Cáceres, T., Venkateswarlu, K., & Megharaj, M. (2019). Acute toxicity of the insecticide methyl parathion and its hydrolytic product p-nitrophenol to the native Australian cladoceran *Daphnia carinata*. *Ecotoxicology*, **28**(6), 680-685.
- Calero, M., Ronda, A., Pérez, A., Yáñez, A., Trujillo, M. C., & Martín-Lara, M. Á. (2016). The scale-up of Cr³⁺ biosorption onto olive stone in a fixed bed column. *Desalination and Water Treatment*, **57**(52), 25140-25152.
- CCB, (2005). A source reduction approach: Integrated bio-based tanning methods and the role of enzymes in dehairing and fibre opening. *Clean Technologies and Environmental Policy*, **7**(1), 3-14.
- Chapra S.C. (1997) Surface water-quality modeling. WCB-McGraw Hill, Boston
- Chapra, S. (1997). Surface Water Quality Modeling, University of Colorado and Boulder. Press McGraw-Hill
- Chowdhary, P., Bharagava, R. N., Mishra, S., and Khan, N. (2020). Role of industries in water scarcity and its adverse effects on environment and human health. In *Environmental concerns and sustainable development* (pp. 235-256). Springer, Singapore.
- Chowdhury, M., Mostafa, M. G., Biswas, T. K., Mandal, A., and Saha, A. K. (2015). Characterization of the effluents from leather processing industries. *Environmental Processes*, **2**(1), 173-187
- Chowdhury, M., Mostafa, M. G., Biswas, T.K., Mandal, A., and Saha, A. K. (2015). Characterization of the effluents from leather processing industries. *Environmental Processes*, **2**(1), 173-187.

- Crossman, J., Futter, M. N., Elliott, J. A., Whitehead, P. G., Jin, L., and Dillon, P. J. (2019). Optimizing land management strategies for maximum improvements in lake dissolved oxygen concentrations. *Science of the Total Environment*, 652, 382-397.
- Dawood, S., and Sen, T. (2014). Review on dye removal from its aqueous solution into alternative cost effective and non-conventional adsorbents. *Journal of Chemical and Process Engineering*, 1(104), 1-11.
- Dhiman, S., and Mukherjee, G. (2021). Biotechnological approaches towards treatment and recycling of wastewater from tanneries and leather industry. In *Microbial Ecology of Wastewater Treatment Plants* (pp. 249-268). Elsevier.
- Dhungana, T. P., and Yadav, P. N. (2009). Determination of chromium in tannery effluent and study of adsorption of Cr⁶⁺ on saw dust and charcoal from sugarcane bagasse. *Journal of Nepal Chemical Society*, 23, 93-101.
- European Commission (2009). *Integrated pollution prevention and control (IPPC). Draft Reference document on best available techniques for the tanning of hides and skins.*
- European Food Safety Authority. (2012). Health risk of ammonium released from water filters. *EFSA Journal*, 10 (10), 2918.
- FAO/WHO Codex Alimentarius Commission. (2001). Food Additives and Contaminants. Joint FAO/WHO Food Standards Programme; *ALINORM 01/12A, 1-289.*
- GoK (2008). *National Development Plan, 2008 on Effective Management for Sustainable Economic Growth and Poverty Reduction.* Government Printer, Nairobi.

- Goltara, A., Martinez, J., and Mendez, R. (2003). Carbon and nitrogen removal from tannery wastewater with a membrane bioreactor. *Water science and technology*, **48**(1), 207-214.
- Hasegawa, C. M., Barbosa, A. M., and Takashima, K. (2011). Biotreatment of industrial tannery wastewater using *Botryosphaeria rhodina*. *Journal of the Serbian Chemical Society*, **76**(3), 439-446.
- Hashmi, G. J., Dastageer, G., Sajid, M. S., Ali, Z., Malik, M. F., & Liaqat, I. (2017). Leather industry and environment: Pakistan scenario. *International Journal of Applied Biology and Forensics*, **1**(2), 20-25.
- Heidemann, E. (2005). Leather. Ullmann's Encyclopedia of Industrial Chemistry immune system. *FEMS Immunol Med Microbiol*. **34**: 1–7.
- Kagira, E. K., Kimani, S. W., and Githii, K. S. (2012). Sustainable methods of addressing challenges facing small holder tea sector in Kenya: A supply chain management approach. *J. Mgmt. & Sustainability*, **2**, 75.
- Kanagaraj, J., Velappan, K. C., Babu, N. K., and Sadulla, S. (2006). *Solid wastes generation in the leather industry and its utilization for cleaner environment-A review*.
- Kannaujiya, M. C., Mandal, T., Mandal, D. D., & Mondal, M. K. (2019). Treatment of leather industry wastewater and recovery of valuable substances to solve waste management problem in environment. In *Environmental Contaminants: Ecological Implications and Management* (pp. 311-340). Springer, Singapore.

- Khan, Z., and Anjaneyulu, Y. (2005). Influence of soil components on adsorption–desorption of hazardous organics-development of low-cost technology for reclamation of hazardous waste dumpsites. *Journal of hazardous materials*, **118**(1-3), 161-169.
- Kieu, H. T., Müller, E., & Horn, H. (2011). Heavy metal removal in anaerobic semi-continuous stirred tank reactors by a consortium of sulfate-reducing bacteria. *Water research*, **45**(13), 3863-3870.
- Kimani, M. K. (2013). Constraints Impeding Effective Land Use Plan Implementation.
- Kiruthu, S. (2002). Benchmarking the African leather sector (UNIDO-ESALIA).
- KNBS (2019). Kenya Population and Housing Census Volume 1: Population by County and Sub-County, 2019. Kenya Population and Housing Census.
- Kobyá, M., Can, O. T., and Bayramoglu, M. (2003). Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes. *Journal of hazardous materials*, **100**(1-3), 163-178.
- Kotaś, J., and Stasicka, Z. J. E. P. (2000). Chromium occurrence in the environment and methods of its speciation. *Environmental pollution*, **107**(3), 263-283.
- Kurt,U., Apaydın, O. and Gonullu, M.T. (2007).Reduction of COD in wastewater from an organized tannery industrial region by electro-Fenton process.*Journal of Hazardous Materials*, **143**, 33- 40.
- Liang, P., and Sang, H. (2008). Speciation of chromium in water samples with cloud point extraction separation and preconcentration and determination by graphite furnace atomic absorption spectrometry. *Journal of hazardous materials*, **154**(1-3), 1115-1119.

- Machado, R. (2002). Removal of trivalent Cr³⁺ from solution by biosorption in cork power. *J. Chem. Technol. Biotechnol.*, **77(12)**: 1340-1348.
- Martinez, J. M., Goltara, A., and Mendez, R. (2003). Tannery wastewater treatment: comparison between SBR and MSBR. *Water Science and Technology: Water Supply*, **3(5-6)**, 275-282.
- Memon, S., Memon, N., Mallah, A., Soomro, R., and Y Khuhawar, M. (2014). Schiff bases as chelating reagents for metal ions analysis. *Current Analytical Chemistry*, **10(3)**, 393-417.
- Mishra, S., and Bharagava, R. N. (2016). Toxic and genotoxic effects of hexavalent chromium in environment and its bioremediation strategies. *Journal of Environmental Science and Health, Part C*, **34(1)**, 1-32.
- Mollah, M. Y. A., Schennach, R., Parga, J. R., and Cocke, D. L. (2001). Electrocoagulation (EC)—science and applications. *Journal of hazardous materials*, **84(1)**, 29-41.
- Mook, W. T., Chakrabarti, M. H., Aroua, M. K., Khan, G. M. A., Ali, B. S., Islam, M. S., & Hassan, M. A. (2012). Removal of total ammonia nitrogen (TAN), nitrate and total organic carbon (TOC) from aquaculture wastewater using electrochemical technology: a review. *Desalination*, **285**, 1-13.
- Muchangi, J. (2012). New law won't end carnage, research shows, The star. Accessed on September 19, 2013, at <http://www.the-star.co.ke/news/article-15826/new-law-wont-end-carnage-research-shows>.
- Muchie, M. (2001). Paradoxes of Industrialisation and Unilateral Liberalisation in Africa: A Case of Unrealised Potential of Value-added Leather Manufacture in Kenya. *Science, Technology and Society*, **6(2)**, 397-417.

- Murali Mohan, A., Hartsock, A., Bibby, K. J., Hammack, R. W., Vidic, R. D., and Gregory, K. B. (2013). Microbial community changes in hydraulic fracturing fluids and produced water from shale gas extraction. *Environmental science & technology*, **47**(22), 13141-13150.
- Murugesan, G., and Fox, P. L. (1996). Role of lysophosphatidylcholine in the inhibition of endothelial cell motility by oxidized low density lipoprotein. *The Journal of clinical investigation*, **97**(12), 2736-2744.
- Murugesan, V., Arabindoo, B., and Elangovan, R. (1996). Treatability Studies and Evaluation of Biokinetic Parameters for Chrome Tanning Waste Admixture with Sewage. *Journal of industrial pollution control*, **12**, 41-53.
- Mwinyihija, M. (2007). Assessment of anaerobic lagoons efficacy in reducing toxicity levels of tannery effluent in Kenya. *Res J Environ Toxicol*, **1**, 167-175.
- Mwinyihija, M., Meharg, A., Dawson, J., Strachan, N. J., and Killham, K. (2006). An ecotoxicological approach to assessing the impact of tanning industry effluent on river health. *Archives of environmental contamination and toxicology*, **50**(3), 316-324.
- Mwonderu, J. M., Ombui, J. N., & Onyuka, A. S. (2020). A Survey of leather waste generation and disposal mode in selected counties in Kenya. *Journal of Sustainability, Environment and Peace*, **3**(1), 8-14.
- Nagarajan, P., and Ramachandramoorthy, T. R. (2002). Oil and grease removal from steel industry wastewater by chemical treatment. *Journal Of Ecotoxicology and Environmental Monitoring*, **12**(3), 181-184.

- Navaraj, P. S., & Yasmin, J. (2012). Toxicological evaluation of tannery industry wastewater on *Oreochromis mossambicus*. *African Journal of Environmental Science and Technology*, *6*(9), 331-336.
- Njiru, P. K. (2009). *Children and the Mau Mau: a case study of Kikuyu Division of Kiambu District, 1952-1960* (Doctoral dissertation, University of Nairobi, Kenya).
- Nölte, J. (2021). *ICP Emission Spectrometry: a practical guide*. John Wiley & Sons.
- Noorjahan, C. M. (2014). Physicochemical characteristics, identification of fungi and biodegradation of industrial effluent. *J. Environ. Earth Sci*, *4*(4).
- Noorjahan, C. M., Sharief, S. D., and Dawood, N. (2004). Characterization of dairy effluent. *Journal Of Industrial Pollution Control.*, *20*(1), 131-136
- Nyabaro, O. M., Mosoti, D., Muthoka, T. M., and Onyancha, E. (2013). Determination of Pollution Levels of Wastewater from Nakuru Tanners, Kenya. *African Journal of Education, Science and Technology*, *1*(3), 200-210.
- Onyango, C., Musyoka, P., Shibia, A. G., & Laibuni, N. (2019). *Towards Revitalizing Kenya's Skins, Hides and Leather Products Industry*. Kenya Institute for Public Policy Research and Analysis.
- Onyango, C., Musyoka, P., Shibia, A. G., and Laibuni, N. (2019). *Towards Revitalizing Kenya's Skins, Hides and Leather Products Industry*. Kenya Institute for Public Policy Research and Analysis.
- Organización Mundial de la Salud (OMS), (2003). Guidelines for drinking-water quality Chemical Aspects.
- Orhon, D., Karahan, Ö., and Sözen, S. (1999). The effect of residual microbial products on the experimental assessment of the particulate inert COD in wastewaters. *Water Research*, *33*(14), 3191-3203.

- Papp, J. F., & Lipin, B. R. (2006). Chromite Industrial Minerals & Rocks: Commodities. *Markets, and uses, 7th ed., SME.*
- Parveen, R., Ashfaq, M., Qureshi, J., Ali, S. M. M., and Qadri, M. (2013). Estimation of chromium in effluents from tanneries of Korangi industrial area. *Pakistan Journal of Chemistry, 3*(1), 29-33.
- Parveen, S., Bharose, R., and Singh, D. (2017). Assessment of physico-chemical properties of tannery wastewater and its impact on freshwater quality. *International Journal of Current Microbiology and Applied Sciences, 6*(4), 1879-1887.
- Porra, L., Monfraix, S., Berruyer, G., Le Duc, G., Nemoz, C., ThomLinson, W., and Bayat, S. (2004). Effect of tidal volume on distribution of ventilation assessed by synchrotron radiation CT in rabbit. *Journal of Applied Physiology, 96*(5), 1899-1908.
- Radeny, M., Mungai, C., Amwata, D., Osumba, J., and Solomon, D. (2020). Climate change, agriculture, food and nutrition security policies and frameworks in Kenya. *CCAFS Working Paper.*
- Rakhunde, R., Deshpande, L., and Juneja, H. D. (2012). Chemical speciation of chromium in water: a review. *Critical reviews in environmental science and technology, 42*(7), 776-810.
- Ram, B., Bajpai, P. K., and Parwana, H. K. (1999). Kinetics of chrome-tannery effluent treatment by the activated-sludge system. *Process biochemistry, 35*(3-4), 255-265.
- Resolution, G. A. (2015). 70/1, Transforming Our World: The 2030 Agenda for Sustainable Development. *Geneva: United Nations.*

- Roether, W., Klein, B., Beitzel, V., and Manca, B. B. (1998). Property distributions and transient-tracer ages in Levantine Intermediate Water in the Eastern Mediterranean. *Journal of Marine Systems*, **18**(1-3), 71-87.
- Sabumon, P. C. (2016). Advances in Recycling & Waste Management: Open Access. *Advances in Recycling & Waste Management*, **1**(1), 1-10.
- Sabur, M. A., Rahman, M. M., and Safiullah, S. (2013). Treatment of tannery effluent by locally available commercial grade lime. *Journal of Scientific Research*, **5**(1), 143-150.
- Santos T. (2010). Effluent's determination of Bogota municipality. *MSc Thesis university of Bogota*
- Saxena, D., Joshi, N., and Srivastava, S. (2002). Mechanism of copper resistance in a copper mine isolate *Pseudomonas putida* strain S4. *Current microbiology*, **45**(6), 0410-0414.
- Saxena, G., Chandra, R., and Bharagava, R. N. (2016). Environmental pollution, toxicity profile and treatment approaches for tannery wastewater and its chemical pollutants. *Reviews of Environmental Contamination and Toxicology Volume 240*, 31-69.
- Schenk, H., Wiemann, M., and Hegemann, W. (1999). Improvement of anaerobic treatment of tannery beamhouse wastewater by an integrated sulphide elimination process. *Water science and technology*, **40**(1), 245-252.
- Schrank, S. G., Jose, H. J., Moreira, R. F. P. M., and Schröder, H. F. (2004). Elucidation of the behavior of tannery wastewater under advanced oxidation conditions. *Chemosphere*, **56**(5), 411-423.

- Sempele, B. S. (2017). *An Analysis of Kenya Vision 2030's Efforts Towards Achieving Sustainable Development Goal 10* (Doctoral dissertation, United States International University-Africa).
- Shahzad, K., Akhtar, S., and Mahmud, S. (2006). Prevalence and determinants of asthma in adult male leather tannery workers in Karachi, Pakistan: a cross sectional study. *BMC public health*, **6**(1), 1-7.
- Shrivastava, R., Upreti, R. K., Seth, P. K., and Chaturvedi, U. C. (2002). Effects of chromium on the immune system. *FEMS Immunology & Medical Microbiology*, **34**(1), 1-7.
- Smrithi, A., and Usha, K. (2012). Isolation and characterization of chromium removing bacteria from tannery effluent disposal site. *Int J Adv Biotechnol Res*, **3**(3), 644-652.
- Smrithi, A., Poornima, V., and Usha, K. (2010). Bioremediation Potential of Brassica Juncea against Tannery Effluent. *Advances in Applied Research*, **2**(2), 74-80.
- Song, Z. Wasiams, C. and Edyvean, R.G. (2004). Treatment of tannery wastewater by chemical coagulation. *Desalination* **164** (3); pp 249-259
- Song, Z., Williams, C. J., and Edyvean, R. G. J. (2000). Sedimentation of tannery wastewater. *Water Research*, **34**(7), 2171-2176.
- Soomro, M. S., Akhtar, M. S., and Memon, K. S. (2011). Drinking water quality assessment in Southern Sindh (Pakistan). *Environmental monitoring and assessment*, **177**(1), 39-50.
- Sreeram, K. J., and Ramasami, T. (2003). Sustaining tanning process through conservation, recovery and better utilization of chromium. *Resources, conservation and recycling*, **38**(3), 185-212.

- Srivastava, M. P., Srivastava, N., Sharma, N., and Sharma, Y. K. (2018). Bioremediation of Toxic Heavy Metals Cr⁶⁺ from Tannery Effluent using Micro-Organisms: Biotechnological Potential. *International Journal of Plant and Environment*, **4**(01), 41-48.
- Stepniewska, K., Taylor, W. R., Mayxay, M., Price, R., Smithuis, F., Guthmann, J. P., and White, N. J. (2004). In vivo assessment of drug efficacy against *Plasmodium falciparum* malaria: duration of follow-up. *Antimicrobial agents and chemotherapy*, **48**(11), 4271-4280.
- Sugasini, A., and Rajagopal, K. (2015). Characterization of physicochemical parameters and heavy metal analysis of tannery effluent. *International Journal of Current Microbiology and Applied Sciences*, **4**(9), 349-359.
- Suthanthararajan, R. Ravindranath, E. Chitra, K., Umamaheswari, B., Ramesh, T. and Rajamani, S., (2004b). Membrane application for recovery and reuse of water from treated tannery wastewater. *Desalination*, **164**, 151-156.
- Suthanthararajan, R., K. Chitra, E. Ravindranath, B. Umamaheswari, S. Rajamani, and T. Ramesh (2004a). Anaerobic treatment of tannery wastewater with sulfide removal and recovery of sulphur from wastewater and biogas. *J. Amer. Leather Chemists* **99**(2):67-72
- Tamilchelvan, P. and Dhinakaran, M, (2012) Anaerobic Digestion Treatment of Tannery Waste Water, *International Journal of Engineering Research and Applications*, Vol. 2, Issue 3, pp.932-936.
- Tang, K., Baskaran, V., and Nemat, M. (2009). Bacteria of the sulphur cycle: an overview of microbiology, biokinetics and their role in petroleum and mining industries. *Biochemical Engineering Journal*, **44**(1), 73-94.

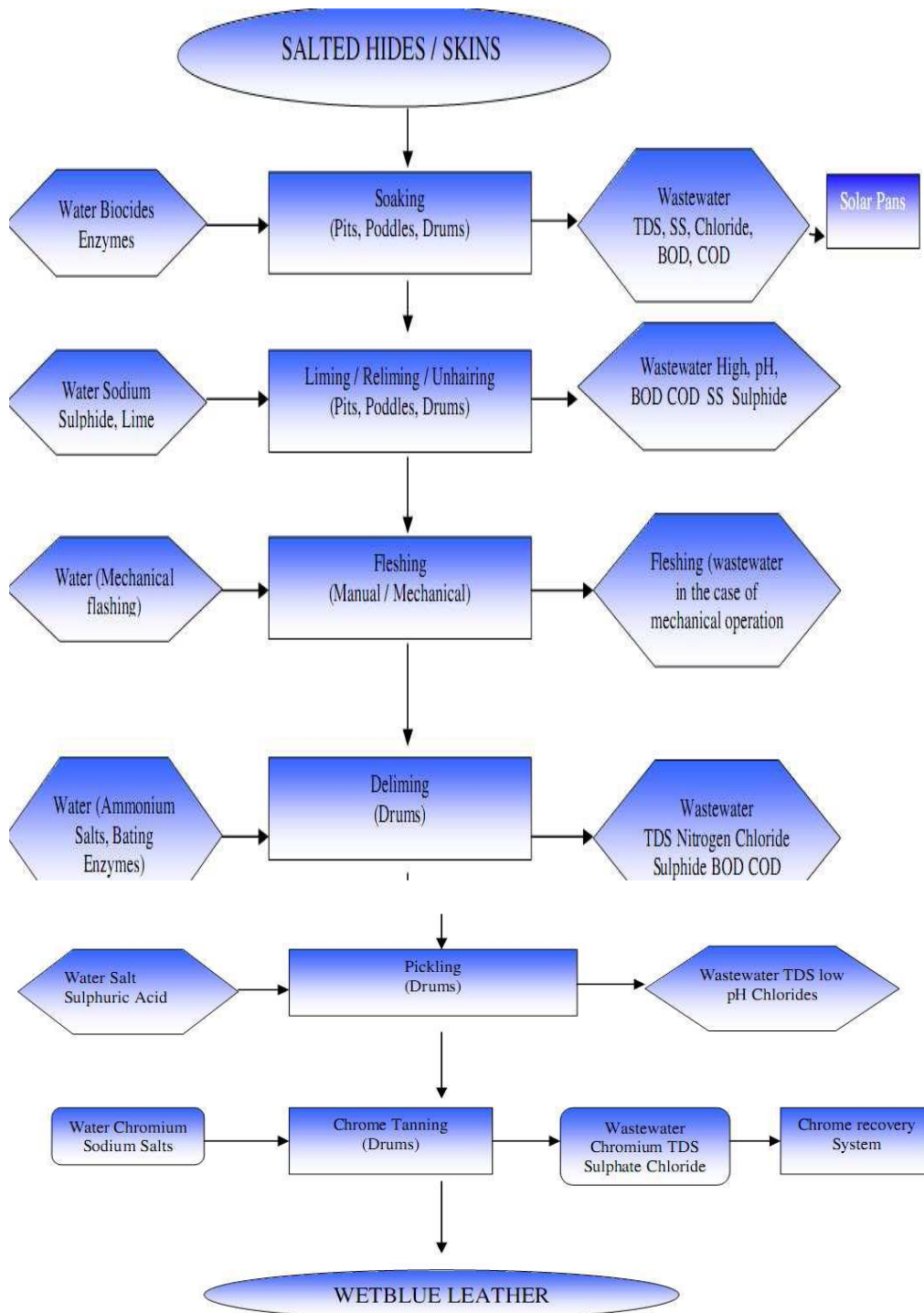
- Tariq, M., Ali, M., and Shah, Z. J. S. E. (2006). Characteristics of industrial effluents and their possible impacts on quality of underground water. *Soil Environ*, **25**(1), 64-69.
- Tchobanoglous, G., Ruppe, L., Leverenz, H., and Darby, J. (2004). Decentralized wastewater management: challenges and opportunities for the twenty-first century. *Water Science and Technology: Water Supply*, **4**(1), 95-102.
- Uddin, M. N., Ahmed, S. S., and Alam, S. R. (2020). Biomedical applications of Schiff base metal complexes. *Journal of Coordination Chemistry*, **73**(23), 3109-3149.
- Uddin, M. N., and Salam, M. A. (2014). Bis (salicylaldehyde) phenylenediamine-a noble reagent for the trace determination of metal ions in environment.
- UNEP (1991). *Tannery and the Environment: A Technical Guide to Reducing the Environmental Impact of Tannery Operations*. Paris: UNEP/IEO, UN Publication series III. ISBN 92-807-1276-4.
- UNIDO (2000). Environmental impact assessment (EIA) on the industrial activities at Hazaribagh area, Dhaka (Project - US/RAS/97/137-EIA), Final Report, Government of the Peoples Republic of Bangladesh & United Nations Industrial Development Organization.
- UNIDO (2005). Cost of tanned waste treatment, 15th session of the leather and leather products industry panel Leon, Mexico. Vienna: United Nations Industrial Development Organization.
- UNIDO, (2011). Introduction to treatment of tannery effluents Vienna.
- Verheijen, L., Weirsema, L. and Dewit, J. (1996). *Livestock and the Environment: Finding a Balance Management of Waste from Animal Product Processing*. International Agriculture Centre, Wageningen, The Netherlands **2**, p.22

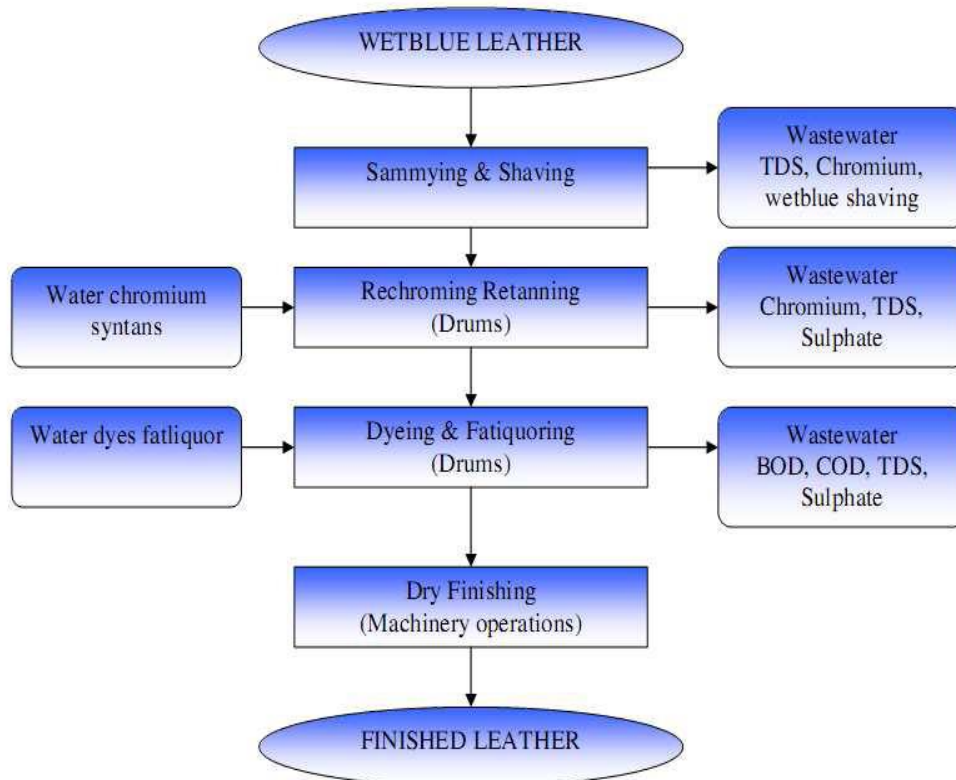
- Verma, T., Ramteke, P. W., and Garg, S. K. (2008). Quality assessment of treated tannery wastewater with special emphasis on pathogenic E. coli detection through serotyping. *Environmental monitoring and assessment*, **145**(1), 243-249.
- Vincent, J. B. (2007). "Recent advances in the nutritional biochemistry of trivalent chromium". *Proceedings of the Nutrition Society* **63** (1): 41–47.
- Wang, M., Janssen, A. B., Bazin, J., Strokal, M., Ma, L., and Kroeze, C. (2022). Accounting for interactions between Sustainable Development Goals is essential for water pollution control in China. *Nature communications*, **13**(1), 1-13.
- Wang, Y., Li, W., Irini, A., & Su, C. (2014). Removal of organic pollutants in tannery wastewater from wet-blue fur processing by integrated Anoxic/Oxic (A/O) and Fenton: Process optimization. *Chemical Engineering Journal*, **252**, 22-29.
- Wangui, A. (2016). *The Performance of Hides and Skins Sub-Sector and Associated Economic Losses in Wajir County, Kenya* (Doctoral dissertation, University of Nairobi).
- Wei, Wei, Robert Kläbe, Hong-Fei Ling, Fang Huang, and Robert Frei. "Biogeochemical cycle of chromium isotopes at the modern Earth's surface and its applications as a paleo-environment proxy." *Chemical Geology* **541** (2020): 119570.
- Welker, A. F., Moreira, D. C., Campos, É. G., and Hermes-Lima, M. (2013). Role of redox metabolism for adaptation of aquatic animals to drastic changes in oxygen availability. *Comparative Biochemistry and Physiology Part A: Molecular & Integrative Physiology*, **165**(4), 384-404.

- Wiemann, M, Schenk, H., and Hegemann, W. (2018). Anaerobic treatment of tannery wastewater with simultaneous sulphide elimination. *Water research*, **32(3)**, 774-780.
- Yu, Y., Lin, Y., Zeng, Y., Wang, Y. N., Zhang, W., Zhou, J., & Shi, B. (2021). Life cycle assessment for chrome tanning, chrome-free metal tanning, and metal-free tanning systems. *ACS Sustainable Chemistry & Engineering*, **9(19)**, 6720-6731.
- Yun, Y. S., Park, D., Park, J. M., and Volesky, B. (2001). Biosorption of trivalent chromium on the brown seaweed biomass. *Environmental science & technology*, **35(21)**, 4353-4358.
- Zywicki, B., Reemtsma, T., and Jekel, M. (2002). Analysis of commercial vegetable tanning agents by reversed-phase liquid chromatography–electrospray ionization–tandem mass spectrometry and its application to wastewater. *Journal of Chromatography A*, **970(1-2)**, 191-200.

APPENDICES

Appendix I: Process Flowchart for Tannery and Associated Pollution





(Source: Andhra Pradesh pollution control board, 2005)

Appendix II: Chemical Properties of Water

	S1	S2	S3	S4
TDS (mg/l)	270.21	201.81	137.71	196.52
	270.11	200.71	136.55	194.11
	271.21	200.11	135.55	194.31
	270.00	198.98	134.32	193.11
pH	S1	S2	S3	S4
	1.52	4.41	8.21	6.02
	1.51	4.40	8.20	6.00
	1.50	4.41	8.21	6.01
	1.50	4.40	8.20	6.02
DO (mg/l)	S1	S2	S3	S4
	8.1	8.42	10.62	9.72
	8.0	8.39	10.55	9.70
	7.9	8.38	10.59	9.69
	8.0	8.38	10.60	9.70
	S1	S2	S3	S4
EC (mS/cm)	1348.22	1360.56	1385.64	1359.32
	1353	1363.55	1382.66	1362.56
	1350	1362.36	1381.33	1360.21
	1348	1360.34	1385.44	1360.23
	S1	S2	S3	S4
BOD (mg/l)	3741.11	5477.56	4897.77	4768.67
	3740.87	5477.32	4897.82	4766.89

	3741.23	5478.78	4896.67	4764.90
	3740.43	5477.65	4898.56	4765.89
	S1	S2	S3	S4
COD (mg/l)	5986.25	9093.31	8095.71	7916.98
	5988.65	9094..54	8017.65	7918.98
	5986.87	9095.87	8056.87	7920.54
	5985.43	9092.11	8088.45	7918.55
	S1	S2	S3	S4
Cr ⁶⁺ (mg/l)	0	912.22	672.23	656.68
	0	913.11	672.45	655.56
	0	912.43	671.32	656.45
	0	913.65	670.45	655.56
	S1	S2	S3	S4
Cr ³⁺ (mg/l)	0	912.22	672.23	656.68
	0	912.67	676.67	651.67
	0	912.00	671.56	655.89
	0	911.32	670.56	655.67
Total chromium	0	935.45	690.75	670.45
	0	934.78	689.43	671.67
	0	935.56	690.42	670.78
	0	935.34	689.89	671.65

Appendix III: Physical Properties of Water Comparison with WHO Standards

	S1	S2	S3	S4
Temperature(⁰ C)	27.30	22.41	27.48	23.34
	27.98	22.60	27.65	23.54
	26.99	22.56	27.90	23.43
	27.34	22.66	27.91	23.45
TSS (mg/l)	282.67	216.76	206.45	233.22
	282.54	216.56	206.32	233.32
	282.21	216.45	206.21	232.78
	282.21	216.23	206.23	233.11
TS (mg/l)	552.76	414.45	288.45	402.43
	552.45	414.21	288.89	402.54
	551.98	414.45	288.67	402.00
	552.76	414.78	288.67	404.77
Colour (TCU)	668.54	786.89	718.55	488.45
	667.55	785.56	718.90	488.90
	668.98	784.33	718.45	488.98
	666.23	781.11	718.90	489.00

Appendix IV: Similarity Report

Turnitin Originality Report

QUANTIFICATION OF Cr +3, Cr +6, TOTAL CHROMIUM, AND PHYSICOCHEMICAL CHARACTERISTICS OF TANNERY WASTEWATER EFFLUENTS: A CASE STUDY OF BATA TANNERIES, KENYA by Maritim Geoffrey

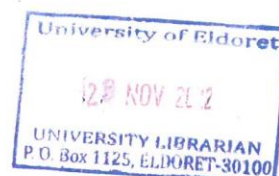


From Theses (Theses)

- Processed on 14-Nov-2022 11:25 EAT
- ID: 1953454095
- Word Count: 20368

Similarity Index
26%
Similarity by Source

Internet Sources:
25%
Publications:
7%
Student Papers:
10%



sources:

- 1 6% match (Internet from 27-Sep-2022)
<http://erepository.uoeld.ac.ke/bitstream/handle/123456789/1649/Maritim%20et%20al%2c%202022.pdf?isAllowed=y&sequence=1>
- 2 2% match (Internet from 12-Nov-2021)
<http://erepository.uoeld.ac.ke/bitstream/handle/123456789/87/Obed%20thesis.pdf?isAllowed=y&sequence=1>
- 3 1% match (Internet from 13-Oct-2022)
<http://erepository.uoeld.ac.ke/bitstream/handle/123456789/1524/ERICK%20MAINYA%20OMANWA.pdf?isAllowed=y&sequence=1>
- 4 1% match (Internet from 22-Jul-2020)
<http://erepository.uonbi.ac.ke/bitstream/handle/11295/95168/Msc%20Thesis%20Final%203-11-2015.pdf?sequence=1>
- 5 1% match (Internet from 04-Nov-2015)
<http://www.readbag.com/cwc-nic-in-main-hp-download-standard-analytical-procedures>
- 6 1% match (Internet from 03-Nov-2018)
<http://gujenvic.nic.in/PDF/final%20coal%20study.pdf>
- 7 1% match (Internet from 23-Apr-2015)
<http://www.sachajournals.com/documents/image/kenya25sjes002.pdf>